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THESIS ABSTRACT

Oxide nanostructures of some transitional metals

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CONTENT

THESIS ABSTRACT

CHAPTER 1. INTRODUCTION

Synthesis, characterization and applications of titanium dioxide and related titanates significantly evolved and were dominant in the last decades. But, emerging nanotechnology introduced a new investigation paradigm of these materials. Over the last years, nanostructured titanium oxides, with dimensions less that 100 nm and various morphologies were the target investigation for many research groups over the world, which developed different synthesis techniques and investigated new properties and new application possibilities of the materials.

Synthesis of carbon nanotubes and, shortly after, of inorganic metals dicalcogenides nanotubes, attracted the increasing interest of scientific community, because these findings opened the possibility to produce different nanostructured compounds with nanotubular morphology, nanoporous and uniform diameters, that confer exceptional properties to these materials. Since then, many one dimension nanostructures metal oxides were studied and synthesized. For titanium dioxide, nanofibers and nanotubes are relatively recently studied and the research is following the constant improvement of semiconducting, redox and catalytic properties of the materials for improved efficiency in applications. Furthermore, beside properties improvement, new properties of these nanomaterials are investigated, to extend the already wide application panel of titanium dioxide and related titanates.

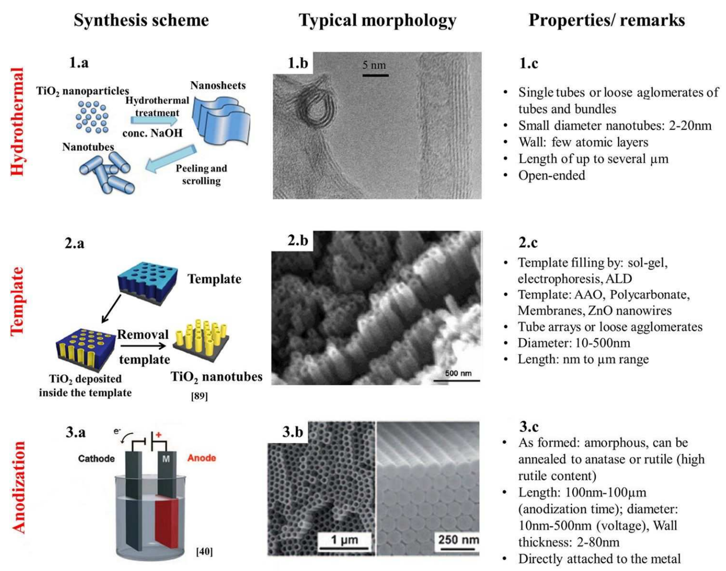
First titanium dioxide nanotubes synthesis was reported by Hoyer et al.[1] that obtained the nanotubes by template technique, using nonporous alumina and a polymer matrix. This technique and chemical matrix related techniques, further developed, have the disadvantage to use polymers matrices and templates, which implies their elimination at the end of the process in order to obtain the titanate based nanotubes, generating a costly procedure with low interest for industrial applications.

An interesting alternative emerged with the first direct synthesis of titanate based nanotubes, without using of polymers and templates, reported by Kasuga et al.[2]. Of remarkable simplicity, this method is based on the hydrothermal treatment of commercial titanium dioxide in alkaline aqueous solution, followed by acid washing. Moreover, titanate based nanostructures with nanotubular morphology have diameters of 10 nm or less, a feature difficult to obtain by other synthesis techniques.

Of course, this synthesis technique attracted an increased interest for scientific groups, including the author of this thesis adopted this technique for nanostructured materials synthesis, and, furthermore, characterization. Even the procedure is simple, in one step reaction; the formation mechanism of the nanotubes is still under debate. Moreover, controversies over the thermodynamic stability or photocatalytic activity of these as obtained nanostructured materials are still investigated and discussed. The disparities on this subject are evident in the literature data, widely reviewed in the second chapter of this work. Apparent simplicity of implementing to industrial scale of this technique and the variety of potential applications of the nanostructured materials determined us to develop this activity, aiming to contribute with new scientific insights and to spread information about this technology and nanostructured materials with tubular morphologies.

CHAPTER 2. LITERATURE REVIEW

Over the past 20 years, a considerable number of different strategies to synthesize TiO_2 and titanate nanotubes or titanate nanotube arrays have been elaborated. In the figure below is presented an overview of typical morphologies and characteristic features of tubes synthesized by different approaches[3].



General overview of different synthesis techniques of titanate based nanotubes: (a) synthesis route scheme; (b) typical morphologies and (c) features of the nanotubes obtained by different techniques

Roughly one may divide the main routes into templating, hydrothermal, and anodic self organization approaches.

From literature data, on may notice that in similar hydrothermal conditions, using different precursors and post-reaction parameters, similar morphologies of the titanate based nanotubes are obtained, but different structures are reported[4]. Establishing a unique and correct structure for titanate based nanotubes remains an open challenge.

CHAPTER 3. OBJECTIVES

In the chapter 3 of this work the general objective and specific objectives are described.

The general objective of this study was the investigation of synthesis parameters of nanostructured titanates by conventional and microwave assisted hydrothermal method, as well as investigation of obtained nanomaterial's characteristics, aiming improvement of state-of-the-art of both techniques and insights over some issues not well-defined in the literature data.

