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PALERMO ITALY 2019

EAST WEST

Chemistry Conference

November 13-15, 2019

The Campus of the University of Palermo

▶ ABSTRACT & PROCEEDING
BOOK

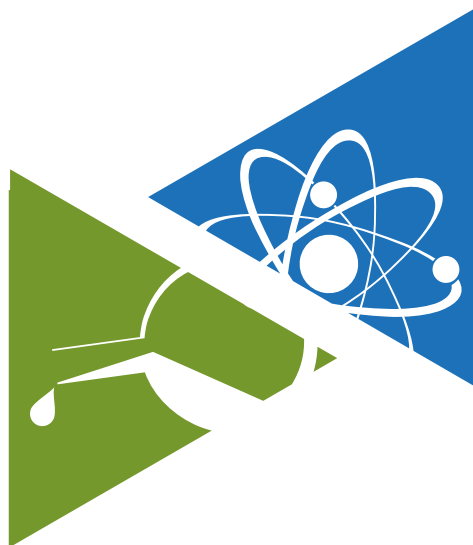
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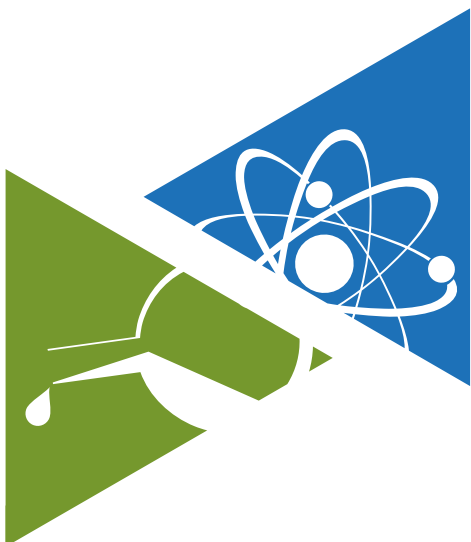
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INDEX

Foreword	5
Committees	6
Scientific Program	8
Poster Program	11
Invited Speakers	12
Oral Presentations	18
Posters	48



Dear Colleagues,

Chemistry as a central science has a dramatic impact on advancement of societies. From new synthesis methods, new drug molecules and polymers and development of novel materials to understanding the molecular machinery in living systems, chemistry plays a significant role. The conferences are the platforms for exchange of ideas, scientific development of young scientists, and establishing new collaborations. With this in mind, the Turkish Chemical Society and University of Palermo have joined the forces to organize EastWest Chemistry Conference in 2019. We welcome contributions from all branches of chemistry and related areas such as nanoscience and nanotechnology, and bio-nano-materials. We hope that the conference will be a very interdisciplinary scientific platform benefitting from all branches of chemistry.

We aim to keep the conference standards high and we hope that it will be a unique opportunity for scientists from a wide variety of chemical disciplines to exchange and inspire new ideas for collaboration. Therefore, your participation to the EastWest Chemistry conference in Palermo in 2019 will be invaluable. We are looking forward to seeing you during the conference.

Sincerely yours,

Prof. Dr. Mustafa Culha
Congress Chair

Prof. Dr. Giuseppe Lazzara
Congress Chair

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SCIENTIFIC PROGRAM

November 13, 2019

11:00-14:00	REGISTRATION
14:00-14:30	Opening Chair: Prof. G. Lazzara
	Prof. S. Milioto <i>Head of the Department of Physics and Chemistry</i> Prof. S. Buscemi <i>Head of the Department of Biological, Chemical and Pharmaceutical Sciences and Technologies</i> Prof. F. D'Anna <i>President of Sicily Section for Italian Chemical Society</i> Prof. Onder Metin <i>Turkish Chemical Society Associate</i>
14:30-15:40	Chair: Prof. F. D'Anna
14:30-15:00	PLENARY-1: Prof. Julia Perez Prieto - <i>University of Valencia, Spain</i> "Gold Nanomaterials as Colorimetric and Luminescent Sensors"
15:00-15:20	S-001 - Giulia Raimondi , PCFC cathode materials: influence of structure and local distortions on proton uptake
15:20-15:40	S-002 - Giuseppe Cavallaro , Halloysite/Keratin mixtures for hair treatment purposes
15:40-16:00	COFFEE BREAK
16:00-17:10	Chair: Prof. Onder Metin
16:00-16:30	PLENARY-2: Prof Rui Fausto - <i>University of Coimbra, Portugal</i> "Infrared-Induced Chemistry: From Changes in Molecular Shape to Chemical Reactions and Unusual Crystals"
16:30-16:50	S-003 - Cemil Alkan , Theoretical Through Microencapsulated Phase Change Materials for Thermal Energy Storage and Thermochromicity Applications
16:50-17:10	S-004 - Hüseyin Akbaş , Some Ionic Liquids As Phase Change Materials And Their Microstructural Constitutions
17:10-18:30	POSTERS

SCIENTIFIC PROGRAM

November 14, 2019

08.30-09.00	REGISTRATION
09:00-10:10	Chair: Prof. Rawil Fakhrullin
09:00-09:30	PLENARY-3: Dr. Erwan-Nicolas Paineau-Lanone <i>French National Centre for Scientific Research CNRS, France</i> "Synthetic imogolite nanotubes: a flexible building block with multipurpose applications"
09:30-09:50	S-005 - Giuseppe Arrabito , Printing Biology for Advanced Synthetic Biosystems
09:50-10:10	S-006 - Ömer Işıldak , Complexes for Thermal Energy Storage Applications
10:10-10:30	COFFEE BREAK
10:30-12:40	Chair: Prof Rui Fausto
10:30-11:00	PLENARY-4: Prof. Sinan Akgöl <i>Ege University, Turkiye</i> "Polymeric nanomaterials for Biomolecules"
11:00-11:20	S-007 - Aurelio Bonasera , Superhydrophobic Titania-based Hybrid Nanocomposites for Cultural Heritage Protection
11:20-11:40	S-008 - Salvatore Cataldo , Activated Biochar From Posidonia Oceanica. A New Adsorbent Material Of Hydrocarbons From Wastewater
11:40-12:00	S-009 - Elena Kovaleva , Evaluation of Stability, Antioxidant Activity and Antidiabetic Effect of Isoflavones Extracted from Raw Sources Using Natural Deep Eutectic Solvent
12:00-12:20	S-010 - Georgii Sokolsky , Green polymer packaging coating on metals with volatile inhibitors and improved degradation rate
12:20-12:40	S-011 - Melike Sevim , mpg-C ₃ N ₄ Supported NiPt Alloy Nanoparticles: Efficient Heterogeneous Catalyst for the Transfer Hydrogenation of Nitroarenes
12:40-14:30	LUNCH
14:30-15:40	Chair: Prof. Sinan Akgöl
14:30-15:00	PLENARY-5: Prof. Ignazio Blanco - <i>University of Catania, Italy</i> The Rediscovery of POSS; a molecule rather than a filler
15:00-15:20	S-012 - Serena Riela , Chemical modification of halloysite nanotubes for biological application
15:20-15:40	S-013 - Marina Massaro , Synthesis of ZnO nanoparticles supported on halloysite nanotubes for catalytic applications
15:40-16:00	COFFEE BREAK
16:00-17:10	Chair: Prof. Ignazio Blanco
16:00-16:30	PLENARY-6: Assoc. Prof. Dr. Onder Metin - <i>Koc University, Turkiye</i> "Nanocatalysis: A key for the development of sustainable organic synthesis methodologies and efficient energy systems"
16:30-16:50	S-014- Vincenzo Campisciano , Covalent Modification of Carbon Nanoforms and SBA-15 Surfaces with Imidazolium-based Salts for Pd species immobilization: Design of Efficient Catalysts
16:50-17:10	S-015 - Svyatoslav Nastyshyn , Silver nanoparticles embedded into thermo-switchable polymer grafted brushes: morphology, shape, temperature-responsivity and toxicity
17:10-18:30	POSTERS
20:00-12:00	CONFERENCE DINNER

SCIENTIFIC PROGRAM

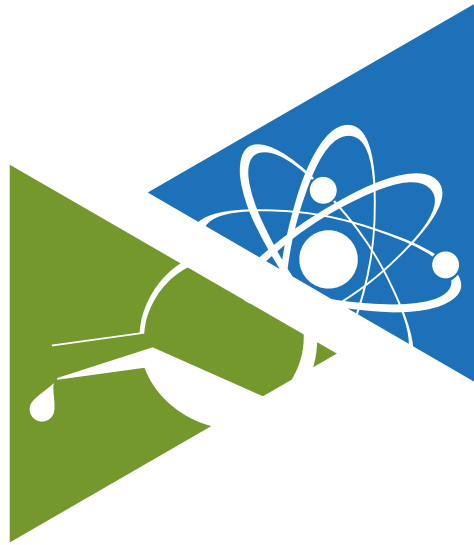
November 15, 2019

09:00-10:30	Chair: Prof. Andrei Rotaru
09:00-09:30	PLENARY-7: Prof. Rawil Fakhruллин - <i>Kazan Federal University, RF</i> "A ray of light in the darkness: dark field/hyperspectral microscopy for imaging and characterisation of nanoscale particles"
09:30-09:50	S-016 - Riccardo Rozza , The computational approach to the study of a complex nanotubular system
09:50-10:10	S-017 - Ketevan Kupatadze , Popularisation chemistry for Teaching Chemistry (Georgian Experience)
10:10-10:30	S-018 - Ostap Lishchynskyi , Grafted Polymer Brushes: Poly(Butyl Methacrylate) vs Poly(Butyl Acrylate): Influence of Temperature on the Wettability, Morphology, Protein Adsorption
10:30-12:20	Chair: Prof. Giuseppe Lazzara
10:30-11:00	PLENARY-8: Prof. Andrei Rotaru - <i>University of Craiova & INFLPR, Romania</i> "Thermokinetic and (micro)structural study of various types of ligno-cellulosic materials"
11:00-11:20	S-019 - Merve Dandan Doğancı , Synthesis and Characterization Of Star Shaped PCL Polymers Having Different Arm Numbers and Their Blends with PLA
11:20-11:40	S-020 - Almila Cerci Izmit , Production of Biodegradable Film by Using Ternary Blends with Mineral Filler
11:40-12:00	S-021 - Filippo Parisi , Clay Mineral Composites for green and sustainable applications
12:00-12:20	S-022 - Nagihan Özbek , Preparation of Functional Surfaces with Light-Induced Tetrazine Click Reaction
12:20-12:40	CLOSING

POSTERS

POSTER PRESENTATIONS

P-01	Asmaa Abu El-Soad, Alexander Pestov, D. Tambasova, Viktoria Osipova, Giuseppe Lazzara and Elena Kovaleva. Silylation of halloysite nanotubes with (3-chloropropyl)-trimethoxy silane
P-02	M. M. H. Desoky, P. Quagliotto, C. Barolo, G. Viscardi, A. Di Carlo and N. Yaghoobi Niab. Effect of regioregularity and molecular weight control of HTMs on perovskite solar cells performance
P-03	Fulden Ulucan, Kevser Kusat Ol and Sinan Akgol. Nanopolymeric System Development for Glycoproteins Recognition
P-05	Antonio Palumbo Piccionello, Paola Marzullo, Silvestre Buscemi, Sonya Vasto and Marta Di Carlo. Synthesis of quinalzolin-4-ones, with potential anti-diabetic activity, through reductive rearrangement of 1,2,4-oxadiazoles
P-06	Gulce Ogruc Ildiz and Rui Fausto. Conformational Analysis and Photochemistry of 2-Chloro-6-fluorobenzoic Acid Monomers in Solid Xenon
P-07	Liudmyla Khrokalo and Victoria Vorobyova. Bactericidal Effect for AgNPs System Obtained on a base of AgNO ₃ and Currant Pomace Extract
P-08	Olga Nosovska. Arsenic removal from natural water by adsorption/membrane filtration
P-09	Mihail Tereshkov, Svitlana Nahirniak, Tetiana Dontsova, Grygorii Krymetz, Andrii Lapinsky and Ravi Singh. Remote Monitoring of Quality of Agricultural Soils
P-10	Olena Chygyrynets, Viktoriya Vorobyova and Anastasiia Shakun. Chemical Characterization of Apricot Pomace: A Possible Use of an Agricultural Waste
P-11	Dar'Ya Nechyporuk. Effective Liquid Coagulants from Secondary Raw Materials
P-12	Erdinç Doğancı and Merve Dandan Doğancı. Effects of Diisocyanate Compatibilizers on the Properties of Star-Shaped Poly(ϵ -caprolactone) /Poly(lactic acid) Blends
P-13	Nataliia Tolstopalova, Olga Sanginova and Ihor Asterlin. Water Harmony Projects: Impact on Water Related Education
P-14	Tatyana Zhuk, Vladislav Bakhonsky, Viktoria Vorobyova, Pavel Gunchenko, Andrey Fokin, Bifu Li, Hongyan Chen and Jing Li. Selective Metal-Free Aerobic Oxidations of Toluene to Benzaldehyde with N-Hydroxyphthalimide in Trifluoroacetic Acid
P-15	Viktoriya Semeniv, Anna Myhalchuk and Oleksandra Berezhnytska. Silver Complexons as Anti-Microbial Additives to Cosmetic Products
P-16	Yana Shymborska, Kamil Awskiuk, Joanna Raczowska, Monika Brzychczy-Włoch, Andriy Kostruba, Halyna Ohar, Ostap Lishchynskyi, Andrzej Bernasik, Andrzej Budkowski, Svyatoslav Nastyshyn and Yuriy Stetsyshyn. Polymer-based coatings with self-activating temperature-dependent antibacterial properties
P-17	Tetiana Shevtsova, Zoriana Demchuk, Andriy Voronov, Stanislav Voronov and Sanjana Choudhary. The Feasibility of Synthesis of Latex Materials Made from Fully Renewable Monomers
P-18	Georgii Sokolsky, Olena Chygyrynets, Luiza Zudina, Eugenii Boldyrev and Victor Andreev. NH ₄ ⁺ -templated and co-doped with Fe ²⁺ and Co ²⁺ at electrodeposition OMS-2 hollandite
P-19	Georgii Sokolsky, Victor Andreev, Tamara Tomila, Michail Kompanets, Olena Chygyrynets and Maria Trubchaninova. FTIR Study of Non-Enzymatic Collagen Cross-Links Formation Induced by Aminoacid Copper Coordination Compound
P-20	Yana Aleeva, Aurelio Bonasera, Clara Chiappara, Michelangelo Scopelliti, Delia Chillura Martino and Bruno Pignataro. Titanium Dioxide Nanocomposites with Remarkable Hydrophobicity and Catalytic Activity for Cultural Heritage Applications
P-21	Giuseppe Arrabito, Vito Errico, Adele De Ninno, Felicia Cavaleri, Vittorio Ferrara, Bruno Pignataro and Federica Caselli. Impact of Inkjet Printed Oil Droplets onto Immiscible Water Interfaces: Fragmentation and Electrical Characterization
P-22	Gulce Ogruc. Vibrational Spectroscopy as a Tool to Diagnose Psychiatric and Neurodevelopmental Disorders, Through Chemometrics Analysis of Spectral Data of Blood Plasma Samples



