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Ph D THESIS ABSTRACT

TiO_2 based oxide nanomaterials with application in energy and catalysis

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CONTENTS

Key words: TiO_2 based films, TiO_2 based powders, V doping, sol-gel method, microwave assisted sol-gel method

1. Introduction

Nanomaterials are materials which have at least one dimension in the nanometer range (1-100 nm) [1, 2]. According to Siegel [3], nanomaterials can be divided into: zero-dimensional (nanoparticles), one-dimensional (nanowires, nanofibers, nanotubes), two-dimensional (films) and three-dimensional (bulk).

The field of inorganic nanostructured materials has enjoyed a growing interest due to the fact that nanomaterials exhibit electrical, optical, mechanical and magnetic properties superior to their bulk counterparts [2]. This can be explained by the fact that nanomaterials have small dimensions, large surface area, high surface-volume ratio and the ability to form highly reactive surfaces with high resistance and long life [4].

From the nanostructured materials category, metal oxides, particularly semiconductor oxide with wide band gap, received over time a particular interest, due to their electrical and optical properties. They can be transparent in visible and infrared and can be both insulating and semiconducting. Among metal oxides with broadband, a particular applicability has the titanium dioxide.

TiO_2 is mainly used in photocatalytic processes, due to the specific properties such as high resistance to corrosion, high band gap values for its polymorphic modifications (3 eV-rutile and 3.2 eV-anatase), long life of excited electrons, etc. The main drawback of its applying in such processes is the small percentage of the solar energy (7%) used [5]. The current attempts are directed towards obtaining catalysts based on titanium dioxide with high reactivity into visible light ($\lambda > 400$ nm) [6, 7]; a method to achieve this goal is to dope the titanium dioxide with metal or non-metal elements.

Among the metals used to improve the TiO_2 photocatalytic activity an increasing interest is given to vanadium. One possible explanation for the improvement produced by doping TiO_2 with this metal, would be the fact that, by irradiation with visible light, excited vanadium centers donates electrons in the conduction band of the TiO_2, which allows the oxidation of molecules adsorbed on the surface. Vanadium appears to be an interesting candidate to obtaine doped titanium dioxide with valuable properties [5].

Titanium dioxide can be prepared with various morphologies (nanoparticles, nanowires, nanotubes, mesoporous) [8], for its obtaining a variety of methods being available, in both liquid phase: hydrothermal/solvothermal method, sonochemical method, electrochemical synthesis, sol-gel method, microwave synthesis [9], and vapor phase: spray pyrolysis, atomic layer deposition, chemical vapor deposition, physical vapor deposition [10].

Among these methods, sol-gel technique is an efficient and versatile method for pure or doped TiO_2 films or powder preparation. Various metal oxides were produced by this method, such as: ZrO_2, ZnO, WO_3, Al_2O_3, Nb_2O_5, TiO_2, rare earth oxides, etc. [11].

By following the alkoxide route, the synthesis is carried out using alkoxides as Ti precursors, alcohol as a solvent, water for hydrolysis and inorganic acids, as catalysts. In the sol-gel reaction, dense cross-linked three-dimensional structures are formed , that turns into gels, and these, by an appropriate heat treatment into amorphous or crystalline nanostructures (films, powders).

TiO_2 films are obtained by solution deposition on various substrates, using diferent film coating techniques (spin-coating, deep-coating, spraying) [12].

The benefits of sol-gel method are numerous, as: obtaining of nanomaterials with high purity, requiring relatively low processing temperature, allowing stoichiometry control, obtaining materials with different shapes and/or predetermined structure [13, 14].

Since the conventional sol-gel method still presents a series of disadvantages (long synthesis duration, high temperature calcination, leading to particle aggregation and poor catalytic performance), the researchers are trying to improve it, for example by combining with microwaves irradiation [15, 16]. Under microwave irradiation, the conditions to obtain monodisperse nanoparticles by heating the sample directly and rapidly are created, which leads to instantaneous decomposition of the precursors and getting a supersaturated solution. The energy is directly transferred to the reactants, thus allowing uniform growth of the nanocrystals [8, 17].

Microwave energy is transmitted to the material by the interaction of electromagnetic field on the molecular level, the heating being produced by mechanisms of dipole polarization and ionic conduction. Polarization is the process of dipoles formation, and dipoles from the sample are aligned in the direction of the applied electric field. The conduction is the process in which the ions from the sample oscillate under the influence of the field produced by microwave. Collisions resulting from rotation during polarization and dipole charge carriers during conduction, give energy of atoms and molecules in solution in the form of heat [18].

So far, the beneficial action of the microwaves in the sol-gel synthesis, has been mainly used in the process of drying and heat treatment, but not for the actual realization of the synthesis. Therefore, the results presented in this thesis have original character by the fact that microwaves were used for iradiation of sol-gel solution.

The main objective of this thesis was *to obtain, by sol-gel and microwave assited sol-gel method, nanofilms and nanopowders based on pure and vanadium doped titanium dioxide, with possible applications in energy and catalysis*. Also, it was investigated the *microwave irradiation effect on the properties of the final products, as well as the correlation between composition, structure and properties of the obtained oxide materials.*

The first research direction was represented by *obtaining and characterization of vanadium doped titanium dioxide films with possible applications in transparent conductive oxide*, direction which was less approached. *In order to obtain solutions for films deposition, sol-gel and microwave assisted sol-gel method was used and film characterization was performed in terms of morphological, structural and optical properties.*

The second research direction was the *study of vanadium doped titanium dioxide nanopowders obtained from the thermal treatment of gels obtained from conventional sol-gel and microwave assisted sol-gel method. The powders were characterized in terms of thermal, structural and morphological properties,being tested in photocatalytic reactions and water splitting.*

The third direction of research was *to establish the influence of microwaves on sol-gel process and therefore on the properties of the obtained nanofilms and nanopowders. Microwave irradiation of the solutions has led to the occurrence of different molecular species that was reflected in both the different thermal behavior of the gels, and the optical properties of the films or the photocatalytic properties of the powder.*

The present thesis is structured in three chapters aimed to fulfilling its goals.

