

*VŠB – Technical University of Ostrava
Nanotechnology Centre, CEET*

NanoOstrava 2023



8th Nanomaterials and Nanotechnology Meeting

*May 15-18, 2023
Ostrava*

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Book of Abstracts, Programme and General Information
(International conference)

NanoOstrava 2023 – 8th Nanomaterials and Nanotechnology Meeting

Dolní Vítkovice, DOV, Ostrava, Czech Republic

May 15-18, 2023

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Ing. Sylva Holešová, Ph.D.

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Dear Conference participants, Visitors and Colleagues,

We welcome you to the NanoOstrava 2023 - 8th international biennial 'Nanomaterials and Nanotechnology Meeting' in Ostrava, which is the centre of the Moravian-Silesian region and, at the same time, the third largest city in the Czech Republic.

This year's conference will be held in the unique location "**Dolní Vítkovice – DOV**", which is an industrial monument now serving as an educational, social and cultural centre.

The conference is organized under cooperation of scientists from the Nanotechnology Centre, CEET, VŠB - Technical University of Ostrava and Institute of Geonics AS CR.

The meeting will be providing plenty of opportunities for open discussions between scientists, students and company representatives interested in the research and development of nanomaterials and nanotechnology.

The **three scientific sessions dedicated to energy, environment and materials characterization** in nanoscience will be packed with world-renowned scientists and a number of scientists and speakers from industry. The conference supports young scientists and enthusiastic students and helps open doors to scientific careers.

We wish you successful and fruitful conference – and enjoy Ostrava!

Organizing committee of NOM 2023

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Biology Centre, Czech Academy of Sciences, České Budějovice, Czech Republic

Ladies and gentlemen, dear colleagues, dear participants,

It is a great honor to welcome you on behalf of the organizing committee to the 8th biannual NanoOstrava international conference, more precisely for this year NanoOstrava 2023.

This year is all the more significant for us, because after the 7th year, which was organized only online, we are again meeting face to face here in Ostrava. Your participation and your interest are a confirmation for us that the COVID 19 pandemic has not stopped the continuation of this amazing conference and that we can continue to meet, present and share our results, conduct scientific discussions and establish new contacts and cooperation for the future.

This year, the conference is focused on current hot topics in which nanotechnology plays an important role, namely the application of nanotechnology, nanomaterials, nanocomposites and advanced materials in energy and environmental applications. We hope that the prepared scientific program will be interesting and informative for you. Over 100 participants from more than 10 countries around the world will present their work over three days.

The discussion on the main topics of the application of nanotechnology in the field of energy and the environment is very relevant right now here in Ostrava, where projects are starting to enable the region and people to solve the social, economic and ecological impacts of the transformation, which is aimed at achieving the goals of the European Union in the field of energy and climate for 2030 and a climate-neutral Union economy by 2050. Nanotechnology can make a significant contribution to addressing these impacts.

I wish you a pleasant time spent at the NanoOstrava 2023 conference, which takes place in the charming and breathtaking environment of the Dolní Vítkovice region, which demonstrates the historical past of Ostrava connected with heavy

industry. I also wish you the acquisition of new and interesting scientific ideas as well as other inspiration and contacts for your work.



Daniela Plachá

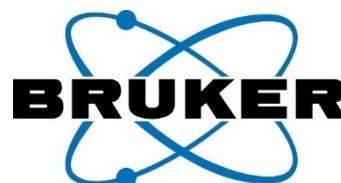
Conference chairman, NanoOstrava2023

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PROGRAMME

NanoOstrava 2023

Monday
15 May, 2023

16:00	18:00	Afternoon registration
16:00	18:00	Welcome party

Tuesday
16 May, 2023

8:00		Morning registration	Hall No. 1					
9:00	9:45	Opening Ceremony	Plachá Daniela Snášel Václav Mišák Stanislav Janovská Kamila Foldyna Josef Bláha Karel					
9:45	10:30	Plenary presentation	Fornasiero Paolo					
10:30	10:45	Coffee Break						
10:45	11:15	T2 (In)	Zbořil Radek					
11:15	11:45	T2 (In)	Jagadeesh Rajenahally					
11:45	12:15	T2 (In)	Mazare Anca					
12:15	13:00	Lunch						
13:00	13:30	T1 (In)	Hall No. 1		13:00	13:30	T2	Hall No. 2
13:30	13:45	T1	Sara Pakseresht Simha Martynková Grażyna		13:30	13:45	T2	Kmentová Hana Grando Gaia
13:45	14:15	T1 (Specion)	Celine Eypert		13:45	14:00	T2	Filip Jan
14:15	14:30	T1	Šindler Matyáš		14:00	14:15	T2 (JEOL)	Brunetti Guillaume
14:30	14:45	Coffee Break					Coffee Break	
14:45	15:00	T1 (In)	Foldyna Martin		14:45	15:00	T1	Tokarčíková Michaela
15:00	15:15	T1	Halagačka Lukáš		15:00	15:15	T1 (Měřicí technika Morava)	Schott Norman
15:15	15:30	T1	Dušenka Adam		15:15	15:30	T1	Castellani Gaia
15:30	15:45	T1 (Thermo Fisher Scientific)	Priece Peter		15:30	15:45	T1	Ingle Avinash
15:45	16:00	T1	Liu Jiaming		15:45	16:00	T1	Férová Marta
16:00	16:15	T1	Mascaretti Luca		16:00	16:15	T1 (Tescan)	Kláštorecký Michal
17:00	19:00	DOV guided tours (for those interested)						

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17 May, 2023**

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8:00					
9:00 9:30	T1 (In)	Rummeli Mark H.	9:00 9:30	T3	Bačáková Lucie
9:30 9:45	T1	Kallio Tanja	9:30 9:45	T3	Malić Marina
9:45 10:00	T1	Matějka Vlastimil	9:45 10:00	T3	Doubková Martina
10:00 10:15	T1 (Měřicí technika Morava)	Horák Jakub	10:00 10:15	T3	Antończyk Agnieszka
10:15 10:30	T1	Kubáň Vít	10:15 10:30	T3 (Carl Zeiss)	Samadi Khoshkhoo Mohsen
10:30 10:45	Coffee Break		10:30 10:45	Coffee Break	
10:45 11:15	T2	Kment Štěpán	10:45 11:15	T3	Nakonieczny Damian
11:15 11:30	T2	Praus Petr	11:15 11:30	T3	Taratuta Anna
11:30 11:45	T2	Pikal Petr	11:30 11:45	T3 (Anamet)	Válek Lukáš
11:45 12:00	T2 (Nicolet)	Šec Karel/Pásztor Ján	11:45 12:00	T3	Havrlant David
12:00 12:15	T2	Vani Sankaralingam Nivitha	12:00 12:15	T3	Černý Šimon
12:15 13:00	Lunch				
13:00 13:30	T3 (In)	Hobza Pavel	13:00 13:30	T1	Bakandritsos Aristeidis
13:30 14:00	T3	Nachtigallová Dana	13:30 13:45	T1	Syrový Michal
14:00 14:15	T3	Tokarský Jonáš	13:45 14:00	T1	Deshmukh Megha
14:15 14:30	T3	Svoboda Ladislav	14:00 14:15	T1 (Anton Paar)	Špringer Jiří
			14:15 14:30	T1	Toběrný Jakub
14:30 14:45	Coffee Break		14:30 14:45	Coffee Break	
14:45 15:15	T2 (In)	Kukutschová Jana	14:45 15:15	T3	Rubáčková Kateřina
15:15 15:30	T2 (LANIK)	Iliushchenko Valeriia	15:15 15:30	T3 (PREVAC)	Miensopust Dominika
15:30 15:45	T2	Sportelli Giuseppe	15:30 15:45	T3	Melchionna Michele
15:45 16:00	T2 (Pragolab)	Kolouchová Anna	15:45 16:00	T3	Krishnamoorthy Baby Monish
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19:00 23:59	Conference dinner				

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9:30 9:45	T3	Henrotte Olivier
9:45 10:00	T3	Smijová Julie
10:00 10:15	T3 (NenoVision)	Komarov Pavel
10:15 10:30	Coffee Break	
10:30 11:00	T1 (In)	Faria Joaquim Luís
11:00 11:15	T1	Ahmad Razi
11:15 11:30	T1	Rej Sourav
11:30 11:45	T1	Raza Waseem
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12:00 13:00	Lunch	

Monday, May 15

16:00-18:00

Registration and Welcome party (DOV, Gong)

Tuesday, May 16

from 8:00

Registration (DOV, Gong)

9:00 - 9:45

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9:45 - 10:30

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(Hall No. 1)

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Invited lecture

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Invited lecture

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Topic 1 – Materials and technology for energy and transportation

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DOV guided tours (for those interested)

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(Hall No. 1)

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(Hall No. 1)

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Topic 1 – Materials and technology for energy and transportation

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Wednesday, May 17

16:30 - 18:00

(DOV - Gong, 1st floor, gallery in front of Hall No.1)

You can set up your poster from Wednesday morning time.

Posters should be prepared in format A0 approx. 90 x 120 cm or smaller. Special evaluation committee will be established and during the poster section posters will be evaluated. The best **3 student's posters** will be awarded with diploma and prize.

We kindly ask all student participants to take a part in the evaluation of poster competition during the conference evening.

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TOPIC 1

Materials and technology for energy and transportation

Chair: Gražyna Simha Martynková

Smart sustainable materials

Batteries

Photovoltaics

Additive technology

Nano in automotive



Invited lectures (IL):**Synthetic Fuels and Green Hydrogen: Paving the Way for a Sustainable Development**

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ABSTRACT

A chariot pulled by pack horses from city to city should be a vision of a past to be set aside as humankind evolves to a sustainable future. Energy for transportation is a big civilizational issue. Daily personal or communitarian displacements would become primarily electrified in a predictable short-term future. However, heavy-duty ground and air transport will continue to depend on liquid fuels due to critical issues associated with volumetric energy density considerations.

Most liquid fuels are still obtained by processing naturally occurring crude oil. According to the European Commission's 2050 Long-term Climate Strategy [1], an integrated solution with the contribution of several alternative fuel options is likely to be required for the future of low-emission mobility. In the near future, Gas-to-Liquids (GtL) processes that convert natural gas into longer-chain liquid hydrocarbons (e.g., jet fuel, gasoline or diesel) will be a decisive alternative to oil refining. The Fischer–Tropsch (FT) synthesis forms the core of GtL processes, using the conversion of syngas ($\text{CO} + \text{H}_2$) through catalyst-assisted chain growth [2]. In the first part of this contribution, the merits of cobalt-supported catalysts for FT synthesis will be discussed as a means to more efficient GtL processes at much smaller scales than those currently used, competing against other emerging small-scale microchannel FT reactors [3].

Hydrogen is an important part of the process, and supplying hydrogen to industrial users is now a significant business worldwide. Demand for hydrogen is rising continuously but is primarily provided by fossil fuels. Only approximately 1% of global hydrogen production currently comes from renewable energies [4]. Solar energy utilization to harvest hydrogen from water can greatly contribute to the cleanliness and sustainability of energy supply and fuel sources. We will describe the use of additive manufacture to create photocatalyst architectures developed by customized design to fit dedicated solution reactors [5].

KEYWORDS

Fischer–Tropsch (FT) synthesis; Cobalt catalysts; Photocatalysis; Additive manufacture.

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REFERENCES

1. European Alternative Fuels Observatory. <https://alternative-fuels-observatory.ec.europa.eu/> (accessed 2023-04-23).
2. K. Jeske, A.C. Kizilkaya, I. López-Luque, N. Pfänder, M. Bartsch, P. Concepción G. Prieto, ACS Catalysis 11 (2021) 4784-4798.
3. D.F. Aguillar. Emerging Catalytic Systems for the Sustainable Production of Synthetic Fuels. M.Sc. Dissertation, Faculty of Engineering, University of Porto, Portugal, 2023.
4. The Energy Transition Blog. <https://energytransition.org/2023/03/green-hydrogen-solution-or-hyped-dream-part-i/> (accessed 2023-04-23).
5. M.A.R.O. Silva. Structured Photocatalysts Manufactured by 3D Printing for Green Hydrogen Generation. M.Sc. Dissertation, Faculty of Engineering, University of Porto, Portugal, 2021. https://sigarra.up.pt/feup/en/teses.tese?P_ALUNO_ID=124129&p_processo=26413 (accessed 2023-04-23).

Silicon nanowires for solar energy harvesting and storage

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ABSTRACT

Efficient harvesting of solar energy and potential storage of energy for later use are some of the most important problems of the societal transition to renewable energy. We will discuss here the potential of using nanostructured devices based on silicon nanowires with large surface areas to harvest solar energy and store it in the form of hydrogen fuel. Previously, the efficient harvesting of solar energy using silicon nanowire devices with radial junction configuration has been demonstrated [1]. In an effort to store the solar energy in hydrogen gas using a water-splitting reaction, there is a need to increase the potential difference on electrodes in order to efficiently perform the reaction. For typical catalysts used for the hydrogen production from water splitting a potential difference of 1.8 to 2 V is required [2]. This brings a necessity to provide devices with open circuit voltage (V_{oc}) of 2 V or more to enable efficient production by a single integrated device.

We will show the latest results of radial multijunction devices based on silicon nanowires able to provide large V_{oc} above 2 V [3]. In addition, as such devices have a very large surface area due to their nanostructured surfaces, it is beneficial to use them directly as photoelectrodes with proper catalysts in a single integrated device. Such devices, which do not need external wiring or connection to the source, but instead perform water splitting by themselves when dipped into the water and exposed to the sunlight, are called artificial leaves. The potential of using artificial leaves as an alternative way to store solar energy in hydrogen fuel will be discussed.

KEYWORDS

Silicon nanowires, solar cells, solar hydrogen, renewable energy, energy storage

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REFERENCES

1. S. Misra, L. Yu, M. Foldyna, P. Roca i Cabarrocas, IEEE Journal of Photovoltaics 5 (2015) 40.
2. S.Y. Reece et al., Science 334 (2011) 645.
3. C. Wang, M. Foldyna, E.V. Johnson, P. Roca i Cabarrocas, Solar RRL 6 (2022) 2200248.

Solid State Lithium-Ion Batteries: Bridging the Gap Between Performance and Safety

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ABSTRACT

Solid state lithium-ion batteries (SSLBs) have emerged as a promising alternative to traditional liquid electrolyte lithium-ion batteries due to their potential for improved safety, higher energy density, and longer cycle life [1]. SSLBs are constructed using a solid-state electrolyte, which eliminates the need for a flammable liquid electrolyte and can reduce the risk of thermal runaway. However, challenges remain in the development and commercialization of SSLBs, including achieving high ionic conductivity in the solid-state electrolyte, optimizing the interface between the electrolyte and electrode materials, and ensuring manufacturability and scalability [2]. Despite these challenges, SSLBs have the potential to bridge the gap between performance and safety in lithium-ion batteries and offer exciting possibilities for future energy storage.

Here, we are exploring surface modification and protective layer coating techniques to enhance the interfacial properties, which can improve the stability, conductivity, and lifespan of SSLBs.

KEYWORDS

Lithium batteries, Solid electrolytes, Safety, Coating

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REFERENCES

1. F. Zheng, M. Kotobuki, S. Song, M. O. Lai, L. Lu, J Power Sources, 389 (2018) 198–213.
2. A. Manthiram, X. Yu, S. Wang, Nature Reviews Materials 2, (2017).

Towards atom precise synthesis and engineering with electron microscopes

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ABSTRACT

In this presentation, I will provide an overview of my research endeavors in several areas. These areas include the synthesis of nano-materials, nano-bio studies, nano-materials in ion insertion batteries, and electron beam materials science. A common thread throughout much of my work is the exploration of structure-property relationships, such as the chiral dependence of single wall carbon nanotubes on their electrical properties, or the biological cell response in relation to nanomaterial type, size, and morphology.

A key aspect of my research is the development of a transmission electron microscope (TEM) into an atomic-scale laboratory, enabling the fabrication, modification, and characterization of samples with high spatial and temporal resolution. As such, the core of my presentation will focus on various electron beam-driven chemical reactions and electron beam engineering techniques that allow for the fabrication and manipulation of nano-materials at the atomic level.

KEYWORDS

Nano-materials, electron microscopy, in situ, synthesis & engineering

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Oral presentations (OP):**Design of Stable Lead-Free Double Perovskite Nanocrystals for Optoelectronic and Photocatalysis Application**

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ABSTRACT

In the past decade, lead halide perovskites (LHPs) exhibited enormous potentials for energy conversion and lighting applications due to their unique optical and electronic properties.^[1] However, material instability and toxicity of LHPs are the main limiting factors towards their practical application.^[2] In this view, recently developed lead-free double perovskites (DPs) are under spotlight due to superior material stability and compositional flexibility.^[3] However, low photoluminescence quantum yield (PL QY) and relatively larger band gap of DPs materials are the main bottlenecks towards their optoelectronic and photocatalysis application.^[4] Therefore, doping and compositional engineering of DP nanocrystals (DP NCs) are the straight forward strategies to enhance the emission properties and to extend the light harvesting abilities of DP NCs for their applications in optoelectronic devices and photocatalysis.^[4,5] However, poor colloidal, photophysical and structural instabilities during purification due to desorption of surface capping ligands hampered their uses in optoelectronic devices and photocatalysis.^[6] Moreover, reduction of silver ions by amine during synthesis is the major culprit for low quality of silver based DP NCs.^[7]

In this talk, I will present the design, synthesis and purification strategies of efficient and stable blue emitting Sb-doped Cs₂NaInCl₆ and warm-white light emitting Bi-doped Cs₂AgInCl₆ DP NCs. The DP NCs were synthesized by utilizing strongly coordinating silver-trioctylphosphine (Ag-TOP) complex along with additional TOP as a co-ligand. The role of Ag-TOP complex is to prevent the early reduction of silver ions during synthesis into metallic silver.^[8] On the other hand, TOP could facilitate the nucleophilic reaction with benzoyl chloride during nucleation and growth stage and results benzoyl trioctylphosphonium chloride intermediate that serve as both halide source and surface capping ligand.^[9] The extensively washed DP NCs exhibited high colloidal, photophysical, and structural stability due to efficient surface passivation by robust dual cationic ligand of benzoyl trioctylphosphonium and oleylammonium cations along with oleate anion. Moreover, I will explore Fe³⁺ doped Cs₂Ag_xNa_{1-x}InCl₆ DP NCs, including synthesis strategies, optoelectronic properties and their application in photocatalytic CO₂ reduction.

REFERENCES

- [1] M. A. Green, A. Ho-Baillie, H. J. Snaith, *Nature Photon.* 8 (2000) 506–514.
- [2] Z. Xiao, Z. Song, Y. Yan, *Adv. Mater.* 31 (2019) 1803792.
- [3] A. H. Slavney, T. Hu, A. M. Lindenberg, H. I. Karunadasa, *J. Am. Chem. Soc.* 138 (2016) 2138–2141.
- [4] F. Locardi, E. Sartori, J. Buha, J. Zito, M. Prato, V. Pinchetti, M. L. Zaffalon, M. Ferretti, S. Brovelli, I. Infante, L. De Trizio, L. Manna, *ACS Energy Lett.* 4 (2019) 1976–1982.
- [5] J. Luo, X. Wang, S. Li, J. Liu, Y. Guo, G. Niu, L. Yao, Y. Fu, L. Gao, Q. Dong, C. Zhao, M. Leng, F. Ma, W. Liang, L. Wang, S. Jin, J. Han, L. Zhang, J. Etheridge, J. Wang, Y. Yan, E. H. Sargent, J. Tang, *Nature.* 563 (2018) 541–545.
- [6] R. Ahmad, G. V. Nutan, D. Singh, G. Gupta, U. Soni, S. Sapra, R. Srivastava, *Nano Res.* 14 (2021) 1126–1134.

- [7] Z. Liu, J. Zito, M. Ghini, L. Goldoni, M. Prato, H. Bahmani Jalali, I. Infante, L. De Trizio, L. Manna, *Nano Lett.* 22 (2022) 8567–8573.
- [8] R. Ahmad, L. Zdražil, S. Kalytchuk, A. Naldoni, E. Mohammadi, P. Schmuki, R. Zboril, Š. Kment, *Applied Materials Today*. 26 (2022) 101288.
- [9] R. Ahmad, L. Zdražil, S. Kalytchuk, A. Naldoni, A. L. Rogach, P. Schmuki, R. Zboril, Š. Kment, *ACS Appl. Mater. Interfaces*. 13 (2021) 47845–47859.

Biogenic nanocatalysts for sustainable bioenergy production

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ABSTRACT

The ever-increasing population of the world has continuously increased the demand for various products including energy. The major source of energy is fossil fuels, however, it is well-known fact that burning fossil fuel is responsible for climate change, air pollution, and many other environmental issues. Apart from this, it is forecasted that existing sources of fossil fuels will be exhausted by 2050. Considering these facts, several governmental organizations and environmental protection agencies developed different policies to support the production and use of biofuels as a sustainable alternative to fossil fuels. It was estimated that only in 2019, the global production of biofuels reached equivalent of 1,841 thousand barrels of oil per day. The present biofuel market is expected to reach 153.8 billion U.S. dollars by 2024.

The production of biofuels involves the use of different biocatalysts (i.e. enzymes) which increase the production cost, hence the development and application of nanocatalyst for the green production of bioenergy can be a promising substitute for conventional biocatalysts. To date, several nanocatalysts have been developed and are being used in the production of bioenergy such as bioethanol and biodiesel. It is believed that efficient use of nanocatalysts can significantly improve energy supply, solve the concerns related to climate change, greenhouse gas emissions, and strengthen energy security, social and economic development.

KEYWORDS

Fossil fuels, Bioenergy, Biocatalyst, Nanotechnology, Nanocatalyst

Earth-abundant photocatalyst for cost-and energy-efficient production of amines

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ABSTRACT

Reduction of nitroaromatics to the corresponding amines is a key process to produce polymers, pharmaceuticals, agrochemicals and dyes.¹ However, their effective and selective reduction requires high temperatures, pressurized hydrogen and involves noble metal-based catalysts.¹ Here we report on an earth-abundant, plasmonic nano-photocatalyst (CuFeS₂, Fig. 1a), with an excellent reaction rate towards the selective hydrogenation of nitroaromatics (Fig. 2b). With solar light as the only energy input, the catalyst operates through the combined action of hot-holes and photothermal effects. Ultrafast laser transient absorption and light-induced electron paramagnetic resonance spectroscopies unveiled the energy matching of the hot holes in the valence band of the catalyst with the frontier orbitals of the hydrogen and electron donor, resulting in the formation of an active transient coordination intermediate (Fig. 1c,d). Consequently, the reusable and sustainable CuFeS₂ catalyst delivers previously unattainable turn-over-frequencies, even in large-scale reactions, while the cost-normalized production rate stands an order of magnitude above the state-of-the-art.²

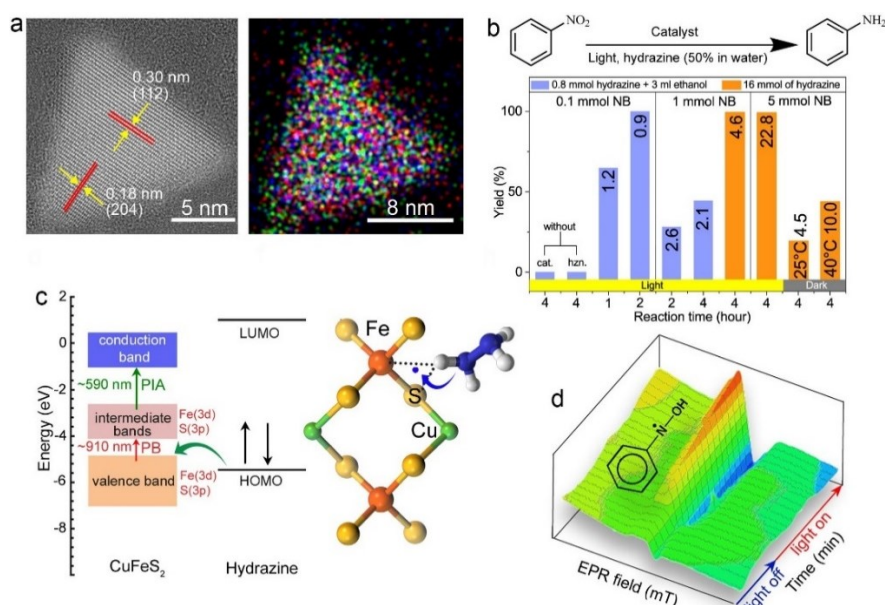


Fig. 1. **a**) HR-TEM of a CuFeS₂ nanocrystal with marked lattice fringes, and the corresponding EDS elemental mapping for Cu, S and Fe. **b**) Reduction of nitrobenzene at various conditions. **c,d**) Energy level diagrams of CuFeS₂ and hydrazine (the e⁻ and H-donor), along with the charge-transfer intermediate, thanks to the energy matching of the hot holes in the valence band of CuFeS₂ with the HOMO of hydrazine.

KEYWORDS

Catalysis, photocatalysis, plasmonics, nitroaromatics, amines.

Acknowledgments: We thank the Czech Science Foundation for support through the EXPRO project no. 19-27454X, and the ERDF/ESF (project no. Z.02.1.01/0.0/0.0/16_019/0000754).

REFERENCES

1. Westerhaus, F.A. et al. *Nat. Chem.* **5**, (2013) 537–543.
2. A. Cheruvasthoor Poulase, G. Zoppellaro, I. Konidakis, E. Serpetzoglou, E. Stratakis, O. Tomanec, M. Beller, A. Bakandritsos, R. Zbořil, *Nat. Nanotechnol.* (2022), 17, 485.

TiN-based photothermal catalyst

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Biomass reforming by harvesting solar energy can provide green hydrogen. Current biomass photoreforming provides H₂ erratically and in limited yield although efficiently, owing to intermittent features of solar light and incomplete degradation of biomass C–C bonds.¹ Here, we overcome these limitations by prioritizing conversion of carbohydrates to liquid hydrogen carriers (LHCs, consisting of HCOOH and CH₃OH), appropriate for transportation. Subsequently, the LHCs can be fully decomposed, releasing only H₂ and CO₂.²



Figure 1. Illustration of H₂ production from biomass and storage in the form of LHCs by a stepwise method.

In this study, we synthesized several core shell CeO₂/TiN-based materials that differ from each other for the thickness of the CeO₂ and TiO₂ shells. Prepared materials were characterized to determine the morphology (TEM and N₂ physisorption), the phase composition and the crystallite dimensions (powder XRD and Raman spectroscopy). This represents a preliminary study for the synthesis of materials. The next steps consist in testing the photocatalysts obtained for the conversion of glycerol (as a model biomass) in liquid hydrogen carriers such as formic acid and methanol.

KEYWORDS

TiN, Plasmonic, Biomass valorization, Hydrogen.

REFERENCES

1. Ren P, Gao Z, Montini T, et al. Stepwise photoassisted decomposition of carbohydrates to H₂. *Joule*. 2023;7(2):333-349. doi:10.1016/J.JOULE.2023.01.002
2. Bulushev DA, Ross JRH. Towards Sustainable Production of Formic Acid. *ChemSusChem*. 2018;11(5):821-836. doi:10.1002/CSSC.20

Electrochemical properties of nano-metal catalyst

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ABSTRACT

To highlight the prospect of green energy production, the development of highly active catalysts for the hydrogen evolution reaction (HER) has become an area of intense research. However, electrocatalyst are widely accepted catalysts in recent era of the renewable energy generation. Electrocatalysis create the formation of chemical bonds by legitimate employment of electrons or holes from an electrical energy input. Electrocatalysts are well known as economical alternative pathways which eliminate the obligation of sacrificial agent and waste generating reagents. On the other hand, copper (Cu) based materials are known as more competitive candidates due to their excellent electrocatalytic activity and stability with relatively lower overpotential to achieve a corresponding current density. In this work, copper low Nuclearity catalyst (LNC) were obtained via an electrochemical transformation of copper chloride (CuCl₃) in 1M KOH solution. To improve conductivity and dispersion of Cu LNCs, the cyanographene (CyanoG) modified glassy carbon electrode (GCE) was used as base for electrochemical deposition of Cu. The resultant Cu-CyanoG/GCE nanocomposite electrochemical activity towards HER in 1M KOH was studied using cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The results indicate that the Cu-CyanoG/GCE may provide a cost-effective alternative to noble metals HER electrocatalyst due to its better mass activity and stability in alkaline solutions.

KEYWORDS

Electrocatalyst, Copper, Green energy, Electrochemical

INTRODUCTION

An electrocatalyst is expected to upgrade the kinetics of the reaction and cost-performance of energy devices that count on HER and OER. In recent era of material science, transition metal oxide (TMO), Ag based, and nitrogen (N) doped carbon catalysts have been widely investigated as search for cost effective and Pt-free electrocatalysts^{2,3}. Effective electrocatalysts play significant role in the development of hydrogen production from water electrolysis, involving low reaction barrier,

lowering energy consumption, encouraging reaction efficiency and rate, etc. Therefore, the research efforts towards economical electrocatalysts become the key task in the evaluation of electrolysis water hydrogen production technology. Therefore, researchers have turned their attention to the relatively inexpensive non-precious metals which found to be effective in electrocatalytic oxidation and reduction of H_2O_2 .

In this study, glassy carbon electrode (GCE) was primarily modified with Cyanographene (CyanoG) ink which was prepared by mixing with nafion and further treated with ultrasonication treatment. CuCl_3 was used as metal precursor in 1M KOH to form electrolyte. Further linear sweep voltammetry (LSV) was used as catalyst deposition technique with potential ranging between 0.10V to -0.40V with 5mV S^{-1} scan rate. The LSV cycles were repeated 10 times to get the even distribution of Cu LNCs on CyanoG modified GCE electrode.

EXPERIMENTAL/THEORETICAL STUDY

All reagents were of analytic reagent grade and used as received without additional purification. 1M KOH was used as electrolyte for the electrochemical analysis. Cyclic voltammetry (CV) and liner sweep voltammetry (LSV) were used to analyse the electrocatalytic activity and stability of the electrocatalyst.

RESULTS AND DISCUSSION

Electrochemical synthesis of Cu LNCs on the Cyano-G modified GCE was done by electrochemical method using LSV technique. Three electrode system was used for the synthesis where, Cyano-G-GCE was used as working electrode, Platinum wire as counter electrode and Ag/AgCl as reference electrode respectively. For the even distribution and facile formation of CU LNCs on electrode surface LSV scans were repeated ten times. From Fig. 1a it can be observed that as the LSV cycles increased the oxidation current for each respective scan is also increased. This evidence reveals that, Cu LNCs are successfully getting deposited on the surface of working electrode. The working electrode was further washed with distilled water and air dried.

The electrochemical activity of the Cu modified CyanoG-GCE electrode was studied by cyclic voltammetry technique compared with bare GCE. Form Fig. 1b we can observe that, Cu modified CyanoG-GCE has shown higher current density compared to bare GCE. It means, Cu-CyanoG-GCE is more electroactive than the bare GCE.

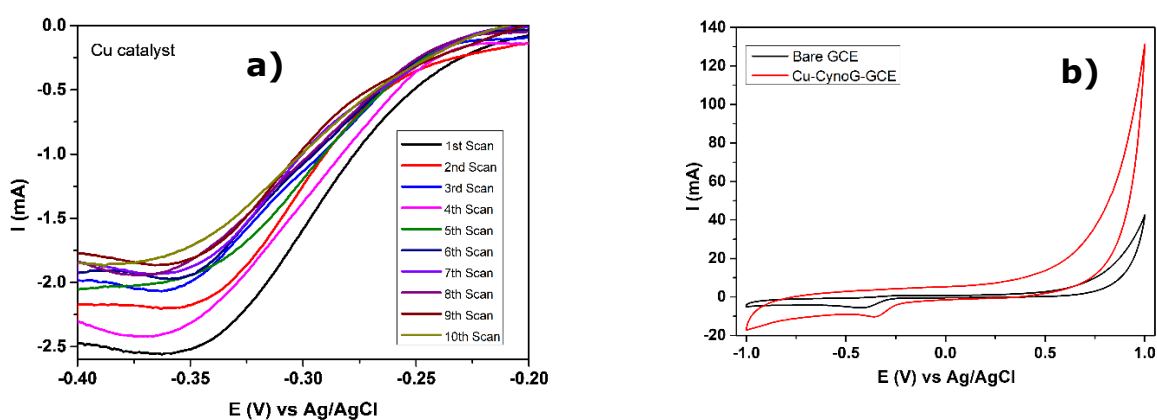


Fig. 1 a) LSV of Cu on CyanoG-GCE and b) CV of bare GCE and Cu-CyanoG-GCE

CONCLUSION

The CyanoG-GCE nanocomposite was obtained by electrodeposition technique applying potential difference between two phases. The prepared Cu-CyanoG-GCE has revealed good electrochemical activity. The results direct that the Cu-CyanoG/GCE may offer a economical alternative to noble metals based electrocatalyst due to its better mass activity and stability in alkaline solutions.

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REFERENCES

1. J. Van der Geer, J.A.J. Hanraads, R.A. Lupton, J. Sci. Commun. 163 (2000) 51–59.
2. W. Strunk Jr., E.B. White, The Elements of Style, third ed., Macmillan, New York, 1979.
3. G.R. Mettam, L.B. Adams, in: B.S. Jones, R.Z. Smith (Eds.), Introduction to the Electronic Age, E-Publishing Inc., New York, 1999, pp. 281–304.

Control of optical properties and surface morphology of ZnO thin films by sputtering deposition conditions

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ABSTRACT

The aim of this work is to analyze influence of deposition conditions, substrate temperature and deposition atmosphere composition on the prepared zinc oxide thin films using RF magnetron sputtering deposition system. Evolution of material optical functions and surface roughness were characterized by fitting of spectroscopic ellipsometric data. The effect of the substrate temperature was studied using X-ray diffraction analysis. It was confirmed, that with increased substrate temperature during the thin film deposition process material tends to form in wurtzite crystalline structure. This corresponds with increase in surface roughness observed in spectroscopic data. Moreover, change in dielectric functions shows that band gap shifts to higher energies for samples prepared at higher temperature.

KEYWORDS

magnetron sputtering, zinc oxide, ellipsometry, thin films

INTRODUCTION

Optical and structural properties of the zinc oxide thin films deposited using radio frequency magnetron sputtering strongly depends on the process conditions.^{1,2} The presented study consists of two parts. First part is focused on estimation of the optimal deposition atmosphere composition, i.e., ratio between working gas (Ar) and reactive gas (O₂). In the study the deposition temperature was

held at room temperature and composition of gas was changed from sample to sample (from pure argon atmosphere to 50 % Ar, 50 % O₂). The evolution of the material optical function was analysed using spectroscopic ellipsometry and optimal deposition conditions were estimated.³ In second study the process gas mixture was fixed, and the substrate temperature varied from room temperature up to 500 °C. The evolution of the material crystallinity was characterized using x-ray diffraction. The experimental data shows, that samples prepared under higher substrate temperature conditions tends to crystallize in hexagonal wurtzite structure. In addition, the higher the temperature was, the more crystalline phase is present in the sample. That corresponds with atomic force microscopy and ellipsometric measurements, where films deposited at higher temperatures had higher surface roughness.

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REFERENCES

1. D. Pranav, K. H. Patel, K. V. Chauhan, A. K. Chawla, S. K. Rawal, *Procedia Technology: 3rd International Conference on Innovations in Automation and Mechatronics Engineering*, 328-335 (2016)
2. Postava, K., Sueki, H., Aoyama, M., Yamaguchi, T., Ino, C., Igasaki, Y., Horie, M., *Journal of Applied Physics*, 87(11), 7820-7824. (2000).
3. A. A. Ahmad., A.M. Alsaad, B.A. Albiss, M. Al-Akhras, H.M. Elnaser, I.A. Qattan. *Physica B: Condensed Matter*, 470-471 (2015)

Molecular characterization of batteries along its lifetime: from development to recycling

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ABSTRACT

Batteries are becoming key elements in our global energy management. Their performances mainly depend on the elements quality and their assembly. Raman microscopy is an ideal technique to molecularly investigate and characterize these different parts of batteries. In this presentation we will demonstrate how Raman can be applied at the different moment of a battery lifetime.

KEYWORDS

Battery, Raman microscopy, Quality control.

INTRODUCTION

In a global warming tendency, governments decide to reduce the use of fossils energies moving to general electrification using nuclear but also renewable energies like wind or hydro-electric sources. The main limitation of these sustainable solutions is coming from their low regularity of energy

production. Consequently, the use of batteries is important to both store this energy during high efficiency periods and deliver it back during low production time. Moreover, this global electrification especially concerns cars and other mobility modalities. The improvement of batteries performances and size reduction become so important factors to investigate, as well as new types of batteries development like hydrogen-based ones, called fuel cells.

Batteries performances strongly depend on both electrodes (quality and reliability over cycling) and electrolyte efficiency. Being able to characterize these different parts of batteries before and after assembly is so very important, as well as during recycling process to reduce the environmental impact of the batteries. Key performance factor is obviously the electric conversion of batteries. Physical and chemical characterization of electrodes and/or electrolytes before, during and after cycling is so critical, inducing the use of non-invasive techniques to do it.

EXPERIMENTAL/THEORETICAL STUDY

Raman microscopy is a key technique for these battery performances characterization. As an optical-based molecular spectroscopy, this non-invasive approach enables a clear molecular characterization of electrodes and electrolyte all along the lifetime of a battery, from its development to its recycling.

RESULTS AND DISCUSSION

Raman can be applied at different levels of battery lifetime. First, raw materials can be analysed for quality control of the electrodes composition. Secondly, as an optical approach, measurements can be performed on battery assembly, meaning that the cell can be characterized after association of the different parts and compared before and after cycling process to do post-mortem cycling investigation and understand the origin of the battery failure. In the same way, electrical performances can be linked to molecular structure in-operando thanks to the coupling of Raman microscopy with electrochemical cells with an optical window allowing the laser access to the battery parts during cycling process. Finally, as for primary material characterization, Raman microscopy can be applied on material characterization during recycling process to support second life applications of these materials.

Fundamental Chemistry	Process Scale-Up	Battery Characterisation	Cell to Module to Pack	System Performance	Re-use and Recycling
▪ Electrochemistry ▪ New material integration ▪ Electrode engineering ▪ Materials analysis	▪ Mixing, coating and assembly ▪ Cell manufacture ▪ Cell instrumentation ▪ 'Like-production' processes	▪ Electrical testing ▪ Mechanical testing ▪ Thermal testing ▪ Abuse testing ▪ Battery forensics	▪ System simulation ▪ Materials and construction ▪ Battery management systems ▪ Manufacturing automation	▪ Pack level and / or in powertrain testing ▪ Climatic testing ▪ 'Real world' testing ▪ Accelerated life testing	▪ Understanding degradation ▪ Remanufacturing and life extension ▪ Second life application ▪ Materials recovery ▪ Economic modelling

Fig. 1. Battery lifetime from development to recycling – Highlighting sections are where Raman microscopy can be used for molecular characterization.

CONCLUSION

Thanks to its non-destructive and molecular discrimination capabilities, Raman microscopy is an ideal technique to investigate and understand battery performances during their whole lifetime as it gives crystallinity, defects, and more others information.

Acknowledgments: The authors would like to acknowledge the global HORIBA application and market network for its support and data sharing.

Green synthesis of nanoparticles using a widely spread weedy plant

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ABSTRACT

The abstract should state briefly the purpose of research, the principal results and conclusions. The text of this part should be **limited to 200 words**. This part will be included to shortened printed version of abstract booklet.

The purpose of this work was to prepare silver nanoparticles (AgNPs) from weedy plant material. Extracts of dried and fresh *Reynoutria leaves* were used for the synthesis of nanoparticles. The extracts were prepared from fresh and dried *Reynoutria leaves* at 100 °C, and from dried leaves at a laboratory temperature 21 °C. AgNPs were prepared by adding 1 mM AgNO₃ and tempered at 70 °C for 24 hours. The changes during the formation of nanoparticles were monitored using UV-vis spectra. Maximum absorbance was detected at 420 nm. The size and stability of the particles were determined by Dynamic Light Scattering method to 70 nm, 85 nm, and their zeta potential was -23.1 and -23.5 mV. In addition, the particle size was checked by SEM. The cold route of green synthesis appears to be a new and energetically beneficial way of preparing AgNPs. The extracts were prepared from dried leaves at laboratory temperature and AgNPs were also synthesized at laboratory temperature by adding 1mM AgNO₃. The shift of absorption maximum to 450 nm was observed, with a particle size of 85 nm. The preparation is three times more time-consuming (72 hours), but without energy costs and from an invasive.

KEYWORDS

Reynoutria bohemica, silver, nanoparticles, green synthesis

Acknowledgments: The authors acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project No. LM2018124.

Charge selective transport materials based on sputtered nickel oxide and tin oxide thin films

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ABSTRACT

Transparent oxide layer providing electrical conductivity are building blocks of wide range of technological applications. Nowadays materials are based on doped high optical band-gap parent oxide material. The aim of this work is to analyze growth process of nickel oxide and tin oxide parent material for hole and electron selective transport thin layers, respectively. The evolution of the material optical properties was analyzed by simultaneous fitting of normal incidence transmittance and spectroscopic ellipsometry data.

KEYWORDS

Transparent conductive oxides, ellipsometry, reactive magnetron sputtering

INTRODUCTION

Transparent conductive oxides (TCO) representing group of material combining electrical conductivity and transparency in visible light spectral range. The key property of parent oxide material is its high optical bandgap to ensure transparency. The dopant has a role of charge donor or acceptor resulting in preferential electron or hole conductivity. The studied thin films were prepared by reactive radio-frequency (RF) magnetron sputtering using high purity (min. 99.95%) Ni, Sn, and Zn targets. The argon, oxygen, and nitrogen were used as working and reactive gases, respectively.

While stoichiometric nickel oxide exhibits as insulator its work function can be modified by the tuning of the concentration of nickel vacancies or oxygen interstices resulting in hole or electron conductivity, respectively.¹ In this study we are focused on evolution of the optical functions of the developed thin films by fitting of spectroscopic ellipsometry data. To promote hole-transport properties of the NiO_x thin films the effect of its doping by zinc is studied.² The zinc is embedded in NiO_x matrix by the process of simultaneous co-sputtering from Ni and Zn targets. The ratio between amount of sputtered Ni and Zn is controlled by delivered RF power on magnetron guns.

The tin oxide is mostly used as n-type TCO. In the case of p-type tin oxide it can be achieved through doping in SnO₂ using elements with a lower valence cation, such as antimony or zinc as the acceptor impurity. Also, nitrogen has been suggested to be an outstanding p-type dopant in SnO₂ due to its suitable ion size and electronegativity.³ To incorporate nitrogen into the tin oxide matrix, the mixture of argon, oxygen and nitrogen is used during the sputtering process and materials are characterized using spectroscopic ellipsometry.

Acknowledgments: The authors acknowledge partial support from the following projects: Czech Science Foundation 22-33060S; Student Grant Agency project SP2023/026, and Ministry of Industry and trade project CZ.01.1.02/0.0/0.0/20_321/0024953.

REFERENCES

1. Itapu, S., Georgiev, D. G., Uprety, P., Podraza, N. J. *Physica Status Solidi (a)*, 214(2), 1600414 (2007)
2. Choi, F. P. G., Alishah, H. M., & Gunes, S.. *Applied Surface Science*, 563, 150249 (2021)
3. S. S. Pan, G. H. Li, L. B. Wang, Y. D. Shen, Y. Wang, T. Mei, and X. Hul, *Appl. Phys. Lett.*, 95, 222112 (2009).

Let's go through the battery

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ABSTRACT

Proper techniques for material research and testing are essential for obtaining accurate and reliable results, particularly in the field of battery research. This contribution briefly discusses several techniques that are appropriate for battery research, including Scanning Electron Microscopy (SEM) with appropriate analytical equipment, 3D X-Ray Microscopy (XRM), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), and Nanoindentation. However, there are many other techniques that can also be applied.

Thanks to aforementioned techniques we can get information about material chemistry, topography, internal structure and material properties at the nanoscale, and we can observe changes that materials undergo under various conditions (e.g., effects of mechanical stress and deformation on battery performance). These techniques can provide valuable information on the chemical and structural changes that occur during battery operation and aging.

Overall, proper techniques for material research and testing are crucial for understanding the properties and behavior of battery materials. These techniques provide valuable insights into the microstructure, morphology, surface properties, and mechanical properties of battery materials, which are essential for designing and developing more advanced and sustainable batteries for the future.

KEYWORDS

battery research, XRM, AFM, Nanoindentation

INTRODUCTION

Materials are the building blocks of everything around us, from the clothes we wear to the devices we use. Understanding the properties and behavior of materials is essential in designing and developing new products, improving existing ones, and ensuring their quality and safety. This is where material research and testing come in, especially for battery research which plays an important role in our everyday life.

Proper techniques for material research and testing are crucial for obtaining accurate and reliable results. Inaccurate data can lead to incorrect assumptions, faulty designs, and even hazardous products. The use of inappropriate or outdated methods can also compromise the validity of the results

and hinder the progress of scientific knowledge. Techniques we use for material research and testing involve a wide range of methods, including microstructural analysis, mechanical testing, spectroscopy, and imaging. Each method has its advantages and limitations and should be carefully selected and applied based on the specific properties and characteristics of the material under investigation.

Overall, the importance of proper techniques for material research and testing cannot be overstated. It is only through careful and rigorous experimentation that we can gain a deep understanding of the materials we use and create more advanced and sustainable products for the future.

CONCLUSION

The proper techniques for material research and testing discussed in the presentation are essential tools for understanding the properties and behaviour of (not-only) battery materials. By gaining a deep understanding of these materials, scientists and researchers can design and develop more advanced and sustainable batteries for the future.

Influence of coatings on nickel rich positive electrode material properties

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ABSTRACT

Nickel-rich layered metal oxide $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) is one of the most promising positive electrode materials for lithium batteries because of its high energy density. However, during battery cycling it suffers from irreversible parasitic reactions and phase changes leading to severe capacity fading and impedance increase. Coating NMC811 with various metal oxides has been shown to effectively suppress those unwanted aging phenomena [1,2]. However, the coatings can also impede lithium transport and consequently, limit performance of a positive electrode. Thus, both physical and chemical properties of an applied coating are effectual factors in providing optimized protection for an electrode material.

We have investigated nanometer scale protective films coated on NMC811 electrodes utilizing atomic layer deposition (ALD), which allows precise control of the deposited film thickness and chemical composition. We have deposited metal oxide and Li-containing metal oxide layers on NMC811 electrodes to investigate how the film chemical composition and thickness affect electrode behavior during a battery operation. Investigations with such characterization methods as Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) and Transmission Electron Microscopy (TEM) confirm that during the deposition the coating diffuses into the NMC811 grain boundaries. Rate capability measurements in half cells and impedance spectroscopy are utilized to study lithium transport while structure stabilizing effect of the thin coatings is evidenced by observing capacity retention during long term cycling. In particular, lithium titanate ($\text{Li}_x\text{Ti}_y\text{O}_z$) is found to effectively hinder the above-mentioned interfacial and structural instabilities while it allows good lithium transport.

In addition to the above-mentioned structural characterization and electrochemical analysis, in-operando dilatometry and in-situ XRD analysis have been carried out to investigate the structural changes occurring during lithium battery cycling. Those results suggest that irreversible volume and structural change observed for the uncoated NMC811 electrodes are notably suppressed when the electrodes are coated with lithium titanate. As the electrode dilation during the cycling generates crack formation and particle degradation, the nanoscale coating is concluded to provide mechanical protection while it simultaneously protects NMC811 from the parasitic reactions with the electrolyte at high potentials.

As summary, we suggest that nanoscale coatings suppress mechanochemical degradation of NMC811 electrodes by suppressing volume changes and reactions at the electrode–electrolyte interphase during the battery cycling. The practical benefits include utilization of higher cut off voltages for the coated NMC811 positive electrodes and increased battery cycle life.

KEYWORDS

lithium battery, positive electrode, nickel rich layered oxide, coating, atomic layer deposition

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REFERENCES

1. W. Li, B. Song and A. Manthiram, High-voltage positive electrode materials for lithium-ion batteries, *Chem. Soc. Rev.* 46 (2017) 3006. DOI: 10.1039/c6cs008752.
2. Z. Ahaliabadeh, V. Miikkulainen, M. Mäntymäki, S. Mousavihashemi, J. Lahtinen, Y. Lide, H. Jiang, K. Mizohata, T. Kankaanpää, and T. Kallio, Understanding Stabilizing Effects of Nano-scale Metal oxide and Li-metal oxide Coatings on Lithium Ion Battery Positive Electrode Materials, *ACS Applied Materials & Interfaces*, 13 (2021) 42773. DOI: 10.1021/acsami.1c11165J.

Thin graphene oxide foil applicable as separator for batteries

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ABSTRACT

Graphene oxide is highly desired material for printing electronics, catalysis, energy storage, separation membranes, biomedicine, and composites. Graphene oxide thin films modified with phytosynthetically prepared silver nanoparticles (nAg) are studied for their functional properties (Fig.1). Graphene oxide (GO) was prepared using a modified Hummers method from two types of flake graphites. nAg with particle size below 20 nm were prepared via reduction using nettle extracts. Along with GO they served as a mix for thin films preparation. The films differ in the graphite and plant precursors used for creation of nanoparticles.

The properties and morphology of the prepared nAg modified GO films were compared with pure GO films. The order of the GO structure decreased slightly after the modification. The surface of the

nAg-modified films was gently smoothed and the overall roughness was reduced. The studied samples were evaluated as hydrophobic by determining the contact angle, which corresponds to their chemistry.

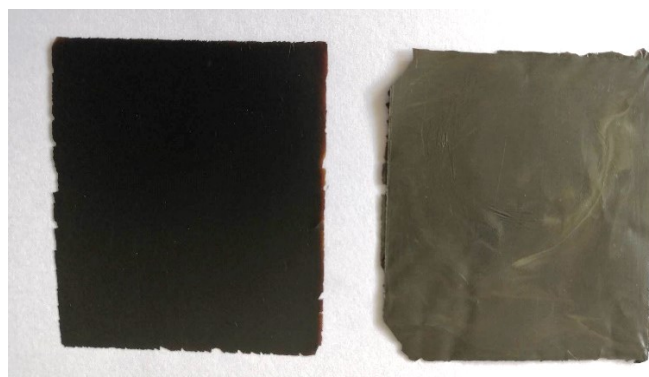


Fig. 1: Real image of Graphene oxide and modified Graphene oxide films

KEYWORDS

graphene oxide, nanosilver, thin film, modification

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Modeling of THz Optical Activity in Biomolecules

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ABSTRACT

Quantities of natural materials exhibit chirality as an asymmetric property. Chiral molecules demonstrate optical activity, which is characterized by different complex refractive indices for left and right circular polarization. In biomolecules such as amino acids and proteins, the vibration modes of these molecular complexes are in the THz frequency range. The plasmonic Born-Kuhn Model act as an intuitive method to describe optical activity in chiral materials. This model simplifies the biomolecule by representing it as two undifferentiated orthogonal coupled oscillators. This conference presentation describes a promotion of the Born-Kuhn Model in more general cases where the orthogonality of coupled oscillators is not required. Based on classical theories of optical activity, the model progressively describes various parameters, such as particle motion, current density, relative permittivity tensor, nonlocality tensor, circular dichroism, and optical rotatory dispersion. This model will contribute to our deeper understanding of the chiral structure of biomolecules.

Broadband TiN solar absorbers with enhanced photothermal properties

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ABSTRACT

Transition metal nitrides (TMNs) are emerging plasmonic materials that can substitute traditional coinage metals, such as gold (Au) and silver (Ag), thanks to their tunable optical response, refractory nature and compatibility with microelectronic industry fabrication processes. In this contribution, we thoroughly discuss the optical tunability of titanium nitride (TiN), the archetypal TMN, to achieve broadband absorption and, therefore, enhanced photothermal properties. We first introduce the general optical properties of TiN thin films that can be measured by spectroscopic ellipsometry. We then consider examples of nanostructured TiN materials as solar absorbers, i.e., nanotubes produced by electrochemical anodization and thermal nitridation¹ and nanoporous tree-like films prepared by pulsed laser deposition.² Such materials exhibit nearly perfect light absorption thanks to the nanostructured morphology and/or partial oxidation, i.e., TiO_xN_y composition. As a result, they exhibit optimal photothermal properties, as confirmed by temperature measurements under moderated light concentration.^{1,2} We finally review selected examples of applications of such materials. TiN nanotubes, in particular, revealed appealing performance in solar steam generation experiments.³ Furthermore, by appropriately coating the same by Rh catalyst nanoparticles, they were also investigated as potential candidates for gas-phase photothermal catalysis.¹

REFERENCES

1. Naldoni, A.; Kudyshev, Z. A.; Mascaretti, L.; Sarmah, S. P.; Rej, S.; Froning, J. P.; Tomanec, O.; Yoo, J. E.; Wang, D.; Kment, Š.; Montini, T.; Fornasiero, P.; Shalae, V. M.; Schmuki, P.; Boltasseva, A.; Zbořil, R. "Solar Thermoplasmonic Nanofurnace for High-Temperature Heterogeneous Catalysis" *Nano Lett.* **2020**, *20*, 3663–3672.
2. Bricchi, B. R.; Mascaretti, L.; Garattoni, S.; Mazza, M.; Ghidelli, M.; Naldoni, A.; Li Bassi, A. "Nanoporous Titanium (Oxy)Nitride Films as Broadband Solar Absorbers" *ACS Appl. Mater. Interfaces* **2022**, *14*, 18453–18463.
3. Mascaretti, L.; Schirato, A.; Zbořil, R.; Kment, Š.; Schmuki, P.; Alabastri, A.; Naldoni, A. "Solar Steam Generation on Scalable Ultrathin Thermoplasmonic TiN Nanocavity Arrays" *Nano Energy* **2021**, *83*, 105828.

Graphitic carbon nitride as the component of friction composites

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ABSTRACT

Both bulk and exfoliated graphitic carbon nitrides (labeled as gCN and TEX6) were tested as components of Cu-free friction composites. For this purpose, Cu-free phenolic resin-based friction mixtures with 4.5, 9, 13.5, and 18 wt% of gCN or TEX6 were used for the preparation of friction

composites in a form of pins using the hot-press molding technique. The friction-wear performance of the prepared pins was tested using a pin-on-disc device. The increase in gCN content in friction composites led to an increase in friction coefficient (COF), while the COF of samples with TEX6 showed the reverse effect. Pin wear decreased with gCN content up to 9 wt%, after this gCN content the wear rate increased. In the case of composites with TEX6 the wear rate decreased up to 13.5 wt.% of TEX6, and above this content increased slightly. The SEM analysis of the friction surfaces revealed better compaction and greater extension of the secondary contact plateau with increasing content of gCN and TEX6. The results obtained revealed that bulk g-CN behaves as rather as a mild abrasive, while exfoliated graphitic carbon nitride behaves as a solid lubricant.

KEYWORDS

Graphitic carbon nitride, Friction composites, Abrasives, Lubricants, Friction-wear performance.

