



## Preparation and photocatalytic activity of the layered titanates

Marija Milanović\*, Ivan Stijepović, Ljubica M. Nikolić

Department of Materials Engineering, Faculty of Technology, University of Novi Sad, Serbia

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### Abstract

Titanate structures were synthesized in highly alkaline solution using hydrothermal procedure. As-prepared powders were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM). A specific surface area of the powders was measured by BET method. Results confirmed formation of layered trititanates, already after one hour of hydrothermal synthesis. To examine the photocatalytic activity of the as-prepared layered titanates, methylene blue (MB) was employed as a target compound in response to visible light at ambient temperature. It was observed that the specific surface area, size distribution and crystallinity are important factors to get high photocatalytic activity for the decomposition of MB.

**Keywords:** layered titanates, hydrothermal synthesis, photocatalytic activity

### I. Introduction

During the past decade, a great research interest has been directed to the development of one-dimensional (1D) nanostructured powders based on oxide ceramics. Compared with bulk materials, one-dimensional nanoscale materials, with their large specific surface areas and possible quantum confinement effects, exhibit distinct electronic, optical, chemical and thermal properties [1–3]. In many cases, 1D nanostructures are superior to their counterparts with larger dimensions. Major advantages of these materials are their extraordinary lengths, flexibility and structure that can allow them to be physically manipulated into various shapes according to the design requirements.

Among the large family of 1D nanomaterials, titanates are of particulate interest. Depending on the synthesis method as well as on the conditions within the method, it is possible to obtain different morphology of titanate structures, such as nanotubes, nanowires, nanofibers, nanorods, nanobelts etc. Titanate based 1D materials are one of the most promising semiconducting ceramic materials because of their wide range of potential applications in nanoelectronics, in optical and sensor devices, in solar cells, pigments, biomedicine etc [1,4–8]. In addition, the high morphological and struc-

tural specificity of 1D titanates (phase composition, high aspect ratio and large specific surface area) may enhance their photocatalytic activity, leading to a higher potential of applications in environmental purification [9–13]. Beside the growing interest in obtaining the one dimensional titanates, the exact mechanism of their formation is still a controversial topic discussed widely in contemporary literature [14–21]. Also, the clarification of the individual stages that precede the formation of the 1D structures, is one of the opened questions; even the composition of these materials is still a subject of debate [1, 22–24].

In this work, layered titanates were synthesized by a hydrothermal method. The main subject of this work was to investigate the photocatalytic activity of the layered structures under irradiation by visible light. These structures can be understood as an early stage in the formation of the one dimensional titanates.

### II. Experimental

The titanate based structures were synthesized through a simple hydrothermal procedure, reported previously [25]. The commercial TiO<sub>2</sub> powder (Degussa P25) was dispersed in an aqueous solution of 10M NaOH and stirred for some time. The hydrothermal reaction was carried out at 150°C for a different time (1, 3, 6 and 10 hours). After hydrothermal treatment the precipitates were washed with distilled water and absolute

\* Corresponding author: tel: +381 21 485 3750, fax: +381 21 450 413, e-mail: [majam@uns.ac.rs](mailto:majam@uns.ac.rs)

ethanol until the neutral pH was reached and separated from the solution by centrifugation. The formed titanates were dried at 120°C for one day. The samples were named Tm-x, where x stands for the time (in hours) of the hydrothermal reaction. The sample notations of the obtained titanates are shown in Table 1, together with the values of specific surface areas.

**Table 1. Sample notations and specific surface areas of titanate samples**

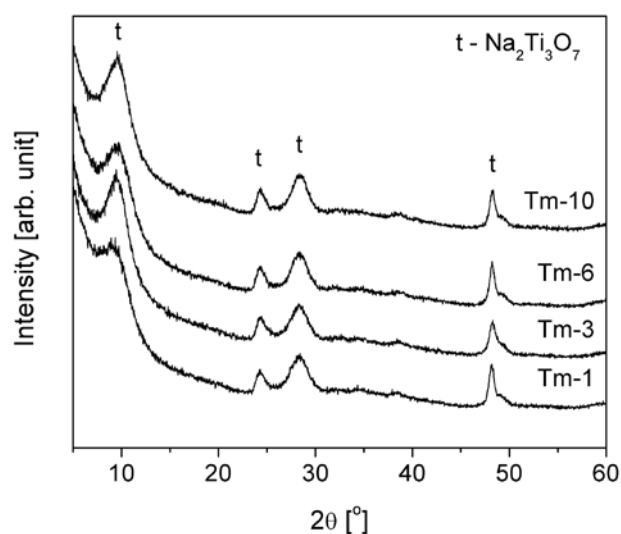
Sample notation	Reaction time [h]	Specific surface area, $S_{\text{BET}}$ [m <sup>2</sup> /g]
Tm-1	1	355
Tm-3	3	219
Tm-6	6	322
Tm-10	10	249