Chapter 1 *provides general information regarding nanomaterials, especially about nanostructured metal oxides, emphasizing the importance of oxide semiconductor nanomaterials with wide band gap such as TiO_2. Also, methods that can improve the properties of TiO_2 were identified, one of these routes, namely doping with vanadium, being aproached in this thesis.*

Chapter 2 *is divided into two subsections. In the first subchapter the main methods of synthesizing oxide nanomaterials, including TiO_2 are described, highlighting the methods used to obtain nanofilms and nanopowders from the present thesis. The second subchapter is dedicated to the presentation of methods for the characterization of oxide nanomaterials in terms of morphology, optical and catalytic properties.*

Chapter 3 *contains the most important results obtained in this thesis and is divided into two subchapters, corresponding to the two types of structured nanomaterials obtained: films and powders.*

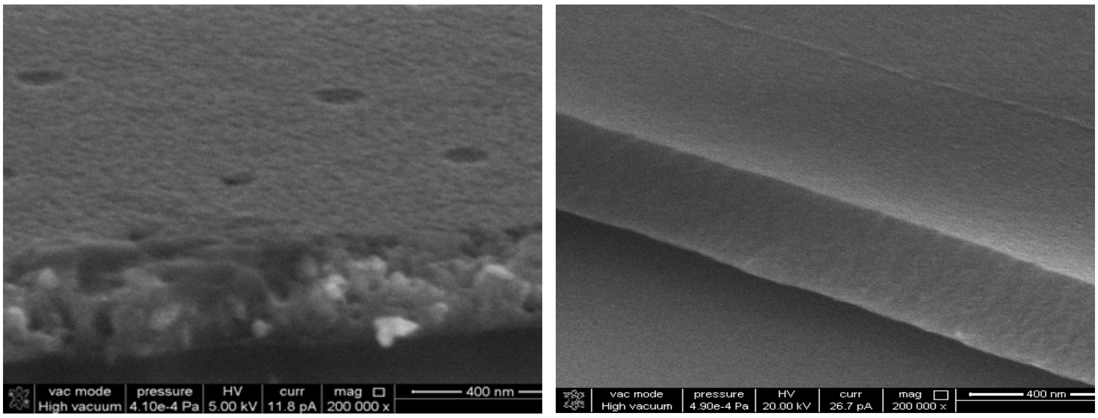
2. Experimental results

Nanostructured films based on V doped TiO_2

<u>The influence of the preparation method on the film properties</u> [19]

In the present thesis pure and V doped TiO_2 films using classical sol-gel and microwave assisted sol-gel method were obtained. In order to investigate the influence of the dopant on the properties of V doped TiO_2 films, two different molar ratios were selected on the basis of literature data [20, 21], respectively TiO_2:V_2O_5 = 99,95:0,05 şi TiO_2:V_2O_5 = 98:2, which corresponds to 1.12 and 0.03 at%. The multilayer films were obtained by successive deposition, by dip-coating and using an immersion and withdraw rate of 5 cm/min.

The films obtained by the two methods used present a smooth and continuous surface, and good adhesion to the substrate. Irradiation of sol-gel solutions with microwave led to films with improved morphology, as compared to films produced by the classical sol-gel method: more dense and homogeneous aspect (Fig. 1), reduced surface roughness (Fig. 2), and higher thickness (Table 1).



(a) **(b)**

Fig. 1. SEM micrographs showing the films cross-section for TiO_2-0.05%V_2O_5 samples with 5 depositions, obtained by: sol-gel method (a) and microwave assisted sol-gel method (b)

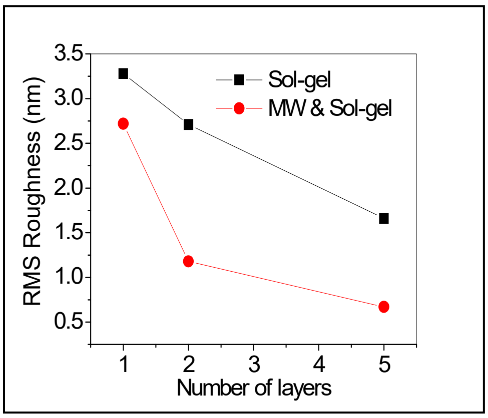


Fig. 2. Roughness variation of the TiO_2-2%V_2O_5 films, with the number of deposited layers

Table 1. Film thickness values obtained by spectroellipsometry (SE)

Probă	d_{SE} (nm)
TO5	188
$(TO5)_{MW}$	202
(TVO5-0,05%)	223
$(TVO5\text{-}0,05\%)_{MW}$	228
(TVO5-2%)	175
$(TVO5\text{-}2\%)_{MW}$	240

Synergic effect of microwave assisted sol-gel method, combined with the presence of 0.05% V_2O_5 content in TiO_2 films, led to improved optical properties for the obtained films: higher refractive index values (Fig. 3), decreased energy band gap (Fig. 4) and a good optical transmission (Fig. 5).

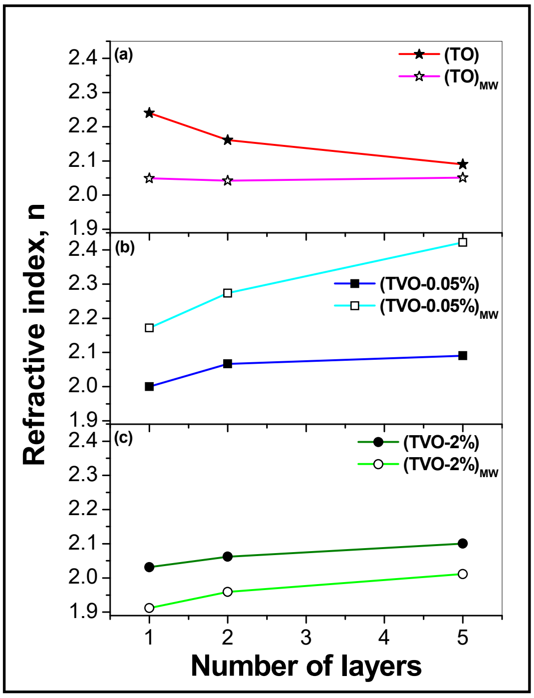


Fig. 3. Variation of the refractive index for the obtained films, function of layer number