PLENARY SPEAKERS

PLENARY-1

Gold Nanomaterials as Colorimetric and Luminescent Sensors

Julia Pérez-Prieto

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Abstract

Sensors and probes are materials that report the presence of specific ions, molecules or molecular events in vitro or in cells by communicating a measurable signal, often a light-based readout. They may function through selective interaction or attachment to a molecule of interest or undergo conformational changes.

Gold NPs larger than 3 nm (AuNPs) possess unique optical and electronic properties that are not available in either molecules or their bulk form. Light excitation with the appropriate wavelength causes the oscillation of the localized electrons in the metallic nanostructure and, as a consequence, they present a strong absorption at the visible light (surface plasmon resonance band, SPB) and their colloids can be clearly observed by the naked eye at nanomolar concentrations. However, they are hardly emissive.

When gold NPs are extremely small (< 3 nm), considerable electronic energy quantization occurs and the nanoparticles exhibit a discrete electronic structure and molecule-like properties. These quantum-sized nanoparticles are new materials and have been termed nanoclusters (AuNCs) to differentiate them from plasmonic AuNPs. They present size-dependent emission with a large Stokes shift.

We comment here on strategies developed by our group for sensing small analytes, based on the relevant properties of these two types of gold nanomaterials.

Keywords: gold nanocluster, gold plasmonic nanoparticles, sensing.

I. Introduction

The peak position and the intensity of plasmonic AuNPs depend on their size and shape (peak between 520 and 550 nm for spherical NPs of 3-50 nm), local environment and, interestingly, the interparticle distance. The assembly of AuNPs with a specific organic capping can lead to a red-shift and widening in the extinction band and blue colloids are obtained in this way. AuNPs are being applied as colorimetric sensors by making use of analyte-induced changes in their aggregation state.

The emission lifetime of the AuNCs depends on the nature of the ligand's anchoring group. Thiolate-capped AuNC photoluminescence occurs in the microsecond scale, while that of phosphate-capped AuNCs occurs in the nanosecond scale. The former originates from ligand-to-metal charge transfer, while the latter is attributed to electronic transitions of the gold core. AuNCs are being used as a promising alternative to two-photon luminophores, due to their strong emission, large two-photon absorption cross-section, and great photostability.

We describe here five assays on the use of gold nanomaterials in sensing, three of them with plasmonic nanoparticles as colorimetric sensors, and two others with AuNCs as photoluminescent sensors.

II. Experimental Set-up and Procedure

The gold nanomaterials were prepared using two different approaches. In the first assay, bare plasmonic AuNPs were prepared by irradiating an aqueous solution of H₂O₂ and HAuCl₄ with a 532-nm laser until the Au³⁺ band disappeared and that of H₂O₂ decreased to approach the absorbance of the plasmon band at 520-525 nm. In the second and third assays, oleilamine-capped AuNPs were reacted with two different nucleoside derivatives to lead to nucleoside-capped AuNPs. The exchange of the oleilamine ligand by the nucleoside was performed in chloroform, thus leading to the assembly of the AuNPs.

On the other hand, the AuNCs were passivated with dinucleotide; they were prepared by initially synthesizing the plasmonic dinucleotide-capped AuNPs and then etching them by adding HCl.

III. Results and discussion

The absence of an organic capping on the bare AuNPs together with the high affinity of the amine groups of the spermine for the nanoparticle surface made it possible to detect, in a highly selective fashion, nanomolar levels of spermine in human urine (healthy donors, cancer patients).

In addition, AuNPs decorated merely with a type of a nucleobase can lead to unique nanohybrids, which selectively or specifically recognise an analyte vs. analogues. These structures make use of the synergistic cooperation between the plasmonic nanoparticle and the nucleoside to build a colourimetric probe based on the formation, in medium polar to polar solvents, of nucleoside channels, whose size and strength play a key role in molecular recognition. The nucleoside channels allow access to the analyte according to their size, and an efficient interaction between the analyte and the nucleobase destabilizes the channels, thus eventually leading to nanoparticle disassembly.

On the other hand, bright dinucleotide-capped AuNCs exhibit an astounding ratiometric fluorescent response to pH variation. Their performance is related to the change, produced by the variation in pH, in the degree of chelation of multidentate ligands, specifically phosphates, on the AuNC surface.

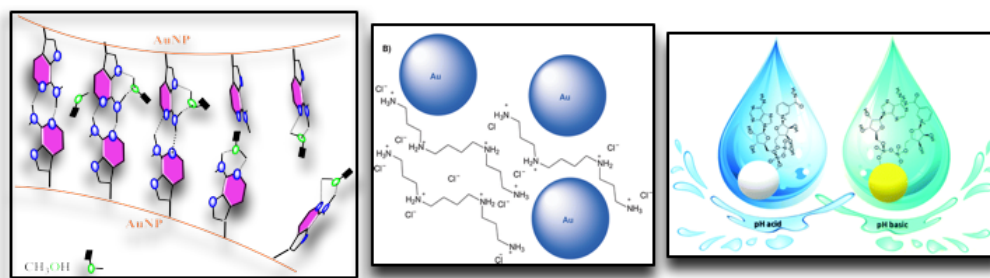


Fig. 1: Different strategies of sensing based on gold nanomaterials; left) formation of nucleoside channels by assembly of nucleoside-capped AuNPs and unzipping caused by the analyte; centre) aggregation of bare AuNPs in the presence of the analyte (polyamines); c) sensing of pH by changing the chelation degree of the ligand on the AuNC surface.

IV. Conclusions

We demonstrate here that bare plasmonic nanoparticles, as well as those decorated with simple nucleosides, can be useful as colorimetric sensors of small analytes by taking advantage of the change in the SPB peak position and intensity of the interparticle distance. On the other hand, AuNCs have proved to be useful as fluorescent pH sensors on the basis of pH-regulated interactions between the ligand anchoring group and the AuNC surface.

Acknowledgements

We thank MINECO (Project CTQ2011-27758, CTQ2014-60174, and CTQ2017-82711) for financial support.

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PLENARY-2

Infrared-Induced Chemistry: From Changes in Molecular Shape to Chemical Reactions and Unusual Crystals

Rui Fausto

University of Coimbra, Portugal

The investigation of infrared-induced chemical is a recent field of research, though its roots may be traced back to the 1963 historical paper by Hall and Pimentel [1], where the relative populations of the two conformers of matrix-isolated nitrous acid could be varied by in situ IR broadband irradiation. Because of lack of efficient selectivity, however, this type of chemistry did not collect, at that time, too much interest among the scientific community. Only 34 years later, the subject gained importance, when high-selectivity in controlling the chemical reactions could be achieved by introduction of narrowband IR excitation [2,3]. Since then, IR-induced chemistry has been developing and, nowadays, it can be used to control the molecular conformation with both high selectivity and efficiency. Furthermore, more recently IR excitation has also been shown to be usable to induce (or facilitate) other types of chemistry [4,5]. The Laboratory for Cryospectroscopy and Biospectroscopy of the University of Coimbra (CQC – Department of Chemistry) has been pioneering this type of investigations, and in this talk I will present a summary of some of our most relevant achievements in the field:

- Efficient control of the molecular conformations by means of narrowband tunable IR excitation, including the generation of rare, elusive conformers otherwise inaccessible to experimentation;
- Application of the research strategy to more complex systems, like dimers;
- Controlling the conformation of selected fragments in a molecule by vibrationally exciting remotely located in space antennas;
- Using vibrational excitation to facilitate tunneling reactions, including processes involving cleavage of chemical bonds;
- Generation of novel high-energy crystals built from high-energy conformers.

Acknowledgements: This investigation has been performed within the Project PTDC/QEQ-QFI/3284/2014 – POCI-01-0145-FEDER-016617, funded by the Portuguese “Fundação para a Ciência e a Tecnologia” (FCT) and FEDER/COMPETE 2020-EU. The Coimbra Chemistry Centre (CQC) is supported by FCT, through the project UI0313/QUI/2013, also co-funded by FEDER/COMPETE 2020-EU.

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PLENARY-4

Polymeric Nanomaterials for Biomolecules

Sinan Akgöl

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Nanotechnology is a multidisciplinary branch of science which has several fields such as biomedical, pharmaceutical, agricultural, environmental, advanced materials and so on. The synthesizing nanomaterials according to purpose, usage field and to observe results of application becomes very important. A great deal of medical applications have been created over the last decades. The ability is in control of the nanosize materials to form different materials. These materials have been used in a wide spectrum from health to the environment. Among these nanomaterials, polymeric nanomaterials play an important role for biotechnologically purposes. Polymeric nanoparticles (PNPs) are defined as particulate dispersions or solid particles of 10-100 nm size. Within these PNPs, therapeutic agents (such as drugs, DNA, proteins, etc.) as well as fluorescent labels can be dissolved, entrapped, encapsulated or can be attached to the nanoparticle matrix. There are different advantages of PNP's. First of all, easily incorporated into other activities related to drug delivery such as tissue engineering. Secondly, delivery of higher concentration of pharmaceutical agent to a desired location. Finally, improvement over traditional oral and intravenous methods of administration in terms of efficiency and effectiveness. The unique physical structure and the excellent chemical capacity are the most effective and the surprising characteristic of the PNP's. There are different type of PNP's such as polymeric nanoparticles, micelles, dendrimers, polymersomes, polyplex, polymer-lipid hybrid, polymer/drug/conjugate systems. Preparation Techniques of PNPs, Surface Modifications of PNP's and Molecular Imprinted Polymers will explained in this speech. In addition to this, different applications such as Medical, Environmental health, and enzyme technologies will also explained.

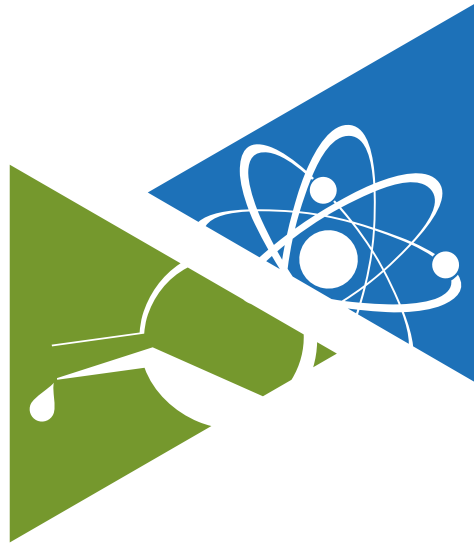
PLENARY-7

A ray of light in the darkness: dark field/hyperspectral microscopy for imaging and characterisation of nanoscale particles

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Nanoscale articles are greatly appreciated by the researchers developing novel drug delivery vehicles. However, imaging, detection and identification of nanosized materials in cells, tissues and organisms is still challenging. Conventional approaches for nanoparticles imaging and characterisation both inside the cytoplasm and/or on the cell or tissue outer surfaces, such as transmission and scanning electron microscopies, are potent tools, having high resolution and supplemented with chemical analysis capabilities. However, imaging and detection of nanomaterials in situ, (i.e. within living isolated cells, microorganisms, protozoans and miniature invertebrates) using electron or atomic force microscopy-based methods is practically impossible. Atomic force microscopy, in several cases, can be used for imaging and mechanical analysis of live cells and organisms under ambient conditions, however this technique allows for investigation of surfaces only. Dark-field microscopy as an optical contrasting technique has been popular among researchers for decades, however until recently the commercially available instrumentation was not well suitable for imaging of nanosized particles. Currently, enhanced dark field microscopy based on using higher numerical aperture oblique light-focusing condensers and variable numerical aperture objectives allow for imaging of nanoscale particles using almost conventional optical microscopy methodology. The use of dark-field/hyperspectral microscopy instrumentation has led to a significant increase of publications featuring the use of dark-field/hyperspectral microscopy to detect nanosized particles used as anticancer drug delivery vehicles and anticancer photoinduced thermotherapy nanoparticles. Apart from imaging nanomaterials in situ, dark-field microscopy is a potent tool to detect larger micron-sized particles, such as microplastics. Hyperspectral imaging can also be realised using the dark-field microscopy instrumentation via spectrometer\CCD camera interfaced with the optical microscope. This talk reports the application of enhanced dark-field microscopy combined with hyperspectral imaging for visualisation and spatial mapping of nanoscale and microscale particles in biological samples, including anticancer drug delivery applications.



