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Characterization of titanate nanotubes for energy applications

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ABSTRACT

In this work we present the synthesis and full structural characterization of hydrothermally synthesized titanate nanotubes (TNTs) for energy applications. It is of interest to characterize the building block of certain nanomaterials and their surface termination. This task is particularly difficult for nanotubes, where the exhibited surface curvature is a limitation for its study. We present the synthesis and thorough structural characterization through several experimental techniques for morphology and compositional characterization. Simulated X-rays powder diffraction patterns (XRPD) of real size nanotubes models are refined with experimental data. The building blocks for the TNT models were obtained from computational simulations by means of Density Functional Theory for $H_2Ti_2O_5{\cdot}0.5H_2O$, $H_2Ti_2O_5{\cdot}H_2O$, $H_2Ti_3O_7$ and $H_2Ti_3O_7{\cdot}0.67H_2O$. Our procedure confirms that open-ended TNTs are obtained, with ~100 nm of length and 6(1) nm of inner diameter. By interpreting the XRPD data, the TNT building block was obtained and found to derive from $H_2Ti_3O_7$, where the distance between [TiO_6] octahedral layers is increased in accordance with $H_2Ti_3O_7{\cdot}0.67H_2O$. This model fully agrees with all the structural characterizations, validating this methodology and suggesting its potential use to study other nanomaterials.

1. Introduction

Since first synthesized by Kasuga *et al.* [1], titania and titanate nanotubes have been extensively researched given their novel properties and potential applications [2]. They have been characterized in terms of energy applications such as: ion-exchange properties, proton conductivity, photocatalytic properties [3], lithium transport [4] and photovoltaic behavior, showing promising results [2,5].Particularly given their high surface area, they are interesting for preparing photoelectrodes to dye sensitized solar cell applications (DSSC). Additionally, this TNT can be used for Li-ion applications such as anodes, and for the composite preparation of polymeric electrolytes.

Despite numerous efforts regarding the synthesis and characterization of titanium dioxide and titanates nanotubes, there is still an open debate about their composition and structural characterization [6], which are crucial to understand their physical properties and surface reactivity. The low periodicity and hence reduction of crystallinity along the radial direction of the high aspect ratio nanostructures increases the complexity of the X-ray powder diffraction (XRPD) pattern interpretation. This is why the XRPD only shows the eventual correspondence with closely related crystal structures, with no mention to the actual 2theta peak positions, relative intensities and broadening. The wrapping along certain crystallographic axes contributes to the broadening of the diffraction peaks associated to particular Bragg planes. In addition, other parameters could increase the complexity of these systems, such as the variable amount of hydration, size distribution and even the presence of secondary phases obtained by soft chemical methods as hydrothermal techniques. Furthermore, the products obtained after acid washing are protonic titanates in which the corresponding positions and crystalline occupations of hydrogen atoms cannot be resolved by conventional XRPD.

Structural characterization is crucial to understand the physical properties, for the eventually system engineering. The aim of this work is to contribute to the elucidation of crystal structure (building block) and geometrical parameters of TNTs by building real radial dimension tubes based on our experimental results and simulating their diffraction patterns. Previously, computational simulation was performed for bulk structural optimization,

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particularly for those crystalline structural phases that do not present experimental refined structures [7], or where the reported crystal structure does not match our experimental and theoretical models [8]. We believe this method helps determine potential solutions by generating models which better explain experimental data. Major efforts are necessary to develop a code that includes size and phase distributions as well as phase coexistence, to properly structure the refinement of nanotube powders.

All these reasons make it necessary to determine the chemical structure of a series of hydrogen titanate nanotubes, in order to understand their role in the physical and chemical properties in all the potential applications. In this work we will show how conventional XRPD can be used to determine the building block of these nanotubes, demonstrating how this tool can be used to characterize other similar nanosystems.

2. Experimental section

2.1. Synthesis of NTs and thermal treatments

Titanate nanotubes were synthesized via hydrothermal method using commercial TiO_2 anatase nanopowder (*ALDRICH, Titanium (IV) oxide, nanopowder, 99.7%, anatase, d < 25 nm*) as the precursor material. 1gr of TiO_2 was dispersed using ultrasonication on 60 mL of NaOH 10 M in a Teflon lined autoclave (total volume ~80 mL). The reactor was kept at 150–155 °C for 24hs without stirring and then air cooled to ambient temperature. The solid was separated through centrifugation, fractioned and then thoroughly washed with HCl 0.1 M and distilled water reaching a final pH ~4. Finally, the sample was dried at 50 °C, see the Supporting information for the complete washing procedure.

