Article

Interaction of Sodium Titanate Nanotubes with Organic Acids and Base: Chemical, Structural and Morphological Stabilities

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Este trabalho relata a interação de nanotubos de titanato de sódio (Na-TiNT) com soluções aquosas de ácido benzóico, ácido fenilfosfônico e anilina. Os Na-TiNT foram obtidos através do tratamento hidrotérmico de TiO$_2$ em solução aquosa de NaOH. Os resultados obtidos através de FTIR, XRD, TEM e análise elementar mostraram que a estabilidade química, estrutural e morfológica dos nanotubos está relacionada à natureza química do meio (básico ou ácido) e às condições de tratamento (temperatura e tempo de contato). A fase α-fenilfosfonato de titânio(IV) foi formada a partir da interação dos Na-TiNT com ácido fenilfosfônico; a quantidade da nova fase foi dependente do tempo de contato e sua cristalinidade da temperatura. Porém, TiO$_2$ ou nanotubo de titanato contendo H$^+$ foram obtidos, em função das condições de tratamento, a partir da interação dos Na-TiNT com ácido benzóico. Quando os Na-TiNT interagiram com a anilina nenhuma mudança estrutural, morfológica ou composicional foi observada.

This work reports the interaction of sodium titanate nanotubes (Na-TiNT) with aqueous solutions of benzoic and phenylphosphonic acids and of aniline. The Na-TiNT were obtained from hydrothermal treatment of TiO$_2$ in aqueous NaOH solution. The results obtained from FTIR, XRD, TEM and elemental analyses showed that the chemical, structural and morphological stability of the nanotubes is related to the medium (acidic or basic) and to the treatment conditions (temperature and contact time). A titanium(IV) α-phenylphosphonate phase was obtained from interaction between Na-TiNT and phenylphosphonic acid. The amount and crystallinity of the new phase were dependent of the contact time and temperature, respectively. On the other hand, TiO$_2$ or proton-rich titanate nanotubes were formed, depending on treatment conditions, from interaction between Na-TiNT and benzoic acid. When Na-TiNT interacted with aniline, no chemical, morphological or compositional change was observed.

Keywords: titanium oxide, titanium oxide nanotubes, phase transformation, adsorption, carboxylic acid

Introduction

Intensive investigation on physical and chemical properties of inorganic one-dimensional (1D) nanostructures such as nanotubes, nanofibers and nanorods has been reported.[1] In particular, titanate nanotubes have attracted great attention from the scientific community due to their potential applications in biosensors, electronic, optical, magnetic, electrochromic and solar cell devices, as well as in heterogeneous photocatalysis.[2-9] Additionally, 1D titanate nanostructures have also been used as support for the immobilization of myoglobin,[10] and as host for platinum oxide and lithium intercalation.[11,12]

Titanate nanotubes can be prepared by hydrothermal treatment of TiO$_2$ powders (anatase or rutile) in aqueous NaOH solutions.[13,14] Although the preparation method is very simple, there is still a great debate in the literature related to the atomic structure and chemical composition of the nanotubes produced by this method. The exact determination of the crystal structure is very difficult because of the small crystallite size and the wrapping of the structure in a crystallographic direction. However, some studies have demonstrated that the three-dimensional structure of the tubes comprises an arrangement of TiO$_6$ octahedrons forming corrugated layers.[15] Thus, as-prepared nanotubes will most likely correspond more closely to the sodium titanate Na$_2$Ti$_3$O$_7$ structure.[16,17] The most acceptable composition of the as-prepared nanotubes is

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$Na_{2-x}H_xTi_3O_7 \cdot nH_2O$ ($0 \leq x \leq 2$), where the sodium content can vary according to the washing conditions (acid solutions or pure water).[16]

In view of the many technological applications of the titanate nanotubes, understanding their chemical, structural and morphological stabilities in several media and their thermal stabilities under several kinds of treatments is an important issue.[18-24] Furthermore, the knowledge of the surface properties of such nanostructured materials is a key point for understanding their reactivity, and potentializing their technological applications. In this work we have focused our investigation on the stability of sodium titanate nanotubes in aqueous solutions of organic base and organic acids and on the characterization of the interaction products.

