

# PREPARATION AND STRUCTURE OF TITANATE NANOTUBES

D. Králová<sup>1</sup>, E. Pavlova<sup>1</sup>, M. Šlouf<sup>1,2</sup>, R. Kužel<sup>3</sup>

<sup>1</sup>*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nam. 2, 162 06 Praha 6, Czech Republic*

<sup>2</sup>*Member of Consortium for Research of Nanostructured and Crosslinked Polymeric Materials (CRNCPM)*

<sup>3</sup>*Department of Electronic Structures, Faculty of Mathematics and Physics, Charles University, 121 16 Praha 2, Ke Karlovu 5, Czech Republic  
kralova@imc.cas.cz*

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## Abstract

This work describes simple and reproducible preparation of dried and stable titanate nanotubes (Ti-NT) in gram-scale amounts using freeze drying. Ti-NT represent a novel type of nanoparticles with interesting morphology and peculiar structure. The morphology, crystalline structure and elemental composition of Ti-NT were investigated by means of scanning and transmission electron microscopy, X-ray and electron diffraction and energy-dispersive X-ray analysis.

## Introduction

In the past decade, fabrication of various inorganic nanoparticles has attracted much attention because of their interesting properties and potential applications. Several recent studies have reported a synthesis of a novel type of TiO<sub>2</sub>-based nanoparticles, whose morphology and crystal structure is completely different from common TiO<sub>2</sub> modifications [1, 2, 3]. Hollow tubular nanoparticles, denoted as titanate nanotubes (Ti-NTs), are formed by a rolled sheet. Majority of authors agree that the plane of a single sheet is formed by octahedrons, identically to well known TiO<sub>2</sub> crystal modifications, such as anatase, rutile and brookite. Nevertheless, the structure and composition of Ti-NT remain unclear and also formation mechanisms of Ti-NTs has not been fully clarified yet [4, 5, 6, 7].

For many potential applications of Ti-NT in materials science it is essential to obtain dry, well separated, chemically and morphologically stable nanoparticles. As for morphological stability, the key point is to preserve single character and high aspect ratio of the particles, i.e. the breaking and the merging of the particles should be minimized. Nonetheless, the authors of available literature focus their attention on structure of single nanotubes [3, 8, 9, 10], their thermal stability [11, 12] or conductive properties [13, 14].

The aim of this study was to develop a straightforward, reproducible preparation technique yielding dried, non-destructed Ti-NT in gram-scale amounts. Synthesis of Ti-NT was based on hydrothermal treatment of TiO<sub>2</sub> powder in concentrated NaOH solution described elsewhere [2]. Three parallel syntheses and three different drying procedures were performed. The morphology of Ti-NT was investigated by means of scanning and transmission electron microscopy, their crystalline structure was studied by

X-ray and electron diffraction and their elemental composition by energy-dispersive X-ray analysis.

