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One-dimensional titanate nanostructures: Synthesis and characterization

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Abstract

One-dimensional (1D) nanostructured titania-based materials were synthesized by hydrothermal processing at 150 °C in a highly alkaline conditions. The investigation was limited on the early stages of the formation of the 1D nanostructures during the hydrothermal treatment of the titania hydrous gel and included the comparison with the common preparation technique from TiO_2 particles. In addition, formation of 1D nanostructures from titania hydrous gel containing Pb during the hydrothermal treatment has also been investigated. The layered titanates ($Na_xH_{2-x}Ti_3O_7$) as well as 1D nanostructures can be formed from the titania hydrous gel. The process is faster than the common technique in which TiO_2 particles are hydrothermally treated under the same conditions. Addition of Pb-acetate to titania hydrous gel accelerates the formation process of thin layers and 1D nanostructures. However, the obtained sheets are amorphous with PbO/TiO_2 crystalline nanometer-sized particles attached to them. In this system, the 1D nanostructures are formed by scrolling of the sheets.

Keywords: Powders-chemical preparation; Titanates

1. Introduction

During the past decade, inorganic one-dimensional (1D) nanostructures (nanotubes, nanowires, etc.) have attracted considerable attention because of their unique physical properties compared to their bulk counterparts resulting from the larger surface area, and because of their many potential applications in nanoelectronics and optoelectronic nanodevices. Among the 1D oxide nanomaterials reported (Co_3O_4, MnO_2, SiO_2, ZnO, ZrO_2, WO_2, etc.),[1] TiO_2 is of particular interest for its wide applications as catalyst supports,[2] semiconductor photocatalysts[3] and sensors.[4] There is also great interest in the development of titanates and TiO_2-based solids with nanoscale dimensions and high morphological specificity, such as nanofibers, nanosheets and nanotubes[5–7] because of their demonstrated potential in solar energy conversion, photocatalysis, photovoltaic devices and carrier for metallic nanoparticles.[5,8,9]

Different processing techniques were used for preparation of TiO_2-based and titanate 1D nanostructures, such as deposition with templates,[10,11] anodic oxidation of titanium,[12,13] but the most common is the hydrothermal method in which TiO_2 particles, crystalline or amorphous, were added in highly concentrated alkaline (NaOH, KOH, etc.) solution and transferred into an autoclave and treated at different temperatures (from 110 °C up to 200 °C)[14] for a long time (from 10 h up to 1 week).[7] By tuning the processing parameters (temperature, time, cooling, washing, etc.) nanostructures of different morphology can be obtained (nanotubes, nanofibers, nanowires, nanorods, etc.). In this paper, we have limited our study on the early stage of the formation of 1D nanostructures during the hydrothermal treatment of titania hydrous gel and compared this with the common preparation technique from TiO_2 powder. In addition, formation of 1D nanostructures from titania hydrous gel containing Pb during the hydrothermal treatment has been investigated.

2. Experimental procedure

One-dimensional nanostructured titania-based materials were synthesized during the hydrothermal treatment of: (i) TiO_2 particles, (ii) pure titania hydrous gel and (iii) titania hydrous gel containing lead originated from Pb-acetate (Table 1).

Titania powders, prepared via reaction of the crystalline TiO_2 powder (P-25, Degusa AG, Germany) and NaOH aqueous solution at 150 °C for 1 and 3 h, have notation T_p-x (where $x = 1$ and

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Table 1
Sample notation

Experiment	Precursor	Sample notation	Pb/Ti ratio
1	TiO_2 particles	T_p	0
2	Titania hydrous gel	T_a	0
3	Titania hydrous gel containing lead	T_aP_0	0
		$T_aP_{0.5}$	0.5
		T_aP_1	1

3, indicate the reaction time). The second powder, synthesized from titania hydrous gel, was formed after hydrolysis of Ti-butoxide ($Ti(OC_4H_9)_4$, Fluka, Switzerland) with distilled water in ethanol (Merck, Germany). The formed titania hydrous gel was added into 4 M NaOH aqueous solution, stirred for 30 min and hydrothermally treated in an autoclave at 150 °C for 1 and 3 h. The as-synthesized powders, having sample notation T_a-x (where $x = 1$ and 3, indicate the reaction time), are washed with distilled water to reach pH of 7 and dried at 120 °C in air for 24 h. The same procedure was carried out for the preparation of the lead-titanate powders containing different Pb/Ti ratio (sample has notation T_aP_1 if Pb/Ti = 1 or $T_aP_{0.5}$ if Pb/Ti = 0.5), only the titania hydrous gel containing lead originated from Pb-acetate ($Pb(CH_3COO)_2\cdot 3H_2O$, Aldrich, USA) was treated under hydrothermal conditions at 150 °C for 1 h.