Anchoring Pt single atom co-catalysts on CdS sensitized single crystal TiO₂ nanoflakes for efficient visible light photocatalytic hydrogen production

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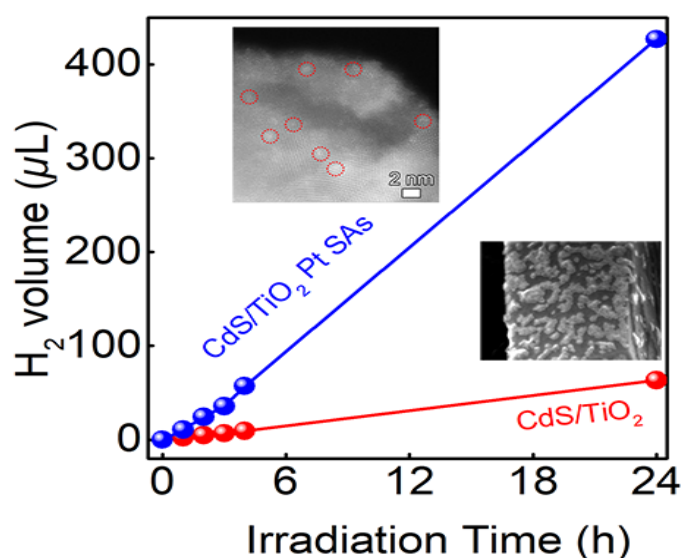
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ABSTRACT

Research on single-atom catalysts (SACs), which have isolated and individual metal atoms anchored on precisely selected supports, has spurred new interest in photocatalysis due to their increased catalytic activity and maximum atom utilization. SACs furnish a one-of-a-kind atomic platform for photocatalysis, not only by providing an increased number of active sites but also by improving the intrinsic activity of each active site. In this study, a Pt single atom was decorated on co-catalysts on CdS-sensitized single crystal anatase TiO₂ nanoflakes heterojunction for increased photocatalytic hydrogen production under visible light illumination. Firstly, vertically oriented TiO₂ nanoflakes were synthesized on a conductive FTO substrate using a one-pot hydrothermal method. Then visible-light-induced photocatalyst was developed by sensitizing with CdS NPs using the SILAR technique. Finally, Pt SAs were firmly anchored on the surface of CdS-sensitized ATNF using a “dark” deposition method. Under optimized conditions, the highest photocatalytic hydrogen evolution on Pt-anchored CdS-sensitized ATNF was 17.8 $\mu\text{L h}^{-1}$ under visible light illumination, which is 15.8 times higher than bare CdS on FTO. The enhanced performance was attributed to the synergistic effect of the Pt single atoms and the CdS/TiO₂ heterojunction, which promoted the separation of photogenerated electron-hole pairs and improved the efficiency of charge transfer. The results suggest that the Pt single atom decorated on CdS/TiO₂ heterojunction is a promising photocatalyst for efficient H₂ production under visible light illumination. The formed Pt-S bonds make the Pt-single atom decorated CdS/TiO₂ nanosheets photocatalyst stable for 120 h of use without losing photocatalytic activity.

KEYWORDS

TiO₂ Nanosheets, Photocatalysis, H₂ Evolution, CdS sensitization, Single-atom catalysis



Plasmonic and Semiconductor Photocatalysis for Solar to Energy Conversion

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ABSTRACT

Recently photocatalytic conversion of solar energy to valuable chemicals and fuels has become an internationally recognized ideal strategy for preventing environmental deterioration and sustainable energy generation. For this reason, plasmonic and semiconductor based photocatalysts have been widely explored to investigate their maximum potential for solar to fuel conversion efficiency. For this reason, we explored plasmonic property of titanium nitride (TiN) nanocubes decorated with platinum (Pt) nanocrystals for visible light enhanced hydrogen production activity. Next, we discovered highly efficient near infrared (NIR) plasmonic activity of TiN nanobars for hydrogen production, along with strong surface enhanced infrared absorption (SEIRA) effect operating in the Mid-IR region for furfural detection. Lastly, 2D TiO₂ bronze nanosheets decorated with Pt single atomic species (SAs) have been explored for photocatalytic hydrogen (H₂) production from water splitting reaction. Such maximum Pt SAs utilization lowers the catalyst cost, without sacrificing high performance.

KEYWORDS

Plasmonic, Titanium nitride, TiO₂ Bronze nanosheets, Pt single atomic species.

RESULTS AND DISCUSSION

Photocatalysts are the centre of the solar to fuel conversion technologies.¹ To explore this goal, plasmonic and semiconductor photocatalysts recently got huge attraction. Here, we investigated refractory, acid-resistant, fuel cell compatible gold-like localized surface plasmon resonance (LSPR) property of titanium nitride (TiN) nanocubes.² Hybrid antenna–reactor complex i.e., TiN–Pt nanocubes synthesised and utilised for efficient hydrogen (H₂) production from ammonia-borane dehydrogenation reaction under solar light. We demonstrated that at high light intensity, H₂ evolution is both an electron- and thermally driven process. Otherwise, upon light illumination, hot electrons are mainly generated in TiN and then transferred to the Pt surface, thus decreasing the energy requirement to access the transition state (TS) of the rate-determining step. Furthermore, light enhanced tandem nitro-reduction to amines also shows excellent potential of TiN/Pt nanocubes as plasmonic photocatalyst, mainly working in visible spectrum of solar light ($\lambda_{\text{max}} = 664 \text{ nm}$). As we all know, the sunlight reaching on earth surface consists broad range of photons with different energies in which near-infrared (NIR, 700–2500 nm), visible (vis, 400–700 nm) and ultraviolet (UV, <400 nm) lights appears around 49%, 46%, and 5% respectively. As NIR photons contribute high percentage in the solar spectrum, development of low cost, stable photocatalyst with efficient NIR light utilization is beneficial for solar to fuel conversion technologies. For that reason, we synthesised TiN nanobars and nanosheets morphology with LSPR absorption spectra extended from visible to NIR region (i.e., 500–2500 nm).³ The H₂ evolution rate of Pt nanocrystals greatly enhanced with the aid of 940 nm NIR plasmonic excitation of TiN nanobars. These plasmonic TiN nanobars also used for the detection of furfural molecule by providing a strong surface enhanced infrared absorption (SEIRA) effect operating in the Mid-IR region. Next, ultrathin two-dimensional (2D) TiO₂ bronze nanosheets (TiO₂-BNS) decorated with Pt single atomic species (SAs) have been explored for photocatalytic hydrogen (H₂) production from water.⁴ With low loading of Pt i.e., 0.05 wt%, TiO₂-BNS-Pt_{0.05} present around 10 times and 99 times higher photocatalytic rates than pristine TiO₂-BNS under solar and 365 nm UV-LED light irradiation respectively. Most excitingly, the in-situ formation of surface exposed defect sites (Ti³⁺) was observed for TiO₂-BNS under light illumination suggesting its significant role in enhancing the H₂ production rate. This self-activation and amplification behaviour of TiO₂-BNS can be extended to other photocatalytic reactions, thus providing a facile approach for fully utilizing noble metal catalysts via the successful formation of SAs.

REFERENCES

1. S. Rej, M. Bisetto, A. Naldoni, P. Fornasiero, J. Mater. Chem. A, 9 (2021), 5915–5951.
2. S. Rej, L. Mascaretti, E. Y. Santiago, O. Tomanec, S. Kment, Z. Wang, R. Zbořil, P. Fornasiero, A. O. Govorov, A. Naldoni, ACS Catalysis, 10 (2020), 5261–5271.
3. S. Rej, E. Y. Santiago, O. Baturina, Y. Zhang, S. Burger, Š. Kment,; A. O. Govorov, A. Naldoni, Nano Energy (104) 2022, 107989.
4. S. Rej, S. M. H. Hejazi, Z. Badura, G. Zoppellaro, S. Kalytchuk, Š. Kment, P. Fornasiero, A. Naldoni, ACS Sustainable Chem. Eng. 10 (2022), 17286–17296.

3D X-RAY MICROSCOPY (XRM) for Battery application

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ABSTRACT

The increasing amount of mobile electronic devices (such as smartphones, smartwatches, Bluetooth headphones, pens and many more) and the growing adoption of electromobility requires the use of highly efficient electrochemical energy storage devices such as batteries and conversion devices such as fuel cells. With ever increasing demands on range and storage capability, the limits of what is technically feasible are being pushed further every day. A variety of measurement systems are available to overcome the associated technical and material hurdles. But only XRM (X-Ray Microscopy), a CT (computed tomography) based imaging technology, allows the user to non-destructively inspect energy storage devices for defects. This can be new production processes, new material composition or the effect of long-term testing on the internal components.

KEYWORDS

NDT (Non-Destructive Testing), X-ray, XRM (X-ray Microscopy), CT (Computer Tomography).

INTRODUCTION

XRM is an imaging technic based on Computer tomography (CT). It is a non-destructive imaging technique that allows scientists to examine the internal structure of materials in great detail, down to an object size of 500 nm. It works by using X-rays to create a 3D image of an object's internal structure. The technique is similar to medical CT scanning but adapted for use with materials.

The process of CT scanning begins with placing an object on a rotating platform, which moves the object through a narrow beam of X-rays. The X-rays pass through the object and are detected on the other side by an array of sensors. The data from the sensors is used to create a 2D image of a slice of the object. By taking many such images from different angles, the computer can reconstruct a 3D image of the object's internal structure.

The resulting 3D image is made up of a series of small cubes called voxels, which represent the data collected by the sensors. The size of the voxels can vary, depending on the resolution of the imaging system and the size of the object being scanned. The voxels can be thought of as 3D pixels, with each voxel representing a small volume element within the object.

The data collected during the CT scanning process is stored in a voxel data set, which can be analysed using specialized software to extract information about the object's internal structure. This data can be visualized as a 3D image, which can be rotated, sliced, and zoomed to examine the object from any angle.

In material science, CT scanning is used to examine a wide range of materials, from metals and ceramics to composites and biological materials. By examining the internal structure of these materials, scientists can gain insights into their properties and behaviour. For example, CT scanning can be used to detect cracks and defects in batteries, which can help improve the design and quality control of manufacturing processes.

RESULTS AND DISCUSSION

At this point I would like to quote an example from one of our customers, the University of Oldenburg, who impressively demonstrated how XRM can make a significant contribution to research with their study: Application of X-Ray Computed Tomography Imaging in the Evaluation of Aging Effects of Batteries and Fuel Cell Components.

The membrane electrolyte assembly (**MEA**) is the core component of the fuel cell (FC) that converts chemical into electrical energy and heat. In this work the degradation process of a high temperature polymer electrolyte membrane (HT-PEM) FC is demonstrated by analysing the influence of contact pressure cycling applied to MEAs. The mechanical changes of the MEA due to different operation strategies between beginning of life and end of test can be detected and visualized by means of microCT investigations [1][2].

The bipolar plate (**BPP**) is an important component for vanadium redox flow batteries (VRFB) as it serves as physical separator and electrical conductor of adjacent cells in a stack. These components are usually carbon based composite materials with complex structure. In the VRFB the BPP can be exposed to acidic media and harsh operational conditions [3]. Thus during battery operation the BPP can undergo significant aging. In order to study the aging propagation within the BPP bulk, pristine and aged graphite-polypropylene composite BPP samples were investigated using microCT.

High resolution nanoCT is also a suitable method for characterization of aging phenomena in **cathodes** for Li-ion batteries. In general, the cathodes for the Li-ion battery technologies consist of active materials such as LiCoO_2 , LiFePO_4 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, conductive additives and polymer binders [4]. Due to the difference in the X-ray absorption coefficients of the active materials and the binder-conductive additive matrix it is possible to perform separate analysis of both components with the nanoCT.

METHOD

MEA: Two studies on contact pressure cycling of HT-PEM MEA consisting of 5 layers with a nominal active area of 25 cm^2 were carried out. The first test was performed in-situ within a test station under real FC operation conditions (H_2 and air supply, current density of 0.2 A/cm^2). The second test was done in a small ex-situ compression unit that was specially developed to fit into the microCT device and that was used without FC operation mode [1][2]. Three repetitive cycles of compression variations using 0.2, 0.5, 1 and 1.5 MPa have been applied in both systems.

BPP: Overload charging conditions were executed on a BPP with an active surface area of 1 cm^2 in an ex-situ electrochemical cell using a current density of 100 mA/cm^2 for 3 h in the positive VRFB electrolyte consisting of 1.6 M vanadium in 2 M sulfuric acid and a state of charge of 90 %.

Cathode: Commercially available 2 Ah Li-ion batteries in pouch cell format were continuously charged and discharged in climatic chambers at 25°C within the voltage range 2.8 to 4.0 V at a C-rate of 1 until reaching different states of health (SOH). After the cell disassembly the different cathodes were characterized using high resolution nanoCT.

CT scanning was performed in order to analyse the inner microstructures of the mentioned single components in energy storage and conversion devices. For the investigations high resolution Skyscan 2011 nanoCT and Skyscan 1172 microCT were applied. 3D reconstruction, image processing, visualization and data analysis were performed by means of included software of the micro and nanoCT equipment (NRecon, DataViewer, CTVox, CTAn, Bruker, Belgium). The scanning parameters are shown in Table 1.

RESULTS

MEA: A cross-sectional image of a MEA compressed with 0.2 MPa serves as ante-mortem reference sample (Figure 1a). After completing three compression cycles in the ex-situ compression device, the mechanical changes can be clearly recognized by many defects and gaps within the catalyst layers (Figure 1b). In comparison, the post-mortem imaging analysis of the MEA, which was treated in-situ in the FC test station, is shown in Figure 1c. Apparently, the result is quite similar to that one gained via ex-situ compression tool. However, here the defect catalyst layers are going through the membrane resulting in short-circuit formation. By comparing these in- and ex-situ post-mortem microCT analyses, it is obvious that the influence of compression cycling is immense while the additional effect of FC conditions is only minor to the mechanical degradation of the MEA [1][2].

BPP: The 3D image of a pristine BPP shows characteristic features of the composite material. It consists of a homogeneously ordered bulk material with integrated segments of local higher density matter and a rough surface texture (Figure 2a). The overload charging conditions led to a damaged surface with increased open porosity, cracks and material loss drawn through the bulk material due to surface oxidation and subsequent CO₂ evolution [5] (Figure 2b). By means of microCT it is possible to visualize the depth of aging effects and the appearance and formation of corrosion events.

Cathode: The quantitative evaluation of the nanoCT images shows a decrease in the average particle size and an increase in number of particles of LiCoO₂ with decreasing SOH of the battery (Figure 3). By means of nanoCT technique the active material particle breaking upon aging was suggested as aging mechanism [6]

Table 1. Overview of scanning parameters.

Parameter	MEA	BPP	Cathode
Device	microCT	microCT	nanoCT
Source Voltage [kV]	78-82	80	80
Resolution [μm]	2.5 – 3.0	1.44	1.00
Rotation step [$^{\circ}$]	0.15	0.20	0.18
Averaging frames	4	5	6
Diameter sample size [mm]	6	16	0.75

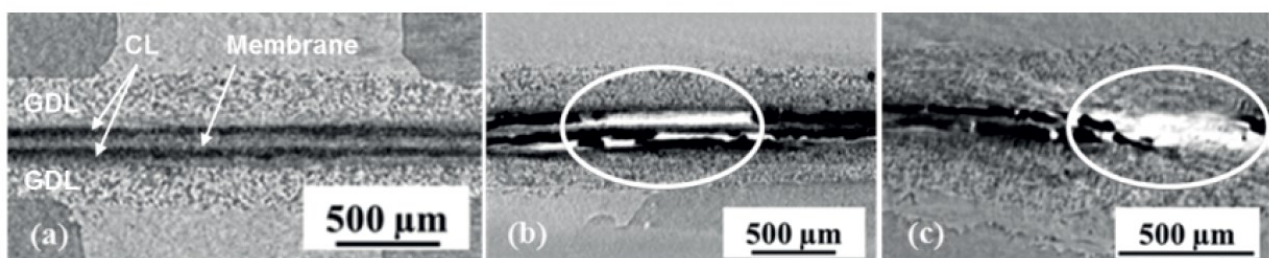


Figure 1: 2D microCT images of MEAs (DataViewer), (a) ex-situ ante-mortem, (b) ex-situ post-mortem and (c) in-situ post-mortem [1]. CL, catalyst layer; GDL, gas diffusion layer.

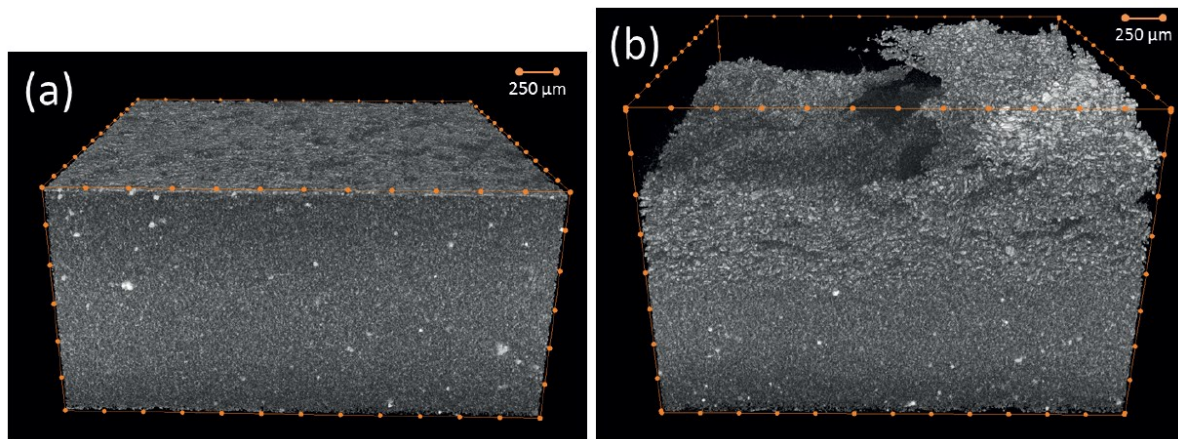


Figure 2: Graphite-polypropylene composite BPP (DataViewer) (a) before and (b) after aging.

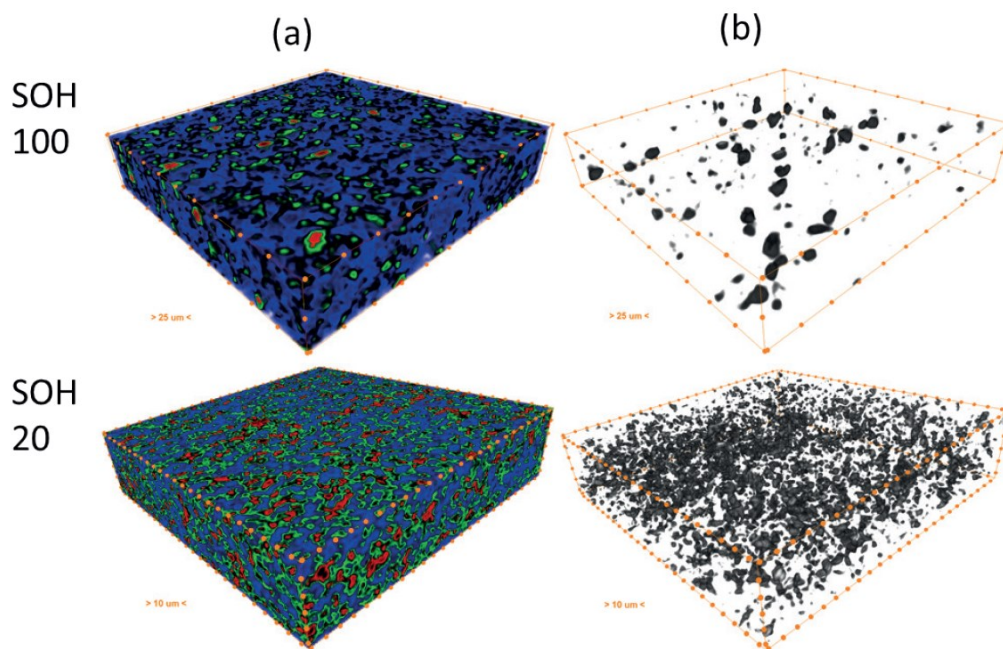


Figure 3: CT images (DataViewer) of (a) LiCoO₂ cathodes with different SOH; (b) Objects with highest densities in the LiCoO₂ cathodes are pointed out [6].

CONCLUSION

The lifetime of fuel cells and energy storage systems is determined by alteration and corrosion of single system components. In order to investigate such critical influences on integral components one assessment criteria is the comparison of interior morphological structures between ante- and post-mortem specimens. Therefore, X-ray micro and nanoCT are powerful and essential tools to analyze their inner texture, characteristics and aging effects. It was shown that CT is applicable to investigate components such as MEAs, BPPs and electrodes from fuel cells and energy storage systems and to give evidence for their aging mechanisms.

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REFERENCES:

1. F.J. Pinar, M. Rastedt, N. Pilinski, P. Wagner, "Effect of Compression Cycling on Polybenzimidazole-based High-Temperature Polymer Electrolyte Membrane Fuel Cells", *Fuel Cells*, 140-149, 2015.
2. M. Rastedt, D. Schonvogel, P. Wagner, "Impact of Load Cycling at High Current Densities on the Degradation Behavior of Membrane-Electrode-Assemblies", *ECS Transactions*, 741-753, 2014.
3. S. Rudolph, U. Schröder, I. M. Bayanov, G. Pfeiffer, "Corrosion Prevention of Graphite Collector in Vanadium Redox Flow Battery" *Journal of Electroanalytical Chemistry*, 93-98, 2013.
4. B. Lestriez, "Functions of Polymers in Composite Electrodes of Lithium Ion Batteries", *Comptes Rendus Chimie*, 1341-1350, 2010.
5. H. Liu, L. Yang, Q. Xu, C. Yan, "Corrosion Behavior of a Bipolar Plate of Carbon-Polythene Composite in a Vanadium Redox Flow Battery", *RSC Advances*, 5928-5932, 2015.
6. L. Komsyyska, S. A. Garnica Barragan, M. Lewerenz, D. Ledwoch, O. Osters, "Detecting Aging Phenomena in Commercial Cathodes for Li-ion Batteries using High Resolution Computed Tomography", *Advances in Science and Technology*, 158-163, 2014.

Conductive ceramics for application in batteries

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ABSTRACT

It has now become evident that ceramics exhibit the full spectrum of electrical properties spanning the gap from superconducting to insulating electronic conductors and from fast ionic to insulating ionic conductors. In many cases, it is the unique combination of desired electrical properties together with the characteristic stability of ceramics that renders them the obvious choice for many technological applications. An all-solid lithium rechargeable battery, which would find many applications if available, is one of the reasons for research of conductive solids. Fast Me^+ -conducting ceramic electrolytes should be contemplated with respect to their electrical properties and crystal structure. Both non-oxide-based ceramics and oxide materials¹ are considered, and the possibilities of further development are pointed out - for example, the preparation of the electrolyte by the thin film technique.

The note of prof. J. Goodenough that "Ion mobilities are greatly increased by aliovalent doping, which introduces mobile vacancies into occupied sites or mobile interstitial ions into empty sites. However, although analogous to doping in semiconductors, the two phenomena differ in an important respect: itinerant electron charge carriers are weakly trapped impurities that introduce them, while mobile ions tend to be strongly trapped."³ is key element for the ceramic/glass materials for next generation of Me ion batteries.

KEYWORDS

Conductive ceramic, solid electrolytes, batteries, structure, stoichiometry

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REFERENCES

1. Huang K, Wan J, Goodenough JB. Journal of materials science. 2001 ;36:1093-8..
2. Duan C, Huang J, Sullivan N, O'Hayre R. Applied Physics Reviews. 2020 3;7(1):011314..
3. Goodenough JB.. Solid State Ionics. 1997 1;94(1-4):17-25.

Chemically modified nanofibrous membranes for CO₂ capture

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ABSTRACT

Nanofibrous materials prepared by electrospinning provide a wide range of applications from biomedical applications to filtration and separation media to catalytic membranes. A key problem in the preparation of nanofiber materials for specific functions is the chemical modification of nanofibers' surfaces. ^[1,2] In this work, we will focus on electrospun polymer (PUR and PAN) nanofibrous membranes modified with different types of amines for CO₂ capture. Electrospinning technology can be used in different variations and in this case we will deal with two main technologies for the preparation of 2D nanofibrous membranes: needle spinning and wire spinning. It turns out that the arrangement of the spinning device has a significant effect on the structure, properties and functionality of the membranes. We will also discuss two approaches to the chemical modification of nanofibrous surfaces: (1) one-step technology, i.e. adding a modifying substance directly into the polymer solution and (2) postspinning modification - subsequent deposition of the modifying substance on the nanofibrous membrane, possibly with a previous plasma or with UV activation of the polymer surface. The effect of all these technological variations will be demonstrated on sorption capacity of membranes based on polyurethane and polyacrylonitrile modified with amines and MOFs.

KEYWORDS

Electrospinning, nanofibers, carbon dioxide, adsorption

INTRODUCTION

Nanofibers, prepared today by the most industrially used method - electrostatic spinning, have unique properties such as a porous structure, a large specific surface area and excellent mechanical properties. These properties predetermine them for application use, such as filter media for the capture of various types of substances, especially gases, but also pathogens, heavy metals, dyes and other undesirable components in air or water. ^[3,4]

To increase the application efficiency of nanofibrous materials, which in themselves show a certain ability to capture various substances - according to the type of polymer material, preparation parameters, defects, etc., the solution is modification, which, by choosing a suitable modifying substance, contributes to the amount of particles or substances captured. The simplest method of modification is to add modifying substances to the spinning solution before electrospinning, but this method is ineffective in some cases and will cause unwanted clogging of the pores of the nanofibrous textile rather than improving the capture ability. In such cases, subsequent modification is chosen, which, however, is more demanding in terms of time requirements, the need for additional tools and chemicals, and therefore financial requirements.

For the capture of acidic gases, such as carbon dioxide or sulfur dioxide, those that contain functional groups of the opposite character, i.e. basic, are usually chosen as modifying substances, which include amines and amine groups containing other substances or particles. ^[5, 6]

For this work, the amines diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and hexadecylamine (HDA) were used to modify polyacrylonitrile (PAN) and polyurethane (PU) nanofiber textiles in one step and subsequently. Metal organic frameworks (MOFs) of the type UiO-66 and NH₂-UiO-66 prepared by solvothermal synthesis were tested as additional modifying substances (only in one step).

EXPERIMENTAL/THEORETICAL STUDY

Electrospinning techniques

Electrospinning is an industrially applicable method of preparing fibers on a micro to nano scale by applying a high voltage of the order of tens of kV to a polymer solution with suitable properties (viscosity, conductivity, surface tension), which in the ideal case leads to the overcoming of surface forces by electrostatic ones and to drawing charged jets of polymer solution towards the oppositely charged or grounded collector electrode. During the flight of the fiber, the solvent evaporates, after its complete evaporation, a rigid fiber and subsequently a non-woven fiber fabric is formed on the collector.

Electrospinning can have different experimental setups, basically two basic types are distinguished - needle spinning and needleless electrospinning. Both of these methods were used and compared in this work for the preparation of nanofibers. The difference in both techniques is that:

Needle electrospinning - the polymer solution exits the capillary under pressure;

Needleless electrospinning - electrospinning from the free surface of the polymer, which is used to cover the surface of a wire or a rotating cylinder. ^[7-12]

Characterization methods

The following techniques were used to characterize the samples and compare the preparation technologies:

Scanning electron microscopy (SEM and HRSEM) for the analysis of the morphology of textiles and individual fibers;

X-ray diffraction to assess the crystal structure;

Infrared spectroscopy for checking the presence of amine functional groups and the chemical binding of amines to the polymer chain;

Air permeability measurement to analyze the amount of gas that can pass through the functional material and thus be sorbed;

CO₂ sorption capacity - a key characteristic for this work, according to which it was assessed which technology and also modification leads to the best results, the measurement was made by the BET CO₂ adsorption/desorption isotherm.

RESULTS AND DISCUSSION

Structure and morphology of textiles and nanofibers

Figure 1 compares PAN nanofibrous fabrics modified with different amines. The higher defectivity of samples **1A - C** prepared by needle spinning compared to sample **1D** prepared by needleless spinning can be observed here. The difference in the preparation of samples by both techniques was mainly in the concentration of the polymer for spinning and also in the general difference in both techniques, i.e. that in needle spinning the solution is forced under pressure through the needle electrode. This pressure then affects the arrangement of the fibers in the fabric and the presence of defects. In general, larger fiber diameters are also typical for needleless spinning, as can be seen from **Figure 1D**.

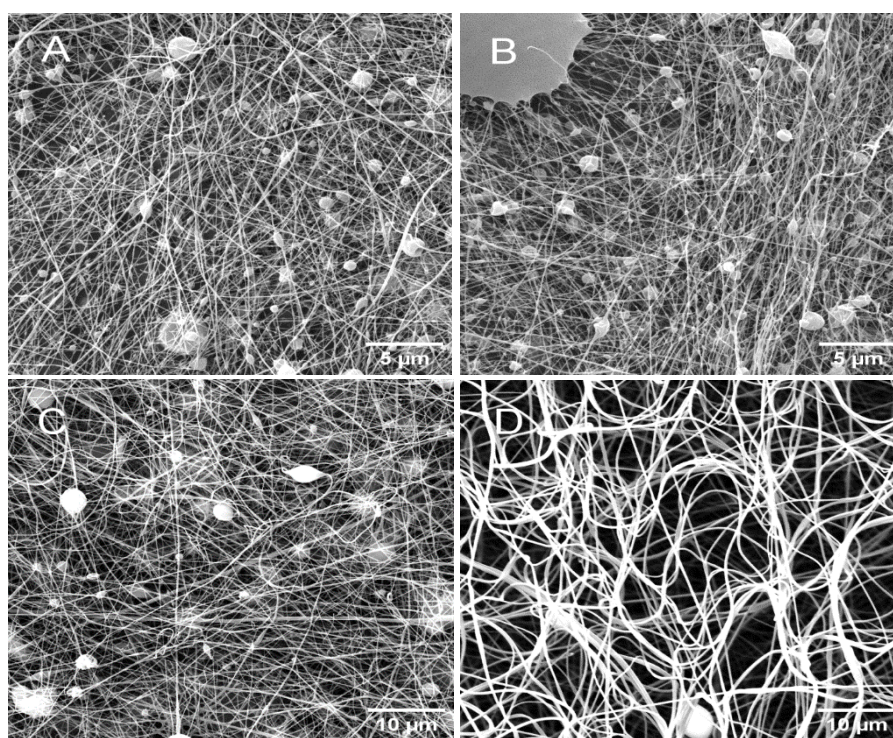


Fig. 1 – SEM images (primary magnification 5kx (A-B) and 10kx (C-D)) - comparison of membrane structure for needle (A - C) and wire technology (D) of electrospinning for amine modified PAN samples: (A) HDA 0.5% w/w, (B) DETA 5% w/w, (C) TETA 2% w/w (needle) and (D) TETA 2% w/w (wire).

Particle modifications of UiO-66 and $\text{NH}_2\text{-UiO-66}$ MOFs were shown to be ineffective for improving CO_2 capture, as it was revealed that a one-step modification, i.e. adding these particles to the spinning solution, causes their encapsulation into the polymer material during spinning. This limits their function as sorbents, and even though MOFs attached in this way are very stable, they do not improve CO_2 capture values. Figure 2 shows MOF particles UiO-66 prepared by solvothermal synthesis (**2A**), their incorporation into a nanofibrous structure (**2B**) and a detail showing the coating of one particle with a polymer material (**2C**).

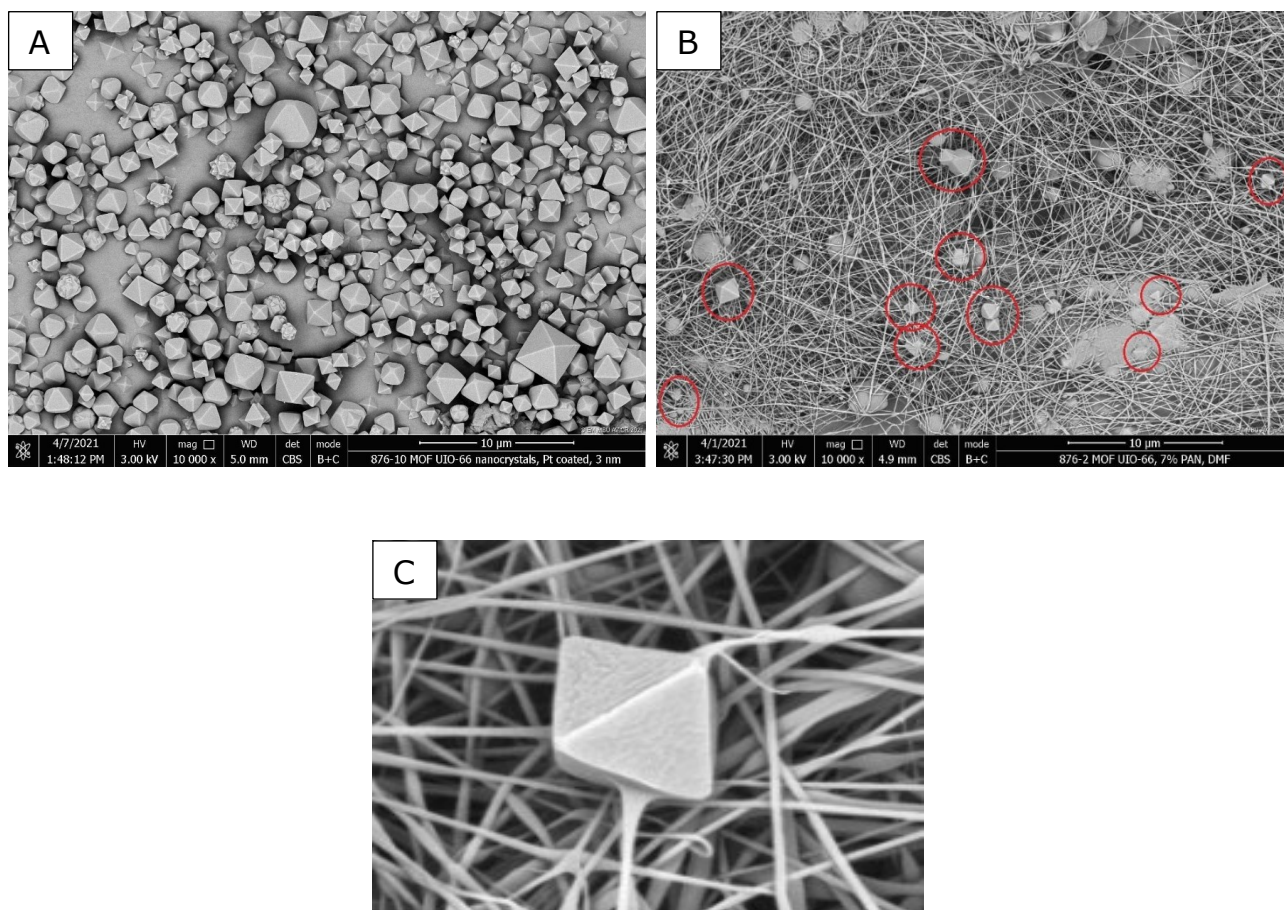


Figure 2 - Prepared MOF particles (A), their incorporation into a nanofibrous structure (B) and a detail of their encapsulation into a polymer material (C).

Table 1 - Fiber diameters, air permeability and sorption capacity for amine- and MOF-modified samples prepared by wire spinning and needle spinning for PAN and PU polymers.

Sample	Mean air permeability	CO ₂ sorption capacity
	[l/m ² /s]	[mmol/g]
PAN_wire_pristine	19.8 ± 0.30	0.19 ± 0.02
PAN_wire_TETA_1%	15.5 ± 0.80	0.30 ± 0.04
PAN_wire_TETA_2%	53.0 ± 4.70	0.51 ± 0.05
PAN_wire_TEPA_1%	18.7 ± 0.60	0.39 ± 0.04
PAN_wire_TEPA_2%	48.3 ± 1.20	0.52 ± 0.25
PAN_needle_pristine	3.17 ± 0.55	0.22 ± 0.03
PAN_needle_TETA_1%	1.8 ± 0.9	0.25 ± 0.03
PAN_needle_TETA_2%	2.3 ± 1.3	0.18 ± 0.02
PAN_needle_TETA_3%	2.8 ± 1.4	0.35 ± 0.04
PAN_needle_TETA_5%	68.5 ± 2.7	0.43 ± 0.04
PAN_needle_TEPA_1%	2.3 ± 1.3	0.30 ± 0.03
PAN_needle_TEPA_2%	4.9 ± 0.5	0.41 ± 0.04
PAN_needle_TEPA_3%	2.6 ± 1.0	0.27 ± 0.03
PAN_needle_TEPA_5%	19.2 ± 2.8	0.30 ± 0.04
PAN_needle_HDA_0.1%	1.9 ± 0.3	max. 0.19 ± 0.02
PAN_needle_HDA_0.5%	1.9 ± 0.3	
PAN_needle_DETA_0.5%	2.0 ± 0.4	max. 0.25 ± 0.03
PAN_needle_DETA_5%	1.9 ± 0.2	
PAN_needle_DETA_10%	1.8 ± 0.3	
PAN_needle_UiO-66_0.5%	3.2 ± 0.5	max. 0.19 ± 0.02
PAN_needle_UiO-66_1%	2.9 ± 0.4	
PAN_needle_UiO-66_2%	2.9 ± 0.3	
PAN_needle_NH ₂ -UiO-66_0.5%	2.9 ± 0.4	max. 0.23 ± 0.03
PAN_needle_NH ₂ -UiO-66_1%	3.8 ± 0.6	
PAN_needle_NH ₂ -UiO-66_2%	2.6 ± 0.6	
PUR_wire_pristine	2.0 ± 0.2	0.12 ± 0.04
PUR/TETA_1%	49.9 ± 4.0	0.36 ± 0.08
PUR/TETA_5%	129.7 ± 20.0	0.36 ± 0.09
PUR/TEPA_1%	79.8 ± 10.0	0.30 ± 0.08
PUR/TEPA_5%	20.0 ± 3.0	0.62 ± 0.10

Polymer-amine bonding, sorption capacity and air permeability

Figure 3 shows the organic groups present in the amine-modified samples, the most important being the amine groups highlighted in red, which confirm successful amine modification.

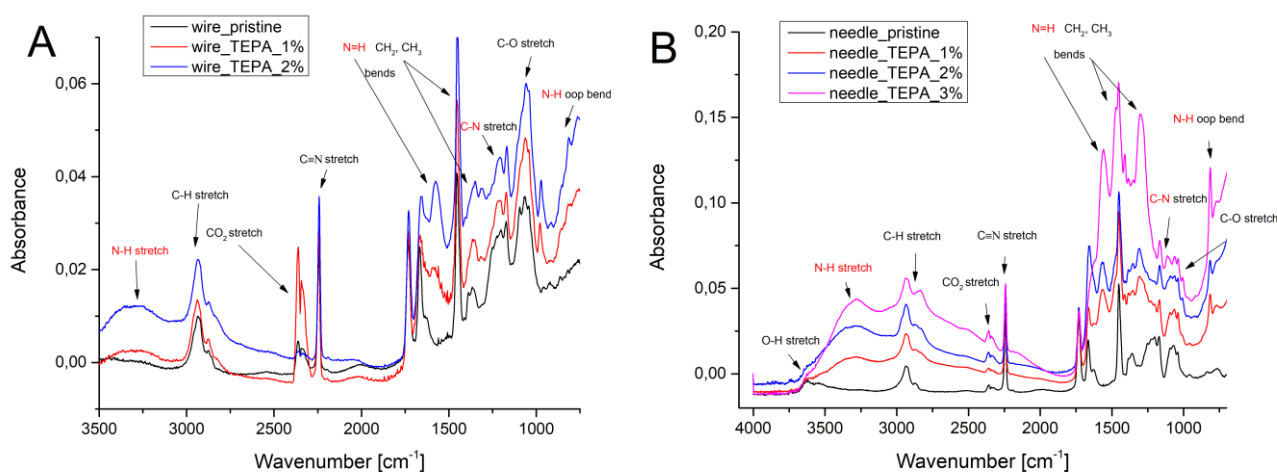


Fig. 3 - IR spectra for TEPA modified samples prepared by (A) wire spinning and (B) needle spinning

Air permeability and sorption capacity

For the development of functional materials of this type, an essential parameter is the air permeability, i.e. the amount of air that can pass through the sample and thus be in contact with the surface of the fibers and the functional groups intended for capture. The sorption results are in **Table 1**.

CONCLUSION

This work was focused on the design and creation of a functional nanofibrous material based on polyacrylonitrile (PAN) and polyurethane (PUR) by one-step modification with different types of amines and MOF particles. This method of modification is more accessible for subsequent production, as it is accompanied by a minimum of technological steps. The best materials appear to be those that have been modified by amines with the largest amount of functional amine groups, i.e. triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). The amine modification diethylenetriamine (DETA) and hexadecylamine (HDA) caused pore clogging and reduced air permeability rather than improving the sorption capacity of the material. Particle modification of MOFs appears to be ineffective, as during spinning the particles are coated with polymeric material and their functionality for capture is inhibited.

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REFERENCES

1. Hoskovec J, Capkova P, Vostiňáková M, Ryšánek P, Kaule P, et al. Permeable Membranes PUR/TETA and PUR/TEPA for CO₂ Capture Prepared with One-Step Electrospinning Technology; *Fibers* 2022;10:100
2. Ryšánek P., Malý M. Čapková P., et al Antibacterial modification of nylon-6 nanofibers: structure, properties and antibacterial activity; *J Polym Res* (2017) 24:208

3. Yalcinkaya F, Yalcinkaya B, Jirsak O. Dependent and Independent Parameters of Needleless Electrospinning. 2016. p. 67-93.
4. Nataraj SK, Yang KS, Aminabhavi TM. Polyacrylonitrile-based nanofibers—A state-of-the-art review. *Progress in Polymer Science*. 2012;37(3):487-513.
5. Khulbe KC, Matsuura T. The Advances of Electrospun Nanofibers in Membrane Technology. *Journal of Membrane Science and Research*. 2020;6(3):251-68.
6. Toriello M, Afsari M, Shon HK, Tijing LD. Progress on the Fabrication and Application of Electrospun Nanofiber Composites. *Membranes [Internet]*. 2020; 10(9).
7. Forward KM, Rutledge GC. Free surface electrospinning from a wire electrode. *Chemical Engineering Journal*. 2012;183:492-503.
8. Zhou F, Gong R, Porat I. Needle and Needleless Electrospinning for Nanofibers. *Journal of Applied Polymer Science*. 2010;115:2591-8.
9. Yalcinkaya F, Jirsak O. Comparison of Needle and Roller Electrospinning System of Polyvinylbutyral. *Journal of Nanomaterials*. 2012;2012.
10. Jirsak O, Petr S, Filip S, Jakub H, Chaloupek J. Polyamic Acid Nanofibers Produced by Needleless Electrospinning. *Journal of Nanomaterials*. 2010;2010.
11. Yalcinkaya F, Yalcinkaya B, Jirsak O. On the Measured Current in Needle- and Needleless Electrospinning. *Journal of nanoscience and nanotechnology*. 2013;13:4672-9.
12. Zhu G, Zhao L, Zhu L, Deng X, Chen W. Effect of Experimental Parameters on Nanofiber Diameter from Electrospinning with Wire Electrodes. *IOP Conference Series: Materials Science and Engineering*. 2017;230:012043.

Heat treated phosphate ceramics for energy applications

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ABSTRACT

An all-solid-state battery would provide a safe power source with high-temperature performance¹. One requirement for this technology is a solid Li⁺-ion electrolyte with a Li⁺-ion conductivity $\sigma_{\text{Li}} > 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ that is stable on contact with a lithium anode. Ceramics based on phosphate $\text{A}_x\text{M}_2(\text{PO}_4)_3$ (A = Li, Na and M = Cr, Zr, Fe, Zn etc.) compounds with the framework have been reported to be fast alkali-ion conductors².

A total of 3 types of ceramics with a combination of metals Li, Cr and Na were studied. The synthesis of advanced phosphate ceramics followed by heat treatment was studied in terms of morphology and phase composition using characterization techniques. Scanning electron microscopy (SEM) revealed a difference in morphology for different ceramic compositions ranging from very well crystallized strength to partially amorphous morphology. The corresponding phase analysis using the X-ray diffraction (XRD) method provided information on the non-uniform composition of the synthesized material and the unification of the phases after heating. XRD analysis confirmed the highly crystalline state of the phosphate ceramics. The application options will be drafted.

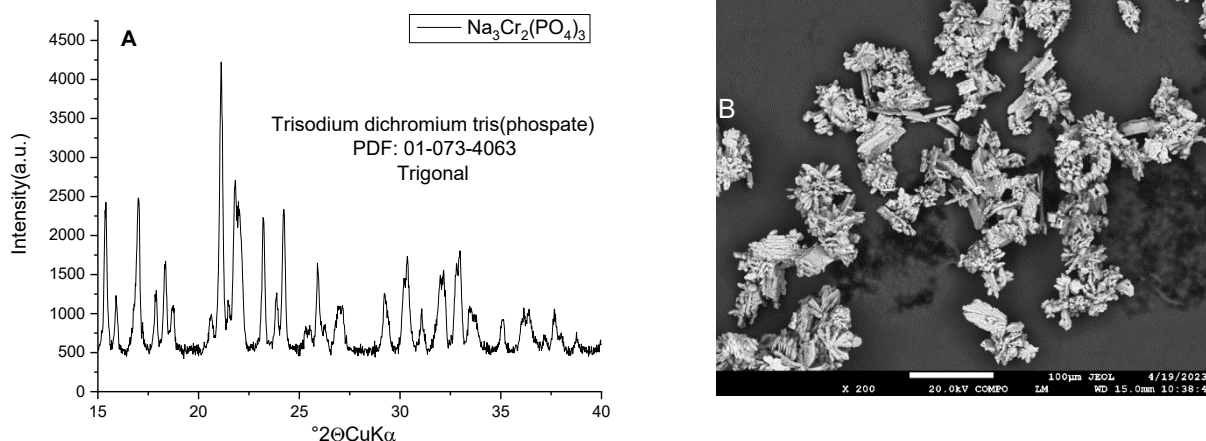


Figure 1A: XRD pattern of synthesized phosphate ceramics; B: SEM image of synthesized phosphate ceramics

KEYWORDS

Phosphate ceramics, heat treatment, morphology, structure

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REFERENCES

1. JB. Goodenough, Nature Electronics. 1 (2018) 204.
2. H. Xie, Y. Li, JB. Goodenough, RSC Advances. 1(9) (2011) 1728-1731.

Optimization of direct laser lithography exposition by modelling of Gaussian beam

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ABSTRACT

Various types of micro-structures can be prepared using direct writing laser lithography. Most of these structures are optical diffractive components, which are in high demand. However, implementation of the desired structure size and shape may be problematic due to the different non-linear responses of different types of photoresists to the exposure dose. Optimizing lithographic

parameters and understanding photoresist chemistry are needed to solve these issues. To characterize the exposure process, the lithographic laser beam is approximated by the mathematical model of the Gaussian beam. Subsequently, the model is used to make a simulation of the real lithographic exposure with photoresist optical constants. By comparing the simulation with the measured data, the optical properties of the photoresist (such as beam divergence and absorption) can be described, and optimization of required parameters can be performed.

KEYWORDS

Direct laser lithography, diffractive optic, microstructure, Gaussian beam

Methods of Lithium-ion Battery Recycling

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ABSTRACT

In recent years, there has been an increasing effort to reduce greenhouse gas concentrations in the atmosphere leading to a significant increase in the construction of renewable energy sources and the use of electricity. The relative ease of obtaining electricity from photovoltaic panels is coupled with the possibility of storing it in battery systems or using it directly to charge, for example, batteries used in cars. Nowadays the application of energy storage has become the most widespread based on lithium-ion batteries (LIBs) ^{1,2}. With the rapid development of this industry, it is also necessary to focus on the disposal and recycling of end-of-life lithium batteries.

To achieve maximum performance, durability and safety, many systems have been developed that are referred to as LIBs. The basic elements of the battery are current collectors, a cathode, an anode, an electrolyte, and a diaphragm (separator). A cathode, an anode, and a diaphragm (separator) are now made from various intercalated Li compounds (a cathode - LiTiS_2 , $\text{Li}_{1-x}\text{CoO}_2$, LiMn_2O_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; an anode - carbon, graphite, LiC_6 ; electrolyte - LiPF_6 , LiBF_4 , LiAsF_6 etc.)⁴. An electrolyte solvent is another key component which can be made from ethylene carbonate, propylene carbonate etc.

The aforementioned information shows, that it will not be easy to develop a recycling method applicable to all types of LIBs. In general, recycling involves three basic stages: discharging, mechanical separation, and element recovery by hydrometallurgical, pyrometallurgical, microbiological, and electrochemical. Therefore, using only one of the recycling techniques to obtain pure elements contained in the batteries, is impossible. Although the number of research papers has increased dramatically in recent years, it is not entirely clear how many techniques are used in practice. The question and the challenge of the recycling process remain the energy and economic aspects of the whole process.

This study aims to contribute to point out some difficulties of LIBs recycling.

KEYWORDS

lithium-ion batteries, recycling

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REFERENCES

1. G. Harper, Sommerville R, Kendrick E, Driscoll L, Slater P, Stolkin R, et al. Recycling lithium-ion batteries from electric vehicles. *Nature* 2019; 575(7781): pp. 75–86.
2. D. Larcher, Tarascon JM. Towards greener and more sustainable batteries for electrical energy storage. *Nat Chem* 2015; 7(1), pp 19–29.
3. Seoa Kim, Jaeyeon Bang, Junsang Yoo, Youngjun Shin, Jihyeon Bae, Juyeon Jeong, Kyumin Kim, Peng Dong, Kyungjung Kwon, A comprehensive review on the pretreatment process in lithium-ion battery recycling, *Journal of Cleaner Production* 294 (2021) 126329
4. T. Guangdong, Yuan G., Aleksandrov A., Zhan T., Li Z., Fathollahi-Fard A. M., Ivanov M. *Sustainable Energy Technologies and Assessments* 53 (2022) pp.102447

Poster presentations (PP):**Synthesis of carbon spheres by chemical vapor deposition with overpressure**

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ABSTRACT

We report on the synthesis of carbon spheres by chemical vapor deposition method with overpressure. The carbon spheres have a diameter of less than a micrometer, good spherical shape, and smooth morphology. Its utilization could be found as a lubricant additive for the improvement of friction and wear resistance.

KEYWORDS

Chemical vapor deposition, chemical vapor deposition with overpressure, carbon spheres, carbon black

INTRODUCTION

Since the first hypothetical explanation of carbon sphere formation¹, the research has had a long journey. The carbon spheres were synthesized through many routes, from chemical vapor deposition and its gas phase synthesis² to hydrothermal synthesis with polymerization of monosaccharides following the nucleation of carbon spheres under high pressure, temperature, and long time³.

Alazami et al. synthesized carbon spheres that could be utilized as an additive to lubricant oil for their smooth surface to improve tribology⁴. Khodabakhshi et al. synthesized porous carbon spheres by the CVD method under certain conditions and precursors that were then used for CO₂ absorption⁵. Jin et al. modified already synthesized carbon spheres with a graphitization step and tested them as lithium anode material⁶.

The synthesis of carbon spheres by chemical vapor deposition can be done with⁷ a catalyst substrate or without it¹. The established routes of chemical vapor deposition synthesis of free carbon spheres can be different from low-pressure chemical vapor deposition (LPCVD)¹ to atmospheric pressure chemical pressure deposition (APCVD)⁸ and to high-pressure chemical vapor deposition (HPCVD)⁹. Herein we refer to chemical vapor deposition with overpressure that has already been used to synthesize pyrolytic carbon⁷.

EXPERIMENTAL/THEORETICAL STUDY

The setup and process of the chemical vapor deposition with overpressure is described in the previous article¹⁰. Briefly, the mixture of ethylene (C₂H₄ 3.0; SIAD) as a precursor and argon (Ar 5.0; SIAD) as an inert gas, have flowed into the quartz reactor to overpressure 2-3 atm. The synthesis took place at a temperature in a range of 800-1000 °C from dozens of minutes to a few hours. The ratio between

precursor and inert gas varied from 1:1 to 1:0. Scheme of chemical vapor deposition with overpressure can be seen in Figure 1.

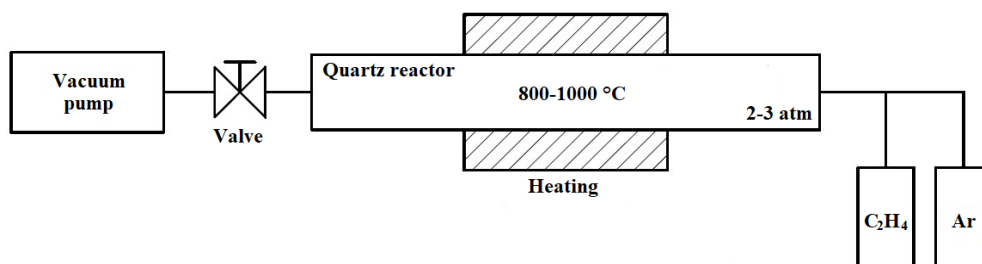


Fig. 1. Scheme of chemical vapor deposition with overpressure. Edited from Czernek et al.¹⁰.

RESULTS AND DISCUSSION

Many experiments were carried out to optimize the synthesis of carbon spheres in the setup of chemical vapor deposition with overpressure. During the synthesis step, an abundance of hydrocarbon precursor has pyrolyzed in high-temperature conditions, and nucleation of carbon spheres takes place. In Figure 2 can be seen carbon spheres that were synthesized for 30 minutes at a temperature of 800 °C with pressure ~3 atm and a ratio of gases 1:1.

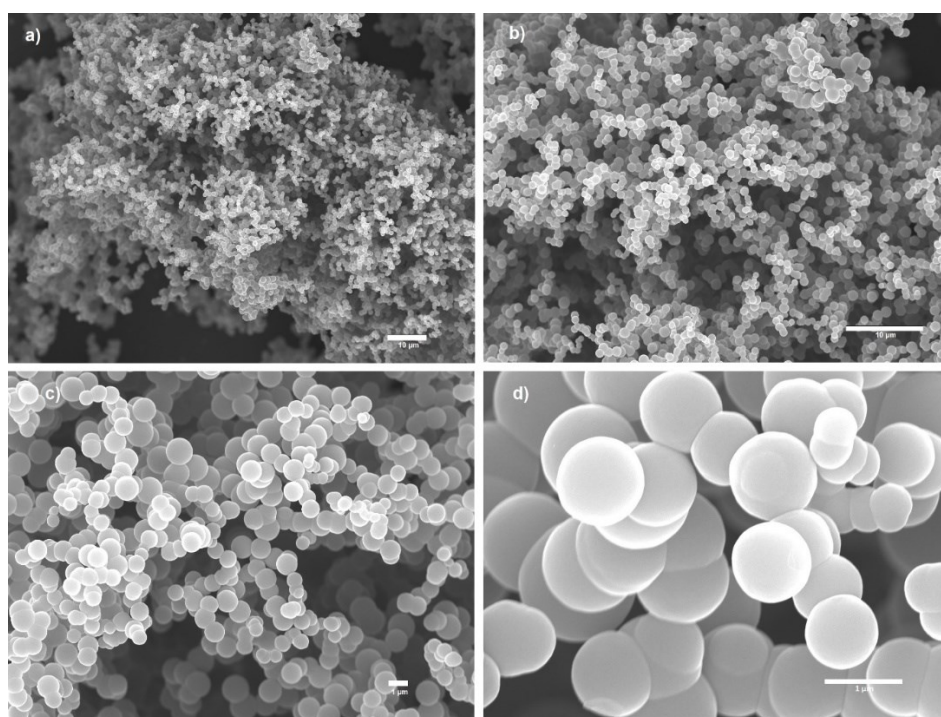


Fig. 2. Scanning electron micrographs from carbon spheres synthesized by CVD with overpressure. Magnification (a) 1 000x, (b) 2 000x, (c) 5 000x and (d) 20 000x.

As can be seen from Figure 2, synthesized carbon spheres have a diameter of less than a micrometer, smooth surface, and good spherical shape. The phenomenon of accretion is also observable¹¹. From a macroscopic point of view, the carbon spheres are synthesized in form of foam. Because of their

morphology and nature, they could be used as lubricant additives to improve friction and wear resistance⁴.

