PREPARATION OF CERIUM PHOSPHATE NANOPARTICLES AND CHARACTERIZATION OF THEIR STRUCTURE DEPENDENT PROPERTIES

Ph.D. thesis

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1. Introduction

The emergence of nanotechnology dates back to the 20th century. Since then, it revolutionized electronics, energetics, chemical industry, medicine, water- and waste treatment. Several promising laboratory and industrial scale achievements have already been accomplished by using nanotechnology. For the widespread application of nanomaterials the development of large scale, reproducible and efficient synthesis methods is of paramount importance.

One dimensional (1D) nanomaterials have been investigated for more than two decades, however, increasing attention has been focused recently on the examination of three dimensional (3D) nano- and microstructures as well. 3D architectures gained scientific interest due to their toxicity being lower than that of small nanoparticles, and their superior performance in many applications as compared to their nanosized and bulk counterparts. For the preparation of 3D nano- and microparticles time-, and energy consuming methods have been suggested in the literature using surfactants, structure directing or capping agents to control the morphology of the product.

The Department of Applied and Environmental Chemistry has a long history with 1D nanomaterials. When I started my work with 1D and 3D cerium phosphate nanomaterials I joined this stream of research of the Department. During my doctoral studies our goals were (i) to develop cost-, time-, and energy-efficient methods for the preparation of cerium phosphate nanostructures, (ii) to investigate their formation mechanism, and (iii) to examine their structure dependent physical properties. In order to deepen our understanding of cerium phosphate architectures the following particular topics were investigated:

1. Hydrothermal synthesis of cerium phosphate nanowires. The examination of the nanowires' recrystallyzation and growth process by Raman spectroscopy, nitrogen adsorption-desorption measurement, thermogravimetry and high-resolution transmission electron microscopy.
2. Cost efficient synthesis of hexagonal cerium phosphate nanowires and nanourchins. Studies on the terbium doping of these nanostructures. Investigation on how the different reaction parameters affect product morphology. The elucidation of the growth mechanisms. The examination of structure-dependent photoluminescence properties.

3. Room temperature synthesis of cerium phosphate spherulites using a flow reaction system. Studies on the terbium doping of these nanostructures. Uncovering how reaction parameters affect the product morphology and the development mechanisms. Elucidation of the growth mechanisms. The examination of structure-dependent photoluminescence properties.
4. The investigation of the thermal stability of hexagonal and monoclinic nanowires.
5. The examination of the room temperature proton conduction properties of hexagonal and monoclinic nanowires under different relative humidity conditions. Studying how the crystal structure and the surface chemical properties of the nanowires can influence their proton conductivity.

2. Experimental

For the preparation of monoclinic cerium phosphate nanowires 60 mL of 0.033 M cerium nitrate hexahydrate and 20 mL of 0.2 M phosphoric acid stock solutions were prepared. Phosphoric acid was poured into the cerium nitrate solution under vigorous stirring. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and put into an electric oven to 200 °C for 4 h. The product was washed with distilled water and ethanol several times by using a centrifuge.

For the preparation of hexagonal cerium phosphate nanourchins the 20 mL, 0.2 M phosphoric acid was poured into the 60 mL, 0.033 M cerium nitrate solution under vigorous stirring. For the preparation of hexagonal nanowires the phosphoric acid was added dropwise (10 seconds/drop) instead of one portion to the cerium nitrate solution. For terbium doped samples an appropriate amount of terbium nitrate was added to the cerium nitrate solution ensuring $[Ce^{3+}]$:$[Tb^{3+}]$ = 9:1 molar ratio.

For the preparation of cerium phosphate spherulites in a flow reaction system a square shaped glass vessel with 14 cm long sides and an inlet hole at the bottom was used. For a typical synthesis 2.3 mL of the precursor solution (a) was pumped (7 mL/h) into 60 mL of precursor solution (b) previously poured into the glass vessel. Pictures were taken from the growing precipitate disc at 3 seconds intervals. In order to investigate the structure dependent photoluminescence properties of the spherulites an appropriate amount of terbium was doped into their structure, ensuring $[Ce^{3+}]$:$[Tb^{3+}]$ = 9:1 molar ratio.

