Oriented Crystal Growth Model Explains the Formation of Titania Nanotubes

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We discuss the formation mechanism of titania nanotubes synthesized by the hydrothermal method. On the basis of a comprehensive analysis of TEM, HRTEM, FT-Raman, and N_2 adsorption data, we point out some major shortcomings of the currently accepted trititanate sheet rollup mechanism. We suggest that a novel formation mechanism, oriented nanotube crystal growth from nanoloop seeds, can explain the experimental findings better than the ones proposed so far.

Introduction

Titanium oxide nanostructures have commanded considerable attention lately because of their numerous potential applications in solar cells,[1,2] electronics,[3] photocatalysis,[4] sensorics,[5] and as catalyst supports.[6] Titania nanotubes are especially interesting, as they combine high aspect ratio and high specific surface area with versatile chemistry, leading to, e.g., larger Li-storage capacity than that of crystalline anatase.[7] The hydrothermal titanate nanotube synthesis process (which was introduced in 1998 by Kasuga et al.[8]) is a cheap one-step reaction, which requires neither expensive machinery nor special chemicals. In a typical synthesis, anatase TiO_2 mixed with 10 M NaOH can be converted into nanotubes with yields close to 100% in an autoclave kept at 130 °C for 24 h. Poudel et al. have shown recently that the volume filling fraction of the autoclave influences the crystallinity of the product.[9]

The exact mechanism of hydrothermal titanate nanotube formation is still a controversial topic debated extensively in contemporary literature. Even the elemental composition of the tube walls is disputed. In their first report, Kasuga et al. assumed a pure TiO_2 anatase wall structure,[8] and this was the conclusion of some later studies[10,11] as well. Other researchers argued in the favor of trititanate $(Na_xH_{2-x}Ti_3O_7)$,[12,13] tetratitanate $(H_2Ti_4O_9 \cdot H_2O)$,[14] or lepidocrocite titanate $(H_xTi_{2-x/4}\square_{x/4}O_4$ where $x \approx 0.7$ and $\square$ = vacancy)[15,16] structures. Authors supporting the $Na_2Ti_3O_7$ wall structure propose that the alkaline treatment leads to the total recrystallization of the starting TiO_2 material into lamellar sodium trititanate,[17] followed by the peeling-off of individual trititanate sheets from the crystallites because of the hydrogen deficiency of the topmost layer.[18] Bavykin et al.

suggested on the basis of high-resolution transmission electron microscopy (HRTEM) observations that several trititanate sheets stuck together may also roll up into a nanotube.[19]

The assumed driving force of the sheet exfoliation in the rollup mechanism is the hydrogen or Na^+ deficiency of the topmost trititanate layer, and the reason for the rollup is the need for dangling bond saturation.[20] This hypothesis is supported by TEM observations[17] and first-principles calculations.[18] On the other hand, no direct experimental evidence has been presented for the mechanism until now. The only report where individual layers were observed to roll up into nanotubes is that of Ma et al. who succeeded in preparing titanium oxide, MnO_2, and $Ca_2Nb_3O_{10}$ nanotubes from colloidal nanosheets.[21] However, they applied an exfoliating agent (tetrabutylammonium hydroxide) to peel the nanosheets off from the lepidocrocite titania crystal and used synthesis conditions differing considerably from those typical in the hydrothermal reaction.

In this letter, we present evidence against the rollup formation model and suggest that titania nanotubes are formed by oriented crystal growth instead.

Results and Discussion

In the course of our work, we optimized the hydrothermal synthesis conditions for titanate nanotubes[22] and devised two different methods for decorating the tubes with CdS nanoparticles.[4,23] The nanotubes were ∼10 nm wide and, on average, 90 nm long with 4−6 walls and exhibited a spiral cross-section (Figure 1A) with some exceptions, which had an onion-like structure (Figure 1B) or even an entangled multiple-spiral (Figure 1C) cross-section instead. It was interesting to find that the average length of the nanotubes could be increased by 1 order of magnitude simply by mixing the synthesis autoclave intensively (Figure 1D vs 1E).

