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BOOK OF ABSTRACTS

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Bioactive, Organic and Inorganic Advanced Materials and Clean Technologies

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BiOrgaMCT

A contract №: BG-RRP-2.004-0002-C01, „BiOrgaMCT“ (Bioactive organic and inorganic materials and clean technologies) By procedure: BG-RRP-2.004 – Creation of a network of research universities in Bulgaria under the National Recovery and Resilience Plan

INDEX

I. First session

II. Second Session

- **Light-Responsive Materials**

1. Sylvain Achelle - The effect of proton on the photophysical properties of pyrimidine chromophores
2. Julien Massue - Excited-State Intramolecular Proton Transfer (ESIPT): A Versatile and Modular Process
3. Biagio Audia - Vectorial holography by multiwavelength optical patterns: an unconventional approach for complex structuring of light-responsive materials
4. Owen Kearney - Water-resistant optical structures with controlled physical and chemical surface properties, for bacteria detection

- **New generation materials**

5. Bárbara Costa - Multifunctional Fe3O4 MNPs: A comparison between co-precipitation and hydrothermal synthesis
6. Francisco Muñoz - Processing and structure influence on the properties of Nd-doped phosphate laser glasses
7. Doris Möncke - Effect of Chemical Composition and Modifier ions on Dissolution Rates of Silicate, Phosphate and Borate glasses
8. Neda Neykova - The Role of the Hole Transport Layer in Perovskite Solar Cells: Simulation and Experimentation Perspectives

- **Biologically active molecules**

9. Kameliya Anichina - Benzimidazole derivatives as multifunctional agents: synthesis and evaluation of antioxidant and photoprotective activity
10. Dancho Danalev - Synthesis and biological studies on bioactive peptides with opioide and anti-inflammatory activity
11. Chavdar Chilev - Kinetic process modeling for extraction of biologically active substances from plant raw materials
12. Ljubica Mihailova - Exploring the Anticonvulsant Potential of CBD oil and CBDA-rich extract: A Path Toward the Brain

III. Third session

Keynote

Stéphane Gérard – Hybrid molecules as strategy for the design of new anti-inflammatory agents

- **Light-Responsive Materials**

1. Luciano De Sio - Polarization-insensitive Chiral Liquid Crystal Reflectors via Thermo-responsive Optical Metastructures
2. Francesca Petronella - Gold Nanorods based platforms for precise detection of pathogens and biomolecules
3. Kosuke Nakashima - The synthesis and photoluminescence properties of spiro oxindole
4. Anton Georgiev - Visible Light Switching of ortho-Functionalized Azo Phthalimides with Tunable Z-Isomer Stability

- **New generation materials**

5. Dimitar Nedanovski - Nonlinear optimization and sensitivity analysis for continuous approximation of true boiling point data for crude oils
6. Nina Penkova - Multiphysics simulation for efficient and reliable systems for low temperature plasma treatment of metals
7. Svetoslav Nenov - A refinement of the crossover selection in the differential evolution method
8. Leandro Gonzalez Rovira - Electrochemical impedance spectroscopy (EIS) to study the corrosion resistance of anodized aluminium alloys

- **Biologically active molecules**

9. Blagovesta Popova - Design of innovative peptide therapeutics for targeting α-synuclein aggregation
10. Elliott J. Price - EIRENE-CZ mass spectrometry resources supporting human exposome research
11. Ognen Pop-Georgievski - Bioactive non-fouling polymer brushes: From design parameters to medical applications

IV. Fourth session

- **Light-Responsive Materials**

1. Atanas Kurutos - Emerging colorimetric and fluorimetric smart materials
2. Lucia Ivanová - Light-harvesting Flavin Derivatives for Hydrogen Evolution Reaction
3. Marcella Salvatore - Programmable Microtexturing of Surfaces through Polarization-Controlled Azopolymer Structuring
4. Francesco Reda - Azopolymer surface reliefs gratings: fabrication & diffraction properties

- **New generation materials**

5. Andriana Surleva - Chemical analysis of new materials - problems and some solutions
6. Petrica Vizureanu - Characterization of Novel Ti-Mo-Nb-Sn Alloys in Biomedical Engineering
7. Andrei Victor Sandu - Properties and Applications of New Ti-Mo-Zr-Ta Alloys for Orthopedic implants
8. Dimka Fachikova - Preparation and characterization of calcium-containing phosphate conversion coatings for biomedical applications

- **Biologically active molecules**

9. Jana Tchekalarova - Anticonvulsant profile of three hemorphin-4 analogues with rhodamine B in mice
10. Stela Georgieva - Chemical behavior and Bioactive Properties of Hemorphin-4 Conjugating to N-[4-(2-phenyldiazenyl) phenyl]glycine and its sensor activity towards metal ions
11. Boryana Borisova - Design and synthesis of novel FELL analogs containing Tyr in the first position instead of Phe
12. Dilyana Dimitrova - Effect Of Modification of Temporin A With Fluorinated Phenylalanine on Antibacterial Activity

V. Fifth session

Keynote:

Christian Rüssel - New Aluminosilicate Glasses for High Power Lasers: Luminescence and Thermomechanical Properties

- **Light-Responsive Materials**

1. Martin Vala - Investigating Ion Exchange in Organic Bioelectronic Devices Using Selective Fluorescence Detection
2. Rayna Bryaskova - Fluorescent Benzimidazole-Hydrazone-Loaded Micelles: A New Tool for Detection and Cancer Treatment
3. Jan Truksa - The influence of water on flavin-derivative spectroscopy
4. Nikolay Georgiev - Aminotriazole containing 1,8-naphthalimides as a platform for AND molecular logic gate and cancer diagnostic tool
5. Rastislav Smolka - Tuning Fluorescence in Stilbene-Based Materials: Host-Guest Systems and Energy Transfer for Enhanced Solid-State and Bioimaging Applications

- **New generation materials**

6. Hristo Georgiev – Bioactive glass-ceramics in the CaO-SiO2-P2O5 system containing high-temperature polymorphs of dicalcium silicate
7. Daniela Angelova - Application of biosorbent for treatment of reactive dye wastewater
8. Tina Tasheva - Study on preparation of glass-ceramic and dense ceramic biomaterials on the base of hydroxyapatite
9. Nadezhda Kazakova - Construction of inorganic and hybrid biosorbents for water purification
10. Nona Shivacheva - Surface treatment of steel surfaces in a three-component phosphating solution before organique coatings applying
11. Tina Tasheva - Synthesis, Structure and Dielectric Properties of Glasses in the TeO2-V2O5- Bi2O3 System

12. Dimitar Dimitrov - Preparation of coatings by dispersing graphene oxide, reduced graphene oxide and zinc titanate in bisphenol-a
13. Zdravka Djumalieva - Formation and characterization of non-chromate conversion coatings on aluminum alloy EN AW 5754
14. Sergei Kusturov - Corrosion Behavior of a High Nitrogen Austenitic Stainless Steel in Aqueous Solutions of Citric and Oxalic Acids

VI. Sixth session

- **Light-Responsive Materials**

1. Jiarong Wu - Photoswitchable Imines Drive Dynamic Covalent Systems to Nonequilibrium Steady States
2. Polya Miladinova - Synthesis and application of some bis(dichlorotriazine) reactive dyes
3. Ventsislav Bakov - Synthesis and study of 1,8-naphthalimide AIEgens designed for the detection of acids and bases in the vapor phase
4. Vladislava Ivanova - Study of optical anisotropy in composite structures based on azo polymer PAZO and GeTe4-In chalcogenide system, prepared by different methods
5. Silvia Angelova - Molecular insights into molecular level interactions and aggregation behavior of an azobenzene-functionalized polymer
6. Jordanka Trifonova - Synthesis, analysis and some optical application of new chalcogenides from the Ge-Te-Cu system
7. Desislava Marinova - Photochromic Properties of Novel Spiroindolines

Poster Sessions

1. Tsvetomila Lazarova-Kyuleva - Synthesis and characterization of High-entropy spinel oxides
2. Daniela Atanasova - Effect of the cotton fabric modification with composite film on antimicrobial properties and release kinetics of biologically active substance
3. Desislava Staneva - The influence of the light and the type of 1,8-naphthalimide chromophore linked to peptide on antimicrobial properties of cotton fabric
4. Georgi Chernev - Low-temperature synthesis, structural properties and applications of self-healing materials
5. Peter Iliev - Utilization of zinc ferrite residue for the production of metals with multifunctional applications
6. Irena Mihailova - Bioactive glass-ceramics in the CaO-SiO2-P2O5 system containing high-temperature polymorphs of dicalcium silicate
7. Stanislav Slavov - Bismuth-titanium-silicate-oxide glass ceramics for various dielectric applications
8. Janna Mateeva - Study of the influence of the partial replacement of feldspar in dental transparent glaze with hydroxyapatite on the phase composition and microstructure of the obtained material
9. Dimitar Dontchev - Transmissibility of rubbers by cyclic disturbtions (LINEAR CASE), Transmissibility of rubbers by cyclic disturbtions (NONLINEAR CASE)
10. Lyubomir Tashkov - Thermal Properties of Unfired Bricks with Additives from Agricultural Materials for Energy-Efficient Construction
11. Nina Penkova - Electrical model of a chamber for low-temperature plasma processing of metal products
12. Vanya Lilova - Comparative study of the bulk and foil zinc anodic behavior kinetics in oxalic acid aqueous solutions
13. Vesislava Toteva - Preparation of a carbon bifunctional catalyst for biofuel synthesis
14. Petar Todorov - Synthesis and study of some physicochemical characteristics of new Rhodamine B-conjugated Hemorphin analogs
15. Stanislava Vladimirova - New pyrrole hydrazones as potential anti-cancer agents
16. Temenuzhka Radoykova - Study of chemical behaviour of novel benzylidenemalononitriles with incorporated nitrogen-containing heterocyclic fragments using molecular absorption and fluorescence spectrometry

17. Meglena Kandinska-Vasileva - Mono- and Polycationic p-Substituted Benzaldehydes as Intermediates for Cyanine Dyes and Fluorogenic Biocompatible Polymer Materials Based on PVA Scaffold
18. Ivan Iliev - Photodynamic Inactivation of Human Herpes Virus with Ga(III) and Zn(II) Phthalocyanines
19. Emilia Naydenova - Design, Synthesis and Anticancer Evaluation of new Analogues of Aurein 1.2 Containing Unnatural Amino
20. Nikolay Lumov - Synthesis, spectroscopic and in vitro studies of triazinobenzeimidazole derivatives
21. Rossitsa Hristova - Novel pyrrole-based hydrazones induce apoptosis and S-phase cell cycle arrest in human SH-4 melanoma cells
22. Veronika Karadjova - Synthesis and characterization new complexe on Zn(II) - peptide ligand BIM25053
23. Maria Elena Stancheva - A high-throughput in vitro assay for preparation of atherosclerotic plaque using magnetic 3D bioprinting
24. Tanya Dimitrova - Quantitative-based cytoskeleton segmentation for accurate measurement of cytoskeleton density in 3D model of atherosclerotic plaque
25. Diana Kichukova - Synthesis and characterization of bioactive composites and their impact on cancer cells
26. Maya Guncheva - Modulation of Matrix Metalloproteinases-2 and -9 in Betulinic Acid Organic Salt-Treated MDA-MB-231 Cells
27. Boryana Yakimova - The health benefits of milk bioactive peptides and their possible involvement in treatment of hypertension
28. Veronika Farková - Synergy between fatty acids and photosensitive components in colostrum
29. Darina Zheleva - Methods of modification of wool fabrics with TiO2 for application in shoe lining
30. Boris Martinov - Stabilization of AU NPS and RGO/AU NPS nanocomposites for application in biomedicine
31. Boris Martinov - Structural characterization, citotoxity and antitumor activityof one step synthesized RGO-AuNPs nanocomposites
32. Aleksey Vasilev - Fluorogenic Biocompatible Polymer Materials Based on PVA Scaffold for Nucleic acids Visualization

Modified Indulines: From Dyestuffs to Theranostic Agents

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Theranostic is a contemporary promising therapeutic approach for the treatment of cancer, combining therapy and diagnosis in a single compound. As such, theranostic molecules mainly consist of an imaging unit combined with a therapeutic agent within the same platform. However, these “multi-component” architectures suffer from difficult synthetic access and high molecular weight, preventing their rapid diffusion across cell membranes and limiting reasonable solubility for biological studies. An alternative to overcome these drawbacks is to use a minimalistic class of molecules that would be directly able to image and treat. Designing a new class of theranostic probes remains nevertheless a major challenge for chemists to access compounds combining three key features: (1) a minimalistic active core (low molecular weight), (2) structural parameters that allow for a high degree of modifications (up to four positions) to fine-tune the properties, and (3) a versatile and straightforward synthesis.

One can turn to triamino-phenaziniums (TAPs) belonging to the induline family, which has a long history as dyestuffs and was so far neglected for biological applications. The presentation, will show theranostic agents based on tunable N-substituted modified TAPs which demonstrate a remarkable biological activity at very low concentrations for (i) cancer cell internalization with a better efficiency compared to healthy fibroblasts; (ii) both one- (1 hv) and two-photon (2 hv) imaging; and (iii) treatment by photodynamic therapy (PDT), with an impressive cancer cell death both in vitro and in vivo upon illumination.

Mechanistic Investigation of the Isomerization of New (and Old) Photoswitches

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Photochemically driven molecular switches and unidirectional molecular motors represent a fascinating fundamental research topic, that has found prospective applications in smart materials and biomedical sciences.[1,2] However, synthesizing molecules tuned for a specific task requires a deep understanding of their motion.

This talk will focus on selected examples of applying the toolboxes offered by organic synthesis, spectroscopy, computational chemistry and physical organic chemistry to predict, construct and investigate photochemically driven switches and motors (Fig. 1).[3-8] This approach allows the understanding of the behavior of new structures and the discovery of the mechanisms underlying their movement at the molecular scale.

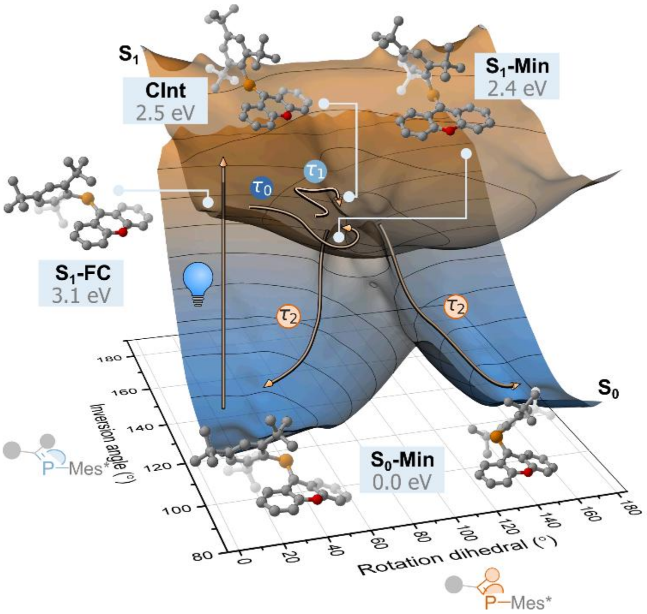

Figure 1. C=P isomerization about the central C=P bond of a novel phosphaalkene switch.[8]

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Photoswitchable Imines: Figuring out the rules

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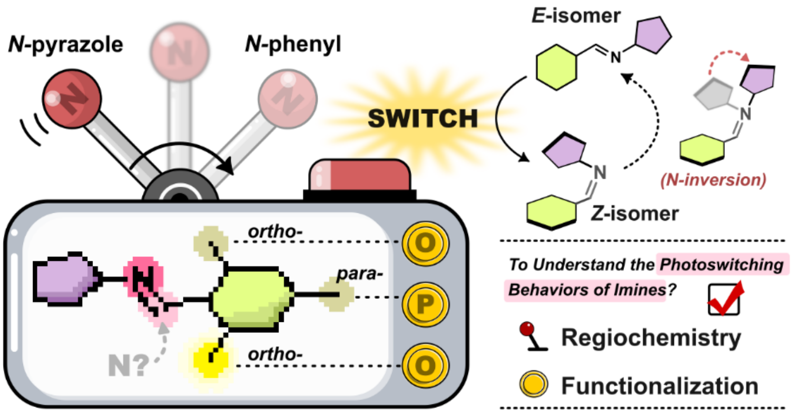
Molecules and materials comprised of dynamic-covalent imine bonds display many desirable properties, including stimuli-responsiveness, recyclability, and effortless preparation, among others. However, the *E*/*Z* photochromism of imines has often been overlooked due to historically poor performance compared to other photoswitches, typically showing less than 50% conversion to the metastable state and thermal half-lives of under one minute.[1] Recently, we developed a strategy that significantly improves these photoswitching properties, achieving quantitative *E*-to-*Z* conversion with visible light and extending the thermal half-lives of the metastable *Z*-state to over one day.[2,3]

With these improved properties, we explored the light-dependent dynamic-covalent chemistry of these photoswitches. To our surprise, we found that they can drive transimination reactions energetically uphill when irradiated with light,[4] operating via a mechanism akin to a light-driven information ratchet.[5] Beyond pushing thermodynamic equilibria into non-equilibrium steady states, we found that the regiochemistry of the C=N bond plays a significant role in the switching behavior.[3,6] Through a systematic investigation, a set of design rules for this novel class of imine photoswitch has now been reported, along with the first crystal structure of an arylimine in its metastable *Z*-conformation.[6] This talk will provide an overview of our recent progress in this area.



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Holographic vectorial morphing of azomaterial surfaces

I Komang Januariyasa, Francesco Reda, Fabio Borbone,
Marcella Salvatore, Stefano Luigi Oscurato

The light-induced structuring of azobenzene-containing material films (azomaterials) enables direct, non-destructive, and reprogrammable surface morphing driven by a light-induced material transport. The surface deformation originates from cyclic trans-cis isomerization of azobenzene molecules under UV/visible light, generating mechanical stress that drives material motion. The phenomenon is highly directional, with both polarization and intensity patterns defining the final surface geometry, enabling vectorial surface lithography.

Holography, which engineers light fields across multiple degrees of freedom, is a powerful tool to exploit azomaterial responses. Holographic morphing has been demonstrated using Computer-Generated Holography (CGH) with a liquid crystal Spatial Light Modulator (SLM). SLMs enable the formation of complex surface reliefs through engineered intensity patterns and support dynamic, all-optical reprogrammability by sequentially inscribing and erasing surface structures.

Polarization-driven reconfiguration of pre-structured surfaces further expands the capabilities of azomaterials by allowing to reprogram the geometry of surface architectures. Functional surfaces fabricated this way benefit from on demand definition of complex topographies. SLMs, operated as computer-controlled polarization rotators, enable time-dependent polarization patterns to guide directional surface deformation in this configuration.

Here, we employ CGH and spatially controlled polarization patterns to fabricate and re-morph azomaterial surfaces solely with light. We achieve high-aspect-ratio reliefs and micro-scale polarization-driven structures, leveraging holographic light's vectorial nature. This method enables reprogrammable diffractive optical elements, including gratings, Fourier surfaces, lenses, and holographic projectors. Our results introduce a new photolithographic paradigm, where structured light directly dictates surface shape and evolution, with applications in photonics, biology, and surface engineering.

