

Synthesis, characterisation and
a novel formation model
of titanate nanotubes

Ph.D. Thesis

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1. Introduction and aims

Nanotubular materials are of great interest because of their unique physical properties and potential applications. Following the discovery of carbon nanotubes, syntheses of some oxide nanotubes have also been achieved in the recent years. Titan-oxide nanotubes have attracted considerable attention because of their potential to combine controlled morphology and high stability with photocatalytic activity. In this way, major effort has focused on developing efficient routes of fabricating nanotubes from TiO_2 . Among the different chemical methods available for titanate nanotube preparation, the hydrothermal process stands out because it has the highest potential for industrial scale-up, since it is a cheap one-step reaction which requires neither expensive machinery nor special chemicals.

Structural information on these nanotubes is essential for a deep understanding of their formation mechanism and their physical and chemical properties. 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. Their high surface area and tubular morphology have initiated heterogeneous catalytic studies where the titanate tubes served as support to metal nanoparticles. Another catalytic research direction is photoactivation by decorating tubes with suitable semiconductor quantum dots.

In the course of our work, we investigated titanate nanotubes in four aspects:

1. Experimental study on the effects of various synthesis parameters on hydrothermal nanotube formation.
2. Investigation of the elemental composition, thermal stability and ion exchangeability of titanate nanotubes.
3. Understand the formation mechanism of titanate nanotubes.
4. Devise simple method which can be used to bestow photocatalytic activity titanate nanotubes and apply as catalysts supports.

2. Experimental

The titanate nanotubes were prepared by alkali hydrothermal method. In a typical synthesis, anatase TiO_2 mixed with 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 24 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. Produced nanotubes are 90-100 nm long and 8-10 nm wide. High resolution transmission electron microscopy (HRTEM) images revealed that titanate nanotubes possess a spiral cross-section.

The quality and the quantity of the prepared nanotubes were examined by transmission electron microscopy (TEM). We have also found Raman spectroscopy a highly useful tool in the investigation of titanate nanotubes. Nevertheless, samples were studied by HRTEM, scanning electron microscopy (SEM), powder X-ray diffraction (XRD), as well as N_2 adsorption.

We made an extensive experimental study on the effects of various synthesis parameters on hydrothermal nanotube formation. Factors varied were synthesis length and temperature, concentration of NaOH solution and the type of the precursor TiO_2 materials.

The comprehensive XRD and spectroscopic characterization allowed the critical evaluation of previous reports on nanotube composition. Above all, we concluded that the exact mechanism of nanotube formation was unclear because some of our experimental findings seem to contradict the simple sheet roll-up theory. On the basis of deep analysis of our experimental data, we pointed out evidence against and some major shortcomings of single trititanate sheet roll-up mechanism. Finally, we worked out a novel formation mechanism.

We devised a novel synthesis method which allows the preparation of titanate nanotubes decorated with CdS nanoparticles in one step. Titanate nanotubes were rendered photochemically active by decorating them with CdS nanoparticles.

We impregnated titanate nanotubes with pre-prepared Pt nanoparticles and tested the as synthesized catalyst in hydrogenation-dehydrogenation reactions of cyclohexene.

3. New scientific results

1. *Optimization of synthesis experiments*

- 1.1. We optimized the effects of various synthesis parameters on alkali hydrothermal titanate nanotubes formation. In the optimum synthesis anatase TiO_2 mixed with 10 M NaOH can be converted into nanotubes with yields 100% in an autoclave kept at 130 °C for 24 h. Synthesized under these conditions, typical nanotubes are 90-100 nm long, 8-10 nm wide with 3-4 nm inner diameter and have 124,7 m^2/g specific surface area.
- 1.2. It was established that the particle size of anatase TiO_2 wasn't influence the size of titanate nanotubes. Nanotubes with the same size were produced although anatase particles were 90, 60, 6 nm, respectively. It clearly showed that the formation of nanotubes is independent from the particle size of raw material.

2. *Characterisation of titanate nanotubes experiments*

- 2.1. We were able to verify that the tube walls have a distorted $\text{Na}_2\text{Ti}_3\text{O}_7$ structure instead of anatase. The XRD profile and the Raman spectrum of the hydrothermally synthesized nanotubes differ characteristically from those of anatase reference. Rather, they exhibit features resembling closely those of $\text{Na}_2\text{Ti}_3\text{O}_7$. The nanotube spectrum contains extra peaks which in turn indicate that the structure is distorted.
- 2.2. The thermal stability of the as-synthesized nanotubes was studied by heating them in flowing N_2 . According to TEM examination nanotube morphology was found to retain up to 500 °C. The corresponding XRD profile and Raman spectrum indicate that the structure starts collapsing at 600 °C and the crystal structure is turning into $\text{Na}_2\text{Ti}_3\text{O}_7$ at 700 °C and stays in this form even at 800 °C.
- 2.3. The nanotubes synthesized in NaOH readily take part in cation exchange reactions. Na^+ ions were successfully exchanged both by alkali and by alkali earth cations. The 660 cm^{-1} and the 905 cm^{-1} peaks in the nanotube Raman spectrum were assigned to vibrations involving framework cations. The mentioned peaks of the sodium form nanotubes experiences blue and red shift with the increasing of the cation.