ORAL PRESENTATIONS

S-001

PCFC Cathode Materials: Influence of Structure and Local Distortions on Proton Uptake

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Doped BaFeO_{3-δ} is a mixed conducting perovskite with oxygen vacancies, holes and protons and can be used as cathode material for Protonic Ceramic Fuel Cells (PCFC), promising energy conversion devices with an operation temperature of 400°C–600°C.

A PCFC cathode material has to fulfill requirements that often are forcing the scientist to compromise of some degree on specific properties. [1] In particular, the cathode needs proton conductivity higher than about 10⁻⁴ S/cm to transfer protons from the electrolyte to the cathode surface making the whole cathode surface catalytically active for oxygen reduction to water. [2] Protons can be incorporated in the structure via hydration at expenses of oxygen vacancies, and their concentration can be determined by thermogravimetric measurements.

The crystal structure and symmetry as well as local distortions have an important impact on the proton uptake. Zn²⁺ and Y³⁺ doping the B-site of (Ba,La)FeO_{3-δ} was proven to be beneficial for the proton uptake. This was tentatively assigned to local lattice distortions induced by these oversized cations (e.g. BO₆ octahedra tilting) which will reduce the covalence of Fe-O bonds and thus enhancing the basicity of oxygen ions involved in the bond.

To support this hypothesis, the local environment of the B-site cations has been probed using Extended X-Ray Absorption Fine Structure (EXAFS). The environment of oxygen ions has been investigated by the recently developed X-Ray Raman Scattering (XRS). Both techniques were applied to oxidized and reduced samples (Fe in mainly 4+ and 3+ oxidation states, respectively) and hydrated samples.

The combination of these techniques with conductivity and water uptake measurements allows for a comprehensive understanding of proton uptake in PCFC cathodes, indicating possibilities to optimize them.

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S-002

Halloysite/Keratin Mixtures for Hair Treatment Purposes

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Abstract

In this work, we explored the adsorption process of keratin onto halloysite (HNTs) surfaces in aqueous medium at variable pH conditions. Within this, electrostatic, colloidal and thermodynamic characteristics of the keratin/HNTs mixtures were studied. Preliminary studies on the keratin solutions at different pH were conducted by means of ζ -potential and UV-vis spectroscopy measurements in order to determine the protein isoelectric point (pH = 4) and, consequently, the peculiar dependence of the keratin surface charge on the pH of the solvent medium. As concerns the HNT/protein mixtures, ζ -potential experiments at pH = 4 evidenced that the addition of halloysite does not alter the keratin surface charge ruling out the presence of electrostatic interactions between the protein and the nanotubes. For pH > 4, the ζ -potential of the mixtures showed a decreasing trend with the HNT/keratin ratio as a consequence of the attractive interactions between the protein and the halloysite inner surface. According to these results, the aqueous colloidal stability of keratin/HNTs mixtures was enhanced in alkaline conditions (pH = 8) as demonstrated by the sedimentation kinetics. Regarding the thermodynamic features, calorimetric measurements highlighted that the adsorption process of keratin onto HNT surfaces is exothermic being that the adsorption enthalpy is positive. Above the keratin isoelectric point, we estimated larger ΔH_{ads} values because of the stronger keratin/HNTs interactions driven by attractive forces. Lastly, the keratin/HNTs aqueous mixtures were tested for the hair treatment by immersion procedure. The protection efficiency of the proposed protocol was investigated by monitoring the cysteine oxidation of the hair samples after their exposure under UV radiation.

S-003

Theoretical Through Microencapsulated Phase Change Materials for Thermal Energy Storage and Thermochromicity Applications

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Abstract

Microencapsulated phase change materials (MEPCMs) are used for energy economy and comfort applications. They are also used for some functional applications like thermochromicity with some colorants and additives. The property development of MEPCMs depends upon the material type, physical situation and morphology. Behind the storage, comfort and temperature sensing properties like thermal conductivity, permeability, life time, material development and property control have been compared to the properties in this work. Hypotheticals are investigated with some theory statements in order to produce characteristic properties.

Keywords: phase change material, thermal energy storage, thermochromicity

S-004

Some Ionic Liquids As Phase Change Materials And Their Microstructural Constitutions

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Abstract

Ionic liquids are liquid at temperatures below 100 °C which can remain fluid in a wide temperature range, while those with higher melting points are referred to as molten salts. Ionic liquids have beneficial properties such as high chemical and thermal stability, negligible vapor pressure, non-flammability, high heat capacity and storage density (Zhu et al., 2009). Thus, the ionic liquids have thermophysical and chemical properties which can be suitable for phase change materials (PCMs) (Wu et al., 2001; Valkenburg et al., 2005).

Some ionic liquids have been synthesized through stoichiometric reaction of fatty acids with an alkanolamine. They were characterized structurally by ¹H-NMR and FT-IR spectroscopic techniques and thermally by DSC, thermal conductivity measuring device and TGA analysis. Their thermal attitudes are important as a structure and property issue for thermal energy storage (TES). In spite that they have shown some ability to serve as TES materials, they could be used also as thermal conductivity enhancers. These materials have also been found as thermally stable.

Keywords: Ionic liquid, thermal energy storage, phase change material

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S-005

Printing Biology for Advanced Synthetic Biosystems

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Abstract

Printing technologies represent a powerful tool for the direct micro- and nano- fabrication of biomolecular structures at the interface between life and materials sciences (Arrabito *et al.*, 2012). Their continuous development over the last years has permitted the onset of man-made biosystems with customizable dimensions (from the micron-scale down to the nanometer scale), composition (organic molecules, DNA, proteins, phospholipids), and relevant functions (molecular interactions, drug screening, cellular biointerfaces, cell-like compartments). In this work, we show the possibility to leverage the fabrication of a wide class of solid-supported or liquid-liquid based synthetic compartments by printing tools at different scales. Scanning probe lithography methodologies will be shown for sub- cellular scale manipulation of living cells or for studies of molecular interactions onto porous surfaces. In particular, DNA-based protein immobilization coupled with dip-pen or polymer pen lithography permits the scalable fabrication of single-cell biochips (Arrabito *et al.*, 2013; Arrabito *et al.*, 2014). Inkjet printing will be shown for the fabrication of size scalable aqueous or oil-based synthetic compartments leading to molecular interaction studies at solid-liquid or liquid-liquid interfaces. The effect of droplet downsizing down to the femtoliter scale will be shown to affect the molecular interactions within aqueous compartments, mimicking the behaviour observed in cellular organelles, in terms of molecular confinement and molecular crowding effects (Arrabito *et al.*, 2019). In the case of oil-based compartments, fragmentation phenomena at surfactant-laden water-based interfaces bring to the formation of femtoliter-scale oil compartments detected by a microfluidic platform (Arrabito *et al.*, 2019).

Keywords: Inkjet Printing, Dip Pen Nanolithography, Molecular Confinement, Synthetic Biology

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S-006

Interpolymer Complexes for Thermal Energy Storage Applications

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Abstract

Interpolymer complexes (IPCs) have rarely been investigated as thermal energy storage materials. Composites prepared for thermal energy storage applications are passive systems called as shape/from stabilised materials and phase change enthalpy arise from the microdomains of the composites with phase change materials (PCMs). They bring seepage as an overcome at high ratios. Also upon usage leakage, phase separation may arise. In IPCs phase change material is bound to the matrices and the enthalpy bearing part becomes the microdomains of the segmental parts of the PCMs, that is they are solid-solid consistent materials. Gluten was the first time used for such and IPC in this work as polyethylene glycole (PEG) is a conventional PCM material. As a result of the analysis of the IPCs, it was found that the produced IPCs had lower phase change tempratures and enthalpies due to the shortened range of chain interactions as expected. However, the temprature and enthalpies were found suitable and considerable for some applications respectively. 50 % PEG IPC was chosen as the best for the condensed storage density and thoroughly investigated.

Keywords: Interpolymer complex, polyethylene glycole, phase change material, thermal energy storage

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S-007

Superhydrophobic Titania-based Hybrid Nanocomposites for Cultural Heritage Protection

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Abstract:

Current research is putting relevant effort into the preparation and investigation of novel composites combining in a single material appealing macroscopic features, chemical stability, and low-cost synthetic strategies.

Among several application fields, cultural heritage protection could benefit of "smart" composites, possessing elevate hydrophobicity (i.e. protection towards humidity), tunable rheology (consolidants and/or protective material), and colour profile compatible with the underlying cultural asset (e.g. a fresco, a marble architectural element, etc.). Thus, an interesting combination could result in merging polysiloxanes and titania (TiO₂) chemistry. Polysiloxanes (PSs) are organic polymers characterized by: i) simple and scalable preparation protocols; ii) inertia under prolonged UV-light irradiation; iii) tunable rheology (Abe, 2004). On the other side, doped TiO₂ nanoparticles (TiNPs) are produced using cheap precursors, possess elevate surface area/volume ratio and efficiently photocatalyze the decomposition of environment pollutants (Gupta, 2011).

Herein, we report the last results regarding the investigation of fluorinated PSs/TiNPs coatings. The preparation methodology has been established combining already-reported protocols (Ding, 2011) and using commercially available precursors. Depending on the nature of the precursors, two different matrices were isolated and exhaustively characterized by means of NMR, FT-IR, SEM and XPS. Then, the polymeric matrices were combined with TiNPs at different wt. percentages, and the modification hydrophobicity was monitored by measuring contact angle values.

Subsequently, photodegradation tests were carried out using a model compound, methylene blue, as a benchmark of the photocatalytic activity. Spectroscopic measurements pointed out the persistent photocatalytic activity by TiNPs, even when embedded by the polymer network, without being released in solution. A correlation between apparent kinetic profile and TiNPs wt. percentage was found.

By employing doped TiO₂, the photocatalytic process can be activated by visible light, thus offering an effective strategy for self-cleaning consolidant and protective smart nanocomposites for cultural heritage applications, such as natural lipidic materials.

Keywords: Cultural heritage, hybrid composites, methylene blue, photodegradation, titania nanoparticles.

Acknowledgements:

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S-008

Activated Biochar From *Posidonia Oceanica*. A New Adsorbent Material of Hydrocarbons from Wastewater

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Abstract

Environmental pollution by petroleum derivatives is a very current topic. In particular, low concentration of this kind of pollutants can seriously compromise the life of animals and plants of aquatic ecosystems (Yu, 2017). The current legislation provides that bilgewater, wastewater produced by boats, can be discharged directly into the sea only if the total hydrocarbon concentration not exceeds 15 mg L⁻¹.

In this work, new activated carbons were tested as adsorbent materials of oil / hydrocarbons from wastewater. Moreover, an instrumental technique able to quickly measure the required low hydrocarbons concentration is also proposed.

The new activated carbons were obtained from bio-oil production waste, a biochar produced by pyrolysis of *Posidonia oceanica*, a marine plant widespread in the Mediterranean sea.

The biochar has been characterized and adsorption experiments were carried out with the pristine biochar (not activated) and with two chemically activated biochars (BCB and BCA) by means of acid or alkali treatments. Moreover, a commercial activated carbon (Filtrisorb 400) has been used for comparison purpose.

Synthetic bilge waters were prepared following reference standards (MEPC, 2003) containing DMA (distillate marine fuel) and SDS (sodium lauryl sulfate).

Batch adsorption isotherms were carried out without ionic medium and at different concentrations of NaCl in order to evaluate the effect of salinity on the adsorption ability of adsorbent materials. The same adsorbents were tested by column experiments. In particular, a bench pilot system was built and breakthrough curves were obtained changing amount of adsorbent material in column, flow rate, initial DMA and surfactant concentrations.

Several instrumental techniques (turbidimetry, TOC, HPLC-FLD) have been used to measure surfactant and hydrocarbon concentrations in experimental samples.

The batch experimental data were fitted with the most used isotherm models (Langmuir, Freundlich, Sips) and important considerations were made on the breakthrough curves of column experiments.

Acknowledgements

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S-009

Evaluation of Stability, Antioxidant Activity and Antidiabetic Effect of Isoflavones Extracted from Raw Sources Using Natural Deep Eutectic Solvent

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Abstract

We developed a method suitable for the quantification of daidzein, genistein and puerarin extracted from soy molasses and dried kudzu root using Natural Deep Eutectic Solvents (NADES) by HPLC-UV, evaluation of their stability, antioxidant activity and anti-diabetic effect. NADES mixture used for the current study was designed using aqueous solution of choline chloride and citric acid (1:2 molar ratio, respectively). A decrease in isoflavone content of extract irrespective of the extraction solvent was dependent on storage time and temperature, there was a higher degree of reduction of isoflavone content of extracts during storage at room temperature as compared to storage at -18°C. The highest isoflavone yield and antioxidant activity using DPPH antioxidant assay by EPR spectroscopy were obtained at sample to NADES volume of 1:20 as compared to other ratios. Diabetic rats treated with the extract at a dose of 100 and 200 mg/kg of animal weight showed decreased levels of fasting blood glucose, glycosylated haemoglobin glucose intolerance, restored changes in histological structure of pancreas and kidneys as compared to untreated diabetic rats.

