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Influence of Synthetic Conditions in the Hydrothermal Preparation of TiO_2 Nanotubes

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Published: 4 December 2015

Abstract: TiO_2 nanotubes have been synthesized using a 2-step strategy that involves the hydrothermal preparation of intermediate titanates followed by a subsequent thermal/hydrothermal treatment of these species to produce the oxide. In the first step the influence of parameters such as temperature, pH or reaction time on the composition, structure and morphology of the intermediate species has been studied. Then we have examined how temperature and the presence of surfactants may affect the composition, structure, morphology and particle size of the titanium dioxide obtained in the second thermal/hydrothermal treatment. In particular, we have studied the effects that the presence of CTAB has upon the morphology of the final product. Both intermediate and final species have been studied by means of X-ray diffraction, transmission electron microscopy, IR spectroscopy and thermogravimetric analysis. This way we have been able to identify $NaTi_3O_6(OH).2H_2O$ and $(TiO_2)_x(H_2O)_y$ as the intermediate titanate species and rutile and anatase as the final TiO_2 polymorphs. Finally, it is worth mentioning the preparation of spindle- or oval-shaped anatase, obtained via hydrothermal synthesis in the presence of CTAB.

Keywords: TiO_2; hydrothermal synthesis; nanotube.

1. Introduction

Titanium dioxide exists as three polymorphs: anatase, rutile and brookite, and although rutile is the thermodinamically stable phase, in the nanoscale anatase becomes very stable too [1]. As a wide-band gap semiconductor, TiO_2 has been widely used in sunscreens, paints and tooth-pastes and, today, especially in photocatalysis [2]. For many of these applications, it is of great importance to maximize the specific surface to achieve a maximum efficiency. In particular, it has been found that in photocatalytic applications, nanotubes and nanorods -that is, 1D nanostructures- may allow for a much higher control of the chemical and physical behaviour [3]. Indeed, by diminishing dimensions to the nanoscale, not only the specific surface area increases significantly but also the electronic properties may change considerably [4].

1D titanium dioxide nanostructures may be obtained by various routes such as sol–gel, template-assisted methods, hydro/solvothermal synthesis or by electrochemical processes [5, 6]. Among them, hydrothermal synthesis has become a promising chemical strategy. This is usually a two-step route that involves, first, the generation of alkali titanate nanofibers by hydrothermal reaction in alkali solution followed by exchange of alkali ions with protons [7], and the subsequent thermal dehydration reactions at high temperature in air. Less frequently, hydrothermal reactions may also be performed to produce the final TiO_2 nanotubes or nanorods [8].1D morphology is already achieved in the first hydrothermal process when alkali titanates are formed, and it is based on the exfoliation of TiO_2 crystal planes in the alkali environment and then stabilization due to the insertion of Na^+ cations between the exfoliated planes. The formed nanolayer sheets are then rolled into tubes during cooling or in the acid treatment [9]. Finally, thermal treatments at 350-450 ºC tend to lead anatase, which seems to favour a faster electronic transport than the rutile phase [10].

Here, we present synthesis of TiO_2 1D nanostructures *via* a 2-step route. Initially, the influence of parameters such as temperature or reaction time on the composition, structure and morphology of the $NaTi_3O_6(OH).2H_2O$ and $(TiO_2)_x(H_2O)_y$ intermediate titanates has been studied. Then, we have examined how temperature can affect the final TiO_2 rutile/anatasa composition in the dehydration process. Finally, we have performed an alternatively hydrothermal route starting from Na-titanate phase in the presence of the CTAB surfactant at different pH values. This way, a spindle- or oval-shaped anatase product was obtained.