As-synthesized powders were characterized by X-ray diffraction, XRD (Philips PW 1710, Philips PW 1050, Cu Kα radiation), scanning electron microscopy, SEM (JEOL JSM 6460LV) with energy-dispersive X-ray spectroscopy, EDS (Oxford INCA EDS system), Fourier-transform infrared spectroscopy, FT-IR (Nicolet-Nexsus 670 FT-IR) and transmission electron microscopy, TEM (Philips EM 400 and Philips CM 20 with High Resolution and EDS capabilities).

3. Results and discussion

The early stage of 1D nanostructures formation from TiO_2 particles (sample T_p-3) or titania hydrous gel (sample T_a-3) has been investigated during the hydrothermal treatment at 150 °C for 3 h. The XRD pattern of the sample T_a-3 (Fig. 1) has very broad diffraction peaks at $2\theta \sim 9.5°$, 24°, 28° and 48°. These peaks have been assigned to the diffraction of $A_2Ti_nO_{2n+1}$-type titanates (A = Na, H).[11] Energy-dispersive X-ray spectroscopy identified that a large amount of sodium is present in the sample, although the pH of the filtrate was neutral. Therefore, the crystal structure of the sample T_a-3 could be attributed to the sodium titanate phase, $Na_xH_{2-x}Ti_3O_7$.[15,16] The presence of 1D nanostructures in the T_a-3 powder, which is hydrothermally treated at 150 °C for 3 h, is obvious on the SEM micrograph shown in Fig. 2(a). These are formed most probably by scrolling of the Na-titanate sheets. On the other hand, the XRD pattern of the sample T_p-3 consists of the characteristic anatase and rutile peaks originated from the TiO_2 precursor powder. The main difference in the XRD patterns between the TiO_2 precursor powder and the hydrothermally treated T_p-3 powder is the appearance of a broad peak at $2\theta \sim 10°$ (Fig. 1), indicating the formation of the amorphous phase. The possible explanation for this may lay in the fact that during the hydrothermal treatment of TiO_2 with concentrated NaOH, some Ti–O bonds broke, leading to the formation of Ti–O–Na or Ti–OH bonds and lamellar frag-

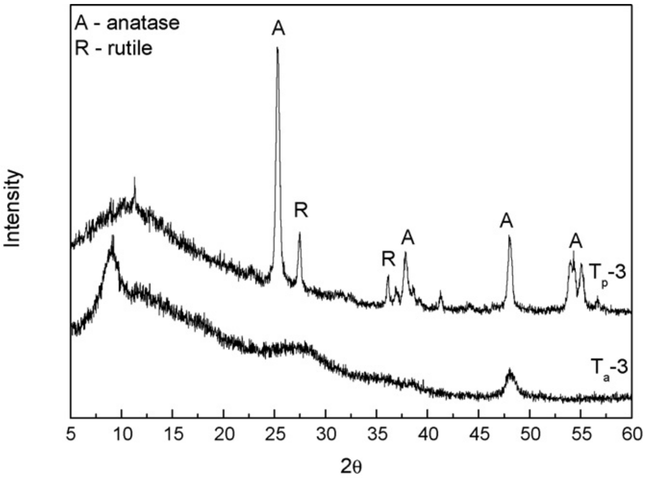

Fig. 1. XRD patterns of the sample T_a-3 obtained from titania hydrous gel and the sample T_p-3 obtained from TiO_2 particles.