CONCLUSION

In this paper, carbon spheres were synthesized by chemical vapor deposition with overpressure in form of foam with a good spherical shape and smooth surface. The utilization could be found in improving tribology because of its carbon nature and smooth surface. We proved that the method of chemical vapor deposition with overpressure is promising in the synthesis of carbon spheres for future research.

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REFERENCES

1. Kroto H., McKay K. The formation of quasi-icosahedral spiral shell carbon particles. *Nature*. 1988. **331**: 328–331. <https://doi.org/10.1038/331328a0>
2. Jin Y. Z., et al. Large-scale synthesis and characterization of carbon spheres prepared by direct pyrolysis of hydrocarbons. *Carbon*. 2005. **43**(9): 1944–1953. <https://doi.org/10.1016/j.carbon.2005.03.002>
3. Sun X., Li Y. Colloidal Carbon Spheres and Their Core/Shell Structures with Noble-Metal Nanoparticles. *Angewandte Chemie International Edition*. 2004. **43**: 597–601. <https://doi.org/10.1002/anie.200352386>
4. Alazami A. A., et al. Ultrasoft Submicron Carbon Spheres as Lubricant Additives for Friction and Wear Reduction. *ACS Appl. Mater. Interfaces*. 2015.
5. Khodabakhshi S., et al. Facile and environmentally friendly synthesis of ultramicroporous carbon spheres: A significant improvement in CVD method. *Carbon*. 2021. **171**: 426–436. <https://doi.org/10.1016/j.carbon.2020.08.056>
6. Yin Y. Z., et al. High temperature annealing effects on carbon spheres and their applications as anode materials in Li-ion secondary battery. *Carbon*. 2006. **44**: 724–729. <https://doi.org/10.1016/j.carbon.2005.09.018>
7. Ma Y., et al. A practical route to the production of carbon nanocages. *Carbon*. 2005. **43**(8): 1667–1672. <https://doi.org/10.1016/j.carbon.2005.02.004>
8. Gutiérrez-García C. J., et al. Synthesis of carbon spheres by atmospheric pressure chemical vapor deposition from a series of aromatic hydrocarbon precursors. *Physica E: Low-dimensional Systems and Nanostructures*. 2019. **112**: 78–85. <https://doi.org/10.1016/j.physe.2019.04.007>
9. Koprinarov N., Konstantinova M. Preparation of carbon spheres by low temperature pyrolysis of cyclic hydrocarbons. *Journal of Materials Science*. 2011. **46**: 1494–1501. <https://doi.org/10.1007/s10853-010-4951-0>
10. Czernek P., Plachá D. Synthesis of pyrolytic carbon by chemical vapor deposition with increased pressure and its formation into scrolled carbon microtubes. Drobíková, K. Skotnicová, K. Novák, D. *PhD students' day FMST 2022*. VŠB – Technická univerzita Ostrava, 2022, 92–95.
11. Deshmukh A. A., et al. Carbon spheres. *Materials Science and Engineering: R: Reports*. 2010. **70**(1–2): 1–28. <https://doi.org/10.1016/j.mser.2010.06.017>

Heterogeneous Electrocatalytic Reduction of CO₂ to Fuels using Metalloporphyrin Complexes

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ABSTRACT

Electrochemical conversion of CO₂ to fuels is one of the most challenging problems for conversion and storage of electrical energy in the form of high-volume energy density molecules. The motivation lies in attaining catalyst design and tuning molecular structures to achieve electronic environment that enable its real-life implementation. In this work, we report heterogeneous electroreduction of CO₂ to ethanol or methanol of an immobilized cobaltporphyrin catalyst system. In moderately acidic aqueous medium, the cobaltporphyrin modified carbon paper electrode exhibits a Faradaic Efficiency of 48 % towards ethanol production. Now keeping the ligand framework fixed, we synthesized Mn(III)Porphyrin where electrochemical reduction of Mn(III) leads to an Mn(II) species, which binds CO₂ and stabilizes the reduced intermediates. This catalyst allows to electrochemically reduce CO₂ to acetic acid in a moderate acidic aqueous medium with a selectivity of 63% and a turn over frequency of 8.25 h⁻¹, when immobilized on a carbon paper electrode. In terms of high selectivity towards acetate, we propose the formation and reduction of an oxalate type intermediate, stabilized at the Mn(III)-porphyrin centre. Comparing both Co(III) and Mn(III) Porphyrins and tallying the chemical reduction study with DFT calculations we arrive to the conclusion that the catalysis is a metal-centred one with the porphyrin ligand stabilizing multiple redox intermediates.

KEYWORDS

Electrochemical, Cobaltporphyrins, Manganeseporphyrin and CO₂ reduction

INTRODUCTION

Molecular metalloporphyrin based catalytic systems has the upper hand of direct coordination of CO₂ to the metal site participating in inner sphere e⁻ transfer pathways resulting in catalytic transformation of the adsorbed CO₂ molecule. Based on the tailored design from the first to second coordination sphere one can infuse different electronic and geometric impact on the redox properties of the complex. Engineering the ligand backbone may in turn increase chemisorption of the reactant species and the robustness of the catalysts upon shuffling of redox states. These catalytic cycles should infuse selectivity for CO₂ reduced to multi-carbon products suppressing possibility of background H₂ evolution which in turn boost the faradaic efficiency and yield. Selecting ligands with π -conjugate backbones or changing the redox potential of the ligands by introducing electron donating or withdrawing moieties one can increase the nucleophilicity of the metal center and make it susceptible to electrophilic attack by CO₂. Ligand modification not only strengthens the immobilization force between solid supports and complexes but also improves the electron transfer kinetics leading to accelerated reaction rates. Thus, engineering of the catalysts should be done keeping the following necessities in mind: 1) formation and stabilization of reaction intermediates by the metal center with

the help of the appended functionalities, 2) using functionalities acting as proton real mediators to increase the H^+ source near the active site 3) to change the redox property of the metal center to boost multi electron reduction, selectivity, most importantly at a low overpotential, 4) choosing superior ligand backbone that can stabilize multiple redox states of the metal center preventing demetallation or associated processes increasing the lifetime of the catalyst.

EXPERIMENTAL STUDY

Cyclic Voltammetry and CPE for CO_2 reduction were performed with a workstation (CH Instruments, Model CHI400A) in a two-compartment, three-electrode electrochemical H-cell, consisting of a gas tight cell with a total volume of 30 mL. Carbon paper was used as the working electrode. Ag/AgCl ($E_{Ag/AgCl} = 0.222$ V filled with 0.1 M KCl) as the reference, and Pt wire as the counter. The reference electrode potential was calibrated with respect to the reversible hydrogen potential using platinum working electrode and platinum wire as counter electrode in 0.5 M H_2SO_4 electrolyte in H_2 atmosphere. This calibration result showed a shift of -0.222 V versus the NHE.

RESULTS AND DISCUSSION

Our efforts to increase the CO_2 reducibility of Corrole based catalytic systems resulted in the synthesis of $(-S-PEG(7)-OMe)_3$ modified Co(III)-Corrole.¹ On heterogeneous electrochemical CO_2

reduction after immobilization over carbon paper electrodes, a 12e reduction of CO_2 to ethanol electrochemically at a low potential of -0.8 V vs R.H.E. Systematic spectroscopic investigation and DFT calculation led to the proposition that shuttling back and forth between Co(III) and Co(I) states the system under electrochemical bias follows two divergent reaction pathways one leading to the 6e reduced product methanol and the other 12e reduced product ethanol. The study has been supported by in-situ spectroelectrochemical FTIR which show the decrease in IR bands of CO_2 and increase in IR-bands of alcohols/acids indicating reduction of CO_2 to ethanol, methanol and acetate. Low operational potential of the catalysts and formation of highly reduced products with C-C step-up was due to the formation of easily reducible glyoxal type intermediate. Besides, our group also conducted CO_2 electroreduction over Mn(III) Corrole $(-S-PEG(7)-OMe)_3$ immobilized over Carbon paper electrodes.² 8e reduction of CO_2 to acetate was resulted with a Faradaic efficiency of 63% and TOF of $8.25\ h^{-1}$.

CONCLUSION

In contrast to the CO pathway the corrole based catalysts proceeds via a formic acid pathway. $HCO\bullet$ intermediate yields methanol, as well as glyoxal which is further reduced to form ethanol serving our catalyst to operate at a low over potential. Heterogenization in the form of supramolecular interactions plays an important role in this catalytic process. CO_2 reduction by Mn(III) Corrole is a metal centred one with the active catalysts being Mn(II) Corrole. CO_2 reduction proceeds via, a carboxyhydroxyl intermediate pathway. The formation and reduction of a Mn(III) bound oxalate intermediate to acetate which was further substantiated by reduction studies of oxalic acid.

Acknowledgments: W.S. and S.G. acknowledges the financial support of the Austrian Science Fund (FWF-P28167-N34 and FWF-P32045-NBL). S.P. acknowledge UGC for fellowships, S.R. acknowledges the start-up, FIRE and PRIS grants from IISER Kolkata, India.

REFERENCES

1. S. Gonglach, S. Paul, M. Haas, F. Pillwein, S. S. Sreejith, S. Barman, R. De, S. Müllegger, P. Gerschel, U.P. Apfel, H. Coskun, A. Aljabour, P. Stadler, W. Schöfberger*, S. Roy*, Nat. Commun. 10, (2019), 3864.
2. R. De, S. Gonglach, S. Paul, M. Haas, S. S. Sreejith, P. Gerschel, U. P. Apfel, T. H. Vuong, J. Rabeah, S. Roy*, W. Schöfberger*, Angew. Chem. Int. Ed. 59, (2020), 10527–10534.

PVDF separator membranes for battery application

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ABSTRACT

In Li-ion batteries, the separator plays one of the main roles in determining efficiency and safety. Separates the cathode and anode and thus prevents free passage of electrons and at the same time allows the passage of metal ions during the charging and discharging cycle. It is important to develop new types of separators that have better electrochemical and thermal properties compared to the polyolefin separators used today, which would improve the performance of the entire battery.¹ Polyvinylidene difluoride (PVDF) is a highly suitable material for this application due to its high thermal stability, chemical resistance, strength and easy processability. Moreover, the properties of PVDF separator membranes can be modified by using suitably selected nanofillers. Zinc oxide nanoparticles, zinc oxide nanoparticles/vermiculite or vermiculite particles with defined particle size used as nanofillers can affect the porosity, thermal stability or conductivity of these materials.² The preparation method of these materials also plays an important role. For example, the heat pressing process influences many properties such as thermal stability, structure or even the representation of the individual PVDF phases. This process can be optimized through the temperature, time and pressure exerted on the material to be processed. The heat press process can also be used as a lamination process to prepare a multilayer membrane separator using a combination of suitable materials.³

KEYWORDS

PVDF nanocomposites, nanofillers, membrane separators.

Acknowledgments: This work was supported by project No. SP2023/026 “Smart nanomaterials for energy storage and savings”.

REFERENCES

1. W. Luo, S. Cheng, M. Wu, X. Zhang, Dan Yang, X. Rui. Review of advanced separators for rechargeable batteries. J. Power Sources 509 (2021) 2200429:1-2200429:20.
2. M. Yanilmaz, Y. Lu, M. Dirican, K. Fu, X. Zhang. Nanoparticle-on-nanofiber hybrid membrane separators for lithium ion batteries via the combination of electrospinning and electrospinning techniques. J. Membr. Sci. 456 (2014) 57-65.
3. F. Yalcinkaya, J. Hruza. Effect of Laminating Pressure on Polymeric Multilayer Nanofibrous Membranes for Liquid Filtration. Nanomater. 8 (2018) 272:1-272:16.

Application of clay minerals for solid electrolyte in batteries

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ABSTRACT

Next generation Li-ion batteries rely on the design and advancement of solid electrolytes and cathode materials. Therefore, various solid electrolytes based on ion conducting polymers and ceramics have been developed. These solid electrolytes showed many advantages, for instance, a high lithium transference number value close to one superior to liquid organic electrolytes¹.

Various types of ceramics and ceramic-like materials is involved into the development of solid-state batteries containing solid electrolyte. Utilization of clay minerals is being effective for the several reasons². The natural material containing ceramic -formative elements such as Si, Al, Mg, Na, therefore being inexpensive source of the precursors. Clay minerals are relatively easy modifiable; therefore, the large number combination can be produced. Additionally, those natural materials will be friendly for recycling respecting circular economy aspects³.

In our study modification of aluminosilicate substrate with conductive metals and conductive polymers is studied. The chemistry along with structure and functional parameters is described. Comparison of various natural minerals is done.

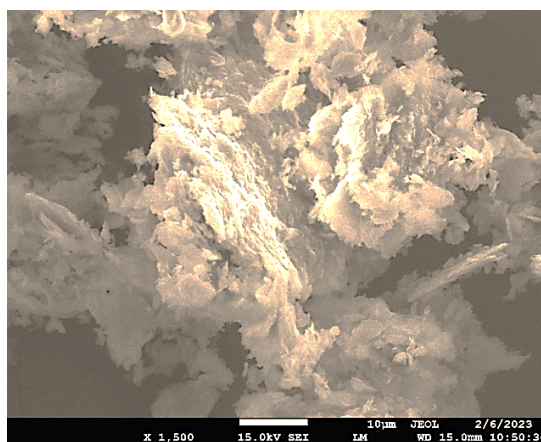


Fig. 1: Acid treated vermiculite intercalated with Li-cation and modified with PVDF.

KEYWORDS

Clay minerals, structure, solid electrolyte, polymers

Acknowledgments: Authors acknowledge financial support from the project MEYS SP 2023/026. This work is supported from the grant programme „Support for Science and Research in the Moravia-Silesia Region 2022” (RRC/12/2022), financed from the budget of the Moravian-Silesian Region.

REFERENCES

1. Tolganbek N, Serikkazyeva A, Kalybekkyzy S, Sarsembina M, Kanamura K, Bakenov Z, Mentbayeva A. Materials Advances. 2022;3(7):3055-69.

2. Yu X, Manthiram A. A review of composite polymer-ceramic electrolytes for lithium batteries. *Energy Storage Materials*. 2021 Jan 1; 34:282-300.
3. Martynková, G.S., Kratošová, G., Brožová, S, Sathish, S.K. in *Lithium-Sulfur Batteries Materials, Challenges and Applications*, Elsevier, 2022, Pages 653-672

Efficient photocatalysts for hydrogen evolution via solar water splitting

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ABSTRACT

Almost a quarter of the worldwide energy sector is dependent on the current catalytic process. For boosting the future economy, photocatalysis research has become the central development regime of new, clean protocols to generate energy. However, single-site catalysis holds a new frontier in the realm of heterogeneous catalysis. The main goal of the present research is to reach significant enhancement in photocatalytic hydrogen evolution via solar water splitting, either by metal-free condition or atomic engineering with single atoms. In the present research, C₃N₄ nanosheet precisely decorated with TiO₂ (extended series) is used as a highly efficient photocatalyst with a band gap from 2.1 to 2.7 eV. C₃N₄ nanosheet and TiO₂ play a significant role in photocatalytic activity for hydrogen generation. An appreciable amount of hydrogen is being evolved under visible-light irradiation in a solution with water and methanol with added designed photocatalyst composite of C₃N₄ and TiO₂. The photocatalytic hydrogen evolution activity under optimal conditions is observed at 300 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which is higher than g-C₃N₄ and TiO₂ photocatalysts separately. These photocatalysts may increase the production of hydrogen due to their high and efficient photocatalytic performance further with single atom engineering. Such formulated energy-based materials will be explored further via enhancing visible light absorption and introduction of tunable band gaps for hydrogen production as green energy storage and environmental protection.

KEYWORDS

Hydrogen, photocatalyst, water splitting, energy

Optimizing the preparation of the MAX phase by the grinding process

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ABSTRACT

MAX phases represent a group of intensively studied materials with potential applications in aerospace, defence, and nuclear industries, and they are also initial materials for the preparation of a novel outstanding group of materials MXenes. In our research, we focused on the synthesis of an MAX phase based on titanium, aluminium, and carbon. The preparation of the MAX phase is usually done in two steps: i) grinding of the mechanical mixture (for example Ti+Al+C) and ii) calcination of this mixture at temperatures higher than 1000 °C. Because it is necessary to heat the furnace to such high temperatures, the calcination process is relatively expensive. As one of the possibilities to reduce economic costs and simplify the preparation of the MAX phase, the optimisation of the grinding process was studied. For this purpose, a Design-of-Experiment (DOE) approach was adopted. The definition of four factors set at two levels resulted in a series of 16 samples. The selected factors included i) grinding time, ii) rotational speed, iii) number of grinding balls, and iv) amount of grinded material. The X-ray diffraction method was used to determine the phase composition of the mixtures after grinding.

KEYWORDS

MAX phases, mechano-chemical preparation, thermal treatment, characterization.

Acknowledgments: This work was supported by VSB – Technical University of Ostrava (Projects No. SP2023/034 and SP2023/043).

Characterization of organic binders for pelletization

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ABSTRACT

An organic binder is a material that is used to hold particles together to form a solid shape or structure. The characterization of an organic binder depends on the specific application and intended use. Nanoparticles can increase the barrier properties of organic binders, such as their resistance to moisture, oxygen, and other environmental factors. The rheological properties of the organic binder,

such as its shear behavior, can affect its flow properties and ability to coat or penetrate particles. Techniques such as powder rheometry was used to determine these properties. And the nanoparticles have been determined. Selected organic binders used to produce pellets were characterized in detail. These were lignosulfonate, flour and starch. From the rheological properties were measured the angle of internal friction, compressibility and angle of repose. The effect of the nanoparticles content in the binder on their further processing was studied. The first results showed that some of the physical-mechanical properties improved after the addition of binders. This research can provide interesting information about the advantages/disadvantages of using organic binders in pellet production.

Acknowledgments: This work was supported by the project No. SP2023/094 "Specific research in selected areas of energy processes".

Smectites composite materials for environmental remediation

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ABSTRACT

Clay minerals from the smectite group are widely used as precursors for composite materials. Clay-based composites represent a current trend in the development of novel materials that can offer a suitable alternative of eco-friendly and affordable materials for pollutant removal in environmental remediation. The study focuses on design and preparation of composites based on selected smectites with manganese oxides and verification of their performance in various applications. The preparation of composites was performed by precipitation of manganese oxides colloids on the surface of chemically modified clay mineral montmorillonit (4 localities). The prepared materials were characterized by X-ray diffraction analysis (XRD), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and X-ray fluorescence spectroscopy (XRFS). The composites were studied for thermal stability, catalytic activity, sorption properties and evaluation of specific surface area. Results showed creation of a manganese oxide phase with a structure of α -MnO₂ (XRD, FT-IR), the α -MnO₂ fibers cover the surface of the clay grains and are much shorter than in the neat reference sample (SEM). The obtained composites exhibited increased efficiency in catalytic combustion of volatile organic compounds (toluene and ethanol). The adsorption procedure in a batch regimen confirmed sufficient sorption ability (over 90%) for two types of broad-spectrum antibiotics.

KEYWORDS

clay minerals, modification, sorption, composites

Acknowledgments: This work was supported by the programme Dynamic Planet Earth of the Czech Academy of Sciences – Strategy AV21.

TOPIC 2

Materials and technology for environment, healthcare, and safety

Chair: Radek Zbořil and Daniela Plachá

Catalysis, photocatalysis and adsorption processes

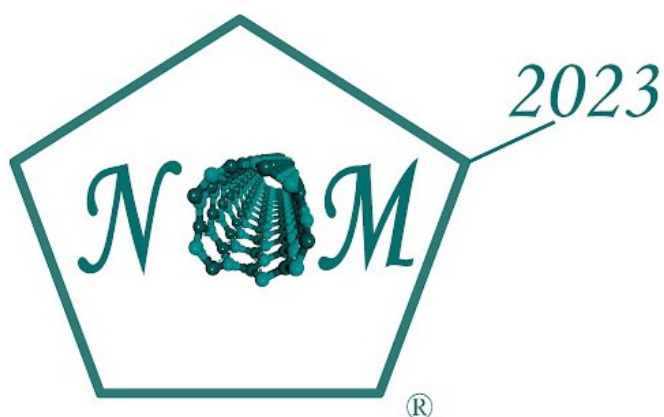
Filters and membranes

Anti-biofouling and antimicrobial surfaces

Green chemistry approaches

Nanomaterials in healthcare

NanoSafety



Plenary lecture (PL):**The metal/non-metal trajectory in sustainable chemistry****P. Fornasiero^{1,2,3}**¹ Department of Chemical and Pharmaceutical Sciences, University of Trieste, via L. Giorgieri 1, Trieste, Italy² ICCOM-CNR UTR Trieste, via L. Giorgieri 1, Trieste, Italy³ INSTM Trieste, via L. Giorgieri 1, Trieste, Italypfornasiero@units.it**ABSTRACT**

Heterogeneous transition metal catalysts are generally based on nanoparticles, that nowadays can be synthesized with uniform size and shape. The extraordinary advances in material science inspired a new vision for nanoscale-inspired design and synthesis of industrially important catalysts, where new synthetic strategies for materials are combined with emerging concepts in catalysis. The possibility to exert a precise structural and morphological control, coupled with the tailored modulation of the metal-support interactions, allowed us to have a step change increase in the activity, selectivity and stability of many industrially and environmentally important catalysts.[1-5] Furthermore, single atom [6], metal-free[7-9] and photothermal[10] catalysts are becoming an essential modern strategy to address current sustainability guidelines, in particular if the reliance on costly elements is abandoned. Such emerging catalysts are deemed to go beyond fundamental research, and will propel industrial interests toward the establishment of green organic synthesis, renewable energy conversion, pollution prevention and control, which represent the real challenges of the 21st century and the focus of the present talk.

KEYWORDS

Sustainable catalysis, metal-support interactions, metal free catalysis, photocatalysis.

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REFERENCES

1. M. Cargnello, V. Doan-Nguyen, T.R. Gordon, R.E. Diaz, E. Stach, R.J. Gorte, P. Fornasiero, C.B Murray, *Science* **2013**, 341, 771-773.
2. M. Cargnello, J.J. Delgado Jaén, J.C. Hernández Garrido, K. Bakhmutsky, T. Montini, J.J. Calvino Gámez, R.J. Gorte, P. Fornasiero, *Science* **2012**, 337, 713.
3. G. Valenti, A. Boni, M. Melchionna, M. Cargnello, L. Nasi, G. Bertoni, R.J. Gorte, M. Marcaccio, S. Rapino, M. Bonchio, P. Fornasiero, M. Prato, F. Paolucci, *Nature Communications* **2016** article number: 13549.
4. N. Luo, T. Montini, J. Zhang, P. Fornasiero, E. Fonda, T. Hou, W. Nie, J. Lu, J. Liu, M. Heggen, L. Lin, C. Ma, M. Wang, F. Fan, S. Jin, F. Wang, *Nature Energy* **2019**, 4, 575-584.
5. S.M. Hossein Hejazi, M. Shahrezaei, P. Błoński, M. Allieta, P.M. Sheverdyayeva, P. Moras, Z. Bađura, S. Kalytchuk, E. Mohammadi, R. Zbořil, Š. Kment, M. Otyepka, A. Naldoni, P. Fornasiero.; *Chem Catal.*, **2022**, 2, 1177-1190.
6. A. Bakandritsos, R.G. Kadam, P. Kumar, G. Zoppellaro, M. Medved', J. Tuček, T. Montini, O. Tomanec, P. Andrášková, B. Drahoš, R. S. Varma, M. Otyepka, M. B. Gawande, P. Fornasiero, R. Zbořil, *Adv. Mater.* **2019**, 31, n° 1900323
7. D. Iglesias, A. Giuliani, M. Melchionna, S. Marchesan, A. Criado, L. Nasi, M. Bevilacqua, C. Tavagnacco, F. Vizza, M. Prato, P. Fornasiero, *Chem*, **2018**, 4, 106

8. G. Filippini, F. Longobardo, L. Forster, A. Criado, G. Di Carmine, C. D'Agostino, M. Melchionna, P. Fornasiero, M. Prato, *Science Adv.* **2020**, 46, eabc9923.
9. A. Actis, M. Melchionna, G. Filippini, P. Fornasiero, M. Prato, E. Salvadori, M. Chiesa, *Angew. Chem. Int. Ed.* **2022**, 61, e202210640[
10. R. Puning, Z. Gao, T. Montini, Z. Zhao, N. Ta, Y. Huang, N. Luo, E. Fonda, P. Fornasiero, F. Wang, *Joule*, **2023**, 7, 333-349.

Invited lecture (IL):

Impact of Nanomaterials on the Environment

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In the last two decades, the field of nanotechnology has changed very rapidly from an uncertain promise of benefits and innovations to numerous effective applications such as medicine, environmental technologies, food manufacturing and other fields where organisms, not only humans, may be in direct contact with nanomaterials, especially nanoparticles and nanofibers. However, biosystems are not exposed to engineered nanomaterials only. Anthropogenic activities generate substantial amounts of nanomaterials, mainly ultrafine particles. These activities involve traffic contributing with its exhaust and non-exhaust particulate emissions, various industrial processes, e.g. welding, but also selective laser melting during 3D printing using metallic powders.

In general, development of new technologies and their products, intentional as well as unintentional, have not traditionally been accompanied by a parallel debate on the broader issues such as ethics and governance of the technology. In case of nanotechnology and nanomaterials, such discussions have occurred as a consequence of documented harm being done to humans and the environment, or the widespread release of the technology and its products by a local market.

Apart from the well known advantages of nanomaterials usage, there are possibilities that these materials may pose a hazard for the environment in a sense that they have the tendency to accumulate in the atmosphere, soil and water environments and even in the food chain. Therefore, it is necessary to work also on preventive measures of this adverse impact prior to fully implementing nanomaterials in products and to deal with responsible research and innovation in nanotechnology for future sustainable development.

Anodic TiO₂ nanotubes and single-atom co-catalysts in photocatalytic H₂ generation

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ABSTRACT

The present work discusses recent progress in the synthesis of TiO₂ nanotubes (NTs) by electrochemical anodization, single-atom (SA) co-catalyst decoration of such nanotubular layers, and the use of such SA decorated NTs in photocatalytic H₂ production. Herein, we show that anodic TiO₂ nanotubes can be used as a platform for the decoration with noble metal single-atoms, SAs, e.g., Pt, Pd, Rh and Au, by a simple “dark deposition” approach, and that such SA decorated TiO₂ NTs provide a high activity for photocatalytic H₂ generation from pure water, i.e., in absence of a sacrificial agent, compared to their nanoparticle counterpart decorated tube layers.

KEYWORDS

TiO₂ nanotubes, co-catalysts, single-atom, H₂ production

INTRODUCTION

Green hydrogen production is a highly researched topic in the past five decades, which started with the report of Fujishima and Honda from 1972, reporting on the use of TiO₂ nanoparticles as a solar-illuminated semiconductor for the splitting of water into H₂ and O₂. However, it was later shown that the formation of H₂ on TiO₂ is kinetically hampered, and to reach reasonable photocatalytic reaction rates, noble metals (Pt, Pd, etc.) are used as co-catalysts on the semiconductor's surface, either as metallic nanoparticles (NPs), nanoclusters or more recently as single-atom (SA).

With respect to TiO₂ nanostructures, anodic 1D TiO₂ nanotubes (NTs) have shown a high surface area, good control over the morphology, directional charge transport and ability to harvest their functionality^[1,2]. Anodization is by far the most used method to obtain TiO₂ nanotubes, as it ensures a well-controllable morphology, as well as the ability to tailor the crystal structure (amorphous, anatase, anatase/rutile mixtures) by the employed annealing treatments. The control over the morphology of the TiO₂ NTs, e.g., tube diameter, length and spacing, can be easily mastered by the used anodization conditions (anodization voltage, time, temperature, pH, electrolyte composition, substrate pretreatment, etc.)^[1,2], and different tubular morphologies can be obtained, e.g., single or double-walled, multi-stacks, super lattice, spaced, etc.^[1–3]. To note that as-formed anodic TiO₂ NTs are amorphous, and can be crystallized to partially crystalline materials, fully crystalline anatase, or anatase/rutile mixtures via adequate annealing treatments^[1].

To overcome the slow electron transfer kinetics encountered on TiO₂ which seriously diminishes the H₂ production efficiency, a co-catalyst is required, typically a noble metal (Fig. 1a). Over the years, significant efforts were made to increase the cost efficiency, to decrease the size of the co-catalyst particle and to enhance the noble metal usage; thus, the development of insulated single atoms of noble metals as co-catalyst. Herein, we will discuss the recent advances in TiO₂ nanotubes growth and their use with SA co-catalyst for an efficient photocatalytic H₂ production.

EXPERIMENTAL/THEORETICAL STUDY

TiO₂ nanotubes were obtained by electrochemical anodization of Ti in a ethylene glycol electrolyte (0.15M NH₄, 3vol.% H₂O), at 60 V, 20 min (room temperature) [4]. Nanotubes were annealed to anatase (air annealed: 450 °C, 1 hour). The single atom Pt, Pd, Rh and Au decoration was obtained by dark deposition (precursor solutions of 2 mM or 0.005 mM of H₂PtCl₆·6H₂O, (NH₄)₂PdCl₆, RhCl₃, and HAuCl₃) - see our recent work [4]. For more details to the used characterization techniques (SEM, XPS, TEM) and H₂ photocatalytic measurements see reference [4].

RESULTS AND DISCUSSION

In a first step we present an overview of anodic TiO₂ nanotubes with different morphologies and how to achieve the single-atom co-catalyst decoration of NTs via dark deposition. We will further discuss different noble metals (Pt, Pd, Rh, Au) [4] deposited as single atoms on TiO₂ NTs via dark deposition [5–7] and shown an overview from our recent work [4] comparing their efficiency for H₂ production in plain water – see Fig. 1b. The different noble metal SAs of Pt, Pd, Rh or Au decorated on the anatase TiO₂ NTs result in an oxygen-coordinated noble metal δ^+ state. Interestingly, a low SA loading from a 0.005mM Pd solution on the TiO₂ NTs is much more effective as co-catalyst for the photocatalytic H₂ generation in plain water than Pt, Rh, or Au SAs (or than corresponding noble metal nanoparticles) [4]. The Pd SAs TiO₂ NTs lead to a H₂ production rate of 0.381 $\mu\text{mol h}^{-1} \text{cm}^{-1}$ (SA density of 0.41×10^5 Pd atoms / μm^2), by suppressing the H₂ and O₂ recombination reactions at the individual SAs used as co-catalysts in photocatalytic splitting [4].

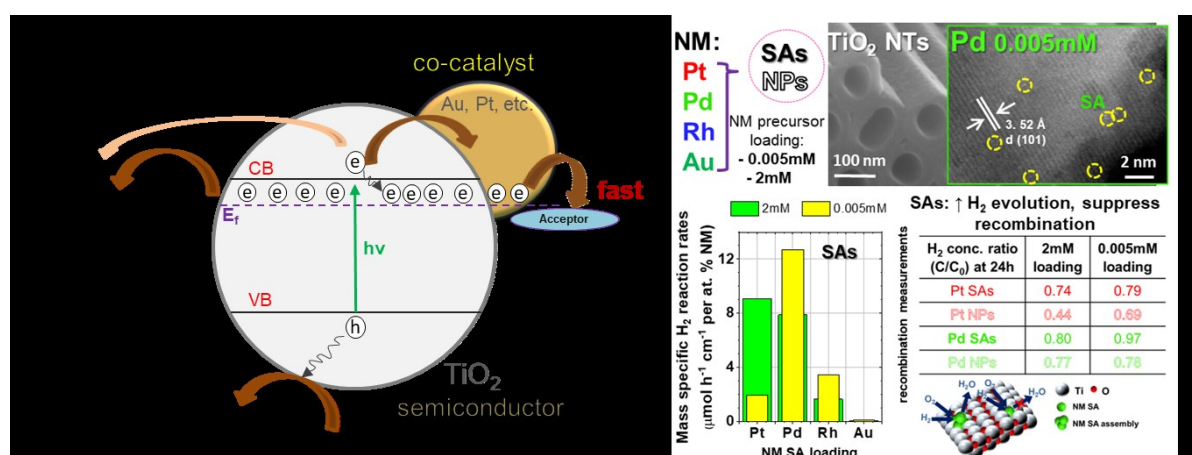


Fig. 2 a) Photocatalytic H₂ production (e.g., on TiO₂ nanoparticle), b) Overview of SA/NP co-catalyst decoration on TiO₂ NTs and representative Pd SA decoration (TEM), mass specific H₂ reaction rates and recombination measurements (b is from Hwang et al. [4], used under Creative Commons CC-BY license).

CONCLUSION

The present work discusses recent advances of TiO₂ NTs obtained via electrochemical anodization and their single-atom co-catalyst decoration via dark deposition. Following, an overview of the photocatalytic H₂ generation efficiency from TiO₂ NTs decorated with different noble metal SAs (Pt, Pd, Rh, Au) or their nanoparticle counterpart is given, clearly showing a strong beneficial effect of using SAs for an efficient H₂ production from plain water.

Acknowledgments: The authors acknowledge the DFG and Operational research program, Development and Education (European Regional Development Fund, Project No. CZ.02.1.01/0.0/0.0/15_003/0000416 of the Ministry of Education, Youth and Sports of the Czech Republic) for financial support.

REFERENCES

- [1] K. Lee, A. Mazare, P. Schmuki, *Chem. Rev.* 114 (2014) 9385-9454.
- [2] J. Park, A. Cimpean, A. B. Tesler, A. Mazare, *Nanomaterials* 11 (2021) 2359.
- [3] S. Ozkan, A. Mazare, P. Schmuki, *Electrochim. Acta* (2018) 268.
- [4] I. Hwang, A. Mazare, J. Will, T. Yokosawa, E. Spiecker, P. Schmuki, *Adv. Funct. Mater.* 32 (2022) 2207849.
- [5] X. Zhou, I. Hwang, O. Tomanec, D. Fehn, A. Mazare, R. Zboril, K. Meyer, P. Schmuki, *Adv. Funct. Mater.* 31 (2021) 2102843.
- [6] G. Cha, A. Mazare, I. Hwang, N. Denisov, J. Will, T. Yokosawa, Z. Badura, G. Zoppellaro, A. B. Tesler, E. Spiecker, P. Schmuki, *Electrochim. Acta* 412 (2022) 140129.
- [7] Z. Wu, I. Hwang, G. Cha, S. Qin, O. Tomanec, Z. Badura, S. Kment, R. Zboril, P. Schmuki, *Small* 18 (2022) 1.

Nanocatalysis for sustainable and advance chemical synthesis

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ABSTRACT

The development of sustainable processes for advanced chemical synthesis, energy technologies and materials as well as valorization of renewable resources/feedstocks is an important goal of chemical research. Notably, catalysis constitutes a key technology for achieving more sustainable processes in the chemical, pharmaceutical and agrochemical industries. As a result, >80 of globally produced chemical products are made using catalytic processes. In this regard, the development of more active, selective, and cost-effective, as well as stable and reusable catalysts is of central importance and essential to produce all kinds of chemicals at present and in the future. Since decades, catalysts based on precious metals have revolutionized organic synthesis at scales ranging from the lab bench to the industrial manufacture of fine and bulk chemicals. However, the higher price and limited availability of these metals have spurred interest in catalysis with more earth-abundant metal alternatives. Hence, the development of non-noble metal-based catalysts is highly desired and crucial for the advancement of sustainable and cost-efficient chemical processes. The major challenge in catalysis is to create catalysts that exhibit extreme stability, remarkable activity and high selectivity. In general, homogeneous catalysts are highly selective but not very stable and difficult to recycle or reuse. On the other hand, heterogeneous catalysts are more stable and easy to recycle or reuse but these ones are less selective. We are dealing on how to combine both homogeneous and heterogeneous catalysis aspects to create essential catalysts, especially based on nanoparticles (NPs) and single atoms (SACs) for advanced organic synthesis. Consequently, in the talk different approaches for the preparation of highly active and selective base metal nanoparticles- and single atom catalysts by using homogeneous complexes or metal organic frameworks will be presented. The importance and applicability of these specific catalytic materials (NPs and SACs) for industrially important synthetic reactions involving functionalized and structurally diverse molecules will be discussed. Next, the talk includes more sustainable catalytic processes for the synthesis of valuable fine and bulk chemicals as well as

molecules used in life science applications. Further, catalytic applications on the valorization of renewable feedstocks and upscaling of waste-plastics will be shown.

REFERENCES

1. V. G. Chandrashekhar, W. Baumann, M. Matthias, R. V. Jagadeesh, *Science*, 2022, 376, 1433-1441
2. R. V. Jagadeesh, K. Murugesan, A. S. Alshammari, H. Neumann, M.-M. Pohl, J. Radnik, M. Beller, *Science*, 2017, 358, 326-332.
3. R. V. Jagadeesh, A. E. Surkus, H. Junge, M. M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, *Science*, 2013, 342, 1073-1076.
4. V. G. Chandrashekhar, T. Senthamarai, R. G. Kadam, O. Malina, J. Kašlík, R. Zbořil, M. B. Gawande, R. V. Jagadeesh, M. Beller, *Nature Catalysis*, 2022, 5, 20-29.
5. T. Senthamarai, V. G. Chandrashekhar, N. Rockstroh, J. Rabeah, S. Bartling, R. V. Jagadeesh, M. Beller, *Chem*, 2022, 8, 508-531.
6. T. Senthamarai, K. Murugesan, J. Schneidewind, N. V. Kalevaru, W. Baumann, H. Neumann, P. C. J. Kamer, M. Beller, R. V. Jagadeesh, *Nature Communications*, 2018, 9, 4123.
7. R. V. Jagadeesh, H. Junge, M. M. Pohl, J. Radnik, A. Brückner, M. Beller, *Journal of the American Chemical Society*, 2013, 135, 10776-10782.
8. K. Murugesan, V. G. Chandrashekhar, C. Kreyenschulte, M. Beller, R. V. Jagadeesh, *Angewandte Chemie International Edition*, 2020, 59, 17408-17412.
9. K. Murugesan, M. Beller, R. V. Jagadeesh, *Angewandte Chemie International Edition*, 2019, 58, 5064-5068.
10. J. Gao, L. Feng, R. Ma, B. J. Su, A. M. Alenad, Y. Liu, M. Beller, R. V. Jagadeesh, *Chem Catalysis*, 2022, 2, 178-194. Cobalt single-atom catalysts for domino reductive amination and amidation of levulinic acid and related molecules to N-heterocycles.

Low-dimensional Graphene Chemistry for Sustainable Technologies

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ABSTRACT

Covalent functionalization of low-dimensional carbon systems, 2D - graphene and 0D – graphene/carbon dots, paves the way for non-metallic magnets, extraordinarily efficient single-atom catalysts, selective sorbents or advanced theranostic agents. Two main strategies based on structural doping with nitrogen and fluorographene chemistry will be discussed. The role of nitrogen substitution in controlling magnetic and photoluminescence properties of graphene along with switching the spin state of molecules will be described [1]. N-doped graphene dots will be explored as unique fluorescence systems allowing to measure temperature inside the living cells or to monitor the water/ice phase transition with the exceptional applicability in medical diagnostics/therapy [2]. In the next part, various examples of selective covalent functionalization of graphene via nucleophilic substitution of fluorographene will be presented. Recently discovered cyano-graphene and graphene acid possess an exceptional affinity towards binding metallic and molecular species. The applicability of these derivatives in environmental and antimicrobial technologies will be discussed [3]. Finally, the use of graphene derivatives as the efficient traps for immobilization of single atom catalysts will be demonstrated with various reaction systems [4].

KEYWORDS

Fluorographene, Graphene Acid, Organic Magnets, Nitrogen Doping, Graphene Dots, Nucleophilic Substitution

REFERENCES

- [1] B. de la Torre, M. Švec, P. Hapala, J. Rolando, O. Krejčí, R. Lo, D. Manna, A. Sarmah, D. Nachtigalová, J. Tuček, P. Blonski, M. Otyepka, R. Zbořil, P. Hobza, P. Jelínek, *Nat. Commun.*, 9, 2831, (2018). b) P. Blonski, J. Tuček, Z. Sofer, V. Mazánek, M. Petr, M. Pumera, M. Otyepka, R. Zboril, *J. Am. Chem. Soc.* 139, 3171-3180, (2017).
- [2] S. Kalytchuk, K. Poláková, Y. Wang, J. P. Froning, K. Cepe, A. L. Rogach, R. Zbořil, *ACS Nano*, 11, 1432-1442, (2017).
- [3] J. Kolařík, A. Bakandritsos, Z. Bad'ura, R. Lo, G. Zoppellaro, Š. Kment, A. Naldoni, Y. Zhang, M. Petr, O. Tomanec, J. Filip, M. Otyepka, P. Hobza, R. Zbořil, *ACS Nano*, 15, 3349-3358, (2021). b) D. Panáček, L. Hochvaldová, A. Bakandritsos, T. Malina, M. Langer, J. Belza, J. Martincová, R. Večeřová, P. Lazar, K. Poláková, J. Kolařík, L. Válková, M. Kolář, M. Otyepka, A. Panáček, R. Zbořil, *Adv. Sci.* 8, 2003090, (2021).
- [4] A. Bakandritsos, R. G. Kadam, P. Kumar, G. Zoppellaro, M. Medved', J. Tuček, T. Montini, O. Tomanec, P. Andrášková, B. Drahoš, R.S. Varma, M. Otyepka, M. B. Gawande, P. Fornasiero, R. Zbořil, *Adv. Mater.*, 31, 1900323, (2019).

Oral presentations (OP):**Beauty of iron nanoparticles: summary of more than 15 years' experience**

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ABSTRACT

Iron nanoparticles (commonly termed as nZVI – nanoscale Zero-Valent Iron particles) attract attention of scientists and environmental engineers for more than twenty years mainly because of their high reactivity and potential to become a new generation of remediation agent in groundwater treatment technologies. At Palacký University Olomouc, we established the intensive research on nZVI particles in 2006 and intensified collaboration with other Czech universities and remediation companies on this topic. Our research covers the synthesis (including up-scaling),¹ surface modification,^{2,3} chemical transformations,⁴ formation of nZVI-based nanocomposites,⁵ reactivity studies,⁶ combination with other remediation processes (like bioremediation⁷ or electric field enhanced remediation⁸), evaluation of toxicity and fate⁹ of nZVI and their reaction products in the environment. Following extensive laboratory research, the industrially prepared nZVI particles have been used in numerous field pilot tests and in full-scale remediations of polluted sites for groundwater restoration. In this presentation, we will overview the most important achievements in the field of nZVI optimization, including their complex evaluation, and will give future prospects and directions of subsequent research dealing with nZVI.

KEYWORDS

Nanoremediation, Synthesis, Surface modification, Groundwater.

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REFERENCES

1. O. Schneeweiss, J. Filip, B. David, R. Zbořil, M. Mašláň, J. Nanopart. Res. 13 (2011) 5677-5684.
2. J. Kašlík, J. Kolařík, J. Filip, I. Medřík, O. Tomanec, M. Petr, O. Malina, R. Zbořil, P.G. Tratnyek, Chem. Eng. J. 354 (2018) 335-345.
3. M. Brumovský, J. Filip, O. Malina, J. Oborná, O. Sracek, T.G. Reichenauer, P. Andrášková, R. Zbořil, ACS Appl. Mat. Inter. 12 (2020) 35424-35434.
4. M. Brumovský, V. Micić, J. Oborná, J. Filip, T. Hofmann, T., D. Tunega, J. Haz. Mat. 442, (2023) 129988.
5. J. Semerád, A. Ševců, N.H.A. Nguyen, P. Hrabák, R. Špánek, K. Bobčíková, K. Pospíšková, J. Filip, I. Medřík, J. Kašlík, I. Šafařík, A. Filipová, J. Nosek, M. Pivokonský, T. Cajthaml, Chemosphere 281 (2021) 130915.
6. S. Klimkova, M. Cernik, L. Lacinova, J. Filip, D. Jancik, R. Zbořil, Chemosphere 82 (2011) 1178-1184.
7. J. Němeček, P. Pokorný, O. Lhotský, V. Knytl, P. Najmanová, J. Steinová, M. Černík, A. Filipová, J. Filip, T. Cajthaml, Sci. Tot. Env. 563-564 (2016) 822-834.
8. M. Černík, J. Nosek, J. Filip, J. Hrabal, D.W. Elliott, R. Zbořil, Wat. Res. 154 (2019) 361-369.
9. J. Semerád, J. Filip, A. Ševců, M. Brumovský, N. Nguyen, J. Mikšíček, T. Lederer, A. Filipová, J. Boháčová, T. Cajthaml, Environ. Sci. Nano 7 (2020) 1794-1806.

Single atoms functionalized carbon nitride for photocatalytic organic synthesis

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ABSTRACT

Carbon nitride derivatives are a family of materials that have found increasing popularity in photocatalysis and sustainability processes¹. In particular new carbon nitride species incorporating single transition metal atoms (CN-M-SAC), provide charges and metastable high-spin states formed upon photo-irradiation of the materials². It has been shown that these features make possible the development of light-driven organic reactions.

The project targets the development of two types of CN-M-SAC to be used as photocatalysts for two classes of organic reactions that incorporate the H₂ evolution or the CO₂ fixation. The metals selected for this research are nickel and cobalt. CN-Ni-SAC is intended to catalyse the carboxylation of allylic alcohols using carbon dioxide³, while CN-Co-SAC is a suitable heterogeneous catalyst for the synthesis of anilines along with the production of H₂⁴.

Particular attention is dedicated on carbon nitrides and their structural modification. Either on the molecular level, for example with the addition of some non-metal atoms, defect engineering or oxidation, or on the surface level, by varying the crystallinity of CN material through amorphization or by changing the surface to volume ratio changing the porosity of the material. The modified carbon nitride will be further functionalized by inclusion of single transition metal atoms.

KEYWORDS

Single-atoms, carbon nitride, H₂ evolution, CO₂ fixation

REFERENCES

1. Gentile, G.; Marchi, M.; Melchionna, M.; Fornasiero, P.; Prato, M.; Filippini, G. U. *Eur J Org Chem* **2022**, 2022 (37).
2. Chen, Z.; Mitchell, S.; Vorobyeva, E.; Leary, R. K.; Hauert, R.; Furnival, T.; Ramasse, Q. M.; Thomas, J. M.; Midgley, P. A.; Dontsova, D.; Antonietti, M.; Pogodin, S.; López, N.; Pérez-Ramírez, J. *Advanced Functional Materials* **2017**, 27 (8), 1605785.
3. Fan, Z.; Chen, S.; Zou, S.; Xi, C. *ACS Catal.* **2022**, 12 (5), 2781–2787.
4. U Dighe, S.; Juliá, F.; Luridiana, A.; Douglas, J. J.; Leonori, D. *Nature* **2020**, 584 (7819), 75–81.

Using foam ceramics as photocatalytic substrate

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ABSTRACT

The emphasis put on the quality of living space has been exponentially increasing in the last decades. Advanced catalytic oxidation processes represent a promising technology for the remediation of contaminated water, air, and soil. Generally, semiconductive photocatalysts are an ecologically friendly and sustainable resource that can convert harmful substances almost waste-free into final products like H₂O and CO₂. The most common photocatalyst representative is titanium dioxide (TiO₂), which excels due to its efficient photoactivity, high stability, ecological integrity, and relatively low cost. Nevertheless, there are some drawbacks related to TiO₂ utilization, such as preparation of suitable suspension, high tendency to create agglomerates, stability of suspensions in time, application technique, etc. Coatings based on titanium dioxide are usually applied on different planar surfaces, such as glass, facades, metals, etc. Researchers are trying to increase TiO₂ activity by doping, surface modification, particle size reduction, etc. The enhancement of the efficacy of TiO₂ coating by its application on a ceramic porous system, where a benefit of a large specific surface area of the substrate is used, was investigated in this study. Then, the influence of the preparation technique on the coating quality and photocatalytic properties was also evaluated.

KEYWORDS

Foam ceramics, photocatalytic activity, surface quality

INTRODUCTION

The phenomenon of photocatalysis has been broadly investigated for the purpose of degradation of harmful chemicals either in air or water for many decades. The efficacy of photocatalysts can be affected by many factors, such as photocatalyst composition, particle size, light source, surface area and morphology of the photocatalyst, presence of other substances, etc. Despite the promising deployment of photocatalytic elements in the industrial sectors, photocatalytic systems have still their limitations. Owing to the fact that photocatalysis is about nanoparticles (NPs), controlling the textural properties, such as particle size, agglomeration degree, and surface area, are not easy tasks to figure out. NP suspensions, known as the first generation of photocatalysts, display impressive photocatalytic activity due to their high specific surface in direct contact with pollutants. Nevertheless, in many cases, these suspensions are applied on solid planar surfaces, which can limit the whole potential of these suspensions¹. The usage of three-dimensional (3D) substrates cannot only compensate mentioned limitations but also improve and extend the suspensions' application field. These 3D substrates are commonly referred to materials such as foam, which crucially offers great potential in terms of photocatalytic efficacy and activity. Foams coated with photocatalytic suspension can reliably interact with irradiated light to form more oxidative species leading to degradation processes with higher photocatalytic efficiency over planar substrates. This study presents a new sight on the application possibilities of photocatalytic suspensions.

Photocatalytic suspension

Titanium dioxide has a predominant role in the photocatalyst field due to its high efficiency, stability, versatility, availability, long history, and low cost. Preparation of stable suspension of TiO₂ NPs is challenging because of their high affinity to agglomerate, due to their large specific surface area. This behaviour is generally connected with Van der Waals attraction forces and can be compensated by repulsive electrostatic forces, steric stabilization, or specific surface treatment². The combination of electrostatic and steric stabilization can be achieved by using polyelectrolytes. Ultrasonication can be additively used to improve the deagglomeration process as well. The presence of agglomerates generally reduces the specific surface area which can negatively affect photocatalytic activity. Nevertheless, even with these options, the deagglomeration process into the primary particles is still challenging.

The powder nano-TiO₂ (n-TiO₂) is usually used in an industrial scale that is necessary to convert to a stable suspension, rather than synthesizing n-TiO₂ suspensions according to different laboratory approaches. Water is usually used as a versatile medium for TiO₂ suspensions. Generally, in water, NPs tend to create multiple larger agglomerates (compared to primary particles), with dimensions larger than micrometer due to the hydrophobic nature of the NPs surface and the electrostatic attraction of the NP powders. Various polymers, organic acids, or surfactants have been adopted to stabilize n-TiO₂ suspensions³. Adding different inorganic salts can also improve the suspension stability^{3,4}. Monitoring the effect of individual stabilizers on photocatalytic activity is essential to avoid depreciation of the primary purpose of TiO₂ coating use.

Last but not least, key parameter which can influence the quality of TiO₂ suspension is the preparation technique. One of the most common equipment used to prepare suspension from powder is a high-shear dispersing machine or in other words – a homogenizer. To brake nanoparticles' clusters and improve suspensions' stability, homogenizers are usually equipped with a specific geometry called a rotor-stator⁵. The rotor is usually a movable inner part, whereas the stator is a fixed outer part with holes or gaps with definite dimensions depending on a target particle size. Due to the high shear force, the agglomerates coming through these gaps are mechanically broken down. Using the homogenizer, the low viscous suspensions are prepared, for the denser ones the pearl mill can be used.

The construction of the pearl mill can be divided into two main parts: dispersing container and the main mill body. Dispersing container serves as a stock vessel, which is continuously homogenizing. The mill part has a rotating mill chamber filled with zirconium balls of definite size (according to the target fineness). The suspension from the stock container enters the milling chamber (here undergoes the milling process), then comes through the exit gap and goes back to the stock vessel. The whole process is a continuous procedure where the suspension undergoes several repeating cycles to achieve the desired fineness.

Foam Ceramics

The first mention of the synthesis of solid inorganic foam dates back to 1965⁶. Nowadays there are several techniques used to make a porous system with controlled porosity: replica, a sacrificial template on direct foaming process. The replica technique to produce foam ceramics is used in our company. This process (**Fig. 1**) is based on the immersion of reticulate polyurethane foam into the ceramic slurry (step 1) followed by drying (step 2) and firing (step 3). A ceramic matrix with a specific internal structure is formed as a result of the firing process since the used polyurethane foam burns out of the final ceramic product. The primary application field for our foam ceramic products is the filtration of molten metals where labyrinths of the foam help to trap inclusions and impurities, and

last but not least to laminarise turbulent flow. According to the literature³, the main types of ceramic matrix for photocatalysis can be divided into two groups: semiconductors (such as SiC) and metal oxide (such as Al₂O₃). The photocatalytic layer can be applied by spraying, immersing, chemical or physical vapor deposition, etc. Depending on the required parameters and applications field, it is possible to use several types of porosity. To specify porosity, the term – Pore Per Inch (PPI) is used, where the given number corresponds to the number of pores in one linear inch. For photocatalytic applications, PPI 10, 20, 30 are usually used.

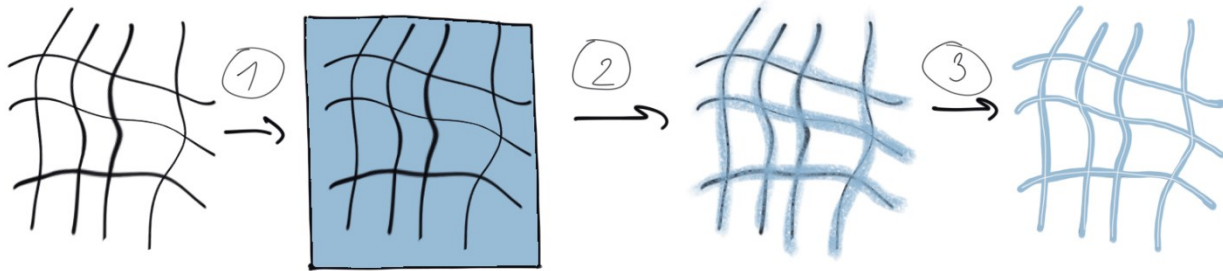


Fig. 1. The ceramic filter preparation approach

The previous study of Lanik research team⁷ has proved that the application of the photocatalytic coating on ceramic foam is about seven times more effective (tested on NO_x degradation) rather than the planar substrate (**Fig. 2**).

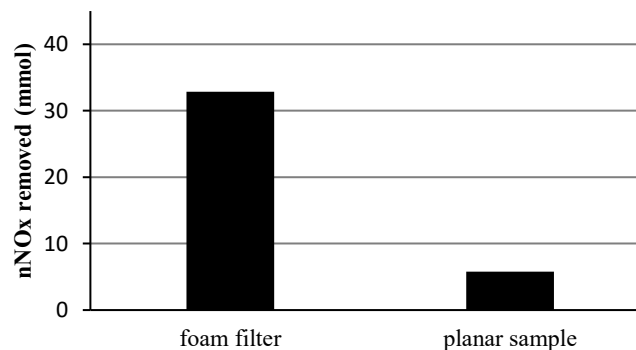


Fig. 2. The photocatalytic efficiency of a porous matrix over the planar sample on NO_x removal⁷

EXPERIMENTAL PART

The main aim of this experiment was to verify the influence of the suspension preparation technique on the compactness of the applied coating on the ceramics' substrate, then to measure the photocatalytic properties of selected suspensions.

For this experiment, LANIK s.r.o. collaborated with a supplier of TiO₂ in the Czech Republic – Precheza a.s. (Přerov). The product PRETIOX CG100 was used (with a specific surface area of 103 m²/g and primary particle size distribution D₅₀ – 15.8 nm) as a nano-powder medium for suspensions preparation.

For the purpose of production of ceramic filters, pure and stable raw materials were used. The ceramic based on aluminium oxide was selected as a matrix for TiO₂-based suspension. Also, this system benefits from the sufficient mechanical stability of the carrier matrix.