Phase transition of the samples was examined by X-ray diffractometry, Raman, and infrared spectroscopy. [Ce^{3+}]:[Tb^{3+}] molar ratio, and potential impurities in the samples were determined by energy dispersive X-ray spectroscopy. The morphology and the nanoscopic features of the particles were investigated by transmission and scanning electron microscopy. The structural stability of the samples was monitored by thermogravimetric measurements. The pore structure and the specific surface area of the particles were examined by nitrogen and water vapor adsorption-desorption methods. The protonation/deprotonation properties of the samples were investigated by potentiometric titration, the amount of surface acidic centers were determined by temperature programmed ammonia desorption. The relative humidity dependent proton conduction properties of the nanowires were examined by impedance spectroscopy and isothermal transient ionic current method. The photoluminescence properties of the samples were investigated by fluorimetry.

3. New scientific results

1. Investigation of the growth properties of monoclinic cerium phosphate nanowires under hydrothermal conditions.

1.1 A simple, fast hydrothermal synthesis was developed for the preparation of monoclinic cerium phosphate nanowires by the optimization of previous methods published in the literature. The average diameter of the nanowires was 15.7 ± 7 nm with an aspect ratio of 40–60.

1.2 The morphological and structural evolution of the nanowires was examined by HRTEM, Raman spectroscopy, nitrogen adsorption-desorption and thermogravimetric measurements. The development of monoclinic nanowires commenced from hexagonal urchin-like nanostructures obtained by the admixture of the precursor solutions. Under hydrothermal conditions the nanourchins broke up into nanorods from which micrometer long nanowires developed by the so-called dissolution/recrystallization process in 3–4 hours.

1.3 A Raman spectroscopic study revealed monoclinic P–O vibrations in the spectrum of the hydrothermally treated sample for 1 h. Hexagonal P–O bands entirely disappeared from the Raman spectrum of the sample treated hydrothermally for 2 h, though TG measurement still showed 0.5 % structural water indicating the incomplete recrystallization of the nanowires. According to Raman spectroscopic and TG

measurements 3–4 h was necessary for the complete recrystallization of the nanowires. Until 1 h the average diameter and specific surface area values of the nanowires changed markedly. Afterwards the specific surface area values of 2–4 h samples slightly decreased, while the average diameters fluctuated around ~15 nm. The standard deviation values of average diameters increased steeply until 2 h. Afterwards they started to decrease. These findings could be explained on the basis of the HRTEM study of the hydrothermally treated sample for 1 h, in which the coalescence of the nanowires along the (100) facets was observed. At the early stage of particle growth two simultaneous thickening mechanisms took place. The nanowires thickened by the traditional layer-by-layer fashion and also by the coalescence of adjacent nanowires along the (100) facet, implying the marked increase of standard deviation. With increasing synthesis time more coalescence occurred, hence the standard deviations decreased.

2. Ambient temperature preparation, terbium doping and structural stability test of hexagonal cerium phosphate nanowires and nanourchins.

2.1 A simple ambient temperature synthesis was developed for the preparation of hexagonal cerium phosphate nanourchins. The average diameter of the urchins and the constituting nanorods were 373 ± 39 nm and 5.6 ± 1.7 nm, respectively.

2.2 Micrometer long hexagonal cerium phosphate nanowires were prepared with an average diameter of 9.8 ± 4.0 nm by the dropwise addition of the phosphate precursor. The nanowires tended to form bundles with an aspect ratio of 40–60.

2.3 The growth process of the nanowires was examined by time monitored synthesis. This approach could not be applied in the case of nanourchins due to their instantaneous formation, hence the core of an opened up nanourchin was examined by HRTEM, searching for structural features related to their growth mechanism. For the formation of nanowires and nanourchins a modified dissolution/recrystallization process and the seeding and radiating mechanism was proposed, respectively. The influence of $[Ce^{3+}]$:$[PO_4^{3-}]$ molar ratio, precursor addition rate and order on the product morphology was also investigated. It was found that only the precursor addition rate affected significantly the fundamental morphology (nanourchin or nanowire) of the nanostructures.

