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**MODIFICATION ROUTES OF ONE DIMENSIONAL TITANATE
NANOSTRUCTURES**

Ph.D. thesis

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I. Introduction and objectives

The history of titanate nanostructures (such as nanotubes and nanowires) goes back to 1998, when Kasuga and his co-workers synthesized titanate nanotubes using a hydrothermal method (reacting TiO_2 powder with 10 M NaOH solution in a static autoclave). In the past twenty years thousands of scientific papers have been published in this field, indicating its significance and the interest of the scientific community.

The structure of titanate nanotubes (TiONT) is reminiscent of a rolled-up carpet. The tubes are open-ended and hollow. Their length is between 100 and 200 nm while their average inner and outer diameters are approx. 5 nm and 8 nm, respectively. A typical nanotube features a spiral cross section composed of 3-5 wall layers. There are numerous scientific publications describing their theory of formation. Early theories commonly accepted that the first step in nanotube formation is the exfoliation of a 2D sheet from the surface of the TiO_2 crystal. The tubular structure forms subsequently, by an up-rolling mechanism of the recrystallized 2D sheet. These theories were disproved by the experiments of Kukovecz and his co-workers at our department, and they suggested a novel formation mechanism. According to their theory the growth of nanotube crystals commences from nanoloop seeds.

Titanate nanowires (TiONWs) can also be prepared by the reaction of TiO_2 and 10 M NaOH solution at 150 °C (or higher) in an autoclave. In contrast to the synthesis method of nanotubes, the autoclave is rotated around its shorter axis at about 28 rpm in this case. The structure of the nanowires differs from that of tubular titanates. They consist of parallel planar titanate sheets, their diameter is between 50-80 nm, while their length can reach 3-5 μm .

Our department has extensive experience in the field of titanate nanostructures. During my doctoral work I was involved in titanate nanostructure research, where my goal was to extend further the scientific knowledge of this field. I explored new methods and extended the previously established techniques to modify one-dimensional titanate nanostructures.

A potential route to modify the titanate nanostructures is the utilization of their ion exchange ability. If the ions are modified/replaced in the nanowire, then its structural and surface properties will be modified as well. Since titanate nanostructures have a very similar framework to zeolites, ion exchange – which is a proven approach in the case of zeolites – can be a promising method to modify the surface acidity of titanate structures.

In my experiments my aim was to create bifunctional catalysts by decorating the titanate surface by metallic nanoparticles. To achieve this goal, two different methods were applied. In the first case Rh decorated nanostructures were prepared by using a wet impregnation technique, while in the second case Co-loaded titanate nanowires were synthesized by the vapor phase deposition of cobalt-carbonyl.

By exploiting the ion exchange ability of titanate nanostructures, titanate nanotubes were also utilized in a water softening process. The ion exchange capacity of the tubes was examined against Ca^{2+} and Mg^{2+} ions. The kinetic parameters of the process and the regeneration possibilities of the exhausted titanate bed were investigated.

II. EXPERIMENTAL

Modification of surface acidic properties

To modify the surface acidic properties of titanate nanostructures their ion exchange abilities were exploited. Protonated nanowires were produced by the ion-exchange reaction of Na-form TiONW and 200 mL 0.1 M HCl solution. After 24 hours of vigorous stirring the solid phase was separated and was washed with distilled water by centrifugation several times. After the washing procedure the nanowires were dried at 60 °C in air.

The ion-exchange method was used to prepare protonated, La, Fe, Co and Cu containing titanate nanotubes from Na-form TiONT. For the metal ion containing samples, Na-form TiONT was added to 200 mL 0.1 M solution of the metal salts, while the protonated sample was prepared by using 200 mL 0.1 M HCl solution. After 24 hours of vigorous stirring the solid phase was separated and washed with distilled water by centrifugation several times. After the washing procedure the nanotubes were dried at 60 °C in air.

