

Self-Standing TiO₂ Nanotubular Membranes for Sustainable Production of Energy

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In this contribution, we present a simple electrochemical approach to obtain large-area free-standing TiO₂ nanotube membranes, via a three-step anodic oxidation of pure Ti sheets in fluoride-containing ethylene glycol. The highly ordered vertically oriented TiO₂ nanotubes were characterized by Field Emission Scanning Electron Microscopy (FE-SEM) and Glancing Angle X-Ray Diffraction (GA-XRD) analysis. In particular, we report some details related to the synthetic procedure by SEM images of the fundamental steps, evidencing the development of the morphology of the catalytic surface. The study was focused on the ability to control the nanotube morphology, length, pore size, wall thickness and packing degree, by varying some parameters during the synthesis (such as voltage, electrolyte, pH, time of anodization, water concentration, etc.). The 1D nanostructured films (well-ordered vertically aligned TiO₂ nanotubes) can be used as electrodic materials for solar devices (dye-sensitized or photo-electrochemical solar cells). Results showed that smooth surface and high aspect ratio TiO₂ nanotube arrays were fabricated, which may have wide applications in the development of micro-confined reactors for a sustainable production of energy.

1. Introduction

The ability to design and synthesize nano-engineered structures as functional materials with unusual and valuable properties has opened new perspectives in the fabrication of electrochemical devices for sustainable production of energy. (Genovese et al., 2013a). In this context, synthesis of tubular one-dimensional (1D) nanostructures grown onto the surface of metals (such as Al, Ti, W) by electrochemical anodization, have attracted growing scientific interest due to their unique size and shape dependent properties that can be exploited in a wide range of applications (Passalacqua et al., 2012). Among the other metal oxides, TiO₂ is the most utilized and studied material for its suitable semiconducting and optical properties, photocatalytic activity, low cost and toxicity (Ampelli et al., 2013). Nanostructured TiO₂ was successfully applied as water-splitting photocatalyst for hydrogen production in photoelectrochemical (PEC) reactors (Ampelli et al, 2011), as photo-anode in dye-sensitized solar cells (Mor et al, 2006) and as gas sensing material in fuel-cell technology (Ampelli et al, 2012) and for safety and control purposes in fermentation processes (Ampelli et al, 2014a). In each of these applications, aspects such as particle size and shape, crystallinity, surface morphology and chemistry of the titania-based materials are the key parameters to be controlled for the process optimization. A precise control of the nanotube morphology, length, pore size, wall thickness and packing degree may strongly enhance their performances, depending on the application where the titania nano-materials are used (Ampelli et al, 2009). Specifically, by varying the fluorides and passing from aqueous to organic electrolytes, smooth surface and high aspect ratio TiO₂ nanotube arrays can be fabricated by controlled anodic oxidation techniques (Ampelli et al., 2008).

In this contribution, free-standing membranes of well-ordered vertically aligned TiO₂ nanotubes (with both the ends open) were fabricated by anodic oxidation technique. This electrochemical approach allowed to obtain large-area free-standing TiO₂ nanotube membranes via a three-step oxidation of pure Ti sheets in fluoride-containing ethylene glycol (EG). The high-quality membranes were obtained with facile and reliable procedures by taking advantage of i) the different mechanical stability between thermal treated and

not treated layers, ii) the less defective nature of the layer anodized at lower temperature and iii) a pulse detaching technique. The resulted 1D TiO₂ nanostructures exhibited unique properties for their special geometry, high surface area and aspect ratio, paving the way for transferring ions, electrons, photons, as well as gases and liquids. Specifically, we reported in this work on some details related to the procedure of synthesis through a characterization by sequential SEM images of the fundamental steps, evidencing the development of the morphology of the catalytic surface.

Due to their smooth surface and high aspect ratio, the TiO₂ nanotube arrays may have wide applications in the development of micro-confined reactors, as photo-active supports where depositing metal nanoparticles (Pt, Au, but also not-noble metals such as Cu, Co) that act as reducing catalytic centres for a sustainable production of energy (Ampelli et al., 2014b).