So far, most studies performed on the nanotubes stability in aqueous media were carried out employing inorganic base and acids such as NaOH and H_2SO_4, HNO_3 and HCl, respectively. Zhu *et al*.[20] reported that a phase transition from titanate nanofibers to TiO_2 polymorphs takes place in acid conditions at temperatures close to ambient. However, the phase obtained depends on the acid concentration. In a diluted (concentrated) HNO_3 solution, these authors observed the anatase (rutile) phase. By studying the influence of different washing post-treatments on the layered titanate obtained from the reaction of TiO_2 and NaOH in a Teflon-lined autoclave at 130 ºC for 24 h, Tsai and Teng[21] observed that an increase in acidity during the acid washing leads to the formation of titanate nanotubes through $Na^+ \rightarrow H^+$ substitution, and eventually the nanotubes can also be transformed into tubostratic anatase TiO_2. Titanate nanotubes have poor stability in dilute inorganic acids even at room temperature and can slowly transform into rutile nanoparticles after several months.[22] The nature of the inorganic acid influences the transformation rate and it is correlated with titanate solubility in the acid medium. It is possible that acid-induced transformation from titanate nanotubes to TiO_2 nanostructures occurs through dissolution of nanotubes along with simultaneous crystallization of TiO_2.

In addition, for some applications, superficial modifications of the titanate nanotubes with organic molecules are demanded, and thus an understanding of the superficial chemistry of these nanoparticles is also very important. Studies on the chemical modification of titanate nanotubes with organosilanes, surfactants, polymers and carboxylic acids have been reported.[25-33] Wang *et al*.[29] reported superficial modifications on proton-rich titanate nanotubes (H-TiNT) with carboxylic acids of different chain lengths in alcoholic solutions. A collapse of the morphology and a crystalline structure

change were observed when the interaction of the H-TiNT was performed with shorter chain acids. On the other hand, neither morphological nor structural changes were observed in the nanotubes when they interacted with longer chain acids, and, consequently, the carboxylic acids were adsorbed on these nanoparticles.

Carboxylic acids are interesting substances to be evaluated as coupling agents on the titanate nanotube surfaces. The adsorption of these acids on the metal oxide surface generally occurs *via* coordination of the carboxylic group, that acts as a ligand at the sites of the metallic ions.[34] Additionally, organophosphorus compounds (derived from phosphates, phosphonates or phosphinates) are also interesting substances that offer promising alternatives as modifiers of metal oxide surfaces. The P-C bond is stable under hydrolysis conditions, and the versatility of phosphorus chemistry allows one to exploit its bonding with a large variety of functional organic groups. The stability of the P−O−M (M = metal) bond is illustrated by numerous examples reported in literature for metal phosphonates and metal phosphates.[35]

In this paper, we have investigated the chemical, structural and morphological stabilities of the nanotubes in aqueous media containing organic acids (benzoic and phenylphosphonic acid) and an organic base (aniline). In addition, we also studied the products obtained through interaction between titanate nanotubes and organic molecules and evaluated the importance of some process parameters, such as contact time and temperature, on the nature of the final products.

Experimental

We have used $TiCl_4$ (Merck, purity 99%), urea (J. T. Baker, purity 99%), NaOH (Merck, purity 99%), phenylphosphonic acid (Aldrich, purity 98% - solubility in H_2O[36] at 25 ºC: 404 g L^{-1}) and benzoic acid (Merck, purity 99% - solubility in H_2O[36] at 30 and 95 ºC: 4.2 and 68.0 g L^{-1}, respectively) as received. Aniline (Synth - solubility in H_2O[36] at 25 ºC: 36 g L^{-1}) was distilled before use.

Titanate nanotubes preparation

TiO_2 anatase was obtained by homogeneous precipitation from $TiCl_4$ using urea as precipitating agent.[37] Titanate nanotubes were prepared as described previously.[16] In a typical synthesis, 2.00 g (25.0 mmol) of TiO_2 were suspended in 60 mL of a 10 mol L^{-1} NaOH aqueous solution for 30 min. The white suspension formed was transferred to a 90 mL Teflon-lined stainless steel autoclave and kept at 165 ± 5 ºC for 170 h. After cooling to room temperature,

Table 1. Experimental conditions used for promoting the interaction of nanotubes with organic molecules

Sample	Organic molecule	Temperature (ºC)	time (h)	pH	Carbon content after the interaction (%)
Na-TiNT+PPH1	PPH	100 ± 3	48	2.5	16.28
Na-TiNT+BA1	BA	100 ± 3	48	3.0	5.77
Na-TiNT+AN1	AN	100 ± 3	48	9.0	0.53
Na-TiNT+PPH2	PPH	32 ± 3[a]	48	2.5	14.82
Na-TiNT+BA2	BA	32 ± 3[a]	48	3.0	3.19
Na-TiNT+AN2	AN	32 ± 3[a]	48	9.0	-
Na-TiNT+PPH3	PPH	32 ± 3[a]	20	2.5	9.68
Na-TiNT+BA3	BA	32 ± 3[a]	20	3.0	1.45

[a] room temperature.

the resulting white solid was washed several times with deionized water until pH 11-12. The samples were dried at $60 ± 10$ ºC for 24 h. These titanate nanotubes have mainly Na^+ ions as counter-ions and were named in this paper as Na-TiNT.