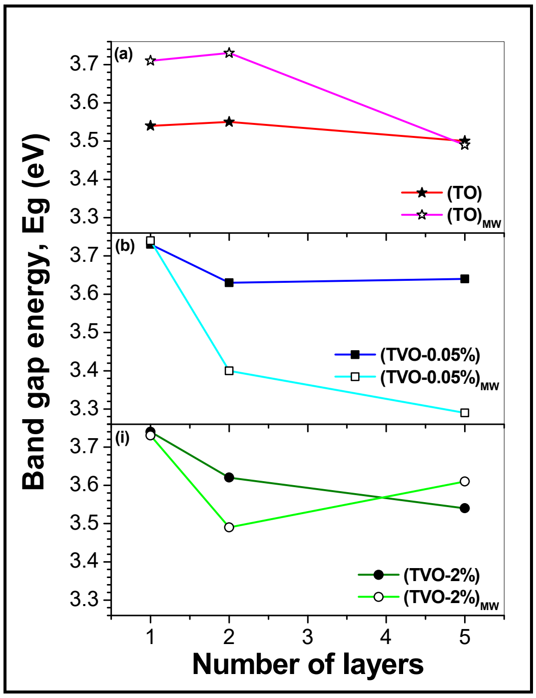


Fig. 4. Variation of the band gap energy for the obtained films, function of layer number

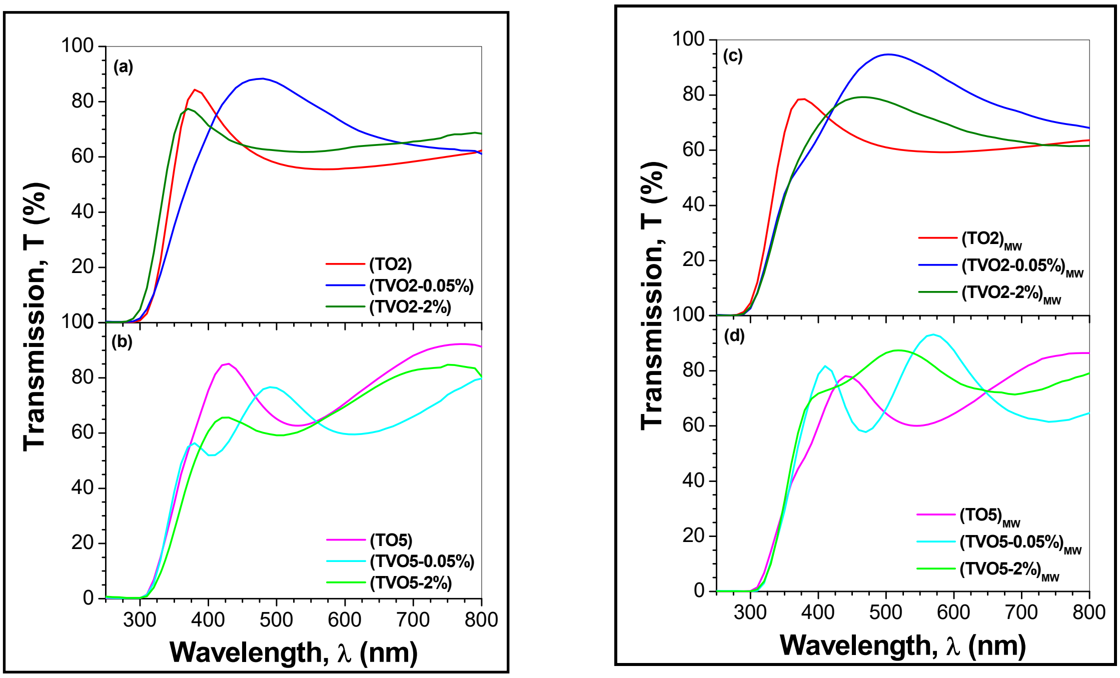


Fig. 5. Optical transmission of the films obtained by sol-gel method (a-b) and microwave assisted sol-gel method (c-d), function of the number of layers and V content

Substrate influence on the films properties [22]

In order to investigated the effect of the substrate nature on the structural, morphological and optical properties of the films, multilayer films were obtained (5 layers) on microscope glass, microscope glass covered with SiO_2 buffer layer (SiO_2/glass) and Si wafer. Pure TiO_2 and vanadium doped TiO_2 films (with 0.05% V) were deposited on various substrates by dip-coating using solutions obtained by sol-gel or microwave assisted sol-gel method. The percentage of dopant was selected based on previous results [19], which led to the conclusion that film with the best morphological and optical properties are obtained by using 0.05% V_2O_5, combined with the use of the microwaves.

By the method of deposition used, undoped and V doped TiO_2 films with similar thickness, intrinsic porosity, low surface roughness (below 2 nm) were obtained (Fig. 6). The roughness and thickness of the films are less influenced by the nature of the substrate.