The as-prepared structures were examined by transmission electron microscopy (TEM), Energy disperse X-ray spectroscopy (EDS), Raman spectroscopy, *in situ* pyridine adsorption FT-IR spectroscopy, X-ray powder diffractometry (XRD) and nitrogen adsorption surface analysis.

Preparation of Rh/TiONT and Rh/TiONW nanocomposites

1.0 and 2.5 wt% Rh containing TiONT and TiONW were prepared by wet impregnation using RhCl₃ solution and protonated titanate nanostructures. The impregnated samples were dried at 90 °C in air and between 200-300 °C under H₂ atmosphere. Impregnated titanate samples were heat treated for one hour at different temperatures between 200-600 °C, by applying 100 °C heating steps. Samples were collected in every thermal step for further characterization.

The as-prepared samples were investigated by TEM, XRD and Raman spectroscopy techniques.

Vapor phase deposition of Co on TiONW

Co-decorated TiONW with 2 and 4 wt% Co content were prepared by the reaction of protonated TiONW and vapor phase Co-carbonyl (Co₂(CO)₈). The reactions were carried out in a self-designed and built fluidized bed reactor. The reactor consisted of two separated,

vertically placed chambers with individual temperature controls. The Co precursor was put into the lower chamber in which the temperature was set to 40 °C, while the TiONW bed was put into the upper one where the temperature was set to 45 °C to avoid the vapor phase condensation of sublimate ($\text{Co}_2(\text{CO})_8$). CO was used as carrier gas to avoid carbonyl decomposition.

After the carbonylation phase the as-prepared structures were treated at 330 °C in N_2 atmosphere to promote the thermal decomposition of adsorbed Co-carbonyl. The treated samples were transported to an X-ray photoelectron spectroscopic sample chamber for further treatment in H_2 and O_2 atmosphere at 330 °C.

The samples were characterized by TEM, EDS, XRD, diffuse reflectance FT-IR spectroscopy (DRIFTS), diffuse reflectance UV-Vis spectroscopy, temperature programmed reaction spectroscopy and mass spectroscopy techniques.

Water softening

The determination of ion-exchange capacity

The water softening ability of titanate nanotubes was investigated in a continuous flow fixed bed apparatus. The ion exchange bed contained 12 g of Na-form TiONTs. Artificial hard water with a total hardness of $\sim 60 \text{ GH}^\circ$ (0.01 M) and $\text{Ca}^{2+}:\text{Mg}^{2+}$ ion ratio of 1:1 was pumped through the reactor with a feeding rate of 1.6 L h^{-1} . For monitoring the ion exchange process, samples were collected in every 20 minutes. The hard ion concentration of the samples was determined by chelatometric titration. DOWEX 50W was used as reference material.

The kinetics of ion-adsorption

3-3 g of Na-form TiONTs were suspended in 600 mL of $\sim 60 \text{ GH}^\circ$ hard water as well as in 600-600 mL of Ca^{2+} and Mg^{2+} containing solution under vigorous stirring. The mixtures were sampled at regular intervals during the course of the 164 h long experiments. The TiONTs were separated from the solutions by centrifugation and the liquid phases were analyzed for Ca^{2+} and Mg^{2+} by chelatometric titration.

The TiONT samples were examined by EDS and XRD techniques.

III. NOVEL SCIENTIFIC RESULTS

T1. A method was developed for the modification of surface acidic properties of 1D titanate nanostructures

T1.1 By exploiting the ion exchange ability of titanate nanostructures we were able to modify the surface acidic properties of titanate nanostructures, which was examined by in situ pyridine adsorption FTIR spectroscopy. Metal cation intercalation was monitored by Raman spectroscopy and EDS measurements.

T1.2 We found that pristine nanotubes and nanowires possess only weak Lewis acidic sites on their surface, while the protonation of the nanostructures introduced Brönsted acidity. Lanthanum and transition metal ion exchanged samples featured stronger Lewis and Brönsted acidic sites compared to their pristine counterparts.