Suspension preparation

Applied suspensions were prepared using two different techniques: dispersing process using high shear dispersing machine (Dispermill Discovery, The Netherlands) with rotor-stator geometry. The mixing parameters were the following: mixing time – 10 minutes, 2 and 6 hours, the mixing speed was 1600 rpm, corresponding to the 5.03 m/s. The next set of samples was prepared by Precheza, using a pearl mill Labstar LS1 (NETZSCH GmbH, Germany) milling for 120 minutes. Parameters of individual suspensions are shown in **Tab. 1**:

Table 1. Parameters of individual suspensions

Suspension number	Preparation technique	TiO ₂ content wt. %	D50 μm	D90 μm
A	High shear dispersing machine	10	5.66	50.40
B			0.55	7.55
C			0.45	1.90
D	Pearl mill	25	0.085	0.126
E		10	0.085	0.123

Prepared suspensions were applied on the ceramic matrix by spraying, using a spraying gun under laboratory conditions (22 °C, RH~38%). The fixation on ceramic substrates was carried out by recalcination in electric at high temperature.

Samples were prepared in two dimensions; for surface analysis, the size was – 10 × 5 mm, and for photocatalytic measurement – 100 × 50 × 20 mm, both sizes were adapted to the individual instrument equipment.

Instrumental methods

Particle size distribution was measured using Horiba LA-960 V2. Scanning electron microscopy (SEM) was used to observe the effect of different preparation techniques of TiO₂ suspensions for surface quality and to monitor the effect of selected stabilizers on coating compactness. The microscope Tescan VEGA 3 was used.

Measurement of photocatalytic properties was carried out according to the modified approach ISO 22197-1 to determine NO_x degradation degree.

RESULTS AND DISCUSSION

First of all, prepared suspensions were evaluated as to the particle sizes, more precisely D₅₀ and D₉₀. The results are shown in Tab. 1. It is obvious that the pearl mill contributes to better deagglomeration about 10 times more than the high-shear dispersing machine.

Then, the compactness and the thickness of each coating on the ceramic substrate were evaluated by SEM analysis. Principal attention was focused on the influence of the suspension preparation procedure on surface quality. Then, selected suspensions were compared in terms of photocatalytic activity on NO_x degradation.

SEM analysis

Using this method, the surface quality and compactness were determined depending on the mixing technique. Homogenizer mixing represents a widespread method in suspension preparation; it was thus chosen as the main mixing technique. Nevertheless, after analysing the quality of the surface, this type of mixing did not bring the expected results. Even after several efforts of testing at different dispersing times, still, none of them met the expectations. As can be seen from **Fig. 3**, the TiO₂-based coating seems to be compact, nonetheless the amount and the size of agglomerations (**Fig. 4**) can negatively affect not only photocatalytic properties but can cause increased undesirable attrition of the coating.

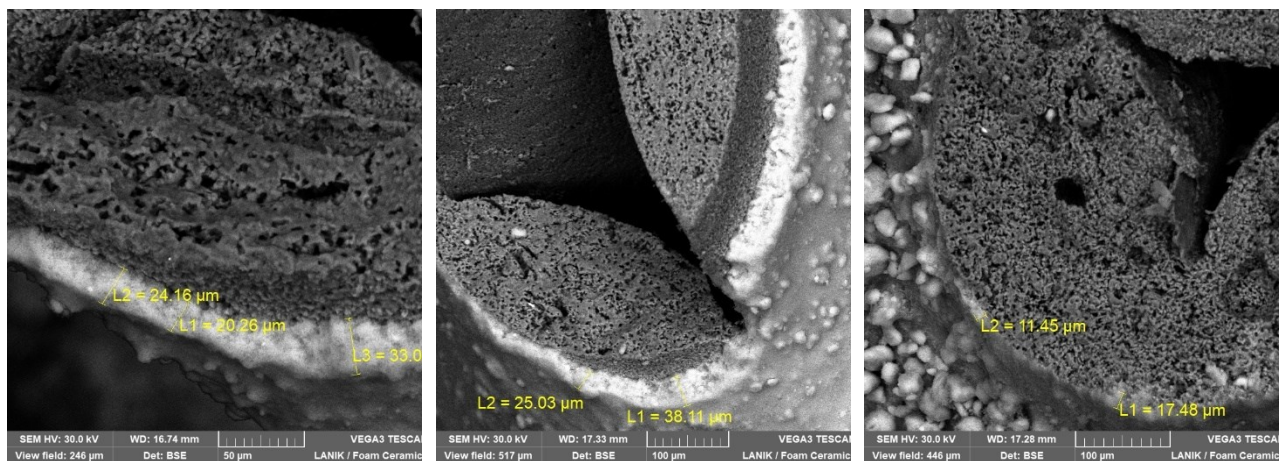


Fig. 3. Different dispersing times on layer thickness (from left to right: A, B, C)

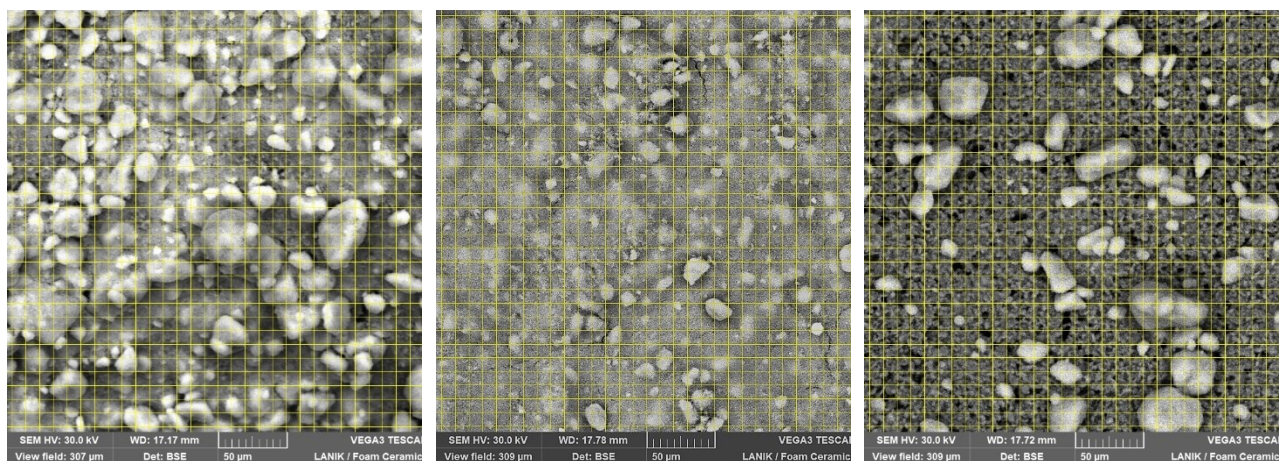


Fig. 4. Different dispersing times on surface quality (from left to right: A, B, C), the cell dimension is 10 × 10 μm

On the other hand, the pearl mill technique brought more satisfactory results in terms of surface quality. Moreover, the pearl mill technique contributes to the higher deagglomeration degree, **Fig. 5**.

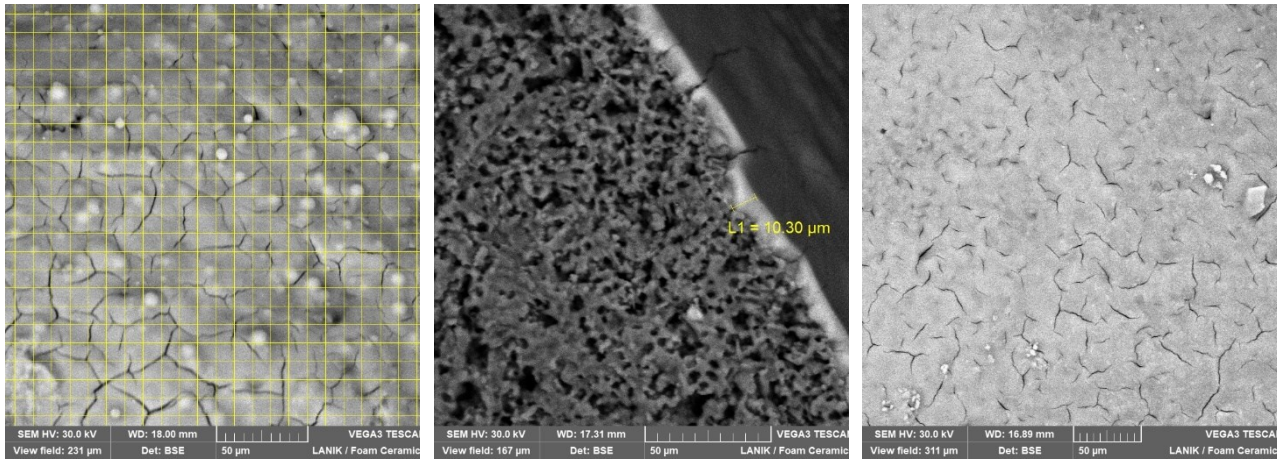


Fig. 5. Different TiO₂ content on surface quality using pearl mill technique, from left D, E, E (the cell dimension is $10 \times 10 \mu\text{m}$)

Photocatalytic properties

Photocatalytic efficacy was measured on suspension prepared by a pearl mill for higher TiO₂ content, suspension D. The photocatalytic activity was determined on NO_x degradation. Evaluation of the photocatalytic activity of the rest of the suspensions will be the subject of further research. The course of one of the measurements is shown in **Fig.6**. The mean value of the degree of conversion NO_x was determined at $49 \pm 3 \%$.

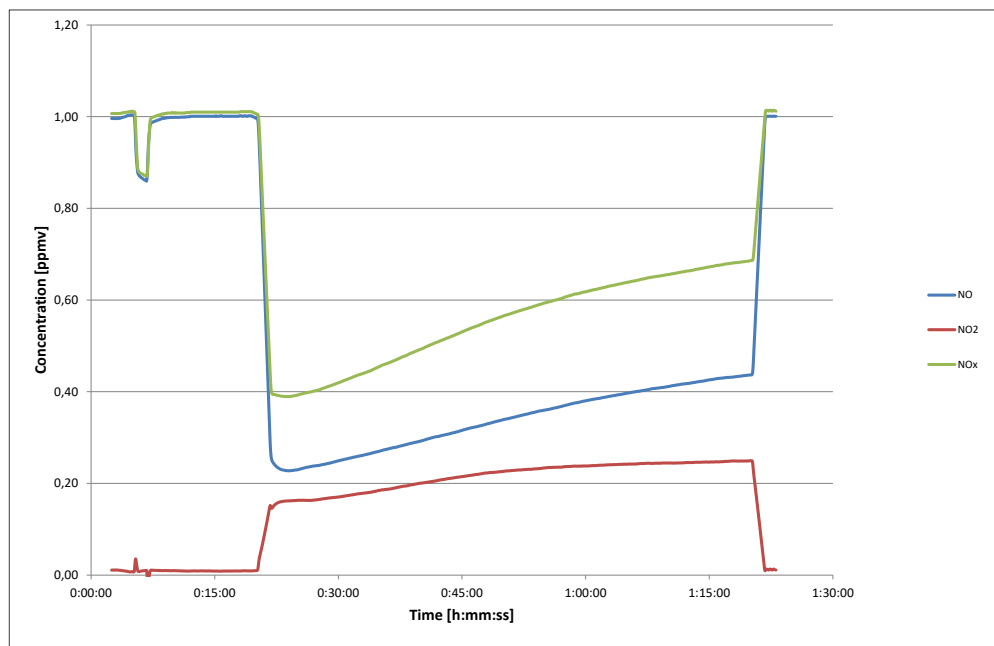


Fig. 6: The example of the measurement process.

CONCLUSION

The aim of this paper was to offer fresh sight into the application of TiO₂-based suspensions. Foam ceramics represent suitable substrates in terms of a high specific surface, chemical stability and innocuousness, and mechanical durability. The influence of the preparation technique on the TiO₂-based surface quality was verified within this work. The preparation technique is a key parameter that influences the deagglomeration degree and the further coating character. The high shear dispersing machine did not bring the expected results. Unfortunately, even the longer mixing (6 hours) did not positively affect the coating quality - the deagglomeration degree was still low. Moreover, the reagglomeration can take place because larger agglomerates (about two times) were monitored in case of 6 hours dispersing against 2 hours of mixing.

On the other hand, the pearl mill technique met expectations and showed better results in terms of surface quality and the deagglomeration degree. In terms of photocatalytic activity, almost 50% of NO_x degradation was achieved. The correlation between different prepared coatings and their photocatalytic activity will be the subject of further research.

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REFERENCES

1. Warren, Z. et al., 2023. Photocatalytic foams for water treatment: A systematic review and meta-analysis. *Journal of Environmental Chemical Engineering*, 11(1). Available at: <https://linkinghub.elsevier.com/retrieve/pii/S221334372202111X>.
2. Monteiro, S. et al., 2014. Stabilization of nano-TiO₂ aqueous dispersions with poly(ethylene glycol)-b-poly(4-vinyl pyridine) block copolymer and their incorporation in photocatalytic acrylic varnishes. *Progress in Organic Coatings*, 77(11), pp.1741-1749. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0300944014002021>.
3. Shih, Y.-H., Liu, W.-S. & Su, Y.-F., 2012. Aggregation of stabilized TiO₂ nanoparticle suspensions in the presence of inorganic ions. *Environmental Toxicology and Chemistry*, 31(8), pp.1693-1698. Available at: <https://onlinelibrary.wiley.com/doi/10.1002/etc.1898>.
4. Farner Budarz, J. et al., 2019. Chlorpyrifos degradation via photoreactive TiO₂ nanoparticles: Assessing the impact of a multi-component degradation scenario. *Journal of Hazardous Materials*, 372, pp.61-68. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0304389417309184>.
5. Bałdyga, J. et al., 2008. Dispersion of Nanoparticle Clusters in a Rotor–Stator Mixer. , 47(10), pp.3652-3663. Available at: <https://pubs.acs.org/doi/10.1021/ic070899u>.
6. Shaw, R.A. & Ogawa, T., Inorganic polymers. Part I. A solid inorganic foam. *Journal of Polymer Science Part A: General Papers*, 3(9), pp.3343-3351. Available at: <https://onlinelibrary.wiley.com/doi/10.1002/pol.1965.100030926>.
7. Mareček, P. et al., 2017. Application of foam ceramic panels as a photocatalytic filters: *Konference Pigmenty a pojiva*, Seč.

Defect engineering for highly active semiconductor photocatalysts

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ABSTRACT

The development of cost-competitive materials capable of producing fuels or electricity directly from the energy harvested from sunlight offers a desirable approach to fulfilling the need for clean, sustainable, and secure energy. Semiconductor metal oxides (*e.g.*, TiO₂, Fe₂O₃, or BiVO₄) are abundant, photoactive, stable and cheap; and thus they have been among the most widely adopted materials for the conversion of solar energy into storable and transportable chemical energy such as *e.g.* hydrogen (H₂). However, despite a huge scientific effort, their overall efficiency for solar-driven applications remains rather low due to several crucial limitations such as particularly fast recombination of photo-generated charges (electron-hole pairs) and sluggish kinetics of the redox surface reactions that hinder the practical application in this field. Defect engineering has become an attractive research direction for improving the optical and electronic properties of semiconductor photocatalysts towards boosting their photo(electro)chemical performance. For example, so-called non-stoichiometric black TiO₂ has demonstrated unexpectedly enhanced photo(electro)chemical activity, which has been attributed to the co-catalytic effect of unsaturated Ti³⁺ ion at the titania surface due to the presence of oxygen vacancies (V_O). Additionally, these unsaturated defects/sites provide a strong affinity to tightly bond or anchor various species such as transition metals single atoms, or carbon dots that can be used as even more effective co-catalysts. In this contribution, recent advancements regarding defect engineering toward significantly enhanced photocatalytic activity of oxide semiconductors will be summarized.

Separated TiO₂ nanotubes with single atoms-based co-catalyst for photocatalytic hydrogen production

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ABSTRACT

This work is focused on the development of novel nanodevices based on separated photoactive TiO₂ nanotubes decorated with suitable co-catalysts in the forms of single atoms for hydrogen production by photocatalytic splitting of water. In order to strongly anchor the co-catalysts on the surface of semiconductors we will first controllably introduce surface oxygen vacancies by a thermal reduction treatment. Since the precise control of the process is crucial for strong bonding of the co-catalysts as well as for controlling its optimal loading, we will investigate the role of defects with respect to physical, physicochemical, and functional properties of the nanotubes. We see a great potential of

highly valuable scientific results since the combination of single atom co-catalysts with separated TiO₂ nanotubes photocatalysts has not been systematically studied.

KEYWORDS

TiO₂ nanotubes, single atom, photocatalysis, hydrogen production

INTRODUCTION

The development of highly efficient energy conversion/storage devices has attracted great attention from scientific and technological researchers due to the increasing concerns for the environment and the depletion of fossil fuels. In this context, the development of cost-competitive materials capable of producing fuels or electricity directly from the energy harvested from sunlight offers a desirable approach towards fulfilling the need for clean, sustainable, and secure energy.

EXPERIMENTAL

TiO₂ nanotubes were grown on Ti foil (0.125 mm, Advent, 99.6+%) via electrochemical anodization technique using a typical organic electrolyte (Diethylene Glycol, 40 mL DI water, and 6 g ammonium bifluoride (NH₄HF)). Ti foil was anodized at 60 V for 3 hours at 40°C. Before anodization the Ti foil was degreased by sonication in EtOH, acetone, and DI water sequentially, and then dried in a N₂ stream. TiO₂ nanotubes were then annealed in air at 450°C for 2 hours (heating rate 2°C.min⁻¹). The reduction process was carried out in a ceramic crucible placed in a tube furnace using hydrogen stream (100 mL.min⁻¹) at 450°C for 1 hour (heating rate 10°C.min⁻¹). Annealed and reduced TiO₂ nanotubes were immersed in 10 mL MeOH (50 vol%) solution containing diluted H₂PtCl₆·6H₂O solution in a closed container for 24 h in dark. Before closing, the solution was purged with Ar to remove residual gases, such as oxygen and nitrogen. After staying in dark for 24 h, the tubes were then soaked in EtOH and DI water for 15 min each. Subsequently, the samples were dried in a N₂ stream. Then the samples were subject of measuring the real hydrogen evolution due to photocatalytic water splitting. The amount of hydrogen produced under irradiation and accumulating in the photoreactor will be determined online by Gas Chromatograph coupled to a Mass Spectrometer (GC–MS).

RESULTS AND DISCUSSION

We successfully prepared the separated TiO₂ nanotubes, decorated them with single atoms of platinum and we efficiently drove hydrogen production under solar light. We systematically investigated the properties of pure TiO₂ and TiO₂/SAs composites through material characterization using different spectroscopic techniques (HRTEM, EPR, XPS).

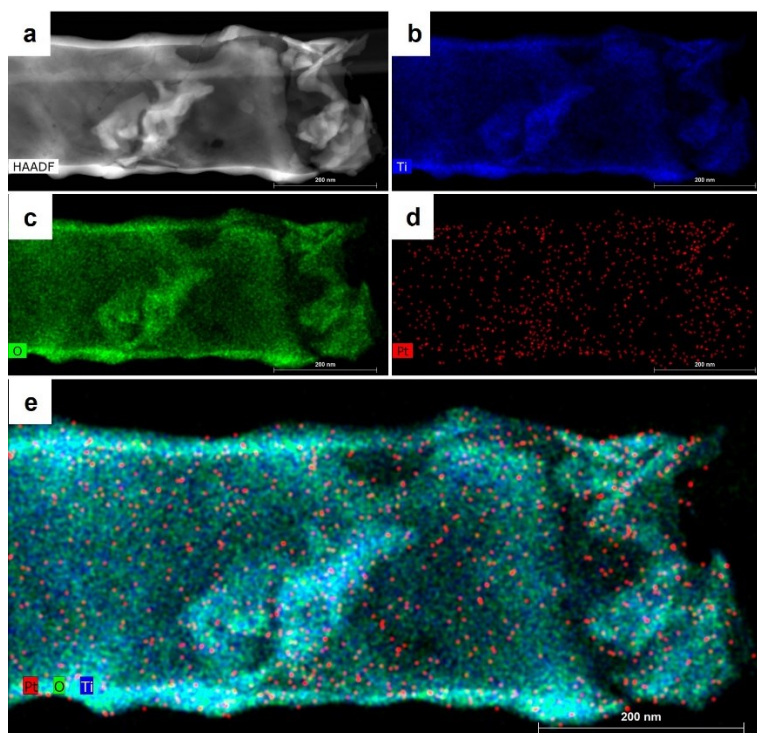


Fig. 1. STEM elemental mapping of the Pt SA-loaded TiO_2 nanotubes fragment.

CONCLUSION

Our results show ability to anchor the platinum single atoms to the surface of TiO_2 nanorods through defects caused by thermal treatment in hydrogen atmosphere and their use in photocatalytic hydrogen generation.

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REFERENCES

1. Naldoni, A.; Shalaev, V. M.; Brongersma, M. L. *Science* 2017, 356, 908.
2. Chen, X.; Liu, L.; Yu, P. Y.; Mao, S. S. *Science* 2011, 331, 746.
3. Xue, Z.H., Luan, D. Y., Zhang, H. B., Lou, X. W. *Joule* 2022, 6, 92-133.

A new insight into nanoparticle mobility

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ABSTRACT

The Brownian motion can be used to describe the nanoscale mobility using the principles of SMLS (static multiple light scattering) and DLS (dynamic light scattering) and together with dedicated algorithms provides the information about nanoparticle size. Furthermore it can be used to see the migration of particles in the sample and phase transitions. This presentation will introduce the portfolio of Cordouan Technologies, the new generation of time-resolved instruments range Vasco using DLS and Thetis the first commercial instrument using the principle of depolarized DLS that allows to measure the length and width of anisotropic particles. Formulation instruments range TurbiScan is focused on formulation stability (mean particle size and migration). Optic method approach observing nanoscale mobility can be also used to see low energy phase transition and it is very useful when describing thin layer formation (instrument range CurinScan).

KEYWORDS

Cordouan Technologies, Thetis, Formulation, TurbiScan

INTRODUCTION

Cordouan Technologies is the French specialist of advanced solutions for characterization (size, charge, etc.) of nanoparticles and nanomaterials. Their unique product portfolio is issued from patented and innovative technologies transferred from prestigious institutes: Institut Français du Pétrole (IFPEN), Karlsruhe Institute of Technology (KIT) or Institut Charles Sadron (ICS). Two instruments will be further introduced. The Vasco KinTM is a new generation of time-resolved instrument for accurate kinetic analyses combined with an in situ and contactless remote optical head. It allows to monitor in real time nanoparticles synthesis, agglomeration or the stability of suspensions. With a single and continuous measurement, Vasco KinTM gives access to all characterization data of a reaction (size distribution, scattered intensity, correlogramms, etc.).

ThetisTM the latest nano-particle size analyzer from Cordouan Technologies represents a new step in the DLS technique for nano-particle size analysis. For the very first time, an instrument allows to measure easily length and width of anisotropic nanoparticles in a colloidal suspension. Anisotropic particles movement can be divided into translational and rotational part providing two different diffusion coefficients. The incoming light is polarized into vertical and horizontal direction. The correlograms with advanced calculation mechanisms provide the length and width ratio of anisotropic particles. The ThetisTM is the first instrument that combines the principle of SLS, DLS and DDL with three different algorithms for nanoparticle size measurement.

Formulation has developed solutions for each step of the formulator's journey from formulation (suspension, emulsion, dispersion, etc.) development to final product. Their analytical solutions allow for directly and accurately measuring end use properties, such as (re)dispersibility, stability and shelf life, curing and drying, gelation, sprayability and injectability without complicated sample preparation and denaturation. Formulations can be used undiluted by not altering the product properties. Structural properties of materials at rest can be described by diffracting wave spectroscopy

(RheoLaserTM instrument range), this technology allows to monitor gel formation, rheological behaviours, network structure evolution and phase transitions.

TurbiScanTM range analysers are using SMLS the most appropriate method for native-state liquid dispersions characterization. Stability and shelf life, dispersibility and particle size of any liquid dispersions in concentrated and opaque samples without any stress/denaturation can be measured. NMA (nanoscale mobility analysis) allows the following microstructure changes in formulas. The high sensitivity of this measurement allows for identifying drying and curing mechanisms (evaporation, skinning, packing, hardening etc.) and characteristics times (open time, dry surface, dry through). This technology embedded in CurinScanTM range, is contactless and applicable on any type of substrate (glass, metal, paper, wood, artificial skin etc.) from RT up to 250 °C with humidity control.

CONCLUSION

Nanoparticle mobility can be used to describe important material properties. With Pragolab's (nano)particle dedicated portfolio including high quality and innovative instruments of Cordouan Technologies and Formulation, we can help you with academic research and industrial applications (process monitoring, quality control, research and development).

Acknowledgments: This contribution uses the materials kindly provided from companies Cordouan Technologies and Formulation.

Nano vs pigment TiO₂ – latest issues from producer's perspective

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ABSTRACT

Titanium dioxide (TiO₂) is the example of material produced both in nano range and as a pigment above the 100 nm threshold. The refractive index of any material dictates how particles of this material interact with electromagnetic radiation. Measuring methods for particle size are numerous and each gives its own value based on physical principles and limitations. Particle size influence the optical properties of the material in the visible light range; therefore, particle sizing is important for every TiO₂ producer. Electron microscopy is decisive method for estimating whether material is nanomaterial or not but it is tedious and difficult to automate, therefore other methods are often used despite of their limitations. We want to present difficulties resulting from poor understanding of particle size measurement principles and differences which has to be considered when using various particle size measurement methods.

KEYWORDS

Particle size measurement, TiO₂ properties, Safety

INTRODUCTION

History of TiO_2 production for pigment use is more than 100 years old. During this time the worldwide production increased from several thousand tons to more than 8 million tons per year. So, the average worldwide TiO_2 consumption is around 1kg/person/year with spread of several grams in developing countries to more than 3kg/person/year in USA or Europe. TiO_2 pigments can be found mostly in paints and plastics and not only to give the white look but also to provide opacity for usually transparent colour pigments.

TiO_2 as a material is not white but transparent¹ and its whiteness is due to combination of high refractory index and small (optimal) particle size. As the refraction index is constant the only way how to change the optical properties of pure TiO_2 is to change particle size so it is utmost importance of any TiO_2 pigment producer to understand principles of particle size measurement.

Particle size and its measurement is source of great confusion even among experts. This presentation is devoted to clarify some issues with particle size measurement, influence of particle size to optical properties of TiO_2 and also to recently raised safety aspects of particulate materials including TiO_2 .

Most of TiO_2 produced is used as a pigment (more than 90%) for quite a long time. TiO_2 nanomaterials are mainly used for catalysis, as UV absorbers or as photocatalysts for approximately 50 years, however in last few years the safety of TiO_2 is questioned and especially in Europe the tendency to ban or classify TiO_2 is strong mostly led by the fear of nanomaterials. The safety of TiO_2 is taken seriously by all producers. The insolubility and inertness of TiO_2 is prerequisite for its safety. The only way, how TiO_2 can interact with body tissues is therefore more or less mechanical and most existing toxicological studies have positive effect only due to overload conditions or when some artificial unnatural conditions are used in tests.

Recently the genotoxicology panel published² thorough overview which states that reviewed datasets do not support a direct DNA-damaging mechanism for TiO_2 in either the nano or micro form. The TiO_2 classification as carcinogen issued in delegated act 2020/217³ was appealed in European court and the judgement⁴ both overruled the reliability of the study used as a base for classification and also emphasized that such classification must be related to inherent material property following RAC Opinion that the mode of action of TiO_2 carcinogenicity could not be regarded as intrinsic toxicity of the material but is similar to any of materials which can be called poorly soluble low toxicity particles (PSLT) materials. If such reasoning that all PSLTs have the same toxicological profile had been accepted, all particulate materials should had been classified without further testing.

EXPERIMENTAL/THEORETICAL STUDY

There are numerous techniques for measuring particle size, some of them easy and some of them quite tedious. Good overview can be found in results of Nanodefine project⁵. In principle each method usually measures some property related to particle size like sedimentation speed, light scattering, hydrodynamic behaviour and others. Special case is electron microscopy where particles are counted and their area or dimensions are estimated. And this is the first source of confusion, each measurement technique works naturally with specific weighting and results are difficult to recalculate from one weighting to another. This is not so important in case of artificial particles with narrow size distribution like metal or latex standards but is the utmost importance in case of technically produced materials like pigment TiO_2 .

Brief overview of methods used to measure particle size

Laser scattering/diffraction

One of the most common methods. Requires suspension of particles in water or some other suitable liquid. The sample has to be diluted, in case of TiO₂ pigment to rather great extent. Scattering of electromagnetic waves by particles can be explained by Rayleigh or Mie theory^{6,7}. Intensity of scattered light is proportional to sixth power of particle diameter. Each equipment producer has its proprietary mathematical procedures of scattered light evaluation and therefore it is difficult to compare results of real samples measured by different equipment. The other drawback is that there is no proof that only primary particles are measured.

Dynamic light scattering

In principle, measured is decoherence of laser beam caused by moving particles due to the Brownian motion of molecules. Big particles tend to move slowly whereas small particles are quicker so the smaller are the particles the quicker is the decoherence of laser beam. This method is often used especially for nanoparticles but the main drawback is similar to static light diffraction – complicated mathematical evaluation, extreme dilution of the sample and inability to evaluate whether only primary particles are measured. Above these drawbacks the method is also sensitive to presence of big particles. On the other hand, due to the principle, results are closer to sedimentation methods than in case of static light diffraction.

Sedimentation techniques

Any particle with higher density than surrounding liquid sediments due to gravitational force and the sedimentation speed is given by Stokes law. The sedimentation velocity is proportional to the volume and density of the particle (in case of laminar region) so the results are volume or mass weighted. The particle concentration is measured by the light/Xray absorption and evaluated in time and space. The recalculation from the measured signal is more straightforward and mathematical apparatus is relatively simple. In case of optical detection and TiO₂ particles the sample must be diluted and the method cannot evaluate if primary particles or agglomerates are measured. One of the drawbacks is also limited range because big particles sediment quickly and may be lost before measurement and small particles will not sediment within reasonable measurement time.

Electron microscopy (EM)

Electron microscopy is a method of choice when measuring if particles are in nano range or not due to the fact that definition of nanomaterial is derived from number based primary particle size distribution. Except for aerosols measurement, EM is one of few methods providing number based minimum diameter and can detect primary particles. The problem is that this method is difficult to automate and the sample preparation and the way how the images are evaluated greatly influences the result, especially when dealing with broad particle size range material. The EM image size is limited and due to geometric constraints, the bigger particles have bigger probability to cross the image border than smaller particles and therefore are systematically undercounted.

Any method has its own strengths and weaknesses. Laser based methods are quick and easy to perform but calculation of particle size is difficult in case of broad particle size distribution. Sedimentation methods are more time consuming but give reasonable values for volume based distribution. Electron microscopy gives number based particle size distribution but requires expensive equipment, trained personnel and is time consuming. Although it is possible to recalculate one distribution to another in principle, it is not recommended in practice as the results can be error prone. The number based distribution to volume based distribution recalculation is probably easiest but still not recommended. Especially considering low number of particles counted on both ends of particle

size distribution the recalculation results are only approximate. One need to be also careful comparing average particle sizes of one sample from different methods. In principle, numeric representation of average particle size increases from number based to intensity based particle size distribution. It is illustrated by example on Fig. 1, where number and recalculated volume based distribution of one sample is compared.

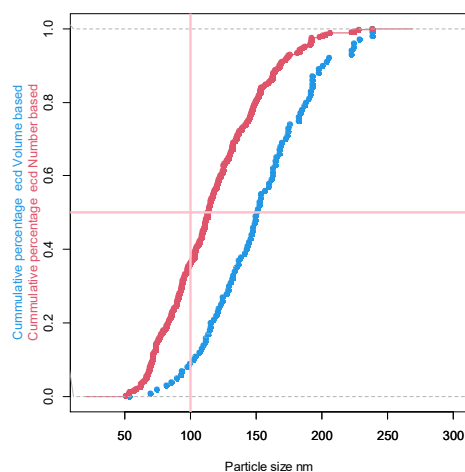


Fig. 1. Comparison of measured number based distribution (red) with calculated volume based distribution (blue) of the TiO_2 sample.

RESULTS AND DISCUSSION

Optical properties of TiO_2 result from its purity, refractive index and particle size. We evaluated how primary particle size influence optical properties measured by ASTM D6131 – 97 in gray paste.

We prepared anatase particles with volume based average particle size from 20 nm to 250 nm by calcination at temperatures from 200 to 1050°C and we measured tinting strength and undertone (blue/yellow) shade. As seen from the Fig. 2 average diameter of particles with highest tinting strength is between 130 and 220nm. Tinting strength sharply decrease above and below these thresholds. This means that the particles of TiO_2 become more transparent for visible light with decreased particle size and nano TiO_2 cannot be used as colorant. The lower is the value of undertone, the more yellow shade is obtained and undertones below 5 are usually not accepted. The optimum particle size for pigmentary anatase TiO_2 is therefore in relatively narrow range 105 to 160nm (number based).

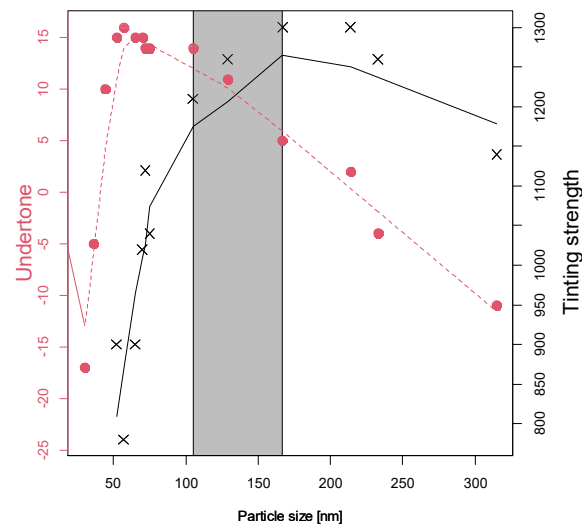
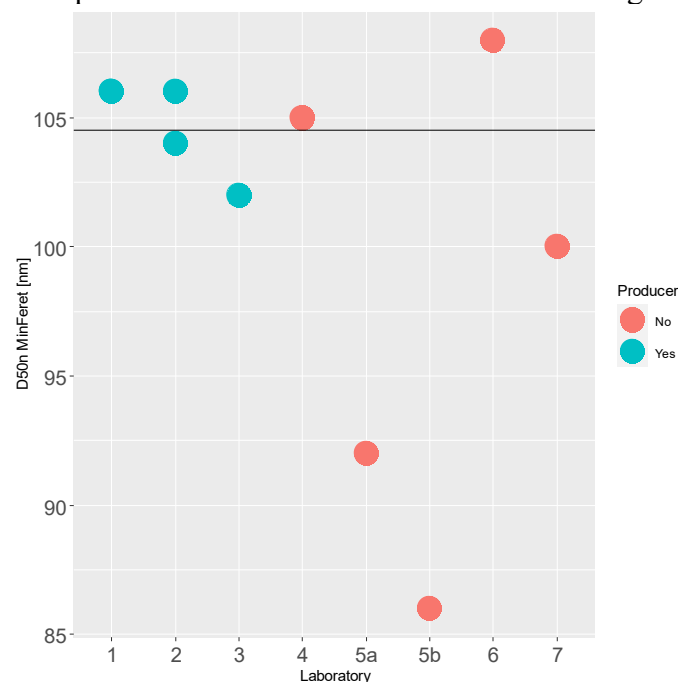


Fig 2 Influence of primary particle size (number based) on tinting strength and undertone of laboratory prepared TiO_2

The importance of correct and precise particle size measurement by electron microscopy is underlined by necessity of decision whether the material is nanomaterial or not especially from regulatory point of view because REACH requirements for nanomaterials are more stringent.



To illustrate the problems with electron microscopy we compared measurement of the same TiO_2 sample from 6 different labs. It can be clearly seen that all three TiO_2 producer labs give consistent results despite of different methodology for particle sizing. Results of other labs are much more variable and both measurement methods of lab 5 put the measured sample to the nanorange.

CONCLUSION

Particle sizing in sub micrometre range is not an easy task and requires good knowledge of all aspects both in technical and theoretical part. Specific attention needs to be devoted when measuring real technical materials which are agglomerated and has broad particle size distribution. Good example is measurement of pigmentary TiO₂ which has number weighted average particle size close to the 100nm threshold dividing nano and bulk (pigmentary) materials. The main problem with interlaboratory comparison and measurement method development is the fact that there is no certified reference material with above mentioned properties.

REFERENCES

1. Liqi Cui and Weitian Wang, "Optical properties of anatase and rutile TiO₂ films deposited by using a pulsed laser," Appl. Opt. 60, 8453-8457 (2021)
2. David Kirkland, Marilyn J. Aardema, Rüdiger V. Battersby, Carol Beevers, Karin Burnett, Arne Burzlaff, Andreas Czich, E. Maria Donner, Paul Fowler, Helinor J. Johnston, Harald F. Krug, Stefan Pfuhler, Leon F. Stankowski, A weight of evidence review of the genotoxicity of titanium dioxide (TiO₂), Regulatory Toxicology and Pharmacology, Volume 136, 2022, 105263, ISSN 0273-2300, <https://doi.org/10.1016/j.yrtph.2022.105263>.
3. https://eur-lex.europa.eu/eli/reg_del/2020/217/oj
4. EUR-Lex - 62020TJ0279 - EN - EUR-Lex (europa.eu)
5. V. Hodoroaba and J. Mielke, "Techniques evaluation report for selection of characterisation methods," NanoDefine Technical Report D3.1.
6. <https://www.scribd.com/document/234650128/Light-Scattering-by-Small-Particles-Min-Zhong>
7. https://en.wikipedia.org/wiki/Rayleigh_scattering

Graphitic carbon nitride for photocatalytic applications

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ABSTRACT

Graphitic carbon nitride (g-C₃N₄) is one of the very promising metal-free photocatalysts with semiconducting properties that has been intensively studied during the last decade. Its important physico-chemical properties are high thermal, physical, and photochemical stability. G-C₃N₄ absorbs visible light as a result of the band gap energy of about 2.7 eV. It can be prepared by physical or chemical vapour deposition (PVD, CVD). However, a bulk synthesis from simple precursors by methods focused on the thermal condensation of nitrogen-rich precursors, such as cyanamide, dicyandiamide, melamine and so forth, allows for a high production at a low cost. However, in as-prepared state, it suffers from certain disadvantages, such as namely low specific surface area and fast recombination of photoinduced electron – hole pairs. They can be overcome by exfoliation [1], forming of heterojunction composites [2], and doping, for instance, with non-metal elements, such as sulphur, phosphorus [3], carbon, and oxygen [4]. Then, g-C₃N₄ can be used for various photocatalytic reactions, such as degradation of organic compounds, evolution of hydrogen, decomposition of nitrous oxide, reduction of carbon dioxide etc. This work summarizes some results of the photocatalytic applications of g-C₃N₄ obtained during last several years.

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REFERENCES

1. Svoboda L., Praus P., Lima M., Sampaio M., Matýsek D., Ritz M., Dvorský R., Faria J.D., Silva C.G., Materials Research Bulletin, 100 (2018) 322.
2. Reli M., Huo P., Sihor M., Ambrožová N., Troppová I., L. Matějová L., Lang J., Svoboda L., Ritz M., Praus P., Kočí K., Journal of Physical Chemistry A, 120 (2016) 8564.
3. Praus P., Smýkalová A., Cvejn D., Losertová S., Koštejn M., Novák V., Diamond and Related Materials, 130 (2022) 109439.
4. Praus P., Smýkalová A., Foniok K., Novák V., Hrbáč J., Journal of Environmental Chemical Engineering, 9 (2021) 105498.

Interfacing BiO_x nanoparticles to carbon nitride for solar fuel production

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ABSTRACT

In order to maintain and preserve terrestrial ecosystems, a lot of concern has been rising around safer and greener conditions, endeavoring the development of less polluting protocols.

This goal includes exploiting photons and electrons to prompt chemical reactions,¹ as the progressive reduction of precious metals while crafting catalysts' active centers.²

On this leitmotiv, we propose the development of novel semiconductor interfaces between the earth-abundant bismuth oxide and carbon nitride, discussing how different synthetic protocols can impact on the hydrogen evolution reaction (HER) from ethanol photoreforming.

Upon slight modifications from the state-of-the-art literature,^{3,4} we got core-shell Bi@BiO_x nanoparticles that were interfaced with carbon nitride before (*composite B*) or after (*composite A*) the complete graphitization.

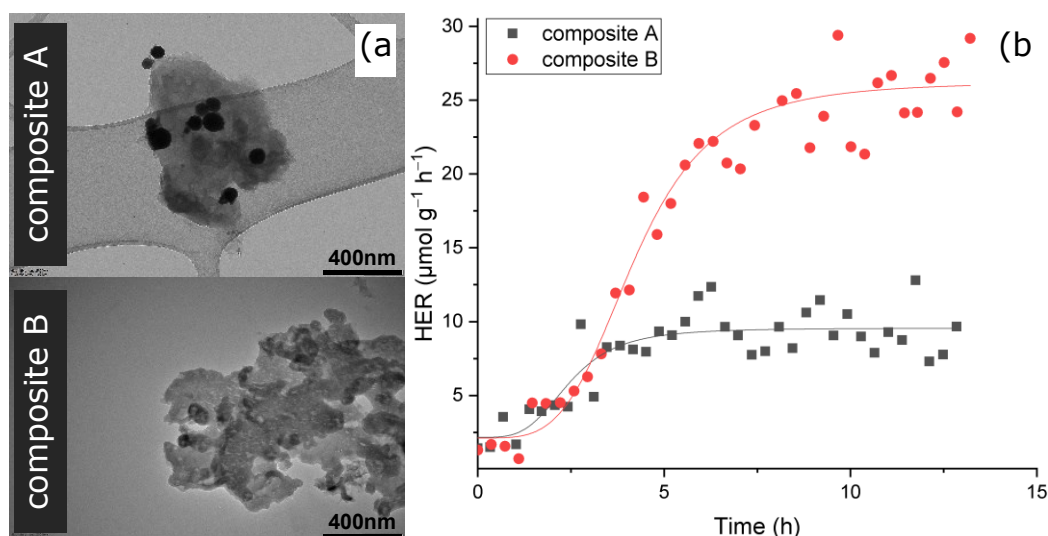


Fig. 1. (a) TEM images (25k magnification) of the two composites presented and (b) their hydrogen evolution rate.

Interface modifications induced a noticeable difference in terms of hydrogen production, with the composite B performing approximately three times more than the other one.

These encouraging preliminary results are pushing us towards more ambitious fields, such as photoreduction of CO₂, known that similar interfaces have been demonstrated to be active under electrocatalytic settings.⁴

KEYWORDS

bismuth oxide, carbon nitride, solar fuels, photocatalysis

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REFERENCES

1. (a) Sportelli, G.; Boselli, T.; Protti, S.; Serpone, N.; Ravelli, D., *Solar RRL* 7 (2023), 2201008; (b) Melchionna, M.; Fornasiero, P.; Prato, M.; Bonchio, M., *Energy Environ. Sci.* 14 (2021), 5861-5833; (c) Osterloh, F.E., *ACS Energy Lett.* 2 (2017), 2, 445-453
2. Kaiser, S.K.; Chen, Z.; Akl, D.F.; Mitchell, S.; Pérez-Ramírez, J., *Chem. Rev.* 120 (2020), 12, 11703-11809
3. (a) Chen, M.; Li, Y.; Wang, Z.; Gao, Y.; Huang, Y.; Cao, J.; Ho, W.; Lee, S. *Ind. Eng. Chem. Res.* 56 (2017), 37, 10251-10258
4. Melchionna, M.; Moro, M.; Adorinni, S.; Nasi, L.; Colussi, S.; Poggini, L.; Marchesan, S.; Valenti, G.; Paolucci, F.; Prato, M.; Fornasiero, P., *ACS Appl. Energy Mater.* 5 (2022), 11, 13356-13366

New advances in molecular (FTIR and Raman) microscopy and nanoscopy

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ABSTRACT

Scattering-type scanning near-field optical microscopy (s-SNOM) is the ideal technology to investigate modern nanomaterials at the real nanoscale. SNOM technique combines highlights of two worlds: high spatial resolution of Atomic Force Microscopy (AFM) and analytical power of optical microscopy and spectroscopy (f.e. IR, FT-IR and Raman). By achieving an unmatched spatial resolution below 10 nanometres this technology opens a new era for modern nano-analytical applications such as chemical identification, free-carrier profiling and plasmonics near-field mapping. We will introduce the basic principles of near-field microscopy for imaging and spectroscopy with 10 nanometres spatial resolution and address their impact and key applications in the field of nanomaterial research.

KEYWORDS

SNOM, Raman, FT-IR, spectroscopy, microscopy

INTRODUCTION

Main limitation of FTIR and Raman microscopy for study of nanomaterials are its spatial resolution limits. Usually is infrared (FTIR) microscopy limited by diffraction limit at approximately 10 micrometres and Raman microscopy around 400 nanometres. Spatial resolution of AFM is on the other hand excellent, but mostly with no optical and chemical information. So, there is logical need to combine analytical power of optical spectroscopy with high spatial resolution AFM. Main focus of this presentation is introduction to this quite new research area via description of some key applications.

EXPERIMENTAL/THEORETICAL STUDY

All examples in this presentation are performed with new line of nanoscopy instruments from German company Attocube systems AG: **neaSCOPE line** (original company Neaspec was founded in 2007 by the world's leading experts of near-field microscopy as a spin-off from the the Max-Planck-Institute of Biochemistry).

RESULTS AND DISCUSSION

As a nano-analytical tool, there is a wide variety of application for SNOM: 2D materials, semiconductors, nanowires, mineralogy, catalysis, polymer research, microplastics in environment, Li-ion batteries research, Plasmonics, bio research etc. Development of new single widely tuneable laser leads to unmatched possibility of fast measurement of infrared spectra (FTIR) in wide range

7140 – 540 cm^{-1} with spatial resolution around 10 nanometres (only limitations are AFM tips properties) and spectral resolution better than 4 cm^{-1} . Imaging (or hyperspectral imaging) of samples leads to comprehensive amounts of information about given samples from AFM map(s) and spectroscopy images in one step of sample analysis. One of the newest additions for overall nanomaterial research is correlative TERS (Tip Enhanced Raman) and nano-FTIR spectroscopy mode using patented dual beam-path design. This option allows fast sample mapping/imaging, where results includes FTIR images, Raman images and AFM modes images: all correlated in one comprehensive results package (see Fig.1).

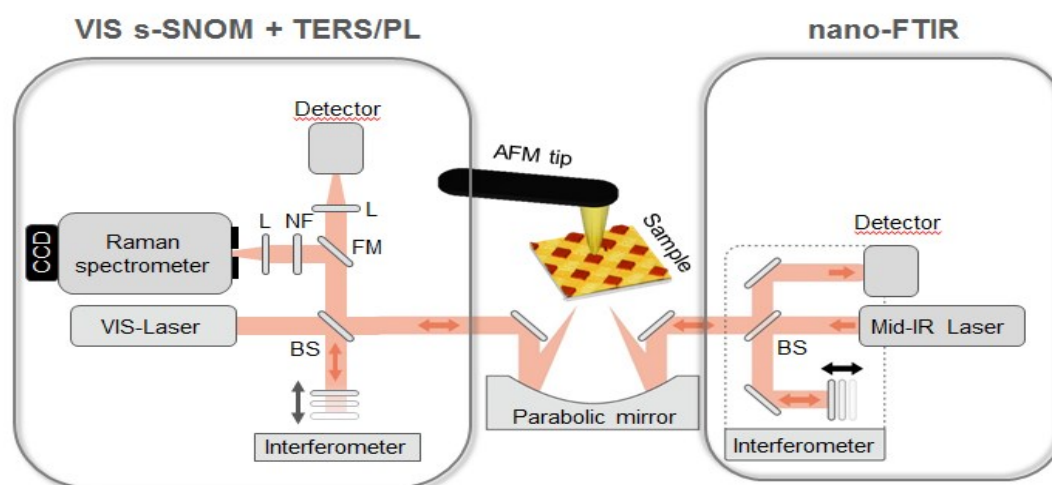


Fig.1. Schema of new TERS / nano-FTIR system: **IR-neaSCOPE^{+TERS}**

IR-neaSCOPE^{+TERS} combines nano-FTIR with TERS and Photoluminescence (PL) spectroscopy for an ultimate characterization using elastic and inelastic light scattering within the same microscope. It allows for simple alignment procedure using complementary IR or visible scattering, which delivers robust nanoscale Raman and PL performance even with standard metallized AFM tips.

s-SNOM applications examples described in presentation:

Chemical mapping of complex polymer nano-composite materials – Car tires

Nano / Microplastics in sea water, ice and snow

Detection of nanoscale domains in polymer brush monolayer(s)

Nano-IR (FTIR) measurements of soft organic biomaterials

Solar cells research

Quantum graphene dots

New Li-ion batteries quality control and future research (E.g. delithiation)

Probing structural changes in single enveloped virus particles

CONCLUSION

Breaking diffraction limits of optical spectroscopy via combination with modern AFM technology leads to new options for nano-imaging of many different kinds of materials and to better material understanding in many different research areas. Focus of this presentation was on real examples of application of this technology in variable research areas.

REFERENCES

1. T. Taubner, R. Hillenbrand, F. Keilmann, Journal of Microscopy, Volume 210, Issue 3, p. 311
 2. A. Cvitkovic, N. Ocelic, and R. Hillenbrand, Nano Letters 7, p.3177
 3. M. Meyns, S. Primpke, G. Gerds, Analytical Methods, Issue 40, p.5195
- All references are listed here: <https://www.neaspec.com/references/publications/>

The effect of metal-related nanoparticles in the germination of selected commercial crop

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ABSTRACT

The application of nanotechnologies and nanoparticles (NPs) is currently integrated into all human activities involving engineering, the energy industry, medical and pharmacology, agriculture, and other related disciplines. Before the widespread application of NPs in natural agronomic environments, it is profitable to deal with the accompanying effects on morphological, physiological, and biochemical pathways and reactions in plants under laboratory conditions. For a precise evaluation, the germination test in interaction with nanoparticles could be provided as an ideal alternative.

In this context, evaluating the type of nanoparticles, their concentration, stability, size, and other physicochemical properties are appropriate. In general, the germination of seeds includes several interconnected processes such as water absorption, initiation of metabolic changes, root growth and the formation of the first leaves.

Currently, toxicological studies employed various metals and metal oxide nanoparticles such as ZnO, TiO₂, CeO₂, Fe₂O₃, SiO₂, CuO, Ag, Al, Cd, Cu, Pb etc., which were categorized into inorganic nanoparticles. Here, zinc oxide is the most frequently used nanoparticle worldwide. Based on plant essentiality, zinc corresponds to micronutrients, including photosynthesis, protein formation, regulation of plant growth and development, and protection against environmental stress. Therefore, the aim of the presented work was to determine the effect of nanoparticles containing zinc and using different concentrations on the germination and initial growth of winter wheat (*Triticum aestivum* L.).

From the results, it is evident that discrepancies were observed in the range of applied zinc NPs with different concentrations to winter wheat in comparison with NPs free control. Certain trends were observed in terms of germination and the length of the plants. However, this inspired us to elaborate on the furthermore sophisticated experiment's trials and methodologies for precise determination mechanisms between the interaction of NPs and other commercial crops.

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Poster presentations (PP):**Towards biofuel molecules in a single pot**J. H. Advani^{1,2}, A. Manal², R. Srivastava²¹Nanotechnology Centre, CEET, VSB-Technical University of Ostrava, Ostrava-Poruba 70800, Czechia;²Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, India

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ABSTRACT

Biofuel production from the platform molecules like Levulinic acid (LA) and furfural is highly compelling. This study involves the synthesis of a bifunctional nanoporous Zr-phosphonate catalyst and its effective utilization in the selective γ -valerolactone (GVL) production via catalytic transfer hydrogenation of LA. A 98.1% LA conversion with 98.2% GVL selectivity was observed using isopropanol as H-donor. The synergic presence of acidic and basic sites on the catalyst favored the formation of biofuel molecules like furfural ether and GVL under mild reaction conditions via tandem furfural transformation. The catalyst afforded 93.4% furfural conversion with 50% furfural ether and 17.6% GVL selectivity in just 2 h. Almost complete furfural conversion with ~90% total biofuel selectivity (65% GVL and 24.5 % furfural ether) was observed in 12 h. The improvement in the GVL selectivity (82%) was realized by incorporating a Brønsted acidic phosphotungstic acid alongside the phosphonate catalyst. The structure-activity correlation and reaction mechanism were predicted by integrating the catalyst optimization studies with the physicochemical characterizations and poisoning tests. The fine tailoring of a single catalyst that enables a cascade transformation of furfural to GVL will highly encourage the researchers and catalysis industries.

KEYWORDSCascade Transformation, Biofuels, Furfuryl ether, γ -valerolactone**INTRODUCTION**

The ever-increasing population has led to a high dependence on the fossil fuels for energy and chemicals, elevating the oil prices. Intensive efforts are focused on the production of these chemicals and fuels from the non-edible biomass. The development of sustainable and efficient technologies to produce these biofuels is highly anticipated. Biodiesel, bioethanol, methylfuran, dimethylfuran, various alkylated furanic ethers, γ -valerolactone, and tetrahydrofurfural are examples of several such molecules.¹ The octane number and energy density of the GVL are almost identical to the ethanol. However, the low vapor pressure of GVL gives an added advantage making it easier to store and transport. Moreover, GVL can be easily transformed into various hydrocarbons, making it extremely important as a fuel additive. On a similar note, furfuryl ethers, produced via much cheaper protocols than the methylfurans, have anti-knocking properties and are more ecofriendly than the methylfurans.

The etherification of furfuryl alcohol to furfuryl ether and hydrogenation of levulinic acid/esters to GVL occur under reducing environments. However, the production of these ethers and GVL from readily available biomass derived molecules like furfural in a single pot can increase overall efficiency of the reaction by reducing the losses that occur during purification steps. This not only improves the process economy but also makes the transformation more sustainable.¹ Under the reductive environment, FFA can be transformed to GVL via furfuryl ether. The earlier reported

literature suggests the integration of two different catalysts or longer reaction time to produce GVL.²⁻⁵ Herein, we demonstrated the utilization of acid-base bifunctional nanoporous catalyst preliminarily for the catalytic transformation of levulinic acid to GVL and later for the cascade conversion of FFA to GVL via furfuryl ethers under milder reaction conditions.

EXPERIMENTAL STUDY

Synthesis of zirconium phosphonate (ZrNPO₃) catalyst:

Nanoporous polymeric ZrNPO₃ catalyst was synthesized by a reacting nitrilotris(methylene)triphosphonic acid with ZrCl₄ in DMF solvent under aging at 80 °C for 12 h.

Catalytic transfer hydrogenation of levulinic acid (LA)/Furfural (FFA) to γ -valerolactone (GVL):

The catalytic transfer hydrogenation (CTH) of LA/FFA was carried using ZrNPO₃ catalyst in Isopropanol as solvent-cum-H-donor under autogenous pressure.

RESULTS AND DISCUSSION

The physicochemical properties of the synthesized ZrNPO₃ catalyst were thoroughly performed using XRD, electron microscopy, elemental mapping, N₂ adsorption-desorption analysis, FTIR, Pyridine adsorbed FTIR, TPD, and XPS.

The preliminary studies for the catalytic transfer hydrogenation were carried using different Zr-based catalysts like ZrO₂, ZrPO₄ and ZrNPO₃. Among different Zr-based catalysts, ZrNPO₃ catalyst showed the highest TOF during the CTH of LA giving a 98.1% LA conversion with 98.2% GVL selectivity in 8 h under the optimized conditions. The kinetic profile for the CTH of LA using ZrNPO₃ catalyst showed a pseudo-first order kinetics. The catalytic activity of the ZrNPO₃ catalyst was found to be comparable to the hereto reported catalysts.