This study was conceived was conceived to rigorously examine the influence of precursor phase and crystallite size, alkaline concentration and hydrothermal reaction time on the formation of alkaline hydrothermally synthesized nanostructures. To achieve this, two commercial and two laboratory made by sol-gel method (amorphous and crystalline TiO_2), pure and phase mixture (anatase and rutile) were used. These powders were treated in alkaline environment and different experimental conditions (method modification and different reaction time).

In this study, X-ray diffraction (XRD), transmission and scanning electron microscopy (TEM and SEM) were used to investigate structure and morphology. Thermal behavior was investigated by thermodifferential and thermogravimetric analyses (DTA/TGA), differential scanning calorimetry (DSC) and in-situ X-ray diffraction (*in-situ* XRD).

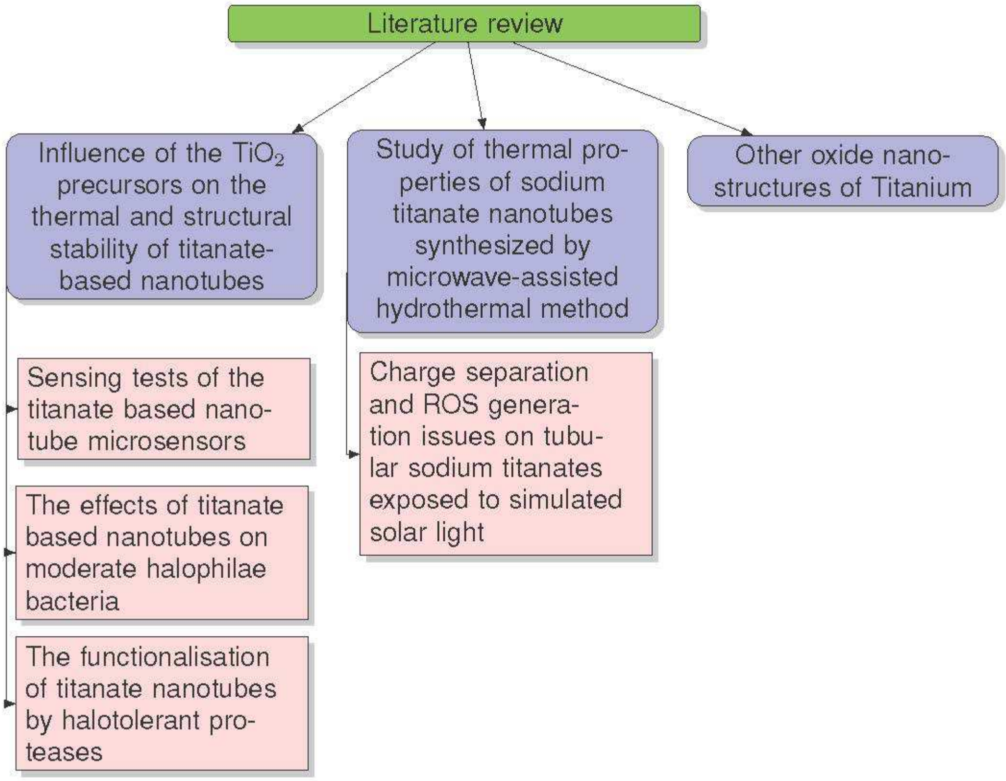
Specific objectives of the research presented in this work were:

1. Analyzing the effect of precursor type and hydrothermal reaction time on the formation of titanate based nanotubes;
2. Analyzing the effect of the post-hydrothermal thermal treatment on the structure and morphology stability of the titanate based nanotubes;
3. Analyzing the influence of physical modification of the hydrothermal method (by exposure to microwave irradiation) and exposure time to microwave irradiation on the morphology, structure and thermal behavior of the titanate based nanotubes;
5. Analyzing the changes of hydrothermal method (conventional and microwave assisted) reaction parameters on the morphology evolution of the titanium based oxide nanostructures;
4. Analyzing the charge separation and ROS generation issues on tubular sodium titanates exposed to simulated solar light;

6. Analyzing the sensing properties of titanate based nanotube microsensors;

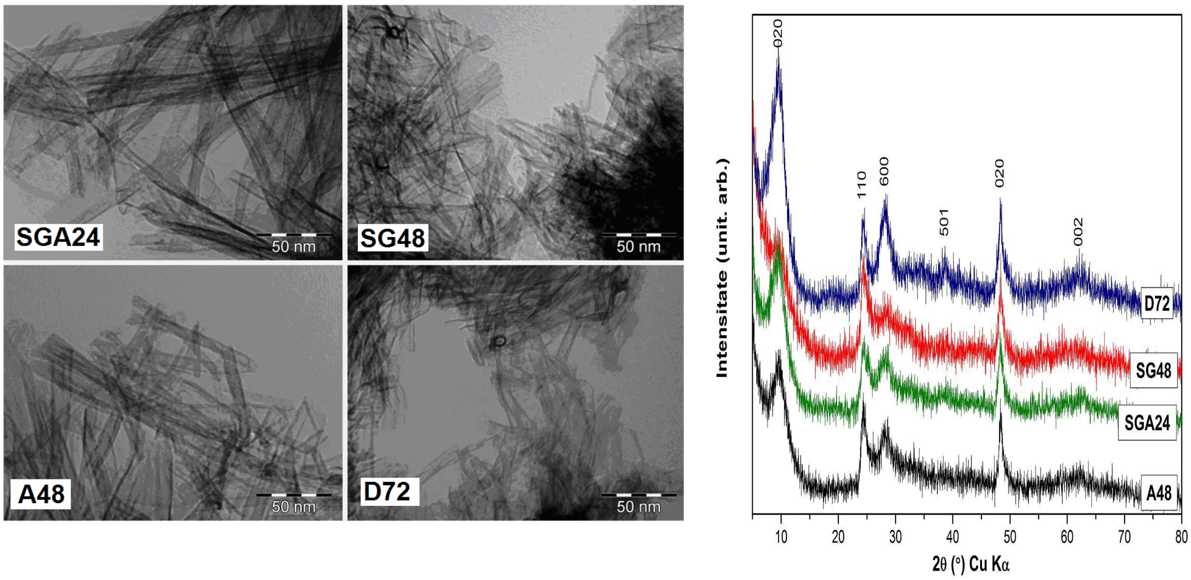
7. Analyzing the antibacterial properties of titanate based nanotubes and functionalisation abilities by biocompounds.