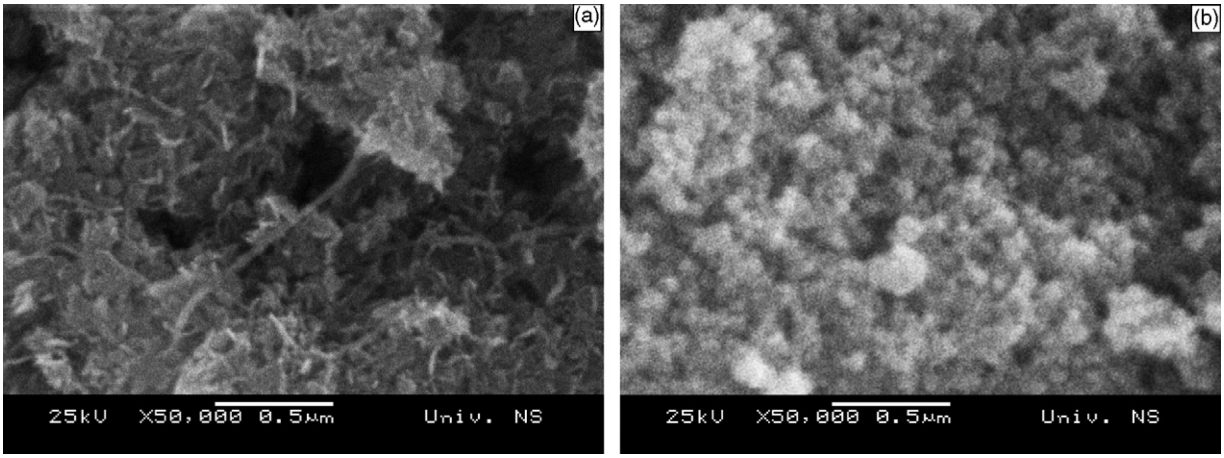

Fig. 2. SEM images of the samples: (a) T_a-3 obtained from titania hydrous gel and (b) T_p-3 obtained from TiO_2 particles.

