The 17th International Conference of Physical Chemistry
ROMPHYSCHEM

ABSTRACTS

ROMPHYSCHEM 17

September 25 - 27, 2023, Bucharest, ROMANIA

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"Ilie Murgulescu" Institute of Physical Chemistry - Bucharest
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Romanian Chemical Society
ALPHA Association

17th International Conference of Physical Chemistry

ROMPHYSCHEM-17

ABSTRACT BOOK

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PLENARY LECTURES

New Ammonia Synthesis Process; Science, Engineering and Society View

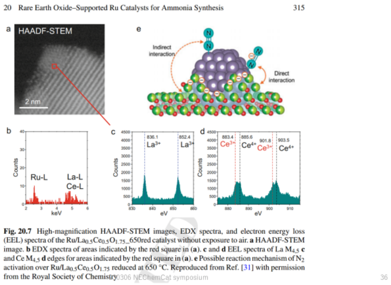
K. Aika

National Institute of Technology (KOSEN), Numazu College , Japan

Without ammonia fertilizer production we cannot obtain enough food at present. Ammonia had been produced through coal-based hydrogen in old days but now is produced with natural gas-based hydrogen. In near future, we must abandon fossil fuel and are obliged to use renewable energy as hydrogen source. For a natural gas reforming-system a bigger sized plant is economic. But water electrolysis units may be free from the size effect, because of the plate electrode structure.

As the background conditions are changed, a small-scale ammonia plant (below 100 t-NH3/d) can be suitable at the cheap-renewable-power-cost region. The process design concept will be changed. For a big sized process using natural-gas water is used both as a reactant and cooling media. As a result of this steam is produced which is used as energy source of turbines. But for renewable ammonia process air cooling and motor pumps will be used because of cheep power cost. The process becomes simple. However, a robust electrolysis unit against unstable power supply, new synthesis catalysts under lower pressure, and new ammonia separation system must be developed.

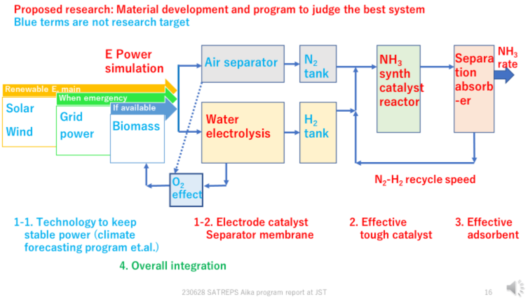
In this paper a new concept of ammonia synthesis process is disclosed as an example of green ammonia process. The material and process design concept are shown in a sense of science and engineering. Finally, it is pointed out that role of ammonia in our society will be increased. Green ammonia will be used as an energy source in addition to fertilizer. Environmental concern by active nitrogen will be discussed.



20 Rare Earth Oxide–Supported Ru Catalysts for Ammonia Synthesis 315

Fig. 20.7 High-magnification HAADF-STEM images, EDX spectra, and electron energy loss (EEL) spectra of the Ru/$La_{0.5}Ce_{0.5}O_{1.75}$_650red catalyst without exposure to air. **a** HAADF-STEM image. **b** EDX spectra of areas indicated by the red square in (**a**). **c** and **d** EEL spectra of La $M_{4,5}$ **c** and Ce $M_{4,5}$ **d** edges for areas indicated by the red square in (**a**). **e** Possible reaction mechanism of N_2 activation over Ru/$La_{0.5}Ce_{0.5}O_{1.75}$ reduced at 650 °C. Reproduced from Ref. [31] with permission from the Royal Society of Chemistry

230306 NEChemCat symposium 36



Proposed research: Material development and program to judge the best system
Blue terms are not research target

1-1. Technology to keep stable power (climate forecasting program et.al.)
1-2. Electrode catalyst Separator membrane
2. Effective tough catalyst
3. Effective adsorbent
4. Overall integration

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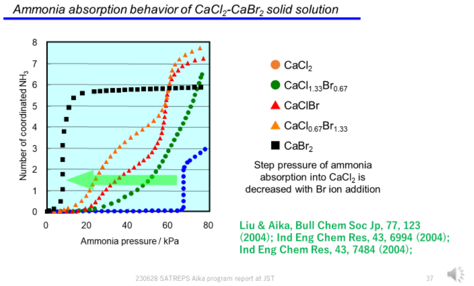

Ammonia absorption behavior of $CaCl_2$-$CaBr_2$ solid solution

Step pressure of ammonia absorption into $CaCl_2$ is decreased with Br ion addition

Liu & Aika, Bull Chem Soc Jp, 77, 123 (2004); Ind Eng Chem Res, 43, 6994 (2004); Ind Eng Chem Res, 43, 7484 (2004);

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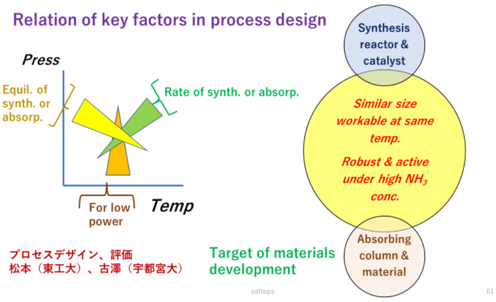
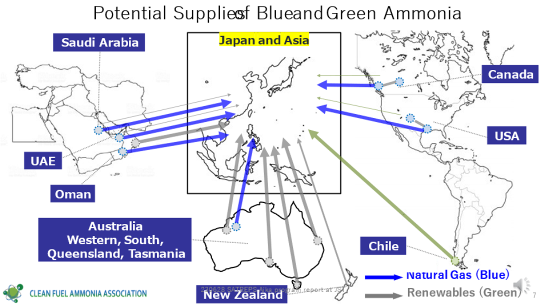


Relation of key factors in process design

プロセスデザイン、評価
松本（東工大）、古澤（宇都宮大）

Target of materials development

satreps 61



Potential Supplies of Blue and Green Ammonia

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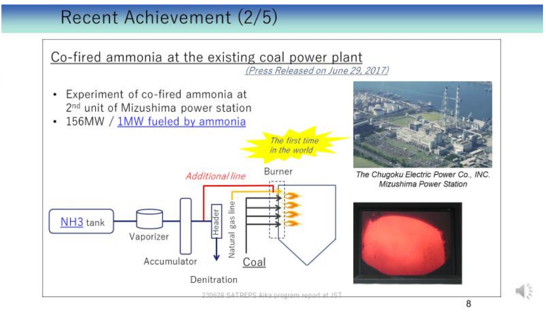

Recent Achievement (2/5)

Co-fired ammonia at the existing coal power plant
(Press Released on June 29, 2017)

- Experiment of co-fired ammonia at 2^{nd} unit of Mizushima power station
- 156MW / 1MW fueled by ammonia

The Chugoku Electric Power Co., INC. Mizushima Power Station

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Upcycling Commodity Polymers – An effective means for the preparation of added value materials

Rabah Boukherroub

Institute of Electronics, Microelectronics and Nanotechnology (IEMN), UMR CNRS 8520,
Avenue Poincaré – CS 60069, 59652 Villeneuve d'Ascq, France

Plastics represent the largest synthetic consumer product in the world. The annual production in 2018 reached 359 million metric tons. Plastics are found in countless products (packaging, construction materials, electronics, biomedical devices, energy storage etc.), owing to their light weight, low cost, easy processability and diverse advantageous properties. However, despite these beneficial features, the end-of-life management of plastic waste is challenging. The mismanagement of plastic products leads to environmental pollution because the plastic' lifetime is several times shorter than its decomposition. According to [UNEP 2021], less than 10% of plastic waste is recycled, making the related environmental issues very challenging.
Therefore, the development of appropriate strategies to reduce, reuse and recycle plastic is of outermost importance.

In this presentation, I will focus on the different recycling strategies of waste polymers and particularly on chemical upcycling and is achieved by either chemically altering a polymer to one that possesses a higher value or by transforming them to entirely new products. The upcycling of polymers is a relatively young but fast-growing field.

1. Waste PET Upcycling to Conductive Carbon-Based Composite Material through Laser-Assisted Carbonization of UiO-66
Dmitry Kogolev, Oleg Semyonov, Nadezhda Metalnikova, Maxim Fatkullin, Raul D. Rodriguez, Petr Slepicka, Yusuke Yamauchi, Olga Guselnikova, Rabah Boukherroub, Pavel S. Postnikov
Journal of Materials Chemistry A 11 (**2023**) 1108-1115

2. "Functional upcycling" of polymer waste towards the design of new materials
Olga Guselnikova, Olg Semyonov, Elizaveta Sviridova, Roman Gulyaev, Alina Gorbunova, Dmitry Kogolev, Andii Trelin, Yusuke Yamauchi, Rabah Boukherroub, Pavel Postnikov
Chemical Society Reviews (under revision)

Molecular Docking, Druglikeness Analysis, and ADMET Prediction of Dihydroxyfumaric acid and its derivatives as potential antiviral compounds

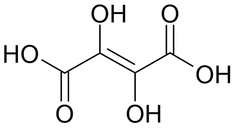
Gh. Duca and N. Bolocan

Laboratory of Physical and Quantum Chemistry, Institute of Chemistry of Moldova,
State University of Moldova

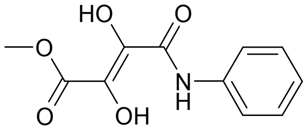
Dihydroxyfumaric acid (DHF) is a natural antioxidant, widely present in living cells as an intermediate in the di- and tricarboxylic acid cycles, bearing structural similarities with ascorbic acid. Novel derivatives with antioxidant/antiradical properties have been previously synthesized from dihydroxyfumaric acid by our group, and their usefulness for the pharmaceuticals and food industry has been discussed. Herein, we report an in silico docking study of DHF and some of its synthesized derivatives, against two proteases of SARS-CoV-2, complemented by ADMET and bioavailability modelling.

Research results show that all studied compounds have good pharmacokinetic profiles, significant druglikeness, and efficiently bind to M^{pro} and PL^{pro}, with binding affinities similar or higher than that of ascorbic acid. Ritonavir, an anti-viral compound used in anti-HIV treatment was used as a reference in this study, and results showed that in the case of binding to M^{pro}, compound 6 and 13 have a binding affinity comparable to that of ritonavir, while in the case of PL^{pro} docking, the binding affinities of compounds 5, 6, 12 and 13 (Fig.1) exceeded that of ritonavir, exhibiting better ADMET and bioavailability profiles.

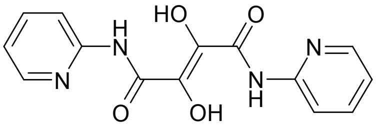
DHF and its tested derivatives meet all Lipinski rules, meaning that the molecular mass is less than 500 g/mol, and the number of donors (HD) and acceptors (HA) of hydrogen bond are less than 5 and 10, respectively. The only exception are compounds 7 and 8, which have one violation, i.e. HD > 5. The topological polar surface area (TPSA) and the number of rotatable bonds (RT) of the investigated compounds are in the range 93.06–139.12 and 2–10, respectively. According to Veber's rule, these compounds should be well absorbed orally. The calculated bioavailability score of 0.56 for DHF and its tested derivatives is equal to the score of ascorbic acid. Ritonavir, on the other hand, has three violations out of five, with a bioavailability score of only 0.17.



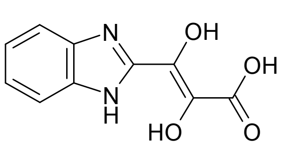
Dihydroxyfumaric acid (DHF)



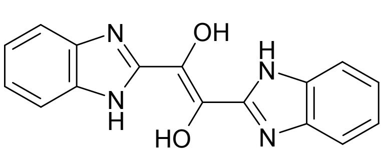
(*E*)-methyl 2,3-dihydroxy-4-oxo-4-(phenylamino)but-2-enoate (compound **5**)



2,3-dihydroxy-N^1,N^4-di(pyridin-2-yl)fumaramide(compound **6**)



(*E*)-3-(1H-benzo[*d*]imidazol-2-il)-2,3-dihidroxiacrilic acid (compound **12**)



(*E*)-1,2-di(1H-benzo[d]imidazol-2-il)etene-1,2-diol (compound **13**)

Figure 1: Chemical structures of DHF and its best performing derivatives.

The current research supports the importance of further studies of dihydroxyfumaric acid derivatives in the desire to discover promising naturally derived candidates for the antiviral treatment of Covid-19.

Active Approach Forward for Comfortable World

A. Fujishima

Tokyo University of Science
fujishima_akira@rs.tus.ac.jp

In 1967, the phenomena of producing oxygen gas on TiO_2 semiconductor surface in aqueous solution by light illumination known as “photosynthetic water oxidation” was first time demonstrated by us. This discovery of “photosynthetic water oxidation” to oxygen gas evolution using TiO_2 is recognized as “artificial leaf”, since out functionality is analogous with plant leaf “natural photosynthesis” in which oxygen and carbohydrates are produced from water and carbon dioxide using sunlight. Later in 1972, our report in “Nature” journal describes the complete water splitting phenomenon resulting in hydrogen and oxygen gas evolution by phenomena. This work has triggered a new scientific theme namely “artificial photosynthesis”, and opens new paradigm of the nature photosynthesis using man-made materials.

The tremendous amount of research that has been carried out in the two closely related fields of semiconductor photoelectrochemistry and photocatalysis during the past three decades continues to provide fundamental insights and practical applications. The principles and measurements obtained TiO_2 with photoelectrochemical studies have led to the research activity on heterogeneous photocatalysis, where the strong photooxidative activity of TiO_2 has been applied to environmental cleanup. This resulted in the concept of “light cleaning”, i.e., deodorizing, disinfection, and decontamination of air, water and surface with TiO_2 thin films and light. In 1997, we reported the novel photo-induced superhydrophilicity of TiO_2 and proposed the concept of self-cleaning superhydrophilic properties of TiO_2.

Recently carbon recycle subject is recognized as a very important field. Carbon dioxide must be used with hydrogen to produce methane, which is very useful chemical. How to get hydrogen using solar energy is very attractive subject. Photocatalysis is one of useful methods.

I will explain and introduce the recent progress of photocatalysis.

New Analytical Tools and Methods to Investigate the Behavior of Nano-Wastes in Solid Waste Treatment Processes

C. Ludwig[1,2]

[1]Paul Scherrer Institute (PSI), ENE LBK CPM, CH-5232 Villigen PSI, Switzerland
[2]École Polytechnique Fédérale de Lausanne (EPFL), ENAC IIE GR-LUD, CH-1015 Lausanne, Switzerland

Over the past decades many efforts have been made to minimize air pollution from thermal waste treatment (TWT) and prevent ground water pollution from waste disposal. However, current waste treatment systems encounter new challenges, such as nano-wastes, i.e. wastes containing engineered nano-particles and nano-objects (NO).

A general evaluation and assessment of the NO behavior during and after a TWT process, including the formation of different compounds, aging and fate, is mandatory. Due to their specific chemical and physical properties, such as the high surface to volume ratio, NO are of particular importance. One can differentiate between NO generated in TWT and those contained as engineered NO (ENO) in the waste feedstock. Their behavior and fate during TWT processes and after disposal of secondary residues is not fully understood. Moreover, analytical tools are missing for the investigation of NO in waste treatment processes (Figure).

My research group is developing and applying reliable analytical techniques for studying the fate of materials in waste to energy and bioenergy technologies. We contribute to the optimization and development of resource efficient waste and bioenergy technologies. The aim is to recycle valuable materials and chemicals as secondary resources as well as to recover energy from the feedstocks. Moreover, waste treatment processes should be designed to avoid or at least minimize emissions to the environment (soil, water, air).

A series of PhD theses have been performed under my supervision to develop on-line analytical techniques to obtain chemical information needed to understand the fate of trace metals in process gases and fluids (Table). More recent work focused specifically on the issue of NO. While analytical tools to measure online particle size distribution of NO are well established, the chemical composition is conventionally made offline. In my presentation I will present some highlights and insights obtained from our analytical work of the past 20 years and will complement my presentation with the recent developments in measuring online NO in aerosols and fluids.

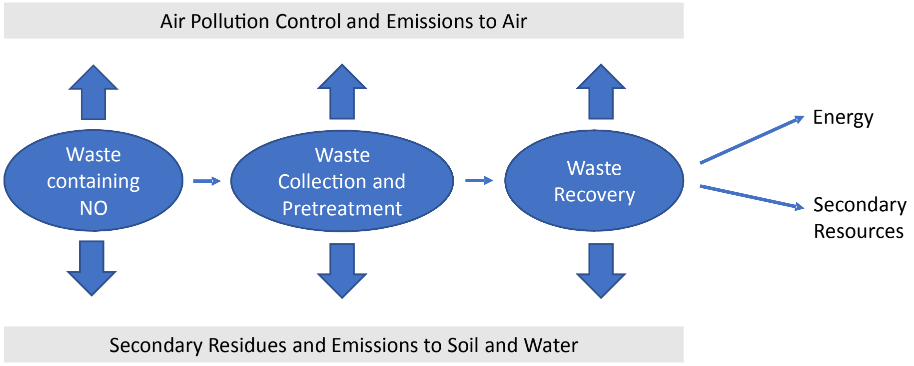


Figure: Our motivation for new analytical tools – Nano-objects in Waste Treatment Processes

Table: PhD theses with important contributions to analytical developments

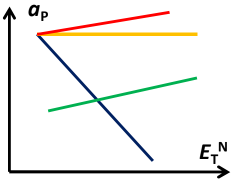
- Cen, T., EPFL PhD theses in preparation (SNF Project 184817)
- Agarwal, A., EPFL PhD theses in preparation (SNF Project 184817)
- Foppiano, D., Hyphenated Analytical Techniques for Studying the Speciation and Fate of Contaminants and Nanoparticles in Waste Treatment and Bioenergy Processes, EPFL PhD thesis 2019
- Edinger, Ph. S., Analysis and Removal of Product Gas Contaminants Present in Gasification Processes, EPFL PhD thesis 2019
- Hess, A., Time-resolved size and element analysis of gas-borne nanoparticles, EPFL PhD thesis 2016
- Hossein, M., Investigations into the Effects of Biofuel Contaminants on Solid Oxide Fuel Cells, EPFL PhD thesis 2016
- Wellinger, M., Development and Application of Devices for Online Trace Element Analysis of Thermal Process Gases from Woody Feedstocks, EPFL PhD thesis 2012
- Hagendorfer, H., New Analytical Methods for Size Fractionated, Quantitative, and Element Specific Analysis of Metallic Engineered Nanoparticles in Aerosols and Dispersion, EPFL PhD thesis 2011
- Kowalski, T., Evaluating a surface ionisation detector for measuring alkalis in biomass gasification, ETHZ PhD thesis 2007
- Lutz, H., Detoxification of filter ashes from waste incinerators - Understanding and influencing the removal of heavy metals during a thermal treatment process, ETHZ PhD thesis 2002

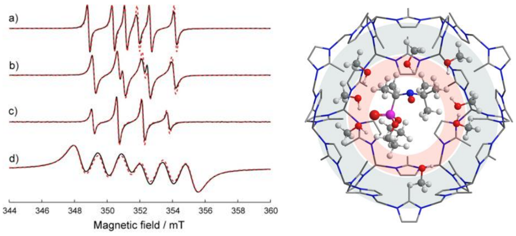
From fundamental solvents effects in nitroxides to probes for (Ultra)-low-filed Overhauser-enhanced Magnetic Resonance Imaging (OMRI)

S. R. A. Marque

ICR, Aix-Marseille University France

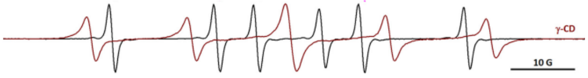
Low field or ultra low field OMRI is a powerful and an unique tool to investigate enzymatic activity involved in pathologies using an imaging technique.[1] In general, OMRI relies on the use of stable radicals, often nitroxides, however, in our case, nitroxides must be sensitive to the enzymatic activity, i.e., to display an EPR signal different before (biodistribution probes) and after enzymatic activity (pathology probes). To reach this aim, our group developed several β-phosphorylated shift-nitroxides which exhibit different before and after selective proteolysis based on the change in conformation affording a significant change in phosphorus hyperfine coupling constant a_P. Hovewer, these nitroxides suffer of two drawbacks: challenging and time-consuming synthesis and a lack of universality, e.g., activities of MMP-2 and MMP-9 enzymes cannot be detected. In the last decade, our group investigated thoroughly and intensively the solvent effects on hyperfine coupling constants of β-phosphorylated nitroxide.[2][3][4][5][6][7] We showed that a_P displays with the Reichardt's polarity constants E_T^N a linear increase, a linear decrease, no change, exponential decaying variation, shot-gun like distribution depending on the structure of the nitroxide, i.e., 40 different models have been investigated. These amazing changes on a_P of several mT were applied to the detection of traces of water in THF,[8][9] to investigate binary mixtures of solvent, and polarity in Metal Organic Framework (MOF).

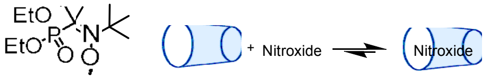




Signal EPR de nitroxyde dans MOF ZIF8 : (a) iPrOH, (b) EtOH, (c) MeOH et (d) air.

Recently, we investigate the host-guest interactions between β-phosphorylated nitroxide and cyclodextrine and observed striking changes in a_P.[10] Such changes are the first step toward the used of rotaxane based on β-phosphorylated nitroxide and peptide as enzymatic activity probes for OMRI.





EPR signal of nitroxide included in γ-cyclodextrine (red line) and of free nitroxide in water (black line). This talk will survey this decade of investigations and will highlight the most striking results.

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Advancing hybrid molecular materials of zinc for cellular differentiation in Diabetes mellitus II.

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A plethora of metabolic disorders emerge dominantly as a challenge to the health care system of numerous countries around the globe. The underlying etiopathology, exemplified through often unclear symptomatology, is ordinarily linked to aberrant insulin secretion or resistance to it in human physiology. Prominent in all respects is the case of insulin resistance, which is intimately associated with Diabetes mellitus II. Under the prevailing conditions, a number of pharmaceutical protocols have been adopted over the years, with several classes of drugs (insulin, thioazolidinones, biguanides, etc.) administered to patients to alleviate the symptoms and prevent further deterioration of human life.

The employed drugs in the case of Diabetes mellitus have been inexplicably associated with several side effects, thereby limiting their efficacy and ultimate efficiency in reducing the symptomatology and/or even rectifying the clinical picture of the patient To that end, alternative drugs that are atoxic, efficient and target-specific have been sought out by the international scientific community. Outstanding among the plethorically arisen efforts are metallodrugs, with metal ions , such as vanadium, having been explored as potential metal-organic forms acting as insulin mimetic agents, thus replacing and/or even enhancing insulin activity in the clinical administration of the disease.

In an effort to pursue alternative metallodrugs capable of fighting hyperglycemia in Diabetes mellitus II, zinc (Zn(II)) has been employed in our research, as a metal ion a) inherently physiological and relevant in insulin packaging and storage in human adipocytes, b) capable of promoting metal-organic chemistry, kinetically and thermodynamically supporting low and high molecular mass biomolecules in human physiology, and c) being atoxically acting as a promoter of molecular species participating in processes, such as the hematopoietic system and immune system enzymes abolishing reactive oxygen species. To that end, binary and ternary zinc-organic substrate species have been designed, synthesized in aqueous media, isolated in pure crystalline form and characterized by numerous techniques, ultimately formulating the physicochemical profile of well-defined soluble forms of zinc.[1]

Based on the physicochemical profile of zinc species characterized, the ensuing in vitro biology research in several cell lines (3T3-L1, etc.) was investigated. Initially, the toxicity profile of a series of well-defined zinc-(hydroxy)carboxylic containing binary and ternary materials was determined, thus giving rise to (physico)chemical characteristics (solubility, bioavailability, morphology, proliferation, migration) justifying further inquiry into their ability to induce cell differentiation of premature adipocytes toward mature adipocytes. The latter stand as competent cellular hosts capable of taking up glucose and catabolizing it, thereby fighting hyperglycemia. Concomitantly, the genetic basis of the cell differentiation potential of the zinc species was investigated (RT-PCR), with genes such as a) PPAR-γ, GLUT (1,4) heavily involved in cell differentiation and cell maturation, and b) ADIPQ, PI3K, MAPK, and others, intimately involved in signal transmission leading to glucose uptake and catabolism. [2]

The collective physicochemical and biological profile of the designed and synthesized zinc species formulate the strategic approaches leading to hybrid molecular materials of low molecular mass, effectively shaping up the pharmaceutical profile of potential metal organic agents mimicking insulin and/or enhancing insulin in diabetic pathologies. Further work into the molecular biology of the species studied is expected to pinpoint the salient features that will guide further employment of the derived molecular materials as functional insulin-mimetic metallodrugs in Diabetes mellitus II.[3]

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Application of atomic layer deposition in nanotechnology

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In the lecture the history, characteristics and potential of atomic layer deposition (ALD) will be presented. ALD is a thin film deposition method from the gas phase, which enables the deposition of uniform, conformal coatings on even highly structured and porous substrates, opening up the way to synthesize novel nanomaterials. Several examples will be shown about how various nanostructures can be obtained by ALD, based on our own experience.

The synthesis of core/shell WO_3/TiO_2, ZnO/TiO_2 and TiO_2/ZnO nanofibers and TiO_2 nanotubes by ALD and electrospinning was performed. By using sol-gel and ALD, PMMA/TiO_2, SiO_2/TiO_2, SiO_2/ZnO, SiO_2/Al_2O_3 core/shell nanoparticles were obtained. Bionanocomposites were manufactured by ALD, e.g. TiO_2 coated lotus leaves or Al_2O_3 covered bird feathers. Carbon nanomaterial (e.g. C_{60}, graphene oxide, carbon aerogels, carbon nanospheres) based nanocomposites were prepared by ALD. Polymer (Kapton)/oxide membranes were also in the focus of research.

The applications ranged from photocatalysis, gas sensing, particle detection, photonic crystals to nanofluids. In the presentation the advantage and disadvantage of ALD films for the various applications will be discussed.

Carbon Neutral Cycles Utilizing Photocatalytic CO_2 Reduction into $C_{1–3}$ Paraffins or Ethene and Propene

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Photocatalytic CO_2 reduction utilizing natural light completes new carbon neutral cycle. CO_2 conversion into solar fuels is one option while the CO_2 conversion into ethene and propene is also highly expected forming essential chemicals to be economically viable in sustainable society. Ni^0-ZrO_2 photocatalyst formed methane from CO_2 under the irradiation of UV–visible light at the formation rate of 980 $\mu mol \cdot h^{-1} \cdot g_{cat}^{-1}$ that is one of the highest rates reported using photocatalyst. CO_2 was adsorbed and photoactivated on O vacancy at ZrO_2 surface while the intermediate COH species hopped onto Ni^0 nanoparticles and was progressively hydrogenated into methane. Co^0-ZrO_2 photocatalyst formed $C_{1–3}$ paraffins at the total formation rate of 330 $\mu mol \cdot h^{-1} \cdot g_{cat}^{-1}$ via the coupling of CH_3 and/or CH_2 species. In clear contrast, using Co^0-ZrO_2 photocatalyst, CO was photoconverted into ethene and propene at the total formation rate of 6.0 $\mu mol \cdot h^{-1} \cdot g_{cat}^{-1}$ with the olefin selectivity of 70 mol%. Based on ^{13}C-isotopic monitoring, FTIR, the analysis of thermal factor in extended X-ray absorption fine structure, and density functional theory calculations, dual site mechanism is proposed comprising O vacancy site at ZrO_2 surface to provide electrons to CO_2 and metallic nanoparticle surface site warmed by UV–visible light irradiation, activated to form hydrocarbons.

SECTION 1

Theoretical chemistry. Molecular spectroscopy.

KEYNOTES

Radiationless relaxation pathways in molecular dimers

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The equilibrium geometries of the ground and first electronic excited states as well as the radiationless deactivation channels of catechol and benzene in their dimer configurations were investigated using the standard linear-response and the spin-flipped TDDFT together with the ωB97X-D3 exchange-correlation functional, as well as by the multireference CASSCF methods, considering the minimally augmented ma-def2-TZVPP and the 6-31G** basis sets. It was found that for the equilibrium geometry the stacking distance between the monomers decreases in the first electronic excited state, due to the stronger intermolecular interaction energy, bringing the two monomers closer together. Intermolecular-type CI geometries can be formed between the two monomers, where both aromatic rings show planar deformation and a weaker, approximately 1.6-1.8 Å long, C-C bonds are formed between the two monomers, with multiple orientation configurations of the monomers relative to each other. It was also shown that, these, intermolecular-type CIs are energetically more favorable than CIs containing only one deformed monomer. The validity of the dimer-type CI geometries obtained by spin-flipped TDDFT was confirmed by CASSCF calculations.

Simple resolution of the standard multispin Hamiltonian in binuclear complexes

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Simple model Hamiltonians play a pivotal role in bridging quantum mechanical (QM) calculations with experimental observations, providing a framework for the rational design of single-molecule magnets (SMMs) with magnetic hysteresis closer to room temperature [1]. Concerning binuclear complexes in the weak-exchange regime, the preferred method for extracting magnetic properties is through the use of a multispin model Hamiltonian ($\hat{H}^{MS}$). This Hamiltonian takes into account the Heisenberg isotropic exchange and the magnetic anisotropy, among others, and can be validated and resolved by means of QM calculations through the effective Hamiltonian theory [2]. However, the use of $\hat{H}^{MS}$ has been abandoned since its resolution often requires to introduce high-order anisotropy tensors in the model [3]. In this keynote, we re-habilitate the use of the standard $\hat{H}^{MS}$ to model magnetic properties in binuclear complexes regardless of the exchange regime. A proposed general extraction procedure will be showcased with binuclear Co(II) complexes and in the framework of spin-orbit configuration interaction (SOCI) calculations that rely on multiconfigurational CASSCF wavefunctions.