Interaction of organic molecules with sodium titanate nanotubes

The sodium titanate nanotubes were submitted to interaction with phenylphosphonic acid (PPH), benzoic acid (BA) and aniline (AN). The treatment was carried out by suspending 50 mg of nanotubes in 25 mL of 0.07 mol L^{-1} aqueous solutions of the organic molecules, except for the experiments carried out with benzoic acid at room temperature, in which saturated solutions were used. The suspensions were maintained under magnetic stirring at different temperatures and for different contact times. In Table 1 we list the experimental conditions used for promoting the interactions of nanotubes with the organic molecules. The solid products were isolated by centrifugation and dried in vacuum.

Characterization techniques

X-ray powder diffraction (XRD) patterns were obtained with a Shimadzu XRD7000 diffractometer using CuK_α ($\lambda = 1.5406$ Å) radiation and operating with 30 mA and 40 kV. A scan rate of $1°$ min^{-1} was employed. Transmission electron microscopy (TEM) images were obtained using a Carl Zeiss CEM-902 setup. Fourier transform infrared (FTIR) spectra were recorded using the KBr pellet technique (from 370 up to 4,000 cm^{-1}) on a Bomen FTLA 2000 spectrophotometer. A total of 32 scans and a resolution of 4 cm^{-1} were employed. Carbon analyses were performed using a Perkin-Elmer 2400 instrument.

Results and Discussion

In Figure 1, we show the FTIR spectra of Na-TiNT before and after interaction with aqueous solutions containing organic compounds. The spectrum of the as-prepared nanotubes (curve a in Figure 1) exhibits a broad and intense band located at about 3,300 cm^{-1} which
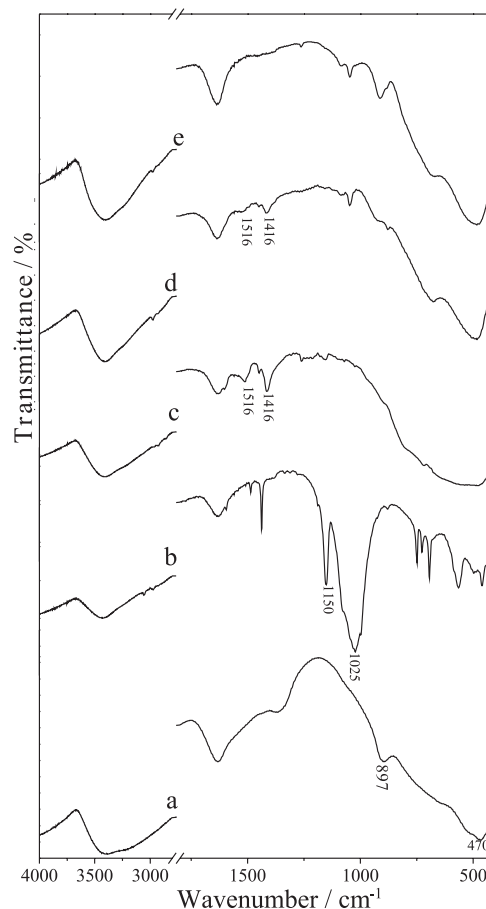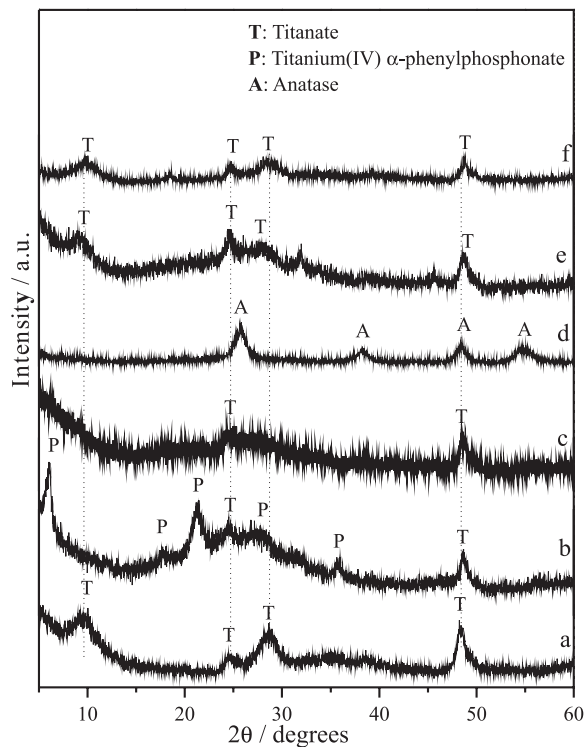