## Experimental

### *Synthesis and drying of titanate nanotubes.*

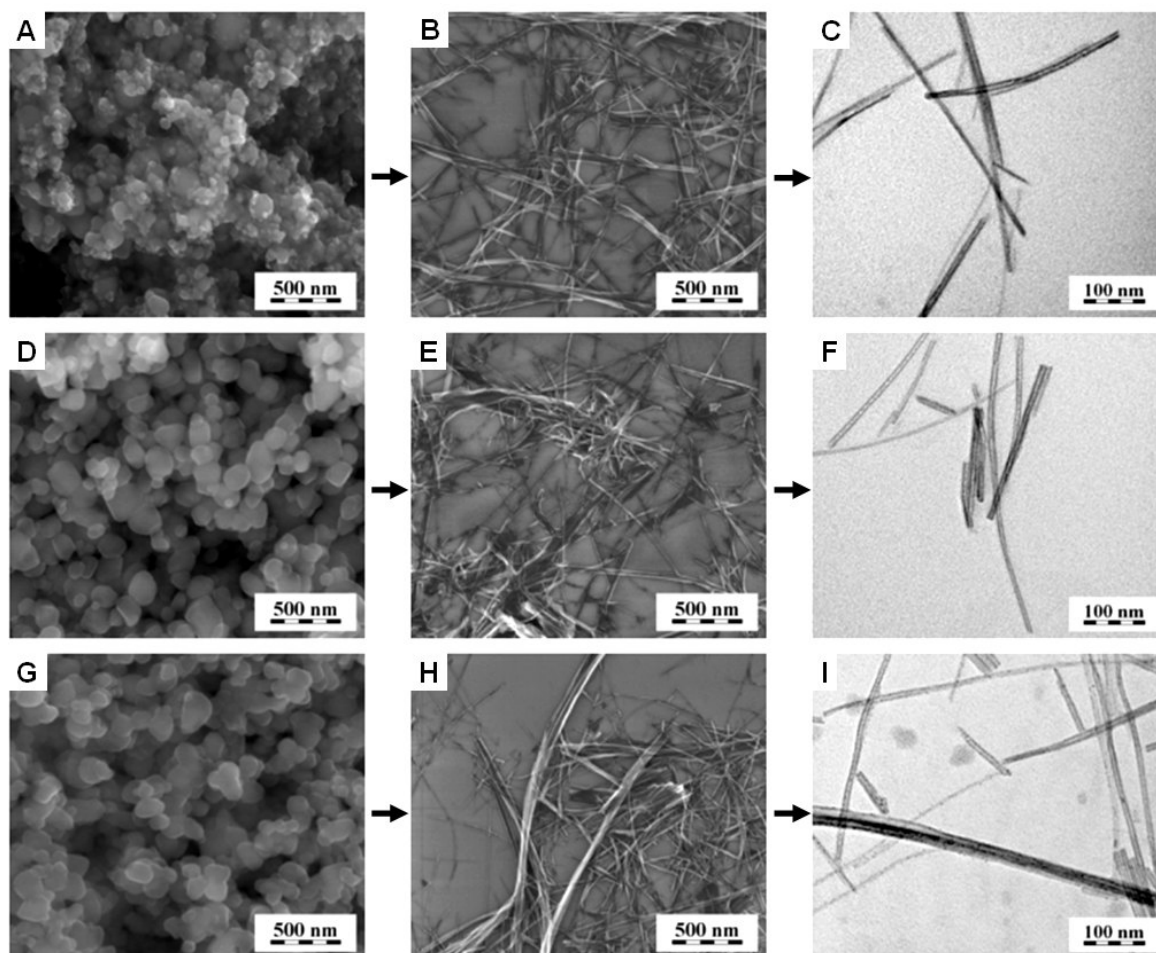
Titanate nanotubes (Ti-NT) were synthesized by hydrothermal treatment as reported in literature [1,2]. Starting TiO<sub>2</sub> modifications included: technical powder (Riedel-de Haën, Sigma-Aldrich), anatase TiO<sub>2</sub> powder (99, 8%; Aldrich) or TiO<sub>2</sub> nanopowder (99, 9%, Aldrich); the other chemicals used were NaOH (Lach-Ner, s.r.o.), HCl (35% p.a., Lach-Ner, s.r.o.) and deionized water.

Ti-NT were prepared by three parallel syntheses (denoted as S20, S28 and S30). Briefly, 6 g of TiO<sub>2</sub> powder in 10M NaOH aqueous solution in a closed vessel was heated at 120 °C for 20 hours and subsequently washed with water to achieve pH = 11.5 (sample denoted S30/11,5). Part of solution was neutralized by 0,1M HCl aqueous solution and subsequently washed with water to pH = 5.5 (sample denoted S30/5.5). The remnant of solution (S30) and solution another synthesis (S20) were dried in six different ways: S20 was filtered and dried on air for 20h (S20/D1), dried at 60 °C for 2 hours (S20/D2), dried at 60 °C for 4 hours (S20/D3), dried at 100 °C for 4 hours (S20/D5) and dried at 60 °C for 4 hours under the vacuum (S20/D6). Part of Ti-NT suspension was dispersed in ethanol, filtered and dried on air for 20 hours (S20/D4) or dried at 60 °C for 4 hours (S20/D7). The rest of S30 and part of S28 were more diluted by distilled water and freeze dried (S28/L1, S30/L1).

Specimens for electron microscopy were prepared as follows: Ti-NT dispersion in water or dried Ti-NTs was dispersed in water. In some cases the Ti-NT were treated in ultrasonic bath for several minutes. The impact of sonication on the Ti-NT structure was examined using the samples sonicated from 1 minute to 25 minutes.

