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Structural characterization of Nb and La doped nanostructured titania powders and coatings

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The aim of this part of research was to elucidate the complex effect of different parameters and phenomena on obtained nanostructured titania powders and coatings suitable for various applications. Through this work we showed that titania coatings exhibit a distinct behavior in respect to their powder counterparts. We have investigated the strong influence of the substrate, temperature, type and concentration of dopants (Nb and La) on nanostructure development in titania coatings. The obtained results were compared to the results of titania powders prepared under the same conditions.

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1. Introduction

Nanostructured titania is one of the most studied semiconducting materials from fundamental and practical point of view, due to their excellent properties, which are useful in many applications such as: optical, sensors and solar devices, photocatalysis, biomaterials etc. Properties of titania depend on many parameters, such as method and conditions of preparation, crystalline phase type (anatase, rutile), grain size, surface area, the presence of dopants or impurities. Since anatase is more suitable than rutile in many fields of applications (monitoring some gases, pollutant photodegradation etc.) it is necessary to stabilize anatase phase at higher temperatures and hinders anatase to rutile transformation [1,2,3,4]. The addition of different concentrations and type of dopants can be a useful way to prevent anatase to rutile transition and to inhibit its grain growth. Although the studies have been attempting to understand how dopants affect titania properties [5,6], there is still limited information concerning the effect of dopants on the phase formation, microstructural development and thus the properties of titania.

Expansion of nanostructured materials, especially coatings, has opened the new opportunities in tailoring of titania properties. However, the application of the titania/anatase coatings in different devices faces the problem of complicated investigations concerning effects of substrate, dopants, and heat treatment on its performances. A great number of results, reported on this subject, are based mostly on the titania powders. However, as expected, the titania properties are quite different depending on whether they are obtained as a powder or in a form of a coating. The results obtained on titania powders concerning application should be used very carefully in the field of titania coatings.

Therefore, we found interesting and necessary to deal with a preparation of titania powders and coatings and with comparison of their structural characteristics, pointing out the fact that coatings exhibit a distinct behavior in respect to their powder counterparts. The aim of this work was to investigate the influence of the substrate, temperature, type and concentration of Nb and La as dopants on nanostructure development in titania coatings. The obtained results were compared to the results of titania powders prepared under the same conditions.

2. Experimental procedure

The sol-gel method was used to obtain titania powders and coatings, starting from transparent titania sols, undoped and doped with 2, 4 and 6 at% of Nb or La. For the prepartion of titania sols, as starting materials were used: titanium-butoxide ($Ti(OC_4H_9)_4$ - Fluka, Switzerland), isobutanol, distilled water and appropriate acid (HCl was used for Nb-doped samples and HNO_3 for La-doped ones). Titania sols were prepared according to the procedure proposed in earlier work [7]. The final molar ratio of starting materials, in all titania sols, was $Ti(OC_4H_9)_4 : H_2O : C_4H_9OH : HCl$ or $HNO_3 = 1 : 2 : 5 : 0.5$ and pH value was about 2. As a dopant source were used $NbCl_5$ (Merck, Germany) aqueos solution which was added to the HCl and $La(NO_3)_3 \times 6H_2O$ (Riedel-de Haën-Germany) which was dissolved in HNO_3.

Undoped and doped titania sols, prepared for titania coatings, were deposited on α-alumina substrate by dip technique with withdrawal speed of 0.02 cm/s. Prior to coatings deposition, the gold comb shaped electrodes were deposited on substrates by physical vapor deposition technique, using sputter deposition on the instrument BAL-TEC SCD 005. Titania gel coatings, obtained on this way, were subjected to the heat treatment at 500°C for 10 min. This procedure was repeated five times and after that, all samples were heated at 560°C, 660°C and 800°C for a selected time. Titania powders prepared from the same sols, after their gelation, were dried at 60°C and 120°C and heated at 450 and 660°C, for a selected time.