In an attempt to verify the trititanate sheet rollup nanotube formation mechanism, we tried rolling up trititanate nanosheets directly from the assumed $Na_2Ti_3O_7$ intermediate. This is a

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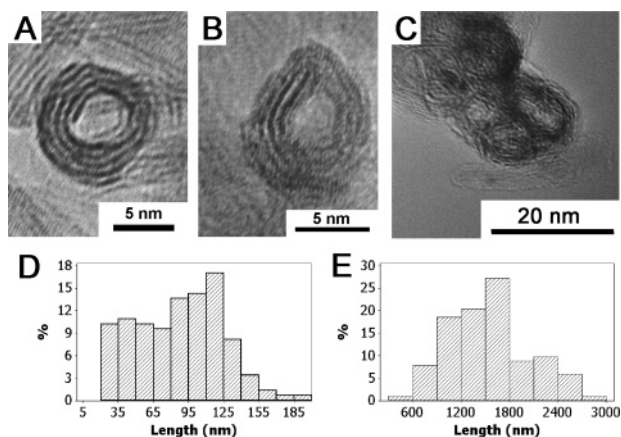† University of Szeged.
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Figure 1. Representative HRTEM images of titania nanotubes with single-spiral (A), onion-like (B), and entangled multiple-spiral (C) cross-sections. The TEM-based length distribution of nanotubes synthesized (130 °C, 10 M NaOH, 72 h) in static (part D) and in intensively mixed (part E) autoclaves is shown as well.
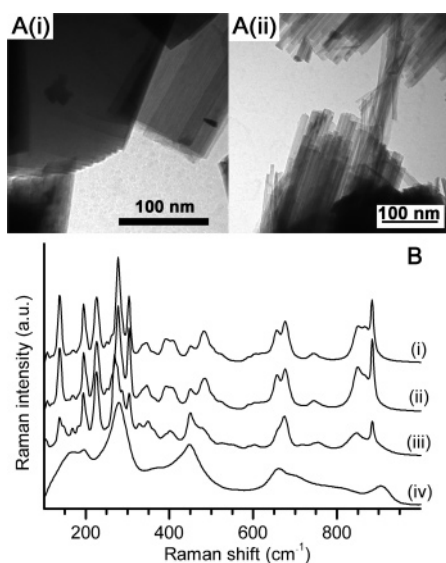

Figure 2. TEM images (part A) and Raman spectra (part B) of (i) the starting $Na_2Ti_3O_7$ material, (ii) $Na_2Ti_3O_7$ treated in 10 M NaOH at 130 °C for 72 h, and (iii) $Na_2Ti_3O_7$ treated in 10 M NaOH at 190 °C for 240 h. The spectrum of the nanotubes grown in one hydrothermal step (10 M NaOH, 130 °C, 72 h) is given in (iv) as reference.

Figure 3. HRTEM images of trititanate nanotubes synthesized at 130 °C in 10 M NaOH using various synthesis times: (A) 1 h, (B) 2 h, (C,D) 3 h. (D) is dark field image after 3 h.

Figure 4. A summary of the proposed hydrothermal formation mechanism of trititanate nanotubes.