### *Scanning electron microscopy and microanalysis.*

The morphology of Ti-NT powders was characterized by scanning electron microscopy (SEM) using a high resolution, field-emission gun SEM microscope Quanta 200 FEG (FEI, Czech Republic) equipped with energy dispersive X-ray spectrometer (EDS). Specimens for morphological investigations (SEM) were prepared by drying of a droplet of Ti-NT dispersion on the carbon support. The specimens were then observed as they were in low-vacuum mode using accelerating voltages from 10 to 30 kV. Specimens for X-ray microanalysis (EDS) were prepared by consolidation of dry Ti-NT into tablets. EDS spectra were collected



**Figure 1.** Synthesis of Ti-NT from various sources: (a,b,c)  $\text{TiO}_2$  nanopowder -mixture of anatase and rutile, (d,e,f) technical  $\text{TiO}_2$  - mixture of rutile and anatase and (g,h,i)  $\text{TiO}_2$  powder - anatase modification. The first column (a,d,g) shows SEM micrographs of original powders, the second column (b,e,h) and the third column (c,f,i) show SEM and TEM micrographs of Ti-NT, respectively.

from several locations at each tablet at acceleration voltage 30 kV.

#### *Transmission electron microscopy and electron diffraction.*

The morphology of Ti-NT powders was simultaneously inspected by transmission electron microscopy (TEM) and crystal structure was analyzed electron diffraction (ED) using a 120 kV TEM microscope Tecnai G<sup>2</sup> Spirit (FEI, Czech Republic). Specimens for TEM investigations were prepared in the same way as those for SEM; the only difference consisted in that a specimen support was a microscopic copper grid covered by thin transparent carbon film. The samples were studied in both bright field (conventional TEM) and electron diffraction without selecting aperture (ED) modes at 120 kV.

#### *Powder X-ray diffraction.*

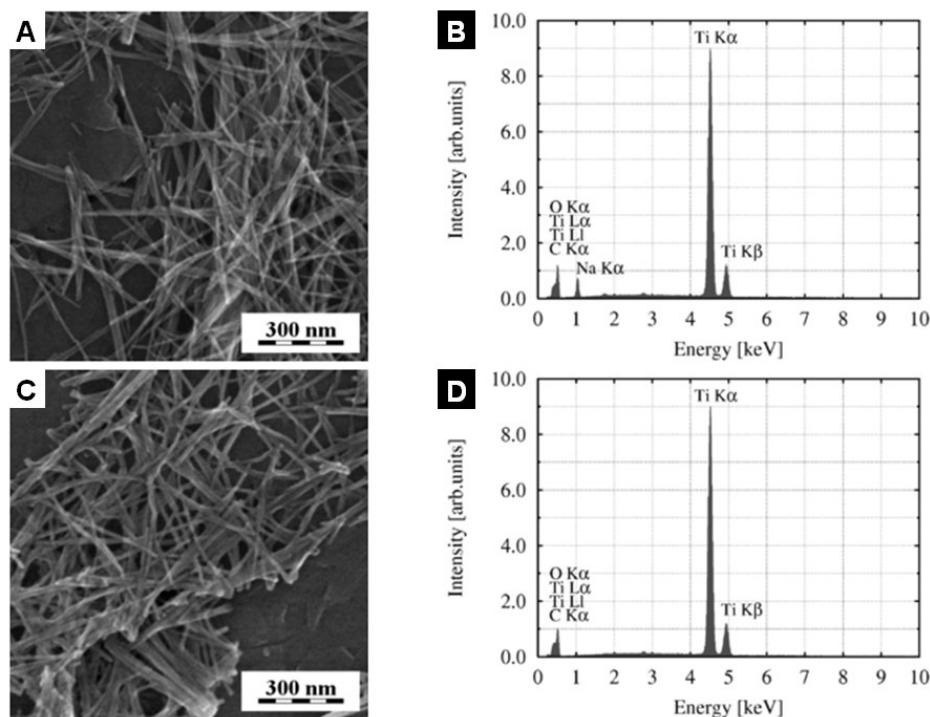
Powder X-ray diffraction (PXRD) measurements of whole patterns were performed mainly on XRD7 (FPM-Seifert) diffractometer with monochromator in the diffracted beam.