2.4 Recrystallization of hexagonal nanowires was investigated by a thermal stability test. Structural characteristics of the calcined samples were examined by XRD, Raman and IR spectroscopy, nitrogen adsorption-desorption and HRTEM. Nanowires could keep their morphology up to 800 °C, while at 1000 °C the wire-like structure collapsed and amorphous particles were formed. In contrast to morphology, the crystal structure of the nanowires started to rearrange at a much lower temperature (400–600 °C). It was also demonstrated that spectroscopic techniques can indicate much smaller changes in the crystal structure than X-ray diffractometry which showed pure hexagonal phase for the sample calcined at 400 °C.

2.5 Terbium doped nanourchins and nanowires were prepared by the methods presented here, then their thermal stability and structure dependent photoluminescence properties were examined. 10 % terbium increased significantly the stability of the nanostructures. Pure nanowires entirely recrystallized into monoclinic phase at 600 °C in 1 h, while the terbium doped samples had to be calcined for 8 h at 600 °C for the complete phase transition. As-prepared nanowires had 13–22 % higher luminescence intensity (depending on wavelength) than their nanourchin counterparts, which can be explained by the higher structural water content of nanourchins (2.6 % for nanourchins and 1.8 % for nanowires), since structural water can effectively quench Tb^{3+} emission. In the case of calcined samples nanourchins had 19–25 % higher luminescence intensity than their nanowire counterparts. Luminescence intensity was much higher for the as-prepared samples than for the heat-treated ones (by approx. ×6 for nanourchins and ×9 for nanowires). This difference can be explained by the partial oxidation of Ce^{3+} to Ce^{4+}, which can effectively quench Tb^{3+} emission.

3. Investigation of the formation and terbium doping of hexagonal cerium phosphate spherulites in flow reaction system.

3.1 Cerium phosphate spherulites were prepared at ambient temperature without the use of structure directing agents.

3.2 It was found that the pumping order of the precursor solutions played a significant role in determining the growth mechanism of the spherulites. When phosphoric acid was pumped into the cerium nitrate solution, 1.6 ± 0.4 μm sized spherulites were formed, while reverse pumping order promoted the formation of 2.6 ± 0.3 μm size spherulites. The origin of the spectacular structural differences between the spherulites was

investigated by HRTEM. According to our HRTEM study the spherulites in the first case were developed by the seeding and radiating process, while their counterparts were formed by crystal splitting. The different growth mechanisms of the spherulites implied the development of different structural features.

3.3 Spherulites developed by seeding and radiating process exhibited 30–35 % higher photoluminescence intensity than their counterparts formed by crystal splitting. This difference can be attributed to the formation of crystal defects during the crystal splitting process, which can effectively quench the particles' luminescence intensity.

4. Examination of structure dependent proton conduction properties of hexagonal and monoclinic cerium phosphate nanowires

4.1 Ambient temperature proton conduction properties of hexagonal and monoclinic cerium phosphate nanowires were examined for the first time.

4.2 The structural and surface chemical properties of the nanowires were investigated by XRD, nitrogen and water vapor adsorption-desorption, potentiometric titration and temperature programmed ammonia desorption techniques. The net proton (0.074 mmol/g), and ammonia consumptions (0.58 mmol/g) for hexagonal nanowires were ~2.3 times higher than for monoclinic nanowires (0.034 mmol/g and 0,25 mmol/g, respectively). After the normalization to specific surface areas (143.5 m^2/g for hexagonal, and 62.0 m^2/g for monoclinic) identical values were obtained, indicating a crystal structure independent surface acidic center density for both nanowires.

