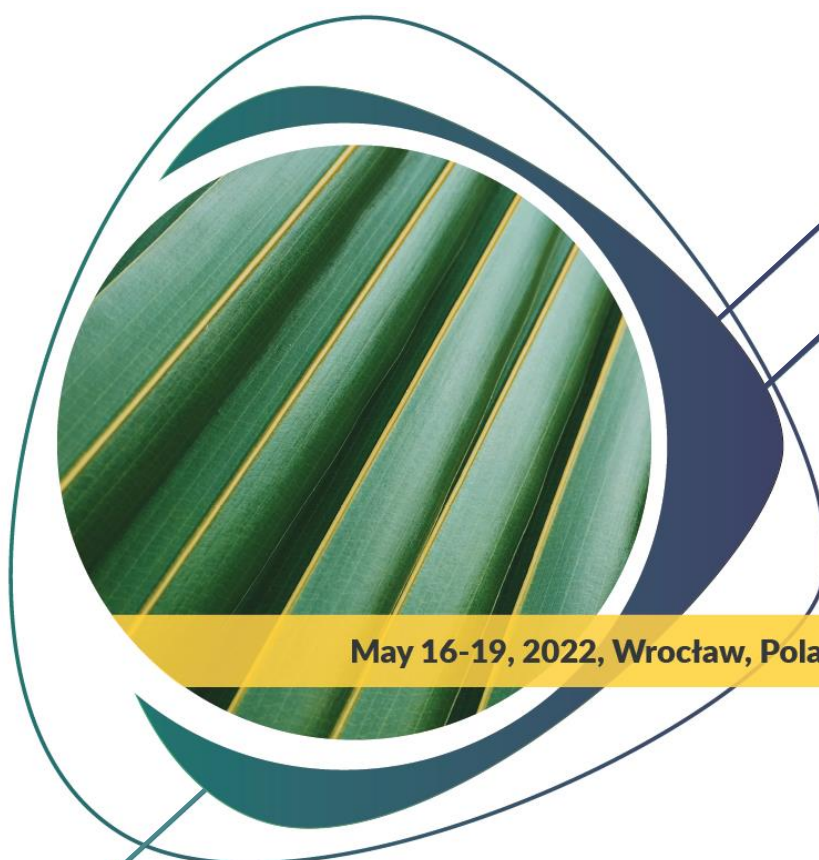




Book of abstracts



May 16-19, 2022, Wrocław, Poland

1st International Conference on
Advanced Materials
for Bio-Related
Applications

AMBRA 2022

Conference venue

Wrocław University of Science and Technology
building D20, ul. Janiszewskiego 8
50-370 Wrocław, Poland
ambra@intibs.pl

Organizers

Division of Optical Spectroscopy
and
Division of Biomedical Physicochemistry
Institute of Low Temperature and Structure Research, Polish Academy of
Sciences
ul. Okólna 2, 50-422 Wrocław, Poland

Department of Mechanics, Materials and Biomedical Engineering
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Special issue in Nanomaterials

**A special issue of Nanomaterials (MDPI, IF=5.076)
will be dedicated to**

AMBRA 2022

Submission of the full manuscripts is open, and will be possible until the deadline of December 31st, 2022. The publication of the Special Issue is expected to occur by the end of 2022. (although single articles will be published immediately after acceptance). If the manuscript is accepted for publication, Authors will have to cover the Article Processing Charges (details will be given later).

Instructions for submission:

- The submission website for this journal is located at:

https://www.mdpi.com/journal/nanomaterials/special_issues/Materials_Bio-Related

- To ensure that all manuscripts are correctly identified for inclusion into the special issue, 'Nanomaterials: Advanced Materials for Bio-Related Applications' must be selected when the "Article Type" step is reached in the submission process.

Guest Editors

Dr. Anna Lukowiak
Prof. Dr. Rafał Jakub Wiglusz



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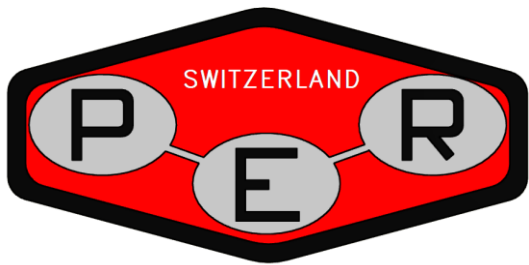
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Welcome Witamy

Dear Colleagues and Friends,

We are pleased to welcome all participants of the "1st International Conference on Advanced Materials for Bio-Related Applications, **AMBRA 2022**" to Wrocław. The organizers, the Institute of Low Temperature and Structure Research of the Polish Academy of Sciences, and the Wrocław University of Science and Technology, with the partnership of the University of Wrocław, are grateful that so many great scientists have chosen to participate in our conference.

The **AMBRA 2022** conference is organized for the first time by the interdisciplinary scientific community from Wrocław. During the event, we wish to initiate a forum to foster and stimulate discussion on advanced materials that find applications in many biological and medical fields. Thus, we are glad to meet experts working in nanotechnology, biomaterials, tissue engineering, cardiac surgery, microbiology, pharmacy, agriculture, and related areas. We trust that we will take part in many important scientific presentations and discussions. Moreover, we are convinced that new scientific collaborations, joint research projects, and original scientific ideas will be born during the conference.

The aim and mission of the **AMBRA 2022** conference is to present the current state of progress in R&D in the field of biomedical sciences and materials engineering, and to create a forum between the participants to discuss cooperation and progress on the subject of the meeting. The conference's subject matter gives hope and looks toward solving the dilemmas related to modern materials in various bioapplications.

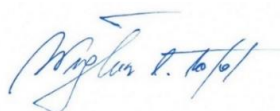
Topics of particular interest include, but are not limited to:

Biomaterials | Nanomaterials | Bio-imaging | Antibacterial agents | Biological and Medical applications

We trust that you will have a very pleasant and memorable stay with us, in our city, and in our academic and scientific community here in Wrocław.

Wrocław was the host European City of Culture in 2016 and we hope that you will also be able to experience and enjoy some of its unique features, history, culture, and cuisine.

Yours sincerely,

A handwritten signature in blue ink, appearing to read "Rafał J. Wiglus".

Rafał J. Wiglus
Conference Co-Chair

A handwritten signature in blue ink, appearing to read "Anna Łukowiak".

Anna Łukowiak
Conference Co-Chair

A handwritten signature in blue ink, appearing to read "Justyna Krzak".

Justyna Krzak
Conference Co-Chair

A handwritten signature in blue ink, appearing to read "Wiesław Strękowski".

Wiesław Strękowski
Chair of the Scientific Committee

Conference programme

16.05 - Monday

9.30	REGISTRATION		(building D20, ul. Janiszewskiego 8)
11.00-11.10	WELCOME		
11.10-11.50	PL1	Michał Giersig	Nanomaterials for biomedical applications
11.50-12.20	I01	Marek Godlewski	Oxides-based fluorescent markers for applications in medicine
12.20-12.50	I02	Jakub Rybka	The laboratory of applied biotechnology – from 3D bioprinted meniscus to covid-19 immunodiagnostics
LUNCH			
14.10-14.40	I03	Stefan Lis	Chosen inorganic nanoluminophores containing with Ln(III) ions focused on biomedical and analytical applications
14.40-15.00	O01	Eugeniusz Zych	Pr-activated grantets for optical thermometry
15.00-15.20	O02	Nicole Nowak	Novel synthesis method of rubidium(I) and europium(III) co-doped hydroxyapatite nanomaterials — potential use in regenerative medicine
15.20-15.40	O03	Magdalena Muszyńska	Elemental analysis of nanoparticles and single cells in relation to advanced biological materials
COFFEE BREAK			
16.00-16.30	I04	Galyna Dovbeshko	2D MoS ₂ nanoparticles as a platform for imaging of cancer cells
16.30-16.50	O04	Marta Wujczyk	Spectroscopic investigation of biocompatible bismuth(III) and europium(III) doped yttrium orthovanadate-phosphate
16.50-17.00	S01	Sylwia Klimas	An in vitro examination of fluoride ions release from selected materials - resin - modified glass ionomer cement (vitremer) and nanohybrid composite material (tetric evoceram)
17.00-17.10	O05	IKA Poland Sp. z o.o.	Organic, aqueous syntheses and fermentation in new IKA reactor systems
17.10-17.50	PL2	Zygmunt Gryczynski	Enhanced fluorescence based detection for biomedical diagnostics and imaging (remote)
18.00-20.00	Welcome reception (H14 building, Wybrzeże Stanisława Wyspiańskiego 40)		

17.05 - Tuesday

9.30-10.10	PL3	Aldo Boccaccini	Biofabrication with composite and multimaterial bioinks: Progress and challenges (<i>remote</i>)
10.10-10.40	I05	Marek Samoć	Toward advanced nonlinear optical materials
10.40-11.00	O06	John Reeks	Response of ZnO micro- and nano-crystals to <i>Staphylococcus aureus</i> bacteria and bacterial growth media
COFFEE BREAK			
11.20-12.00	I06	Thi Ngoc Lam Tran	Glass-based optical transducer platforms for bio-chemo-sensors
12.00-12.10	S02	Weronika Bodylska	Synthesis, characterization and bioactivity of glasses ($\text{SiO}_2\text{-CaO}$) with different sizes
12.10-12.30	O07	Bartosz Bondzior	Decomposition of LaPO_4 microparticles in glass monitored by the Eu^{3+} luminescent probe
12.30-12.50	O08	Beata Borak	Foliar fertilization by the sol-gel particles containing Cu and Zn
12.50-13.10	O09	Sabina Jaros	Bioactive aminophosphine coordination networks: Synthesis, characterization and enhanced antimicrobial activity
LUNCH			
14.30-15.10	PL4	John A. Capobianco	Lanthanide luminescence: From high energy to low energy excitation (<i>remote</i>)
15.10-15.40	I07	Elżbieta Gumienna-Kontecka	Biomimetic analogues of siderophores: from structural probes of ferric ions assimilation to $^{68}\text{Ga}/^{89}\text{Zr}$ nuclear imaging
15.40-16.00	O10	Alexander Kirillov	Bioactive metal-organic networks for antimicrobial applications
16.00-16.20	O11	Maciej Wernecki	Challenges in studying nanomaterials as antibacterial agents
16.30-18.00	POSTER SESSION		
19.45-21.30	Night sightseeing (start from Plac Katedralny, main entrance to Cathedral of St. John the Baptist)		

18.05 - Wednesday

	9.30-10.10	PL5	Luís Carlos	How hot are living cells during magnetic hyperthermia? (remote)
	10.10-10.40	I08	Vadim Kessler	Oligonuclear metal-oxo-alkoxide complexes as molecular models for oxide nanoparticles produced in the sol-gel process
	10.40-11.00	O12	Karolina Elzbieciak-Piecka	Cr ³⁺ -doped GdAl ₃ (BO ₃) ₄ borates as an efficient tool in light-to-heat conversion
	11.00-11.20	O13	Metanel Group SA	TBA
	COFFEE BREAK			
	11.40-12.10	I09	Artur Bednarkiewicz	Photon avalanching: Old phenomenon, new challenges
	12.10-12.40	I10	Marzena Dominiak	Customized 3D allogenic bone blocks in complex dental treatment
	12.40-13.00	O14	Sara Targońska	Investigation of micro and nanostructure of various type of bone substituted materials
	13.00-13.20	O15	Kamila Maciejewska	Synthesis and application of NaYF ₄ nanoparticles as nanoheaters and luminescent nanothermometers
	LUNCH			
	14.40-15.10	I11	Pavla Jendelova	Hydrogels for spinal cord injury repair
	15.10-15.40	I12	Magdalena Wawrzyńska	Coating and surface modification of stents for cardiovascular applications
	15.40-16.00	O16	Martyna Majchrzak	Dissecting the role of prolyl oligopeptidases in cell death by the application of protease-selective prodrugs: From basic research into new anticancer therapeutic strategies
	18.00	Conference dinner with barbecue (Ogród Botaniczny, ul. Sienkiewicza 23 or ul. Kanonia 4)		

19.05 - Thursday

9.30-10.00	I13	Marcin Nyk	Nonlinear optical properties and bio-related applications of advanced colloidal nanomaterials
10.00-10.30	I14	Gulaim A. Seisenbaeva	Hybrid organic inorganic materials as advanced adsorbents and biocatalysts
10.30-10.50	O17	Dominika Wawrzyńczyk	Pr ³⁺ -doped NaYF ₄ and LiYF ₄ nanocrystals combining visible-to-UVC upconversion and NIR-to-NIR downconversion for biomedical applications
COFFEE BREAK			
11.10-11.40	I15	Łukasz Marciniak	Sensitization of lanthanide-based phosphors by transition metals towards high-brightness and sensitive thermometers
11.40-12.00	O18	Marta Gordel-Wójcik	Optical characterization of surface-modified gold nanoshells
12.00-12.20	O19	Anna Szczurek	Protection of polymeric materials with sol-gel coatings for the reduction of plastic waste
12.20-12.40	O20	Adam Watras	Synthesis and structural properties of novel Ln ₄ O ₃ F ₆ (Ln = Ce-Yb) oxyfluorides
12.40-12.50	CLOSING		



Plenary Lectures

NANOMATERIALS FOR BIOMEDICAL APPLICATIONS

M. Giersig*

Institute of Fundamental Technological Research Polish Academy of Sciences

Department of Theory of Continuous Media and Nanostructures

* Corresponding author: mgiersig@ippt.pan.pl

Advances in the controlled growth and characterisation of high-quality nanomaterials are a key factor in laying the foundations of modern nanomaterials for applications in biomedicine. One of the most important challenges of nanotechnology is the design and production of materials starting from the atomic scale, through the molecular scale to the supramolecular scale. The best known description of nanotechnology was developed by the National Nanotechnology Initiative (USA), defining nanotechnology as the manipulation of matter in which at least one of its dimensions lies between 1 and 100 nanometres. The development and creation of a new generation of smart nanomaterials has been made possible by interdisciplinary collaboration. Sophisticated nanomaterials are the result of synergic cooperation between specialists in the following fields: physics, chemistry, biomedicine, materials science, computer science and humanities. The dynamic development of nanotechnology is clearly visible in numerous biomedical and electronic applications and they will be the subject of my lecture. I will present specific examples of nanomaterials due to their production methods determining their specific properties such as size, morphology, structure - electronic and crystallographic, superparamagnetism, superhydrophobicity and biocompatibility, implying their applications.



Prof. Giersig has published over 292 internationally refereed publications covering physics, chemistry, material science, biochemistry, medicine, nanotechnology and engineering. His work has been cited over **23 400 times**, quoted in the ISI Index (without self-citations) at an average of over “82,6” citations per publication, while his **h-index** is currently “**78**” in the World Ranking by Thomson Reuters of the 100 Top Chemists and Material Scientists of the past decade 2000-2010, Giersig is listed in position 75 in chemistry and 83 in material science. Giersig’s most important articles have been published in the following high Impact Index journals: amongst others in: Science (IF 37); Advances in Physics (IF 21); Advanced Materials (IF 19,7); Journal of the American Chemical Society (IF 13,8); Nano Letters (12,7); Nature Communications (IF 12,1); Advanced Functional Materials (IF 12,1); Angewandte Chemie International Edition (11,9); Chemistry of Materials (IF 9,4; Small (IF 8,6)); **PATENTS:** Co-Inventor of 10 patents; **SPIN-OFFs:** Co-Founder of two companies. Prof. Giersig has supervised 22 PhD (several of them with distinction) students and advised 30 MSc graduates. **SCIENTIFIC EXPERTISE:** Synthesis and production of novel metallic, magnetic and semiconductor nanoparticles by wet chemistry and physical methods; Creation/Growth of nanostructures based on carbon (MWCNT, graphene); Nanostructures for applications in life sciences: Cell Manipulation, Tissue Engineering, Diagnostics/ Therapy; Nanostructures for applications in electronics: Solar cells, Photonics, Memory and Detection devices; Sophisticated characterization methods: HRTEM, ELSS; EDX, SEM, AFM, MAFM, SNOM, UPS, XPS, SQUID, UVW, Raman; Image analysis: 3D reconstruction and theoretical modelling the specific properties of nanostructures.

ENHANCED FLUORESCENCE BASED DETECTION FOR BIOMEDICAL DIAGNOSTICS AND IMAGING.

Z.K. Gryczynski*



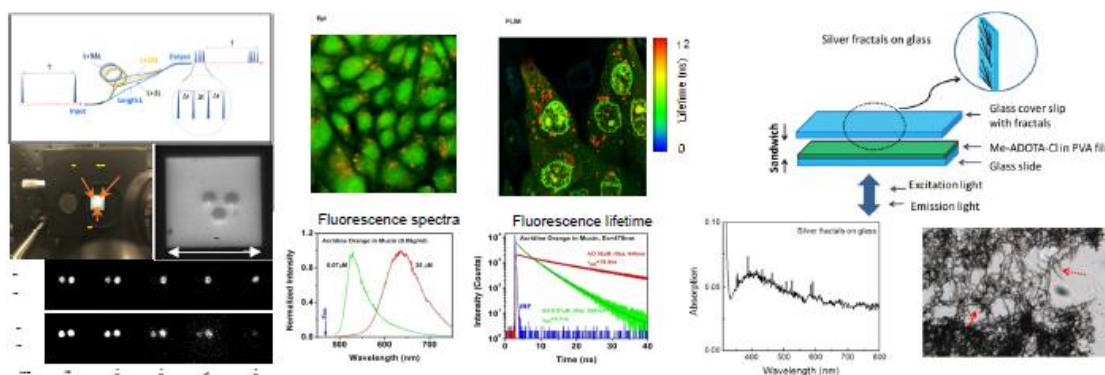
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Optical/fluorescence-based detection plays a prominent role in modern medical diagnostics and biomedical imaging. Recent progress at the interface of biology, physics, micro and nanoscale engineering, nanomaterials, and fluorescence probes development opens new possibilities for biomedical applications. The broad range of applications spreads from biomarkers detection (e.g. cancer markers or cardiac markers), diagnostics tests (e.g. DNA detection or antibody based assays), imaging and monitoring of intra- and extra-cellular environment to practical forensic applications (like sample collection, processing, and amplification).

In this presentation, we will discuss various aspects of recent developments in photonics and nanotechnology that stimulate new ways for developing ultrasensitive assays for medical and chemical applications. Use of long-lived fluorescence probes with excitation pulse manipulation to highly improve detection, diagnostics, and imaging will be presented. We will also present examples of monitoring cellular environment/processes and application of multi-pulse technology with plasmonic platforms for enhanced detection.



BIOFABRICATION WITH COMPOSITE AND MULTIMATERIAL BIOINKS: PROGRESS AND CHALLENGES

A. Boccaccini*

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Keywords: biofabrication, bioprinting, hydrogels, bioactive glass

Biofabrication is a fast expanding research field focusing on the development of 3D hierarchical cell laden structures by automatized additive manufacturing methods, e.g. 3D printing. Bioinks for biofabrication are based on natural or synthetic hydrogels. Alginate-based hydrogels are receiving increasing attention for biofabrication as they exhibit excellent biocompatibility and show a similarity to the extracellular matrix of native tissues in terms of mechanical and structural properties. Current research focuses on improving the printing and cell biology properties of alginate based hydrogels by incorporating bioreactive inorganic fillers, e.g. silica or bioactive glass nanoparticles. The development of such composite hydrogels should lead to improved bioink printability and enhanced functionalities, including superior mechanical properties and cell biology performance [1]. This presentation will review the application of bioreactive fillers in the field of biofabrication. Specifically, a series of reactive silicate fillers as additives for alginate based bioinks of interest in biofabrication will be discussed, analyzing 3D printability, properties of the printed constructs and cell viability. A hydrogel in focus for bioink development is alginate dialdehyde-gelatin (ADA-GEL), which has been combined with sol-gel derived bioactive glass nanoparticles in the silica-calcia system [2]. The use of ion doped mesoporous bioactive glass nanoparticles (e.g. exploring Cu doping for obtaining angiogenic effects) has been also investigated recently [2]. In vitro biocompatibility studies combined with fluorescence staining and cell viability assays showed the superior biological behavior of composite bioinks, with focus on the effect of the silicate filler addition. It was also found that an optimal amount of incorporated inorganic filler in ADA-GEL exists regarding printability. The release of bivalent calcium ions from the particles (sol-gel derived SiO_2 -CaO nanoparticles) can strengthen the network of the hydrogel over time leading to a better stability after printing [3]. It will be shown that composite hydrogels composed of ADA-GEL and inorganic fillers are suitable for biofabrication using a variety of cell types. There is always an optimal filler concentration that leads to improved printability and shape stability of the scaffolds. Challenges in the field, in particular regarding the long-term *in vitro* (and *in vivo*) evaluation of cell laden printed constructs, will be discussed.