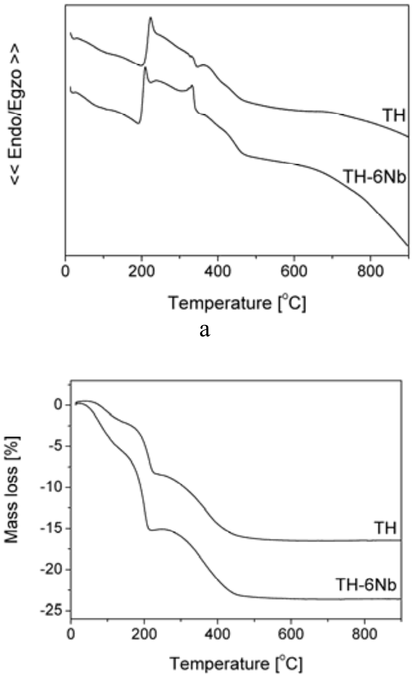
The specific surface area of the titania powders, as well as the pore size distribution, were measured by low-temperature nitrogen adsorption according to the BET method (ASAP 2000). Thermal analysis (DTA/TG, Bähr STA 503) was performed at temperatures up to 900°C with a heating rate of 10^{o}C/min. The XRD data were recorded with a step size of 0.015°/s and a collection mode of 60 s/step (XRD, Philips PW 1820, CuK_{α} radiation). Titania coatings were characterized by X-ray diffraction under the same conditions as powders. The average grain size of anatase and rutile in titania powders and coatings was estimated from the full width at half maximum by Scherrer's equation, $d = 0.94\cdot\lambda/(\beta\cos\theta)$ [8]. The surface, cross section, structure and average grain size of coatings, as well as size and morphology of particles in the powders, were investigated by scanning electron microscope (SEM, JEOL 6460LV).

The undoped titania powders were denoted by letters TH (if HCl was used) or TN (if HNO_3 was used), while THA or TNA denote undoped titania coatings on alumina substrate. In the doped samples, to these notation were added numbers which denote the atomic percentage of dopants (2, 4 or 6) along with chemical symbols of dopants (TH-4Nb for a powder, or TNA-4La for a coating).

3. Results

3.1 Titania Powders

According to the DTA/TG results, in undoped and doped titania powders during heating, the similar effects appeared, which are illustrated in Fig. 1 for TH, and TH-6Nb powders. The broad exothermic peak, Fig. 1a, in the region of 200-470°C was derived, partially, by organic residue decomposition and partially, by the phase transformation of titania powders. The overlapping of these peaks complicate exact determination of the phase transformation temperatures in titania powders. The mass changes appear due to water and hydroxyl group losses and solvent evaporation. These effects are more pronounced in doped powders than in undoped ones, Fig. 1b (for example the total mass loss in the TH powder is about 16.5 wt%, while in the TH-6Nb it is about 23.7 wt%). This difference in mass loss between undoped and doped samples occurs as a result of introducing the different anionic groups associated with dopants.