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Exploring the activity of the zigzag graphene nanoribbon edges and of the graphene quantum dots for the electrochemical Oxygen Reduction Reaction using DFT

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The present study was carried out in the context of the ongoing research to discover more effective catalysts for the oxygen reduction reaction (ORR) in PEM fuel cells. Graphitic materials such as graphene quantum dots (GQD) are gaining attention for this application, due to their abundance in edge sites, low dimensionality. The primary emphasis in this study is to investigate how dopants and various defects, as well as the reduction in the size of the material affects the activity of the edges towards ORR. To achieve this goal, Density Functional Theory (DFT) was employed to explore the activity of the zig-zag nanoribbon edges, undoped, N-doped or with various functionalized defects. Furthermore, as smaller sizes mean higher activity in many cases, the study also evaluates the activity of undoped and N doped GQD of various shapes (triangular, rhombohedral and hexagonal) and sizes, for zig-zag or armchair terminated edges.

Acknowledgements: This work is supported by (UEFISCDI) project PN-III-P1-1.1-TE-2021-0931 and by L'Oreal Woman in Science scholarship

SECTION 1

Theoretical chemistry. Molecular spectroscopy.

POSTERS

Investigating the Relationship between Structure and Biological Activity in Aminodiphenylamine Derivatives

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Diphenylamine derivatives have a wide range of industrial applications, from being used as antioxidants, dye starting materials, to medicine precursors. Molecular properties of these derivatives, such as lipophilicity and total antioxidant capacity (TAC) are important in understanding their structure-activity relationships. Lipophilicity is associated with drug absorption, toxicity, and other drug-receptor interactions, while TAC is related to the ability to fight reactive free radicals and other oxidant non-radical species. Thus, in this study, we utilized nine compounds, derived from aminodiphenylamine, to assess their antioxidant capacity and lipophilicity. Moreover, we also investigated their biological activity, mainly by assessing their MIC (minimum inhibitory concentrations), MBC (minimum bacterial concentrations), and antibiofilm activity, against four bacterial references.

Theoretical study of the reactivity of syringol with atmospheric radicals

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Syringol (2,6-dimethoxyphenol) is a pollutant found in the atmosphere as a component of the smoke resulting from the wood burning process, but it can also be a basic component in the pharmaceutical industry, agriculture or the chemical industry. Using the density functional theory (DFT) [1] with Becke three-parameter exchange and Lee–Yang–Parr correlation (B3LYP) [2] from the ORCA [3] quantum chemistry software package, the most energetically stable conformer and the modes of interaction of syringol with oxygen and some radicals from the atmosphere were determined.

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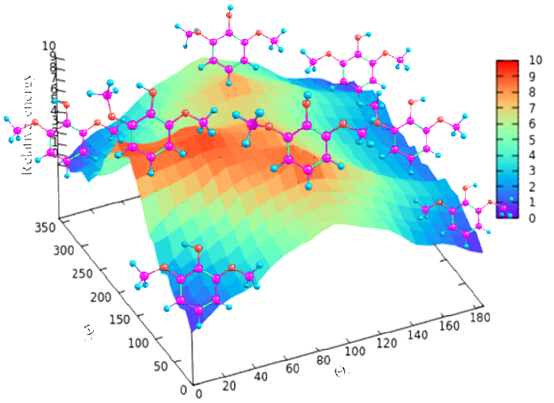

The ORR activity of undoped and N-doped triangle shaped graphene quantum dots using DFT

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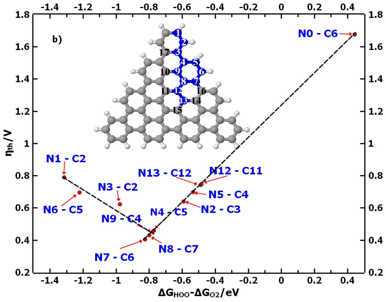

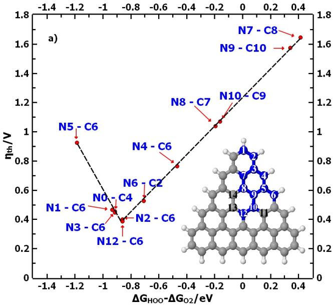

From the thermodynamic point of view, using DFT, we present how N modifies the activity for ORR of triangular shape GQD compared to the pristine structures. Depending on its position within the GQD, N induces less or more reactive sites. We have worked on two types of edges formed directly from cutting graphene, namely three sizes of zigzag (zz) and armchair (ac). Out of many studied structures (using 22 to 84 carbon atoms), below it is shown just two examples of N-doped positions and active sites on which we have done the intermediates adsorption testing. Both contain the theoretical calculated overpotential for the edges of graphene nanoribbon undoped & N-dopped (a. zigzag, b. armchair). The highest activity is exhibited close to the top of volcanoes plot, within the activity plot of the placed structures.

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Physico-chemical methods for the investigation of wooden ancient art pieces

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Art objects investigation by physico-chemical methods emerged in the last decades of the 20th century as a valuable tool for heritage research, evaluation, authentication, conservation or restoration. The wooden support was widely used for the realization of various heritage objects: icons, paintings, sculptures, tools, furniture, boats, machineries, monuments, churches, etc due to its availability, workability and durability. The physico-chemical methods used for the analysis of wooden art objects divide in two classes destructive and nondestructive. In this work we aim to exploit the potential of nedestructive methods, respectively, of the microdestructives ones with special emphasis on spectroscopic techniques. Depending on the techniques and materials used in the realization of the wooden ancient art pieces several methods of analysis could be necessary for obtaining of complete information. The most used methods of investigation are vibrational spectroscopy techniques, FTIR and FT-Raman respectively X-Ray Fluorescence for the analysis of organic and inorganic constituents of works of art, combining molecular and elemental analysis. An investigation protocol is proposed considering the limits of detection of mobile instruments compared to benchtop ones, respectively the size of the sample compartment in case of voluminous objects as well as the complexity of the art objects.

SECTION 2

Chemical kinetics and thermodynamics

KEYNOTES

Reactivity of functionalized silica surfaces with ozone and hydroxyl radicals

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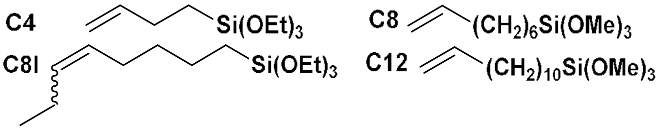
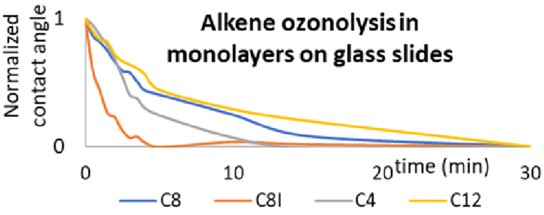
Department of Chemistry, University of York, UK

Understanding chemical reactivity of surface-attached functional groups with gaseous reactive species is critical for many applications including atmospheric chemistry, paints/coatings and sensors. As contributors to the RADICAL consortium working on atmospheric radical sensors[1], we have studied reactions of ozone and non-thermal He/H_2O/O_2 plasma (as a source of hydroxyl radicals) with functionalized self-assembled monolayers on non-porous silica nanoparticles and planar silica substrates. In order to characterize the reaction products on silica nanoparticles, we have developed methodology for removing the monolayer from the surface to yield soluble products that can be analysed by conventional analytical techniques.

We are particularly interested in the effect of monolayer environment (e.g., the presence of adjacent molecules, monolayer thickness, position of the functional group in the monolayer) on the kinetics and chemical reactivity of the monolayers. Initial results suggest that the reactivity follows a similar trend to the bulk condensed phases with higher ozone reactivity for shorter monolayers.





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[1] *https://radical-air.eu/*

Thermodynamic stability evaluation of carbon-supported metal oxides under supercritical water conditions

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Carbon-supported metal oxides (Me_xO_y/C) are employed as catalysts and/or sorbents in processes undergoing in supercritical water (scH_2O)[1,2], the green reaction medium used to obtain energy relevant or value added products [3]. Here we present a thermodynamic approach developed for understanding the effects of various parameters, such as composition, structure, particle size and shape, as well as of the preparation conditions (temperature, pressure and concentration) on the thermodynamic stability of the Me_xO_y/C materials under different operating conditions. A systematic study on the thermodynamic stability of Me_xO_y/C is done by combining several experimental methods in both isothermal and dynamic regimes, such as Drop Calorimetry, and dynamic differential scanning calorimetry (DSC) coupled with thermogravimetry (TG).

Acknowledgments: This research is funded by Romanian CNCS/CCCDI-UEFISCDI, grant number PN-III-P4-ID-PCE-2020-1241. The authors thank to Prof. Ludwig from PSI-CH, Dr. Atkinson from ICF-RO and Dr. Contescu retired from ORNL-USA for valuable support.

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Atmospheric chemistry of aromatic compounds: from gas-phase kinetic to secondary organic aerosol formation

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Aromatic hydrocarbons (AHs) are key species widely spread in urban atmosphere. Their concentration and reactivity highly influence the atmospheric pollution, climate change and human health [1]. Once released in the atmosphere AHs react with OH radicals leading to gas-phase products.

The gas-phase chemical degradation mechanisms of AHs are intensively studied in the atmospheric simulation chambers at the level close to their concentration in the atmosphere. Kinetic rate coefficient investigations [2], gas-phase chemical degradation mechanism and secondary organic aerosol (SOA) formation [3] was studied for the reaction of 2,6-dimethylphenol (26DMP) and 2,6-dimethylbenzoquinone (26DMBQ) initiated by OH radicals. The present work, performed in different atmospheric simulation chambers, adds for first time the information related to the 26DMP and 26DMBQ's reactivity, atmospheric lifetime, gas-phase products and SOA formation yields. The importance and impact of these processes on the atmosphere and modeling studies will be assessed.

Acknowledgement given to UEFISCDI project PN-III-P2-2.1-PED-2021-4119 (SOA-AROMATIC).

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The impact of hydrogen enrichment on flame structure and combustion characteristic properties of premixed hydrocarbon-air flames

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Hydrogen is a valuable alternative to actual fossil fuels, since its combustion produces no carbon dioxide, a well-known greenhouse gas, or carbonaceous particulates. This recommend hydrogen for use in IC (Internal Combustion) engines, in spite of various safety issues of its production, storage and transportation. A more reasonable method is to use hydrogen as an additive to fossil fuels, for enhancing their combustion. The influence of hydrogen is seen in the characteristic ignition and propagation properties of blended hydrocarbon mixtures. Thus, hydrogen addition to fuel-air gaseous mixtures results in the decrease of minimum ignition energy, and in the increase of the laminar burning velocity, as well as in the increase of H radicals pool, accounting for the increase of reaction rate, for the more slowly combusting hydrocarbons. In addition, using hydrogen as additive to hydrocarbons would reduce the emissions of CO and soot; however, NOx emissions increase, due to lower flame temperatures. Data concerning the influence of added hydrogen amount, as well as of other operational parameters of gaseous combustions, on ignition and explosion propagation of ternary hydrogen-hydrocarbon-air mixtures are summarized, using original results on hydrogen-propane-air as well as literature information..

An insight into the thermodynamics of protein interactions with magnetic dextran iron oxide nanoparticles

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The study of the interaction of nanoparticles (NPs) with biological systems is a key issue for both nanomedicine and nanosafety research. In the present work the thermodynamic signature associated with the interaction of one of the most abundant plasma proteins, bovine serum albumin (BSA) with magnetic dextran iron oxide NPs has been investigated. The following issues have been addressed: (i) Analysis of binding characteristics for protein-NPs systems represented by the binding constant, binding stoichiometry, enthalpy, Gibbs energy and entropy obtained by means Isothermal Titration Calorimetry; and (ii) Assessing the effect of NPs on the protein stability by measuring the thermodynamic parameters for the proteins denaturation (denaturation temperature, heat capacity, enthalpy and entropy). The thermal stability of BSA increases in the adsorbed state and no changes of protein secondary structure resulting from adsorption of BSA on NPs surface is expected. The interaction is entropy-driven arising from the release of the hydration water from the binding interface. The information generated by the thermodynamic approach is speaking in favor of a water-mediated binding process offering new opportunities for the future application of these nanosystems.

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SECTION 2

Chemical kinetics and thermodynamics

POSTERS

Gas-phase kinetic and degradation mechanism of the OH radical initiated oxidation of 2-methylstyrene

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Biomass burning release in the atmosphere quite significant quantities of aromatic hydrocarbons (AHs). AHs are strongly correlated with anthropogenic activities and influence the atmospheric pollution, climate change and human health [1]. AHs react with OH radicals in the gas-phase leading to degradation products with high potential impact on human health. A few data on the gas-phase ozonolysis of 2-methylstyrene is known to date [2,3], however, OH chemistry is not known.

In this study has been investigated for the first time, using a relative rate method with mesitylene, propene, isobutene as reference compounds, the gas-phase kinetic rate coefficient for the reaction of 2-methylstyrene with OH radicals.

The degradation mechanism and products formation from the reaction of 2-methylstyrene with OH radicals proved the formation of *ortho*-tolualdehyde as the major product. These studies employed FTIR and PTR-TOF-MS measurement techniques in an atmospheric simulation chamber. The importance and impact of these processes on the atmosphere and modeling studies will be assessed.

Acknowledgement given to UEFISCDI project PN-III-P2-2.1-PED-2021-4119 (SOA-AROMATIC).

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Propagation of premixed hydrogen-hydrocarbon–air flames in a closed spherical vessel with central ignition

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Hydrogen addition on hydrocarbon flames may be interesting by supporting an extended flammability range, more stable flames, a higher burning velocity, resulting in reduced CO_2/HC emissions. The peak explosion pressure and the maximum rate of pressure rise of explosions in confined spaces are key safety parameters to evaluate the hazard of processes running in closed vessels and for design of enclosures able to withstand explosions or of their vents used as relief devices. An experimental investigation on the explosion characteristics of hydrogen-propane-air and hydrogen-butane-air mixtures was carried out in a spherical vessel at room temperature (298 K) and sub-atmospheric pressures (between 0.3 and 1.0 bar). Based on pressure history recordings, maximum explosion pressure (p_{max}), maximum rate of pressure rise ($(dp/dt)_{max}$) and deflagration index (K_G) were derived. Linear correlations $p_{max}=f(p_0)$ and $(dp/dt)_{max}=f(p_0)$ were found. In addition, the heat loss to the walls during the explosion propagation was estimated on the basis of the difference between the adiabatic and experimental measured pressure. All parameters are examined as functions of added hydrogen amount to binary hydrocarbon-air mixtures.

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Optical and viscometric properties for binary mixtures of cyclohexane + aromatic hydrocarbons in the range of normal temperatures and pressures

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The optical and viscometric properties for binary mixtures of cyclohexane with two alylbenzenes, as *n*-propylbenzene and *iso*-propylbenzene, were measured at several temperatures in the range of (298.15 to 318.15) K and p = 0.1 MPa. The experimental data for refractive indices, n_D, and viscosities,η, at temperature of T = 298.15 K are reported. By using the obtained results, the related excess or deviation quantities, as deviation in refractive indices, excess molar refractions, and deviation in viscosities, were calculated and reported in this work. All these excess properties were correlated with the Redlich-Kister equation. The capability of different theoretical (n,ρ) mixing rules to predict the refractive index was evaluated. Different equations, as Grunberg–Nissan, Katti-Chaudry, Hind, Dolezalek, and three-body McAllister interaction model, were used to calculate the viscosities values and a comparison with those values with the experimental data was made.

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Thermophysical properties of *L*-Alanine / Glycine + D-Fructose ternary mixtures at (313.15 and 318.15) K temperatures and pressure of 0.1 MPa

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The thermophysical properties for ternary mixtures of *L*-Alanine (L-Ala) and Glycine (Gly) in aqueous D-Fructose (DF) solvent have been measured at four temperatures in the range of (288.15 up to 318.15) K and atmospheric pressure.

In this study, the experimental data of densities, ρ, speed of sound, c, and refractive indices, n_D, at two (313.15 and 318.15) K temperatures are presented. From measured values for 1.027 $mol \cdot kg^{-1}$ *D*-Fructose solvent and various molalities, between (0.1585 and 0.9807) $mol \cdot kg^{-1}$ of aminoacids, the apparent molar volumes, V_Φ, isentropic compressibility coefficient k_S, and molar refractivity, R_D, for (Gly) and (L-Ala) solutes have been computed. The Laplace and Lorentz-Lorenz equations for isentropic compressibility coefficient, and molar refractivity, respectively, were used in calculus. The physico-chemical behavior for ternary L-Ala/Gly+ D-Fructose mixtures was shown and interpreted graphically.

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Effects of TiO_2 nanoparticles with various particle sizes on protein thermal stability

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The thermodynamic investigation of protein stability in the presence of nanoparticles (TiO_2) and the evaluation of the thermodynamic parameters of thermal denaturation of bound protein, bovine serum albumin (BSA) was performed using a NanoDSC calorimeter (TA Instruments). Calorimetry is a good method to determine the heat of adsorption and these data are an excellent indication of the thermal protein stability in the presence of nanoparticles. The denaturation temperature (T_m) is indicative of the protein stability, and ΔH_{cal} is associated with energetically favorable intramolecular interactions in the protein.

The characteristics of polydisperse samples of nanoparticles (TiO_2) before the thermodynamic measurements have been detected from DLS measurements. The mean hydrodynamic diameter Z-average provided information on aggregate sizes in aqueous solution. PdI is an indicator of the width of particle-size distribution of a sample.

The changes in the adsorption of BSA on the NMs were associated with some rearrangements/unfolding of the protein during adsorption, with the results speaking in favor of the correlation of the increasing of the enthalpic character of interaction with the decreasing of protein's structural stability.

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Hydrogen influence on ignition and quenching of n-butane-air explosions in deflagration regime

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The ignition by electric sparks of stoichiometric n-butane-air mixtures in the presence of various amounts of hydrogen was investigated at ambient initial temperature and various total initial pressures between 0.3 and 1.0 bar. The quenching distances were measured by flanged electrode technique using high voltage inductive-capacitive sparks and were found dependent on total initial pressure p_0 and on concentration of added hydrogen. At constant composition, the quenching distances decrease with increasing pressure according to the following empirical correlation: $d_q=a\bullet p_0^{-\alpha}$, where $a$is a constant and α is the baric coefficient.

The overall kinetic parameters of H_2-blended butane oxidation were calculated as: the overall reaction order n from the baric coefficient of quenching distances ($n=-2\bullet\alpha$) and the overall activation energy E_a from the variation of quenching distances versus the reciprocal value of average temperature of the flame front. Minimum ignition energies for ignition by high voltage sparks, H_{min} were calculated from the quenching distances d_q according to a validated correlation model [1, 2]: $H_{min}=k\bullet p_0\bullet d_q^3$, where k is a proportionality constant and p_0 - the total initial pressure of mixture. All parameters were examined in correlation to the added hydrogen amount to n-butane-air mixtures.

Keywords: quenching distance, hydrogen, n-butane, minimum ignition energy

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Study of the heat transfer to supercritical water during *pseudo*-boiling phase transition

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Water in its supercritical state exhibits two states known as liquid-like (LL) and gas-like (GL), distinguishable during the *pseudo*-boiling phase transition[1,2]. Therefore, the supercritical water (scH_2O) reflects both liquid and gas behaviours, rendering it valuable for a variety of applications, such as the treatment of wastewater, the thermochemical conversion of biomass for the production of biofuels, and the hydrothermal synthesis of nanoparticles [3]. The heat transfer to scH_2O is an essential issue to consider for the working parameters optimization of the reactors used in supercritical water technologies. Here we present the results obtained during isobaric transient experiments at different scH_2O flow rates. The findings revealed that there is a distinct heat requirement difference due to the transition between the LL and GL metastable phases of scH_2O.

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Thermodynamic characterization of hydroxyapatite-based biomaterials used for tissues regeneration

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Hydroxyapatite (HA), ($Ca_{10}(PO_4)_6(OH)_2$), the main mineral constituent of bone, presents excellent biocompatibility with soft tissues such as skin, muscle, and gums and it is able to accelerate bone ingrowths onto the surface of a biomedical implant. Both synthetic hydroxyapatite and hydroxyapatite of biological origin are currently used for bone regeneration in variuos formulation such as granules, blocks and scaffolds.

The interaction between HA-based biomaterials and proteins was the main focus of this study. HA obtained from natural sources (bovine bones and eggshells) and synthetic HA (obtained in acid and basic medium by hydrothermal method) were structural, morphological and thermal investigated and different modifications related to the origin of the samples are reported. The isothermal titration calorimetry (iTC) method considered a "gold standard" for measuring biomolecular interactions, was used to get thermodynamic information about the energetic parameters that drive the interactions between HA and proteins. The obtained results are important in regulating the biomaterials - protein interaction by correlation of the physicochemical properties with the energetic parameters.

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Molecular interactions of fenofibrate with active pharmaceutical ingredients by DSC and FTIR spectroscopy

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Mixtures of active principle ingredients (API) are used in order to obtain drugs with enhanced biodisponibility or synergistic biological activity. The structure and the properties of the API, i.e. the number of hydrogen bond donors/acceptors, solubility, etc. as well as the mixture preparation method may lead in some cases to the formation of eutectics.

In this work binary compositions of fenofibrate with citric acid, caffeine, timolol maleate, betaxolol and paracetamol, obtained by mechanosynthesis, solvent evaporation and recrystallization from melt were studied by dynamic scanning calorimetry and FTIR spectroscopy. The main thermodynamic parameters as well as the characteristic frequencies of single components and of various molar fractions mixtures were used to establish the molecular interactions, hydrogen bonds or van der Waals responsible for the behavior of the prepared API mixtures.

Pressure influence on laminar burning velocity of hydrogen-blended propane-air mixtures

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Recently, the study of alternative and clean fuels has attracted increasing attention with the depletion of fossil fuels and the implementation of stricter regulations on pollutant emissions. In this context, hydrogen and propane could be used as alternative fuels. Knowledge of the explosion parameters of these mixtures is important; the laminar burning velocity is considered to be a fundamental property of fuel-air mixtures with a significant impact on many aspects of combustion.

In this work, the burning velocities of stoichiometric propane-hydrogen-air mixtures (with various concentrations of hydrogen between 0 and 30 vol.%) were investigated at various initial pressures (between 0.3 and 1.0 bar) and ambient initial temperature. The burning velocities were obtained from both experimental measurements of pressure variation during the early stage of closed spherical vessel explosions with central ignition and by a detailed modelling of free laminar premixed flames. It is found that the laminar burning velocity increases with H_2 addition for all initial pressures, as a consequence of increase in total mass fraction of active chemical species. Examination of burning velocities variation against initial pressures of flammable mixtures allowed the determination of baric coefficient and overall reaction orders.

Enthalpies of combustion and formation of some dipeptides with potential biological activity

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Thermal analysis of two dipeptides having alanine (Ala) as first term, namely, L-alanyl-glycine and L-carnosine (β-alanyl-L-histidine), using combustion calorimetry method and simultaneous TG-DSC measurements, have been carried out.

The enthalpies of combustion and formation, the TG-DSC quantities related to the decomposition processes of these compounds, were compared with those of the free amino acids contained in the dipeptides.

Some information on the influence of the components on the decomposition processes of the dipeptides were obtained. The formation enthalpies are the first data in the literature concerning the thermochemical properties of the studied peptides and evidenced new information related to their stability. These results could be used for a better explanation of their behavior when they are involved in different biological processes in the living bodies.

Thermodynamic properties of zinc oxide nanoparticles obtained by supercritical & classical hydrothermal synthesis

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Zinc oxide (ZnO) is a useful material and the preparation method used to obtain ZnO nanoparticles can significantly impact on its properties and potential applications. Since the 90th, the supercritical hydrothermal synthesis has been developed to produce nano-sized metal oxide particles in a mineralizer-free process [1]. In the present study, we compare the thermodynamic properties of ZnO particles obtained by both classical hydrothermal and supercritical water (scH_2O)[2] synthesis methods. Moreover, we use the supercritical hydrothermal synthesis approach to produce carbon-supported ZnO nanoparticles by impregnation in scH_2O. The structural features showing the particularities of the synthesis methods were highlighted by Fourier transform infrared (FTIR) analysis. The thermodynamic characterization of the obtained nanomaterials is performed by dynamic differential scanning calorimetry (DSC) coupled with thermogravimetry (TG).

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Thermodynamic characteristics of the carbon-supported copper oxides obtained by supercritical water impregnation approach

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The supercritical water (scH_2O) is a suitable reaction medium for nanoparticles synthesis due to its unique properties, including low solubility of inorganics, low viscosity, and enhanced mass transfer [1]. There are two metastable phases of scH_2O, known as liquid-like (LL) and gas-like (GL), respectively [2,3], with distinct properties. Here we present the evaluation of the impregnation temperature effect on the thermodynamic properties of carbon-supported copper oxide materials determined by dynamic differential scanning calorimetry (DSC) coupled with thermogravimetry (TG). The operation temperature of the scH_2O reactor has been chosen in such a way to have water density corresponding either to LL or to GL states.

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Thermodynamic properties of some entropy-stabilized oxides

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The understanding of the interrelation composition-structure-properties is a central point in the research activity with impact in the materials science. One of the key parameters responsible for this relationship is the change of the energetic parameters. In order to find new ways to tune, enhance and optimize the properties of novel materials designed for different applications, the thorough knowledge of the thermodynamics of the new materials is essential. The focus of our present research is on new materials called “entropy-stabilized oxides”, which represents a "complex materials" class presenting a large diversity of magnetic, electrical and electrochemical properties. Some specific systems of high entropy oxides with the general formula $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ (named HEOx hereafter) were selected for discussion. In the present paper the HEOx thermodynamic properties have been investigated in the temperature range from ambient to 1273 K. For the first time, the relevant functions suitable for evaluation of the thermodynamic stability in particular temperature ranges associated with structural changes during heating have been measured. The energetic parameters obtained by a couple of measurements (Drop Calorimetry, DSC, Electromotive Force Measurements) together the microstructure, thermal expansion and electrical conductivity data have been analyzed and the relationship of the thermodynamic stability with the defect structure has been revealed.

Thermodynamic properties of the carbon-supported zinc oxide materials prepared by supercritical water impregnation method

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Supercritical water (scH_2O) is a highly attractive reaction medium with two distinct states known as liquid-like (LL) and gas-like (GL)[1]. Moreover, scH_2O is proven effective in the impregnation process of ZnO on activated carbon (ZnO/C) [2]. Understanding the influence of the impregnation temperature on the thermodynamic properties of ZnO/C is crucial to obtain composite materials with well-defined properties. The impregnation temperature has been chosen in such a way to have scH_2O density corresponding either to LL or to GL states of water and the thermodynamic properties have been evaluate by dynamic differential scanning calorimetry (DSC) coupled with thermogravimetry (TG). The results of the present study provide valuable knowledge for designing efficient and controlled impregnation strategies of ZnO on carbon support in scH_2O.

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SECTION 3

Catalysis and Chemical Engineering.

KEYNOTES

Amorphous SiO_2 - intrinsic and added (chemo) reactivity

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Highly defected SiO_2 nanotubes were obtained by using sol-gel method assisted by *in situ* generation of the template. The oxygen-related lattice defects and Si^{3+} act as active photocatalytic sites for degradation of an organic substrate in aqueous media. Further material optimization looks for achieving a higher density of oxygen vacancies able to increase the light absorption and hydrogen generation from organics under light exposure (UV, solar and visible irradiation).Therefore, metal and non-metal modifiers are used for improvement of photo-generated charge separation and modulation of redox processes.

Role of electron polarons and carrier dynamics in the photoreduction of CO_2 on transition-metal oxide surfaces

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The research focused on titanium dioxide (TiO_2) and zirconium dioxide (ZrO_2) among transition-metal oxides (TMOs), which are semiconductors with potential applications in photochemical energy conversion. The presence of excess electrons in TMOs, known as electron polarons (EPs), significantly affects the surface chemistry and is influenced by defects, doping, interstitials, or light irradiation. Surface oxygen vacancies (V_O) in TMOs are reactive sites that give rise to EPs with energy levels between the Valence Band and Conduction Band.

To investigate the phenomena attributed to EPs and carrier dynamics, we performed electronic structure calculations and Ab Initio Molecular Dynamics (AIMD) simulations using the Vienna ab initio simulation package (VASP).

The findings conclude that presence & configuration of EPs significantly influence CO_2 adsorption across different TMOs. Furthermore, we followed the one-electron reduction process of CO_2 adsorbed on V_O-monoclinic-ZrO_2 surface to be $CO_2^{\bullet -}$ by excited electrons in 150 fs using the Non Adiabatic-Molecular Dynamics (NA-MD) simulation.

Oscillations in heterogeneous catalytic oxidation of methanol

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Heterogeneous catalytic reactions are non-linear multi-level chemical reaction systems, far from thermodynamic equilibrium, which could exhibit complex temporal behavior such as instabilities, chemical waves, or oscillations. The oscillatory behavior in the case of the oxidation of the methanol on a solid catalyst is normally observed on a macroscopic scale, either as reaction products oscillations in the outlet of a flow reactor or as oscillations of a quantity that depends on the reaction conversion (i.e. the temperature of the oscillations).

The activation energy of ignition for the thermokinetic oscillations obtained in the reaction of methanol oxidation on a Pd catalyst was determined. For this purpose, new equations were proposed starting: i) from the maximum value of the temperature of the oscillation, T_M, and ii) from its minimum value, T_m.