Photocatalytic activity of the prepared powders was estimated from the change in the concentration of methylene blue (MB) under visible light irradiation. In several glasses containing 0.01 g of titanate powder, a 10 ml of aqueous MB solution (100 ppm) was added and maintained in the dark for 1 hour with stirring. After completion of the adsorption of MB, the solution was kept under irradiation of visible light for a different time (10, 20, 30, 40, 50 minutes). Samples were centrifuged in order to separate the titanates from the solution. The concentration change of MB was then determined by measuring the maximum absorbance at  $\lambda = 665$  nm as a function of irradiation time using a spectrophotometer. Concentration of methylene blue solution was calculated with the absorbency of the methylene blue solution separated from sample. The adsorption degree of titanate powders to methylene blue solution was valued as  $c/c_0$ , where  $c$  is the concentration of methylene blue solution separated from adsorbed sample and the  $c_0$  is the concentration of the original methylene blue solution.

Structural changes caused by the hydrothermal conversion of the starting P25 powder to titanate structures were studied by FT-IR spectroscopy and electron microscopy. Phase composition of the samples was determined by X-ray powder diffraction (XRD). X-ray diffraction patterns of the titanates were collected on a Siemens D500 instrument using Ni-filtered Cu-K $\alpha$  radiation of wavelength 1.5418 Å. The XRD data were recorded with a step of 0.02°/sec. Microstructure and morphology of the samples were analyzed using a Hitachi H9000-NA transmission electron microscope (TEM) operating at 200 KV, capable of performing the selected area electron diffraction (SAED). Fourier-transform infrared spectroscopy measurements were performed using a Nicolet-Nexus 670 FT-IR in the range 400–4000 cm<sup>-1</sup>. Specific surface area of the powders was estimated by low temperature nitrogen adsorption measurements performed on a Quantachrom Autosorb-3B instrument applying BET method.

### III. Results and discussion

Typical XRD patterns of one-dimensional titanates are shown in Fig. 1. Titanate structures are present already after one hour of hydrothermal synthesis, which is an unusually short time. From the Fig. 1, it can be identified four characteristic diffraction peaks at  $2\theta \sim 9.5$ , 24.44, 28.37 and 48.32°, related to the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> type of titanates, (ICDD card 31-1329), in accordance with the literature [24,26]. These peaks could be ascribed to the interlayer spacing typical for one-dimensional titanate structures [24–28]. The intensity of the peak around 9.5° is increasing with the reaction time, indicating the rise in crystallinity.



**Figure 1. XRD patterns of titanate structures prepared under hydrothermal reaction**

The FT-IR spectra of the prepared powders, Fig. 2, are in accordance with the XRD results. The peak at around 900 cm<sup>-1</sup> is typical for one-dimensional structures [3,25]. This peak corresponds to the vibration of Ti-O nonbridging oxygen bonds, and could imply on the formation of Ti-O-Na bonds. The characteristic bands in the range 450–700 cm<sup>-1</sup> are due to the different types of Ti-O vibrations, and they are related with tetrahedrally and octahedrally coordinated titanium ions [29]. As previously reported [25], those peaks are missing in the starting powder and it can be assumed that observed vibrations are the result of the breaking of the Ti-O bonds and formation of titanate layers by the intercalation of Na<sup>+</sup> and OH<sup>-</sup> ions into the structure. Two prominent absorption bands at 3400 and 1600 cm<sup>-1</sup> in all samples have been assigned to the stretching and bending vibrations of the adsorbed water molecules [3,29]. It suggests that these structures are preferred for water to be absorbed on the surfaces and in pores of the materials. The shape and intensity of the observed bands are changing with the duration of the hydrothermal reaction, implying on a structure modification and possible formation of the one-dimensional titanate structure.

