

# Titania Nanotubes for Separation Applications

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## ABSTRACT

We synthesized titania nanotubes arrays in the form of powders and membranes by a cheap, simple and easily scalable anodization method. The nanotubes powders can be compacted inside steel high-performance liquid chromatography (HPLC) columns, or sintered to produce filtration pellets. Furthermore, we were able to successfully functionalize both types of materials described above with ligands such as C18, as a proof of concept regarding possible application in custom tailored filtration needs. Preliminary water-oil filtration experiments show good promise for such applications.

**Keywords:** titania nanotubes, filtration, HPLC

## 1 INTRODUCTION

Titanium oxide (or titania) is an abundant, cheap material, a biocompatible semiconductor with a large bandgap which has multiple uses ranging from white pigments and UV absorber (sunscreens) to photocatalytic and photovoltaic applications. The relatively recent synthesis of nanoporous and nanotubular titania by an inexpensive anodization method tremendously expanded the applications range for this material, especially enhancing the photovoltaic and photocatalytic efficiency by increasing the active surface area by several orders of magnitude. In this work we will focus on the possible application of such nanomaterials in filtration and water treatment.

## 2 TITANIA NANOTUBES SYNTHESIS

After demonstrating for the first time the possibility of nanotubes formations in chloride ions containing solutions [1], our laboratory gained over seven years of experience in producing such nanomaterials by anodization of titanium foil both in fluoride or chloride ions containing solutions, with a good control over the morphological parameters [1-3]. Depending on the anodization conditions, the nanotubes can be synthesized either as powders consisting of micrometer sized bundles of tubes (each tube having a diameter of the order of 25 nm), or as ordered arrays of quasi-hexagonally aligned tubes (which can be connected to the original titanium foil, but also freestanding – square centimeters sized membranes up to hundreds of microns thick).

## 2.1 Nanotubes powders

DC anodization of titanium foil in chloride-ions containing acidic aqueous solutions (figure 1a) results in the rapid formation of titania nanotubes bundles 1-100  $\mu\text{m}$  long and several microns wide. These grains are continuously released in the solution, forming in time a white precipitate (figure 1b) which can be later recovered, washed and dried to a white titania powder (figure 1c) consisting of micron sized uniquely nanostructured grains (see figure 2).

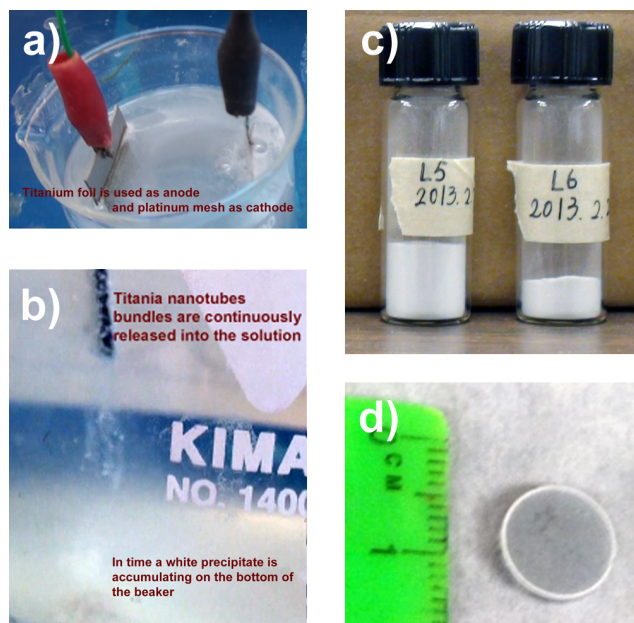


Figure 1: From titanium foil to titanium oxide nanostructured pellets. a) Lab scale anodization setup; b) Nanotubes formation at the anode site; c) Resulted titania powder; d) Pelletized powder (1 cm diameter)

We investigated the optimization of the anodization conditions for the efficient synthesis of large quantity of nanotubes powders. By varying parameters such as chloride ions concentration (0.1-0.5 M), anodization voltage (10-20 V) and pH (1.8-3), we studied their influence on the yield of the final powders. All other conditions such as titanium foil size, distance between anode and cathode, anodization time were kept constant. The yield was estimated in three different ways: by weighing the titanium foil before and after anodization), by weighing the final powder, and by recording the average anodization current which is related to the nanotubes formation rate. Efficiency of titanium to titanium oxide conversion was also calculated as a molar percentage ratio.