2. Results and Discussion

Hydrothermal syntheses were carried out in order to study the influence of temperature and reaction time. Thus, synthesis at 200 ºC for 6, 24 and 48 h were performed. Nanotubes start to appear after 6 h of hydrothermal heating, but the reaction was not complete and crystallinity of the product was low. The products obtained after 24 and 48 h were very similar, both in composition and degree of crystallinity. Syntheses at 170ºC were performed during 24 h but low crystallinity was obtained again. For this reason, the syntheses were carried out at 200 ºC for 48 h (6 sample).

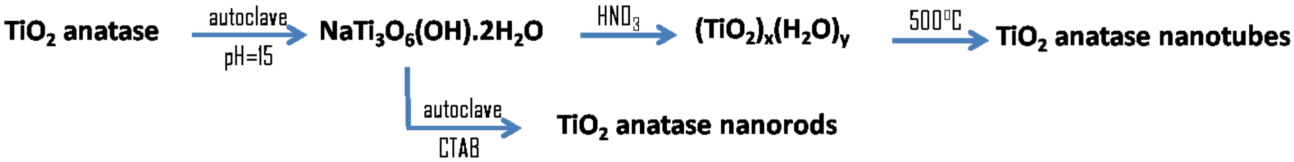
XRD patterns of the most representative as synthesized titanates shown in Fig. 1 indicate the presence of $NaTi_3O_6(OH).2(H_2O)$ [11] and $(TiO_2)_x(H_2O)_y$ [12] phases before and after HNO_3 treatment, respectively. Subsequent thermal treatment in air at 400-500°C leads to the formation of anatase and rutile TiO_2 phases (JCPDF 21-1272 and JCPDF 21-1276) together with some $NaTi_8O_{13}$ (JCPDF 48-0523) impurities. At the same time, after the second hydrothermal treatment anatase phase was also obtained.

Thermogravimetric analysis of titanate samples shows mass losses of about 20 and 15%

in good agreement with the presence of H_2O and some Na_2CO_3 (formed in the basic conditions due to absorption of atmospheric CO_2 [13]) in Na-titanate samples and only H_2O in H-titanate ones. This was confirmed by IR spectroscopy (Figure 2).

TEM images of some representative samples are shown in Figure 3. Nanotubes were already formed in the first hydrothermal step and neither the acidic nor the thermal nor the hydrothermal processes alter significantly the morphology of the samples. Both Na- and H-titanate samples are very similar, 40-80 nm wide, although they widen to 70-170 nm after thermal or hydrothermal treatments when deintercalation and dehydration take place and lead to TiO_2. HTEM images of titanates shown in Figure 3 reveal lattice fringes with plane spacings of about 11 Å and 10 Å corresponding to the interlayer distances in the 2D crystal structures of $NaTi_3O_6(OH).2(H_2O)$ and $(TiO_2)_x(H_2O)_y$. Both of them exhibit similar crystal structures with packed planes formed by titanium oxide octahedra and Na^+, OH^- H^+ and H_2O as inserted species between them [11, 12].

Some authors suggest that the mechanism of formation of the tube shape is based on a topochemical process of exfoliation of TiO_2 crystal planes in the alkali medium [14], after which nanolayer sheets start rolling into tubes during cooling. Na^+ ions are then exchanged by H^+ ions by washing products in acid solutions to form layered hydrogen titanate, from $Na_{2-x}H_xTi_3O_7.2H_2O$ to $H_2Ti_3O_7.yH_2O$ [15, 16, 17]. Finally, the H-titanate transforms into anatase through a dehydration reaction. This is accompanied by an *in situ* rearrangement of the structural units to give 1D TiO_2 nanostructures [8]. In this work, not only traditional heat treatments of H-titanates to obtain anatase TiO_2 nanotubes, but also hydrothermal treatments of Na-titanates in presence of CTAB as surfactant at different pH values were performed. Heating at 400ºC and 500ºC in air led to the formation of anatase and anatase/rutile nanotubes, respectively, about 70-170 nm wide and without significant morphological changes. However, some impurities of $NaTi_8O_{13}$ oxide were also found in XRD, indicating that the exchange of Na^+ ions was not completely achieved. At the same time, hydrothermal processes led to the formation of anatase as the main phase but the morphology of the products was found to be slightly altered depending on pH. Thus, the synthesis at pH=2 led to obtain anatase porous nanotubes, very similar in thickness and morphology to their precursors, but a considerable amount of intermediate titanate remained unaltered. The non-acidified synthesis (pH=8.5) led to a purer and more crystalline product. It seems that CTAB in a slight alkali environtment favoured the extraction of Na^+ ions previous to the stacking of the TiO_2 layers, as thicker and denser nanostructures of 70-170 nm were found. It is possible that the CTAB surfactant made the exfoliation and later rearrangement of oxide layers in Na-titanates easier than in H-titanates, as H^+ could be more strongly bounded to the TiO_6 octahedra. The morphology also changed. Oval- or spindle-shaped anatase was obtained suggesting a non-uniform stacking mechanism. Both hydrothermally synthesized samples did, however show similar microstructures formed by aggregated nanofibres, although these were more densely stacked in the oval-shaped oxides.