Ammonia Synthesis from Nitrogen and Water using Phosphate-based Electrolyte Electrolyzer and Ru catalysts

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Typically, ammonia is a major chemical synthesized from N_2 in the air and H_2 derived from fossil resources. By synthesizing NH_3 from H_2O using renewable energies instead of H_2 from fossil resources, we can obtain carbon-neutral process and utilize ammonia not only as a fertilizer but also as a green fuel. By combining water electrolysis to obtain H_2 and the conventional Haber-Bosch NH_3 synthesis, ammonia can be produced using renewable electricity sources such as solar and wind power plants. However, the integration of these two individual processes is complex and not well-suited for fluctuating electricity supply. One approach we have examined involves the utilization of a novel type of electrochemical cells incorporating Ru ammonia catalysts in a phosphate-based electrolyte water electrolyzer, alongside a Pd-alloy hydrogen-permeable membrane. These cells operate at temperatures ranging from 200 to 250°C. In this presentation, we will demonstrate the progress of research and development regarding the electrochemical ammonia synthesis system. A $Ru/Cs^+/MgO$ catalyst was used for ammonia synthesis and placed on the backside of the cathode of the Pd alloy membrane. The anode consisted of Pt-plated Ti sintered fibers. Ammonia was synthesized with the rate of $12.4\ \mathrm{nmol{\cdot}s^{-1}{\cdot}cm^{-2}}$ ($44.6\ \mathrm{\mu mol{\cdot}h^{-1}{\cdot}cm^{-2}}$) and 12% current efficiency at 0.7 MPa and $30\ \mathrm{mA{\cdot}cm^{-2}}$. Simultaneously, hydrogen production was observed for the remaining part of the current efficiency. Over the past few years, the system has been gradually improved, and it can currently produce ammonia with a current efficiency of 20% at $50\ \mathrm{mA{\cdot}cm^{-2}}$, 2.0 V and 1.0 MPa.

Design of Co Catalysts for Ammonia Synthesis under Mild Conditions by Surface Dynamics during High-Temperature Reduction

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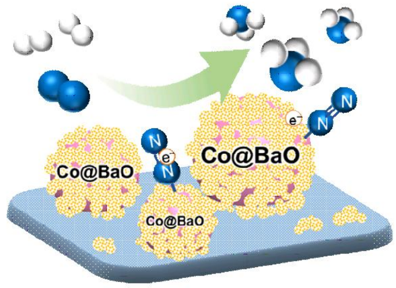
Ammonia has attracted great attenuations as a carbon-free fuel because CO_2 is not emitted when ammonia is combusted in power station. Ammonia is commonly produced by the Haber-Bosch process. In this process, ammonia is produced at high temperatures (>450 °C) and pressures (>20 MPa) over an iron-based catalyst and the use of fossil fuels emits large amount of CO_2. A catalyst that yields ammonia with high efficiency under mild reaction conditions (<400 °C, <10 MPa) would reduce energy consumption in the green ammonia fuel synthesis process.

We discovered that Co/BaO/MgO reduced at unusually high temperature, 700 °C, showed higher ammonia synthesis rate than bench-mark noble metal, Ru, catalysts at 350 °C and 1.0 MPa. At the same temperature the ammonia synthesis rate of Co/BaO/MgO was increased drastically with increase in pressure to 3.0 MPa and was higher than that of active Ru-based catalyst. It was uncovered that the Co nanoparticles (core) are encapsulated by nano-fractions of BaO (shell) and electrons are effectively donated from the nano-fractions *via* Co to antibonding π-orbital of N_2, which results in weakening of N≡N bond, rate determining step for ammonia synthesis.



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Versatile Layered Perovskites for Environmental Applications

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Layered perovskites represent an emerging class of semiconductor materials allowing the incorporation of various spacers into the inorganic matrix, while the structure of perovskite blocks remains unchanged. Their flexible lamellar construction makes them possible to be tailored through ion exchange, pillaring, exfoliation, or restacking methods. Therefore, unique nano architectures with attractive properties are obtained compared with those of the parental compounds. Solar photoconversion is an important environmental-friendly route to solve numerous worldwide issues, including water and air purification. In this regard, layered perovskites are promising candidates for light-related applications due to their unique features.

This study aims to develop visible-light harvester materials based on transition-metal chlorides intercalated into the $RbLaTa_2O_7$ host, which can remove pollutants from wastewater. Different compounds of the form $(\mathit{Me}Cl)LaTa_2O_7$ (*Me* = Cu, Fe, and Ni) were synthesized and characterized by various techniques to investigate their physicochemical properties. Intercalation of the (*Me*Cl) spacers led to a redshift in the absorption edge of the $RbLaTa_2O_7$ host toward the visible-light domain. The (*Me*Cl) insertion gives rise to a valence band located at a higher energy level than that of O_{2p} orbitals, narrowing thus the band gap of the host. The performance of the catalysts has been evaluated for the photodegradation of various pollutants under simulated solar irradiation.

Synergistic Interaction between Ti and Fe, Co, Ni Oxides Supported on Micro-Mesoporous Zeolite Y with Effect on Mechanism and Efficiency of Photocatalytic Pollutant Degradation

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Isolated Ti sites on zeolite supports exhibit valuable photocatalytic effects for a wide spectrum of pollutants from wastewater. Recently, several studies were concentrated on the photocatalytic properties of materials based on group VIII metals (Fe, Co, Ni) supported on oxides such as TiO_2, SiO_2 Al_2O_3. Here, Fe, Co, Ni ions were supported by impregnating their nitrate solutions on Ti-modified zeolite Y with micro- and micro-mesoporous structure. The significant effect of zeolite Y and hierarchical zeolite Y supports on TiO2 species, their interaction with Fe, Co, Ni oxides and the resulted photocatalytic properties were evaluated. The variation of metals oxidation state with effect on efficiency and mechanism of the photocatalytic reactions was assessed by H_2-TPR, photoluminescence, Raman and XPS spectroscopy. The mechanism of the antibiotic (amoxicillin) degradation from water was investigated under UV and visible light irradiation in the presence of scavengers. The different activity was attributed to the presence of the group VIII metals ions and (M^{2+} and M^{3+}) which influence the band gap energy and photogenerated e^-/h^+ recombination. The highest value of the photocatalytic efficiency was obtained for a higher percentage of M^{3+} ions.

Insights into the catalytic and photocatalytic nitrate removal over nanostructured Pt-based catalysts

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TiO_2-supported mono and bimetallic catalysts (Pt, Pt-Cu, Pt-Ni, and Pt-Co) were prepared by impregnation or deposition protocols. The samples were characterized using TEM, XRD, fractal analysis, UV-Vis, TPR, and CO chemisorption techniques. The catalytic and photocatalytic reduction of nitrate in an aqueous solution was studied using TiO_2-supported mono/bimetallic catalysts. Additionally, the photocatalytic hydrogen generation by water splitting was investigated under simulated solar light and UV-Vis light irradiation. The influence of the structural features on the catalytic and photocatalytic performance, the synergistic effect and the interaction between platinum and non-noble metal nanoparticles are discussed.

SECTION 3

Catalysis and Chemical Engineering.

POSTERS

W/TiO_2-CeO_2/Activated Carbon Composite Photocatalysts Obtained by Sol-gel Method with Application in Degradation of Textile Dyes from Water

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The Ce-doped TiO2 photocatalysts frequently has a lower band gap than TiO2, depending on the Ce content and the synthesis method. This study presents the synthesis of TiO2-CeO2 by sol-gel method in presence of Brij 58 and activated carbon as soft, respectively hard templates. The materials were dried at 60 °C and calcined at 450 °C and 600 °C. The thermal analysis in air of the as-synthesized samples showed more significant mass loss in the range of 300 oC, attributed to nitrate decomposition, and a significant exothermic effect between 500 and 600°C atributed to transformation of anatase phase to rutile. Thermal analysis in nitrogen showed only mass loss in three steps till 460 °C. The properties of the W/TiO2-CeO2/activated carbon composites were characterized by X-Ray diffraction, nitrogen physisorption, Dynamic Light Scattering, TPR with hydrogen, FTIR, Raman, photoluminescence (PL) and UV-Vis spectroscopy. The optical properties were correlated with the photocatalytic properties of the obtained composite materials. The decrease in intensity of PL spectra was explained by the presence of defects that act as non-radiative centers. The photocatalytic properties were evaluated in degradation of dyes in the degradation of dyes (Congo Red, Crystal Violet) as pollutants in water. The effects of structure, Ce, W, activated carbon on the photocatalytic degradation efficiency were evidenced and associated with the mechanism of reactions.

Catalytic Ozonation of Ammonia in Water over Composite Metal Catalysts

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Although ammonia nitrogen represents one of the nitrogen sources for the primary producers having a positive role in plant growth, the excess of ammonia in water and soil has severe and persistent effects on aquatic and terrestrial ecosystems leading eventually to health concerns for the human population. That is why it is imperative to find efficient solutions to limit the presence of ammonia in water bodies. This work investigate the potential of the catalytic ozonation in the removal of NH_4^+ from water. In this respect mono and bimetallic catalyst based on copper, cobalt, and iron oxides supported on γ-Al_2O_3 were prepared and characterized by X-ray diffraction (XRD), electronic microscopy (SEM-EDX), H_2-temperature-programmed reduction (H_2-TPR), O_2-temperature-programmed oxidation (O_2-TPO). The oxidation tests performed on synthetic solutions of 10 ppm NH_4^+ reveled higher activity and selectivity to N_2 for Cu-Co/Al_2O_3 catalysts. For these systems, the effect of Cu loading on bimetallic catalysts and of reaction parameters (e.g. pH) on the process performance were also studied.

Computing the Energetic Fractal Dimension using the Adsorption Isotherms

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The adsorption fractal isotherms, such as fractal Dubinin-Radushkevich or fractal Freundlich adsorption isotherms, can be obtained assuming fractal behavior of energetic and/or geometric heterogeneities. Applying these adsorption fractal isotherms together with a complementary method of geometric fractal dimension determination, like micrographs images analysis, both geometric fractal dimension and energetic fractal dimension can be computed. The method will be applied to compute the energetic fractal dimension of some nanoparticle catalysts (Rh/Al_2O_3, Rh/TiO_2, Rh/WO_3).

Hydrothermal-Assisted Surfactant Synthesis of TiO_2-CeO_2 Mixed Oxides Doped with Tungsten as Photocatalysts in Textile Dyes Degradation

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Most of the syntheses of mesoporous oxides involve the use of a series of soft or hard templates. Here, mesoporous W/CeO_2-TiO_2 photocatalysts were synthesized by hydrothermal synthesis in presence of Brij 58 and activated carbon with phosphate groups. The thermal analysis in air of the as-synthesized samples revealed a slow loss of mass, up to 600 °C, and a significant exothermic effect around 510 °C and 580 °C atributed to TiO_2 phase transformation from anatase to rutile. The crystalline structure, mesoporous structure, zeta potential (ζ) and optical properties of the obtained materials with 2.5% CeO_2 and 1% W were characterized by various techniques as X-Ray diffraction, nitrogen physisorption, Dynamic Light Scattering, FTIR, Raman, photoluminescence and UV-Vis spectroscopy. The photocatalytic properties were evaluated in degradation of dyes in the degradation of dyes (Congo Red, Crystal Violet) that are often present in waste water from the textile industry. The obtained results evidenced the synthesis of active photocatalysts in degradation of dyes. The effect of composition and dye structure (cationic, anionic|) on photocatalytic degradation efficiency was evaluated in UV and visible light and results were correlated with mechanism and kinetic of reaction. The increase of the photocatalytic activity was obtained for samples doped with Ce and W. The photocatalytic activity was attributed to the hetero-conjunction at TiO_2 surface.

Iron oxide/zeolite-based thin films for advanced photocatalytic applications

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Thin films and coatings with semiconductor behavior, which thickness ranges from nano- to submicron-domains, are used in various self-cleaning, antimicrobial, and photocatalysis applications.

Solution-based materials with oxide cores and functional outer shells of polymers, silica, zeolites, and carbon are used for a wide range of applications in chemical separation and catalysis, environmental remediation and monitoring, biotechnology and medicine.

In this paper, superparamagnetic iron oxide (core)-silica (shell 1)-zeolite (shell 2) nanoparticles and corresponding thin films, obtained by co-precipitation and ultrasonic-assisted sol-gel methods and deposed by spin-coating technique, respectively, are investigated for nanosorbtion and advanced photocatalysis in UV and visible light.

The morpho-structural properties of the powder and 80-250nm thick thin films were investigated by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDX), X-ray diffraction, Raman spectroscopy, and Brunauer–Emmett–Teller physisorption measurements. The absorption coefficient and band-gap energy values were evaluated from the optical transmission spectra acquired at room temperature in the 200–1100 nm spectral range. The sorption–photocatalytic activities and kinetics were investigated under dark or UV/Vis/solar irradiation respectively, by spectrophotometric monitoring (665 nm peak) of the methylene blue degradation.

Keywords: Iron oxide, zeolite, thin films, advanced photocatalytic applications

Silver Nanoparticles Deposited on Various Supports with Applications in Water Treatment

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Ammonia is one of the common inorganic pollutants in surface waters, it can come from a wide range of sources through the discharge of wastewater (industry, agriculture, municipal waters). Catalytic ozonation reaction can efficiently remove ammonia nitrogen without introducing other pollutants, and improve the nitrogen selectivity of reaction products by controlling the reaction conditions.

Silver nanoparticles (AgNPs) based catalysts have shown excellent O_3 decomposition performance, therefore they are promising catalysts for catalytic ammonia ozonation due to their high reactivity, stability and selectivity to N_2.

In this study, we synthesized well-defined silver nanoparticles (Ag NPs) of 3-5 nm by alkaline polyol method and then dispersed them on solid supports (Fe_3O_4, TiO_2, and WO_3). Both colloidal NP's and supported NPs were characterized using various experimental methods (TEM, XRD, UV-Vis, H_2-TPR) to gather information about their specific morphology, structure and chemical state. The effects of the nature of the support on the catalytic behavior of Ag NPs for the catalytic ozonation of ammonia in water were studied.

Activated Carbon for dye based wastewater depollution

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Activated carbon (AC) is one of the best adsorbents for wastewater treatment. The precursor materials are mainly carbonaceous materials or lignocellulosic materials. Thus, coffee is almost the most consumed beverage in the world, which means a large amount of wastes that can be a source to obtain activated carbon. In this study, coffee grounds were used as a precursor for the production of activated carbon using the chemical activation method in the presence of the activating agent H_3PO_4. Activated carbon was evaluated in the process of adsorption of the dye Brilliant Blue from water.

Four activated carbon samples were prepared by varying the concentration of H_3PO_4 and method of treatment. X-ray diffractograms indicate for all the samples, a structure with a general amorphous character. As the phosphorus content, highlighted by X-ray Fluorescence, decreases, microcrystalline components were formed. The SEM images indicate irregularly shaped particles that tend to become spherical in the case of samples with highest phosphorous content. Treatment concentrated phosphoric acid creates a more irregular surface structure, larger pores and high surface area (938 and 1114 m^2/g). Samples with higher surface area were used as adsorbents for Brilliant Blue FCF (BB) dye in water. Adsorption equilibrium was modeled using the Langmuir and Freundlich isotherms. The maximum adsorption capacity was 42.2 mg/g and the kinetic study of the adsorption process indicated 2-kinetic order.

Elemental composition of the surface and stability of $MnOx\text{-}Na_2WO_4/SiO_2$ catalyst under the conditions of oxidative conversion of methane

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This report presents results based on the use of a ThermoFisher Phenom Pro G6 SEM with a BSD detector, a Bruker D2 PHASER XRD diffractometer, and an EMXmicro electron magnetic resonance spectrometer, a Belsorp Mini II device from BEL, Japan Inc. and an integrated mass-spectrometer-microreactor system from Hiden Analytical, UK, to characterize the elemental and phase composition of the surface, magnetic particles, textural properties (specific surface area, pore size and volume), and catalytic activity of $MnNaW/SiO_2$ samples in the oxidative conversion (coupling, condensation) of methane (OCM), depending on the reaction conditions (temperature, CH_4/O_2 ratio, contact time, duration). The thermodynamic analysis of phase equilibria arising between the sodium tungstate melt, manganese and silicon oxides under the conditions of the OCM reaction has been carried out.

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The influence of the support over Rh nanoparticles catalysts for dry reforming of methane reaction

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The conversion of methane and carbon dioxide into synthesis gas is a significant, sustainable and attractive process because it can mitigate the greenhouse effect and can produce valuable chemical compounds. This study investigates the impact of supports (TiO_2, Al_2O_3, WO_3 and MgO) on the performance of supported rhodium nanoparticles in the dry reforming of methane reaction (DRM). The alkaline polyol method synthesized Rh nanoparticles of 1-2 nm which were dispersed on Al_2O_3, TiO_2, WO_3, and MgO supports with 1.0 wt% Rh nominal loading. The synthesized catalysts were characterized using various experimental methods BET, XRD, TEM, fractal analysis, H_2 chemisorption, XPS, H_2-TPR, and CO_2-basicity to obtain information about their specific morphology, structure and chemical state.

The obtained catalysts Rh/Al_2O_3, Rh/TiO_2. Rh/WO_3 and Rh/MgO exhibited remarkable catalytic performance and stability for DRM reaction at 400–750 °C temperature towards syngas production. The highest conversions of CH_4 and CO_2 were obtained at 625 °C for Rh/TiO_2 and Rh/Al_2O_3 at weight hourly space velocity (WHSV) 14 400 mL/min, gas flow reactant mixture composition 2 vol.% CH_4, 12 vol.% CO_2, and 10 vol.% Ar.

Ti-Incorporated ZeoliteY Modified with Fe, Co, Ni as Efficient Photocatalysts for Degradation of Antibiotics

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TiO_2/zeolite materials were reported as atractive photocatalysts with superior efficiency in degradation of β-lactam antibiotics. Here, titanium was incorporated in zeolite Y network by direct synthesis (1 and 2% TiO_2). The obtained TiO_2/zeolite Y materials were modified by impregnation of Fe, Co or Ni nitrate solutions to obtain photocatalysts with 5% oxide of each metal. The formation of zeolite Y structure and its microporous texture were evidenced, for all the materials, by XRD, Raman and N_2 physical adsorption. XRD and Raman spectroscopy results were correlated to reveal the stability of the zeolite Y crystallinity upon modification, the presence of anatase and metal oxides. The UV-Vis absorbtion edge of photocatalysts shifted to visible region after Fe, Co or Ni addition. Photocatalytic activity was evaluated under UV and visible light irradiation. The photocatalytic mechanism was investigated using ethanol, p-benzoquinone and KI as $\bullet OH$, $\bullet O_2^-$ radicals and hole (h^+) scavenger. The photoluminiscence spectra showed diferent type of emision peaks which were assigned to self-traped excitations, oxygen vacancies (OVs) and surface states (OVs and adjacent ions). It was noticed a different contribution of reactive oxygen species to degradation depending on the metal species used to modify the zeolitic support. All of these were correlated with the photocatalytic results. Better degradation efficiencies were obtained for Ni containing photocatalysts.

Au-TiO_2-CeO_2 Supported on Zeolite Y as Active Catalysts in CO Oxidation

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The performances of gold catalysts in CO oxidation are strongly influenced by Au-support interaction and morphology/shape of nano-scale support. Here, Ti was incorporated during zeolite Y synthesis (1%, 2%, 5% wt.TiO_2) while Ce (1% wt. CeO_2) and Au (1% wt.) were added by impregnation method. The catalytic activity was evaluated in CO oxidation. The crystalline structure, typical for zeolite Y, was confirmed by X-Ray diffraction and Raman spectroscopy for samples with 1 and 2% TiO_2. The significant decreasing of zeolite cristallinity was evidenced for samples with 5% titania. UV-Vis spectra indicated the red shift of absorption and surface plasmon resonance effect for all the samples modified with gold and ceria. The highest Au^0/Au^{3+} and Ce^{3+}/Ce^{4+} atomic ratios were obtained for samples with higher titania loading. These XPS results were compared with those obtained by H_2-TPR. The low-temperature peaks of the H_2-TPR profiles (160 °C, 340 °C) were attributed to reduction of the cationic gold and of the surface oxygen species. The latter are associated to TiO_2 and CeO_2 strongly bound with the gold species and are catalytically active for CO oxidation. The third peak of reduction (650 °C), more significant for samples with 5% titania, was attributed to TiO_2-CeO_2 mixed oxides reduction. A significant effect of cerium and titanium concentration on CO conversion was evident.

Thermal stability of mono- bi-, and trinuclear carbinol derivatives of ferrocene and thermodynamics of their pyrolysis

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Mono-, bi-, and trinuclear carbinol derivatives of ferrocene $C_5H_5FeC_5H_4$-$C(CH_3)_2OH$ (I), $[C_5H5FeC_5H_4]_2C(CH_3)OH$ (II), $[C_5H_5FeC_5H_4]_3C$-OH (III), the thermal stability and thermodynamics of the pyrolysis of these compounds have been studied. The composition and structure of the synthesized compounds have been established. IR and NMR spectra show two types of OH groups involved in the formation of intra- and intermolecular associates. The electronic absorption spectra indicate the presence of characteristic absorption bands in compounds I-III at λ_{max} = 270 (I), 278 (II), and 285 nm (III). It is shown that when samples are heated from room temperature to 700 °C in an inert gas flow, the residual mass of compounds I-III is 2.05, 20.24, and 66.96% of the initial mass, respectively, and these compounds decompose to form nanosized iron /iron oxide and carbon particles. It is shown that the pyrolysis of ferrocene and its derivatives I-III with the formation of iron/iron oxide and carbon structures in the range of 700-1500K is characterized by negative values of free energy. Reactions with the formation of iron and/or iron oxide proceed with an increase in entropy, and with an increase in temperature, their negative values of free energy increase.

Fractal patterns of TiO_2-supported Pd-Au nanoparticles with controlled morphology - efficient photocatalyst for water splitting

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Mono (Pd, Au) and bimetallic (Pd-Au) nanoparticles protected with PVP, having various molar ratios were synthesized using a modified protocol of the alkaline polyol method.

The as obtained nanoparticles were characterized using various techniques TEM (Transmission Electron Microscopy), XPS (X-Ray Photoelectron Spectroscopy), XRD (X-ray powder diffraction) and fractal analysis to elucidate their morphology, structure and chemical state. The physico-chemical properties as well as their reactivity towards hydrogen reduction of titania-supported Au, Pd, and Au–Pd catalysts were also investigated by means of various methods (TEM, XRD, XPS, UV-Vis spectroscopy and CO chemisorption.

It was observed that Pd, Au and Pd-Au nanoparticles dispersed on TiO_2 showed a good and stable activity for photocatalytic water splitting reaction. However, the individual nanoparticles (Au or Pd dispersed on TiO_2) exhibited poorer photocatalytic properties compared to bimetallic ones. Therefore, Pd-Au/TiO_2 can be successfully used as catalyst due to the synergetic effect between gold and palladium.

Effect of ultrasound on the activity of iron-containing mordenite particles in hydroxylation of phenol to dihydroxybenzenes with hydrogen peroxide in liquid phase catalytic system based on in situ DLS, FTIR and EMR data

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Iron-containing catalysts are most preferred for the hydroxylation of phenol to dihydroxybenzenes (DHB) because of the low toxicity and cost of iron [1]. This report presents the results of a study by in situ dynamic light scattering (DLS), infrared Fourier spectroscopy (IR) and electron magnetic resonance (EMR) of the effect of ultrasound (US) on the distribution of catalyst particles on size, reaction products adsorbed on catalyst particles, magnetic properties of the particles during the hydroxylation of phenol to DHB with hydrogen peroxide in a liquid-phase system depending on the reaction temperature in the range of 278–343 K, phenol/hydrogen peroxide ratio, catalyst concentration. A Hielscher UP200S with a frequency of 26 kHz and a power of 200 W was used as an US source. It has been shown that the effect of ultrasound on the activity of the catalytic system in the liquid-phase hydroxylation of phenol to DHB with hydrogen peroxide leads to a change in the particle size distribution with a decrease in average size of particles and cleaning of the surface of the particles from the reaction products.

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SECTION 4

Electrochemistry. Corrosion. Ionic liquids.

KEYNOTES

Anodic Processes on Ti Involving Various Deep Eutectic Solvent Formulations

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Titanium and its alloys represent attractive materials for a large range of industrial and decorative applications. Among various Ti surface modifications, anodization process is particularly interesting, as depending on the applied operation parameters, anodic oxide films possessing different characteristics could be obtained. A quite novel approach to produce anodic titanium oxide either as nanostructured layers or powders takes into consideration the use of deep eutectic solvents (DESs) as electrolytes. Therefore, the paper presents some experimental results regarding the anodic oxidation of Ti electrode in various DES based formulations, including: (i) choline dihydrogen citrate-oxalic acid-ethylene glycol (1:1:1 molar ratio), choline chloride-oxalic acid (1:1 molar ratio) and choline chloride-lactic acid (1:2 molar ratio) eutectic mixtures that have been found to be adequate to form thin colored anodic titania layers and (ii) choline chloride-urea and choline chloride-ethylene glycol (1:2 molar ratio) suitable to produce anodic TiO_2 nanopowders with enhanced photocatalytic characteristics under UV irradiation and visible light irradiation, as well. A description of anodization procedures and of some characteristics of the obtained nanostructured materials, from appearance, composition, morphology viewpoints, also associated with their envisaged applications, will be presented, too.

Studies on tetrahydroacridines with potential use in Alzheimer’s desease treatment

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Besides their applications in dye industry and metal chemo sensing for organic electronics and organic light-emitting diodes, tetrahydroacridines have received increased attention in medicinal chemistry due to their ability to inhibit topoisomerase enzymes and block DNA transcription. In particular, they have been widely explored for the treatment of Alzheimer’s disease, human cancer and tuberculosis. New tetrahydroacridines have recently been synthesized in our group by Pfitzinger condensation of 5,5’-(ethane-1,2-diyl) diindoline-2,3-dione (2) with cyclanones. Their optical and electrochemical properties were investigated using UV-Vis spectroscopy, cyclic voltrammetry, differential pulse voltammetry, and rotating disk electrode voltammetry. DFT calculations were also performed.

Maximizing adsorption efficiency for electrochemical determinations of catechins in wine

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The accurate measurement of antioxidants in wine plays an essential role in assessing its quality and health benefits. Catechins, as prominent antioxidants present in wine, significantly contribute to its overall antioxidant capacity. Catechins are polyphenolics antioxidants found in wine and they play an important role in the stabilization of wine color during aging. Electrochemical determinations offer a reliable method for quantifying catechins in wine due to their sensitivity and specificity. However, optimizing the adsorption efficiency of catechins onto electrode surfaces is crucial to improve the accuracy and precision of these determinations.

This study aims to investigate strategies for enhancing adsorption efficiency in electrochemical determinations of catechins in wine. To maximize the adsorption of catechins onto the electrode surface, various approaches are explored, such as evaluating the impact of graphite type and particle sizes, assessing the influence of binding oil and its percentage, investigating the adsorption time, and optimizing several experimental conditions. Following the completion of method optimizations, actual wine samples sourced from various regions of Albania were subjected to testing. The measurements of catechins in wine samples were performed using the differential pulse voltammetry (DPV) technique, which offers high sensitivity and selectivity in detecting and quantifying these antioxidant compounds. The successful implementation of the investigated adsorption enhancement strategies has demonstrated a substantial improvement in the accuracy and precision of catechin determination in wine samples.

PEDOT-AuNPs nanocomposite modified glassy carbon electrode for epinephrine sensing

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This work aims to present the development of a nanocomposite material based on a poly (3,4-ethylenedioxythiophene) conductive polymeric matrix and Au nanoparticles employing sinusoidal current method for epinephrine (EPI) determination. The electrochemical sensor was successfully implemented for its detection in synthetic probes, exhibiting satisfactory results such as a linear response over a wide concentration range (10-320 µM), a detection limit of 7 µM, and a sensitivity of 0.024 µA/µM. Consequently, EPI sensing through a simple, cost-effective and reliable assay still remains one active research due to the increased prevalence of neurological disorders associated with the imbalance of the catecholamine neurotransmitter.

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A new approach for the synthesis of Co-Ni mixed oxide-based anodes for oxygen evolution

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Tiny amounts of Co were deposited on Ni substrates and mixed before calcination to produce oxygen evolution anodes. The electrochemical measurements have shown that this method was able to generate highly efficient electrodes, having the lowest onset potential and also the lowest Tafel slope. Accordingly, the superior activity originates in the highly active catalytic centers. X-Ray photoelectron spectroscopy revealed that the thus obtained surface structure possesses a certain oxidation resistance that provides stability to the electrocatalytic active species in the water oxidation process.

The ex-situ method of electrochemical determination of catechins in wine in comparison with the ins-situ method

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Electrochemical determination techniques play a vital role in various fields, including analytical chemistry, pharmaceuticals, and food science. This study focuses on comparing the advantages of ex-situ electrochemical determination with in-situ techniques, specifically in the context of catechin analysis in wine. Catechin, a natural polyphenolic compound widely found in plants and beverages, is known for its antioxidant properties and health benefits.

Traditional in-situ electrochemical measurements involve analyzing samples directly at the electrode surface, providing real-time information but presenting challenges such as electrode fouling and interference from complex sample matrices. In contrast, ex-situ electrochemical determination involves an indirect measurement of an analyte in a solution which doesn't contain it. This method offers several advantages including improved sensitivity, selectivity, and reduced matrix effects. Our findings show that ex-situ electrochemical determination exhibits increased sensitivity and selectivity for catechin detection, enabling accurate quantification even in complex sample matrices.

To sum up, this study demonstrates the advantages of ex-situ electrochemical determination over in-situ techniques for catechin determination in wine. These findings highlight the potential of ex-situ approaches in enhancing the accuracy and reliability of electrochemical analysis of catechin and other similar compounds in various applications.

Influence of additives on Ag electrodeposition from Deep Eutectic Solvents

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Silver layers are involved in a large range of applications, due to their excellent physio-chemical properties, good corrosion resistance, high bulk conductivity, and decorative features. Usually, high quality Ag deposits are electrochemically prepared using cyanide- based electrolytes at the lowest cost. However, due to the environmental and human health constraints, in the last decade sustained efforts have been made to minimize the toxic effects of certain electrochemical technologies. Under these circumstances, the use of deep eutectic solvents (DESs) as a green alternative to highly erosive inorganic acids, toxic co-ligands or hazardous organic solvents-based electrolytes has attracted an increased interest. It is well-known that the presence of certain organic compounds as additives to the electrolyte could favorably contribute to the entire electroplating process, including the improvement of cathodic efficiency and the modification of the deposit morphology, with a strong influence on its further characteristics. However, relatively few information related to the influence of these types of complexing agents in DES based electrolytes is reported.