a

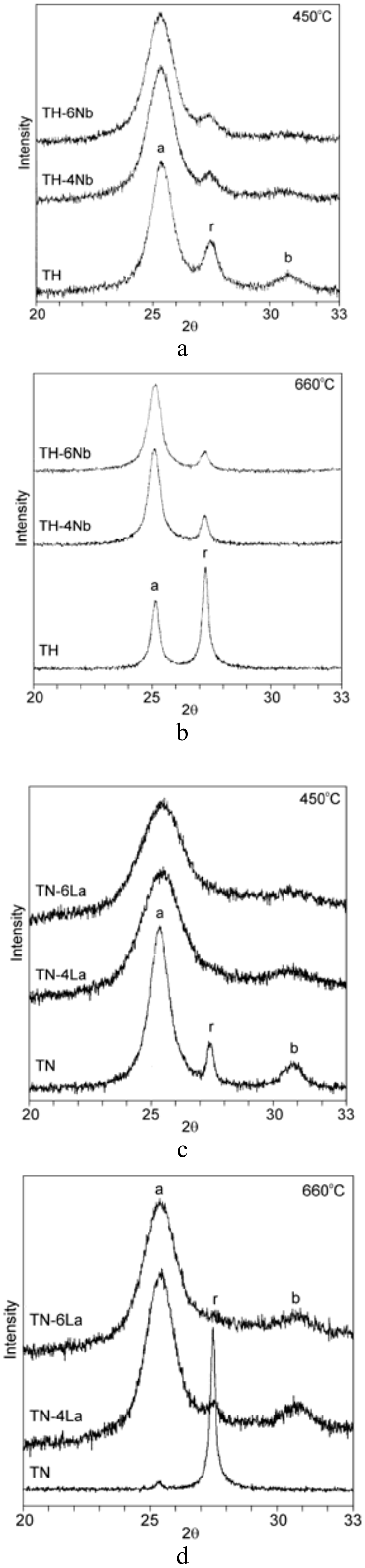
b

Fig. 1. DTA (a) and TG (b) curves of TH and TH-6Nb powders.

According to BET method, the specific surface areas of titania powders calcined at 450°C, are relatively high and increase with doping. The surface area of the TN powder is around 80 m^2/g (corresponding to the average particle size of 18.3 nm) in respect to the TN-6Nb powder with the surface area of about 203 m^2/g (corresponding to the average particle size of 7.2 nm).

XRD patterns of undoped and Nb- and La-doped titania powders after heat treatment at 450°C and 660°C during 5h, are presented in Fig. 2.

XRD patterns for undoped and Nb- and La-doped powders show the differences in intensity and shape of the characteristic peaks of titania crystalline phases (for anatase at $2\theta \sim 25.3°$, for rutile at $2\theta \sim 27.4°$ and for brookite at $2\theta \sim 31°$). The undoped powders, TH and TN, after heat treatment at 450°C/5h consist of anatase, rutile and brookite phases (brookite phase is more pronounced in the TN than in the TH samples), Fig 2a,c. With increasing heat treatment at 660°C/5h, brookite phase completely disappears, the portion of anatase decreases, while the phase transformation to rutile progresses. In the TN sample, rutile becomes the dominant phase, Fig. 2d. This suggests that presence of chlorine ions (TH powder) suppresses anatase to rutile transition. In the Nb-doped powders, rutile is present at 450°C and its quantity increases with the temperature, but also decreases at higher concentration of niobium. On the other hand, in La-doped powders, rutile is not detected at 450°C and it started to appear at 660°C in very small quantities. This clearly indicated that doping with Nb and La stabilize the anatase phase.



a

b

c

d

Fig. 2. XRD patterns of undoped, Nb-doped (a, b) and La-doped (c, d) powders after heat treatment at 450°C/5h and 660°C/5h (a-anatase, r-rutile, b-brookite).

The average crystallite size, estimated from the anatase (101) and rutile (110) diffraction peaks, using the Scherrer formula, are given in Table 1. For undoped powders heated at temperatures up to 660°C the average crystallite size of anatase is in the range from 8.1 to 25.4 nm, and decreases when dopants (Nb or La) are added. Thus, besides the stabilization effects, dopants effectively suppress growth of particles.

Table1. Average grain size of anatase and rutile in titania powders estimated by XRD.

Sample notation	450°C		660°C	
	$d_{anatase}$ *[nm]*	d_{Rutile} *[nm]*	$d_{Anatase}$ *[nm]*	d_{Rutile} *[nm]*
TH	8.1	9.6	25.4	38.6
TH-4Nb	7.4		19.6	22.0
TH-6Nb	7.1		16.3	19.5
TN	11.1	19.4		47.9
TN-4La	4.2		7.9	
TN-6La	4.1		6.0	

3.2 Titania Coatings

The phase composition in titania coatings on alumina substrate was different in respect to corresponding titania powder after similar heat treatment. XRD results in Fig. 3, showed that in the undoped titania coating on alumina substrate (sample THA without gold electrodes) after heat treatment even up to 660°C for 5h, anatase is a dominant phase, with average grain size of about 25 nm, but at the same time characteristic peak of rutile phase appeared, although it is small in intensity. According to these results as well as to those presented earlier [7], alumina as a substrate, hinders phase transformation anatase to rutile.