Figure 1. FTIR spectra of a) Na-TiNT, b) Na-TiNT+PPH1, c) Na-TiNT+BA1, d) Na-TiNT+BA2, e) Na-TiNT+AN1.

is attributed to the O–H stretching mode, indicating the presence of surface hydroxyl groups and water molecules adsorbed on the surface and in the interlayer space of the nanotubes. Water molecules were confirmed by the presence of the band at 1,630 cm^{-1} that is assigned to the H–O–H deformation mode. The band observed at 897 cm^{-1} can be attributed to the Ti–O stretching mode which involves non-bridging oxygen atoms.[16] The band at 470 cm^{-1} is related to Ti–O–Ti vibrations of the interconnected octahedra that are rigid units responsible for the formation of the nanotube walls.[16]

The products obtained after the interaction of Na-TiNT with phenylphosphonic acid, using different process parameters, presented new bands in the FTIR spectra. The same spectral features were observed for all products, so that we show here only the FTIR spectrum for the sample obtained for 48 h at 100 °C (curve b in Figure 1). The strong bands, one at 1,150 and other at 1,025 cm^{-1}, are attributed, respectively, to the P–C$_6$H$_5$ group and to the stretching of PO$_3$. Furthermore, the expected bands at 2,700 and 2,250 cm^{-1}, respectively related to P–OH stretching and P–OH deformation modes, were not observed. Bands at 1,220 cm^{-1} (characteristic of P=O group) and 940 cm^{-1} (P–OH) were not observed either.[35,38] The absence of the bands related to P=O and P–OH groups, along with the presence of the signal related to the PO$_3$ group, indicates the formation of phenylphosphonate as a result of the interaction process. Moreover, we did not observe in the spectrum (curve b, Figure 1) the typical bands of titanate nanotubes in the spectral region below 1,000 cm^{-1}. Thus, these results suggest chemical and structural changes of the as-prepared nanotubes.

The typical X-ray pattern of the titanate phase is observed in curve a (Figure 2) for pristine titanate nanotubes.[16] However, the XRD pattern of the product obtained after the interaction of the nanotubes with PPH under heating (curve b in Figure 2), presented a new diffraction pattern characteristic of the Ti^{IV} α-phenylphosphonate phase, (Ti(O$_3$PC$_6$H$_5$)$_2$),[38,39] suggesting a reaction between the titanate nanotubes and PPH. This result is in agreement with that observed in the FTIR measurement (curve b in Figure 1). Nevertheless, we still observed characteristic peaks of titanate nanotubes at about 24 and 48° (curve b in Figure 2), indicating that the reaction was not complete. On the other hand, when the interaction was carried out at room temperature for 48 h, we observed only the characteristic peaks of the titanate nanotubes at about 24 and 48° in the XRD pattern (curve c in Figure 2). The absence of the peak at about 10° in this sample, related to interlayer space of titanate nanotubes, indicates a possible disordering of the nanotube walls.


Figure 2. X-ray diffraction patterns of a) Na-TiNT, b) Na-TiNT+PPH1, c) Na-TiNT+PPH2, d) Na-TiNT+BA1, e) Na-TiNT+BA2 and f) Na-TiNT+AN1.

In order to correlate the spectroscopic and structural data with the morphology we carried out electron microscopy measurements (Figure 3). Pristine nanotubes (Na-TiNT) are multi-walled with an average outer (inner) diameter of approximately 10 nm (5 nm) and a length of several tens of nm (Figure 3a). When the nanotubes were submitted to interaction with PPH at 100 °C, the TEM images showed the total collapse of the tubular morphology (Figure 3b), in agreement with structural and vibrational data. However, nanotubes could still be observed when Na-TiNT interacted with PPH at room temperature for 48 or 20 h (Figure 3f). The electron microscopy measurements revealed that the formation of the Ti^{IV} α-phenylphosphonate along with the increase of the temperature led to the loss of the tubular morphology.