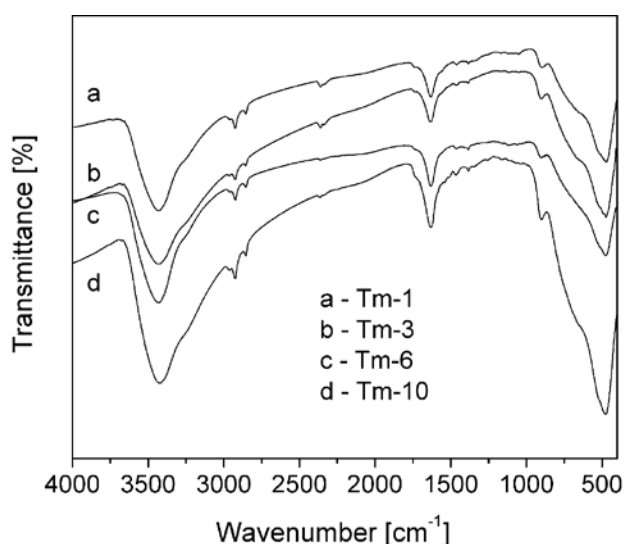


Figure 2. FTIR spectra of one dimensional layered titanate structures

TEM images of titanate structures, shown in Fig. 3, are in good agreement with previously presented results. Formation of lamellar titanate sheets is obvious already after 1 hour of hydrothermal synthesis, Fig. 3a. Complete transformation of P25 nanoparticles into titanate nanosheets indicates that the rate of hydrothermal reaction is very high in the early stages of layer formation. As the reaction proceeds, formed nanosheets grow together with a tendency to curl at their edges, leading to the formation of nanotubes. Hence, similarly to our findings reported earlier [30], obtained results implied that the most probable formation mechanism of titanate nanotubes is a transformation of titania nanoparticles into titanate nanosheets due to the attack of sodium hydroxide during the hydrothermal reaction. These results have shown that the formation of one dimensional titanate structures (layered titanates) is possible after unusually short time, but com-

plete transformation into the nanotubes requires a longer time for the synthesis than 10 hours tested in this work.

Efficiency of the formed layered titanates in water purification is shown in Fig. 4. Photocatalytic activity of the prepared powders was estimated from the change in the concentration of methylene blue (MB) under visible light irradiation. It can be seen that obtained layered titanates have shown high efficiency in the photocatalytic degradation of MB. It was particularly noteworthy that the process showed an extraordinary fast initial rate of adsorption, which can be verified by the fact that the amount of adsorbed MB onto Tm-6 and Tm-10 samples within 10 minutes achieved almost 60% in respect to the initial concentration. With increasing the time of irradiation, the concentration of MB decreases, indicating the rise of titanates activity. These changes are clearly noticeable from the transition of the solution colour from dark blue to light blue shades with increasing time of excitation, Fig. 5. The remarkable photocatalytic activity of the layered titanates can be attributed to their defective structure and high specific surface area. The BET specific surface area, Table 1, increases following the order: Tm-3 < Tm-10 < Tm-6 < Tm-1, which does not correlate with the crystallinity of the powders, but is probably caused by the different porous nanostructure in the investigated samples. Further analyses regarding the pore shape and size distribution are needed to explain this behaviour. With respect to the starting powder ( $S_{BET}(P25) = 80 \text{ m}^2/\text{g}$ ), the high specific surface area of as-synthesized layered titanates made it possible to adsorb pollutant molecules into the surface of the pores, thus favouring the photocatalytic degradation mediated with these structures. It can be seen that after completion of the MB absorption, the most effective titanates in MB degradation are those with the highest specific areas.