The diagram below shows the structure of the work, by highlighting the relations of objectives and results.



CHAPTER 4. INFLUENCE OF THE TiO_2 PRECURSORS ON THE THERMAL AND STRUCTURAL STABILITY OF TITANATE-BASED NANOTUBES

In this chapter, the influence of different TiO_2 precursors (laboratory-prepared sol–gel powders, dried and thermally treated at 400 °C, and commercial powders such as anatase by Aldrich and P25 Aeroxide by Evonik) on the structure and morphology of the titanate nanotubes obtained by hydrothermal method was investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements. In all cases, titanate-based nanotubes were obtained, having similar structure and morphology. The effect of the thermal treatment on the structural stability was also studied by differential thermal analysis and thermogravimetry analysis (TG/DTA) and differential scanning calorimetry (DSC) measurements up to 600 °C, to determine the transformation of titanate nanotubes into other phases[5]. Complementarily, by XRD investigation, the phases that develop after the thermal treatment of the titanate nanotubes in 110–400 °C temperature range were identified.

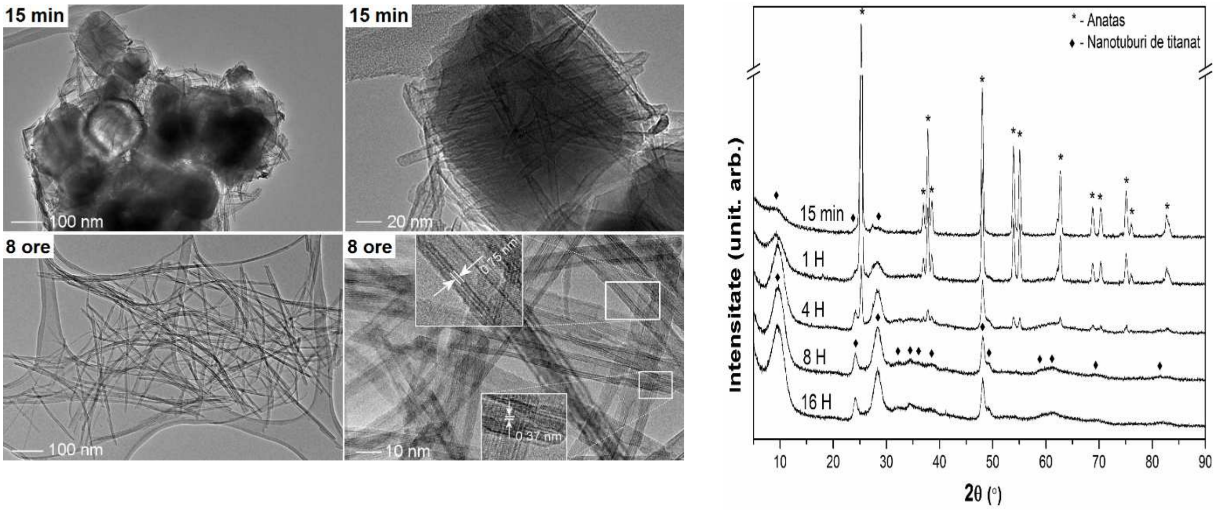


TEM micrographs (left) and X-ray diffractograms (right) of titanate based nanotubes, prepared by conventional hydrothermal method

The TEM micrographs come to confirm the deterioration of morphology and transformation from nanotubes to particles. The thermal stability of the investigated nanotubes led to the conclusion that this property depends not only on the sodium content but also on the type of precursor. The highest thermal stability was noticed for the nanotubes synthesized starting with anatase (Aldrich) commercial powder. As it can be noticed if the figure above, in all cases, titanate-based nanotubes were obtained having similar structure and morphology. Thermal analyses of the nanotubes investigated by DTA/TG combined with DSC analysis have shown a similar behavior. No specific thermal effects assigned to phase transformation could be observed, but the important structural transformation takes place in the 200–500 °C temperature range. The different thermal behavior of the investigated samples was determined by XRD investigations of the samples thermally treated in the 100–400 °C temperature range. All samples undergo phase transformation but at different temperature. The thermal phase transformation of the samples depends not only on the Na content in the composition of the nanotubes but also on the structure of the TiO_2 precursor used in their synthesis. The titanate nanotubes obtained starting from anatase (Aldrich) precursor presents the highest thermal stability.

