

## Hydrothermal Synthesis of Nanostructured Titania

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**Abstract.** Titania ceramics have many applications due to its surface properties and, recently, its nanostructured compounds, prepared by hydrothermal treatments, have been described to improve these properties. In this work, commercial titanium dioxide was treated with 10% sodium hydroxide solution in a pressurized reactor at 150°C for 24 hours under vigorous stirring and then washed following two different procedures. The first one consisted of washing with water and ethanol and the second with water and hydrochloric acid solution (1%). Resulting powders were characterized by X-ray diffraction, N<sub>2</sub> gas adsorption and field emission gun scanning and transmission electronic microscopy. Results showed that from an original starting material with mainly rutile phase, both anatase and H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> phase could be identified after the hydrothermal treatment. Surface area of powders presented a notable increase of one order of magnitude and micrographs showed a rearrangement on the microstructure of powders.

### Introduction

Titanium dioxide (titania) has been extensively investigated for a variety of applications such as photocatalysis, solar cells, environmental purification process, electroluminescent devices, biocompatible layers in bone implants and others[1]. These properties arise from the peculiar surface properties of titania and structures with nanometer dimensions that are decisive factors to improve the properties of powders or ceramics. In fact, as the most properties of solids depend on its microstructure, a drastic reduction on the particle dimensions will cause a variation of physical and chemical properties of the bulk material. Generally, it is accepted that materials with grain dimensions less than 100 nm are called nanostructured materials[2]. Thus, titania nanoscaled materials as nanopowders, nanotubes, nanowires and nanorods are object of a great number of investigations[3,4].

In the case of titania nanotubes (TNT), fabrication process comprises the assisted template-method, sol-gel process, electrochemical anodic oxidation and hydrothermal treatment. These processes have advantages and drawbacks. In this work the hydrothermal treatment in highly alkaline media was chosen due to its simplicity, low cost and effectiveness. This process was first reported by Kasuga et al [5], using TiO<sub>2</sub>-SiO<sub>2</sub> powders and a sol-gel method that was modified in a later work [6] to a hydrothermal treatment of TiO<sub>2</sub> in aqueous solution media of 5-10 M NaOH for 20h at 110°C. They concluded that TNT with anatase symmetry are formed when this procedure is followed by treatment with HCl aqueous solution and distilled water. Using the same process, other authors [7] proposed that nanotubes are formed without HCl washing step and that the crystalline structure do not agree with neither anatase or rutile phase of TiO<sub>2</sub>. TNT formation mechanism and its crystalline structure are still matter of discussion. Zhang et al [8] prepared nanotubes with a 40% w/w NaOH solution in a teflon vessel refluxed in a oil bath at 100°C for 20 h and proposed the formation of H<sub>2</sub>T<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> and Na<sub>2</sub>Ti<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub>, where Ti bonds are broken by the action of OH<sup>-</sup> ions rearranges in a form of a flexible and planar fragments of (-Ti-O-Ti-O-) that can form the

nanotubes. Some other authors proposed a similar formation mechanism for the TNT and structures as anatase [9,10,11] or hydrogen trititanate ( $H_2Ti_3O_7$ ). [4, 12]

In this work the process for the preparation of TNT from commercial titanium oxide using hydrothermal treatment in 10 M NaOH solution was carried out and some physical and chemical properties of the synthesized material are characterized.

### Experimental procedures

Starting materials were PA grade titanium oxide ( $TiO_2$  or titania) from CAAL, Brazil and sodium hydroxide from Nuclear, Brazil. The experiment was conducted in a Parr 4566 pressure reactor with a teflon vessel.  $TiO_2$  powder (05 grams) was mixed with 100 ml of 10M sodium hydroxide aqueous solution in the vessel that was coupled to the equipment. Temperature was raised to  $150^\circ C$ , promoting an autogenously pressure rise to 30 PSI and these conditions was kept for 24 hours under agitation. Obtained solids were separated from the mother liquor, washed with water and divided in two samples. One of them were treated with 0,1 N hydrochloric acid solution and the other sample treated with PA grade absolute Ethyl Alcohol (99% EtOH – CAAL Brazil). Characterizations were done in three samples as shown in Table 01.

Table 01. Sample codification

Sample	Code
Commercial titania	$TiO_2$ com
TNT treated with HCl	TNT-HCl
TNT treated with EtOH	TNT-EtOH

Specific surface area values of samples were determined by a  $N_2$  gas adsorption BET method (Quantachrome - Nova 1200), crystalline structures were determined by X-ray diffraction (Rigaku - DMAX 3000) and microstructure were observed by Field Emission Gun Scanning Electron Microscopy (JEOL - JSM 6710F) and a Transmission Electron Microscopy (JEOL - JEM 2100).