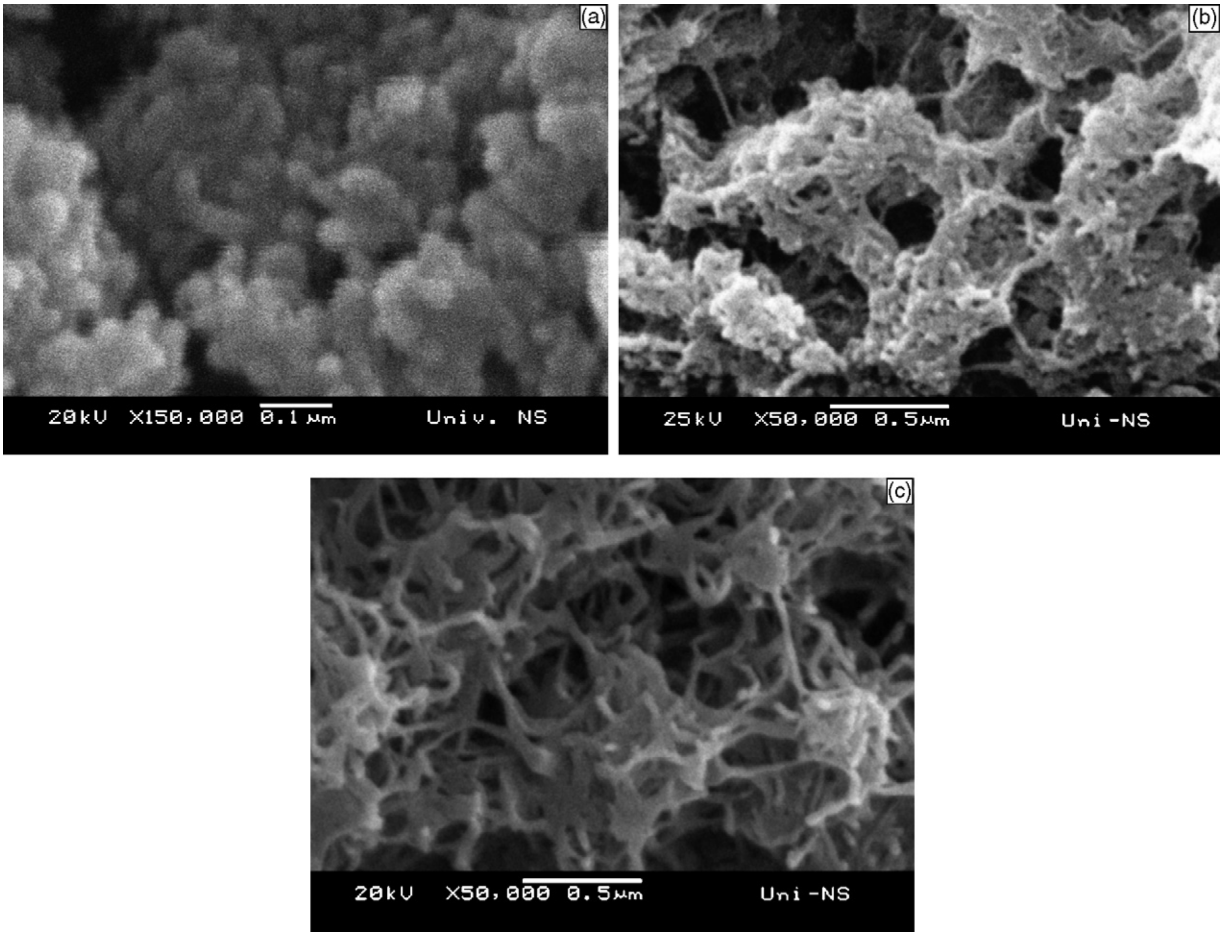

Fig. 3. SEM images of powders synthesized at 150 °C for 1 h, with different amount of lead: (a) T_aP_0 without Pb, (b) $T_aP_{0.5}$ with Pb/Ti = 0.5 and (c) T_aP_1 with Pb/Ti = 1.

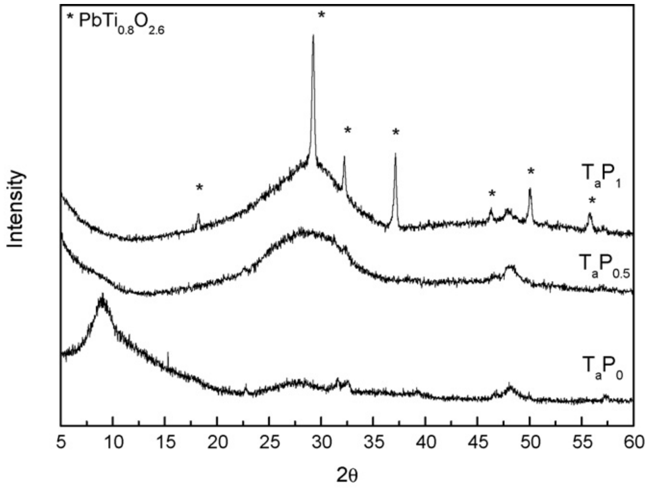

Fig. 4. XRD patterns of powders synthesized at 150 °C for 1 h with different amount of lead: T_aP_0 (without Pb), $T_aP_{0.5}$ (Pb/Ti = 0.5) and T_aP_1 (Pb/Ti = 1).

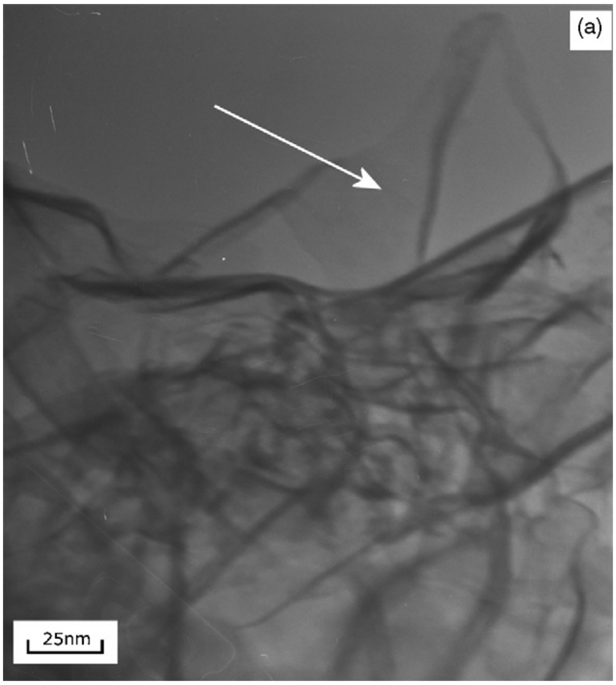

Fig. 5. TEM bright field images of the T_aP_1 powder synthesized at 150 °C for 1 h (existence of a lamellar titanate structure is indicated by an arrow).

