

STRUCTURE AND STABILITY OF MODIFIED TITANATE NANOTUBES: ION-EXCHANGE, DOPING AND HETEROSTRUCTURES

Ph.D. thesis

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1. Introduction

Increasing atmospheric concentration of CO₂ and depletion of fossil energy sources are just a few examples for today's major environmental challenges that materials science needs to be working on. Nanotechnology offers a new point of view because it deals with matter with at least one dimension in the 1 to 100 nm range and the size control brings about different physical and chemical properties compared to the bulk phase. There are many kinds of nanomaterials such as quantum dots, nanotubes and nanowires, nanosheets with thickness of a few atomic layers, or hierarchical structures. These materials can be applied as sensors, in energy storage, biomedicine or as catalyst supports because of their favorable properties.

Discovery of carbon nanotubes made the '90s the decade of tubular nanostructures. In 1998, *Kasuga* firstly reported about trititanate nanotubes synthesized by an alkaline hydrothermal route. These rolled-up nanotubes have layered structure with a length of 100-200 nm, diameter of 10-12 nm and specific surface area of 200-300 m²/g. Protonated trititanate nanotubes (TiONT) transform into different types of titanium-dioxides upon heat treatment. Thus, from the application point of view, the investigation of TiONTs is as appropriate as that of TiO₂.

Since 1972, TiO₂ has become one of the most investigated semiconductors especially in the field of heterogeneous photocatalysis, owing largely to *Fujishima's* and *Honda's* groundbreaking photoelectrochemical study. Titanium-dioxide exhibits photocatalytic activity only under UV irradiation. However, modifications such as doping or the formation of heterostructures can push its activity into the visible light region.

The Department of Applied and Environmental Chemistry has been active in 1D titanate nanostructure research for nearly 15 years now. This was the research direction that I joined when I started my work at the Department. The goals of my doctoral studies were to prepare modified (ion-exchanged, doped, heterostructure based) titanate nanotubes and to investigate their heat stability and photocatalytic properties. In order to deepen our understanding of these nanostructures the following particular topics were investigated:

- Synthesis and heat stability of bismuth and/or antimony ion-exchanged titanate nanotubes: structural and morphological investigation.

- Investigation of nitrogen doping by thermal and ion-implantation methods. Study of the chemical environment of the incorporated nitrogen. Revealing the effect of dopants and post heat treatments on the structure and morphology of TiONT.
- Preparation of bismuth- and antimony-oxychloride based TiONT heterostructures by immobilization of oxychloride nanoparticles on the surface of nanotubes. Investigation the heat stability of composites and studying their photo-activated methyl orange dye decolorization properties.

2. Experimental

Titanate nanotubes were synthesized via the alkaline hydrothermal method. 50 g TiO₂ was stirred in 10 M NaOH solution, then the obtained suspension was transferred to a PTFE-lined stainless steel autoclave and kept at 130 °C for 24 hours with continuous rotation at 3 RPM. The as-prepared product was neutralized by deionized water, then protonated in 0.01 M HCl for one week. After the protonation step remnant Cl⁻ ions were washed out of the system by deionized water. The product was finally dried at 60 °C for 2 days.

In order to prepare bismuth and/or antimony ion-exchanged titanate nanotubes 2 g of TiONT was suspended in 100 ml deionized water by ultrasonic homogenization and subsequently bismuth-acetate, antimony-acetate or both of them were added to the system. The total metal content was set to 10 w/w% in all cases. The mixture was stirred for 24 hours then the solid product was separated by filtration. Remnant acetate ions were washed out by deionized water, then the ion exchanged nanotubes were dried at 60 °C for 2 days. All samples underwent heat treatment at 600, 750 or 900 °C for 1 hour.