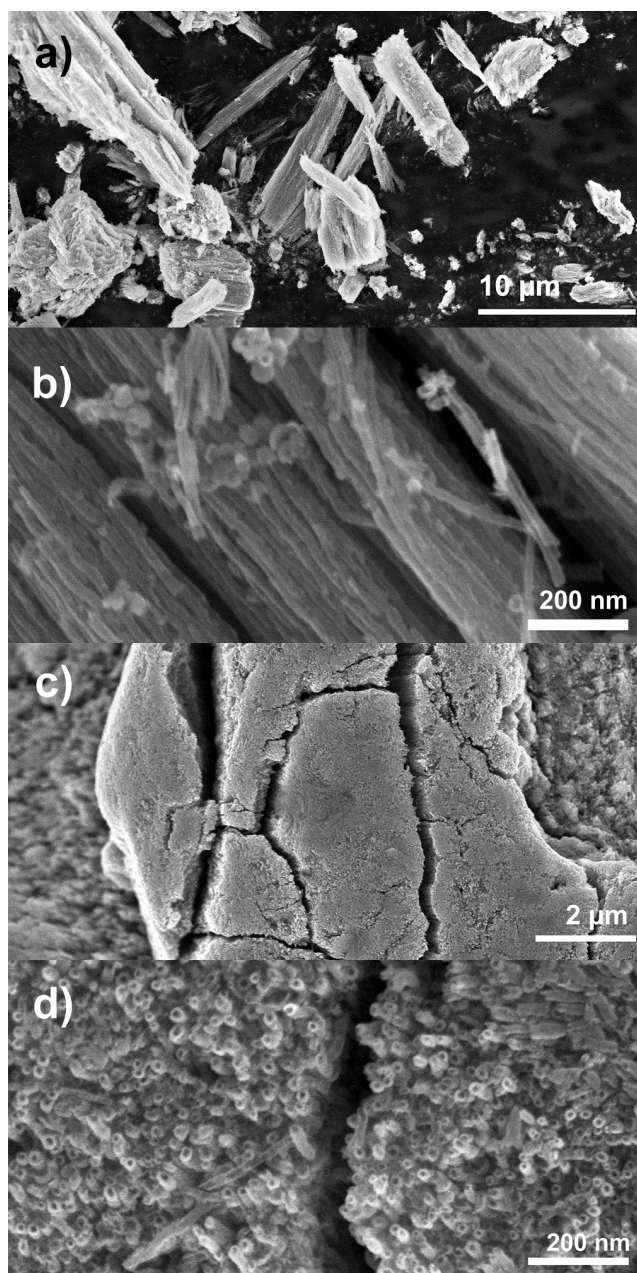


Figure 2: a) SEM images of powder grains several microns in size; b) Higher magnification side view revealing the nanomorphology of a grain – 25 nm diameter tubes tightly bundled; c) Top view of such a bundle; d) Higher magnification of an area from the previous image, again revealing the nanotubular structure.

We discovered that the formation rate is increasing with increasing voltage, chloride ions concentration and decreasing pH (figure 3). However, there is a limitation given by the fact that high anodization currents (associated with ultra-fast formation of nanotubes) result in the heating of the solution and violent bubbling at the cathode, thus destabilizing the anodization process. Such phenomena have been observed for voltages above 16 V and chloride concentrations above 0.2 M.