Elemental analyses (Table 1) showed 16.28, 14.82 and 9.68% of carbon in samples obtained from the treatments of nanotubes with PPH at 100 °C for 48 h, at 32 °C for 48 h and at 32 °C for 20 h, respectively. The calculated carbon content for the titanium(IV)α-phenylphosphonate compound is 40%. Thus, considering the results of carbon elemental analyses and XRD measurements, we can suggest that the titanate nanotubes did not react completely with PPH. Additionally, a small part of the carbon content could arise from adsorbed phenylphosphonate on the titanate nanoparticle surface.
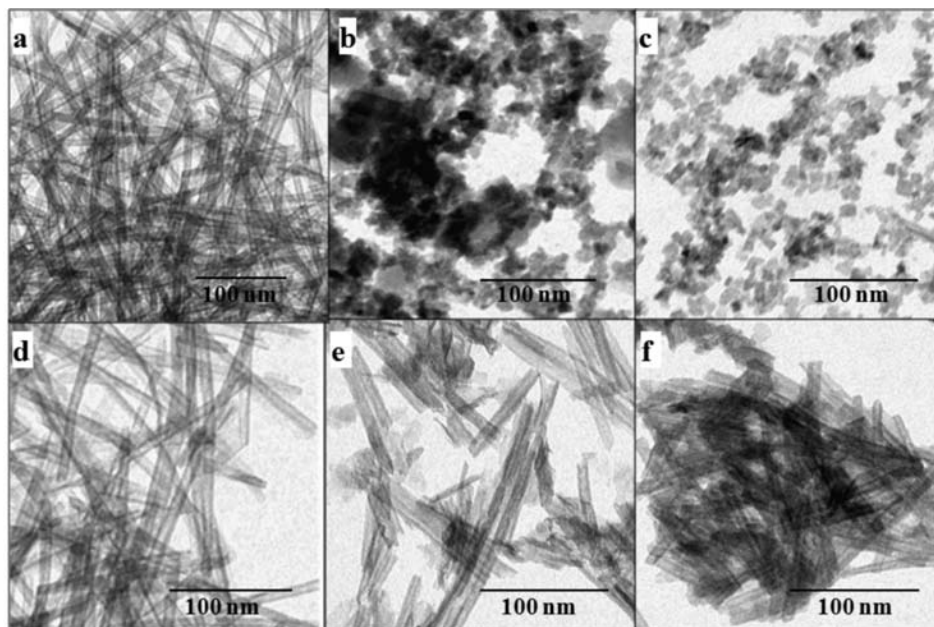
Figure 3. TEM imagens of a) Na-TiNT, b) Na-TiNT+PPH1, c) Na-TiNT+BA1, d) Na-TiNT+AN1, e) Na-TiNT+BA2 and f) Na-TiNT+PPH3.
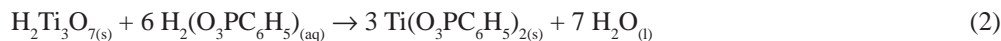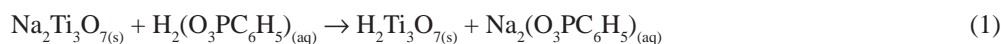
Studies reported in the literature about titanate nanotube treatments in aqueous media containing inorganic acids describe the transformation of titanate nanotubes into TiO_2 (rutile or anatase) through a mechanism of dissolution and crystallization.[22] Considering our results for the interaction between Na-TiNT and PPH, we propose that initially an ion exchange reaction of Na^+ by H^+ takes place (reaction 1). This is possible due to the dissociation of the phenylphosphonic acid into H^+ (see pH value in Table 1) and phenylphosphonate. The proton-rich phase could then dissolve, releasing Ti^{IV} to the solution, with simultaneous precipitation of Ti^{IV} α-phenylphosphonate (reaction 2) due to the presence of phenylphosphonate in the medium. The complete process is represented by reaction 3. In all these reactions, the water content of the nanotubes was disregarded.
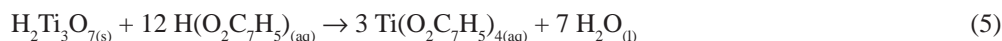
By analyzing the reaction parameters such as temperature and contact time, we verified that when the reactions between Na-TiNT and PPH were carried out at 100 °C or 32 °C for 48 h, the carbon contents in these products were analogous (see Table 1). However, comparing their XRD diffractograms (curves b and c in Figure 2) we clearly observed that the increase in the temperature promoted the crystallization of the Ti^{IV} α-phenylphosphonate phase. Furthermore, when the reactions were carried out reducing

the contact time from 48 to 20 h and maintaining the temperature at 32 °C, we observed a reduction in the carbon content. Our results point out that the medium and contact time play an important role in the products formed through interaction of titanate nanotubes with PPH.