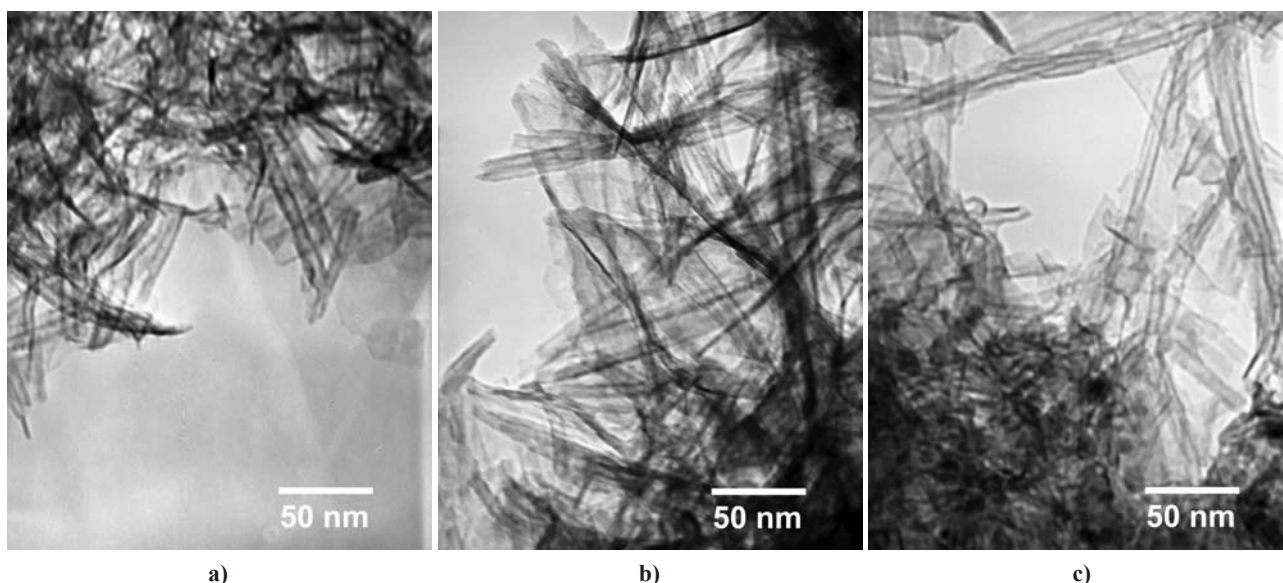


Figure 3. TEM images of one dimensional layered titanate structures: a) Tm-1, b) Tm-3 and c) Tm-10

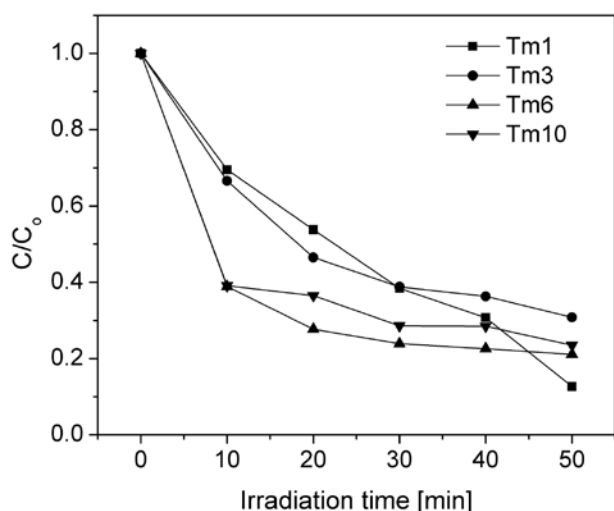


Figure 4. Photocatalytic degradation of MB onto layered titanate structures under visible light excitation

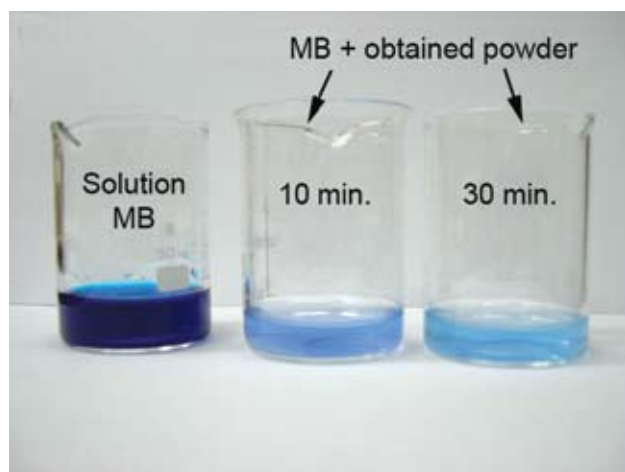


Figure 5. Change of the solution color influenced by MB degradation onto layered titanate structures