lamellar crystal (Figure 2A(i)) possessing low specific surface area ($A_S = 5.1$ m^2/g) due to the strong stacking of the trititanate layers. As-synthesized $Na_2Ti_3O_7$ crystals[24] were subjected to the same alkaline hydrothermal treatment (130 °C, 10 M NaOH, 72 h) that was sufficient[22] for converting anatase TiO$_2$ into nanotubes with a yield close to 100%. However, the TEM image clearly shows that, instead of nanotube formation, the trititanate sheets were only cut into blocks of stripes 20 nm wide and over 300 nm long (Figure 2A(ii)). The Raman spectrum (Figure 2B) did not show any signs of crystal structure distortion due to sheet curvature, and the specific surface area was practically unchanged ($A_S = 5.5$ m^2/g for 72 h and 7.4 m^2/g for 168 h reaction length). Thus, even though the stripes have the right dimensions to form nanotubes, this final step does not happen, and the synthesis stops at this point. Repeating the reaction with $Na_2Ti_3O_7$ crystals ground in a ball mill for 1 h or using more aggressive conditions (190 °C, 10 M NaOH, 240 h) did not change the outcome of the experiment: The trititanate sheet blocks were cut into stripes but did not roll up into nanotubes.
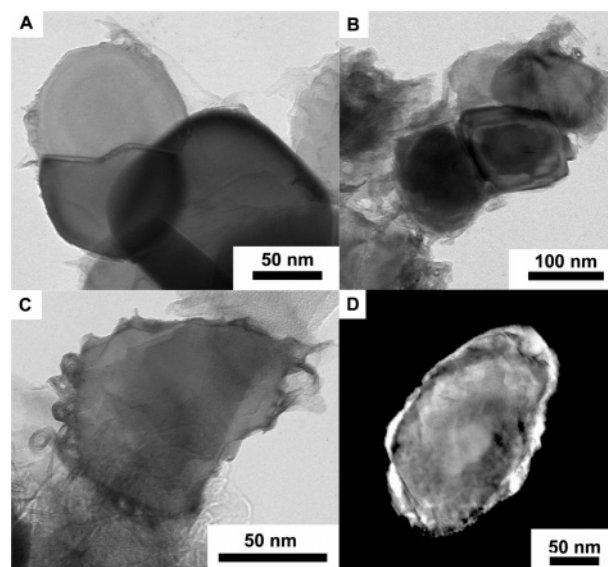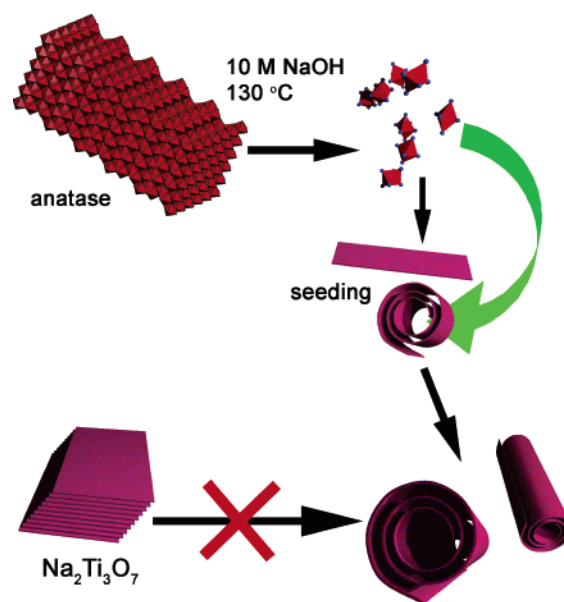
The specific surface area was the highest (11.9 m^2/g) in the case of the 190 °C, 240 h sample; however, this is still an order of magnitude smaller than that of the trititanate nanotubes. This indicates that no exfoliation takes place. It seems possible that blocks of trititanate stripes represent the most stable titania form in the synthesis mixture, and therefore, no nanotubes are formed.

A series of HRTEM images (Figure 3) were taken after 1, 2, and 3 h of reaction time in order to study the first steps of titanate nanotube formation in the original hydrothermal reaction. The two most peculiar features of these images are as follows: (i) Small curved objects ("nanoloops") attached to the anatase crystallites appear as early as 1 h after the reaction is initiated, and (ii) after 3 h of reaction time, the crystal surfaces have broken up into small terraces. Tilting the sample holder between 0° and 45° revealed that the nanoloops are not longer than 10 nm. The final product (obtained after 72 h of reaction) does not contain any nanoloops, only full-sized nanotubes.