Keywords: Isoflavones, Antioxidant activity and Stability, Natural deep eutectic solvents (NADES), diabetic rats, Biochemical and Histological Characteristics

I. Introduction

Isoflavones are part of the human diet all over the world. In most parts of Asia, the traditional cuisine is rich in soy products that contain high concentrations of isoflavones, whereas in Western world soy is, in general, less regularly consumed. They are also phytochemicals of pharmacological relevance owing to a plethora of epidemiological, animal, and cell studies findings supporting their beneficial health effects. In plants consumed as part of the human diet (including dietary supplements), the extensive concentrations of isoflavones have been observed in soy (*Glycine max* L.), red clover (*Trifolium pratense*), and kudzu (*Pueraria lobata*) [Mortensen et.al., 2009]. Soya molasses is a waste product of soya concentrate processing. It contains around 1-3 % of isoflavones with respect to dry substances. The extraction of these compounds has been plagued by the use of organic solvents, hence the need for alternate green solvents. Stability, antioxidant activity and potential of isoflavones extracted in prevention and treatment of different diseases including *Diabetes mellitus* are very important are very important characteristics under study.

II. Experimental Set-up and Procedure and Analysis

NADES mixture used for the current study was designed using aqueous solution of choline chloride and citric acid (1:2 molar ratio, respectively). Extraction of isoflavones with methanol was done using Soxhlet apparatus for 12hrs, whereas that with NADES was performed at 60 °C for 1hr. The stability of extracts obtained using NADES and methanol was evaluated for 14 days storage period at different temperature (room temperature, 4°C, and -18°C). The effect of different water concentration in NADES composition (10%, 20%, and 30%) on extractability of isoflavones was also investigated. The effect of sample to of NADES volume ratio on extractability of isoflavones was also evaluated.

The tissues collected from animals were fixed in 10% formalin for 24hrs, processed for customary histological evaluation, and embedded into paraffin blocks using an automatic processor (Leica EG 1160). Tissue sections of 3-4 mm thick were made using a microtome and stained with hematoxylin and eosin (H&E) dye. Kidney tissues were further

stained with Periodic Acid Schiff (PAS).

III. Analysis

The antioxidant activity of extracts was performed using 2, 2-diphenyl -1-picrylhydrazyl (DPPH) antioxidant assay (J. Polak, 2013) by EPR spectroscopy on EPR-CV Elexys E-500 spectrometer (Bruker, Germany). Identification and quantification of isoflavone content in extracts was performed using HPLC-UV method on HPLC-UV chromatograph Agilent 1200 Infinity LC System, USA. The plasma glucose levels was determined using the glucose oxidase method as described by (Danilova I.G., 2017 et al.). Glycosylated hemoglobin (HbA1c) was measured using affinity chromatography (TOR 9398240-16404416-01, Fosfosorb OJSC, Russian Federation). Biochemical tests were conducted using a DU-800 spectrophotometer (Beckman Coulter Int. S.A., Switzerland). Tissues were examined under light microscope (Leica DM 2500), and image analysis was done using Video TesT-Morphology 5.0 software.

IV. Results and discussions

Despite detecting daidzein, genistein and puerarin in extracts obtained from kudzu roots using NADES, only puerarin was quantifiable, whereas the 3 isoflavones were detected and quantified in methanolic extracts obtained from the same source. Although the isoflavone content in extracts obtained from kudzu roots using NADES was 60% lower as compared to methanolic extracts, the stability of isoflavone content of NADES extracts during 14 days storage at room temp. was higher as compared to methanolic extracts. It was found that decrease in isoflavone content of extract irrespective of the extraction solvent was dependent on storage time and temperature, there was a higher degree of reduction of isoflavone content of extracts during storage at room temp. as compared to storage at -18°C. The highest isoflavone yield was obtained at sample to NADES volume of 1:20 as compared to other ratios, it could be suggested that the extractability of NADES was dependent on viscosity. While the extractability of puerarin from kudzu root increased with water content of NADES composition, an inverse effect was observed in the extractability of isoflavones (genistein and daidzein) from soy molasses. The antioxidant activity of both kudzu roots and soy molasses extracts obtained using NADES was higher compared with methanolic extracts. Furthermore, the antioxidant activity of NADES extracts revealed a higher scavenging activity at sample to NADES volume of 1:20 as compared to other ratios.

The antidiabetic potential of the isoflavones-rich extract at a dose of 100 and 200 mg/kg of animal weight was evaluated in alloxan-induced diabetic rats, and it was found that diabetic rats treated with the extract showed decreased levels of fasting blood glucose and glycosylated haemoglobin, and decreased glucose intolerance as compared to untreated diabetic rats. Pancreas sections of diabetic rats treated with the extract showed an increased number of immunostained insulin and Ki67 positive cells, and restoration of the pancreatic islet structure compared with untreated diabetic rats. Similarly, kidney sections of diabetic rats treated with the extract showed reduced hypercellularity of the glomerulus compared with untreated diabetic rats.

V. Conclusions

The method suitable for the quantification of daidzein, genistein and puerarin extracted from soy molasses and dried kudzu root using Natural Deep Eutectic Solvents (NADES) by HPLC-UV. The stability of isoflavone content of NADES extracts during 14 days storage at room temp. was higher as compared to methanolic extracts. The highest isoflavone yield and antioxidant activity using DPPH antioxidant assay by EPR spectroscopy were obtained at sample to NADES volume of 1:20 as compared to other ratios. Diabetic rats treated with the extract at a dose of 100 and 200 mg/kg of animal weight showed decreased levels of fasting blood glucose, glycosylated haemoglobin glucose intolerance, restored changes in histological structure of pancreas and kidneys as compared to untreated diabetic rats.

Acknowledgements

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S-010

Green Polymer Packaging Coating on Metals with Volatile Inhibitors and improved Degradation Rate

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Abstract

Polymer films containing a volatile inhibitor with a polymer decomposition catalyst provide adequate temporary corrosion protection to supply metal for customers. The most effective volatile inhibitors have been established for different plant raw materials and investigations on model substances. Photocatalytic effects and, in turn, improved polymer degradation rate make films with titania more eco-friendly. Although TiO₂ acts under UV-irradiation, coupling and doping effects, composite with better conductors could improve its activity up to the visible light range.

Keywords: polymer film, volatile inhibitor, titanium dioxide, corrosion protection, polymer degradation

I. Introduction

Green and sustainable approaches in chemical technology are of high demands nowadays. Significant efforts have been made to reconsider corrosion protection procedures introducing inhibitors based on aqueous extracts of natural origins: drupaceous and other parts of different plants (Chygyrynets', Lipatov, 2003). High inhibitor activities demonstrate alcohol extracts of plant raw materials as the next after aqueous ones (Vorobyova, Chygyrynets', 2018). These volatile inhibitors are eco-friendly and able to act independently or together with polymer coatings with main task to support temporary corrosion protection for metal supply to customers. Nevertheless, the application of polymers causes their recycling problem that could be solved by addition of photocatalytic materials (García-Montelongo, 2014). These materials should possess optimal performance for films that are polymer packaging inhibitor materials on metals during their operation. Doping operation is very important in the search for more photoactive catalysts. Main strategies except for doping could be coupling with other semiconductors with small band gap energy, surface decoration with noble metals, using conductive materials like polyaniline, graphite, maxene and etc. The aim of this work was to study opportunities of combined application of polymer film with volatile inhibitor and TiO₂ (doped) photocatalyst.

II & III. Experimental Set-up and Procedure and Analysis

Titanium dioxide nanodispersed sample with anatase structure synthesized in I. Frantsevich's Institute for Problems of Materials Sciences NASU was utilized. The polymer polyethylene films with TiO₂ were prepared as shown in (García-Montelongo, 2014). UV-source was 30W Hg-quartz lamp. Polymer films containing a volatile inhibitor were synthesized by the procedure published elsewhere (Vorobyova, Chygyrynets', 2018). Titanium dioxide nanodispersed sample was studied by XRD, SEM, TEM, EPR, porometry (G.Sokolsky et al, to be published). The degradation rate was studied by FTIR on a FSM-1201 Fourier spectrometer. The composition of a plant volatile extracts was studied by liquid chromatography coupled with mass spectrometry (LC-MS). Standard accelerated corrosion tests for volatile inhibitors under atmospheric corrosion conditions have been carried out.

IV. Results and discussions

Nanoparticles of TiO₂ of about 10 nm size were observed by TEM method. Anatase structure was confirmed by XRD. Self-doping by Ti³⁺-ions detected by EPR was the reason of slight band gap decrease to 2.75 eV in the sample. Its positive

effect is also mentioned in the literature, resulting in increased electrical conductivity and red shift to visible light absorption. The active degradation of aminoazodye on sample TiO_2 studied was revealed in (G.Sokolsky et al, to be published). C=O, C-O, and O-H vibrations were detected on FTIR spectra after 40 hours of UV-irradiation of the series of polymer films with TiO_2 . The procedures of TiO_2 electrolytic doping by Mn-ions and coupling of TiO_2 with MnO_2 and/or graphite, carbon nanotubes are currently under investigation. As a result of the series of different plant raw materials studied, the volatile inhibitors were obtained. The most effective components of plant extracts and raw materials have been established and investigated on model substances. The pathways of polymeric composite material preparation for temporary corrosion protection of metals with subsequent selfdegradation were formulated.

V. Conclusions

Therefore, titanium dioxide additives to polymer films containing inhibitor could be prospective to develop functional protective and degradable polymer coatings on metals since materials are safe and have no aggressive behavior toward a metal and environment.

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S-011

mpg-C₃N₄ Supported NiPt Alloy Nanoparticles: Efficient Heterogeneous Catalyst for the Transfer Hydrogenation of Nitroarenes

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Abstract

In this study, we report a novel and simple protocol for the synthesis of NiPt/mpg-C₃N₄ nanocatalysts for the reduction of nitroarenes via transfer hydrogenation reactions using AB as a hydrogen donor. This is the first example of the synthesis of NiPt alloy NPs supported on mpg-C₃N₄ and their catalysis in the transfer hydrogenation of nitroarenes. We studied on the effect of the different support materials like reduced graphene oxide and Ketjen Black for hydrogenation of nitroarenes.

Keywords: alloy nanoparticles; nitroarenes; transfer hydrogenation; ammonia borane

I. Introduction

Graphitic carbon nitride (g-C₃N₄) that is cost-efficient, abundant, non-toxic, metal-free, and stable material [1-3]. g-C₃N₄ is a polymeric material which merely consists of C, N, and O, with a typical band gap of 2.7 eV. Ammonia borane (AB, H₃N-BH₃) is considered to be the most promising candidate for hydrogen storage applications among all other practical hydrogen storage materials [4] owing to its impressive specialities that hydrogen content of 19.6% wt, stability in the solid state under ambient conditions, and nontoxicity. Addressed herein we emerge these two materials, namely NiPt alloy nanoparticles supported on mpg-C₃N₄. NiPt/mpg-C₃N₄ for the transfer hydrogenation of aromatic nitro compounds using ammonia borane as a hydrogen source and performed in aqueous methanol solution in a pressure glass tube at room temperature.

II. Experimental Set-up and Procedure

Synthesis of support material mpg-C₃N₄

mpg-C₃N₄ materials used in our study were prepared from the thermal polycondensation of GndCl in the presence of LudoxHS40 colloidal silica as the template [5] In this synthetic protocol, 4.0 g of GndCl was dissolved in 4 mL of water in a glass vial and added dropwise into 10 g of Ludox HS40 colloidal silica under vigorous stirring. The mixture was heated at 50 °C for over-night. The white solid heated heated to 550 °C with under Ar(g) flow and kept at this temperature for 2 h in a horizontal quartz-tube oven. The yellow solid w reacted with NH₄HF₂ solution for 2 days for etching silica. Finally, obtained solid sample were washed with water and ethanol twice times in order to remove the all the impurities. After the BET analyses; The surface area of mpg-C₃N₄ is nearly 200m²/g.

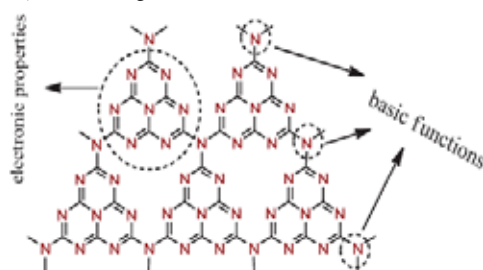


Figure 1: The scheme of mpg-C₃N₄

Synthesis of NiPt NPs

In a typical synthesis of NiPt NPs, according to organized recipe; Monodisperse NiPt NPs were synthesized via the reduction platinum(II) acetylacetonate and nickel(II) acetate by BTB in OAm and 1-octadecene (ODE). In the synthesis, under magnetic stirring, OAm acted as the surfactant, BTB served as the reducing agent, and ODE was used as a solvent. Pt(a-

cac_2 and $\text{Ni}(\text{ac})_2$ dissolved in a mixture of OAm (3 mL) and ODE (7 mL) in a four-necked glass reactor. The temperature is arranged to the 100 °C and the reaction was stirred. 0.2 g of BTB was dissolved in 3 mL OAm and precursors were injected to the reactor at 100 °C and stayed at 100 °C for 1 h. The NP product was separated by adding 50 mL acetone and then centrifuged at 9000 rpm, 10 min and the second centrifuge was done with ethanol. NiPt NPs were collected by dispersing into hexane.

