Abstract:

Title: **NANOTUBES BASED ON TITANIUM DIOXIDE WITH A HIGH ASPECT RATIO AND A METHOD OF THEIR PREPARATION**

Abstract: Nanotubes based on titanium dioxide with a high aspect ratio (>50) and a new type of crystal structure characterized by three main maxima of electron diffraction pattern at the values of diffraction vector $q = 1.75 \text{Å}^{-1}$, $2.05 \text{Å}^{-1}$ and $3.35 \text{Å}^{-1}$ and two other broad peaks at $q = 4.20 \text{Å}^{-1}$ and $5.25 \text{Å}^{-1}$ (diffraction vector $q$ is defined by the equation $q = 4\pi \sin(\theta)/\lambda$, where $\theta$ is the diffraction angle and $\lambda$ is the wavelength of accelerated electrons).
Nanotubes based on titanium dioxide with a high aspect ratio and a method of their preparation

Technical field

The invention concerns a new crystalline modification of titanium dioxide in the form of nanotubes with a high aspect ratio and a method of preparation of this modification of TiO₂.

Background Art

common structures such as \( \text{H}_2\text{Ti}_3\text{O}_7 \) or \( \text{Na}_2\text{Ti}_3\text{O}_7 \), or lepidocrite titanates [Kubota Y, Kurata H
and Isoda S 2006 Mol. Cryst. Liq. Cryst. 445 107]. Finally, most authors agreed that TiNT
show the structure of rolled layers of titanate octahedrons [Wang W Z, Varghese O K,
Mater. 15 1310]. On the basis of diffraction measurement results given in the cited sources, it
can be stated that the TiNT described so far show predominantly the well-known crystalline
modifications derived from \( \text{TiO}_2 \). In addition, the TiNT so far described often show residues of
starting \( \text{TiO}_2 \) from which they were prepared (anatase, rutile, etc.).

In recent years, there were patented methods of preparation of nanotubes with the
structure of pure anatase [Kasuga et al., Japanese application 8-259182, US Patent 6,027,775
and a US Patent 6,537,517], nanotubes with the structure of a mixture of anatase and rutile
[CZ Patent 297 774] and nanotubes with the structure of perovskite [Wong et al., US Patent
7,147,834].

The original Japanese application 8-259182 and US Patent 6,027,775 derived
therefrom concern nanotubes 5-80 nm in diameter and of wall thickness 2-10 nm, with
anatase crystalline modification, characterized by high absorption in the UV region and are
designed as photoactive catalysts of oxidation reactions. The preparation of the nanotubes
according to US Patent 6,537,517 is based on treatment with 30-50% aqueous NaOH
solution of crystalline \( \text{TiO}_2 \) at elevated temperature and pressure. The method of preparation
of TiNT according to the mentioned documents is aimed at reaching their photoactivity and
catalytic activity as high as possible and then, indirectly, at obtaining specific surface as high
as possible, on which the investigated properties depend. The aspect ratio (defined as the ratio
of nanotube thickness to its total length) is not the object of main interest in the given
documents. Nevertheless, it can be deduced from the examples that the obtained aspect ratios
are not higher than 50.

The nanotubes according to the invention of Wong et al. (US Patent 7,147,834), in
contrast to those mentioned above, are characterized by a relatively high length and a high
aspect ratio. According to chemical composition they are titanates of calcium, strontium and
barium. For their electric properties, they are designed primarily for ferroelectric applications.

Czech patent no. 297 774 concerns the invention of a photoactive \( \text{TiO}_2 \) modification in
the form of nanofibres as a catalyst of oxidation reactions.
Disclosure of Invention

The essence of the invention is nanotubes based on titanium dioxide which do not show the drawbacks of the so far known nanotubes but are superior to them, first of all because of their high aspect ratio, high structure purity of the material without traces of residual anatase, rutile or perovskite as primary materials for their preparation. Moreover, they show a different crystal structure, which manifests itself, e.g. in electron diffractograms. The nanotubes according to the invention show a uniform morphology. The method of preparation of the nanotubes according to the invention is characterized by the possibility of controlling their aspect ratio in a wide range without the necessity of performing some steps of the procedure in inert atmosphere.