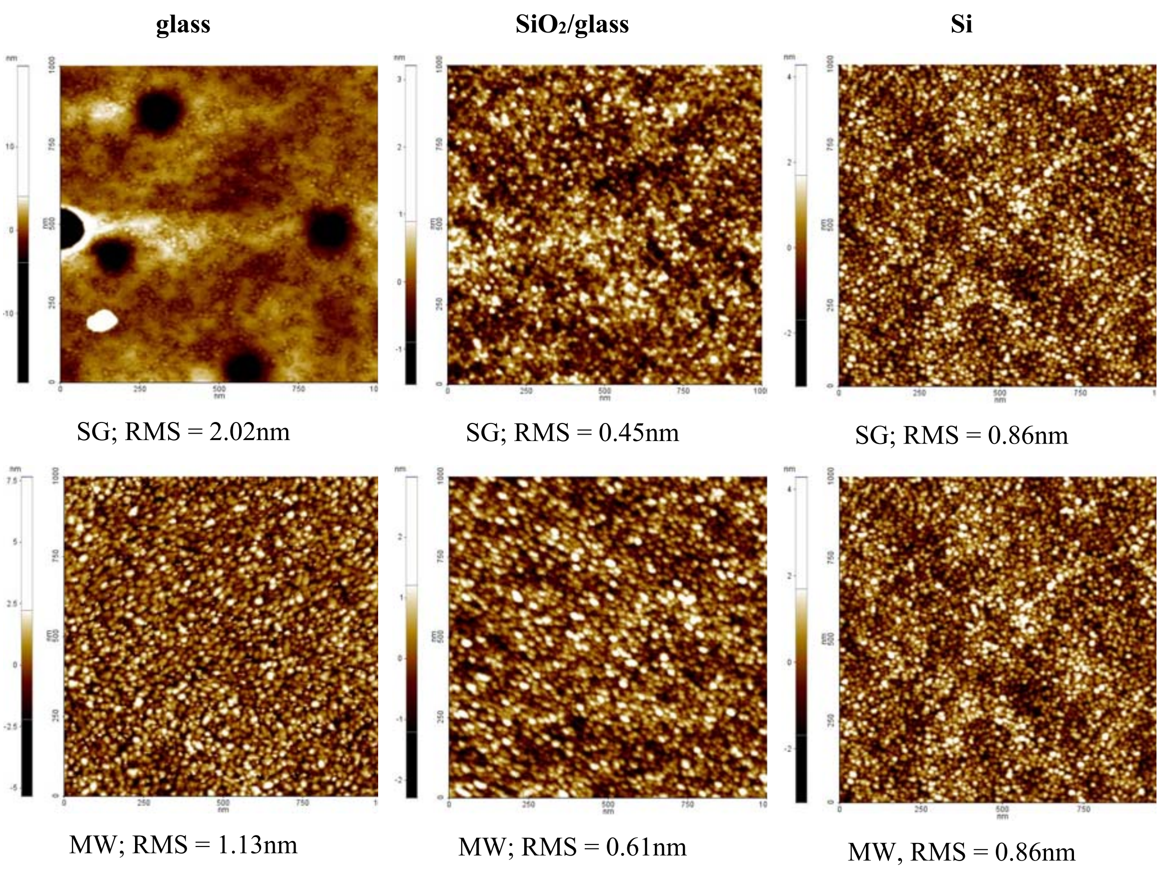


Fig. 6. Morphology of the TiO_2 films doped with 0.05% Vanadium deposited on glass, SiO_2/glass and Si

By X-ray diffraction (Fig. 7 and 8), for all the obtained films, regardless of the nature of the substrate used, the presence of anatase crystalline phase was revealed. The influence of the different substrates used was connected to their degree of crystallization, being well known that the crystalline substrates induce the crystallization of the deposited films.

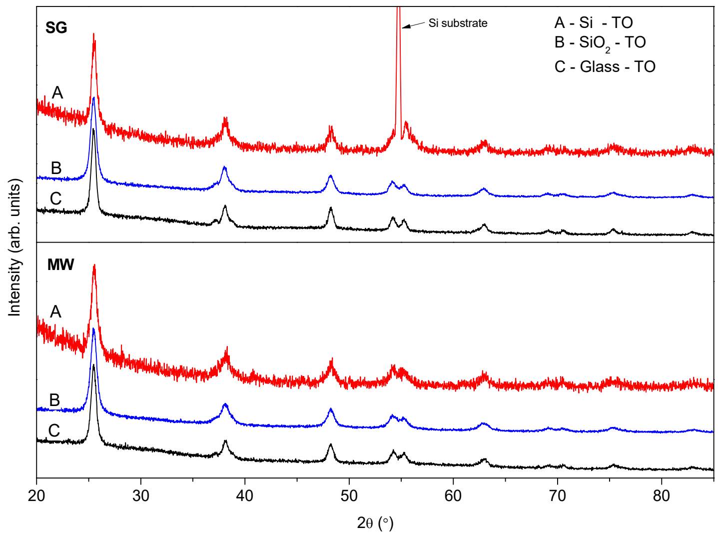


Fig. 7. X-ray diffraction patterns of the TiO_2 films obtained by sol-gel and microwave assisted sol-gel method: A - Si (red), B - SiO_2/glass (blue) and C – glass (black)

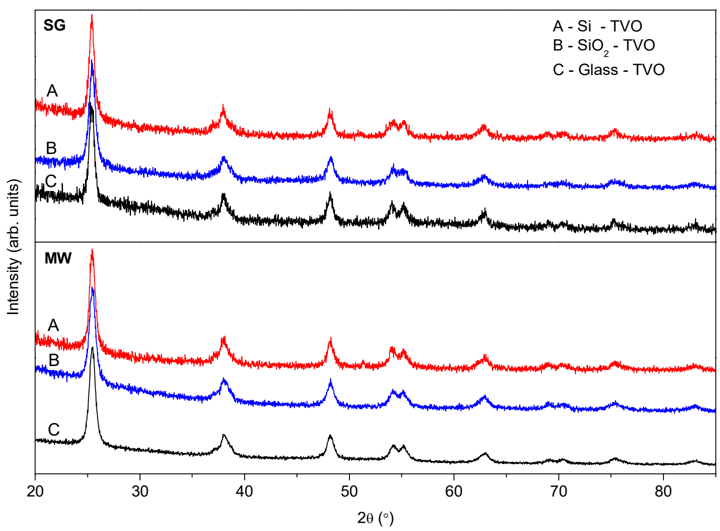


Fig. 8. X-ray diffraction patterns of the V - doped TiO_2 films obtained by sol-gel and microwave assisted sol-gel method: A - Si (red), B - SiO_2/glass (blue) and C - glass (black)

The influence of substrate on the refractive index is more evident the in case V-doped TiO_2 films, obtained by microwave-assisted sol-gel method (Fig. 9), leading to significant higher refractive index on glass and SiO_2/glass substrates. This trend is opposite as compared to TiO_2 films.