Therefore, the influence of certain additives including nicotinic acid, 5,5-dimethylhydantoin and uracil on the morphological and structural characteristics on the electrodeposited Ag coatings under direct and pulsed current conditions onto Cu substrates from DES based electrolytes is discussed.

SECTION 4

Electrochemistry. Corrosion. Ionic liquids.

POSTERS

Potentiometric determination of pyridoxine by perturbation of a homogeneous oscillating chemical reaction

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Pyridoxine (PY) or vitamine B6 is water-soluble and plays an important role in good function of immune and nervous systems, can reduce the severity of diabetes, stress even for patients infected with Covid-19. Therefore, the analytical determination of PY in real samples, biological fluids can be vital.

The Belousov – Zhabotinsky (BZ) oscillating reaction has been used as a method for the determination of several organic and compounds. This analytical technique has some advantages as simplicity, cheap, short rate of determination and good reproducibility of experimental results. The principle of the BZ oscillating reaction applied in analytical chemistry is based on the perturbation in the oscillation pattern promoted by different species. Both period of the oscillations and oscillation amplitude are used as analytical parameters. Also, the BZ reaction serves as a biomimetic system, imitating the succession of redox reactions taking place in human bodies, which aids in understanding the antioxidant properties of PY and its mechanism of action.

In this work we present the electrochemical behaviour of PY studied by cyclic and differential pulse voltammetry. An oscillation system based on the Belousov–Zhabotinsky reaction for the quantitative determination of pyridoxine was utilized. The influence of added amount of PY on BZ reaction is evaluated by means of changes in oscillations amplitude and period.

Investigation of corrosion protection performance of new composite coating for cobalt based alloy in hydrochloric acid solution obtained by electrochemical methods

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In this study, potentiostatic, galvanostatic and cyclic voltammetry deposition processes were used for the obtained of a new composite polymer: 3-methylpyrrole-sodium lauryl sulfate and dioctyl sulfosuccinate sodium/poly 2-methylthiophene (P3MPY-SLS-AOT/P2MT) coatings over cobalt based alloy sample for corrosion protection. The sodium lauryl sulfate and dioctyl sulfosuccinate sodium as a dopant ions used in the electrochemical polymerization process can have a significant result on the corrosion protection of the composite polymeric layer by preventing the penetration of aggressive ions. The composite coatings were characterized by cyclic voltammetry, Fourier transform infrared spectroscopy and scanning electron microscopy techniques. The anticorrosive performance of P3MPY-SLS-AOT/P2MT coated cobalt alloy was examined by potentiostatic and potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) procedures in 1 M HCl solution. The corrosion estimate of P3MPY-SLS-AOT/P2MT covered cobalt alloy was observed to be ~9 times lower than of uncoated cobalt alloy. The effectiveness of these protective coatings of this composite layer is greater than 90%. The highest efficacy is achieved by the electrochemical deposition of P3MPY-SLS-AOT/P2MT obtained at 0.9 V and 1.1 V potential applied and at 0.5 mA/cm^2 and 1 mA/cm^2 current densities applied in molar ratio 5:1. Corrosion tests results indicated that the ccomposite coatings provide good corrosion protection of cobalt alloy in corrosive environments.

Electrosynthesis of Polypyrrole with Drug Incorporation using NADES

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This paper presents research on electrochemical synthesis and characterization of adherent polypyrrole (Ppy) structures electrodeposited from Natural Deep Eutectic Solvents (NADES), an emerging field of green chemistry, with an emphasis on their interaction with a widely used CoCr dental alloy. The research aims to explore the ability of these structures to encapsulate a widely used antibiotic, amoxicillin (Amox), and analyze its subsequent release in an Afnor artificial saliva-based environment resembling the oral cavity. This investigation operates under the premise that Ppy may serve as an effective matrix for controlled drug release. The electrodeposited films were morphologically investigated using scanning electron microscopy (SEM) with an EDX module, and polypyrrole and antibiotic were both identified using structural FT-IR analysis. The film's characterization was completed with an evaluation of hydrophilic–hydrophobic balance, with electrochemical stability measurements in PBS and with antibacterial inhibition. A decrease in the value of the contact angle was observed covered with PPy and drug incorporated. Additionally, an improvement in the anticorrosive properties of the coating was observed by increasing the efficiency in the case of alloy covered by PPy–Amox. A kinetic study of drug release was performed as well. A non-Fickian behavior was established as a mechanism for the release profiles of the gentamicin from the polymer layer.

Electrodeposition of Tin-Reduced Graphene Oxide Composite from Choline Chloride - Ethylene Glycol Eutectic Mixtures

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The development of electrodeposited tin-graphene oxide (Sn-GO) composite coatings has shown promising electrochemical performance related to various industrial applications such as corrosion protection, electronics fabrication or anode material for lithium ion batteries. In addition the incorporation of graphene related materials into Sn and Sn alloys acting as lead-free solders (i.e. SnAgCu, SnBi, SnZn and SnIn) facilitated an improvement of their wetting property but an insignificant change in their melting point.

Therefore the paper presents some experimental results regarding the direct electrodeposition of Sn-rGO from a deep eutectic solvent (DES), namely using choline chloride-ethylene glycol eutectic mixtures. Raman spectroscopy demonstrated that GO is also reduced during the tin electrodeposition. The analysis of current-time transients involving Scharifker & Hills model has shown that Sn-rGO composite deposition process corresponds to a nucleation and tridimensional growth controlled by diffusion, with nucleation evolving from progressive to instantaneous upon increasing the overpotential. The corrosion performance during continuous immersion in aerated 0.5 M NaCl aqueous solution at 25 °C for 144 h and the solderability performance will be also discussed.

New composite materials based on iron-nickel powder encapsulated by phosphorous pentoxide: structure, magnetic properties, and corrosion resistance

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The elaborated magnetic samples were subjected to corrosion, in synthetic seawater by immersion test over 328 days at ~ 25° C. The calculated gravimetric data show low corrosion rate and fairly low penetration index. Metallographic micrographs obtained showed few surface changes after corrosion, results confirmed by SEM images in which the ordered globular structures are not much modified after corrosion. The AFM morphological characteristics of the sample were detailed by subtracting the area of the scanned area ($1\mu m \times 3\mu m$). The RMS roughness related to the selected line scan in initial sample is 15.9 nm, while the peak to valley parameter in the same profile is 70.2 nm. After the corrosion experiments, small and large pits are randomly formed on the surface of sample, which leads to increased waviness, as indicated by the RMS value and a peak-to-valley parameter. The XRD patterns show that the initial alloy crystal structure is a superposition of an ordered FCC and a second BCC α-phase, with no additional reflexes after corrosion. Through the ponderomotive method, it was demonstrated that the studied material retains its ferromagnetic properties after corrosion with small insignificant changes.

Corrosion behavior of a novel TixTa9Nb8Zr2Ag in various biofluids for surgical applications

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In this study the corrosion behavior of TixTaNbZrAg alloy (with different percentages Ta) was studied by electrochemical methods (the open circuit potential, electrochemical impedance spectroscopy and potentiodynamic polarization) in biofluid solutions (PBS and AS) for 168 hours at 37^0C. The properties of these quaternary alloys were investigated in relation to its use in surgical applications (orthopedic and dental applications). Corrosion parameters were estimated by Tafel extrapolation and the results have highlighted the lower corrosion rate ($R_{cor} < 10\ \mu m\ y^{-1}$) and nobler potential corrosion ($-65\ mV < E_{cor} < 87\ mV$) for Ti**10Ta**9Nb8Zr2Ag alloy in both biofluids, artificial saliva (AS) and phosphate buffer solution (PBS), placing these alloys in very stable (Ti**10Ta**9Nb8Zr2Ag alloy) and stable (Ti**20Ta**9Nb8Zr2Ag alloy) corrosion resistance class, according to ISO 8044: 2020-Corrosion of metals and alloys. The corrosion behavior of the alloys was also confirmed by the EIS results illustrated in Nyquist and Bode plots, that display high impedance values which is attributed to the formation of a passive protective film on the surface. Moreover, the results presented in this study underlined the influence of the tantalum content in the chemical composition of the alloy on the corrosion resistance, and point out that the Ti**10Ta**9Zr8Nb2Ag alloy might be successfully used for medical implant.

Trends in Materials Development for Nuclear Energy

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The aim of the current research is focused on the characterization of some materials used in sustainable nuclear energy. In this regard, the paper's primary goals are to improve the performance of alloys by covering them with adherent, anti-corrosive coating. Thus, the corrosion behavior of a Cr-coated zircaloy, as well as CrN-coated 310 H stainless steel under simulated supercritical water conditions was studied.

Metallographic examination, scanning electron microscopy (SEM) with an energy dispersive spectra detector (EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) investigations were used to characterize the surface coating before and after exposure to extreme conditions specific to nuclear energy. The thickness of the Cr or CrN coatings was determined from SEM images. Oxidation kinetics, porosity, and protection efficiency were determined using the gravimetric method, electrochemical impedance spectroscopy (EIS), and potentiodynamic tests.

Pt-PEDOT Based Electrochemical Sensing Platform For Serotonin Quantification

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An electrochemical sensing platform based on Pt nanoparticles (PtNPs) and poly(3,4-ethylenedioxythiophene) (PEDOT) composite material has been developed by means of innovative sinusoidal current (SC) method. The PEDOT layer has been prepared onto glassy carbon disk electrode by using a SC with 100 mHz frequency and 1.5 μA amplitude, superimposed on a dc current of 5 μA, with deposition time of 300s. Afterwards, PtNPs have been electrodeposited onto the PEDOT layer using a SC of 100 mHz frequency and selected amplitude of 25 μA superimposed on a cathodic current of (-25) μA. The detection of serotonin has been successfully accomplished using the developed PEDOT-PtNPs based sensing platform with a low detection limit of 1.0 μM and a linear response over the concentration range from 4 to 100 μM serotonin.

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Investigation of Different Synthesis Parameters in Developing of an innovative AgNPs-PEDOT Based Electrochemical Sensor for Quercetin Determination

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Quercetin (3,3',4',5,7-penta hydroxyl flavones), a natural flavonoid with outstanding properties on human health including anti-viral, anti-ulcer, anti-cancer, and anti-oxidant effects has drawn the attention of researchers during the last decades. The synthesis parameters of the SC (Sinusoidal Current) and SV (Sinusoidal Voltage) procedures such as the amplitude of the sinusoidal current/voltage, I_{sin}/E_{sin}, the frequency of the sinusoidal current/voltage, f, the value of the constant current/voltage I_{dc}/E_{dc}, and the electrodeposition time, t_{dep} have been investigated. The AgNPs-PEDOT based electrochemical sensor prepared with the optimized parameters was successfully used in quantification of quercetin with a linear response over the range of 1-150 μM and a low detection limit of 0.5 μM. AgNPs-PEDOT coatings synthesized by SV and SC methods proved to have a large surface electroactive and high electron transfer rate that improved significantly the sensitivity of the sensor.

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Tungstate-Borate Ionic Liquids:
Structure, Electrochemical Behavior and Electrodeposition of Tungsten Coatings

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To study the ionic composition of Na_2WO_4-B_2O_3 melts, EMF measurements of electrochemical circuits containing platinum-oxygen indicator and tungsten electrodes relative electrodes versus platinum-oxygen reference electrodes were performed. Experimental dependences of the potential of platinum-oxygen and tungsten electrodes on the B_2O_3 concentration are explained by the formation of ditungstate ions $W_2O_7^{2-}$ in the melt. Studies of the electroreduction of ditungstate ions indicate that the electrode process is controlled by the electroactive particles diffusion to the electrode. At the same time, the formation rate of these electroactive particles does not limit the electrode process. Charge transfer occurs reversibly, which is confirmed by the electrochemical measurements results in stationary and non-stationary polarization modes. Thus, in Na_2WO_4-B_2O_3 melts, realization of multi-electron equilibrium and electroreduction of tungsten from its dimeric anionic form is possible. The obtained results served as the basis for the development of tungsten coatings electrodeposition processes. Corrosion potentials of electrodes made of substrate materials (copper, nickel, steel) were measured. The influence of B_2O_3 concentration, temperature, cathodic current density and duration of electrolysis on the composition and structure of cathodic deposits was studied, and the optimal parameters of the reverse deposition mode were found.

Capacitive performance of electrodes based on intermetallic $FeNi_3$ nanoparticles anchored on graphene oxide

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Carbon-based material decorated with the intermetallic nanoparticles, like $FeNi_3$, might be preferred as active electrode materials in the supercapacitors field because of their outstanding properties such as good stability and high capacity storage. In this respect, capacitive performance of some new $FeNi_3$-based electrodes was investigated. These electrodes were obtained by coating the $FeNi_3$ nanoparticles, grafted on graphene oxide (GO), on nickel foam support ($FeNi_3$/GO/Ni). Graphene oxide, synthesized through a modified Hummers method from expanded graphite precursors, was herein used as a platform for grafting $FeNi_3$. The $FeNi_3$/GO nanostructured composite was synthesized by a combined sol-gel technique, using iron and nickel salts. Capacitive performance of these $FeNi_3$/GO/Ni electrodes was assessed by cyclic voltammetry (CV) and galvanostatic charge-discharge (CD) in alkaline media. The specific capacitance of $FeNi_3$/GO/Ni, estimated from charge-discharge, at a current density of 0.5 A/g, is around 148 F/g. For comparison, the specific capacitance of graphene oxide coated on Ni foam (GO/Ni) was also estimated by CV and CD. The results attested that $FeNi_3$/GO/Ni has a better charge storage capacity than GO/Ni, pointing out that the synergetic effect of GO and $FeNi_3$ nanoparticles is actually responsible for the good capacitive performance of these new $FeNi_3$-based electrodes.

Design of an Electrochemical Sensor for Sensitive Determination of Antioxidants

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Lipoic acid or 1,2 dithiolane-3-pentanoic acid ($C_8H_{14}O_2S_2$) is an important antioxidant used in therapy of stroke, cancer, neurological disorders, liver affections, etc. as it reduces the level of reactive oxygen species and plays a protective role against oxidative stress. In this work, we report on the development of an electrochemical sensor based on poly(3,4-ethylenedioxythiophene) (PEDOT)-Prussian blue nanoparticles (PBNPs) and its application to LA determination. The sensor was prepared via a two-step method involving the sinusoidal voltage electrodeposition of ferrocyanide–doped PEDOT on glassy carbon electrode (GCE) followed by the in situ formation of PEDOT-PBNPs. The GCE/PEDOT-PBNPs modified electrode obtained using sinusoidal voltage of 0.247 V amplitude with 50 mHz frequency superimposed on 0.6 V dc potential for 20 minutes exhibited electrocatalytic activity toward LA oxidation, a stable amperometric response within the range comprised between 10 μM and 1 mM LA and a detection limit of 3.8 μM LA.

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Investigation of Tricyclic Active Compounds in Commercial Antidepressant Drugs by Electrochemical Methods

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World Health Organization reports show that the COVID-19 pandemic has led to an increase in people suffering from depression. This mental illness is treated, in combination with psychotherapy, with antidepressant drugs to positively influence the individual’s mood. Thus, these drugs have seen a recent boom in prescription and consumption rates worldwide.

This work is an investigation of tricyclic active compounds (amitriptyline, doxepin, imipramine, clomipramine, trimipramine) in some antidepressant drugs commercially available on the European market by electrochemical methods. Specifically, three electrochemical methods of detection and quantification (anodic cyclic voltammetry, differential pulse voltammetry, and rotating disc electrode voltammetry) were developed, validated intra-laboratory, and applied for the quality control of active compound content in commercial pharmaceutical formulations. The methods are very convenient and may present interest to quality control laboratories across the globe.

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Electrochemical investigation of an N,N-bis-tetrahydroacridine diacide with anti acetyl cholinesterase activity

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Tetrahydroacridines have received increased attention in medicinal chemistry due to their ability to inhibit topoisomerase enzymes and block DNA transcription. In particular, they have been widely explored for the treatment of Alzheimer's disease, human cancer, and tuberculosis. New tetrahydroacridines were recently synthesized by Pfitzinger condensation of 5,5'-(ethane-1,2-diyl) diindoline-2,3-dione with several cyclanones. We herein report the synthesis of several bis tetrahydroacridines derivatives. Their optical and electrochemical properties were investigated by use of UV–Vis and electrochemical measurements.

Development of Aptasensing Platforms by Controlled Grafting of Aryldiazonium Salts

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The electrochemical reduction of protected aryldiazonium salts represents an efficient approach for electrode surface functionalization, that can both prevent multilayers growth, and also to control the surface density of the tethered molecules. In this study, glassy carbon surfaces grafted with protected ethynyl aryldiazonium salts, followed by deprotection and post-functionalization with azide-modified DNA aptamers by “click” chemistry are applied for developing well-organized aptasensing platforms. In particular, we demonstrate that by employing silyl protecting groups of different sizes we are able to generate spatially ordered reactive layers, and to regulate the detection sensitivity when the grafted aromatic groups function as anchors for the immobilization of the receptor molecules. The surface coverage of the electrodes grafted with ethynylphenyl groups after their post-modification with suitable derivatization reagents has been estimated by XPS, cyclic voltammetry and chronocoulometry techniques. The results corelated well with the protective group size, for the largest protective group, the lowest surface concentration being obtained. Further, we have developed an electrochemical aptasensor, and demonstrated the possibility to effectively tune its analytical performance through the size of the employed silyl protecting group.

Structure, magnetic properties, and corrosion of Monel-400 in Mediterranean Seawater

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Monel-400 is a copper-nickel alloy with high resistance to corrosion in various environments and it is used in marine technology for production equipment in the chemical industry.

The corrosion processes of special steels Monel-400 in Mediterranean Seawater at 298 K has been investigated by immersion method. Immersion data within 400 days showed that the corrosion rate has a big sharp increase and then decreases. The final corrosion rate (CR) was $1.697\cdot10^{-4}$ g/m^{2}h and the penetration index was found to be 0.169 mm/year, which means a stable corrosion resistance of Monel-400 in Mediterranean Seawater. These results are much better than those obtained for OL52 carbon steel (CR=$5.026\cdot10^{-4}$ g/m^{2}h) in the same corrosion conditions.

Micrographic images before and after corrosion, obtained with a metallographic microscope, with camera acquisition, sustain the corrosion data. The influence of the corrosion process on the crystal structure and specific magnetization of the studied steels was carried out by using X-ray diffraction and ponderomotive methods. No significant changes were observed on both structure and magnetic properties after corrosion in Mediterranean Seawater.

Ni/SnO_2 for bioethanol electrooxidation

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In recent decades, fuel cells have attracted the attention of researchers as a renewable energy source and a potential alternative to fossil fuels for mitigating the energy crisis and greenhouse gas emissions due to their high fuel conversion and electrical efficiency. Metal oxides such as SnO_2, NiO, Fe_2O_3, TiO_2, MnO, Cu_2O, and ZnO mixed with conducting polymers are widely used as anodes in both acidic and basic media. In this study, we proposed different Ni deposition methods on the SnO_2 surface. A small amount of Graphene Nanopletelets (GNP) incorporated or mixed with the oxidic phases improves the electrochemical activity. A comprehensive study of the structure, morphology and surface chemistry was carried out using a complex of physicochemical methods (XRD, Raman, BET, SEM, TEM, XPS).All the electrochemical experiments for the bioethanol electrochemical oxidation were performed in a three-electrode glass cell. We highlighted the effect of the different chemical species, deposited by different deposition protocols, on the electrocatalytic performance.

Nitrite Anodic Oxidation at Ni/SnO_2–Carbon Composites: Synergistic effects and analytical applications

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Mesoporous SnO_2 was obtained by a procedure involving a hydrothermal treatment of a micellar aqueous solution of $SnCl_4\times$and Brij®35 surfactant, followed by an additional thermal treatment. Nickel chemical deposition was afterword carried out and the suspension was ultrasonicated, dried, and then thermally treated for 2 hours at 200ºC. In some cases, the Ni/SnO_2 electrocatalyst was mixed, before sonication, with a small amount of Black Pearls 2000 (BP) and the activity for nitrite anodic oxidation of the thus obtained composite (Ni/SnO_2-BP) was compared to that of the pristine Ni/SnO_2. Linear sweep voltammetric, steady-state and EIS experiments have demonstrated an enhanced activity of the Ni/SnO_2-BP composite which is actually the synergistic effect of several factors: the larger specific surface area, the better electrical conductivity and the fact that the carbonaceous component can provide additional active sites for the process. These features enabled the use of Ni/SnO_2-BP electrodes for accurate nitrite voltammetric determination within a noticeably wide dynamic concentration range (0.05÷20 mM), with excellent sensitivity ($384\ \mu A\cdot cm^{-2}\cdot mM^{-1}$).

SECTION 5

Advanced materials science

KEYNOTES

Challenges, lessons and successes in the search for new antitumor and antiviral agents

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Cancer and viral infections are two of the leading biomedical and societal challenges of our time. The aim of our study is to summarize some of the most important problems accompanying the development of antitumor and antiviral agents arising from both the characteristics of cancer cells and viruses on one hand and their "relationships" with the host organism on the other. Why is it so difficult to create antivirals, even when we can inactivate the virus simply with soap and water? Why, despite all efforts, do we still not have a universal cure for cancer, and can one ever be prepared? Special attention will be given to model systems used in preclinical studies in these areas. What are the advantages and disadvantages of different types of cell cultures and how can we get the most reliable information about the biological activity of the compounds investigated with their help? Why do test compounds sometimes show promising antitumor or antiviral activity in vitro but do not fare well in vivo? What are the main challenges facing researchers in the laboratory and can we optimize the experimental design to improve the quality and in formativeness of the information obtained.

Comparative study
between hydroxyl and carboxyl functionalized carbon nanotubes and their nanofluids

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Nowadays efficient energy utilization is a critical factor, which needs to be accounted for. One way to do so is the use of so-called "nanofluids", which are engineered work fluids with increased thermal conductivity, thus increasing heat transfer efficiency.Nanofluids are a kind of dispersion with highly conducting nanoparticles dispersed in a base fluid (e.g. water, ethylene glycol or mineral oils).

Multi walled carbon nanotubes have an exceptionally high longitudinal thermal conductivity of around 3000 W/mK, but the dispersion of MWCNT in a polar continuous phase (e.g. water) is challenging due to the apolar surface of the particles. Our study aims to discover the effect of polarizing surface functionalization on stability of MWCNT nanofluids.

We characterized hydroxyl and carboxyl functionalized MWCNTs with TG/DTA, FTIR, XRD, TEM and EDX. We prepared stable nanofluids in three concentrations (150, 500 and 1000 ppm(V)) with Na-DBS surfactants in deionized water. The nanofluids viscosity, thermal conductivity and light penetration depth was measured. We also analyzed the aggregates zeta potential and particle size using DLS.

Assessment of Synthetic Approaches for Titanium Dioxide-based Nanoparticles in Photocatalysis

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The present investigation offers an in-depth examination of the synthetic procedures employed for the production of Ag/Zn/Cu-doped TiO_2 photocatalysts supported on zeolite or graphene oxide substrates, with the objective of attaining surfaces capable of effectively inducing photodegradation under UV-A radiation. Two distinct methodologies have been scrutinized: the sonochemical and microwave-assisted approach, as well as the sol-gel method coupled with a microwave treatment. The synthesis process successfully yielded pure forms of anatase and rutile titanium dioxide, which were subsequently subjected to metal doping and supported within graphene oxide sheets, enabling a comprehensive evaluation of their respective photocatalytic properties. The physical-chemical attributes of both the samples and the raw materials, including fly ash and zeolites, were characterized through the utilization of SEM, TEM, XRD, and XRF techniques.

Barium strontium titanate functional materials: from nanopowders to multiscale-structured bulk ceramics

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Dense, single-phase and multiscale-structured bulk $Ba_{1-x}Sr_xTiO_3$ (BST) ceramics (x = 0 – 0.4) have been prepared by alternative consolidation techniques starting from nanopowders synthesized *via* sol-gel method. In the microstructured ceramics obtained after conventional sintering at 1400°C/4 hours, increasing Sr addition produces the reduction of tetragonality and unit cell volume, as well as the grain size decrease. These changes are accompanied by the gradual decrease of Curie temperature value, so that, while at room temperature the ceramics with x = 0 – 0.35 are found in their ferroelectric state, the compositions with x = 0.375 and 0.4 Sr are in the cubic paraelectric phase. Fine-grained $Ba_{1-x}Sr_xTiO_3$ samples (x = 0.20 and 0.40) with grain sizes of 70 – 240 nm were also obtained by spark plasma sintering carried out in various conditions (1000°C/4 min, 1050°C/2 min and 1050°C/4 min), in order to analyze the influence of the so-called "size effects" on the functional (dielectric and ferroelectric) properties of the mentioned BST ceramics. Common to all the BST fine-grained ceramics is the more diffuse character of the ferroelectric-to-paraelectric phase transition, with Curie point settled at about 335 K for the compositions with x = 0.20 and 280 K for the samples with x = 0.40. Compared to coarse-grained ceramics with grain size in the order of microns and maximum permittivity of about 10^4, the permittivity maximum in the fine-grained BST ceramics is strongly flattened and, with grain-size decreasing, is drastically reducing down to a few hundreds.

The monuments of Dobrudgea: scientific diagnosis and conservation with nanomaterials

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During the last decades, some innovative research led to the development of some materials and methods, as well as nanotechnologies for applications in cultural heritage monuments. In this work, several monuments are analyzed, such as: the Sacidava fortress (Geto-Dacian settlement and Roman castrum, from the Roman era (Trajan era)), Constanța, the Roman Mosaic from Constanța, the Chalk Churches from Basarabi - Murfatlar, in order to identify the origin of the raw materials and the deterioration processes. Some nanomaterials, such as hydroxyapatite and its derivatives, have been used for the conservation of the surfaces. Appropriate analytical techniques such as: Scanning Electron Microscopy (SEM), Optical Microscopy (OM), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Raman Spectroscopy, Polychrome analysis (by color parameters), mechanical properties, or some nuclear techniques (X-ray fluorescence wavelength dispersive (WDXRF), neutron activation analysis (NAA)), applied for the initial and treated surface of the samples mentioned above will be presented and discussed in this paper.

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Synthesis and characterization of TiO_2 decorated with calcium and copper ions

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The nanomaterials containing titanium oxide TiO_2 decorated with calcium and copper ions were synthesized by the sol-gel method presented here and characterized by the following analytical methods: UV-Vis spectroscopy, TEM electron microscopy, X-ray diffraction (XRD), X ray Photoelectron Spectroscopy (XPS), voltammetry and Fourier transform infrared spectroscopy (FTIR).

From UV-Vis optical absorption spectra in the wavelength range 330–1000 nm for the decorated TiO_2 sample compared to the spectrum of the rutile TiO_2 sample, relatively equal strong absorption is observed for both samples only in the 330-370 nm range, there is a strong increase in light absorption in the wavelength range between 400 and 850 nm, with a broad maximum between 400 and 650 nm (Kubelka-Munk function). The XRD, TEM and XPS analyzes demonstrated that the surface of TiO_2 crystals is decorates with calcium and copper particles.

Antimicrobial efficiency was also evaluated using standard qualitative and quantitative methods on standard clinical microbial strains, both in the light and in the dark.

Inverse opal structures for photocatalytic purposes

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Inverse opals have a porous, high surface area structure, which due to the repeating spherical void patterns. This hollow structure can interact with light of comparable wavelength and create some unique optical properties, such as the photonic band gap and the “slow” photon effect. The preparation of this materials is doable with the bottom-up methodology using vertical deposition and various nanospheres (carbon, polystyrene) as sacrificial templates. Atomic layer deposition makes it possible to create inverse opals with high precision and from photocatalytically active materials.

In our work, we explore the relation between the inverse opal structure and its optical properties and photocatalytic activity. Inverse opal wall thickness’ and the sacrificial templates effect is researched by experiments and simulations. TiO_2/ZnO and ZnO/TiO_2 inverse opal heterojunctions are synthesized, and the optical, photocatalytic and surface wettability are explored. Addition of another nanostructure such as nanorods with two different synthesis route was explored using hydrothermal growth for the nanorods.

ZnO-Al_2O_3 composite inverse opals for enhanced photocatalysis

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The excellent photocatalytic properties of zinc oxide (ZnO) inverse opal (IO) are well-known, while aluminum oxide (Al_2O_3) provides structural stability and support. Combining these materials creates a composite of ZnO-Al_2O_3 structures that demonstrate enhanced photocatalytic performance compared to each material individually. In this study, we successfully grew ZnO and ZnO-Al_2O_3 combined IO structures on the surface of a 600 nm polystyrene (PS) nanosphere template using thermal atomic layer deposition (TALD) and plasma-enhanced atomic layer deposition (PEALD). An ultra-thin film of Al_2O_3 was also deposited on top of the IO either through TALD or PEALD, forming composite IO structures (ZnO-Al_2O_3). The as-prepared IO composite materials were characterized using SEM-EDX, Raman, XRD, PL, UV-vis, and photocatalysis. SEM, Raman, and XRD confirmed the presence of visible microporous, well-ordered, and crystalline hexagonal wurtzite ZnO IO structure, with an amorphous Al_2O_3 structure on top. This study confirms that ZnO/TALD-Al_2O_3 exhibits improved photocatalytic activity compared to bare ZnO and ZnO/PEALD-Al_2O_3 IO counterparts.

Synthesis of Resveratrol co-crystals under mechanochemical conditions

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Natural antioxidant compounds, such as trans-resveratrol, could be used as an alternative for the antibiotics used in meat production, without their disadvantages. The unique physical properties exhibited by novel solid forms of a drug, such as co-crystals, can impact key pharmaceutical parameters, including storage stability, compressibility, density as well as dissolution rates and solubility, which are essential factors in achieving suitable bioavailability.