The nanotubes according to the invention show the diameters (D) between 8 and 40 mm at lengths (Z) at least 1-20 μm, their average aspect ratio (L/D) always amounting to more than 50 and reaching the values 100-500 at least. The walls of the nanotubes according to the invention are made by at least 2 and at the maximum by 12 layers of a planar crystalline modification of titanium dioxide, which differs from the crystalline modification of starting TiO₂ and is characterized by characteristic peaks on electron diffractograms at certain values of diffraction vector q. Diffraction vector q is defined by the equation \( q = 4\pi \cdot \sin(\theta) / \lambda \), where \( \Theta \) is the diffraction angle and \( \lambda \) is the wavelength of accelerated electrons. Three most intensive characteristic peaks on diffractograms appear at the values \( q = 1.75 \) Å⁻¹, 2.05 Å⁻¹ and 3.35 Å⁻¹ and two further broad peaks appear around \( q = 4.20 \) Å⁻¹ and 5.25 Å⁻¹. In dependence on the conditions of TiNT preparation and of electron diffraction measurement, the nearest peaks, \( q = 1.75 \) Å⁻¹ and 2.05 Å⁻¹, can partly overlap.

The procedure of preparation of the nanotubes according to the invention consists of three consecutive steps. In the 1st step, a suspension of TiO₂ in NaOH solution is prepared, the TiO₂ concentration in suspension being at least 0.01 g/100 mL and 6 g/100 mL at the maximum and the NaOH concentration being at least 2M and 16M at the maximum. In the 2nd step, the TiO₂ suspension is thermostated under constant stirring at 60 °C at the minimum and 160 °C at the maximum, for at least 12 h. In the 3rd step, the nanotubes from the reaction mixture are separated and dried, to advantage by lyophilization. The NaOH solution after isolation of nanotubes can be used again for preparation of TiO₂ suspension in the first step of the procedure. During isolation, TiNT can be neutralized with HCl without affecting the quality of the final product.
In the preparation of nanotubes by the procedure according to the invention, the average aspect ratio of the resulting nanotubes can be controlled by the mean size of particles of the starting TiO₂, by modification of the starting TiO₂ and by the ratio of concentrations of the starting TiO₂ and NaOH in suspension, in combination with the reaction temperature and time, as well as by the method of drying the final product. A specific procedure of preparation consists first of all in combination of reactant concentrations, average particle size and crystalline modification of input TiO₂, reaction temperature and the method of product drying. Applying suitable reaction conditions, the resulting TiNT product with the above described characteristic properties is formed. The interrelations of reactant concentrations, crystalline modifications of the starting TiO₂, average particle size of TiO₂ powder, reaction temperature and time can be described in principle as follows:

(1) the average aspect ratio of TiNT increases with decreasing TiO₂ concentration,

(2) the particle size and crystalline modification of the starting TiO₂ affect together the length and diameter of TiNT whereas the high aspect ratio remains retained,

(3) the average aspect ratio of TiNT rises with increasing reaction temperature, time and NaOH concentration up to a certain value.

The nanotubes according to the invention are, in contrast to others, are very well tolerated by living tissues. From this fact and in combination with their unique morphology, it follows that TiNT according to the invention are an ideal reinforcing component of living tissues, first of all of bone tissue and cartilage, and also of their synthetic replacements based on TiNT-reinforced composites. An advantage of the TiNT according to the invention is that its high aspect ratio and an extraordinarily small proportion of agglomerates makes it possible to adjust mechanical properties of the composite material of implant in a sufficiently wide range so that the implants show the same deformation behaviour as the parts of bones or cartilages to be replaced in specific applications.

**Brief Description of Figures**

Fig 1: Table: Effect of crystalline modification and the mean particle size of source TiO₂ on the morphology and aspect ratio of TiNT; the TiNT were prepared at TiO₂ concentration 0.1 g/ 100 mL, NaOH concentration 10 M, at 120 °C for 20 h.