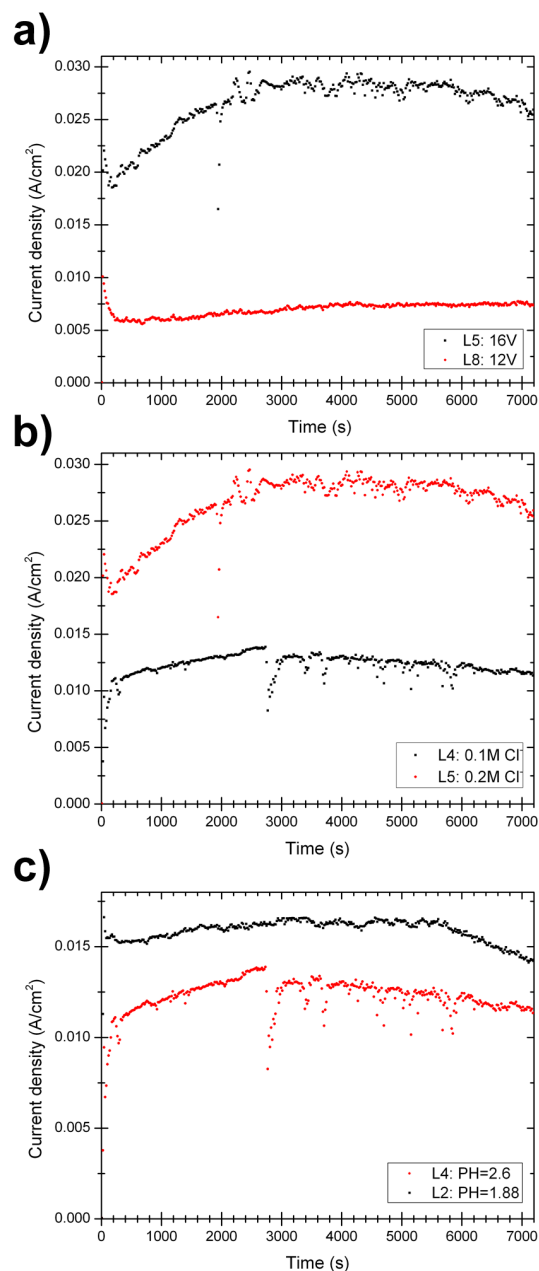


Figure 3: Variation of the anodization current over 2 hours for a) Different voltages; b) Different chloride ions concentrations; c) Different solution pH.

This imposes a limitation on the anodization parameters. For our lab scale experiment (12 cm<sup>2</sup> samples in 250 ml solution anodized for 2 hours) we identified concentrations of 0.1-0.2 M, a pH below 2 and a voltage of around 16V to be the optimal conditions for the fast synthesis of titania nanotubes powders. This resulted in powder yield rates approaching 1g/hour, for a process which can be easily scalable to industrial size, and a further scaling up of the synthesis in our lab is already in progress.

The titanium to titanium oxide molar percentage conversion ratio was above 70% for the optimal conditions.



However, due to the losses of powder during repeated washing and centrifuging, losses which are bigger in percentage as the initial mass is smaller, we cannot yet draw pertinent conclusions out of the efficiency calculations. More efficient powder recovery methods such as self-filtration should significantly increase the overall conversion efficiency. Also, it is well known that the as anodized nanotubes are somewhat deficient in oxygen, thus the molar mass ratio of titanium to titania is bigger than 48:70 in this case.