Azo dyes for polarization recording: Comparative analysis of the photoinduced anisotropy in thin films containing various azo dyes and polymer matrices

Lian Nedelchev, Blaga Blagoeva, Polya M. Miladinova, Dimana Nazarova

The azo dye-based guest-host polymer systems were the first highly efficient photoanisotropic materials that proved the practical applicability of polarization holography. These systems, containing azo dye embedded in a polymer matrix, offer an easy to produce and cheap alternative of the commonly used azopolymers. A detailed literature survey is performed in order to identify the most commonly used azo dye-polymer matrix systems. In spite that numerous studies on the properties and potential for applications of azo dyes have been published, a detailed comparative analysis of these systems is still missing. Here, we present a comprehensive study of the photoanisotropic parameters (maximal value of the photoinduced birefringence, response time and stability) of different azo dye-polymer matrix thin film systems with varying concentrations of the azo dye. Both commercially available azo dyes and azo dyes synthesized in the University of Chemical Technology and Metallurgy are studied. To induce birefringence in the thin film samples we use a range of recording lasers in the UV and visible with wavelengths varying from 355 to 532 nm. Our aim is to determine the optimal concentration and recording wavelength for each of the azo dyes, as well as to compare the photoanisotropic parameters of the different azo dyes.

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Keywords:

azodyes, guest-host systems, photoinduced anisotropy, polarimetry, thin films

Fluorescent Detection of Protein Immobilzation on Ultrananocrystalline Diamond Surfaces

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Friedrich W. Herberg, Cyril Popov

Diamond is an ideal candidate for biomedical and biotechnological applications, such as platforms for biosensors and DNA-chips, due to its biocompatibility, excellent mechanical properties, large electro-chemical potential window and high chemical stability. In the current project we are investigating the non-covalent and covalent binding of proteins on the surface of ultrananocrystalline diamond (UNCD) films prepared by microwave plasma chemical vapor deposition. For both pathways green fluorescence protein (GFP) was used allowing direct measurement of the fluorescence signal by a microplate reader. As a first step, the UNCD surface was nanostructured by plasma etching to increase the area for interaction with proteins. In the case of non-covalent immobilization, UNCD surfaces with hydrogen, oxygen or fluorine terminations, achieved after different plasma modifications, were studied. These processes resulted in change of the wettability, revealed by contact angle measurements, and of the surface composition, as shown by X-ray photoelectron spectroscopy. The intensity of the fluorescence signal due to binding of GFP from solutions with concentrations between 10 μM and 500 pM increased in the order F-UNCD < H-UNCD < O-UNCD, i.e. with the increase of the hydrophilicity of the surface. For the covalent immobilization photochemical grafting of ω-alkene, e.g. of TFAAD (10-Trifluoro-acetamidodec-1-ene), as linker on H-terminated UNCD was firstly applied for direct binding of GFP. In a second series of experiments nanobodies able to bind GFP from solutions were immobilized by the same linker molecules. In order to reduce the physical adsorption and to realize GFP capturing mostly by the binding nanobodies, milk powder was applied as a blocking protein before the exposure to GFP solutions. In both cases the average fluorescence intensity increased with the concentration of GFP in a non-linear relation, which can be attributed to saturation in the higher concentration range and to depletion in the lower one. These initial results can serve as a starting point for further investigations of structured and functionalized UNCD as a bioplatform for immobilization of different binding proteins with high affinity and specificity toward target molecules.

Microwave radiation: applications in metrology and materials synthesis

Luís Cadillon Costa

Microwaves, using low power radiation levels, can be used for the measurement of the electrical properties of materials. The complex permittivity, ε^*=ϵ´-i ϵ´´, can be calculated using the small perturbation theory. In this method, the resonance peak frequency and the quality factor of a cavity, can be used to calculate the complex dielectric permittivity. This technique has been used to distinguish the living seeds of tomato, containing mostly bound water, and the death seeds, containing particularly free water.

For high power radiation levels, it can be used for materials synthesis. The curing systems of the cork agglomerates, particularly which used in the manufacture of stoppers, are mainly based on simple convective systems that use hot air at temperatures in the range from 120 º C to130 º C. Using microwave radiation, we can obtain reduced synthesis times and lower energy consumption contributing to a more sustainable and environmentally friendly synthesis process. The developed system was scaled from laboratory setup to industrial applications, making it suitable for mass production of stoppers.

Modification of 45S5 Bioglass: Tailoring Antioxidant and Pro-Oxidant Properties through Ion Incorporation

J.F.C.S. Regadas, S.R. Gavinho, M.P.F. Graça

Bioglasses are extensively used as biomaterials due to their bioactive composition, which promotes favorable interactions with biological systems. Modifying the composition through the incorporation of various ions, such as cerium (Ce) and iron (Fe), imparts additional functional properties, including the modulation of reactions with reactive oxygen species (ROS), allowing bioglass to act as either an antioxidant or pro-oxidant agent. This study investigates the effects of CeO2 and Fe2O3 incorporation into 45S5 Bioglass, focusing on their influence on ROS interactions. A comprehensive analysis, including structural, morphological, electrochemical, and biological characterizations, was conducted. The results indicated that higher ion concentrations induced thermal and structural alterations, but these changes did not compromise the desired functionalities. Notably, an increase in Ce concentration led to a decrease in the Ce3+/Ce4+ ratio, suggesting that higher Ce content enhances the material’s antioxidant properties. Electrochemical analysis further revealed that ion incorporation facilitated improved charge transfer dynamics. Based on these findings, the 5Ce sample was identified as a potent antioxidant agent, while the 5Fe sample exhibited pro-oxidant behavior.

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Barium Titanate-Based Glass-Ceramics Crystallized from Multicomponent Oxide Glasses: Phase Composition and Microstructure

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The interest in the synthesis of new dielectric materials is caused by their potential application in various electronic and sensors devices as well as in a large variety of electronic components. The present work reports on the synthesis of glasses in the system $Na_2O/Al_2O_3/BaO/ZrO_2/TiO_2/B_2O_3/SiO_2$ prepared by the melt-quenching technique. Subsequently, these glasses were transferred to glass-ceramics by controlled thermal treatment. X-ray diffraction is used to characterize the phase composition and reveals the precipitation of $BaTiO_3$ or $BaZr_xTi_{1-x}O_3$ and, for longer annealing times, $Ba_2TiSi_2O_8$. The microstructure is studied by scanning electron microscopy and shows the presence of bright, globular crystalline structures with a densely-branching morphology which, with increasing annealing time, start to merge. Tomography is used to gather information on the volume fraction and average crystal size as an effect of the applied temperature-time schedule. Longer annealing times lead to a higher volume fraction and increasing average size of the obtained crystalline structures.

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Influence on the concentration of the bioactive compounds of waste lavender extract through membrane separation and crystallization

Stoyko Petrin, Nevena Lazarova-Zdravkova, Yoana Stoyanova, Dimitar Peshev

Huge amounts of solid waste are generated from plant biomass, during the distillation process of lavender oil. This waste is usually disposed of, which leads to environmental problems, and on the other side to the loss of valuable bioactive compounds with antioxidant activity. This study investigates the influence of membrane separation and the following crystallization on the concentration of valuable bioactive components from an extract of lavender waste biomass. After the membrane separation results show that the concentration of the compounds increases about 5 times. The further process of crystallization shows that only a small part of the components remains in the sediment, which indicates that the antioxidant components can be separated and concentrated by crystallization because they pass into the supernatant. The obtained results are also confirmed by the studied antioxidant activity of the samples before and after crystallization.

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Cu and Pt complexes of 1H-benzimidazole-2-yl hydrazones: synthesis, structural insight and cytotoxicity

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2. University of Chemical Technology and Metallurgy
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1H-benzimidazole-2-yl hydrazones have showin promising in vitro cytotoxic activity towards MCF-7 and AR-230 cancer cell lines, especially pronounced for some of the derivatives, containing ortho-hydroxy- and methoxy-benzylidene fragments. In view of the fact that coordination with metal atom could significantly affect the cytotoxicity profile of the ligands, series of copper and platinium complexes of 1H-benzimidazole-2-yl hydrazones were obtained. The possible coordination modes were studied by quntum-chemical calculations at B3LYP/LANL2DZ level of theory and confirmed by elemental analysis, SEM-EDX, IR, micro-Raman, and UV spectroscopy. The in vitro cytotoxicity of the metal complexes of 1H-benzimidazole-2-yl hydrazones on leukemic (AR-230) and epithelial carcinoma (MCF-7) as well as normal murine fibroblast cells (CCL-1) was evaluated using MTT test. The non-metal and metal-based analogues showed distinguished differences in their cytotoxic behavior. The modulatory activity of selected representatives was studied on key kinase signaling pathways in MCF-7 and AR-230 in vitro tumor models in a comparative manner to the reference drugs tamoxifen and imatinib.

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Bioactive Stent for Atherosclerosis Therapy and Enhanced Vascular Healing

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Atherosclerosis, a progressive systemic disease, remains the leading cause of morbidity and mortality in cardiovascular health. Coronary Artery Disease (CAD), the most prevalent form of heart disease, occurs when the coronary arteries narrow due to plaque buildup, restricting blood flow to the heart muscle. This reduction in blood supply can lead to angina (chest pain) and heart attacks. Currently, percutaneous coronary intervention is the most widely used treatment for CAD. This procedure involves the permanent implantation of a stent within the affected artery, restoring blood flow and providing symptomatic relief. Coronary stents, typically made from metal alloys, offer the necessary radial strength to maintain vessel patency. However, stent implantation triggers neointimal tissue formation by inflammation and excessive smooth muscle cell proliferation, which can lead to arterial thickening and late lumen loss. Drug-eluting stents have become the gold standard in interventional cardiology to mitigate restenosis, as they release therapeutic agents to inhibit excessive tissue growth. Over the past decade, extensive research has focused on developing next-generation stents that effectively prevent restenosis while promoting re-endothelialization. This presentation will introduce the development of an innovative cardiovascular stent featuring a unique multi-layered coating designed to enhance biocompatibility and therapeutic efficacy. The novel stent incorporates:

1. A nitrogen-containing titanium oxide (TiOxNy) sub-coating is a bioactive surface capable of controlled nitric oxide release to promote vascular healing.

2. A hybrid nanocomposite biodegradable nanoparticle-containing sub-coating with an anti-plaque effect to prevent atherosclerotic progression.

3. A biodegradable polymer matrix top layer, composed of polylactic acid embedded with chemically functionalized detonation nanodiamonds for enhanced performance. This advanced stent design holds the potential to not only prevent plaque formation and facilitate plaque removal but also to improve endothelialization, reducing the risks of restenosis and thrombosis.

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Structural insights into polyphosphate glasses in the K2O-Na2O-CaO-MgO-P2O5 system: spectroscopic analysis and thermodynamic modeling

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While spectroscopic techniques like Nuclear Magnetic Resonance (NMR), Raman or FTIR provide valuable insights into glass structure, theoretical models offer complementary advantages in experiment planning and result interpretation. In this study, the thermodynamic model of Shakhmatkin and Vedishcheva (SVTDM) is applied to calculate the structure and molar volume of phosphate glasses within the system x K2O – (18-x) Na2O – 15 CaO – 22 MgO – 45 P2O5, where x varies from 0 to 18. This model treats glasses as ideal solutions formed by the interaction of constituent oxides, offering generalizability across compositions without adjustable parameters. Its predictive capability has been previously demonstrated across various glass systems, including silicate, borate, and borosilicate glasses. Additionally, physicochemical properties such as molar volume can be derived from the model. The results obtained from this model are then compared with experimental data from density and 31P and 23Na MAS-NMR measurements, showing a good agreement between experimental and modeling results for both structure and molar volume. In principle, the model can also predict the arrangement of modifiers along Qn groupings, but further experimental work is needed to validate these results.

The effect of proton on the photophysical properties of pyrimidine chromophores

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Lionel Sanguinet, Mihalis Fakis, Julián-Rodríguez-López

During the past two decades a large library of pyrimidine chromophores have been designed for applications ranging from (bio)chemical sensors, two-photon absorption chromophores and emitters for OLEDs.[1]

These chromophores can be easily and reversibly protonated at the nitrogen atom of the heterocyclic ring and this can cause dramatic colour changes.[2]

This presentation will highlight the last results we have obtained regarding the effect of proton on the photophysical properties of pyrimidine derivatives. This will include halochromism, white-light emission by controlled partial protonation,[2] bimodal molecular switches and multilevel systems,[3] two-photon absorption switches based on protonation,[4] excited state intramolecular proton transfer (ESIPT),[5] and anti-counterfeiting platinum complexes with pyrimidine ligands.[6]

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Excited-State Intramolecular Proton Transfer (ESIPT): A Versatile and Modular Process

Julien Massue

Excited-State Intramolecular Proton Transfer (ESIPT) is a photophysical process corresponding to a photoinduced proton transfer in the excited-state, occurring in heterocyclic systems that exhibit strong hydrogen bonding in their ground state (e.g. enol fragments). This very fast process (picosecond) leads to either the sole emission of the keto (K*) tautomer, a dual E*/K* emission when ESIPT process is partially frustrated. In selected cases, a competition with deprotonation is also possible, leading to highly emissive anionic species and paving the way to fluorescence molecular switches. Heterocyclic dyes displaying ESIPT fluorescence are characterized by enhanced photostability, solid-state fluorescence and environment-dependent emission profile. As such, applications of ESIPT emitters include optoelectronic devices, bio-medical imaging, ratiometric sensing and security inks. Molecular engineering studies in our group around different organic scaffolds led to the development of highly stimuli-responsive dyes, displaying multi-state fluorescence, which can be fine-tuned upon electronic substitution or environment (polarity, temperature, hydration). Additional properties such as aggregation-induced emission (AIE) or acid/base-mediated stabilization of supramolecular rotamers, can also be envisioned.

Innovative applications of ESIPT luminescence for the ratiometric sensing of pH variations at the interface of electrodes or as linkers for supramolecular metallic assemblies' switches will be also discussed in this presentation.

Vectorial holography by multiwavelength optical patterns: an unconventional approach for complex structuring of light-responsive materials

Dr. Biagio Audia

Since 1948, when a pioneer Denis Gabor introduced it, the holographic technique has made giant steps forward both in terms of fundamental research and practical applications. Nowadays, holographic methods represent a standard in fields such as anticounterfeiting and data storage and symbolize the future in the framework of virtual and augmented reality. Additionally, thanks to the remote control offered by light over different photo-induced processes, holography provides a unique tool for the photo-structuring of light responsive materials. Indeed, this technique allows, via the illumination with well-defined light patterns, for a large-area, single-step, and cost-effective structuration. However, traditional methods face limits in achieving a high degree of complexity and nanometric spatial resolutions. Here, an unconventional approach to overcome these limitations is presented. Instead of using canonic monochromatic light, we involve wavelength as an additional degree of freedom. We generate and record optical patterns using a multiwavelength laser beam composed by close lines originated from the same source and coupled in the same Gaussian mode. To demonstrate the capability of the approach we exploited the photo-response of an azobenzene polymer, processed into two different geometries: confined and free-surface film. By adjusting parameters such as the number of lines, their amplitude and polarization, result possible to simultaneously and independently encode multiple sinusoidal profiles with nanometric spatial resolution and high-fidelity. One of the main outcomes of the investigation is the possibility to multiplex, in confined samples, mixed holograms that result crosstalk-free and with a unique diffractive and polarizing behaviour. In free-surface samples, the illumination with the multiwavelength patterns allows the inscription of extremely precise Fourier surfaces, where beat phenomena lead to a never observed hierarchical topography. Combined with the feasibility of the method the multiwavelength approach introduces a powerful tool for material structuring. Additionally, it provides insight into new generation optics and in the field of Fourier surfaces, offering real perspectives on the scaling up of ultracompact structured devices.

Water-resistant optical structures with controlled physical and chemical surface properties, for bacteria detection

Owen Kearney, Alan Casey, Izabela Naydenova

Water-resistant optical structures with controlled physical and chemical surface properties have potential in detecting antibiotic-resistant pathogens, such as E. coli in liquid samples. The discovery of antibiotics significantly improved global life quality; however, these benefits are disproportionately experienced in developed countries, where more than 95% of deaths from diseases like AIDS, malaria, and respiratory infections occur in developing regions. Addressing this disparity requires effective disease monitoring and accurate diagnostic tests, which are often inaccessible in resource-limited settings. The WHO's REASSURED criteria outline the ideal characteristics for point-of-care diagnostic tests, emphasizing accessibility and practicality over purely technical accuracy. An inexpensive test with moderate accuracy may be more beneficial in reaching and treating a larger population than an expensive, highly accurate test available to few. This work seeks to develop a compact, label-free optical device for bacterial detection and quantification. Designed to be simple, cost-effective, and user-friendly, employing diffraction principles, through controlled surface topography. The device will operate as a diffractive surface sensor, with the operating principle stemming from a measurable output, proportional to refractive index change in the device surface, due to bacteria presence. Surface modification involves photopolymer materials irradiated with spatially modulated laser light to create precise surface relief structures. The two methods utilised in achieving these patterns differ in their approach to controlling light intensity. Post-recording thermal treatment is utilised in order to enhance the amplitude of the surface relief patterns. Correlations between the chemical composition of the photopolymers and the resulting surface structures are analysed, assisting in optimizing device performance. A protocol for fabrication of the water-resistant surfaces by copying in PDMS is developed. Current challenges associated with this approach of bacteria detection are discussed. Further empirical evidence is needed to validate the effectiveness of this approach for bacteria detection in real time.

Multifunctional Fe3O4 MNPs: A comparison between co-precipitation and hydrothermal synthesis

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Multifunctional Magnetic Nanoparticles (MNP) have been widely used for biomedical applications. From cancer treatment to drug delivery, the use of these multifunctional MNP is growing exponentially, leading to a rising interest from the scientific community. This work focused on a primary study on how the synthesis conditions can influence the properties of the MNP. Therefore, Fe3O4 MNP were synthesized using two different methods: co-precipitation and hydrothermal synthesis. By adding different amounts of NaOH, distinct MNP were obtained with different synthesis pH values, varying from 9 to 12. The structural characterization of the samples was performed using X-ray diffraction (XRD), while their morphology was examined through transmission electron microscopy (TEM). The magnetic properties and magnetic behaviour were analysed using a superconducting quantum interference device (SQUID), while the Capability to be used for magnetic hyperthermia was evaluated through specific absorption rate (SAR). Furthermore, cytotoxicity was assessed using SRB and MTT assays. It was found that the co-precipitation method allowed the synthesis of Fe3O4 MNP with a pure composition of Fe3O4 with smaller size, in comparison with the hydrothermal synthesis. In terms of SAR, both presented elevated values (>45 W/g), acceptable to be used for magnetic hyperthermia. Additionally, in terms of cytotoxicity, both methods were able to synthesize Fe3O4 MNP that appear to not be cytotoxic for concentrations below 20 mg/mL.

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Processing and structure influence on the properties of Nd-doped phosphate laser glasses

Mónica Muñoz-Quiñonero, Crystal Guillet, Jon Azkargorta, Ignacio Iparraguirre, Gregory Tricot, Chongyoun Shao, Rafael J. Jiménez-Riobóo, Joaquín Fernández, Rolindes Balda, Francisco Muñoz

Neodymium doped phosphate glasses are one of the preferred hosts for high power repetition laser systems. Despite their relatively low chemical durability and mechanical resistance, phosphate compositions have been successfully employed in fusion energy experiments, notably at the National Ignition Facility in the USA, due to their high optical performance. One of the most important drawbacks for the preparation of high-quality phosphate laser glasses lies in their ability to retain water during the melting process. We have managed this issue through a preparation procedure that consists of a second melting under a constant flow of N_2 using a graphite crucible, which allows the preparation of glasses with very low water contents and a high degree of optical homogeneity. In this work, we will review the results of the dehydroxylation processing in alumino-phosphate glasses, by studying factors such as melting temperature, time or mass of remelted glass. Furthermore, the main spectroscopic properties of Nd^{3+} ions in glasses of the system Na_2O-K_2O-BaO-Al_2O_3-P_2O_5-Nd_2O_3 will be shown together with their structure as obtained by Nuclear Magnetic Resonance and Electron Paramagnetic Resonance spectroscopies. On the other hand, the mechanical properties of the glasses, such as elastic modulus, thermal expansion and conductivity, and fracture toughness, which altogether are needed to evaluate the thermal shock resistance of the glasses while in operation, have been studied as a function of the chemical composition.