Trans-Resveratrol is a promising bioactive compound with antibacterial activity, but low bioavailability due to its low aqueous solubility. Mechanochemical synthesis is an alternative route to solution-based co-crystal synthesis, offering higher energy efficiency, reduced solvent waste, high yields and improved recovery of the final product. The aim of this study is the mechanochemical synthesis of resveratrol (R) – piperazine (P) co-crystals, used as nutraceutical compounds. Different synthesis conditions (the nature and amount of added solvent, reaction time) were investigated and their influence on the co-crystal phase and purity were determined. A reaction time of up to 1 h is sufficient for the completion of the reaction. Non-toxic solvents (water, ethanol) can be used to obtain a desired co-crystal phase with high purity.

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Design and synthesis of Piezoelectric Materials for Energy Harvesting Applications

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Society requires materials and methodologies for energy harvesting to develop smart materials and embed automation. Energy harvesting is one of the keys enabling technologies. Energy harvesting materials can dynamically harvest energy from the surroundings generating electrical power for sensors and devices. Different environmental resources can be used: mechanical vibration, motion, magnetic field, heat.

Piezoelectric materials (inorganics, polymers, composites) are widely used for sensors, actuators, motors, resonators, and energy harvesting devices. The most widely used piezoelectric ceramics are based on lead titanate zirconate $xPbTiO_3$-$(1-x)PbZrO_3$ solid solution (PZT), due to their good properties and possibilities for modifying their structure and properties by different dopants. Hazardous Substances Directive (RoHS), restrict the use of hazard substances such as Pb and PbO in electrical and electronic equipment devices.

The search for alternative lead-free piezoceramic materials to replace PZT became a subject of increasing importance for researchers. Piezoelectric families of materials with ABO_3 perovskite structure with different cations either in the A or B positions were investigated. Here we present the thermodynamic modelling for $(Ba_x, Ca_{1-x})(Ti_y, Zr_{1-y})O_3$ synthesis and sintering modeling by active factorial experiment.

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When a nitronyl nitroxide ligand meets amines to form Schiff bases. Ligands design and their complexes

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The design of the ligands with coordination sites aimed for specific metal ions is mostly in conjunction with the pursued properties.

2,6-Diformyl-*p*-cresol is a versatile molecule used to build compartmental ligands [1]. The corresponding nitronyl nitroxide radical, i. e. 2-(2-hydroxy-3-formyl-5-methylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide (HL), has been synthesized and further used to generate metal complexes with metal ions from d and f blocks.

Moreover, additional binding sites are grafted to the ligand HL via the free formyl group that is reacted with various amines to form Schiff bases with different topologies, among with a special mention is the tripodal obtained from tris(2-aminoethyl)amine. The polydentate paramagnetic ligands have been reacted with different Ln(III) hexafluoroacethylacetonato complexes giving rise to mono- and oligonuclear complexes with exciting magnetic properties.

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Magneto-Structural Phase Transition Behavior and Magnetocaloric Properties in Bulk and Nanocrystals of MnAs Compound

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The simulation of magnetic properties in extended quantum spin networks can be done in good conditions with Ising models within Monte Carlo-Metropolis algorithms, as our systematic studies employing original computer codes proved. The present analysis provides interesting insights into the exchange interactions governing the magnetic behavior in bulk and nanocrystals of the MnAs compound. The magnetic and structural ordering are highly correlated due to the interplay between lattice and spin degrees of freedom, as expected for a magneto-structural transformation.

On the basis of the Monte Carlo Metropolis algorithm, the variation with temperature and magnetic field strength was obtained for the following physical quantities: magnetization $M(T,H)$, the product of the magnetic susceptibility and temperature $\chi_{mol}*T$, magnetic specific heat $C(T,H)$, entropy variation $\Delta S(T,H)$, and statistics of spin projections $m_{Sz}^{Mn(i)}(T)$. The magnetic exchange interaction $J_{Mn\text{-}As\text{-}Mn}$ were also obtained from calibration with experimental first- and second-order phase transitions temperatures and magnetocaloric properties in bulk and nanocrystals of MnAs compound.

Exploring the Potential of Photoswitchable Ligands: Novel Cu(II) Complexes Incorporating Azo Derivatives of *ortho*-Vanillin

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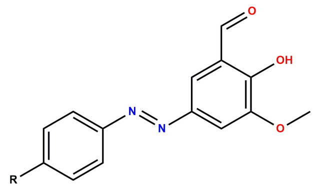
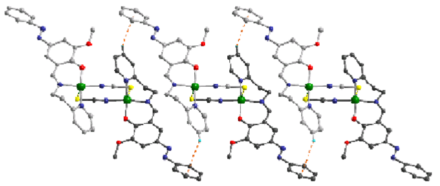
Ortho-vanillin exhibits a diverse coordination chemistry owing to its ability to readily form Schiff base compounds[1] leading to both homo- and heterometallic complexes.[2] Continuing our research, we focused on enhancing the photoactive properties of organic and coordination compounds by incorporating an azobenzene moiety into *o*-vanillin molecule, resulting in the synthesis of three proligands: (E)-2-hydroxy-3-methoxy-5-(phenyldiazenyl)benzaldehyde (HL^1, R = H), (E)-2-hydroxy-3-methoxy-5-(p-tolyldiazenyl)benzaldehyde (HL^2, $R = CH_3$), and 2-methoxy-4-((E)-phenyldiazenyl)-6-((E)-((2-(pyridin-2-yl)ethyl)imino)methyl)phenol (HL^3), and their corresponding mononuclear copper complexes $[Cu(L^1)_2Na(hfac)]$(**1**), $[Cu(L^2)(bipy)]\cdot 3H_2O$(**2**). A new Schiff base ligand is generated employing this photoshwitchable aldehyde, as well as a dinuclear tiocyanato-bridged complex, $[Cu_2(L^3)_2(SCN)_2]$(**3**).



$HL^{1,2}$



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Effect of SiO_2 and ZnO nanoparticles on the viscosity and thermal conductivity of aqueous media

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Since the last three decades nanofluids have been the focus of interest because of the industrial demand of better heat transfer fluids. In recent years more and more studies have been published on hybrid and composite nanofluids. Most of the articles are about the stability and thermophysical properties of the dispersions. Some of them determine different parameters of the particles, but there are only smaller number of articles where clusters are also examined.

In our research SiO_2 and ZnO nanofluids were examined. SiO_2 and ZnO nanoparticles were purchased from Sigma-Aldrich and Nanografi. The average particle diameter is 10-20 and 18 nm respectively. TEM images, XRD diffractograms IR spectra were made about the particles. SiO_2 and ZnO particles in 0.5 v/v% were dispersed in H_2O by an ultrasonic homogenizer. The volume ratio of SiO_2: ZnO was 1:0, 1:1, 0:1. When using the two different particles quick aggregation was observed. We changed the basefluid to ethylene glycol, but this did not solve the problem, so we had to use different surfactants. Gum arabic was the most effective in aggregation prevention, so this surfactant was used to make stable suspensions with the original basefluid. SiO_2, ZnO and hybrid nanofluids were made in 0.5, 1.0 and 1.5 v/v% concentration. Zeta potential, viscosity, and thermal conductivity of the nanofluids were measured.

[Ln$_2$(hfac)$_4$(ac)$_2$(OH$_2$)$_2$(OMe)$_2$] - a useful precursor for luminescent d-f metal-complexes

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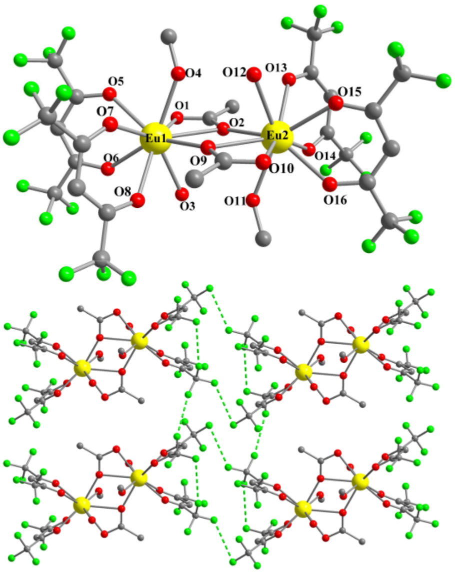

The synthesis of lanthanide hfac-acetato-compounds was reported by Matsumoto et. al. and, so far, the structure for this precursor has been described as consisting of mononuclear species.[1] In this work we show that these useful precursors are actually binuclear species, consisting of two 4f metal ions linked by two acetato-bridging ligands. Using these precursors and optically active Schiff bases, we obtained chiral *syn-syn* acetato-brided hetrodinuclear d-f complexes. By changing the acetate unit with enantiopure carboxylato-moiety, we intend to achieve the transfer of the optical information to the lanthanide ions.

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Emerging Techniques for Cocrystal Preparation: Investigation of Ultrasound-Assisted Solution Cocrystallization and Microwave-Assisted Methods

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Cocrystals have garnered considerable attention in contemporary times due to their ability to modify the physical characteristics of solid-state materials, particularly in the realms of pharmaceuticals and nutraceuticals. As the commercialization of cocrystals continues to grow, it is imperative to explore novel manufacturing approaches that offer both environmental sustainability and efficiency. This research study presents diverse methods for cocrystal preparation and focuses on the utilization of emerging techniques, namely ultrasound-assisted solution crystallization and microwave-assisted methods. The advantages of these techniques and their effects on material properties are comprehensively examined. Multiple physicochemical properties, including thermal stability, granulometric attributes, and water solubility, are thoroughly investigated. The findings unequivocally demonstrate that the choice of preparation technique significantly impacts the final properties of cocrystals, encompassing aspects such as purity, morphology, and water solubility.

Acknowledgments
This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS-UEFISCDI, project number PN-III-P2-2.1-PTE-2021-0393, contract number PTE 98/2022.

SECTION 5

Advanced materials science

POSTERS

Novel chromogenic and fluorogenic nitrobenzofurazan derivatives

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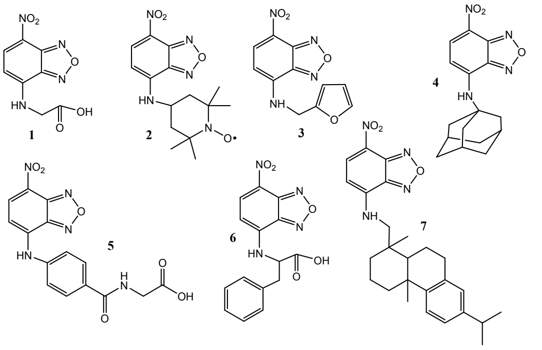
Starting from different amines and NBD-chloride, compounds **1-7** were obtained and characterized by UV-Vis, fluorescence, ESR, NMR, MS, X-ray crystal structure, etc., as appropriate.

Compounds **3-7** are novel oxadiazole derivatives and their physico-chemical and some biological properties were compared with those of the known compounds **1** and **2**.

Theoretical semi-empirical calculations (AM1 and PM3) and the fragmental method for the hydrophobicity evaluation were employed to get a close structural insight.

As such compounds can have strong and important chromogenic and fluorogenic properties they are bound to be used as sensors and probes in different chemical or biological systems.



Sweets essence under analysis: UV-VIS-NIR spectra and other physical properties of cake flavor extracts

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This paper presents the results of the analysis of the most common flavor extracts in commercial liquid form, i.e. almond, lemon, orange, rum and vanilla extracts, respectively, from the point of view of mostly never studied combination of physical properties: density, dynamic viscosity coefficient, superficial tension coefficient, and the refractive index. The possible correlations between these magnitudes were also studied. It resulted that the density, dynamic viscosity coefficient and refractive index are very close to those of water, while the superficial tension coefficient is smaller than that of water. Strong negative correlation (-0.70) was found between density and the dynamic viscosity coefficient, while a strong positive correlation (0.86) was identified between the dynamic viscosity coefficient and the refractive index. Moreover, the 190-1100 nm transmission spectra of all five chosen liquid flavor extracts were obtained and analyzed, revealing both similarities and relevant differences. Stronger absorption was noticed for rum and vanilla extracts for most of the investigated spectral range, while almond, lemon and orange exhibited fluorescence along the entire visible range, most likely due to the ethanol content. All the investigated physical magnitudes will be further investigated as it can correlate with the food quality and use of these flavoring substances.

Ru(II)/Ru(III) Complexes-loaded mesoporous silica with anticancer and antimicrobial properties

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Despite significant progress in understanding the molecular biology of cancer development, the design of new cytotoxic anticancer drugs remains the cornerstone of modern antitumor therapy. The use of metallodrugs to treat cancer has grown very much since the discovery of cisplatin, in 1960. Recent studies have highlighted a variety of ruthenium-based compounds with very promising anticancer properties that could serve as viable alternatives to cisplatin and its derivatives. In some cases, their limited solubility in water can make their administration difficult, leading to a weak therapeutic effect. Therefore, alternative methods to deliver these types of drugs are essential for maximizing their therapeutic performance. In this context, the aim of our study was to develop a new series of hybrid nanosystems based on Ru(II)/Ru(III) complexes with Schiff base ligands loaded in SBA-15 mesoporous silica and to evaluate their antimicrobial and anticancer properties. The results of the antibacterial activity showed the promising potential of some of them for the development of novel antibacterial drugs, being efficient against *S aureus* and *E. faecalis* Gram-positive strains, two of the most fearful resistant opportunistic nosocomial pathogens. Some of the compounds proved to have high cytotoxic activity on A549 lung tumor cells.

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Electrical properties for gas sensing of Sn, Ti, Zn and Pr mixed oxides

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This work presents a comparison between the powder obtained at 800 °C and the film treated at 450 °C for mixed oxides of Sn, Ti, Zn, and Pr obtained by sol-gel deposition for gas sensing applications. The materials were characterized by X-ray diffraction, XPS spectroscopy, SEM electron microscopy, and EIS electrochemical impedance spectroscopy.

Response and sensor recovery characteristics for CO were also investigated and the gas sensing mechanism explained. The results indicated that the mixed oxide thin film exhibited high sensitivity for CO compared to the investigated powder. The findings of this work provide insight into the potential of the mixed oxides for CO gas sensing.

Functionalization of a tripodal Mannich base as nitronyl-nitroxide and Schiff-base ligands and their complexes

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Mannich bases are organic molecules frequently employed as ligands [1]. One important advantage associated to Mannich reactions, with respect to Schiff condensations, is the formation of strong bonds between the building units of the target molecule, resulting in stable ligands.

A tripodal Mannich base was synthesized, starting from 5-bromosalicylaldehyde and tris[2-(methylamino)ethyl]amine, resulting in a ligand with two compartments able to accommodate metal ions. The three remaining formyl groups of the 5-bromosalicylaldehyde moieties are available for further functionalization. Thus, a nitronyl-nitroxide derivative of the Mannich base could be obtained. Such ligands have paramagnetic properties, due to the presence of unpaired electrons in the nitronyl-nitroxide free stable radical moiety.

Another functionalization was performed by Schiff reactions, using various amines. As a result, an increase of the number of compartments was observed and, consequently, there was an increase of the nuclearity of the resulting coordination compounds.

[1] J. D. Crane, D. E. Fenton, J. M. Latour, A. J. Smith, *J. Chem. Soc., Dalton Trans.*, **1991**, 2979-2987

Novel functional bidimensional coordination polymers

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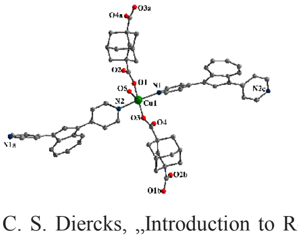
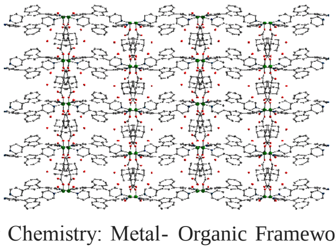
Metal-organic frameworks, a class of highly ordered porous materials consisting of metal-containing nodes connected by organic linkers, have been widely investigated for their ability to separate and accommodate specific molecules[1]. Employing 3d metal ions as nodes and spacers such as the C_2-symmetric ligand 1,3-adamantanedicarboxilic acid (H_2ada), 4,4'-bipyridine (bipy) or 1,3-bis(4-pyridyl)azulene (azbpy), we synthesized and characterized new coordination polymers: $^{\infty}{}_{2}[Zn_2(ada)_2(bipy)(H_2O)_{1.5}]\cdot(bipy)_{0.5}\cdot 3H_2O\cdot CH_3OH$, $^{\infty}{}_{2}[Zn_2(ada)(bipy)(H_2O)]\cdot H_2O$, $^{\infty}{}_{2}[Cu_2(ada)(bipy)]_2$ and $^{\infty}{}_{2}[Cu(ada)(azbpy)(H_2O)]\cdot 2H_2O$. The metal-organic frameworks will be investigated for their gas storage ability.





[1]O. M. Yaghi, M. J. Kalmutzki, C. S. Diercks, „Introduction to Reticular Chemistry: Metal- Organic Frameworks and Covalent Organic Frameworks", Wiley-VCH Verlag GmbH.-KGaA, **2019**, ISBN:9783527345021

Syntheses and molecular structure of mononuclear lanthanide complexes with salicylaldehyde

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The luminescence of lanthanide ions can be enhanced by the organic ligands, such as 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), β-diketonates, which play the role of antenna. Mixed ligand complexes [Ln(diketonato)$_3$(AA)] (AA = bipy, phen and their substituted derivatives) even intensify the luminescence. In this communication we report on the use of anion of salicylaldehyde for the synthesis of mononuclear lanthanide complexes [Ln^{III}(sal)$_3$(phen)]], where Hsal = salicylaldehyde, phen = 1,10-phenanthroline, Ln = Nd (1), Eu (2), Tb (3), Dy (4), Er (5), Yb (6). Complexes 2-4 and 6 were obtained by reactions of suitable [Ln(phen)$_2$(NO$_3$)$_2$] precursors with three equivalents of salicylaldehyde, and compounds 1 and 5 are formed by *in situ* reaction of Ln(NO$_3$)$_3$·6H$_2$O (Ln = Nd^{III}, Er^{III}), salicylaldehyde, Et$_3$N and phen. The crystalline phase purity of the samples 1-6 was confirmed by PXRD experiments, and their crystal structures were established by single crystal X-Ray diffraction studies. The compounds 1- 6 are isostructural. The Ln^{III} centers are surrounded by six oxygen donor atoms of three sal$^-$ ligands coordinated in bidentate chelate mode. Coordination number 8 is completed by the two N-donor atoms of the 1,10-phen, while SHAPE software indicates a square antiprism coordination polyhedron in all complexes.

New Insights in the Design of Materials Based on Polysulfones with Potential Applications in Biomedical Field: Structure–Properties Relationship

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The design and development of new polysulfone-based materials with tunable properties for various applications in the biomedical field have been accomplished by structure modification and control using the quaternization (QPSF) and sulfonation (SPSF) reactions. The evaluation of the solubility parameters of functionalized polysulfones (QPSF and SPSF), applying predictive methods for the selection of suitable solvents, has been a useful tool for predicting the physical properties and performance of these polysulfones. The obtained information offers the possibility to estimate the properties of the analyzed materials and to optimize the design and processing conditions to obtain membranes with specific features to the intended applications. Subsequently, structural parameters evaluation, surface chemical analysis, and morphological properties were investigated to establish the relationship between the structure of the polymers and their surface characteristics. Considering the obtained results, the quality and functionality of these materials are guaranteed, being validated for applications in the biomedical field.

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Homo- and heteropolynuclear complexes using a Schiff base derived from 2,3-dihydroxybenzaldehyde: synthesis and characterization

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The Schiff base ligands derived from *o*-vanillin [1] are known for their ability to form various homo- and heterometallic coordination clusters with interesting magnetic and photophysical properties [1,2]. Another intriguing, structurally related, aldehyde, which can be used to obtain different Schiff base ligands in order to generate multinuclear metal complexes, is 2,3-dihydroxybenzaldehyde.

In this study, we report the synthesis of four new homo- and heteropolynuclear complexes using as ligand a Schiff base formed by the condensation of 2,3-dihydroxybenzaldehyde with 2-(2-aminoethyl)pyridine (H_2L) and different Zn(II) and/or Ln(III) salts: $[Zn_4L_2(CH_3COO)_4]\cdot 2H_2O$ (**1**), $[Zn_2Gd_2L_2(CH_3COO)_6(MeOH)_2]\cdot MeOH$ (**2**) and $[Ln_{14}(CH_3COO)_{28}(HL)_{14}]$, where Ln = Gd (**3**), Eu (**4**). All compounds have been characterized by single crystal and powder X-ray diffraction, UV-VIS and IR spectroscopy. Also, the photoluminescence analysis of these complexes reveals that compound **1** exhibits fluorescent properties.

[1] Andruh, M. *Chem. Commun.* **2011**, 47, 3025.
[2] Li, X.Z.; Tian, C.B.; Sun, Q.F. *Chem. Rev.* **2022**, 122(6), 6374.

Porous spherical ZnO-alginate family prepared by a dual-template method for biological applications

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Self-assembled ZnO-alginate hierarchical spherical morphologies have been built up through a total green hydrothermal procedure using alginate (SA) and triethanolamine (TEA) as templates. The optimization of the properties displayed by the resulting composites is based on: (*i*) the ability of triethanolamine to form Zn^{2+}-TEA coordination systems with distinct dimensionalities and topologies, and (*ii*) the particular ionogelation of the alginate. The *in vitro* biotoxicity assays towards several randomly chosen Gram-positive and Gram-negative bacteria and fungal strains demonstrate the capability of these materials to act as biocides.

Acknowledgements. This study was financially supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-2020-2324, within PNCDI III.

Processing of Quaternized Polysulfone/Cellulose Acetate Phthalate/Polyvinylidene Fluoride Solutions by Electrospinning to Obtain Bioactive Fibrous Membranes

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The present work promotes a promising strategic way to obtain of bioinspired fibrous membranes with morphological and surfaces properties tailored for various applications from biomedical field. In order to obtain uniform, continuous, bead-free electrospun fibrous membranes, the choice of solvents (DMF and/or NMP) and composition of polymers mixture (quaternized polysulfone (PSFQ)/cellulose acetate phthalate (CAP)/polyvinylidene fluoride (PVDF)) for the electrospinning process of ternary solutions, as a result of the obtained rheological parameters, had an important role. Additionally, the morphological changes of obtained membranes, which were analyzed by SEM microscopy, were influenced by the solution properties and implicitly, the different macromolecular rearrangements in membranes structure, as a result of the functional groups orientation during electrospinning experiments. Therefore, the relationship between polymers structure, solution properties, and membranes functionality can be considered as an indicator for future practical applications.

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Versatile Multilayered Hydrophobic and Antibacterial Coatings

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The goal of the current study is to create new "eco-friendly" polyelectrolyte coatings with unique qualities intended for superior long-term protection. The objective of the study is to increase the polyelectrolyte (PE) coatings hydrophobicity, which is a crucial component in the production of coatings with low wettability qualities. For LbL protective coatings, a new technique for making hydrophobically modified polyelectrolytes multilayered coatings will be adopted. LbL deposition on a different substrate was used to build the complex coatings with hydrophobically modified poly(acrylates)/chitosan/surfactant, with or without ZnO nanoparticles. AFM, SEM, FT-IR, CA, were used to analyze the obtained LbL multilayers. The contact angle values of the PE coatings grow with the presence of nanoparticles. The film's thickness and roughness follow the same general pattern as its wettability. The innovative coatings have benefited from increased transparency and chemical compatibility and will carefully preserve the artefacts' aesthetic and chromatic characteristics.

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Plant-Based Biosynthesis of Magnetic Cobalt Ferrite

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In the recent years, cobalt ferrite ($CoFe_2O_4$) has received a renewed research focus due to its interesting properties and, implicity, due to its multiple biomedical applications. A special attention is paid to the biogenic routes to obtain cobalt ferrite. These green synthesis methods are simple and environmentally friendly, using nontoxic and biocompatible reagents. Due to the content of active biomolecules (flavonoids, polysaccharides, carbohydrates, amino acids, etc.), plant extracts are ideal candidates to be used as biological agents in the synthesis of nanoparticles.

In this work, $CoFe_2O_4$ was synthesized by a green approach of wet ferritization method using eucalyptus leaves extract as a reducing/chelating/capping agent. The structure, morphology and magnetic properties of $CoFe_2O_4$ were investigated by XRD, SEM, IR and Raman spectroscopy, thermal analysis and magnetic measurements. The M - H loops, recorded at room temperature, highlighted a superparamagnetic behavior of cobalt ferrite. The biosynthesized $CoFe_2O_4$ exhibits promising antimicrobial and antibiofilm activity.

Spinel Aluminates Obtained through Malate Route

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For decades, aluminates have been considered as a practical option for various industrial and technological applications. Spinel aluminates represent an extensive domain of research for its prospective use, including pigments, thermal and optical control coatings on spacecraft, catalysts / photocatalyst, sensors or supports for enzyme immobilization. A special attention was given to cobalt and nickel aluminates, due to their interesting properties: low surface acidity, good thermal stability and mechanical resistance, hydrophobicity.

MAl_2O_4 (M = Co, Ni) nanoparticles were prepared through precursor method, using malic acid as ligand. We have performed a study on the systems: $2Al^{3+}:(1-x)Co^{2+}:xNi^{2+}:4C_4O_5H_4^{2-}$, where $0 \leq x \leq 1$, $C_4O_5H_4^{2-}$ = malate anion. The isolated coordination compounds were characterized by elemental chemical analysis and physicochemical measurements (IR and UV-Vis spectra). Multiple characterization procedures were also conducted to investigate the structure, morphology and physicochemical properties of the spinel aluminates.

Novel multifunctional organo-modified silica coatings for metallic historic objects

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The main goal of this study was to obtain an eco-friendly coating material for anticorrosive protection of metal artifacts, using organo-modified silane derivatives. As anticorrosion agents various essential oils (EO) such as thyme and cinnamon leaf oils were employed, encapsulated in the silica matrices. The silica coatings were obtained using triethoxy silane (TEOS) and 3 –Glycidyloxypropyl trimethoxysilane (GPTMS) in various molar ratio. The influence of the fluorosilane addition on the hydrophobicity of the deposited films was also investigated.

The copper coupons were used as model metal, and various coating materials with or without essential oils were deposited using brushing method. The films were characterized by optical microscopy, contact angle, UV-VIS and FTIR, in order to evaluate the morphology, hydrophobicity and optical properties of the coating materials. The antimicrobial properties of the EO loaded coatings were tested against Aspergillus Niger, a fungus often found on the surface of artifacts. The anticorrosion efficiency of the silica coatings, with or without EO was evaluated on coated Cu plates subjected to corrosion in saline solution by using potendiodynamic polarization. The corrosion rate determined from linear sweep voltammetry (LSV) measurements show good protective effect of silica-EO coatings, as compared with coatings with bezotriazole as reference anticorrosion agent. observed. As part of the cleaning protocol, we propose that the microemulsions should be removed with cinnamon essential oil, thus obtaining an anti-corrosion protection layer on the metal surface.

Strategies to prevent healthcare associated infections

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The prevention and control of the spred of infections associated with medical care represents a real challenge for the biomedical community, with particular importance in epidemiological, clinical and economic terms. Recent research has shown that over 80% of nosocomial infections are associated with the formation of biofilms generated by opportunistic pathogens that frequently develop high levels of antibiotic resistance and virulence, leading to the accumulation of biomass on solid surfaces.

Considering the above, a 2-year study was carried out using the Q-field photocatalytic paint, applied in a section of a hospital unit. Sanitation tests were performed (in situ), the circulation of pathogenic bacterial strains in the palliative care ward was evaluated. It is observed that, although at the level of the hospital there was an increasing trend in the number of cases confirmed by IAAM, at the level of Q-field paint Palliative Care Department the number of cases associated decreased.

The Q-field product based on inorganic agents, shows bacterial activity on Gram negative and positive strains, fungi and viruses. The microaerobiota measurements of the last 2 years (2021-2022) showed a very low load compared to the period before the application of the paint sample in the clinic rooms.

Preparation of Nb-doped TiO_2 by combustion method

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In this study, we describe the combustion-based production of titanium dioxide (TiO_2) nanoparticles doped with niobium (Nb). The goal was to look at how Nb doping affected the structural and morphological characteristics of TiO_2 and to consider its possible uses. To start the combustion reaction, a fuel material (glycine) was mixed with a precursor to titanium dioxide (Ti(IV) iso-propoxide) and niobium (ammonium niobate(V)), which was then homogenized and ignited. Titanylnitrate was produced and then combined for one hour while stirring with glycine, ammonium niobate(V). The resulting solution was well mixed and then maintained in a furnace. The reaction parameters, including combustion temperature and residence time, were carefully controlled to achieve the desired Nb doping levels and nanoparticle sizes. X-ray diffraction (XRD) analysis confirmed the formation of crystalline TiO_2 with the desired doping concentration, and scanning electron microscopy (SEM) revealed the formation of uniform nanoparticles.

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Functional Model for Upscaling Cocrystal Preparation of Resveratrol/Piperazine Nutraceutical Product

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The upscaling process of cocrystal preparation involves increasing the scale or quantity of cocrystals produced while maintaining the desired properties and quality. In the present work we propose a functional model for the production of a nutraceutical product based on resveratrol and piperazine (coformer). For this upscaling process several steps were necessary: 1. Process Optimization, 2. Batch Size Determination, 3. Equipment Selection, 4. Safety Considerations, 5. Mixing and Dissolution, 6. Crystallization Control, 7. Filtration and Drying, 8. Characterization and Quality Control, 9. Scale-Up Validation, 10. Process Monitoring and Optimization. It is important to note that upscaling a cocrystal preparation process can be complex, and it may require iterative adjustments and fine-tuning to achieve the desired results. The designed and executed model can produce batches up to one kg and produces good quality resveratrol/piperazine cocrystal.

Functional model for resveratrol/piperazine cocrystal preparation.

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Co(II) and Cu(II) homometallic complexes with Schiff base ligands bearing amino acids: structural characterization and cytotoxic activity on tumor cells

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Amino acids, the building blocks of proteins, are particularly important in biochemistry due to their biological functions. These molecules contain uncharged amino groups at physiological pH that can be used to synthesize Schiff bases, molecules that play a key role in coordination chemistry. The use of inorganic compounds, especially transition metal coordination compounds, as anticancer agents has been known for decades, although the organic molecules are most widely employed.