#### IV. Conclusions

We have successfully synthesized layered titanates through a simple hydrothermal procedure. Layered titanates can be understood as an early stage in the formation of the titanate nanotubes. The XRD patterns have shown that the particulate structure of the starting powder is completely altered already after one hour of hydrothermal treatment at 150°C and layered titanates have started to appear. The structure of the obtained titanates corresponds to the sodium titanates. The crystallinity of the powders increases with the time of hydrothermal reaction. As-prepared layered titanates have very high values of specific surface area, up to 355 m<sup>2</sup>/g in contrast with 80 m<sup>2</sup>/g of the starting powder, P25 Degussa. The obtained layered titanate structures have shown the high efficiency in photocatalytic degradation of MB, already after 10 minutes under visible light excitation. Remarkable photocatalytic activity of the layered titanates can be attributed to their defective structure and high specific surface area. Additional investigations regarding the pore size distribution are

needed in order to explain the influence of the titanate pore structure on their photocatalytic efficiency.

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#### References

- H.-H. Ou, S.-L. Lo, "Review of titania nanotubes synthesized via the hydrothermal treatment: Fabrication, modification and application", *Sep. Purif. Technol.*, **58** (2007) 179–191.
- E.I. Kapinus, T.A. Khalyavka, V.V. Shimanovskaya, T.I. Viktorova and V.V. Strelko, "Photocatalytic activity of spectro-pure titanium dioxide: Effects of crystalline structure, specific surface area and sorption properties", *Inter. J. Photoen.*, **5** [3] (2003) 159–166.
- J.A. Toledo-Antonio, S. Capula, M.A. Cortes-Jacome, C. Angeles-Chavez, E. Lopez-Salinas, G. Ferrat, J. Navarrete, J. Escobar, "Low-temperature FTIR study of CO adsorption on titania nanotubes", *J. Phys. Chem. C*, **111** (2007) 10799–10805.
- M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, "Environmental applications of semiconductor photocatalysis", *Chem. Rev.*, **95** (1995) 69–96.
- W. Wang, H. Lin, J. Li, N. Wang, "Formation of titania nanoarrays by hydrothermal reaction and their application in photovoltaic cells", *J. Am. Ceram. Soc.*, **91** [2] (2008) 628–631.
- M. 'Ou Li, X. Xiao, R. Liu, "Synthesis and bioactivity of highly ordered TiO<sub>2</sub> nanotube arrays", *Appl. Surf. Sci.*, **255** [2] (2008) 365–367.
- A. Corma, "From microporous to mesoporous molecular sieve materials and their use in catalysis", *Chem. Rev.*, **97** (1997) 2373–2420, and the references therein.
- F. Dong, W. Zhao, Z. Wu, "Characterization and photocatalytic activities of C, N and S co-doped TiO<sub>2</sub> with 1D nanostructure prepared by the nano-confinement effect", *Nanotechnol.*, **19** (2008) 365607.
- L. Xionga, Y. Yang, J. Maia, W. Suna, C. Zhang, D. Wei, Q. Chen, J. Ni, "Adsorption behavior of methylene blue onto titanate nanotubes", *Chem. Eng. J.*, **156** (2010) 313–320.
- P. Wena, H. Itoh, W. Tang, Q. Feng, "Transformation of layered titanate nanosheets into nanostructured porous titanium dioxide in polycation solution", *Microporous Mesoporous Mater.*, **116** (2008) 147–156.
- C.-W. Peng, M. Richard-Plouet, T.-Y. Ke, C.-Y. Lee, H.-T. Chiu, C. Marhic, E. Puzenat, F. Lemoigno, L. Brohan, "Chimie douce route to sodium hydroxo titanate nanowires with modulated structure and conversion to highly photoactive titanium dioxides", *Chem. Mater.*, **20** (2008) 7228–7236.
- Z.-J. Chen, B.-Z. Lin, B.-H. Xu, X.-L. Li, Q.-Q. Wang, K.-Z. Zhang, M.-C. Zhu, "Preparation and characterization of mesoporous TiO<sub>2</sub>-pillared titanate photocat-