Fig 2: Table: Effect of concentration of input TiO₂ on the aspect ratio of TiNT; the TiNT were prepared at NaOH concentration 10M, at 120 °C for 20 h.
Fig. 3: Table: Effect of reaction conditions on the aspect ratio of TiNT; the TiNT were prepared from anatase of the mean particle size 1 µm and at TiO₂ concentration 0.1 g/100 mL.

Fig. 4: The experimental electron diffractograms (dashed lines) and calculated X-ray diffractograms (solid lines) for TiNT (a), anatase (b) and rutile (c), which prove that the crystalline structure of TiNT essentially differs from common TiO₂ modifications. The TiTN diffractogram corresponds to Example 1; in the other Examples, the same TiNT diffractogram is obtained, the only exceptions are Examples 5-7, where the TiNT diffractograms show also the peaks of residual anatase, which correspond to diffractogram (b).

Fig. 5: FESEM micrographs of the TiNT from Example 3 illustrate an exceptionally high aspect ratio of the prepared nanotubes. (The TiNT in FESEM are displayed as white fibres on dark background). From the measured average thicknesses of nanotubes (D) and nanotube lengths (L), it can be estimated that the aspect ratio (D/L) is at least 500. This is a lower estimate as most nanotubes are so long that they exceed the real width of the image at given magnification.

Fig. 6: HRTEM micrographs of TiNT obtained in Example 1, which illustrates that nanotube walls are usually formed by three layers of TiO₂ sheets. (The TiNT in HRTEM are displayed as black hollow tubes on light background; the inset in the upper right corner shows a Fourier transform illustrating two main types of periodicities in TiNT).

Examples of Carrying out the Invention

Example 1
Starting TiO₂ in the form of anatase, ground to powder with the mean particle size 1 µm, was suspended in 10M NaOH solution, the concentration of TiO₂ in suspension amounting to 0.1 g/100 mL. The suspension was then thermostated in a stirred autoclave at 120 °C for 20 h. The solid was filtered off, washed with water and dried by lyophilization. In the dry product, the particle diameter and length were determined by FESEM (field emission gun scanning electron microscopy) and from TEM (transmission electron microscopy) microphotographs. The crystalline structure of TiNT was determined by diffraction methods PXRD (powder X-
ray diffraction) and SAED (selected area electron diffraction), chemical purity was checked by microscopic and spectroscopic methods, EDX (energy dispersive analysis of X-rays) and Raman spectroscopy (RS). The number of layers was determined by HRTEM (high resolution transmission electron microscopy). It was found that the nanotube diameter \((D)\) amounted to 20 nm and their mean length \((L)\) was at least 2 \(\mu\)m, so that the average aspect ratio of prepared nanotubes \((D/L)\) estimated by image analysis showed a value higher than 100. According to HRTEM, the nanotube walls were most often formed by three layers of TiO\(_2\) in planar arrangement; the presence of residual anatase was not detected by SAED, PXRD, or RS. On electron diffractograms of resulting nanotubes, three most intensive characteristic peaks were found at the diffraction vector values \(q = 1.75 \, \text{Å}^{-1}, 2.05 \, \text{Å}^{-1}\) and \(3.35 \, \text{Å}^{-1}\) and two other broad peaks around \(q = 4.20 \, \text{Å}^{-1}\) and \(5.25 \, \text{Å}^{-1}\).

**Example 2**
Starting TiO\(_2\) in the form of anatase, ground to powder with the mean particle size 200 nm, was suspended in 10M NaOH solution, the concentration of TiO\(_2\) in suspension amounting to 0.1 g/100 mL. From this suspension, TiNT were prepared under the conditions described in Example 1. The properties of resulting TiNT were evaluated by the procedure described in Example 1. The nanotube diameter \((D)\) amounted to 15 nm and their mean length \((L)\) was at least 2 \(\mu\)m, so that the average aspect ratio of prepared nanotubes \((D/L)\) was at least 130. The average number of TiO\(_2\) layers in planar arrangement, as observed on HRTEM photographs, was three, like in Example 1. On an electron diffractogram of resulting nanotubes, characteristic peaks were again found: three most intensive characteristic peaks were at the diffraction vector values \(q = 1.75 \, \text{Å}^{-1}, 2.05 \, \text{Å}^{-1}\) and \(3.35 \, \text{Å}^{-1}\) and two other broad peaks around \(q = 4.20 \, \text{Å}^{-1}\) and \(5.25 \, \text{Å}^{-1}\).

