

Nanostructured titanate compounds – Effect of ZrO₂ addition and its influence on microstructure

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Abstract

Zirconium oxide (zirconia) and titanium oxide (titania) can form solid solution for a relatively high extent, about 20 to 30 mol%. Exploring these property of the oxide mixture, titanate nanotubes were synthesized by hydrothermal method where to the rutile phase TiO₂ powder, zirconium hydroxide was added in amounts of 5,10 and 15 mol%, to obtain titanate nanotube with zirconia (TNT-ZrO₂). The reaction was carried out with all the chemicals together in a pressure reactor. The influence of zirconium on both titanate microstructure and structural rearrangement were investigated using X-ray diffraction and scanning electron microscopy. Results showed that with increasing amounts of zirconium, TNT powders surface area lowers and the particles enlarges, while structure of nanocompounds varies from nanotubes to nanorods and nanosheets, with increase of ZrO₂ content.

Keywords: Titanate nanotube; zirconia; hydrothermal synthesis, nanostructured materials

Introduction

Titanium oxide, also known as titania, is one of most important raw material for catalysis due to its surface properties as the photocatalytic activity, excellent optical absorption and other properties as low toxicity, high chemical stability and availability in various forms¹. Titania has three main allotropes, rutile, anatase and brookite, where the first one is the most stable specimen and the other two are metastable forms, but anatase is known to have better catalytic properties².

To improve titania properties, many authors proposed the use of its nanostructured compounds, such as nanopowders, nanotubes and nanowires³.

Among these structures, titania nanotubes (TNT) has received attention due to its properties as high surface area, pore volume, ion-exchange ability, photocatalytic activity and enhanced light absorption due to the high aspect ratio⁴.

There are at least three well established routes for synthesis of TNT, assisted template method, electrochemical anodic oxidation and alkaline hydrothermal method. In the last one, firstly reported in 1998 by Kasuga et al⁵, titanium nanotubes were synthesized by an hydrothermal treatment and has been object of interest of many researchers because its very small tubular structure, high aspect ratio, pure and oriented crystalline phase, self assembling morphology and can be made with simple apparatus and low operation cost.

The drawbacks of the nanotubes are the high energy band gap that lies between 3,3 and 3,87 eV and can only be excited by UV light^{6,7}, thermal degradation at relatively low temperatures as 300 to 400°C⁸ and poor mechanical properties.

By the other hands, titania can form solid solution with some metal oxides and the binary composite formed with zirconia has attracted the attention of a many works in various applications^{9,10}.

The aim of this work is to modify the process developed by Kassuga et al⁵ by adding zirconium hydroxide to the titanium oxide / sodium hidroxide mixture in order to synthesize a titanium nanostructured material doped with zirconia. The obtained compounds properties were characterized and the influence of zirconia on nanotube microstructure was investigated.

Experimental procedures

Experiments were conducted in a pressure reactor Model 4566 MiniReactor, Parr Instrument, with a PTFE vessel. Employed chemicals were commercial PA grade titanium oxide procured from CAAL, Brazil, zirconium oxychloride from Ipen, Brazil and all others chemicals were ACS grade reagents. Zirconium oxychloride was previously precipitated as zirconium hydroxide with ammonium hydroxide solution, filtered and washed with water in order to minimize the influence of chloride ions in the steel vessel and on the basic media necessary to the reaction.

As stated above, the synthesis was based on the pioneering work of Kassuga et al and was described elsewhere¹¹. Briefly, all chemicals were put together in the reactor and temperature was raised to 150°C, agitation speed was set do 100 rpm and reaction was maintained for 15 hours and the achieved pressure was 30 psi. The obtained product was a paste that is easily washed with water, forming a suspension of a powder like structures, easy to wash by filtering and sedimentation, very similar to TNT suspensions. These compounds were washed till neutral pH, dried overnight at 60°C and then thermally treated in an oven varying temperature through room temperature (RT), 400, 600 and 800 °C. All samples were characterized by density measurements by a Ar gas pycnometer (Quantachrome - Ultrapycnometer 1000), N₂ gas sorption surface area analysis according to BET (Quantachrome - NOVA 1200), x-ray diffraction (Rigaku - Multiflex), Transmission electron microscopy - TEM (JEOL - JEM 2100) and Field Emission Gun Scanning Electron Microscopy - FESEM (JEOL – JSM 6710F). Samples codification is as indicated in table 01, and for zirconium concentration was calculated as ZrO₂.