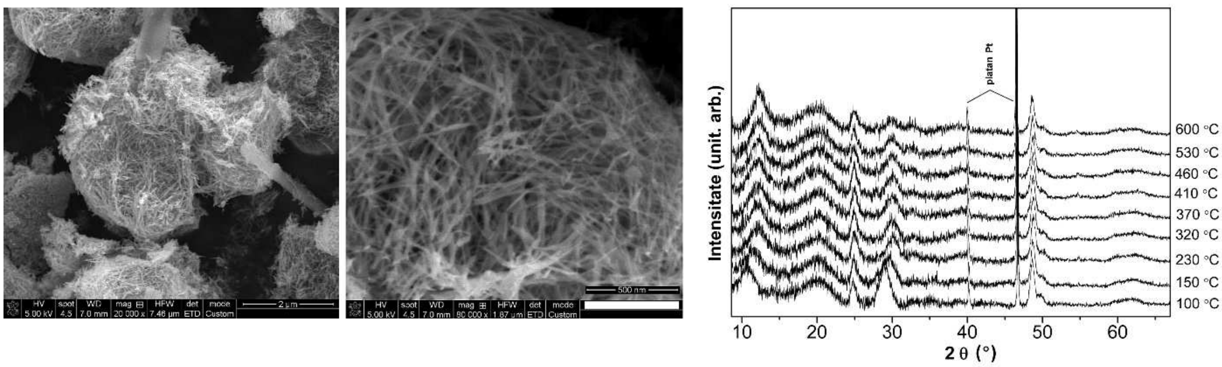
CHAPTER 5. A STUDY OF THERMAL PROPERTIES OF SODIUM TITANATE NANOTUBES SYNTHESIZED BY MICROWAVE-ASSISTED HYDROTHERMAL METHOD

In this chapter, a study on the thermal properties of titanate based nanotubes, obtained by microwave assisted hydrothermal method was performed. Sodium titanate nanotubes were synthesized by microwave-assisted hydrothermal treatment of commercial TiO_2, at constant temperature (135 °C) and different irradiation times (15 min, 1, 4, 8 and 16 h)[6].



TEM micrographs (left and middle, different magnifications) and X-ray diffractograms (right) of titanate based nanotubes, prepared by microwave assisted hydrothermal method

The products were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, differential scanning calorimetry and specific surface area measurements. The irradiation time turned out to be the key parameter for morphological control of the material. Nanotubes were observed already after 15 min of microwave irradiation.



SEM micrographs (left and middle) and in-situ X-ray diffractograms (right) of titanate based nanotubes, prepared by microwave assisted hydrothermal method

The analyses of the products irradiated for 8 and 16 h confirm the complete transformation of the starting TiO_2 powder to titanate based nanotubes. The nanotubes are open ended with multi-wall structures, with the average outer diameter of 8 nm and specific surface area up to 210 m^2/g. The morphology, surface area and crystal structure of the sodium titanate nanotubes synthesized by microwave-assisted hydrothermal method were similar to those obtained by conventional hydrothermal method.

A combination of hydrothermal conditions and microwave irradiation significantly reduced reaction time needed for the complete conversion of anatase particles to sodium titanate nanotubes. In comparison with conventional hydrothermal treatment the time reduced for about 3-times. Further, the TEM measurement of the outer nanotube diameters revealed that the diameter of these nanotubes is ~8 nm and is for 2–3 nm smaller than of the nanotubes synthesized under conventional hydrothermal conditions. In addition, due to the shortened reaction times the microwave assisted hydrothermal method can be considered as environmental friendly as shorter reaction time also affect the lower energy consumption.

CHAPTER 6. CHARGE SEPARATION AND ROS GENERATION ISSUES ON TUBULAR SODIUM TITANATES EXPOSED TO SIMULATED SOLAR LIGHT

In this chapter, the research focuses on few key points concerning the light-driven processes taking place on TiO_2 anatase and sodium titanates with tubular morphology such as relationship between morphology and activity for H_2 and CO_2 production, density of surface hydroxyl groups, ROS (•OH and $•O_2^-$) production and photocatalytic activity, and charge separation at interface of semiconducting domains and enhancement of activity. It is evidenced that one of the main advantages of tubular morphology of sodium titanate is conferred by its significantly higher surface area compared to parental anatase.

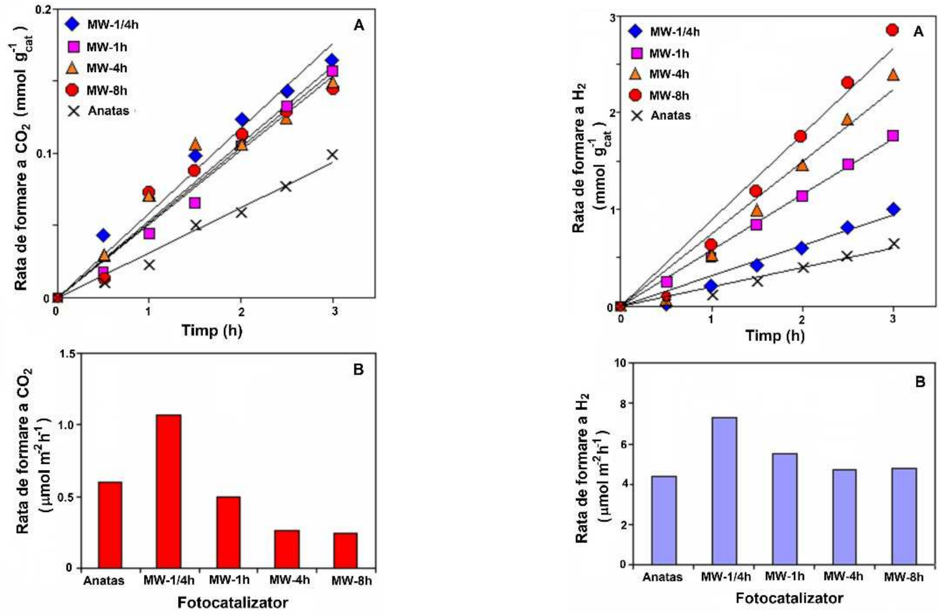
Composition and surface relative density of –OH groups on titanate based nanotubes