**Example 3**
Starting TiO\(_2\) in the form of rutile, ground to powder with the mean particle size 200 nm, was suspended in 10M NaOH solution, the concentration of TiO\(_2\) in suspension amounting to 0.1 g/100 mL. From this suspension, TiNT were prepared under the conditions described in Example 1. The properties of resulting TiNT were evaluated by the procedure described in Example 1. The nanotube diameter \((D)\) amounted to 40 nm and their mean length \((L)\) was at least 20 \(\mu\)m, so that the average aspect ratio of the prepared nanotubes \((D/L)\) was at least 500. The typical number of layers of TiO\(_2\) in planar arrangement, observed on HRTEM photographs, increased to six, equally as in Example 1. On an electron diffractogram of
resulting nanotubes, characteristic peaks were again found: three most intensive peaks were found at diffraction vector values \( q = 1.75 \ \text{Å}^{-1} \), \( 2.05 \ \text{Å}^{-1} \) and \( 3.35 \ \text{Å}^{-1} \) and two other broad peaks around \( q = 1.75 \ \text{Å}^{-1} \) and \( 5.25 \ \text{Å}^{-1} \).

Example 4
Starting TiO\(_2\) in the form of rutile, ground to powder with the mean particle size 50 nm, was suspended in 10M NaOH solution, the concentration of TiO\(_2\) in suspension amounting to 0.1 g/100 mL. From this suspension, TiNT were prepared under the conditions described in Example 1. The properties of resulting TiNT were evaluated by the procedure described in Example 1. The nanotube diameter (\( D \)) amounted to 8 nm and their mean length (\( L \)) was at least 1 \( \mu \text{m} \), so that the average aspect ratio of the prepared nanotubes (\( D/L \)) was at least 125. The typical number of layers of TiO\(_2\) in planar arrangement, as observed on HRTEM photographs, increased to six, as in Example 1. On an electron diffractogram of resulting nanotubes, characteristic peaks were again found: three most intensive peaks at the diffraction vector values \( q = 1.75 \ \text{Å}^{-1} \), \( 2.05 \ \text{Å}^{-1} \) and \( 3.35 \ \text{Å}^{-1} \) and two other broad peaks around \( q = 4.20 \ \text{Å}^{-1} \) and \( 5.25 \ \text{Å}^{-1} \).

Example 5
Starting TiO\(_2\) in the form of anatase, ground to powder with the mean particle size 1 \( \mu \text{m} \), was suspended in 10M NaOH solution, the concentration of TiO\(_2\) in suspension amounting to 1.0 g/100 mL. From this suspension, TiNT were prepared under the conditions described in Example 1. The properties of resulting TiNT were evaluated by the procedure described in Example 1. Sporadic isometric anatase particles and aggregates of adherent nanotubes were found and the average aspect ratio of prepared nanotubes decreased by ca. 20 %. On an electron diffractogram of the resulting product, in addition to characteristic diffractions of nanotubes (three main peaks at \( q = 1.75 \ \text{Å}^{-1} \), \( 2.05 \ \text{Å}^{-1} \) and \( 3.35 \ \text{Å}^{-1} \) and two other broad peaks around \( q = 4.20 \ \text{Å}^{-1} \) and \( 5.25 \ \text{Å}^{-1} \)), also the diffractions due to anatase were observed (the most intensive peaks at \( q = 1.80 \ \text{Å}^{-1} \), \( 2.55 \ \text{Å}^{-1} \) and \( 3.30 \ \text{Å}^{-1} \)).