3. Formation of titanate nanotubes experiments

- 3.1. We discovered that titanate nanotubes can be synthesized in concentrated Na₂S solutions. Since the S²⁻ anion is a strong Brønsted base and the 10 M Na₂S solution provides a highly basic environment, the Na₂S-based synthesis is likely to be governed by the same mechanism as the NaOH-based one.
- 3.2. In the course of our TEM observations, the nanotubes were exhibited a spiral cross-section with some exceptions, which had an onion-like structure or even an entangled multiple-spiral cross-section instead. 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-section.
- 3.3. It was established that even if the starting material would recrystallize in a lamellar Na₂Ti₃O₇ form, this would not transform into nanotubes under the circumstances applied but cut into stripes. It seems possible that blocks of Na₂Ti₃O₇ stripes represent the most stable titania form in the synthesis mixture, and therefore, no nanotubes are formed.
- 3.4. Intense mixing the autoclave which ensured turbulent mixing of the reagent mixture was shown to result ten times longer nanotubes than the static reactor. The longer nanotubes formation can occur because mixing takes the reaction out of diffusion control and provides a continuous supply of TiO₆ octahedral building blocks to grow nanotubes, allowing them to reach longer lengths.
- 3.5. Experimental evidence was presented against the currently accepted exfoliated sheet roll-up model and a novel formation mechanism was suggested that oriented nanotube crystal growth from nanoloop seeds, can explain the experimental findings better than the ones proposed so far. A very small amount of material is removed from the anatase crystallite, leaving behind terraces on the surface. The material recrystallizes into a Na₂Ti₃O₇ 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 into nanotubes by oriented crystal growth, supplied with TiO₆ building blocks by the alkaline dismantling of the anatase raw material.

4. *Modification of titanate nanotubes experiments*

- 4.1. Titanate nanotubes were successfully decorated with CdS and ZnS semiconductor nanoparticles both by a two-steps simple wet chemical method and by a complex-assisted one-step synthesis method. The two-step process involves bubbling H₂S through an aqueous suspension of Cd²⁺-exchanged titanate nanotubes at room temperature. The other one is the novel complex-assisted one-step synthesis of CdS-decorated titanate nanotubes. The key feature of the process is controlling the rate of CdS formation by introducing Cd²⁺ ions as a Cd-EDTA complex into the synthesis mixture. There are two characteristic differences between the methods: (i) the complex-assisted method gave significantly smaller CdS particles (mean diameter of 5,3 nm vs. 6,0 nm for the two-step method) and (ii) the surface of the nanotubes is completely covered by nanoparticles when using the complex-assisted method.
- 4.2. Titanate nanotubes decorated with CdS were shown to have photocatalytic activity to otherwise inactive titanate nanotubes. The photosensitization appears to be originating from the strong coupling between the CdS nanoparticles and the titanate support.
- 4.3. Preliminary catalytic investigations were carried out using pre-prepared platinum nanoparticles supported on titanate nanotubes and tested in hydrogenation-dehydrogenation reactions of cyclohexene. The results showed that this type of catalyst exhibits interesting properties as compared to conventional catalysts.

4. Application of the results

Results of our research have importance mainly in the field of fundamental studies. However, finding good conditions to the large-scale and selective production of a nanomaterial, like titanate nanotubes, always carries potential practical significance.

Hereafter these good quality nanotubes could be modified easily by semiconductor nanoparticles, which may be important to their further applications. We devised two different methods for decorating the tubes with CdS nanoparticles and took steps to prove that after modifications the nanotubes can be used as photocatalyst or catalyst support.