### Results and Discussions

The conversion rate of commercial  $TiO_2$  to TNT are very high in the conditions employed in this work. This evaluation was based on visual observation of the original raw material particles remaining in the processed materials.

The expressive increase in the specific surface area of TNT, when compared to the original commercial  $TiO_2$  (Table 02) is a clear evidence of a rearrangement of the rutile structure. Surface area values for TNT washed with HCl and EtOH are also quite different between them. This result is consequence of high concentration of  $Na^+$  ion in TNT samples, even after washing with water. EtOH treatment withdraws water molecules adsorbed on the TNT structure, but keeps the  $Na^+$  ion and this is believed to increase the specific surface area, despite the reduction of thermal stability. Acid washing exchanges  $Na^+$  ion by  $H^+$  ions and causes an early collapse of tube structure and reduces surface area [3,13].

Table 02. Specific surface area of commercial titania and synthesized TNT samples

Sample	Surface area ( $m^2.g^{-1}$ )
$TiO_2$ com	24.9
TNT-HCl	257.2
TNT-EtOH	164.7

X-ray diffraction pattern of samples (Fig. 01) are compared to strongest reflections of anatase, rutile and hydrogen trititanate ( $H_2Ti_3O_7$ ), corresponding to PDF files 86-1157, 77-0446 and 47-0561, respectively. Commercial  $TiO_2$  is essentially composed by anatase phase, the diffraction profile for the TNT structure has only four well defined peaks in the studied range (05-80 degrees) and detected reflections does not match with rutile pattern and has some peak coincidence with the anatase profile but keeps major similarity with trititanate pattern. The peak height for 29.8 degrees reflection for the HCl washed TNT are smaller when compared to EtOH washed TNT. This is a result of the ion exchange capacity of TNT and can be attributed to the substitution of  $Na^+$  by  $H^+$  ions. Small height and broad width of TNT peaks could be interpreted as poor crystallinity but in fact is an evidence of preferential orientation.

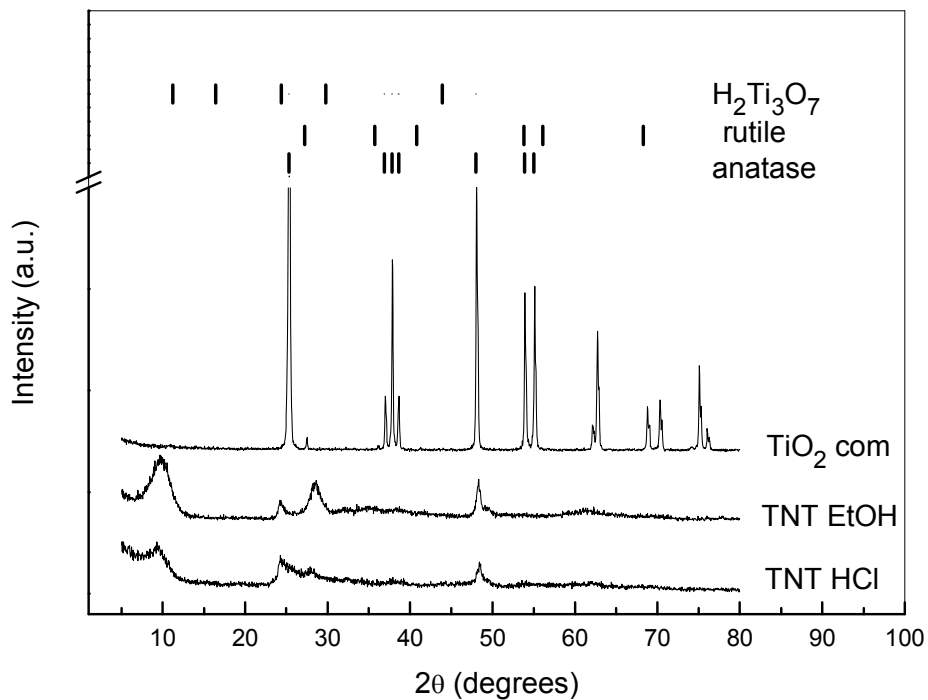


Figure 01. XRD diffraction pattern of commercial titania and synthesized TNT samples.

FEG-SEM micrographs of TNT are shown in Fig.02. Nanotubes are randomly distributed, the diameters are mainly about 20 nm, though some are as thick as 50 nm and lengths are in the range of tens to hundreds nanometers, showing structures with high aspect ratio. Micrographs (a) and (b) are related to samples treated with HCl and (c) and (d) refers to those treated with EtOH. There is no significant difference between them, but the last samples seem to be a little more damaged. Higher magnification (Fig.2d) shows that the ends of tubes are closed and, along its sides, surfaces are not smooth, showing some wrinkled structures.