Example 6
Starting TiO\(_2\) in the form of anatase, ground to powder with the mean particle size 1 \( \mu \text{m} \), was suspended in 10M NaOH solution, the concentration of TiO\(_2\) in suspension amounting to 6.0 g/100 mL. From this suspension, TiNT were prepared under the conditions described in
Example 1. The properties of resulting TiNT were evaluated by the procedure described in Example 1. Isometric anatase particles and nanotube aggregates were present so that the average aspect ratio of the prepared nanotubes decreased by ca. 40%. On an electron diffractogram of the resulting product, in addition to characteristic diffractions of nanotubes (three main peaks at $q = 1.75 \ \text{Å}^{-1}$, $2.05 \ \text{Å}^{-1}$ and $3.35 \ \text{Å}^{-1}$ and two further broad peaks around $q = 4.20 \ \text{Å}^{-1}$ and $5.25 \ \text{Å}^{-1}$), also the diffractions due to anatase were observed (the most intensive peaks at $q = 1.80 \ \text{Å}^{-1}$, $2.55 \ \text{Å}^{-1}$ and $3.30 \ \text{Å}^{-1}$).

Example 7

TiNT were prepared under the same reaction conditions as in Example 1, except for a shorter reaction time (8 h instead of 20 h). A reaction product similar to those in Examples 5 and 6 was obtained, with sporadic presence of isometric anatase particles. The nanotube aggregates decreased the average aspect ratio of nanotubes roughly by 20% (instead of 100, it was approximately 80).

Example 8

TiNT were prepared under the same reaction conditions as in Example 1, except for a longer reaction time (60 h instead of 20 h). The same reaction product as in Example 1 was obtained including the average aspect ratio amounting to more than 100.

Example 9

TiNT were prepared under the same reaction conditions as in Example 1, except for a lower reaction temperature (60 °C instead of 120 °C). The resulting product was similar to that in Examples 5 and 6. The presence of isometric anatase particles and nanotube aggregates decreased the average aspect ratio of nanotubes roughly by 40% (ca. 60 instead of the value 100).

Example 10

TiNT were prepared under the same reaction conditions as in Example 1, except for a higher temperature (160 °C instead of 120 °C). The same final product as in Example 1 including the average aspect ratio higher than 100.
Example 11
TiNT were prepared under the same reaction conditions as in Example 1, except for a lower NaOH concentration, which was 5 M (instead of 10 M). The resulting product was similar to those in Examples 5 and 6 except for a decrease in the average aspect ratio of nanotubes by ca. 30% (ca. 70 instead of 100).

Example 12
TiNT were prepared under the same reaction conditions as in Example 1, except for a higher NaOH concentration, which was 16 M (instead of 10 M). The same final product as in Example 1 including the average aspect ratio higher than 100.

Example 13
TiNT were prepared under the same reaction conditions as in Example 1, except for the drying procedure. In Example 1, nanotubes were dried by lyophilization, whereas in this Example nanotubes were dried in vacuum at 60 °C or in air at laboratory temperature (25 °C). The same results were obtained as in Example 1, except for the fact that the nanotubes tended to fuse in aggregates and clusters. In that way, their average thickness increased and their aspect ratio decreased to ca. 60.

Example 14
TiNT were prepared under the same reaction conditions as in Example 1. The resulting product was washed with distilled water and neutralized with a few drops of concentrated HCl. The neutral medium is natural for biological applications. Then the resulting product was washed with distilled water. The product was the same as the final product in Example 1 including the average aspect ratio, which was higher than 100.