- alyst”, *J. Porous Mater.*, DOI 10.1007/s10934-010-9369-1.
13. S.-Y. Kim, T.-H. Lim, T.-S. Chang, C.-H. Shin, “Photocatalysis of methylene blue on titanium dioxide nanoparticles synthesized by modified sol-hydrothermal process of  $\text{TiCl}_4$ ”, *Catal. Lett.*, **117** (2007) 3–4.
  14. N. Viriya-empikul, N. Sano, T. Charinapanitkul, T. Kikuchi, W. Tanthapanichakoon, “A step towards length control of titanate nanotubes using hydrothermal reaction with sonication pretreatment”, *Nanotechnol.*, **19** (2008) 036501.
  15. Z. Y. Yuan, B. L. Su, “Titanium oxide nanotubes, nanofibers and nanowires”, *Colloids Surf., A* **241** (2004) 173–183.
  16. A. Thorne, A. Kruth, D. Tunstall, T. S. J. Irvine, W. Zhou, “Formation, Structure, and stability of titanate nanotubes and their proton conductivity”, *J. Phys. Chem. B*, **109** (2005) 5439–5444.
  17. Q. Chen, G.H. Du, S. Zhang, L.-M. Peng, “The structure of trititanate nanotubes”, *Acta Crystallogr. B*, **58** (2002) 587–593.
  18. Y. Yang, X. Wang, L. Li, “Crystallization and phase transition of titanium oxide nanotube arrays”, *J. Am. Ceram. Soc.*, **91** [2] (2008) 632–635.
  19. B. Poudel, W.Z. Wang, C. Dames, J.Y. Huang, S. Kunwar, D.Z. Wang, D. Banerjee, G. Chen, Z.F. Ren, “Formation of crystallized titania nanotubes and their transformation into nanowires”, *Nanotechnol.*, **16** (2005) 1935–1940.
  20. E. Horvth, A. Kukovecz, Z. Knya, I. Kiricsi, “Hydrothermal conversion of self-assembled titanate nanotubes into nanowires in a revolving autoclave”, *Chem. Mater.*, **19** 4 (2007) 927–931.
  21. A. Kukovecz, M. Hodos, E. Horvth, G. Radnczi, Z. Knya, I. Kiricsi, “Oriented crystal growth model explains the formation of titanate nanotubes”, *J. Phys. Chem. B*, **109** 38 (2005) 17781–17783.
  22. C.-C. Tsai, H. Teng, “Structural features of nanotubes synthesized from NaOH treatment on  $\text{TiO}_2$  with different post-treatments”, *Chem. Mater.*, **18** (2006) 367–373.
  23. S. XuChun, E. Yang, Z. YiFan, “Synthesis of  $\text{M}_x\text{H}_y\text{-Ti}_3\text{O}_7$  nanotubes by simple ion-exchanged process and their adsorption property”, *Chin. Sci. Bull.*, **52** [18] (2007) 2491–2495.
  24. M. Qamar, C.R. Yoon, H.J. Oh, N.H. Lee, K. Park, D.H. Kim, K.S. Lee, W.J. Lee, S.J. Kim, “Preparation and photocatalytic activity of nanotubes obtained from titanium dioxide”, *Catal. Today*, **131** (2008) 3–14.
  25. Lj. M. Nikolic, M. Maletin, P. Ferreira, P. M. Vilarinho, “Synthesis and characterization of one-dimensional titanate structure”, *Process. Appl. Ceram.*, **2** (2008) 109–114.
  26. A-L. Sauvet, S. Baliteau, C. Lopez, P. Fabry, “Synthesis and characterization of sodium titanates  $\text{Na}_2\text{Ti}_3\text{O}_7$  and  $\text{Na}_2\text{Ti}_6\text{O}_{13}$ ”, *J. Solid State Chem.*, **177** (2004) 4508–4515.
  27. D.V. Bavkin, V.N. Parmon, A.A. Lapkin, F.C. Walsh, “The effect of hydrothermal conditions on the mesoporous structure of  $\text{TiO}_2$  nanotubes”, *J. Mater. Chem.*, **14** (2004) 3370–3377.
  28. J. Yu, M. Zhou, “Effects of calcination temperature on microstructures and photocatalytic activity of titanate nanotube films prepared by an EPD method”, *Nanotechnol.*, **19** (2008) 045606.
  29. E. Morgado Jr., M.A.S. de Abreu, G.T. Moure, B.A. Marinkovic, P.M. Jardim, A.S. Araujo, “Characterization of nanostructured titanates obtained by alkali treatment of  $\text{TiO}_2$ -anatases with distinct crystal sizes”, *Chem. Mater.*, **19** [4] (2007) 665–676.
  30. Lj.M. Nikolić, M. Milanović, S. Nedić, K. Giannakopoulos, A.G. Kontos, “Hydrothermal conversion of Nb-anatase nanoparticles into layered titanates”, *Ceram. Int. submitted*.