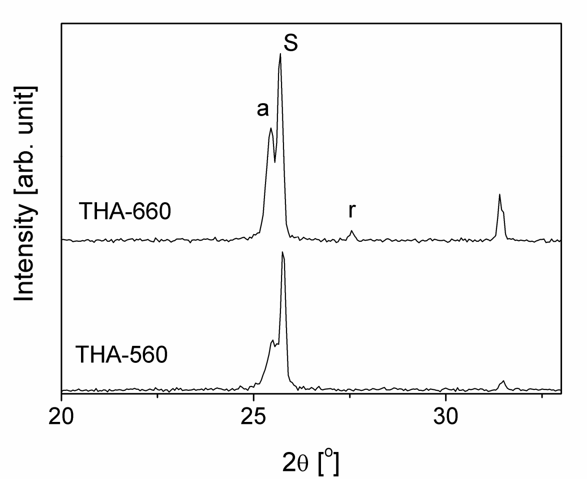
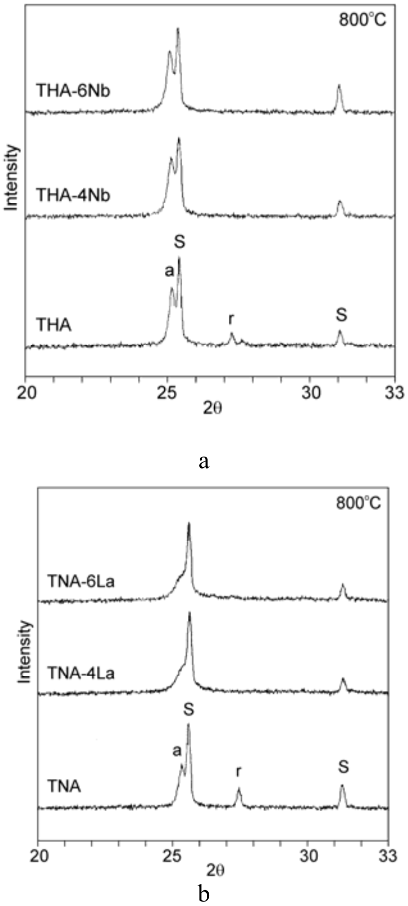


Fig. 3. XRD patterns of THA coatings on alumina substrate without gold electrodes after heat treatments at 560°C/7h and 660°C/5h (a-anatase, r-rutile, S-substrate)

However, the same titania coatings, THA, on alumina substrate with gold electrodes (deposited before coatings), showed an increase of the anatase thermal stability. This is obvious from XRD results presented in Fig 4., obtained after heating of these coatings up to 800°C for 3h, which besides peaks characteristic for alumina substrate, consist of intensive anatase peak while the peak of rutile is negligible in intensity. Comparing above mentioned results, it can be concluded that gold behaves as the anatase phase stabilizer.



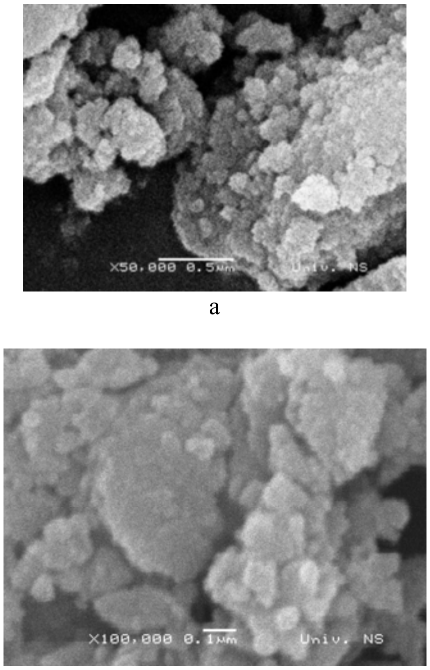
a

b

Fig. 4. XRD patterns of undoped, Nb-doped (a) and La-doped (b) titania coatings after heat treatment at 800^{o}C/3h (a-anatase, r-rutile, S-substrate)