Curves c and d (Figure 1) show the FTIR spectra for the sodium titanate nanotubes that interacted with benzoic acid at 100 °C (48 h) and 32 °C (48 h), respectively. The band at 1,516 cm^{-1} (1,416 cm^{-1}) was observed in both spectra; it was attributed to asymmetric (symmetric) stretching modes of carboxylate groups,[35] indicating the presence of BA in these products. However, for the spectral region of the Ti−O vibrations (below 1,000 cm^{-1}) we clearly observed a difference between the band features of these two products (curves c and d in Figure 1). For the sample obtained from interaction of BA with nanotubes at 32 °C, the spectrum is similar to that of the as-prepared nanotubes. On the other hand, for the sample obtained at 100 °C we observed a broader band, indicating a possible structural change.

In the diffractogram of the interaction product of Na-TiNT and BA at 100 °C for 48 h (curve d in Figure 2), we observed characteristic peaks of the anatase TiO_2 phase, showing a phase transformation from titanate to anatase TiO_2. Similar behavior was also observed by other authors.[20-22,29] Nevertheless, in the diffractograms of the

$$Na_2Ti_3O_{7(s)} + H_2(O_3PC_6H_5)_{(aq)} \rightarrow H_2Ti_3O_{7(s)} + Na_2(O_3PC_6H_5)_{(aq)} \qquad (1)$$

$$H_2Ti_3O_{7(s)} + 6\ H_2(O_3PC_6H_5)_{(aq)} \rightarrow 3\ Ti(O_3PC_6H_5)_{2(s)} + 7\ H_2O_{(l)} \qquad (2)$$

$$Na_2Ti_3O_{7(s)} + 7\ H_2(O_3PC_6H_5)_{(aq)} \rightarrow 3\ Ti(O_3PC_6H_5)_{2(s)} + Na_2(O_3PC_6H_5)_{(aq)} + 7\ H_2O_{(l)} \qquad (3)$$

$$Na_2Ti_3O_{7(s)} + 2\ H(O_2C_7H_5)_{(aq)} \rightarrow H_2Ti_3O_{7(s)} + 2\ Na(O_2C_7H_5)_{(aq)} \qquad (4)$$

$$H_2Ti_3O_{7(s)} + 12\ H(O_2C_7H_5)_{(aq)} \rightarrow 3\ Ti(O_2C_7H_5)_{4(aq)} + 7\ H_2O_{(l)} \qquad (5)$$

$$3\ Ti(O_2C_7H_5)_{4(aq)} + 6\ H_2O_{(l)} \rightarrow 3\ TiO_{2(s)} + 12\ H(O_2C_7H_5)_{(aq)} \qquad (6)$$

$$Na_2Ti_3O_{7(s)} + 2\ H(O_2C_7H_5)_{(aq)} \rightarrow 3\ TiO_{2(s)} + 2\ Na(O_2C_7H_5)_{(aq)} + H_2O_{(l)} \qquad (7)$$

products obtained from interaction of Na-TiNT with BA at room temperature for 48 h (curve e in Figure 2) and 20 h (not shown here), we observed the maintenance of the titanate structure.

TEM images (Figure 3c) show that the interaction of Na-TiNT with BA under heating leads to the collapse of the tubular morphology, converting titanate nanotubes into TiO_2 nanoparticles. However, for Na-TiNT that interacted with BA at room temperature, the tubular morphology was preserved (Figure 3e).

Elemental analyses (Table 1) show 5.77, 3.19 and 1.45% of carbon content in samples obtained from treatments of nanotubes with BA at 100 ºC for 48 h, at 32 ºC for 48 h and at 32 ºC for 20 h, respectively. Thus, based on results of carbon elemental analyses, XRD and FTIR measurements, we suggest that the adsorption of benzoate occurs on both TiO_2 and titanate nanotube surfaces.

Considering the results obtained from interaction between Na-TiNT and BA at 100 ºC, we propose that the transformation from titanate to TiO_2 occurs in several steps. In the first step, probably an ion exchange substitution reaction of Na^+ by H^+ takes place (reaction 4), as in the case of the interaction of nanotubes with PPH. This is possible due to partial dissociation of benzoic acid into H^+ and benzoate in the aqueous medium (see pH value in Table 1). The evidence that an ion exchange reaction occurred is in the intensity inversion between the peaks located at 24 and 28º in the diffractogram of the sample obtained from interaction between Na-TiNT and BA at room temperature (curve e in Figure 2). This intensity inversion is characteristic of proton-rich titanate nanotubes.[16] In the second step, due to the low pH of the medium, the proton-rich phase could be dissociated, releasing soluble forms of Ti^{IV}. A product that could be formed when Ti^{IV} was released in the medium would be Ti^{IV} benzoate (reaction 5). However, this product is probably unstable and can not precipitate leading to crystallization of the anatase TiO_2 (reaction 6). Reactions 4, 5 and 6 can be summed, resulting in a general equation for the interaction process between Na-TiNT and BA (reaction 7). For the sample obtained at room temperature the phase transformation from titanate to TiO_2 did not occur. This fact may be related to the smaller dissociation

rate of the proton-rich phase in the medium when the temperature was reduced from 100 to 32 ºC.