To assemble the NiPt nanoparticles, we used the liquid phase self assembly method. 50mg of as-synthesized NiPt NPs were dissolved in 25 mL of hexane and mixed with 100.0 mg of $\text{mpg-C}_3\text{N}_4$ in ethanol. The resultant ethanol/hexane mixture which includes nanocomposites was sonicated for 2 h. Next, the resultant mixture was centrifuged at 7500 rpm for 10 min and the yielded catalysts were washed with ethanol. The resultant yield is NiPt/ $\text{mpg-C}_3\text{N}_4$. Nitrobenzene was first employed as a model compound to explore the optimized reaction parameters and the nitroarene derivatives were converted to the aniline derivatives.

III. Analysis

As clearly seen by the TEM image, the NPs have homogen dispersion with an average particle diameter of 2.4 nm. There no agglomeration NiPt nanoparticles, the cloudy region belongs to the $\text{mpg-C}_3\text{N}_4$ structure. As we can see the nanoparticles supported on the surface homogeneously (Figure 2).

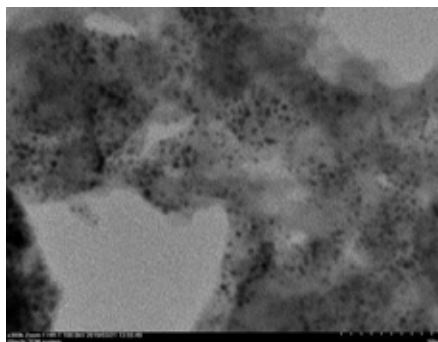


Figure 2. TEM images of NiPt/ $\text{mpg-C}_3\text{N}_4$ nanocomposites.

IV. Results and discussions

Firstly, monodispersed NiPt NPs were synthesized using a one-pot organic solution-based thermal decomposition that included the reduction of $\text{Pt}(\text{acac})_2$ and $\text{Ni}(\text{ac})_2$ in the mixture of OAm and ODE. In the protocol, OAm served as a surfactant and BTB is reducing agent, ODE was used as the solvent, respectively. The new synthesis protocol used for NiPt NPs and 2.4 nm NiPt NPs were synthesized. NiPt NPs are decorated onto the $\text{mpg-C}_3\text{N}_4$ and this nanocomposite is used for transfer hydrogenation of nitroarenes. There are several parameters (temperature, catalyst amount, AB amount and reusability) are investigated.

V. Conclusions

We reported a facile method for the preparation of $\text{mpg-C}_3\text{N}_4$ -assembled monodispersed NiPt NPs and its impressive activity for transfer hydrogenation of nitroarenes. The transfer hydrogenation of nitroarenes, were achieved in a commercially available pressure tube at room temperature within only 1hour and 70-100% conversion yield.

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S-012

Chemical Modification of Halloysite Nanotubes for Biological Applications

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Halloysite nanotube, an aluminosilicate of the kaolin group, is an emerging nanomaterial which possesses peculiar chemical characteristics. By means of suitable modifications, such as supramolecular functionalization or covalent modifications, it is possible to obtain novel nanomaterials with tunable properties for several applications. In this context the covalent grafting of suitable organic moieties on the external surface or in the halloysite lumen has been exploited to improve the loading and release of several biologically active molecules. The resulting hybrid nanomaterials have been applied as drug carrier and delivery systems, as fillers for hydrogels, in tissue regeneration and in the gene delivery field. Furthermore the loading and release of specific molecules have been also investigated for environmental purposes.

S-013

Synthesis of ZnO Nanoparticles Supported on Halloysite Nanotubes for Catalytic Applications

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Halloysite nanoclays (HNTs) are promising nanomaterials because of their versatile properties, such as hollow tubular morphology and tunable surface chemistry. HNTs are biocompatible, non-toxic and abundantly available at low cost. Due to these characteristics HNTs are suitable for development of hybrid sustainable materials, which are perspective for wastewater remediation, green packaging and drug delivery.^{1,2}

Functionalized halloysite constitutes a valuable support for metal nanoparticles, promoting catalytic applications with tunable properties. The peculiar tubular shape of HNTs favors the dispersion and surface availability of the supported metal nanoparticles that are active in the catalytic path. Moreover, the presence of an empty lumen opens new perspectives for the production of nanoarchitectures with synergistic catalytic effects, due to the increase in local concentrations and confinement. Among the various alternative catalysts, zinc oxide received much attention due to its cheap, nontoxic, thermally stable, and amphoteric properties.

Herein, we report the synthesis of a novel versatile catalyst based on halloysite and zinc oxide (HNT@ZnO). It was found that the presence of halloysite improved the UV-*vis* spectral absorption ability of ZnO. The hybrid was successfully used as photocatalyst for the methyloange and rhodamine B degradation. In addition, after eight consecutive cycles for the methyloange photodegradation, the hybrid did not exhibit significant reduction in its photocatalytic performances confirming its stability. Based on trapping experiments and calculated energy bands we also proposed a photocatalytic mechanism.

Furthermore, to evaluate the versatility of the synthesized HNT@ZnO hybrid, we used it as catalyst for biodiesel production from soybean oil, too. Also, in this case, the hybrid showed good catalytic performance and recyclability.

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S-014

Covalent Modification of Carbon Nanoforms and SBA-15 Surfaces with Imidazolium-based Salts for Pd species immobilization: Design of Efficient Catalysts

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Abstract

Both carbon nanoforms (CNFs), namely multi-walled carbon nanotubes (MWCNTs) and carbon nanohorns (CNHs), and mesoporous silica (SBA-15) were suitably modified with a polymerized bis-vinylimidazolium salt and an imidazolium-modified polyhedral oligomeric silsesquioxanes (POSS). The materials obtained were used as supports for Pd species and employed as efficient catalysts for C–C coupling reactions (Suzuki and Heck). A thorough characterization of all obtained hybrid materials was carried out, including TEM, TGA, solid-state NMR, XPS, SAXS, and BET analyses.

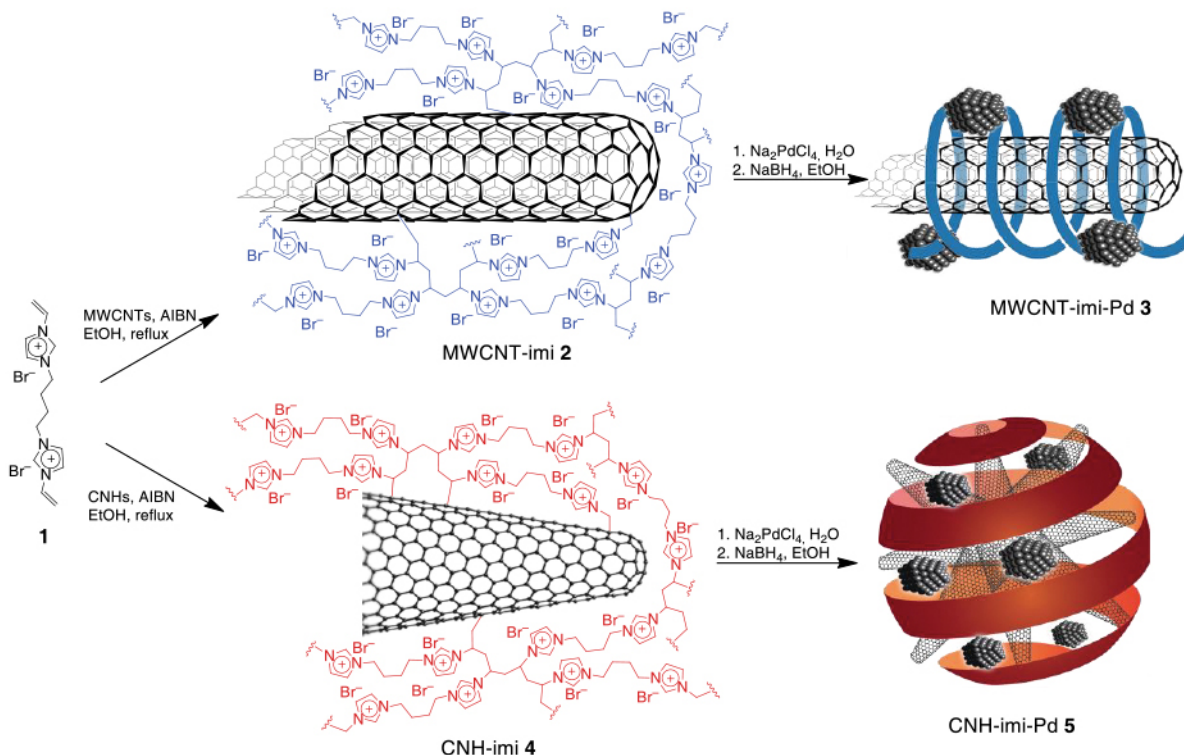
Keywords: Carbon nanoforms, mesoporous SBA-15, C–C coupling

I. Introduction

In the field of heterogeneous catalysis, the choice of the proper support material that can ensure both a good dispersion of the catalytic species onto its surface and the diffusion of reactants and products toward and from the catalytic centre, respectively, constitutes the main goal for the production of efficient catalysts. For the foregoing reasons, a rational functionalization of the surface of pristine support material in order to improve interactions with catalytic species is of paramount importance. The choice of MWCNTs, CNHs, and SBA-15 as bases of the catalysts architecture was conceived with the aim to properly functionalize each support with specific procedures that could maximize performances of the final catalytic materials. In order to achieve this goal, two different approaches involving radical polymerization of a bis-vinylimidazolium salt^[1] and grafting of an imidazolium-modified POSS^[2] were adopted for CNFs and SBA-15, respectively.

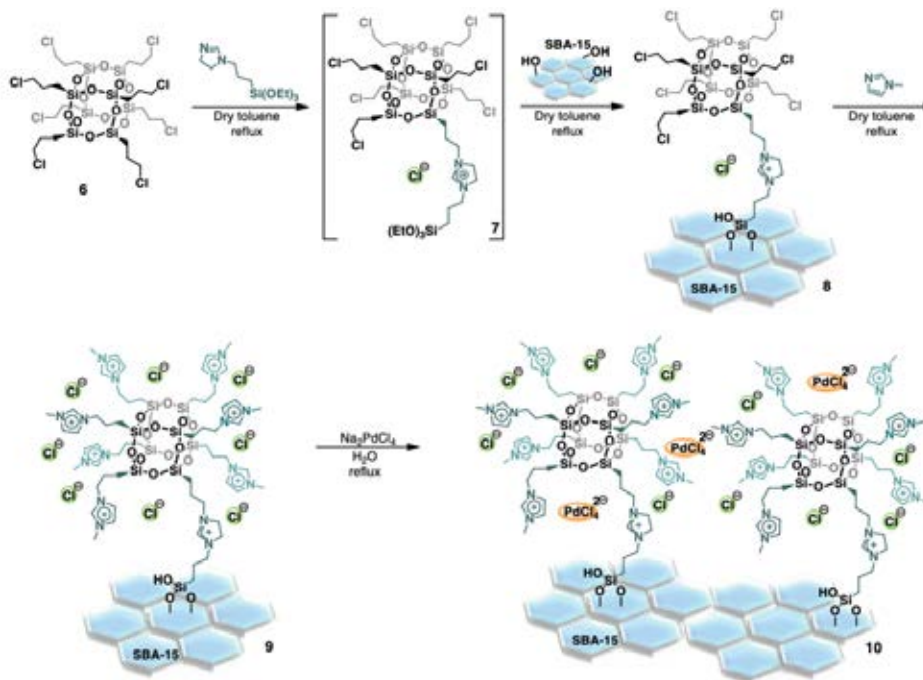
II. Experimental Set-up and Procedure

The procedure followed for the production of hybrid materials **3** and **5** involving radical polymerization of bis-vinylimidazolium salt on support materials and the subsequent immobilization of Pd species is depicted in **scheme 1**.



Scheme 1: Synthetic procedure for the preparation of materials MWCNT-imi-Pd 3 and CNH-imi-Pd 5

SBA-15 was functionalized by grafting imidazolium-tagged POSS followed by ion-exchange of chloride ions with PdCl_4^{2-} , the whole procedure is reported in **scheme 2**.



Scheme 2: Synthetic procedure for the preparation of material 10

III. Results and discussions

High-resolution TEM investigation showed that the CNFs structures acted as templates for the growth of the highly crosslinked imidazolium network, which perfectly covers their whole surfaces creating a cylindrical or spherical coating for MWCNTs and CNHs, respectively (**Figure 1**). On the other hand, the textural properties of SBA-15 allowed for the functionalization of the inner pore walls with POSS nanocage making material **10** as a sort of nanoreactor (**Figure 2**).

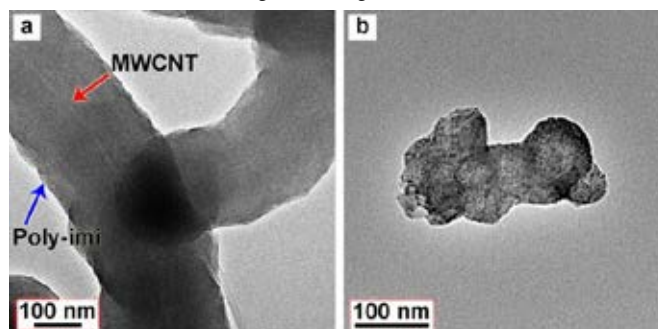


Figure 1: HRTEM images of materials a) **3** and b) **5**.

IV. Conclusions

The rational structural design of hybrid materials **3**, **5**, and **10** with imidazolium-based salts for the immobilization of Pd species allowed them to be used as efficient and recyclable catalysts for the Suzuki and Heck cross-coupling reactions.