In the case of thermal nitrogen doping 12 g of urea and 1 g of TiONT were transferred into a PTFE-lined stainless steel autoclave with a volume of 0.4 dm³. The precursors were physically separated from each other. The sealed system was kept at 200 °C during which ammonia gas developed in situ by the thermal decomposition of urea served as the dopant source. The doping time was 2, 4, 8, 12 or 24 hours. Pristine and doped materials underwent heat treatments between 400–900 °C for 1 hour.

Ion bombardment was performed in the analytical chamber of an X-ray photoelectron spectrometer using a hot-filament equipped ion gun (Kratos MacroBeam) fed with high-purity (5N5) N₂. The ion beam (spot size of approximately 2 mm, non-mass-selected, incident at mean

angle of 55° to the surface normal) was rastered over a sample surface of approximately 8×8 mm. The accelerating voltage was 3 kV and the energy of the incident ions was 1.5 keV.

Plasma treatment was performed in the stainless steel sample preparation chamber of the XPS instrument (base pressure $<1 \times 10^{-4}$ Pa). High purity N₂ (5N) or NH₃ flow of a few ml/min (STP) was regulated by a bleeding valve that set the pressure to 5–7 Pa. Constant RF power of 100 W at 13.56 MHz was applied through a matching circuit to a copper coil fixed outside of a glass dome attached to the preparation chamber. The sample bias was set to negative values between 100 and 300 V. Treatment time varied from 5 to 30 min. After treatment the sample was transferred to the analysis chamber without exposing it to the ambient air.

TiONT supported bismuth oxychloride was prepared by a precipitation reaction. 1 g TiONT was suspended in 50 ml deionized water by ultrasound treatment for 2 hours, then bismuth(III)-chloride was added to the system. The atomic ratio of Ti:Bi was set to either 10:1 or 100:1. The suspension was stirred for 24 hours, then filtered and washed with deionized water. Powder samples were dried at 60 °C for 48 hours. In order to prepare reference bulk BiOCl, 2 g of the precursor salt was mixed in 200 ml deionized water. The as-prepared suspension underwent the same treatments as the supported counterparts. Samples were heat treated between 200-900 °C.

Antimony-oxychloride/TiONT systems were prepared by the solvothermal route. In all cases, the Sb content was set to 15 w/w%. In a typical synthesis, antimony(III)-chloride was stirred in 0.28 dm³ 50/50 v/v% ethylene glycol and deionized water mixture. The pH of the medium was 1–2 in this step, while pH = 4–5 and pH = 8–9 samples were prepared by adding the necessary amount of 6 mol dm³ NaOH solution. After 1 hour of intensive stirring, the suspension was transferred into a 0.4 dm³ PTFE-lined stainless steel autoclave and kept at 120 °C for 12 hours. The pale yellowish product was washed with deionized water to remove chloride ions and dried at 60 °C for 24 hours. The pristine and nanoparticle decorated samples were subjected to thermal annealing at 100, 200, 300, or 400 °C for 1 h. The product materials were characterized after each annealing step. Commercial anatase TiO₂ was decorated and heat treated by following exactly the same protocol, and used as the reference material.

The morphology of samples was studied by transmission and scanning electron microscopy. X-ray diffraction, selected area electron diffraction and Raman spectroscopy were applied for structural examination. The elemental composition was studied by energy dispersive X-ray spectrometry and the chemical environment was investigated by X-ray photoelectron

spectroscopy. The specific surface area and pore volume were determined by nitrogen adsorption measurements. The light absorption properties of semiconductor samples were investigated by diffuse reflectance UV-Vis spectroscopy. Surface functional groups were identified by diffuse reflectance Fourier transform infrared spectroscopy.

The photocatalytic activity was studied in methyl orange dye decolorization test reactions under UV-Visible or visible light irradiation. Dye concentrations were measured by UV-Vis spectrophotometry.