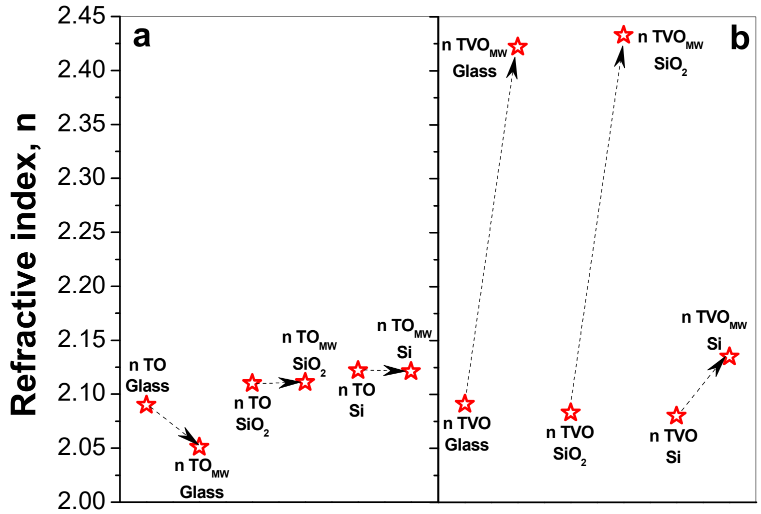


Fig. 9. Refractive index of TiO_2 (a) and TiO_2-V (b) films determined at λ = 630 nm

The following partial conclusions were established:

- The films obtained by microwave assisted sol-gel method had improved properties, compared to the films obtained by the conventional sol-gel method, namely: (i) a compact and continuous structure with very low roughness, (ii) films with increased thickness (iii) higher refractive index and increased transmission.
- The best optical properties (transmission > 90%, high refractive index, low band gap energy) were obtained for TiO_2 films doped with 0.05% V_2O_5 obtained in the presence of microwaves, improved optical characteristics recommending these films for applications in the transparent conductive oxide.
- Interaction between film and substrate is important only for the deposition of the first layer. The influence of the substrate is no longer noticeable in the 5 layered films: they have similar properties: thickness, porosity, roughness, crystalline phase
- The influence of the substrate is visible in the variation of the refractive index of V doped TiO_2 films deposited by microwave assisted sol-gel method.

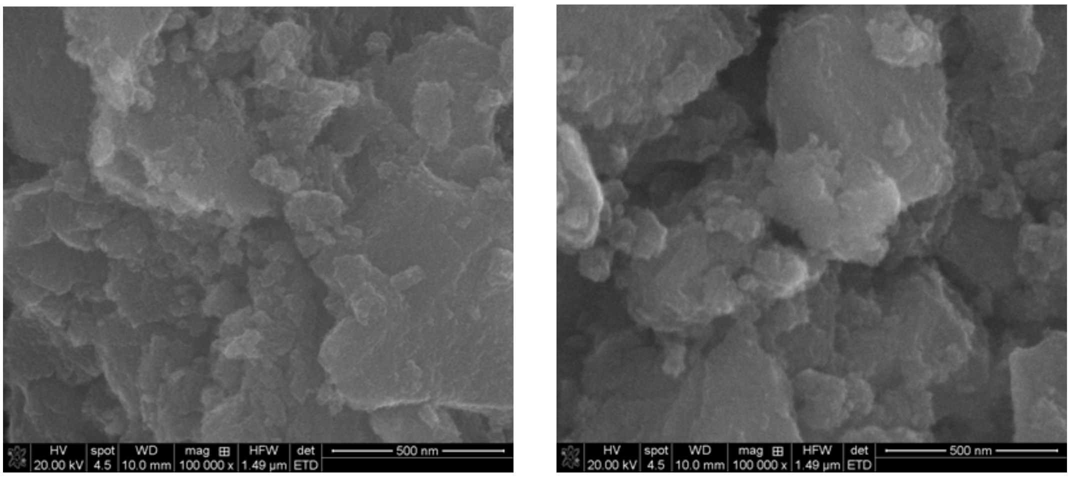
Nanostructured powders based on V doped TiO_2

Sol-gel powders [23]

In the present thesis, powders based on vanadium doped TiO_2, obtained by gelling the solutions used to deposition of the films were also studied. The obtained gels were dried at 100 ºC for 16 h, followed by a thermal treatment for 1 h at 300 °C or at 450 °C, with a heating rate of 1°C/min. in order to eliminate the water and organic residues. The thermal treatment was established based on thermogravimetric and thermo-differential analysis.

The powders were characterized in terms of structural, morphological, as well as adsorption properties.

It has been found that different concentration of vanadium used for doping TiO_2 (0.05% or 2% V_2O_5) did not affect the structural and morphological properties of the samples (Fig. 10).



(a) (b)

Fig. 10. SEM images of (a) TiO_2-0.05%V_2O_5 sample and (b) TiO_2-2%V_2O_5 sample

The EDX analysis revealed the presence of V only in the case of Ti-V 2% sample (1.12% at.), in the amount closely to the predicted value (Fig. 11).

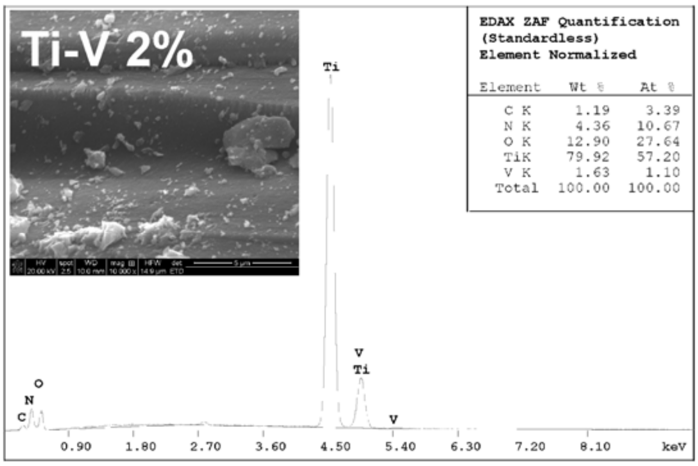


Fig. 11. EDX spectra of TiO_2-2%V_2O_5 sample

The textural parameters (specific surface area (S_{BET}), total pore volume (V_{total}) increased with increasing the percentage of vanadium, while average pore diameter (D) decreased (Table 2).