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Effect of Chemical Composition and Modifier ions on Dissolution Rates of Silicate, Phosphate and Borate glasses

Doris Möncke

Metasilicate and Metaphosphate and to a lesser degree borate glasses are typical bioactive glass systems whose dissolution in the body can be controlled by careful adjustments of the composition.

An overview will be given on typical silicate, phosphate and borate network structures, and how these facilitate dissolution rates. Small additions of high field strength ions can change the chemical stability significantly. For silicates – but even more so for phosphates, the choice of crucible material can lead to the incorporation of high field strength elements, such as Si4+, Nb5+ or Al3+, which will change the glass structure and properties.

In phosphates, nitrogen uptake in the melt can lead to a stronger network via nitridification.

Changing the modifier cations of the alkali or alkaline earth series will also change the properties and allows for fine tuning of dissolution rates. This effect can be theoretically assessed by the glass optical basicity, the electron donor power of the glass matrix that is related to the anion polarizability.

This presentation will show various case studies to highlight intentional and un-intentional compositional changes as function of raw materials, crucible materials and initial water content. Especially in low melting phosphate glasses, the initial water content can be a crucial factor in structure and properties.

Finally, the addition of active dopants that facilitate anti-microbial properties, blood vessel formation or near infrared fluorescence will be briefly addressed.

The Role of the Hole Transport Layer in Perovskite Solar Cells: Simulation and Experimentation Perspectives

Neda Neykova, Eva Horynova, Naini Jain, Ognen Pop-Georgievski, Jakub Holovsky

The Hole Transport Layer (HTL) is a critical component in perovskite solar cells (PSCs), facilitating efficient hole extraction and transport from the perovskite layer to the anode, while minimizing charge recombination. It ensures proper energy level alignment, optimizing open-circuit voltage and overall efficiency. Additionally, the HTL enhances device stability by protecting the perovskite layer from moisture and oxygen, and improves adhesion between the perovskite and electrode. Common HTL materials, including organic compounds like Spiro-OMeTAD and inorganic alternatives such as NiO, play a key role in optimizing PSC performance, stability, and scalability. This study investigates the preparation of NiOx thin films as hole transport layers in perovskite solar cells using pulsed laser deposition (PLD), combining simulation and experimental methods. The goal is to enhance the understanding of hole transport in PSCs and contribute to the development of more stable, efficient devices. NiOx films were deposited under varying oxygen pressures, substrate temperatures, and laser frequencies, with experimental results validating trends observed in simulations. Characterization techniques including photothermal deflection spectroscopy (PDS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were used to assess the films. PSC devices incorporating NiOx as the HTL were fabricated, and their performance was evaluated through J-V measurements. This study analyzes how PLD parameters influence NiOx properties and determines optimal conditions for fabricating NiOx films for PSC applications.

Benzimidazole derivatives as multifunctional agents: synthesis and evaluation of antioxidant and photoprotective activity

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A series of benzimidazole derivatives were synthesized efficiently via a one-step process. The compounds were characterized through IR, 1H NMR, and 13C NMR spectroscopy, while their structural properties were further analyzed using DFT methods.

An in vitro study demonstrated the photoprotective potential of these newly synthesized benzimidazoles. Their absorption spectra, recorded in DMSO, showed maximum absorption peaks in the range of 280–300 nm, closely matching the commercial UV filter 2-phenyl-1H-benzimidazole-5-sulfonic acid (PBSA), which has a peak at 302 nm.

The antioxidant activity of the derivatives was evaluated using the DPPH radical scavenging assay, revealing a strong dependence on the number and position of hydroxyl groups on the aryl ring at position 4. Introducing a second hydroxyl group notably improved the activity. Furthermore, the position of hydroxyl groups was critical, as the 2,5-dihydroxy derivative exhibited significantly greater activity compared to its 3,4-dihydroxyphenyl analog.

Preliminary cytotoxicity assessment of the benzimidazole derivatives was conducted on two normal fibroblast cell lines, 3T3 (mouse embryonic fibroblasts) and CCL-1 (murine fibroblasts). Cellular viability, measured using the MTT assay after 72 hours of incubation with compound concentrations ranging from 1 to 250 μg/mL, indicated no cytotoxicity (IC50 > 100 μM) in both cell lines.

These results highlight the potential of the new benzimidazole derivatives as UVB filters in cosmetic formulations, combining photoprotective and antioxidant properties with low cytotoxicity.

Keywords: benzimidazoles; multifunctional agents; UVB filters; antioxidant activity;

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Synthesis and biological studies on bioactive peptides with opioide and anti-inflammatory activity

Dancho Danalev, Boryana Borisova, Hristina Nocheva, Hristina Zlatanova-Tenisheva, Stoyko Petrin, Petya Romanova, Marie Cochard, Stéphane Gérard

Independently of the origine the pain is unpleasant feeling. It worsens the life of the person affected and often leads to mental trauma and depression. Pain is one of the main health problems affecting million people worldwide. Currently, many substances, such as opioids and non-steroidal anti-inflammatory drugs (NSAIDs), are used in medicinal practice in order to assure better life of people touched by chronic or acute pain. Unfortunately, many of these molecules are often associated with severe side effects and risks of addiction. Most of inflammation processes in the organism are related to some kind of pain. Taking into account all mentioned above, there is a growing need to develop new analgesic and anti-inflammatory therapeutics, which exclude or overcome these limitations.

The prohormone submandibular rat 1 (SMR1), can be cleaved to produce polypeptides with analgesic, erectile function, and anti-inflammatory activities. The human protein calcium-binding protein spermatid-specific 1 (CABS1) contains a similar sequence to the anti-inflammatory sequence in rat SMR1. The peptide FELL derived from the human CABS1 protein were tested in an animal model of antigen-induced intestinal anaphylaxis and it was revealed that this molecule significantly inhibited ileal contractions at 10-6 M concentration. Laurent et al. postulated that the sequence FELL contains the core anti-inflammatory component [1]. Thus, our studies were directed to the tetrapeptide molecule FELL. Many modifications in the primary structure of the tetrapeptide were done with desire to influence positively pharmacokinetic and pharmacodynamic of the parent molecule as well as the biological activity. The obtained results on structure-activity relationship will be discussed.

Acknowledgement:

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Kinetic process modeling for extraction of biologically active substances from plant raw materials

Ch.Chilev, D.Peshev, B.Stoilov, A.Balinova

The revival of interest in natural products and traditional herbal medicine has highlighted the need for efficient extraction methods for bioactive compounds from plants. Efficient extraction of phenolic compounds from plants is vital for optimizing industrial applications. Solid-liquid extraction, particularly for phenolic compounds, presents unique challenges due to the complex and varied structure of plant materials, storage influences, and anisotropic properties, all of which affect extraction efficiency. Optimizing these processes is crucial to maximize yield and minimize costs in industrial applications.

This study investigates the extraction kinetics of phenolic compounds from Melissa officinalis (lemon balm), identifying optimal parameters across different solvents and temperatures. Kinetic studies were performed in a stirred vessel with deionized water, 40% ethanol, and 70% ethanol at 30°C and 40°C, under controlled agitation to ensure internal diffusion-limited conditions. Total phenolic content was quantified using spectrophotometry. Two calculation methods for effective diffusion coefficients were applied: the Standard Function Method (SFM), assuming constant diffusion rates, and the Regular Regime Method (RRM), which allows for variable diffusion.

While SFM assumes constant diffusion coefficients, RRM accounts for variations due to structural changes in the solid phase during extraction. Results indicated minimal differences in diffusion coefficients between solvents at similar temperatures. The RRM produced more accurate fits to experimental data, highlighting the importance of accounting for dynamic diffusion rates. Faster extraction rates were observed for 40% ethanol, which achieved higher phenolic yields compared to deionized water and 70% ethanol.

Optimal extraction conditions for phenolic compounds from Melissa officinalis were achieved at 40°C using 40% ethanol. The study demonstrates the reliability of RRM for modeling extraction systems with variable diffusion coefficients, providing valuable insights for industrial-scale applications.

Exploring the Anticonvulsant Potential of CBD oil and CBDA-rich extract: A Path Toward the Brain

Ljubica Mihailova, Jana Tchekalarova, Dushko Shalabalija,
Marija Glavas Dodov, Gjoshe Stefkov

Epilepsy remains a complex neurological disorder, shaped by an intricate interplay of excitotoxicity, neuronal damage, and disrupted signaling between inhibitory and excitatory pathways. For centuries, Cannabis sativa has been revered in traditional medicine, with its therapeutic potential stretching across cultures and generations. Among its many medicinal virtues, its application in neurological disorders, particularly epilepsy, has remained an area of growing scientific interest. While modern research has begun to unravel the anticonvulsant properties of cannabidiol (CBD) and cannabidiolic acid (CBDA), much remains to be explored in optimizing their pharmacological potential and targeted brain delivery. Therefore, our main focus was investigation of possible anticonvulsant activity of 12% CBD oil and CBDA-rich extract obtained from wild growing Cannabis sativa on the territory of N Macedonia, in order to point out the role of this plant as potential source for the development of bioactive compounds and therapeutic drug delivery systems for epilepsy.

This study evaluates the anticonvulsant efficacy of 12% CBD oil and a CBDA-rich extract in acute seizure models of mice, offering new insights into their therapeutic promise. Using the maximal electroshock seizure threshold (MEST), 6 Hz-induced psychomotor seizure threshold, and intravenous pentylenetetrazol (PTZ) tests, we examined the chosen extracts' ability to modulate seizure activity in comparison to carbamazepine, as a conventional antiepileptic drug. Neurotoxicity was assessed through the rotarod test to determine safety profiles. Our findings reveal a dose-dependent anticonvulsant effect, with CBD oil displaying robust seizure protection and CBDA exerting unique modulatory effects that may influence synaptic plasticity and neurotransmitter balance.

Our study not only underscores the therapeutic potential of CBD and CBDA but also highlights the pressing need for innovative drug delivery strategies to enhance their bioavailability and brain targeting. By bridging the gap between traditional botanical medicine and modern pharmacology, our research paves the way for further exploration of cannabinoid-based epilepsy treatments, offering renewed hope for patients with refractory epilepsy syndromes.

Hybrid molecules as strategy for the design of new anti-inflammatory agents

Stephane GERARD, UFR of Pharmacy, URCA, France

Our team, within the Institute of Molecular Chemistry of Reims (ICMR, UMR CNRS 7312), has specialized for several years in the design of new scaffolds of therapeutic interest. Among the different "hit to lead" programs we work on this presentation will focus on the design of innovative dual entities and the challenging development of new hybrid strategies.

Polarization-insensitive Chiral Liquid Crystal Reflectors via Thermo-responsive *Optical Metastructures*

Luciano De Sio

Bottom-up approaches combined with plasmonic nanomaterials are exciting solutions for realizing large area and randomly organized optical components that exploit the optical and thermo-optical properties of stimuli-responsive metastructures.[1-3] Cholesteric liquid crystals (CLCs) represent a fascinating class of materials characterized by their 1D periodic structures. CLCs organize themselves into layers without the positional ordering of molecules within each layer. This study presents and analyzes a novel integration of a large-area optical metasurface-perfect absorber and randomly organized gold nanorods array combined with CLC Bragg reflectors. By utilizing the photo-thermal characteristics of the optical metastructures, the reflection properties of the CLC layer can be manipulated by varying the CLC's pitch, which modifies the reflection band's spectral positioning. Furthermore, changes in the CLC pitch lead to variations in the refractive index, impacting the absorption band's spectral location on the metastructures. This combination heralds a new era in optical technology, offering enhanced versatility and performance in manipulating light.

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Gold Nanorods based platforms for precise detection of pathogens and biomolecules

Francesca Petronella

One of the key lessons learnt from the COVID-19 pandemic is the impact of current lifestyle paradigms, along with climate change, and overpopulation, on the spread of infectious disease. Novel diagnostic tools are therefore required for fast and reliable monitoring of pathogenic microorganisms both as point-of-use and point-of-care devices. In this perspective, biosensors based on nanostructured materials can offer valuable support.

A particular emphasis is on metallic nanoparticles (M-NPs) as optical transducers. M-NPs exhibit the localized surface plasmon resonance phenomenon (LSPR). The LSPR in M-NPs can be easily identified by UV-visible absorption spectroscopy as it involves visible and near-infrared (NIR) radiation. Interestingly, the absorption spectrum of M-NPs is dependent on their size, shape and surrounding medium where M-NPs are dispersed.

Indeed, the Ganz theory demonstrates that a change in the medium in which M-NPs are dispersed (for example, due to intentional or unintentional contamination) corresponds to a change in the refractive index (n) and, therefore, in the wavelength of LSPR plasmon bands (1).

For this reason, M-NPs are utilized as efficient optical transducers.

The present contribution will describe our recent results on the realization of plasmonic nanostructures with excellent optical and morphological features suitable for fabricating optical biosensors with a focus on gold nanorods (AuNRs). Among M-NPs, AuNRs are the ideal candidates as optical transducers for biosensing. AuNRs, due to their anisotropy, are featured by two LSPR plasmon bands, corresponding to transverse and longitudinal plasmon oscillations, respectively. The shift of the LSPR longitudinal plasmon band (LSPR-l), being more sensitive to n variation, is selected as a readout parameter.

After reviewing the main properties and the mainstream synthesis protocols, some examples of AuNRs surface (2.) functionalization for biosensing and nanomedicine applications will be discussed. However, to realize a technologically relevant device it is necessary to reproduce on a substrate the same optical features of a colloidal dispersion on a substrate. This topic will be addressed in the second section of this presentation which will overview our recent result in the realization of bioactive AuNRs arrays (3.) for optical biosensing applications, giving rise to versatile optical devices for immune-sensing or gene-sensing.

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The synthesis and photoluminescence properties of spiro oxindole

Kosuke Nakashima, Aoi Imamura, Yasuyuki Matsushima, Shin-ichi Hirashima,
Dancho Yordanov, Tsuyoshi Miura, Anton Georgiev

Molecules with indole motifs play an important role in materials science and medicinal chemistry. Spirooxindoles are attractive targets in synthetic chemistry. They are widespread in natural products and exhibit diverse biological activities such as antitumour and antibacterial. We have recently demonstrated the asymmetric synthesis of spirooxindoles using organocatalysts and their photoluminescent behavior. The squaramide organocatalyst efficiently promoted the asymmetric Friedel-Crafts alkylation of indoles with α, β-unsaturated trifluoromethyl ketones, affording the corresponding products bearing both the indole motif and the trifluoromethyl group in high yields with excellent enantioselectivities (up to 99% ee). The transformation of the obtained adduct into chiral spiroindolin-3-one was also demonstrated. A chiral and non-conjugated C2-spirooxindole substituted at the C3 position by a phenyl ring was studied for its unusual photoluminescence behavior. The compound exhibited an unusual solvent-dependent visible emission in the range of 440-540 nm with a good quantum yield. The C3-phenyl ring was found to play a central role in the unusual visible emission, allowing rotation through a single bond. We have studied the acid-triggered rearrangement in two C2-spirooxindoles to 2-hydroxyhemi-indigo and chromenoindole derivatives, which are promising for biomedical and optical applications. The N-H spirooxindole shows a double proton translocation and its conversion to the (Z)-2-hydroxyhemi-indigo photo-switch with trifluoroacetic acid, while the N-methyl-spirooxindole undergoes a structural rearrangement to the chromenoindole. 2-Hydroxyhemi-indigo exhibits visible light-activated Z/E switching with high thermal stability of the E-switched form due to intramolecular hydrogen bonding stabilization.

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Visible Light Switching of ortho-Functionalized Azo Phthalimides with Tunable Z-Isomer Stability

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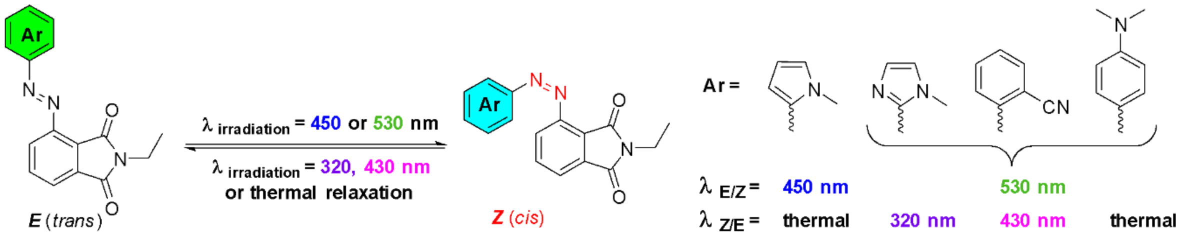

Light plays a vital role in nature and photonic technologies. Looking at nature, we witness a number of collections of molecular switches and machines, for example, vision cycle with rhodopsins and photosynthesys. Molecular photoswitches are artificial photoactive tools that respond to light stimuli and convert light energy based on their photoisomerisation from thermodynamically stable to metastable isomers. The design of new azo compounds with improved performance is an emerging area of research due to the increasing demand for photoswitchable molecules in a wide range of applications.

Azoheteroarenes are a class of bistable E/Z photoswitches that are triggered by light in both directions. A novel class of azo photoswitches based on a 3-substituted phthalimide that undergoes reversible E/Z isomerisation under visible light irradiation has been designed and synthesised by our group. The idea is based on *ortho*-functionalization by EW imide ring and *ortho* ED or EW groups in heteroaryl and phenyl rings. The photoswitching performance was compared by *para*-dimethylaminophenyl azo compound. Depending on the heteroaryl/phenyl rings, they exhibited different wavelengths of visible light E/Z isomerization ranging from 450 to 530 nm and different thermal stability of the metastable Z isomer from seconds to days. They exhibited good fatigue resistance and near qualitative E/Z switching in the range of 60-80%. DFT calculations have revealed different thermodynamic stability of the metastable Z isomers, which is reflected in their rate of thermal back Z/E isomerisation.

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Nonlinear optimization and sensitivity analysis for continuous approximation of true boiling point data for crude oils

Dimitar Nedanovski, Svetoslav Nenov, Dimitar Pilev

Six functions, four of which distribution-like Weibull, Weibull extreme, Beta and Gamma distributions, depending of a certain number of free parameters, have been investigated as model functions for approximating True Boiling Point (TBP) data of all types of crude oil. The initial data originate from practical measurements in Lukoil Neftohim - Burgas.

Nonlinear regression, subsequent sensitivity analysis and application of Akaike Information Criterion (AIC) and Bayes Information Criterion (BIC) have been performed for each of these functions in order to determine the number of parameters and optimal parameters values. The AIC and BIC suggest the six-parameter Weibull extreme function as best fit for the TBP data of all crude oil types, allowing construction of a correct TBP curve and detection of measurement errors.

The results of this research contain some unpublished calculations related to I. Shishkova, D. Stratiev, I.V. Kolev, S. Nenov , D. Nedanovski, K. Atanassov, V. Ivanov, S. Ribagin, Challenges in Petroleum Characterization - A Review, Energies, no. 20, Article number 7765, 2022.

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Multiphysics simulation for efficient and reliable systems for low temperature plasma treatment of metals

N. Penkova, B. Varhoshkov, V. Todorov, H. Anchev, K. Krumov, V. Iliev

Mathematical models of the coupled electromagnetic, fluid flow and thermal processes in periodic chambers for low temperature plasma treatment of metal products have been developed. The specific electrical conductivity of the ionized gas has been calibrated on the basis of an electrical model of the chamber and measurements of temperatures and the current in the circuit in situ. The models were solved numerically via the finite volume method in the ANSYS/CFX software. The three-dimensional fields of pressure, temperature, velocity, turbulent characteristics, electric current density and voltage in the chamber have been simulated and analyzed in order to estimate the possibilities for improvements of the efficiency and the reliability of the equipment. Ways for further development and application of the models and the computational algorithms for technological and constructive enhancement of the plasma treatment systems are discussed. The researches were conducted in the framework of the project BG-RRP-2.004-0002 BiOrgaMCT, funded by the European Union-NextGenerationEU through the National Recovery and Resilience Plan of the Republic of Bulgaria.