The cascade transformation of FFA to GVL was further evaluated using the different Zr-based catalysts under the optimized reaction conditions. The high Lewis acidity of the ZrNPO₃ catalyst activated the >C=O bond of the FFA/levulinate, favoring the reaction to proceed in the forward direction, giving almost complete FFA conversion with 90 % selectivity towards the biofuels (65 % GVL and 24.5 % furfuryl ether) at 180 °C in 12 h. The kinetic studies with time suggested a major FFA conversion (93.4%) producing 50 % furfuryl ether, and 17.6 % GVL in just 2 h.

To evaluate the role of the acid-base sites in the catalyst, the catalyst was individually poisoned using benzoic acid and pyridine as passivates. The poisoning experiments demonstrated that the GVL selectivity was 6-7% more in the proximity of the pyridine than that involving benzoic acid signifying the importance of the base which in synergy with the acid sites favor the formation of the GVL. The catalytic optimization studies were combined with poisoning studies and the detailed physicochemical characterization to acquire insight into the structure-activity correlation and reaction mechanism.

CONCLUSION

A bifunctional acid-base inorganic-organic hybrid nanoporous ZrNPO₃ catalyst with high surface area was synthesized and used to produce biofuel molecules using isopropanol as H-donor. High GVL selectivity was obtained for the hydrogenation of LA. The catalyst was also efficient in the MPV reduction of FFA producing furfuryl ether and GVL with combined selectivity of 90 % at 180 °C. A high IPMF yield (58.4 %) with only 11 % GVL was obtained in just 1.5 h at 180 °C. On allowing the

reaction to proceed further, IPMF was converted to subsequent products giving the highest selectivity of 65 % for GVL in 12 h. The absence of the Brønsted acidity in the ZrNPO_3 catalyst was responsible for the incomplete furfural ether conversion. This fact was verified by the increase in the GVL selectivity when a Brønsted acidic phosphotungstic acid was added alongside the ZrNPO_3 catalyst. The excellent catalytic activity and recyclability was attributed to the Lewis acidic Zr^{4+} sites, presence of basic sites from the phosphonates and large surface area with high pore volume. The facile catalyst synthesis and the exemplified protocol to produce highly demanding furfuryl ether/GVL biofuel molecules is highly beneficial to be practiced on an industrial scale.

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REFERENCES

1. A.K. Manal, J.H. Advani, R.S. Srivastava, *ChemCatChem* 14 (2022) e202200576.
2. L. Bui, H. Luo, W.R. Gunther, Y. Roman-Leshkov, *Angew. Chem. Int. Ed. Engl.* 2013, 52, 8022-8025
3. S. Zhu, Y. Xue, J. Guo, Y. Cen, J. Wang, W. Fan, *ACS Catal.* 2016, 6, 2035-2042
4. S. Song, L. Di, G. J. Wu, W. L. Dai, N. J. Guan, L. D. Li, *Appl. Catal. B.* 2017, 205, 393-403
5. H. P. Winoto, Z. A. Fikri, J. M. Ha, Y. K. Park, H. Lee, D. J. Suh, J. Jae, *Appl. Catal. B* 2019, 241, 588-597

Photosensitization of Singlet Oxygen via Adsorption-Induced Emission Phenomena in Hybrid Systems of Porphyrins and Layered Silicates

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ABSTRACT

The ability of various dyes to sensitize highly reactive singlet oxygen is a useful tool with potential applications in synthetic photochemistry, environmental and medical fields, such as antibacterial materials. However, for many of these applications, it is necessary to immobilize the photosensitizers on solid carriers, which can pose a challenge due to molecular aggregation of the dye molecules, leading to reduced singlet oxygen production.

This study investigates the relationship between molecular aggregation of two metallo-porphyrin-based photosensitizers and singlet oxygen production efficiency in hybrid systems with synthetic saponite Sumecton SA. We controlled the molecular aggregation of porphyrins by varying the silicate/dye ratio ($n_{\text{dye}}/m_{\text{silicate}}$ - mmol/g) and/or by pre-modifying saponite with cetyltrimethylammonium cation. In addition, we observed the phenomenon of adsorption-induced emission caused by the planarization of metalloporphyrins on the smectite surface. This planarization suppressed the non-radiative deactivation of molecules.

Overall, these findings provide insights into optimizing singlet oxygen production in photosensitizer immobilization on solid carriers, which could have significant implications for the development of new applications in various fields.

KEYWORDS

Singlet oxygen, Hybrid materials, Molecular aggregation, Adsorption induced emission.

INTRODUCTION

Photogenerated reactive oxygen species (ROS), such as singlet molecular oxygen ($^1\text{O}_2$) are a group of highly reactive oxygen compounds that play a crucial role in the field of environmental chemistry. They are involved in a range of chemical reactions, including the photooxidation of organic substances in the environment. Therefore, singlet oxygen's unique ability to efficiently oxidize organic pollutants has made it a valuable tool in the field of environmental technologies. In water and wastewater treatment, $^1\text{O}_2$ can be used to eliminate organic pollutants from contaminated water sources because $^1\text{O}_2$ can oxidize a wide range of organic compounds, such as pesticides, pharmaceuticals, and dyes, making it an effective treatment method for various water pollutants.

$^1\text{O}_2$ is commonly prepared through a process known as photosensitization, where organic molecules such as porphyrins or phthalocyanines are used as photosensitizers. After photoexcitation of the photosensitizer molecule to its excited triplet state, it can transfer its excitation energy to ubiquitous molecular oxygen leading to $^1\text{O}_2$ formation.¹

The use of $^1\text{O}_2$ in environmental technologies is limited by several factors, including low quantum yields, low selectivity of reactivity, and the need to remove the photosensitizer from purified water.²

One solution to the limitations of $^1\text{O}_2$ in environmental technologies is to fix the photosensitizer molecule on a solid support, such as layered silicates like smectites.³ Adsorbing organic dyes onto the smectite surface under suitable conditions, the molecular aggregation of dyes can be suppressed, which can effectively control the photosensitization quantum yield. In addition, an observed phenomenon of adsorption-induced emission, where the adsorption of the photosensitizer onto the smectite surface can lead to a suppression of non-radiative relaxation of the excited state and, therefore, an increase in the quantum yield.⁴ Another benefit of fixing the photosensitizer molecule onto solid support is that the modified smectite can also act as an organic pollutant adsorbent in the system. This can increase the selectivity of the $^1\text{O}_2$ reaction because the organic pollutant becomes more accessible to $^1\text{O}_2$. The aim of the work is to study the effect of the fixation of two metalloporphyrins on the smectite surface on their ability to produce singlet oxygen.

EXPERIMENTAL/THEORETICAL STUDY

The synthetic layered silicate Saponite Sumecton SA (Sap), known for its small particles and lower cation exchange capacity (CEC - $0.73 \pm 0.02 \text{ mmol} \cdot \text{g}^{-1}$) was used. This saponite was therefore modified by cetyltrimethylammonium bromide (CTA^+) to 50% of the CEC of Sap. This surfactant is a modifier that changes the hydrophilic surface of Sap to a hydrophobic one, allowing the adsorption of neutral organic molecules through hydrophobic interaction. The Sap/ CTA^+ (0.4 g of Sap) was modified by the aquatic solution of Pt (III) meso-Tetra (N-Methyl-4-Pyridyl) Porphyrine (PtTMPyP^{4+}) or Pd (III) meso-Tetra (N-Methyl-4-Pyridyl) Porphyrine (PdTMPyP^{4+}) of concentrations of $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, to achieve the dye/Sap ratio of 0.1; 1; 5; and 10% of CEC of the Sap. The hybrid suspensions were stirred for 24 h at room temperature and subsequently were centrifuged and dried for 24 h at 50°C . Subsequently, the samples were manually crushed using an agate mortar. Thus, the samples were prepared for characterization and further experiments.

By the same procedure, the sample of Sap (0.4 g of Sap), but without modification by CTA^+ was modified by PtTMPyP^{4+} or PdTMPyP^{4+} , respectively.

Prepared materials were characterized by XRD and IR techniques to understand the structure and basic properties. The UV-Vis absorption spectroscopy and fluorescence spectroscopy were used to analyze the effect of dye/Sap interaction on the spectral properties of the porphyrin dyes.

The generation of singlet oxygen was tested using the sensor molecule anthracenediyl-bis(methylene) dimolonoic acid (ADMA), which can be decomposed by reaction with singlet oxygen, which can be measured using UV-Vis spectroscopy.

RESULTS AND DISCUSSION

Our experimental results showed that the most effective production of singlet oxygen was observed in samples with the lowest loading of photosensitizer on smectite. We attribute this to the suppression of molecular aggregation of the dye, which can lead to a decrease in the efficiency of singlet oxygen production. Furthermore, our results confirmed the phenomenon of increasing the quantum yield of singlet oxygen due to adsorption-induced emission. In addition to loading, we found that premodification of smectite with a surfactant also had an effect on dye aggregation. The surfactant modification further suppressed molecular aggregation, leading to an increase in the efficiency of singlet oxygen production. However, it should be noted that all prepared samples effectively degraded ADMA within 3 hours.

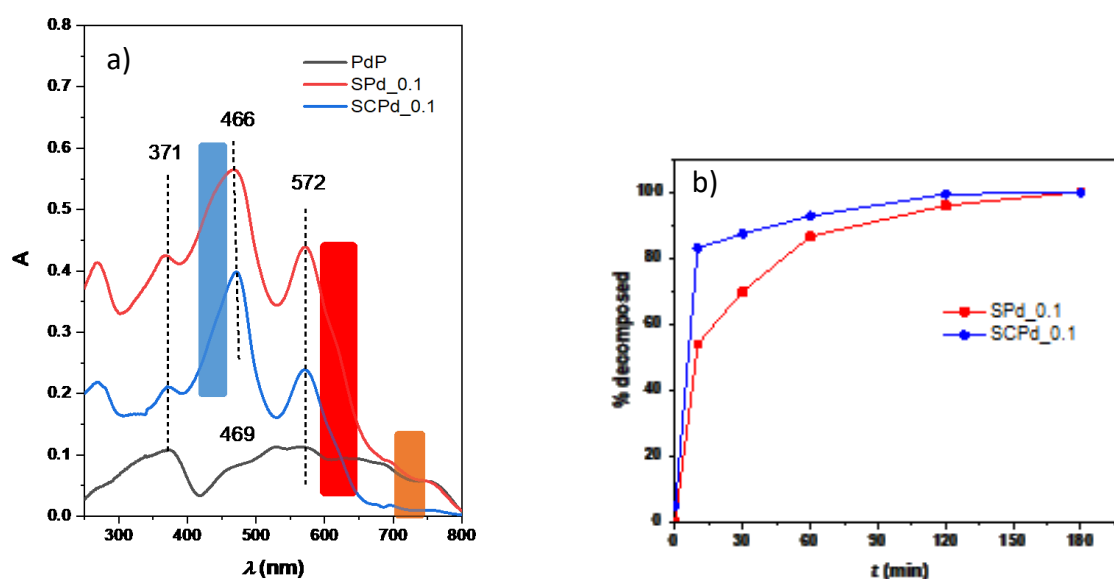


Fig. 1. a) The absorption spectrum of Saponite samples with PdTMPyP⁴⁺ with (SCPd) and without (SPd) CTA⁺ modification with the loading of 0.1. b) The decomposition rate of ADMA.

The adsorption efficiency of the ADMA molecule after 3 hours was measured as well. We found that Saponite alone did not show significant affinity towards ADMA. However, when Saponite was modified with porphyrin dyes, a weak level of adsorption was observed.

Interestingly, a significant increase in ADMA adsorption efficiency was observed when Saponite was pre-modified with the addition of CTA⁺. While the difference in aggregation between the compared samples with and without the addition of CTA⁺ was not significant, we hypothesize that the higher

efficiency of ADMA decomposition observed in the modified samples is likely due to its higher adsorption.

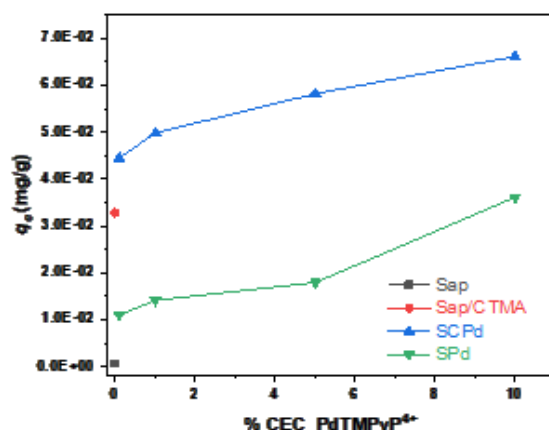


Fig. 2. Adsorption of ADMA after 3 hours.

The increased adsorption of ADMA on the modified Saponite samples may make it more accessible to singlet oxygen, leading to more effective degradation of the organic pollutant. These results suggest that pre-modification of Saponite with CTA⁺ can enhance the adsorption and degradation of organic pollutants, making it a promising approach for environmental technologies.

CONCLUSION

The most effective production of singlet oxygen occurred in samples with the lowest loading of photosensitizer on smectite, which was attributed to the suppression of molecular aggregation of the dye. The study also confirmed the phenomenon of increasing the quantum yield of singlet oxygen due to adsorption-induced emission. The pre-modification of smectite with a surfactant was found to suppress molecular aggregation and increase the efficiency of singlet oxygen production as well as enhance the adsorption of ADMA, which led to more effective degradation. All prepared samples effectively degraded ADMA within 3 hours, with modified Saponite samples showing higher efficiency due to increased adsorption capacity.

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REFERENCES

1. P.R. Ogilby, Chem. Soc. Rev. 39 (8) (2010) 3181–3209.
2. I. Pibiri, S. Buscemi, A. Palumbo Piccionello, A. Pace, ChemPhotoChem. 2 (7) (2018) 535–547.
3. T. Fujimura, T. Shimada, T. R. Sasai, S. Takagi, S. Clays Clay Miner. 67 (6) (2019) 537–544.
4. J. Bujdák, T. S. Baranyaiová, P. Boháč, R. Mészáros, J. Phys. Chem. B. 127 (5) (2023) 1063–1073.

Template assisted plasmonic nanomaterial assembly

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ABSTRACT

The optical properties of gold nanoparticles (AuNPs) substrate were obtained by adjusting the number of nanoparticles inside every anodic aluminum oxide (AAO) nanopore. AuNPs was embedded into nanopores with the assistance of ultrasonic wave. The UV-Vis absorbance spectra were clearly red-shifted when increasing AuNPs per nanopore from monomer M1 ($N = 1$) to clusters of M2 ($N = 3 \pm 1$), M3 ($N = 5 \pm 1$), and M4 ($N = 7 \pm 1$). COMSOL simulation results based on 2 nm nanogap distance among AuNP in nanopore which also consistent to the experimental absorbance of gold substrates with approximately 2nm length of Oleylamine ligand covering AuNP. The more hotspot occurred by elevating the nano number of nanoparticles which catalyze the coupling of 4-nitrobenzenethiol (4-NTP) to p,p'-dimercaptoazobisbenzene (DMAB) under 633 nm illumination. The Raman peak positions of DMAB were gradually appeared at M3 and become stronger for M4. Our process for fabricating the plasmonic substrate should be meaningful for adjusting photocatalysis by tuning the numbers of nanoparticles inside nanopores.

KEYWORDS

Hot electrons, Metal nanoparticles, Photocatalysis, Raman spectroscopy.

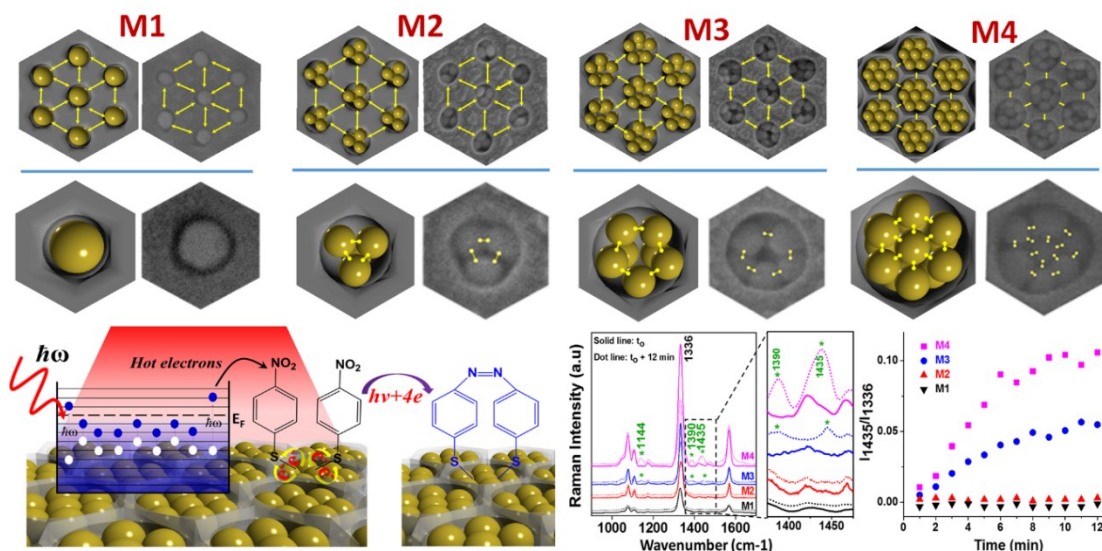
EXPERIMENTAL/THEORETICAL STUDY

To prepare AuNPs¹, HAuCl₄ (70 mg) was dissolved in toluene and oleylamine (1:1.2, v/v). Then, the solution was quickly injected into a preheated (80 °C) mixture of toluene and oleylamine (10:1, v/v) and refluxed at 120 °C for 2 h. After that, AuNPs were collected and purified by centrifugation and stored in toluene. The whole reaction cycle was repeated three times and five times to obtain the AuNPs of diameters of ~28 and ~43 nm, respectively.

To fabricate AAO templates², as-annealed aluminum foils were chemically electropolished in solution of perchloric acid and ethanol (1:5, v/v) at 5 °C and 15 V. The first anodization was performed in a 0.3 M oxalic acid solution at 10 °C, 40 V for 7 h and was then etched away by a solution of phosphoric acid and chromic acid. The length of AAO nanopores was controlled by the second anodization under the same conditions as the first anodization. The diameter of the nanopores was adjusted by a pore-widening step in phosphoric acid (5 wt %) at 30 °C.

AuNPs and AuNPs@AAO substrates were characterized using a field-emission scanning electron microscope (FE-SEM, JSM 7500F, JEOL), transmission electron microscope (TEM, Tecnai G2 F30, FEI). The UV-vis absorption spectra were obtained using a Shimadzu UV-3600 plus spectrometer equipped with an ISR 603 integrating sphere attachment. The Raman spectra were recorded by a Renishaw RM 1000 micro spectrometer and the laser spot diameter was ~2 μm diameter. Finite-difference time domain (FDTD) numerical simulation was performed using a Lumerical software to yield the scattering and absorption spectra of the AuNP aggregates including the electromagnetic enhancements between the nanogaps. NBT and DMAB calculations were performed via GAUSSIAN 09 at the B3LYP level with either 6-31G(d) basis set or the LanL2DZ basis set for the Au atoms.

RESULTS AND DISCUSSION



CONCLUSION

AuNPs were facily inserted into the AAO nanopore by ultrasonication method. The number of AuNPs in every AAO nanopore could be changed though controlling the size of AuNPs or the dimension of the AAO nanopore. All of the AuNPs substrates exhibited high reproducibility and stability for SERS detection and photocatalytic reaction by taking advantage of the plasmonic effect of substrates.

REFERENCES

1. Mourdikoudis, S.; Liz-Marzán, L. M., Oleylamine in Nanoparticle Synthesis. *Chemistry of Materials* **2013**, 25 (9), 1465-1476.
2. Lee, W.; Park, S.-J., Porous Anodic Aluminum Oxide: Anodization and Templated Synthesis of Functional Nanostructures. *Chemical Reviews* **2014**, 114 (15), 7487-7556.

Low temperature preparation of the PCL/PVDF composite materials

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ABSTRACT

PVDF (polyvinylidene fluoride) is a semicrystalline thermoplastic fluoropolymer with good mechanical and chemical resistance and piezoelectric properties. PCL (polycaprolactone) is a thermoplastic polyester often used for its good biodegradability and biocompatibility. Both polymers have been studied in detail, but little is known about their properties in composite materials or

mixtures. Therefore, this work focused on interaction between these polymers and their structural and phase properties. Composite films based on PVDF/PCL were prepared using hydraulic presses at different low temperatures. They were prepared from pure PCL thin films and PVDF thin films, some of which were modified with vermiculite in the amount of 1 wt% and 3%. These composites were then characterized by optical microscopy (OM), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetry (TGA). The prevailing phase of PVDF was observed to be α for unmodified layers and γ for those that were modified.

KEYWORDS

PVDF/PCL composites, vermiculite, structural properties, phase properties.

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REFERENCES

1. V. Tiwari, G. Srivastava, Effect of thermal processing conditions on the structure and dielectric properties of PVDF films, Dordrecht, 2014.
2. T. Wu, H. Jin, S. Dong, et al., A Flexible Film Bulk Acoustic Resonator Based on β -Phase Polyvinylidene Fluoride Polymer, Hangzhou, 2020.
3. L. Jiang, J. Zhang, Biodegradable Polymers and Polymer Blends 109-128.
4. Y. Kong, Y. Ma, L. Lei, X. Wang, H. Wang, Crystallization of Poly(ϵ -caprolactone) in Poly(vinylidene fluoride)/Poly(ϵ - 47 caprolactone) Blend, Shaanxi, 2017.

Polyurethane nanofiber membranes modified by amines for CO₂ capture

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ABSTRACT

The development of composite nanofibrous sorbents for CO₂ capture is primarily based on surpassing the already achieved values of sorption capacities for this important greenhouse gas. However, in this race to achieve the highest sorption values, very important issues related to real-world applicability, such as the simplicity, portability, usability and economic returns of such materials, are neglected. This research does not forget these important issues, and in this spirit, electrostatic softening of polyurethane (PUR Larithane) with a mixed amine TETA/TEPA modification was used to achieve them, meaning that both the electrostatic softening itself and the modification of the nanofibers were carried out in a single step. Not only due to computer modelling predicting the resulting interaction

nature between the polymer and modifier, a 10 times more breathable PUR/TEPA 5 wt.% nanofibrous material was successfully designed and softened simultaneously with 5 times higher CO₂ sorption capacity compared to the unmodified PUR nanofibrous membrane. Thus, this work provides a matrix and technology that is readily industrially transferable with the potential application of cyclic CO₂ capture.

KEYWORDS

CO₂ adsorption, Electrospinning, Sorption capacity, Solid supported adsorbent

INTRODUCTION

Carbon dioxide and other greenhouse gases are released into the atmosphere, causing changes in the Earth's climate. Many research groups are focusing on finding ways to capture and reduce CO₂ emissions. There are various methods of capturing CO₂, such as absorption technologies in liquid media, adsorption technologies using solid materials and membrane separation technologies. However, not all methods are effective both in terms of CO₂ sorption and energy consumption. For example, the amine purification method is very effective in capturing CO₂, but is energy intensive and potentially hazardous. On the other hand, there are also membrane technologies/materials available where nanofibrous materials have their penetration, which are economically, health and often environmentally friendly, but generally not as effective against liquid CO₂ capture technology. To address this shortcoming, most published methods use carbonization of polymeric nanofibrous materials to achieve excellent sorption capabilities that can be further enhanced by subsequent activation. However, the disadvantage of these technological approaches is the resulting sorption medium in the form of a powder in addition to the high number of technological steps. This complicates the design of a functional unit operating in the waste gas stream. Therefore, this work focuses on the development of permeable CO₂-absorbing membranes based on chemically modified polymer nanofiber membranes prepared by one-step electrospinning technology, i.e. the modifying agent is added directly to the solution during spinning. This technology, hence the material, strikes a balance between economical, application transferable and functional levels for targeted CO₂ capture with potential for cyclic process repeatability. For the spinning technology, we have chosen a wire spinning technology (nanospider technology) that is easily transferable to industrial production lines.¹

EXPERIMENTAL/THEORETICAL STUDY

One-step electrostatic membrane preparation and modification

Nanospider electrospinning technology (needle-free elspin. technology) using a wire as a spinning electrode was used. The most used technology using free-surface spinning electrodes is collectively assigned to the device called Nanospider, which in its earliest form worked with a spinning electrode in the form of a conductive cylinder, later replaced by wire to better control the fiber diameter. Nanofiber membranes have been prepared using wire electrospinning technology with a commercial Nanospider™ NS 1WS500U device from Elmarco. One-step technology has been used in present work that means modifying agents (TETA, TEPA amines) were dissolved in spinning solution. This process can generally be referred to as blend electrospinning.

Membrane characterization methods

The prepared samples of the PUR/TETA and PUR/TEPA membranes were characterized with a series of analytical methods: scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, hydrophobicity, electrokinetic analysis of surface chemistry, NMR analysis, and air permeability measurements. Atomistic molecular simulations were used to elucidate the interactions of polymer amines. Finally, CO₂ sorption tests were performed to determine the sorption capabilities of the formed nanofibrous materials with respect to CO₂.

RESULTS AND DISCUSSION

By comparing the SEM images in Figure 1, we could conclude that both amines led to changes in fiber morphology, i.e., significant decreases in fiber diameters (Table 1) and the straightening of the fibers (Figure 1b,d). With increasing amounts of applied amine, one can see a higher concentration of defects in the form of spindle fibers and continuous layers of material (Figure 1c,e). This negative effect of amines on the fiber structure is more pronounced in the case of the TETA amine. These changes in fiber morphology, and consequently, in membrane structures, are due to the chemical modifications that resulted in significant increases in air permeability in Table 1, measured under the standard conditions of a test area of 20 cm² and a constant pressure gradient of 100 Pa.

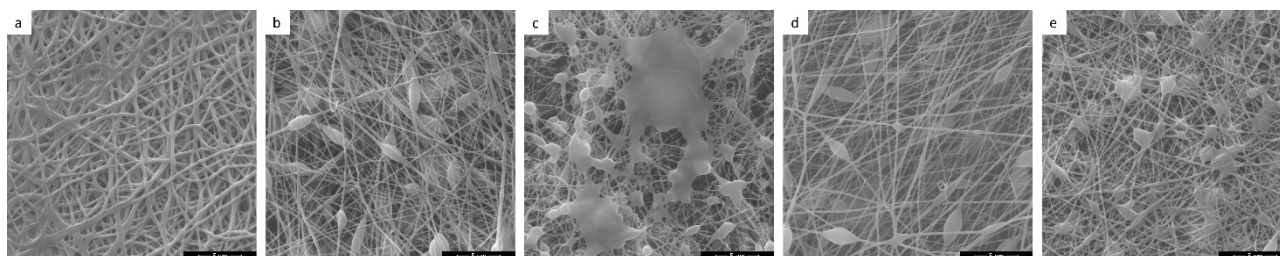


Fig. 1. Original SEM images (a) pristine PUR; (b) PUR/TETA (1 wt.%); (c) PUR/TETA (5 wt.%); (d) PUR/TEPA (1 wt.%); (e) PUR/TEPA (5 wt.%).

Table 1 summarizes the values of the fiber diameters, air permeability, and CO₂ sorption capacities for the measured samples, and it is evident that the chemical modifications increased the air permeabilities. It can be seen that the chemical treatment led to a significant increase in the sorption capacity and, at the same time, an increase in air permeability compared to the pure PUR membrane. The maximum sorption capacity for the PUR/TEPA sample (5 wt.%)~13.9685 cm³/g was accompanied by a reduction in air permeability compared to other modified samples (Table 1).

Table 1. Average values of the nanofiber diameters (in nm) obtained in the MMD measurements and air permeability for the pristine PUR membrane and the TETA- and TEPA-modified amine membranes (1 and 5 wt.%) and the CO₂ sorption capacity in g/cm³ (third column).

Sample	MMD Nanofiber Diameter (nm)	Air Permeability (m/s)	CO ₂ Adsorbed Volume (cm ³ /g)
PUR	290 ± 37	0.002 ± 0.0002	2.7 ± 0.9
PUR/TETA (1 wt.%)	170 ± 24	0.05 ± 0.004	8.1 ± 1.9
PUR/TETA (5 wt.%)	164 ± 35	0.13 ± 0.02	8.09 ± 2.0
PUR/TEPA (1 wt.%)	174 ± 40	0.08 ± 0.01	6.8 ± 1.8
PUR/TEPA (5 wt.%)	166 ± 45	0.02 ± 0.003	13.9 ± 2.3

The XRD structure analysis confirmed the crystallization of PUR during the spinning process (Figure 2). The diffraction profile at $2\theta \sim 20^\circ$ corresponds to the parallel arrangements of the PUR chains in the fiber axis. This position of the main peak for PUR Larithane is shifted to a lower angle in comparison with the XRD profiles for electrospun polyamide(6)^{2,3} and polyvinylidene fluoride⁴, indicating the higher space requirement for PUR Larithane chains due to their larger volume (isophorone diisocyanate and one hexane-1,6-diol). Electrospun membrane samples are always strongly textured, which means that the diffraction profiles corresponding to the crystallographic planes perpendicular to the fiber axis are missing. In addition, the large width of the diffraction profiles shows very small PUR crystallites, which means no observable reflections were present at high 2θ angles. The intensity of the XRD profiles decreased with an increasing amine concentration, as the amount of crystalline PUR decreased in samples due to the lower fiber diameters. In the case of the PUR/TETA samples with 5 wt.% of TETA, the diffraction profile exhibited additional peaks corresponding to crystalline TETA. The crystallization tendency of TETA affected the surface morphology of the modified fibers and reduced the values of the sorption capacity for PUR/TETA (5 wt.%) in comparison with PUR/TEPA (5 wt.%).

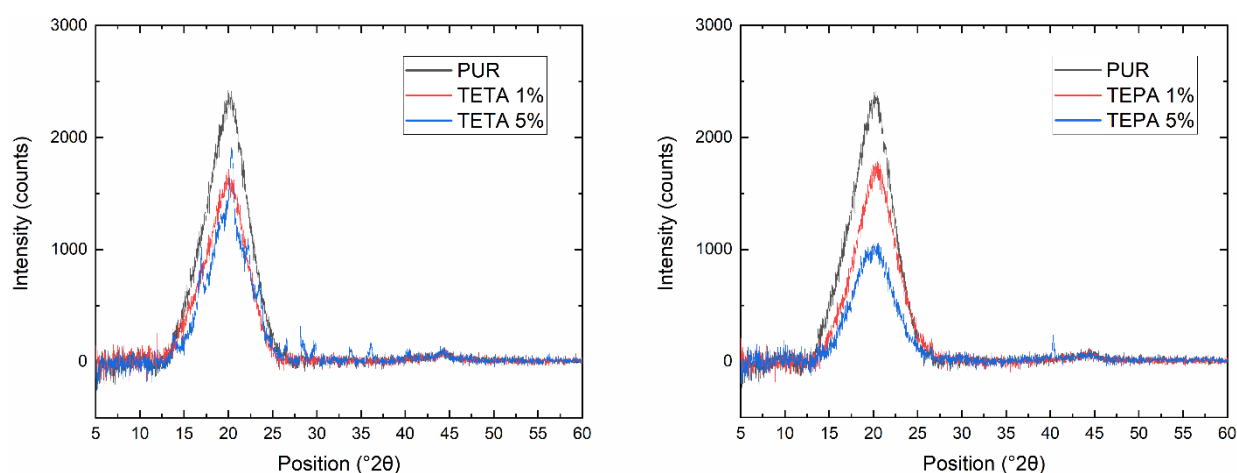


Fig. 2. Diffractograms (CuK α) comparing the structural characteristics of the unmodified PUR membrane with the membranes modified with amines TETA (**left**) and TEPA (**right**).

Based on the above findings from SEM and XRD analysis, a more challenging high-resolution SEM (HRSEM) analysis was performed on the PUR/TEPA samples, which revealed other interesting features of the membrane structure (Figure 3). The amine-modified PUR nanofibers showed a tendency to stick together in bundles and at higher concentrations these bundles formed continuous surfaces. This behaviour has not been observed with short amines or other modifiers^{2,3,4} and suggests the importance of polymer-modifier and modifier-modifier interaction energy on membrane structure. Therefore, we used molecular modelling (force field calculations) to analyze the intermolecular interactions in the PUR/TETA(TEPA) samples and to elucidate the effect observed in the HRSEM analysis (Figure 3).

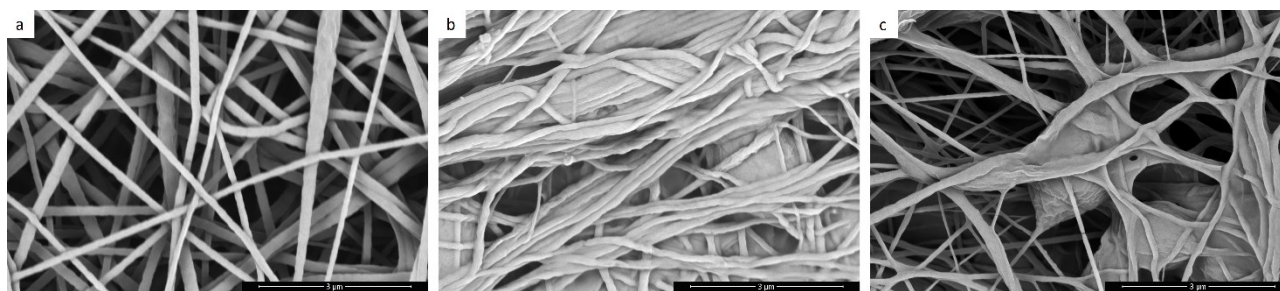


Fig. 3. HRSEM images (a) pristine PUR without the occurrence of glued parallel fiber bundles or fused bands and layers; (b) PUR/TEPA (1 wt.%). A distinct characteristic feature of this sample is parallel bundles of fibers alternating with an irregular network; (c) PUR/TEPA (5 wt.%). After increasing the TEPA concentration to 5 wt.%, the individual fibers were fused into continuous strips and layers.

Based on the PUR structure determined with the NMR spectrum¹, one segment of the model chains consisted of one isophorone diisocyanate (the solid part) and one hexane-1,6-diol (the soft part) (Figure 4, left part). A number of PUR chains with different numbers of segments were built, and the E_{int} values for TETA and TEPA with each of these chains were determined.

The predominant component of the interaction energy of PUR-TETA/TEPA belonged to the hydrogen bonding between the functional groups on both of the interacting subjects, where the key factor was the distance of the functional group pairs in both the amine and PUR chains (Figure 4, left part).

The structural similarity of the distances of the functional groups in the PUR and TETA(TEPA) structures drove the amines to energetically advantageous positions, more or less parallel to the PUR chain (Figure 4, right part). Figure 4 (right part) illustrates two models for two extreme mutual positions of the PUR and amines, corresponding to the maximum absolute values of the interaction energies for the parallel- and cross-positions. A large number of functional groups guarantees considerable interaction energies even for cross-positions and provides a chance to connect the chains and nanofibers to each other, i.e., to facilitate the cross-linking of the membrane and its subsequent mechanical strengthening.

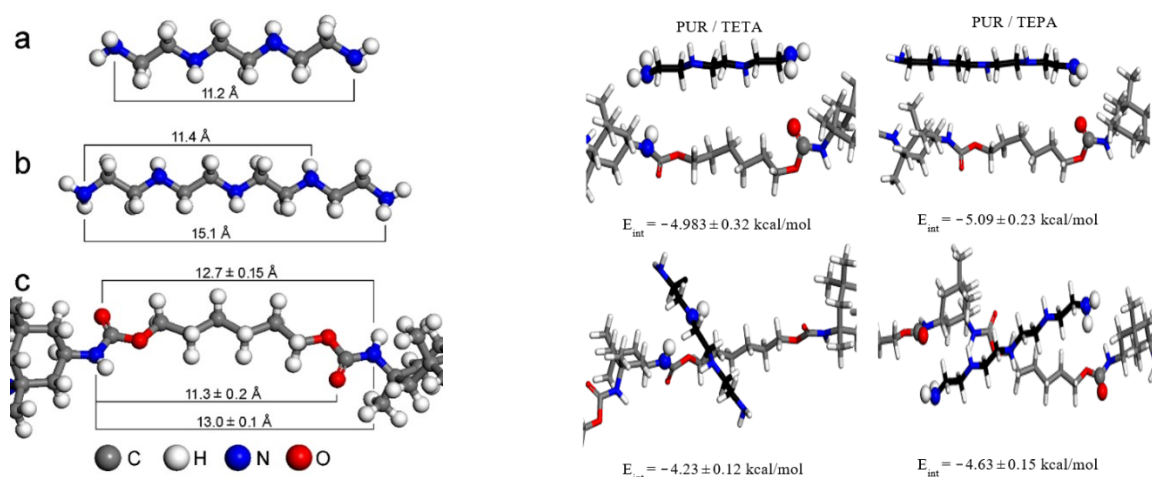


Fig. 4. Left part - Functional groups' distances in geometry optimized (a) TETA, (b) TEPA, and (c) PUR models used for the docking calculations. In the case of PUR, all segments in all PUR models were measured, and the average distance values, along with the standard deviations, were determined. Right part - Mutual positions of PUR/TETA/TEPA corresponding to their maximum interaction energy for two extreme mutual positions, i.e., parallel and crossed. The atoms of the functional groups sharing hydrogen bonds are displayed as balls. For clarity, the carbon atoms in the amines are black.

Consequently, the models containing two PUR chains (78 segments each) and the number of amines corresponding to the amount provided by weight percentage (1 or 5 wt.%) were prepared for energy optimization. The models containing amines exhibited higher absolute values of interaction energies compared to models containing only two PUR chains without amines (Table 2). For 5 wt.% of amine, ~18 and ~14 molecules of TETA and TEPA, respectively, belonged to two PUR (78 segments) chains (Table 2). The decrease in the E_{int} (i.e., the enhanced strength of interactions) compared to the models containing only two PUR chains is evident. Table 2 clearly shows that the presence of amines on the PUR fiber surfaces increased the interaction energies of the fibers and explains the sticking of fibers observed with the HRSEM (Figure 3).

Table 2. Models of two PUR chains (78 segments each) with different amounts of amines expressed by the number of molecules and weight percentages. The interaction energies (E_{int}) of two PUR chains with different amounts of amines are provided in the third column (E_{int} values for the same models without amines are provided in parentheses).

Sample	Amine (wt.%)	E_{int} (kcal/mol)
2PUR (78 seg)	0.00	-1959 ± 21
2PUR (78 seg) + 4TETA	1.13	-2152 ± 32 (-1977 ± 25)
2PUR (78 seg) + 3TEPA	1.10	-2153 ± 30 (-1939 ± 20)
2PUR (78 seg) + 18TETA	4.91	-3038 ± 47 (-1951 ± 22)
2PUR (78 seg) + 14TEPA	4.94	-2982 ± 41 (-1971 ± 22)

CONCLUSION

The goal of this work was to prepare an electrospun membrane for CO₂ sorption that is air permeable. The combination of these two properties, i.e., the maximum CO₂ sorption capacity and air permeability, would significantly simplify the design of functional units for practical use. Another important requirement is the one-step spinning technology, i.e., modifying substances directly in the spinning solution so that no subsequent technological steps are necessary. The sample PUR/TEPA (5 wt.%) was shown to meet this condition with a sorption capacity 5 times higher and air permeability 10 times higher than pure PUR membranes. Increasing the concentration above 5 wt.% hindered the spinning process. This work confirms the influence of mutual intermolecular interactions on the structure and properties of chemically-modified membranes and shows the usefulness of computer design in the case of chemically-modified nanofibrous membranes. The technology proposed in this work is easily transferable to industrial production lines. On the other hand, even the technology used by us has its limits, which were achieved in this work, so future research must be focused on modifying the spinning technology so that we can prepare porous nanofibers with a rough surface using special additives dissolved in the spinning solution to increase the total surface area of the fibers. We would still be looking for single-stage technology and reasonable air permeability.

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REFERENCES

1. J. Hoskovec, P. Čapková, M. Vostiňáková, P. Ryšánek, P. Kaule, J. Tokarský, O. Benada, V. Blechta. Permeable Membranes PUR/TETA and PUR/TEPA for CO₂ Capture Prepared with One-Step Electrospinning Technology. *Fibers* **2022**, *10*, 100. <https://doi.org/10.3390/fib10110100>
2. P. Ryšánek, P. Čapková, J. Štojd, J. Trögl, O. Benada, M. Kormunda, Z. Kolská, M. Munzarová. Stability of antibacterial modification of nanofibrous PA6/DTAB membrane during air filtration. *Mater. Sci. Eng. C* **2018**, *96*, 807–813. <https://doi.org/10.1016/j.msec.2018.11.065>
3. P. Čapková, M. Kormunda, Z. Kolská, J. Trögl, M. Munzarová, P. Ryšánek. Electrospun Antimicrobial PVDF-DTAB Nanofibrous Membrane for Air Filtration: Effect of DTAB on Structure, Morphology, Adhesion, and Antibacterial Properties. *Macromol. Mater. Eng.* **2018**, *303*, 1700415. <https://doi.org/10.1002/mame.201700415>.
4. P. Ryšánek, M. Malý, P. Čapková, M. Kormunda, Z. Kolská, M. Gryndler, O. Novák, L. Hocelíková, L. Bystrianský, M. Munzarová. Antibacterial modification of nylon-6 nanofibers: Structure, properties and antibacterial activity. *J. Polym. Res.* **2017**, *24*, 208. <https://doi.org/10.1007/s10965-017-1365-6>.

Nanostructured filtration materials for air filtration. Interchangeability of standards for facemasks and respirators. Effect of nanofibers in filter media.

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ABSTRACT

Plenty of media discussion run over the interchangeability of various norms for assessment of textile materials used for facemasks and respirators during the Covid-19 pandemic. The main panelists were sales representatives of large melt blown producers, several producers of nanofibers and of course politics. Discussed are picked European, American and Chinese standards used for testing of facemasks and respirators. Some aspects of applied measurement conditions and their influence on consequent properties (first filtration efficiency and pressure drop) are presented. Results obtained by measurements in accordance with different standards (it unfortunately means at different conditions) are not interchangeable.

The positive effect of nanofibers presence in filtration materials for facemasks and respirators is demonstrated on improvement of their filtration efficiency and pressure drop. Improvement of filtration characteristics can be reached by preparation of nanostructures combining layers made from thick and thin nanofibers. Such a nanostructure possesses filtration efficiency at maximum penetrating particle sizes (MPPS) about 98% in comparison with nanostructure made from thin nanofibers (70% only). Of course, the pressure drops of both compared nanostructures were the same - around 152 Pa.

KEYWORDS

Covid-19, standards, electrospinning, morphology of nanostructures

INTRODUCTION

The medical staff were using surgical masks in the beginning of pandemic Covid-19, which suit the requests of standards e.g. Chinese (YY 0469) and European (EN 14683:2019). Both of these standards work with bacteria sizes of 3 000 nm, which is unfortunately 30 times higher than the size of coronavirus SARS-CoV-2 (Fig. 1, virus size 80 through 150 nm in base – without any cover by salts and enzymes) and cannot be applied. In the beginning of pandemic a lot of facemasks and

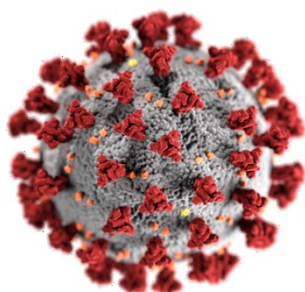


Fig. 1. SARS-CoV-2

respirators on the market were made of poor quality materials and the facemasks properties measured in accordance with standards did not respond requested values. Most of the standards for characterization of filtration materials in use during the pandemic were working with penetration of particle sizes around 400 nm (e.g. European EN 149-2001 and Chinese GB 2626-2006). Since the 1970s, with the availability of discrete particle counters, new standards for testing HEPA and ULPA filters have been developed. The best test methods for evaluation of protection against coronavirus penetration through air filtration materials are in accordance with American IEST-RP-CC 001, European EN 1822:2009 and EN ISO 29463 which work with interception of particle

sizes tens through hundreds nm.

Application of nanofibers¹ in air filter media improves the most requested filtration properties – increasing the filtration efficiency simultaneously with decreasing of pressure drop². Membranes prepared from interpenetrating and layered electrospun nanofibrous composite structures were used also for water purification³.

EXPERIMENTAL

For the spinning process in electrostatic field the solutions of polyvinylidene fluoride (PVDF) Kynar Flex 2801-00, ARKEMA, PA, USA and polyurethanes (PU) Elastolan B 95 A, BASF, Germany and Permuthane SU-22-542, STAHL, The Netherlands) were prepared. PVDF solution in dimethyl formamide (DMF) possessed mass concentration of 20 %, viscosity of 1.5 Pa.s and electrical conductivity of 80 $\mu\text{S}\cdot\text{cm}^{-1}$. PU solution for preparation of thin fibers was prepared from PU Elastolan B 95 A in DMF with concentration of 18 % by weight, viscosity of 1.3 Pa.s and conductivity of 230 $\mu\text{S}\cdot\text{cm}^{-1}$. PU solution for preparation of thick fibers was made from PU Permuthane SU-22-542 in mixture of DMF and toluene (80/20) solvents with concentration 19 % by weight, viscosity 1.5 Pa.s and conductivity 55 $\mu\text{S}\cdot\text{cm}^{-1}$. The electrical conductivity was adjusted in all cases by means of sodium tetraborate decahydrate and citric acid.

Nanostructures were prepared from polymeric solutions by means of electrospinning machine SpinLine 40 (SPUR Zlín, Czech Republic) equipped with 2 lines of nanofibers forming nozzles. The used experimental conditions for PVDF nanofibers preparation were: temperature 22–24°C, relative humidity 31–34%, applied electric voltage 75 kV, dosing of polymer solution 2.3 $\text{ml}\cdot\text{min}^{-1}$, distance between electrode 180–210 mm, speed of substrate collecting nanofibers varied from 0.2 to 1.0 $\text{m}\cdot\text{min}^{-1}$ in context of requested basis weight preparation. The experimental conditions for PU combined layered nanostructure preparation were as follow: temperature 23°C, relative humidity 32%, applied electric voltage 60 kV, dosing of polymer solution 0.9 $\text{ml}\cdot\text{min}^{-1}$, distance between electrode 210 mm, speed of substrate collecting nanofibers 1.0 $\text{m}\cdot\text{min}^{-1}$. Layers of thick and thin nanofiber were made by supplying of two various PU solutions separately in first or second spinning line respectively. Nanofibers were collected on polypropylene (PP) nonwoven textiles with basis weight of 30 $\text{g}\cdot\text{m}^{-2}$.

Filtration materials were characterized by scanning electron microscopy (SEM, Vega 3, Tescan, Czech Republic), assessment of mean fiber diameter by means of ImageJ program and determination of nanostructure basis weights. Pressure drops (p) and filtration efficiencies were evaluated on protective mask filter tester PALAS PNFT 1000 (Karlsruhe, Germany).

RESULTS AND DISCUSSION

Overview and critical survey of standards for characterisation facemasks and respirators properties

Compared are the two most important standards used during the pandemic in Czech Republic - European EN 149-2001 and Chinese GB 2626-2006. Values presented in Table 1 are corresponding to requests of classes FFP2 (EN standard) and KN95 (GB standard) respectively. Unfortunately, both of them work with different particle sizes (aerosol of NaCl has been used), testing and evaluating conditions (Table 1).

Table 1. Comparison of standards for facemasks and respirators.

Standard / Followed Property	EN 149-2001	GB 2626-2006	Differences	Conclusions
MMAD* particle size (nm)	600	300	Different ways of capture measurement	Along BG - easier intersection of aerosol
Filtration efficacy (%)	> 94	> 95	EN at 95 l/min GB at 85 l/min	EN is stricter, it is easier to fulfill GB
Pressure drop (Pa)	< 240	< 300	Various shapes of testing heads	EN is severer and EN is measured at flux 95 l/min comparing GB (85 l/min)

*MMAD – mass median of aerodynamic average

We can conclude that test results according to the compared standards are comparable but not interchangeable and that there does not exist uniform standard for evaluation and consequential comparison of filtration materials. For the assessment of filtration materials in terms of protection against bacteria and viruses, the standards working with filtration efficiency in the area of ultrafine particle separation (at least 20 through 400 nm) have to be used, e.g. American IEST-RP-CC 001, European EN 1822:2009 and EN ISO 29463 which measure and evaluate properties of HEPA and ULPA filters. Unfortunately, the test results provided in accordance with these standards on filtration materials applied during pandemic were rather sporadic, frequently were disparaged and deliberately misinterpreted.

Effect of nanofibers on filtration properties

Filtration efficiencies in the area of ultrafine particle separation measured according to EN 1822 for PVDF nanostructures with various pressure drops are depicted in Fig. 2. Nanostructured materials ensured very good filtration efficiencies at low pressure drops. The mean fiber diameter was 155 nm. The values were measured at flux 95 l.min^{-1} and corresponding face velocity 19 cm.s^{-1} . While respiration intensity at flow 30 l.min^{-1} (face velocity 5.7 cm.s^{-1}) corresponds to breathing at normal walk, respiration intensity at flow 95 l.min^{-1} (face velocity 19 cm.s^{-1}) corresponds to breathing at running. It is rather surprising that even very low area mass (0.06 g.m^{-2} , Fig. 3) is already capable capture of more than 10% of ultra-fine particles. With lower pressure drop the filtration efficiency is decreasing.

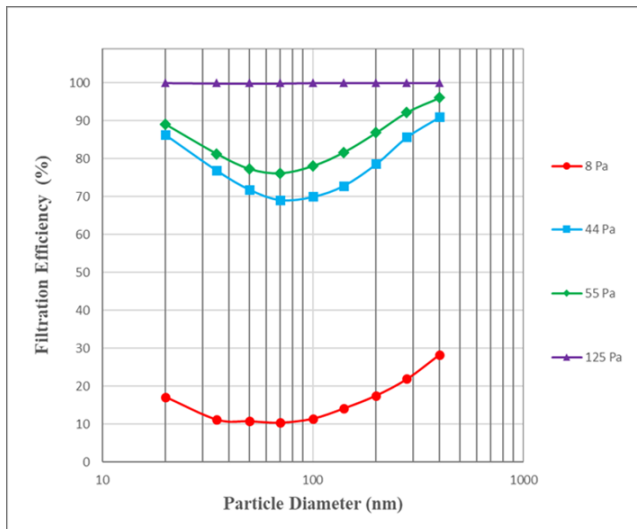


Fig. 2. Filtration efficiencies of PVDF nanostructures with various pressure drops. Measured at flux $95 \text{ l} \cdot \text{min}^{-1}$ and corresponding face velocity $19 \text{ cm} \cdot \text{s}^{-1}$.

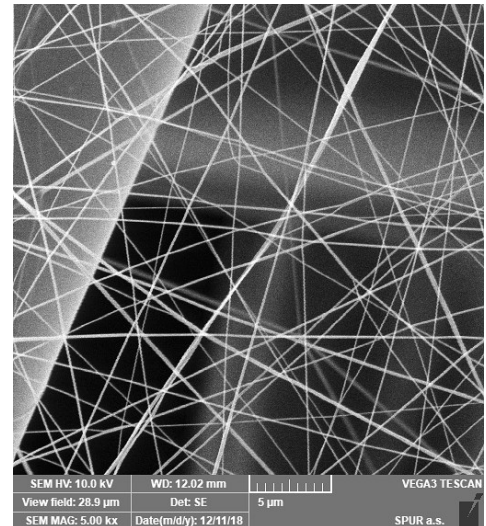


Fig. 3. Straight PVDF nanostructure, $p = 8 \text{ Pa}$, basis weight = $0.06 \text{ g} \cdot \text{m}^{-2}$ only, magnification $5000\times$.

Effect of combination layers from thick and thin nanofibers on filtration properties

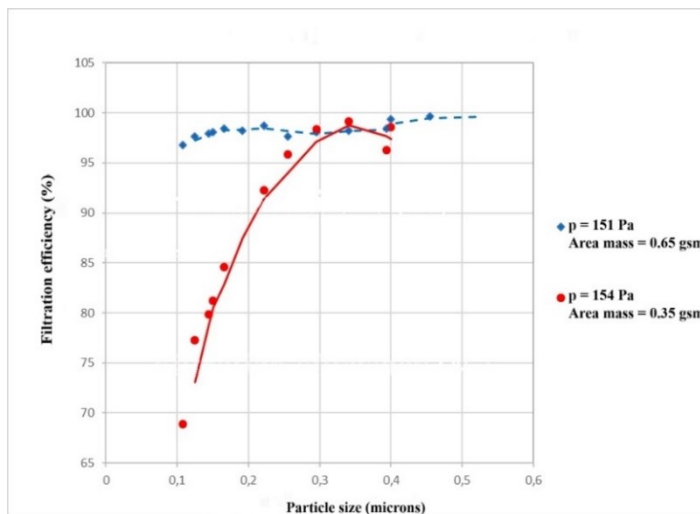


Fig. 4. Filtration efficiencies of PU nanostructures prepared from nanofibers with mean fiber diameter 170 nm and bimodal nanofiber distribution at 170 nm and 350 nm respectively.

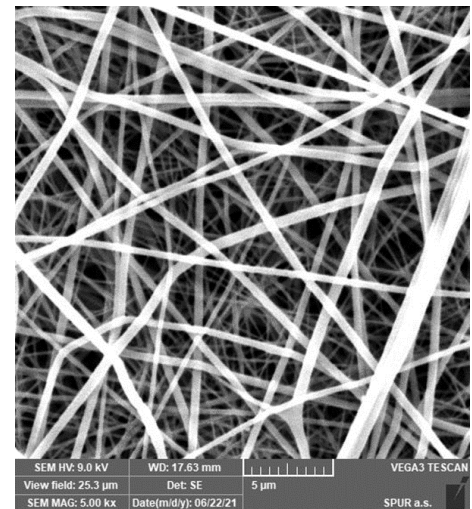


Fig. 5. Combined nanostructure from alternating layers of thick and thin nanofibers, $p = 151 \text{ Pa}$, basis weight = $0.65 \text{ g} \cdot \text{m}^{-2}$, magnification $5000\times$.

Two PU nanostructures with the same pressure drops (151 and 154 Pa) but different morphologies are compared in Fig. 4. Nanostructure with mean fiber diameter of 170 nm (red points) and area mass of $0.35 \text{ g} \cdot \text{m}^{-2}$ exhibit worse filtration efficiency than nanostructure in Fig. 5 with area mas of $0.65 \text{ g} \cdot \text{m}^{-2}$ (blue points) formed by 6 layers of alternating thick (mean fiber diameter 350 nm) and thin nanofibers (mean fiber diameter 170 nm).

CONCLUSION

Nanostructures prepared from nanofibers are gradually becoming increasingly demanded materials for applications in air filter media for separation of ultrafine particles, bacteria, fungi, yeasts and viruses from the air. Prepared PVDF nanostructure with pressure drop of 44 Pa possesses filtration efficiency at MPPS around 70%, nanostructure with pressure drop 125 Pa possess filtration efficiency already around 100%, corresponding to quality of HEPA 13 and HEPA 14 filtration materials. Procedures allowing to prepare homogeneous nanofiber structures of the desired morphology (e.g. combination of thick and thin nanofibers described in this study) are used for quality improvement of facemasks and respirators i.e. increasing of filtration efficiency simultaneously with decreasing of pressure drop. Prepared nanostructures combining layers made of thick and thin nanofibers possess filtration efficiency for particle sizes 150 nm about 98% in comparison with nanostructure made from thin nanofibers (around 70% only). Of course, the pressure drops of both compared nanostructures were the same – around 152 Pa.

Proper measurement of filtration properties has to be supported by clear standards which allow proper comparison of filtration materials.