T2. We demonstrated that nanosized Rh clusters can be prepared by simple wet impregnation on the surface of titanate nanotubes and nanowires, furthermore it was observed that the presence of Rh in the titanate structure facilitates different phase transition pathways in nanotubes and nanowires during annealing.

T2.1 Heat treatment was applied to Rh decorated and protonated titanate nanotubes and nanowires. We concluded that in the case of nanotubes the Rh content enhanced the titanate-anatase recrystallization process, whereas in the case of nanowires the Rh content promoted the formation of β -TiO₂ phase during the heat treatment process.

T2.2 Heat treatment of previously impregnated samples in reductive atmosphere lead to the formation of nanosized Rh particles on the surface of the titanate nanostructures. The average Rh particle diameter was 1.9 ± 1.4 and 2.8 ± 0.7 nm in the case of nanowires and nanotubes, respectively.

T3. Co-loaded titanate nanowires were prepared by the vapor deposition of cobalt-carbonyl

T3.1 Cobalt-carbonyl was successfully deposited on the surface of titanate nanowires at low temperature. The success of the deposition was confirmed by DRIFTS measurements.

T3.2. MS measurement, during the thermal decomposition of deposited cobalt-carbonyl, indicated the formation of CO₂ gas. The evolution of CO₂ was interpreted as

the sign of oxygen vacancy formation in the titanate support caused by the reaction of framework oxygen and the CO ligand of the cobalt-carbonyl.

T3.3. Depending on the metal loading, after the decomposition of $\text{Co}_2(\text{CO})_8$, Co was stabilized on the nanowires in Co^{2+} form by ion exchange at 2 w% Co content. This sample showed a significant decrease in the band gap energy. At higher metal loading (4 w%) the band gap did not change significantly, however, the formation of Co nanoclusters attached to the generated O vacancies was observed.

T4. The ion exchange ability of titanate nanostructures was utilized for water softening process.

T4.1. The ion exchange capacity of titanate nanotubes in water softening process was determined to be 1.2 mmol g^{-1} .

T4.2. We demonstrated that there are two types of ion exchange positions in the titanate nanotube framework. These sites are distinguishable on the basis of their ion exchange kinetics. Cations can be rapidly adsorbed on the inner and outer surface and on the tips of the tubes, whereas ion exchange is significantly slower at sites located between the layers.

T4.3. It was also shown that the adsorption of Ca^{2+} ions is preferred over Mg^{2+} ions in titanate nanostructures. Furthermore, while the ion exchange of Mg^{2+} is reversible, there is a limitation to the recoverability of Ca^{2+} ion exchange capacity.

IV. PUBLICATIONS RELATED TO THE THESIS

1. **Madarász, D.**; Szenti, I.; Nagy, L.; Sápi, A.; Kukovecz, Á.; Kónya, Z.
Fine tuning the surface acidity of titanate nanostructures
Adsorption - Journal of the International Adsorption Society (2013), **19**: 695-700 (IF: 2,074)
2. Pótári, G.; **Madarász, D.**; Nagy, L.; László, B.; Sápi, A.; Oszkó, A.; Kukovecz, Á.; Erdőhelyi, A.; Kónya, Z.; Kiss, J.
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3. **Madarász, D.**; Pótári, G.; Sápi, A.; László, B.; Csudai, Cs.; Oszkó, A.; Kukovecz, Á.; Erdőhelyi, A.; Kónya, Z.; Kiss, J.
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4. **Madarász, D.**; Szenti, I.; Sápi, A.; Halász, J.; Kukovecz, Á.; Kónya, Z.
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V. OTHER PUBLICATIONS

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Fabrication of SiC-Particles-Shielded Al Spheres upon Recycling Al/SiC Composites
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(2011), **42**: 1439-1443

2. Győri, Z.; Havasi, V.; **Madarász, D.**; Tátrai, D.; Brigancz, T.; Szabó, G.; Kónya, Z.;
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Luminescence properties of Ho³⁺ co-doped SrAl₂O₄:Eu²⁺, Dy³⁺ long-persistent phosphors synthesized with a solid-state method.
Journal of Molecular Structure (2013), **1044**: 87-93

3. Malikov, E.Y.; Muradov, M.B.; Akperov, O.H.; Eyvazova, G.M.; Puskás, R.;
Madarász, D.; Nagy, L.; Kukovecz, Á.; Kónya, Z.