ments as an intermediate phase in the formation process of the 1D nanostructures. However, there is no evidence of 1D nanostructure in the SEM images of the powder synthesized from the TiO_2 particles presented in Fig. 2(b). According to this, it can be concluded that the layered titanates ($Na_xH_{2-x}Ti_3O_7$) as well as 1D nanostructures can be formed from the titania hydrous gel. The process is faster than the common technique in which TiO_2 particles are hydrothermally treated under the same conditions.

It is well known that preparation of 1D nanostructures based on other titanates (e.g. Pb-titanate, Ba-titanate, Sr-titanate, etc.) still remains a challenge in materials science and engineering. Thus, formation of 1D nanostructures from titania hydrous gel containing Pb has been investigated during the hydrothermal treatment at 150 °C for 1 h. Fig. 3 illustrates SEM images of powders hydrothermally synthesized at 150 °C with different amount of Pb. The images show that as-synthesized powders have different particle morphology. The powder synthesized without Pb-acetate, T_aP_0, consists of spherical particles (Fig. 3(a)). With addition of Pb-acetate in titania hydrous gel, some 1D nanostructures are formed (Fig. 3(b and c)). Those images clearly show that with increase of the Pb/Ti molar ratio (from 0.5 to 1), the amount of the 1D nanostructures increases.

XRD analysis, Fig. 4, shows that only the powder T_aP_0 has diffraction peaks characteristic for Na-titanates. The XRD pattern of the $T_aP_{0.5}$ powder indicates on its amorphous structure, whereas the crystalline peaks observed in the XRD pattern of the sample T_aP_1 (Fig. 4) correspond to PbO–TiO_2 solid solution.[17] However, a very weak peak at $2\theta \sim 48^\circ$ (character-