Scheme 1. Scheme of the syntheses of TiO_2 nanotubes

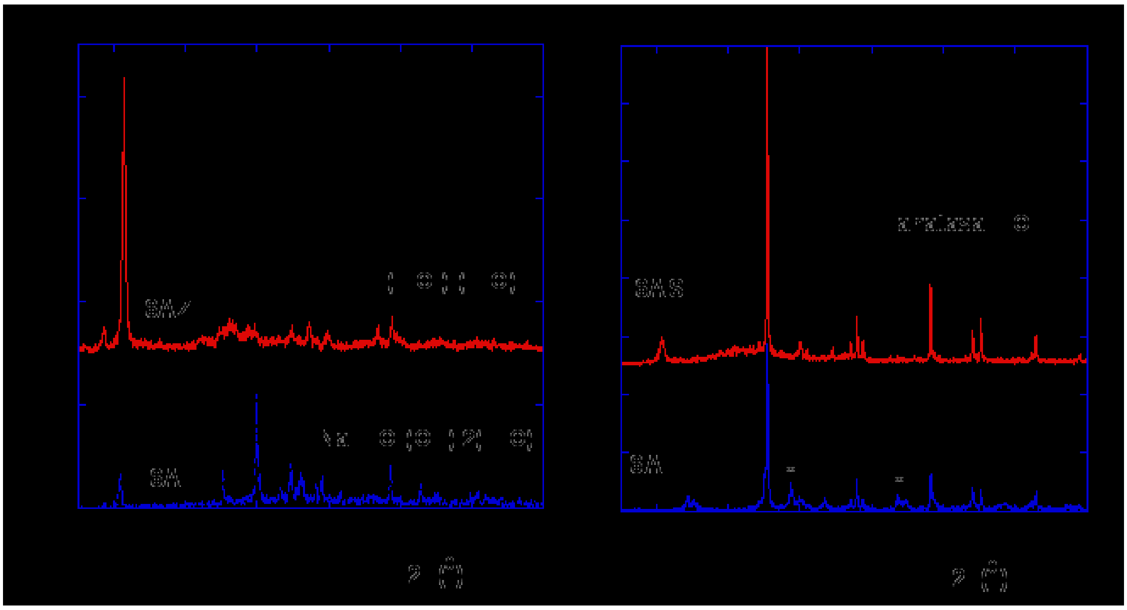


Figure 1. XRD patterns of 6A (after first hydrothermal treatment), 6AZ (acidified sample), 6AZT (after thermal treatment) and 6AS (after second hydrothermal treatment with CTAB).