References

- [1] A. Leite, et al., *Biofabrication* 8 (2016) 035005.
- [2] H. Zhu, et al., *Small* 18 (2022) 2104996.
- [3] S. Heid, et al., *Bioprinting* 26 (2022) e00200.

LANTHANIDE LUMINESCENCE: FROM HIGH ENERGY TO LOW ENERGY EXCITATION

G.A. Mandl, J.A. Capobianco*

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Concordia University, Montreal Quebec, Canada*

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In this plenary lecture, I will discuss the versatile means through which lanthanide doped nanomaterials can be utilized for biological applications. X-ray mediated photodynamic therapy (X-PDT) utilizes radioluminescent nanoparticles to induce the generation of reactive oxygen species and kill cancer. We have developed a Pr^{3+} based nanoparticle system that works in tandem with 5-ALA therapy to produce an X-PDT-Radiotherapy effect utilizing endogenously produced Protoporphyrin IX. Utilizing low-energy near-infrared light, we are developing biocompatible dye-sensitized PDT systems utilizing $\text{Er}^{3+}/\text{Yb}^{3+}$ doped nanoparticles. Together, these two avenues of excitation utilizing lanthanide doped nanoparticles demonstrate the potential for these biologically relevant materials.

HOW HOT ARE LIVING CELLS DURING MAGNETIC HYPERTHERMIA?

Y. Gu,¹ R. Piñol,¹ C.D.S. Brites², A. Millán¹, L. D. Carlos²

¹ INMA, Institute of Nanoscience and Materials of Aragon, CSIC-University of Zaragoza, Zaragoza, Spain

² Phantom-g, CICECO-Aveiro Institute of Materials, Department of Physics, University of Aveiro Campus de Santiago, 3810-193 Aveiro, Portugal

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Keywords: luminescence thermometry, intracellular temperature, magnetic hyperthermia

The emergence of luminescent nanothermometry during the last decade opened up the possibility of measuring thermal flows at spatial scales below 10 μm , unreachable by conventional electrical methods [1]. Diverse phosphors capable of providing a contactless thermal reading through their light emission properties have been examined, e.g., polymers, DNA or protein conjugated systems, organic dyes, quantum dots, and trivalent lanthanide (Ln^{3+}) ions incorporated in organic-inorganic hybrids, multifunctional heater-thermometer nanoplatforms, upconverting, downconverting and downshifting nanoparticles. The implementation of these Ln^{3+} -based phosphors (with an emphasis on upconverting nanoparticles) as ratiometric thermometers was extensively reviewed in the past five years [1].

In the last couple of years, the focus of luminescence thermometry has gradually shifted from the fabrication of more sensitive nanoarchitectures towards the use of the technique as a tool for thermal bioimaging and the unveiling of properties of the thermometers themselves and their local surroundings, as, for instance, the instantaneous ballistic velocity of Brownian nanocrystals suspended in both aqueous and organic solvents [2].

After a general perspective of the work done on luminescence nanothermometry since the explosion of the field one decade ago, the lecture will be focused on an example [3] illustrating the potential of the technology to measure the intracellular temperature, including recent results of those measurements during magnetic hyperthermia.

References

- [1] C. D. S. Brites, S. Balabhadra, L. D. Carlos, *Adv. Opt. Mater.* 7 (2019) 1801239.
- [2] C. D. S. Brites, X. Xie, M. L. Debasu, X. Qin, R. Chen, W. Huang, J. Rocha, X. Liu, L. D. Carlos, *Nature Nanotech.* 11 (2016) 851.
- [3] R. Piñol, J. Zeler, C. D. S. Brites, Y. Gu, P. Téllez, A. N. Carneiro Neto, T. E. da Silva, R. Moreno-Loshuertos, P. Fernandez-Silva, A. Isabel Gallego, L. Martinez-Lostao, A. Martínez, L. D. Carlos, A. Millán, *Nano Lett.* 20 (2020) 6466.



Invited Lectures

OXIDES-BASED FLUORESCENT MARKERS FOR APPLICATIONS IN MEDICINE

**M. Godlewski^{1,*}, J. Kaszewski¹, J. Rosowska¹, P. Kielbik²,
M. M. Godlewski²**

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Keywords: oxides, nanoparticles, fluorescence labels, cancer

The new application of nanoparticles of wide band gap oxides will be discussed, allowing early detection of cancer. For this we applied so-called fluorescent markers (FMs). Several types of such markers were tested and discussed in the literature [1]. The new generation of FMs, developed by us, is based on nanoparticles doped with rare earth ions. As a matrix nanoparticles of wide band gap oxides (mainly ZnO and ZrO₂) are selected due to their bio-neutrality. Rare earth doping of the markers results in an efficient and spectrally sharp photoluminescence (PL) in a visible light spectral region. Importantly, for these FMs a stable PL is observed, without any blinking and photo-bleaching.

We then tested the ways to introduced FMs to organisms. Direct injection to a blood system may be dangerous – FMs can aggregate blocking blood circulation. Moreover, the chemicals used to stabilize nanoparticles in suspension (i.e. PEG) affect strongly their trafficking mechanisms, rendering them nearly useless for intra-tumor deposition. This why we tested a new method of FMs introduction – Intra-gastric (IG). This innovative method of introducing of markers to organisms was developed by us. We observed that after IG introduction FMs are distributed through the organism. Importantly, after IG introduction, FMs penetrate and gradually accumulate in tumors, including the difficult to diagnose and treat lungs tumor.

Tests were performed to check selectivity of our method. It turned out that blood - lungs barrier is very tight. FMs cannot enter to healthy cells but easily penetrate membrane for the region of tumor. An effective trafficking of FMs to the areas of lung cancer was thus observed, whereas surrounding tissue was impermeable for nanoparticles. The data obtained confirm 100% selectivity of the method. This shows a high potential of studied FMs in direct tracing of the extent of cancer spread in lungs.

Importantly, FMs developed by us can also be used as MRI contrast agents. Moreover, we performed tests of using developed FMs as transport agents. FMs were used to selectively introduce a given medicine to area of tumor. A directed therapy is thus possible.

References:

[1] M.M. Godlewski, J. Kaszewski, P. Kielbik, J. Olszewski, W. Lipinski, A. Slonska-Zielonka, J. Rosowska, B.S. Witkowski, M.A. Gralak, Z. Gajewski, M. Godlewski, *Nanotechnology Reviews* 9 (2020) 274.

THE LABORATORY OF APPLIED BIOTECHNOLOGY – FROM 3D BIOPRINTED MENISCUS TO COVID-19 IMMUNODIAGNOSTICS

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Keywords: applied biotechnology, bionanotechnology, 3D bioprinting, tissue engineering, covid-19 immunodiagnostics

The topics of our research revolve around tissue engineering, 3D bioprinting, meniscus regeneration, and most recently, COVID-19 diagnostics. We are also actively participating in efforts directed towards the automation and robotization of biotech laboratories. Our mission is to venture beyond the boundaries of basic science and bridge academic discoveries with real-life applications. We strive to establish meaningful partnerships with both scientific and industrial entities to drive innovation in biotechnology.

3D bioprinting allows mimicking spatial characteristics of biological structures with the use of bioinks, composed mainly of biocompatible hydrogels. 3D bioprinting enables precise cell deposition while providing optimal conditions for cellular growth and proliferation. This technology is suitable for the creation of various models, reflecting tissue environment more precisely in comparison to monolayer cell cultures. Additionally, 3D bioprinting as a part of novel tissue engineering approaches offers a possibility to restore the physiological functions of an organ without resorting to artificial implants. Our main focus is to utilize 3D bioprinting for meniscus regeneration.

The main diagnostic tool utilized to detect ongoing infection with SARS-CoV-2 is based on the real-time polymerase chain reaction (RT-PCR), which detects viral genetic material in patients. It is a precise and reliable method to determine the carriers of the infection. Immunodiagnostics of COVID-19 is a crucial supplement for RT-PCR diagnostics, as the gradual development of herd immunity may affect policies employed to countermeasure the effects of the ongoing pandemic. Additionally, it will be crucial for the evaluation of the vaccines, including long-term immunity, and their efficacy against novel strains of the virus. Our team is focused on developing an in-house, high-throughput system for COVID-19 diagnostics, utilizing a robotic station and optimized ELISA.

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CHOSEN INORGANIC NANOLUMINOPHORES CONTAINING WITH Ln(III) IONS FOCUSED ON BIOMEDICAL AND ANALYTICAL APPLICATIONS

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Keywords: nanoparticles, lanthanides, sensitized emission, applications

The presentation shows and discusses examples of effective nanoluminophores doped with lanthanide ions (Tb^{3+} lub Eu^{3+}) and their surface functionalized with organic compounds hybrid systems for biomedical and analytical applications. Luminescent nanoparticles doped with Ln^{3+} ions in systems functionalized with the desired organic ligand molecules, such as: $\text{LaF}_3: \text{Tb}^{3+}$ 5%, Ce^{3+} 10%@ $\text{SiO}_2\text{-NH}_2$ nanoparticles with acetylsalicylic acid (aspirin) coated on the surface [1], or ligand sensitized (Fig. 1): 2,6-Pyridine dicarboxylic acid (2,6-PDA) capped- $\text{LaF}_3: \text{Eu}^{3+}$ and adenosine capped- $\text{SrF}_2: \text{Eu}^{3+}$ nanoparticles (NPs) [2], showed high hemocompatibility and therefore can be successfully used in biomedical research. NPs functionalized with organic compounds have also proved to be very useful for analytical purposes. We have developed new highly selective fluorescence methods based on energy transfer from the analyte ion to the Tb^{3+} ion (3,5-Dihydroxy Benzoic Acid-Capped $\text{CaF}_2: \text{Tb}^{3+}$ NPs [3], or Tb^{3+} ion (Adenosine capped $\text{CaF}_2: \text{Eu}^{3+}$ nanocrystals [4] and DPA capped- $\text{LaF}_3: \text{Eu}^{3+}$ NPs) for the determination of metal species (e.g. WO_4^{2-} , MnO_4^- , Cu^{2+}) in real water samples.

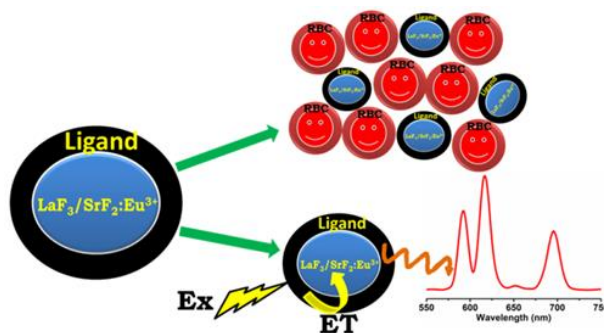


Fig. 1. Ligand sensitised $\text{LaF}_3/\text{SrF}_2: \text{Eu}^{3+}$ NPs, hemocompatibility and intense Eu^{3+} ion emission via ligand sensitisation.

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2D MoS₂ NANOPARTICLES AS A PLATFORM FOR IMAGING OF CANCER CELLS

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Keywords: 2D-MoS₂, confocal microscopy, cancer cell imaging, DOX

Modern 2D materials with graphene-like structures have unique physical and chemical properties and can be used for different biomedical applications. In the current work, 2D-MoS₂ particles (Aldrich) were characterized by X-ray, element analysis, electronic microscopy, FTIR, Raman spectroscopy and used together with doxorubicin (DOX) for imaging of cancer cells.

The effect of 2D MoS₂ nanoparticles and 2D MoS₂ – DOX complex on the cell line LLC/R9 - a highly angiogenic low-metastatic variation of the original Lewis lung cancer (LLC) - was examined. For two days, cells were cultivated in a cultural medium under standard conditions and in a CO₂ atmosphere. The treatment consisted of an aqueous suspension of 2D-MoS₂ at a concentration of 0.1 mg/ml. Reference cells were incubated under the same settings and parameters but without the inclusion of nanoparticles. Confocal images were registered using LCM 510 confocal microscope (Carl Zeiss, Germany) with FSet10wf, FW1-2: FSet20wf filters under the ultraviolet lamp and laser excitation. All images were registered using an LD Plan-Neofluar 40x/0.6 Korr lens.

At the apoptosis stage, a little portion of the cell's membrane is destroyed. Luminescence is not observed when a UV lamp is used for excitation. The effect of 2D MoS₂ nanoparticles on cells leads to the appearance of luminescence in the green range. After treatment of cells with DOX, the images clearly show that all the cells have a damaged membrane and are at different stages of death.

The complex 2D- MoS₂- DOX nanoparticles (Fig.1) lead to complete staining of the cell as a whole in green range and clear luminescence in green and red region.

Our study has shown that 2D nanoparticles can be used as markers for cell structure visualization in order to detect apoptosis, necrosis, and redistribution of anti-cancer drug DOX inside the cell.

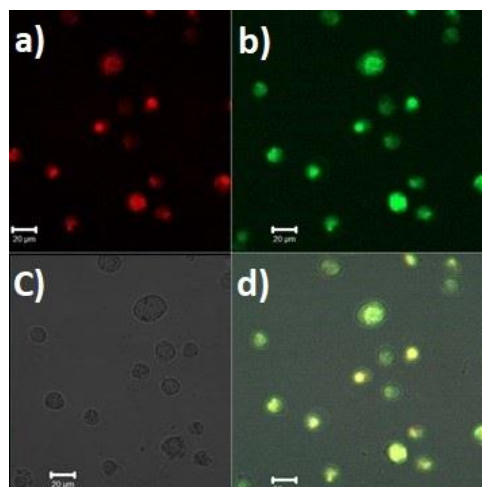


Figure 1. Confocal images of cells after treatment with 2D- MoS₂ nanoparticles with doxorubicin: a,b,d) excitation: Laz 543 nm T1 60%, 488 nm T2 50% 405 nm T3 30%, beam splitters FW1-1: FSet10wf, FW1-2: FSet20wf, c) UV excitation, without filters, in transmission mode.

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TOWARD ADVANCED NONLINEAR OPTICAL MATERIALS

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Keywords: nonlinear absorption, two-photon absorption, multiphoton absorption, photoacoustic effect

A material is usually considered “advanced” if at least one of the following features is true: i) its properties are markedly better than those of the hitherto existing materials, ii) it can be used in novel, non-standard applications, iii) it is multifunctional. In the domain of materials exhibiting nonlinear optical (NLO) properties, such as frequency conversion, nonlinear absorption and nonlinear refraction, much activity has always been directed at finding novel materials with possibly much enhanced NLO coefficients. Many published accounts presenting such data have to be taken with caution, but there are numerous “emerging” materials and nanomaterials that do show promising NLO properties [1,2]. We have postulated that some of those materials that we nicknamed “NLO pigments” can find numerous applications. Among the mechanisms that can lead to enhancements, we have explored quantum size effects in various nanostructures, aggregation effects and, recently, doping in 2D semiconductor platelets [3], which was found to provide increased two-photon absorption and refraction cross sections. One notes that any comparisons between various materials have to be carried out using parameters which account properly for differences e.g. in sizes of nanoparticles and their composition.

Various applications of NLO properties, especially of the two-photon absorption, call for the presence of specific photophysical and/or photochemical properties of an NLO material. Examples include here the presence of high luminescence quantum yield, high singlet-oxygen generation efficiency [4], good photocatalytic properties etc. Less is known about the use of NLO absorbing materials for exploiting properties such as photoelectric, photomagnetic, photoelastic and photoacoustic effects. Recently, we have initiated studies of generation of high-frequency photoacoustic effects by multiphoton absorption of femtosecond pulses in thin (a few tens of nanometers) films of a multifunctional NLO pigment, quinacridone. The initial results [5] point out to high sensitivity of the technique for studying NLO absorption in various structures, including systems that are unsuitable for usual techniques such as Z-scan or multiphoton-induced luminescence.

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GLASS-BASED OPTICAL TRANSDUCER PLATFORMS FOR BIO-CHEMO-SENSORS

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Keywords: optical transducers, optical waveguides, glass photonics, photonic crystals, optical resonators

In the environmental, agri-food and biomedical sectors, there is a current need of online and real-time bio-chemical detection and monitoring. For such purposes, glass-based optical sensors are appealing candidates. These optical sensors offer unique advantages such as high thermo-chemical resistance, immunity from electromagnetic interference, low signal attenuation loss, multiparameter detection, and high integration ability. Unlike the popular chemical and electrochemical sensors, optical sensors generally do not require frequent maintenance and calibration, paving a way for online and remote sensing. This talk gives an overview of potential glass-based optical transducer platforms for bio-chemo-sensors focusing on optical waveguides[1], optical resonators[2], and photonic crystals[3] (1D and 3D). Principles of optical signal-transducing based on refractive index, fluorescence, and optical absorption are outlined. Conclusions regarding the perspectives of future developments of novel optical transducers are discussed with special attention to rare-earth-based glass structures. The rare-earth-based structures can act as a light source and an optical transducer at once in a laboratory-on-chip system. Such optical transducer platforms have great potentials because they can simplify the supporting equipment needed for their operation and, therefore, their cost, as well as the complexity of their operating procedure[4].

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BIOMIMETIC ANALOGUES OF SIDEROPHORES: FROM STRUCTURAL PROBES OF FERRIC IONS ASSIMILATION TO $^{68}\text{Ga}/^{89}\text{Zr}$ NUCLEAR IMAGING

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Keywords: siderophores, hydroxamic acids, biomimetics, Fe(III), Ga(III), Zr(IV)

Under iron-deficient conditions most aerobic microorganisms secrete low molecular-weight, highly specific iron(III) chelating compounds – siderophores, which actively transport ferric ions into the cells via specific receptors in the microbial membranes.¹ The difficulties in synthesis of structurally complicated natural siderophores has directed the siderophore research towards biomimetic chemistry, aiming at mimicking or reproducing the function of the natural product rather than its detailed structure. This approach allowed us to diversify the arsenal of biologically active siderophore-type molecules, introduce additional desired chemical and/or physical properties, and provide means to identify general motifs governing an interplay between structure and function in biological activity.¹⁻⁴

Taking into account, that siderophores are absent in the host cells, they are tempting targets for microbial imaging; ^{68}Ga and ^{89}Zr are positron emitters that have recently become the subject of great interest for molecular imaging applications using positron emission tomography (PET). Of the evaluated siderophores, ^{68}Ga -ferrioxamine E (FOXE) and its close biomimetic analogs were shown as the most promising for possible applications in PET imaging of *S. aureus*.⁴ On the other hand, desferrioxamine B (DFO) is currently the most commonly used chelator to radiolabel biomolecules with ^{89}Zr .⁵ However, its *in vivo* stability has proven insufficient, and transchelation has been observed. Our Zr(IV) – DFO solution studies provided information on the actual chemical form of the complex in biological media, and this can contribute to a better understanding of the *in vivo* speciation and differences in the biological activity of this and other chelators.^{6,7}

Overall, proposed derivatives may hold potential as inert and stable carrier agents for Fe(III), Ga(III) and Zr(IV) ions for diagnostic medical applications. They could also allow identifying critical microbial compartments in which siderophores accumulate and thus illuminate key targets for specific drugs against bacterial/fungal diseases.

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OLIGONUCLEAR METAL-OXO-ALKOXIDE COMPLEXES AS MOLECULAR MODELS FOR OXIDE NANOPARTICLES PRODUCED IN THE SOL-GEL PROCESS

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Keywords: metal oxide sol-gel, ligand grafting, drug delivery, nano medicine

Sol-Gel process in case of metal oxides proceeds via nucleation of an oxide phase in a coordination equilibrium type process [1]. The nuclei are particles with well-defined and often even crystalline metal-oxide core, mimicking the structure of relate oxide material, and are capped by residual organic ligands or hydroxide entities [2]. They are thus resembling polyoxometalate species – well known non-cluster coordination aggregates. Understanding of their structure and reactivity on molecular level can be achieved investigating the formation and behavior of oligonuclear metal oxo-alkoxide complexes. We proposed to denote this kind of species as metal oxo Paperbags, to distinguish these highly reactive species from clusters, which contain metal-metal bonds and are often displaying relative chemical stability. The insight into structure of paperbag compounds brings light on how the molecules of medicines actually attach to specific inorganic nanostructured matrices and provide basis for understanding the kinetic features of ligand desorption and, in particular, drug release processes [3] (see Fig. 1).