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REFERENCES

1. Kimmer, D., Slobodian, P., Petras, D., Zatloukal, M., Olejnik, R., Saha, P.: Polyurethane/Multiwalled Carbon Nanotube Nanowebs Prepared by an Electrospinning Process, *Journal of Applied Polymer Science*, 2009, Vol. 111, p. 2711-2714.
2. Kimmer D., Vincent I., Lovecka L., Kazda T. Giurg A., Skorvan O.: Some Aspects of Application Nanostructured Materials in Air Filtration, Water Filtration and Electrical engineering. In Conference proceedings vol. 1843 of Novel Trends in Rheology VII, 26-27 July 2017, Zlín, Czech Republic, New York, USA: AIP Publishing, p. 060001-1–060001-11.
3. Liu X., Ma H. and Hsiao B. S.: Interpenetrating Nanofibrous Composite Membranes for Water Purification, *ACS Appl. Nano Mater.* 2019, 2, 3606-3614.

New generation of agronomical perspective nano-fertilizes: Exploring thermodynamics and sustainability

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Nanotechnology has begun to revolutionize agricultural research, with a particular emphasis on the development and application of nanofertilizers. The small size and high surface-to-volume of nanoparticles (NPs) and nanomaterials (NMs) predefine them to an extensive agronomical application. Despite this potential, the thermodynamic behavior of nanofertilizers remains

understudied and warrants further exploration, especially concerning nutrient release, mobility, and bioavailability. Contrasting traditional fertilizers and macro-sized agrochemicals, nanoformulations such as NPs and NMs integrated into gels, emulsions, and dispersions exhibit distinct thermal movement, diffusion, and sedimentation properties. These characteristics can be more predictably assessed through surface and physical chemistry, as well as electrochemistry. As a result, both inorganic and organic nanomaterials are being harnessed to create a new generation of nanofertilizers, with various types of pure and mixed materials being employed. With advancements in preparation techniques and a growing focus on climate change resilience, the development and testing of nanofertilizers are poised to surge in the coming years. These innovations hold the potential to significantly impact agriculture by ensuring crop yield sustainability in the face of an increasingly-changing global environment.

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Green solvents for electrospinning

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ABSTRACT

Electrospinning is a technique that is widely used to produce nanofibrous materials for various applications in different industries. The solvent choice is one of the important parameters of electrospinning because only a limited range of solvents can dissolve the relevant polymers and ensure subsequent fiber formation. Traditional solvents commonly used in the production of polysulfone (PSU) and polyurethane (PU) nanofibers, such as dimethylformamide, are harmful to the environment and pose a risk to the health and safety of production workers. One solution is to use alternative, green solvents. The possibilities of preparing PSU and PU polymer solutions based on a system of mixtures of alternative solvents cyclopentanone, ethyl lactate and methyl lactate were studied. Nanofibers were prepared by electrospinning technology using green solvent-based polymer solutions. The effect of the conductivity enhancing additive content in the polymer solution on the thickness of the obtained nanofibers was evaluated. The applied green solvents can be used as a substitute for toxic organic solvents, while the polymer solution properties and processing conditions need to be optimized.

KEYWORDS

electrospinning, nanofiber, green solvent

INTRODUCTION

Electrospinning is a well-established technique widely used to produce nanofibrous materials for a variety of applications in different industries. The electrospinning technique can process a huge variety of polymers, but often requires the use of organic toxic solvents. Traditional solvents commonly used in nanofiber production, such as *N,N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP) and dimethylformamide (DMF), are harmful to the environment and pose a risk to the health and safety of production workers. The European REACH Regulation has identified them as Substances of Very High Concern (SVHC).¹ The solution is to use alternative, so-called green solvents. The definition of green solvents expresses the goal to minimize the environmental impact resulting from the chemical production until the disposal of the solvents. For each solvent, an EHS (environmental, health and safety) indicator is established and subjected to a series of detailed risk analyses.²

The solvent choice probably represents the most important parameter in electrospinning, since only a limited range of solvents and compositions can dissolve the respective polymers and subsequently achieve fiber formation. The diameter and morphology of polymer nanofibers are influenced by both the properties of the polymer solution and the process parameters.^{2, 3, 4}

Polysulfone (PSU) and polyurethane (PU) nanofiber structures are widely used in water and air filtration membranes due to their desirable properties such as stability, high mechanical strength, and ease of modification.^{5, 6} The preparation of PSU and PU solutions for electrospinning is limited by the solubility of the polymer in green solvents. A group of green solvents based on renewable sources, e.g. Cyrene (dihydrolevoglucosenone), γ -Valerolactone (GVL), *N*-butylpyrrolidinone (NBP) meet the solubility condition of PSU and PU polymers, but are unsuitable for the nanofiber preparation process by electrospinning due to the low evaporation rate.^{7, 8} Cyclopentanone (CPO), ethyl lactate (EL) or methyl lactate (ML) are becoming interesting solvents for replacement options.⁹ These solvents not only meet the solubility conditions of these polymers and allow electrospinning, but are also more economically acceptable and easier to recycle. This fact is also of interest for an industrial scale electrospinning where controlled waste management is required.²

EXPERIMENTAL STUDY

Materials

Polysulfone (PSU), Ultrason S 6010 was obtained from BASF Company (Ludwigshafen, Germany) and polyurethane (PU), Desmopan 2590A was obtained from Bayer MaterialScience AG (Leverkusen, Germany). Cyclopentanone (CPO), ethyl lactate (EL), methyl L-lactate (ML), sodium tetraborate decahydrate, citric acid and tetraethylammonium bromide (QAS, Quaternary ammonium salt) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA).

Polymer solutions and nanofibers preparation

The polysulfone and polyurethane solutions were prepared by dissolving them in a mixed solvent system at a given ratio (Tables 1 and 2). The conductivity of the solutions was increased by the addition of QAS or BC (a combination of sodium tetraborate decahydrate and citric acid in a ratio of 1/3). The polymer solutions were stirred for 12 h at laboratory temperature and 4 h at 40 °C followed by conductivity measurements.

Table 1. The solvent system, additive and conductivity of 14% (w/w) PSU solutions

Solvent system, ratio	Conductivity enhancing additive	Conductivity enhancing additive content per solution [w/w %]	Conductivity [$\mu\text{S}\cdot\text{cm}^{-1}$]
CPO	QAS	0.08	30.1
CPO/EL, 90/10	QAS	0.4	50.1
CPO/EL, 70/30	QAS	0.8	109.6
CPO/EL, 80/20	QAS	1.0	130.1
CPO/ML, 90/10	BC	1.5	50.1
CPO/ML, 80/20	BC	3.0	108.1

Table 2. The solvent system, additive and conductivity of 12% (w/w) PU solutions.

Solvent system, ratio	Conductivity enhancing additive	Conductivity enhancing additive content per solution [w/w %]	Conductivity [$\mu\text{S}\cdot\text{cm}^{-1}$]
CPO/EL, 80/20	QAS	1.0	160.2
CPO/EL, 80/20	QAS	0.8	133.2
CPO/ML, 80/20	QAS	0.8	148.5
CPO/ML, 90/10	BC	1.5	56.4
CPO/ML, 80/20	BC	3.0	112.3

The nanofibers were prepared by electrospinning device SpinLine 40 (SPUR a.s., Czech Republic) with simultaneous drying of the interior of the equipment to a relative humidity of 25-30 % using a Munters ML180 (Munters, Germany) dryer. A voltage of 75 kV was applied to spin a drop of polymer solution from the test stick, the electrodes distance was 18 cm. The nanofibers were collected on a polypropylene non-woven fabric.

The structure, surface morphology and fiber diameters of the nanostructured materials were evaluated by SEM – scanning electron microscopy (Vega 3, Tescan, Czech Republic). The samples of nanofibrous material were coated with a thin layer of palladium to increase their electric conductivity before SEM imaging commenced.

RESULTS AND DISCUSSION

The process of nanofibers formation by electrospinning is mostly influenced by the properties of polymer solutions and the processing parameters. The resulting properties of the nanofibers - diameter and morphology are mainly influenced by the conductivity and viscosity of the polymer solution. Several issues need to be dealt with simultaneously when looking for a green solvent for the electrospinning solution preparation. In particular, the solvent must ensure complete solubility of both the polymer and the conductivity modification additive.

The selected solvent, cyclopentanone, is a good solvent for both polysulfone and polyurethane. Based on the experience with the successful spinning of these polymers in the organic solvents DMF and DMAc, the additives, quaternary ammonium salt (QAS) and a combination of borax and citric acid (1/3), were chosen to increase the conductivity of the polymer solutions. The limited solubility of these additives in CPO was solved by creating a mixed solvent system. Ethyl lactate (EL) and methyl lactate (ML) were selected as co-solvents from a group of alternative solvents. Water, acetone and dimethyl sulfoxide (DMSO) were found to be unsuitable for this purpose after screening.

The minimum solubility limit of PSU and PU was found to be 70/30 for the solvent combination CPO/EL, CPO/ML.

The effect of the conductivity enhancing additives content in the polymer solution on the nanofiber thickness was investigated (Table 3 and 4).

Table 3. PSU nanofiber diameter

Solvent system, ratio	Conductivity enhancing additive	Conductivity enhancing additive content per solution [w/w %]	Mean nanofiber diameter [nm]
CPO	QAS	0.08	606.9 ± 245.6
CPO/EL, 90/10	QAS	0.4	242.9 ± 74.5
CPO/EL, 70/30	QAS	0.8	224.5 ± 84.5
CPO/EL, 80/20	QAS	1.0	209.6 ± 74.1
CPO/ML, 90/10	BC	1.5	197.4 ± 70.8
CPO/ML, 80/20	BC	3.0	210.9 ± 69.3

Table 4. PU nanofiber diameter

Solvent system, ratio	Conductivity enhancing additive	Conductivity enhancing additive content per solution [w/w %]	Mean nanofiber diameter [nm]
CPO/EL, 80/20	QAS	1.0	165.7 ± 60.5
CPO/EL, 80/20	QAS	0.8	220.3 ± 89.6
CPO/ML, 80/20	QAS	0.8	201.8 ± 79.4
CPO/ML, 90/10	BC	1.5	218.0 ± 88.3
CPO/ML, 80/20	BC	3.0	296.6 ± 130.5

The thinnest polysulfone nanofibers were obtained using 1% (w/w) QAS additive and CPO/EL solvent system in 80/20 ratio (Fig. 4). This corresponds to the highest conductivity of the polymer solution. This nanofibrous structure is free of defects, compared to other systems with QAS additive (Fig. 1–3).

In the solutions where conductivity was enhanced by the BC combination, precipitation of the conductivity enhancing additive occurred when EL was used as a co-solvent. The precipitation problem was solved by substituting ethyl lactate with methyl lactate. Although even thinner polysulfone nanofibers are achieved when using BC and CPO/ML solvent system, the nanofibrous structure contains defects – beads (see Fig. 5, 6).

Following the results obtained in the spinning of PSU nanofibers, it was possible to set up the solvent system for electrospinning of polyurethane. Again, the thinnest fibers were again achieved with a CPO/EL solvent system in an 80/20 ratio containing 1% (w/w) QAS which conductivity was the highest. However, visible traces of QAS additive can be observed on the nanofiber surface (see Fig. 7). This problem was solved by reducing the QAS additive content in the solution to 0.8% (w/w per solution) (Fig 8, 9). The addition of BC is not a suitable means to increase conductivity. The nanofibrous structure contains defects and the nanofibers are glued together at the contact points (Fig. 10, 11).

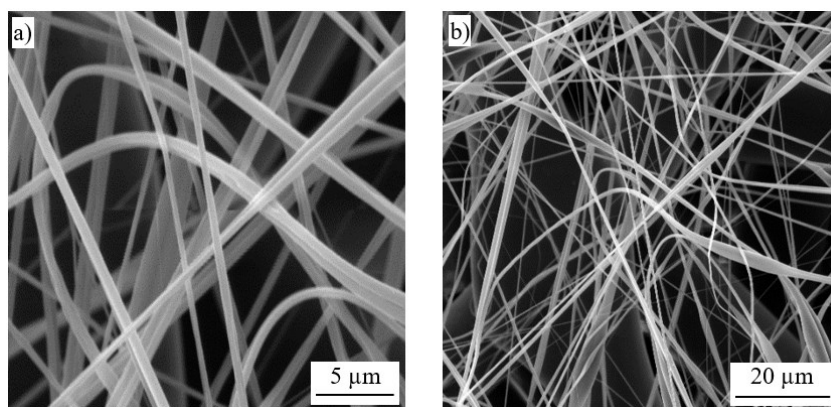


Fig. 1. SEM image of PSU nanofibers prepared from 14% (w/w) PSU in CPO, 0.08 % QAS (w/w).

Magnification (a) 5000 $\times$; (b) 1500 $\times$.

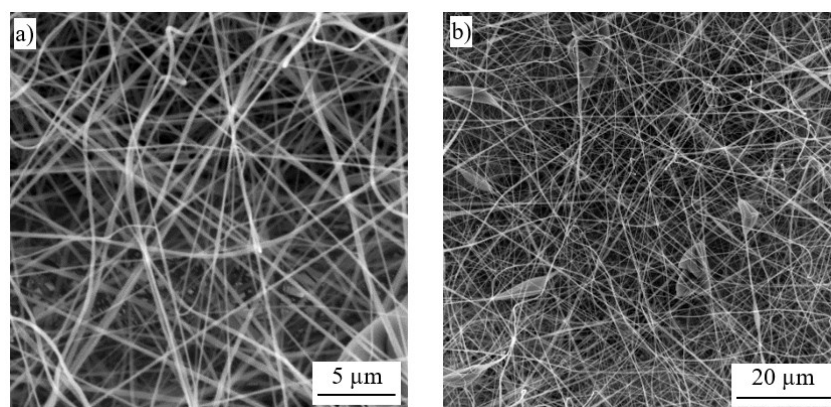


Fig. 2. SEM image of PSU nanofibers prepared from 14% (w/w) PSU in CPO/EL, ratio 90/10, 0.4 % QAS (w/w).

Magnification (a) 5000 $\times$; (b) 1500 $\times$.

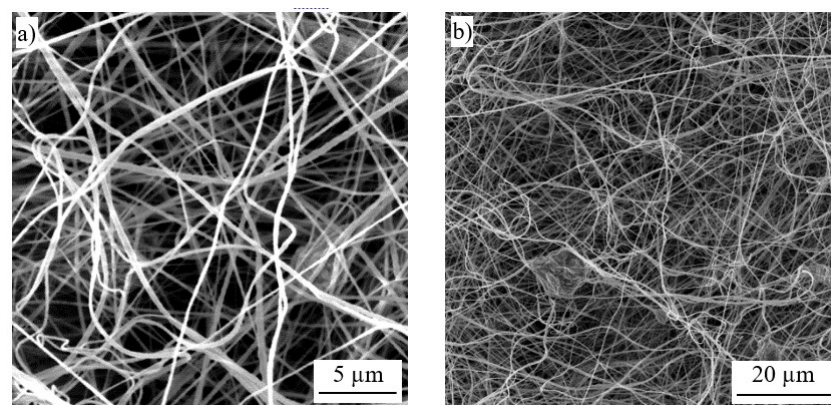


Fig. 3. SEM image of PSU nanofibers prepared from 14% (w/w) PSU in CPO/EL, ratio 70/30, 0.8 % QAS (w/w).

Magnification (a) 5000 $\times$; (b) 1500 $\times$.

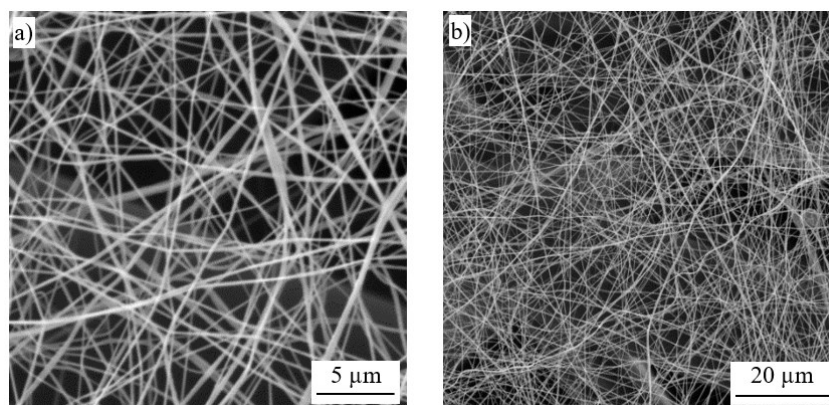


Fig. 4. SEM image of PSU nanofibers prepared from 14% (w/w) PSU in CPO/EL, ratio 80/20, 1.0 % QAS (w/w). Magnification (a) 5000 $\times$; (b) 1500 $\times$.

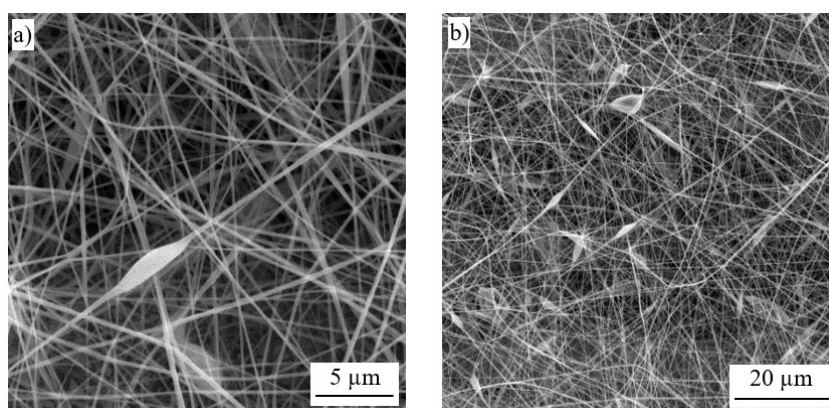


Fig. 5. SEM image of PSU nanofibers prepared from 14% (w/w) PSU in CPO/ML, ratio 90/10, 1.5 % BC (w/w). Magnification (a) 5000 $\times$; (b) 1500 $\times$.

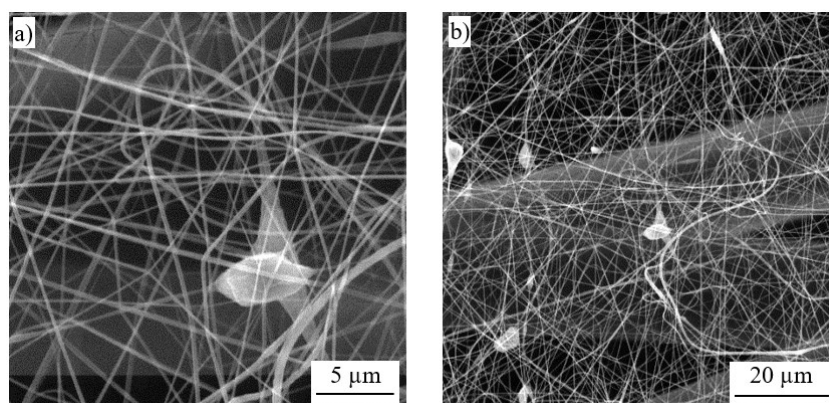


Fig. 6. SEM image of PSU nanofibers prepared from 14% (w/w) PSU in CPO/ML, ratio 80/20, 3.0 % BC (w/w). Magnification (a) 5000 $\times$; (b) 1500 $\times$.

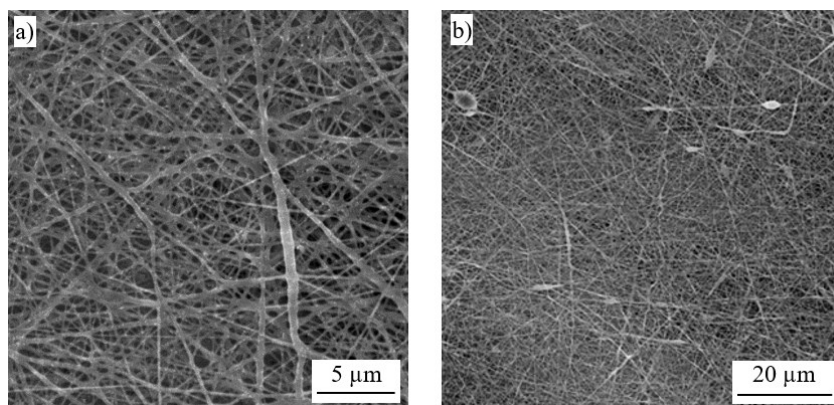


Fig. 7. SEM image of PU nanofibers prepared from 12% (w/w) PU in CPO/EL, ratio 80/20, 1.0 % QAS (w/w). Magnification (a) 5000 $\times$; (b) 1500 $\times$.

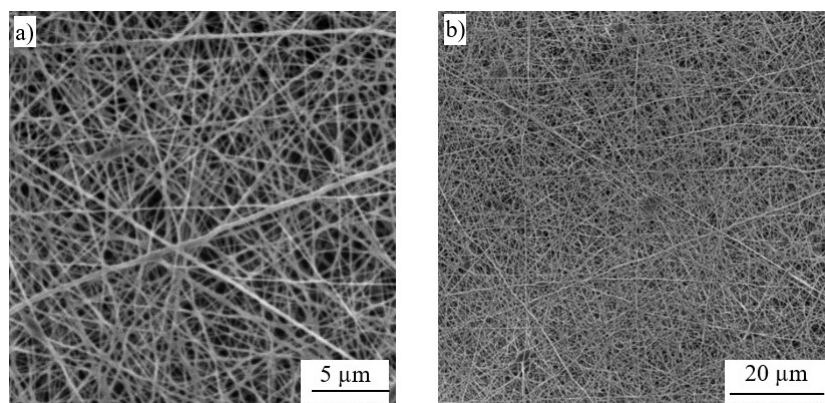


Fig. 8. SEM image of PU nanofibers prepared from 12% (w/w) PU in CPO/EL, ratio 80/20, 0.8 % QAS (w/w). Magnification (a) 5000 $\times$; (b) 1500 $\times$.

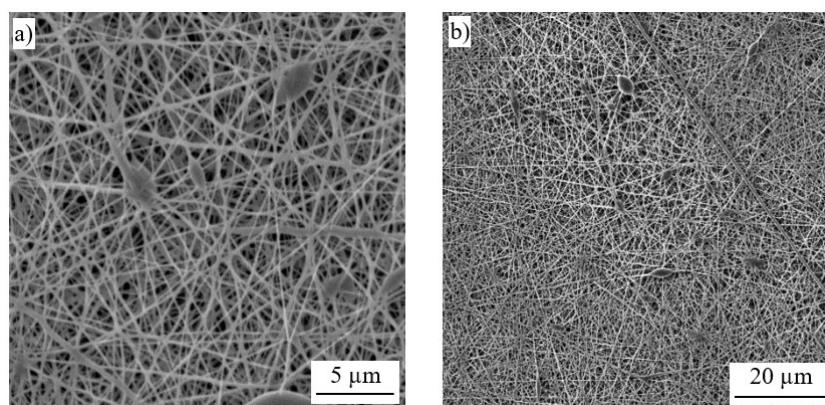


Fig. 9. SEM image of PU nanofibers prepared from 12% (w/w) PU in CPO/ML, ratio 80/20, 0.8 % QAS (w/w). Magnification (a) 5000 $\times$; (b) 1500 $\times$.

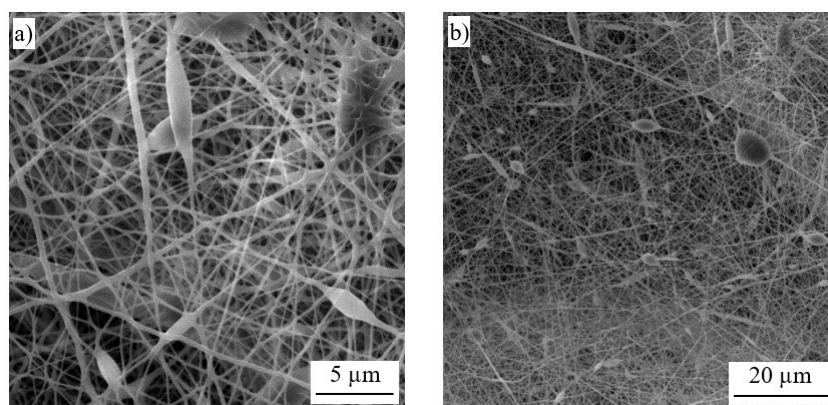


Fig. 10. SEM image of PU nanofibers prepared from 12% (w/w) PU in CPO/ML, ratio 90/10, 1.5 % BC (w/w). Magnification (a) 5000 $\times$; (b) 1500 $\times$.

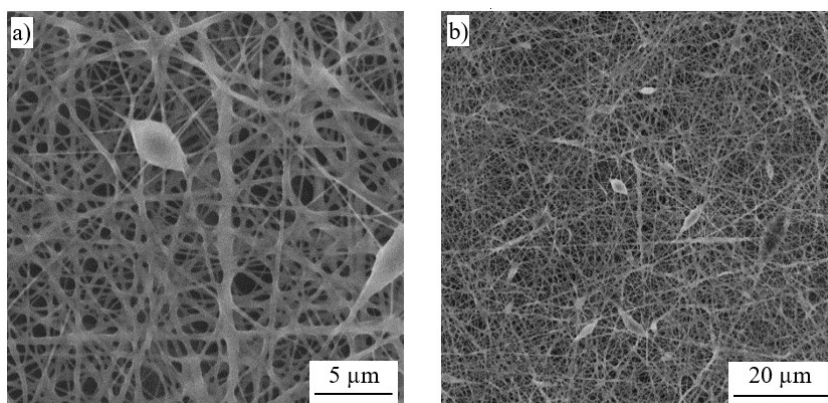


Fig. 11. SEM image of PU nanofibers prepared from 12% (w/w) PU in CPO/ML, ratio 80/20, 3.0 % BC (w/w). Magnification (a) 5000 $\times$; (b) 1500 $\times$.

CONCLUSION

For the preparation of PSU and PU nanofibers by electrospinning, alternative solvents such as cyclopentanone, ethyl lactate or methyl lactate can be used. These green solvents can replace the organic solvents DMF, DMAc, NMP, when optimal electrospinning conditions and polymer solution properties are adjusted. The experimental results show the necessity of modifying the conductivity of the spinning solution, which together with other parameters affects the nanofiber thickness and structure. Large-scale nanofiber spinning using a jet system must be preceded not only by optimization of the desired properties of the polymer solution, but also of the electrospinning process parameters and the ambient conditions. PSU and PU nanofibers prepared by electrospinning from solutions based on green solvents can be applied in water and air filtration membranes with subsequent testing of functional properties.

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REFERENCES

1. W. Xie, T. Li, A. Tiraferri, E. Drioli, A. Figoli, J.C. Crittenden, B. Liu. Toward the Next Generation of Sustainable Membranes from Green Chemistry Principles. *ACS Sustain. Chem. Eng.*, 2021, 9, 50-75. <https://dx.doi.org/10.1021/acssuschemeng.0c07119>
2. J. Avossa, G. Herwig, C. Toncelli, F. Itel, R.M. Rossi. Electrospinning based on benign solvents: current definitions, implications and strategies. *Green Chem.*, 2022, 24, 2347-2375. <https://doi.org/10.1039/D1GC04252A>
3. Y. Tang, Z. Cai, X. Sun, C. Chong, X. Yan, M. Li, J. Xu. Electrospun Nanofiber-Based Membranes for Water Treatment. *Polymers*, 2022, 14, 2004. <https://doi.org/10.3390/polym14102004>
4. C.Z. Mosher, P.A.P. Brudnicki, Z. Gong, H.R. Childs, S. Won Lee, R.M. Antrobus, E.C. Fang, T.N. Schiros, H.H. Lu. Green electrospinning for biomaterials and biofabrication. *Biofabrication*, 2021, 13, 035049. <https://doi.org/10.1088/1758-5090/ac0964>
5. S. CH. Mamah, P. S. Goh, A. F. Ismail, N. D. Suzaimi, L. T. Yogarathinam, Y. O. Raji, T. H. El-badawy. Recent development in modification of polysulfone membrane for water treatment application. *Journal of Water Process Engineering*, 2021, 40, 101835. <https://doi.org/10.1016/j.jwpe.2020.101835>
6. R. Ding, S. Chen, H. Xuan, B. Li, Y. Rui. Green-solvent-processed amphiphobic polyurethane nanofiber membranes with mechanically stable hierarchical structures for seawater desalination by membrane distillation. *Desalination*, 2021, 516, 115223. <https://doi.org/10.1016/j.desal.2021.115223>
7. S. A. N. Mehrabani, V. Vatanpour, I. Koyuncu. Green solvents in polymeric membrane fabrication: A review. *Sep. Purif. Technol.*, 2022, 298, 121691. <https://doi.org/10.1016/j.seppur.2022.121691>
8. J. Lopez, S. Pletscher, A. Aemissegger, Ch. Bucher, F. Gallou. N-Butylpyrrolidinone as Alternative Solvent for Solid-Phase Peptide Synthesis. *Org. Process Res. Dev.*, 2018, 22, 4, 494–503. <https://doi.org/10.1021/acs.oprd.7b00389>
- A. Duereh, H. Guo, T. Honma, Y. Hiraga, Y. Sato, R. L. Smith, H. Inomata. Solvent Polarity of Cyclic Ketone (Cyclopentanone, Cyclohexanone): Alcohol (Methanol, Ethanol) Renewable Mixed-Solvent Systems for Applications in Pharmaceutical and Chemical Processing. *Ind. Eng. Chem. Res.*, 2018, 57, 7331–7344. <https://doi.org/10.1021/acs.iecr.8b00689>

Effectiveness of Moringa biosynthesized AgNPs to reduce *Clavibacter michiganensis* subsp. *michiganensis* severity in tomato (*Solanum lycopersicon*)

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ABSTRACT

The aim of this study was to evaluate the antibacterial activity of AgNPs synthesized with *Moringa oleifera* extract (Mo-AgNPs) by reducing the disease severity in tomato plants caused by *Clavibacter michiganensis* subsp. *michiganensis* (*Cmm*). The in vivo efficacy of Mo-AgNPs was evaluated during four weeks against *Cmm* in tomato plants. The treatments were sprayed once a week, no inoculated tomato plants; Mo-AgNPs preventive + *Cmm*; *M. oleifera* extract preventive + *Cmm*; and positive control *Cmm*. Plant height, basal stem width, number of leaves, and disease severity according to the scale of Baysal et al. were measured twice a week. The tomato plants treated with Mo-AgNPs were not the ones with the highest vegetative performance; they even had low averages compared to the other treatments. Disease severity was analyzed by Kruskal-Wallis H, then Dunns test $p < 0.05$. The results showed differences between the treatments with the positive control (*Cmm*). The disease severity in treatment Mo-AgNPs preventive + *Cmm* reached 9%; the *M. oleifera* extract preventive +

Cmm reached a disease severity of 13.2%; while positive disease control reached 36.6 % severity in the fifth week. This study demonstrates that Mo-AgNPs have the potential to delay the disease progress caused by *Cmm* in tomato plants.

KEYWORDS

Biosynthesized NP, plant pathogenic bacteria, *Clavibacter*, quarantined bacteria

INTRODUCTION

Bacterial wilt and canker of tomato is a devastating disease caused by *Clavibacter michiganensis* subsp. *michiganensis* (*Cmm*), a quarantined pathogen in the European Union and other countries. Currently, this disease has no cure and no resistant cultivars. It spreads rapidly causing severe loss in productivity¹. Thus, new alternative technologies are required for the management of this pathogen, as a possible alternative the use of biosynthesized silver nanoparticles (AgNPs) using *Trichoderma harzianum* extracts that have been applied against *Cmm*². Green synthesis of AgNPs has gained popularity due to its advantages over chemical synthesis by reducing toxic reagents. Thus, the aim of this study was to evaluate the antibacterial activity of green synthesized AgNPs by reducing the disease severity in tomato plants caused by *Cmm*. AgNPs were biosynthesized with *Moringa oleifera* extract. The novelty of this study is the search for new control options to incorporate into the integrated management of quarantined bacteria such as *Cmm*.

EXPERIMENTAL/THEORETICAL STUDY

The in vivo efficacy of Mo-AgNPs was evaluated for four weeks against *Cmm* in tomato plants in greenhouse conditions. The following treatments were sprayed once a week: C = no inoculated tomato plants; T1= Mo-AgNPs preventive + *Cmm*; T2= *M. oleifera* extract preventive + *Cmm*; T3= *Cmm* positive control. Tomato plants in completely randomized design (Fig 1). Plant height, basal stem width, number of leaves, and disease severity according to the scale of Baysal et al. were measured twice a week.



Fig. 1. Tomato plants in completely randomized design

RESULTS AND DISCUSSION

The results showed significant differences between treatments and the infected tomato plants in the fifth week (Dunns < 0.05). The tomato plants treated with Mo-AgNPs were not the ones with the highest vegetative performance; they even had low averages compared to the other treatments.

Disease severity was analyzed by Kruskal-Wallis H test $p < 0.05$. The results showed differences between all treatments compared to the positive control (*Cmm*). The disease severity in treatment Mo-AgNPs preventive + *Cmm* reached 9% (T1); the *M. oleifera* extract preventive + *Cmm* (T2) reached a disease severity of 13.2%; while positive disease control (T3) reached 36.6 % severity in the fifth week (Fig 2).

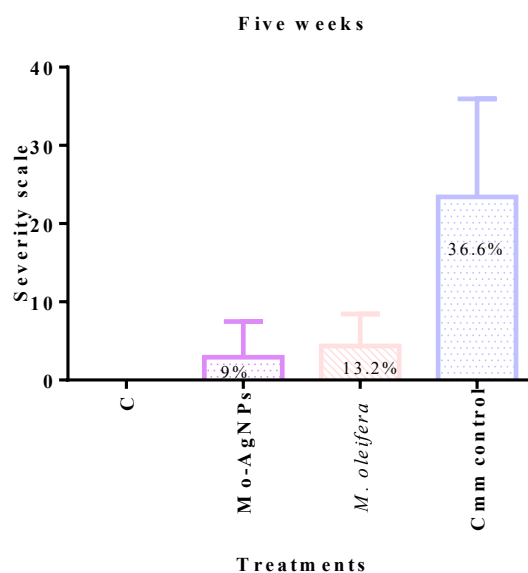


Fig. 2. Disease severity on tomato plants 5 weeks after inoculation of *Cmm*. C= no inoculated tomato plants. T1= Mo-AgNPs preventive + *Cmm* (9%); T2= *M. oleifera* extract preventive + *Cmm* (13.2%); T3= positive disease control *Cmm* (36.6 %).

CONCLUSION

The disease severity in treatment Mo-AgNPs preventive + *Cmm* reached 9%, while the control tomato plants inoculated with *Cmm* reached 36.6 % severity in the fifth week. This study demonstrates that Mo-AgNPs have the potential to delay the disease progress caused by *Cmm* in tomato plants. Future research can be carried out with metallic NPs originating from biosynthesis, in addition to combining plant extracts to try to reduce the disease severity.

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REFERENCES

1. I. Montenegro, A. Madrid, M. Cuellar, M. Seeger, J.F. Alfaro, X. Besoain, ... *Molecules*, 23(8) (2018) 2053.
2. A. Noshad, M. Iqbal, L. Folkers, C. Hetherington, A. Khan, M. Numan, S. Ullah *J. Nano Res.* 58, 10-19. Trans Tech Publications Ltd. 2019.
3. O. Baysal, E.M. Soylu, S. Soylu. *Plant Pathol* 52(6) (2003) 747-753.

Study of implants as a possible source of particles in human tissues

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ABSTRACT

Implants are widely used in traumatology to fix broken bones. The metal components of implants for these purposes are most often made of titanium alloy or stainless-steel alloy. While the bulk forms of these alloys are considered biologically inert, metal particles and ions released from the surface of the implant due to wear can cause a negative response in the human body. Scanning electron microscopy was used to determine the number of particles and their chemical composition in 10 biopsy tissue samples. The most frequently detected particles were FeCrNi, FeCr, FeNi, TiAlV, TiAl, TiAlNb. The detected particles had the same composition as the material used for implants.

KEYWORDS

Biopsy samples, implants, particles, scanning electron microscopy

INTRODUCTION

Fixation of fractures with implants is used for proper alignment and healing of bones ¹. However, in some cases, postoperative complications may occur due to the reaction of the surrounding tissue to the antigen (in our case, metal particles and ions). Particularly in the field of orthopaedics, the abrasion of osteosynthetic material in joint replacements and the associated health complications in patients are well described. In these cases, large metal friction surfaces are involved where metallic material can be released into the surrounding tissue ^{2,3}. In the types of implants we have studied, the metal friction surfaces are smaller and therefore it is assumed that either there is no release of metal particles from the implant surface or the abrasion of material is minimal. For this reason, similar studies have not received as much attention.

EXPERIMENTAL STUDY

Biopsy samples were obtained in cooperation with the University Hospital in Ostrava. Tissue samples were collected from 10 patients (ethics committee; reference number 317/2019). Biopsy samples were taken in close proximity to the implant in patients who had to undergo revision surgery due to implant failure. Sample preparation consisted of several steps. The first step was to fix the tissue in a buffered formalin solution for 24 hours. This was followed by decalcification and dehydration of the samples in a series of alcohols. This was followed by embedding the tissue samples in paraffin blocks from which thin sections were prepared on slides. The slides containing the tissue sections were dewaxed. Finally, the samples were sputter coated with a thin layer of Au/Pd. The samples thus prepared were analysed to scanning electron microscope analysis.

RESULTS A DISCUSSION

Ten biopsy samples were evaluated by scanning electron microscopy. The presence of metal-based particles, their morphology and elemental composition were evaluated Table 1. The elemental composition of the implants was used also evaluated Table 1. The elemental composition was determined by EDS analysis.

Table 1. NUMBER OF DETECTED PARTICLES AND TYPE OF THESE PARTICLES

Sample number	Number of detected particles	Type of detected particles	Type of implants material	Sample number	Number of detected particles	Type of detected particles	Type of implants material
1	2	stainless steel	FeCrNi	6	2	titanium alloy	Ti ₆ Al ₄ V
2	3	stainless steel	FeCrNi	7	3	titanium alloy	Ti ₆ Al ₄ V
3	4	stainless steel	FeCrNi	8	11	titanium alloy	Ti ₆ Al ₄ V
4	9	stainless steel	FeCrNi	9	19	titanium alloy	Ti ₆ Al ₄ V
5	10	stainless steel	FeCrNi	10	28	titanium alloy	Ti ₆ Al ₄ V

Metal-based particles were detected in all biopsy samples. Based on the EDS analysis data obtained, only titanium particles were detected in the biopsy samples collected from patients with titanium implants and only steel particles were detected in the biopsy samples collected from patients with steel implants. It can therefore be assumed that implants may be the source of these particles. In our case, the implants were implants in which the frictional metal surfaces are smaller than, for example, in the case of joint replacements³. This may be related to the number of particles detected, which was low.

CONCLUSION

Ten biopsies of tissue taken in close proximity to the implant were obtained from 10 patients. The biopsy samples were studied by scanning electron microscopy. The presence of metal-based particles, their morphology and elemental composition were evaluated. The method used proved to be suitable for this type of evaluation. Both micron and submicron sized metal-based particles were detected with compositions corresponding to the implants. Abrasion of implants used for fracture fixation was shown to be related to the particles detected in the biopsy samples.

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REFERENCES

- [1] TSAI, Ya-Yun, Ming-Kai HSIEH, Po-Liang LAI, Ching-Lung TAI a Shu-Wei CHANG. Predicting pullout strength of pedicle screws in broken bones from X-ray images. *Journal of the Mechanical Behavior of Biomedical Materials* [online]. 2022, **134**. ISSN 17516161. Dostupné z: doi:10.1016/j.jmbbm.2022.105366
- [2] GARNIER, Robert, Joël POUPON, Nouzha DJEBRANI-OUSSÉDIK a Jérôme LANGRAND. Titanium cutaneous metallosis after reverse total shoulder arthroplasty. *JSES Reviews, Reports, and Techniques* [online]. 2022, **2**(2), 190-193. ISSN 26666391. Dostupné z: doi:10.1016/j.xrtr.2022.01.006
- [3] PISANU, Francesco, Matteo ANDREOZZI, Enrico FIORI, et al. Surgical management of hip prosthetic failure in metallosis: A case series and literature review. *Journal of Orthopaedics* [online]. 2021, **28**, 10-20. ISSN 0972978X. Dostupné z: doi:10.1016/j.jor.2021.10.002

Composites based on smectites for removal of pharmaceutical micropollutants

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ABSTRACT

The aim of this work is comparison of ability of prepared organo-smectite composites for the removal of diclofenac (DC) from aqueous environment due to increasing wastewater pollution related to high consumption of pharmaceuticals, mainly widely prescribed non-steroidal anti-inflammatory drugs. The montmorillonite (MMT), beidellite (BEI), hectorite (HEC) and nontronite (NTN) were modified with benzalkonium chloride (BA) and prepared composites were checked as potential sorbent for analgesic drug DC from aqueous solutions. X-ray diffraction confirmed the intercalation process of organic substance into all used smectite samples. Also, the results obtained by thermal analysis proved BA intercalation into clay matrix by decrease of dehydration temperature due to an increase of the hydrophobicity of modified smectites. The removal of DC from aqueous solution reached up to 97 % sorption efficiency for MMT and NTN composites, 95 % for BEI composite and 92 % for HEC composite. The sorption characteristics including the sorption isotherms were determined too. These results suggest that the modification of smectites can lead to preparation of potential inexpensive materials with sufficient sorption ability for the removal of non-steroidal anti-inflammatory drugs from aqueous solution with respect to their occurrence in relatively low concentrations in wastewaters.

KEYWORDS

smectites, benzalkonium chloride, diclofenac, sorption

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Halloysite as suitable adsorbent of atrazine and diuron

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ABSTRACT

Halloysite mineral with its spiral shape nanotube morphology was tested as suitable adsorbent for herbicides atrazine and diuron, which have negative impact on the environment and fauna. Halloysite nanotubes are widely used for absorption due to their unique properties like a large specific surface area, porosity, high adsorption capacity, various charge distribution on inner and outer surface and colloidal behavior. Mutual interactions of both herbicides with the halloysite nanotubes were calculated¹. Calculations of herbicide conformations with minimum energy, geometry optimization and molecular dynamics of halloysite models with herbicides were done in Materials Studio² using COMPASS force field³. Various amount of herbicide loading was tested on inner and outer surface of halloysite to find the most reliable model. It was shown that both surfaces can interact with herbicides and loading and arrangement of herbicides depend on their concentrations and mutual interactions. The inner surface of the halloysite showed stronger interactions with both herbicides than the outer surface, and especially with diuron (e.g., binding energies for atrazine and diuron were -115 ± 2 and -130 ± 3 kJ·mol⁻¹, respectively). Poster contribution is based on published paper “How herbicides like atrazine and diuron interact with spiral halloysite structure.”¹

KEYWORDS

Halloysite, Atrazine, Diuron, Molecular simulations

INTRODUCTION

The main goal of this work was the study of the immobilization of atrazine and diuron molecules in the tubular structure of halloysite. In addition, the characterization of possible interactions on different surfaces of this clay was studied in the Materials Studio modeling environment² using molecular mechanics methods with the COMPASS force field³, which is commonly used for organic polymers, inorganic metals, zeolites and clay minerals, while these last two structures are similar in some respects⁴⁻⁶. In addition, COMPASS force field can parameterize organic compounds containing H, C, N, O, S and P, as well as metal cations, leading to an appropriate selection of tested herbicides. The level of current theory provides us with a broad description of the local environment in herbicide-halide systems, allowing us to identify the primary and boundary conditions for the use of halloysite structures as an effective interaction platform for herbicides and other pollutants.

EXPERIMENTAL/THEORETICAL STUDY

The halloysite structure model has an outer diameter of 62.68 Å and an inner one of 45.29 Å, while the model is composed of 5130 atoms. Various sets of initial models of halloysite with atrazine or diuron and water molecules were created to investigate mutual interactions between the halloysite surface and herbicides. The number of calculated water molecules was set to keep a reasonable

balance between the computational costs and the most suitable approach of the real system that means in a low relative humidity environment.

In order to investigate the preferred position and arrangement of herbicides' molecules with respect to halloysite surfaces, a set of initial models with atrazine molecules only in the inner, only in the outer part, or in the various ratios on both parts of the halloysite surfacere were created.

The binding energies of the herbicides' molecules in the halloysite structure (E_{bind}) were measured by the average of the five best models, as derived from the 51 models of molecular dynamics trajectory, with respect to the energy point of view, based on the following equations:

$$(1) E_{\text{bind}} = E_{\text{Total}} - (E_{\text{Hal+Wat}} + E_{\text{Herb}}),$$

where E_{Total} is the total energy of the system, $E_{\text{Hal+Wat}}$ is the total energy of halloysite and water molecules and E_{Herb} is the total energy of herbicide molecules only.

The binding energy per one herbicide molecule ($E_{\text{bind/nA}}$) was calculated as below:

$$(2) E_{\text{bind/nA}} = E_{\text{bind}} / n_{\text{Herb}}.$$

Mutual binding energy per one herbicide molecule (E_{mut}) with surrounding of other herbicide molecules, where n_{Herb} is the number of all herbicide molecules present in the model (total energy of herbicides alone without surrounding is divided by the number of all herbicides in the system), was calculated as:

$$(3) E_{\text{mut}} = E_{\text{Herb}}/n_{\text{Herb}}.$$

RESULTS AND DISCUSSION

Molecular mechanics calculation revealed that comparison of both atrazine and diuron herbicides show similar behaviour when interacting with the surface of halloysite nanotube. Both herbicides were preferably absorbed on the inner surface that means that strongly interacted with the octahedral sheet instead of the tetrahedral sheet. The main H-bonding of atrazine molecule with the halloysite surface was formed by the CH_3 , CH_2 , and NH groups and partially by the triazine ring, whereas diuron molecules interacted through CH_3 , NH , and carbonyl groups, and partially by the N atom and the chlorophenyl ring. For both calculated herbicides, the calculated halloysite structure easily interacted with 32 molecules onto the inner tube and present comparable weak interactions with a higher loading (37 herbicide molecules) on the inner surface. The binding energy per herbicide molecule evidenced that the interactions were very alike in both concentrations, being the energies slightly lower when the haloysite mineral interacted with fewer molecules. In the complexes, both herbicides presented weaker interactions, including vdW, with the outer surface than with the inner one, where the electrostatic contributions dominated, i.e. H-bonding. As the same concentration of diuron and atrazine molecules was selected for the investigation and comparison of the structural stability, diuron presented better interactions on the inner surface of the halloysite structure than the atrazine (lower $E_{\text{bind/nD}} = -130 \pm 3 \text{ kJ}\cdot\text{mol}^{-1}$ and $E_{\text{bind/nA}} = -115 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$ for the models with diuron and atrazine, respectively).

CONCLUSION

Halloysite structures with atrazine and diuron molecules were investigated for the evaluation of the systems' stabilities by molecular simulations methods. Simulations have shown that atrazine and diuron molecules can interact on outer and inner halloysite surfaces, setting up a planar arrangement which is parallel with the surface but only when free space is available. Higher herbicide

concentrations report the arrangement which is more perpendicular to the surface due to the mutual herbicide repulsive interactions. In addition, herbicides preferably interacted with the inner octahedral surface of the halloysite showing a preference for arrangement when all the molecules are placed in the inner part of the structure. The diuron molecule presented higher stability (i.e. a lower binding energy per diuron molecule) than atrazine on the inner surface of the halloysite owing to higher polarity shown by the diuron molecule that helps to better interact with the polar OH groups from the octahedral surface of the halloysite structure.

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REFERENCES

1. E. Gianni, D. Moreno-Rodríguez, L. Jankovič, E. Scholtzová, M. Pospíšil, *Journal of Environmental Chemical Engineering*, 10 (2022) 108785.
2. Accelrys Software, Materials Studio modelling environment, (2004).
3. H. Sun, *J. Phys. Chem. B* 102 (1998) 7338–7364.
4. S.A. Boyd, J.F. Lee, M.M. Mortland, *Nature* 333 (1988) 345–347.
- 5 A. Borrego-Sánchez, C.I. Sainz-Díaz, L. Perioli, C. Viseras, *Molecules* 26 (2021) 4392.
6. W. Li, X. Pang, C. Snape, B. Zhang, D. Zheng, X. Zhang, *Energy Fuels* 33 (2019) 765–778.

Effect of plasma treatment on the properties of PVDF/CeO₂ nanofiber membrane

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ABSTRACT

Polyvinylidene fluoride (PVDF) nanofibrous membrane has been prepared by electrospinning and its surface was modified by CeO₂ nanoparticles by immersion in a water colloidal solution with CeO₂ nanoparticles (CeO₂ NPs). Two ways of the deposition of CeO₂ nanoparticles on the PVDF nanofiber membrane were used: (1) deposition of CeO₂ NPs on the pristine electrospun membrane and (2) the immediate deposition CeO₂ NPs on the DBD plasma treated electrospun membrane. We investigated the effect of plasma treatment on the amount of CeO₂ NPs deposited on PVDF nanofiber surfaces and on the Ce³⁺/Ce⁴⁺ ratio in CeO₂ NPs deposited on PVDF. The amount of CeO₂ on nanofiber surfaces was determined by XPS (X-ray photoelectron spectroscopy) and SEM analysis. Results showed a significant increase of CeO₂ NPs amount on the plasma treated PVDF membrane, accompanied by slight decrease of Ce³⁺/Ce⁴⁺ ratio in CeO₂ NPs adherent on plasma treated PVDF surface in comparison with pristine PVDF surface. Detailed analysis of XPS spectra – C1s, O1s, and

Ce_{3d} indicated a possibility of the chemical bonding of CeO₂ NPs on the plasma treated PVDF surface.

KEYWORDS

polyvinylidene fluoride, nanofiber, nanoparticle, plasma treatment

INTRODUCTION

Cerium oxide nanoparticles (CeO₂ NPs) exhibit unique properties with wide application potential^{1,2}. CeO₂ as a valuable catalytic material whose properties vary dramatically from that of the bulk material to NPs.

Just recently has been shown that some types of cerium oxide are highly effective in the degradation of organophosphate pesticides (parathion methyl, fenchlorphos, chlorpyrifos, dichlofenthion, and prothiofos) and some types of phosphate-based flame retardants^{3,4}.

Thanks to many exciting properties cerium oxide attracted the attention of investigators designing nanofibrous membranes to create nanocomposite membranes polymer/CeO₂ for a wide scale of specific functions^{5,6,7}.

This work was focused on the optimization of the technology for functionalization of CeO₂ /PVDF nanofibrous membranes using plasma pre-treatment and to determine the effect of plasma treatment on the amount of deposited CeO₂ on the membrane surface and the effect of plasma treatment on the ratio Ce⁴⁺/Ce³⁺ on the membrane surface, which is responsible for all the unique properties of CeO₂ NPs.

EXPERIMENTAL

Nanofibrous membranes were prepared using Nanospider technology. The modification of membranes was performed by immersion of nanofibers and DBD plasma modified nanofibers directly into the colloidal solution of CeO₂ nanoparticles. Prepared samples were characterized by SEM, contact angle measurement and XPS spectroscopy to show the impact of plasma treatment on the properties of resulting nanocomposite.

RESULTS AND DISCUSSION

The contact angle measurement was used to determine the influence of plasma treatment on the surface properties of nanofibers. The lowest value of contact angle was reached for 10s treatment. This time was used as an optimal for plasmatic modification.

SEM analysis of pristine PVDF nanofibers showed almost none influence of DBD plasma on the nanofiber morphology. On the contrary the SEM images of CeO₂ modified nanofibers showed larger amount of nanoparticles on the plasma treated nanofibers. This result confirmed the activation of nanofiber surface by DBD plasma. The EDS mapping revealed the homogenous distribution of Ce on the NPs decorated plasma treated CF membrane. The EDS calculated amount of Ce on the plasma treated membrane is about 5 at.%.

Results of XPS analysis are quantitatively evaluated in the Table 1. The XPS measurements show the presence of expected carbon, fluorine, cerium (if applicable) and oxygen, and other impurities (Na,

P). The impurities originate from the source material solution and they are expected to be concentrated on the surface of the fibers by the electrospinning process.

Table 1: Comparison of atomic concentrations in the samples

	C	F	O	Ce	P	Na
	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]
CF membrane	49.6	38.3	8.4	-	2.0	1.6
washed CF membrane	54.2	39.8	5.4	-	0.4	0.3
CF/CeO ₂	54.5	34.3	8.3	1.6	0.8	0.5
plasma treated CF/CeO ₂	54.5	22.0	19.3	3.1	0.8	0.3

It is evident from Table 1 that the cerium content is doubled on the plasma treated membrane necessarily accompanied by an increase in oxygen and a decrease of fluorine content as the oxide is part of the CeO₂ NPs.

CONCLUSION

It could be concluded that plasma treatment has a double effect on the preparation of nanocomposite membrane PVDF/CeO₂ NPs: (1) twice the amount of CeO₂ NPs on plasma treated membrane compared to a pristine PVDF membrane and (2) stronger binding of CeO₂ NPs to the membrane and therefore higher stability of the nanocomposite membrane. Moreover, both of these advantages do not imply a substantial reduction in the Ce³⁺ concentration which is significant for the desired membrane functionality.

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REFERENCES

1. Younis A, Chu D, Li S, Cerium oxide nanostructures and their applications, in: M. A. Farrukh (Ed.) Functionalized Nanomaterials, IntechOpen.
2. Sun C, Li H, Chen L, Nanostructured ceria-based materials: synthesis, properties, and applications. *Energy Environ Sci* 2012; 5:8475-8505.
3. Janoš P, Henych J, Pfeifer J, Zemanová N, Pilařová V, Milde D, Opletal T, Tolasz J, Malý M, Štengl V, Nanocrystalline cerium oxide prepared from a carbonate precursor and its ability to breakdown biologically relevant organophosphates, *Environ. Sci.: Nano*, 2017;4;1283-1293.
4. Janoš P, Ederer J, Došek M, Some Environmentally Relevant Reactions of Cerium Oxide; *Nova Biotechnol. Chim.* 2015; 13;148-161.
5. Rather HA, Thakore R, Singh R, Jhala D, Singh S, Vasita R, Antioxidative study of Cerium Oxide nanoparticle functionalized PCL-Gelatin electrospun fibers for wound healing application, *Bioactive Mat.* 2018;3;201-211.
6. Breitwieser M, Klose C, Hartmann A, Büchler A, Klingele M, Vierrath S, Zengerle R, Thiele S, Cerium oxide decorated polymer nanofibers as effective membrane reinforcement for durable, high-performance fuel cells, *Adv. Energy Mater.* 2017;1602100.
7. Vazquez-Velez E, Lopez-Zarate L, Martinez-Valencia H, Electrospinning of polyacrylonitrile nanofibers embedded with zero valent iron and cerium oxide nanoparticles, as Cr(VI) adsorbents for water treatment; *J. Appl. Polym. Sci.* 2019;48863.

Crystallization of submicron steroid drug particles by supercritical fluid extraction and ultrasound precipitation

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ABSTRACT

This work is focused on submicron crystallization of drug particles with anti-inflammatory properties. The methods used in the preparation were fluid crystallization based on ultrasound assisted crystallization and precipitation and further supercritical fluid extraction. In fluid crystallization based on ultrasound crystallization, the optimal flow rate was determined and finally Tween 80 was added to prevent agglomeration. This arrangement was analyzed by scanning electron microscopy (SEM) and particles size distribution (PSD) by FBRM probe. Supercritical fluid extraction was used in the rapid expansion of the supercritical solution mode (RESS) and gas antisolvent mode (GAS). The produced particles were analyzed by scanning and transmission (STEM) electron microscopy and particles size distribution. Subsequently, the results of both methods of preparation were compared. The SFE method yielded particles of smaller size (0.299 – 0.245 μm) than the ultrasonic antisolvent precipitation method (4.5 μm).