3. New scientific results

1. We were the first to synthesize bismuth and/or antimony ion-exchanged titanate nanotubes and investigate their thermal stability

- 1.1. We incorporated bismuth and/or antimony ions into the structure of titanate nanotubes by taking advantage of their ion-exchange property. Successful ion exchange was verified by EDS, TEM and XRD measurements.
- 1.2. We proved by TEM measurements that bismuth promotes the thermally induced collapsing of the tubular morphology. TiONT turns into particles with size of 20-30 nm upon heat treatment at 600 °C. The effects of thermal annealing at 600, 750 and 900 °C were investigated by XRD and Raman spectroscopy. We demonstrated that bismuth ion-exchange promotes the trititanate–anatase–rutile phase transition compared to the pristine TiONT. At 900 °C the conversion to rutile is 100%.
- 1.3. We proved by TEM measurements that the presence of antimony inhibits the thermally induced collapsing of the tubular morphology. After heat treatment at 600 °C, nanotubes are still observable in the sample and they even exhibit a higher aspect ratio than the pristine ones. The effects of thermal annealing at 600, 750 and 900 °C were investigated by XRD and Raman spectroscopy. We demonstrated that antimony-containing trititanate turns into B-TiO₂ besides the anatase phase. Moreover, at 900 °C the anatase–rutile phase transition is lower than in the case of pristine TiONT at the same temperature. The formation of intermediate B-TiO₂ was affected by Sb³⁺ because of its favorable ionic radius.
- 1.4. We proved that bismuth segregates on the surface as bismuth-titanate nanoparticles with size of 2.5-3 nm when a sample with 10 w/w% Bi content is annealed between 600-900 °C. The structure of the sample calcined at 900 °C was identified as rutile TiO₂/Bi₂Ti₄O₁₁, which is applicable in the field of heterogeneous photocatalysis. Our experiment serves a new and easy method for the synthesis of this nanostructure.

2. We devised a thermal nitrogen doping method and investigated the stability of doped structures

- 2.1. We doped titanate nanotubes with nitrogen using ammonia gas that was prepared in situ by the thermal decomposition of urea at 200 °C in a purpose-built reactor. The doping time was chosen as 2, 4, 8, 12 or 24 hours. TEM and XRD investigations revealed that

nanotubes became partially fragmented after 8 hours of doping and a mixed trititanate/anatase was formed. After 12 hours cubic and octahedrally shaped anatase nanoparticles were formed. The crystallinity degree of TiO₂ increased after 24 hours doping time. Using our experimental setup we succeeded in preparing nitrogen doped TiO₂ nanoparticles using ammonia gas as the dopant source at the lowest temperature so far.

- 2.2. By EDS analysis we showed that the nitrogen content changes between 0.11-6.6 at.% during the 2-24 hours doping time. XPS and DRIFTS measurement revealed that the incorporated nitrogen is in interstitial position as NH₄⁺ and NH₂ in the 24 hours doped sample.
- 2.3. By thermal stability investigation between 400 and 900 °C we demonstrated that increasing doping time promotes the transformation of nanotubes into nanorods and then into smaller nanoparticles. This observation was confirmed by TEM and SEM image analysis and the calculation of average particle length and circularity. These two parameters exhibited similar characteristics as a function of doping time.
- 2.4. An XRD study revealed that both elongated doping time and increased temperature results in anatase (101) crystallite size growth. The extent of the anatase–rutile phase transition was increasing with the doping time at 900 °C: in the case of pristine TiONT the rutile content is ~5 w/w%, whereas after 24 hours doping time it is almost 40 w/w%.
- 2.5. The effects of doping time and heat temperature on the structure and morphology were summarized in a phase diagram. This can be a useful tool for the design of nitrogen topped titan-oxide nanostructures.

3. Nitrogen doping of trititanate nanotubes by different ion implantation methods

- 3.1. We were the first to dope titanate nanotubes by nitrogen using nitrogen bombardment, nitrogen and ammonia plasma treatment.
- 3.2. The chemical environment of nitrogen in trititanates was analyzed by XPS. The amount of incorporated surface nitrogen was 1.1, 7.0 and 18.6 at.% in the case of N₂⁺ bombardment, N₂ plasma, and NH₃ plasma treatment, respectively. All samples contained both substitutional and interstitial nitrogen.