2. Experimental

The self-standing titania nanotube (TNT) membranes were prepared via a three-step anodic oxidation (AO) process. Prior to AO, pure titanium discs (Alfa Aesar, thickness 0.025 mm x 35 mm dia.) were ultrasonically cleaned with ethanol followed by a deionized water rinse. The AO was performed at room temperature in a two-electrode electrochemical cell with a Ti foil as working electrode and a Pt rod as counter electrode, applying 50 V for 10 h in EG containing 0.3 wt. % NH₄F and 2 vol. % H₂O. For the AO, an Agilent E3612A DC power supply was used, coupled with a multimeter Keithley 2000/E to record the resulting current. After the AO, the samples were rinsed thoroughly with deionized water and then dried under a nitrogen stream. The annealing processes were conducted in air with heating and cooling rate of 2 °C/min for 3 h at 200 °C and then at 450 °C. The morphology of the samples was analyzed by scanning electron microscopy using FEI mod. XL-30 with FEG (Field Emission Gun). Glancing Angle X-Ray Diffraction (GAXRD) measurements were performed to assign the crystal structure. A X-ray diffractometer Philips X-pert 3710 has been used with monochromatic CuK α radiation at 40 kV and 30 mA. A 2 θ scan rate of 0.02°/s was used. Spectra were collected at 0.5° incident angle. The samples were studied in the range 20° < 2 θ < 80°.

3. Results and discussion

Different techniques have been employed in literature for the synthesis of tubular TiO₂ nanostructures, such as atomic layer deposition (ALD) (Huang et al., 2012), hydrothermal synthesis (Suzuki and Yoshikawa, 2004), sonochemical (Zhu et al., 2001) and microwave (Wu, 2004) methods. However, the most suitable technique to obtain tailored nanoarchitectures seem to be the electrochemical anodization technique, as it is easy, scalable, tunable and low-costly.

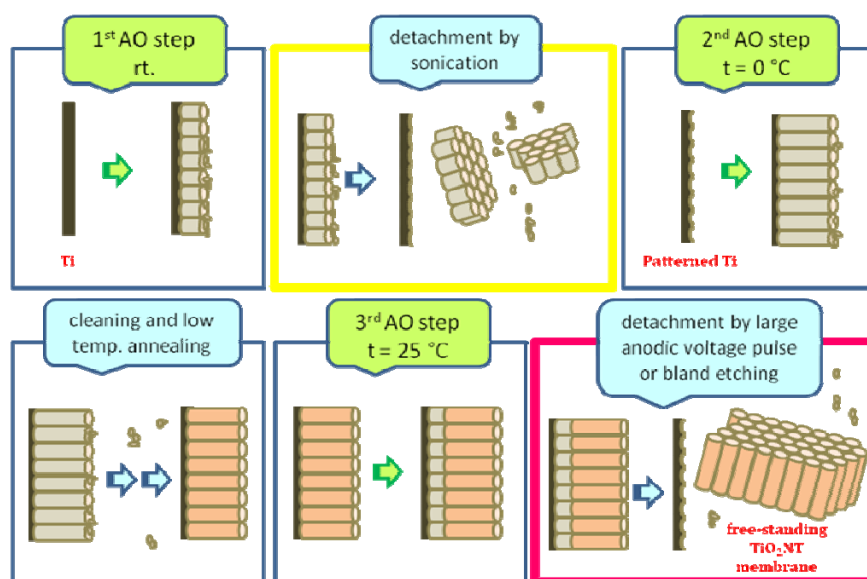


Figure 1: Scheme of the procedure for obtaining free-standing TNT membranes.

The method of fabricating self-standing TNT membranes uses an approach at constant anodization voltage, consisting of six stages in total, including three successive AO steps. Figure 1 shows a scheme of the overall process. Firstly, a Ti sheet is anodized to form a TNT array membrane supported on Ti. After the detachment of the TNT membrane by sonication, a Ti foil whose surface has a honeycomb-like patterned morphology is obtained. Using this patterned Ti foil, a second AO step is carried out under the same conditions than the first step but at lower temperature (0 °C), followed by calcination at 200 °C (see experimental part). Thereafter, a third AO process is performed forming a thin amorphous underlayer on the as annealed TNT/Ti foil. Finally, the detachment of the thermal treated layer was obtained by selective dissolution of the third amorphous TNT layer from the Ti substrate by a large anodic voltage pulse. As a result, a free-standing TNT membrane with both the ends open is fabricated. After the electrochemical preparation process the membrane was amorphous, but it crystallized in anatase phase by annealing in air at 450 °C.