Table 2. BET surface area (SBET), total pore volume (Vtotal) and pore size (D) of the samples

Sample	S_{BET} (m²/g)	V_{total} (cm³/g)	D (nm)
TiO_2-0.05% V_2O_5	150.1	0.11	3.1
TiO_2-2% V_2O_5	242.7	0.13	2.5

Microwave assisted sol-gel powders [24]

Research in this thesis also includes the results on the influence of microwaves on the thermal behavior of the pure TiO_2 and vanadium doped TiO_2 gels, compared with the conventional sol-gel method.

The thermal stability of the resulted gels, in the presence and in the absence of the microwave field, was investigated by thermogravimetric and thermo-differential analysis (TG/DTG/DTA) and thermogravimetric and thermo-differential analysis coupled with evolved gas analysis (TG/DTA/EGA).

For undoped TiO_2 powder, from the TGA/DTA/DTG curves, it can be seen that thermal decomposition of gels was not influenced essentially by the method of preparation (Fig. 12).

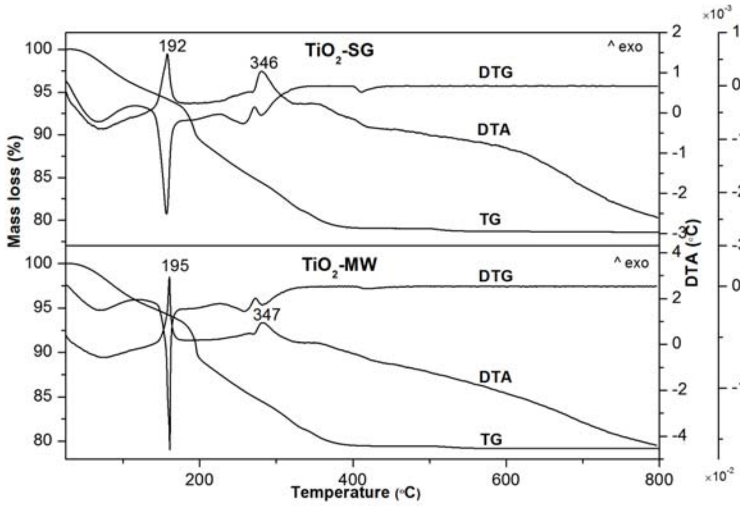
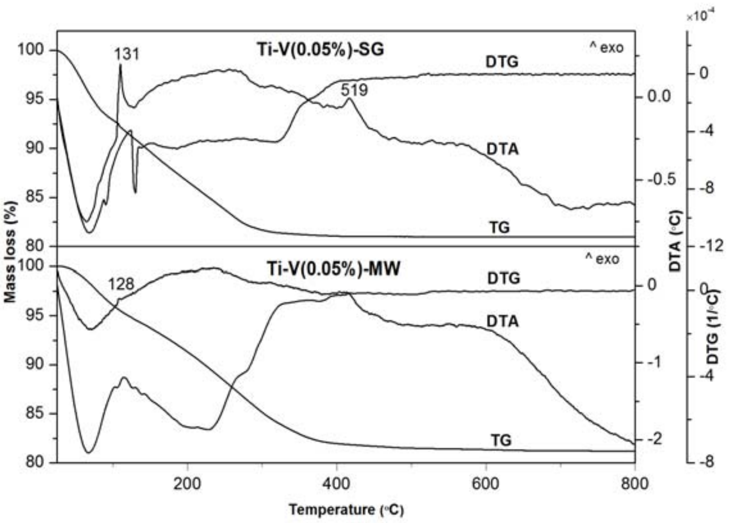
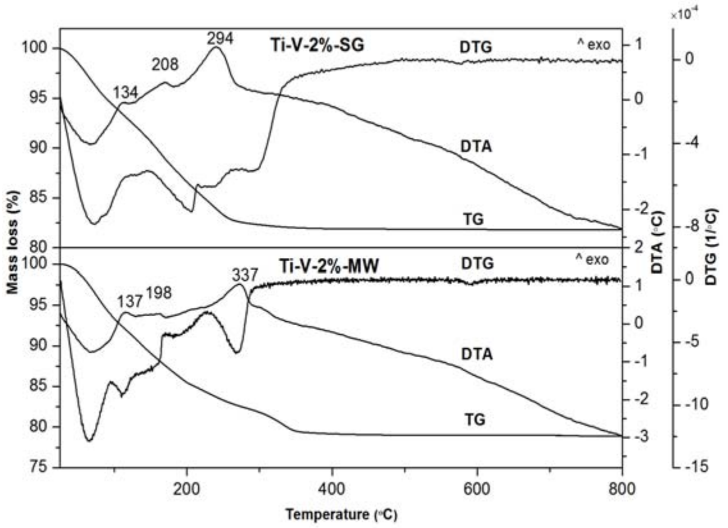


Fig. 12. DTA/TGA/DTG curves of the TiO_2 samples

In the case of V doped TiO_2 samples, the influence of the dopant and the preparation method on the TiO_2 decomposition, was put in evidence (Fig. 13). The differences in the behaviour of the samples could be correlated to the different molecular species present in the resulted gels obtained by different preparation method (sol-gel or microwaves assisted sol-gel method) and the amount of dopant.