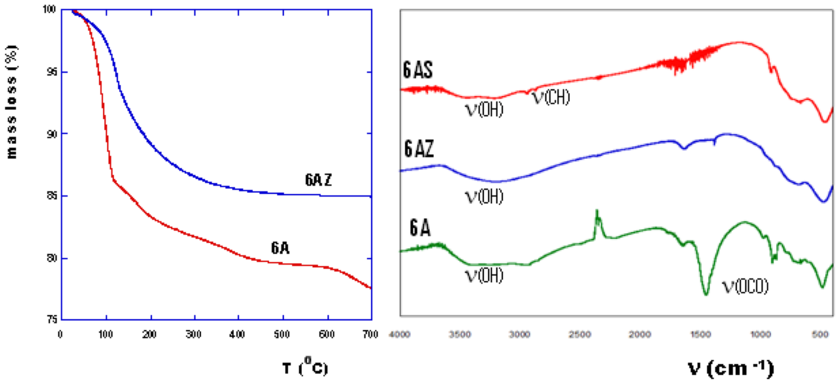


Figure 2. TG curves and IR spectra of synthesized samples.

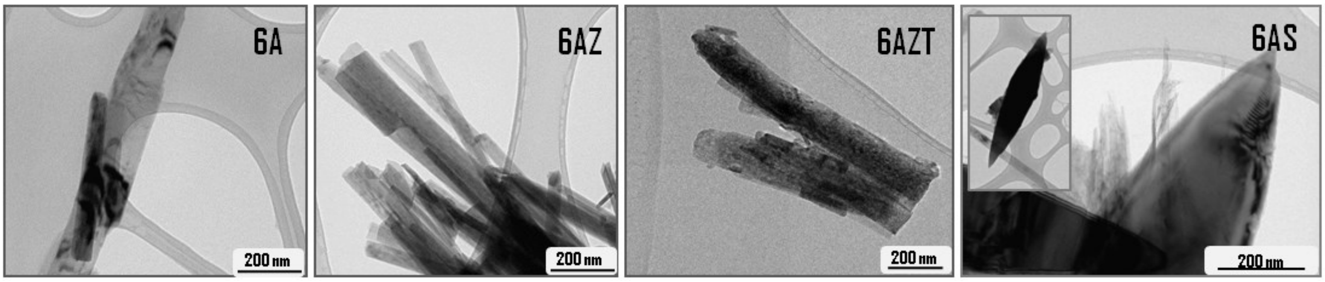


Figure 3. TEM images of 6A (after first hydrothermal treatment), 6AZ (acidified sample), 6AZT (after thermal treatment) and 6AS (after second hydrothermal treatment with CTAB).

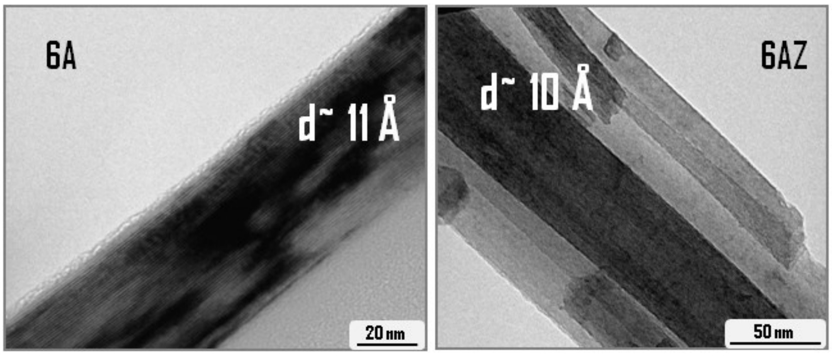


Figure 4. HRTEM images of 6A and 6AZ, Na- and H-titanate samples.

3. Materials and Methods

Sodium hidroxide (97%), titanium (IV) oxide (99,8%), cetyltrimethylammonium bromide (CTAB) (99%), nitric acid (65%) and acetone were purchased from Sigma-Aldrich and used as received without further purification. Hydrochloric acid (37%) was purchased from Panreac.