An additional intriguing aspect in behavior of nanoparticles is their capacity to strongly interact with biomolecules, in particular, with proteins. The nature of bonding and reactivity of nanoparticle-biomolecule complex can be modeled by revealing the structures and bonding parameters of related paperbag models. Such studies can provide insight into the possibility to apply sol-gel nanoparticles as nano medicines in, in particular, anti-viral media [4].

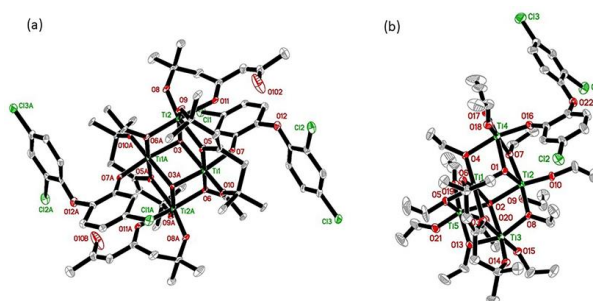


Fig. 1. Molecular structures of Ti-oxo-alkoxide Ti_5 (a) and Ti_4 (b) Paperbags bearing a diclofenac ligand [3].

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PHOTON AVALANCHING: OLD PHENOMENON, NEW CHALLENGES

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Keywords: photon avalanche, superresolution imaging, biosensing

Among upconversion processes leading to the anti-Stokes emission, the photon avalanche (PA) became an interesting research topic since 1979, when it was first observed in Pr³⁺ doped LaCl₃ [1]. There are several essential requirements necessary to satisfy to observe PA in a given system the PA, such as (i) the presence of efficient ESA transition and negligible GSA at the pumping wavelength and (ii) the presence of efficient the cross-relaxation (CR) processes required to populate intermediate excited level. As a consequence, the luminescence intensity of PA increases by several (2-3 typically) orders of magnitude when exciting with power density slightly exceeding the PA threshold. Until recently, PA was observed mostly in lanthanide doped bulk materials and fibers, often in cryogenic temperatures aiming to get new laser lines or detect medium IR photons. Only recently its PA emission was also demonstrated for NaYF₄ nanoparticles doped with Tm³⁺ at the room temperature under 1064 and 1450 nm photoexcitation and 800 nm emission [3].

The wide application potential of PA (e.g. superresolution imaging [3], biosensing [4], nanothermometry [5] etc.) makes it extremely interesting to further study the PA in various lanthanides and various matrices of various sizes. In this lecture, we will summarize the current state-of-the-art on PA emission, we will discuss the PA emission in nano, micro and bulk LiYF₄ crystals and discusses the peculiarities of photon avalanche emission in wider context as the paradigm shift in luminescent materials design.

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CUSTOMIZED 3D ALLOGENIC BONE BLOCKS IN COMPLEX DENTAL TREATMENT

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Keywords: bone reconstruction, orthodontic-orthognathic treatment, allogenic 3D bone block

The morphological structure of the alveolar ridge of the maxilla and/or mandible is an important predictor of the possibility of gingival recession development. The narrow alveolar ridge in the lip-lingual dimension, especially with the thin biotype of the gingiva, is one of the factors predisposing to the development of this pathology. It may hinder or prevent the course of orthodontic treatment as an independent therapy method or as part of the orthodontic-orthognathic treatment. In addition, the reconstruction of the narrow alveolar ridge may be an alternative procedure in relation to some orthognathic procedures, making it possible to carry out treatment in a minimally invasive manner [1].

The aim of the presentation will be to present the bone reconstruction method using a 3D allogenic bone block in the prevention and treatment of gingival recession in the course of orthodontic treatment

Assessment will be given to a group of patients after or before orthodontic treatment with a narrow bony ridge as a primary morphological defect or as a complication of orthodontic treatment.

All patients underwent an original 3D reconstruction of the bone. Prior to the procedure, the periodontal status was assessed, including the gingival biotype, thickness and width, and the occurrence of gingival recession.

In the case of existing recessions, the first stage of the procedure was rebuilding of the keratinized gingiva, followed by bone reconstruction. In the case of the primary morphologically defect, bone reconstruction was performed after the orthodontic analysis.

The lecture will present the rules for the qualification of patients for the treatment, the procedure including the methodology of bone graft surgery and long-term effects of the performed procedures. The complications associated with the treatment will also be analyzed.

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HYDROGELS FOR SPINAL CORD INJURY REPAIR

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Spinal cord injury (SCI) is a serious trauma, which often results in a permanent loss of motor and sensory functions, pain and spasticity. Despite extensive research, there is currently no available therapy that would restore the lost functions after SCI in human patients. Advanced treatments use regenerative medicine or its combination with various interdisciplinary approaches such as tissue engineering or cell therapy. An important repair strategy is tissue reconstruction by bridging the SCI lesion with a supportive and stimulatory milieu that would enable axonal rewiring. Methacrylate hydrogels have been extensively used as bridging scaffolds in experimental spinal cord injury (SCI) research. As synthetic materials, they can be modified, which leads to improved bridging of the lesion. We have characterized methacrylate hydrogels modified with different bioactive molecules, such as Fibronectin, SIKVAV or laminin. We have also prepared hydrogels with oriented pores. Hydrogels were evaluated as stem cell carriers and/or suitable bridges for bridging spinal cord injury in rats. We observed partial tissue reconstruction and axonal ingrowth depending on the hydrogel modifications. However, chemically-synthesized materials cannot fully mimic the complex morphological structure and chemistry of the native ECM, therefore hydrogels from natural materials, such as decellularized extracellular matrix or hyaluronic acid were prepared. These hydrogels were characterized *in vitro* in terms of their biochemical composition and adhesion, as well as their possible use as cell carriers. In vivo experiments confirmed their suitability as material for filling tissue cavities and modulating immune response. To further enhance cell-polymer interactions and axon growth, gene therapy based on integrin expression in neurons can facilitate the axon growth on long distance and can be possible approach for further therapies in neural tissue engineering.

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COATING AND SURFACE MODIFICATION OF STENTS FOR CARDIOVASCULAR APPLICATIONS

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Keywords: medical implants, graphene coating, cardiovascular stents, hemocompatibility

Implantable medical devices, especially vascular stents, are often coated with various types of coatings to improve the properties of these devices. In the case of endovascular stents, coatings positively influence physiological processes in the vessel tissue after stent implantation, e.g., enhancing desired processes in pathologically altered tissues. Stent coatings inhibit inflammation that occurs in the immediate vicinity of the stent. The use of inert carbon coatings and especially graphene coatings seems to be very promising in this field. Technologies for deposition of graphene coatings in general on various metallic substrates are known and can be based on methods such as chemical vapor deposition (CVD), epitaxy on crystalline substrates, graphite oxide reduction, exfoliation and others. A medical device coated with these coatings has very good surface hemocompatibility properties, resulting in a reduced incidence of complications after stent implantation, such as thrombus formation on the implant surface. Thrombosis associated with intravascular implants is an important clinical problem that can be overcome by using graphene-coated devices. In the in vitro application studies conducted in this study on vascular endothelial cells on graphene-coated stents, the growth of HUVECs was 51% higher than on reference stents without graphene coating. This indicates that the graphene coating promotes endothelial cell colonization, and the graphene-coated implant showed features of faster healing of the tissue surrounding the material after implantation than the non-graphene-coated implant. The results of the hemocompatibility test, understood as the ability to inactivate blood clotting processes, further indicated that the Co-Cr alloy samples (type L-605), covered with a graphene layer did not show a procoagulant effect of the obtained layer.

NONLINEAR OPTICAL PROPERTIES AND BIO-RELATED APPLICATIONS OF ADVANCED COLLOIDAL NANOMATERIALS

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Keywords: nanomaterials, nonlinear optics, two-photon absorption, biophotonics

The growing availability of short-pulse laser sources is bringing numerous advantages to using optical processes in biological and medical applications. The possibility of exciting nanoluminophores by multiphoton processes can be the key to better diagnostic and therapeutic procedures, especially in combination of this with advantages of being able to engineer multifunctional advanced nanosystems. For example, an important new direction for nanomedicine is the use of nanoplateforms called “theranostics agents (therapy + diagnosis)” which combine therapeutic and diagnostic functionalities.

The main object of this study is to find procedures to relate the properties of hybrid nanomaterials to their structure, with special emphasis put on the wide spectra range nonlinear optical response (measurement of a third order electric susceptibility $\chi^{(3)}$, with the use of the femtosecond laser techniques, including z-scan and two-photon excited emission) of extended group of advanced nanostructured materials of colloidal hybrid nanomaterials with various shape, size and compositions, by defining and comparing the optical merit factors relevant for many photonic applications in nanophotonics and biophotonics. This study provided both fundamental knowledge about materials engineering of a new class of inorganic nanomaterials, i.e. optimization of synthesis and surface modification, as well as fundamental knowledge about how to correctly characterize those materials using a new approach of femtosecond laser techniques. A comprehensive study of various groups of more complex structures, constructed of more than a single nanocomponent, i.e. semiconductor quantum dots [1] or quantum 2D nanoplates [2], nanoplasmonic [3] and lanthanide-doped nanoparticles [4,5], where also more than a single functionality is present, will be discussed.

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HYBRID ORGANIC INORGANIC MATERIALS AS ADVANCED ADSORBENTS AND BIOCATALYSTS

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Keywords: functional silica, bio-based polymer matrices, enzyme immobilization, water purification, recycling

Hybrid organic-inorganic materials open broad perspective of application due to combination of functional components. They can be based on inorganic matrices such as porous or dense silica, aluminosilicates and metal oxide materials grafted with organic or bio-ligands. An alternative approach starts from bio-based polymers such as (nano) cellulose or other carbohydrates like chitin or chitosane or lignin. In the latter case, an inorganic functional component – a metal oxide, is introduced to broaden the spectrum of their characteristics. Nano components are applied to exploit the large surface area, specific properties related to nano dimensions and nano confinement, and increase the load of active functions.

Application of different organic functions permits to address simultaneously different classes of water pollutants using a single column of a hybrid adsorbent [1]. The grafted ligand layer can be tailored to become highly specific, permitting to selectively separate different metal cations even with very close chemical properties [2]. Combining chelating functions with enzyme bio-catalysts it is possible to create materials for enzymatic water treatment very stable to presence of hazardous metal cations in solution [3]. Bio-based matrices open for fully biocompatible soft materials with prospects of application in bandages, drug delivery, and even soft tissue regeneration [4]. Even fully green materials for water purification process can be designed starting from natural mineral matrices or bio-polymers. Strong synergy can be obtained combining chemical and photochemical pathways in application of hybrid organic-inorganic materials.

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SENSITIZATION OF LANTHANIDE-BASED PHOSPHORS BY TRANSITION METALS TOWARDS HIGH-BRIGHTNESS AND SENSITIVE THERMOMETERS

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Keywords: luminescence thermometry, lanthanide ions, transition metal ions, high sensitivity

Although the applicative potential of lanthanide ions (Ln^{3+}) based luminescence thermometry has already been confirmed by many studies[1-3] the main limitations that reduced the accuracy of temperature readout of this type of temperature sensor is the relatively low emission intensity of Ln^{3+} ions resulting from the low absorption cross section of $4f-4f$ absorption bands and the low relative sensitivity of this type of luminescent thermometers. Therefore to address these issues co-doping with transition metal (TM) ions is proposed. During this talk, the strategy of sensitization of Ln^{3+} luminescence through $\text{TM} \rightarrow \text{Ln}^{3+}$ energy transfer will be proposed. It will be proved that by taking advantage of a much stronger absorption cross-section of TM with respect to Ln^{3+} the emission brightness of Ln^{3+} can be significantly enhanced. Moreover due to the lack of energetic resonance between excited states of TM and Ln^{3+} the probability of phonon-assisted $\text{TM} \rightarrow \text{Ln}^{3+}$ energy transfer reveals strong thermal susceptibility. Hence TM-co-doping has a beneficial influence on the relative sensitivity of Ln^{3+} based luminescent thermometers[4].

During this talk, the benefits of using TM as an Ln^{3+} luminescence sensitizer and the limitations of this strategy will be discussed using Cr^{3+} co-dopant as a case study.

Acknowledgements

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Oral talk

Pr-ACTIVATED GARNETS FOR OPTICAL THERMOMETRY

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Keywords: optical thermometry, garnets, Pr³⁺-luminescence

It has been recognized a long time ago that garnets allow for relatively long-wavelength (low-energy) 5d→4f luminescence of such ions as Ce³⁺ or Pr³⁺. This property led to important applications of garnet-based phosphors, among which is the generation of the yellow component in white LEDs. The relatively low-energy emitting levels of the two dopants are accompanied by their suitably positioned absorption bands. In garnets, the first 4f→5d absorption of Ce³⁺ is typically around 450 - 460 nm and in the case of Pr³⁺ it is about 270 - 280 nm. Hence, even Pr³⁺ can be easily excited with commonly offered light sources. Furthermore, the 4f→5d excitation bands are broad and intense as they result from allowed transitions. This translates into efficient excitation of Pr³⁺, which is important in thermometry.

Despite the 5d→4f luminescence, Pr³⁺ produces also two different emissions related to 4f→4f transitions. In the greenish blue part of the spectrum (and partly in red) luminescence resulting from the ³P₀→³H₄ transitions appear and in the red region ¹D₂→³H₄ luminescence is seen. Relative contributions of the three emissions of Pr³⁺ depend on quite a few factors, among which one should especially consider the host phonons energy, Pr concentration, the physical form of the phosphor (single crystal, (nano)powder, sintered ceramic, glass), and temperature. As always, the phosphor fabrication procedure, purity of the starting materials, and processing conditions (atmosphere, temperature, heat-treatment duration etc.) also affect the luminescence of the product.

The mentioned high efficiency of the excitation of Pr³⁺-activated garnets in a suitable spectral region we considered advantageous for thermometric purposes. Furthermore, we proved that some luminescent properties of Pr³⁺ in garnets can be tuned by employing bandgap engineering of the host lattice of the phosphor [1,2]. This can be done, for example, by mixing Al and Ga in different proportions in Y₃(Al,Ga)₅O₁₂:Pr phosphors. Higher content of Al enlarges the host bandgap allowing for the 5d→4f luminescence to be less susceptible to thermal quenching, while higher contents of Ga make the quenching possible at very low temperatures. We found such properties greatly useful in designing luminescent thermometers according to specific needs. In the presentation, this subject will be discussed in detail and experimental data and thermometric properties of some garnets activated with Pr³⁺ will be presented and discussed.

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NOVEL SYNTHESIS METHOD OF RUBIDIUM(I) AND EUROPIUM (III) CO-DOPED HYDROXYAPATITE NANOMATERIALS - POTENTIAL USE IN REGENERATIVE MEDICINE

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Keywords: Hydroxyapatite, rubidium ions, regenerative medicine

Nanotechnology gained great success in biological and medical fields as well as in chemistry sciences and physics. Through the innovative features like improved pharmacokinetics and pharmacodynamics, increased biocompatibility, minimized toxicity and targeting capacity, it makes new possibilities for personalized medicine.

Hydroxyapatites by their mechanical properties, biocompatibility and bioactivity are able to create strong bond with living bone tissue. Synthetic hydroxyapatites have highly developed specific surface and when incorporated in bone loss can induce osteoinductivity and lead to regenerative processes. They can be also used as a biomedical sensors through their properties to photostabilize the luminescence of rare earth ions [1]. Rubidium element is essential for human bone development but it is also known from its anti-depressant activity and moreover from anti-cancer properties [2,3,4].

In our research the structural and morphological properties of the obtained nano hydroxyapatite doped with rubidium and europium ions were determined by using XRD (X-ray powder diffraction) and TEM (transmission electron microscopy) techniques. The luminescence properties were evaluated by measuring the excitation and emission spectra. In the present study, we evaluated biocompatibility toward rat's red blood cells to exclude potential cytotoxic features of our compounds. Experimental *in vitro* bioactive properties of hydroxyapatite based nanoparticles doped with Rb⁺ and Eu³⁺ by using mouse osteoblast model, were established and discussed in detail as novel approach in the field of personalized medicine.

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ELEMENTAL ANALYSIS OF NANOPARTICLES AND SINGLE CELLS IN RELATION TO ADVANCED BIOLOGICAL MATERIALS

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Keywords: nanoparticle, single cell, ICP-MS, SP-ICP-MS

Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is a promising technique for nanoparticle analysis. It allows to obtain quantitative information on the number, size and size distribution of nanoparticles as well as the concentration of the ionic form of the examined element in the solution (an example shown on Fig 1).

The study of changes in nanoparticles in the environment requires the determination of a number of their physicochemical parameters (including size, metal concentration in ionic and NPs form, dissolution and agglomeration efficiency). Every of these parameters, until recently, would have required the use of a separate measurement technique, often with an extended stage of sample preparation. This confirms the attractiveness of the SP-ICP-MS technique as a tool for the potential high-throughput characterization of nanoparticles in various tested systems.

Another interesting technique, a modification of SP-ICP-MS, is single cell ICP-MS (SC-ICP-MS) Single cell ICP-MS (SC-ICP-MS) is a specific combination of two worlds – iuji of elemental analysis and biochemistry, which takes elemental analysis to a completely new level - the level of a single cell. The SC-ICP-MS allows to determine the content of a given metal in a cell, metal distribution in the cell population and the number of cells containing metal or metal nanoparticles and the number of nanoparticles per cell [1]. This technique requires a much smaller amount of sample (100–200 µL) compared to conventional methods.

A concentration of as little as 100 000 cells / mL is sufficient for the measurement. The specially designed spray chamber allows to obtain results after delivering the cells to the plasma. This chamber in combination with a high-performance nebulizer, effectively delivers undamaged cells to the plasma, and a dedicated autosampler transmits the sample at a very low, precisely controlled rate of 10–20 µL / min, which in practice translates into a very small sample volume needed for the analysis - 200 µL of the solution is sufficient to obtain the measurement results.

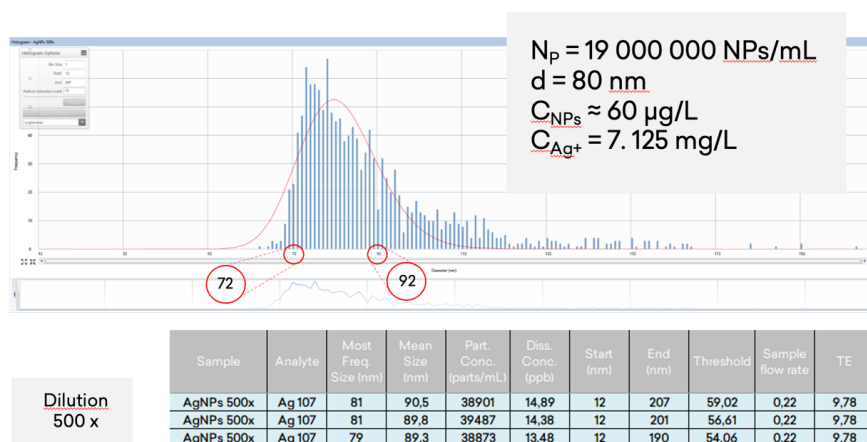


Fig. 1. Example of silver nanoparticle solution characteristics performed with SP-ICP-MS.

SPECTROSCOPIC INVESTIGATION OF BIOCOMPATIBLE BISMUTH(III) AND EUROPIUM(III) DOPED YTTRIUM ORTHOVANADATE-PHOSPHATE

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Metal-based materials are widely being developed for potential use in bio-imaging, theranostics, therapy, and biosensing. Furthermore, bismuth-rich compounds are currently applied in cosmetics, biomedicine, medicinal chemistry, and theranostics [1,2]. Bismuth compounds are used to treat *H. pylori* infections, chronic gastritis, peptic ulcers, and wound and burn dressings.

Yttrium orthophosphate and orthovanadate doped with optically active ions have potential applications as sensors, fluorescent labels, etc. [3,4]. In this work, these compounds are co-doped with europium(III) and bismuth(III) ions for two purposes. The first is to enhance the Eu^{3+} ion emission by facilitating energy transfers [5]. The second is to increase biocompatibility for their potential application in medical treatments or cosmetics.

Yttrium orthovanadate and orthophosphate crystalize in the zircon-type tetragonal system with the $I4_1/a$ space group [6,7]. These isostructural compounds can form a continuous solid-state solution of yttrium orthovanadate-phosphate ($\text{YV}_x\text{P}_{1-x}\text{O}_4$, where $0 \leq x \leq 1$). This study focuses on the investigation of luminescent properties of bismuth(III) and europium(III) co-doped $\text{YV}_{0.5}\text{P}_{0.5}\text{O}_4$. Additionally, their biocompatibility was investigated. Cytotoxicity assay toward L929, LOVO, and A549 cell lines confirmed full biocompatible properties of tested compounds, even in the highest tested concentration. Furthermore, the normal morphology of used cell lines was visualized via fluorescence microscopy and supported the cytotoxicity test. Therefore, obtained materials are suitable to use in the bio-imaging field.