A refinement of the crossover selection in the differential evolution method

Dimitar Nedanovski, Svetoslav Nenov, Dimitar Pilev

A refinement of the crossover selection in the differential evolution method (DEM) for global optimization and some benchmarks in order to test and compare the results have been proposed. In the tested cases the introduced refinements lead to better results relative to the original DEM.

Besides we present a typical case in which we apply DEM - optimizing and analysing a nonlinear least squares, used to model gas oil viscosity on the base of Walther's empirical equation, using initial database of 41 primary and secondary vacuum gas oils.

Electrochemical impedance spectroscopy (EIS) to study the corrosion resistance of anodized aluminium alloys

Gonzalez-Rovira, Leandro

Anodizing of aluminum alloys is an electrochemical technology that produces the formation of anodic aluminum oxide (AAO) layers on the surface of the alloy. Barrier layers and porous layers can be obtained depending on the electrolyte employed.

Porous aluminum oxide layers (PAAO) are produced in moderate acid electrolytes and have been widely used in fields as varied as architecture, sporting goods, packaging, aerospace or automotive. Anodized parts often undergo post-treatments that take advantage of the porous nature of the anodic layer to enhance their properties, such as corrosion or wear, or for aesthetic purposes, such as color or gloss. These post-treatments include painting, application of adhesives to enable the bonding of the anodized part to another part, or introduction of dyes and pigments into the porous structure. After the application of the dye, the pores must be sealed to prevent leaching or desorption. Likewise, when PAAO do not need painting, adhesives, or dyes, they require a post-treatment to seal their pores to significantly improve their corrosion resistance.

Electrochemical impedance spectroscopy (EIS) is a powerful technique which can provide information about the corrosion resistance of the anodized element, the quality of sealing and the mechanisms of both the sealing and the evolution/degradation of the PAAO layers in contact with a corrosive media.

This contribution summarizes the employment of different equivalent electrical circuits (EEC) as a tool to understand the EIS spectra of anodized aluminum, both sealed and unsealed, and justifying the correspondence of their electrical elements (basically resistances and capacitors) with the different zones of the PAAO layers.

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Design of innovative peptide therapeutics for targeting α-synuclein aggregation

Blagovesta Popova

Peptide drug development is emerging as a promising strategy in the fight against neurodegenerative diseases like Parkinson's Disease (PD). PD affects millions of people worldwide and is expected to become even more common as the population ages. The disease is caused by the death of specific brain cells due to the harmful aggregation of a protein called α-synuclein. This small, unfolded protein aggregates into toxic oligomers and prefibrillar structures, disrupting normal brain function and leading to the typical symptoms of PD. Developing drugs to stop or reverse α-synuclein aggregation has been challenging. However, recent advancements in designing peptides as targeted inhibitors of protein aggregation using computer models have shown significant potential in reducing toxic protein aggregates, paving the way for innovative treatments that could slow or halt the progression of PD. We identified two peptides that significantly inhibited α-synuclein oligomerization and aggregation in vitro and partially rescued cytotoxic effects in vivo. In this study, in silico mutagenesis was employed to design new peptides with improved characteristics based on these sequences. Computational tools were used to model peptide structures and predict their interactions with α-synuclein fibrils. The most promising candidates were co-expressed with α-synuclein in yeast cells, demonstrating improved rescue ability by reducing cytotoxicity, inhibiting in vivo α-synuclein aggregation, and decreasing reactive oxygen species caused by α-synuclein. This in silico optimization approach represents a valuable method for developing aggregation inhibitors, advancing peptide-based drug research for PD.

EIRENE-CZ mass spectrometry resources supporting human exposome research

Elliott J. Price, Frank L.N.A. Acquaye, Eliška Benešová, Thomas A.A. Contini, Kateřina Coufalíková, Gabriela Přibyl Dovrtělová, Kristína Gömöryová, Helge Hecht, Akrem Jbebli, Štěpán Koudelka, Kapil Mandrah, Wudmir Y. Rojas, Hana Seličová, Romana Ševčíková, Žiga Tkalec, Veronika Vidová & Jana Klánová

Mass spectrometry (MS) is a leading technology for measuring proteins and small molecules in molecular phenotyping. However, concerns about the reproducibility and replicability of MS-based molecular phenotyping persist. This presentation will introduce the open MS resources of the Czech node of EIRENE, the first European infrastructure dedicated to supporting human exposome research. These resources are designed to i) enable the MS-based profiling of human exposure to chemical agents, ii) support the quantitation of clinically relevant protein and metabolite biomarkers and iii) facilitate the high-throughput processing of MS data. Examples of ongoing applications in clinical studies and population cohorts will be highlighted and the prospects for MS-guided precision (environmental) health and chemical early warning systems discussed.

Bioactive non-fouling polymer brushes: From design parameters to medical applications

Diego Dorado Daza, Radoslava Sivkova, Jan Svoboda, Tomas Riedel, Andres de los Santos Pereira and Ognen Pop-Georgievski

The success or failure of interventions involving medical devices and biomaterials is often defined by interactions at their surface with the biological environment they interface. Rapid non-specific deposition of proteins (termed fouling) can lead to life-threatening complications. The adsorbed proteins can trigger blood coagulation, which can lead to thrombus formation. Adsorbed proteins promote immune responses, such as inflammation on implants or complement activation on drug carriers, leading to their rapid clearance. In the lecture we will report on our work towards the development of coatings to mitigate protein fouling. Their preparation relies on the “grafting to” the surface of pre-formed polymer chains or “grafting from” the surface via surface-initiated polymerizations. We will show that the latter approach provides brushes of superior fouling resistance owing to the attainability of thicker layers and higher grafting densities. By endowing the polymer brushes with reactive groups, we can incorporate peptide sequences and biorecognition elements to target various biomedical applications.

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Emerging colorimetric and fluorimetric smart materials

Atanas Kurutos

Optical chemical sensors and instruments transmute chemical information into a suitable chromo-fluorogenic signal. Fluorescence-based methodologies are extensively utilized owing to their exceptional efficiency, selectivity, reproducibility, safety, and rapid detection capabilities. Enhancing the luminous properties and functional control of organic dyes while simultaneously reducing synthesis costs and improving the economic viability of molecular material production continues to present considerable challenges. Wavelength-ratiometric methodologies demonstrate considerable advantages in fluorescence sensing and imaging when contrasted with approaches that rely on intensity variations at a singular wavelength. As a result, they are increasingly preferred in fluorescence probing and sensing due to their provision of an internal reference for the output signal, which mitigates experimental artifacts, thereby enhancing the sensitivity and reliability of assays. Recent advancements suggest that this strategy can enhance outcomes by utilizing a diverse range of novel fluorophores, thereby leveraging the complete spectrum of photophysical and photochemical effects, as well as incorporating a wide array of assay designs. The application domains encompass a wide array of areas, including onsite environmental monitoring, point-of-care diagnostics, and personal testing needs. Selected examples of the detection of various analytes within chemical and biological systems demonstrate numerous opportunities for the integration of the analyte-sensor interaction in the fabrication of new smart materials.

Light-harvesting Flavin Derivatives for Hydrogen Evolution Reaction

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This research explores the design and synthesis of a novel, vitamin B2-inspired, metal-free organic photosensitizer tailored for sustainable energy applications. Flavins, derivatives of riboflavin are π-conjugated molecules that possess unique optical, redox, and photosensitizing properties. Molecular tuning through organic synthesis enables their optimisation for a suitable light-harvesting application.

Preliminary evaluation of flavin photosensitising properties was conducted using a simple setup. The HER measurements utilised quasi-homogeneous system consisting of flavin photosensitiser, water reduction co-catalyst and sacrificial electron donor. The primary goal was to prove viability of the photocatalytic system and establish optimal composition as a foundation for future study.

This study showcases the use of a nature-inspired, metal-free molecular organic photosensitizer, which demonstrated superior photostability and stable performance over 29 hours. It produced 100 μmol of H_2 (TON of 400) under visible light irradiation using a low-power output white LED. Remarkably, the system operated reliably and reproducibly under these basic conditions. The highlight of this study lies in the application of the nature-inspired metal-free molecular organic photosensitiser, which exhibited superior photostability and stable performance over 29 hours, yielding 100 μmol of H2 (TON of 400) upon visible light irradiation with white LED with low power output. Notably, the system was robust enough to reliably and reproducibly work under such primitive conditions, which is remarkable. Further, the LED lamp is energy-saving compared to solar simulators or high-power xenon lamps. The study highlights the potential of flavins as cost-effective, scalable, and sustainable materials for green hydrogen production, offering a compelling alternative to traditional noble metal-based systems.

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Programmable Microtexturing of Surfaces through Polarization-Controlled Azopolymer Structuring

Marcella Salvatore, I Komang Januariyasa, Francesco Reda, Fabio Borbone, Stefano Luigi Oscurato

The ability to engineer surface properties is closely linked to the complexity and anisotropy of superficial structures. Traditional micropatterning techniques enable the precise and repeatable fabrication of intricate textures. However, these methods are often costly, time-consuming, and require a predefined design of the final structure, limiting their flexibility.

An alternative and more versatile strategy involves photolithographic approaches based on light-induced mass transport in azopolymers. These materials offer the advantage of being dynamically and reversibly structured on a large scale using a simple optical setup, without the need for additional processing steps. When exposed to spatially structured UV/visible light fields, azopolymer films undergo surface modulations due to the cyclic transitions between trans and cis isomerization states of azomolecules. This molecular rearrangement drives mass transport across the film, leading to controlled topographical changes. The final surface geometry depends on the intensity distribution and polarization state of the incident light, which determine both the amplitude of deformation and its directional anisotropy.

By leveraging polarization-driven mass transport, it is possible to generate large-scale surface textures with tunable levels of complexity. In this work, a straightforward illumination scheme is used to reconfigure the pre-structured azopolymer microtextures, initially arranged as 2D square arrays of cylindrical microvolumes. This approach is further extended by accounting for the wavelength-dependent light penetration depth within the material, which affects the structuring process in three dimensions. The combination of these effects enables the tailored design of the final texture, enhancing control over both surface and volume structuring.

This technique opens new possibilities for designing functional surfaces with tailored properties, such as tunable wettability and diffraction behavior. Additionally, the ability to further modify the microstructures post-fabrication ensures adaptability for various application requirements, making this a highly flexible and scalable method for advanced surface engineering.

Azopolymer surface reliefs gratings: fabrication & diffraction properties

Francesco Reda (*), Marcella Salvatore, I Komang Januariyasa, Fabio Borbone,
Stefano Luigi Oscurato

Diffraction gratings are crucial in photonic technologies, but their fabrication by traditional methods is still challenging, influenced by factors such as resolution, size, and throughput. Azobenzene-containing polymers (azopolymers) offer a promising alternative. These polymers enable light-driven surface structuring through cyclic isomerization of azobenzene. These molecular motions generate stress in the polymer matrix, causing a stable plastic deformation and forming surface reliefs in a single illumination step. In this work, we report on the fabrication of azopolymer light-induced surface reliefs gratings (SRGs) using both interference lithography and computer-generated holographic illumination. A scalar diffraction model is developed to quantitatively relate the results of a Fourier analysis of the surface profile to the accurate measurement of the diffraction efficiencies in the transmitted diffraction orders. This model is further extended for a novel diffraction-based method to measure the refractive index of structured thin films, which is successfully estimated by simply incorporating the measured surface topography and the diffraction efficiency of the grating over a wide spectral range into the scalar theory-based diffraction model. Finally, we present a real-time holographic setup for the reconstruction of SRG morphology during inscription. By embedding a probe beam into the experimental setup, we collect and analyze the evolving diffraction pattern in real time, using Fourier decomposition to accurately reconstruct the periodic surface geometry, including any deviation from an ideal sinusoidal profile. The accurate diffraction model and the ability to reconstruct the evolving surface geometry in real time provide unprecedented control over the final diffractive functionality, potentially representing a cornerstone in the fabrication of azopolymer diffraction gratings.

Chemical analysis of new materials - problems and some solutions

Andriana Surleva

The chemical characterization of new materials and the precursors of their obtaining is a challenging task that imposes for development of a specific analytical chemistry strategy. Nevertheless the line of general and specific guidelines, still the verification of methods of estimation of chemical and physical characteristics of specific samples needs development of innovative approaches. In this report the limitations of well-known approaches are discussed together with the developed alternatives to demonstrate specific issues encountered in the research laboratory analyzing new materials or characterizing new properties of materials.

Gergana Ilieva

Presentation topic will be added

Characterization of Novel Ti-Mo-Nb-Sn Alloys in Biomedical Engineering

Petrica Vizureanu , Madalina Simona Baltatu, Andrei Victor Sandu, Dumitru Doru Burduhos-Nergis, Manuela Cristina Perju, Dragos Cristian Achitei

Many fields use titanium alloys because of their unique properties. The work aims to obtain and characterize alloys from the Ti-Mo-Nb-Sn system using the vacuum arc melting method, aiming to improve materials for medical alloys. These alloys were designed to overcome existing problems such as inadequate mechanical properties and allergic reactions commonly associated with biometals, such as 316L stainless steel and Co-Cr-Mo alloys. Ti–Nb–Sn–Mo alloys have a dual-phase structure (β and α"+β), and they have a high flexural strength (1145–1255 MPa) and a low elastic modulus (53–63 GPa), which is very similar to the mechanical properties of human bone. They also exhibit a superior modulus of resistance, making them ideal for high-load applications. The Ti–5Mo–11Nb–7Sn alloy, in particular, shows exceptional promise due to its high strength, suggesting extensive potential in implantology. This alloy not only improves implant longevity and performance but also aims to replace less compatible materials, meeting the growing demand for more efficient biomedical technologies.

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Properties and Applications of New Ti-Mo-Zr-Ta Alloys for Orthopedic implants

Andrei Victor Sandu, Madalina Simona Baltatu, Petrica Vizureanua, Dumitru Doru Burduhos-Nergis, Manuela Cristina Perju, Dragos Cristian Achitei

The orthopedic applications of titanium alloys, as depicted in various studies and clinical reports, highlight their important role in surgical implants. However, challenges like low wear resistance have prompted ongoing research and innovation. Enhancing wear resistance and incorporating antibacterial properties have become focal points in the evolution of β-Ti alloys, with a keen emphasis on bone regeneration capabilities. This paper focuses on the development of titanium-based TiMoZrTa (TMZT) alloys, considering their properties, using a vacuum remelting system: Ti15Mo7Zr5Ta, Ti15Mo7Zr10Ta, Ti15Mo7Zr15Ta, Ti20Mo7Zr5Ta, Ti20Mo7Zr10Ta, and Ti20Mo7Zr15Ta. EDX microanalysis confirmed the precise chemical composition of these alloys and their uniform distribution without chemical heterogeneities. Optical microscopy revealed various grain structures, from dendritic boundaries in some alloys to uniformly distributed large β grains in others. X-ray diffraction identified a dual-phase structure consisting of a centered cubic β-phase and an orthorhombic α”-phase. Thermal analysis showed stability of the TMZT alloys at body temperature, with no phase transformations observed between 30-40º C. Microhardness tests indicated hardness values ranging from 321.31 HV to 462.33 HV, while indentation tests revealed elastic moduli between 43.57 and 76.88 GPa. The presence of β-stabilizing elements like Mo, Zr, and Ta effectively reduced the elastic modulus, closely approximating that of human bone (17-30 GPa), with a noteworthy improvement in the modulus by 44% when molybdenum content was increased from 15% to 20% and alloyed with 10% tantalum.

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Preparation and characterization of calcium-containing phosphate conversion coatings for biomedical applications

Dimka I. Fachikova, Gergana P. Ilieva, Daniela S. Lilova

Calcium phosphate conversion coatings obtained on metal implants are widely used for biomedical applications. The mechanical strength, good adhesion to the substrate, and high corrosion resistance in the human body of calcium phosphate conversion coatings on metal implants make them widely used for biomedical purposes. This work presents the results obtained during phosphating of high nitrogen stainless steel simples in calcium-containing phosphate solutions. The influence of composition and concentration of the components on the density, pH, conductivity, total and free acidity of the phosphating preparations are determined, as well as the effect of concentration and temperature of the working solutions on kinetics of obtaining coatings was also determined. The surface morphology of the coatings was investigated using scanning electron microscopy (SEM). The chemical state and phase composition were determined using energy dispersive spectroscopy (EDS) and X-ray diffraction analysis (XRD), respectively. The behavior and stability of phosphate coatings on high nitrogen stainless steel in various physiological solutions, close to these in human body, was also investigated.

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Anticonvulsant profile of three hemorphin-4 analogues with rhodamine B in mice

Jana Tchekalarov, Petar Todorov, Tsveta Stoyanova

Epilepsy is a neurological disorder with symptoms closely related to convulsive or non-convulsive seizures. Hemorphins, are products of hemoglobin metabolism considered as bioactive atypical oligopeptides containing four to ten amino acids. Recently, our team reported a synthesis and characterization of three N-modified analogues of hemorphin-4 with rhodamine B (Todorov et al., 2021). In the present study, the three compounds, Rh-1, Rh-2, Rh-3, were evaluated in vivo for their antiseizure activity in the 6-Hz test and the maximal electroshock (MES) test. As referent drugs, phenytoin and diazepam were used for comparative analysis. Further, the most effective dose of the three compounds, were characterized in a pentylenetetrazole (PTZ) kindling model of epilepsy in mice. The role of opioid receptors underlying their mechanism of action was also evaluated.

The R-3 compound showed efficacy against psychomotor seizures in the 6-Hz test and tonic-clonic seizures in the MES test at four doses tested whereas the R-1 and R-2 compounds showed activity only at the highest doses of 10 µg/5 µl after icv infusion in mice. A combination of the selective opioid receptor antagonists of DOR, KOR, and, MOR with the highest doses of R-1, R-2, and R-3 compounds, respectively, was used to elucidate the possible role of opioid receptors in the underlying mechanism related to their protective activity against the MES-induced seizure spreading. Only the selective antagonist of DOR, natrindole, suppressed the anti-seizure effect of the R-1 peptide analogue while the opoid antagonists were unable to suppress anti-seizure activity of R-2 and R-3. The three Rh analogs suppressed clonic seizures in fully kindled mice, which effect was comparable to that of the referent drug diazepam However, the opioid receptor antagonist naloxone inhibited the anti-seizure effect only of Rh-1. Our results suggest that the R-1 compound as the most potent anti-seizure hemorphine analogue, which activity is mediated by opioid receptors.

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Chemical behavior and Bioactive Properties of Hemorphin-4 Conjugating to N-[4-(2-phenyldiazenyl)phenyl]glycine and its sensor activity towards metal ions

Stela Georgieva, Petar Todorov, Temenuzhka Radoykova, Spas Nikolov

This study focuses on the synthesis and characterization of a novel azobenzene analog, namely N-[4-(2-phenyldiazenyl)phenyl]glycine (Azo), which is related to hemomorphin-4 (Tyr-Pro-Trp-Thr-NH2). The synthesis was conducted utilizing a modified solid-phase peptide synthesis (SPPS) technique employing the Fmoc methodology. An investigation was conducted to establish the spectroscopic, electrochemical, and biological properties of the newly synthesised molecule, Azo-Tyr-Pro-Trp-Thr-NH2. Analysis of the physicochemical parameters revealed that the fluorescence intensity and voltammetric behaviour of the azopeptide compound were significantly influenced by the polarity of the solvents. The pK value of the azopeptide derivative in aqueous solution as well as the stoichiometry and stability of the metal (Zn, Hg, Cd, Cu, Pb and Au) chelates show the stoichiometry is predominantly 1:2 (ML2) with constats corresponding to high complex stability. The findings demonstrated the effective utilization of the novel azopeptide compound for the detection of copper in water within a concentration range of 1.3x10-7 to 3.0x10-6 mol L-1. The method exhibited satisfactory precision (Sr = 1.5%) and accuracy.