3.1. Synthesis of sodium and hydrogen titanates nanorods. 0,4 g commercial TiO_2 was dispersed in 20 mL of 10M NaOH with magnetic stirring for 30 minutes. The white suspension was then transferred into a Teflon-lined autoclave of 25 mL capacity. After being heated at 170-200 °C for 6-48 h, the autoclave was naturally cooled to room temperature. The resulting products were filtered and washed several times with diluted HCl [18, 19] and dried at 80°C for 2 h.

3.2. Synthesis of sodium and hydrogen titanates nanorods. For the ion-exchange, the sodium titanate samples were immersed into a 0.2 M HNO_3 solution for 6 h and 1-2 hour in an ultrasonic bath [20]. After that, they were washed with deionized water for several times, filtered and dried at 80°C for 2 h.

Finally, different hydrothermal [21] and thermal treatments were carried out. 0,3 g of previously synthesised Na-titanate were mixed with 0,5 g CTAB in 20 mL of distilled water and transferred again into a Teflon-lined autoclave and heated at 200°C-tan for 24 h. In one case, before heating, the pH was acidified by adding HCl 0,1M. In the other hand, some H-titanates were heated at 400-500 °C for 4-5 h.

3.4. Characterization. IR spectra (400-4000 cm^{-1}) were recorded on a MATTSON FTIR 1000 spectrophotometer with samples prepared as KBr pellets. The powder X-ray diffraction (XRD) pattern was taken using a Philips PW1710 diffractometer. Thermogravimetric measurements were performed in a Netzsch STA 449C thermogravimetric analyzer. Crucibles containing 9 mg of sample were heated at $10^{\circ}C.min^{-1}$ under dry argon. For microstructure analysis, powders were dispersed in acetone, dropped-cast onto copper grid and examined using a CM200 transmission electron microscope.

4. Conclusions

1D anatase samples with different shapes had been obtained by a 2-step method that implied an initial hydrothermal treatment in alkali environment followed by acid exchange and final thermal/hydrothermal heating. 1D nanostructures were already achieved in the first stage during the formation of sodium titanates and remained without significant morphological alteration, except a slight broadening, until the formation of anatase TiO_2 nanotubes. Exceptionally, a second hydrothermal heating in the presence of CTAB of the alkali intermediates led to an oval-shaped anatase sample where TiO_2 fibres seemed to be more densely stacked.

Acknowledgments

This work has been supported by institutional funding from MINECO and Basque Government under Projects MAT2013-41128-12 and IT-570-13, respectively.

Author Contributions

This text is based on "**Final Degree Project"** made by E. Ereño.

Conflicts of Interest

The authors declare no conflict of interest.