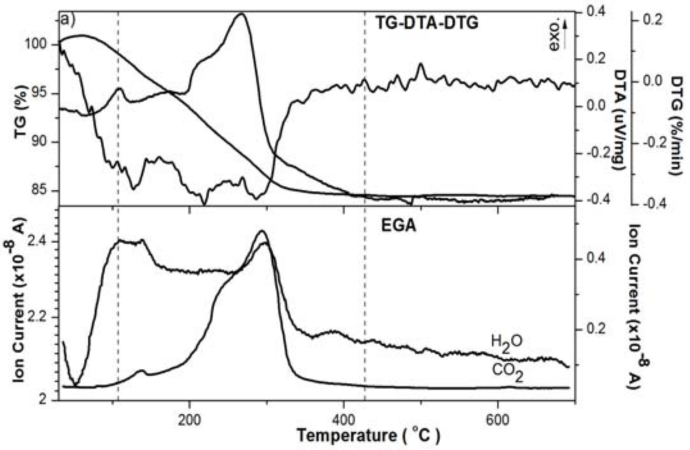
(a)



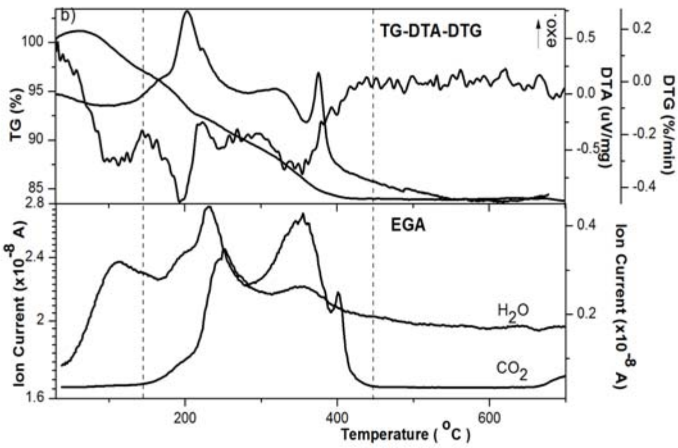
(b)

Fig. 13. DTA/TGA/DTG curves of the: TiO_2-0.05%V_2O_5 samples (a) and TiO_2-2%V_2O_5 samples (b)

TG/DTA/EGA measurements confirmed the different thermal behavior of V doped TiO_2 gels obtained by the microwave assisted sol-gel. Regardless of the method used, the same gases were evolved (CO_2 and H_2O), but their release occurred at different temperatures and in different amounts (Fig. 14).



(a)



(b)

Fig. 14. TG/DTG/DTA/EGA curves of TiO_2-2%V_2O_5 samples obtained by sol-gel method (a) and microwave assisted sol-gel method (b)

Catalytic studies of the vanadium doped TiO_2 powders [23]

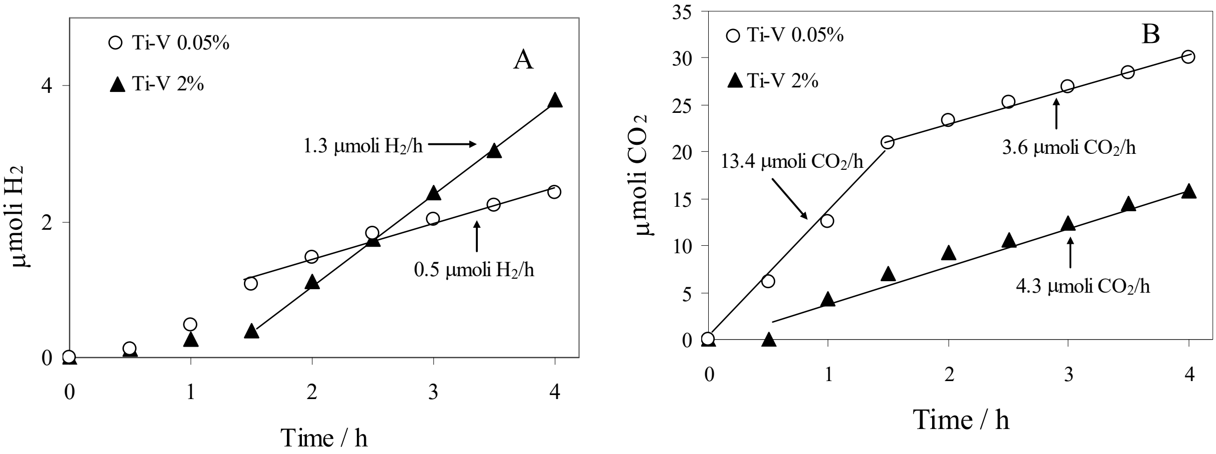
The photocatalytic tests under simulated solar light were carried out in order to observe whether improvements are achieved when TiO_2 host material is doped with V_2O_5. Previous studies reported that the vanadium doping has a beneficial effect on the photocatalytic activity of TiO_2 [25], decreasing TiO_2 band gap being considered to be the main reason for the observed improvement activities.

Vanadium doped TiO_2 nanopowders obtained by sol-gel and assisted sol-gel method were tested in the reactions of water spliting and for methanol oxidation. The reaction rates, expressed as μmol H_2 or CO_2/g of catalyst was calculated in the linear domain of the activity plots, after the steady state was established.

For the sol-gel catalysts, the sample with higer amount of dopant (TiO_2-2%V_2O_5) was more active to produce H_2 (1.3 μmol H_2/h) compared to the sample with low vanadium content (TiO_2-0.05% V_2O_5, 0.5 μmol H_2/h).

The rate of CO_2 formation in the linear domain was relatively close for the two investigated catalysts; 3.6 μmol CO_2/h over TiO_2-0.05% V_2O_5 and 4.3 μmol CO_2/h over TiO_2-2% V_2O_5, respectively (Fig. 15).

In the case of microwave assisted sol-gel powders, the sample with lower amount of dopant (TiO_2-0.05% V_2O_5) was more active both to produce H_2 (0.64 μmol H_2/h, compared to 0.23 μmol H_2/h for TiO_2-2%V_2O_5), and for methanol mineralization (4.7 μmol CO_2/h, compared to 1.27 μmol CO_2/h for TiO_2-2%V_2O_5) (Fig.