The in vivo potential anticonvulsant effect of the new biopeptide Azo-Tyr-Pro-Trp-Thr-NH2 was also studied using the 6-Hz seizure test and maximal electroshock (MES) test in ICR mice. The impact of both 1 and 5 Âµg compounds was similar to that of the positive control valproate in the 6-Hz test. The test chemical exhibited no neurotoxic effects in the rotarod test. Our findings indicate that the biopeptides that have been altered at the N-terminus of hemomorphin-4 using azobenzene should be studied further as potential candidates with significant biological activity, namely in the area of anticonvulsant properties.

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Design and synthesis of novel FELL analogs containing Tyr in the first position instead of Phe

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Pain is defined as a major health problem worldwide, essentially affecting quality of life. It also presents a challenge for effective long-term management [1]. Accurately characterizing and localizing pain, regardless of whether being acute or chronic, mild or intense, is challenging due to the diverse possible origins [2]. Currently, existing therapies, such as opioids and non-steroidal anti-inflammatory drugs (NSAIDs), are often associated with severe side effects and risks of addiction. Therefore, there is a growing need to develop new analgesic therapeutics, which exclude or overcome these limitations.

Our previous works were focused on the development of several series of the anti-inflammatory FELL (Phe1-Glu2-Leu3-Leu4) analogs [3,4]. Moreover, our in-vivo evaluation had identified the parent tetrapeptide and newly created analogs as promising analgesic agents.

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The present research aimed to enhance pharmacological properties of the parent tetrapeptide FELL by modifying the amino acid primary sequence. The performed changes include substitution of the proteinogenic Phe at the 1st position with L- or D-tyrosine (Tyr), alongside with C-terminal amidation. Introducing an aromatic hydroxyl group that could facilitate additional hydrogen bonding and electronic interactions, potentially enhancing the peptides' bioactivity and specificity. Herein, we report design, synthesis, and structural characterization of four new Tyr-analogs of FELL.

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Effect Of Modification of Temporin A With Fluorinated Phenylalanine on Antibacterial Activity

Dilyana Dimitrova, Veronica Nemska, Tsvetelina Foteva, Nelly Georgieva, Dancho Danalev

Antimicrobial resistance (AMR) has reached almost critical proportions, ranking it as one of top ten global health threats according to WHO. This threat necessitates a solution in terms of new agents that can combat AMR. A promising new alternative is a group of bioactive compounds called antimicrobial peptides (AMPs). With that focus of research in mind, the incorporation of fluorinated amino acids in bioactive compounds such as peptides has proved to be beneficial. Fluorinated amino acids enhance pharmacological characteristics as they increase stability in metabolic processes and hydrophobicity. In this study we examined the impact of the substitution of the Phe in position 1 with fluorinated such in two different places in the molecule of Temporin A – DT4F (Phe(4-F)-LPLIGRVLSGILNH2) and DT2F (Phe(2-F)-LPLIGRVLSGIL-NH2) on the antibacterial activity in comparison to the parent peptide. The novel peptides were synthesized following the Fmoc/OBut strategy for SPPS and analyzed for structure and purity using HPLC-MS technique. The antibacterial activity of the newly synthesized analogues was assessed against Bacillus subtilis NBIMCC 3562 in order to obtain the minimal inhibitory concentration (MIC) using broth microdilution method in 96-well plates in concentration range from 0 to 320 µg/mL and compared to the parent temporin A.

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New Aluminosilicate Glasses for High Power Lasers: Luminescence and Thermomechanical Properties

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Glasses as luminescence materials for high power laser applications have to meet various physical properties. Among these are optical properties, such as high transparency and long fluorescence life times as well as thermomechanical properties, high Young's modulus and small coefficient of thermal expansion. Traditionally, active laser glasses are phosphate glasses due to their good optical properties. However, these glasses suffer from their very high coefficient of thermal expansion ($>10x10^{-6}\cdot K^{-1}$). Aluminosilicate glasses have excellent mechanical properties and coefficients of thermal expansion in the range from 3 to $6x10^{-6}\cdot K^{-1}$. Various ternary and quaternary MO_x-Al_2O_3-SiO_2 with M = Mg, Ca, Sr, Ba, Pb, Zn, Li, Na, K, Y and La, doped with Yb_2O_3, Sm_2O_3 or Eu_2O_3 were prepared and characterize with respect to their luminescence behavior as well as their thermomechanical properties. Special attention has been paid to the minimization of the water concentration of these glasses, because the fluorescence especially of Yb_2O_3 doped glasses strongly decreases with increasing water concentration. Best results were obtained by bubbling the melt with dried argon and by doping the glass with few mol% fluoride. Finally, the damage threshold of optimized glass compositions is discussed.

Investigating Ion Exchange in Organic Bioelectronic Devices Using Selective Fluorescence Detection

Martin Vala, Marková Aneta, Ivaylo Zhivkov, Jan Víteček and Martin Weiter

With the increasing number of diseases such as Parkinson's and Alzheimer's diseases, epilepsy, heart disease, depression, diabetes, and cancer, there is a growing need for targeted treatments that maximize effectiveness while minimizing side effects. Organic bioelectronics offers a promising approach that enables precise, electronically controlled stimulation and detection. One such device, the organic electrochemical transistor (OECT), is based on the ion exchange between organic semiconductors and environment (cells). Organic semiconductors for OECT's offer a unique ability to convert ionic conductivity into electronic conductivity. Due to this ion-to-electron conductivity and "softer" (lower Young modulus) mostly polymeric structure, these devices provide more efficient communication between living tissues and electronic components compared to conventional technologies.

This study focuses on real-time analysis of ion exchange and transport in OECTs. Despite significant research advancements, much of our current understanding of ion exchange relies on indirect or delayed detection methods. However, a precise understanding of ion movement is essential to optimizing the performance of organic bioelectronic systems.

To address this, we combine electrical, and optical measurements to quantify ion exchange and transport in real-time. By correlating the outputs of these detection methods, we achieve a more accurate in situ assessment of ionic activity. This approach allows for a detailed investigation of drug exchange between organic semiconductors and targeted environments, providing valuable insights into OECT's potential applications in bioelectronics.

Fluorescent Benzimidazole-Hydrazone-Loaded Micelles: A New Tool for Detection and Cancer Treatment

Rayna Bryaskova, Nikoleta Philipova, Kameliya Anichina, Rumiana Tzoneva

Fluorescent micelles designed for controlled release of a novel anticancer drug have been developed to enable simultaneous intracellular imaging and cancer treatment. These nanosized fluorescent micellar systems incorporate the new anticancer drug through the self-assembly of well-defined block copolymers. These copolymers are based on amphiphilic poly(acrylic acid)-block-poly(n-butyl acrylate) (PAA-b-PnBA), which is synthesized using Atom Transfer Radical Polymerization (ATRP), along with the hydrophobic anticancer drug benzimidazole-hydrazone (BzH). Using this method, well-defined nanosized fluorescent micelles were prepared, consisting of hydrophilic polyacrylic acid (PAA) shell and a hydrophobic poly(n-butyl acrylate) (PnBA) core. The BzH drug was embedded within the micelles due to hydrophobic interactions, resulting in very high encapsulation efficiency. The size, morphology, and fluorescent properties of both the blank and drug-loaded micelles were investigated using various methods. The BzH drug-loaded micelles demonstrated enhanced antiproliferative and cytotoxic effects on MDA-MB-231 cells, resulting in prolonged alterations to microtubule organization, along with apoptotic changes and preferential localization in the perinuclear region of cancer cells.

The influence of water on flavin-derivative spectroscopy

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Flavins and lumazines are naturally occurring derivatives of pteridine, exhibiting specific structure-dependent photoactive properties. They are well-known for their role in redox cofactors and electron shuttling in cellular metabolism [1]. In this study, we focused on four pteridine derivatives – lumazine, its cyanated derivative, alloxazine, and the fluorinated derivative of alloxazine – and investigated their spectroscopic behavior in water and dimethyl sulfoxide (DMSO) mixtures.

Experimental samples were dissolved in DMSO, with water gradually added to modulate their optical properties. The results showed that the cyanated lumazine derivative exhibited a significant blue shift in its spectrum upon the addition of water, suggesting the potential for using this effect to detect specific water concentrations in solution. Noteworthy findings were also observed in samples containing a 65% water and 35% DMSO mixture, where a marked decrease in absorption and emission intensities was registered, likely due to the formation of $DMSO{\cdot}2H_2O$ trimers [2]. This phenomenon has been previously documented and points to the potential of these molecules in optical sensors for probing specific microenvironments [3].

Furthermore, it was found that substituting polar groups significantly enhances water solubility, allowing these molecules to penetrate cell membranes more easily than larger flavins. This opens up opportunities for their use in in vitro imaging of living cells.

The spectroscopic properties of the studied molecules were also theoretically modeled using density functional theory (DFT), incorporating both implicit DMSO solvent models and explicit water molecules, providing valuable insights for future applications of these molecules in bioimaging and chemical sensing.

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Aminotriazole containing 1,8-naphthalimides as a platform for AND molecular logic gate and cancer diagnostic tool

Nikolai I. Geogiev

A family of novel fluorescence sensing 1,8-naphthalimides containing aminotriazole unit in C-4 position was synthesized and investigated. It was found that in the novel probes occurred a TICT process in excited state which fluorescent efficiency was strongly pH and viscosity dependable. Due to the remarkable fluorescence changes as function pH and viscosity, an AND molecular logic gate operating in the physiological range was constructed. The fluorescent output of obtained AND gates was enabled simultaneously at high acidity and viscosity which often was associated with cancer. Also the prepared aminotriazole containing 1,8-naphthalimides demonstrate low cyto toxicity and cell permeability which show the high potential of the novel probes to act as diagnostic tool in medicine.

Tuning Fluorescence in Stilbene-Based Materials: Host-Guest Systems and Energy Transfer for Enhanced Solid-State and Bioimaging Applications

Smolka Rastislav, Kolaříková Adéla, Čekal Jozef, Pauk Karel, Luňák Stanislav Jr., Imramovský Aleš, Anton Georgiev and Vala Martin

Photoluminescent materials based on organic conjugated molecules have been widely studied for their unique optical properties, color tunability, and potential applications in various fields. Intense solid-state fluorescence (SSF) is particularly useful for technologies such as organic light-emitting diodes (OLEDs), light-emitting field-effect transistors, and water-dispersible nanoparticles for bioimaging. This study focuses on the properties of stilbene-based photoluminescent materials in both solid-state form and molecular mixtures. Their fluorescence primarily arises from intramolecular charge-transfer (CT) transitions, which allow for a broad range of emission colors.

However, in red-emitting materials, band-gap narrowing can reduce fluorescence quantum yields due to increased rate of non-radiative processes. One way to overcome this is through host-guest (HG) systems, where a mixture of two structurally similar molecules with different band-gap energies enhances fluorescence via Förster resonance energy transfer (FRET). In these systems, the donor molecule transfers energy to the acceptor, boosting its fluorescence beyond its typical levels. When formulated as nanoparticles, these materials exhibit stronger acceptor-like photoluminescence. By carefully selecting donor-acceptor pairs and their ratios, it is possible to achieve partial energy transfer, leading to materials that emit a balanced combination of both components—creating bright white-light-emitting (WLE) materials.

Materials with strong solid-state fluorescence are highly desirable for many applications. WLE materials are particularly useful in OLEDs and field-effect transistors, while far-red (FR) emitting nanoparticles play a crucial role in bioimaging. In biological applications, FR fluorescence offers several advantages, including reduced background autofluorescence, lower light scattering, and improved tissue penetration. These factors contribute to better optical contrast and reduced photodamage, making FR-emitting materials especially valuable for imaging applications. This study highlights the importance of carefully designing photoluminescent materials to optimize their performance for specific technological and biomedical uses.

Bioactive glass-ceramics in the CaO-SiO2-P2O5 system containing high-temperature polymorphs of dicalcium silicate

Irena Mihailova, Lachezar Radev, Petya Dimitrova, Hristo Georgiev, Radostina Ivanova, Ralitsa Teodosieva

The CaO-SiO2-P2O5 system is one of the main systems studied with a view to the synthesis of new bioactive materials for bone regeneration – glasses, glass-ceramics and ceramics. The interest in materials containing calcium-silicate-phosphate phases is determined by their characteristics in a biological environment: biocompatibility, biodegradability and bioactivity. By a modified sol-gel method, including heating as a final stage, respectively at 700, 1200 or 1400 °C, three types of materials in the CaO-SiO2-P2O5 system were obtained with the same chemical composition, corresponding to the stoichiometry of Ca15(PO4)2(SiO4)6. The phase-structural evolution of the samples, depending on the synthesis temperature, was monitored using the following experimental methods: thermal analysis, X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) and BET analysis. After thermal treatment at 700 °C, a predominantly amorphous sample was obtained. The phase composition of the materials obtained at 1200 and 1400 °C confirmed the literature data on the role of P2O5 as a stabilizer of high-temperature polymorphic modifications of Ca2SiO4: β-Ca2SiO4 (monoclinic) α'-Ca2SiO4 (orthorhombic) and α-Ca2SiO4 (hexagonal). The phase composition and structure of the synthesized materials define them as promising biomaterials for bone regeneration. An in vitro bioactivity test of the glass-ceramic in a simulated body fluid (SBF) was conducted for up to 21 days. The experimental results of XRD, FTIR, SEM and EDS validated the ability of the glass-ceramic samples to form a layer of hydroxyapatite on their surface in vitro.

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Application of biosorbent for treatment of reactive dye wastewater

Daniela Angelova, Georgi Georgiev

In the present study, the possibilities of application of carbon material obtained from cocoa husks for purification of reactive dye-contaminated waters are considered. After thermochemical treatment, the obtained carbon material is characterized by a high specific surface area determined by the BET method (1694 m2.g-1). The analysis data show that micropores predominate in the structure of the obtained carbon material (about 78%). Adsorption experiments were carried out at different temperature in dynamic conditions. It was found that as the temperature increased, the carbon material adsorbed 93% of the pollutant in three minutes.

Study on preparation of glass-ceramic and dense ceramic biomaterials on the base of hydroxyapatite

Tina Tasheva, Janna Mateeva, Albena Yoleva, Hristo Georgiev

The development of advanced materials for biomedical applications is among the most important problems facing modern materials engineering. This study is focused on the synthesis of new glass-ceramic materials on the base of hydroxyapatite and glass-forming oxides on the one hand and dense hydroxyapatite ceramic with pre-melted and milled sodium borosilicate glasses as sintered additives on the other hand. Hydroxyapatite powder used in this investigation was prepared from Black Sea Rapana venosa shells and monocalcium phosphate monohydrate Ca(H2PO4)2.H2O by solid-state synthesis at 1180oC. Series 1 was prepared by homogenization and melting of powdered quartz, H3BO3, Na2CO3, NaNO3 and 30 mass % of HA powder in a corundum crucible at 1200oC and melt-quenched in water. The second series was synthesized by the mixture of hydroxyapatite powder and pre-melted and milled glass with the following composition in mass %: 35 B2O3, 45 SiO2, 10 Al2O3, 10 Na2O. The obtained dense ceramic samples with dimensions of 3 x 0.5 cm at a pressure of 50 MPa on a hydraulic press were pressed and fired at 1200oC with 2 hours hold at maximum temperature. The density of the samples were measured on a hydrostatic balance Mettler Toledo New Classic ME 104 equipped with density determination kit for solids using distilled water as the immersion liquid. The amorphous and crystalline structure of the obtained samples of both series was studied by X-ray diffraction (DRON 3M diffractometer, Cu Ka radiation, wavelength 1.7903 Å, 28 mA current and 40 kV voltage). The FTIR spectra are recorded in the 4000 - 400 cm-1 range by using FT-IR spectrometer Varian 600-IR. The samples for these measurements were prepared in the form of KBr–discs. The precision of the absorption maxima was ±3 cm-1. The SEM images were took by scanning electron microscope Carl Zeiss GmbH, model EVO 10, brand ZEISS were used. The bioactivity behaviour of studied HA containing compositions, were traced in a simulated body fluid (SBF) medium of pH 7.4 in a water bath at 37oC for during residence time in SBF medium 10 and 20 days.

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Construction of inorganic and hybrid biosorbents for water purification

Nadezhda Kazakova, Georgi Chernev, Hristo Karakostov

Environmental protection is one of our most important mission. Water purification from heavy metals is one of the most important industrial task. The hybrid biosorbents demonstrated significant efficiency in removing the tested heavy metal ions. This study evaluated the potential of hybrid biosorbents, which consist of both low and high molecular weight heteropolysaccharides, to eliminate Cu(II), Cd(II), and Ni(II) ions from aqueous solutions. Inorganic sol-gel sorbents based on Tetraethylorthosilicate (TEOS) were utilized as a control for the hybrid biosorbents. Their structural characterization was conducted using various methods. The maximum adsorption capacities were observed for biosorbents that incorporated immobilized algal biomass, as well as for those containing TEOS and high molecular algal heteropolysaccharide. The adsorption of the toxic ions Cu(II), Zn(II), and Ni(II) across the four types of sorbents proved effective. Notably, a high percentage of these ions was removed during the initial hours of the adsorption process.

Surface treatment of steel surfaces in a three-component phosphating solution before organic coatings applying

Nona N. Shivacheva, Dimka I. Fachikova

Phosphating as a surface treatment of carbon steels is the most widely used method in practice due to its ease of preparation, low cost, and excellent adhesion to paint or polymer coatings. The coating is formed as a result of topochemical reactions, which causes the steel surface to integrate as part of a phosphating film.

The presented work investigates the influence of various factors (concentration and temperature of the medium, exposure time) on the kinetics of formation of crystalline phosphate films on carbon steel surfaces prepared in a three-component phosphate solution. Using gravimetric, electrochemical and physical analytical methods, the indicators characterizing the phosphating preparation (density, pH, conductivity and acid capacity), as well as the thickness, composition and roughness of the phosphating films, were determined.

The adhesion, elasticity and impact strength of three types of organic coatings, with and without phosphating of the steel surfaces, were measured. The corrosion resistance of the combined coatings in a sodium chloride model solution was determined.

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Synthesis, Structure and Dielectric Properties of Glasses in the TeO2-V2O5- Bi2O3 System

Tina Tasheva, Stanislav Slavov

Developments in the field of electronic conductivity of glasses have been one of the most important high-tech areas in the last few decades. Two series of glasses with compositions (90-x)TeO2-xV2O5-10Bi2O3 and (80-x)TeO2-xV2O5-20Bi2O3, where x = 20, 30, 40 mol % were synthesised. The initial materials of TeO2, Bi2O3 and V2O5 were homogenized in an agate mortar and the obtained batches were melted in a corundum crucible at 950 °C for 20 minutes in an electric furnace. The melts were stirred several times during heating, and then they were melt-quenched on an aluminium plate and pressed to a thickness of 1~2mm by a copper plate.

Powder X-ray diffractograms collected in the range from 5.3 to 80◦ 2θ with a constant step of 0.03◦ 2θ and a counting time of 52.5 sec/step on a Bruker D8 Advance diffractometer (Germany) with Cu Kα radiation and a LynxEye detector were recorded on the obtained samples. The experimental density of the glasses was measured using the Archimedes principle, using a Mettler Toledo New Classic ME 104 analytical balance equipped with a kit for determining the density of solid samples and distilled water as an immersion liquid. The molar volume and oxygen packet density were calculated. Infrared spectra were recorded in the range of 2000-400 cm-1 using the Varian 600-IR FT-IR spectrometer. Raman spectra were measured with the LabRAM HR Visible Raman spectrometer in the 90-1280 cm-1 range. The photoelectron spectra were recorded on an ESCALAB MK II X-RAY photoelectron spectrometer with a non-monochromatic X-ray source Al under a vacuum above 10-7 Pa at a 45-degree take-off angle and a total instrumental resolution of 1eV. The dielectric characteristics were measured with the Zanner CM6 Impedance spectrometer. The measurements were made with a standard sample holder with a two-electrode method. The samples were polished and plane-parallel, and silver electrodes were applied to them. Measurements of all samples were taken in the frequency range of 1Hz-1mHz at room temperature.