## Results and discussion

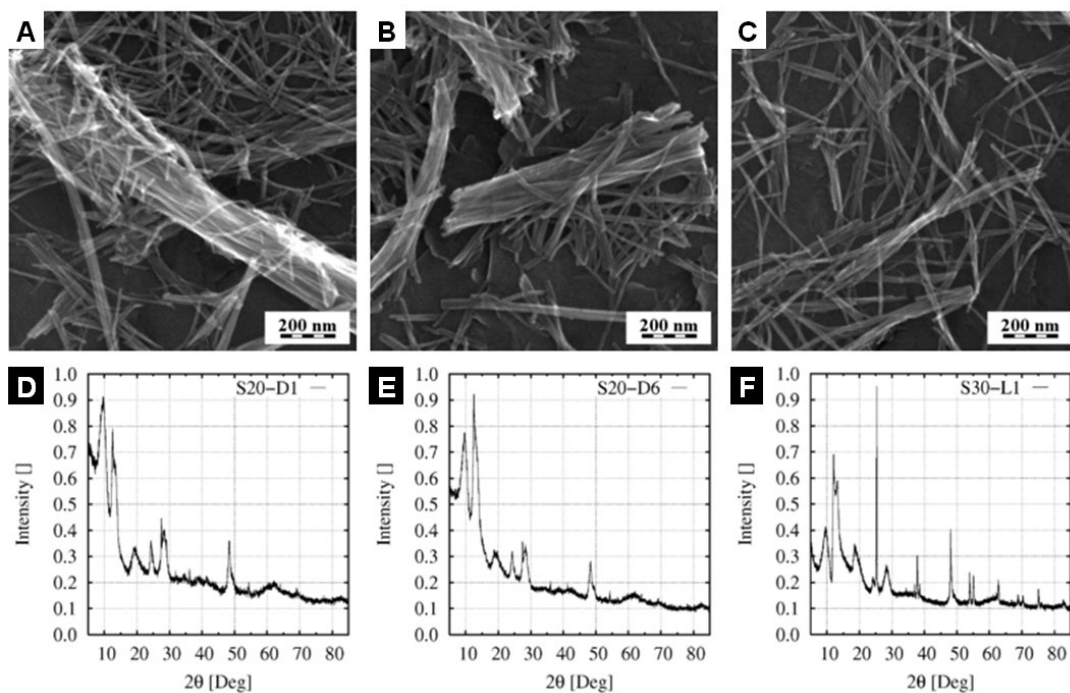
Suspension of titanate nanotubes have been prepared from  $\text{TiO}_2$  powders by standard method described in the literature [1, 2, 3]. We repeatedly succeed in preparing Ti-NT from a mixture of different types  $\text{TiO}_2$  crystal modifications (Fig. 1) not only from pure anatase as stated in some papers [3]. The amount, morphology and structure of Ti-NT were not affected by the modification of starting  $\text{TiO}_2$ .

In addition, the assumption that formation of nanotubes in aqueous solution is completed after hydrothermal treatment was confirmed. In contrast to some studies [1, 2, 15], we show that neutralization by HCl is not necessary for their formation (Fig. 2). The Ti-NT were observed both after washing with water (Fig. 2a) or HCl (Fig. 2b). It was also proved by EDS that  $\text{Na}^+$  ions are not necessary to stabilize Ti-NT, which persist both in presence (Figs. 2a-b) or absence (Figs 2c-d) of sodium. Nevertheless, it was observed that the stability of Ti-NT decreases from several months in strong alkaline solutions to several weeks in solutions with lower pH. Ti-NT are further impaired if they are transferred to non-aqueous medium as evidenced by both SEM and TEM.

Drying procedure is a critical step to obtain gram-scale amounts non-destructed Ti-NT because the nanotubes tend



**Figure 2.** Synthesis of Ti-NT from solutions with various pH: (a,b) pH = 11.5 and (c,d) pH = 5.5. SEM micrographs (a,b) showed almost identical morphology and EDS spectra (b,d) proved that removal of sodium was not