16).

Fig. 15. Comparative H_2 (A) and CO_2 (B) evolvement for sol-gel obtained catalysts

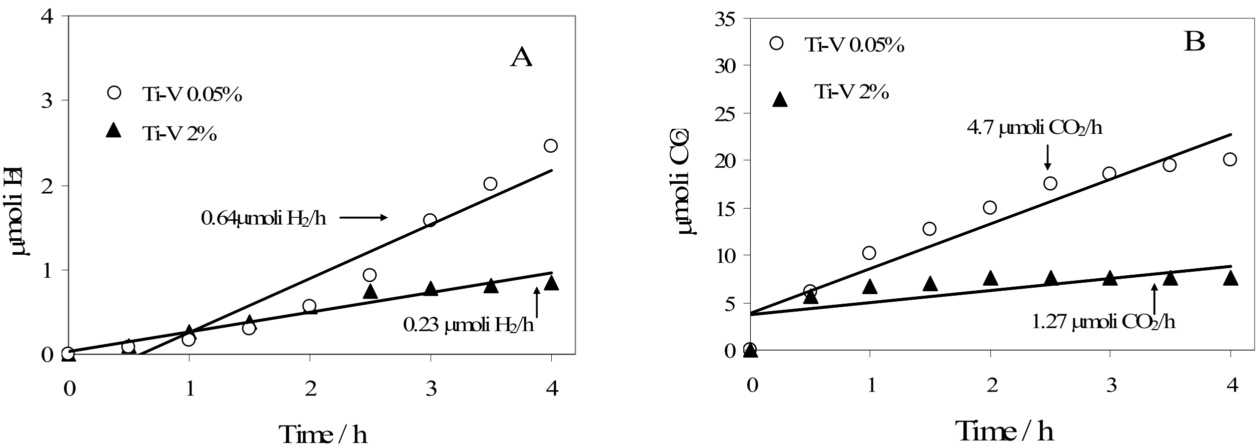


Fig. 16. Comparative H_2 (A) and CO_2 (B) evolvement for microwave assisted sol-gel obtained catalysts

It should be noted that, the catalyst with lower content of dopant (TiO_2-0.05%V_2O_5) obtained by microwave assisted sol-gel method is the most active in terms of photocatalytic activity (0.64 μmol H_2/h, respectively 4.7 μmol CO_2/h), compared to the similar catalyst obtained by sol-gel method (for which were obtained 0.5 μmol H_2/h, respectively 3.6 μmol CO_2/h), under the same reaction conditions.

The following partial conclusions were established:

- A more complex thermal decomposition of the gels obtained by microwave assisted sol-gel by can be attributed to the presence of various species and a large number of molecular species in the gel. The formation of different molecular species in the solution during the gllation process can influence the properties of the resulted powders.
- No significant differences were observed in the structural and morphological properties of the sol-gel doped TiO_2 powders with different amounts of vanadium (0.03% and 1.12%), but the sample TiO_2-2%V_2O_5 have specific surface area with almost 100 m^2/g higher than the sample TiO_2-0,05%V_2O_5, which is expected to influence the photocatalytic activity of the samples.
- The comparative results of the photocatalytic tests under solar irradiation conditions of vanadium doped TiO_2 samples obtained by sol-gel method showed that TiO_2-2%V_2O_5 sample is a better catalyst for the dissociation of water, while the catalyst TiO_2-0,05%V_2O_5 is more active in methanol oxidation.
- The TiO_2-0.05%V_2O_5 sample obtained by microwave irradiation of the solutions showed the best fotocatalitic activity, for both tests performed.

3. Conclusions:

- Using sol-gel method and microwave assisted sol-gel method, pure and vanadium doped TiO_2 films and powders with different amount of vanadium, 0.05% V_2O_5 (0.03 at.%V) and 2% V_2O_5 (1.12 at.%V) were obtained.
- The obtained multilayer films (with 2 and 5 layers) were characterized in terms of morphology, structural and optical properties, while the powders were characterized from the point of view of structural, morphological, thermal behavior and the catalytic properties.
- The irradiation of sol-gel solutions with microwaves lead to different behavior of the solutions and of the obtained gels. Thus, the solutions obtained by microwave assisted sol-gel method presented an increased stability compared with the solutions obtained by sol-gel method. An increased stability of the solution is very important for multilayer films preparation.
- Also, films obtained by microwave irradiation solutions, presented enhanced features compared with those obtained by conventional sol-gel method. The best optical properties (optical transmission over 90%, high refractive index, low band gap energy) were obtained

for TiO_2 films doped with 0.05% V_2O_5 in the presence of microwaves, improved optical characteristics recommending these films for TCO applications.

- The influence of microwaves was also reflected in the thermal behavior of the vanadium doped TiO_2 gels, which present more complex decomposition than in the case of gels obtained by conventional sol-gel method. Complex thermal decomposition can be attributed to the different type and number of molecular species present in these gels.
- Lastly, different molecular species present in the solution in the moment of gelation can influence the resulted powder properties. Preliminary photocatalytic investigations for water splitting and methanol oxidation showed that the catalyst with lower amount of vanadium (TiO_2-0.05%V_2O_5) obtained by microwave assisted sol-gel method exhibited the highest photocatalytic activity compared to powder obtained by conventional sol-gel method.

4. Original contributions:

The original contributions of the thesis, based on the results obtained, are:

- Using for the first time a microwaves assited sol-gel method for preparing V-doped TiO2 fims and powders.
- Obtaining solutions with enhanced stability and prolonged gellation time, by microwaves irradiation that are particularly important for multilayer films preparation.
- Obtining vanadium doped TiO_2 films with enhanced optical properties (high refractive index, low energy band gap), which recommended these films for TCO applications.
- Improving the photocatalytic activity (water splitting and methanol oxidation) of vanadium doped TiO_2 powders by irradiating solutions with microwave.

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Note: * - The second number corresponds to reference number from the Thesis