It is also important to mention a significant dopant effect on anatase phase stability in titania coatings. According to XRD results in Fig 4., it can be concluded that in Nb- and La-doped coatings, anatase is stable phase even after heat treatment up to 800°C for 3h, since there is no evidence of rutile phase. Anatase to rutil transformation occured only in undoped titania coatings, THA and TNA. From these patterns it is evident that peak of anatase phase becomes broader, both in the Nb- and La-doped coatings, indicating that these dopants hinder grain growth. Characteristic peak of anatase phase is more pronounced in coatings doped with Nb than in La doped titania coatings, Fig 4., showing that La has the same effect on anatase stabilization and its grain growth, as in powders.

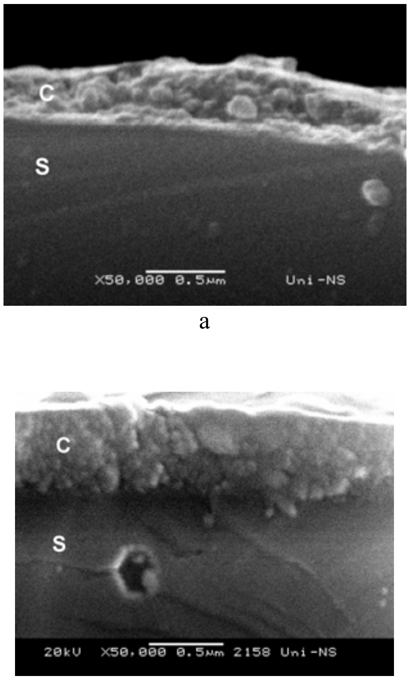
SEM micrographs of titania powders, Fig. 5, show that particles are agglomerated, but still with the sizes less than 30 nm. According to the SEM micrographs of titania coatings, Fig. 6, they have good adherence to the substrate, a uniform thickness less than 1 μm and fine nanograin structure.



a

b

Fig. 5. SEM micrographs of a) TN and b) TN-6La titania powdersafter heat treatment at 450^{o}C/5h.



a

b

Fig. 6. SEM micrographs of a) THA and b) THA-6Nb titania coatings after heat treatmant at 560 ^{o}C/7h (C-coating, S-substrate)

4. Discussion

The presented results clearly show that stability of anatase phase is increased when dopants (Nb and La) are added, but also when titania is prepared in the form of a coating on alumina substrate. In addition, the average crystalline size of anatase decreases with addition of dopants. In the same powder if the rutile phase exists, the sizes of their crystallites are always larger than the size of anatase crystallites (Table 1). This can be explained by thermodynamic analysis [9, 10], which suggests that below a critical size (which was determined to be 14 nm) rutile have a higher surface energy, than anatase, so that anatase is a stable phase. Thus, rutile starts to form when the fine anatase particles reach the critical size, providing appropriate sites for the nucleation of the rutile phase. In nanocrystalline titania the rate of anatase to rutile transformation is limited by rutile nucleation. Models for this transformation that have been proposed in literature [11] included three different modes of rutile nucleation such as: interface nucleation, surface nucleation and bulk nucleation, which are operative in various temperature range. The nucleation mechanism is temperature dependent and the derived kinetic equations carry particle size terms. The dominant mechanism of rutile nucleation at temperatures below 500°C is interface nucleation. At higher temperatures, it is expected that surface nucleation mechanism is operative. However, in nanocrystalline titania at these temperatures, coalescence of neighboring anatase grains is very fast and more anatase particles are in contact with each other. This causes the movement of grain boundaries and cooperative atomic rearrangement which affect anatase grain growth and rutile nucleation on their surfaces, Table 1. The change in anatase grain size from 8.1 to 25.4 nm suggests mentioned operative mechanism anatase to rutile transformation and could confirm that the critical size for the anatase to rutile transformation changes with temperature (increases with the increase of temperature).