In this study, we obtained and structurally characterized two series of mononuclear Co(II) and Cu(II) complexes with Schiff bases derived from *o*-vanillin and various amino acids. Evaluation of their cytotoxic/antitumor activity against human carcinoma and rat sarcoma cells revealed that Cu(II) complexes show higher cytotoxic activity compared to Co(II) complexes containing the same ligands. The most pronounced cytotoxic effect in both groups of investigated metal complexes is expressed by the complexes containing Schiff base ligand derived from *o*-vanillin and serine.

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Time Stability and Dye Adsorption Study for Magnetite-PGL-Chitosan Nanocomposites

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Surface functionalization of the magnetic nanoparticles allows using a new material for an efficient adsorption of the dyes from waste water. The employed nanocomposite was obtained by electrostatic deposition on iron oxide (magnetite) (M) particles of an interpolymeric complex (CP) between chitosan, a natural polisaccharide and biocompatible polyglycidol (PGL), in alternance with sodium dodecylsulfate (SDS) (S). After each sequential deposition the resulted material (MS, MSCP, MSCPS) was analized by FTIR and SEM. The size histogram of M particles indicates a majority population with a mean diameter of 55 nm which considerably increases for the covered particles. In the same time, the successful deposition was observed by the modification of electrokinetic potential and the increase of hydrodynamic diameter. The bare and covered magnetic particles were dispersed in water or 5 mM SDS and studied by DLS and Zeta potential method. All the systems were more stable in 5 mM SDS than in water and MSCPS was the most stable material even after 35 days. Also, MSCPS efficiently adsorbed methylene blue from water. UV-Vis absorption measurements allowed obtaining the respective adsorption isotherm which fitted well with the Freundlich model, indicating a heterogeneous multilayer adsorption. The new magnetic nanocomposite with iron oxide core presented a good colloidal stability, being also eco-friendly and effective for wastewater treatment.

Trans-$[M^{III}(valen)(CN)_2]^-$ - versatile tectons in constructing heterometallic coordination assemblies

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Heteroleptic *trans*-dicyanidometallates $[M^{III}(valen)(CN)_2]^-$ are rarely used as building blocks in designing heterometallic assemblies (M^{III} = Cr^{III}, Ru^{III}, H_2valen is the Schiff base obtained by condensation of *o*-vanillin and ethylenediamine). These tectons can interact with a second metal ion through the cyanido groups, the $O_2O'_2$ compartment or both of them.

Herein, we report the synthesis and structural characterization of two new dicyanido-Cr^{III} complexes containing the valen^{2-} ligand, $[K(H_2O)(CH_3OH)Cr^{III}(valen)(CN)_2]_2$ (**1**) and $PPh_4[Cr^{III}(valen)(CN)_2]\cdot 8.5H_2O$ (**2**). A solid-state transformation is observed in compound **1** involving ligand exchange upon heating and air exposure through a rare process of cracking crystals to self-healing. By employing $[Ru(valen)(CN)_2]^-$ metalloligands and $[Ln(hfac)_2(ac)(Hhfac)(H_2O)_2]$ as assembling nodes in constructing heterometallic systems, cation complex-anion complex, $[Ru(valen)(CN)_2Ln(ac)(H_2O)_5][Ru(valen)(CN)_2]$, Ln^{III} = Eu^{III} (**3**), Tb^{III} (**4**), Dy^{III} (**5**), Sm^{III} (**6**), Pr^{III} (**7**) and binuclear discrete, $[Ru(valen)(CN)_2Ln(hfac)_2(H_2O)_4]$, Ln^{III} = Eu^{III} (**8**), Pr^{III} (**9**), species yielded (Hhfac = hexafluoroacetylacetone, ac$^-$ = acetate anion).

Influence of Synthesis Route on Properties of Cu-doped ZnO Nanoparticles

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Zinc oxide is a non-toxic oxide with high refractive index, high thermal conductivity and antibacterial properties. Zinc oxide was doped with copper ions in order to obtain nanoparticles with improved electrical and optical properties. Coper-doped zinc oxide was prepared by different methods and using different precursors and solvents. Obtained solutions and powders were investigated by Infrared Spectroscopy (FTIR), Visible Spectroscopy (UV-VIS), Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES), volumetric/gravimetric chemical analysis and Photoluminescence Spectroscopy (PL). The nanoparticles were investigated supplementary by X-ray fluorescence (XRF) and Scanning Electron Microscopy (SEM). The results shows that the bandgap decreases in ZnO doped with coper compared with zinc oxide. The influence of precursors and synthesis route on the properties of the Cu- doped ZnO nanoparticles was established.

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Doped ZnO Nanopowders for Nanofluids

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Nanofluids have novel properties that make them useful in applications in heat transfer, including microelectronics, fuel cells, domestic refrigerator. The nanofluids are colloidal suspensions of nanoparticles (oxide, metal) in a base fluid (water, oil). Zinc oxide is a non-toxic oxide with high thermal conductivity and high refractive index. Zinc oxide was doped with different ions in order to obtain nanoparticles with right properties for nanofluids. Doped zinc oxide nanopowders were prepared by sol-gel method. The thermal treatment of the doped zinc oxide powders is established based on thermogravimetric (TG) and differential thermal analysis (DTA). The X-Ray Diffraction patterns of the thermally treated powders show the crystallization of zincite, belonging to wurtzite-type structure. Moreover, the incorporation of doping ions into ZnO lattice was also confirmed by infrared spectroscopy (FTIR). The influence of synthesis parameters on the morphology was studied by field emission scanning electron microscopy. The main applications being pursued involve nanofluids, photocatalysts, energy storage materials, and microelectronics.

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An Improved Pathway to Produce Biogenic Silica from Wheat Straws

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Wheat is one of the most planted food crops in the world. Wheat straw are by-products generated in large quantities every year. Beside animal feed or fertilizer, wheat straws are used as fuels for heat or additives in building materials, causing significant environmental issues. More recently, wheat straw has been applied as the raw material for silica obtaining, in order to produce porous silica with low cost and high efficiency. In this study, the wheat straws potential as raw material for biogenic silica extracting was investigated. High-purity biogenic silica (more than 94 wt.% SiO_2) was obtained from agriculture wastes, in particular wheat straws. Two different morphological forms of biogenic silica were obtained. The wheat straws were cut in small pieces and soaked in ultrapure water for 24 h, in order to swell the cell walls. The wet biomass was leached using 5 M sulfuric acid and 5% citric acid for a defined period, then calcined at 550 °C. The final products were characterized by XRF, FTIR, TG analysis, specific surface, pores distribution, and SEM. The obtained silica presented a microstructure composed of accessible, interconnected, and intra-particle mesopores (around 3.7-5 nm pores diameter) and high specific surface are (around 150 m^2/g).

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An Overview on the Utilization of Crown Ethers in Lithium Isotopes Separation

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The two naturally occurring isotopes of lithium (^{6}Li and ^{7}Li) have a natural abundance of about 7.5% and 92.5%, respectively. Many of the lithium isotope separation techniques have environmental impact, the mercury method use being the most harmful. The two isotopes (^{6}Li and ^{7}Li) play an important role in nuclear energy domain. High isotope separation of Li isotopes is usually achieved using the polydentate complex technique. Crown ethers are considered the most efficient for isotopes separation due to their selective-complexing ability with metal cations. It was demonstrated that they play multiple roles: phase transfer, selective chelation, dehydration, and retention during the electromigration process. This overview highlights the types of crown ethers and composite membranes that incorporate them applied in lithium isotopes separation. Crown ethers influence the lithium ions migration from the anode solution into the organic solution and enrichment of ^{6}Li at the interface resulting in the enrichment effect in organic solution.

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Antimicrobial Systems Based on Hydroxypropyl Methylcellulose and Silver Nanoparticles: Structural-Morphological Characterization

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The preparation of antimicrobial systems based on hydroxypropyl methyl cellulose (HPMC) with a high inhibitory effect on microbial growth was achieved by embedding silver nanoparticles (AgNPs), applying the thermal reduction method, using poly(N-vinylpyrrolidone) (PVP) as a stabilizing agent. Thus, the catching mechanism of silver in polymeric matrix can be explained by taking into account the hydrophilic nature of the amide groups and the hydrophobic nature of the vinyl groups of the PVP. The rheological parameters emphasized the multifunctional role of PVP which helps to control the size and distribution of AgNPs and prevent their precipitation but also the optimization of some properties of the studied materials. The silver amount was quantified using the spectroscopy techniques (XRF, EDX), while formation of the AgNPs was confirmed using FTIR, XRD, TEM, and DLS methods. Also, the morphological examination by means of the texture roughness parameters (AFM and SEM) has evidenced favorable characteristics for targeted applications. Antibacterial activity was tested against *Escherichia coli* and *Staphylococcus aureus* and was found to be substantially improved when silver was added in the studied systems. We can conclude that the structural and surface properties of these materials confirm their functionality and biological activity.

Exploring Niobium Doping for Enhanced Photocatalytic Activity of Titanium Dioxide under Visible Light Irradiation

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The research presented in this study focuses on the exploration of niobium (Nb) doping as a strategy to enhance the photocatalytic properties of titanium dioxide (TiO_2). By doping TiO_2 with transition metal ions such as Nb, it is possible to extend its light absorption range and improve its photocatalytic activity. The main objective of this research is to investigate the influence of Nb doping (5-35%) on the structural, morphological, and optical properties of TiO_2 prepared by the auto-combustion technique. To achieve these goals, a comprehensive set of characterizations is performed, including X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) to analyze the chemical composition, structural properties, and changes induced by Nb doping. UV-visible spectroscopy is employed to examine the modifications in the band structure and bandgap of TiO_2 resulting from the incorporation of Nb atoms. Nb doping leads to a controlled incorporation of Nb atoms into the TiO_2 structure. This incorporation induces structural and morphological changes in TiO_2, including modifications in its band structure and a narrowing of the bandgap. Consequently, the doped TiO_2 material becomes capable of absorbing visible light, thereby expanding its photocatalytic activity to a broader spectrum of light wavelengths.

Oxidic systems for energy applications

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The compositional versatility of the glasses and their glass ceramics recommends them for various applications in the field of energy production and storage.

Thus, several zirconia and lanthanum-doped glasses and glass ceramics are prepared and tested as vitreous pore-free, and homogenous candidates for solid oxide fuel cells (SOFCs).

Structural, thermal, and electrical characterization was attained by means of XRD, Raman spectroscopy, SEM, DSC, dilatometry, and electrical conductivity measurements. X-ray diffraction (XRD) and Raman spectroscopy were used to quantify the crystalline degree as well as the Q^n units (where n stands for bridging oxygen atoms of the SiO_4 units) in the vitreous phase of the as-prepared samples and their 100h aged counterparts at 850 °C. Tailored linear thermal expansion coefficient around 8.25×10^{-6} K^{-1} and electrical conductivity values within the 10^{-5} to 10^{-10} S/cm range enable using of these materials for sealant purposes.

Electrospun zeolite-modified polyvinylidene fluoride (PVDF) membranes

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The electrospinning method represents an emerging approach for obtaining polymer fibers with high surface area to produce multi-functional membranes for the pollutant's filtration and/or degradation from water and air. This paper discusses the effects of zeolite incorporation on the morpho-structural, opto-electric, surface, and photocatalytic properties of the electrospun polyvinylidene fluoride (PVDF) membranes.

For this purpose, scaning electron microscopy with energy dispersive spectroscopy (SEM-EDX), X-ray diffraction, Raman spectroscopy and Brunauer-Emmett-Teller physisorption measurements were used. Also, the absorption coefficient and band-gap energy values were evaluated from the optical transmission spectra in the 200–1100 nm spectral range. The sorption–photocatalytic activities were investigated under dark or UV/Vis/solar irradiation respectively, by spectrophotometric monitoring (665 nm peak) of the methylene blue dye degradation.

Non-ionic surfactants based lyotropic liquid crystals as transdermal drug delivery systems for Curcumin and essential oils

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Lyotropic liquid crystals can be used as drug delivery systems due to their properties, including but not limited to biocompatibility, being stable in excess water and their specific morphology, which allows for a higher quantity of bioactive compounds to be encapsulated, compared to other carriers.The aim of this study was to develop and characterize a lyotropic liquid crystal-based drug delivery system for the transdermal application of hydrophobic active principles. A lyotropic liquid crystal formed in a polyoxyethylene (20) sorbitan trioleate (Tween 85), polyoxyethylene (20) sorbitan monooleate (Tween 80) and water mixture has been obtained and characterized. We discuss the possibility of a synergistic effect in surfactants mixture, the morphology of the obtained system at various molar ratios and the effect of active principle (curcumin, tea tree essential oil) encapsulation onto the systems. Physicochemical characterization of the system (with and without active principle encapsulated) was performed by polarizing optical microscopy, dynamic light scattering, small-angle x-ray scattering and rheology. The release kinetics of the active principle from the optimized lyotropic liquid crystal system has also been investigated.

Sustainable Packaging Applications
Utilizing Organophosphorus Reinforced Poly(vinyl alcohol) Nanocomposites

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A novel approach to eco-friendly multifunctional nanocomposites with superior characteristics, involves the creation of semi-interpenetrated nanocomposite films using poly(vinyl alcohol) (PVA) covalently and thermally crosslinked with oxalic acid (OA), reinforced with a unique organophosphorus flame retardant (PFR-4). Additionally, the nanocomposite films are doped with silver-loaded zeolite L nanoparticles (ze-Ag). To evaluate the structure and composition of the prepared PVA/OA films and their semi-interpenetrated nanocomposites with PFR-4 and ze-Ag, scanning electron microscopy (SEM) was utilized to examine the morphology, while energy dispersive X-ray spectroscopy (EDX) provided insights into the homogeneous distribution of the organophosphorus compound and nanoparticles within the nanocomposite films. The results demonstrated that the composites with low phosphorus content exhibited significantly improved flame retardancy, with a reduction of up to 55% in the peak heat release rate. Furthermore, the reinforced nanocomposites exhibited significantly increased ultimate tensile strength and elastic modulus. Moreover, the samples containing ze-Ag nanoparticles displayed a considerably enhanced antimicrobial activity. These findings highlight the potential of these nanocomposites for various sustainable applications.

Influence of the dopant content and sintering method on the properties of hafnium-modified barium titanate ceramics prepared by the sol-gel method

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The synthesis and characterization of $BaTi_{1-x}Hf_xO_3$ (BTH) ceramics with varying Hf content (x= 0.03, 0.05, 0.10, 0.20, 0.30) using different sintering techniques was investigated. The powders were prepared using "acetate" variant of the sol-gel method and consolidated through conventional sintering (CS) or spark plasma sintering (SPS). The relative density was higher for BTH-SPS samples compared to BTH-CS samples. Electrical measurements showed that the addition of Hf decreased the ferroelectric-paraelectric phase transition temperature, regardless of the consolidation technique. BTH-CS ceramics with lower Hf content exhibited sharp permittivity maxima, indicating typical ferroelectric behavior. As the proportion of Hf increased, the phase transitions shifted to higher temperatures, resulting in a single "pinched" ferroelectric-paraelectric phase transition for BTH-CS ceramics with $x \geq 0.20$. BTH-SPS ceramics generally had higher relative permittivity values than BTH-CS ceramics of similar composition. The permittivity maxima were highest for ceramics with $x = 0.20$. BTH-SPS specimens also exhibited higher dielectric losses compared to BTH-CS ceramics.

Carbonaceous Materials Containing TEMPO Stable Free Radical: Blackberry-like Hydrochars with Enhanced Electrocatalytic Activity

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Stable free organic radicals and biomass-derived hydrochars have emerged as appealing, green, multifunctional materials, but their association has not been explored till now. Herein we developed a general, green and one step scalable incorporation protocol of 4-amino-TEMPO onto/into sustainable hydrothermal carbonaceous (HC) matrix. The synthetic pathway confirmed for the 4-amino-TEMPO and sucrose pair allows the configuration of benign, robust, stable redox active blackberry-like (Figure 1) or spherical hydrochar materials, and unveil the power of HCs as an active scaffold for materials used for diverse electrochemical purposes.

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Polysaccharide-assisted synthesis of hybrid Prussian Blue/C particles

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Prussian Blue (PB) and its analogs (PBA) materials, with the general formula $A_hM_k[M/M'(CN)_6]_l \cdot mH_2O$ (h, k, l, m = stoichiometric numbers; A = alkali metal cations; M, M' = transition metal ions), are well-established for their intriguing electrochemical, photochemical, biochemical, and magnetic properties. The exceptional nature of these properties together with their three-dimensional (3D) face-centered cubic structures render PB/PBA-modified electrodes highly suitable for a range of applications, including (bio)sensors and electrochromic display devices [1]. The PB/PBA-C hybrid or composite materials, with the potential improvement of PB/PBA properties anticipated through the inclusion of carbonaceous support, have received relatively limited exploration in research endeavors.

Herein, we report on the hydrothermal synthesis and characterization of a new class of hybrid PB/C and PBA/C particles by employing cyanide-based $K_4[Fe^{II}(CN)_6]$ or $K_3[M^{III}(CN)_6]$ (M = Fe, Co) complexes as starting materials and (poly)saccharides (glucose, fructose, starch) as carbon sources. The morpho-structural, thermal, and optical properties of the as-obtained materials will be discussed.

Acknowledgment: This work was supported by a UEFISCDI Research Project Number PN-III-P4-ID-PCE2020-2324.

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Novel (poly)saccharide-derived porous carbonaceous materials as efficient support for next-generation copper-based/C composites

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Porous carbonaceous materials have gained significant attention as promising supports for highly conductive metal/metal oxide/C composites. In this context, (poly)saccharides offer a favorable "green" alternative for obtaining carbonaceous materials through hydrothermal carbonization. Nonetheless, the resulting C-based materials are amorphous and achieving porous textures of the hydrothermal carbons (HC) is quite a challenge. The *soft template* approach is highly suitable for acquiring mesoporous HC by employing block copolymers, followed by hydrothermal carbonization at a moderate temperature under self-generated pressures. The subsequent heating at high temperatures, in a low-oxygen environment, using the double crucible method [1] improves the surface area and pore size distribution of the HC. We report on the synthesis via *soft template* method of new porous HC using glucose, chitosan, and carrageenan as carbon sources. The post-synthesis impregnation of the as-obtained porous HC with copper particles afforded Cu-based/C composites. The optical, morpho-structural, and textural properties of the carbonaceous matrix and of the corresponding copper-containing composites will be discussed.

Acknowledgment: This work was supported by a UEFISCDI Research Project Number PN-III-P4-ID-PCE2020-2324.

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Dioxidovanadium(V) heterometallic complexes with symmetrical bis-hydrazone ligands

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Recently, dioxidovanadium(V) complexes with hydrazone ligands involving alkali metals have proven their potential in terms of medicinal applications. As a contribution to this topic we report here the synthesis and crystal structure of four new heterometallic V^V/M^I complexes, namely $[(M(H_2O)_4(VO_2)_2(HL^1)]$ (M = Na **1**, K **2**), and $[(M_2(H_2O)_4(VO_2)_2(L^2)]$ (M = Na **3**, K **4**). Compound **1**-**4** were obtained by reactions of $[VO(acac)_2]$ with bis(salicylaldehyde)diaminoguanizone (H_4L^1) or bis(salicylaldehyde)carbohydrazone (H_4L^2) and an alkali metal carbonate M_2CO_3 (M = K, Na) in $MeOH/H_2O$ mixture. Single-crystal X-ray diffraction study for compounds **1-4** reveals that ligands behave as binucleating and coordinate to metal centers as tri- and tetrabasic acids, forming $[(VO_2)_2(HL^1)]^-$ and $[(VO_2)_2(L^2)]^{2-}$ complex anions, respectively. These are interconnected with monovalent aquated alkali metal ions, resulting in the formation of distinct heterometallic discrete (**1**) and polymeric networks (**2-4**). The vanadium(V) atoms adopt distorted square-pyramidal coordination geometries, completing their coordination sphere by two cis-oxido-O atoms. In the solid state the extended structures are stabilized by strong electrostatic and hydrogen bond interactions.

Bentonite clay - low cost adsorbent for pyridine: Equilibrium and kinetic study

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Raw bentonite as a representative nonmetallic clay mineral has good performance in adsorbing contaminants by cation exchange. In this study, sodium saturated bentonite as well as modified with a cationic surfactant was used as adsorbent to remove pyridine, an organic pollutant, from aqueous solutions. The process took place at room temperature and basic pH. The influence of contact time and of the initial contaminant concentration on the pyridine uploading was determined by GS-MS. The physical and chemical properties of bentonite and of cethyltrimethyl ammonium bromide (CTAB) modified bentonite were evaluated before and after being in contact with the pyridine solution by BET specific surface area and porosity, XRD and FTIR. Protonated pyridine species generated in contact with hydroxyl group of bentonite caused interactions with the clay and surfactant removal. The adsorption efficiency of pyridine at equilibrium was 82.88% for surfactant modified bentonite and 97.82% for sodium bentonite. The results indicate that Freundlich isotherm model and pseudo-second order kinetic model describe well the adsorption process and that chemical adsorption prevailed over partition/physical adsorption in both cases.

Copper-based/C composites on new eco-friendly carbonaceous polysaccharides-derived platforms: synthesis and characterization

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The low cost, non-toxic copper oxide materials proved to be promising p-type semiconductors with a high Hall mobility and optical properties that were of interest in (photo)catalysis, photodetectors, energy storage, sensors, biocidal agents and in antitumoral therapy.[1] The performances of copper-based nanoparticles are strongly influenced by their composition, size/shape, dispersibility degree, hierarchical arrangement of crystallites, and texture properties, prompting the developing of efficient soft chemistry strategies to design best fit nanoscaled materials. Moreover, the incorporation/deposition of the copper-based materials into the carbonaceous supports are expected to improve their physico-chemical properties. Herein, we report on the synthesis of Cu_xO oxides ($x = 1, 2$) and/or Cu-based/C composites obtained through solution-based methods and using (poly)saccharides as source of carbon. Their morpho-structural and optical properties were discussed.

Acknowledgment: This work was supported by a UEFISCDI Research Project Number PN-III-P4-ID-PCE2020-2324.

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SECTION 6

Biophysical and pharmaceutical physical chemistry

POSTERS

Studies on polyphenols extraction and their embedding in porous supports

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Polyphenols, valuable substances synthesized by plants, have attracted attention due to their benefits on human health such as anti-inflammatory, antioxidant, antibacterial, antiproliferative etc.[1]. This study aimed to develop effective processes for polyphenols extraction from grape *Vitis vinifera* pomace of Pinot Noir cultivar (Murfatlar), which is the main winemaking by-product. Herein, we report the influence of the extraction method (ultrasound-assisted, high-pressure extraction, conventional method) and temperature on the chemical profile of hydroethanolic extracts that were characterized by spectrometric determinations and HPLC-DAD. Then, the extracts with good antioxidant activity were encapsulated in mesoporous silica pristine and functionalized with amino moieties (MCM-NH_2), fucoidan-coated MCM-NH_2 (Fuc@MCM-NH_2) and diatomite. The cell viability of mouse macrophage cell line was around 90% when treated with a dose of 10 μg/mL sample, which indicated a safe concentration. The anti-inflammatory potential of extract free and encapsulated into Fuc@MCM-NH_2 was evaluated using NO assay and 10 μg/mL concentration was safer to the macrophage and better at reducing the inflammation than 100 μg/mL causing a higher percent of NO inhibition (33.07 % and 32.81 % of free and encapsulated extract, respectively).

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Binding interaction of epirubicin with bovine serum albumin

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Epirubicin is an anthracycline chemotherapy drug that is used in the treatment of various types of cancer. It is derived from the natural compound doxorubicin but has a modified structure that gives it certain advantages in terms of efficacy and safety. Bovine serum albumin (BSA) is a commonly used protein model to study drug-protein interactions.

The interactions of epirubicin with bovine serum albumin (BSA) were studied by spectroscopic methods. The binding constants was evaluated and we can say that quenching of fluorescence of serum albumin by this drugs was found to be a static quenching process. Based on the Föster theory of non-radiation energy transfer, the binding distances between the drugs and tryptophane were calculated and the value obtained suggests that there is a non-radioactive energy transfer between BSA and Epirubicin. The site for binding of Epirubicin to BSA was identified using competitive binding experiments with warfarin and ibuprofen.

This work provide insight that will guide development of future pharmacological applications of epirubicin.

Biophysical properties of some nitrobenzofurazan derivatives

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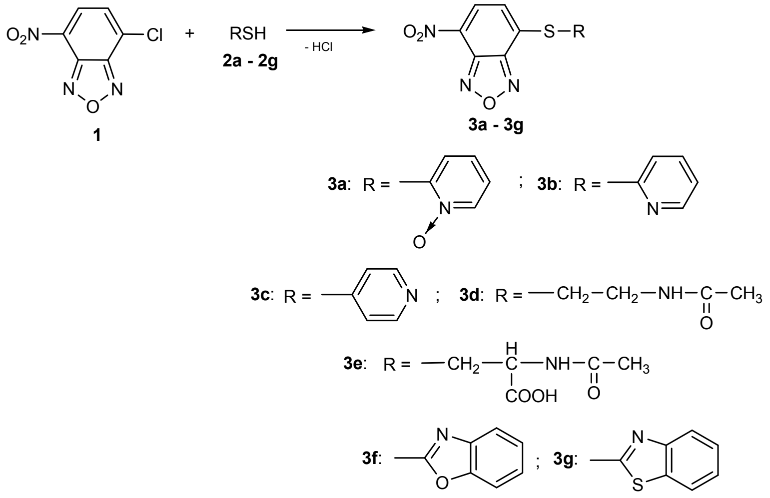
The purpose of our study was to evaluate antitumor activity of some nitrobenzofurazan derivatives previously reported. In this regard, their cytotoxic effect, influence on eukaryotic cell cycle, and on some genes implicated in apoptosis were evaluated. Compounds **3b**, **3c** and **3d** induced apoptosis through both, intrinsic and extrinsic, pathways, while compound **3a** activated only the intrinsic pathway. The most toxic proved to be compound **3d.** This compound also slightly increased S phase and decreased G0/G1 phase in a dose dependent manner.



Research on the effectiveness of ascorbic acid incorporation into water-in-oil emulsions with parsley (*Petroselinum Crispum*) extract

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Water-in-oil emulsions have a high potential for various pharmaceutical formulas used in the cosmetic industry as delivery systems of natural hydrophilic compounds. This paper presents the results of the preparation of inverse emulsions from a natural oil (grape seed oil) in order to evaluate the incorporation of ascorbic acid extracts from parsley. Thus, the stability of the emulsions was evaluated according to the storage time at room temperature. Also, the degree of ascorbic acid release over time from the prepared emulsions was evaluated. The microscopic analysis and that of certain characteristic physical parameters, confirmed the type of emulsions, both for the control emulsion, and for those containing ascorbic acid extract. Moreover, the incorporation of the extract into the internal phase of the emulsions contributed to changes observed microscopically on the size of the droplets and on their appearance. Analysis of the kinetics of ascorbic acid confirmed that the emulsions have a long-lasting effect on its decomposition as compared to the behavior of the free extract. This can be associated with pharmaceutical creams based on inverse emulsion with a sustained release of ascorbic acid over time. The kinetic results of the basic inverse emulsion (without hydrocolloids or secondary emulsifying agents), stored at room temperature, were best associated with a first-order reaction ($R^2 = 0.91$)

Exploring (BSA - micellar carrier – drug) systems with pyrene

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The medicine transport to target needs biocompatible carriers and the nonionic surfactants with their small critical micellar concentrations and low toxicity successfully accomplish this demand. Besides, the nonionic ethoxylated surfactants (NES) have a valuable stabilizing effect upon the conformation of serum albumins and therefore deserve more scientific interest. New perception can be obtained by exploring mixtures of serum albumin and NES with pyrene (Py), as an external probe.

This work mimics a drug delivery process by incorporating Py into NES micelles, used as drug carriers, and then adding bovine serum albumin (BSA). Pyrene plays both the role of model drug and extrinsic sensor for the BSA - micellar carrier interaction. Two nonionic surfactants with different alkyl chains and ethoxylation degrees are employed to obtain micellar carriers with unlike dimension and polarity. The investigation is performed by means of static and dynamic fluorescence, UV-Vis absorption and circular dichroism. The fluorescence approach uses complementary spectroscopic data, obtained by exciting either the intrinsic (tryptophane in BSA) or the extrinsic (Py) fluorophore. The acquired results characterize these complex systems and shed light upon the modes of drug transport with NES carriers. In addition, the study shows that the protective effect of ethoxylated surfactants upon the secondary structure of BSA is maintained as well in the presence of pyrene.

Interfacing metal ion enhancement of natural product antioxidant potency with neuroprotection

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Natural products have been at the forefront of pharmaceutical development over the past decades, with key molecular components exhibiting antioxidant, anti-carcinogenic, anti-inflammatory, and antidiabetic activity. To that end, plant flavonoids exhibiting antioxidant activity against Reactive Oxygen Species (ROS) and oxidative stress have been under scrutiny, due to epidemiological association with neurodegenerative diseases (Alzheimer, Parkinson). Poised to investigate the physicochemical profile of select natural product-containing antioxidants, under the interactive influence of well-defined metal-organic zinc-citrate (ZnCit) species, against neurodegeneration, the in vitro toxicity profile and antioxidant capacity of Cronus mas L. aqueous extracts was studied in the presence/absence of ZnCit, thereby establishing links to combating oxidative stress.[1] The results show that the enhancement effect of ZnCit reflects interactions with plant extract molecular components and neuronal cell (N2a,SH-SY5Y) cytosolic targets, thereby averting ROS-induced aberrations, ultimately providing plant extract neuroprotection and justifying biomedically functional food formulations.[2]

Acknowledgements: This research has been conducted in the framework of the Regional Operational Programme Central Macedonia 2014-2020. co-financed by Greek national funds and the European Union.

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Characterisation of 2-hydroxypropyl-β-cyclodextrin inclusion complexes with natural antiinflamatory agents. Enthalpies of combustion and formation.