4.3 Ambient temperature proton conductivity was measured by IS and ITIC methods under different relative humidity conditions. When conductivity was plotted against relative humidity hexagonal nanowires showed 1.5 times higher conductivity than their monoclinic counterparts, especially at low RH%. With increasing relative humidity, the difference between the nanowires decreased, then entirely disappeared at 100 RH%. An opposite tendency was observed when conductivity was plotted against the adsorbed amount of water. In this case, monoclinic nanowires exhibited ~2.5 times higher conductivity than hexagonal ones, especially at low adsorbed amounts. After conductivity was normalized to the number density of surface acidic centers, and the adsorbed amount of water was normalized to the specific surface area of the nanowires, the originally distinct curves collapsed into a master curve. Relaxation

times plotted against adsorbed amount of water showed similar characteristics than the conductivity vs. adsorbed amount of water plot. The identical dependence of relaxation times on conductivity implies a common origin of conduction, and their interdependency suggests that we simply observe the same process from different perspectives. These results indicated a crystal structure independent conduction mechanism in cerium phosphate nanowires.

4. Papers related to the present thesis

1. Structural stability test of hexagonal $CePO_4$ nanowires synthesized at ambient temperature

P. Pusztai, T. Simon, Á. Kukovecz, Z. Kónya

Journal of Molecular Structure, 2013, 1044 (24), 94–98

IF_{2013}: 1,599

2. Green synthesis of biomimetic $CePO_4$:Tb nanostructures using the simplest morphology control

P. Pusztai, Á. Kukovecz, Z. Kónya

RSC Advances, 2014, 4 (91), 49879–49887

IF_{2014}: 3,840

3. Structure-independent proton transport in cerium(III) phosphate nanowires

P. Pusztai, H. Haspel, I. Y. Tóth, E. Tombácz, K. László, Á. Kukovecz, Z. Kónya

ACS Applied Materials & Interfaces, 2015, 7 (18), 9947–9956

IF_{2014}: 6,723

4. A simple method to control the formation of cerium phosphate architectures

P. Pusztai, E. Tóth-Szeles, D. Horváth, Á. Tóth, Á. Kukovecz, Z. Kónya

CrystEngComm, 2015, 17 (44), 8477–8485

IF_{2014}: 4,034

5. Presentations, posters, attending conferences

1. Synthesis and characterization of one-dimensional cerium phosphate nanostructures

P. Pusztai, Á. Kukovecz, Z. Kónya

The Ninth Students' Meeting, Újvidék, 2011, presentation

2. Characterization of one-dimensional cerium phosphate nanostructures prepared by rapid hydrothermal and sonochemical method

P. Pusztai, Á. Kukovecz, Z. Kónya

10th Multinational Congress on Microscopy, Urbino, 2011, presentation

3. Synthesis and characterization of cerium and silver based one-dimensional nanostructures

P. Pusztai, Á. Kukovecz, Z. Kónya

NAPEP meeting, Baku, 2011, presentation

4. Synthesis and characterization of one-dimensional nanostructures

P. Pusztai Á. Kukovecz, Z. Kónya

Magyar Mikroszkópos Társaság, Siófok, 2011, presentation

5. Nervous system and general toxic effects in rats after subacute intratracheal application of nanosized lead oxide

G. Oszlánczi, E. Horváth, A. Szabó, A. Papp, **P. Pusztai**, M. Szabó, G. Kozma, A. Sápi, Z. Kónya, T. Vezér

Neuroforum 2011, 17 (1), T11-11B, 1 p., abstract

6. A különböző méretű MnO2 nanorészecskék hatására kialakuló pulmonáris morfológiai elváltozások

E. Horváth, G. Oszlánczi, A. Sápi, **P. Pusztai**, P. Ragó

Egészségtudomány 2011, 55 (2) 123-124, abstract

7. Komplex környezeti kadmium expozíció idegrendszeri hatásainak modellezése patkányban

E. Horváth, Zs. Máté, A. Lukács, A. Szabó, **P. Pusztai**, A. Sápi

Egészségtudomány 2012, 2 123-124, abstract

8. Az oldott és nanopartikuláris állapotú mangán neurotoxikológiai hatásai patkány modellben

E. Horváth, Zs. Máté, Sz. Takács, A. Szabó, A. Sápi, **P. Pusztai**, Z. Kónya, A. Papp

A Magyar Élettani Társaság, a Magyar Anatómusok Társasága, a Magyar Biofizikai Társaság és a Magyar Mikrocirkulációs és Vaszkuláris Biológiai Társaság Kongresszusa, Debrecen, 2012, abstract