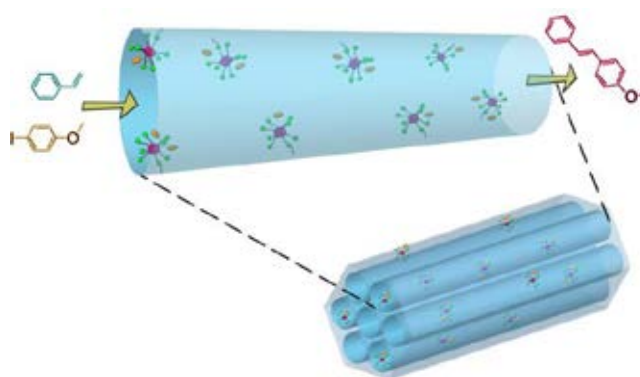


Figure 2: Graphical representation of hybrid material **10**.

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S-015

Silver Nanoparticles Embedded into Thermo-Switchable Polymer Grafted Brushes: Morphology, Shape, Temperature-Responsivity and Toxicity

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Abstract

The “smart” antibacterial surfaces have a great potential for health and industrial applications, as they can prevent bacterial attachment and biofilm formation especially using a “kill-release” strategy.

We fabricated and studied in details the smart antibacterial coatings based on poly(di(ethylene glycol)methyl ether methacrylate) (POEGMA) and silver nanoparticles. The presence and shape of silver nanoparticles in POEGMA were inspected using the X-ray photoelectron spectroscopy and scanning electron microscopy. The lower critical solution temperatures of POEGMA were determined, measuring the temperature dependence of the water contact angles. Moreover we showed that the polymer grafted brushes can be employed to control the shape of nanoparticles.

At finish we found that the POEGMA brushes with embedded silver nanoparticles is capable of the thermo-switchable killing of bacteria. In addition, the influence of the POEGMA brush coatings without nanoparticles and with the silver nanoparticles was examined for the control of proliferation of human cells.

S-016

The Computational Approach to the Study of a Complex Nanotubular System

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Abstract

Halloysite (HNT, with stoichiometric formula is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) is one of the most popular nanotubular aluminosilicate used in chemical field and material science. Structurally, it is characterized by an internal layer of AlO_6 octahedra and an external one of SiO_4 tetrahedra. The different chemical environment inside and outside the nanotube as well as its low-cost and its bio-friendly behaviour (Lisuzzo, 2019) have been made the HNT one of the most exploited clay material. Furthermore, the outer-inner layer differences can be willingly tuned through chemical modifications or just by changing the pH (Abdullayev, 2008).

The computational approach applied on the HNT and its nanocomposites can actually be a big hand of help in developing new HNT based materials and in understanding the substrate-adsorbate interactions between HNT and molecules of technological interest. Modelling such a complex system is not an easy task. In this work we show how to deal with the HNT modelling for smart material-design. The starting point is the building of a reliable HNT model which is obtained by cropping a portion from a previously investigated spiral nanotube, characterized by means of DFTB (Ferrante, 2015). The so constructed model is then used for the adsorption study of small organic molecules on the HNT surfaces with DFT calculations, in order to design new corrosion inhibitor HNT nanocomposites. Two promising candidates were identified for this purpose: salicylaldehyde and quinaldic acid. In the end, the HNT nanocomposite of these two species were experimentally tested by means of TGA, DSC and UV- vis spectroscopy. (Rozza, 2019).

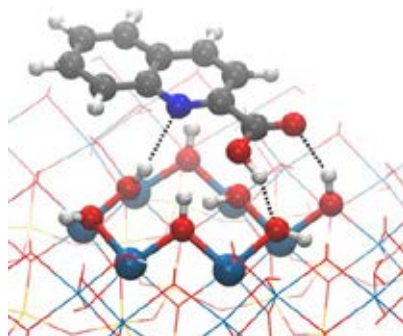


Fig. 1: Adsorption geometry of Quinaldic acid on the inner HNT layer

Keywords: Halloysite, corrosion inhibitors, DFT.

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S-018

Grafted Polymer Brushes: Poly(Butyl Methacrylate) vs Poly(Butyl Acrylate): Influence of Temperature on the Wettability, Morphology, Protein Adsorption

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Abstract

Poly(n-butyl methacrylate) (PBMA) and poly(n-butyl acrylate) (PBA) grafted polymer brushes attached to glass were fabricated in a three step process involving surface initiated atom transfer radical polymerization. The thicknesses and composition of the PBMA and PBA coatings were examined using ellipsometry and time-of-flight secondary ion mass spectrometry (ToF-SIMS), respectively.

For PBMA, the glass transition temperature constitutes a range close to the physiological temperatures, which is in contrast to PBA, where the glass transition temperature is around -55 °C. Atomic force microscopy studies at different temperatures suggest a strong morphological transformation for PBMA coatings, in contrast to PBA, where such essential changes in the surface morphology are absent. Besides, for PBMA coatings, protein adsorption depicts a strong temperature dependence.

The combination of bovine serum albumin and anti-IgG structure analysis with the principal component analysis of ToF-SIMS spectra revealed a different orientation of proteins adsorbed to PBMA coatings at different temperatures.

Keywords: grafted polymer brushes, stimuli-responsive polymer coatings, glass transition temperature, cells, orientation of the proteins.

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S-019

Synthesis and Characterization of Star Shaped PCL Polymers Having Different Arm Numbers and Their Blends with PLA

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Poly(lactic acid) (PLA) is a commercialized biodegradable polymer that can be obtained from renewable resources such as whey, corn, and potato (Drumright, 2000). However, it is a brittle and rigid polymer due to its relatively high glass transition temperature (T_g). In order to be used in industrial fields it needs to be plasticized or blended with other flexible polymers that have lower T_g . One of the biodegradable polymers that can be used for toughening PLA is poly(ϵ -caprolactone) (PCL) (Lopez-Rodriguez, 2006; Deokar, 2016; Wang, 2019).

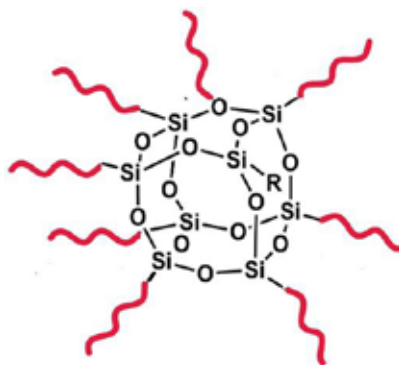


Figure 1. Schematic illustration of 8-armed star shaped PCL polymers with POSS core.

The aim of this study is to investigate mechanical and thermal behavior of PLA/star-shaped PCL blends. Star-shaped PCL polymers having different arm numbers (3, 4, 6) were synthesized via ring-opening polymerization (ROP) (Pan, 2019; Wang, 2019). Also, 8-armed star shaped PCL polymers were synthesized via combination of ROP and “click” chemistry. Then, the blends of PLA and star-shaped polymers were prepared in a twin-screw extruder. Thermal and mechanical properties of PLA/star-shaped PCL polymers were investigated.

Keywords: PLA/PCL Blends, Star Polymer, Click Chemistry

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S-020

Production of Biodegradable Film by Using Ternary Blends with Mineral Filler

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Abstract

New regulations in packaging and textile market increase the demand for eco friendly polymer materials that are more harmless. Specially disposable products, which can be degraded in nature, make them preferable by consumers. To produce polymeric film with biodegradable blends can solve environmental waste problem. In this study, ternary blends of polyesters, thermoplastic starch and mineral filler were mixed in various formulations and a biodegradable compound and film were prepared. During compounding and film extrusion, the difficulties in process were eliminated by working various machine parameters. The effect of different formulation and process parameters on mechanical and rheological properties of film were examined.

Keywords: Biodegradable, mineral, film, blends, ternary, compound, extrusion, eco friendly, disposable

S-021

Clay Mineral Composites for Green and Sustainable Applications

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Abstract

Sustainable consolidation and protection of paper, wood and waterlogged archaeological wood plays a relevant role within the cultural heritage issue. Innovative composites formed by clay nanotubes and biopolymers are proposed. In this work, these composites are used to safeguard the weakened, material structures in an appropriate way. Additionally, the nanotubes are used like nanocontainers for loading and triggered release of different species. The incorporation of $\text{Ca}(\text{OH})_2$ into the nanotube lumen retards the carbonatation. The obtained materials were tested for wood protection and consolidation. The obtained composites are characterized through morphology, wettability, thermal degradation and tensile properties. The treatment with pristine halloysite nanotubes did not alter the thermal properties of the woods. The penetration of the nanotubes into the waterlogged archaeological woods was investigated using X-ray tomography. The co-presence of polymer and $\text{Ca}(\text{OH})_2$ loaded nanoparticles generated a more uniform nanotubes distribution in the lignin channel structures and a significant enhancement of the mechanical properties with respect to the pristine halloysite treatment. This work proposes the use of halloysite/polymer mixture in a new method for waterlogged archaeological wood consolidation and represents a starting point to develop, with a biocompatible approach, a smart composite material in which the nanotube cavity is filled with active species for wood protection and active response to external stimuli. These features are promising for a composite nanoadditive in long-term smart protection of waterlogged archaeological woods.

S-022

Preparation of Functional Surfaces with Light-Induced Tetrazine Click Reaction

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Abstract

Light-induced chemistry has been utilized many years in materials science because of the ability of light to provide precise spatial and temporal control over chemical processes (Truong vd., 2017). In particular, photo inducible reactions have emerged as a method for turning on biorthogonal reactions with temporospatial control (Zhang vd., 2016). The Diels–Alder (IEDDA) reaction stands out from other bioorthogonal reactions by under its unmatched kinetics, excellent orthogonality, and biocompatibility (Oliveira vd., 2017).

The aim of this research is to modify the glass surfaces using the light-induced version of the Diels Alder (IEDDA) reaction with the inverse electron requirement. In this reaction, it is planned to obtain the tetrazine molecule by means of photooxidation. For this, the dihydrotetrazine (dHTz) molecule, the tetrazine precursor, was prepared and dHTz would be converted in situ to the tetrazine molecule during the modification of the glass surface. IEDDA will be performed on the glass modified with trans-cyclooctene (TCO) which is the partner molecule of Diels-Alder Click reaction. For this purpose, dHTz was synthesized primarily with dipridyl precursors having cyano group and attached to the terminal group of polymers such as carboxylic acid-terminated Polystyrene (PSt-COOH) and Poly (N-isopropylacrylamide) (PNIPAAm-COOH). On the other hand, TCO functionalized glass surfaces were obtained with the aid of 3-aminopropyltriethoxysilane. The modified glass surfaces were characterized by surface contact angle measurement, FT-IR and SEM / EDS methods, respectively. **The key point here is to ensure that the oxidation step during the transformation of dHTz to tetrazine is performed by photochemical reaction.** With this study, it is aimed to develop a new method for the modification of different surfaces by means of fast, effective, light-induced tetrazine click reaction which will enable the modification of the material surface in advanced technological applications.

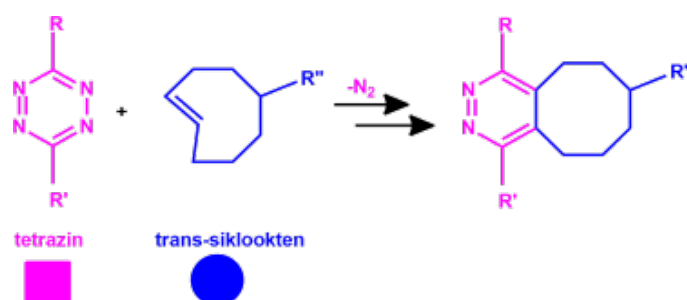


Figure 1. Tetrazine-*trans*-siklooktene Diels-Alder Click Reaction.

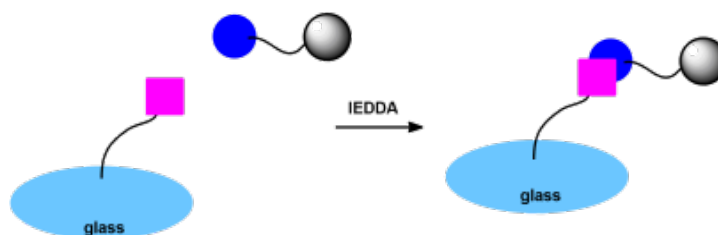


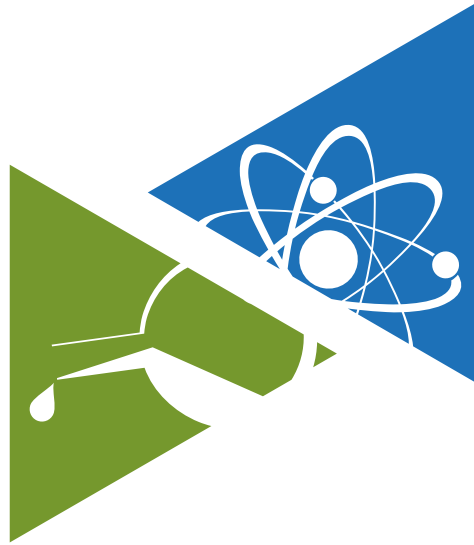
Figure 2. Two different molecule connection via Tetrazin Diels-Alder Click Reaction.

Keywords: “Tetrazin Diels-Alder Click reaction, functional surfaces, photooxidation, glass surface modification”

Acknowledgments: This work was financially supported by The Scientific and Technological Research Council of Turkey (TUBITAK, Project # 217Z057).

