

## Steps in growth of Nb-doped layered titanates with very high surface area suitable for water purification



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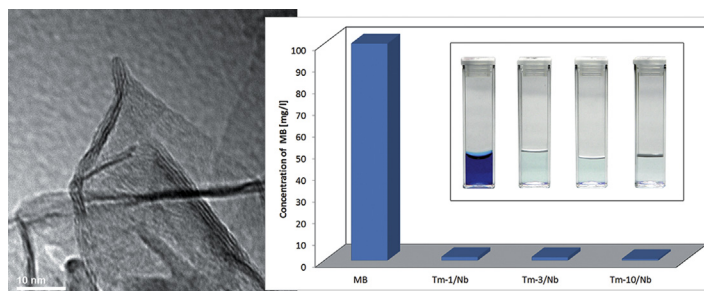
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### HIGHLIGHTS

- Nb-doped layered titanates have been prepared by a hydrothermal procedure.
- Introduction of Nb to precursor lowers the rate of layered titanate formation.
- Steps in growth of Nb-doped layered titanates are considered.
- Nb-doped layered titanates show high/fast MB adsorption from concentrated solution.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Nb-doped layered titanates, as highly efficient adsorbents, have been synthesized by hydrothermal reaction for variable duration and at 150 °C in a highly alkaline solution with  $\text{NbCl}_5$  as the Nb source. The results have shown the formation of nanosheets already after 1 h of hydrothermal processing, but morphology and phase composition change as the reaction proceeds. The prepared layered titanates have been structurally investigated via scanning and transmission electron microscopy, X-ray diffraction, as well as Raman and Fourier transform infrared spectroscopies. The steps of layered titanate growth have been followed and an intermediate layered anatase phase is identified. Thus optimized growth of mesoporous titanate materials with 10% Nb atomic content present very high specific surface area of  $345.3 \text{ m}^2 \text{ g}^{-1}$ , and perform as very efficient adsorbents for wastewater treatment applications.

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## 1. Introduction

Since Kasuga et al. [1] applied the alkaline hydrothermal method for the synthesis of titania nanotubes, substantial effort has been devoted to obtain various nanostructured titanates with specific elongated morphologies, including nanorods, nanofibers

and nanosheets. Elongated titanate nanostructures possess unique combinations of structural and physicochemical properties (high surface area, large ion-exchange capabilities and electro-conductivity) that can provide a wide range of possible applications, such as those in photocatalysis, lithium batteries, sensor applications, hydrogen production and storage, water purification etc. [2–4].

Recently, a lot of scientific interest has been directed towards investigations of two dimensional (2D) titanates (nanolayers or nanosheets) as a group of elongated titanates, from several points of view [5].

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Titanate nanolayers represent a transitional shape in nanotube formation, whose mechanism, despite a large number of relevant publications is still not very well understood. Namely, the mechanism of transformation of TiO<sub>2</sub> particles into nanotubes under the alkaline conditions is associated with many uncertainties, while the formation of the intermediate lamellar fragments is also not very clear. Concerning the formation of these layers, three mechanisms stand out according to the current literature: 1) nanosheets exfoliate from the precursor; 2) the precursor is partially dissolved in the alkali solution, and this is followed by the nucleation of titanates and their subsequent growth; 3) a combination of the two [6,7]. Under hydrothermal conditions the weaker Ti–O bonds break down and form linear fragments, which then exfoliate and, with the aid of O–Na–O ionic bonds, link to each other and grow on planar fragments or nanosheets.

Another important and attractive aspect of layered titanates is their use as building blocks in the fabrication of more complex nanostructured units or even devices [8]. Furthermore, 2D titanates present unique structural features such as tunable interlayer distances, high surface area and high cation exchange capacity [9,10]. These multi properties provide plenty of active sites for adsorption, rendering these nanostructured mesoporous materials very efficient in wastewater treatment.

Doping of TiO<sub>2</sub> with transition metal elements, such as Nb, has been theoretically and experimentally confirmed as a feasible way to inhibit the anatase to rutile phase transition and obtain tunable crystal structures with excellent hydrogen sensing performance, increased photoemission properties, enhanced efficiency in dye-sensitized solar cells, and modified TiO<sub>2</sub> conductivity [11–14]. In the present work, we have controlled the titania nanotubes formation by applying hydrothermal treatment of a TiO<sub>2</sub> precursor in highly alkaline solution with niobium dopant source. In this way, layered titanates were obtained with exceptionally high surface area presenting very efficient adsorption of cationic methylene blue (MB) dyes from water.