9. General toxicity, neurotoxicity, and the corresponding metal levels in rats treated with nanoparticulate and dissolved mangenese

E. Horváth, Zs. Máté, Sz. Takács, A. Szabó, A. Sápi, **P. Pusztai**, Z. Kónya, A. Papp

SIWAN5, Szeged, 2012, poster

10. Nervous system effects of a modelled complex environmental cadmium exposure in rats

E. Horváth, Zs. Máté, A. Lukács, A. Szabó, **P. Pusztai**, A. Sápi, Z. Kónya, A. Papp

14th DKMT Euroregional Conference on Environment and Health, Szeged, 2012, poster

11. Structural stability test of cerium phosphate nanowires for a potential application in solid oxide fuel cells

P. Pusztai, T. Simon, Á. Kukovecz, Z. Kónya

EUCMOS, Kolozsvár, 2012, presentation

12. Thermal stability test of one-dimensional $CePO_4$ nanostructures for a potential solid oxide fuel cell application

P. Pusztai, T. Simon, Á. Kukovecz, Z. Kónya

SIWAN5, Szeged, 2012, poster

13. **The influence of synthesis methods, different dopant ions and ratios on the luminescence of $SrAl_2O_4$ nanoparticles**
Z. Győri, V. Havasi, **P. Pusztai**, D. Madarász, Á. Kukovecz, Z. Kónya
EUCMOS, Kolozsvár, 2012, presentation

14. **General toxicity, neurotoxicity and the corresponding metal levels in rats treated with nanoparticulated and dissolved manganese**
E. Horváth, Z. Máté, S. Takács, A. Szabó, A. Sápi, **P. Pusztai**, Z. Kónya, A. Papp
SIWAN5, Szeged, 2012, poster

15. **The influence of different CO-activators on the photoluminescence properties of $SrAl_2O_4$ phosphors**
Z. Győri, V. Havasi, **P. Pusztai**, D. Madarász, Á. Kukovecz, Z. Kónya
SIWAN5, Szeged, 2012, poster

16. **Controlled synthesis of copper nanocrystals with various shapes**
M. Mohl, D. Dobó, **P. Pusztai**, Á. Dombovári, Á. Kukovecz, Z. Kónya, K. Kordás
The Annual Meeting of the NGS-NANO, Turku, 2012, poster

17. **Thermal stability of cerium phosphate nanowires: A spectroscopic study**
P. Pusztai, Á. Kukovecz, Z. Kónya
Tavaszi Szél konferencia, Sopron, 2013, presentation

18. **Humidity dependent conduction properties of hexagonal and monoclinic $CePO_4$ nanowires**
P. Pusztai, H. Haspel, V. Bugris, Á. Kukovecz, Z. Kónya
International research and practice conference NANOTECHNOLOGY and NANOMATERIALS, Bukovel, 2013, presentation

19. Humidity dependent conduction properties of hexagonal and monoclinic $CePO_4$ nanowires

P. Pusztai, H. Haspel, V. Bugris, Á. Kukovecz, Z. Kónya

International research and practice conference, 2nd International Summer School for young scientists "NANOTECHNOLOGY: from fundamental research to innovations, Bukovel, 2013, poster