Acknowledgments

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RESPONSE OF ZNO MICRO- AND NANO-CRYSTALS TO *STAPHYLOCOCCUS AUREUS* BACTERIA AND BACTERIAL GROWTH MEDIA

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Keywords: antibacterial, spectroscopy, Zinc Oxide, optoelectronics

Antibacterial action of micro- and nanoscale ZnO is well-documented and has been thoroughly studied in recent years. There are several prevalent hypotheses regarding the mechanisms by which ZnO inhibits bacterial growth, but the fundamental nature of interactions between ZnO and bacteria is still not well identified. In our studies, we investigated changes in morphology and optoelectronic properties of ZnO micro- and nano-crystals in response to ZnO interactions with *Staphylococcus Aureus* and various growth media. Such approach was designed to further elucidate the nature of mechanisms behind bacterial growth inhibition by ZnO and possibly other antimicrobials. In this work, minimum inhibitory concentration (MIC) assays of ZnO with *Staphylococcus Aureus* were utilized to monitor bactericidal dynamics; additionally, novel exposure assays were used to expose sub-MIC concentrations of ZnO to bacterial growth environments. Scanning electron microscopy experiments revealed significant changes to sample morphologies after exposure to bacteria and different growth media. Photoluminescence and surface photovoltage studies detected changes in electronic structure and near-surface charge dynamics resulting from these exposures.

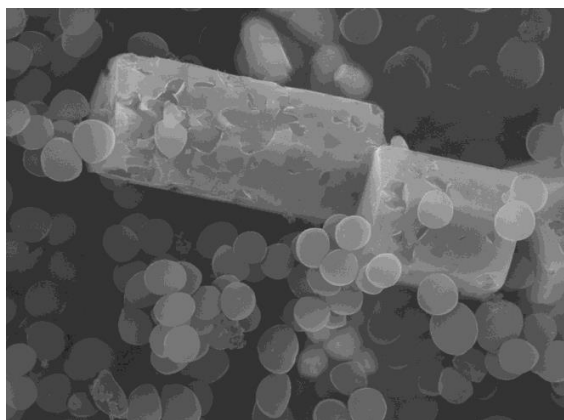


Fig. 1. Scanning Electron Microscope image of Staphylococcus Bacteria around ZnO micro-crystals

DECOMPOSITION OF LaPO_4 MICROPARTICLES IN GLASS MONITORED BY THE Eu^{3+} LUMINESCENT PROBE

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Keywords: direct doping, bioactive, glass, luminescent probe

The methods to directly introduce crystals of known chemistry, size, and optical properties in a glass matrix are useful to circumvent some limitation of growing crystalline phases in glass-ceramics[1,2].

The LaPO_4 : 10% Eu^{3+} (LP1) crystals were prepared by conventional solid-state method and were added and mixed into the glass melt before quenching them on the brass plate. The studied set of glasses comprised of bioactive systems P_2O_5 -CaO-SrO- Na_2O (Si-0) with addition of 5% of SiO_2 (Si-5) or 5% of B_2O_3 (B-5) and NaPO_3 – NaF/ CaF_2 . The glasses were chosen based on their wide range of T_g and reactivity. The emission spectrum of LP1 is characteristic for highly symmetrical coordination of Eu^{3+} and very distinct from the emission spectrum of Eu^{3+} in amorphous host, which, along with XRD and EDS methods, has been used to determine the state of the crystals embedded in the glass.

The SEM/EDS results indicate that the crystals form clusters of $\sim 50\ \mu\text{m}$ in diameter and do not dissolve as they keep their chemical composition. However, the XRD and luminescence results suggest that the highly symmetrical crystal structure is maintained only for samples Si-0 and NaPO_3 -NaF, where the R parameter (ratio between the electric and magnetic dipole-type transitions) is close to the one of as prepared crystals and the XRD results show peaks matching to the LaPO_4 pattern. The rest of the glasses exhibit no peaks on XRD diffractograms and luminescence characteristic for Eu^{3+} in amorphous host. The decomposition of the LP1 crystals does not correlate with the melting temperature but does correlate with the depolymerization of the phosphate chains and more rigid glass network.

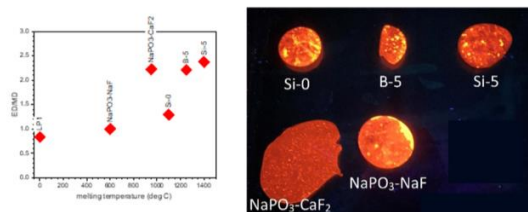


Fig. 1. The R parameter (left) of the samples, photographs of glass samples under UV excitation (right).

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FOLIAR FERTILIZATION BY THE SOL-GEL PARTICLES CONTAINING Cu AND Zn

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Keywords: foliar fertilization, sol-gel particles, Cu, Zn

Plants are the main source of food for humans. It is estimated that by 2050 there will be 9.7 billion people in the world [1]. Hence, it is essential to increase plant production to feed the world's growing population. Plants absorb macro- and micronutrients from fertilizers but most conventional chemical fertilizers are characterized by poor utilization and uptake efficiency due to the loss of fertilizer caused by leaching and volatilization [2]. Foliar fertilizers may be more environmentally friendly and target oriented way for plant nutrition than soil fertilization [3].

Silica particles containing Ca, P, Cu or Zn were synthesized by the sol-gel method and tested as a new and innovative fertilizers for foliar application. Three plant species: maize *Zea mays*, wheat *Triticum sativum* and rape *Brassica napus* L. var *napus* growing on two types of soils: neutral and acid, were examined.

The aqueous suspensions of the tested particles were sprayed on the chosen leaves and also on the whole tested plants. At a specific stage of development determined according to the BBCH scale, the leaves and the whole plants were harvested and dried, and with the AAS method, the content of Cu and Zn in them was determined. The concentration of Cu in the sprayed leaves and leaves of the sprayed plants was higher compared to the content of these components in the leaves of the control plant. Cu accumulates more in the leaves, low amount of Cu was observed for the all sprayed maize and rape. Zn showed different behavior. For the maize cultivated in acid soil, the higher Zn content was observed in the whole sprayed plant than in individual sprayed leaves. For the rape the amount of Zn in sprayed leaves and the all sprayed plant are comparable. No significant differences were observed in the Cu or Zn content provided as a suspension of SiO₂ particles containing Cu or Zn respectively, and an aqueous solution of copper or zinc sulfate (0,1%), which contain metals in the ion form. Generally a greater amount of studied micronutrients Cu and Zn was observed in the plants growing in acidic soil than in neutral soil. All SiO₂ particles tested as a foliar fertilizers were characterized by SEM and EDX.

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BIOACTIVE AMINOPHOSPHINE COORDINATION NETWORKS: SYNTHESIS, CHARACTERIZATION AND ENHANCED ANTIMICROBIAL ACTIVITY

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Keywords: antimicrobial materials, coordination polymers, bioactive MOFs, silver, aminophosphine ligands

Bioactive silver(I) metal-organic frameworks (bioMOFs) and coordination polymers (bioCPs) represent a fascinating group of materials characterized by versatility, complexity, and diverse biological properties. In general, the physical and biological properties of such compounds depend on coordination geometry, lipo- and hydrophilicity, number and type of bioactive organic building blocks. Among a wide range of multidentate ligands, cage-like aminophosphine ligands such as PTA (1,3,5-triaza-7-phosphaadamantane) and its various derivatives stand up as particularly attractive building blocks due to several reasons, including water solubility, air stability, and rich connectivity [1,2].

In this work, our recent examples of new biologically active Ag(I)-based bioMOFs and bioCPs driven by PTA and carboxylate linkers will be highlighted, showing their design, synthesis, full characterization, and structural features. Selected examples will be presented in terms of their diverse utility and potential applications as bioactive materials with remarkable antimicrobial and antiviral properties.

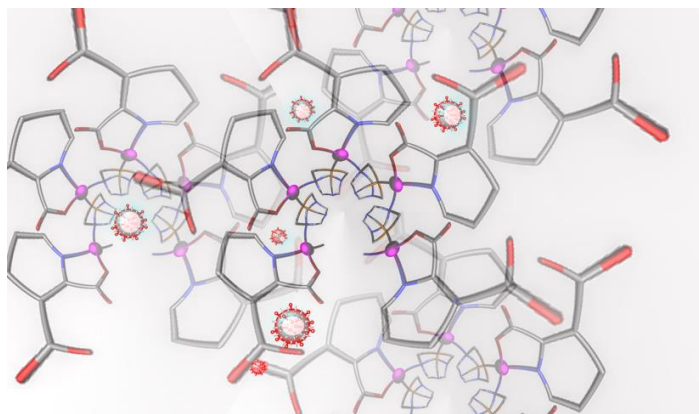


Fig. 1. Antiviral silver(I) quinolate coordination polymer.

Acknowledgments

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BIOACTIVE METAL-ORGANIC NETWORKS FOR ANTIMICROBIAL APPLICATIONS

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Keywords: metal-organic frameworks, coordination polymers, antimicrobial materials, biopolymers

This presentation will highlight our recent research on the self-assembly synthesis, crystallization methods, structural features and applications of a wide diversity of functional metal-organic architectures, including bioactive metal-organic frameworks (bioMOFs), coordination polymers (bioCPs) and derived materials with potent antimicrobial properties.¹⁻³ The following topics will be discussed:

- (1) Self-assembly generation and structural diversity of silver(I) and copper(II) coordination polymers derived from carboxylic acids, aminoalcohols and/or aminophosphines.
- (2) Application of these compounds as efficient antimicrobials against different types of Gram-positive and Gram-negative bacteria, and bacterial biofilms.
- (3) Design of bioCP-doped polymer films, based on epoxidized soybean oil acrylate (ESOA) or potato starch (PS) as model biopolymer materials.
- (4) Antibacterial and biofilm inhibition activity of the obtained biopolymer films as a function of bioCP dopant type and loading, biopolymer matrix, and metal ion release rates (Fig. 1).

This multidisciplinary study expands antimicrobial use of bioactive coordination polymers and hybrid biopolymer materials obtained from renewable biofeedstocks such as soybean oil and potato starch.

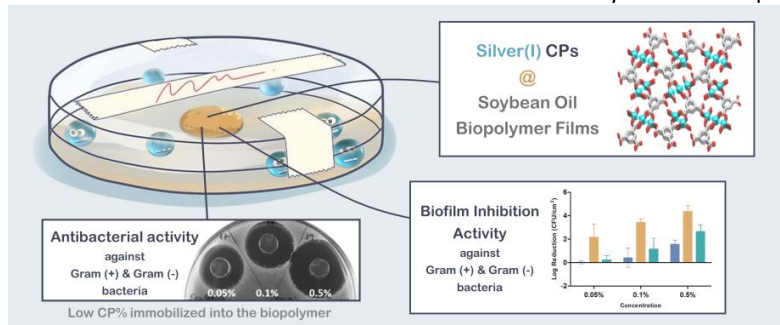


Fig. 1. Antimicrobial bioCP-doped Biopolymer Films.

Acknowledgments

We thank the FCT (PTDC/QUI-QIN/29697/2017, LA/P/0056/2020, UIDB/00100/2020, Portugal) and National Science Center (Grant No. 2019/35/D/ST5/01155, Poland) for financial support.

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CHALLENGES IN STUDYING NANOMATERIALS AS ANTIBACTERIAL AGENTS

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Keywords: antibacterials, resistance, nanomaterials, silver nanoparticles

The issue of resistance to antibacterial agents concerns subjects of both medical treatment (resistance to therapeutics) and disinfection (resistance to products used in industry, households and hygiene). Nanotechnology provides alternative antibacterial agents and new carriers for agents already in use. Research shows that it can be effective against resistant bacteria, even those multi-drug resistant as carbapenem-resistant *Acinetobacter* strains or various Enterobacteriaceae family members, listed by CDC among currently urgent threats in healthcare [1, 2, 3].

However, bacteria can possibly adapt to novel nano-sized formulations of substances. Their ability to resist new agents lies in their high variability and wide range of stress responses, as we have already observed in the case of silver nanoformulations [4, 5]. Therefore, identifying those nanomaterials that are initially effective but fail shortly after deployment may be an essential step in the development of antimicrobial nanomaterials. Even a detailed characterisation of the physicochemical properties of nanomaterials does not make it possible to determine a priori what their bactericidal mechanism is and what type of resistance can be expected.

An available solution is to utilise a lab-scale adaptation experiment, exposing bacteria chronically to nanomaterials. It is possible to mimic an evolutionary process of adaptation and trace bacterial susceptibility changes in time [6]. Gaining knowledge in this way appears to be an essential step towards enabling theoretical modeling of the phenomenon of nanomaterials resistance, as is being done in the case of antibiotic research [7, 8].

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Cr³⁺-DOPED GdAl₃(BO₃)₄ BORATES AS AN EFFICIENT TOOL IN LIGHT-TO-HEAT CONVERSION

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Keywords: Cr³⁺ ions, borates, nanoheaters, heat generation

Nowadays, a remarkable advances made in the field of nanotechnology have contributed to the development of many specialized measurement, sensing and diagnostic techniques [1-4]. One of the examples especially significant for biomedical applications could be targeted therapy like photothermal therapy (PTT) frequently called hyperthermia of tumors that enable in vivo treatment of cancerous tissues [5-6]. For this purpose, nanoparticles that have the ability to convert incident light into heat are involved, causing local overheating and destruction of the affected tissues. However, the effectiveness of the heat generation process depends strongly on the kind of used photothermal agent. In the literature could be found many works about effective heat generation in Ln³⁺-doped nanomaterials [7]. But, in case of lanthanide ions could be encountered a limiting factor which is low absorption cross-section. For this reason, a new approach in light-to-heat conversion that involves powders doped with Cr³⁺ ions was proposed in presented research. The choice of transition metal ions was dictated by the fact that they possess a larger cross-section for absorption than lanthanides ions. Hence, transition metal ions could be able to absorb much more energy, which as an effect of nonradiative relaxation is released in the form of heat. Therefore, materials doped with transition metal ions will be more efficient heaters than those based on lanthanide dopants. The main purpose of this work is to verify the influence of the selected high phonon energy host matrix and Cr³⁺ dopant concentration on the efficiency of light induced heat generation.

Acknowledgements

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INVESTIGATION OF MICRO AND NANOSTRUCTURE OF VARIOUS TYPE OF BONE SUBSTITUTED MATERIALS

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Keywords: bone reconstruction, bone nanostructure, allografts, xenografts, processed tooth

During our live people are unfortunately exposed to the list of diseases and accidents. As a result of lots of those live situation our bone maybe lost and the reconstruction can be necessary. Successfully, the surgical field of science offers a numbers various methods of bone reconstruction procedures. In recent years an industry of biomaterials has been expanded quickly. Commonly known are the autogenic procedures, allogenic graft material, xenografts and alloplastic materials. All of them are used for the different examples because of a differences between their structure and properties [1,2].

From the materials construction point of view bone structure is a composition of an inorganic phase (apatite) located in an organic matrix (collagen fibers). Those two phases are organized with highly hierarchical structure. From the nanoscale, the apatite crystals are surrounded with collagen fibril. On the next level the collagen fibers are rolled up into osteons which form Haversian canals.

The presented study includes five bone-substituted materials: three allografts from biobanks, one xenogenic bone graft and the processed tooth. Between the bone grafts characterized by different origin are observed a physical-chemical differences. A list of measurements technics were used to determine the nanostructure of various material. The list includes x-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FT-IR) as well as scanning electron microscopy (SEM).

The main goal of bone grafts nanostructure investigation is to explain the differences on the bone rebuilding process after using the various materials. It is important to understand the mechanism of healthy bone structure reconstruction. We hope, those knowledge will be helpful to the surgeons to make a decision, which material is dedicated for specific kind of reconstruction.

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SYNTHESIS AND APPLICATION OF NaYF_4 NANOPARTICLES AS NANOHEATERS AND LUMINESCENT NANOTHERMOMETERS

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Keywords: luminescent nanothermometry, light-to-heat conversion, transition metal ions

Photothermal therapy [1] is a local treatment method that uses nanoparticles, which absorb energy and converts it into heat after stimulation with electromagnetic radiation. In photothermal therapy, temperature is a critical parameter, and it must be precisely controlled to destroy cancer cells and to prevent overheating of healthy cells. Therefore, it is of vital importance that temperature is measured with a spatial sub-micron resolution. The possibility of such a precise reading and temperature regulation is possible thanks to luminescent nanothermometers [2]. This technique enables contactless temperature reading by using nanoparticles showing luminescence after excitation by laser beam. Therefore, combining these two functionalities, i.e. light-to-heat conversion and luminescence thermometry into a single system particle present significant advantages for targeting therapies. However, the combination of these two techniques is a great challenge both in terms of synthesis and instrumentation so that much effort is still needed to obtain a material that meets all these requirements.

In view of the above, the present work is undertaken to synthesize biocompatible LNPs acting as: a nano-heater and a luminescent nanothermometer in a single system. The research conducted will enable the analysis of multifunctional $\text{NaYF}_4:\text{Cr}^{3+}, \text{Nd}^{3+}$ nanocrystals for light-induced heating and real-time temperature monitoring and their application potential will be discussed.

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DISSECTING THE ROLE OF PROLYL OLIGOPEPTIDASES IN CELL DEATH BY THE APPLICATION OF PROTEASE-SELECTIVE PRODRUGS: FROM BASIC RESEARCH INTO NEW ANTICANCER THERAPEUTIC STRATEGIES.

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Keywords: cell death, pyroptosis, prolyl oligopeptidase, prodrugs

Regulated cell death is a key process during which dangerous or nonfunctional cells are removed from an organism to maintain its homeostasis. To date the best characterized type of cell death is apoptosis, which being immunologically silent is a suicidal cell death as a result of caspases activation. In contrast to apoptosis, pyroptosis is highly inflammatory cell death. This process is triggered by various external stimuli including viral and bacterial infection, or by microparticles such as alum, or silica. Such infections result in the cell blebbing, membrane rupture, and the leakage of the cellular content into the external environment. In pyroptosis, viruses and bacteria induce the innate immune reaction, and the microparticles can lead to multiple diseases, including life style diseases. Given that it is of special importance to dissect the molecular mechanisms underlying pyroptosis, which could be further beneficial for the development of efficient treatment. Recently, it was demonstrated that pharmacological inhibition of prolyl proteases in cancer cells triggers pyroptosis, which is against long-standing dogma that these enzymes are key players in apoptosis. To better understand this pleiotropic function of prolyl oligopeptidase, we profiled its substrate specificity using combinatorial libraries of fluorescent substrates, and developed prodrugs that are selectively activated by this enzyme. Our approach might shed a light on the bidirectional role of prolyl oligopeptidases in cell death process.

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Pr³⁺-DOPED NaYF₄ AND LiYF₄ NANOCRYSTALS COMBINING VISIBLE-TO-UVC UPCONVERSION AND NIR-TO-NIR DOWNCONVERSION FOR BIOMEDICAL APPLICATIONS

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Keywords: lanthanides, nanoparticles, UVC, upconversion, downconversion, imaging

Lanthanide-doped fluoride nanocrystals are known to exhibit optical properties of much interest to biological applications such as photon upconversion (UC) and downconversion (DC) which are useful for both imaging and photoactivated processes such as sterilization. Efficient near infrared (NIR)-to-visible (VIS), NIR-to-NIR and VIS-to-ultraviolet (UV) UC, as well as NIR-to-NIR or VIS-to-NIR DC processes occurring in those materials have proven application potentials for photo-activation processes[1], sensing[2] and imaging[3].

Herein, we report, for the first time, the possibility to merge VIS-to-UVC UC with NIR-to-NIR DC processes occurring in Pr³⁺ and Yb³⁺ co-doped nano-scale materials. Such materials, exhibiting the desired bimodal optical features, should allow for efficient germicide action with simultaneous imaging possibilities. In particular, we report the synthesis of series of NaYF₄ and LiYF₄ NCs co-doped with Pr³⁺ and Yb³⁺ and further demonstrate the VIS(447 nm)-to-UVC (ca. 275 nm) UC photoluminescence. At the same time, these materials provide NIR-I (980 nm)-to-NIR-II DC PL (peaked at ca. 1320 nm). Thus, both damaging DNA and RNA of targeted microorganisms and viruses and imaging in the are possible. As a proof-of-concept, we demonstrate degradation of DNA caused by UVC emission generated by Pr³⁺/Yb³⁺ doped NCs excited with 447 nm laser. Along with that, a NIR-II DC PL imaging capability of these NCs is also demonstrated, both in steady-state and time-gated imaging modes.