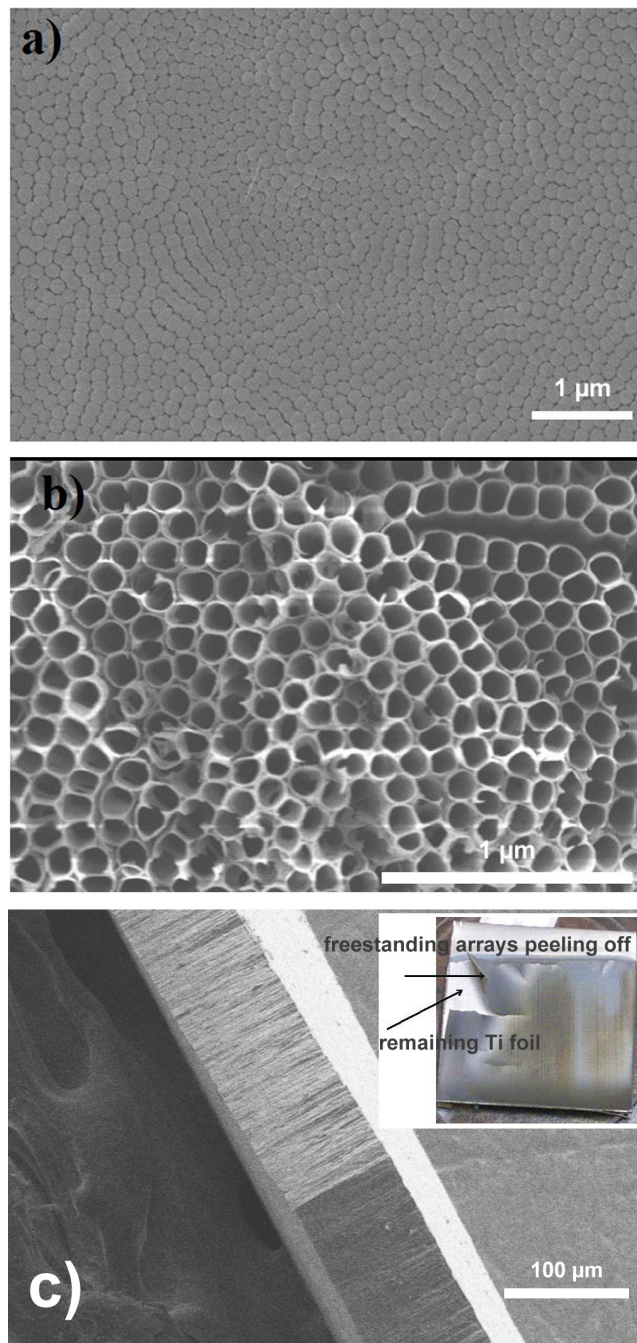


Figure 4: Freestanding titania nanotubes arrays a) Bottom view; b) Top view; c) Side view (inset shows a digital picture of the membrane peeling off the titanium foil).

## 2.2 Nanotubes freestanding membranes

Another possibility for creating titania nanotubes based membranes is by synthesizing freestanding arrays having a flat surface area of the order of few square centimeters and with a thickness (corresponding to the length of the nanotubes) of tens of microns (figure 4). Such structures are synthesized by anodization in fluoride-ions containing non-aqueous (for example ethylene glycol based) solutions, at DC voltages between 30 and 75V. The anodization voltage controls the average diameter of the nanotubes, while the anodization time is the parameter controlling the thickness of the final membrane. When the amount of water in the solution is below 2%, the contact between the titania nanotubes arrays and the remaining titanium foil becomes very loose, making it easy to peel off upon drying once the anodization is stopped. Photo-activated liquid filtration and pollutants mineralization has been already demonstrated for such membranes [4], and applications similar to those of currently available alumina nanoporous membranes are envisioned. Titanium oxide is having the advantage of being non-toxic, naturally anti-bacterial, so it can be readily used in water purification.

## 3 NANOTUBES FUNCTIONALIZATION

We tested the possibility of sensitizing the titania nanotubes with various ligands for custom filtration or chromatography application. We particularly studied the bonding of octadecyl (C18), a compound commonly used as functionalizing agent in HPLC.

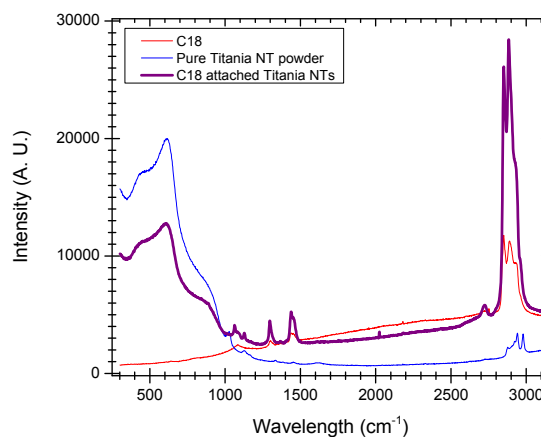


Figure 5: RAMAN spectra of a sample of titania nanotubes powder after C18 ligand was attached (in violet). A pure titania nanotubes powder spectrum (in blue) and correspondingly pure C18 spectrum (in red) were also recorded for comparison.

Titania nanotubes produced by either of the two DC anodization methods described in the previous section were

immersed for 5-10 minutes in a 90:6:4 methanol/water/C18 solution, and then repeatedly washed with methanol and subsequently dried back at around 60°C. Alternatively, during the C18 exposure, the samples were sonicated for a more vigorous interaction.

After drying the samples, a RAMAN analysis was performed on the powders. Figure 5 is presenting a characteristic spectrum, compared with references of pure titania nanotubes powder and pure C18 respectively. While maintaining the three peaks at around 450, 610 and 830  $\text{cm}^{-1}$  specific to amorphous titania, the C18 treated powders also exhibited clear peaks at around 1300, 1440, 2720, 2850 and 2885 (with a shoulder at around 2925)  $\text{cm}^{-1}$  specific to C18. The pure titania are exhibiting (as expected) some carbon-specific signal themselves, because of well documented carbon surface contamination. However, the position and the ratio of the 610  $\text{cm}^{-1}$  peak to the 2700-3000  $\text{cm}^{-1}$  peaks demonstrate that (a significant amount of) C18 indeed bonded to the samples.