Figure 2 shows the glancing angle x-ray diffraction patterns of the TNT membrane as-prepared (a), after a thermal treatment at 450 °C (b) or at 500 °C (c) for 3 h. The GAXRD measurements revealed that no reflections due to crystalline phase are present at temperature below 200 °C and there is only a broad peak in the 20-30 2θ range, indicating the presence of amorphous TiO₂. For the sample annealed at 450 °C, instead, reflections due to anatase phase were detected; moreover, at 500 °C reflections due to rutile phase also began to appear in addition to the anatase ones. TNT membranes prepared by this three-step AO approach evidenced a good level of transparency, as the photo in Figure 3a shows for a 0.35 mm-diameter titanium disc anodized for 6 h; Figure 3b, instead, reports the corresponding FESEM image, evidencing a layer thickness of about 90 μm. In order to obtain a better understanding of the procedure of nanotubular membrane formation and its detachment from the underlying metallic Ti disc, the samples were analyzed by Scanning Electron Microscopy with FEG (field emission gun). The most significant images of the membrane at different steps of AO preparation are collected in Figure 4. The 4a image shows the TiO₂ layer and the Ti substrate after the first AO step, whereas images 4b and 4c show the metal oxide structure after the second AO step at two different magnifications. In 4d image, the micrograph of the patterned titanium substrate after the detachment of the first AO layer, is reported.

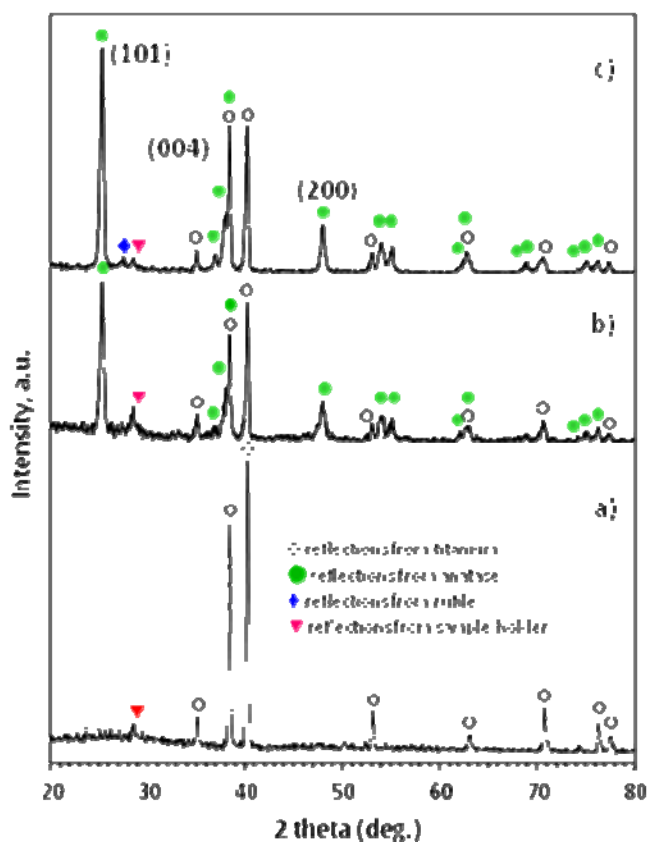


Figure 2: Glancing angle x-ray diffraction patterns of the TNT membrane a) as-prepared, b) after thermal treatment at 450 °C and c) at 500 °C, for 3 h.

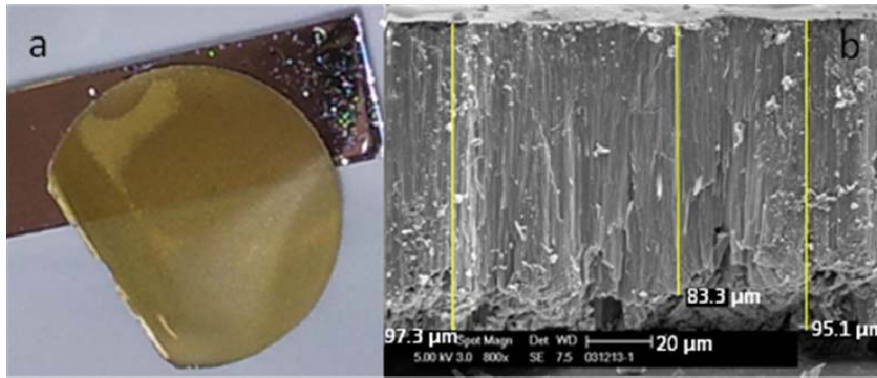


Figure 3. Photograph of a TNT membrane a) after the AO preparation and b) the corresponding FESEM image.