5. List of publications on which the thesis is based

- 1. Photosensitization of ion-exchangeable titanate nanotubes by CdS nanoparticles**
M. Hodos, E. Horváth, H. Haspel, Á. Kukovecz, Z. Kónya, I. Kiricsi
Chemical Physics Letters 399 (2004) 512-515
IF: 2,438 Cited: 20
- 2. Catalysis by pre-prepared platinum nanoparticles supported on trititanate nanotubes**
M. Hodos, Z. Kónya, I. Kiricsi
Reaction Kinetics and Catalysis Letters 84 (2005) 341-350
IF: 0,475
- 3. Complex-assisted one-step synthesis of ion-exchangeable titanate nanotubes decorated with CdS nanoparticles**
Á. Kukovecz, M. Hodos, Z. Kónya, I. Kiricsi
Chemical Physics Letters 411 (2005) 445-449
IF: 2,438 Cited: 2
- 4. Oriented crystal growth model explains the formation of titania nanotubes**
Á. Kukovecz, M. Hodos, E. Horváth, Gy. Radnóczy, Z. Kónya, I. Kiricsi
Journal of Physical Chemistry B 109 (2005) 17781-17783
IF: 3,834 Cited: 13
- 5. Vibrational spectroscopic studies on the formation mechanism of ion-exchangeable titania nanotubes**
M. Hodos, H. Haspel, E. Horváth, Á. Kukovecz, Z. Kónya, I. Kiricsi
Proceedings of the XIX. Winterschool on Electronic Properties of Novel Materials
(Edited by H. Kuzmany, J. Fink, M. Mehring)
AIP Conference Proceedings 786 (2005) 345-348

6. Conference lectures and posters related to the thesis

- 1. Titania nanotubes doped with CdS nanoparticles**
Hodos M., Kiricsi I.
Surface Chemistry and Nanostructures Committee of Hungarian Academy of Sciences
Szeged, 22/10/2003 (Oral presentation in Hungarian)
- 2. Porous tubular alkali titanate – Synthesis and characterization**
Hodos M., Kónya Z., Horváth E., Radnóczy Gy., Kiricsi I.
XI. Zeolite Forum,
Wysowa, 29/08-03/09/2004 (Oral presentation in English)
- 3. Tubular alkali titanate based photocatalyst-Synthesis and characterization**
I. Kiricsi, M. Hodos, E. Horváth, Gy. Radnóczy, Z. Kónya
7th Pannonian International Symposium on Catalysis,
Srní, 12-16/09/2004 (Oral presentation in English)

4. **Let's roll up alkali titanate nanotubes!**
M. Hodos, Z. Kónya, E. Horváth, I. Kiricsi
2nd Szeged International Workshop on Advances in Nanoscience,
Szeged, 30/09-02/10/2004 (Oral presentation in English)
5. **Vibrational spectroscopic studies on the formation mechanism of ion-exchangeable titania nanotubes**
M. Hodos, H. Haspel, E. Horváth, Á. Kukovecz, Z. Kónya, I. Kiricsi
XIX. International Winterschool on Electronic Properties of Novel Materials,
Kirchberg, 12-19/03/2005 (poster)
6. **Titania nanotubes – Synthesis and Characterisation**
Hodos M.
Catalysis Science Committee of Hungarian Academy of Sciences
Budapest, 22/02/2005 (Oral presentation in Hungarian)
7. **Let's roll up the mystery of titania nanotubes!**
Hodos M.
Physical and Nanoscience Committee of Hungarian Academy of Sciences
Budapest, 30/03/2005 (Oral presentation in Hungarian)

7. Other publications, conferences

1. **Tubular inorganic nanostructures**
I. Kiricsi, Á. Fudala, D. Méhn, Á. Kukovecz, Z. Kónya, M. Hodos, E. Horváth, M. Urbán,
T. Kanyó, É. Molnár, R. Smajda
Current Applied Physics 6 (2006) 212-215
IF: 1,116 Cited: 1
2. **Catalytic detoxification of C₂-chlorohydrocarbons over iron-containing oxide and zeolite catalysts**
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IF: 1,440 Cited: 1
3. **Spectroscopic studies on the transfer of surface chemistry from 2D to 3D systems**
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4. **Encapsulation of platinum nanoparticles into the mesoporous SBA-15 structure**
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Tuczno, 21-26/09/2003 (Oral presentation in English)

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J. Halasz, M. Hodos, Sz. Lorincz, I. Kiricsi

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Prague, 01-04/09/2003 (Oral presentation in English)

6. Catalytic hydrodechlorination of C₂-chlorohydrocarbons

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Timisoara, 14-15/11/2002 (poster)

7. Decomposition of chlorinated C₂-compounds over simple and mixed oxide catalysts

Hodos M., Halász J., Hannus I., Kiricsi I.

9th Symposium on Analytical and Environmental Problems
Szeged, 30/09/2002 (Oral presentation in Hungarian)

8. Oxidative and reductive destruction of halogenated organics over mixed and zeolite catalysts

Halász J., Imre B., Kanyó T., Gungl A., Hodos M., Tóth M., Hannus I., Kiricsi I.

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