Industrial applicability

The nanotubes based on titanium dioxide according to the invention are utilizable as a reinforcing component of polymer composites, in particular of the composites designed for production of skeletal replacements and medicine implants; further as a component of
augmentation materials for medical applications and as a material for production of special filters, membranes and ion exchangers.
1. Nanotubes based on titanium dioxide characterized in that they have medium diameter $D$ $8^{10}$ nm and medium length $L$ 1-20 μm and the aspect ratio $L/D$ higher than 50 while the nanotube walls are formed by 2-12 layers of planar crystalline titanium dioxide, characterized by three main maxima of electron diffraction pattern at the values of diffraction vectors $q = 1.75 \, \text{Å}^{-1}$, $2.05 \, \text{Å}^{-1}$ and $3.35 \, \text{Å}^{-1}$, and two other broad peaks at $q = 4.20 \, \text{Å}^{-1}$, $5.25 \, \text{Å}^{-1}$, the diffraction vector $q$ being defined by the equation $q = 4\pi \sin(\theta)/\lambda$, where $\Theta$ is the diffraction angle and $\lambda$ is the wavelength of accelerated electrons.

2. Nanotubes based on titanium dioxide according to Claim 1 characterized in that the aspect ratio is at least 100-500.

3. Nanotubes based on titanium dioxide according to Claim 2 characterized in that their mean average is 20 nm, the mean length is at least 2 μm and their aspect ratio is at least 100.

4. Nanotubes based on titanium dioxide according to Claim 2 characterized in that their mean diameter is 15 nm, the mean length is at least 2 μm and their aspect ratio is at least 130.

5. Nanotubes based on titanium dioxide according to Claim 2 characterized in that their mean diameter is 40 nm, the mean length is at least 20 μm and the aspect ratio at least to 500.

6. Nanotubes based on titanium dioxide according to Claim 2 characterized in that their mean diameter is 8 nm, the mean length is at least 1 μm and the aspect ratio is least 125.

7. Method of preparation of nanotubes according to Claim 1, characterized in that a suspension of TiO$_2$ of the average particle size 0.01-5 μm in a 5-16 M NaOH aqueous solution of concentration 0.01-6 g/100 mL is prepared, which is under constant stirring thermostated at 60-160 °C for at least 8 h and the formed solid product, after isolation from the suspension, is washed and dried.

8. Method of preparation of nanotubes according to Claim 7 characterized in that the NaOH solution is of concentration 10 mol/L.
9. Method of preparation of nanotubes according to Claim 7 or 8 characterized in that the thermostatting time is 20 h.

10. Method of preparation of nanotubes according to Claim 7 or 8 or 9 characterized in that the suspension is thermostated at 120 °C.

11. Method of preparation of nanotubes according to Claim 7 or 8 or 9 or 10 characterized in that the suspension concentration is 0.1 g/100 mL.

12. Method of preparation of nanotubes according to Claims 8, 9, 10 or 11 characterized in that the average particle size of TiO$_2$ in the anatase modification is 1 µm.

13. Method of preparation of nanotubes according to Claims 8, 9, 10 or 11 characterized in that the average particle size of TiO$_2$ in the anatase modification is 0.2 µm.

14. Method of preparation of nanotubes according to Claims 8, 9, 10 or 11 characterized in that the average particle size of TiO$_2$ in the rutile modification is 1 µm.

15. Method of preparation of nanotubes according to Claims 8, 9, 10 or 11 characterized in that the average particle size of TiO$_2$ in the rutile modification is 0.05 µm.

16. Method of preparation of nanotubes according to Claims 11-15 characterized in that the product is neutralized.

17. Method of preparation of nanotubes according to Claims 11-16 characterized in that the product is dried by lyophilization.
### Figure 1

<table>
<thead>
<tr>
<th>Example</th>
<th>Crystalline modification of source TiO₂; average particle size</th>
<th>Average diameter of TiNT; nm</th>
<th>Average length of TiNT; μm</th>
<th>Average aspect ratio of TiNT</th>
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<td>1</td>
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<tr>
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### Figure 2

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<th>Example</th>
<th>Crystalline modification of source TiO₂; average particle size</th>
<th>TiO₂ concentration g/100 ml</th>
<th>Average aspect ratio of TiNT</th>
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### Figure 3

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<tr>
<td>12</td>
<td>16</td>
<td>120</td>
<td>20</td>
<td>&gt; 100</td>
</tr>
</tbody>
</table>

### Figure 4

![Graph showing intensity vs. q [1/Å] for TiNT, Anatase, and Rutile](image-url)