The cross-section of the membrane is shown in 4e and, finally, the 4f image reports a particular of the bottom side of the membrane, which is the layer previously attached to the metallic Ti substrate. Upon closer examination of the SEM micrographs, it is found that the morphology of the top surface is slightly different from that of the bottom where the tube wall is thicker. Moreover, reducing the time of the extra electric pulse used to detach the membrane from the metal support and analyzing the bottom of the TNT membrane so obtained, the bottoms of the nanotubes are closed. To open them it is necessary prolonging the time of the extra pulse (see details reported in Figure 5 in which the opening of the tube bottom is starting and Figure 4f where the tubes are fully opened).

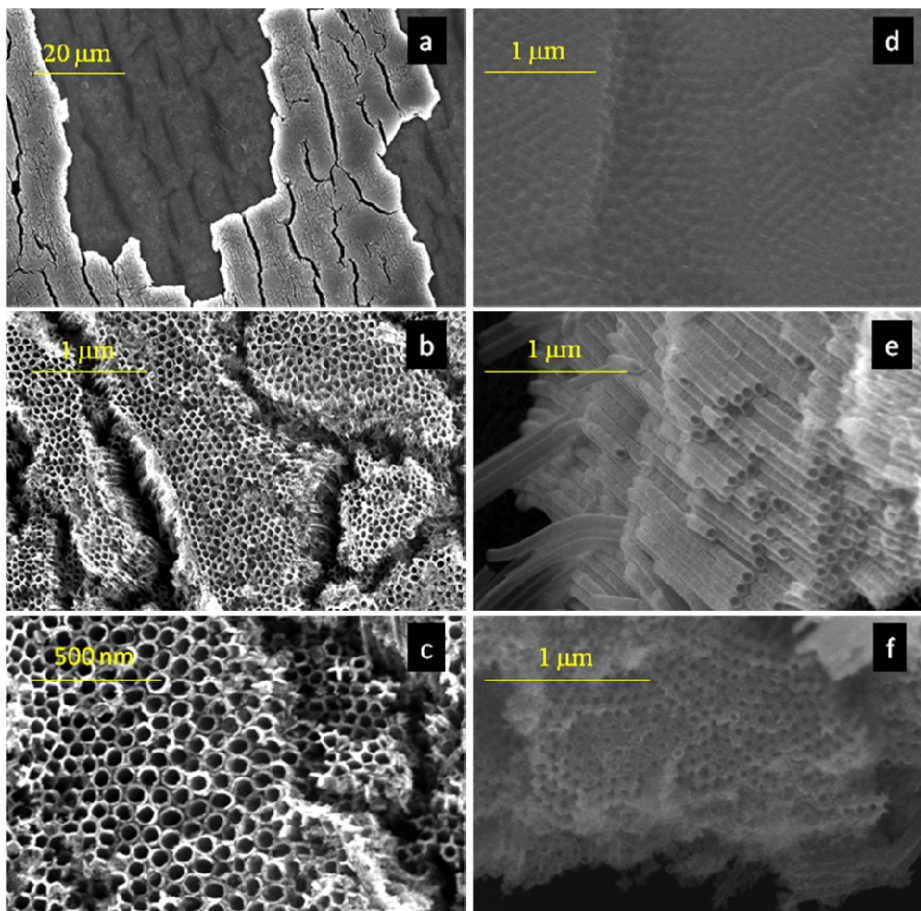


Figure 4. FESEM micrographs at different times during the anodization procedure for the preparation of TNT self-standing membranes.

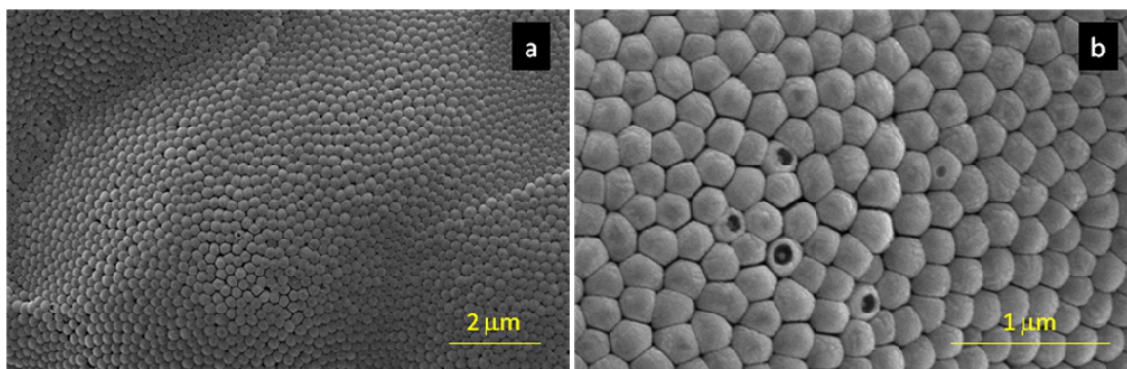


Figure 5. FESEM micrographs of the bottom of the TNT membrane detached from the metallic substrate by an extra potential pulse of different durations: a) short and b) long to highlight that the opening of the nanotube bottom is starting.