FTIR spectra for both samples obtained from interaction of the Na-TiNT with aniline at 100 ºC for 48 h (curve e in Figure 1) and at 32 ºC for 48 h (not shown here) did not exhibit any typical bands of aromatic amine. Additionally, we did not observe any drastic change in the Ti–O vibrations related to the signature of the nanotubes (spectral region below 1,000 cm^{-1}). Thus, these results suggest that AN has a weak interaction with Na-TiNT and, probably, does not modify its structure nor its composition. XRD patterns for samples obtained under heating (curve f in Figure 2) and at room temperature (not shown here) showed the maintenance of the crystalline structure of the pristine nanotube. Theses results are in agreement with FTIR measurements.

Elemental analyses for Na-TiNT interacting with AN showed that, when the interaction was performed under heating, only a small quantity of carbon (0.53%) was incorporated, and when the interaction was carried out at room temperature, no carbon was detected (Table 1). Therefore, carbon analyses also suggest a weak interaction between Na-TiNT and AN. TEM images for the sample obtained under heating conditions (Figure 3d) and at room temperature (not shown here) indicate that the tubular morphology was preserved. Based on these results, we propose that, due to the higher pH of the medium (see Table 1), the ion exchange reaction of Na^+ by H^+ did not occur and the dissociation of the sodium titanate nanotubes was thus much lower. Consequently, we observed the conservation of the sodium titanate nanotubes in these experimental conditions.

Conclusions

The chemical, structural and morphological stabilities of sodium titanate nanotubes towards interaction with aqueous solutions of organic base and acids were investigated, as well as the influence of reaction parameters on the nature of the final products. When the nanotubes were heated in an acidic medium, the nanoparticles exhibited changes in their composition, crystalline structure and morphology. The changes occurred due to a $Na^+ \rightarrow H^+$ ion exchange

reaction in the nanotubes. The new proton-rich phase can dissociate releasing soluble Ti^{IV} species to the medium. Consequently, the soluble Ti^{IV} can react with the counter-ion of the organic acid. For the phenylphosphonic acid, the Ti^{IV} α-phenylphosphonate phase was obtained. In the case of benzoic acid, on the other hand, the formation of anatase TiO_2 was probably due to the instability of the product given by benzoate and Ti^{IV}, which could not precipitate.

When the interaction between sodium titanate nanotubes and organic acids was carried out at room temperature, the stability of the nanotubes depended on the nature of the acid. For the phenylphosphonic acid, the structure of Ti^{IV} α-phenylphosphonate was formed, and the reaction was favored by the contact time. However, for benzoic acid, the morphology and structure of the nanoparticles were maintained, but their chemical composition was modified. After the reactions, the organic counter-ion adsorbed on the surface of the final products. Furthermore, the Na-TiNT basic character was revealed by its weak interaction with aniline.

Acknowledgments

References

1. Remskar, M.; *Adv. Mater.* **2004**, *16*, 1497.

2. Liu, A.; Wei, M.; Honma, I.; Zhou, H.; *Adv. Funct. Mater.* **2006**, *16*, 371.

3. Xu, X. G.; Ding, X.; Chen, Q.; Peng, L. M.; *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 035423.

4. Xu, X. G.; Ding, X., Chen, Q.; Peng, L. M.; *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 165403.

5. Tokudome, H.; Miyauchi, M.; *Angew. Chem., Int. Ed.* **2005**, *44*, 1974.

6. Alves, O. L.; Duran, N. E. D.; Moraes, S. G.; Ferreira, O. P.; *Br PI0505217-3*, 2005.

7. Bavykin, D. V.; Friedrich, J. M.; Walsh, F. C.; *Adv. Mater.* **2006**, *18*, 2807.

8. Bavykin, D. V.; Walsh, F. C.; *Eur. J. Inorg. Chem.* **2009**, *8*, 977.

9. Wei, M.; Konishi, Y.; Zhou, H.; Sugihara, H.; Arakawa, H.; *J. Electrochem. Soc.* **2006**, *153*, A1232.

10. Liu, A.; Wei, M.; Honma, I.; Zhou, H.; *Anal. Chem.* **2005**, *77*, 8068.

11. Ma, X.; Feng, C.; Jin, Z.; Guo, X.; Yang, J.; Zhang, Z.; *J. Nanopart. Res.* **2005**, *7*, 681.

12. Li, J.; Tang, Z.; Zhang, Z.; *Electrochem. Commun.* **2005**, *7*, 62.

13. Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K.; *Langmuir* **1998**, *14*, 3160.

14. Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K.; *Adv. Mater.* **1999**, *11*, 1307.

15. Zhang, S.; Peng, L. M.; Chen, Q.; Du, G. H.; Dawson, G.; Zhou, W. Z.; *Phys. Rev. Lett.* **2003**, *91*, 256103.

16. Ferreira, O. P.; Souza Filho, A. G.; Mendes Filho, J.; Alves, O. L.; *J. Braz. Chem. Soc.* **2006**, *17*, 393.

17. Pradhan, S. K.; Mao, Y.; Wong, S. S.; Chupas, P.; Petkov, V.; *Chem. Mater.* **2007**, *19*, 6180.

18. Umek, P.; Cevc, P.; Jesih, A.; Gloter, A.; Ewels, C. P.; Arcon, D.; *Chem. Mater.* **2005**, *17*, 5945.

19. Langhuan, H.; Zhongxin, S.; Yingling, L.; *J. Ceram. Soc. Jpn.* **2007**, *115*, 28.

20. Zhu, H. Y.; Lan, Y.; Gao, X. P.; Ringer, S. P.; Zheng, Z. F.; Song, D. Y.; Zhao, J. C.; *J. Am. Chem. Soc.* **2005**, *127*, 6730.

21. Tsai, C.-C.; Teng, H.; *Chem. Mater.* **2006**, *18*, 367.

22. Bavykin, D. V.; Friedrich, J. M.; Lapkin, A. A.; Walsh, F. C.; *Chem. Mater.* **2006**, *18*, 1124.

23. Nian, J. N.: Teng, H.; *J. Phys. Chem. B* **2006**, *110*, 4193.

24. Morgado, E.; de Abreu, M. A. S.; Pravia, O. R. C.; Marinkovic, B. A.; Jardim, P. M.; Rizzo, F. C.; Araujo, A. S.; *Solid State Sci.* **2006**, *8*, 888.

25. Zhang, C.; Jiang, X.; Tian, B.; Wang, X.; Zhang, X.; Du, Z.; *Colloids Surf., A* **2005**, *257*, 521.

26. Niu, H.; Cai, Y.; Shi, Y.; Wei, F.; Mou, S.; Jiang, G.; *J. Chromatogr., A* **2007**, *1172*, 113.

27. Shi, Z.; Xueping, G.; Deying, S.; Zhou, Y.; Yan, D.; *Polymer* **2007**, *48*, 7516.

28. Tang, X.; Mezick, B. K.; Kulkarni, H.; Wu, Y.; *J. Phys. Chem. B* **2007**, *111*, 1507.

29. Wang, C W.; Zhang, J.; Huang, H.; Wu, Z.; Zhang, Z.; *Colloids Surf., A* **2008**, *317*, 270.

30. Gao, Y.; Gao, X.; Zhou, Y.; Yan, D.; *Nanotechnology* **2008**, *19*, 495604.

31. Gai, L.; Du, G. ; Zuo, Z.; Wang, Y.; Liu, D.; Liu, H.; *J. Phys. Chem. C* **2009**, *113*, 7610.

32. Byrne, M. T.; McCarthy, J. E.; Bent, M.; Blake, R.; Gun'ko, Y. K.; Horvath, E.; Konya, Z.; Kukovecz, A.; Kiricsi, I.; Coleman, J. N.; *J. Mater. Chem.* **2007**, *17*, 2351.

33. Lu, M.; Yang, S.; *J. Colloid Interface Sci.* **2009**, *333*, 128.

34. Gratzel, M.; *Heterogeneous Photochemical Electron Transfer*, CRC: Boca Raton, FL, 1989.

35. Guerrero, G.; Mutin, P. H.; Vioux, A.; *Chem. Mater.* **2001**, *13*, 4367.

36. Budavari, S.; O'Neil, M. J.; Smith, A.; Heckelman, P. E.; Kinneary, J. F.; *The Merck Index,* 12th ed., Merck & Co., Inc.: Whitehouse Station, NJ, USA, 1996.

37. Daly, F. P.; Ando, H.; Schimitt, J. L.; Sturm, E. A.; *J. Catal.* **1987**, *108*, 401.

38. Medeiros, M. E.; Alves, O. L.; *J. Mater. Chem.* **1992**, *2*, 1075.

39. Anillo, A. A.; Villa-García, M. A.; Llavona, R.; Suárez, M. S.; Rodríguez, J.; *Mater. Res. Bull.* **1999**, *34*, 627.