Photocatalysts	C at. %	O at. %	Ti at. %	Na at. %	$[OH]_{surface}$ [a]	Specific surface area m^2/g
1/4h	16.2	52.9	17.5	13.4	18.2	49.4
1h	12.3	55.2	18.7	13.8	11.2	109.9
4h	8.9	56.4	20.5	14.2	7.2	179.9
8h	7.3	58.3	19.7	14.7	6.5	210.5

[a] *Surface relative density of –OH groups determined from O1s photoemission spectra, deconvoluted*

FTIR and XPS analyses evidence that the density of surface hydroxyl groups decreases with development of tubular morphology. Radical trapping experiments find out that variation of surface hydroxyl density is followed in great lines by the activities for •OH and $•O_2^-$

generation as well as by the photocatalytic production of H_2 and CO_2 from water/methanol mixture. It comes out that ROS, formed by action of photogenerated electrons and holes on adsorbed O_2 and hydroxyl groups, respectively, play an important role in determining the photocatalytic activity of titania-based materials. The other major aspect revealed by this research is that charge separation at anatase/sodium titanate crystalline phases has a remarkable effect on activity by enhancing the formation rates of H_2 and CO_2.



Photocatalytic test results: CO_2 (left) and H_2 (right), release by time, normalized to photocatalytic amounts (A) and corresponding reaction rate, calculated to surface unit (B)

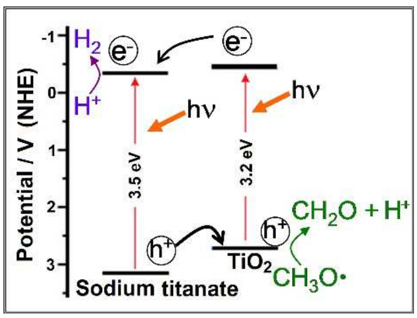
Photocatalytic reforming of methanol was employed to witness key points of light-driven processes taking place on TiO_2 anatase and sodium titanates with tubular morphology. This work analyses essential aspects of photocatalytic processes such as relationship between:

(i) morphology and activity for H_2 and CO_2 production,

(ii) density of surface hydroxyl groups and $\cdot OH$ generation,

(iii) ROS ($\cdot OH$ and $\cdot O_2^-$) production and photocatalytic activity, and

(iv) charge separation at interface of semiconducting domains and enhancement of activity.



Energy level diagram of nanotubes/ anatase

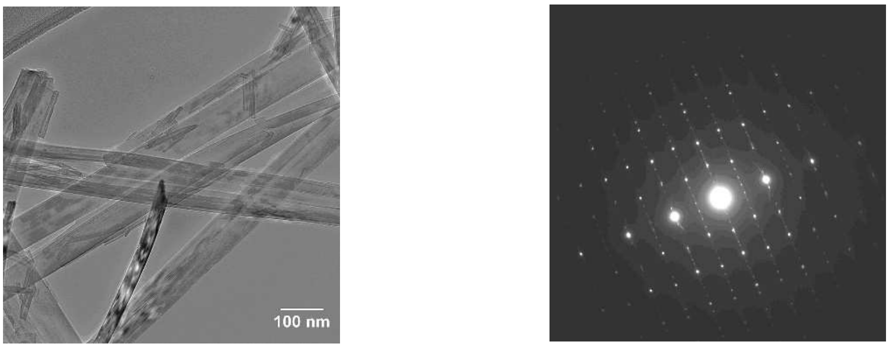
The main finding of present research can be summarized as follows. One of the main advantages conferred by tubular morphology of sodium titanate is the significantly higher surface area compared to parental anatase. The density of surface hydroxyl groups decreases with development of tubular morphology. This trend is followed in great lines by the activities for •OH and $•O_2^-$ generation as well as by the photocatalytic production of H_2 and CO_2. It comes out that ROS, formed by action of photogenerated electrons and holes on adsorbed O_2 and hydroxyl groups, respectively, play an important role in determining the photocatalytic activity of titania-based materials. The other major aspect revealed by this research is that charge separation at anatase-sodium titanate phase has a remarkable effect on activity by enhancing the formation rates of H_2 and CO_2.

CHAPTER 7. OTHER OXIDE NANOSTRUCTURES OF TITANIUM

In chapter 7 experimental results on the preparation of other titanium based oxide nanostructures, particularly nanorods, are presented. Titanate based nanotubes or titanium based oxide nanostructures are, generally, promising materials, with unique properties, but, in the same time, have disadvantages: difficult to model in bulk ceramic shapes, and even harder to obtain as layers, films and coatings. Other disadvantage is the difficulty to dope by *in-situ* methods, and only by ion-exchange methods. In many synthesis processes, nanorods and nanoparticles compete with nanotubes formation for applications where shaping nanotubes are difficult to obtain. Nevertheless, even a reaction fulfill all conditions for nanotubes synthesis, the end product may have nanoparticles or nanorods morphology. Nanorods are, no doubt, a less versatile host with regard to nanotubes because of the absence of an interior volume, but, nanorods have other advantages, as a better thermal stability. Thus, if the synthetic aim to obtain hollow anisotropic nanostructures (e.g., nanotubes) is sacrificed, then, a wide range of synthesis routes is opened for the obtaining of nanowires, nanorods, nanoribbons, nanofibers and others.