To reduce effectively the defects on the TNT surface, the Ti foil was pre-anodized in 0.3 wt % NH_4F ethylene glycol solution at 50 V for 2 hour and this first TNT layer was then peeled-off. Subsequently, the textured Ti substrate was anodized for the second time at a lower temperature thus reducing the formation of defects. At the end of the second AO step, the membrane was thermal treated at low temperature 200°C for 3 h with heating and cooling rates of 1 °C/min to have a more robust layer. The bottom of the tubes thermal treated at low temperature is amorphous and it can be penetrated during the successive third AO step. Afterwards, the third AO step was performed in the same condition of the second step but at room temperature. At the end, the detachment of the membrane layer could be obtained by bland etching in 1M HCl solution or, to avoid the use of environmentally unfriendly corrosive etching solutions, by a large anodic voltage pulse ($V_p = V_a + 60$ Volts) for a short time, typically 30 seconds. The third AO step was performed at higher temperature to favour the detachment of the TNT layer, which is more defective. Finally, a high thermal treatment allowed to obtain a more robust TNT membrane. Another characteristic of the obtained TNT membrane is the presence of numerous connections on the wall of the nanotubes that link the TNTs each to other (see details of a TNT membrane in Figure 6).

Structuring the surface of titania in terms of arrays of nanotubes can be viewed as an ensemble of micro-confined reactors, which may ideally enhance the process performances due to the high positive effect of confinement within the catalytic microspaces. In order to develop this idea and exploiting the narrow distribution of diffusion paths along the channels for multi-site catalytic reactions, preliminary permeation tests were performed using a dye molecule methylene blu (MB). By filling MB in one side of a double-chamber reactor and distilled water in the other side, we observed that after about 22 h in the dark the MB was equally distributed in the two compartments of the reactor by passing through the TNT membrane, thus equilibrating the concentration gradient of the dye.

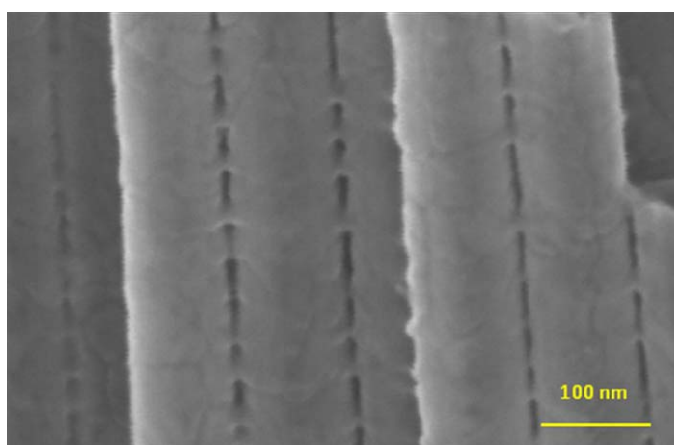


Figure 6. FESEM micrograph of a TNT membrane which shows the connections between adjacent nanotubes.

4. Conclusions

In the present work, free-standing membranes of well-ordered vertically aligned TNTs with both the ends open were fabricated. The high-quality of the membranes described here was obtained with facile and reliable procedures that occurred through a three-step anodic oxidation technique. By controlling accurately the synthetic parameters during each step, it was possible to tailor the desired nanoarchitecture of the self-standing TNT membranes, depending on the catalytic application of the TiO₂ layers. In particular, we followed the different AO steps by sequential SEM images, in order to understand the mechanism of formation of the self-standing TNT membranes. These one-dimensional nanostructures exhibit unique properties because of their special geometry, high surface area and aspect ratio. They are very versatile and further modifications of the membranes by incorporating metal/metal oxide nanoparticles are also possible. Therefore the capability of structuring the TiO₂ surface and tuning the hierarchical structure of the material, opens new perspectives for both a sustainable chemical production and to implement materials for energy conversion and storage, i.e. from water photo-electrolysis and photo-reforming of waste organics to CO₂ conversion processes to liquid fuels (Genovese et al., 2013b).

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