KEYWORDS

Ultrasound assisted crystallization, RESS (Rapid expansion of supercritical solution), GAS (Gas antisolvent), flow crystallization.

INTRODUCTION

Recently, processes have been developed in the pharmaceutical industry that focus on the continuous production of drug particles. These processes tend to be faster, easier to control and more robust than batch production. There is also a new need to reduce drug particle size to make it easier to reach the site of action and also make the drug more bioavailable or comfortable to the user. For example, particles larger than 1 μm in eye drops tend to cause discomfort to the user, but particles with a smaller size are imperceptible.¹

EXPERIMENTAL STUDY

The first method used for preparation was ultrasonic precipitation in a cell. This was done by mixing a stream of drug dissolved in acetone and an antisolvent (purified water). The mixed suspension was then analyzed using an FBRM probe (FBRM PI-9.5-14/206, Mettler Toledo) and SEM (TM3030Plus, Hitachi).

The second preparation method used supercritical fluid extraction (SFE) with supercritical carbon dioxide acting as an antisolvent. A prominent technique that was used was GAS. The drug solution was dissolved in acetone and precipitated with supercritical carbon dioxide during rapid nozzle expansion.² Different supercritical conditions (temperature and pressure) were applied. The resulting particles were analyzed using the disc particle size analyzer (Disc Centrifuge DC24000, CPS) and

STEM (JEOL JSM-7610F Plus, JOEL). Tween 80 was added to solutions to stabilize the final crystals.

RESULTS AND DISCUSSION

Using ultrasound assisted crystallization and precipitation, particles of approximately 4.5 μm in size were created. Smaller particles were prepared using SFE in GAS mode. The difference between the particles size distribution is shown in Figure 1 and Figure 2a,b. The figures showed that the particles prepared by SFE are much smaller than those prepared by ultrasonic crystallization. The difference between Figures 2a) and 2b) is due to the addition of Tween 80, which prevented the particles from agglomerating.

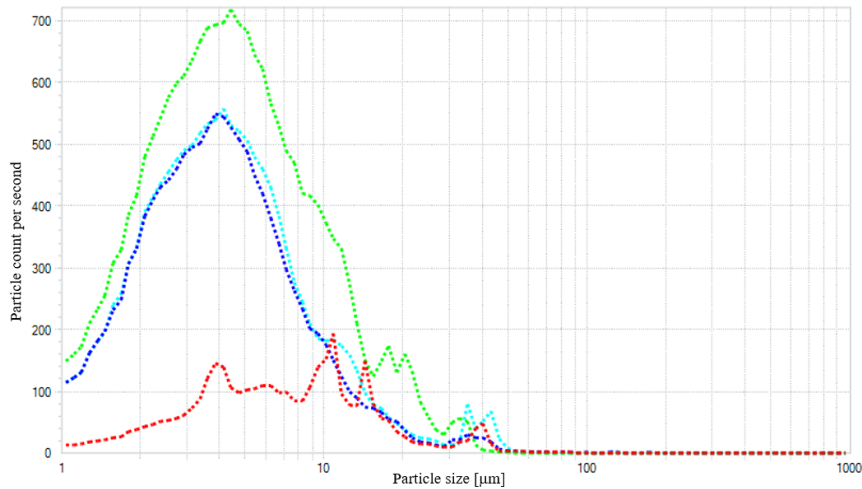


Fig. 1. PSD measured using FBRM, the particles were prepared by ultrasonic precipitation over time.

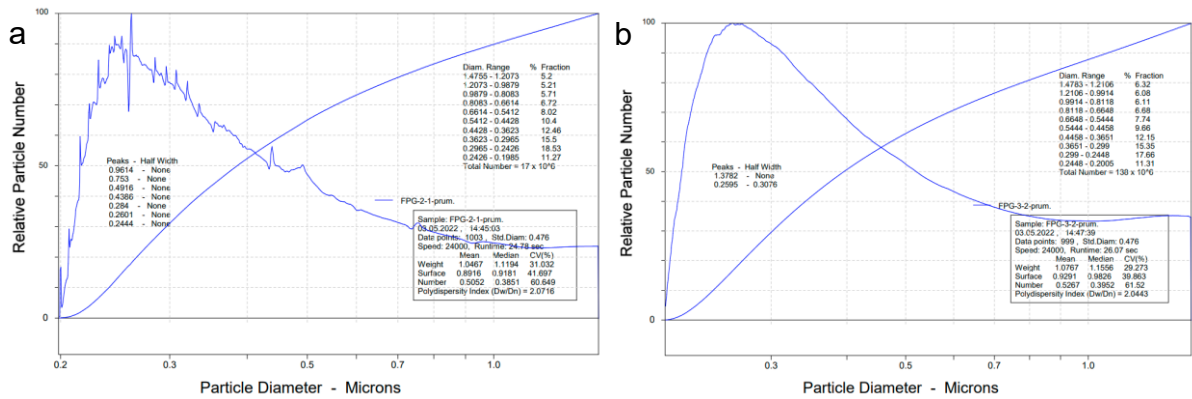


Fig. 2. (a) PSD for sample prepared using SFE without Tween 80; (b) PSD for sample prepared using SFE with Tween 80.

Based on the SEM analysis, it was concluded that both methods led to the formation of drug particles of the similar shape. The typical shape of the drug used is "needle". This can be seen in Figure 3, where the results of both used methods are compared.

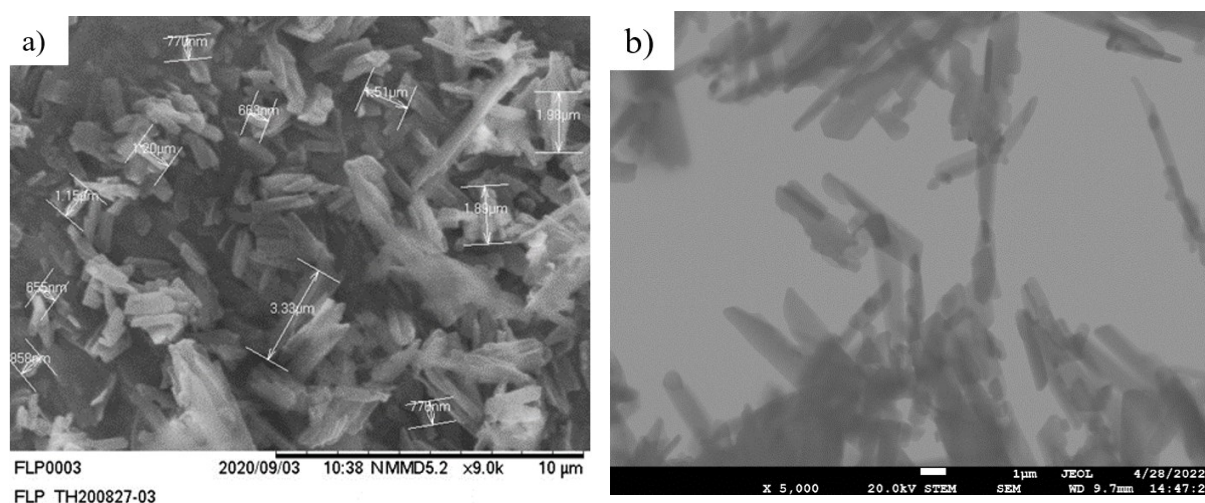


Fig. 3. (a) SEM image of drug microparticles prepared by ultrasound precipitation; (b) STEM image of drug submicron particles prepared by SFE.

CONCLUSION

The SFE method yielded particles of smaller size ($0.245 - 0.299 \mu\text{m}$) than the ultrasound assisted crystallization method ($4.5 \mu\text{m}$). The addition of Tween 80 to the processed solutions prevented agglomeration of the final product. The SFE production process was robust and particles prepared by this method at different temperatures and pressures achieved similar particle size distributions. SFE is a very promising method for the continuous production of drugs of defined particle size, but this requires further research.

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REFERENCES

1. Teva Czech Industries intern information's
2. SHETH, Pratik, Harpreet SANDHU, Dharmendra SINGHAL, Waseem MALICK, Navnit SHAH and M. SERPIL KISLALIOGLU. Nanoparticles in the Pharmaceutical Industry and the Use of Supercritical Fluid Technologies for Nanoparticle Production. *Current Drug Delivery* [online]. 2012, 9(3), 269–284. ISSN 15672018. Available at: doi:10.2174/156720112800389052.

Composites g-C₃N₄/TiO₂ for photocatalytic applications

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ABSTRACT

TiO₂ in anatase form and g-C₃N₄ are semiconductors that have been intensively studied for photocatalytic applications. To evoke the photocatalytic activity of anatase with band gap energy 3.2 eV the light of wavelength approximately 380 nm and lower is necessary. In contrast to TiO₂, g-C₃N₄ with a band gap energy 2.7 eV requires the light of wavelength approximately 460 nm, which predetermines this photocatalyst for a broad range of photocatalytic applications operating at day light. Combining both photocatalysts, the composite g-C₃N₄/TiO₂ can be obtained with improved photodegradation performance compared to both individual components. In our research, we used the thermal hydrolysis of titanyl sulphate suspension with bulk g-C₃N₄ to obtain g-C₃N₄/TiO₂ composites. The prepared samples were characterized using the methods of chemical and phase analysis, the morphology of the particles was studied using SEM technique, and the specific surface area was determined using physisorption of nitrogen. The band gap energies of the prepared samples were evaluated using UV-VIS DRS spectrometry. UV and VIS light induced degradation of rhodamine B was used to evaluate the photocatalytic performance of prepared composites.

KEYWORDS

TiO₂, g-C₃N₄, composites, characterization, photodegradation activity.

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Production of PVB/g-C₃N₄ photocatalytic active fibrous membranes for environmental application

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ABSTRACT

In recent times, fibrous membranes have developed a crucial role in the filtration of pollutants from air or water. Unfortunately, if the filter membrane is used for several hours or days, it leads to a gradually increasing concentration of pollutants on the membrane surface. However, this

contamination can be effectively eliminated by the presence of photocatalytic submicroparticles as part of the fibrous membrane. We prepared several polyvinylbutyral fibrous membranes and compared their photocatalytic activities by phenol degradation. The blend method is the most widely used. Active particles are added to the polymer solution prior to the electrospinning process. This approach seems logical and effective. Unfortunately, this method led to particle encapsulation by a polymer within the fibre and to a decrease in photocatalytic activity ($k = 0,00115 \text{ min}^{-1}$). Another method is called thermal treatment. This method led to the attachment of the particle to the fibre surface, allowing its significantly more effective surface action ($k = 0,00176 \text{ min}^{-1}$). However, the thermal method caused changes in the fibre size distribution. Using a combination of the methods mentioned above, the last membrane was prepared and tested with the highest photocatalytic activity ($k = 0,00281 \text{ min}^{-1}$).

KEYWORDS

Electrospinning, photocatalysis, degradation kinetics, phenol

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Use of supercritical fluid technology for preparation of antimicrobial nanomaterials

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ABSTRACT

Development of new antimicrobial material, whose are not toxic to human not any other higher living organism is new challenge of today science. Each of newly developed material can be used in biomedicine, coating, etc. Using commonly used biopolymer polylactide and cationic polymer based on methacrylic acid seems to be effective in use against antimicrobial resistance. Polylactide, as bioplastic that is easily degradable, recyclable, and mass-produced, is very suitable for replacing oil-based polymers on market. Also, the development of 3D printing in the context of this initiative, and the actual use of PLA as one of the main materials used for this printing, make the technology around the preparation and modification of PLA quite logical. Supercritical fluid technology is environmentally friendly and energy saving technology, which allow us to extend or use at all expensive and in many cases also toxic solvents.

In a first approach, polylactide nano- and microparticles and structures were prepared by supercritical fluid extraction. The RESS (rapid expansion supercritical fluid solution) method is easier to optimize and shows better particle size control. However, the yield of this method is very low.

On the contrary, a highly porous structure was obtained using the SAS (supercritical antisolvent) method. In this method we need to use a solution of polylactide in an organic solvent. Resulted

microparticles prepared by SAS method, in shape of fibres in micron size. The yield of the reaction was higher.

Second approach was done with preparation of particles of antimicrobial polymer and polylactide/antimicrobial polymer. Created microparticles prepared by RESS method had similar shape as particles prepared from pure PLA by RESS.

KEYWORDS

polylactide, antimicrobial polymers, supercritical fluid technology

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TOPIC 3

Advanced materials characterization

Chair: Jan Neuman

Advanced testing
Nanomaterials detection
Surface properties
Structure characterization
Morphology and topography



Invited lectures (IL):**Digital olfaction**G. Cuniberti

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ABSTRACT

Olfaction is an ancient sensory system that allows us to access sophisticated information about our environment. Drawing inspiration from biology, carbon nanomaterials-based gas sensors combined with machine learning algorithms aim at replicating this performance and digitizing the sense of smell. This lecture presents is about gas discrimination and identification performance of carbon nanomaterials-based nanosensors. Functionalized carbon nanomaterials-based nanosensors were fabricated on multiple-channel gas sensor devices, and the sensing signal was acquired when exposed to various gases. The transient features of the gases were then extracted from the sensing signal and fed to a machine-learning algorithm to discriminate and identify the gases. The developed carbon nanomaterials-based electronic olfaction system shows excellent gas identification performance for different gases. This platform can be used to miniaturize e-noses, digitize odors, and distinguish various gases and volatile organic compounds (VOCs) for applications such as pathogen detection, environmental monitoring, and disease diagnosis.

Anisotropic charge distribution on halogen atom, σ -hole, really exists: atomic force microscopy and high-level quantum chemical calculationsP. Hobza^{1,2}

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ABSTRACT

Halogen bonds, which are bonds between halogens and electron donors, play an important role in chemical, biological, and nanomaterial sciences. The existence of halogen bonds was long a puzzle because it involves a bond between electronegative atoms that should carry a negative charge. At the beginning of the century, Clark and Politzer explained this phenomenon by showing that the electron density on the halogen atom, which is covalently bonded to an electronegative atom (e.g. carbon), is not homogeneous but forms a so-called sigma hole, which is positively charged. In a halogen bond, the negatively charged electron donor interacts with the positively charged sigma hole on the halogen. The existence of the sigma hole was theoretically predicted, but direct experimental confirmation did not exist.

Using Kelvin probe force microscopy, which belongs to scanning probe force microscopy, we studied sigma holes in the molecules tetrakis (4-fluorophenyl) methane and tetrakis (4-bromophenyl) methane. Through a combination of experiments and advanced quantum mechanical calculations, we confirmed the existence of the sigma hole in the second molecule and the absence of this hole in the first molecule. The experiments fully agreed with the theoretical prediction based on the molecular electrostatic potential.

REFERENCES

B. Malada, A. Gallardo, M. Lamanec, B. de la Torre, V. Spirko, P. Hoibza, P. Jelínek, *Science* 2021, 374, 863-867.

Oral presentations (OP):**Nanostructured biomaterials as analogs of extracellular matrix for adhesion and growth of cells in tissue engineering – a review**

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ABSTRACT

Tissue engineering is defined as an interdisciplinary field, that applies the principles of engineering and the life sciences toward the development of biological substitutes that restore, maintain, or improve the function of damaged tissues and organs [1]. There are two main components of a tissue-engineered construct: cells and their scaffolds, i.e. biomaterials that fulfill the function of extracellular matrix (ECM). These biomaterials (i.e. materials that enter into an interaction with the biological environment) can be of nature-derived or synthetic origin – for example, various natural and synthetic polymers, metals and their alloys, ceramics, or carbon-based materials. The cell-material interaction is strongly dependent on the physical and chemical properties of the material surface, e.g. its chemical composition, polarity, wettability, electrical charge and conductivity, rigidity or deformability, and also the surface roughness and topography. The nanostructure of the material surface, i.e. presence of irregularities or other domains than 100 nm in size, mimics the natural nanoarchitecture of native tissues and organs, such as various curvatures on the ECM molecules (e.g. collagen helices), the structure of the cell cytoplasmic membrane with the extracellular parts of integrin adhesion receptors, etc. Moreover, nanostructured materials support the adsorption of cell adhesion-mediating molecules (e.g. vitronectin, fibronectin, collagen) in an appropriate conformation, enabling the binding of cell adhesion receptors to the active sites of these molecules, such as specific amino acid sequences (RGD) or carbohydrate ligands. Among these molecules, vitronectin is adsorbed preferentially to the nanostructured substrates due to its relatively small and linear molecule, and then it is preferentially recognized by osteoblasts over other cell types, making the nanostructured substrates particularly suitable for bone tissue engineering (for a review, see [2]). In accordance with this, our laboratory is participating in the development of various nanostructured layers for surface modification of bone implants in order to increase their osseointegration, such as nanocrystalline diamond films, films of TiO₂ or other oxides, zeolites or MXenes, or polymeric nanofibrous scaffolds reinforced with ceramic, metallic or carbon nanoparticles for potential bone tissue engineering [3-5].

KEYWORDS

Nanoscale roughness, nanofibers, osteogenic differentiation, nanomedicine

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REFERENCES

1. R. Langer, J.P. Vacanti, *Science* 260 (1993) 920-926.
2. L. Bačáková, E. Filová, M. Pařízek, T. Ruml, V. Švorčík, *Biotechnol. Adv.* 29 (2011) 739-767.

3. M. Steinerová, R. Matějka, J. Štěpanovská, E. Filová, L. Staňková, M. Rysová, L. Martinová, H. Dragounová, M. Domonkos, A. Artemenko, O. Babchenko, M. Otáhal, L. Bačáková, A. Kromka, Mater. Sci. Eng. C Mater. Biol. Appl. 121 (2021) 1117924.
4. R. Gabor, L. Cvrček, M. Doubková, V. Nehasil, J. Hlinka, P. Unucka, M. Buřil, A. Podepřelová, J. Seidlerová, L. Bačáková, Mater. Des. 219 (2022) 1108115.
5. A. Brož, I. Jirka, R. Matějka, J. Štěpanovská, M. Doubková, P. Sajdl, J. Drahokoupil, O. Volochanskyi, T. Futóová, L. Bačáková. Mater. Des. 224 (2022) 111373.

Electronical and optical properties of carbide molybden modifications

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ABSTRACT

In my work, I introduce MXenes, a new type of single-layer material. I focus on modifications of carbide molybdenum and their isomers. More specifically, on their up to now preliminary or even completely undescribed electronic and optical properties. In comparison to all available sources, I describe them on a substantially higher level and consequently determine whether the materials lead the electric current or not and whether they absorb wavelengths of visible light. The key outcome will have the form of values of band gaps calculated by means of the Perdew-Burke-Ernzerhof method, also known as PBE, by means of the hybrid method, also known as HSE06, and finally by means of the many-body perturbation method GW, and absorption of wavelengths of visible light. I find exact values of lattice constant and energetic levels of isomers, thereby contributing to the general development of the single-layer world and helping next workers -- SOČ students and researchers. In the end, I focus on exact description of optical properties by means of the Bethe–Salpeter equation, BSE, that includes excitons. I reflect all data in graphs and charts and interpret them. I suggest potential practical application of gained pieces of knowledge.

Surface modification of metallic bone implants for improved osseointegration

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ABSTRACT

Titanium and its alloys have a wide range of applications in biomedicine - from temporary or permanent implants such as bone screws or femoral stem implants, to wireless systems for controlled drug delivery. Their high biocompatibility and good physical and mechanical properties make them suitable for use in the fields of orthopaedics and dentistry. Ti6Al4V alloy is one of the most commonly used materials for construction of bone implants. However, development of new surface modifications to eliminate the possible release of Al and V ions and to further promote implant integration into bone remains highly desirable. We will present results of *in vitro* and *in vivo* analyses of Ti6Al4V materials surface-modified by two different methods. The first set of materials was modified by a combination of physical vapour deposition (PVD) and micro-arc oxidation (MAO) to develop Ti and ZrTi oxide surface layers [1]. The second set of samples was coated with thin film of nanocrystalline diamond (NCD) using chemical vapour deposition (CVD) method, oxidized and functionalized with human bone morphogenetic protein (BMP-7), which is a key modulator of bone and cartilage formation and repair [2]. To assess the osteoinductive and osteoconductive potential of these modifications we have analyzed them in interaction with bone marrow mesenchymal stromal cells (hBMSC) and human fetal osteoblast cells (hFOB). We studied the morphology and proliferation of cells with fluorescence microscopy and metabolic tests, cell phenotypic maturation and differentiation by the level of enzymatic activity of alkaline phosphatase, gene expression of selected osteogenic markers and the mineralization of extracellular matrix by Alizarin Red staining up to 21 days of cell culture. Hybrid ZrTi layers deposited by the combination of PVD-MAO methods showed increased corrosion and wear resistance, reduced coefficient of friction, and at the same time it stimulated osteogenic cell differentiation better than the unmodified alloy. CVD-modified samples coated with NCD film promoted faster mineralization and bone formation than control both *in vitro* and *in vivo* study in rabbits. The adsorption of BMP-7 on NCD surface further increased and accelerated the process, making it a great candidate to improve the bioactivity of Ti6Al4V implants.

KEYWORDS

Orthopaedic implants, coatings, nanocrystalline diamond, osteogenic differentiation

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REFERENCES

1. R. Gabor, L. Cvrček, M. Doubková, V. Nežasil, J. Hlinka, P. Unucka, M. Buřil, A. Podepřelová, J. Seidlerová, L. Bačáková. Mater. Des. 219 (2022) 110811.
2. I. Nemčáková, A. Litvinec, V. Mandys, S. Potocký, M. Plencner, M. Doubková, O. Nanka, V. Olejníčková, B. Sanková, M. Bartoš, E. Ukraintsev, O. Babčenko, L. Bacáková, A. Kromka, B. Rezek, D. Sedmera. Sci. Rep. 12 (2022) 5264.

Stem cells growth observations and material aimed to engineer bone tissue replacements and appropriate scaffolds

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ABSTRACT

The ultimate objective of my year internship at Physiological institute of Czech Academy of Sciences was to select an appropriate scaffold for colonization and long-term proliferation of cells. It focused on the impact of scaffolds on cell activity. This research represents the first step towards the engineering of bone tissue replacement. Bone tissue replacements could reduce the risk of immune reaction and decrease the need for reoperation caused by implanted replacements overuse or damage; thus, they promote consequent progressive blending in the rest of the tissue. Particularly, the development of polymer scaffold by 3D printing presents an opportunity to manufacture the replacements in any arbitrary shape.

The objects of selection were three basic kinds of scaffolds differing by material, their processing and inner 3D structures, namely FDM 3D printed prints, honeycomb structure scaffolds and SLA 3D resins. The first tests were carried out on 10 types of three-dimensional print structures with fiber width either 240 μm or 200 μm and space between them from 0 μm up to 200 μm . The second kind of scaffolds were structures resembling honeycomb structure by shape. Their structure was two-dimensional, and they were exposed to radiation of varying intensities and the aim of which was to determine the impact of radiation processing on the proliferation of cells. The third kind of scaffolds were resins printed on SLA 3D printer with three-dimensional ladder structure and with fiber and space width 100 μm .

The experiment consisted of ASC stem cells seeding isolated from human fat tissue on the above mentioned three kinds of scaffolds. The cells were cultivated in thermostat for up to 10 days in static conditions. Their growth was evaluated based on either the images from the Dragonfly 503 confocal microscope or the Olympus IX71 optical microscope, summing up the nuclei dyed by fluorescent dye Hoechst 33258 or MTS metabolic test.

The cells colonized all the 10 types of prints. However, the depth of colonization differed. According to the images from the confocal microscope, the most efficient penetration occurred in types number 2, 3 and 8. Regarding of honeycombs, MTS tests and nuclei sums revealed that long-term proliferation is best supported by scaffold radiated by level 1,000, where the cells reached higher levels of proliferation than in polystyrene positive control. The MTS tests on resins proved sufficient proliferation and deep penetration was obvious from IX71 optical microscope.

Multiscale investigation of plasmon-driven photocatalysts by scanning electrochemical microscopy

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ABSTRACT

Plasmon-driven photocatalysts received soaring interest due to the possibility of using plasmonic effects to enhance reaction rates or activate unexpected reaction pathways [1]. The surface plasmons decay by generating non-thermal (hot) electron-hole pairs having enough energy to drive chemical reactions when excited by an electromagnetic field (e.g., sunlight). Extensive research efforts demonstrated the significance to investigate the interactions between molecules and nanomaterials at multiscale to discover and understand the lush applicability provided from plasmon-driven photocatalysis [2-4]. So far, the only technique enabling the local study of the chemical production from purely photocatalytic processes and unlocking the local in situ mapping of those chemicals produced through plasmon-driven reactions is the scanning electrochemical microscope (SECM).

Herein, we present a methodology to study locally the photo-material by SECM enabling 2D quantitative mapping of plasmon-driven reaction products at different scale (from mm to hundreds of nm). The experimental results coupled with diffusion model enable the quantification of the material quantum efficiency. The methodology elucidates structure-activity relationships at the origin of the plasmonic activity.

The presented results demonstrated the methodology thanks to a reference model including Au NPs deposited on a semiconductor/charge collector substrate formed by a TiO₂/ITO substrate, which is already well-referenced in the literature [5]. Ultimately, the methodology will be applied to shed light on the correlation between the system properties (e.g. size, shape, composition, interface and embedding media) and the photoproduced molecules at multiple scales.

REFERENCES

1. Zhang, Y.; He, S.; Guo, W.; Hu, Y.; Huang, J.; Mulcahy, J. R.; Wei, W. D., 2018, *Chem. Rev.*, 118, 2927–2954.
2. Sytwu, K.; Vadai, M.; Hayee, F.; Angell, D. K.; Dai, A.; Dixon, J.; Dionne, J. A., 2021, *Science*, 371, 280–283.
3. Cortés, E.; Xie, W.; Cambiasso, J.; Jermyn, A. S.; Sundararaman, R.; Narang, P.; Schlücker, S.; Maier, S. A., 2017, *Nat. Commun.*, 8, 14880
4. Oksenberg, E.; Shlesinger, I.; Xomalis, A.; Baldi, A.; Baumberg, J. J.; Koenderink, A. F.; Garnett, E. C., 2021, *Nat. Nanotechnol.*, 16, 1378–1385.
5. Yu, Y.; Wijesekara, K. D.; Xi, X.; Willets, K. A., 2019, *ACS Nano*, 13, 3629–3637.

LiteScope 2.5: Pushing the boundaries of correlative AFM-in-SEM microscopy

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ABSTRACT

The LiteScope 2.5 is a new generation of “plug & play” atomic force microscopy (AFM) microscope that can be easily integrated into a scanning electron microscopy (SEM) system for correlative multimodal sample analysis. This microscope offers several unique features, making it an excellent tool for in-situ sample characterization and precise localization of regions of interest.

Firstly, our microscope offers correlative multimodal sample analysis by combining the high-resolution imaging capabilities of AFM (and 12 more related techniques) with the capabilities of SEM material analysis. This combination allows for a more comprehensive understanding of a sample's properties, leading to better insights into its structure and behavior.

Secondly, it enables in-situ sample characterization, allowing researchers to analyze samples under laboratory-controlled conditions, including temperature and humidity. This capability is crucial for research on oxidation-sensitive samples, whereas with LiteScope 2.5 offer a way to prepare and measure the sample without the need to take the sample out of a vacuum.

Finally, LiteScope provides precise localization of the region of interest, enabling researchers to target specific areas of a sample with high accuracy. This feature is handy in analyzing complex samples, where it can be difficult to isolate specific regions of interest.

KEYWORDS

AFM, SEM, Correlative microscopy, CPEM

INTRODUCTION

With the advancement of sample preparation techniques which allow the fabrication of more complex samples, the need for a tool which increases the effectiveness of sample analysis arises even more. The proper complex analysis must be done to understand advanced material science and nanotechnology research samples. To ease this chore, we present a new-generation LiteScope 2.5, combining the benefits of AFM, SEM and their related techniques. LiteScope is an AFM microscope integrable with the majority of SEMs. The sample can then be measured simultaneously with both techniques, and results can be correlated using a patented correlative probe and electron microscopy (CPEM) technology.

Thanks to the wide view field of SEM and fast ability to change scanned area, it is effortless and fast to navigate the AFM probe to the region of interest and precisely approach the surface of the sample.

With the fixed position of both the AFM tip and SEM electron beam, the scanner starts to scan with the sample, acquiring both data sets at once from the same area. Combining the data from the AFM technique with material or chemical analysis of SEM-related technique result in complex and comprehensive information about the studied sample¹⁻⁴.

EXPERIMENTAL/THEORETICAL STUDY

LiteScope implementation into the SEM is fast and easy. Firstly, the LiteScope is installed into the SEM chamber via an adaptation plate compatible with most standard SEM stages. Two cables (signal output and scanner control) are then led out of the chamber through a grommet into the NenoBox controller, together with the signals from the SEM detectors.

After localizing the area of interest with SEM, all the measurement is controlled via the user-friendly interface NenoView.

Apart from the previously mentioned AFM, LiteScope offers 12 complementary techniques. With LiteScope, the mechanical, magnetic, electro-mechanical, and electrical properties can be measured. Apart from imaging techniques, LiteScope can perform spectroscopy measurements with F - z or I - V curves.

On top of all these techniques, the CPEM technique can correlate multiple layers of data information.

To demonstrate the capabilities of new generation LiteScope 2.5, we present here the state-of-the-art measurement output of the following techniques:

Atomic force microscopy: AFM allows high-resolution topography measurements of a wide range of samples with the noise floor around 35 pm.

Conductive AFM: Conductive AFM provides a high-resolution local conductivity map of the sample by applying a bias between the sample and the conductive probe.

Kelvin probe force microscopy: KPFM is a two-pass technique estimating the local distribution of surface potentials.

Magnetic force microscopy: MFM enables high-resolution imaging of the magnetic properties of different materials and visualization of the magnetic domain on the surface.

RESULTS AND DISCUSSION

We present two experiments highlighting the unique capabilities of LiteScope 2.5. Figure 1 shows the first measurement of the in-situ analysis of battery material. Thanks to the ability to utilize FIB or GIS milling, the sample prone to oxidation is repolished in the vacuum chamber. The subsequent analysis is done without any air exposure.

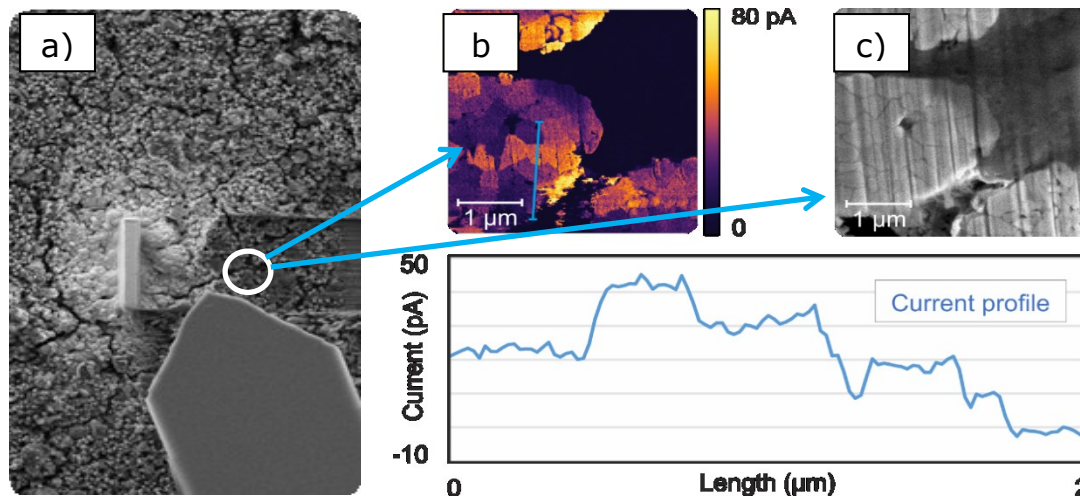


Fig. 1. (a) SEM overview of AFM probe approaching FIB milled trench. (b) C-AFM measurement of local conductivity of cathode material. The blue line indicates the measured current profile. (c) SEM image of the measured area.

Due to the ability to precisely navigate the AFM probe to the region of interest, the researchers can choose the best place for repetitive analysis, which is impossible without using LiteScope 2.5. The results of the experiment are shown In Figure 1. where it is shown how the probe is navigated into the fibbed trench, where the exposed bulk material is then studied with conductive AFM. The measurement outcomes clearly show the conductivity of the individual grains.

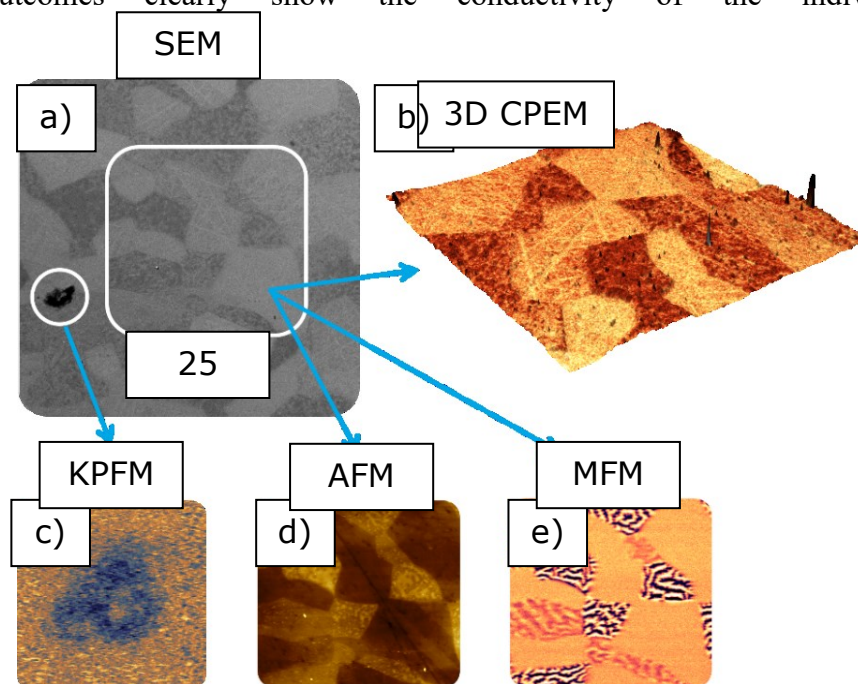


Fig. 2. (a) SEM overview image of duplex steel with the highlighted area where complex measurement was done. (b) 3D CPEM image showing the morphology of the sample. (c) KPFM analysis of surface impurity. (d) AFM topography of the clean area of the duplex steel. (e) MFM measurement shows the qualitative analysis of the sample's magnetic stray field.

The second measurement shows the ability to localize the exact location on the sample repetitively, allowing us to do complex multimodal analysis. The duplex steel was analyzed with AFM, KPFM, MFM and SEM. The measurement analysis provides information about the local magnetic stray fields of the individual grains of the duplex steel. Using KPFM can provide information about impurities on the sample and their surface potential for better determination of the origin and material composition of the impurities. NenoView also allows users to use unique AI-driven multidimensional correlative imaging CPEM. Combining data from multiple measurement modes under the same experimental conditions yields more reliable results and saves time in acquiring data.

CONCLUSION

The new generation LiteScope 2.5 microscope represents a significant advance in microscopy technology, offering unprecedented opportunities for researchers to attain superior resolution in a variety of experimental techniques. This cutting-edge microscope is poised to become the ultimate tool for complex correlative analysis.

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REFERENCES

1. VANECKOVA, Tereza, et al. Scientific Reports, 2019, 9.1: 11840.
2. CHRONOPOULOS, Demetrios D., et al. Chemical Communications, 2019, 55.8: 1088-1091.
3. UKROPCOVÁ, Iveta, et al. Advanced Materials Interfaces, 2023, 10.2: 2201963.
4. Applied Surface Science, 2022, 587: 152839.

Interaction of metal oxide nanoparticles with plant under the influence of electric field

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ABSTRACT

The application of electrical energy is a common thing that is observed in daily human activity. One of the fields where electrical energy can be applied and benefitted is agriculture. Currently, the use of the electric field (EF) in agriculture is orientated into environmental remediation of contaminated areas, especially soils, to reduce decontamination and minimise the negative side-effect of inorganic and organic pollutants. Here, electro-culture with applied EFs and magneto-culture used by magnetic fields could be another alternative for agricultural practices of various commercial crops.

Generally, in the case of direct current (DC), the mode of action is based on the transportation and redistribution of ionic (on non-ionic) chemical species situated between “working” electrodes with different polarities under external electrical fields.

In electroculture, few prospective outcomes appeared nowadays, e.g., alternating current (AC) intensifies the mobility of nitrogen in the soil environment. By use of DC, several pilot studies were carried out with positive results, such as enhanced plant resistance against pathogens and increased seed germination and yield. Additionally, fruit quality was measured, and it showed an increased phenol concentration in cultivated radish (*Raphanus sativus* L.), which ultimately enhanced its antioxidant activity. However, most of the studies in this field utilized conventional fertilizers. Despite this, in our experiment's trials, we used metal oxide micronutrient-zinc in nanoparticulate forms as a new generation of nano-fertilizers with selected crops under low voltage DC treatment. Nano-fertilizers, in comparison with traditional counterparts, used their specific properties based on lower concentration range, smaller size, and higher surface-to-volume, and could be used as nutrients delivery device and initiate more target agronomical effects.

Our outcomes confirmed that the case of DC with zinc nanoparticles showed a higher germination percentage than the other treatments. However, this result does not correspond to the quantitative growth parameters of the crop, where the statistically most significant treatment was the control variant (NPs-free, no DC-treatment) in comparison with the zinc nanoparticles variant.

For this reason, in the agronomical context in the near future, the combination of electric fields and nanotechnology will introduce new disciplines and procedures majorly applicable under regulated conditions of hydroponic farming and plant culture techniques. Moreover, it can be employed in cultivating nutritious crops on other planetary bodies, including Moon, Mars etc., for future people who are willing to colonise outside the Earth.

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Modified nanofibrous membranes for tissue engineering

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ABSTRACT

Nanofibrous membranes are widely used in biomaterial research and tissue engineering because of their ability to mimic the structure of extracellular matrix (ECM). They can be prepared from natural, synthetic or composite materials [1]. Poly (ϵ -caprolactone) (PCL) is a synthetic polymer with

excellent biocompatibility and has therefore been extensively investigated in tissue engineering in form of various scaffolds. However, due to its hydrophobic nature and poor mechanical properties, PCL should be modified to overcome these limitations and widen its area of application [2]. In this study, we developed nanofibrous membranes based on PCL and modified them with magnetic nanoparticles (MNPs) and *L*-ascorbic acid (AA) for bone regeneration applications. The incorporation of MNPs into the membranes provides a unique opportunity for non-invasive mechanical and magnetic stimulation of cellular activity [3], while AA plays an essential role in collagen synthesis and bone development [4].

MNPs were synthesized by the coprecipitation method followed by the grafting of ϵ -caprolactone through ring-opening polymerization. Such surface-modified nanoparticles were introduced into the PCL matrix solution which was further functionalized with AA and used for the production of fibers by the electrospinning method. We investigated the effect of different MNPs and AA content in the membranes on their physiochemical properties and their biological response toward SAOS-2 osteosarcoma (bone cancer) cells. Modification of PCL membranes with MNPs resulted in an increase in Young's modulus and enhancement in tensile strength, while modification with AA improved mechanical properties only at higher concentrations. The metabolic activity of cells gradually decreased over time on the membranes. Furthermore, higher content of AA significantly deteriorated the metabolic activity of the cells compared to the control membranes without AA. Our findings suggest that modification of nanofibrous membranes with MNPs improved their mechanical properties and higher content of AA impeded metabolic activity of SAOS-2 cells, which could potentially make them a good biomaterial for bone regeneration of osteosarcoma patients. Further experiments will be conducted in the future to evaluate the osteogenic properties of the membranes.

KEYWORDS

Nanofibrous membrane, bone tissue engineering, magnetic nanoparticles, ascorbic acid.

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REFERENCES

1. X. Yan, H. Yao, J. Luo, Z. Li, J. Wei. Functionalization of Electrospun Nanofiber for Bone Tissue Engineering. *Polymers (Basel)*, 2022, 20;14(14):2940.
2. R. Dwivedi, S. Kumar, R. Pandey, A. Mahajan, D. Nandana, D.-S. Katti, & D. Mehrotra. Polycaprolactone as biomaterial for bone scaffolds: Review of literature. *J Oral Biol Craniofac Res.* 2020 Jan-Mar;10(1):381-388.
3. H.-M. Yun, S.-J. Ahn, K.-R. Park, M.-J. Kim, J.-J. Kim, G.-Z Jin, ... E.-C. Kim. Magnetic nanocomposite scaffolds combined with static magnetic field in the stimulation of osteoblastic differentiation and bone formation. *Biomaterials*, 2016, 85, 88–98.
4. P. Aghajanian, S. Hall, M.-D. Wongworawat, S. Mohan. The Roles and Mechanisms of Actions of Vitamin C in Bone: New Developments. *J Bone Miner Res.* 2015 Nov;30(11):1945-55.

Electrochemical synthesis of hydrogen peroxide by carbon-based catalyst: a look beyond the surface

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ABSTRACT

The electrochemical oxygen reduction (ORR) lies at the heart of fuel cell devices. However, a new paradigm has been shaped very recently to exploit this reaction for the synthesis of hydrogen peroxide (H_2O_2).¹ H_2O_2 is a highly relevant industrial chemical, and its sustainable synthesis is one of the central goals of current research. Being ubiquitous in many commercial products, the sensing of H_2O_2 is also an important matter to fulfil current European regulations on the acceptable limits of chemicals within commercial products.

Carbon nanostructures (CNSs) represent one of the latest forefront materials in heterogeneous catalysis. The electrosynthesis of new metal-free CNS based catalyst for selectively triggering ORR to produce H_2O_2 is an outstanding achievement that matches current guidelines on sustainability. Our group has been exploring the rational development of functionalized, doped, or metal modified carbon nanostructures for triggering selective electrocatalytic 2-electron O_2 reduction to H_2O_2 with high activity and selectivity, discovering several important structural features to be accounted for in this catalytic process.

Here, the trajectory towards carbon-based catalysts with ever improved efficiency is outlined, starting from our very first contribution, that set in 2018 one of the state-of-the art in H_2O_2 electrosynthesis, based on carbon nanohorns (CNHs) enveloped within a shell of graphitized polydopamine (Figure 1).²

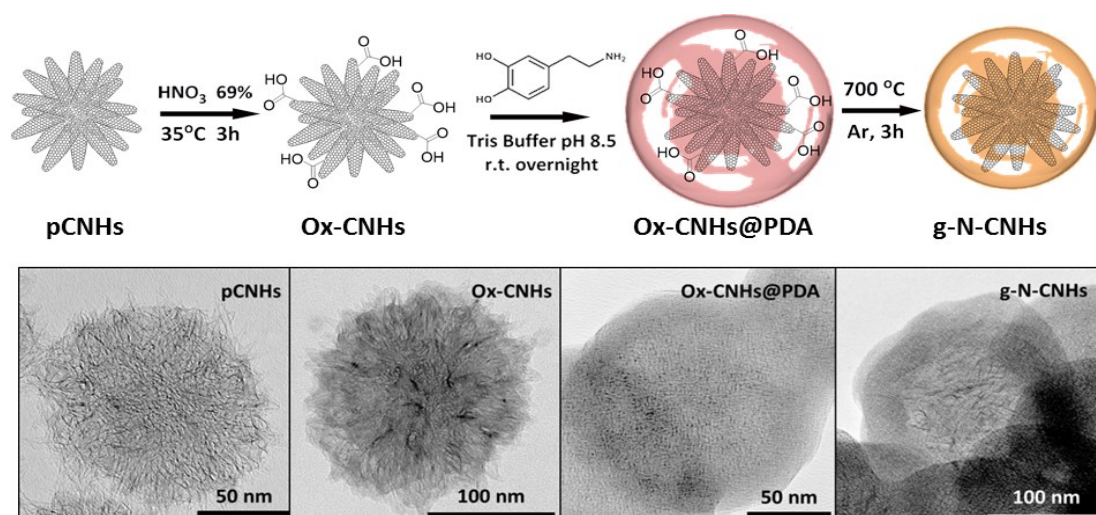


Figure 1: Synthetic scheme of the electrocatalyst for H_2O_2 synthesis and TEM images of all intermediates

The talk will then dig deep into the integration of metal cores within doped carbon shell,³ and discuss in-depth analysis of the ORR framework in acidic environment,⁴ also uncovering the criticality of surface vs bulk composition of catalysts in the design of 2-electron ORR electrocatalysts. A flavor on transferring fundamental work onto macro-scale setups for real application will be finally given, with an example of our recent efforts in cell design and parameter optimization.⁵

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REFERENCES

1. M. Melchionna, P. Fornasiero, M. Prato *Adv. Mater.* **2019**, 31, 1802920.
2. D. Iglesias, A. Giuliani, M. Melchionna, S. Marchesan, A. Criado, L. Nasi, M. Bevilacqua, C. Tavagnacco, F. Vizza, M. Prato, P. Fornasiero *Chem* **2018**, 4, 106-123.
3. A. Lenarda, M. Bevilacqua, C. Tavagnacco, L. Nasi, A. Criado, F. Vizza, M. Melchionna, M. Prato, P. Fornasiero *ChemSusChem* **2019**, 12, 1664-1672.
4. M. Ferrara, M. Bevilacqua, M. Melchionna, A. Criado, M. Crosera, C. Tavagnacco, F. Vizza, P. Fornasiero, *Electrochim. Acta* **2020**, 364, 137287
5. J. Filippi, H. A. Miller, L. Nasi, M. V. Pagliaro, A. Marchionni, M. Melchionna, P. Fornasiero, F. Vizza *Mater. Today Energy* **2022**, 29, 101092

On the characterization of TiO₂ anatase surface using a computational approach

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ABSTRACT

TiO₂ has the capability to act as a photocatalyst by generating electron-hole particles on its surface when exposed to UV radiation. This electron-hole pair has the ability to catalyze various reactions, including the decomposition of water and the formation of the H₂ molecule. However, the efficiency of TiO₂ photocatalyst is limited due to its narrow absorption spectrum, low quantum efficiency, and high recombination rate of electron-hole pairs.

The effectiveness of TiO₂ photocatalysts depends on several factors, such as the coordination of the Ti atom, which includes 3-, 4-, or 5-coordinated Ti atoms. These coordination types influence electronic properties, such as multiplicity, resulting in varying reactivities of these sites. To understand the reactivities of a specific surface type, a detailed characterization of surfaces in terms of these properties is essential.

In this contribution, we focus on investigating the electronic properties of anatase surfaces and their characterization using IR spectra of CO probe molecule, which is readily available through the experimental method. To achieve this, we consider different computational approaches like cluster models and periodic crystal model calculations. Furthermore, we analyze the influence of water molecules on these surfaces using both molecular dynamics simulations and static calculations. This

provides a more realistic model of the system and enhances our understanding of the electronic properties of anatase surfaces.

The approach discussed here provides an opportunity to establish a connection between Ti sites of varying coordination, and hence electronic properties, with different levels of effectiveness in various photocatalyzed reactions.

Acknowledgements: The work was supported by the Czech Science Foundation, project 19-27454X.

Polyamide PA-12 ceramic oxide reinforced composites: manufacturing and degradation tests

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ABSTRACT

The main aim of this research was the preparation of a polymer–ceramic composite with PA-12 as the polymer matrix and modified aluminosilicate cenospheres (CSs) as the ceramic filler. The CSs were subjected to an early purification and cleaning process, which was also taken as a second objective. The CSs were surface modified by a two-step process: (1) etching in Piranha solution and (2) silanization in 3-aminopropyltriethoxysilane. Second aim was to conduct artificial ageing tests on polymer-ceramic composites prepared from polyamide PA-12 polymer matrix for medical applications and three different variants of ceramic fillers: zirconia, alumina and cenospheres. Before ageing, the samples were subjected to ethyl oxide sterilization. The composite variants were prepared for 3D printing using the fused deposition modeling method. The control group consisted of unsterilized samples. Samples were subjected to artificial ageing in a high-pressure autoclave. Ageing conditions were calculated from the modified Hammerlich Arrhenius kinetic equation. Ageing was carried out in artificial saliva. After ageing the composites were subjected to mechanical (tensile strength, hardness, surface roughness) testing, chemical and structural (MS, FTIR) analysis, electron microscopy observations (SEM/EDS) and absorbability measurements.

KEYWORDS

PA-12 Composites. Oxide Ceramics. Degradation Tests. 3D Printing.

INTRODUCTION

Polymer–ceramic composites (PCCs) are increasingly used in biomaterials engineering as functional layers, structural materials, and degradable elements in the human body^{1,2}. Due to their potential for replacing metals and their alloys, much hope is placed on PCCs for structural applications³ and most attention has focused on composites with polymer matrixes of PEEK, PET, PA, and PU^{4,5}. PEEK is a good alternative to ceramics and some metal alloys, especially when used in dental prosthetics for fixed prosthetic frameworks or generally fixed prostheses. However, it suffers from significant costs and problems during manufacturing, i.e., high injection temperatures and high unit prices. PA-12 is used increasingly in additive manufacturing and allows extensive processing for additive manufacturing.

EXPERIMENTAL/THEORETICAL STUDY

FTIR. Tests were carried out using a Shimadzu IR Tracer-100 Fourier Transform Infrared Spectrophotometer (Michelson interferometer, beam splitter: KBr germanium coated, light source: high-energy ceramics, detector: DLATGS detector) using a multi-reflection ATR attachment equipped with a diamond prism.

MS. High resolution MS analyses were performed on a Waters Xevo G2 Q-TOF mass spectrometer (Waters Corporation, Milford, MA, USA) equipped with an electrospray ionization (ESI) source operating in positive ion modes. MS data were collected from 100 to 2000 Da in positive ion mode with scan time of 0.1 s.

SEM/EDS. Morphology observations of samples were made using a TESCAN VEGA scanning electron microscope (SEM) equipped with secondary electrons (SE) and backscattered electrons (BSE) detectors in low vacuum. Chemical composition was determined using energy dispersive X-ray spectroscopy (EDS, Oxford Instruments EDS probe with Aztec software).

CONCLUSION

In this study, we evaluated the effect of artificial ageing in SBF for PA-12 composites with zirconia, alumina and CSs. The ageing model was calculated according to Hammerlich's modified Arrhenius kinetic equation. The artificial ageing test was calculated so that the entire degradation process corresponds approximately to the exposure of human saliva at 37 °C for 365 days.

Acknowledgements: The research was partially supported by the Rector's of The Silesian University of Technology Habilitation Grant 07/020/RGH20/0062 and Grant of Polish Ministry of Science and Higher Education 07/020/BK_22/0073. This work was also partially supported by the project IT4Innovations national supercomputing centre—path to exascale project (CZ.02.1.01/0.0/0.0/16-013/0001791) and “Science without borders” projects CZ.02.2.69/0.0/0.0/16_027/0008463 within the Operational Programme Research, Development and Education, Ministry of Education, Youth and Sport of the Czech Republic SP2021/106 and SP2022/31.

REFERENCES

1. Alizadeh-Osogouei, M.; Li, Y.; Wen, C. *Bioact. Matter.* 4, (2019), 22–36.
2. Guo, Z.; Poot, A.A.; Grijpma, D.W. *Polym. J.*, 149, (2021), 149, 110388
3. Iftikhar, S.; Jahanzeb, N.; Saleem, M.; Rehman, S.U.; Matinlinna, J.P.; Khan, A.S. *Saudi Dent. J.* 33, (2021), 33, 229–238.
4. Pugliese, R.; Beltrami, B.; Regondi, S.; Lunetta, C. *Ann. 3D Print. Med.* 2, (2021), 100011
5. Shirvan, A.R.; Nouri, A.; Wen, C. *Biomater.* (2021), 395–439.

From Lab Scale to Fabrication

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ABSTRACT

The Nanospider™ machines can produce nanofibers from a wide range of polymers. Elmarco product portfolio includes lab equipment intended for in-house research and development, semi-industrial equipment for high value and low volume products, and fully industrial equipment capable of high volume production.

Since Elmarco laboratory equipment uses the same Nanospider™ needle-free electrospinning technology as in the industrial production lines, the experimental work and research can be readily transferred to industrial production equipment which aides in commercializing different ideas.

High spatial resolution X-ray microscopy - a new technology approach for the research laboratory

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ABSTRACT

The progress of scientific research and technology development depends heavily on effective imaging solutions to characterize the properties and behaviors of materials. Revealing details of microstructure, ideally in 3D, is a critical part of this understanding, whether developing and confirming models that describe material properties and behavior, or simply visualizing structural details. ZEISS offers 3D X-ray microscopes (XRM): advanced imaging solutions that have overcome major hurdles to three-dimensional imaging by providing high-contrast, sub-micron imaging, even for relatively large samples. These breakthrough advances in nondestructive, three-dimensional (3D) imaging enable a wide range of engineering disciplines.

The nondestructive nature of X-ray microscopy (XRM) enables multiscale or multimodal imaging of the same sample for analysis the hierarchical structures. Two families of X-ray microscopes are available for this purpose and will be presented in this talk. These include the Zeiss Xradia Versa and Zeiss Xradia Ultra laboratory-based X-ray microscopes. They provide the highest resolution for the study of internal structures at true spatial resolutions from submicron (< 450 nm for Versa) to nanometer (< 50 nm for Ultra). 3D-XRM architectures feature several key advantages, including characterization of large samples without loss of resolution, high contrast for improved clarity, minimal sample preparation, the ability to perform in situ experiments, and synchrotron-quality imaging in a laboratory system. Whereas traditional CT systems rely on single-stage geometric magnification, Xradia Versa features a combination of unique two-stage magnification optics and a high flux X-ray source to produce faster sub-micron scale resolution images across the widest range of intact sample sizes and types. In addition, it provides excellent contrast capabilities through different imaging modes, i.e., (i) absorption, (ii) absorption and propagation phase contrast, (iii) dual-

energy scanning modes, and (iv) diffraction contrast tomography. On the other hand, the innovative Xradia Ultra architecture, with unique X-ray optics adapted from synchrotron technology, features absorption and phase contrast resolving the microstructure down to 50 nm spatial resolution.

These unique features make all families of X-ray microscopes powerful tools for applications in a very wide range of scientific and industrial fields. Correlative workflow from XRM to FIB-SEM is also presented as a unique technique for comprehensive multiscale characterization of a large number of samples.

Photocatalytic activity of nano-ZnS under different types of radiation

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ABSTRACT

The assessment of reaction conditions on the photocatalytic activity (PA) of nano-ZnS samples under UV and sunlight radiation is performed. Two methods were used for nano-ZnS synthesis: conventional hydrothermal method and microwave-assisted hydrothermal method. X-ray powder diffraction (XRPD), scanning electron microscopy, UV-VIS diffuse reflectance spectroscopy (DRS), Fourier-transform infrared (FTIR) spectroscopy and Raman spectroscopy were used for the characterization of samples prepared under various reaction conditions. The XRPD, FTIR and Raman spectroscopy results indicate that all samples have cubic ZnS phase (i.e. sphalerite). UV-VIS DRS was used to determine the direct band gap energy. Nano-ZnS prepared by conventional hydrothermal synthesis with reaction time 3.5 h and sulphur : zinc molar ratio 1 : 2 showed the highest PA value under the UV radiation. Photocatalytic tests under the sunlight radiation led to the very similar PA results for both synthesis methods, even with a slightly faster onset, and PA > 90 % was recorded after 8 h. Although both methods are suitable for preparation of highly photocatalytic nano-ZnS, the microwave-assisted hydrothermal synthesis has a great potential mainly for its short reaction time (0.5 h) compared to the lengthy conventional hydrothermal synthesis.