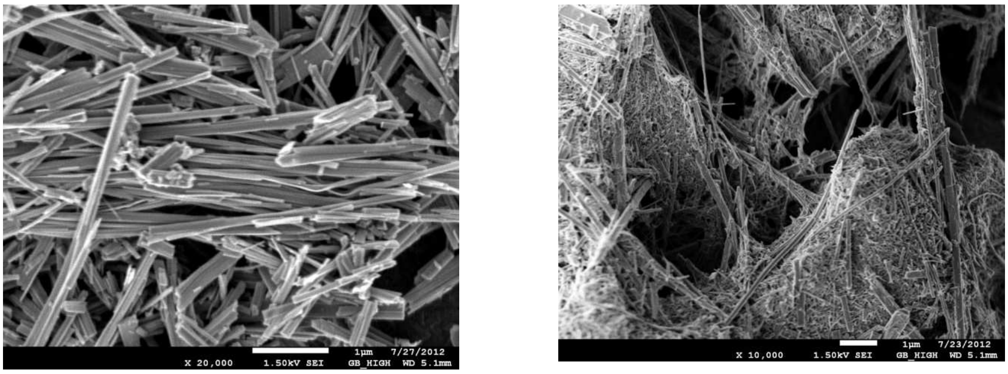
For the sake of clarity, all non-hollow anisotropic nanostructures were noted as nanorods, where rods represent fiber, wire, ribbon, etc.

Titanate based nanorods were prepared by the methods describes in the chapters 4 and 5. The precursor used for nanorods preparation was the commercial anatase powder, from Aldrich.



TEM micrograph (left) and selected area electron diffraction image (right) of the titanate based nanorod, obtained by conventional hydrothermal method

Regarding the oxide nanostructure with non-hollow morphology, it was demonstrated that the conventional hydrothermal method was more appropriate compared to microwave assisted method for obtaining a unique nanorod phase and morphology.



SEM micrographs of various nanorods morphologies, obtained by conventional (left) and microwave assisted (right) hydrothermal method

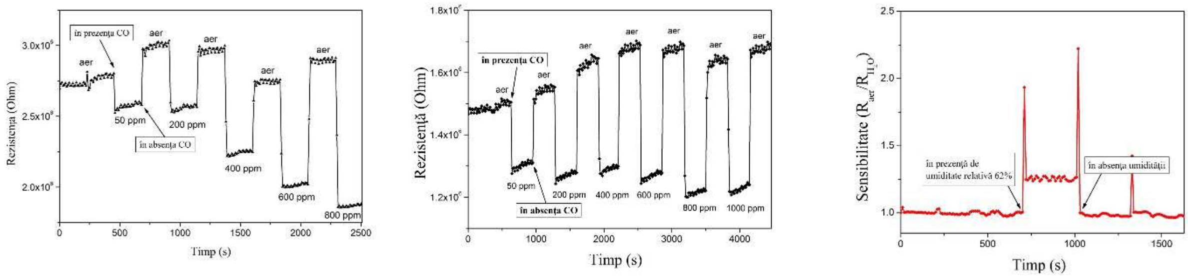
Even the conventional hydrothermal method has the disadvantage of a longer reaction time; this method proves to be more appropriate for nanorods preparation, whereas the microwave assisted hydrothermal method is recommended for nanotube preparation, with a shortened reaction time by 4-5 folds.

CHAPTER 8. APPLICATIONS

The synthesized materials described in the previous chapters were tested for sensing and biocatalysis applications.

8.1 Sensing tests of titanate based nanotube microsensors

The nanotube based sensitive films were deposited by drop-casting method, on transducers with different compositions of the support (Si and Al_2O_3). The number of layers varied from 3 to 9. The electric measurements were performed in environmental conditions, inside controlled atmosphere ovens, with a gas flow controlled by a mass flow– MFC. The electric answer on the deposited layers was measured for different concentrations of CO, CO_2, CH_4, C_3H_8, in 50-2000 ppm range, as well as 62 % relative humidity.



CO response/recovery of the sample with 5 layers (left) and 9 layers (middle), at 260 °C and titanate based nanotube's sensitivity to humidity (right), all samples on Al_2O_3 transducers

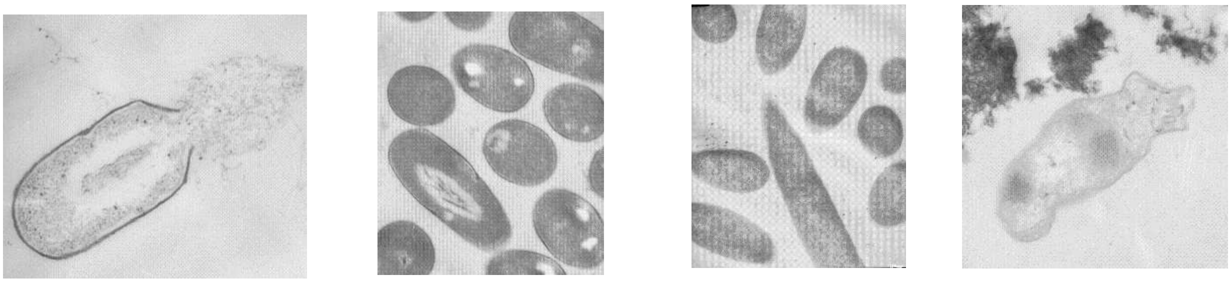
The response of titanate based nanotubes microsensors is driven by the number of deposited layers. More layers, better response to CO gas. The recovery is complete and the signal is reproducible, as it can be noticed in the figure above, middle. Other factors that influences the sensors response, on alumina support, beside working temperature and the number of layers, is the sensitivity to certain stimuli (gas, humidity, etc.). The sensors were tested to 62% relative humidity (water vapors). In the right side figure it can be noticed that the titanate based nanotubes sensors presented a response to humidity and the recovery was completed at room temperature, but the sensitivity was rather low. The titanate based nanotubes's microsensors response is driven by the number of deposited layers and, for CO gas, more layers of titanate nanotube, more intense the response to CO.