Letters

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The presented new findings cannot be explained within the framework of the available single trititanate sheet rollup theory. How could the same synthesis conditions applied to sodium trititanate induce exfoliation in one case and not in another? Why are the particle surfaces cut up into small terraces instead of being peeled off layer by layer? How can we interpret the presence of the 10-nm-long nanoloops, and why are they not observable after the conversion into nanotubes is complete?

We suggest that the rollup theory is in effect only when local concentration fluctuations generate extreme conditions at the surface of nanoparticles. A very small amount of material is removed from the anatase crystallite, leaving behind terraces on the surface. The material recrystallizes into a trititanate sheet, which curves up into a nanoloop of single-spiral, multiple-spiral, or onion-like cross-section. The bulk of the material is then transformed from anatase TiO_2 into nanotubes by oriented crystal growth, supplied with TiO_6 building blocks by the alkaline dismantling of the anatase raw material. The same seeds are probably formed also when pre-made $Na_2Ti_3O_7$ is used as the starting material. However, since sodium trititanate is already the most stable titanium oxide phase under the reaction conditions (10 M NaOH, 130 °C), it is not destroyed by NaOH, and thus, recrystallization into nanotubes does not occur.

Moreover, the exfoliated single-sheet rollup theory implies that the length distribution of the nanotubes should be narrow, which is certainly not the case as evidenced by Figure 1D. Such a broad distribution indicates that nanotubes grow independent of each other from different sources and for different times. Performing the synthesis in a mixed autoclave resulted in fewer but longer nanotubes (Figure 1E). This finding also fits well into the crystal growth theory, because (i) the probability of local concentration extrema is lower in a homogenized vessel, thus fewer crystal seeds are formed, and (ii) mixing takes the reaction out of diffusion control and provides a continuous supply of octahedral building blocks to grow nanotubes, allowing them to reach longer lengths.

Figure 4 offers a quick overview of the mechanistic considerations detailed above. Even if the starting material would recrystallize in a lamellar trititanate form, this would not transform into nanotubes under the circumstances applied. On the other hand, local concentration fluctuations on the crystallite surfaces initiate the formation of nanoloops from the anatase starting material, which then become seeds for an oriented crystal growth process leading to titanate nanotubes. The shape of the cross-section is determined by the curvature of the seeding nanoloop. Since these are flexible ensembles only a few nanometers in length and diameter, they can give rise to spiral, onion, or even multiple-spiral nanotube cross-sections.