#### 4 NANOTUBES BASED PELLETS AND FILTRATION EXPERIMENTS

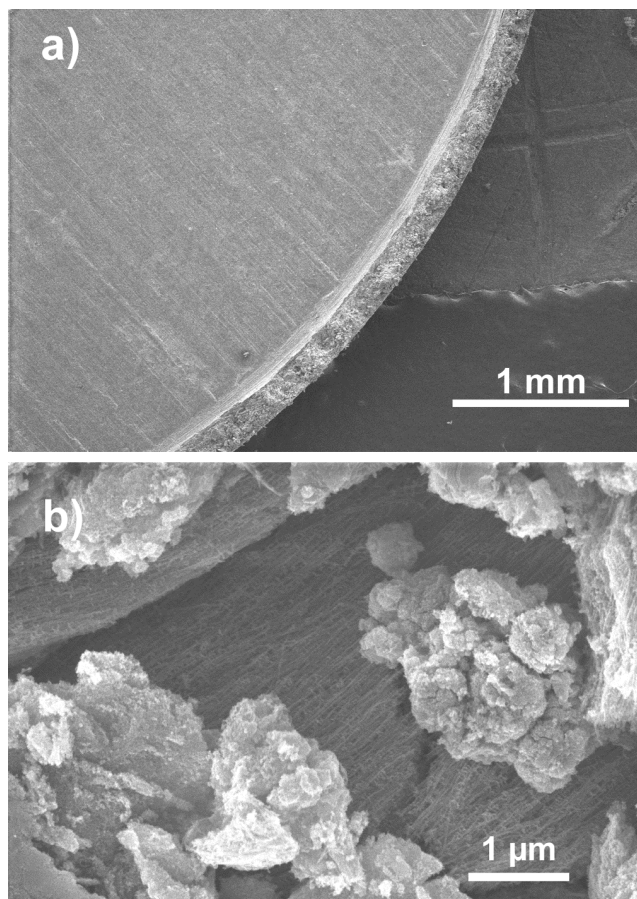


Figure 6: SEM image of a pellet made of titania nanotubes bundles. a) Low magnification image presenting the flattened surface and a thin indentation on the edges; b) High magnification image demonstrating that the grains didn't lose the nanotubular morphology after compression

Titania nanotubes powders produced as described in section 2.1 were subsequently pelletized using a hydraulic manual press under pressures up to 5000 psi (~35 MPa). The porosity of the 1 cm diameter and 1-3 mm thickness pellets that we obtained (figure 1d) was calculated to be about 40% of the single crystal anatase. SEM imaging (figure 6) revealed that the grains can withstand such pressure without being crushed, thus maintaining the nanotubular morphology. Subsequent sintering can be performed if better durability is needed [5].

Preliminary experiments performed with the as is pellets employed in a simple filtration setup showed permeability to water for trans membrane pressure (TMP) below 1 atm, and resistance to kerosene. The membrane clogged after a few water-kerosene cycles, but this should happen much harder in a crossflow setup.

The intrinsic nanomorphology of the powders and nanoporosity of the membranes offers higher active surface area, and should translate into higher permeability of the membrane (higher flowing rate) without affecting the filtration efficiency. Other advantages of the material include better resistance and robustness in high temperature or highly acidic media.

#### 5 CONCLUSION

We demonstrated the possibility of large scale production of titania nanotubes based powders by a simple anodization method. Furthermore, the powders can be compacted (and, optionally, sintered) into millimeter thick pellets which can be employed as filtration membranes. Alternatively, membranes consisting of vertically aligned, quasi-hexagonally ordered titania nanotubes arrays have been produced, and good control over tubes diameter and length has been achieved. Functionalization of such materials with specific ligands such as C18 has been demonstrated. Experiments are in progress for employment of the membranes, either separated or combined, in crossflow filtration setups for water treatment and water-oil separation tests. Experiments involving titania nanotubes powders compacted into steel HPLC columns are also envisioned.

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