The structure modification can be seen from the sequence of TEM micrographs. Fig.03a shows a typical micrograph of original commercial  $TiO_2$  with large rounded particles. Micrograph of TNT washed with HCl and EtOH are shown in Fig.3b and Fig.3c, respectively. From these images, nanotube dimensions can be estimated more precisely and diameter is about 10 nm. Moreover the tubular nature and crystalline structure of samples becomes evident.

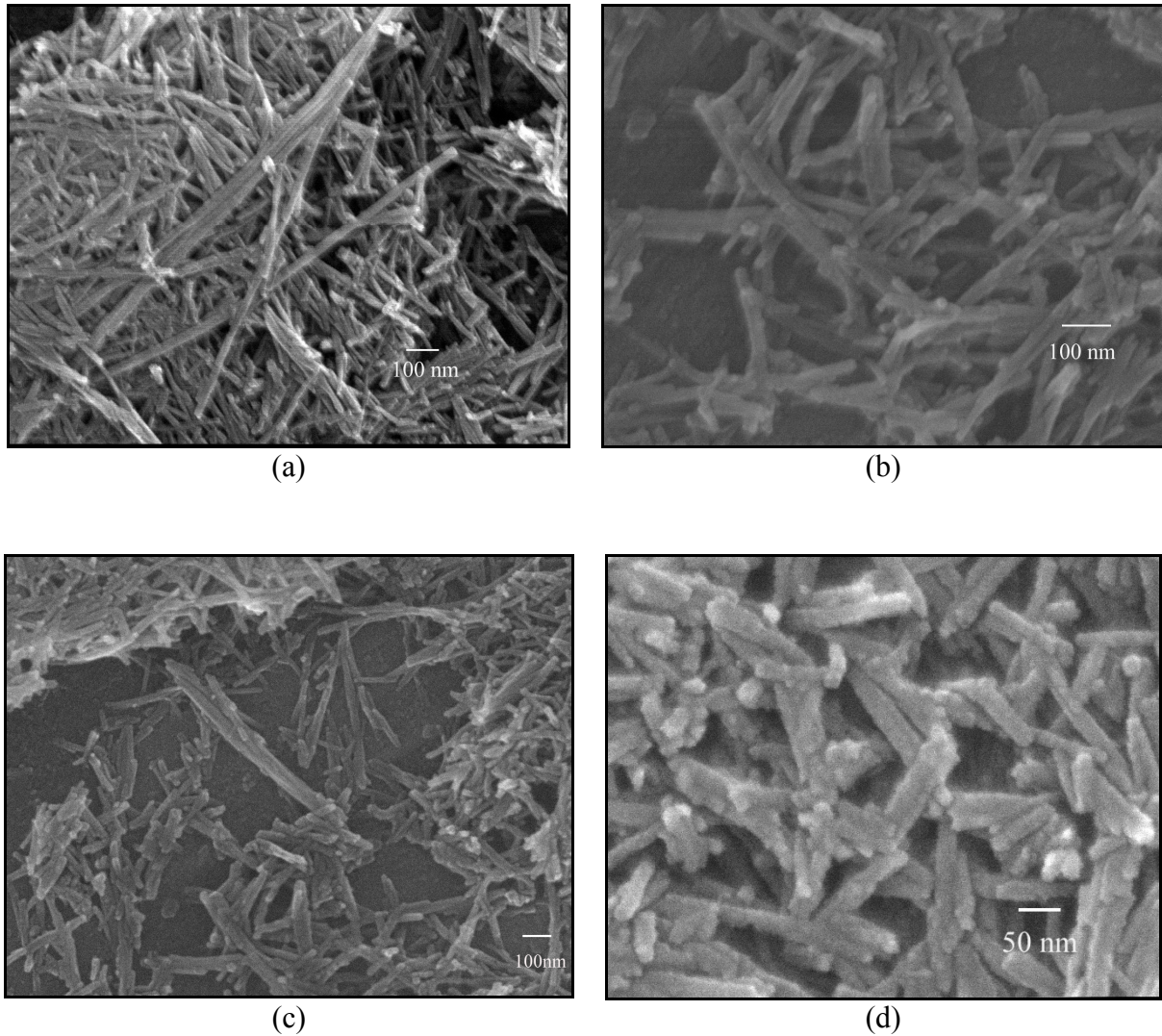


Figure 02. FEG-SEM micrographs of TNT after HCl washing (a) and (b); and after EtOH washing (c) and (d).

It was supposed that the small dimensions of TNT and its random distribution on the samples could show a polycrystalline response on DRX profile, but actual pattern shows a preferentially oriented structure. This can be attributed to the high aspect ratio and the strongly oriented structure of nanotubes. Some authors [8], assuming the nanotubes are formed by  $H_2Ti_3O_7$  layers, concluded that it grows along the [010] direction.