8.2 The effects of titanate based nanotubes on moderate halophilae bacteria

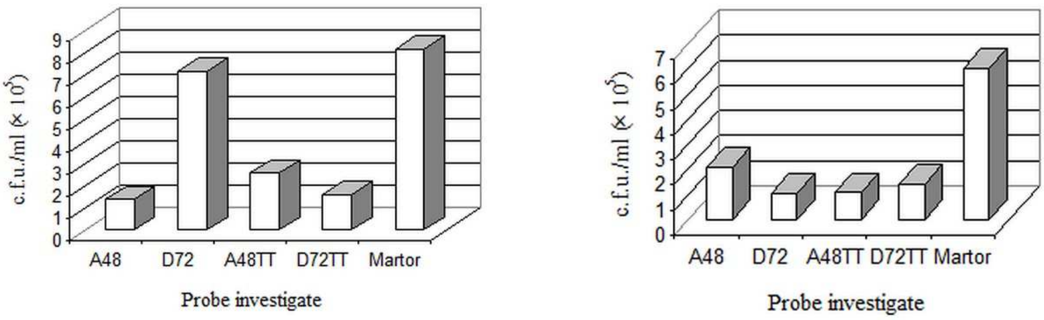
This application focused on the interaction of titanate nanotubes with several halotolerant microorganisms belonging to genera *Virgibacillus* and *Bacillus* revealing the some antibacterial properties of these nanostructured materials. Subsequently, the antibacterial activity of the obtained nanosystems on the above mentioned bacterial cells are determined and discussed. The obtained results show a significant dependence of the functional performances on the system's compositional and morphology. In particular, the antimicrobial activity of investigated nanotubes is correlated with preparation methods in various experimental conditions. Up-to-date, no reports subjecting the investigations of the titanate nanotube effect on halotolerant microorganisms, *Virgibacillus halodenitrificans* and *Bacillus subtilis*, isolated from subterranean salt rock dated from Neogene period, were identified in the literature data.

The obtained and reported results[7] some antibacterial properties of tested nanostructured materials towards halotolerant microorganisms belonging to genera *Virgibacillus* and

Bacillus. The data showed that the interaction between bacterial cells and nanotubes conducted also to different inhibition degree consequently of the composition of the bacterial cells wall. The titanate based nanotubes, starting from P25 Aeroxide commercial precursor, only dried at 110 °C or thermally treated at 400 °C presented a good antibacterial activity. Given the correlation of antimicrobial interaction between the titanate based nanotubes and the structure of the bacteria cell wall, a bactericide mechanism is possible, the presence of the potential target for the nanotubes at the level of cell wall, or interaction is randomly one.



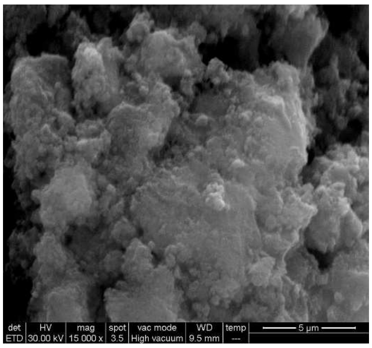
Different mechanism for modifying the cell wall of Virgibacillus halodenitrificans



Total number of c.f.u. at 24 hours of incubation of Bacillus subtillis 1/9 (left) and V. halodenitrificans 1/13 (right) strains, by titanate based nanotubes sample type

8.3 The functionalisation of titanate based nanotubes by halotolerant proteases

Salted environments are the natural habitat of certain halophilic microorganisms, both bacteria and *archaea* extremophiles which are a source of enzymes (*extremozymes*) with extreme stability. Taking into account that extremozymes are stable and active under hard conditions of pH and ionic strength, their study as biocatalysts is attractive. Many halophiles secrete proteolytic enzymes which enable the degradation of proteins and peptides in the natural hypersaline environments. The interactions of various nanostructures with biological molecules attracted a serious interest in the last years in order to understand their use for human life purposes and benefits. This application deals with approaching the functionalization of titanate nanostructures with halotolerant proteases. Since salted environments are widely used in Romania for recreational activity, it is of high interest to investigate the impact of new materials like titanate nanotubes on metabolites of halophilic microorganisms that populated such areas. To the best of the author's knowledge, this is the first report on the investigation of the functionalization of titanate nanostructures with halotolerant proteases of moderately halophilic bacterial strains isolated from salt massif dated from Neogene period[8].