- 3.3. We succeeded in incorporating a record high amount (8-10%) of nitrogen into titanate nanotubes in substitutional position by ammonia plasma treatment. We identified NH_4^+ , CH_2 and CH_3 functional groups on the surface by DRIFTS measurements.
- 3.4. XRD and TEM measurements revealed that unlike thermal nitrogen doping, ammonia plasma treatment does not affect the structure or morphology of TiONTs.

4. Preparation, heat stability and photocatalytic activity of bismuth-oxichloride/titanate nanotube heterostructures

- 4.1. We were the first to synthesize titanate nanotube supported bismuth-oxichloride nanoparticles. During the precipitation reaction BiOCl nanoparticles formed with the size of ~5 nm as determined by TEM. We identified their structure as tetragonal BiOCl (XRD).
- 4.2. By XRD and TEM investigations we proved that TiONT turns into anatase nanotubes at 400 °C. Supported nanoparticles grew to ~10 nm and lose their crystal structure. XRD analysis showed that although BiOCl became partially decomposed, its components Bi, O and Cl still remained in the system. DR-UV-Vis absorption spectra exhibited a red shift compared to those of pristine nanotubes, which may be related to the dissolution of Bi^{3+} into the anatase structure during the heat treatment at 400 °C.
- 4.3. We performed an XRD based thermal stability investigation between 200 and 900 °C. We found that in the case of 100:1 Ti:Bi atomic ratio samples, the anatase–rutile phase transition was advanced like in the case of bismuth ion-exchanged ones compared to pristine TiONT. The 100:10 Ti:Bi atomic ratio favors the formation of tetragonal BiOCl nanoparticles. The carrier stability is similar to that in pristine TiONT. According to the XRD measurements BiOCl turns into amorphous phase around 300-400 °C.
- 4.4. The sample with 100:10 Ti:Bi atomic ratio was heat treated at 400 °C and subsequently decomposed 88% of the model compound (methyl orange) under visible light irradiation. The visible light activity originated from the incorporation of Bi^{3+} into the anatase structure and the dye sensitization effect promoted by methyl orange adsorbed on the surface. Electron transfer between TiO_2 and BiOCl is also possible, but its direction is undetermined.

5. Synthesis and photocatalytic properties of antimony-oxichloride/titanium-oxide heterostructures

- 5.1. We were the first to synthesize antimony-oxychloride/titanate nanotube and antimony-oxychloride/titanium-dioxide heterostructures. Nanoparticles with sizes between 8-11 nm were successfully immobilized on the surface of TiONT, while in the case of TiO₂, we did not observe any supported nanoparticle formation during the pH regulated solvothermal synthesis.
- 5.2. The heterostructures underwent thermal annealing between 100 and 400 °C and each annealed sample was examined by XRD. We described the effect of the different titanium-oxide supports on the formation of antimony-oxychlorides and antimony-oxides for the first time. We compared our results with literary data to determine the structure of various solvothermally synthesized products. In the presence of TiONT support, at pH = 1-2 SbOCl or Sb₄O₅Cl₂, at pH = 4-5 Sb₈O₁₁Cl₂ or Sb₈O₁₁Cl₂(H₂O)₆, and at pH = 8-9 α-Sb₂O₃ was formed. In the case of TiO₂, at pH = 1-2 Sb₈O₁₁Cl₂(H₂O)₆, at pH = 4-5 Sb₈O₁₁Cl₂(H₂O)₆ or Sb₈O₁₁Cl₂(H₂O)₃, and at pH = 8-9 α-Sb₂O₃ and β-Sb₂O₃ was formed.
- 5.3. DR-UV-Vis measurements revealed that the light absorption of TiONT based samples changes continuously during the formation of different antimony oxychlorides and oxides because of the trititanate–anatase phase transition of the support. In the case of TiO₂ based heterostructures there is no significant change in the optical properties.
- 5.4. Each sample was tested in methyl orange decolorization under UV-Vis irradiation. Apparent reaction rates in the presence of TiONT supported oxychlorides are higher by one order of magnitude than those measured in their TiO₂ based or antimony-oxide containing counterparts. We attributed this effect to the continuously changing structure of both the support and the oxychlorides during the heat treatment.