Table 01. Composition of the samples

Code	Composition (mol%)	
	TiO ₂	ZrO ₂
TNT (pure)	100	0
TNT-Zr 05	95	5
TNT-Zr 10	90	10
TNT-Zr 15	85	15

Results

The specific surface area of samples, are shown in table 02 just for comparison, because the difficulties in the determination of samples density. Pure TNT sample has large surface area and with increasing addition of

zirconium, surface area decreases substantially, indicating strong structural changes.

Table 01. Specific surface area of as synthesized samples

Sample	Specific surface Area (m ² .g ⁻¹)
TNT (pure)	257,2
TNT Zr 05	74,5
TNT Zr 10	61,6
TNT Zr 15	17,2

FESEM micrographs of prepared compounds at room temperature are shown in figure 01. While pure TNT (fig.1a) structures have diameter of about 10 nm and are hundreds of nanometers long, with the addition of 05 mol% ZrO₂ (fig.1b), morphology seems to be kept but nanotubes diameters grows to about 50 nm and the structure of TNT-Zr 10 are similar, but thicker and structures with more than 50nm diameter can be seem. Finally, with addition of 15 mol%, structures are not more rounded, but flattened like a board.

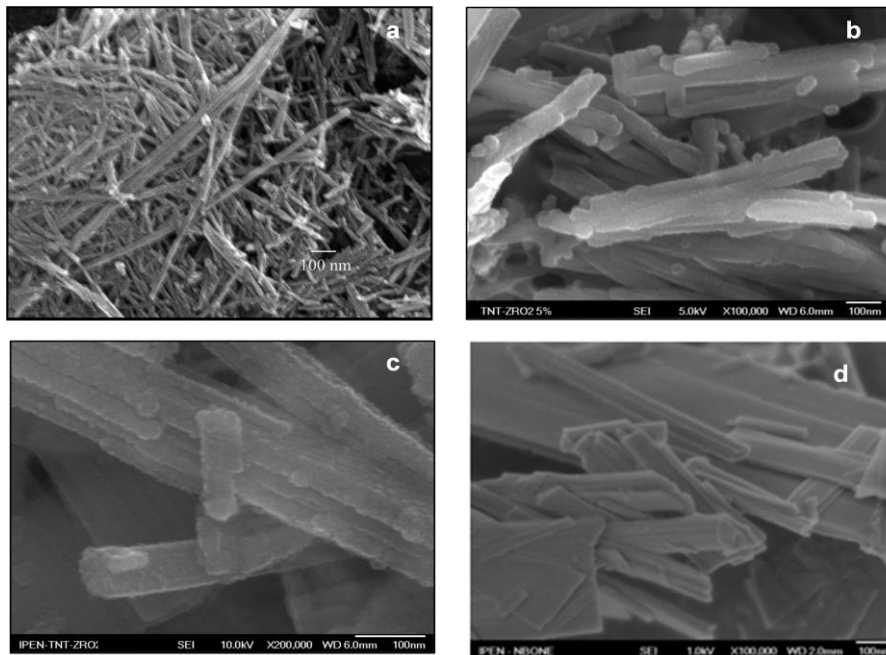


Fig. 01 FESEM micrographs of room temperature TNT samples with a) pure TNT, b) 5 mol% ZrO₂, c) 10 mol% ZrO₂ and d) 15 mol% ZrO₂.

The same samples under observation by TEM are presented in figure 02. The tubular nature of pure TNT can be seen from the multiwalled elements in the fig.2a with a fragment showing the cross section of a nanotube illustrating that the structure is probably formed by a wrapping of a titanate sheet¹². Micrograph of the TNT Zr 05 sample in fig.2b shows that it still keeps tubular structure but also have some nanorod characteristics. From fig.02c it can be seen that structures of TNT Zr 10 are compact, rather than tubular. Finally TNT Zr 15 samples seems to be unable to finish the wrapping process, showing a tendency to remain flattened.