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POSTERS

P-01

Silylation of halloysite nanotubes with (3-chloropropyl)-trimethoxy silane

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Abstract

Modified halloysite nanotubes (HNTs-Cl) was synthesized by a coupling reaction with (3-chloropropyl) trimethoxysilane (CPTMS). The grafting of chloro-silane onto HNTs surface develops chloro- groups, which have a great chemical activity and are considered to be good nominees for employing as active sites that react with other active molecules for further modification of HNTs surface properties. The aim of this study is to determine the best conditions for silylation of HNTs with (3-chloropropyl) trimethoxysilane. Many parameters such as nature of solvent, molar ratio of (HNTs / CPTMS / H₂O), refluxing time and the effect of catalyst have been studied. The best modified HNTs sample was evaluated by FT-IR, Elemental analysis, TGA and SEM image. The results obtained from elemental analysis were used for calculating the degree of functionalization. The highest degree of functionalization was achieved by using toluene as a media for the silylation process, the molar ratio of (HNTs / CPTMS / H₂O) was (1:1:3) and the refluxing time was 4 hours. Addition of 7.169 mmol of Et₃N and 25.97 mmol of NH₄OH led to a great effect on increasing the number of silane groups which have been grafted on HNTs surface.

Keywords: Silylation, Halloysite nanotubes, Chloro-silane.

I. Introduction

Halloysite is a naturally occurring dioctahedral 1:1 clay mineral that belongs to the kaolin groups. The unit layer of kaolin group minerals is composed of one SiO₄ tetrahedral sheet and one AlO₂(OH)₄ octahedral sheet. Therefore, the different inner and outer-compositions of these materials allow to accomplish different chemical reactions on either surface (Massaro et al., 2014a; Li et al., 2008; Du et al., 2010; Vergaro et al., 2010). In recent decades, tubular halloysite has attracted significant scientific interest because of its excellent physicochemical properties. For instance, halloysite has been widely used as a filler in polymers, as a carrier for the loading and controlled release of guest molecules and as an adsorbent for pollution remediation (Abdullayev et al., 2009).

II. Experimental Set-up and Procedure

The halloysite was treated with 3-chloropropyltrimethoxysilane (CPTMS) in toluene, THF, Ethanol, n-hexane, 1,4 dioxane for 4 h at the boiling point of each solvent and then washed with the used solvent. The effect of catalyst (triethyl amine, urea and ammonia solution) on the proceeding of the reaction has been performed and moistening of the reaction media has been tested as mentioned at Table 1.

III. Analysis

Elemental analysis of carbon, hydrogen and nitrogen (EA) of the modified HNT samples which were grafted using 3-chloropropyltrimethoxy silane was carried out using an elemental analyzer Perkin Elmer PE 2400. FT-IR diffuse reflectance spectra were obtained with a Spectrum-One spectrometer, Perkin Elmer. The measurements were performed in the wave number range (4500-500) cm⁻¹. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo instrument for the pristine halloysite nanotubes and the best sample of (HNTs-CPTMS). Scan electron microscope (SEM) images were obtained by using a Carl instrument Zeiss EVO LS 10. They were used to study the morphology of the pristine halloysite

nanotubes and the best sample of (HNTs-CPTMS).

IV. Results and discussions

According to the data obtained from Table 1. the lowest degree of functionalization was obtained by using polar solvents like THF and ethanol. The use of (silane/ H₂O) ratio 1/3 mol/mol increased the degree of functionalization from 24.29 % to 36.5%. The HNT sample with the molar ratio (HNTs / CPTMS / H₂O) equal (1:1:3), toluene as solvent, refluxing time 4 hours and refluxed at 110°C was selected as the best sample in terms of HNTs surface functionalization with CPTMS. Addition of 7.169 mmol of Et₃N and 25.97 mmol of NH₄OH to the reaction media have a great effect on increasing the number of silane groups which have been grafted on HNTs surface.

Tab. 1: The different parameters which have been performed for the grafting process and the results obtained from elemental analysis.

Molar ratio (HNTs/ CPTMS/H ₂ O)	Solvent	Catalyst	Temperature	Refluxing Time	Content, %		Degree of functionalization %
					C	H	
1:1:0	20 ml toluene		110°C	4 hours	2.17	1.83	24.29
1:1.33:0	20 ml THF		66°C	4 hours	1.20	1.63	11
1:1:3	20 ml toluene		110°C	4 hours	3.26	2.22	36.5
1:1:0	20 ml ethanol		79°C	4 hours	0.96	1.53	10.75
1:1.33:0	5 ml toluene		110°C	4 hours	1.40	1.90	12.84
1:1:0	20 ml toluene		110°C	35 hours	2.01	1.86	22.5
1:1:0	20 ml toluene		110°C	48 hours	1.89	1.97	21.16
1:2:0	20 ml toluene		110°C	4 hours	2.41	2.03	17.13
1:2:0	17 ml toluene		110°C	48 hours	2.98	1.95	21.19
1:1:3	20 ml toluene	0.5 ml Et ₃ N	110°C	7 hours	4.31	2.85	48.26
1:1:3	20 ml toluene	0.2 g urea	110°C	4 hours	6.63	2.97	27.77
1:1.33:0	20 ml n-hexane	1 ml Et ₃ N	69°C	4 hours	3.69	2.14	33.83
1:1.33:0	20 ml 1,4 dioxane	1 ml Et ₃ N	100°C	4 hours	2.65 5	2.175	24.34
1:1.33:0	20 ml 1,4 dioxane		100°C	4 hours	1.56	1.86	14.3
1:1:3	20 ml toluene	0.5 ml Et ₃ N	110°C	4 hours	4.84	2.22	54.19
1:1:3	40 ml toluene	0.5 ml Et ₃ N	110°C	4 hours	4.55	2.13	50.95
1:1:3	20 ml toluene	0.5 ml Et ₃ N + 0.5 ml NH ₄ OH	110°C	4 hours	7.26	2.55	81.35
1:1:0	20 ml toluene	3 drops (EtO) ₄ Ti	110°C	4 hours	3.17	2.1	35.49
1:1:3	20 ml toluene	0.5 ml Et ₃ N + 0.138 ml NH ₄ OH	110°C	4 hours	4.52	2.24	50.67

V. Conclusions

HNTs has been modified with 3-chloropropyltrimethoxy silane. The grafting conditions have been carried out; the best solvent is toluene and the optimal molar ratio (HNT/CPTMS/H₂O) for the most effective grafting was 1:1:3. The grafting process is greatly affected by the addition of base catalyst.

Acknowledgements

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P-02

Effect of Regioregularity and Molecular Weight Control of HTMs on Perovskite Solar Cells Performance

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Among alternative energy sources, Perovskite Solar Cells (PSCs), raising in efficiency from 3.2% to 22-23% in only few years,¹ are the new frontier of the photovoltaic research. The polymeric Hole Transport Materials (HTM) extract holes and protect perovskite from moisture degradation due to their superior sealant ability.² We prepared several P3HT and PTAA conductive polymers. P3HT structure was modulated in molecular weight (20 to 300 kDa) and regioregularity (78-100%), to search for correlations between structure and solar cell efficiency.³ The P3HT were prepared by different synthetic methods (oxidative,⁴ C-H activation⁵ and Grignard Methatesis⁶).

The PTAA were prepared by polymerization of dibromo-substituted linkers with different anilines, with a Pd catalyst bearing a NHC ligand,⁷ obtaining polymers with short to medium molecular weight. Upon characterization, the polymers showed a very good stability and the estimation of energy levels was compatible with the most common perovskites used in perovskite solar cells. Those HTMs were used in crystal engineering perovskite⁸ solar cells, reaching a photoconversion efficiency of 17% and 13.4% respectively, confirming their good potential as HTMs for PSCs.

Acknowledgements

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P-03

Nanopolymeric System Development for Glycoproteins Recognition

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Abstract

Glycoproteins are well known among biomarkers for inflammatory and cancer diseases. Changes in glycosylation can be shown development of diseases like inflammation and cancer. Because tissue- and disease-specific modifications of outer membrane and secreted proteins are common, many N- and mucin-type O-glycoforms are good marker candidates and also serve as targets for imaging agents and therapeutics.

Our research focuses on developing a nanopolymeric system that can recognize glycoproteins due to lectin affinity. We synthesized a specific polymeric nanomaterial (p(HEMA)) with mini-emulsion polymerization technique and modified it with triethoxy-3-(2-imidazolin-1-yl)propylsilane (IMEO) and Concanavalin A. Nanopolymer was characterized with several advanced characterization methods. MUC1 was used as the model glycoprotein whose overexpression have a significant correlation with cancer cell proliferation, metabolism, invasion, metastasis, angiogenesis and chemoresistance. This nanopolymeric system also can be used revelation surface for other glycoproteins such as cancer antigens or Immunoglobulins.

Keywords: glycoproteins, disease, polymeric nanomaterial

I. Introduction

Markers for identification of diseases and treatment success are becoming increasingly important while developing new methodologies. Glycoproteins have high potential to be as markers for a variety of biological processes. Glycosylation of immunoglobulin and prostate-specific antigen, among many other proteins, represents well documented examples of disease-related alterations in site-specific protein glycoforms. Additionally, secreted glycoproteins are accessible in serum that makes them excellent candidates for the development of noninvasive serological assays (Chandler et.al., 2013). Different strategies exist for determination of glycoproteins such as carbohydrate/glycan arrays, lectin arrays, glycoprotein arrays, mass chromatography. Also there are some combined strategies, for example lectin capture strategies have been combined with other techniques, such as MS, for the discovery of serum glycoprotein biomarkers (Zhao et.al., 2008). MUC1 was used as the model glycoprotein whose overexpression have a significant correlation with cancer cell proliferation, metabolism, invasion, metastasis, angiogenesis and chemoresistance (Nath et.al., 2014).

II. Experimental Set-up and Procedure

Hydroxyethylmethacrylate (HEMA) based polymeric nanomaterial was synthesized with mini-emulsion polymerization technique and modified it with triethoxy-3-(2-imidazolin-1-yl) propylsilane (IMEO) and Concanavalin A. Concanavalin A binding were performed with optimization studies with respect to pH, time and concentration parameters.

III. Analysis

Nanopolymer was characterized with several advanced characterization methods such as scanning electron microscope (SEM), Zeta size and potential analysis, atomic force microscopy (AFM), Fourier Transform Infrared Spectroscopy (FTIR), elemental analysis, thermal characterization, surface area calculations.

IV. Results and discussions

From the SEM images, nanoparticles have been developed with app. 80 nanometers size and spherical shape. Zeta size results also indicate that their sizes are app. 180 nm. The difference between SEM results is due to Brownian effect on suspen-

sion. FTIR analysis shows that modification and derivation of p(HEMA) nanomaterial was successful due to specific bands of silanization agent and lectin. Amide I stretch bands are observed at 1636 cm⁻¹. The band at 1522 cm⁻¹ can be interpreted as belonging to the tyrosines in ConA. Si-O-C stress specific to the presence of IMEO are seen at 1245 cm⁻¹. The tension bands of the Si-O-Si bond were observed at 1145 cm⁻¹. From the AFM results it can be said that modification and derivation of p(HEMA) nanomaterials was resulted with changing in surface topology and porosity.

V. Conclusions

This nanopolymeric system were developed for recognition of MUC1 with high surface area, high specificity and low cost property. It can also be used as revelation surface for other glycoproteins such as cancer antigens or Immunoglobulins. It has a great potential in order to use biosensor and drug delivery systems.

Acknowledgements

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P-05

Synthesis of Quinalzolin-4-ones, with Potential Anti-diabetic Activity, through Reductive Rearrangement of 1,2,4-oxadiazoles

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1 Quinazolinones are benzo-fused N-heterocyclic compounds. The 4(3H)-quinazolinone is the structural element of a wide variety of natural products and biologically active compounds with different therapeutic and pharmacological properties like: antimicrobial, anticonvulsant, anticancer, antimalarial, antihypertensive, anti-inflammatory, anti-diabetic (1). In view of this fact, enormous efforts have been made to perfect efficient and affordable strategies for the construction of the quinazolinone skeleton and above all of the 2-substituted quinazolinones. The aim of this work has been the synthesis of quinazolinone derivatives through a new method of reduction of 1,2,4-oxadiazoles using ammonium formate as reducing agent and palladium as catalyst. The new method allows not very drastic conditions of reaction, easily available solvents and reagents. There are also a reduction in times of synthesis and a maximization of yields compared to the classical methods. The synthetic way used has allowed to get different quinazolinone derivatives variously substituted in positions 1 and 2. Among the synthesized quinazolinones there is the alkaloid glycosine whose hypoglycemic effect is known (2). A preliminary in vitro biological evaluation of the synthesized quinazolinone derivatives has been performed, in particular, cell viability on different cell lines and protection from the oxidative stress were considered.

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P-06

Conformational Analysis and Photochemistry of 2-Chloro-6-fluorobenzoic Acid Monomers in Solid Xenon

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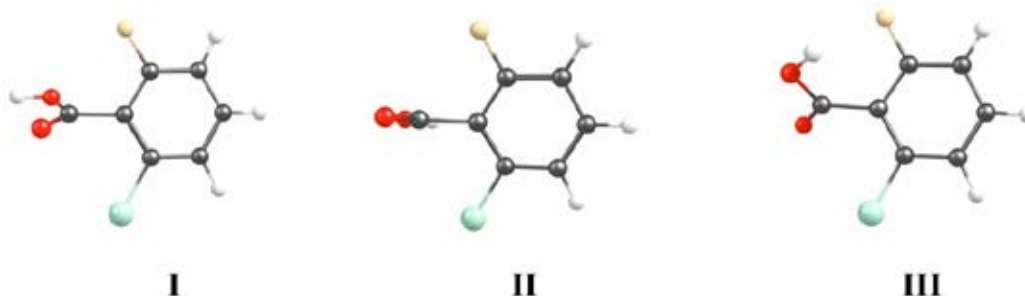
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In this study, the conformational space of 2-chloro-6-fluorobenzoic acid (CFBA) has been investigated theoretically using density functional theory, with the B3LYP functional and the 6-311++G(d,p) basis set, and experimentally by matrix isolation infrared spectroscopy.