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OPTICAL CHARACTERIZATION OF SURFACE-MODIFIED GOLD NANOSHELLS

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Keywords: gold nanoshells, surface functionalization

Plasmonic nanoshells have attracted significant interest due to their resonant optical properties providing excellent spectral tunability, promising for various biophotonic applications. In this work we discuss our experimental and theoretical results related to the synthesis and optical characterization of surface-modified gold nanoshells (Fig. 1).

Numerical simulations provide further insight into the plasmon resonances (electric dipole and electric quadrupole) contributing to the optical extinction spectrum, as well as into the effect of structural nonuniformity of the gold layer on these resonances. This includes local field enhancements in plasmonic hot spots, which are shown to reach a factor of ~ 10 times in completed NSs, boosted up to ~ 100 times in uncompleted NSs. [1]

The described properties of uncompleted NSs could be of interest in the context of photothermal therapy and sensing applications in biology and medicine, motivating further research on gold nanoshells and their appropriate functionalization.

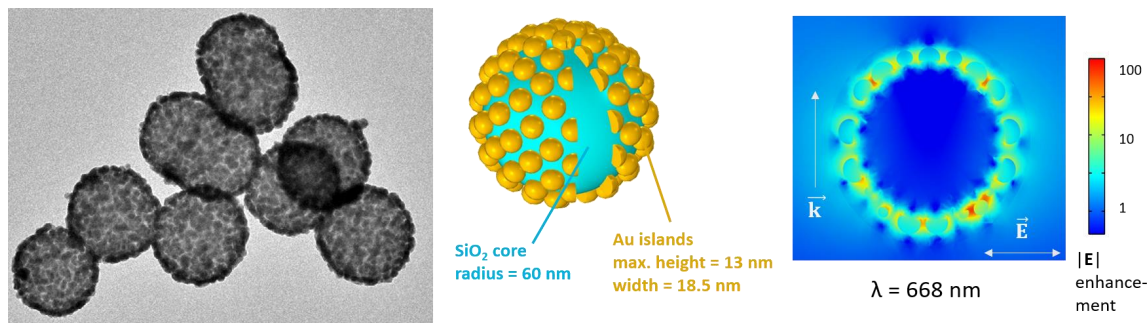


Fig. 1. TEM pictures of uncompleted gold nanoshells (left). Schematic illustration of the geometry assumed in the model for the uncompleted nanoshells (center). Calculated electric field distributions (plotted in logarithmic color scale) near the resonance peaks (right).

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PROTECTION OF POLYMERIC MATERIALS WITH SOL-GEL COATINGS FOR THE REDUCTION OF PLASTIC WASTE

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Keywords: protective coatings, sol-gel method, silica-titania, organically modified, polyethylene terephthalate

One of the biggest ecological problems of nowadays world is a huge amount of plastic waste, which has a very long degradation time. Plastic production in the last years is growing exponentially [1]. Even though increasing actions in field of materials segregation and recycling have been made, the plastic waste problem is a global crisis. Moreover, the recycled polymeric materials exhibit reduced quality in comparison to virgin plastics and the purification of polymeric waste, which can contain different types of contaminants and processing additives, is technologically challenging [2]. Alternatives to polymeric materials recycling are inter alia incineration or using biodegradable plastics, however, all the options have different disadvantages. The incineration of plastics produces energy, but during this process, a lot of harmful pollution is released [2]. Biodegradable polymeric materials are, whereas, characterized by reduced mechanical and thermal stability and poor barrier properties in the relation to the costs [3]. In this work, we propose an alternative method, which could be used for the reduction of plastic waste production. By modification of PET (polyethylene terephthalate), which is one of the most commonly used polymeric materials, with organically functionalized SiO₂-TiO₂ coating, the protection against the deterioration of its most crucial properties has been revealed [4]. A reduction of various temperatures effects on the shape deformation, transparency and mechanical properties deterioration, by the proposed coating is presented in this work. The use of such protective coatings allows the enhancement of products life expectancy and thus reduction of the frequency of plastic elements replacement.

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SYNTHESIS AND STRUCTURAL PROPERTIES OF NOVEL $\text{Ln}_4\text{O}_3\text{F}_6$ ($\text{Ln} = \text{Ce-Yb}$) OXYFLUORIDES

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Keywords: oxyfluorides, nanomaterials, bio-imaging

The novel inorganic materials designed to work as bio-imaging phosphors or sensors for luminescence thermometry are mostly prepared in nanoscale. In recent years huge effort has been put on synthesis and characterization of different kind of nanophosphor – oxide, fluoride, nitrides, etc.. Also materials belonging to $\text{Ln}_2\text{O}_3\text{-LnF}_3$ family has been studied, but to the best of our knowledge, there are only few reports on spectroscopic $\text{Ln}_4\text{O}_3\text{F}_6$ group and all of them treat on $\text{Gd}_4\text{O}_3\text{F}_6$ oxyfluoride co-doped with different rare earth ions. It is known that other lanthanides can be part of the matrix, therefore studying their properties and its influence on energy transfer mechanism between optically active rare-earth dopants is worth investigating, because of its potential use in such applications like bio-imaging or temperature sensing.

The series of materials were manufactured through microwave-stimulated hydrothermal method. The XRD patterns of prepared $\text{Ln}_4\text{O}_3\text{F}_6$ were measured. Since theoretical pattern is available only for $\text{Gd}_4\text{O}_3\text{F}_6$ it can be seen that this sample is pure. However, knowing that lanthanide series should be isostructural, some conclusions can be made. Only for the $\text{Ce}_4\text{O}_3\text{F}_6$ sample other phase is achieved. For the rest of prepared samples diffraction patterns are very similar and are shifting with increasing the lanthanide ion size therefore it can be supposed that these samples have the $\text{Ln}_4\text{O}_3\text{F}_6$ structure.

For selected samples ($\text{Ln} = \text{Pr, Eu and Yb}$) SEM micrographs were made. As can be seen in Fig. 1 the morphology of these materials is different. $\text{Pr}_4\text{O}_3\text{F}_6$ oxyfluoride has square rod-like shape with about 0.7 μm length and up to 100 nm in cross-section. There are also smaller grains with dimensions below 100 nm. $\text{Eu}_4\text{O}_3\text{F}_6$ sample has shape of rice grains, but they are much bigger than $\text{Pr}_4\text{O}_3\text{F}_6$ – average length is 3.3 μm , while average diameter 1.2 μm . Finally $\text{Yb}_4\text{O}_3\text{F}_6$ oxyfluoride has shape of broken sticks or splinters with average length 18.4 μm and average cross-section 1.9 μm . The common feature of all measured samples is prolongation in one direction.

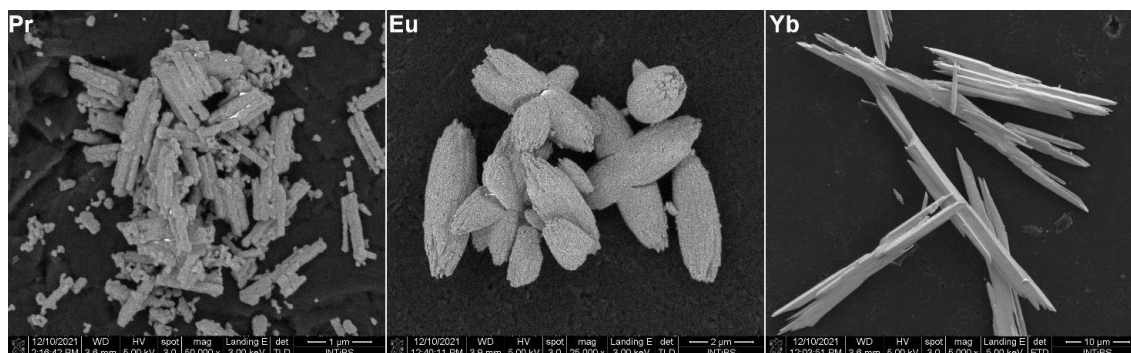


Fig. 1. SEM micrographs of $\text{Pr}_4\text{O}_3\text{F}_6$ (left), $\text{Eu}_4\text{O}_3\text{F}_6$ (center) and $\text{Yb}_4\text{O}_3\text{F}_6$ (right).



Short communication

AN IN VITRO EXAMINATION OF FLUORIDE IONS RELEASE FROM SELECTED MATERIALS - RESIN - MODIFIED GLASS IONOMER CEMENT (VITREMER) AND NANOHYBRID COMPOSITE MATERIAL (TETRIC EVOCERAM).

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Keywords: fluoride ions release, nanohybrid composites, resin-modified glass ionomers, tooth decay prevention

The aim of this study is to examine a short-term fluoride ions release from selected materials - resin-modified glass ionomer - Vitremer (3M ESPE) and nanohybrid universal composite - Tetric EvoCeram (Ivoclar Vivadent). Release of fluoride ions ($\mu\text{g}/\text{mm}^2/\text{h}$) from Tetric EvoCeram and Vitremer into nine environments (artificial saliva, deionized water and 0.9 % NaCl) differing in composition of the solution and pH was determined. Six samples were prepared for each solution. In the short-term study the measurements were taken after 1, 3, 24, 48, 72, 168 hours. The cumulative values as well as levels of fluoride ions released at concrete time intervals were compared. Within 7 days (168 hours) both materials showed variable level of fluoride ions release. The highest value of fluoride ions release from nanohybrid Tetric EvoCeram material was reported in deionized water (8) after 24 hours (1.550 ± 0.014 ($\mu\text{g}/\text{mm}^2/\text{h}$)) and the lowest value was read in AS pH 7.50 (5) after 1 hour (0.022 ± 0.001 ($\mu\text{g}/\text{mm}^2/\text{h}$)). What's more the highest value of F⁻ release from Vitremer was found in deionized water (8) after 168 hours of immersion (24.021 ± 2.280 ($\mu\text{g}/\text{mm}^2/\text{h}$)) and the lowest value was in AS without CaCl₂ pH 4.5 (6) (0.303 ± 0.249 ($\mu\text{g}/\text{mm}^2/\text{h}$)). Cumulated release of F⁻ after 7 days was significantly bigger from resin-modified glass ionomer material - Vitremer in AS, which imitates the environment of oral cavity. Therefore, we can assume that Vitremer has better remineralization potential and it will constitute more effective method of tooth decay prevention.

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SYNTHESIS, CHARACTERIZATION AND BIOACTIVITY OF GLASSES (SiO₂–CaO) WITH DIFFERENT SIZES

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Keywords: bioactive glass, biomaterial, hydroxyapatite, bioactivity

Bioglass® 45S5, produced by Larry Hench, is the first example of bioactive glass that has a strong bone-binding capability and can therefore be used in orthopaedics and dentistry [1]. Currently, new materials based on bioactive glass are continuously developed to meet clinical requirements. Since their size, chemical composition, and porosity strongly influence bioactivity, thus the synthesis process is crucial. Bioactive glasses are usually produced using the traditional melting process or the sol–gel method [2]. By adjusting sol–gel processing parameters, the physicochemical properties such as particle size of glasses or specific surface area may be controlled.

Drawing the potential, the aim of our study was to develop the synthesis of highly bioactive glass in a binary system using calcium hydroxide as a precursor. Furthermore, the goal was to determine the effect of particle size on bioactivity. Sol–gel synthesis allowed to obtain four amorphous glasses named: A_75S, B_78S, C_75S and D_90S. The bioactivity of newly synthesized glasses was examined *in vitro* in Dulbecco's phosphate-buffered saline (DPBS) by monitoring the formation of hydroxyapatite on the glass surface during a different time of incubation. The composition, structure, and morphology of the powders before and after incubation were characterized using various techniques such as: DLS, EDS, XRD, IR-ATR, TEM or SEM microscopy (Fig. 1), and N₂ sorption (77 K). The potential bioapplication was determined by biocompatibility tests using fibroblasts (HDF) and osteoblasts (MC3T3) as model cell lines.

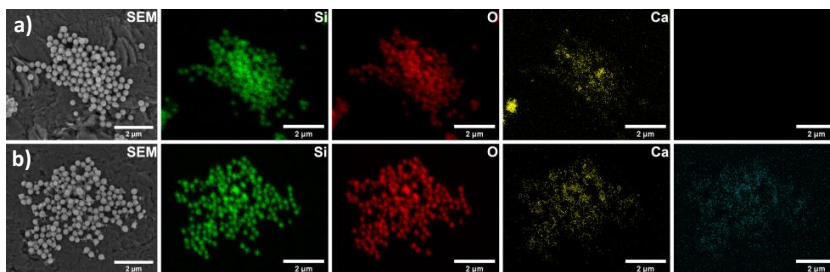


Fig. 1. SEM images and EDS elemental mapping of Si, O, Ca and P before (a) and after 21 days of incubation in DPBS for sample D_90S.

The research was performed within projects 2016/22/E/ST5/00530 and 2019/36/D/ST5/00243 of the National Science Center.

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Posters

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Lp	Name	Title
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P-22	Justyna Rewak- Soroczyńska	ANTIPSEUDOMONAL ACTIVITY OF NANOHYDROXYAPATITES DOPED AND CO-DOPED WITH Cu ²⁺ AND Eu ³⁺ IONS OBTAINED VIA CO-PRECIPITATION AND HYDROTHERMAL METHODS
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P-32	Michał Biały	PROSPECTIVE Zr-BASED BULK METALLIC GLASSES AS ADVANCED MATERIALS FOR NEW GENERATION IMPLANTS AND SURGICAL TOOLS
P-33	Adam Strzęp	ERBIUM DOPED CaF ₂ -SrF ₂ CRYSTALS FOR ~3 μM LASER

MULTIMODAL POLYMER ENCAPSULATED NANOPARTICLES WITH IMPROVED BIOCOMPATIBILITY FOR TWO-PHOTON AND TEMPERATURE STIMULATED BIOAPPLICATIONS

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Keywords: quantum dots, ferrite, encapsulation, nonlinear optics

An important issue to address in nanomaterials in bio-related applications is the lack of their multimodality and hydrophobicity.[1] That is why, we have focused on nanostructures offering multifunctional features in single nanomaterial dispersible in water. An nanoemulsification/solvent-evaporation approach was used to co-encapsulate two different hydrophobic nanocomponents i.e.: semiconductor CdSe quantum dots (QDs) and magnetic Fe₃O₄ nanoparticles (NPs) in order to combine the features of both nanostructures within single multimodal core-shell nanocapsules (NCs).[2] As a result, colloidal NCs exhibiting dual one- and two-photon induced luminescence and magnetic properties were obtained, whereas encapsulation process allowed transfer of both hydrophobic nanostructures (QDs and NPs) into an aqueous environment. Transmission electron microscopy (TEM), X-ray scattering technique, and energy dispersive X-ray analysis (EDX) were used to comprehensively characterise the morphology of NCs. Upon UV excitation, NCs show one-photon induced visible emission, while upon near-infrared fs laser excitation two-photon induced visible emission was detected. It was evidenced that the presence of strongly absorbing magnetic Fe₃O₄ NPs does not significantly influence the luminescence properties of co-encapsulated CdSe QDs. Additionally, applying an 808 nm laser stimulation and/or an alternating magnetic field (AMF) result in temperature increase of the NCs. Moreover, cytotoxicity studies reveal the safe potential of using the high concentration of NCs in potential medical applications. This study explores, for the first time, using the CdSe/Fe₃O₄ co-loaded NCs as a multifunctional agent for bioimaging and hyperthermia-based anti-cancer treatments.

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NEW Ca-MOF/GLASS COMPOSITE AND ITS BIOAPPLICATION POTENTIAL

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Keywords: bioactive glass, biocompatibility, MOF, composite

The Bioglass® 45S5, created by Larry Hench in the 1970s, is the first example of bioactive ceramics that has the ability to bond with bones and soft tissues, thus the material offers many perspectives for its use in implantology or tissue engineering [1]. To increase the functionality of biomaterials, materials chemistry is developing towards the synthesis of composites with greater application possibilities.

Following this topic, combining the properties of bioactive glass (SiO₂–CaO) and Ca-based Metal-Organic Framework (UTSA-280) [2], a new type of composite was obtained. Ca-MOF/glass was prepared based on facile and green mechanochemical synthesis.

The newly obtained composite was characterized structurally, spectroscopically, and texturally using many techniques such as XRD, IR, TG, CO₂ sorption analysis, SEM and TEM (Fig. 1). The bioactivity was assessed during incubation of the material in simulated body fluid (SBF) at 37 °C for 21 days. The MOF component did not decrease the biocompatibility of the bioactive glass, which was confirmed against human dermal fibroblasts (HDF) and mouse osteoblast precursor cells (MC3T3).

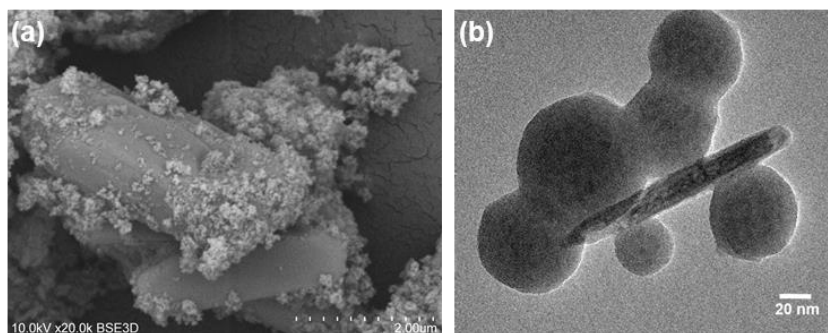


Fig. 1. SEM of Ca-MOF/glass (a) and TEM of Ca-MOF/glass with hydroxyapatite (b) formed after 7 days of incubation in SBF.

Acknowledgements

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STRUCTURAL CHANGES OF ZGO:Cr³⁺ NANOPOWDERS AND THEIR EFFECT ON THE PERSISTENT LUMINESCENCE

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Keywords: ZnGa₂O₄:Cr³⁺ spinel, persistent luminescence, antisite defects, Raman markers

Luminescent markers specific to cell components and external factors (pH and temperature) are widely used in modern biological and medical research. One of these promising markers is persistent nanophosphors (PersL NP) with emission in the "biological window" range [1]. One of the most promising PersL NP with emission in the NIR region is ZnGa₂O₄:Cr³⁺ [2].

In this work, we present ZnGa₂O₄ doped with 0.5% Cr³⁺ synthesized using the hydrothermal method and subsequently calcinated at 650, 750 and 850 °C. The Raman band centred at around 670 cm⁻¹ can be assigned to the A_{1g} symmetric stretching vibration of the Zn-O bonds in the [ZnO₄] tetrahedral site which is characteristic of the inverse spinel (Zn₂MO₄). The two maxima at around 70 °C and 140 °C, observed in the TL curves, are due to Zn_{Ga} and Ga_{Zn} anti-site defects [3] and to oxygen vacancy defects [4], respectively. Thus, the correlation between the degree of inversion (band A_{1g}^{*}) and the available traps (evolution of the band at around 140 °C) can be argued (Fig. 1).

The structural changes and their effect on persistent luminescence will be discussed in detail. In addition to the study of Raman modes of the investigated NP, Raman spectra of NP in the presence of biological molecules will also be discussed.

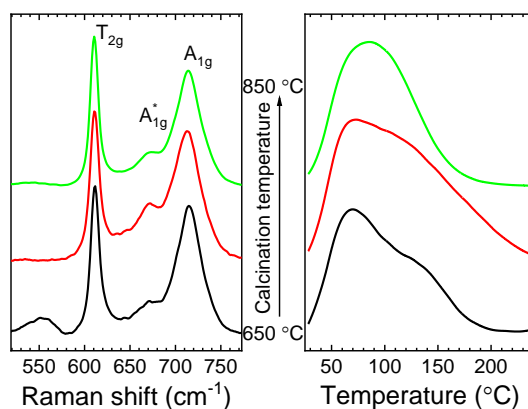


Fig. 1. Raman spectra and TL curves of the ZGO:Cr as a function of calcination temperatures

Acknowledgement: This work was supported by OPUS 11 2016/21/B/ST5/02385

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3D RECONSTRUCTION PECULARITIES OF SCANNING ELECTRON MICROSCOPY IMAGES: ADIPOSE TISSUE

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Keywords: 3D reconstruction, SEM, biological tissue, adipose

3D surface reconstruction of SEM images using stereo-photogrammetry has been introduced a long time ago, but only in recent years it started receiving more interest. The same workflows could not be easily applied on SEM micrographs since different nature of images. In the present study three different ways to obtain 3D view of SEM images of biological tissue by using only free available software were demonstrated.