References and Notes

1. Hanaor, D.A.H.; Sorrell, C.C. Review of the anatase to rutile phase transformation. *J. Mater. Sci.* **2011**, *46*, 855–874
2. Abdullah, N; Kamarudin, S.K. Titanium dioxide in cell fuel technology: an overview. *J. Power Sources* **2015**, *278*, 109-118.
3. Roy, P.;Beger, S.; Schmuki, P. TiO_2 nanotubes; synthesis and applications. *Angew. Chem. Int. Ed.* **2011**, *50*, 2904-2939.
4. Henglein, A., Small-particle research: physicochemical properties of extremely small colloidal metal and semiconductor particles. *Chem. Rev.* **1989**, *89*, 1861-1873.
5. Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara K., Formation of Titanium Oxide Nanotube. *Langmuir* **1998**, *14*, 3160;
6. Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara K. Titania Nanotubes Prepared by Chemical Processing. *Adv. Mater.* **1999**, *11*, 1307-1311.
7. Yang, D.; Liu, H.; Zheng, Z.; Sarina, S.; Zhu H. Titanate-based adsorbents for radioactive ions entrapment from water. *Nanoscale*, **2013**, *5*, 2232-2242.
8. Sui, X.L.; Wang, Z.B.; Li, C.H.; Zhang, J.J.; Zhao, L. Effect of pH value on $H_2Ti_2O_5/TiO_2$ composite nanotubes as Pt catalyst support for methanol oxidation. *J. Power Sources* **2014**, *271*, 196-202.
9 . Suzuki, Y.; Yoshikawa, S. Synthesis and Thermal Analyses of TiO_2-Derived Nanotubes Prepared by the Hydrothermal Method. *J. Mater. Res.* **2004**, *19(4),* 982-98
10. Aradi, B. ; Deak, P.; Huy, H.A.; Rosenauer, A., Frauenheim, T. Role of Symmetry in the Stability and Electronic Structure of Titanium Dioxide Nanowires, *J. Phys. Chem. C* **2011**, *115*, 18494–18499.
11. Andrusenko, I.; Mugnaioli, E.; Gorelik, T.E.; Koll, D.; Panthöfer, M.; Tremel,W.; Kolb, U. Structure analysis of titanate nanorods by automated electron diffraction tomography. *Acta Crystallogr B* **2011**, *67(3),* 218-25.
12. Yang, J.; Jin, Z.; Wang, X.; Li, W.; Zhang, J.; Zhang, S.; Guo, X.; Zhang, Z. Study on composition, structure and formation process of nanotube $Na_2Ti_2O_4(OH)_2$. *Dalton Trans.* **2003**, 3898–3901.
13. Andrusenko, I.; Mugnaioli, E.; Gorelik, T.E.; Koll, D.; Panthöfer, M.; Tremel,W.; Kolb, U. Structure analysis of titanate nanorods by automated electron diffraction tomography. *Acta Crystallogr B* **2011**, *67(3),* 218-25
.14 Lee, L.; Park, H.; Paik, U.; Han, T.H. Exfoliation of titanium dioxide powder into nanosheets using hydrothermal reaction and its reassembly into flexible paper for thin-film capacitors. *J. Solid State Chem.* **2015**, *224*, 76-81.
15. Du, *G.* H. ; Chen, Q.; Che, R. C.; Yuan, Z. Y.; Peng, L. M. Preparation and structure analysis of titanium oxide nanotubes. *Appl. Phys. Lett.* **2001**, *79, 3702 – 3704.*

16. Suzuki, Y.; Yoshikawa, S. Synthesis and Thermal Analyses of TiO_2-Derived Nanotubes Prepared by the Hydrothermal method. *J. Mater. Res.* **2004***, 19,* 982.
17. Peng, C.W.; Richard-Plouet, M.; Ke, T.-Y.; Lee, C.-Y; Chiu, H.-T.; Marhic, H.; Puzenat, E.; Lemoigno, F.; Brohan, L. Chimie douce Route to sodium hydroxo titanate nanowires with modulated structure and conversion to highly photoactive titanium dioxides. *Chem. Mater*. **2008**, *20*, 7228-7236.
18. Yuxiang, L.I.; Mei, Z.; Min, G.; Xidong, W. Hydrothermal growth of well-aligned TiO2 nanorod arrays: Dependence of morphology upon hydrothermal reaction conditions. *Rare Metals* **2010**, 29(3), 286.
19. Yu, J.; Wang, G.; Cheng, B.; Zhou, M. Effect of hydrothermal temperature and time on the photocatalytic activity and microstructures of bimodal mesoporous TiO_2 powder. *Applied Catalysis B: Environmental* **2007**, *69*, 171-180
20. Zhu, K.; Gao, H.; Hu, G.; Shi, Z. A rapid transformation of titanate nanotubes into single-crystalline anatase TiO_2 nanocrystals in supercritical water. *J. of Supercritical Fluids* **2013**, *83*, 28-34.
21. Dorian, A.H.; Hanaor, C.; Sorrel, C. Review of the anatase to rutile phase transformation. *J. Mater. Sci*. **2011,** *46*, 855-874.