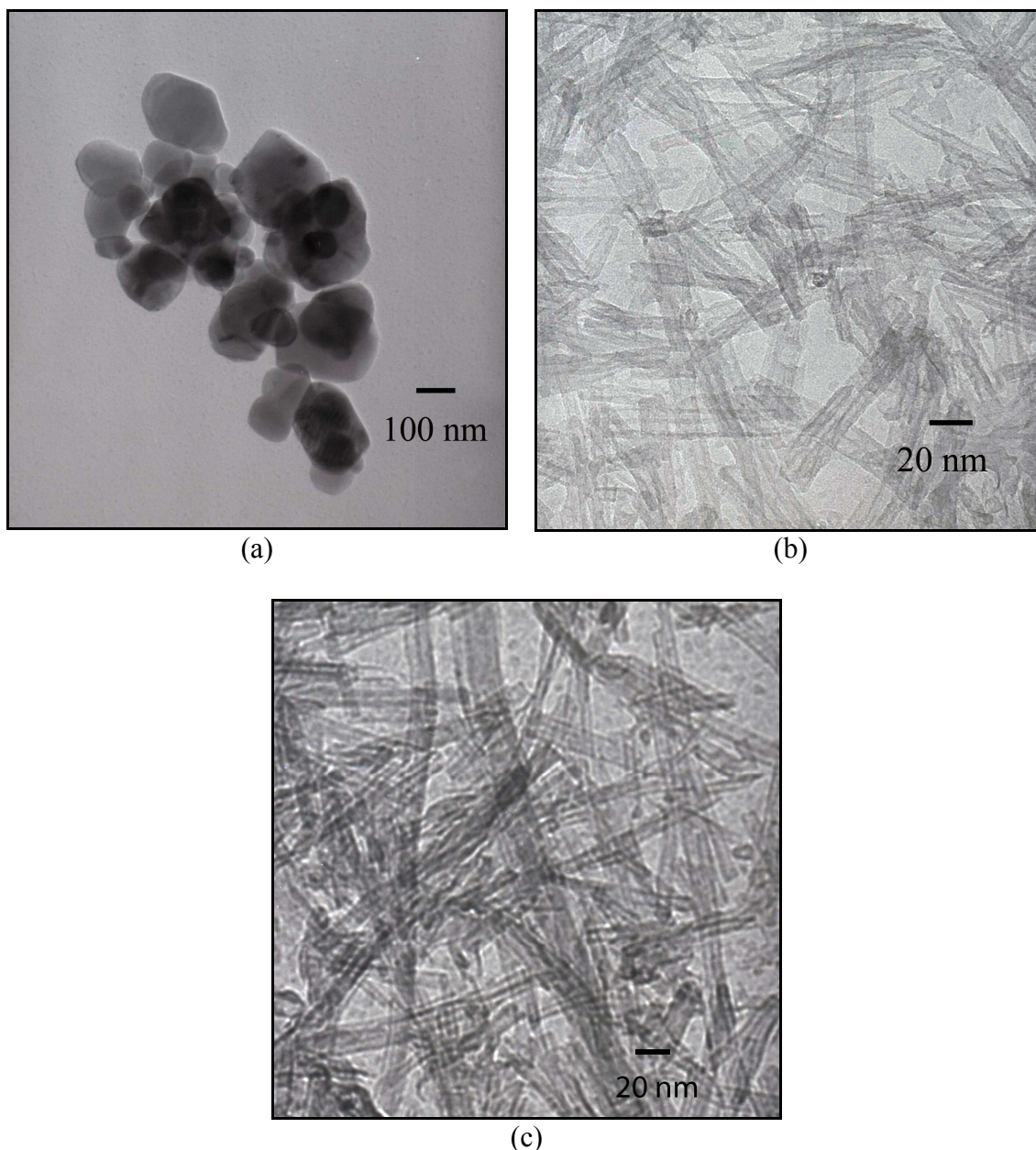


Figure 3. TEM micrographs of commercial TiO<sub>2</sub> powder (a); TNT after HCl (b) and EtOH (c) washing.

## Conclusions

Hydrothermal synthesis of nanostructured titania in 10% aqueous sodium hydroxide solution resulted in titania nanotubes. Reaction conversion rate is very high, and no clear difference in microstructure was visible from materials washed with HCl solution or ethanol but specific surface area values and XRD profiles indicated that spatial arrangement is affected. materials. Crystalline structure has similarity with H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> (hydrogen trititanate) and anatase, despite the discrepancies of peak equivalence with both phases. Nanotubes reduced dimensions and random distribution indicates that it could have a polycrystalline response on XRD, but in fact it shows preferentially orientated structure, caused by its high aspect ratio and orientation.

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