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Preparation of coatings by dispersing graphene oxide, reduced graphene oxide and zinc titanate in bisphenol-a

Dimitar Dimitrov, Boris Martinov, Anna Staneva

The resistance of microorganisms to modern antimicrobial agents is a current challenge in healthcare. Studies of graphene materials (GO, RGO), as well as metal and oxide nanoparticles, confirm the presence of antimicrobial activity against biofilm-forming microorganisms. Bisphenol-a- epichlorohydrin (BPA) coatings are used in optics due to their suitable refractive index and transparency in the visible spectrum. However, the formation of a biofilm on the surface would deteriorate their optical properties and the safety of their use. On the other hand, the dispersion of carbon and oxide nanomaterials in polymer matrices is an ongoing challenge, since their uniform distribution is essential for the isotropic properties of the coatings.

In the present study, we developed a suitable path for obtaining thin-film coatings with the participation of zinc titanate and graphene structures (ZnTiO3, GO, RGO,) and composites between them, by stabilization using BISPHENOL-A. Sonication using an ultrasonic reactor, centrifugation and subsequent addition of BPA were performed. The coatings were applied on glass substrates by the Dip Coating method and were polymerized at 100°C for 1 hour. TEM has shown that in the compositions with the participation of GO, the sizes of ZnTiO3 nanoparticles of the order of 10 nm are preserved. It has been shown that ZnTiO3 nanoparticles are stable, evenly distributed in the polymer matrix of Bisphenol and attach to the surface of GO and RGO nanolayers.

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Formation and characterization of non-chromate conversion coatings on aluminum alloy EN AW 5754

Zdravka K. Djumailieva, Dimka I. Fachikova, Sergei D. Kusturov, Gergana P. Ilieva

Conversion surface treatment of aluminum and its alloys is the most common method for obtaining films with protective, decorative and functional properties, and especially as a substrate for subsequent paint and polymer coatings - due to the excellent adhesion between them.

The proposed work describes the preparation and characterization of thin non-chromate conversion coatings on the surface of aluminum-magnesium alloy EN AW 5754, intended for the production of radio-electronic equipment. Using physical, chemical and electrochemical research methods, the following were determined: the chemical composition of the alloy; the kinetics of obtaining conversion coatings in solutions with different concentrations, temperatures and duration of the processes. The chemical composition of the formed films, their topography and morphology were determined. The stability and protective ability were studied in model sodium and ammonium chloride environments.

The optimal conditions for obtaining conversion coatings of uniform thickness, homogeneous composition and with the best protective properties have been determined.

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Corrosion Behavior of a High Nitrogen Austenitic Stainless Steel in Aqueous Solutions of Citric and Oxalic Acids

Sergei Kusturov, Dimka Fachikova, Daniela Lilova

The results obtained in studying the corrosion-electrochemical behavior of high-nitrogen austenitic stainless steel, Cr18Mn12N in aqueous solutions of citric and oxalic acids are presented in this work. The investigations were carried out by using electrochemical methods (potentiodynamic polarization measurement - PPM, measurement of open circuit potential - OCP), light and scanning electron microscopy (LM, SEM), as well by energy-dispersive spectroscopy (EDX).

It has been found that as temperature rises (20÷60oC) the corrosion potential of the steel under study in citric acid shifts to more negative values, and the corrosion current, icorr, increases at all acid concentrations (1.0, 10.0 and 20.0%). Under the same conditions, in oxalic acid solutions, Ecorr becomes more positive, while icorr maintains the same trend as with citric acid.

Using physical analytical methods, the composition and microstructure of the steel under study, the topography and the elemental composition of the film formed on the surface of steel in passive state in the solutions of the two acids have been determined.

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Photoswitchable Imines Drive Dynamic Covalent Systems to Nonequilibrium Steady States

Jiarong Wu

Imines (RCH=NR’) are well-known for their dynamic-covalent properties and are widely used in the field of self-assembly and in designing self-healing materials due to their reversible condensation/hydrolysis behaviour. However, as analogues to azo-based photoswitches, which can undergo E/Z photoisomerization, their photoswitching properties have long been overlooked. This can be attributed to their poor photoswitching properties, for example, thermal half-lives of their metastable state being less than 1 minute at room temperature and low amounts of the metastable Z-isomer being generated under photoirradiation.

Earlier this year, we discovered imines that exhibit much improved, and useful, photoswitching properties.[1] Specifically, we significantly optimized the photoswitching behavior of imines, achieving thermal half-lives of up to 19.2 hours and an almost quantitative conversion from E- to Z-isomer under visible light. Further investigations into imine-based photoswitches, including iminobispyrazoles (IBPs)[2] and various regiochemistries and functionalizations of aryliminopyrazoles (AIPs),[3] provided deeper insights into the design of photoswitchable imines. The longest thermal half-life of a Z-imine achieved so far exceeds one day, which enabled the crystallization of the Z-isomer—the first reported Z-arylimine crystal to date.[3]

Building on this foundation, our recent work showcases the coupling of the imine photoswitching process with a thermal transimination equilibrium.[4] By utilizing light, we successfully drove a exchange process energetically uphill, to a non-equilibrium steady state (NESS). This system, remarkably simple with just one aldehyde and two different amine components forming a distribution of two imines, contains much more information within, making the entire system an "information ratchet".

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Synthesis and application of some bis(dichlorotriazine) reactive dyes

Polya M. Miladinova

Environmental problems arising as a result of the colouring of textile and polymer materials can occur at three different stages: during the dyeing of the textile or polymer material, during the use of the coloured material and at the moment of washing and cleaning. All these problems are a result of the weak chemical bonds (hydrogen, ionic or Van der Waals forces) of the dyes with the material. One successful solution of the problems was the discovery of reactive dyes. A characteristic structural feature of reactive dyes is the reactive group attached to the chromogenic system. The reactive group, generally based on halogen heterocycle is capable to form a covalent bond with the fibres under alkaline conditions. Considering the advantages and disadvantages of the widely used mono and dichlorotriazine dyes, in order to achieve a hider degree of exhaustion and fixation and lower water pollution the world investigation have been focused on developing reactive dyes with two and more reactive groups, situated in different part of the dye molecule.

Two bis(dichlorotriazine) reactive dyes with orange and magenta colour were synthesized. They were characterized by thin layer chromatography and spectrophotometrically. The dyes were evaluated on cotton and compared to commercial dichlorotriazine dye C.I. Reactive dye 1. The degrees of exhaustion and fixation were assessed. The optical properties - L*, a*, b*, C*, and h* from the CIE Lab colour space of the resulting textile samples have been examined.

As a conclusion of the studies, it was found that both reactive dyes could have application for dyeing of cotton with higher degree of exhaustion and fixation in comparison with some commercial used reactive dyes.

Keywords: bis(dichlorotriazine)reactive dyes, exhaustion and fixation

Acknowledgment:

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Synthesis and study of 1,8-naphthalimide AIEgens designed for the detection of acids and bases in the vapor phase

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For quite some time, the development of fluorescent chemosensory materials has gained significant attention due to their rapid response, high sensitivity, and real-time monitoring capabilities. These materials are particularly valuable for non-invasive imaging, essential in biomedical applications.

Fluorescence-based sensing mechanisms such as PET (photoinduced electron transfer), ICT (intramolecular charge transfer), and AIE (aggregation-induced emission) have been widely employed. The PET “fluorophore-spacer-receptor” model, introduced by de Silva, remains a popular approach due to its simplicity and efficiency. However, designing PET-based fluorescent probes with enhanced properties, such as higher quantum yields and improved selectivity, remains a challenge.

AIE-active fluorophores offer an advantage over traditional fluorophores, which suffer from aggregation-caused quenching (ACQ). AIE-based materials exhibit strong fluorescence in the solid state, making them promising for sensor development and bioimaging.

This study focuses on 1,8-naphthalimides due to their bright fluorescence and stability. The investigated compounds were designed as PET sensors using a tertiary amine receptor attached at either the N-position (Upper receptor) or the C-4 position (Lower receptor) of the naphthalimide core. Both configurations exhibited PET activity, but in the “Lower receptor” system, the process was enhanced, whereas in the “Upper receptor” system, an internal repulsive field restricted it. This effect was reduced in certain derivatives, particularly those with halogen substitution. These findings provide insight into the design of improved fluorescent sensors for targeted applications.

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Study of optical anisotropy in composite structures based on azo polymer PAZO and GeTe4-In chalcogenide system, prepared by different methods

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New bulk chalcogenide materials from the GeTe4-In system have been synthesized by melt-quenched technique. Their structure and morphology have been studied by X-ray powder diffraction and scanning electron microscopy. Some physicochemical properties of the obtained materials, such as density, compactness, molar and free volume, and their dependence on the composition, have been determined.

Composite films based on the azopolymer PAZO doped with newly synthesized chalcogenides of the GeTe4-In system were obtained through the following methods: thermal vacuum evaporation of the chalcogenide and centrifugal deposition of the azo polymer, centrifugal deposition of a suspension of the PAZO polymer and GeTe4-In particles, and by electrospray deposition.

The kinetics of birefringence was studied in order to determine the influence of the method of preparation of the composite materials on the magnitude of the optical anisotropy induced in them.

Keywords: chalcogenide glasses, melt-quenching technique, physico-chemical properties, azopolymer PAZO, optical anisotropy**.**

Molecular insights into molecular level interactions and aggregation behavior of an azobenzene-functionalized polymer

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Poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) exhibits a number of unique physical properties that are important for the diverse applications of this functional polymer in photonics, optoelectronics, memory devices, and sensors. Molecular modeling tools are used in the current study to investigate the PAZO interactions (including photoinduced cooperative molecular reorientation) that determine its distinct properties. In particular, the molecular level motions according to the classification of Nathanson and Rochon1 fall in the scope of the research. The photoinduced orientation phenomena in polymer films are widely studied due to their importance for a number of applications, including optical and photonic. Numerous studies have reported an axis-selective trans-cis-trans photoisomerization in azobenzene-based molecules and photo-cross-linkable polymer materials to generate photoinduced optical anisotropy. A better understanding of the interactions and aggregation behavior of a widely used polymer such as PAZO at a molecular level can guide the design and development of new improved materials.

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Synthesis, analysis and some optical application of new chalcogenides from the Ge-Te-Cu system

Yordanka Trifonova, Ani Stoilova, Deyan Dimov, Branimir Ivanov, Dimana Nazarova, Lian Nedelchev, Vania Lilova, Vladislava Ivanova

New bulk chalcogenides from the system (GeTe6)1-xCux, where x=5, 10, 15 и 20 mol %, has been synthesized. The composition of the materials was studied using X-ray powder diffraction (XRD) and energy dispersive spectroscopy (EDS). Scanning electron microscopy (SEM) has been applied to analyze the surface morphology of the samples. Some thermal characteristics as glass transition, crystallization and melting temperature and some physicochemical properties as density, compactness, molar and free volume were also determined. The XRD pattern shows sharp diffraction peaks indicating that the synthesized new materials are crystalline. The following four crystal phases were determined: Te, Cu, CuTe и Cu2GeTe3. The results from the EDS confirm the presence of Ge, Te and Cu in the bulk samples in a concentration in good correspondence with those theoretically determined. The SEM images reviled single crystals on the surface of the bulk samples, which with increasing the cooper concentration become larger and form clusters.

To study the applicability of the synthesized new materials as media for optical record of information, layers has been deposited from the bulk samples via vacuum thermal evaporation and the diffraction efficiency kinetics has been investigated.

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Photochromic Properties of Novel Spiroindolines

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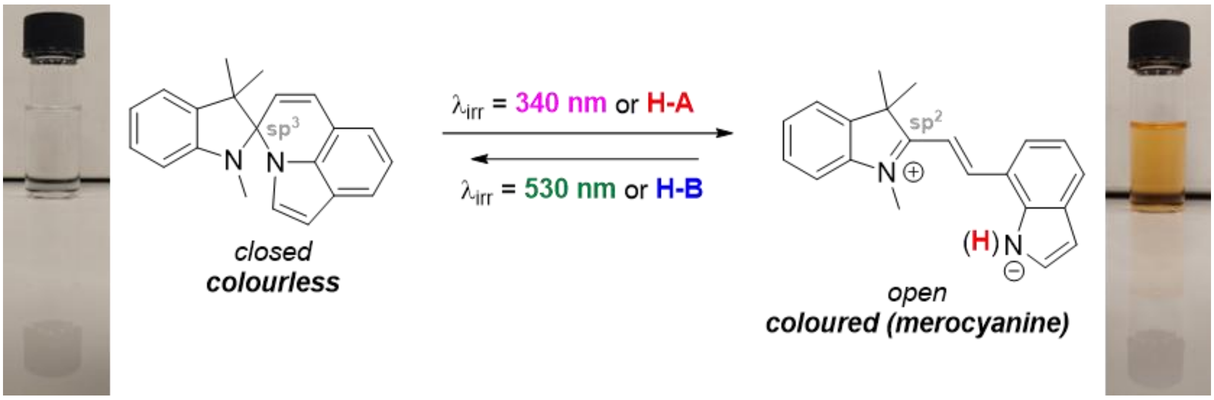

Photochromic spiro-compounds have been known for a long time and are usually associated with spiropyrans and spirooxazines, which undergo an open-closed photochromic reaction by UV light. The open form of merocyanine covers a broad visible spectral range from 450 to 700 nm, making them applicable in photonics and biotechnology. In this study, we have designed and synthesised a new class of photochromic spiro-compounds known as spiroindolines, in which the nitrogen plays a central role in the open-closed reaction by both light and acid-base. The closed forms are colourless and exhibit emission in the blue-cyan region, while the open merocyanine form emits in the NIR region.

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Synthesis and characterization of High-entropy spinel oxides

Tsvetomila Lazarova-Kyuleva, Diana Kichukova, Katerina Tumbalova, Consolato Rosmini, Grigoria Theochari

High-entropy oxides (HEOs) are a new class of oxide systems based on the concept of high-entropy alloys. Since the discovery of high-entropy alloys more than a decade ago, the search for new non-metallic materials stabilized by high entropy has greatly increased the interest in the study of this new category of advanced materials. High-entropy oxides with spinel-type structure attract wide interest from researchers due to good thermal/chemical stability, magnetic, electrical properties, attractive catalytic and adsorption properties. Various oxide materials based on (CoMnFeNi) have been synthesized, with a suitable ion from the group of Cu, Cr, Mg, Zn, Al selected as the fifth element by the solution combustion synthesis method. After that, the samples were heat treated at temperatures in the range of 400 to 700oC and analyzed by powder X-ray diffraction, low temperature adsorption with nitrogen and infrared spectroscopy.

The authors are thankhul to Project KP-06-M89/3 "Synthesis and characterization of High-entropy spinel oxides with applications in catalysis" for the financial support.

Effect of the cotton fabric modification with composite film on antimicrobial properties and release kinetics of biologically active substance

Daniela Atanasova

The study aims to modify cotton fabric with a chitosan film crosslinked with polycarboxylic acid. The preparation of the materials includes impregnation of the cotton fabrics with a crosslinker, then drying at room temperature. Solutions of pure chitosan and chitosan containing an anti-inflammatory agent are prepared. After soaking the samples with the latter solutions, two of the samples are subjected to heat treatment and two are dried at room temperature. The obtained materials are characterized by infrared spectroscopy and optical and thermal analysis. The composite materials were tested for antimicrobial activity against Gram-negative and Gram-positive bacteria. Kinetic models were used to identify the mechanism of biologically active substance BAS release from the composite materials. The obtained materials have the potential to be applied as antimicrobial wound dressings, releasing controlled BAS.

The influence of the light and the type of 1,8-naphthalimide chromophore linked to peptide on antimicrobial properties of cotton fabric

Desislava Staneva

The cotton fabric was modified with peptides linked to 1,8-naphthalimide chromophore with different substituents in the fourth position, and its colour characteristics were analyzed. The NO2 substituent is the reason for the light absorption from 350 nm to 500 nm, and the fabric's colour is yellow-green. The light absorption of the materials treated with the compounds containing H or Cl substituents is outside the visible electromagnetic spectrum. The NO2 substituent quenched the fluorescent emission of 1,8-naphthalimide fluorophores. In contrast, fluorophores with the other two substituents emit blue light with weak intensity, act as optical brighteners for the pristine fabric, and increase the fabric's lightness. After deposition of the fluorescent peptide on the cotton surface, their fluorescence spectra exhibit a well-defined vibronic structure with maxima at 410 nm, 424 nm, 426 nm, and 460 nm, which are bathochromically shifted relative to those in solution. The tight fixation of the peptides on the cotton surface limits the possibility of conformational changes in the molecules and causes aggregation of the 1,8-naphthalimide fragments.

The iodometric method confirmed that the release of singlet oxygen was the fastest for NO2-NIVal fabric, followed by Cl-NIVal fabric, and is slowest for H-NIVal fabric. The antimicrobial activity of the fabrics has been investigated against model Gram-positive Bacillus cereus and Gram-negative Pseudomonas aeruginosa bacteria. In the dark, NO2-NIVal fabric exhibits more pronounced activity than other fabrics. The illumination with visible light enhances the antimicrobial efficiency of all fabrics, and the effect was better pronounced against P. aeruginosa than B. cereus.

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Low-temperature synthesis, structural properties and applications of self-healing materials

Georgi Chernev, Hristo karakostov, Nadezhda Kazakova, Silviya Hristova, Lyudmila Angelova

Sol-gel processes are promising strategies for preparing materials that exhibit synergetic or complementary behavior between a polymer and an inorganic matrix interacting at the molecular scale.

The main objective of this work is to investigate the sol-gel synthesis, structure, and application of nanocomposite silica hybrid materials containing varying amounts of the organic component methylmetacrylate (MMA).

In this work, hybrid inorganic–organic hybrids based on different silica precursors and addition of organic compound SP were prepared by sol–gel technique. Acid catalyzed solutions of tetraethylorthosilane (TEOS) or methyltriethoxysilane (MTES) containing were used as an inorganic precursor.

The structural evolution of the hybrid materials containing different amounts of sepharose was examined by XRD, FTIR, BET and SEM. The formation of silica nanocomposites by the self-assembly was studied by AFM and roughness analysis.

The results prove that all the studied hybrids have an amorphous structure. The surface area of the pores in the hybrids decreases from 287 m2/g to 154 m2/g with the increasing of the quantity of MMA. The average size of nanoparticles on the sample surface is about 7 to 14 nm and it can observe the formation of their self-organized structures. The hybrid sample surfaces have different structures. No correlation was found between the roughness of the surfaces and the amount of organic component in the materials.Hybrids are used to immobilize bacterial cells that produce thermostable enzymes. These biocatalysts demonstrate good operational stability over an extended period of 18 days, as well as high thermostability. Additionally, encapsulated cells within the hybrid matrix exhibit superior capability.