The adipose samples were taken from volunteer patients at the Department of General Surgery of Vilnius University Hospital. Men and women aged 18–65 years with a BMI more than 30 kg/m² were enrolled in the study. The study protocol was approved by the Lithuanian Ethics Committee. Adipose tissue samples were stored in –70 °C temperature before the chemical analysis was performed. The adipose tissue samples were homogenised and extracted using a modified Folch extraction procedure. Morphology of adipose tissue samples were evaluated by field emission scanning electron microscopy (FE-SEM, SU70, Hitachi) equipped with the energy dispersive X-ray spectrometer, and the spectrometer was controlled by the INCA software (Oxford Instruments) or by Hitachi TM3000 and Helios NanoLab 650 instruments. The database of SEM images of the adipose tissue taken from 3 layers of adipose tissue (subcutaneous, preperitoneal and visceral) was collected (Fig. 1) [1]. There were compared three different techniques approaches to obtain 3D view of adipose tissue engaging only the freely available software: Stereoscopic view, Interactive 3D Surface Plot plugin for Fiji and Extrapolation of spatial data.

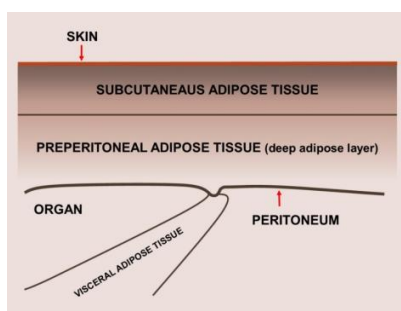


Fig. 1. A schematic diagram of adipose tissues in human body [2].

The 3D reconstructed model by VisualSFM and MeshLab free available software gave the best and the most promising results.

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NEW SUN-LIKE WHITE LIGHT EMISSION SOURCE FOR BIOLOGICAL APPLICATION

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Keywords New light emission source; White light emission; Up-conversion; Intervalence charge transfer

The laser-diode-driven white light-emitting source has received much attention in recent years due to its high efficiency, brightness, and lifetime. One of the most popular sources of white light is light-emitting diodes (LEDs). However, the emission spectra for LED family are characterized by a strong power peak at 450 nm and, at the same time, absence of intense emission in the red part [1]. The use of a novel NIR laser-driven white light emission (LIWE) source may offer another possible route to construct laser-driven light. Despite the fact that the overall efficiency might be lower compared with LEDs, this NIR LIWE source offers obvious advantages, such as tunable color temperature, which depends only on excitation density. This discovery was interesting enough to attract the attention of many research groups around the world. As a result, the number of scientific publications relating to laser-induced broadband white luminescence since 2010 is growing steadily.

In this work, a focused laser beam (1064 nm) with an excitation spot diameter of 175 μm was used (3.4 W, 10^8 W/m^2). The occurrence of LIWE phenomenon and its intensity largely depended on the site of excitation of the pellet. Because the sample is transparent, the laser beam penetrates the entire volume of the sample. When the excitation light was focused on a surface of ceramic and its power exceeded a certain threshold, the samples generated LIWE (Fig. 1). LIWE covers the entire visible and near-infrared range between 28000 cm^{-1} - 10000 cm^{-1} or more [2,3]. Power dependence of integrated emission shows that 4-6 photons are involved in the LIWE process, which corresponds to ~ 38000 - 57000 cm^{-1} . In conclusion, due to relatively high emission intensity and color index, LIWE-based sources can be promising for biological applications as compact sun-like emission sources.

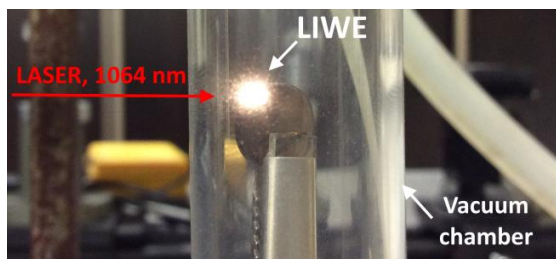


Fig. 1. The photo of LIWE under CW excitation of the transparent Cr:YAG ceramics.

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This work was supported by Polish National Science Centre, grant: PRELUDIUM-18 2019/35/N/ST3/01018.

SYNTHESIS AND INVESTIGATION OF PHYSICOCHEMICAL AND LUMINESCENT PROPERTIES OF Tb³⁺ AND Sr²⁺ CO-DOPED PHOSPHATE-VANADATE HYDROXYAPATITE

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Keywords: spectroscopy; phosphate-vanadate hydroxyapatites; Tb³⁺ and Sr²⁺ co-doping; hydrothermal method

Hydroxyapatites' biomedical usefulness is well known. However, to understand the basic physicochemical properties is essential before starting a biological research [1-4]. In this study new phosphate-vanadate hydroxyapatites co-doped with Sr²⁺ and Tb³⁺ ions were obtained by the hydrothermal method. The concentration of the dopants was set at 1 and 2 mol% for Sr²⁺ ions, and 0.5, 1, and 2 mol% for Tb³⁺ ions in a molar ratio of calcium ion amount.

To evaluate the structure and morphology of the obtained materials, the XRPD (X-ray Powder Diffraction) technique, SEM-EDS (Scanning Electron Microscopy-Energy-Dispersive Spectrometry) and FTIR (Fourier Transform Infrared) spectroscopy were performed. Moreover, the chemical formula was confirmed using the ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry).

Furthermore, the study of the spectroscopic properties (emission, emission excitation and emission kinetics) of the obtained materials as a function of optically active ions and annealing temperature at 500, 600 and 700°C was carried out.

Finally, the research focused on determining the cytocompatibility of the phosphate-vanadate hydroxyapatiteco-doped with Sr²⁺ and Tb³⁺ ions.

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NOVEL BIORESORBABLE POLY(L-LACTIDE-CO-D,L-LACTIDE)-BASED BLENDS FOR 3D-PRINTED BONE-RECONSTRUCTION IMPLANTS

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Keywords: poly(L-lactide-co-D,L-lactide), nanohydroxyapatite, biocomposite, co-rotating twin-screw extrusion, bone-fixation material

A novel, bone-reconstruction dedicated polymeric-nanohydroxyapatite material has been prepared for 3D-printed implant *via* co-rotating twin-screw extrusion. The thermogravimetric analysis proved a successful preparation of the nanohydroxyapatite and its nanocomposites. Mechanical results in conjunction with density values, reported as close to human bone, evidenced usability of this novel material for internal bone fixation implant. Based on these results, supported by numerous advanced research techniques (please see reference [1]), it was proved that the PLDLLA-based composite can be an excellent candidate for bone reconstruction implants.

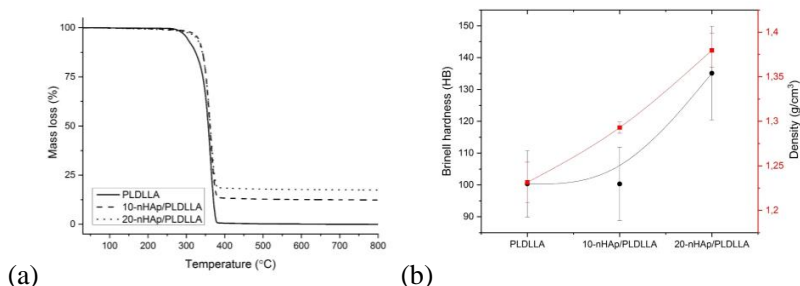


Fig. 1. Thermogravimetric curves (a) and Brinell hardness and density (b) of PLDLLA and nHAp/PLDLLA composites in a function of composition

This kind of reinforced material can be utilized in many medical fields, including orthopedic, oral, maxillofacial, craniofacial, as well as plastic and reconstructive surgeries. Its excellent usefulness to these purposes is supported not only by the material superior mechanical properties but also by its bioactivity and complete resorbability. Our biomaterial has already been embedded into the human skull, mandible and maxilla.

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The research was carried out as part of the project entitled "Development of customised biodegradable implants for bone reconstruction procedures" led by Syntplant sp. z o.o. and by Poznan University of Technology under the project no. 0613/SBAD/4710. Moreover, the authors would like to acknowledge the National Science Centre, Poland (NCN) for financial support within the project "Preparation and characterisation of biocomposites based on nanoapatites for theranostics" (no. UMO-2015/19/B/ST5/01330).

PHOTON AVALANCHE IN Pr^{3+} AND Yb^{3+} CO-DOPED $\beta\text{-NaYF}_4$ NANOCRYSTALS

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Keywords: photon avalanche, nanocrystals, praseodymium, lanthanide ions

Among different anti-Stokes emissions, where emitted photons have larger energy than the absorbed photons, Photon Avalanche (PA) phenomenon is very unique. It owes a very non-linear increase of luminescence intensity in response to minute rise of excitation intensity above some threshold pump power density, called as a PA threshold. PA was first observed in the year 1979 in Pr^{3+} doped LaCl_3 quantum counters [1]. Since then, PA became an interesting topic and was investigated in various bulk materials doped with lanthanide ions such as Tm^{3+} , Pr^{3+} , Ho^{3+} , Er^{3+} [2], [3]. It became a challenge to demonstrate PA at a smaller scale materials, and only recently PA at nanoscale was achieved for Tm^{3+} doped NaYF_4 and LiYF_4 nanocrystals [4],[5]. Here, we investigated $\beta\text{-NaYF}_4$ nanocrystals doped with Pr^{3+} and co-doped with Pr^{3+} and Yb^{3+} ions in order to check PA occurrence. Spectral properties of the nanomaterials were investigated using home-built microscope setup in which all samples were excited with 852 nm focused laser light. While the singly Pr^{3+} doped nanoparticles did not exhibit PA features, Pr^{3+} co-doping with Yb^{3+} ions enabled to successfully show photon avalanche emission at 480 nm and 610 nm. In the case of $\beta\text{-NaYF}_4$ core-shell nanocrystals co-doped with 0.5% Pr^{3+} and 15% Yb^{3+} ions PA threshold was observed at around 400 kW/cm^2 for both emissions. Maximal slopes for this sample at 387 kW/cm^2 was 8.9 and 9.2 for 480 nm and 610 nm, respectively. Presented results suggest that such Pr^{3+} based nanoscale avalanching materials might be very promising for further applications in bioimaging and biodetection.

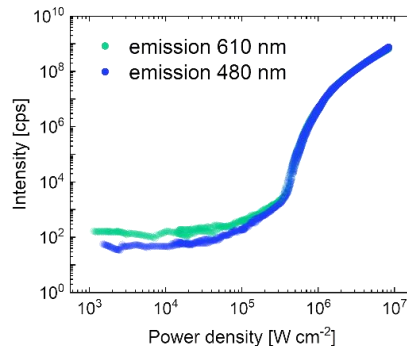


Fig.1. Luminescence intensity in a function of pump power density for sample $\text{NaYF}_4:0.5\%\text{Pr}^{3+}, 15\%\text{Yb}^{3+}@\text{NaYF}_4$

Acknowledgements: Research was supported by project 2018/31/B/ST5/01827 funded by the National Science Centre, Poland.

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ANTIMICROBIAL EFFECT OF UVC RADIATION GENERATED VIA UPCONVERSION PROCESS IN LANTHANIDE DOPED Y_2SiO_5 PHOSPHORS

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Keywords: upconversion, UVC radiation, lanthanide doped phosphors, antimicrobial therapy

UVC radiation (200-280 nm) drew the general attention as it was discovered to damage DNA and RNA of microorganisms, which does not allow them for further multiplication. [1] For that reason it is widely exploited for surface disinfection purposes. However, the classical approach of antimicrobial inactivation has to be performed with the usage of UVC lamps in the areas where no other living organism is present, which remains challenging e.g. at hospitals. [2] One of the possible solutions for overcoming the obstacle is to prepare surface made of material doped with lanthanide ions, within which ladder like energy level structure upconversion could be realized, even under visible sunlight excitation. [3] Such an approach for UVC antimicrobial treatment could be performed *in situ* and would be safe for people.

In our work the results of spectroscopic experiments conducted on Y_2SiO_5 phosphors bearing optimized amount of different rare earth elements are presented. For example, the 447 nm laser diode irradiation of $\text{Y}_2\text{SiO}_5 : \text{Pr}, \text{Tm}, \text{Yb}$ phosphor induces anti-Stokes upconversion emission from Pr^{3+} (wide band emission between 250-350 nm) and Tm^{3+} (emission band at 370 nm). Incorporation of Li^+ ions into host matrix increases the energy transfer probability from Pr^{3+} to Tm^{3+} , thus significant Tm^{3+} luminescence intensity enhancement is observed. On the contrary, excitation with a 980 nm laser diode promotes the energy transfer from Yb^{3+} to Tm^{3+} , hence the only emission below 400 nm comes from Tm^{3+} . The antimicrobial performance of UVC radiation emitted by upconverting Y_2SiO_5 phosphors, studied on *Staphylococcus aureus*, provided encouraging results, which will be useful for development of light triggered anti-Stokes emitting materials for germicidal purposes.

Acknowledgments

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FUNCTIONAL MATERIALS BASED ON HYDROXYAPATITE NANOPARTICLES AND MOFs

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Keywords: hydroxyapatite, MOF, composite, antibacterial

Biocompatible chemically-synthesized hydroxyapatite (HA) is extensively used in bone treatments, controlled drug release, and dental implants [1]. HA coatings on metal alloy substrates have gained much attention for bone replacement because they exhibit high biocompatibility and acceptable mechanical properties. Nevertheless, infection with medical implants and injection materials is still one of the common causes of failure for bone repair [1]. The fabrication of HA-based composite materials with antimicrobial properties could be an intriguing solution.

Following this topic, as a promising approach to increase the antibacterial properties, coating of HA nanoparticles with a Cu-based Metal-Organic Framework (MOF) layer such as Cu-HKUST-1 [2] was proposed. Its antibacterial profile was evaluated against several Gram-positive and Gram-negative strains. To determine the biocompatibility of the composite, *in vitro* cell viability was tested by MTT assay using the human dermal fibroblasts and the MC3T3 mouse osteoblast cells as model cell lines.

MOFs can provide biomaterials with a multifunctional character and we have shown it using another example of MOF such as MIL-100(Fe). This core-shell composite based on biocompatible HA nanoparticles and Fe-based MOF has demonstrated to act as efficient heterogeneous catalysts toward the biomimetic oxidation of 1-aminocyclopropane-1-carboxylic acid into ethylene gas, a stimulator that regulates fruit ripening [3].

New MOF@HA composites were characterized structurally, spectroscopically, and texturally using different techniques, e.g. XRD, IR, TEM and N₂ sorption (77 K) analysis.

Acknowledgements

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DEVELOPMENT OF A PROTOTYPE TISSUE ENGINEERING PRODUCT FOR THE REGENERATION OF CORNEAL INJURIES

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Keywords: Tissue engineering, corneal injuries, regenerative medicine

The cornea is a highly specialised tissue, whose essential feature is full translucency. Many corneal diseases lead to neovascularisation, fibrotic changes, inflammatory infiltration, opacity and degenerative pigmentary changes of the corneal surface [1]. In this case, isolated corneal stromal cells can be used as a source of mesenchymal stem cells. The cells are a promising source of cellular material with high regenerative potential. Compared to bone marrow mesenchymal stem cells, corneal stromal cells are closer to eye tissues and provide better corneal healing [2]. In cases of unilateral stem cell deficiency, a corneal stromal autograft can be harvested and transferred from a healthy eye.

The aim of the present study was to develop a method for manufacturing a prototype tissue engineering product designed to regenerate damaged corneal structures in the course of treating complicated corneal ulcers, and to treat opaque scars after the healing process has been completed.

In order to procure the prototype, isolations of ocular stromal cells were performed from material obtained from 20 donors of the clinic's patients (dogs and cats). A primary culture of the eye-slice cells was isolated from the collected material. The obtained cells were used to develop a method for the production of a collagen scaffold containing a 3D culture of the cells isolated from the corneal stroma. It was observed the process of cell proliferation in the fabricated capsule. Moreover slow overgrowth of the collagen structure by cells was noticed. After 7 to 10 days of culture, a lens-shaped product was obtained, which can be implanted in patients to regenerate corneal apparatuses Fig 1. An experimental therapy using a prototype product is planned in the very near future.

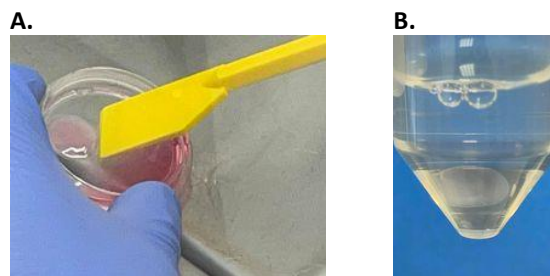


Fig. 1. Tissue engineering product prototype (A) culture vessel, (B) product prepared for implantation.

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BIOACTIVE $\text{SiO}_2\text{--CaO}$ and $\text{SiO}_2\text{--CaO--P}_2\text{O}_5$ GLASS POWDERS DOPED WITH $\text{Tm}^{3+}/\text{Yb}^{3+}$ IONS

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Keywords: bioactive glass, sol-gel method, rare-earth, up-conversion

Bioactive glass is described as inorganic material, non-toxic to cells, biocompatible, non-inflammatory and able to form an hydroxyapatite (HA)-like surface layer when immersed in a simulated body fluids similar to the blood plasma [1]. During recent years, studies focus on up-conversion luminescent properties in bioglass expected to investigate degradation behaviour *in vivo* [2].

In this study, $\text{SiO}_2\text{--CaO}$ (SC) and $\text{SiO}_2\text{--CaO--P}_2\text{O}_5$ (SCP) glass powders doped with 0.3 mol% of Tm^{3+} and 4 mol% of Yb^{3+} ions were prepared by the sol-gel method. For four weeks, the samples were immersed in a buffer simulating physiological fluids (Dulbecco's phosphate-buffered saline, DPBS) to investigate their bioactivity. During this time, glass powders were characterized morphologically, structurally, and optically. X-ray diffraction showed that before incubation in DPBS, the samples had amorphous structure. After 14 days or 7 days of immersion for SC and SCP, respectively, we observed reflections at $2\theta = 26^\circ$ and 32° , which corresponded to the (002) and (211) reflections of HA crystal structure. The surface morphology of tested glass samples has been investigated by transmission electron microscopy. In all samples after 21 and 28 days of incubation in DPBS buffer, we observed the shapes of spongy growth nuclei formation on the sample surface reflecting presence of apatite layer. The formation of HA on all samples after immersion in DPBS buffer was confirmed by IR-ATR and Raman spectroscopies. The bands appearing at around 540 and 610 cm^{-1} in SC and SCP powders after 3 days were assigned to the P-O bending vibrations. An existence of PO_4^{3-} symmetric stretching modes of apatite phase at 960 cm^{-1} wave number region was also observed. The course of changes in ion concentration shows the dynamics of ion release indicating the glass mineralization process. During incubation, the concentration of silicon decreased and content of phosphorus and calcium increased in the all tested samples. Furthermore, the up-conversion emission spectra were measured under 980 nm excitation wavelength in resonance with the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ absorption of Yb^{3+} . For all glasses, energy transfer from Yb^{3+} to Tm^{3+} was observed. The thulium emission bands were observed around 475, 650, and 800 nm corresponding to the $^1\text{G}_4 \rightarrow ^3\text{H}_6$, $^1\text{G}_4 \rightarrow ^3\text{F}_4$, and $^3\text{H}_4 \rightarrow ^3\text{H}_6$ transitions, respectively. For each sample, decrease of luminescence intensity after prolonged soaking in buffer was observed. The up-conversion emission decay curves were also monitored and showed consequent lifetime shortening with the immersion time in the buffer.

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NEW APPROACH TO BIODESIGN RELATED TO TISSUE ENGINEERING

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Keywords: tissue engineering, biodegradable polymers, hydroxyapatite, bone augmentation

Nowadays, regenerative medicine and tissue engineering have become the fastest growing field of medicine. There are sought advanced therapies all over the world that can improve regeneration processes of the damaged tissues. Progenitor cells in conjunction with a polymer have been recognized as functional components of regenerative therapy as a scaffold or bioactive material. The trend of modern medicine is personalized health care focusing on precisely defined problems and preferences of the patient. In this case, it has been obtained multifunctional bioactive system that would not only act as a material filling bone defects inducing the formation of bone tissue but also at the same time bond a matrix for MMC stem cells obtained from a given patient supporting the regeneration of the damaged tissue.

The aim of this work was to design and develop multifunctional composite systems based on nanostructured apatites embedded in synthetic biodegradable polymers.