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In this work, thermodynamic properties of (2-hydroxypropyl)-β-cyclodextrin (HPβCD) inclusion complexes with thymol, carvacrol and eugenol are reported.

The melting temperatures and the enthalpy of fusion were determined by differential scanning calorimetry.

Combustion calorimetry method was applied in order to obtain the enthalpies of combustion and formation for the complexation compounds. In order to verify the formation of inclusion complex in solid phase, FT-IR and DSC methods were used. The transformation points and the associated thermal effects were determined from the DSC curves in the temperature range from ambient up to 400ºC. The obtained results indicated that (2-hydroxypropyl)-β-cyclodextrin (HPβCD) improved the stability of thymol, carvacrol and eugenol.

Influence of dietary antioxidants on drug-albumin binding

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Due to their biological activity, antioxidants, as dietary supplements, are of tremendous interest. The formation of antioxidants-albumin complexes has recently been the subject of extensive research, with a particular emphasis on structure-affinity connections. Drug-food interactions can lead to an increase in the amount of free drugs in the blood, which can influence how they are transported and/or disposed of and, in certain situations, cause harmful or toxic effects.

This study used fluorescence and absorption spectroscopy to investigate how bovine serum albumin (BSA) interacted with the nimesulide (NIM), a non-steroidal anti-inflammatory drug, and the fluoroquinolone bactericidal antibiotic, levofloxacin (LEV), in the presence of two antioxidants, quercetin (QUE), and ascorbic acid (ASC), in an aqueous solution under physiological conditions. NIM/LEV significantly quenched the fluorescence of BSA, and the quenching mechanism was thought to be static quenching by generating a stable ground complex. The binding distance between the amino acid residue of BSA and NIM/LEV was estimated. The lowered association constants of NIM/LEV binding to BSA in the presence of either QUE or ASC were both attributable to competitive binding to protein.

Therefore, when treating specific pathologies, the consumption of antioxidants-rich foods and beverages should be taken into account in order to prevent the negative effects caused by changes in plasma protein binding.

Apparent kinetics of bovine serum albumin thermal denaturation. Analysis of microDSC data via Arrhenian windows.

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Thermal denaturation of BSA (fatty acids free, 98% purity) was investigated in phosphate buffer, pH = 7.4, at various ionic strengths (IS = 0.0265M, 0.053M, 0.106M, 0.265M) and heating rates (0.4 K/min. 0.6 K/min, 0.8 K/min, 1 K/min, 1.2 K/min), utilizing a μDSC7 evo calorimeter (Setaram).

The obtained results proved that kinetics of BSA thermal denaturation is difficult to approach, at least within the experimental conditions investigated. Unfavorable signal-to-noise ratio and the complexity of the process itself are probably the main causes. The activated nature of the denaturation was clearly evidenced by the simple Kissinger test. The influence of the buffer ionic strength was manifest, with an obvious trend of protein stabilization in buffer with higher concentration.

Thermograms decompositions into two contributions did not result in a regular behavior of the two components with either heating rate or ionic strength, thus making advanced isoconversional methods unsuitable. A simplified model-based approach, based on Arrhenian windows of the experimental data, offered a promising alternative for apparent denaturation kinetics.

Enhanced binding at fever temperatures between HER2 in complex with trastuzumab and pertuzumab

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Fever follows the administration of trastuzumab and pertuzumab used in HER2-relevant immunotherapy, but is often eliminated in clinical practice. We sought to explore the role of temperature (37˚-39˚) on the formation of immune complexes between HER2 with either trastuzumab or pertuzumab, or with both antibodies. Using molecular dynamics simulations and free energy calculations, the binding between HER2 and these immunotherapeutic monoclonal antibodies was investigated under different temperatures. Trastuzumab and pertuzumab present the highest free binding energy to HER2 at febrile temperatures (39˚), or when HER2 is in complex with both antibodies. Performing molecular dynamics simulations under fever temperatures may be important for delineating their role in enhancing the binding affinity of mature antibodies used in immunotherapy.

Interaction of anticancer drug actinomycin D with bile salts micelles

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Due to the presence of different tunable binding sites, bile salt micelles are found to be interesting host systems capable of carrying both hydrophobic and hydrophilic guest molecules depending on the structure and size of the guests.

This work is focused on exploring the interaction of actinomycin D (ActD) anticancer drug with two bile salts of different hydrophobicity (sodium cholate (NaC) and sodium deoxycolate (NaDC) and the influence of these bile salts aggregates on the ActD–DNA complex by UV-Vis spectroscopy (absorption and thermal denaturation).

The binding strength of ActD to NaDC is higher than for NaC, attesting stronger hydrophobic interactions between ActD and NaDC micelles. Also, the partition coefficient is significantly higher for NaDC micelles than for NaC micelles, in line with larger aggregates formed by NaDC. The spectral profile of ActD molecules in NaC and NaDC micelles, in comparison with different solvents, implies that ActD molecule experiences a hydrophobic environment in bile salts micelles.

Regarding the influence of NaC and NaDC aggregates on the ActD–DNA complex, it was shown that the presence of both bile salts micelles do not induce the deintercalation of ActD molecules from DNA duplex.

Zinc(II) complexes containing pyridyl-type ligands for fluorescent detection of antiinflammatory drugs

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The past few decades have witnessed an increasing interest in the chemistry of d^{10} metal systems because of their rich photochemical properties, catalytic applications and use in drug discovery. In recent years we have undertaken a systematic exploration of the structural features displayed by mixed-ligand compounds of diverse coinage metal salts with pyridine nitrogen and tertiary triaryl phosphorus donors with diverse profiles and electronic characteristics, together with the influence of the counterions, the metal/ligand ratios, metal coordination number, stereochemistry and nuclearity, and the consequences for the physicochemical properties of the final compounds. The present work presents a series of four complexes based on zinc(II) bromide with pyridyl-type ligands, with the general stoechiometric formula $[Zn(L)Br_2]$ (L = 2,2':6',2"-terpiridine (tpy); 2,2'-biquinoline (bq); 2,2'-bipyridine (bpy); 2,2'-dipyridylamine (dpa)). The obtained complexes were found to display photoluminescent properties and, due to this property, they were subjected to fluorescent detection investigations of sodium diclofenac, a substance from the antiinflammatory class.

A coarse-grained model of chitosan for a physical cross-linking pattern

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Phytic acid (PA) represents a cyclic polyphosphate, mainly used as a cross-linking agent in novelty studies to formulate chitosan (CT)-based microspheres, nanoparticles or hydrogels designed as nanocarriers with unique biological properties. To explore and predict the underlying reticulated pattern responsible for the structural design in the CT-based models we put forth a coarse-grained parametrization of the PA employing specifically the Martini 2.2 force field implementation.

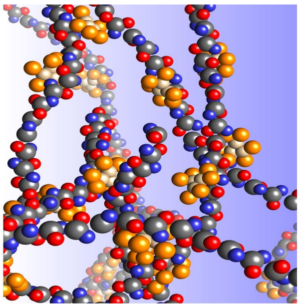

Figure 1. The architecture of CT-PA network

SECTION 7

Green chemistry and environmental engineering

KEYNOTES

Growth of calcium carbonate coating on pure Mg

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Carbonate deposition from carbonated water containing calcium ions can be used as a simple technique for surface modification of materials designed for biomedical use. In this work, rapid deposition of carbonate clusters and nanoparticles under non-equilibrium conditions, from a saturated carbonated aqueous solution, was investigated in order to elucidate the growth mechanism of coating formation and the evolution of the carbonate coating with immersion time of pure magnesium disks (Matthey) in carbonation solution. For this purpose, Raman and EDS spectroscopies, XRD, SEM and AFM microscopies were involved. SEM and AFM observations confirm that the calcite coating is continuous and that lateral growth of the calcite nuclei leads to two-dimensional coalescence to a polycrystalline coating. The mechanism of the hydrophobic coating formation involves surface nucleation of carbonates mediated by the dissolution of the native brucite corrosion product, surface conversion to hydroxyl-carbonates, calcite surface nucleation, and nanoparticle attachment during coating formation, leading to the lateral growth of a continuous coating layer of intertwined calcite microcrystals. The grown carbonate films grown have high potential to be used as a non-toxic protective coating with possible application in biodegradable implants.

SECTION 7

Green chemistry and environmental engineering

POSTERS

Enzymatic degradation of epirubicin

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The presence of pharmaceuticals in groundwater is a serious issue nowadays; these substances can have harmful effects on any living being, including cytotoxicity, genotoxicity, mutagenicity, teratogenicity, and endocrine disruption. Therefore, in order to keep them out of the environment, it is crucial to develop efficient and "green" procedures for their degradation. One of the advanced oxidation techniques (AOPs) being researched to remove pharmaceuticals from wastewaters is the use of enzymes. Among them, horseradish peroxidase (HRP) was proved to be able to eliminate many phenolic compounds when hydrogen peroxide is present as a cosubstrate.

Epirubicin is an anthracycline drug used in combination with other medications to treat breast cancer in patients who have had surgery to remove the tumor; due to the rise in breast cancer incidence worldwide, this type of medication is significantly more prevalent in aquatic environments.

This study was focused on the degradation of epirubicin in the presence of HRP and hydrogen peroxide in unbuffered media, using a spectrophotometric method (variation of absorbance at λ=480 nm in time) at different initial concentrations of all components. The kinetic parameters corresponding to a simplified ping-pong model were estimated, showing that HRP has a high affinity for epirubicin. Furthermore, since HRP's operational inactivation constant is lower than the values observed for other substrates, the approach may be used to remove such pharmaceuticals from wastewaters.

Efficient Recovery of Antidepressants from Aqueous Media by Microemulsion Extraction System

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Tricyclic antidepressants are environmental pollutants whose occurrence started to be investigated more only recently, with the advent of analytical methods sensitive enough to detect their extremely low levels in environmental samples. In our study, we present some results of our experiments on the preparation and application of some microemulsion systems for the separation and concentration of several tricyclic antidepressant drugs. For the construction of phase diagrams, organic esters were used and nonionic surfactant polyoxyethylene (4) lauryl ether (Brij 30).

The optimal extraction conditions using these types of systems (water-oil-surfactant) correspond to high ratios of aqueous phase and a small amount of surfactant, resulting in Winsor II systems. A green method was developed to extract from aqueous medium the antidepressants at concentrations between 20-100 mg/L, and then quantify their remaining concentrations by gas chromatography coupled with mass spectrometry, without the need of derivatization.

Acknowledgment: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2021-1216, within PNCDI III.

Multifunctional biocompatible hydrogels for biomedical applications

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Hydrogels are a class of fascinating materials in the form of a three-dimensional network structure widely used for biomedical applications such as tissue engineering and controlled delivery of biologically active agents. Starting from relatively simple single polymer networks, they can form multifunctional composite hydrogels that simulate the complex features of living tissues. Depending on the source of the constituents, hydrogels can contain bio-based polymers such as polysaccharides or proteins which can be derived from plants, microorganisms or animals. They demonstrate several advantages, such as biodegradability and biocompatibility and can incorporate different nanoparticles, antibiotics, anesthetics or other bioactive components.

In the present research, the development of new biocompatible polysaccharide-based hydrogels with the desired multifunctional characteristics for biomedical applications was presented. The morphologies of the obtained hydrogels were studied using SEM microscopy. The rheological properties of the hydrogels were determined. The results demonstrated that the novel polysaccharide-based hydrogels could provide the required and suitable biophysical and biochemical properties capable of inducing an effective biological solution for both *in vitro* and *in vivo* biomedical treatments.

Keywords: *hydrogels, biocompatibility, biopolymers, biomedical applications*

Dynamics of PM, TCVO and CH_2O concentrations in the city of Galati

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According to the World Health Organization (WHO), air pollution is the greatest environmental risk to human health and to the health of terrestrial and aquatic ecosystems. People in urban areas are mainly exposed to this risk. Particulate matter, nitrogen dioxide and ground-level ozone are the air pollutants thought to be responsible for most premature deaths. In 2020, in Romania, according to European Environment Agency estimates, at least 21,556 people died prematurely because of exceeding the PM 2.5 threshold, while 3,110 died prematurely because of nitrogen dioxide pollution, and over 1,000 because of ozone exposure. The objective of this paper was to study the spatial variation of particulate matter (PM10 and PM2.5) on the territory of Galati city, Romania. In addition to PM, two other pollutants were monitored: volatile organic compounds and formaldehyde. The values of the European Air Quality Index, temperature and humidity were also considered. The measurements were taken for three time intervals during each day: 8-9 A.M., 12–1 P.M., and 4 –5 P.M., respectively, in over 40 points of the city. To quantify the influence of meteorological factors on the PM concentrations in the atmosphere, correlation coefficients were calculated and ANOVA methods were used. PM 2.5 and PM 10 concentrations were within normal limits. European air quality index values calculated using particulate matter concentrations ranked air quality as good or fair. As for formaldehyde and volatile organic compounds, in more than 48 % of the total measurement points, the allowed values were far exceeded, the level of concern regarding human health being high.

High capacity recovery of Ag(I) from aqueous solution by mesoporous silica sorbent

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A simplified sol-gel method was developed for the preparation of thiol functionalized porous silica particles using (3-mercaptopropyl)-trimethoxy-silane (MPTMS) for co-gelation in the presence of micellar templates. The resulting short range ordered porous silica microparticles are exceptionally effective sorbents of aqueous Ag(I). The binding of aqueous Ag(I) is almost stoichiometric in the broad pH range between 4.0 and 9.0 even at low Ag(I) concentrations until reaching the limiting ca. 200 mg g^{-1} sorption capacity. The sorbent displays high selectivity towards Ag(I), which was tested in the simultaneous presence of several different metal compounds. The practically complete recovery of Ag(I) and the regeneration of the sorbent was achieved by washing with a $Na_2S_2O_3$ solution. X-ray photoelectron spectroscopy (XPS) revealed that silver is not reduced on the surface of the sorbent. The reason for the strong and selective binding of Ag(I) is the formation of layered thiolate coordination compounds on the functionalized silica surface that display characteristically high stability.

Evaluation of adsorption capacity of NH_2- and SH- functionalized silica towards Hg(II) from synthetic residual waters

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In recent years, adsorption became one of the most appropriate approach for mercury removal from wastewaters due to many advantages such as: simplicity and safety of the technique, low cost, environmental friendliness, the ease of adsorbents regeneration and high recovery efficiency.

The objectives of the present study were: (i) to investigate and establish the optimum conditions of pH, sorbent dose, mercury concentration and temperature for the sorption capacity and removal efficiency in non-competitive conditions; (ii) to model the kinetic and equilibrium of mercury adsorption in order to evaluate the kinetic and isotherm parameters; (iii) to explain the adsorption mechanism by using theoretical chemistry (DFT method); (iv) to establish the level of reusability of the sorbents during consecutive sorption/desorption cycles.

The synthesis of the sorbents was realized by a condensation reaction between the –OH active groups from the surface of the silica and the methoxy groups of the (3-Mercaptopropyl)-trimetoxysilane or (3 Aminopropyl)-trietoxysilane. The functionalized silica were then used to remove mercury (Hg(II)) from aqueous solutions in batch adsorption experiments.

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Phytosomes use as Vectors to Improve Active Compounds Efficacy

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The main goal of the current work was to design new bio-vectors, phytosomes, able to improve active compounds bioavailability for nutraceutical and cosmeceutical applications. The formulation of new biovectors was based on solvent injection method, using lecithin, solvents biliary salts as solvents (sodium cholate, respectively sodium deoxycholate, aqueous solutions), while active compounds were either standard rutin and epicatechin, or hydrophilic respectively lipophilic extracts from *Hippophae rhamnoides* berries. Extracts were normalized in rutin content, respectively epicathechin content. For better control of particle size and dispersion, Poloxamer 407 or Tween 80 were added during synthesis process. Designed vectors were characterized as morphology (particle size, zeta potential, TEM) and structural specificity (FTIR analysis). It was proven that the bio-vectors are appropriate for targeted applications, based on dimension and morphological characteristics. The structural characterization supported the inclusion of active compound in the nano-carrier, proofs of hydrogen bonds and changes in the intensity and wavenumber of the specific lecithin groups being provided. Release profile was drawn, for both formulas, bio-vectors -total extract, respectively bio-vectors-standard compound, around 80% from rutin being released in first 120 minutes. Swelling tests were performed in order to prove the safeness of bio-vectors use for nutraceutical applications.

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Study on the variability of the ozone ground concentration between 2015-2023 in the South East area of Europe. A comparison of numerical methods of investigation

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The study of air quality parameters has recently become a very important topic. In this sense, many researches in the field have highlighted, by conducting studies on narrow specific areas, the existence of some processes that can conveniently describe the dynamics of the variation of the different quality parameters and especially the evolution of the concentrations of the polluting factors in the atmosphere. In the present study, we took the data from the air quality monitoring system in Romania, data covering a number of 50 monitoring stations over a period of 8 years.

With the help of these data, we were able to build seasonal and annual distribution maps for ozone concentration at ground level and we were able to highlight the existence of significant differences between neighboring stations. Also, we were able to investigate the quality of the prediction that could be achieved by comparing two evaluation methods: a non-linear regression method - using RBF neural networks. The obtained results are compared with MANOVA statistical analysis methods using a minimal set of measured parameters. The obtained models highlighted the dependence of ozone concentration at ground level on both meteorological parameters and the level of solar radiation. In the last part, a mechanism is proposed that can explain the diurnal variability of this concentration at the soil level.

Research on the dynamics of nitrogen oxide concentrations in the South East area of Europe in the period 2015-2023

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The study of the dynamics and the recording of the level of nitrogen concentrations in the lower layers of the atmosphere is a topical issue. Based on continuous observation data of surface nitrogen oxide concentrations from fifty automatic air monitoring stations and by using meteorological data from weather recording points related to these stations, it was possible to highlight the temporal and spatial variations of concentrations of nitrogen oxides. It was also possible to evaluate and study the relationships between the concentration values and the meteorological factors. Thus, with the help of the evaluations of the correlations between these parameters and with the help of ANOVA-type methods, the dynamics and spatial variability were investigated during the period 2015-2023. Mainly, it was possible to build an automatic calculation module using non-linear and ANN-type interpolation methods to be able to build distribution maps for monthly, annual or daily average values. It was also possible to highlight the existence of a significant decrease in pollution recorded at most automatic air monitoring stations during the COVID-19 pandemic. Also, we were able to investigate the quality of the prediction that could be achieved by comparing two evaluation methods: a non-linear regression method - using RBF neural networks. The obtained results are compared with MANOVA statistical analysis methods using a minimal set of measured parameters. In the last part, a mechanism is proposed that can explain the diurnal variability of this concentration at the soil level.

Multifunctional fluorescent polymer sensing phenothiazinium dye and metal ions

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This study reports about smart and emissive pyrene labeled poly(acrylic acid) sensing methylene blue and various metal ions. Different methods as surface tension, UV-vis, steady-state and time-resolved fluorescence, electrokinetic potential, dynamic light scattering, microscopy or FTIR investigated the photophysical behavior and the structure of the supramolecular materials. The influence of the surfactant and polymer concentration or pH on the pyrene photophysics was analyzed. The binding mechanism and the analysis of interactions between methylene blue or metal ions and pyrene labeled poly(acrylic acid) were evaluated by fluorescence quenching measurements. The detection limit (for metal ions), the quenching and binding constants (for methylene blue and metal ions) were assessed.

The fluorescent polymer showed high sensitivity and binding ability for methylene blue, Cu^{2+} and Fe^{3+}. The outcome may be useful in waste water treatment or in biomedical applications.

Influence of size and chemical composition of titanium dioxide surface modified with silver nanoparticles based on aminated hyaluronic acid in vivo toxicity

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We proposed an efficient, "environmentally friendly" chemical reduction protocol for the synthesis of aminated hyaluronic acid-based silver nanoparticles on modified surface of titanium dioxide nanoparticles for biological investigations. The physical-chemical and optical properties of silver nanoparticles have been known and studied for many years, so the focus of the latest data in the literature remains on the biological effects, given their size and toxicity. For this, we developed a novel aminated hyaluronic acid (HA-NH_2)-based protocol to obtain silver nanoparticles, in which HA-NH_2 was used for the first time as a reducing and stabilizing agent. Finally, the article focuses on the effect produced by the size of silver nanoparticles on the titanium dioxide surface and the chemical composition of the materials for in vivo toxicity study.

Laccase - ABTS as an efficient system for recalcitrant dye degradation

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One of the main sources of pollution is the significant use of synthetic dyes in the textile industry and their direct discharge into neighboring water and land resources. To give unique remediation solutions in contrast to present treatment technologies, environmental engineers and biotechnologists must design an effective, cheap, and environmentally safer bioremediation methodology. A new treatment option for wastewater streams with refractory organic pollutants is revealed via enzymatic methods.

The ability of laccases to degrade synthetic dyes in wastewater has been established, and the degradation byproducts of these enzymatic reactions are less hazardous than parent dyes. In terms of the effectiveness of synthetic dyes' biodegradation, this study analyzes the potential of laccase enzyme as agent for laccase-catalyzed degradation of an azo-dye Orange G (OG).

The degradation of OG was followed by a spectrophotometric method, monitoring the decrease of OG concentration in time at λ=477 nm, in citrate buffer, at pH=4.5. The degree of decolorization increases when ABTS mediator is used. In the presence of the mediator, the reaction proceeds in two stages; in the first stage, which is much faster, ABTS oxidation occurs to the radical cation $ABTS^{\bullet+}$, after which it oxidizes the dye. A degree of decolorization of approximately 40% is achieved within 15 minutes at a laccase concentration of 40 nM.

The estimated kinetic parameters show a good affinity of laccase for OG and a specificity close to those obtained in literature for other phenolic substrates.

WORKSHOP 8

Advanced ellipsometric and spectroscopic techniques: applications in environment, energy and sensing

KEYNOTES

The use of UV Visible spectroscopy for the characterization of semiconductors

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Diffuse Reflectance (DR) UV-Vis spectroscopy is a useful technique for the characterization of solid samples, powders or films. Its strength lies in the following characteristics: simple to use, non-destructive, and doesn't require special sample's processing. DR UV-Vis spectroscopy allows to determine some important properties of catalytic/sensor materials such as: the oxidation state and the local coordination of a metal ion in compounds, the band gap of semiconductors, the quality of deposition in case of thin films, and the refractive index and the thickness of the thin films.

The aim of the current study is to exemplify how DR UV-Vis spectroscopy could be applied in the characterization of solid materials used in catalysis/photocatalysis. Thus, first application studied was the identification of the oxidation state and the local coordination of vanadium ions in V_2O_5/Al_2O_3, from the deconvolution of the recorded spectra. Another application discussed will be the determination of the band gap (E_g) of semiconductor oxides. The effect of the calculation method, the experimental characteristics and the data processing method on the values obtained for E_g will be follow.

Nanocarbon based hybrid materials for chemoresistive sensing

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Recently, nanocarbon-based hybrid materials have received particular attention as potential sensing layers for chemoresistive environmental sensors. We report on synthesizing binary, ternary, and quaternary carbon nanohorns (both pristine and oxidized) and graphene oxide-based hybrids and their structural characterization. Using interdigital transducer structures ("in-house designs" and commercial ones) realized on solid and flexible substrates, we did demonstrate the sensing capabilities of the synthesized hybrids for relative humidity (RH), alcohol, and oxygen. The functional characterization included the response analysis regarding sensitivity, linearity, response and recovery times, and hysteresis. The results obtained are compared with those provided by industrial-grade sensors. Sensing mechanisms and potential optimization routes are discussed.

Supercapacitor technology: Quo vadis?

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The family of the electrical energy storage devices was enlarged in the year 1954, by the invention of the supercapacitor, (US Patent 2800616) under the name of "Low voltage electrolytic capacitor" by H. I. Becker, who was not aware of the Helmholtz's electrical double layer (EDL) theory (year 1853), at the interface between a solid electronic conductor and a liquid ionic conductor. The ultrahigh value of the (super)capacitance was due to the very high specific surface area of the two activated carbon electrodes immersed in a liquid electrolyte. This first supercapacitor stores the electric charge by the electrostatic principle, and it is still commercially available these days. Replacing the activated carbon by a conducting metal oxide like hydrous ruthenium oxide (RuO_2) in the year 1970 (Trasatti and Buzzanca) triggered the discovery of the pseudocapacitor devices, where ten times higher values of the (super)capacitance were obtained by storing the electrical charge via redox reaction at and near the interface of hydrous RuO_2 and electrolyte (Conway, 1978). The high cost and scarcity of the RuO_2 electrode have triggered the work aiming to replace the noble metal with cheaper electroactive materials able to store electrical charge by the redox electrochemical reactions. It is the purpose of this presentation to present the major milestones of the material research and spectroscopic methods used for creating new avenues in the supercapacitor technology based on transition metal oxides, nanocarbonic materials and/or metallic transition metal dichalcogenides.

Composite photocatalytic beads based on TiO_2 and carbon derivates for wastewater treatment

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The study reports on composite thin films deposited on glass beads (with high surface area and easy retrieval) for the treatment of trace organic pollutants from wastewater through photocatalysis. The sol-gel coatings (TiO_2-GO=TGO and TiO_2-gC_3N_4=TCN) were deposited using two layers (a TiO_2 seeding layer, followed by the composite one). Annealing went up only to 150°C (1 h) for TGO to preserve de derivate intact and to 450°C (3h) for the TCN. Accordingly, the crystallinity degree of the two samples was 48% (TGO) and 54% (TCN). Raman and EDX analyses confirmed GO and gC_3N_4 the inclusion in the composite. The TGO thin films were more porous, but lead to a methylene blue photodegradation of only ~40% compared to 70% (for TCN).

This work was supported by a grant of Ministry of Research and Innovation, CNCS-UEFISCDI, project number PN-III-P2-2.1-PED-2021-2928, Contract no. 598PED/2022.

Future improvements in Breast cancer diagnostics: The Case for Deep Raman spectroscopy

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Breast cancer is currently the one of leading type of cancer globally, comprising 11.7% of new cancer cases diagnosed in 2020. While various imaging methods such as X mammography, ultrasound, MRI, and PET are used for detecting and clinically managing breast cancer, they are limited in their ability to provide information about the chemical nature of the malignancy. Thus, additional excisional biopsy and histopathological assessment are necessary for a definitive diagnosis. This research aims to develop a non-invasive Raman spectroscopy approach to probe the composition of inorganic chemicals buried deep within biological samples, including breast tissue. The method is based on Transmission Raman Spectroscopy (TRS) and allows for chemical-specific detection of molecules within a large sampling volume. The research focuses on detecting specific molecular markers such as calcium hydroxyapatite and calcium oxalate, which are observed in breast calcifications, as well as water content that accumulates in large amounts during cancerous tumor development. The proposed method can provide more detailed and accurate information about the composition of breast tissue, leading to improvements in diagnosis, and treatment of the breast cancer.

Smart Systems for environment monitoring and biomedical applications

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National Institute for R&D in Microtechnologies

Environment monitoring represents a stringent necessity under the drastic conditions of Climate change and the increased pollution of the environment (air, water, food) in the big cities but also in small villages. On the other side, Biomedical devices, patients monitoring, and health care system represent the bottleneck of citizen wellbeing, of medical services and at the end of the economy.

Approaching these two important sectors, environment and biomedical, by advanced micro nanotechnology devices and systems we expect: a) to increase connections with industry and enhance cooperation with business actors for commercialization of environmental monitoring technologies with a special focus on air monitoring; b) to reinforce dialogue with end-user associations, policy makers, investors, and society; c) to offer technologies and devices and systems, IoT connected ready to use for monitoring and remediation of the air/ water, d) to design and fabricate new, miniaturized, portable/wearable devices and systems for patients, medical centers, family doctors in order to measure, monitor, advertise on different diseases in an early stage; e) to help remediation of people disabilities by implantable devices; f) to increase areas such as the data analysis, communication, robots, human-machine interfaces. The extended presentation will detail some results already achieved or expected and will figure out future developments.

Ellipsometry for Investigating Combinatorial and Low-Dimensional Structures: Applications in Interface Monitoring and biosensing

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The properties of structures at the interface play a crucial role in determining the performance of biosensing devices. These properties encompass various aspects such as chemical, electronic, optical, and physical characteristics. It is essential for these properties to not only enhance optical sensitivity but also be chemically compatible with interface processes, including the adsorption or selective adsorption of target molecules for biosensing. One effective approach to increase the electric field is through the utilization of plasmons in combination with Bragg multilayers inspired by the absorption peaks of the adsorbed molecules. Combinatory techniques provide a means to explore a wide range of compositions and properties, offering the opportunity for integration into a flow cell combined with plasmonics. Immobilizing genetically engineered molecules with selective affinity, such as Ni and As, enhances the chemistry and sensitivity to specific ions and molecules. To understand interface phenomena and develop such systems, the combination of cyclic voltammetry and ellipsometry is demonstrated for the deposition of gold nanoparticles and flagellar filaments.

Raman Spectroscopy a Label-free bio-photonic tool, from stem-cells to plant biology to molecular sensing

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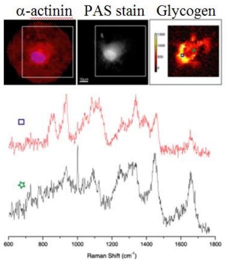
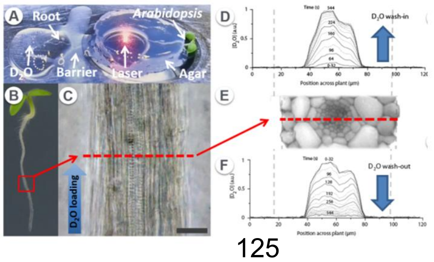
Since its discovery by Raman and Krishnan in 1926, the Raman effect has enjoyed an explosion of new applications. The past 30 years in the Raman spectroscopy history are perhaps the most exciting for biology with the demonstration of the first Raman application on live cells by Puppels in 1990. Soon after, a plethora of new applications emerged that demonstrate the true potential of Raman technology in biology. This presentation will showcase three examples where Raman spectroscopy shines as a tool in Regenerative Medicine - in-vitro differentiation of stem cells inside micro-bioreactors under physiological conditions while detecting bio-molecular changes taking place inside intact embryoid bodies during cardiogenic differentiation; Plant Biology - monitoring hydrodynamics within living root tissues by imaging the water-transporting through xylem vessels in Arabidopsis thaliana; and Molecular sensing - novel nanomembranes for the sensitive detection of low concentrations of target analytes using the Surface Enhanced Raman Scattering(SERS) effect.