Utilization of zinc ferrite residue for the production of metals with multifunctional applications

P. Iliev, B. Lucheva, N. Kazakova, I. Stoyanova, V. Stefanova

The article presents the results of a number of analyses used to characterize the zinc-ferrite residue that is generated after the leaching of zinc calcine. This zinc residue is a fine-grained material that primarily contains zinc ferrite, plumbojarosite, anglesite, and gypsum. The material also contains precious metals that are not extracted during the Waelz process but remain in the clinker, ultimately being irretrievably lost. From both ecological and economic perspectives, hydrometallurgical processing of the zinc-ferrite residue is the most profitable option. To perform the thermodynamic analysis of leaching, the variant of sulfuric acid leaching is chosen. This analysis is conducted using the software HSC Chemistry ver. 10.5.4.4. Various technological parameters are evaluated, including temperature, solid-to-liquid ratio (S:L), and solution acidity, to determine their influence on the stability of ionic and nonionic regions of the substances present in the solution. Sulfuric acid leaching of the zinc ferrite residue is performed and the leaching products are analyzed. It is established that when the leaching is carried out with 200 g/l sulfuric acid, a solid:liquid ratio of 1:10 and a temperature of 90°C, the degree of recovery for the main metals are as follows: 98.30% Zn, 96.40% Cu and 92.72% Fe. The insoluble residue contains 27% Pb and 554 g/t Ag. Based on the obtained results, a hydrometallurgical technology for utilizing zinc-ferrite residue will be developed, aimed at producing metals and materials (Cu, Ag, Pb, ZnSO4, Fe2O3) with multifunctional applications.

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Bioactive glass-ceramics in the CaO-SiO2-P2O5 system containing high-temperature polymorphs of dicalcium silicate

Irena Mihailova, Lachezar Radev, Petya Dimitrova, Hristo Georgiev, Radostina Ivanova, Ralitsa Teodosieva

The CaO-SiO2-P2O5 system is one of the main systems studied with a view to the synthesis of new bioactive materials for bone regeneration – glasses, glass-ceramics and ceramics. The interest in materials containing calcium-silicate-phosphate phases is determined by their characteristics in a biological environment: biocompatibility, biodegradability and bioactivity. By a modified sol-gel method, including heating as a final stage, respectively at 700, 1200 or 1400 °C, three types of materials in the CaO-SiO2-P2O5 system were obtained with the same chemical composition, corresponding to the stoichiometry of Ca15(PO4)2(SiO4)6. The phase-structural evolution of the samples, depending on the synthesis temperature, was monitored using the following experimental methods: thermal analysis, X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) and BET analysis. After thermal treatment at 700 °C, a predominantly amorphous sample was obtained. The phase composition of the materials obtained at 1200 and 1400 °C confirmed the literature data on the role of P2O5 as a stabilizer of high-temperature polymorphic modifications of Ca2SiO4: β-Ca2SiO4 (monoclinic) α'-Ca2SiO4 (orthorhombic) and α-Ca2SiO4 (hexagonal). The phase composition and structure of the synthesized materials define them as promising biomaterials for bone regeneration. An in vitro bioactivity test of the glass-ceramic in a simulated body fluid (SBF) was conducted for up to 21 days. The experimental results of XRD, FTIR, SEM and EDS validated the ability of the glass-ceramic samples to form a layer of hydroxyapatite on their surface in vitro.

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Bismuth-titanium-silicate-oxide glass ceramics for various dielectric applications

Stanislav Slavov

Storing energy in an optimal way is one of the most important problems nowadays. The synthesis of materials with improved dielectric properties is of great importance because of the possibility of their application as resistive sensors and as components of energy storage devices.

The samples in the system Bi2O3-TiO2-SiO2-Nd2O3 were carried out by the method of supercooled melt with a cooling rate of 102 K/s in two stages: with temperatures respectively at 1150 °C and 1450 °C and rapid cooling to room temperature. For characterization of the resulting materials are used the following equipment: X-ray phase analysis XRD - TUR M62, Cu-Kα.,

Electrical impedance measurements of selected glass-ceramics make it possible to estimate conductivity and dielectric constants over a wide temperature range from room temperature to 300 °C, for frequencies from 100 Hz to 100 kHz. The impedance and phase angle values determined for the investigated ranges are of the order of 108 Ohm and -90°, respectively.

Changing the starting composition of the oxide mixture allows control of the dielectric properties, such as dielectric constant and dielectric loss, and also the resulting samples have a wide range of Curie temperatures. The classical method of synthesis gives reason to obtain new dielectric materials that meet all environmental norms (using ecological raw materials) and with reduced production costs.

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Study of the influence of the partial replacement of feldspar in dental transparent glaze with hydroxyapatite on the phase composition and microstructure of the obtained materials

Janna Mateeva, Albena Yoleva, Adriana Batsova

In the present study we investigate the influence of partial replacing the starting raw materials sodium and potassium feldspars with hydroxyapatite (HA) in dental glaze on the phase composition and microstructure of the obtained materials. Hydroxyapatite was obtained by us based on Black Sea rapanes and monocalcium phosphate. In our previous scientific works new multicomponent glasses based on sodium feldspar, potassium feldspar, sodium carbonate, sodium nitrate, potassium carbonate, barium carbonate, lithium carbonate, boric acid have been developed for application as glaze layers on dental zirconia ceramic to smooth the surface of dental ceramics and improve optical properties. In present scientific research we partial replacing the sodium and potassium feldspars with hydroxyapatite (HA) in quantity 10, 20 and 30 mass% in transparent dental glaze and the influence of this replacing on the phase composition, microstructure and photoluminescent properties of the obtained materials was studied. Four glass compositions were melted at temperature at 1200oC.

Powder X-ray diffraction analysis of the obtained materials was performed with PAN analytical EMPYREAN Diffractometer system with a goniometer radius of 240 mm, operating at 40 kV and 30 mA, with CuKa radiation, equipped with 3D-pixel detector. SEM (Carl Zeiss GmbH, EVO 10) was used to observe to microstructure of studied samples. The ATR-FTIR-spectra of the studied glass materials were recorded on a Thermo Nicolet iS50 infrared spectrometer at room temperature in the range of 4440-600 cm-1 with a diamond crystal ATR accessory at a resolution of 2 cm-1 and 64 scans. The photoluminescent properties of the obtained materials were studied on an apparatus FLS1000 Photoluminescence Spectrometer, Edinburgh Instruments.

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Transmissibility of rubbers by cyclic disturbtions

(Part 1)

Dontchev D., Stankov V., Slavov S., Hadjov K.

In this paper the authors use the nonlinear hereditary theory of Boltzmann to describe the elastoviscous behaviour of rubbers and introduce them to the dynamic mechanical analysis (DMA). This research concerns Butadiene-nitril and Polyisoprene rubber with 10% and 70% Carbon black volumetric inclusions (CB) respectively. Similar materials are often used as dampers for vibration attenuation. Elastoviscous behaviour, loss factor and transmissibility (ratio of the force transmitted to the force applied over a system) for such elastoviscous solids as a function of imposed angular frequency and imposed strain amplitude are obtained in accessible form for engineering practice. The Boltzmann nonlinear hereditary theory with sum of singular kernels is used here in order to take into account the extremely high stress relaxation and creep velocity at the beginning and to enlarge the experimental time interval. Nonlinearity is taken into account using the Ogden equation. One has obtained the loss factor by cycling and the respective transmissibility curves of such a rubbers for two imposed regimes – sinusoidal and pulsation loads. Experimental results illustrate the applicability of the proposed approach

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Transmissibility of rubbers by cyclic disturbtions (nonlinear case)
(Part 2)

Dontchev D., Stankov V., Slavov S., Hadjov K.

This research concerns the dynamic mechanical analysis (DMA) for Butadiene-nitril and Polyisoprene rubber with 10% and 70% Carbon black volumetric inclusions (CB) respectively. Similar materials are often used as dampers for vibration attenuation. Elastoviscous behavior, loss factor and transmissibility (ratio of the force transmitted to the force applied over a system) for such elastoviscous solids as a function of imposed angular frequency are obtained in accessible form for engineering practice. The Boltzmann hereditary theory with sum of singular kernels is used here in order to take into account the extremely high stress relaxation velocity at the beginning and to enlarge the experimental time interval.

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Thermal Properties of Unfired Bricks with Additives from Agricultural Materials for Energy-Efficient Construction

Lubomir Tashkov, Penka Zlateva, Mariana Murzova

Unfired bricks with additives from agricultural materials, such as straw and rice husks, represent a sustainable construction alternative that combines low energy consumption in production with effective thermal insulation properties. The present study analyzes the impact of different additive percentages (10%, 25%, 50%, 75%) and wall thicknesses (25 cm, 35 cm, 45 cm) on the thermal resistance and heat storage capacity of the materials. Through numerical simulations based on experimental data for thermal conductivity, density and specific heat capacity, the thermal properties of different variants were investigated. The results show that the higher additive content significantly improves thermal resistance (up to 2,33 $(m^2K)/W$ with 75% additives and 35 cm thickness) but simultaneously reduces heat storage capacity (from 504,000 $J/(m^2K)$ with 10% additives to 336,000 $J/(m^2K)$ with 75% additives for the same thickness).

Based on the results obtained, a strategy for the optimal selection of material composition and wall thickness is proposed, depending on climatic conditions. For cold regions, bricks with a higher content of additives (50-75%) and thicknesses of 35-45 cm are recommended to minimize heat loss. In warm regions with large temperature fluctuations, lower additive percentages (10-25%) and moderate thickness (25-35 cm) provide better thermal inertia. The study highlights the importance of the balanced approach in designing energy-efficient buildings using unfired bricks with agricultural additives. The findings offer valuable insights for optimizing construction materials and their practical application in sustainable construction.

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Electrical model of a chamber for low-temperature plasma processing of metal products

V. Todorov, H. Anchev, B. Varhoshkov, N. Penkova

An electrical model of a vacuum chamber for low-temperature plasma processing of metal products is developed and calibrated. The electrical resistances and the conductivities of the solid and fluid domain of the chamber during the operation are determined, based on the measured input values of the current and voltage. They are checked in two modes: at direct current and alternating current. A comparison of the results, obtained at the solution of the electrical model and additional model of the electrohydrodynamic processes and conjugate heat transfer in the chamber is made. It was proved that the two models complement each other and allow a detailed analysis of the processes in the plasma and the treated material. This combination enables algorithmic numerical study of the three-dimensional electrical, thermal ad fluid flow fields in the chamber at different locations of the gas inlets, outlets, electrical connections and ways of arranging the metal products.

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Comparative study of the bulk and foil zinc anodic behavior kinetics in oxalic acid aqueous solutions

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The anodic behavior of zinc electrodes is important for energy storage, corrosion protection, electrochemical processing, and other practical applications. This study investigates the anodic polarization of zinc foil and bulk electrodes in aqueous oxalic acid solutions, revealing significant differences in their electrochemical behavior, particularly in induction period durations. The induction period's duration depended on electrolyte concentration, current density, and temperature. Notably, the temperature dependence of the kinetics exhibited contrasting trends: the induction period for foil electrodes increased with temperature, while that of bulk electrodes decreased. Chemical analysis and polishing treatment comparisons showed no significant differences between the foil and bulk electrodes. However, SEM observations of samples anodized at different temperatures, combined with ICP-OES analysis of dissolved electrode material, provided insights into the distinct anodic behaviors. XRD studies further confirmed these findings, revealing a crystallographic orientation dependence of the anodic behavior. These results offer valuable insights into the electrochemical properties of zinc electrodes, with implications for optimizing their performance in various applications.

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Preparation of a carbon bifunctional catalyst for biofuel synthesis

Vesislava Toteva, Georgi Georgiev, Daniela Angelova

Liquid fuels used by modern society are still based on fossil resources, mainly crude oil, and the search for ways to a more sustainable development model is imperative. Biomass, and in particular carbohydrates derived from waste biomass, e.g. lignocellulosic, are low-cost and are extremely suitable raw materials for the production of chemicals and value-added products. Fructose and glucose have been widely studied for the production of valuable chemicals and polymer monomers, but much less so for synthetic fuels. Sustainable production of biofuels still has unresolved problems, such as the development of new catalysts for synthesis reactions. The potential of synthetic fuels, along with hydrogen and other renewable energy sources, needs to be expanded to minimize dependence on fossil fuels and maintain sustainable development. Biofuels are produced through catalytic reactions that require expensive catalysts. However, they can be replaced by those obtained on the basis of biocarbon materials. The best results are achieved with bifunctional catalysts. In this study, a carbon catalyst derived from waste biomass was developed. Its surface was modified using ZnCl2 to create Lewis acid sites and H2SO4 to establish Brønsted acid sites. A number of instrumental methods were used to characterize them: low-temperature nitrogen adsorption, scanning electron microscopy (SEM), Raman spectroscopy, Energy-dispersive X-ray analysis (EDAX). The results show that they have potential for use as catalysts for the synthesis of biofuels based on the conversion of carbohydrates.

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Synthesis and study of some physicochemical characteristics of new Rhodamine B-conjugated Hemorphin analogs

Petar Todorov, Stela Georgieva, Petia Peneva

The Xanthene dyes are widely used in medicinal and bioorganic chemistry as biologically active compounds alone or conjugated. Hemorphins in turn, are endogenous opioid peptides found in nature and are part of the hemorphin family. These peptides perform a variety of biological actions, including anticancer, antidiabetic, antihypertensive, and antiepilepsy. That is why we synthesized and physiochemically studied some novel rhodamine B-conjugated hemorphin analogs, which could be sensitive fluorescent probes in biological applications. A modified solid-phase peptide synthesis via Fmoc-strategy was used, with Rhodamine-B reacting directly to the resin with the N-terminal amino group to form the hemorphin analogs. The crude peptides were purified using an RP-HPLC, and their molecular weights were measured using ESI-MS. The aromatic peptide systems were evaluated for their conformational states, and anisotropy, as well as specific angles of optical rotation. The electrochemical properties were also discussed, and it was proven that some alterations in the amino acid skeleton affect the electrochemical behavior of aromatic systems by affecting the reactivity of the redox function group. Furthermore, the compounds' second structures are studied using FT-IR and CD-dichroism to corroborate the conformational and anisotropy of these novel aromatic peptide systems. Biological studies are to be performed and the structure-property relationship will be explained.

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New pyrrole hydrazones as potential anti-cancer agents

Stanislava Vladimirova, Ivan Iliev, Rossitsa Hristova

Cancer is a group of diseases characterized by uncontrolled growth and spread of abnormal cells in the body. Annually, more than 18 million new cases of cancer were reported worldwide. Despite the successful solutions found in the therapy of some types of cancer, the search for new active and low-toxic anti-cancer agents is a main goal of a number of research teams. The current study describes the synthesis and biological evaluation of a new hydrazones, containing two pyrrole rings. The structures of the newly synthesized compounds were confirmed by spectral techniques. The newly synthesized pyrrole hydrazones were tested for safety (cytotoxicity/phototoxicity) by BALB 3T3 NRU assay. Antiproliferative activity was tested on the normal cell line HaCaT (keratinocytes) and the tumor cell line SH-4 (melanoma) by MTT dye reduction assay. The tested compounds are of low toxicity and no phototoxic. Some of these hydrazones exhibit high antiproliferative activity in tumor cells SH-4.

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Study of chemical behaviour of novel benzylidenemalononitriles with incorporated nitrogen-containing heterocyclic fragments using molecular absorption and fluorescence spectrometry

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The present study focuses on the synthesis and characterization of three new benzylidene malononitriles with introduced BOC-piperazine, 3-methylpiperidine or thiomorpholine rings in their structure, namely MKI(CN)2 -2, MKI(CN)2 -4 and MKI(CN)2 -8. The newly obtained benzylidenemalononitriles were synthesized by the Knoevenagel reaction, isolated in high yields, and their structure and analytical purity were proven using 1 H- and 13 C-NMR spectroscopy and by melting temperatures. A study was conducted to establish the spectral properties of the newly synthesized compounds (fluorescent and UV-Vis) in organic and aqueous media. The analysis of the physicochemical parameters revealed that the fluorescence intensity and absorption of the benzylidene malononitriles are significantly affected by the polarity of the solvents. Their acid-base constants in aqueous solution were determined by two spectral graphic methods. To determine simultaneously metal ions in media with different matrix compositions, the possibility of obtaining new complex compounds between benzylidenemalononitriles and metal ions (Hg2+, Cd2+, Cu2+) in different buffer media at different ligand: metal ion ratios, was tested. The obtained chelates show high complex stability.

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Mono- and Polycationic p-Substituted Benzaldehydes as Intermediates for Cyanine Dyes and Fluorogenic Biocompatible Polymer Materials Based on PVA Scaffold

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Biocompatible and biodegradable polymers with structural fragments like polyvinyl alcohol (PVA), polylactic acid, polyglycolic acid, polycaprolactone or (and) polyethylene glycol are widely used in a broad range of applications in the field of medicine. Among the most promising and most useful biomaterials is the polyvinyl alcohol possessing good film-forming properties and good biocompatibility. The most common ways to control hydrophobicity of PVA involve modification reactions via hydroxyl groups, graft copolymerization of hydrophobic monomers and crosslinking. Usually as bioactive compounds some fluorogenic biomolecular probes specific for definite cell compartments are used. Such fluorogens are helpful tools for exploration the function and properties of newly developed polymer materials for drug delivery via fluorescent microscopy techniques. Our main idea is the functionalization of the PVA matrix by attachment of fluorogenic reporter cyanine dyes. The goal of the present work is the synthesis and purification of a large series of aldehydes as intermediates for the preparation the target dyes and polymers. In current study, we apply a modified synthetic procedure to obtain p-substituted benzaldehydes bearing one or more cationic centers. After purification of the mentioned compounds using flash column chromatography or fractional recrystallization, the chemical structure of the cationic substances was proven by analytical methods such as NMR, Mass spectrometry, IR and UV-Vis spectroscopy.

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Photodynamic Inactivation of Human Herpes Virus with Ga(III) and Zn(II) Phthalocyanines

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Photodynamic inactivation (PDI) has been revealed as a valuable approach against viral infections because of the fast therapeutic effect and low resistance development. The photodynamic inhibition of the infectivity of human herpes simplex virus type 1 (HSV-1) at different stages of its reproduction was studied. PDI was determined on extracellular virions, on the stage of adsorption to the MDBK cells and inhibition of the viral replication by application of zinc and gallium phthalocyanines (ZnPcMe and GaPcMe) upon 660 nm light exposure. The PDI was evaluated on extracellular virions and virus adsorption by the terminal dilution method and the change in viral infectivity. The decrease in viral titer was determined. The effect on the replicative cycle of the virus was determined using the cytopathic effect inhibition assay. The direct influence on the virions showed a remarkable effect with a decrease in the viral titer more than 4 ($\Delta lg > 4$). The influence of the virus to the cell on the stage of adsorption was significantly affected by the exposure time and the concentration of applied photosensitizers. A distinct inhibition was evaluated for ZnPcMe at the viral replication stage, which demonstrated a high photoinactivation index (PII = 33.0). This study suggested the high efficacy of PDI with phthalocyanines on HSV-1, with full inhibition caused by singlet oxygen.

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Design, Synthesis and Anticancer Evaluation of new Analogues of Aurein 1.2 Containing Unnatural Amino

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Antimicrobial peptides (AMPs) are promising alternative agents for treating multidrug-resistant bacterial infections. Many antimicrobial peptides also act as anticancer peptides (ACPs) [1]. They have the ability to pass through cell membranes and destroy bacteria or cancer cells. These peptides offer several advantages, including a short interaction timeframe, low toxicity, specificity, and good tumor penetration, positioning them as promising candidates for future chemotherapy treatments. Aurein 1.2 (Gly1-Leu2-Phe3-Asp4-Ile5-Ile6-Lys7-Lys8-Ile9-Ala10-Glu11-Ser12-Phe13-NH2) is a multifunctional antimicrobial peptide isolated from the green and golden bell frog, Litoria aurea, and the southern bell frog Litoria raniformis skin secretions.The aurein peptides can be classified into five discrete groups (aureins-1–5), among which, aurein-1 peptides are regarded as among the shortest of α-helical peptides with antimicrobial and anticancer activities [2]. Aurein 1.2 was chosen as a template for rational modification to achieve more potent biologically active peptides. Aurein 1.2 was modified at position 7 and 8. Lysine residues were replaced sequentially and simultaneously with the unnatural amino acids. New modified analogs followed the structure Gly-Leu-Phe-Asp-Ile-Ile-Xxx-Xxx-Ile-Ala-Glu-Ser-Phe-NH2 where Xxx is Orn, Dab (diaminobutyric acid) or Dap (diaminopropanoic acid). The peptides were synthesized by standard solid phase peptide chemistry methods Fmoc-strategy.