Synthesis and characterization of polyvinyl alcohol based multiwalled carbon nanotube nanocomposites
Physica E-Low-Dimensional Systems & Nanostructures (2014), **61**: 129-134

4. Altay, M. C.; Malikov, E. Y.; Eyvazova, G. M., Muradov, M. B.; Akperov, O. H.;
Puskás, R.; **Madarász, D.**; Kónya, Z.; Kukovecz, Á.;

Facile synthesis of CuS nanoparticles deposited on polymer nanocomposite foam and their effects on microstructural and optical properties
European Polymer Journal (2015), **68**: 47-56

5. De Luca, P.; Poulsen, T.G.; Salituro, A.; Tedeschi, A.; Vuono, D.; Kónya, Z.;
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Journal of Thermal Analysis and Calorimetry (2015) **122**: 1257-1267

6. Malikov, E.Y.; Altay, M.C.; Muradov, M.B.; Akperov, O.H.; Eyvazova, G.M.; Puskás, R.; **Madarász, D.**; Kukovecz, Á.; Kónya, Z.
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7. Anojčić, J.; Guzsvány, V.; Vajdle, O.; **Madarász, D.**; Rónavári, A.; Kónya, Z.; Kalcher, K.
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8. Kovács, D.; Igaz, N.; Keskeny, Cs.; Bélteky, P.; Tóth, T.; Gáspár, R.; **Madarász, D.**; Rázga, Zs.; Kónya, Z.; M Boros, I.; Kiricsi, M.
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Scientific Reports (2016), **6**: 27902 1-13
9. Kovács, D.; Szőke, K.; Igaz, N.; Spengler, G.; Molnár, J.; Tóth, T.; **Madarász, D.**; Rázga, Zs.; Kónya, Z.; Boros, I.; Kiricsi, M.
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Chemical Engineering & Technology (2017) **40**: 1323-1331
13. Budai, D.; Vízvári A.D.; Bali, Zs.,K.; Márki, B.; Nagy, L.V.; Kónya, Z.; **Madarász, D.**; Henn-Mike, N.; Varga, Cs.; Hernádi, I.
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PLoS ONE (2018), **13**: e0193836.

VI. PRESENTATIONS, POSTERS, ATTENDING CONFERENCES

In English

1. **Madarász, D.**; Sápi, A.; Kukovecz, Á.; Kónya, Z.
Investigating the properties of ion-exchanged titanate nanowires
NAPEP, Nanotechnology Platform for Electronics and Photonics
22-28 May 2011, Oulu, Finland
2. Sápi, A.; Nagy, L.; **Madarász, D.**; Kukovecz, Á.; Kónya, Z.
Environmental application of titanate nanostructures,
14th DKMT Euroregional Conference on Environment and Health,
18-19 May 2012, Szeged, Krakow
3. **Madarász, D.**; Szenti, I.; Sápi, A.; Kukovecz, Á.; Kónya, Z.
Fine tuning of titanate nanostructures' surface acidic sites,
ISSHAC VIII, Eighth International Symposium - Effects of Surface Heterogeneity in
Adsorption and Catalysis on Solids
27-31 August 2012, Krakow, Poland
4. Kiss, J.; **Madarász, D.**; Pótari, G.; László, B.; Sapi, A.; Nagy, L.; Oszkó, A.; Kónya,
Z.; Erdőhelyi, A.
*Structure and stability of clean and Au-Rh containing titanate nanowires and
nanotubes*
CMD-24 (ECOSS-29, CMMP-12, ECSCD-11)
3-7 September 2012, Edinburgh, UK
5. **Madarász, D.**; Kukovecz, Á.; Kónya, Z.
Surface acidity and its modification on titanate nanostructures
NAPEP, Nanotechnology Platform for Electronics and Photonics
21-23 March 2013, Szeged, Hungary