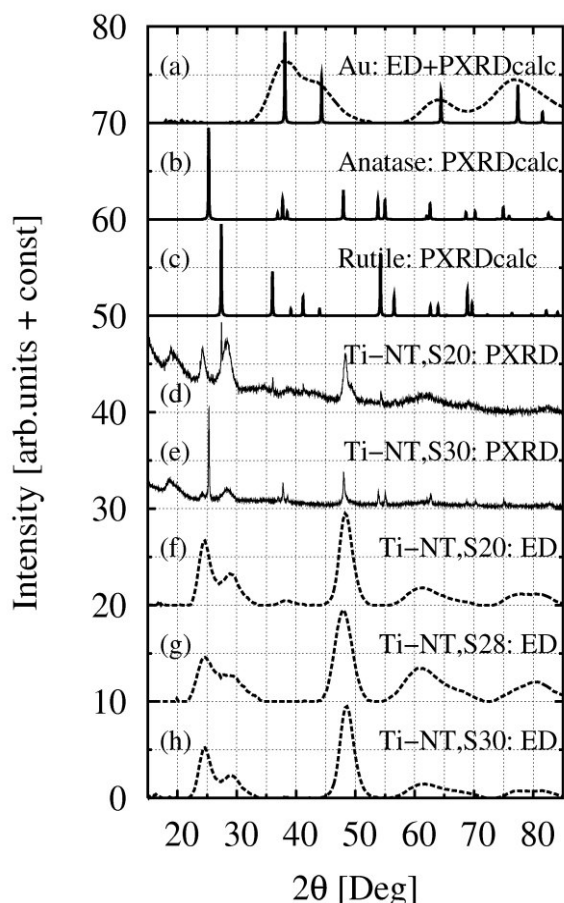


**Figure 3.** Influence of drying on Ti-NT external morphology and internal crystalline structure. (a, d) drying in air - sample S20-D1, (b, e) drying in vacuum - sample S20-D6, (c,f) freeze drying - sample S30-L1. SEM micrographs (a, b, c) and corresponding PXRD patterns (d, e, f).

to merge and break when they are isolated from solution. This was proved by examination of seven different ways of drying in air and *in vacuo*, as described in experimental section. Representative electron micrographs of air drying (Fig. 3a) and vacuum drying (Fig. 3b) showed agglomeration and merging of the nanotubes, which decreased their desirable high aspect ratio. During freeze-drying the morphology of Ti-NT was similar to that observed after drying

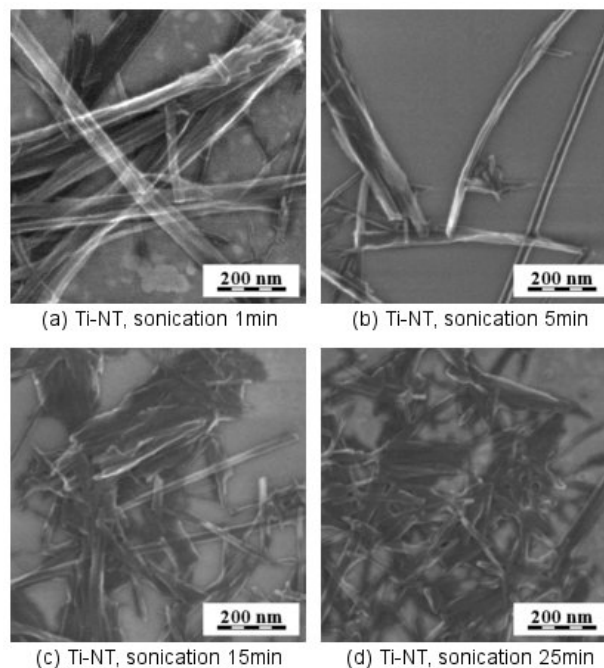
in air or vacuum, but the nanotubes were much less agglomerated and merged (compare Fig. 3a-b with Fig. 3c). The crystalline structure of Ti-NT did not change as proved by PXRD (Figs. 3d-f)

The PXRD results were compared with simulated powder diffraction patterns (calculated by program PowderCell [16]) and experimental ED diffraction patterns (processed by program ProcessDiffraction [17]). Reliability and preci-



**Figure 4.** Comparison of experimental and calculated diffraction patterns of Ti-NT, which were dried in different ways. (a) Experimental ED and calculated PXRDCalc of standard Au specimen, (b) calculated PXRDCalc of anatase, (c) calculated PXRDCalc of rutile, (d) experimental PXRDCalc of air-dried Ti-NT, synthesis S20-D2, (e) experimental PXRDCalc of freeze-dried Ti-NT, synthesis S30-L1, (f) experimental ED of air-dried Ti-NT, synthesis S20-D2, (g,h) experimental ED of freeze-dried Ti-NT, syntheses S28-L1 and S30-L1.