## 2. Experimental

### 2.1. Synthesis of layered titanates

The TiO<sub>2</sub> powder (Degussa P25 with 75% anatase and 25% rutile phase) was used as a starting material for the preparation of the layered titanates. The TiO<sub>2</sub> powder was dispersed in an aqueous solution of 10 M NaOH which was then stirred vigorously. The source of niobium was NbCl<sub>5</sub> (Merck, Germany); niobium chloride was dissolved in water and added to the previous mixture. The atomic percent of niobium in respect to titanium was set to 10 at.%. After a treatment in ultrasonic bath, the specimen was transferred into a sealed vessel and the hydrothermal reaction was carried out at 150 °C for different periods of time, up to 10 h. After the completion of the hydrothermal treatment, the powders were washed with distilled water and absolute ethanol, until a neutral pH was reached. The formed layered titanate-based structures were dried at 120 °C for 1 day. In order to elucidate the effect of niobium, the samples without Nb were prepared under the same conditions. Details for the preparation of the undoped samples are given by Milanovic et al. [15]. Undoped samples were given the names Tm-x, while the doped ones were marked as Tm-x/Nb; in both notations x stands for the time duration (in hours) of the hydrothermal reaction (1, 3 and 10 h).

### 2.2. Characterization techniques

The structural changes caused by the hydrothermal conversion of P25 powder to layered titanates were studied by Raman and FTIR spectroscopy, X-ray powder diffraction (XRD) and electron microscopy. In order to reveal the porosity of materials, a low

temperature nitrogen adsorption method was used. X-ray diffraction patterns of the as-synthesized structures were collected on a Philips PW 1050 instrument using Cu–K $\alpha$  radiation of wavelength 1.5404 Å. The XRD data was recorded with a step of 0.02° s<sup>-1</sup>. The microstructure and morphology of the samples were analyzed using a JEOL JSM 6460LV scanning electron microscope (SEM) and the layered structure was revealed by a Philips CM20 transmission electron microscope (TEM) operating at 200 kV, equipped with an energy-dispersive X-ray spectroscopy tool (EDS) and capable of performing the selected area electron diffraction (SAED) required. Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Nicolet–Nexus 670 spectrometer in the range 400–4000 cm<sup>-1</sup>. Raman spectra were measured in backscattering geometry using the InVia Renishaw micro-Raman spectrometer operating in normal mode and the 514.5 nm line of an Ar<sup>+</sup> laser as the excitation source. The incident laser power on the sample was 0.4 mW and was applied to a spot diameter of 1.2  $\mu$ m. Surface area of the powders was estimated by low temperature nitrogen adsorption measurements performed on a Quantachrom Autosorb-3B instrument applying the BET method.

### 2.3. Batch adsorption experiments

To examine the adsorption behavior of the layered titanates, methylene blue was employed as a target compound at ambient temperature. For the measurement of the MB adsorption capacities of the layered titanates, adsorption kinetics experiments were conducted. 50 mg of titanate powder was dispersed into 50 mL of MB solution with a desired concentration of 100 mg L<sup>-1</sup>. The suspension was continuously stirred in dark until adsorption equilibrium was reached. In regular contact time intervals, aliquots were withdrawn from the suspension and the adsorbents were separated from the suspension via centrifugation. The MB concentration remained in the solution was measured by a Carl Zeiss Jena EK5 visible spectrophotometer at the maximum absorption wavelength of MB ( $\lambda = 664$  nm). It was observed that the adsorption equilibrium is achieved after 1 h of stirring in the dark. To explore the adsorption isotherm, the initial MB concentration was varied from 1 to 50 mg L<sup>-1</sup> and the material dosage was maintained at 0.1 g L<sup>-1</sup> in the solutions.

## 3. Results and discussion

### 3.1. Materials characterization

XRD patterns of Nb-doped titanates are shown in Fig. 1. In order to follow the structural changes in the powder after the hydrothermal reaction, the XRD pattern of the starting material is given too. By comparing the XRD patterns of the starting P25 powder and the powder obtained after 1 h of hydrothermal reaction, it is obvious that the basic structure of the starting powder has changed after very short reaction times. The intensity of characteristic peaks of anatase and rutile are significantly reduced, and are accompanied with the formation of an amorphous phase. By further extending the reaction time, this tendency is continued and after 10 h of hydrothermal reaction, the characteristic peaks of the starting material completely disappear. Finally, the diffraction pattern of the Tm-10/Nb sample exhibits four weak and broad peaks at  $2\theta \sim 9.5, 24.4, 28.3$  and  $48.4^\circ$ , related to the layered titanates [16–19]. However, there are still disagreements related to the composition of the titanate nanostructure and the three characteristic peaks positioned at  $2\theta \sim 24.4, 28.3$  and  $48.4$  in the diffraction patterns have been assigned to the diffraction of titanates such as Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>·nH<sub>2</sub>O (JCPDs no. 72-0148) [16,19]. The structure of layered titanates is composed of TiO<sub>6</sub> octahedra with shared edges

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