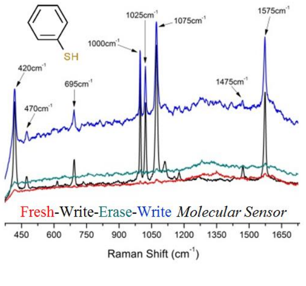
Reg. Medicine



Watching Plants Drink



Molecular sensing



Engineering Functional Materials for Diagnostic Devices

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The clinical use and acceptance of point-of-care and point-of-need diagnostic tools for the detection of pathogens and disease biomarkers is evolving and in need of a functional technical toolkit for effective implementation. There exists, however, a gap of knowledge on how to improve both technical performance and availability of rapid and low-cost testing when difficult to access and costly laboratory level infrastructure is still the only diagnostic solution.

We have demonstrated that whole-cell foodborne pathogens such as *E. Coli* O157:H7 and *Salmonella Typhimurium* can be rapidly screened for, either as single-target or multiplexed fashion, with printed low-cost paper based microfluidic devices (μPADs), aptamer technologies, biofunctionalization strategies, and quantitative color quantification, without the need of breaking down the cells and extracting the DNA. The diffusion and sample to response time is of 5 minutes or less. An insignificant change in colorimetric response for non-target bacteria indicates the aptasesnors are specific. The reported multiplexed colorimetric paper based microfluidic devices is likely to perform well for on-site rapid screening of pathogenic bacteria in water and food products.

Influence of sol-gel technological conditions on thin TiO_2 films properties

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The influence of the preparation methods on the structure of thin TiO_2 films and their optical and electrical properties is investigated. The films were prepared by sol-gel deposition method in two different ways. At the first series of samples, the wafers were dip-coated in $[Ti(OC_2H_5)_4]$ solution and dried in air at room temperature for 24 h and then annealed in air at 700 ^oC for 1 h. In the second series, TiO_2 multilayers were formed by successive deposition cycles from $[Ti(OCH_2CH_3)_4]$ solution. After each deposition, a densification treatment at 300 ^oC for 30 min was applied to the intermediate layers and, a final thermal treatment at 450 ^oC for 1 hour was used. The thickness and optical parameters of the films were determined by ellipsometric measurements. XRD data analysis has revealed crystalline films with either rutile or anatase TiO_2 phase depending on the applied sol-gel technological conditions.

To study the electro-physical properties, TiO_2 films were incorporated in metal-insulator-semiconductor (MIS) structures. From the analysis of the frequency-dependent admittance characteristics the parameters of the deep levels in the energy band gap of TiO_2 have been evaluated. The current-voltage characteristics taken at different temperatures have revealed the inter-trap tunneling as charge transport mechanism in these TiO_2 films.

Nanoscale features of the sol-gel film crystallization

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The crystallization process of the as deposited amorphous sol-gel films was investigated by high resolution transmission electron microscopy. The thermal annealing used in different situation was performed by classical furnace treatment (CFA), rapid thermal annealing (RTA) and pulse laser annealing (PLA). The investigations were performed using TEM specimens prepared by plan view and cross section methods. Some crystallization effects were produced by the electron irradiation during TEM observations. HRTEM studies were performed on ATO, ITO, ZnO and HfO2 sol-gel films. The main characteristics of the sol-gel films crystallization is the high density nucleation and a quite homogeny morphology, which lead to a final uniform nanocrystalline structure. Some stress field and texture appear in some cases.

WORKSHOP 8

Advanced ellipsometric and spectroscopic techniques: applications in environment, energy and sensing

POSTERS

Bio-derived smart thin film for biosensors

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Biosensors have shown immense potential for medical diagnosis and environmental monitoring. The development of biosensors is an interdisciplinary process, an amalgam of science, information technology, and engineering. Fundamental to biosensors is the biointerface consisting of a recognition element (biological or biologically derived) integrated or associated with a transduction platform. Biointerface performance plays a crucial role in defining the stability, sensitivity, and shelf life of a biosensor. Favorite substrates for biosensing include metals and metal oxides, silica-based materials, polymers, bio-derived polymers or a combination of these materials in the form of thin layers. The thickness determination and in situ, advantage of ellipsometry make this optical technique particularly suitable for studies of thin active layers of biological interest. Quantification of sensing and microstructural parameters of thin active layers on planar surfaces and in porous layers is of great interest, especially in fields such as biosensors and surface bio interaction. Furthermore, by combining ellipsometric measurements and bio-specificity, the possibilities for developing biosensor concepts are enhanced. A major general challenge is the integration of bio-derived materials and obtaining efficient biosensors.

Keywords: Biosensors, thin films, ellipsometry, electrochemical, biopolymers

Sensor processes based on gold nanoparticle bonded modified proteins

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The aim of our work is to develop a field-applicable heavy metal detection sensor which is able to monitor contaminations in water samples set into the ppm range by international health standards. The sensor structure is based on an evaporated gold electrode on a silicon substrate while the sensing process is provided by genetically modified bacterial flagellin proteins.

In order to provide adsorption of the protein and proper coverage of the electrode gold nanoparticles were deposited onto the surface prior tot he protein deposition. The golden nanoparticles were formed on the surface by electrochemical deposition from $H(AuCl_4)$ solution. The modified protein layer was attached to the surface using potential cycles. Morpholgy and size distribution of the golden naoparticles, the coverage and stability of the attached protein layer were monitored by Spectroscopic Ellipsometry (SE) and SEM microscopy. A special three layer SE modell was introduced for *in situ* monitoring of the protein layer formation.

Cyclic voltammetry (CV) measurements carried out on the sensors in Ni ion contaminated solutions showed that the sensor is capable of quantitative measurement in the range of 1 μM Ni concentration, i.e. for testing around the EPA health limit. CV measurements showing the selectivity of the sensor against Fe, Cu and Zn ions will also be demonstrated.

The effect of the doping on optical parameters of ZnO thin films synthesized by sol-gel method

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The ZnO and doped-ZnO thin films were deposited on glass substrate by sol-gel (dipping) method. The thin films of zinc oxide (ZnO) were doped with different dopants the Li, Al and Li-Ni (co-doped). The thin films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and spectroscopic ellipsometry (SE) to show structure, morphological and optical properties respectively. XRD and AFM revealed the hexagonal wurtzite structure and a low surface roughness of the doped ZnO thin films. The optical analysis (SE) indicated that the doped ZnO films have good transmittances (70–90%) in the visible range and the value of the optical band gap increases with doping from 3.2 eV to 3.5 eV. The optical band gap is correlated with Urbach energy, used as a measure of disorder in the film matrix after doping. In order to determine the optical energy gap (Eg) different numerical methods (e.g. Moss, Wemple or Ravindra) were used. The Eg values were found to be in good agreement with the literature data.

WORKSHOP 9

Sol-gel science and applications.

KEYNOTES

Bioactivity of sol-gel materials

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Sol-gel nanostructures, especially SiO_2 and TiO_2, are known as biocompatible materials and have been largely used as carriers for enzymes, drugs, biological markers. Antimicrobial properties of such engineered matrices can be obtained by modulating the synthesis conditions and by using modifiers. In the case of optic active materials, their light exposure was also used in order to photogenerate reactive oxygen species inducing antimicrobial mechanisms. Some recent results concerning ROS generation and the antibacterial activity of SiO_2, TiO_2 and IrOx based materials, tailored by lysozyme loading and light irradiation, will be presented.

Mesoporous silica-based composite materials for therapeutic applications

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Mesoporous silica, hollow spheres or nanoparticles, is widely investigated as support for biologically active compounds, due to its ability to host a high amount of organic molecules and the possibility to tailor its surface properties by linking organic groups or attaching inorganic nanoparticles, which could tune host-guest interactions. Recently, a lot of research has been directed towards the use of natural compounds for therapeutic applications. Herein, we report the obtaining of polyphenolic extracts from *Vaccinium myrtillus* fruits and leaves that were further embedded into mesoporous supports. The properties of prepared extracts were evaluated before and after encapsulation into functionalized silica supports. The results showed improved features for encapsulated extracts like good cytocompatibility, anti-inflammatory potential on human keratinocytes and antimicrobial activity.

Acknowledgement: The financial support from UEFISCDI through project PCE no. 117/2022 is highly appreciated.

Coatings for absorption fiber-optic sensors prepared by sol-gel method

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Materials prepared by sol-gel method have been broadly investigated for the development of optical pH sensors. By using such materials, absorption and fluorescence pH indicators have been immobilized in detection parts of these sensors employing optical waveguides, glass slides, etc. Usually, sensing characteristics of such pH sensors are reported, such as time response, and sensitivity. Only some papers have described effects of the immobilization of pH indicator in sol-gel matrices on their physico-chemical properties. This paper deals with characteristics of absorption pH indicator, methyl red, immobilized in a xerogel silica coating applied on the detection part of a U-shaped fiber-optic probe. The performance of such a probe for pH detection of saliva samples is also shown.

The fiber-optic coatings were obtained from sol prepared on the basis of TMOS, HCl, water, ethanol and methyl red. The sol was applied on a U-shaped fiber by dip-coating technique and the gel layer was dried at 80 °C for 24 hours. For comparison, the sol was applied on a glass slide at the same condition. Transmission spectra of the fiber-optic probe immersed in different calibration pH buffers were measured and employed for the determination of the indicator constant, and the probe sensitivity. Then, pH values of saliva samples were measured with the probe. The transmission spectrum of the coated slide in air was also measured and used for the characterization of the coating. It has been found that the sol-gel coating changes the indicator constant in comparison with that in bulk solutions.

Influence of Microwaves on Sol-Gel Chemistry

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The sol-gel technique is a versatile and efficient method for the preparation of pure or doped metal oxide films or powders. Combining sol-gel processing with the effects of ultrasound or microwaves further enhances the versatility of sol-gel chemistry. The microwave-assisted sol-gel approach has most frequently been used to obtain nanocrystalline, monodispersed oxide nanoparticles or to transform amorphous gels into well crystallized nanopowders. However, less focus has been directed towards the influence of microwaves on the sol-gel reactions in solutions. In the presentation some contribution for the sol-gel chemistry and for the influence of the microwaves irradiation on the chemical reactions that take place during the sol-gel synthesis will be given, as well as on the properties of the resulting samples.

WORKSHOP 9

Sol-gel science and applications

POSTERS

Functionalized three-dimensional (3D) scaffolds based on natural marine sponges and sol-gel derived mesoporous bioactive glasses for enhanced bone tissue regeneration

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In this study, the bioactivity and biocompatibility of vitamin D3 functionalized cerium-containing 3D scaffolds prepared based on sol-gel derived mesoporous bioactive glasses (MBG) and natural marine sponges were evaluated. Cholecalciferol, also known as vitamin D3 plays a crucial role as a regulator in the absorption of calcium and phosphorus, supporting osteoblasts and osteoclasts functions and promoting bone tissue regeneration. The obtained scaffolds were immersed in Simulated Body Fluid (SBF) for different periods to assess their bioactivity. Scanning electron microscopy and FTIR analyses confirmed the formation of a thin hydroxyapatite (HA) layer after only three days of immersion. Cytotoxicity and genotoxicity tests showed that non-functionalized and functionalized scaffolds were non-cytotoxic and non-genotoxic toward osteoblasts cells. In vitro, osteogenic differentiation using Alizarin Red S staining highlighted the beneficial effect of vitamin D3 functionalization on promoting osteogenesis.

Boronic acid-functionalized mesoporous silica for targeted drug delivery

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Targeted delivery of chemotherapeutic agents has received increasing attention lately in cancer therapy research, as it can address the drawbacks of classical therapeutic approach. Boronic acid derivatives have an active targeting capacity towards overexpressed sialic acid receptors found on tumor cells [1]. In this study, mesoporous silica nanoparticles (MSN) are used as carriers, due to their high surface area and porosity, which allow the loading of various functional groups as well as drug molecules. Herein, several MSN carriers were functionalized with boronic acid derivatives and loaded with doxorubicin. The properties of the obtained drug delivery systems were evaluated. The release profiles of the chemotherapeutic agent were also studied. The functionalized MSN show good biocompatibility on BJ dermal cells and antitumoral effect on BT474 cancer cells line.

Acknowledgements: The financial support of the UEFISCDI funding agency (Romania) through project no. PED 576/2022 is greatly appreciated.

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The SiO_2 based gels obtained by microwaves assisted sol-gel method

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In case of SiO_2 based gels, a comparative study was conducted in order to establish the influence of the precursors and the preparation method on thermal behaviour, morphology and structural properties of the gels obtained by the sol-gel (SG) and microwave assisted (MW) sol-gel methods. As precursors tetraethoxysilan (TEOS) or methyltriethoxysilan (MTEOS) are used for obtaining xerogels. The gelling process of the prepared solutions and xerogels obtained were characterized by Fourier-transform Infrared Spectroscopic (FTIR) and their decomposition was performed by thermal analysis (TG/DTG/DTA). The thermal stability of the gels is influenced by their composition rather than by the conditions of the preparation process. Hybrid Si-alkoxides lead to gels that show differences due to different organic fragments linked to the inorganic network. The morphology and structure of thermally treated samples were investigated by Scanning Electron Microscopy (SEM), respectively X-ray Diffraction (XRD). Their properties will be influenced by the observed differences in the structure of the gels.

Cu doped TiO_2 nanostructures obtained by microwave assisted sol-gel and sol-gel methods

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Different methods are available for preparation of pure and doped TiO_2 powders or films. In the present work the results of obtaining Cu doped TiO_2 nanostructures by the sol-gel (SG) and the microwave-assisted sol-gel (MW) methods are presented. The comparative investigations of the structure and morphology of the as-prepared gels and of the nanopowders obtained by annealing was realized by FT-IR, TG/DTA-MS, SEM, X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS).Thermal analysis studies have shown substantial differences in the decomposition of gels depending on the method of preparation and on the amount of the dopant (2.0 and 5.0 mol % CuO). The thermally treated gels at 450 ^{o}C showed for the samples obtained by the SG method the formation of TiO_2 anatase phase, while in the case of samples obtained by the MW method beside anatase phase, the presence of small amounts of rutile was observed. The different crystalline structure of the mentioned samples could be correlated both with method of preparation and with the presence of cooper ions with different valence.

Cu doped Zinc Oxide Nanoparticles for Nanofluids: Synthesis and Characterization

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Due to its outstanding properties, ZnO is one of the most researched oxides. It possesses excellent heat conductivity, a high refractive index, and antimicrobial qualities. Doped ZnO has been manufactured in a variety of ways, but the sol-gel method has drawn the most attention due to its stability, and affordability. The synthesis of Cu-doped ZnO nanostructures, with a focus on the sol-gel method, is summarized in this study, along with the many variables affecting the morphological, structural, and optical characteristics of the materials generated. CuO has been extensively used in the creation and production of super-capacitors, semiconductors, electric and magnetic materials. The thermogravimetric and differential thermal analysis were performed to determine the influence of reactants utilized as well as the effect of copper content on the thermal behavior of the resulting gels. The intended thermal treatment was established based on the thermal analysis results in order to achieve the desired qualities in the powders that were produced. The results of the XRD analysis of the powder showed that the samples had zincite structure. Additionally, infrared spectroscopy confirmed the incorporation of doping ions into the ZnO lattice. The primary areas of interest are microelectronics, photocatalysts, energy storage materials and nanofluids.

Acknowledgments The Romanian Academy–Hungarian Academy of Sciences Joint Research Project 2023-2025 entitled "Composite nanofluids for providing effective heat transfer" is acknowledged.

WORKSHOP 10

Physical chemistry of soft materials

KEYNOTES

Mesoscale structure formation in solutions of ionic liquids

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Aqueous solutions of a prototypical set of methyl-imidazolium (MIM) - based ionic liquids is investigated by UV Raman spectroscopy and Small-Angle Neutron Scattering in the water-rich domain. Selected Raman signals in different wavenumber ranges provide insights into the local organization of cation-anion pairs as a function of the increasing amount of water in a wide range of concentrations. The high-frequency range of Raman spectra is analyzed by a differential method to extract from the OH stretching profile of water the solute-correlate (SC) spectra, which emphasize the molecular structuring of the interfacial water present in the hydration shells around the selected anions. The neutron scattering data show the water – IL segregation at nanoscale.

The peculiar solvation behavior for the different MIM-based mixtures was related to the hydrogen bonding features of the hydrating water molecules. The ionic liquid [MIM][Cl] seems more sensitive to hydration than [MIM][TfO] even in an extremely hydrated regime.

Multiple nanoaggregation strategies for multi-stimuli responsive amphiphilic block copolymers

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Formation or disassembly of nanoaggregates in solution is one of many behaviors that can be triggered on stimuli-responsive materials by physical or chemical changes. This study focuses on an amphiphilic block polymethacrylate that combines a PEG-based thermally-responsive hydrophilic block with one that, through the versatile 2-(hydroxyimino)aldehyde (HIA) functional group, is sensitive to pH changes and exposure to light or metal cations. Thereby, multiple nanoaggregation strategies are available for this copolymer in solution, namely block-selective solubility, a pH-induced switch from double-hydrophylic to amphiphile or metal cation ligation. The different nanoaggregates obtained with a single polymer through these strategies are discussed. The impact of nanoaggregation on the photochemistry of the HIA group is also highlighted.

Acknowledgements: This work was supported by Sapienza University of Rome (research grants AR120172B31E3F4A, AR12117A85B1E4F2, B84I19004610005, and B89C20002540001) and by the CNRDISBA project "NutrAge" (FOE 2021).

Structure and reactivity of gels and colloidal solutions probed by EPR

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A PEG–Tyr block copolymer forms a colloidal solution in water at room temperature which spontaneously converts into a gel upon heating. A micellar solution and a gel can therefore be studied under identical experimental conditions. We used EPR spectroscopy of spin-labelled copolymers to compare physical properties of micelles and gels and then explored their chemical reactivity (photochemical degradation and dimerisation of tyrosine).

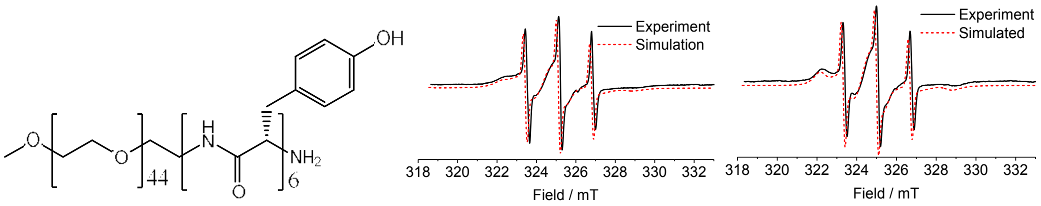

Fig. 1. X-band EPR spectra of spin labelled PEG2000–Tyr$_6$ (left) micelles (centre) and gel (right).

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Redox Processes Mediated by Gold Nanoparticles Encapsulated in Polymeric Gels Evidenced by Spectroscopic Methods

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Gold nanoparticles (AuNPs) stabilized on solid supports are used in a variety of applications in catalysis, materials science and life sciences. We explore here the catalytic properties of hard/soft hybrid materials prepared by reduction of an Au^{3+} salt by biocompatible polymer matrices: covalent polymeric gels obtained by reaction of isocyanate-functionalized polyethylene glycol (PEG900) with β-CD[1] and polysaccharide gels (alginate, chitosan). Two redox processes mediated by the hydrogel-embedded AuNPs are investigated: i) the reduction of 4-nitrophenol by NaBH$_4$, followed by UV-Vis spectroscopy, and ii) the reduction of nitroxide radicals (TEMPO, as either spin probe or spin label) and oxidation of their corresponding hydroxylamines, followed by EPR spectroscopy. The catalytic activity of the materials increases in the order chitosan/AuNPs < alginate/AuNPs < PEG900/β-CD/AuNPs. For alginate/AuNPs, two domains with different reaction rate constants are observed, the second coinciding to a loss of structural integrity of the material, most probably due to displacement of Ca^{2+} ions from the gel network by Na^{+} ions. The EPR data show that the catalytic efficiency of the PEG900/β-CD/AuNPs material decreases with increasing ratio of PEG900 chains to β-CD units.

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The poloxamers' aggregation behaviour in water and the influence of an anionic nonsulfated glycosaminoglycan on the micelle formation

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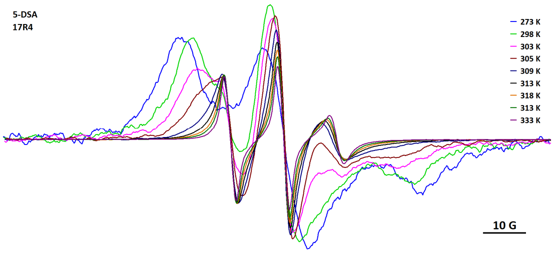
Poloxamers are linear block copolymers used in pharmaceutical formulations to optimize the drug delivery. In solution, Pluronics display interesting properties. While the reverse Pluronics can form different types of aggregates, the regular type of those amphiphilic surfactants form micelles. The aggregation behaviour of Pluronics and the influence of hyaluronic acid (HA), on the micelle formation have been investigated using EPR spectroscopy, μDSC, rheology and DLS methods.

In 17R4, the presence of HA has a striking influence on the spectral features of the 5-DSA spin probe. In the absence of HA, the dynamic of 5-DSA is highly restricted. The μDSC thermogram for F127 shows two endothermic peaks corresponding to micellization and to micelle-to-gel transition. For 10R5, DLS data indicate the presence of small aggregates. HA induces a significant increase of the aggregate size. At 290 K the hydrodynamic radius is 35 nm, while at 295 K it is only 18.6 nm.



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WORKSHOP 10

Physical chemistry of soft materials

POSTERS

Supramolecular polymeric assemblies formed by host-guest interaction

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Efforts have been made in recent decades to develop advanced supramolecular materials as well as investigate their applications in environmental remediation, catalysis, nanomedicine, electronic devices, sensors, and more. The host-guest supramolecular assemblies generated between functionalized alginate (Alg) with cyclodextrin (CD) units and functionalized polyacrylic acid (PAA) with alkyl chains were investigated in this study. Methods used to describe the behavior of polymers and their mixtures include, FTIR spectroscopy, dynamic light scattering, surface tension, fluorescence spectroscopy along with electron paramagnetic resonance (EPR) spectroscopy.

The surface tension of Alg-CD decreases significantly in the presence of hydrophobically modified polyacrylates, highlighting the effect of alkyl chain length. The fluorescence study demonstrates that that probe is solubilized closer to the nonpolar core in the presence of hydrophobically modified polyacrylates. The local changes in the EPR spectra of the mixtures of spin-labelled Alg-CD and polyacrylates are small, which can be explained by the fact that the main components involved in Ca^{2+} complexation and host-guest interactions are diamagnetic. The study revealed that the mixture between Alg-CD units and PAA-alkyl chains develop supramolecular host-guest assemblies which are strongly dependent on the alkyl chain length attached to polyacrylate.

Formation and hosting properties of smart systems consisting of surfactant, polymer and their mixtures

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The investigation of polymer-surfactant interactions is important not only from academic point of view, but practical one because mixtures of polymer and surfactant are extensively used in a wide range of domestic, industrial, and technological applications. In this work it is mainly investigated the interaction between some polyacrylic acid based polymers (unmodified and hydrophobically modified polyacrylic acid and polyacrylates) and surfactants. It is shown that, depending on surfactant, the interaction occurs cooperatively by hydrophobic attraction, hydrogen bonds or electrostatic forces leading to earlier micelles formation. This means that the polymer favors the surfactant aggregation inside its coil (it wraps around the micelles) so the critical aggregation concentration (CAC) is lower than the critical micellar concentration (CMC). The formed complexes permit a better solubilization of hydrophobic and less hydrophobic compounds. These systems, as individuals or their mixtures, respond to external stimuli such pH, temperature etc., which make them the so called smart systems. The biocompatibility of the investigated surfactants and polymers, the very low CMC and CAC, their ability to host hydrophobic or less hydrophobic compounds make them very attractive for many and various domains.

Spin labelled polysaccharides as probes for the formation of Alginate/Chitosan Interpenetrated Networks

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This study analyzes the physico-chemical properties of interpenetrated and semi-interpenetrated polymer networks resulting from cross-linking chitosan with glutaraldehyde and alginate with Ca^{2+} cations. These properties highlight the influence of the order of addition of the cross-linking agents on the polymer mixture. In order to observe the difference between the studied systems, two methods were used: electron paramagnetic resonance spectroscopy (EPR) and infrared vibrational spectroscopy (IR). While IR spectroscopy is a frequently used method for the characterization of gels, EPR spectroscopy is less used but the latter method provides information about the dynamics of systems from the region where the radical is located. The IR spectra of samples resulting by adding Ca^{2+} as the first cross-linker are similar to that of the alginate gel, and the spectra of samples in which glutaraldehyde is firstly added resemble the chitosan gel spectrum. Using spin-labelled alginate and spin-labelled chitosan allowed monitoring the changes occurring in the dynamics of the systems. The results show that the dynamics of interpenetrated networks influences the order of addition of the cross-linking agents, and that the formation of the alginate networks determines the characteristics of the system.

Laccase immobilized onto CS-PAA microspheres applied for synthetic dyes decomposition

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Synthetic organic dyes are ubiquitous contaminants of water bodies that hinder efforts to obtain safe and available clean water. Ideally, the harmful effects of synthetic dyes can be mitigated by selective decontamination of water using enzymes. The main disadvantage of these natural catalysts is created by unstable structure, that is easily destabilized by unfavorable chemical and physical factors. Therefore, we proposed a procedure to improve the resistance of the *Trametes versicolor* Laccase against pH, temperature and storage by immobilization on a solid support formed from chitosan (CS) and polyacrylic acid (PAA). To understand how the polymeric mixture stabilizes and improves the catalytic properties of laccase, kinetic studies were performed using a classic substrate. As a practical application, the immobilized enzyme was tested in the decomposition of an azo dye and the degradation mechanism was proposed. Finally, the molecular docking was used and the optimum binding mode between azo dye and enzyme was predicted.

The behaviour in surfactants and oligo(ethylene glycols) of a newly synthesized spin labelled-curcumin

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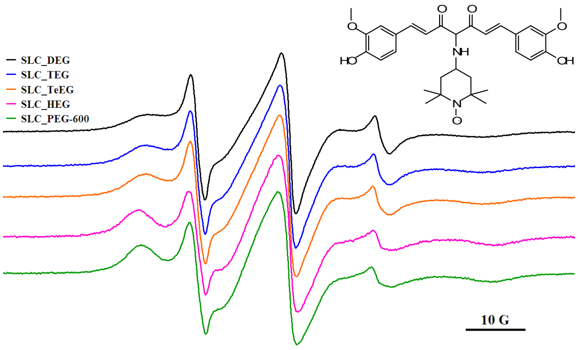
Curcumin is a natural compound with diaryl-heptanoid structure, and the recent studies show the pharmaceutical effects of this 1,3 β-diketone. The reactive methylene group can generate new derivatives of curcumin with a pronounced antitumoral activity. A new spin labelled-curcumin (SLC) was synthesized and characterized and its behaviour in non-ionic, cationic and anionic surfactants has been investigated through Electron Paramagnetic Resonance (EPR) spectroscopy. In solutions of reverse pluronics, 10R5 and 17R4, the spin probe has a fast motion ($\tau \sim 2\text{x}10^{-10}$ s). The EPR parameters of SLC are sensitive to SDS assemblies. A drastic change in spin probe dynamics reflected in EPR spectrum by a distortion of the spectral lines was observed in oligo(ethylene glycols).



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Insights into the Interaction of Gold Nanoparticles with *Trametes versicolor* Laccase

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The interaction of gold nanoparticles (AuNPs) with laccase from Trametes versicolor (Lc) was investigated by spectroscopic (Fluorescence, Circular Dichroism - CD) and calorimetric (differential scanning microcalorimetry – µDSC, isothermal titration calorimetry - ITC) methods. The complex action of AuNPs on the enzyme activity was studied using 2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS). Molecular docking was employed to predict the optimum binding mode and the nature of interaction forces between ABTS and Lc. The thermal stability of the enzyme was determined both in water and in sodium phosphate buffer pH 6, in the absence and presence of AuNPs.

The study exposes new features of enzyme-gold nanoparticles interaction, and provides a deeper insight into the complex action of nanoparticles on enzyme kinetics. The results may offer valuable information for laccase-based bio-nanoconjugates and their applications in the environmental remediation field.

Physico-Chemical Changes Induced by Gamma Irradiation on Some Structural Protein Extracts

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In this study, the effect of gamma irradiation at the dose of 10 kGy and UV radiation, on proteins structure was investigated by calorimetric (μDSC) and spectroscopic (ATR-FT-IR, circular dichroism and EPR) methods. Proteins were extracted from fish scales, cowhide and sheep wool. The protein were stabilized by mixing them with a riboflavin solution. The μDSC experiments showed that gamma irradiation influences differently the thermal stability of proteins depending on their structure. After gamma irradiation, the thermal stability of keratin decreases, while a resistance to thermal denaturation was observed for collagen and gelatins. The ATR-FT-IR spectra have shown that gamma irradiation induces changes in the vibrational modes of the amide groups. These changes are associated with protein denaturation, most meaningfully were observed for keratin. The circular dichroism analysis have evidenced that gamma radiation produces more significant changes in secondary structure of proteins than exposure to UV radiations. Riboflavin has different effects on the secondary structure of the investigated proteins. For keratin and fish gelatin, a stabilizing effect was observed while a destabilizing effect for bovine gelatin was, observed in both irradiated and non-irradiated samples. The EPR spectroscopy shows the presence of the free radicals centered on oxygen for the gamma-irradiated samples, and the increase in their EPR signals over time owed to the presence of riboflavin.

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