sion of ED in our TEM microscope was verified by means of standard Au specimen (Fig. 4a). Theoretical powder diffraction patterns of anatase and rutile were calculated with program PowderCell (Fig. 4b-c). Experimental PXRDCalc results from previous experiments were included for comparison (Figs. 4d-e). Finally, ED diffraction patterns from all three parallel syntheses (S20, S28, S30) were collected (Figs. 4f-g). Comparison of all diffraction patterns in Fig. 4 clearly showed that the crystalline structure of Ti-NT was different from both common TiO<sub>2</sub> modifications. Surprisingly enough, all three ED patterns of Ti-NT were the same, whereas two PXRDCalc patterns of Ti-NT differed both from each other and from the corresponding ED patterns. The first discrepancy between ED and PXRDCalc consisted in several strong and sharp reflections on PXRDCalc (Fig. 4d-e), which were not observed in ED. Sharp character of the reflections suggested that they originated in some bigger crystallites. Comparison of calculated and experimental PXRDCalc patterns showed that these sharp reflections came from anatase (confront Fig. 4b and Fig. 4e) or rutile (confront Fig. 4c and Fig. 4d). In ED the anatase/rutile reflections were not observed, because no big crystallites of



**Figure 5.** Impact of sonication on morphology of Ti/NT. Sonication for (a) 1 min, (b) 5 min, (c) 15 min and (d) 25 min. More than 5 min of sonication breaks the nanotubes.

anatase/rutile were found in TEM microscope. This indicated that *number* of the anatase/rutile crystallites in the samples was quite small, although the anatase/rutile reflections were quite strong in PXRDCalc due to relatively high *volume* of big anatase/rutile microcrystals in comparison with tiny titanate nanotubes. Moreover, the specimens for PXRDCalc may have contained higher volume of anatase/rutile than corresponding specimens for ED due to differences in specimen preparation techniques. As the two PXRDCalc diffraction patterns (Fig. 4d and 4e) were different, the anatase/rutile microcrystals probably grew during drying procedures, which were also different, whereas both syntheses should have been identical. The second discrepancy between PXRDCalc and ED was strong diffraction around  $2\theta = 18\text{deg}$  in PXRDCalc (Fig. 4f-h), which was completely missing in ED. This diffraction could not be observed in TEM microscope because it was too close to the beamstopper, which had to shield CCD camera from central beam; different experimental setup might help in this case. Nevertheless, strong and broad diffractions around  $2\theta = 24, 28$  and  $48\text{deg}$ , which corresponded neither anatase nor rutile, were observed in both ED and PXRDCalc diffraction patterns of all prepared Ti-NT (Fig. 4d-h).

We also studied possibilities to improve dispersion of Ti-NT by sonication before drying. SEM micrographs demonstrated that sonication of Ti-NT in solution yields less merged nanotubes but sonication times higher than 5 minutes break the nanotubes (Fig. 5). As a result, we used in all experiments zero or very short sonication times.



## Conclusion

Titanate nanotubes (Ti-NT) were prepared using a hydrothermal synthesis described elsewhere. Ti-NT represent a novel type of nanoparticles with peculiar structure. In this study we show that gram-scale amounts of Ti-NT can be isolated from solution by freeze drying.

Three parallel syntheses and three drying procedures were used to prepare dried Ti-NT in gram-scale amounts. Impact of preparation and drying on external morphology and internal crystal structure of Ti-NT was investigated by microscopic (SEM, TEM, EDS) and diffraction (PXRD, ED) methods.

SEM and TEM micrographs showed that the Ti-NT were quite stable, especially if they were kept in alkaline solution. The basic morphology of the nanotubes did not change, their diameters were approx. 10 nm and their lengths were usually in micrometer scale. Nevertheless, during drying the nanotubes tended to break and merge, which decreased their high aspect ratio that is advantageous for many potential applications in materials science.

PXRD and ED proved that the crystalline structure of Ti-NT during all applied drying procedures (air, vacuum, freeze drying) did not change. Breaking and merging of nanotubes during drying in air and *in vacuo* had negligible effect on internal crystalline structure. Ti-NT crystalline structure after drying did not correspond to any common crystal modifications of TiO<sub>2</sub>.

It has been demonstrated that freeze drying is the best technique to prepare high amounts of dried, single, non-merged Ti-NT with high aspect ratio.

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