20. Adsorbed water induced electrical conduction properties of hexagonal and monoclinic $CePO_4$ nanowires

P. Pusztai, H. Haspel, Á. Kukovecz, Z. Kónya

Magyar Mikroszkópos Társaság, Siófok, 2014, presentation

21. Formation and characterization of gold nanoparticles on titanate nanotubes and nanowires

P. Pusztai, R. Puskás, L. Nagy, E. Varga, A. Erdőhelyi, Á. Kukovecz, Z. Kónya, J. Kiss

JVC, Bécs, 2014, presentation

6. Other publication

1. Low-Temperature large-scale synthesis and electrical testing of ultralong copper nanowires

M. Mohl, **P. Pusztai**, Á. Kukovecz, Z. Kónya, J. Kukkola, K. Kordas, R. Vajtai, P.M. Ajayan

Langmuir 2010, 26 (21), 16496–16502

IF_{2010}: 4,268

2. Repeated simultaneous cortical electrophysiological and behavioral recording in rats exposed to manganese-containing nanoparticles

Sz. Takács, A. Szabó, G. Oszlánczi, **P. Pusztai**, A. Sápi, Z. Kónya, A. Papp

Acta Biologica Hungarica 2012, 63 (4), 426–440

IF_{2012}: 0,504

3. **General and electrophysiological toxic effects of manganese in rats following subacute administration in dissolved and nanoparticle form**

E. Horváth, Zs. Máté, Sz. Takács, **P. Pusztai**, A. Sápi, Z. Kónya, L. Nagymajtényi, A. Papp

The Scientific World Journal 2012, Paper Article ID 520632, 7 p.

IF_{2012}: 1,730

4. **Synthesis and characterization of WO_3 nanowires and metal nanoparticle-WO_3 nanowire composites**

M. Szabó, **P. Pusztai**, A-R. Leino, K. Kordás, Z. Kónya, Á. Kukovecz

Journal of Molecular Structure 2013, 1044 (24), 99–103

IF_{2013}: 1,599

5. **Photocatalytic decomposition of formic acid and methyl formate on TiO_2 doped with N and promoted with Au. Production of H_2.**

A. Gazsi, G. Schubert, **P. Pusztai**, F. Solymosi

International Journal of Hydrogen Energy 2013, 38 (19), 7756–7766

IF_{2013}: 2,930

6. **Influence of gold additive on the stability and phase transformation of titanate nanostructures**

P. Pusztai, R. Puskás, E. Varga, A. Erdőhelyi, Á. Kukovecz, Z. Kónya, J. Kiss

Physical Chemistry Chemical Physics 2014, 16 (48), 26786–26797

IF_{2014}: 4,493

7. **Photocatalytic H_2 evolution using different commercial TiO_2 catalysts deposited with finely size-tailored Au nanoparticles: Critical dependence on Au particle Size**

Á. Kmetykó, K. Mogyorósi, **P. Pusztai**, T. Radu, Z. Kónya, A. Dombi, K. Hernadi

Materials 2014, 7 (12), 7615–7633

IF_{2014}: 2,651

8. **Photocatalytic H_2 production using Pt-TiO_2 in the presence of oxalic acid: Influence of the noble metal size and the carrier gas flow rate**

Á. Kmetykó, K. Mogyorósi, V. Gerse, Z. Kónya, **P. Pusztai**, A. Dombi, K. Hernadi

Materials 2014, 7 (10), 7022–7038

IF_{2014}: 2,651

9. **Decoration of titanate nanowires and nanotubes by gold nanoparticles: XPS, HRTEM and XRD characterization**

J. Kiss, **P. Pusztai**, L. Óvári, K. Baán, G. Merza, A. Erdőhelyi, Á. Kukovecz, Z. Kónya

e-Journal of Surface Science and Nanotechnology 2014, 12, 252–258

IF: –

10. **Probing the interaction of Rh, Co and bimetallic Rh-Co nanoparticles with the CeO_2 support: catalytic materials for alternative energy generation**

E. Varga, **P. Pusztai**, L. Óvári, A. Oszkó, A. Erdőhelyi, C. Papp, H-P. Steinrück, Z. Kónya, J. Kiss

Physical Chemistry Chemical Physics 2015, 17 (40), 27154–27166

IF_{2014}: 4,493

Peer-reviewed papers total: 14	out of this, related to the topic of this thesis: 4
Cumulative impact factor: 41.515	out of this, related to the topic of this thesis: 16.196
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