4. Papers related to the present thesis

1. Structure and stability of pristine and Bi and/or Sb decorated titanate nanotubes

A. Rónavári, **B. Buchholz**, Á. Kukovecz, Z. Kónya

Journal of Molecular Structure, 1044, 2013, 104-108

IF₂₀₁₃: 1,599

2. Low temperature conversion of titanate nanotubes into nitrogen-doped TiO₂ nanoparticles

B. Buchholz, H. Haspel, Á. Kukovecz, Z. Kónya

CrystEngComm, 16, 2014, 7486-7494

IF₂₀₁₄: 4,034

3. pH-regulated Antimony Oxochloride Nanoparticle Formation on Titanium Oxide Nanostructures: A Photocatalytically Active Heterojunction

B. Buchholz, H. Haspel, T. Boldizsár, Á. Kukovecz, Z. Kónya

CrystEngComm, 19, 2017, 1408-1416

IF₂₀₁₇: 3,304

4. Titania nanotube stabilized BiOCl nanoparticles in visible-light photocatalysis

B. Buchholz, H. Haspel, A. Oszkó, Á. Kukovecz, Z. Kónya

RSC Advances, 7, 2017, 16410-16422

IF₂₀₁₇: 2,936

5. Morphology Conserving High Efficiency Nitrogen Doping of Titanate Nanotubes by NH₃ Plasma

B. Buchholz, K. Plank, M. Mohai, Á. Kukovecz, J. Kiss, I. Bertóti, Z. Kónya

Topics in Catalysis, 61, 2018, 1263-1273

IF₂₀₁₇: 2,439

5. Presentations, posters, attending conferences

1. Synthesis and characterization of nitrogen-doped titanate nanotubes

B. Buchholz, Á. Kukovecz, Z. Kónya

Hungarian Society for Microscopy, 2013, Siófok, presentation

2. Preparation and modification of vanadium-oxide nanowires

M. Szabó, **B. Buchholz**, Á. Kukovecz, Z. Kónya

Hungarian Society for Microscopy, 2013, Siófok, presentation

3. Structure and stability of pristine, Bi and/or Sb decorated titanate nanotubes

A. Rónavári, **B. Buchholz**, Á. Kukovecz, Z. Kónya

Hungarian Society for Microscopy, 2013, Siófok, presentation

4. Synthesis, structure and stability of pristine and Bi and/or Sb decorated titanate nanotubes

A. Rónavári, **B. Buchholz**, Á. Kukovecz, Z. Kónya

NANO-2013, 2013, Bukovel, poster

5. Nitrogénnel adalékolt TiO₂ nanorészecskék alacsony hőmérsékletű előállítás a titanát nanocsövekből

B. Buchholz, H. Haspel, Á. Kukovecz, Z. Kónya

XXXVI. kémiai Előadói Napok, 2013, Szeged, presentation

6. Photocatalytic activity of the different stoichiometry antimony-oxychloride decorated titanate nanotubes

B. Buchholz, Á. Kukovecz, Z. Kónya

SM-2013, 2013, Újvidék, presentation

7. Nitrogénnel adalékolt TiO₂ nanorészecskék alacsony hőmérsékletű előállítás a titanát nanocsövekből

B. Buchholz, H. Haspel, Á. Kukovecz, Z. Kónya

Termoanalitikai szeminárium, 2014, Szeged, presentation

8. Low-temperature conversion of titanate nanotubes into nitrogen-doped TiO₂

B. Buchholz, H. Haspel, Á. Kukovecz, Z. Kónya

3rd nanoPT, 2015, Porto, poster

9. Nitrogénnel adalékolt TiO₂ nanorészecskék alacsony hőmérsékletű előállításáa titanát nanocsövekből

B. Buchholz, H. Haspel, Á. Kukovecz, Z. Kónya

XXXVIII. kémiai Előadói Napok, 2015, Szeged, presentation