In the proposed system, the polymer constitutes a sufficiently strong support base for the regeneration of bone tissue defects and the pure, highly crystalline nanoapatites increase the bioactivity of materials and offer a possible bioimaging function.

In the preliminary studies, eight bone substitutes based on PLLA, PCAP and hydroxyapatite were obtained. The internal morphology of the substitute was determined by means of scanning electron microscopy (SEM) and the physicochemical analysis of the obtained composites was performed using X-ray powder diffraction (XRPD), absorption, infrared and Raman spectroscopy, as well as differential scanning calorimetry (DSC).

Four materials were selected for biological research. Cytotoxicity studies were performed on a normal mouse fibroblast line in the contact test. The susceptibility of biomaterials to the adhesion of microorganisms and the formation of biofilm was also investigated. No toxicity of the material was observed in cell-based experiments.

SYNTHESIS AND CHARACTERIZATION OF $\text{Gd}_2\text{O}_3: \text{Er}^{3+}, \text{Yb}^{3+}$ DOPED WITH Mg^{2+} , Li^+ IONS—EFFECT ON THE PHOTOLUMINESCENCE AND BIOLOGICAL APPLICATIONS

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Keywords: upconversion, nanoparticles, biocompatibility, 4T1 cell

The efficiency of the upconversion process is quite low. There are few strategies for improving the efficiency of the upconversion processes in nanoparticles with rare earth (RE) ions. One possible strategy is an inert shell coating. One more viable strategy is connecting the emitters to noble metal surfaces or particles. But the most promising strategy is, in our opinion, doping of the matrix with additional ions such as Li^+ (ionic radius (IR)=59 pm), Ca^{2+} , K^+ , Sc^{3+} , Mg^{2+} , Zn^{2+} (IR=60 pm) and we chose this method in our present studies. Doping with these non-rare earth, non-luminescence ions, allows for the modification of the local structure (crystal field symmetry) around the activator (Er^{3+}) which in turn results in an increase of the upconversion process.

In our research, we chose ions with the smallest ionic radii, such as Mg^{2+} and Li^+ with respective IR=57 and 59 pm, because they easily incorporate into the crystal lattice of Gd_2O_3 and they are much smaller than the Gd^{3+} ion (IR=93.8 pm). In this study, two new materials based on Gd_2O_3 were analyzed in order to improve their upconverting efficiency. A series of samples of Gd_2O_3 : 1% Er^{3+} , 18% Yb^{3+} , x % Mg^{2+} (x=0–50) and Gd_2O_3 : 1% Er^{3+} , 18% Yb^{3+} , 2.5% Mg^{2+} y% Li^+ (y=0.5 to 2.5) doped with Mg^{2+} and Li^+ ion were prepared by homogeneous precipitation synthesis.

We observed a 8-fold increase in red luminescence for samples suspended in DMSO solution for 2.5% of Mg^{2+} doping. The x-ray analysis shows that for the concentration of 2.5% Mg, the size of the crystallites in the NPs is the largest, which is mainly responsible for the increase in the intensity of the upconversion luminescence.

Synthesized nanomaterials with very effective upconverting luminescence, can act as luminescent markers *in vitro* imaging. The cytotoxicity of the nanoparticles was evaluated on the 4T1 cell line for the first time [1].

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SOLVOTHERMAL SYNTHESIS OF CALCIUM HYDROXYAPATITE IN WATER-ORGANIC SOLVENT MEDIA

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Keywords: calcium hydroxyapatite, α -tricalcium phosphate, water-organic solvent system, solvothermal synthesis

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp] is a major inorganic component in hard tissue [1-3]. Hap is biocompatible and biodegradable substance with a great promise for bone regeneration [4]. It was observed that bone has a great affinity for implants containing high percentages of HAp [5].

In the present work, the effects of various organic solvents and solvothermal conditions on the formation of HAp via hydrolysis of α -tricalcium phosphate (α -TCP) were investigated. The hydrolysis reaction was performed in solutions with different water to organic solvent (W:O) ratios under solvothermal conditions at 120 °C for 3 h and at 200 °C for 5 h. Ethyl alcohol (EtOH), isopropyl alcohol (PrOH), and butyl alcohol (BuOH) did not inhibit the hydrolysis of α -TCP while methyl alcohol (MeOH) and ethylene glycol (EG) had a more prominent inhibitory effect on the formation of single-phased HAp. The samples treated with organic solvent only showed no evidence of HAp formation. This was true for all the organic solvents used under different solvothermal treatments. The morphology of the obtained samples varied from plate-shaped to rod-shaped (Fig. 1). From all the solvents analysed, EG had the highest impact on the sample morphology.

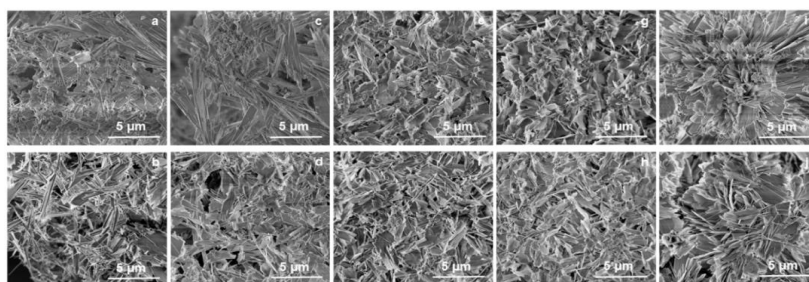


Fig. 1. SEM images of the samples after solvothermal treatment with W:O ratio 40:60: a) W:EG (120 °C); b) W:EG (200 °C); c) W:MeOH (120 °C); d) W:MeOH (200 °C); e) W:EtOH (120 °C); f) W:EtOH (200 °C); g) W:PrOH (120 °C); h) W:PrOH (200 °C); i) W:BuOH (120 °C); j) W:BuOH (200 °C).

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PHOTON AVALANCHE IN MICROCRYSTALS DOPED WITH DIFFERENT CONCENTRATION OF TULIUM

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Keywords: photon avalanche, bioimaging, luminescence

Lanthanides are widely used in biological, diagnostic, therapeutic, photodynamic and theranostic aspects. They can be used in bioimaging because of their properties: they are photostable, non-toxic, have long lifetimes, and emit in the optical window range of biological samples and tissues. Therefore, they can be used for subcutaneous tissue or small animal bio-imaging, bio-sensing or super-resolution imaging. In addition, in lanthanides a very unique up-conversion phenomenon of photon avalanche (PA) emission can occur[1].

PA is one type of upconversion process. As a result of this phenomenon it is possible to obtain photons with higher energy, than the energy of the excitation photon (so called anti-Stokes emission). One of the characteristics feature of the PA is very steep relationship between pumped power density (I_p) and luminescence intensity (I_L), within photon avalanche region ($I_L = (I_p)^S$, with $S > 10$) observed above some critical pumping power density (so called PA threshold). As this relationship is highly nonlinear, we get an S-shaped graph. Another feature, characteristic of PA, is the slowing of the luminescence rise time near the PA threshold [1,2,3].

In this work we present a study of the phenomenon of PA in microcrystals doped with various concentration of Tm^{3+} in $LiYF_4$ under 1059 nm excitation wavelength. The relationship between the excitation power density and luminescence intensity was measured and demonstrated characteristic S-shape dependence. Moreover, we observed changes in the S-shape characteristics as a function of different concentrations. Multicolored emission at 800 nm and 475 nm was obtained. Moreover we measured the luminescence lifetime and an increase in rise times in the PA region was observed in accordance with expectations. This knowledge opens new opportunities in bioimaging and biosensing.

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UPCONVERSION FRET SENSING: THE ROLE OF DONOR PHOTOEXCITATION MODE AND COMPOSITIONAL ARCHITECTURE ON THE DECAY AND INTENSITY BASED RESPONSES

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Keywords: Förster Resonance Energy Transfer, FRET, nanocrystals, up-conversion, lanthanides ions, Yb, Er, Rose Bengal, organic dye

Lanthanide doped nanoparticles offer long luminescence lifetimes, narrowband absorption and emission spectra, and efficient anti-Stokes emission. These features are highly advantageous for Förster Resonance Energy Transfer (FRET) based detection. However despite the existing problems of molecular FRET systems, such as photobleaching and quantitative analysis issues are solved by using up-converting nanoparticles (UCNPs) as donors, new challenges arose with them such as multiple donor-multiple acceptor interaction or disrupted kinetic response to FRET. For these reasons, we have studied and quantitatively compared luminescence rise and decay kinetics of Er^{3+} emission using two types of architectures donor UCNPs (core-only NaYF_4 : 20% Yb, 2% Er and core-shell NaYF_4 : 20% Yb @ NaYF_4 : 20% Yb, 5% Er) under three photoexcitation schemes: (1) direct short-pulse photoexcitation of Er^{3+} at 520 nm; indirect photoexcitation of Er^{3+} through Yb^{3+} sensitizer with (2) 980 nm short (5-7 ns) or (3) 980 nm long (4 ms) laser pulses. The donor luminescence kinetics and steady state emission spectra differed between the UCNP architectures and excitation schemes (Fig. 1).

The experimental and theoretical results underline the complexity of the excitation and RET mechanisms, which affect nanoparticles (UPNPs) donor responses to acceptor and suggest ways to optimize the photoexcitation scheme and the architecture of the UCNPs used as luminescent donors, when aiming for highly sensitive kinetic up-conversion FRET.

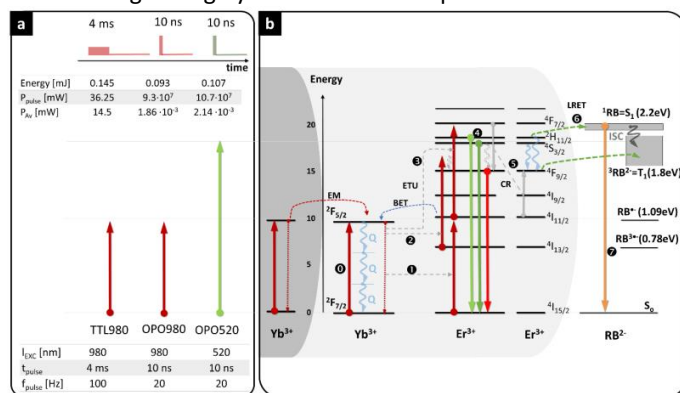


Fig. 1. The excitation schemes and mechanism of UC-LRET between Yb/Er donor NPs and Rose Bengal acceptor. (a) Three different excitation schemes used, 4 ms and 10 ns pulse and 10 ns pulse of 520 nm. (b) Energy scheme and transfer in $\text{Yb}^{3+} / \text{Er}^{3+} - \text{RB}$ system.

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COMPARISON OF LIGHT-TO-HEAT CONVERSION EFFICIENCY IN NANOMATERIALS FOR PHOTOTHERMAL THERAPY

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Keywords: nanomaterials, photothermal conversion efficiency, nanoheaters, photothermal treatment

Nanomaterials (NMs) capable to efficiently convert light energy into heat converting are promising tool for localized photothermal therapy of cancers (PTT). However, quantitative comparison and selection of the most promising NMs for PTT is still a challenge as the materials of different composition and structure have different photo-physical and chemical properties and may interact with biological environment differently. In terms of photophysical properties, the most relevant information to rank NMs is the light-to-heat conversion efficiency, which, however, provide only the information of how much of the absorbed energy is converted into heat and thus, is not sufficient alone to evaluate the suitability of NMs for PTT. We therefore propose external heat conversion efficiency, which allows to create a ranking of heating NMs. Herein, we evaluate the light-to-heat conversion properties of NMs belonging to five classes (i.e. plasmonic, semiconductor, lanthanide-doped nanocrystals, carbon nanocrystals, and metal oxides). The results we have obtained showed the distinct differences between the samples on a logarithmic level. These results provide quantitative information about the heating performance of different NMs and will set a new standard in the characterization of NMs for PTT.

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ANTIFUNGAL ACTIVITY OF HYDROXY- AND FLUORAPATITES DOPED WITH SILVER IONS

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Keywords: hydroxyapatite, fluorapatite, silver, antifungal, yeast-like pathogens

Hydroxy- and fluorapatites (HAp and FAp, respectively) are commonly used in medicine e.g., as implants or teeth fillings. The structure modification by doping with antimicrobial metal ions is one of the ways to improve biological properties [1-3]. Silver is one of the widest studied metal towards the antimicrobial activity. Its antibacterial and antifungal properties against various pathogenic strains are well documented as well as an apatite dopant. The activity of such composites against bacteria is widely described in the literature [4]. Antibacterial properties are desired because of nosocomial infections that occur during surgeries are not uncommon. On the other hand, yeast-like fungi are also noted as potential threat in hospital environment because some of the opportunistic pathogens are inhabitants of human microflora [5]. There were investigated novel hydroxy- and fluorapatites doped with 1 mol% and 10 mol% silver ions and their activity against yeast-like human pathogens: *Cryptococcus neoformans*, *C. gattii*, *Trichosporon beigeli* and *Rhodotorula rubra*. The apatites were obtained via a hydrothermal process. The hydrothermal process was conducted under autogenous pressure (42–45 bar) for 90 min at 250°C. Afterwards, the obtained nanocrystals were heat-treated. The antifungal potential was tested by cfu/ml counting. As was shown, the hydroxyapatites showed better antifungal potential against the studied strains than fluorapatites, and doping with 10 mol% silver ions completely inhibited fungal growth for HAp, while the growth of fungi treated for FAp with 10 mol% Ag⁺ ions was inhibited but not completely abolished. Interestingly, there were some differences in sensitivity level among tested fungi. It appeared that *C. neoformans* was the least sensitive to silver-doped HAp and FAp. After further studies it could be possible to apply those composites e.g., as bone replacements with lower risk of an infection during the surgical procedures.

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DEVELOPMENT OF A TISSUE ENGINEERING PRODUCT FOR USE IN PERIODONTAL MUCOSAL REGENERATION

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Keywords: dental pulp, periodontitis, stem cells

The periodontitis is the one of most important problem in dogs and cats. In the course of this disease there is a loss of attachment of the teeth and their loss. The aim of the research was to develop a prototype of an advanced therapy medicinal product and collagen glue based on the method of extraction and preparation of MSC (mesenchymal stem cells) from the pulp of extracted deciduous teeth of dogs and the development and methods of culturing the cells for subsequent use in the treatment of oral mucosal defects and periodontitis. The practical use of dental pulp stem cells is widespread in regeneration therapies: pulp stem cells isolated from extracted teeth can be used to rebuild own tissues. In the course of the research conducted, a method was firstly developed to culture the cells in collagen matrices. Subsequently, a method for obtaining valuable biological material from extracted teeth was developed and methods for isolating and culturing dental pulp stem cells (DPSCs) were described by modifying their culture conditions *ex vivo*. In this way, a prototype tissue-engineered therapeutic product combining collagen matrix and dental pulp cell culture has been designed and manufactured as part of the study. The use of stem cells in veterinary medicine will enable a significant increase in the potential of therapies for the regeneration of mucosal defects and will significantly increase the chances of success of treatments, even in difficult cases [1].

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THE DENTAL SEALANTS – A COMPARISON OF PHYSICO – CHEMICAL PROPERTIES OF COMMERCIALLY AVAILABLE MATERIALS

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Keywords: dental sealants, biomaterial, fluoride, water contact angle

Since their introduction in 1960s, photocurable dental sealants are a golden standard in caries prevention [1]. Their successful clinical application ultimately depends not only on their mechanical behavior and abrasion-resistant properties but on other physico-chemical properties. They play vital role in the aforementioned application, especially when it comes to cohesion between enamel and sealant, plaque accumulation and fluoride release. Moreover, water contact angle indicates the hydrophobic-hydrophilic properties and implies a behavior in a moist environment of the oral cavity.

Fluoride is an important element in caries prevention. Its impact has been proved on both cariogenic bacteria and on balancing the processes of demineralization and remineralization. It may disturb bacteria's metabolism and adherence to enamel [2]. Therefore, its presence and amount in the sealant composition as well as its secretion mechanism has major clinical importance.

The presented comparative study involves 9 commercially available sealants and compares their chemical composition, fluoride content, water contact angle and efficiency of adhesion to curved enamel surface. Moreover, the FT-IR spectroscopy analysis allowed for analysis of the characteristic peripheral chemical bonding occurring in the material.



Fig. 1. Commercial dental sealants, commonly used in dental clinics, which have been evaluated.

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ANTIPSEUDOMONAL ACTIVITY OF NANOHYDROXYAPATITES DOPED AND CO-DOPED WITH Cu^{2+} AND Eu^{3+} IONS OBTAINED VIA CO-PRECIPITATION AND HYDROTHERMAL METHODS

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Keywords: *Pseudomonas aeruginosa*, nanohydroxyapatite, antibacterial activity, nanotechnology

A growing bacterial resistance to various types of antimicrobials, including antibiotics, is one of the most urgent problem of the modern medical science [1]. Therefore, a wide range of nanoparticles with an antibacterial activity are currently developed. Among them, the most effective are nanomaterials doped with metal ions such as Cu^{2+} which is well-known from strong antibacterial activity. These cations could be used as dopants and co-dopant in hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ - HAp), a bioactive material that promotes bone regeneration[2]. Additional luminescent properties of nanomaterials could be obtained if the Eu^{3+} ions are added.

The tested nanomaterials were obtained using hydrothermal and co-precipitation methods, and their physicochemical properties were assessed using X-ray powder diffraction (XRPD), scanning electron microscope (SEM) and various spectroscopic methods. To evaluate the exact dopant's content, the Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) measurements were performed. To test the efficacy of developed nanomaterials against *Pseudomonas aeruginosa*, different microbiological methods were applied. In order to evaluate whether tested nanomaterials influence bacterial growth, *P. aeruginosa* cultures were incubated with nanopowders and optical density was measured after 24 and 48 h. Moreover, the effect of tested materials on the biofilm formation was evaluated using confocal laser scanning microscope (CLSM) with LIVE/DEAD staining.

The obtained results suggest that co-precipitation method allowed to obtain nanomaterial with greater cation dopants and the biggest differences in dopant content were seen in nanomaterials co-doped with Eu^{3+} and Cu^{2+} . Interestingly, higher Cu^{2+} dopant did not always result in enhanced antibacterial activity, what may suggest that not only the Cu^{2+} cation influenced bacterial growth, but also the nanomaterial itself. Moreover, the analyses revealed that the nanomaterials which were pre-released in the medium for 24 hours before bacterial inoculation, seemed to be more active than their non-pre-released equivalents.

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IMATINIB-FUNCTIONALIZED GALACTOSE HYDROGELS LOADED WITH NANOHYDROXYAPATITE AS A DRUG DELIVERY SYSTEM

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Keywords: Drug delivery system, Hydrogels, Imatinib, Nanohydroxyapatite

Galactose-based hydrogels loaded with nanohydroxyapatite (nHAp) are very attractive as drug carriers due to their high biocompatibility and good cell adhesion [1]. The strategy involving their surface functionalization may be a promising alternative to the conventional method of drug delivery, making the therapeutic system more precise and effective. Nowadays, our interest is focused on the well-described cytostatic - Imatinib (IM) used in anticancer targeted therapies [2]. The Saos-2 and U-2OS osteosarcoma cell lines were selected, because they are cancer cell lines derived from nanoapatite-rich bone tissue and are one of the most commonly used models for in vitro studies on the bone tissue.

This study reports the impact of structure (XRPD, FT-IR) and surface morphology (SEM-EDS) of Imatinib-functionalized galactose hydrogels, loaded and un-loaded with nHAp, on osteosarcoma cell lines. The effect of various Imatinib doses on cell cultures has been demonstrated. It was also investigated how the rough surface of hydroxyapatite-modified hydrogel influences the release of the drug and, consequently, the interaction with the examined osteosarcoma cells.



Fig. 1. Photo of the fabricated porous galactose hydrogel form.

The cytotoxic and pro-oxidative activity of the materials was slightly weaker than that of the directly administered IM. An increase in the amount of p53 protein as well as caspases 9 and 3 was observed, regardless of the form of administration - directly to the culture or to the hydrogels. Administration from hydrogels loaded with nHAp significantly increased the accumulation of Rh-123 in the cells. Administration of IM by hydrogel is expected to reduce the risk of multi-drug development by inhibiting P_{gp}.