6. Varga, E.; Baán, K.; Erdőhelyi, A.; **Madarász, D.**; Kukovecz, Á.; Oszkó, A.; Kónya, Z.; Kiss, J.

Interaction of rhodium with ceria supported cobalt nanoclusters

The Seventh Edition of the Symposium with International Participation - New Trends and Strategies in the Chemistry of Advanced Materials with Relevance in Biological Systems, Technique and Environmental Protection

5-6 June 2014, Temesvár, Romania

In Hungarian

1. **Madarász, D.**; Budai, I.; Mekler, Cs.; Kaptay, G.

Separation of Al/SiC composites

MicroCAD - International Scientific Conference

18-20 March 2010, Miskolc, Hungary

2. **Madarász, D.**; Kukovecz, Á.; Sápi, A.; Kónya, Z.

Investigating the properties of ion-exchanged titanate nanostructures

Hungarian Microscopy Conference - HSM Annual Meeting,

19-21 May 2011, Siófok, Hungary

3. **Madarász, D.**; Szenti, I.; Sápi, A.; Kukovecz, Á.; Kónya, Z.

Fine tuning of titanate nanostructures' surface acidic sites,

Hungarian Microscopy Conference - HSM Annual Meeting,

12-14 May 2012, Siófok, Hungary

4. **Madarász, D.**; Kukovecz, Á.; Kónya, Z.

Modification of surface acidity of titanate nanotubes with transition-metal ions

Hungarian Microscopy Conference - HSM Annual Meeting,

29-31 May 2014, Siófok, Hungary

Posters

1. Mekler, Cs.; **Madarász, D.**; Kaptay, G.; Budai, I.

Surface phase transition and Marangoni convection in the Fe-O system

VII. Hungarian conference on material science

11-13 October 2009, Balatonkenese, Hungary

2. **Madarász, D.**; Szenti, I.; Kukovecz, Á.; Kónya, Z.
Modification of acidic sites on the surface of titanate nanostructures
SIWAN5, Szeged International Workshop on Advances in Nanoscience,
24-27 October 2012, Szeged, Hungary

3. Győri, Z.; Havasi, V.; Pusztai, P.; **Madarász, D.**; Kukovecz, Á.; Kónya, Z.
The influence of different co-activators on the photoluminescence properties of SrAl₂O₄ phosphors
SIWAN5, Szeged International Workshop on Advances in Nanoscience,
24-27 October 2012, Szeged, Hungary

4. Malikov, E.; Akperov, O.; Muradov, M.; Kukovecz, Á.; Puskás, R.; **Madarász, D.**
In situ synthesis of Maleic anhydride – Octene 1 – Vinyl Butyl/CdS and Maleic anhydride – Octene 1 – Vinyl Butyl/ZnS nanocomposites and their characterization with several investigation methods
SIWAN5, Szeged International Workshop on Advances in Nanoscience,
24-27 October 2012, Szeged, Hungary

5. Varga, E.; Baán, K.; Erdőhelyi, A.; **Madarász, D.**; Kukovecz, Á.; Oszkó, A.; Kónya, Z.; Kiss, J.
Interaction of rhodium with cobalt nanoclusters on CeO₂
15th Joint Vacuum Conference
15-20 June 2014, Wien, Austria

VII. SCIENTOMETRIC DATA

Peer-reviewed papers total: 18

out of this, related to the topic of this thesis: 5

Cumulative impact factor: 50.2

out of this, related to the topic of this thesis: 11.8

Independent cites total: 73

out of this, related to the topic of this thesis: 31