SEM micrographs of the titanate based nanotubes sample, functionalized with biomaterial

Titanate based nanotubes, following the biocatalyst testing, appear to be embedded into the biomaterial matrix. Due to the nanometer dimensions, these nanostructures are difficult to highlight by scanning electronic microscopy, but it is important to notice the biomaterial, clearly grouped and developed around the nanotubes. This higher capacity of immobilization of the titanate nanotubes could be assigned to their composition, structure and morphology. The enzymatic activity appears similar when using for immobilization partially purified enzyme. Specific surface area, the total pore volume of pores and the local chemical interactions explain the capacity of immobilization.

CHAPTER 9. CONCLUSIONS. NEW SCIENTIFIC OUTCOMES

In chapter 9 new outcomes concerning the investigation of titanate based nanostructures synthesis parameters, prepared by conventional and microwave assisted hydrothermal method are presented. Nanomaterials characteristics were thoroughly studied, following the aim of the improvement of the state-of-the-art of both techniques and insights over some issues not well-defined in the literature data:

1. Synthesis method optimization

1.1. Various synthesis parameters of both conventional and microwave assisted hydrothermal methods were optimized. The optimum synthesis for 100% conversion to titanate based nanotubes requires a TiO_2 powder (amorphous, crystalline, anatase or anatase-rutile mixture) precursor to be well-dispersed and homogenized in 10 M NaOH aqueous solution for no longer than 24 hours reaction time, at 140 °C. By microwave assisted hydrothermal method, the TiO_2 powder precursor may be converted to 100% titanate based nanotubes only after 8 hours, at 135 °C.

1.2. The nature of TiO_2 precursor has no influence on titanate based nanotubes formation. All involved precursors, regardless their state (crystalline or amorphous) and polymorphism (anatase or anatase-rutile mixture) were converted to titanate based nanotubes, after hydrothermal treatment.

2. Titanate based nanotubes characterization

2.1. By high resolution transmission electron microscopy studies it was highlighted the variation of the interlayer distance forming the nanotube wall, in direct relation with the number of constitutive layers of the wall structure. The distance between the rolled nanosheets is governed by the existent defects in the nanosheets structure, consequently, the higher the number of defects in the nanosheets, the higher the interlayer distance in the nanotube wall. Moreover, the driving force of the nanosheets rolling-up is higher for multiple rolls-up (e.g. multiwalls nanotubes), rendering smaller interlayer distance and, consequently, a smaller inner diameter.

2.2. The thermal stability of the titanate based nanotubes was studied, by thermal analysis and calorimetry and by structure investigations, by *in-situ* X-ray diffraction. It was determined that the structure and the morphology of the hydrogen titanate based nanotubes (low sodium content) are stable up to 350-400 °C, whereas the sodium titanate based nanotubes are stable up to 600 °C, without any damage of the structure and morphology.

3. Investigations of the photocatalytic activity of the titanate based nanotubes

3.1. Essential aspects of photocatalytic processes such as relationship between morphology and activity for H_2 and CO_2 production, density of surface hydroxyl groups and •OH generation, ROS (•OH and $•O_2^-$) production and photocatalytic activity, were investigated.

It comes out that ROS, formed by action of photogenerated electrons and holes on adsorbed O_2 and hydroxyl groups, respectively, play an important role in determining the photocatalytic activity of titania-based materials.

3.2. Compared to single phase systems (anatase or titanate only), the charge separation at interface of semiconducting domains of anatase/titanate nanotubes plays a remarkable role on photocatalytic activity, by improving the formation rate of H_2 and CO_2.

Generally, by association of two semiconductors with aligned energy levels (apparently, the case of anatase/titanate based nanotubes system), a better charge separation is obtained, and the charges does not combine radiative. If the charges do not recombine, then congregate to catalytic reaction and the formation rate of targeted product is higher.

4. Applications of titanate based nanotubes

4.1. The response of titanate based nanotubes microsensors to gas and humidity (CO, CH_4, C_3H_8 and 62% relative humidity) was tested. It was found that a direct relation between the amounts of titanate based nanotubes (more layers) and the response of the microsensors, and the recovery capacity. The titanate based nanotubes sensors presented a response to humidity and the recovery was completed at room temperature, but the sensitivity was rather low.

4.2. The response/recovery features of titanate based nanotubes sensors are related to support type. The nature of the substrate, as porosity, chemical composition, influences the reproducibility of measurements and the recovery capacity of the sensors after injecting the analyzed gas.

4.3. Working temperature influences the electric response of the sensors. Optimal temperature for titanate based nanotube sensors was determined to be 250 °C.

4.4. Antibacterial properties of nanostructured materials towards halotolerant microorganisms belonging to genera *Virgibacillus* and *Bacillus* were tested. Given the correlation of antimicrobial interaction between the titanate based nanotubes and the structure of the bacteria cell wall, a bactericide mechanism was proposed.

4.5. By functionalization of titanate based nanotubes with moderate halotolerant bacteria strains proteases, it was noticed that the nanotubes have a high capacity of immobilization. Titanate based nanotubes, following the biocatalyst testing, appear to be embedded into the biomaterial matrix.

5. Originality

The first Romanian research group that publishes the results in ISI ranked journal, with the subject of preparation and characterization of titanate based nanotubes by conventional and microwave assisted hydrothermal methods.

To the best of the author's knowledge, we published the first report on the investigation of the functionalization of titanate nanostructures with halotolerant proteases of moderately halophilic bacterial strains isolated from salt massif dated from Neogene period.

The observations on charge separation at interface domain of biphasic system anatase/titanate based nanotubes are original and new, these data are not yet published.

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