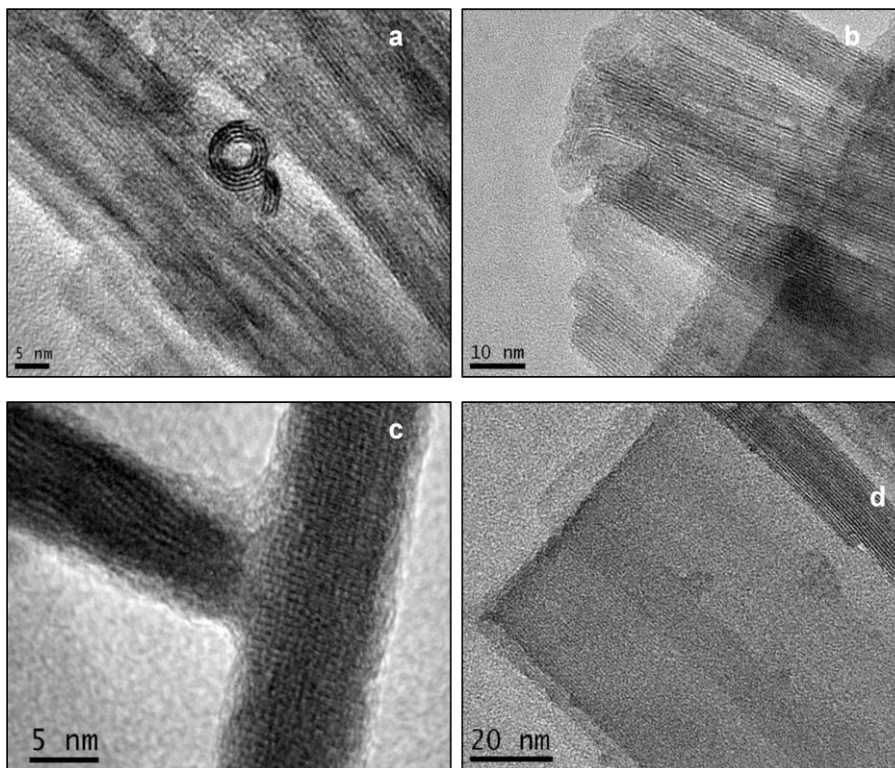


Fig. 02 TEM micrographs of room temperature TNT samples with a) pure TNT, b) 5 mol% ZrO₂, c) 10 mol% ZrO₂ and d) 15 mol% ZrO₂.

Room temperature X ray diffraction patterns of samples are shown in figure 03. Pure TNT profile have a strong and broad peak in $2\theta=10$, and weaker peaks at 26, 28 and 48 degrees, that can be attributed to a titanate type structure and neither anatase nor rutile was clearly identifiable. For the samples with ZrO₂, the strong peak get narrower but remains strong and weak peaks

almost disappears and a weak peak at $2\theta=30$ indicates the presence of tetragonal or cubic zirconia.

From the results, it can be seen that zirconium hydroxide added prior to TNT hydrothermal synthesis seems to be incorporated to nanotube structure, and are not clearly identified in the XRD profile, even in larger amount as 15 mol percent. The influence of the presence of zirconium alter extensively the surface area of powders and the structural changes are confirmed by the observations at the scanning and transmission electron microscopy. Addition of 05 mol% of ZrO_2 causes a growth of particles, and subsequently the structure changes to nanorods or nanobars and finally to nanosheets. To clarify The influence of ZrO_2 addition on titanate nanotubes, samples prepared here will be investigated for mechanical properties and for ageing under thermal treatment.

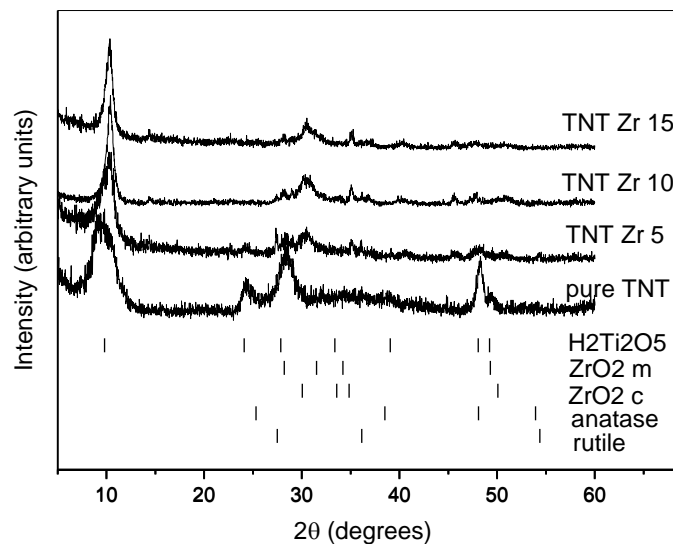


Fig. 03 Room temperature X ray diffraction profiles of pure and ZrO_2 doped TNT samples.

Conclusions

When added before TNT synthesis, zirconium hydroxide seems to be completely incorporated to nanotubes structure, but causes profound structural changes on it. Surface area of TNT powders, initially high, decreases more than 10 times with the increase of ZrO_2 amounts to 15 mol%. Particles initially grows

up with the increase of ZrO₂ and then loses its tubular nature, rearranging progressively to nanorod and finally to nanosheet. In the sequence of this work, mechanical properties and thermal degradation of doped TNT will be investigated.

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