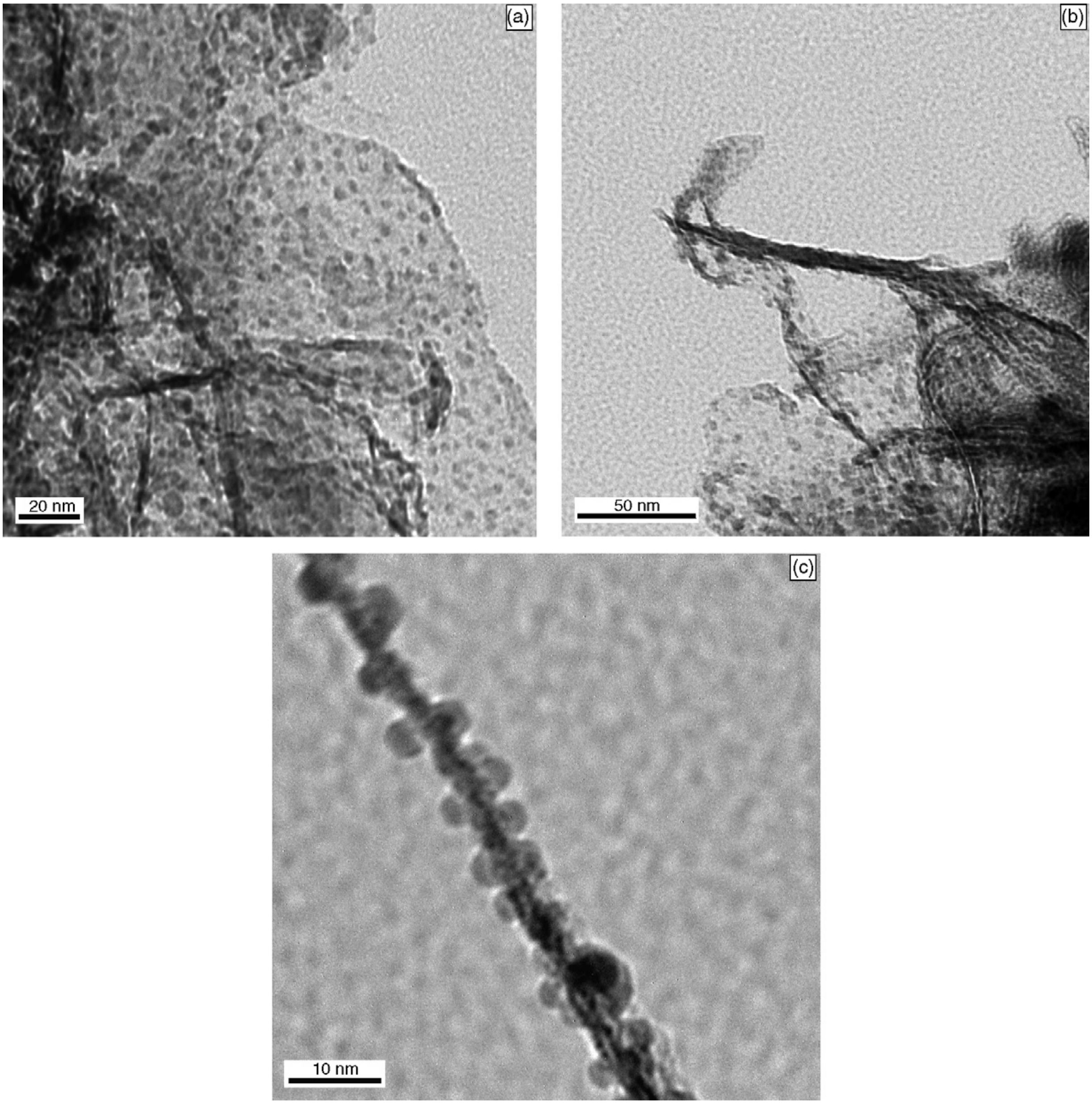

Fig. 6. TEM images of T_aP_1 powder synthesized at 150 °C for 1 h show that: (a) the formed layer is an amorphous sheet with crystalline nanometer-sized particles attached to it, (b) scrolling of thin layers is responsible for formation of 1D nanostructures and (c) the formed 1D nanostructures have diameters of few nanometers, sometimes even with crystalline nanometer-sized particles attached to them.

istic for titanates) is present in both XRD patterns ($T_aP_{0.5}$ and T_aP_1) a fact that suggests that a small portion of the Na-titanate phase is also formed. Energy-dispersive X-ray spectroscopy identifies a presence of sodium in both powders, but in a much smaller quantity than in the T_aP_0 powder.

The detailed structures of the T_aP_1 powder were examined using TEM and some typical images are presented in Figs. 5 and 6. The low-magnification TEM image of Fig. 5 confirms the presence of large portion of 1D nanostructures and indicates the possible existence of the lamellar titanate structures (layer indicated by an arrow). However, at higher magnification (Fig. 6(a)) it is obvious that these thin layers are not crystalline titanates, but amorphous sheets with crystalline nanometer-sized particles attached to them. XRD analysis (Fig. 4) revealed that the crystal structure of the nanoparticles corresponds to $PbO–TiO_2$ solid solution. Fig. 6(b) indicates that during hydrothermal treatment, scrolling of these thin layers takes place, which is a phenomenon responsible for formation of the observed 1D nanostructures. The formed 1D nanostructures have diameters from ~5 to 10 nm and lengths from several tens to several hundreds of nanometers.

4. Conclusions

The early stage of the formation of 1D nanostructures from TiO_2 particles or titania hydrous gel has been investigated during their hydrothermal treatment at 150 °C in a highly alkaline conditions. The layered titanates ($Na_xH_{2-x}Ti_3O_7$) as well as 1D nanostructures can be formed from the titania hydrous gel, and even faster than from the TiO_2 particles. Addition of Pb-acetate to titania hydrous gel accelerates the formation process of thin layers and 1D nanostructures. However, the obtained sheets are amorphous with PbO/TiO_2 crystalline nanometer-sized particles attached to them. In this system, the 1D nanostructures are formed by scrolling of the sheets.

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