KEYWORDS

nano-ZnS, photocatalytic activity, sunlight radiation, UV radiation

Radiation-assisted synthesis of nanocomposites

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ABSTRACT

Radiation-assisted synthesis of nanocomposites involves using mostly ionizing radiation, such as gamma rays or electron beams, to induce chemical reactions that result in the formation of nanoscale materials. This method is often used to produce metal or metal oxide nanoparticles, as well as other types of nanomaterials with unique properties. The process typically involves exposing a solution containing metal ions or precursor molecules to radiation, which leads to the formation of radicals or other highly reactive species. These species then react with the metal ions or precursors to form nanoparticles or other nanoscale structures. One advantage of radiation-assisted synthesis is that it can be performed at ambient temperature and pressure, making it a relatively simple and cost-effective method for producing nanomaterials. Additionally, in some cases non-ionizing radiation like UV and visible light can be used for preparation of nanomaterials as well. All these methods can be used to control final properties of the resulting nanocomposites, which can be tailored for specific applications. However, radiation-assisted synthesis can also have some drawbacks, such as the potential for radiation-induced damage in the final nanocomposites. For this reason, it is important to be careful in the use of these types of preparation methods.

KEYWORDS

ZnO, Ag nanoparticles, radiation, g-C₃N₄, nanocomposites

Acknowledgements: This work was supported by the student project SP2023/095 of the VSB-Technical University of Ostrava.

Study of the change in corrosion resistance of NiTi alloy wires coated with a thin layer of tantalum pentoxide

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ABSTRACT

The Nickel-titanium alloy is widely used for implants in the circulatory system, such as stents and occluders. The injection of any foreign material into the body is associated with possible side effects. The risk regarding NiTi implants are the formation of blood clots or the release of nickel ions into the body. One of the possibilities to improve hemocompatibility properties is to use different types of coatings. Potential for use in cardiovascular system due to its good corrosion resistance and resulting biocompatibility have tantalum compounds, therefore, a Ta₂O₅ coating was applied to the NiTi alloy.

The aim of the tests was to determine the corrosion resistance before bending (0°) and after bending the wire by angles of 40°, 80° and 120° angles without and with coating. For the study, electropolished NiTi alloy wires with a diameter of 0.178 mm were used. Then, a Ta₂O₅ coating was applied by the Atomic Layer Deposition method. Pitting corrosion resistance tests were carried out using the potentiodynamic method at 37 °C, in phosphate-buffered saline (PBS) solution. The results allowed to determine the effect of bending the Ta₂O₅ coating on the corrosion resistance of the NiTi alloy.

KEYWORDS:

NiTi alloy, biomaterials, thin films, Atomic Layer Deposition

Simple method for prediction of preferred crystallographic orientation

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ABSTRACT

Preferred crystallographic orientation of two crystalline materials can be predicted by calculating the number of overlapping atoms of two adjacent (*hkl*) planes, each of which belongs to one of the materials. Originally developed as an auxiliary tool for computer modeling of metal oxide nanoparticles on crystalline substrates, the method of determining the preferred crystallographic orientation has proven to be a stand-alone tool that is simpler and faster for the given purpose compared to the modeling. In this method, the crystalline material is represented by one layer of atoms from a given (*hkl*) plane. The atoms from (*hkl*) plane of one material are overlapped by the atoms from (*hkl*) plane of the other material so that all atoms lie in the same Euclidean plane. The average number of overlaps after rotating one (*hkl*) plane relative to the other (*hkl*) plane by 360°

quantifies the structure compatibility of the two planes – the higher the average number of overlaps, the higher the probability of the preferred crystallographic orientation. The method was verified by comparison with experimental observations of real samples as well as with the results of molecular modeling.

KEYWORDS

crystalline structure, (*hkl*) plane, preferred orientation

Atomic resolution of AFM in 5 minutes; news in nanoparticle characterization

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ABSTRACT

The behavior and properties of many modern materials highly depend on their structural, mechanical and electrical properties at the nanoscale. AFM with its extreme x-, y-, and z-resolution is nowadays instrument to understand the properties of a large variety of materials at this scale. Thereto, AFM not only measures the 3D topography of materials but also offers a large suite of measurement modes that allow correlating topography with the respective properties.

With the DriveAFM, Nanosurf recently introduced a new tip-scanning AFM which not only provides high-performance AFM measurements but also impresses with the integration of full system motorization and CleanDrive photothermal excitation. Here, we will show, how the technological advances of the DriveAFM provide ease of use, enable new, fast imaging techniques, and most importantly deliver insights into material properties down to the level of atomic lattices. Examples given will include different types of measurements on 2D materials, polymers, biological samples, electric and magnetic materials.

Other techniques and news for nanoparticle characterization will be also mentioned.

KEYWORDS

AFM, KPFM, nanostructures, graphene, nanoparticles.

Poster presentations (PP):

Albumin-stabilized metal nanoclusters as a potential dual imaging probe and sensitizer for the treatment of tumors

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ABSTRACT

Metal nanoclusters have attracted much attention due to their unique abilities. For instance gold-based nanoclusters have been studied due to their optical and potential application in photothermal and radiation therapy as well as contrast agent¹. Therefore, *in vivo* toxicity of gold clusters has received much interest. It has been found that gold clusters toxicity depends on size, shape, exposure dose and surface coating or envelope¹. Radiation therapy (RT) in which ionizing radiation is employed to trigger DNA damage and kill cancer cells, has been extensively used in clinical cancer treatment in the past several decades². However, RT has its limits of application for example hypoxia of tumor tissues within many solid tumors. It is known that oxygen plays an important role in RT-induced cell death, owing to the mechanism whereby oxygen can stabilize the radiation-induced DNA breaks and prevent them from being repaired by cells themselves. Therefore, the inadequate oxygen supply in the tumor microenvironment caused by the rapid growth of tumor cells can often lead to the resistance of tumors to radiotherapy. To increase the level of oxygen or other reactive species in tumors and challenge the hypoxic tumor microenvironment, many methods have been reported including the employment of nanomaterials (e.g., perfluorocarbon) or gold nanoclusters to generate reactive species in the tumors^{2,3}. By encapsulating Fe in albumin-stabilized metal nanoclusters, together with the targeted agent paclitaxel as a theragnostic agent for MRI and photothermal therapy of cancer cells, a better effect can be achieved, as shown in Figure 1⁴.

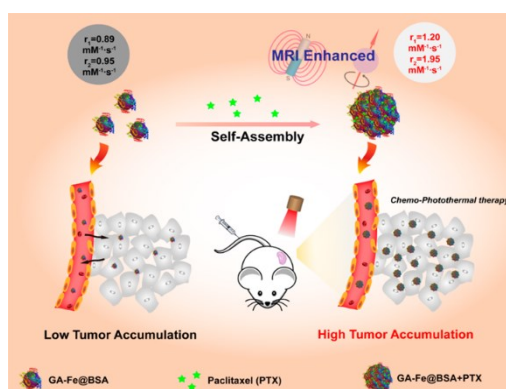


Fig. 1: Schematic representation of the fabrication process and application of GA-Fe@BSA-PTX self-assembled nanoclusters in tumor therapy under a laser. Extracted from⁴.

KEYWORDS

Albumin, Nanoclusters, Fluorescence, Probe, Imaging

Acknowledgments: We thank for the financial support to SGS project number SP2023/095.

REFERENCE

1. X.D. Zhang, D. Wu, X. Shen, P.X. Liu, F.Y. Fan, S.J. Fan, In vivo renal clearance, biodistribution, toxicity of gold nanoclusters, *Biomaterials*. 33 (2012) 4628–4638. <https://doi.org/10.1016/j.biomaterials.2012.03.020>.
2. J. Chen, Q. Chen, C. Liang, Z. Yang, L. Zhang, X. Yi, Z. Dong, Y. Chao, Y. Chen, Z. Liu, Albumin-templated biomineralizing growth of composite nanoparticles as smart nano-theranostics for enhanced radiotherapy of tumors, *Nanoscale*. 9 (2017) 14826–14835. <https://doi.org/10.1039/c7nr05316a>.
3. G. Song, C. Liang, X. Yi, Q. Zhao, L. Cheng, K. Yang, Z. Liu, Perfluorocarbon-Loaded Hollow Bi₂Se₃ Nanoparticles for Timely Supply of Oxygen under Near-Infrared Light to Enhance the Radiotherapy of Cancer, (n.d.). <https://doi.org/10.1002/adma.201504617>.
4. L. An, C. Yan, X. Mu, C. Tao, Q. Tian, J. Lin, S. Yang, Paclitaxel-Induced Ultrasmall Gallic Acid-Fe@BSA Self-Assembly with Enhanced MRI Performance and Tumor Accumulation for Cancer Theranostics, *ACS Appl. Mater. Interfaces*. 10 (2018) 28483–28493. <https://doi.org/10.1021/acsami.8b10625>.

Effects of external electric fields on the structure of oligo(ethylene glycol) in explicit solvents by molecular dynamics simulations

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ABSTRACT

The structure of polymers subjected to electric fields is of interest in several applications, notably in the electrospinning technology¹. In this contribution, we attempt to model the structural response of an oligo(ethylene glycol) (OEG) chain of various lengths to an external electric field of several different intensities in water or methanol. In a molecular dynamics (MD) simulation, we characterize the anisotropy of the average shape of the coil by quantities derived from the gyration tensor. The distribution of the cosine of the angles of the monomer unit vector and the dipole moment vector with respect to the electric field direction is calculated. Results show that the coil in both solvents becomes an increasingly anisotropic and adopts oblate average shape with stronger fields. The monomer units of the chain in water and in methanol orient at angle of around 70° and perpendicular to direction of the electric field, respectively. The monomer dipoles of the chain in both solvents point an increasingly in field direction.

KEYWORDS

Molecular dynamics, Polymer solution, Structure, External electric field

INTRODUCTION

The interaction of polar molecules with an external electric field provides a tool for manipulating molecular structure. And this is also the case for polar polymers, which can undergo complex structural changes due to the external electric field. The study of such changes in the polymer structure is of great importance, for example, for the technology of electrospinning¹. The microscopic changes caused by the electric field influence both the quality of the electrospinning process and the properties of the resulting materials. In previous molecular modeling studies¹, special attention was paid to modeling the dynamics of the initial stages of the process of electrospinning of polymer solutions. In this contribution, our recent molecular dynamics simulation study² is extended by including short ethylene glycol oligomers. In an effort to explain the results of work², molecular dynamics simulations are carried out to study the structure of mono-, di-, tetra-, octa- and hexadecaethylene glycol in water and methanol.

EXPERIMENTAL/THEORETICAL STUDY

All MD simulations were performed with the GROMACS software³ (version 5.1.1) using the leap-frog integrator with a 2 fs time step. The oligo(ethylene glycol) chain and methanol were described by using the GROMOS 53A6OXY+D forcefield⁴. The simple point charge (SPC) model⁵ was used for water molecules. The polymer chain was placed and solvated in a dodecahedral rhombic box. The simulations were performed with periodic boundary conditions in all directions. All of the molecular dynamics simulations were carried out in canonical (NVT) ensemble at a constant temperature of 300 K without an electric field first, then with the applied external electric field in the positive z-axis direction. The intensity of the electric field ranged from 1 V/nm to 5 V/nm. The bond lengths in the OEG chain and the full rigidity of methanol molecules were constrained using the P-LINCS algorithm⁶. The full rigidity of the water molecules was enforced by means of the SETTLE algorithm⁷. The particle-mesh Ewald method⁸ was used to calculate long-range electrostatic interactions. The molecular dynamic simulation time was 500 ns.

RESULTS AND DISCUSSION

The system consisting of a single hydroxyl-terminated OEG chain (comprising 1, 2, 4, 8 or 16 ethylene glycol units) and a solvent (water or methanol) was simulated at a constant temperature of 300 K without the presence of an electric field and with an applied electric field in the positive z-axis direction. The deformation ratios at different intensities of the electric field in both solvents were calculated. The deformation ratio of the coil in both solvents decreases. Originally isotropic coil deforms into a spheroidal average shape with the applied electric field. In both solvents the spheroid is oblate. The distribution of the cosine of the angles between the monomer unit vector and the electric field direction, and between the dipole moment vector and the electric field direction was calculated. In water, the monomer units of the chain orient at angle of around 70° whereas, in methanol, the monomer units orient perpendicular to the electric field. The monomer dipoles of the chain in both solvents tend to point in the direction of the field.

CONCLUSION

The effects of external electric fields on the molecular structure of a single OEG chain of different lengths in water and in methanol were investigated using molecular dynamics simulations at 300 K. The deformation of the average shape of the coil is not isotropic. The deformation ratio shows growing deviations from spherical coil towards an oblate shape for both water and methanol. The monomer units of the chain in water and in methanol orient at angle of around 70° and perpendicular

to the field direction, respectively. The orientation of the monomer dipoles of the chain in both solvents is parallel to direction of the electric field.

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REFERENCES

1. J. Jirsák, P. Pokorný, P. Holec a Š. Dědičová: A Molecular-Level Picture of Electrospinning. *Water*, 12(9):2577:1–31, 2020.
2. Š. Dědičová, J. Dočkal, F. Moučka a J. Jirsák: Molecular dynamics simulation study of the effect of a strong electric field on the structure of a poly(oxyethylene) chain in explicit solvents. *Journal of Molecular Liquids*, 338(2):116622, 2021.
3. M.J. Abraham, D. Van Der Spoel, E. Lindahl, B. Hess, the GROMACS development team, GROMACS User Manual version 5.1.1, 2015.
4. P.F.J. Fuchs, H.S. Hansen, P.H. Hünenberger, B.A.C. Horta, A GROMOS parameter set for vicinal diether functions: properties of polyethyleneoxide and polyethyleneglycol, *J. Chem. Theory Comput.* 8 (2012) 3943–3963.
5. H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, J. Hermans, Interaction models for water in relation to protein hydration, in: B. Pullman (Ed.), *Intermolecular Forces*, Reidel, Dordrecht, 1981, pp. 324–331.
- a. Hess, P-LINCS: A parallel linear constraint solver for molecular simulation, *J. Chem. Theory Comput.* 4 (2008) 116–122.
6. S. Miyamoto, P.A. Kollman, SETTLE: An analytical version of the SHAKE and RATTLE algorithm for rigid water models, *J. Comput. Chem.* 13 (1992) 952–962.
7. U. Essmann, L. Perera, M.L. Berkowitz, T. Darden, H. Lee, L.G. Pedersen, A smooth particle mesh Ewald method, *J. Chem. Phys.* 103 (1995) 8577–8593.

Properties of biodegradable polymer coatings containing nanoparticle substances on a titanium alloy substrate

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ABSTRACT

The aim of the study was to determine the physical and chemical properties of biodegradable polymer coatings containing nanoparticle hydroxyapatite. Coatings were applied by ultrasonic spraying and exposed to a simulated body environment (PBS solution, 37°C). The scope of the research included scanning electron and acoustic microscope studies, XRD tests, coating adhesion tests by scratch test method, potentiodynamic tests, EIS measurements and ion release studies. The results show

beneficial effect of polymer coatings on the biocompatibility of the titanium alloys and indicate the suitability of the applied coatings in biomedical applications.

KEYWORDS

titanium alloys, biodegradable polymer coatings, biomaterials, ultrasonic spray coating

INTRODUCTION

Due to corrosion resistance in the tissue environment, biocompatibility, and the value of Young's modulus similar to the bone elasticity modulus, titanium alloys are widely used in medical applications, especially in orthopedics. However, it is necessary to propose a surface modification method to improve their biocompatibility¹. The most commonly used method is anodic oxidation, which provides high corrosion resistance, but does not eliminate the presence of metal ions released to the environment². The method, which may reduce the release of alloying element ions, is the application of polymer coatings³. Moreover, biodegradable coatings can also be a matrix for the release of mineral substances, such as hydroxyapatite, which can stimulate the process of bone union.

EXPERIMENTAL/THEORETICAL STUDY

The surface of Ti6Al7Nb alloy substrate was ground, sandblasted and anodically oxidated with the use of the electrolyte based on phosphorus and sulphuric acid at the voltage 97 V. Polymer coating based on poly(D,L-lactide-coglycolide) PLGA(85/15) was synthesized in bulk by the ring opening polymerization of glycolide and D,L-lactide at argon atmosphere. Solution of 1% PLGA in CH₂Cl₂ was enriched with 20% of synthetic nanoparticle hydroxyapatite powder (<200 nm particle size) (Merck). Coatings was applied by ultrasonic spray system ExactaCoat (Sono-Tek) with Impact nozzle with following parameters: ultrasound frequency 60 kHz, ultrasound power 1,5 W, speed of nozzle motion 10 mm/s and liquid's flow rate 1 cm³/min. Coatings was composed of 15 layers. Samples were immersed in PBS's solution at 37°C for 3, 6 and 9 weeks.

The morphology of the samples was analyzed by scanning electron microscopy (Quanta 250 FEG, FEI Company). Structure of the coatings was characterized by X-Ray diffraction studies (D8 Advance, Bruker). Adhesion of the coating to the substrate was tested by scanning acoustic microscopy and (KSI Evo II) and scratch test method (CSM Micro-Combi Tester). Electrochemical investigation included resistance to pitting corrosion test by the potentiodynamic method (AUTOLAB PGSTAT 302N, Metrohm) and electrochemical impedance spectroscopy (PARSTAT 4000). The samples were tested both in the initial state and after exposure to PBS's solution.

RESULTS AND DISCUSSION

The PLGA coatings were homogeneous, continuous and transparent (Fig. 1). The distribution of hydroxyapatite was uniform throughout the coating. The coatings are characterized by good adhesion to the Ti6Al7Nb substrate which was confirmed by scanning acoustic microscopy and a scratch test. The application of the coating improved the parameters describing the corrosion resistance in relation to the metallic substrate. Exposure of the coating to the simulated environment of the organism did not cause delamination of the coating, which was confirmed by SAM and XRD. In addition, the use of the coating reduced the density of alloying element ions released from the surface (Fig. 2). However, it is apparent that the longer the period of contact between the samples and PBS, the lower the resulting impedance and hence, the corrosion resistance. With the increase in the exposure time,

an increase in the density of alloying elements released from the surface and the release of hydroxyapatite from the coating was observed.

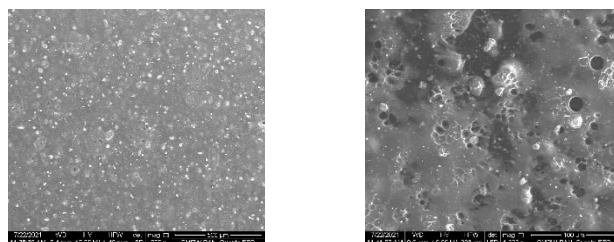


Fig. 1. Scanning electron microscopy (SEM): surface of PLGA coating containing 20% of HAp

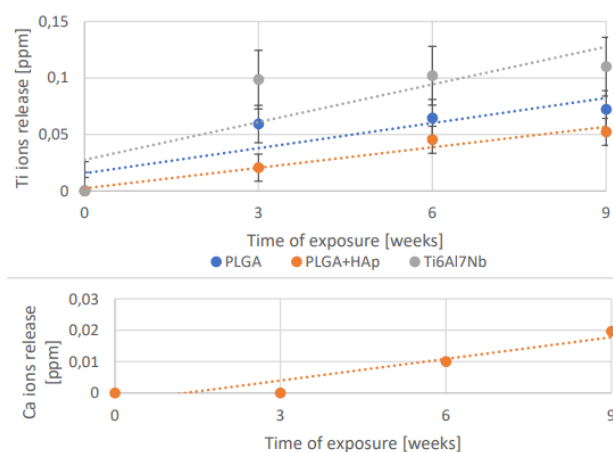


Fig. 2. Results of ions release studies

CONCLUSION

Homogeneous polymer coatings containing the nanoparticles (HAp) can be produced on the surface of anodized titanium implants for osteosynthesis by the ultrasonic spray coating. This method of surface modification could improve the biocompatibility and biofunctionalization of the surface of titanium implants, by limiting density of metal ions' release and stimulating the bone healing process by release of hydroxapatite.

REFERENCES

1. J. Marciniak, J. Szewczenko, W. Kajzer, Surface modification of implants for bone surgery, *Archives of Metallurgy and Materials* 60(3): 2123-2129, 2015.
2. Y. Okazaki, E. Gotoh, Comparison of metal release from various metallic biomaterials in vitro, 26(1), 2005.
3. J. Szewczenko, W. Kajzer, M. Grygiel-Pradelok, J. Jaworska, K. Jelonek, K. Nowińska, M. Gawliczek, M. Libera, A. Marcinkowski, J. Kasperczyk, Corrosion resistance of PLGA-coated biomaterials, *Acta of Bioengineering and Biomechanics*, 19(1), 2017.

The method of toxicity characterization TiO₂ nanoparticles

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ABSTRACT

Today and every day we encounter nanoparticles in both positive and negative senses. They are ubiquitous, which is why it is necessary to characterize their properties not only physico-chemically, but in relation to us as living organisms as well. It is necessary to find out their input into the body, their concentration, and their action in the body chronically or acutely. In this context is also necessary to find out remains concentration in the organism in the long term, or how long it takes for a given nanoparticle to be eliminated from the organism. Nanoparticles can be present in air, water and soil, they can enter to the body in several ways.^{1 2}

Considerable attention has been paid in recent years to airborne nanoparticles. Their effect on living organisms can be studied by two approaches, a) dry or b) wet deposition. Wet deposition takes a very short time and carries the nanoparticles over a smaller distance. From the air, it is transported by rain and snow. Dry deposition, on the other hand, is a longer-term phenomenon, the nanoparticles travel long distances and are transported by wind back to the ground until they become trapped on an object or organism. A typical dry deposition for us Europeans is the Sahara sand, which sometimes falls on our Czech territory.²

This paper focuses on the effect of a frequently used type of nanoparticles - titanium dioxide (TiO₂). The titanium dioxide is found not only in paints, toothpastes, food additives, paper, ink, medicines, plastics or products used for personal hygiene. Other uses include water purification, the manufacture of energy equipment and soil remediation.³

A problem arises with the characterisation of the toxicity of TiO₂, where it was originally classified as a benign material. However, with increased use, its toxic properties are emerging. When used in sunscreens, one must be present in the sun for the EC50 value to drop almost 500 times. Toxicity is also reduced by the formation of clumped TiO₂ particles.³ For these reasons, the toxicity of TiO₂ nanoparticles must continue to be studied.

KEYWORDS

TiO₂, toxicity, nanoparticles, characterization

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REFERENCE

1. TURAN, Nouha Bakaraki, Hanife Sari ERKAN, Guleda Onkal ENGIN a Mehmet Sinan BILGILI. Nanoparticles in the aquatic environment: Usage, properties, transformation and toxicity—A review. *Process Safety and Environmental Protection* [online]. 2019, **130**, 238-249 [cit. 2023-01-16]. ISSN 09575820. Dostupné z: doi:10.1016/j.psep.2019.08.014
2. ABBAS, Qumber, Balal YOUSAF, AMINA, Muhammad Ubaid ALI, Mehr Ahmed Mujtaba MUNIR, Ali EL-NAGGAR, Jörg RINKLEBE a Mu NAUSHAD. Transformation pathways and fate of engineered nanoparticles

- (ENPs) in distinct interactive environmental compartments: A review. *Environment International* [online]. 2020, **138** [cit. 2023-01-17]. ISSN 01604120. Dostupné z: doi:10.1016/j.envint.2020.105646
3. HAIDER, Adawiyah J., Zainab N. JAMEEL a Imad H.M. AL-HUSSAINI. Review on: Titanium Dioxide Applications. *Energy Procedia* [online]. 2019, **157**, 17-29 [cit. 2023-01-11]. ISSN 18766102. Dostupné z: doi:10.1016/j.egypro.2018.11.159

Growth and Characterisation of WO_x and WTe₂ Nanowires

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ABSTRACT

Tungsten ditelluride (WTe₂) possesses Type-II Weyl semimetal band structure and is predicted to host topologically protected one-dimensional hinge states in certain crystallographic directions making it a potential candidate for future applications in spintronics, and for fundamental studies of exotic charge transport via topologically protected states. Nanowire geometry is particularly important to study and exploit unconventional properties, as WTe₂ bulk semimetallic behaviour hinders topologically protected state charge transport.¹

In this study two-step chemical vapor deposition method was used to obtain WTe₂ nanowires. Tungsten oxide (WO_x) nanowires were initially produced, and their growth was observed to rely on various synthesis parameters, such as pressure, growth time, substrate and precursors. Two approaches were employed to obtain the nanowires: with NaCl precursor additive and without. Subsequently, obtained WO_x nanowires were converted to WTe₂ by tellurization. The W:Te stoichiometry of the resulting nanowires was found to be influenced by various synthesis parameters such as temperature, synthesis time, and distance between the WO_x nanowire substrate and tellurium precursor.

KEYWORDS

Type-II Weyl semimetal, Nanowires, Tungsten ditelluride

INTRODUCTION

Weyl semimetals and Higher-order Topological Insulators (HOTIs) are complementing class of topologically nontrivial materials, hosting unconventional, conducting states where charge carrier transport is protected against scattering. Tungsten(IV) telluride (WTe₂) is one of the most prominent member among these materials, and it has gained significant attention in recent years due to its unique electronic and thermoelectric properties.²

In addition to the properties of Type-II Weyl semimetal, WTe₂ also has high magnetoresistance, and in a few - layer thin structures – superconductivity. These properties are important for the study and demonstration of various fundamentally new effects, for example exotic particles - Majorana fermions. Topologically non-trivial materials in the form of nanowires are particularly important in

these studies, because nanowires have a significantly reduced number of conductance channels, which facilitates the detection and isolation of unconventional charge transport.^{1,3,4}

EXPERIMENTAL/THEORETICAL STUDY

The synthesis was carried out in a two-zone tube furnace on Si or Si/SiO₂ substrates. WTe₂ nanowires were obtained by tellurization of previously grown WO_x nanowires using two-step chemical vapor deposition method. In both steps synthesis parameters such as temperature, time, precursors etc. were investigated. The morphology and chemical composition of the WTe₂ nanowires were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Electron beam lithography (EBL) was used for fabrication of electrical contacts to individual nanowires.

RESULTS AND DISCUSSION

WO_x nanowires were grown on Si and SiO₂ substrates, using WO₃:NaCl or pure WO₃ powder as source material. For the growth of WO_x nanowires from the WO₃:NaCl, the most optimal synthesis parameters were established. Growth pressure of 3 Torr facilitates formation of droplet-like structures, while at lower pressure conditions nanowires are found to nucleate from the droplet-like structures. The droplet-like structures only form on Si/SiO₂ substrates, while Si substrate provides growth of “free standing” nanowires, rooted on the Si substrate, indicating different growth mechanism. By varying the growth time, it is possible to control the dimensions of the nanowires.

Na-free WO_x nanowires growth requires higher temperature (950°C) and longer time for sublimation of WO₃ powder, however, these nanowires have smaller diameters (20 – 50 nm) than those synthesized from the WO₃:NaCl (70 – 300 nm).

WTe₂ nanowires were obtained from the WO_x, grown on different substrates, via tellurization in H₂/Ar environment. By varying the temperature and the synthesis time, W : Te stoichiometry close to ratio of 1:2 was obtained.

Fabricated nanowire devices were measured at room temperature and initial characteristics such as electrical contact properties were determined.

CONCLUSION

Relatively small-diameter nanowires and nanoribbons of WTe₂ can be fabricated via conversion of WO_x nanowires, grown from pure WO₃ powder, on Si substrates. In order to obtain W : Te stoichiometry close to 1 : 2, *ambient* pressure conditions and H₂/Ar flow is essential. In the further studies of the nanowire charge transport properties, method for fabrication of ohmic contacts to the WTe₂ is of great importance.

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REFERENCES

1. J.M. Woods, D. Hynek, P. Liu, M. Li, J.J. Cha, ACS Nano 13 (2019) 6455–6460.
2. Y. Hou, T. Zhang, J. Sun, L. Liu, Y. Yao, Y. Wang, Chinese Physics B 29 (2020) 097304.
3. Y. Yomogida, M. Nagano, H. Hamasaki, K. Hirahara, Y. Miyata, K. Yanagi, Jpn. J. Appl. Phys. 60 (2021) SCCD02.
4. P. Marra, Journal of Applied Physics 132 (2022) 231101.

Application of jet-milled zinc phosphate dihydrate in metal surface treatment by phosphating

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ABSTRACT

Corrosion is a spontaneous reaction between a material, often a metal, and its surroundings. This process leads to the deterioration of the material. The protection of metal objects against unwanted corrosion is a key issue in the chemical industry. There are several corrosion prevention methods that aim to create a protective barrier between the metal surface and corrosive stimulators. Such methods most often include surface modifications, barrier coatings, and paint systems. At the beginning of the 20th century, the tri-cationic phosphating method was developed. This newly established corrosion prevention method is a type of conversion coating and today, it is commonly used in many industries. The process of tri-cationic phosphating can be divided into two main steps – the activation step and the phosphating step. The activation step plays an important role in this process as it can determine the qualitative and quantitative nature of the resulting phosphate layer. However, this process is burdened using heavy metals, such as nickel and cobalt. This study concerns the first innovation phase of this process and compares different grinding methods. Their optimization of these methods leads to the development of an effective grinding process that would be used in the preparation of novel, heavy metals-free activation concentrates.

KEYWORDS

Zinc phosphate, phosphating baths, micronization, corrosion, jet grinding

INTRODUCTION

Corrosion prevention is one of the most comprehensive fields of industrial chemistry. Protecting the surface from corrosive stimulators, such as ambient moisture, hostile ions, and molecular oxygen, can be done in a variety of ways. One such method is conversion coatings, which consist of an insoluble layer of inorganic substance or an amorphous film. Conversion coatings are formed between the surface of a metal and a solution in which the metal is immersed. The chemical reaction between the metal's surface and the solution partially modifies the metal's outermost layer into compounds with a lesser sensitivity to undercorrosion. Phosphating, a type of conversion coatings, is the surface conversion process for steel that is typically used as a basis for organic topcoats. Tricationic phosphating, a crucial step in the phosphating process, consists of zinc dihydrogen phosphate and additional cations, such as Zn^{2+} , Co^{2+} , Ni^{2+} , and Mg^{2+} . However, cobalt and nickel ions are environmentally hazardous and banned from industrial processes. suitably micronized zinc phosphate dihydrate, $\mu\text{-Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, has been hypothesized to reduce or eliminate heavy metals from the phosphating process. The micronized zinc phosphate dihydrate acts as a nucleus on the metal surface and generates a phosphate layer of adequate purity. [1] [2]

EXPERIMENTAL/THEORETICAL STUDY

The quality and characteristics of the resulting phosphate layer, such as thickness, are greatly impacted by the metal surface activation step. The purpose of this comparative study is to determine the quality of different grinding methods in terms of their resulting particle size distribution. The input zinc phosphate dihydrate particle size was analyzed by Mastersizer 3000 particle analyzer. The samples were ground by one of the three distinct mills: the planetary mill, the vibrating disc mill, or the jet mill. Particle size analysis of input material was repeated after grinding.

RESULTS AND DISCUSSION

The results of the particle dispersion analysis are summarized in Table 1. The particle sizes $D_x(10)$, $D_x(50)$, and $D_x(90)$ represent the respective proportion of particles with a diameter smaller than or equal to the specified D_x value. Hence, the D_x value is an essential indicator of particle size values inside a given system. To quantify the width of the particle distribution, the particle distribution span was determined as the difference between $D_x(90)$ and $D_x(10)$ over $D_x(50)$. The M 12–60 sample had the largest variation, rendering it unsuitable for application as it could result in an inconsistent and of poor-quality coating. Despite the low span of the Nubirox sample, it was deemed unsatisfactory due to its high $D_x(90)$ value, which was the highest of all the evaluated samples. Despite the desirable grain dimensions of the ZP-10 material, it was not used in further investigation due to its instability (grain redistribution) during particle dispersion measurement. Zinc phosphate PZW2 was chosen as the input material for additional testing because its particle size distribution was the most ideal for utilization in phosphating due to its somewhat low span, resulting in a uniform coating, and fine grain size as determined by its low $D_x(90)$. In addition, the material's stability prevented the oversaturation of particles and their subsequent expansion as a result of the precipitation of dissolved phosphate. In the following investigation, PZW2 was ground using either the planetary mill, the vibratory disc mill, or the jet mill. Our results show that jet milling (method C) achieves the smallest particle size and the shortest distribution range. The particle size distribution of PZW2 samples ground using the planetary mill (A0-A5), the vibratory disc mill, (B0-B5), and the jet mill (C1), are shown in Figure 1. The corresponding particle distribution range is shown in Figure 2. Method A, the FRITSCH Pulverisette 6 planetary mill, yields a $D_x(90)$ as low as 33.50 μm , as depicted in Figure 1. In accordance with technique B, the RS 200 vibratory disc mill, the average $D_x(90)$ was 156.00 μm . With technique C, the STURTEVANT jet mill, the measured $D_x(90)$ was 3.20 μm . This difference in $D_x(90)$ between milling procedures A and B could be attributed to the differing grinding medium or grinding speed, however these were chosen to provide the most efficient grinding in industrial settings. In Fig. 2. it is feasible to discern a causal relationship between techniques A and B, as the particle size drops and subsequently grows. This phenomenon is the result of the Ostwald ripening physico-chemical processes that occur spontaneously during grinding to achieve a more thermodynamically stable state.

Table 1. Particle Size Distribution.

Sample	$D_x(10)$ (μm)	$D_x(50)$ (μm)	$D_x(90)$ (μm)	Span (μm)
Nubirox	3.91	10.8	20.4	1.547
Zinc Phosphate PZW2	2.29	6.67	15.5	1.988
ZP-10	1.71	4.37	8.64	1.610
M 12-60	1.11	6.01	20	3.107

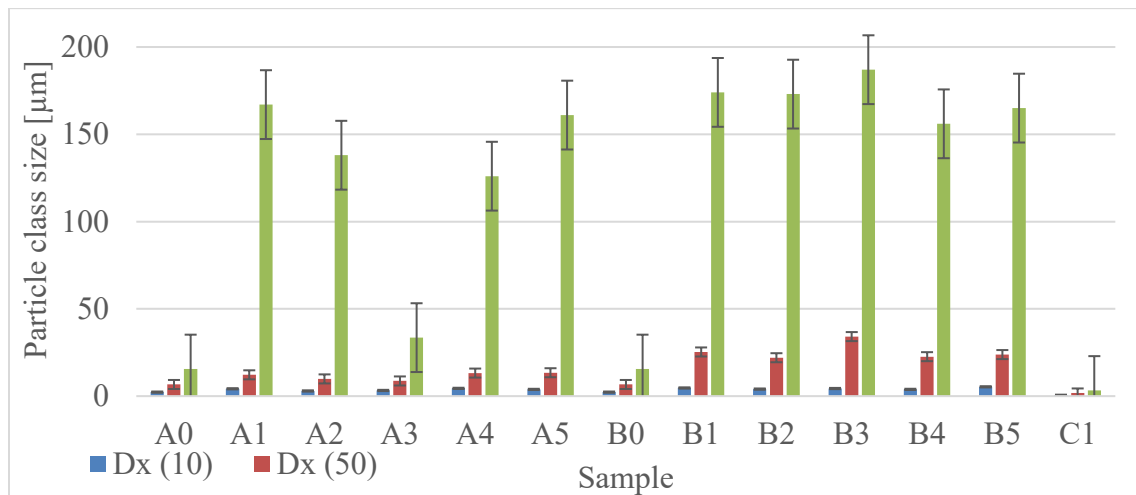


Fig. 1. Particle size Dx(10), Dx(50) and Dx(90) of 13 PZW2 samples.

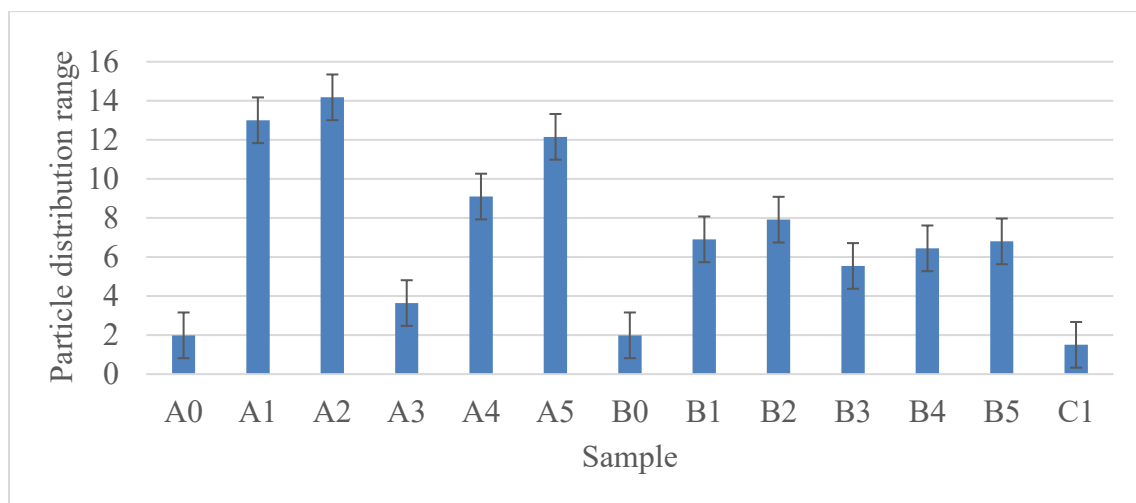


Fig. 2. Particle size distribution of PZW2 samples.

CONCLUSION

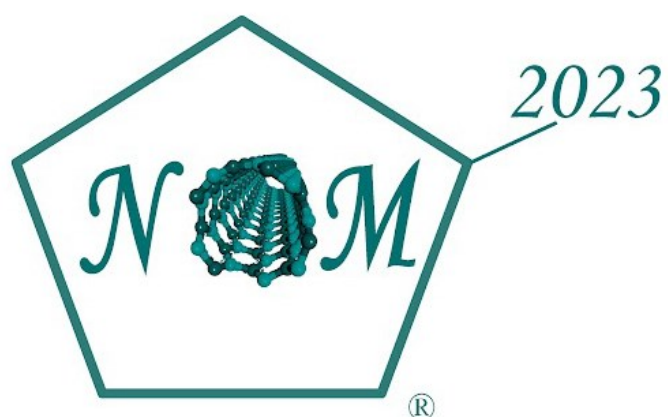
The results of this preliminary investigation indicate that the jet milling method produces superior outcomes when compared to the other milling methods described in this study. This variance is considered due to the nature of jet milling. In the corundum chamber, the particles are crushed against each other at high speed and energy, as opposed to being milled by a friction force as in processes A and B. It is feasible to achieve a smaller particle size and a narrower particle size dispersion with the jet milling process. In order for a high-quality phosphate layer to form on a metal surface, jet milling has the ability to prepare micronized zinc phosphate dihydrate as a nucleus. The development of this technique could result in safer and more environmentally friendly phosphating processes and hence deserves more attention. In order to evaluate if the differences in Dx (90) are a result of the varied milling medium or other factors, it is required to repeat the measurements with the same speed and volume for mills A and B in future research. In order to acquire statistically meaningful results, it is necessary to repeat the jet milling measurements with a larger sample size. The authors plan to study other zinc phosphate dihydrate samples and milling techniques in the future.

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REFERENCES

1. Pokorný, P., Mejta V., Szelag P. *Povrchová úprava: Příspěvek k teoretickým základům tvorby fosfátového povlaku*. Hradec Králové: IMPEA, s. r. o. [online] 2011, 8 [cit. 2020-03-06]. ISSN 1801-707X.
2. Liu, Bing, Zhang, Xian, Xiao, Gui-yong and Yu-peng Lu. *Phosphate Chemical conversion coatings on metallic substrates for biomedical application: A Review*. Materials Science and Engineering [online] 2015, 47: 97–104. Dostupné z: doi:10.1016/j.msec.2014.11.038

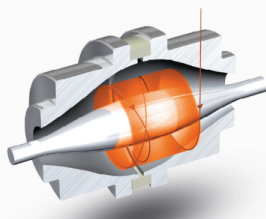
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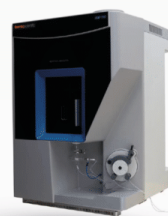
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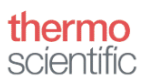


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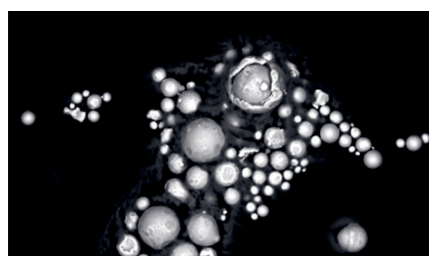


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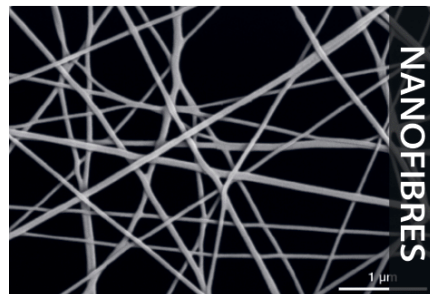


NANOPARTICLES





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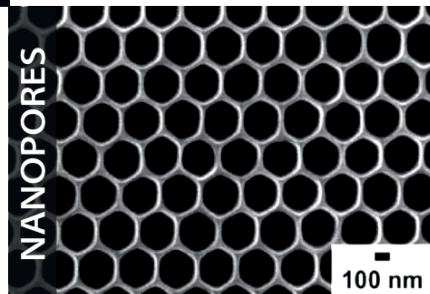


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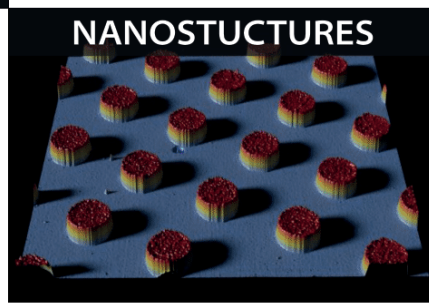
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NANOSTUCTURES



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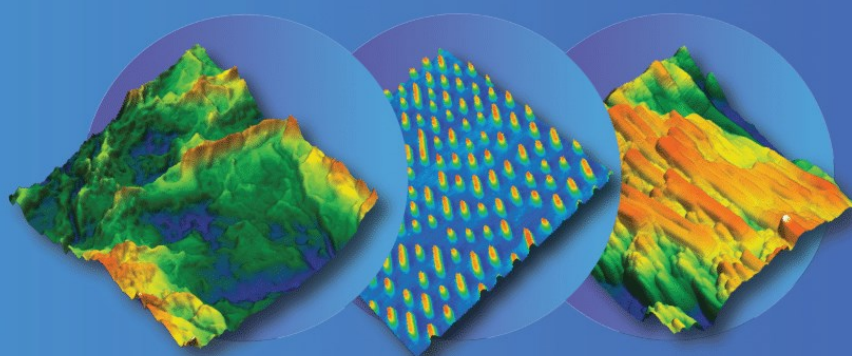
dataphysics
Understanding Interfaces

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Novinka na českém trhu

icspi

Unikátní mikroskop atomárních sil nGauge od firmy ICSPi



Získejte 3D záznamy v nanoměřítku s rozlišením až 1 000 000 x

Získejte data ve třech snadných a rychlých krocích

Unikátní technologie AFM na čipu

Dostupný pro každou laboratoř

Velmi jednoduchá obsluha

Cenová dostupnost

V případě zájmu dozvědět se více či o ukázkou přístroje přímo u Vás v laboratoři, neváhejte nás kontaktovat.

HPST, s.r.o.
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The advertisement features a large, detailed image of the JEOL F2 transmission electron microscope (TEM) on the left. The microscope is white and black, with 'JEOL' and 'JEM-F200' visible on its side. It is positioned on a black base with a control panel. The background is a solid blue with a subtle geometric pattern. On the right side, the text 'F2' is prominently displayed in a large, white, sans-serif font. Below it, the phrase 'Entirely revolutionized TEM' is written in a smaller, white, italicized font. The JEOL logo is in the top right corner. A list of 'New features of F2' is provided, including improved Cold FEG, advanced EELS & EDS, SpecPorter, new STEM detectors (SAAF, OBF, etc.), Python scripting, and time-resolved IDES integration. The website 'www.jeol.com' is at the bottom right. A row of 12 small, colorful icons representing various scientific instruments is at the bottom left.

F2

Entirely revolutionized TEM

JEOL

New features of F2 :

- Improved Cold FEG
- Advanced EELS & EDS
- SpecPorter
- New STEM detectors: SAAF, OBF, etc.
- Python scripting
- Time-resolved IDES integration

www.jeol.com

12 small icons representing various scientific instruments are displayed in a row at the bottom.

LANIK HOLDING

Group of Highly Specialized Industrial Companies



LANIK s.r.o.

Manufacturing of ceramic foam filters and refractory technical ceramics for the foundry, as well as many other industries

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Metsch Refractories Inc.

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ROMILL s.r.o.

Design and manufacturing of industrial equipment with microwave heating

Brno, Czech Republic

www.lanikholding.com

*"Spot the detail, see the whole.
Vidět detail, poznávat celek."*





Surface analysis and imaging

- Atomic force microscopy (AFM, bioAFM, UHV AFM)
- Nanoindentation and Tribology
- Surface analysis (XPS, SIMS, etc.)
- Tabletop Scanning Electron Microscopes (SEM)
- 3D optical and mechanical profilometers
- Electron microscope analyzers (EDS, WDS, EBSD, mXRF...)



Thin layer deposition and characterization

- CVD – Chemical Vapor Deposition, ALD
- Ellipsometry and reflectometry
- PVD – Evaporation and sputtering systems, PLD, MBE
- Plasma assisted depositions and etching – PECVD, RIE, PEALD



X-Ray analytical techniques

- X-ray fluorescence spectrometers
- X-ray single crystal diffractometers
- X-ray fluorescence μ -XRF and TXRF
- X-ray powder diffractometers
- 3D X-Ray Microscopy (mCT, nCT)



Laboratory equipment

- Glove boxes, GMS, Purification systems
- Nanoindentation and AFM Probes and another accessories
- XRF consumables
- Mills, presses and sieves
- Fusion machines
- Presses



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- Propojení s FTIR mikroskopem, Ramanem, TGA, ...
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- Časově rozlišená spektroskopie (až 110 spekter/s)



Vakuový FTIR
spektrometr Vertex 80v
s mikroskopem HYPERION II

SENTERRA II

Vysoce automatizovaný Ramanův mikroskop

- Až 5 excitačních laserů v rozmezí 488–1064 nm
- Možnost kombinace FT-Ramana s disperzním
- Jednoduché a rychlé mapování až 130 spekter/s
- Prostorové rozlišení pod 500 nm

Ramanův
mikroskop
SENTERRA II



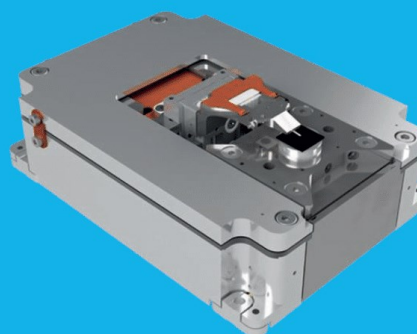
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NenoVision

AFM Designed for SEM Integration

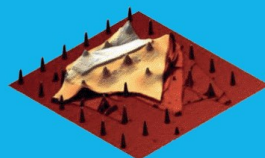
- Plug-and-play AFM solution for SEM microscopes
- The advantage of combined AFM and SEM techniques
- Precise AFM tip navigation with nm precision
- Advanced in-situ sample surface analysis (depth/height profiling, roughness estimation, in-situ 3D imaging, topography vs. material contrast, local spectroscopy measuring)



LiteScope

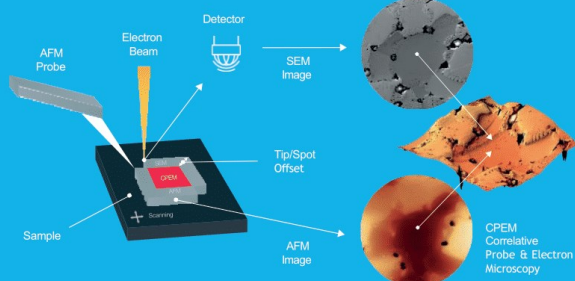
Explore a Variety of Applications

- 2D Materials
- Multifunctional materials and alloys
- Advanced analysis of the TEM lamellas
- Batteries research
- Powders and particles



Characterization of 2D WSe₂ layers
on 1D Si nanopillars

In-Situ Correlative Sample Analysis Using Cutting-Edge CPEM Technology



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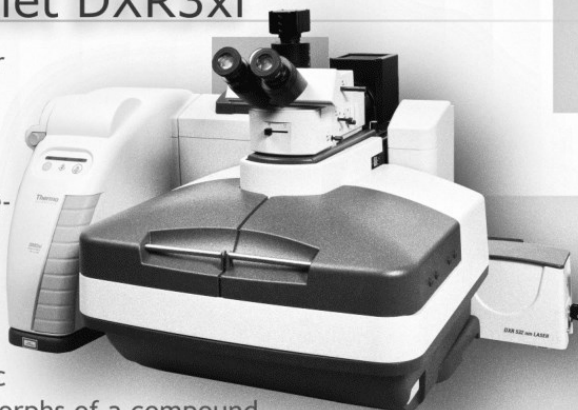
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See the nanoworld

with IR-SNOM and Raman spectroscopy

Raman microscope Nicolet DXR3xi

- High-performance imaging EMCCD detector
- 0.4 μ m resolution
- Non-destructive measurements
- Millions of spectra within tens of minutes
- Compatible with AFM (topography measurements), SPM and TERS
- Safe radiation source (UV, VIS or NIR laser)
- User friendly and intelligent software
- Suitable for studies of deposited graphene layers, pharmaceutical specimens, forensic analysis, distinguishing of individual polymorphs of a compound and many others



NeaScope SNOM

- 10nm resolution
- IR-SNOM/Raman combined experiments
- Ultra-fast chemical imaging and topography measurement
- Non-destructive measurements
- Tunable broad-band IR laser as a safe radiation source
- User friendly and intelligent software
- Studies of plasmons, hyperbolic materials, polymer blends (molecule orientation), organic and inorganic semiconductors, structural disorder of materials, charge distribution and electronic nanomotion, graphene layers, protein and virus complexes, nanomaterial properties, and many others



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The ultimate X-ray diffractometer, with a powerful rotating anode source and two selectable wavelengths



XtaLAB Synergy-ED

The world's first electron diffractometer designed to be used by crystallographers



RIGAKU POWDER XRD SOLUTIONS

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COMPACT X-RAY DIFFRACTOMETER
Advanced quality control system

- 100% compatible with standard sample holders
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MiniFlex
BENCHTOP POWDER X-RAY
DIFFRACTION (XRD) INSTRUMENT
Qualitative and quantitative phase analysis of polycrystalline materials



SmartLab
AUTOMATED MULTIPURPOSE X-RAY
DIFFRACTOMETER WITH GUIDANCE SOFTWARE

Powder diffraction, thin-film, SAXS, in-plane scattering, *operando* measurements

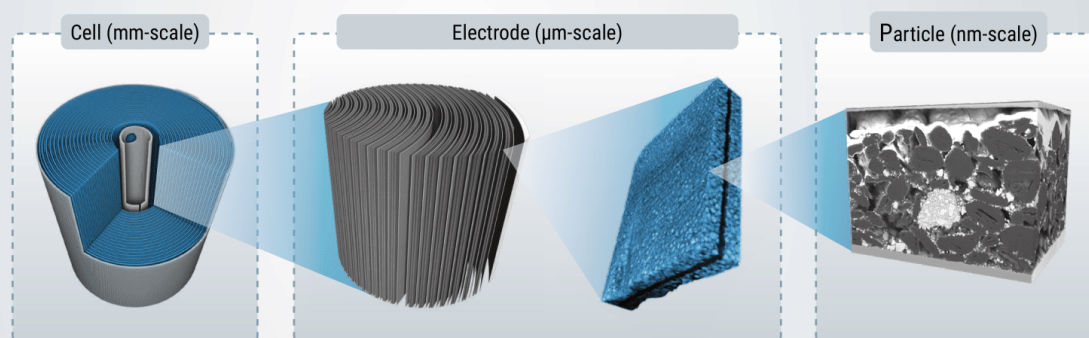


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TESCAN offers solutions tailored to characterization of battery materials at every stage of the battery production value chain. Our multimodal and multiscale analytical workflow incorporates SEMs, FIB-SEMs, micro-CTs, and proprietary analytical techniques that all provide valuable data for improved battery designs and definitive quality control.



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- ✓ **Drive battery performance improvements and innovation** with comprehensive structural and chemical evaluations of electrodes, separators, and their interfaces using high-resolution 3D tomography on a FIB-SEM or X-ray tomography on a micro-CT.
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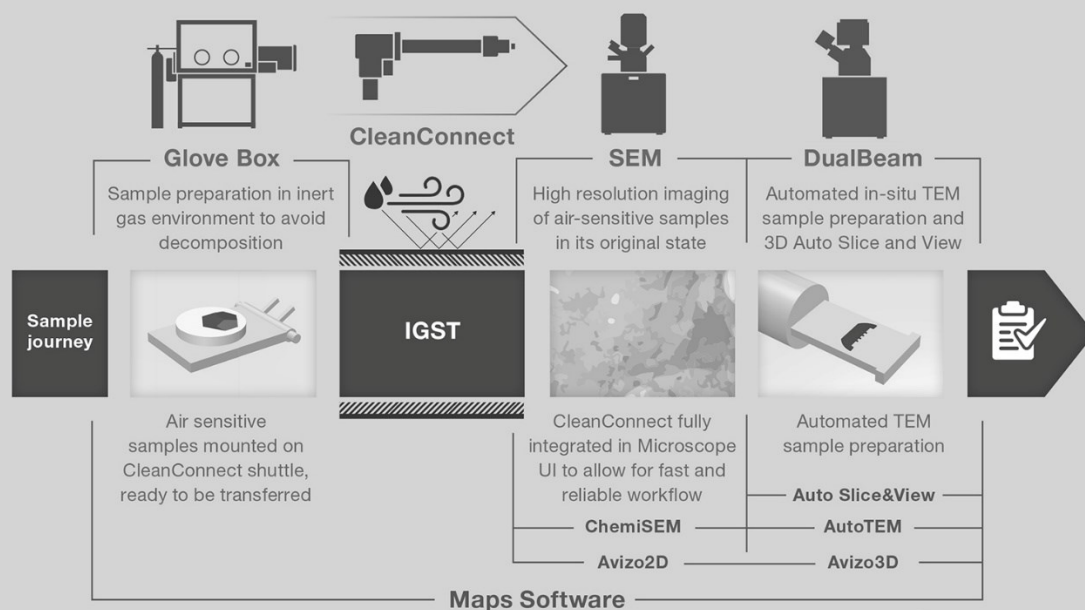
Seamless inert gas sample transfer workflow

Analyze air-sensitive battery materials in their native state

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ZEISS Xradia Versa family 3D X-ray Microscopy

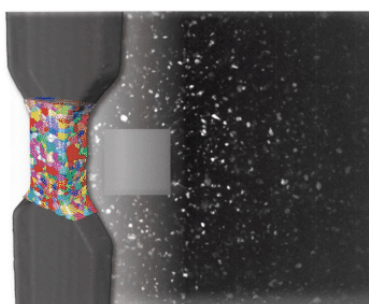


Laboratory-based, Synchrotron Quality Image

ZEISS X-ray microscopes (XRM) are advanced imaging solutions that have removed major hurdles for 3D imaging by achieving high contrast and submicron resolution imaging even for relatively large samples.

Field of Application

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- ✓ **Natural Resources**
- ✓ **Electronics and Semiconductor**
- ✓ **Manufacturing Technology**
- ✓ **Battery and Energy Storage**



CrystalCT_PI-Slide19-f

Benefits

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- XRM Python API for customized instrument control

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Seeing beyond

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