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PREFORMED CROWNS IN PEDIATRIC DENTISTRY– COMPOSITION AND MICROBIOLOGICAL PROPERTIES

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Keywords: pediatric crowns, material composition, biofilm

Pediatric crowns are a prefabricated solution for full crown restoration of deciduous teeth. Historically, preformed crowns have been widely available for the past 50 years. The clinical performance of preformed crowns has evolved to meet higher functional, mechanical, and aesthetic demands. They are available in sets containing different sizes and shapes dedicated to primary teeth. They are made from a variety of biomaterials such as stainless steel, aluminum, acrylic polymers, polycarbonate polymers and zirconia[1]. The use of crowns allows to obtain a tight restoration of the crown tissues of the tooth. Lack of a tight restoration condemns a deciduous tooth to extraction. Pediatric crowns are also very good solution when it is necessary to rebuild teeth with tooth tissue developmental disorders or changes of non-carious origin [2]. In presented study, pediatric steel crowns were exposed to various microorganisms, which are the main components of cariogenic biofilm, in order to evaluate its deposition on the biomaterial surface. This is important, since low microbial deposition is associated with easier cleaning of the restoration, its longer durability and lower risk of endodontic complications and pain. The study is based on qualitative and quantitative biofilm evaluation and the use of electron and confocal microscopy.

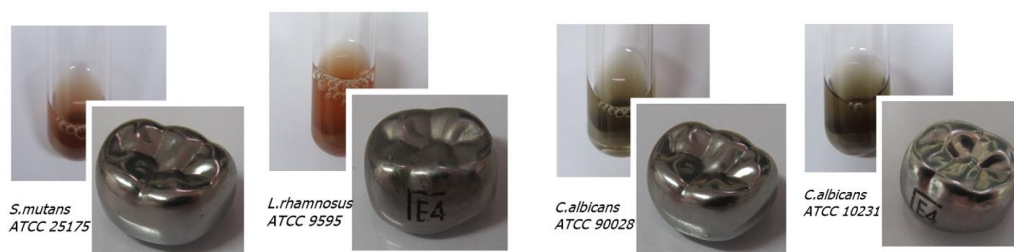


Fig. 1. MTT (for *C. albicans*) and TTC (for *S. mutans*, *L. rhamnosus*) reduction on the crown surfaces results.

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STRUCTURAL AND SPECTROSCOPIC PROPERTIES OF Tb³⁺-DOPED STRONTIUM CHLORAPATITE DESIGNED FOR REGENERATIVE MEDICINE AND BIOIMAGING

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Keywords: strontium chlorapatite, terbium ions, spectroscopy, bioimaging

The development of civilization leads to an increase in the requirements for the life quality of an aging community but also to an increase in the incidence of civilization diseases causing disability and premature death. The ability of the human body to regenerate most tissues and organs is limited, especially, when they are severely damaged. In such cases, the rescue is regenerative medicine and tissue engineering, which focus on stimulating the natural mechanisms of regeneration or tissue reconstruction in the human body. An additional consequence of their efforts is the extension and improvement of people's quality of life. Biomaterials based on apatite compounds are the most promising materials designed for these applications [1]. Moreover, it seems a good idea to dope it with various ions, such as Mg²⁺, Sr²⁺, Zn²⁺, CO₃²⁻ etc. with biological functions, such as Ag⁺, F⁻, Cl⁻ with antibacterial properties, such as RE, TM ions enabling bioimaging. Strontium is a trace element found in human bones and teeth that affects strength, healing, microarchitecture, and bone formation [2,3]. In order to achieve this goal, it is first necessary to carry out basic research on the structural, morphological and spectroscopic properties of the new material.

The Tb³⁺-doped strontium chlorapatite nanosized powders (Sr₁₀(PO₄)₆Cl₂) were synthesized by a hydrothermal method and post heat-treated in 600°C. The structural properties of the obtained materials were checked by the XRD (X-ray powder diffraction) and FTIR (Fourier Transform Infrared) spectroscopy. The chemical formula of obtained materials was confirmed by the ICP-OES technique (Inductively Coupled Plasma-Optical Emission Spectrometry). The luminescence properties (emission, excitation, decay time) as a function of the dopant concentration and post heat-treatment temperature of the Tb³⁺-doped Sr₁₀(PO₄)₆Cl₂ were investigated. The luminescence intensity depending on the ambient temperature was measured to study an influence of temperature to emission spectra.

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FABRICATION OF THREE-DIMENSIONAL HYDROGEL MATERIALS USING NEWLY DEVELOPED WATER-SOLUBLE RADICAL PHOTOINITIATORS BY 3D-VAT PRINTING

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Keywords: water-soluble photoinitiators, radical photopolymerization, hydrogels, 3D-VAT printing

Light-initiated polymerization processes are currently widely used in various industrial fields. Technological advances have led to the use of photopolymerization for biomedical applications as well, including the fabrication of three-dimensional hydrogel structures, cell encapsulation or in drug delivery systems. In recent years, polymeric hydrogels have attracted considerable interest for their potential application, because their structural and biochemical properties are similar to those of the extracellular matrix (ECM) of most tissues. Although hydrogels can be formed by conventional polymerization methods, such as by thermal polymerization, light-induced polymerization has attracted significant interest. A key role in these processes is played by the photoinitiator, which not only determines the process (e.g., its speed) but also is responsible for the properties of the final material. The initiator used in photopolymerization processes for biomedical applications should meet several characteristics, including the compatibility of the absorption characteristics of the initiator with the emission characteristics of the used light sources, high initiation efficiency, lack of toxicity, and water solubility. Therefore, much attention is now being given to the search for new photoinitiators/photoinitiating systems that meet the above requirements and allow the fabrication of hydrogel materials for biomedical applications. In the present work, a group of previously unknown water-soluble radical photoinitiators were designed, synthesized and tested. These initiators were subjected to detailed spectroscopic analysis and their performance in radical photopolymerization of methacrylate monomers was investigated using real-time FTIR technique. The studied resins containing the developed initiators were used in a 3D-VAT printing in order to produce three-dimensional polymeric and hydrogel materials with predefined structures.

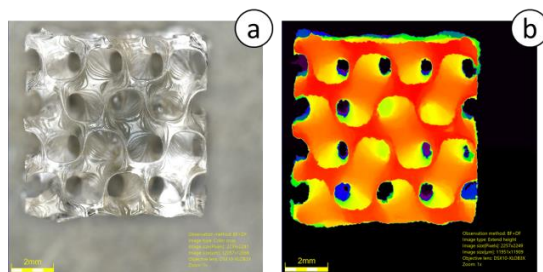


Fig. 1. The nature-inspired gyroid structure obtained using 3D-VAT printing process, using newly synthesised water-soluble photoinitiator.

Acknowledgements

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UVC UPCONVERSION AND NIR DOWNCONVERSION EMISSION FROM Pr^{3+} DOPED FLUORIDE PHOSPHORS FOR STERILIZATION AND BIOIMAGING

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Keywords: UVC upconversion, lanthanide, fluoride phosphors, germicide

Utilization of ultraviolet C (UVC) radiation is one of the simplest and direct method for sterilization or germicide as it can inhibit the replication of RNA and DNA via crosslinking the thymine and the neighbouring cytosine.^{1,2} However, the current UVC generators are hazard to environment especially the production of ozone.³ Pr^{3+} doped phosphors are found to be promising candidate to generate UVC (ca. 260 nm) through photon upconversion emission process from visible light as excitation source. Incorporation of Pr^{3+} into fluoride based inorganic phosphors are particularly beneficial due to the possibility to fine-tune the crystal sizes, shapes and crystal structures ranging from micro-scale to ultra-small nanocrystals.^{4,5} This features allow applications of Pr^{3+} doped fluoride based phosphors not only as bulk materials on surface disinfection purposes, but also possible to apply as nanocrystals for *in-vivo* usage. Moreover, various strategies can also be utilized in this type of fluoride based phosphors in order to enhance the UVC emission and resulting in more efficient disinfection, as well as near infrared (NIR) emission for Bioimaging. Herein, a series of Pr^{3+} doped LiYF_4 and NaYF_4 are discussed for potential biomedical applications.

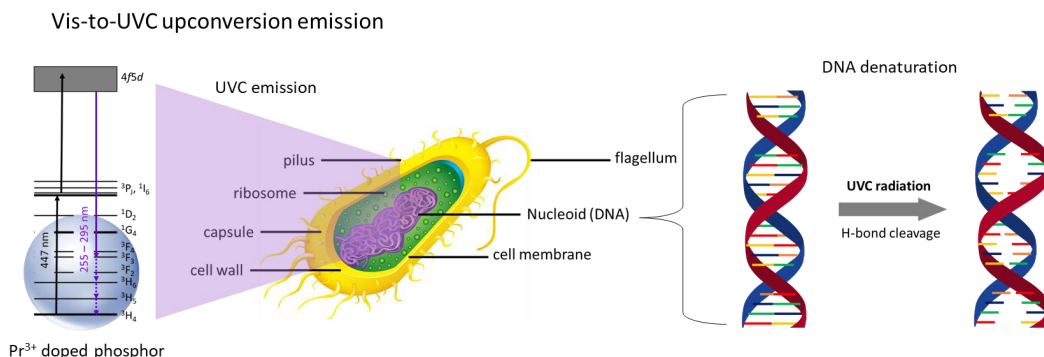


Fig. 1. Generic scheme of Pr^{3+} doped fluoride based phosphors for disinfection application through upconverted UVC emission from visible light. Mechanism of Vis-to-UVC emission of Pr^{3+} doped phosphors (left) and DNA denaturation after UVC radiation (right)

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GRAPHENE COATING OBTAINED IN A COLD-WALL CVD PROCESS ON THE CARDIOVASCULAR STENTS FOR MEDICAL APPLICATIONS

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Keywords: graphene coating, cardiovascular stents, cold-wall chemical vapor deposition method

Graphene is one of the most prospective materials in terms of its unique properties for many applications in the field of electronics, sensors including biosensors etc. [1]. Recent studies revealed that graphene and its derivatives exhibit also intrinsic biological properties, which may facilitate and expand its use in biomedicine [2]. The rising interest in the field of graphene research led to the discovery of different synthetic routes allowing to obtain the high-quality layers of graphene: mechanical cleavage, liquid-phase exfoliation, epitaxial growth, chemical vapor deposition (CVD), as well as chemical cleavage (graphite oxidation followed by chemical reduction of obtained oxide) [3]. Of all listed methods, CVD allows obtaining the graphene with the smallest amount of surface defects and with the highest 2D crystals domain sizes on copper or nickel [3]. Meanwhile, a few reports confirm that the synthesis of graphene via CVD is also possible on metal alloys containing copper but also medical ones like stainless steel or nitinol [4]. And cold-walled CVD (CW-CVD) method allows to successfully obtain a high-quality large-area graphene layer for Cu [5], cobalt [6], and cobalt-nickel alloy [7]. Recently we reported the possibility of obtaining graphene coating by CW-CVD on the surface of Co-Cr (L-605 alloy) [8].

In the present work graphene coating on the cardiovascular stents was optimized and successfully carried out by a CW-CVD method. Functional and radial force tests of the stents was performed to confirm the achievement of appropriate mechanical parameters. A uniform layer of graphene was confirmed by Raman mapping coated area and analyzing specific G and 2D bands. Allergy and toxicity tests performed on small animals did not show any adverse effects and allowed to proceed to preclinical studies on a typical for stents domestic pig model.

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ALGINATE COMPOSITES CONTAINING NIMESULIDE ON A NANOHYDROXYAPATITE MATRIX - THE PRELIMINARY STUDY

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Keywords: nanohydroxyapatite-nimesulide composites, drug release, functionalized surface of nanohydroxyapatite

Nanohydroxyapatite (nHAp) is used as a drug carrier for controlled drug release systems. The aim of this study was to prepare and investigate composites containing nimesulide (N-(4-Nitro-2-phenoxyphenyl)methanesulfonamide) from the group of non-steroidal anti-inflammatory drugs with nanohydroxyapatite matrix. The drug system was obtained using an adsorption process related to an unmodified and functionalized surface of nHAp by biodegradable polyethylene polymer (PEG) and folic acid. The matrices were tested for drug bound amount, stability and hydrodynamic size at physiological condition. In the experimental, it was used the UV-Vis spectroscopy, ATR-FTIR spectroscopy, dynamic light scattering spectroscopy and the thermogravimetric method. The DLS spectroscopy showed a reduction in the degree of aggregation of the modified nHAP matrix (combinations with PEG and folic acid) by approx. 6% compared to nHAP which may affect the effectiveness of the drug-carrier system. The analysis of nimesulide release from alginate composites by spectrophotometric method showed that the process follows the Korsmeyer-Peppas model, and its mechanism is based on the Fick diffusion process. Nimesulide was released from the composites with the nHAp functionalized matrix in 48% at 96 hours, and in 90% from the composites without nHAP. The study of the thermal stability of the composites showed that the drug was stable in the temperature range of 25-120°C.

APPLICATION OF NANOFLUOROAPATITE IN ALVEOLAR BONE REGENERATION SURGERY

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Keywords: nanofluoroapatite, nanomaterials, regeneration, alveolar bone

This study presents the physicochemical characteristics of nanofluoroapatite for regenerative surgery of alveolar bone. Nanofluoroapatite is characterized by its ability to release fluoride, which provides inhibition of microbial activity [1]. In addition, it is a biocompatible material, which has been confirmed in a cytotoxicity assessment according to the ISO standard dedicated to this type of testing. Nanostructured scaffolds provide a closer structural support with natural bone [2]. The results of this study will allow for further use of nanofluoroapatite in experimental animal studies and clinical trials.

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IMPACT OF SYNTHESIZED FLUORINE-SUBSTITUTED HYDROXYAPATITE ADDITION ON PHYSICAL PROPERTIES AND CYTOTOXICITY OF EPOXY RESIN-BASED ENDODONTIC SEALERS

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Keywords: endodontic sealers, epoxy resin-based sealers, fluorohydroxyapatite

Epoxy resin-based endodontic sealers are a group of materials used in root canal treatment among other sealing materials. In combination with gutta-percha, the sealants enable a precise filling of the root canal. Epoxy resins are currently regarded as some of the best root canal sealants available on the market. [1, 2] The aim of this work is to determine the effect of synthesized fluorine-substituted hydroxyapatite added to epoxy resin on the resin properties. The resin used in this study is AH26 Silverfree 1-1 (Dentsply Sirona). The synthesized powders were added in 2% and 5% into the epoxy resin-based sealer. Cytotoxicity studies were performed on the normal mouse fibroblast line Balb/3T3. The degree of cytotoxicity of the materials was determined at toxicity level 4 on a four-grade scale cytotoxicity assessment scale. This proves strong cytotoxicity of the evaluated materials.

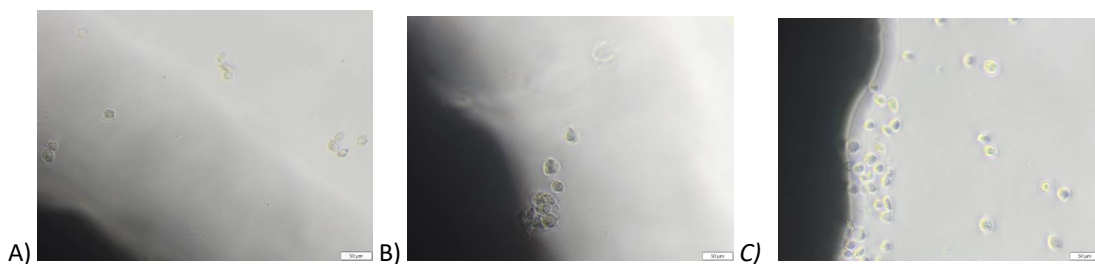


Fig. 1. Morphological image of Balb/3T3 fibroblasts after 24 h incubation with tested materials (direct contact): A) AH26; B) AH26 + 2% fluorohydroxyapatite; C) AH26 + 5% fluorohydroxyapatite

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PROSPECTIVE ZR-BASED BULK METALLIC GLASSES AS ADVANCED MATERIALS FOR NEW GENERATION IMPLANTS AND SURGICAL TOOLS

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Keywords: bulk metallic glasses, cytotoxicity, fibroblasts, mechanical properties, biomedical materials

Zr-based bulk metallic glasses (BMGs) belong to a group of advanced engineering materials – metallic alloys with amorphous internal structure. Their manufacturing requires a particular chemical composition and high cooling rates which prevent the reorganization of atoms into a crystal lattice in the solidification process. These alloys exhibit enhanced mechanical properties, such as high hardness and strength, low elastic modulus, low macroscopic range of plastic deformations, and a high range of elasticity exceeding 2 % [1]. Zr BMGs are also characterized by excellent corrosion resistance and biocompatibility defined as the ability to be inert in the living organisms' environment and to show little or no cytotoxic effect [2].

Our study on Zr-based BMGs revealed that the relative viability of fibroblasts in direct contact is higher for $\text{Zr}_{40}\text{Ti}_{15}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ and $\text{Zr}_{40}\text{Ti}_{15}\text{Cu}_{10}\text{Ni}_5\text{Si}_5\text{Be}_{25}$ than for commonly used in implantology and biomedicine materials like 316L steel and Ti6Al4V alloy (Fig.1(a)). It is well visible in Fig. 1(b) that their morphology and surface adherence to $\text{Zr}_{40}\text{Ti}_{15}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ sample are proper and they exhibit ongoing proliferation. The mechanical and biomedical properties of studied BMGs along with their ability for thermoplastic processing like polymers [3] make them promising materials for new generation implants and surgical tools.

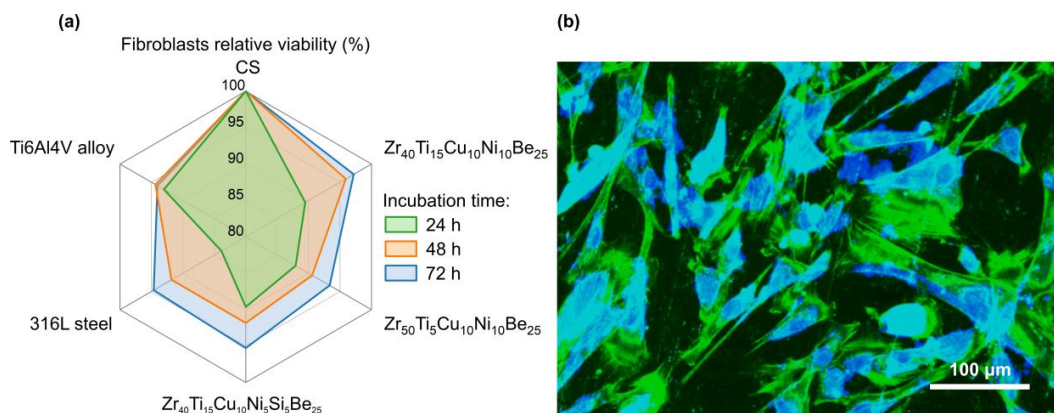


Fig. 1. Relative viability of IMR90 cell line human fibroblasts in direct contact with tested samples after 24, 48 and 72 hours (a) with a representative image of proliferating fibroblasts on $\text{Zr}_{40}\text{Ti}_{15}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ sample (b). Cell viability on the glass control sample (CS) was taken as 100 % after each time.

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ERBIUM DOPED $\text{CaF}_2\text{-SrF}_2$ CRYSTALS FOR $\sim 3\ \mu\text{M}$ LASER

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Keywords: CaF_2 , SrF_2 , Erbium, $3\mu\text{m}$ laser

Erbium doped crystals/glasses are common solid state laser materials. Their attractiveness resides in the wavelengths generated. There are two groups of interesting wavelengths corresponding to these materials: one in the region of $2.7\text{--}3\ \mu\text{m}$ (Cr:Tm:Er:YAG , Er:Cr:YSGG , Er:YAG). The second span from $1.5\ \mu\text{m}$ to $1.7\ \mu\text{m}$ (Er:glass , Er:YAP , Er:YLF). Absorption of water is very strong in $2.7\text{--}3\ \mu\text{m}$ region, what is significant for medical tissue cutting/burning. The active materials from the second group generate wavelengths in part of the spectrum called the 'eye safe' region, which poses very little hazard to the human eye [1, 2].

The problem of $2.7\text{--}3\ \mu\text{m}$ lays in the bottleneck effect. This wavelength is generated from transition between the second and first excited levels of Er^{3+} ion ($^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ respectively). The problem is, that lifetime of bottom level is longer than lifetime of metastable level. Due to this only pulse operation with relatively low repetition rates is available. To overcome this problem a high dopants concentration is used. Heavy doping decrease lifetime of bottom laser level, but decrease thermal conductivity of the material as well. In case of $\text{CaF}_2\text{-SrF}_2$ materials doping level may be kept low, due to natural aggregation of Ln^{3+} ions in these matrices.

Poster will be focused on recent advances in spectroscopic investigations on Er^{3+} doped $\text{CaF}_2\text{-SrF}_2$ single crystals

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