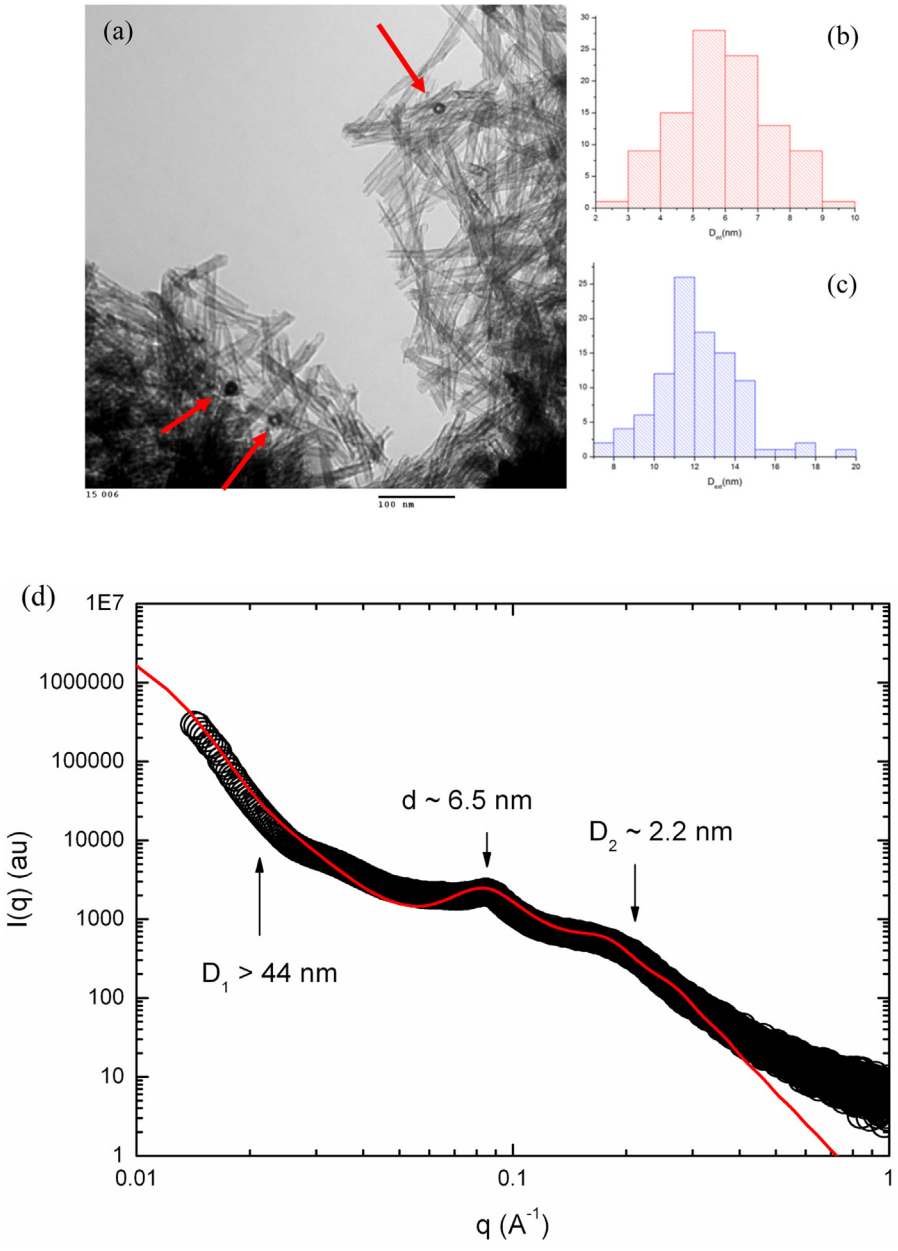

Fig. 1. (a) TEM image of prepared protonic titanate nanotubes, with (b) inner and (c) outer diameter distributions respectively. (d) The GI-SAXS data and Beaucage fitting for hydrogen titanate nanotubes, and the three main coherence distances are sketched.