10. Structure and stability of boron doped titanate nanotubes and nanowires

B. Buchholz, E. Varga, T. Varga, J. Kiss, Z. Kónya

JVC-16, 2016, Portoros, presentation

11. Modified titanates for visible light photocatalysis

B. Buchholz, H. Haspel, Á. Kukovecz, Z. Kónya

YISAC-2016, 2016, Újvidék, presentation

12. Low-temperature N,F co-doping of layered titanate nanotubes and bulk anatase TiO₂: a comparative study

B. Buchholz, K. Plank, H. Haspel, Á. Kukovecz, Z. Kónya

SIWAN7, 2016, Szeged, poster

13. Synthesis of photoactive antimony oxyiodide hierarchical nanostructures

T. Boldizsár, **B. Buchholz**, H. Haspel, Z. Kónya, Á. Kukovecz

SIWAN7, 2016, Szeged, poster

14. pH-regulated Antimony Oxychloride Nanoparticle Formation on Titanium Oxide Nanostructures: A Photocatalytically Active Heterojunction

B. Buchholz, H. Haspel, Á. Kukovecz, Z. Kónya

21st Topical Meeting of the ISE, 2017, Szeged, presentation

15. Synthesis and characterization of new antimony-oxide based photocatalysts

A. Ochirkhuyag, **B. Buchholcz**, Á. Kukovecz, Z. Kónya

Hungarian Society for Microscopy, 2017, Siófok, presentation

16. Nitrogen doping of titania nanomaterials using thermal and plasma activation

B. Buchholcz, K. Plank, M. Mohai, Á. Kukovecz, J. Kiss, I. Bertóti, Z. Kónya

ecoss33, 2017, Szeged, poster

17. Grafén-oxid hatása az aerob granulátumos szennyvíztisztítási technológiára

A. Kedves, **B. Buchholcz**, O. Kedves, L. Sánta, A. Rónavári, J. Halász, Z. Kónya

XIV. Kárpát-medencei Környezettudományi Konferencia, 2018, Gödöllő, poster

18. Titanát nanoszerkezetek fotoérzékenyítése alacsony hőmérsékletű N,F koadalékolással

K. Plank, **B. Buchholcz**, Á. Kukovecz, Z. Kónya

Hungarian Society for Microscopy, 2018, Siófok, presentation

19. Titanát nanocső alapú fotokatalizátorok előállítása: adalékolás és heterostruktúrák

B. Buchholcz, H. Haspel, K. Plank, Á. Kukovecz, Z. Kónya

Hungarian Society for Microscopy, 2018, Siófok, presentation

20. Synthesis of Au supported B-doped titanate nanotubes

B. Buchholcz, K. Plank, Á. Kukovecz, J. Kiss, Z. Kónya

SIWAN8, 2018, Szeged, poster

21. Insight into the impact of graphene-oxide (GO) nanoparticles on aerobic granular sludge (AGS) under shock loading

A. Kedves, **B. Buchholcz**, T. Varga, A. Rónavári, J. Halász, Z. Kónya

SIWAN8, 2018, Szeged, poster

6. Other publication

1. Structure and stability of boron doped titanate nanotubes and nanowires

B. Buchholz, E. Varga, T. Varga, K. Plank, J. Kiss, Z. Kónya

Vacuum, 138, 2017, 120-124

IF₂₀₁₇: 2,067

Peer-reviewed papers total: 6	out of this, related to the topic of this thesis: 5
Cumulative impact factor: 16,379	out of this, related to the topic of this thesis: 14,312
Independent cites total: 20	out of this, related to the topic of this thesis: 17