References and Notes

(1) O'Regan, B.; Gratzel, M. *Nature (London)* **1991**, *353*, 737.
(2) Barbe, C. J.; Arendse, F.; Comte, P.; Jirousek, M.; Lenzmann, F.; Shklover, V.; Gratzel, M. *J. Am. Ceram. Soc.* **1997**, *80*, 3157.
(3) Croce, F.; Appetecchi, G. B.; Persi, L.; Scrosati, B. *Nature (London)* **1998**, *394*, 456.
(4) Hodos, M.; Horvath, E.; Haspel, H.; Kukovecz, A.; Konya, Z.; Kiricsi, I. *Chem. Phys. Lett.* **2004**, *399*, 512.
(5) Mor, G. K.; Carvalho, M. A.; Varghese, O. K.; Pishko, M. V.; Grimes, C. A. *J. Mater. Res.* **2004**, *19*, 628.
(6) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.
(7) Kavan, L.; Kalbac, M.; Zukalova, M.; Exnar, I.; Lorenzen, V.; Nesper, R.; Graetzel, M. *Chem. Mater.* **2004**, *16*, 477.
(8) Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. *Langmuir* **1998**, *14*, 3160.
(9) Poudel, B.; Wang, W. Z.; Dames, C.; Huang, J. Y.; Kunwar, S.; Wang, D. Z.; Banerjee, D.; Chen, G.; Ren, Z. F. *Nanotechnology* **2005**, *16*, 1935.
(10) Yao, B. D.; Chan, Y. F.; Zhang, X. Y.; Zhang, W. F.; Yang, Z. Y.; Wang, N. *Appl. Phys. Lett.* **2003**, *82*, 281.
(11) Wang, W.; Varghese, O. K.; Paulose, M.; Grimes, C. A.; Wang, Q.; Dickey, E. C. *J. Mater. Res.* **2004**, *19*, 417.
(12) Du, G. H.; Chen, Q.; Che, R. C.; Yuan, Z. Y.; Peng, L.-M. *Appl. Phys. Lett.* **2001**, *79*, 3702.
(13) Sun, X.; Li, Y. *Chem.—Eur. J.* **2003**, *9*, 2229.
(14) Nakahira, A.; Kato, W.; Tamai, M.; Isshiki, T.; Nishio, K.; Aritani, H. *J. Mater. Sci.* **2004**, *39*, 4239.
(15) Ma, R.; Bando, Y.; Sasaki, T. *Chem. Phys. Lett.* **2003**, *380*, 577.
(16) Ma, R. Z.; Fukuda, K.; Sasaki, T.; Osada, M.; Bando, Y. *J. Phys. Chem. B* **2005**, *109*, 6210.
(17) Chen, Q.; Du, G. H.; Zhang, S.; Peng, L.-M. *Acta Crystallogr., Sect. B* **2002**, *58*, 587.
(18) Zhang, S.; Peng, T. Y.; Chen, Q.; Du, G. H.; Dawson, G.; Zhou, W. Z. *Phys. Rev. Lett.* **2003**, *91*, 256103.
(19) Bavykin, D. V.; Parmon, V. N.; Lapkin, A. A.; Walsh, F. C. *J. Mater. Chem.* **2004**, *14*, 3370.
(20) Wang, Y. Q.; Hu, G. Q.; Duan, X. F.; Sun, H. L.; Xue, Q. K. *Chem. Phys. Lett.* **2002**, *365*, 427.
(21) Ma, R.; Bando, Y.; Sasaki, T. *J. Phys. Chem. B* **2004**, *108*, 2115.
(22) Hodos, M.; Haspel, H.; Horváth, E.; Kukovecz, Á.; Kónya, Z.; Kiricsi, I. Vibrational spectroscopic studies on the formation of ion-exchangeable titania nanotubes. XIX. Winter School on Electronic Properties of Novel Materials, Kirchberg in Tirol, 2005.
(23) Kukovecz, Á.; Hodos, M.; Kónya, Z.; Kiricsi, I. *Chem. Phys. Lett.* **2005**, *411*, 445.
(24) $Na_2Ti_3O_7$ was prepared as described originally by Andersson and Wadsley (*Acta Crystallogr.* **1961**, *14*, 1245). The nanotubes were prepared by stirring 2 g of anatase TiO_2 in 140 mL 10 M NaOH aqueous solution until a white suspension was obtained, then aging the suspension in a closed, PTFE-lined autoclave at 130 °C for 72 h without shaking or stirring and, finally, washing the product with deionized water to reach pH 8, at which point the slurry was filtered and the nanotubes were dried in air. TEM observations were performed on Philips CM10 and CM20 instruments using copper-mounted holey carbon grids; HRTEM was done on a JEOL 4000EX microscope using copper-mounted lacey carbon grids. SEM observations were performed on Philips XL-20 instrument. Stokes FT-Raman spectra were recorded on a Bio-Rad FT-Raman instrument operating with 1064 nm excitation wavelength at room temperature in air. Spectra were averaged from 256 scans performed at 4 cm^{-1} resolution. The specific surface area was calculated using the BET method from N_2 adsorption isotherms measured at 77 K on a Quantachrome NOVA 2000 instrument.