It is well known [12, 13] that transformation kinetics depend on the type and number of vacancies in titania structure. In anatase and rutile structure Ti is sixfold coordinated, but the number of shared octahedral edges increases from two in rutile to four in anatase. The shared edges should lead to cation–cation repulsion and structural destabilization. Thus, the presence of cation vacancies could help in stabilization of the anatase phase [12]. On the other hand, the oxygen vacancies placed in anatase planes act as nucleation sites for the anatase to rutile phase transformation [12]. From the processing point of view, the temperature at which the phase transformation occurs depends on the preparation method, precursors, dopants etc. Solubility of Nb in titania lattice is relatively high, as ionic radius of Nb^{5+} (0.70 Å) and Ti^{4+} (0.68 Å) are similar. Ruiz et al. [13] have observed that some of Nb ions enter inside the crystallites and they are located in substitutional Ti sites. The remaining Nb ions are segregated and/or located on the surface, what was confirmed by XPS analyses [13]. Thus, the observed inhibition of particle growth (Table 1) can be explained with the fact that higher concentration of Nb on the surface of titania nanoparticles can effectively hinder the particle coarsening by restricting diffusion of Ti ions. In addition, the growth of TiO_2 crystallites could be inhibited by the slight stress, introduced in titania lattice due to difference between ionic radius of Nb^{5+} and Ti^{4+} [12]. The observed stabilization of the anatase phase (Fig. 2) could be also obtained by the creation of one Ti cation vacancy as a consequence of the charge compensation of Nb^{5+} in substitution to Ti^{4+}.

On the other hand, due to much larger ionic radius of La^{3+} (1.016 Å) than Ti^{4+} (0.68 Å) and its 3+ oxydation state, someone may expect different behaviour of La in comparison to Nb. However, inhibition of crystallite growth and thus stabilization of the anatase phase is even more pronounced with La addition (Fig. 2). It is difficult for La^{3+} to replace Ti^{4+} inside the lattice, because the La^{3+} ionic size is much larger than Ti^{4+} one [14]. However, it is believed that La incorporates into titania at low temperatures by the formation of Ti-O-La bonds on the surface of small particles. This inhibits the movement of surface Ti atoms and particle coarsening by restricting direct contact of neighboring crystallites, causing the observed stabilization of the anatase phase. At high concentration La segregates as ternary when rutile is formed [15]. The presented results indicate that La^{+3} as a dopant is even more efficient than Nb^{+5} for hindering the grain growth and stabilization of anatase phase.

Some researches have been emphasizing [11] a well-known effect of gold as anatase stabilizer, but still its mechanism should be more thoroughly elucidated. Gold can appears in different oxididation states (besides metallic gold Au) with different ionic radii. According to some literature data [11] related to the mechanism of gold influence on anatase to rutile transformation (and also related to the high diffusive rate of nanosized gold particles [16]) most probably suggestion is that gold is present as a metallic Au, mainly on the surface of anatase and hinders its transformation to rutile.

5. Conclusions

The obtained results show very complex effect of different variables such as heat treatment conditions, substrate, the dopant type and concentrations on the development of nanostructured sol-gel titania coatings, phase transition, as well as the stability of anatase phase and its average grain size. In respect to titania coatings, titania powders undergo the phase transformation anatase to rutile at lower temperature (450°C) than in coatings (at 660°C in the coatings without gold electrodes and at 800°C in the coatings with gold electrodes). It has been indicated more complex phenomena in titania coatings in respect to powder, mainly because of very important effect of substrate. It is also shown that in titania coatings as well as in powders, La as a dopant is more efficient in hindering anatase to rutile transition and suppressing grain growth than Nb as a dopant.

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