The crude peptides were purified on a reversed-phase high-performance liquid chromatography (RP-HPLC) and the molecular weights were determined, using electrospray ionization mass-spectrometry. The obtained new analogues were tested in vitro for cytotoxicity, phototoxicity and antiproliferative activity on a panel of tumor and normal cell lines, which demonstrated a positive effect on biological activity.

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Synthesis, spectroscopic and in vitro studies of triazinobenzeimidazole derivatives

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Parasitic diseases are a serious medical problem. They are widespread throughout the world, affecting even the more developed countries. The helminth parasite Trichinella spiralis causes serious health problems, including severe muscle pain, fatigue, fever, and difficulty breathing. They are flatworms and can be found in both wild and domestic animals, and they also pose a danger to humans. Infection is caused by consuming undercooked meat. [1].

Benzimidazole is a very important pharmacophore and its derivatives are known for various biological properties such as anticancer, antibacterial, anthelmintic [2]. Photoprotective ingredients containing a benzimidazole fragment in their structure are also used. 1,3,5-triazines are a class of compounds that have shown excellent properties in the fight against malaria. There is evidence that the combination of albendazole (a benzimidazole-based medicine) and antimalarial drugs has shown good results against trichinellosis. The triazine structure can also be found in some photoprotection products [3].

Based on this information, we decided to use a combination of benzimidazole and 1,3,5-triazine fragments. The target compounds were obtained by a one-step synthesis from 2-guanidino-benzimidazole. The purity of the products thus obtained was confirmed by IR and NMR spectroscopy. The anti-trechinella activity of the compounds was tested by an in vitro method and showed good results. Better activity was observed in the derivatives with a substituent at the 3-position compared to the 4-substituted ones. The spectroscopic sun protection factor (SPF spectroscopic) was calculated by UV spectroscopy data.

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Novel pyrrole-based hydrazones induce apoptosis and S-phase cell cycle arrest in human SH-4 melanoma cells

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Melanoma is the deadliest form of skin cancer, arising from melanocytes, the pigment-producing cells in the skin. Effectively treating melanoma remains a significant challenge due to its ability to evade the immune system, develop resistance to therapies, and spread aggressively to other organs. In our laboratory new pyrrole-based carbohydrazide (1) and hydrazones (1A-D) were created, analyzed, and examined using spectroscopic techniques. These hydrazones were produced by reacting a pyrrole hydrazide with substituted pyrrole aldehydes. The initial carbohydrazide was synthesized through a selective reaction of hydrazine with ethyl N-pyrrolylcarboxylate.The biological activity of these newly synthesized compounds was assessed in vitro on a variety of tumor and non-tumor cell lines. Mouse embryonic fibroblasts (BALB 3T3 clone A31) were utilized to evaluate their safety (BALB 3T3 NRU assay). Anti-proliferative activity was measured on keratinocytes (HaCaT) and melanoma (SH-4) cells using the MTT assay. Safety testing revealed low cytotoxicity and no evidence of phototoxicity. Among the novel pyrrole hydrazones, compound 1C demonstrated the highest selectivity (SI = 3.83) in human melanoma cells and exhibited significant anti-proliferative activity (IC50 = 44.63 ± 3.51 μM). The cytotoxic effect of 1C is associated with its ability to induce apoptosis and disturbe cell cycle progression in the S phase. Furthermore, our results indicate that hydrazones formed by condensation with β-aldehydes possess greater biological activity compared to those formed with α-aldehydes.

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Synthesis and characterization new complexe on Zn(II) - peptide ligand BIM25053

Atanas Shopov, P. Romanova, Dancho Danalev, Veronika Karadjova

Peptides are molecules normally present in the human body, as they perform a number of important functions such as hormones, neurotransmitters, neuromodulators, etc. In addition, peptides show specific feature to form complexes with different metals due to specific groups of amino acids in their primary structure. Many metals are object of deep studies as anti-tumor chemotherapeutics.

Zinc (Zn) is an important biologically active metal that participates in over 300 enzymatic reactions in the human body. Zinc forms stable complexes with peptides and proteins, which stabilizes their structures and supports their function. Zinc complexes can be used as antimicrobial, anti-inflammatory and anti-cancer agents. The synthesis and characterization of zinc complexes are of great interest for the development of new pharmaceutical and biochemical applications.

In this work, we present our research on the synthesis and investigation of new Zn(II) - peptide complexes with potential anticancer activity. We combine zinc with a peptide ligand BIM25053 (D-Phe-Phe-Phe-D-Trp-Lys-Thr-Phe-Thr-NH2) with already proven anticancer properties [1]. The complexes with basic structure Zn(II) - Se(VI)/Cl(I) - BIM25053 were synthesized and characterized. The differences in the structures, as well as the proof of the inclusion of zinc ions, are realized using FTIR, elemental and ICP analysis, as well as X-ray powder diffraction. All analytical data obtained will be presented and discussed.

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A high-throughput in vitro assay for preparation of atherosclerotic plaque using magnetic 3D bioprinting

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Three-dimensional (3D) cell culture models provide a valuable tool for bridging the gap between traditional in vitro cell cultures and in vivo responses. They replicate the natural in vivo environment more accurately by mimicking key factors and cellular responses.

Atherosclerosis is characterized by the buildup of plaque made up of fat, cholesterol, calcium, and other substances on the walls of arteries. This buildup can lead to narrowing of the arteries, reducing blood flow and increasing the risk of cardiovascular events. Stenting has become an effective minimally invasive therapy. Globally, over 10 million cardiovascular stents are implanted annually.

To meet the demand for higher throughput in vitro stent testing, we created a magnetic 3D bioprinting-based preparation of an atherosclerotic plaque model. Magnetic levitation was used to form 3D ring cultures of Immortalized Human Coronary Artery Smooth Muscle Cells, as reported previously [1, 2, 3], and the atherosclerotic plaque was formed following [4] with some modifications. The goal of the study is to test a new generation of stents using a three-layer coating made of biocompatible nitrogen-coated titanium oxide, a hybrid nanocomposite that serves as an anti-deposition agent on the surface of the stent, and a top coating layer formed by a biodegradable polymer matrix made of PLGA with incorporated functionalized detonation nanodiamonds (arDND [5]).

The 3D model was tested with different concentrations of DNDs. It showed greater sensitivity to treatment with DND and arDND, increasing the number of dead cells by 15%. These results give valuable information into the conditioned toxicity of DNDs and arDNDs, advancing our understanding of their safe and practical application in developing new stents.

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Quantitative-based cytoskeleton segmentation for accurate measurement of cytoskeleton density in 3D model of atherosclerotic plaque

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Coronary artery disease is caused by hardening and narrowing of the coronary arteries by atherosclerotic plaques, resulting in reduced arterial blood flow and perfusion of the myocardium, leading to angina, localised ischaemia, and eventually infarction. Drug-eluting stents (DES) were designed to reduce in-stent neointimal proliferation and minimise in-stent restenosis, a significant disadvantage of percutaneous coronary interventions with bare-metal stents. In recent years, concern has been raised regarding the long-term safety of DES and the risk of in-stent thrombosis and late restenosis due to neoatherosclerosis.

Our study aims to develop a new generation of stents featuring a three-layer coating: a TiOxNy base, a hybrid nanocomposite middle, and a top layer from PLGA embedded with chemically functionalized detonation nanodiamonds (DND).

Here, we captured biologically relevant characteristics of the endothelial cytoskeleton in the 3D model of atherosclerotic plaque through a network-driven imaging-based approach, allowing us to assess the dynamic features of the cytoskeleton quantitatively.

By introducing this 3D model of atherosclerotic plaque, we demonstrate that the cytoskeletal networks exhibit properties required for cell proliferation, differentiation, and cell-cell interaction, as well as with the stent’s base material. We further show that the advantageous features of 3D model of atherosclerotic plaque are maintained during temporal cytoskeletal re-arrangements involving F-actin, β-Catenin, and E-cadherin.

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These results give valuable information into the conditioned 3D model of atherosclerotic plaque, advancing our understanding of their safe and practical application in developing new stents.

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Synthesis and characterization of bioactive composites and their impact on cancer cells

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According to a report from the World Health Organization (WHO), cancer cases worldwide are projected to increase by 77% by 2050 compared to those diagnosed in 2022. Research indicates that lung cancer was the most commonly diagnosed cancer in 2022, followed by breast cancer, colorectal carcinoma, prostate cancer, and stomach cancer. Standard therapeutic agents often have side effects that can adversely affect various organs and systems. Consequently, scientists are focusing their efforts on developing new, more effective, and body-friendly therapeutic substances.

Medicines derived from natural sources play a significant role in pharmaceutical care. The most effective method for discovering phytodrug candidates is through the extraction and evaluation of the bioactivity of these natural extracts.

This study focuses on the preparation of composites made from chitosan combined with the plant extract of Tanacetum parthenium, as well as zeolite combined with the same plant extract. These composites have the potential for delayed release and increased cytotoxicity against cancer cells. The composites of chitosan and Tanacetum parthenium, along with zeolite and Tanacetum parthenium, were synthesized and characterized using techniques such as powder X-ray diffraction, infrared spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Their effectiveness was tested against various tumor cell lines.

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Modulation of Matrix Metalloproteinases-2 and -9 in Betulinic Acid Organic Salt-Treated MDA-MB-231 Cells

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Betulinic acid (BA) is a pentacyclic triterpenoid with immense pharmaceutical potential. However, its poor solubility in aqueous media remains a significant challenge for clinical applications. Our recent studies have demonstrated that converting BA into organic salts can enhance its solubility and improve its bioavailability. Notably, the formation of amino acid ethyl ester salts has been shown to increase its in vitro anticancer activity by 1.5 to 5 times, depending on the cell type.

In this study, we report the synthesis of mono- and di-lysine ethyl ester salts of BA and evaluate their impact on cell morphology and the activity of matrix metalloproteinases (MMPs) 2 and 9—key enzymes involved in extracellular matrix remodeling and cancer metastasis. By assessing their influence on MMP expression and activity, we aim to elucidate the potential of these BA derivatives as improved therapeutic agents targeting tumor progression.

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The health benefits of milk bioactive peptides and their possible involvement in treatment of hypertension

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Hypertension is a lifelong disorder and the most important therapeutic strategy for treating chronic high blood pressure is to inhibit the angiotensin-converting enzyme I (ACE I).

Recently, food-derived ACE inhibitory peptides have gradually received attention and are considered gentler and safer alternatives to synthetic medicines for blood pressure control. Among food sources, commercial milk-based products such as cheese, yogurt, sour milk, skim milk, etc. have been widely recognized as promising sources of ACE I bioactive peptides to control blood pressure. This study aimed to identify new short peptides during fermentation by lactic acid bacteria (LAB) utilizing their proteolytic system to produce a variety of peptides with inhibitory potential. Lactobacillus helveticus strain NS1—found in artisanal yogurt produced on a small farm in the Central Balkan was used as a single starter and in combination with lactobacilli of various species and origins to create a multibacterial recipe.

For the separation of milk proteins was developed a procedure by centrifugation at 4°C at 10000 × g, with molecular mass cut -off (MWCO) membranes of 3 and 10 kDa.

The samples with molecular mass below 3 kDa were further separated by ultrafiltration by dialysis cell (cut off membrane 1 kDa) by continuous stirring at room temperature. The milk fractions between 1-3 kDa and under 1 kDa molecular mass were characterized by UPLC-MS/MS. The ACE I inhibitory activity of fractions with different molecular masses was determined and compared using the FAPGG (N-[3-(2-Furyl) acryloyl]-L-phenylalanyl-glycyl-glycine) degradation method.

In silico tools are used to evaluate the ADME properties (absorption, distribution, metabolism and excretion) of selected isolated peptides to identify those that would have superior drugability.

Important details regarding the ACE I inhibitory effect of peptides derived from fermented milk are provided by the experimental and computational results obtained. These peptides can be used as nutraceuticals to inhibit ACE I and to enrich knowledge regarding the binding of different peptide structures to the active site of ACE I.

Keywords: Angiotensin-converting enzyme I, inhibitory peptides, LAB, ADME

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Synergy between fatty acids and photosensitive components in colostrum

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The interplay between unsaturated fatty acids and bioactive components in colostrum offers promising opportunities for exploring photoactive systems with potential applications in medicine, food preservation, and environmental remediation. Colostrum, a nutrient-rich biological fluid, contains a variety of photosensitive molecules, such as riboflavin, lactoferrin, and antioxidants like vitamin E, which can synergistically enhance the photoactivity of unsaturated fatty acids (FAs). Unsaturated FAs are known to generate reactive oxygen species (ROS) under light exposure. The combination of these components could lead to innovative applications, including antimicrobial systems, photodynamic therapy, and photocatalysis. However, the interactions remain insufficiently studied, and their practical potential is still unexplored.

Firstly, we focused on optimizing the extraction and qualitative of FAs from colostrum and tracking their changes during the first four days of lactation to evaluate their possible impact. Bovine colostrum samples were obtained from ten Czech Fleckvieh cows kept on a private dairy farm (L. Klíčová, Božice, Czech Republic), with samples collected from morning milking. Comprehensive two-dimensional gas chromatography with a vacuum ultraviolet detector (GC×GC-VUV) was used to achieve better separation, identification, and semi-quantitation of FAs in this complex biological matrix. By identifying key unsaturated fatty acids and analyzing their interaction with colostrum-derived photosensitizers, we aim to understand their synergistic effects under controlled light exposure. Our study can explore their potential to enhance antimicrobial properties, improve oxidative stability, and enable photodynamic treatments while minimizing cytotoxic effects. These findings could pave the way for designing novel photoactive systems harnessing the unique properties of colostrum and its fatty acid profile.

Methods of modification of wool fabrics with TiO2 for application in shoe lining

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The shoe lining materials are extremely important for ensuring good sanitary-hygienic properties and for preventing the bacterial growth, causing a number of skin diseases on the human foot. Woolen materials are very often used as lining details for shoes, which are a suitable environment for the development of fungi and bacteria. There are a number of studies on the application of nanoparticles of various metals and metal oxides to impart antibacterial properties. TiO2 nanostructures have been widely studied as antimicrobial agents due to their photocatalytic activity under UV light and possessing excellent antibacterial properties.

In this study, methods for modification of wool fabrics with TiO2 were developed for application in shoe lining to improve antibacterial properties. Titanium dioxide particles were deposited and fixed to the wool substrate using a cross-linked gelatin hydrogel. The titanium dioxide particles were synthesized in situ with oxalic acid as a precursor and deposited in the gelatin film. Microscopic analyses showed the presence of TiO2 nanoparticles, which were unevenly distributed in the wool sample. Analysis of the physicomechanical parameters of the modified samples containing TiO_2 nanoparticles showed the preservation of these properties. The color fastness and rubbing properties were unchanged compared to those of the control sample. Hygienic parameters such as adsorption and water permeability were also preserved and even improved in some of the samples. Antibacterial studies need to be conducted to confirm the assumptions made about the antibacterial and antifungal properties of the wool composites with the applied finish.

Keywords: TiO2 nanostructures, gelatin film, wool composites, finish coating

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Stabilization of AU NPS and RGO/AU NPS nanocomposites for application in biomedicine

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The stability of Au nanoparticles is one of their most important properties for their application in practice. Gold nanoparticles have exceptional potential for biomedical applications due to their unique physicochemical properties, such as chemical stability, biocompatibility, and interesting optical properties that depend on their size. Au NPs are highly biocompatible, making them safe for use in medical instruments, implants, and devices. Au NPs have many possibilities for modification by adding various functional groups to their surface, which allows easy adaptation to specific medical applications. Graphene has wide applications in electronics and in creating and modeling new batteries. Graphene-based materials show great potential for electrochemical biosensor electrode materials because they increase the sensing area and improve the electron transfer rate. RGO-AuNPs can overcome the barriers that limit the potential of currently available traditional materials due to their excellent properties, which include their high specific surface area. In the present study, a single-step route for the synthesis of a composite based on Au nanoparticles and RGO is proposed. The process of synthesis of Au nanoparticles takes place directly on the surface of the pre-synthesized GO layers. Through TEM and HRTEM analysis, the deposition of well-shaped spherical Au nanoparticles on the surface of the graphene layers is observed. In addition, the RGO sheets are well-defined in the TEM images. The size of Au nanoparticles in the graphene composite has been determined to be in the range of 2 to 20 nm. The crystal lattice parameter of the obtained Au nanoparticles has been determined by Selected Area Electron Diffraction (SAED). The proposed explanation for the size difference is the formation of aggregates of different-sized Au nanoparticles.

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Structural characterization, citotoxity and antitumor activity of one step synthesized RGO-AuNPs nanocomposites

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Gold nanoparticles are widely used with an important role in medicine. Graphene has wide applications in electronics and in creating and modeling new batteries. Graphene-based materials show great potential for electrochemical biosensor electrode materials because they increase the sensing area and improve the electron transfer rate. With the increasing demand for contemporary technological solutions, combining these two materials is expected to find an increasingly wide application in practice. RGO-AuNPs can overcome the barriers that limit the potential of currently available traditional materials due to their excellent properties, which include their high specific surface area. In the present study, a single-step route for the synthesis of a composite based on Au nanoparticles and RGO is proposed. The process of synthesis of Au nanoparticles from chloroauric acid ($H[AuCl_4]$) and reduction using sodium citrate (Na3C6H5O7) takes place directly on the surface of the pre-synthesized GO layers. By TEM, SAED, HRTEM, and XRD analysis, the formation of gold nanoparticles and graphene structures in the obtained composites was confirmed. Through TEM and HRTEM analysis, the deposition of well-shaped spherical Au nanoparticles on the surface of the graphene layers is observed. In addition, the RGO sheets are well-defined in the TEM images. The size of Au nanoparticles in the graphene composite has been determined to be in the range of 2 to 20 nm. The proposed explanation for the size difference is the formation of aggregates of different-sized Au nanoparticles. Overall, the study confirms the potential of RGO/Au nanocomposites for applications in both antibacterial treatments and potentially targeted cancer therapies, while also identifying areas for further optimization. Future work could focus on fine-tuning the size and distribution of gold nanoparticles within the composite to enhance its selectivity and efficacy. Additionally, investigating the influence of surface modifications of the RGO-Au nanocomposites on their biocompatibility could provide insights into developing more versatile biomedical

applications, particularly those requiring a balance between cytotoxicity and biocompatibility. HaCaT keratinocyte cells were used to study cell viability and morphology after treatment with different concentrations of RGO-AuNPs nanocomposites.

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Fluorogenic Biocompatible Polymer Materials Based on PVA Scaffold for Nucleic acids Visualization

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The fast development of the biomedical equipment for analysis and diagnostics necessitates the discovery of new and more sensitive reagents for the recognition of biological macromolecules. The recognition of nucleic acids by small organic molecules based on the changes in the fluorescence signal of the samples is well known. However, there is an urgent need for more sensitive organic materials with improved photophysical properties compared to the known ones, which will inevitably lead to an increase in the accuracy of the bioanalytic methods they are applied. Among the goals of the present work is the development of new fluorogenic biocompatible polymer materials for nucleic acid analysis. The tasks are related to the synthesis of new polymers based on the biocompatible polyvinyl alcohol (PVA) scaffold and new dyes, generating fluorescence only in contact with the corresponding nucleic acids, and subsequent elucidation of their photophysical properties. As a result of the performed research, we obtained organic dyes attached to biocompatible polymers, functionalized polymer membranes and polymeric nanomaterials with improved photostability, low toxicity and higher selectivity towards certain nucleic acids and cell organelles.

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