The calculations allowed identification of 3 different non-planar conformers of the compound, the lowest energy form (**I**) exhibiting the carboxylic acid group in the *cis* arrangement (O=C–O–H dihedral equal to $\sim 0^\circ$), and the two higher energy forms (**II** and **III**) bearing a *trans* carboxylic group (O=C–O–H dihedral equal to $\sim 180^\circ$) (see Figure). The energies of conformers **II** and **III** are larger than that of the most stable conformer **I** by 17.07 and 17.31 kJ mol⁻¹, respectively.

The considerably large energy difference between the two *trans* conformers and the *cis* form implies that only this last species should exist significantly populated in the room temperature gas phase conformational equilibrium. In consonance with the theoretical predictions, only conformer **I** could be trapped from the room temperature vapor of the compound into low temperature (10 K) solid xenon.



The theoretical vibrational characterization of all 3 conformers of CFBA and the assignment of the experimental IR spectrum of conformer **I** were undertaken.

The matrix-isolated monomers of the compound were then irradiated *in situ* using narrowband UV light with $\lambda = 235$ nm. The major observed reaction channel was decarboxylation, leading to production of CO₂ and 1-chloro-3-fluorobenzene. Carbon monoxide was also detected in the infrared spectra of the photolysed solid Xe matrices of the compound, indicated that UV-induced decarbonylation of CFBA takes also place in some extent, though the expected accompanying photoproduct (2-chloro-6-fluorophenol) could not be experimentally sensed.

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P-07

Bactericidal Effect for AgNPs System Obtained on a base of AgNO₃ and Currant Pomace Extract

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Abstract

Susceptibility of *E. coli* to nanodispersed systems obtained from silver nitrate by treatment of pomace extracts has been evaluated. Extract was got by water maceration of berry pomace with ultrasound treatment. Sizes of obtained AgNPs were 50-70 nm. The minimal bactericidal concentration of AgNPs system is 10% and minimal inhibitory concentration is 4,2%.

Keywords: AgNPs, *E.coli*, minimal bactericidal concentration, minimum inhibitory concentration

I. Introduction

In recent time the great research interest takes place to nanosized materials and metal nanoparticles (Hamouda, 2012). Nanosized metal particles with designed surface and structural properties perform an new material with numerous physical, biological and pharmaceutical applications. Bactericidal action of silver nanoparticles strongly depends on size of particles which play an important role in the inactivation of the microorganisms. Nanoparticles less than 100 nm have area of extensive research due to their strong bactericidal properties (Sondi and Salopek-Sondi, 2004).

II. Experimental Set-up and Procedure

Dispersions of silver nanoparticles were prepared by conducted chemical process between argentum nitrate and currant pomace extract. Extract was obtaining by water maceration of plant material with ultrasound treatment with frequency 27 kHz and power 200 W during 1 hour. Dynamic light scattering was employed to measure the hydrodynamic size of nanoparticles in suspensions. The sizes of getting silver nanoparticles were 50-70 nm.

As object for estimation of bactericidal effect of silver nanoparticles solution on Gram-negative bacteria we used strain *Escherichia coli* UKM B-906. Active concentrations estimation in liquid medium meat-peptone broth was conducted by the method of standard evaluation of the antibiotics action (Determination guidelines, 2004). In set of tubes that covered 2 cm³ of nutrient medium we added 2 cm³ of AgNPs solution with concentration range and finally added 2 cm³ of *E.coli* inoculum. In control tube we put 2 cm³ of medium, 2 cm³ of aseptic distilled water, and 2 cm³ of inoculum. Experiment carried out in duplicate for ensure of result reproducibility. All experimental tubes incubated at 37°C in 24 hours. Results was evaluated as difference in the optical density of the suspensions by photoelectric colorimeter at $\lambda = 540 - 670$ nm. As additional control was visual analyze of bacteria grows on selective medium Endo agar.

III. Results and discussion

As result of chemical processes we got colloid system of silver nanoparticles with size 50-70 nm. Low values of optical density at least less than 0,07 as well as the absent of bacteria growth on Endo agar allow us to determinate the minimal bactericidal concentration (MBC) of AgNPs solution. For estimation minimal inhibitory (MIC) concentrations we used graphical method for determination half value of optical density in relation of control tube. Obtained AgNPs system has strong antibacterial action against *E. coli* and determinates MBC is 10 % and MIC is 4,2 %. Thus, currant extract contain compounds that acted as strong reducing agents able to recover cations of the dissociated Argentum salt as well as stabilizers of the obtained disperse system.

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P-08

Arsenic removal from natural water by adsorption/membrane filtration

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Abstract

Arsenic is one of toxic components, which is often present in natural water, especially in groundwater and artesian water. High arsenic content is characteristic for natural waters of many countries, including Ukraine. Concentration of arsenic in drinking water, which is higher than 10 $\mu\text{g/l}$, causes a lot of undesirable consequences (hyperkeratosis, cancer, different disorders). It makes necessary development of new methods and improving of existing methods of dearsenication. Hybride method (combination of adsorption and microfiltration or ultrafiltration) is very perspective in terms of arsenic removal.

Keywords: Arsenic removal, adsorption, hybride method.

I. Introduction

Membrane technologies are very popular both in drinking water and wastewater treatment due to its significant advantages, for example, high process automatization, small physical footprint, high efficiency, simple maintenance, etc. (Fane, Wang & Hu, 2015).

Membranes are also used for arsenic compounds removal in water treatment. Arsenic compounds can be removed from water by reverse osmosis or hybride method (adsorption/micrifiltration) (Litynska et al., 2019).

II. Experimental Set-up and Procedure

Iron (III) oxyhydroxide was precipitated from FeCl_3 solution by thermal hydrolysis of urea. Synthesized adsorbent consisted from small particles with crystal structure of FeOOH (Litynska et al, 2018).

Artesian water from Kwasy (Western Ukraine) was used for experiments.

Mixing of raw water and ferric oxyhydroxide was the first stage. Second step described interaction between adsorbent particles and impurities. Arsenates were immobilized on the particle surface due to formation of insoluble ferric arsenate. Phosphate removal mechanism was the same. Separation was the third step. Adsorbent with immobilized impurities formed protective layer on the membrane surface. Backwash was the fourth stage. Water flow removed adsorbent with immobilized pollutants. After it membrane was as clean as before filtration (Litynska et al, 2019). Water was mixed with ferric oxyhydroxide suspension and separated by fixed in filter holder membrane filter. Arsenic content was determined in filtrate. Total arsenate concentration was detected photometrically in the form of blue compound of redoxing of heteropoly acids (Litynska et al, 2019).

IV. Results and discussions

Initial arsenic concentration in artesian water from Kwasy (Western Ukraine) was 16733 $\mu\text{g/L}$, which is more than 1673 times higher maximum allowable concentration of arsenic in drinking water. pH of this water was 6.46.

Suspension of iron (III) oxyhydroxide was used for arsenic removal. Adsorbent dose was 110 mg/L . After 30 minutes of adsorption arsenic content reduced in 15.7 times and pH increased to 8.15. Thus, this treatment method was very effective in arsenic removal, but for completely effective treatment higher dosages should be used.

V. Conclusions

Combination of adsorption by iron (III) oxyhydroxide and microfiltration for adsorbent removal is effective method of reducing of arsenic content in water. After 30 minutes of adsorption arsenic content reduced in 15.7 times (initial

concentration was 16733 $\mu\text{g/L}$) and pH increased from 6.46 to 8.15. But for completely effective treatment higher dosages should be used.

Acknowledgements

Marta Litynska and Nataliia Tolstopalova are the supervisors of this research.

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P-09

Remote Monitoring of Quality of Agricultural Soils

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The paper presents studies on some of the soils physicochemical characteristics using a portable monitoring system, which is assembled on the basis of a board with the Arduino Mega 2560 microcontroller and sensors of temperature, humidity and CO₂ content. At the same time studies in a closed ground system were conducted. The results of both studies correlate with each other, which allows us to conclude that the development remote monitoring system is very promising.

Keywords: agriculture soils, ground air, gas sensor, remote monitoring system

I. Introduction

The efficiency of agricultural use of soils depends directly on their quality indicators, which include an extended set of characteristics: from data of the geodetic and engineering researches to the component composition of the soil air. Therefore, for a more complete survey of agricultural land in order to determine their qualitative indicators and subsequent application, it is necessary to carry out topographic and geodetic researches, while simultaneously studying the characteristics of soils and their air composition. The solution to this problem is possible with the help of a portable device – remote monitoring system (RMS), which doesn't have analogues to date. Using unmanned aerial vehicles (UAR or drones) and related devices (digital video camera and various detectors), it is possible to monitor agricultural lands and to make their aerial surveys in order to solve a huge number of problems, which include analysis and assessment of soil state, observing changes in their composition, research of the influence of various factors on their quality and control of the fertility level. The digital terrain model can provide information on the state of the environment, simulate the ecological situation of the studied region, and allows preliminary conclusions to be drawn about the possibility of the area usage in agriculture. The additional equipping of the unmanned vehicle with appropriate detectors will allow to determine the basic soil parameters, such as temperature, humidity, content of gas phase components of the ground air (CO₂, CO, O₂ and H₂S). Ultimately, this will not only set the type of soil, but also predict the quality indicators and crop capacity.

II. Experimental Set-up and Procedure

Fig. 1a shows the created portable soil and air monitoring device.

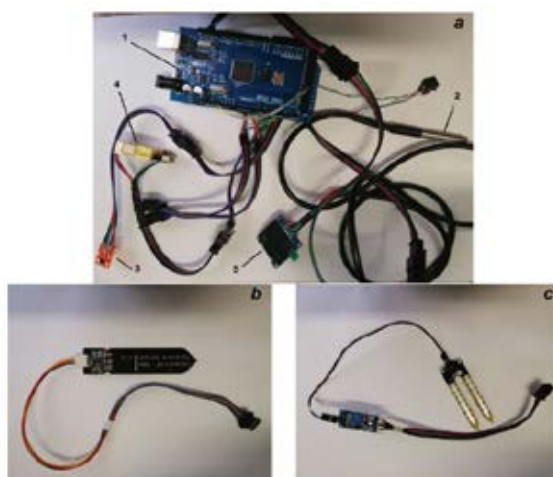


Fig. 1: Experimental installation

The developed system includes following main elements: a board with the Arduino Mega 2560 microcontroller 1; digital contact temperature sensor DS18B20 2; temperature and humidity sensor GY-21 HTU210 3; infrared sensor for the CO₂ content MHZ-19B 4 and display 5. Additionally capacitive soil moisture sensor (Fig. 1b) and soil moisture sensor resistive (Fig. 1c) were used.

III. Analysis

Soil monitoring was carried out in two ways. In the first case, the so-called closed soil system was used (Fig. 2), which in the laboratory was a tight-fitting chamber with a volume of 140 liters with the ability to control and establish temperature and humidity. 1.5 kg of the standardized soil (the content of organic matter = 3.3%, K=4.69; pH = 5) was used to seed with *Agaricus bisporus* and was placed in the chamber. For 2 days ground air was periodically analyzed for O₂ and CO₂ content by an gas-content analyzer "Dozor-5C-M". Additionally soil was examined for a change in pH over time. In the second case, the with a period of 30 minutes soil was constantly analyzed by the developed remote monitoring system RMS. RMS allowed to control temperature and humidity values, as well as change of CO₂ content in ground air.



Fig. 2: Laboratory closed soil system

IV. Results and discussions

As a result of monitoring, it was found that throughout the monitoring period O₂ content decreased slightly, while the percentage of CO₂ increased. A parallel study by the remote monitoring system showed a gradual increase in soil moisture from 7% to 60% (which corresponded to the established moisture value in the closed soil system), and also confirmed the increase in CO₂. In addition, soil pH analysis showed an increase in pH from 5 to 8 in a few hours. In general, the CO₂ content values determined using readings gas analyzer and the monitoring system coincided.

V. Conclusions

Thus, it is expected that created remote monitoring system for the simultaneous study of agricultural soils by the indicators of topographic, geodetic surveys and data on the characteristics of soils will allow determining the quality of soils in order to assess their yield on the basis of the analysis of physicochemical and biochemical soil characteristics and on-line monitoring the quantitative composition of soil air. Such a system will be useful not only for studying soil quality, but also for studying the environmental situation, as well as for determining their safety as a point of view of pesticide contamination and an overdose of fertilizers. It is planned to further modernize the system as well as field testing of the developed remote system. Further RMS will be equipped with gas sensors for the determination of additional components of ground air, such as O₂, NO_x, H₂S, CH₄.

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P-10

Chemical Characterization of Apricot Pomace: A Possible Use of an Agricultural Waste

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Abstract

Different organic solvents were applied for the conventional extraction of Apricot pomace, phenolic contents and antioxidant activities were investigated. Chemical characterization of apricot pomace extracts (APE) was also made by Gas chromatography-mass spectrometry (GC-MS). The extracts were screened for free radical-scavenging potential, using a 1,1-diphenyl-2-picrylhydrazyl in vitro model system. The extracts exhibited significant radical-scavenging activity and the EtOH/2-propanol APE showed the highest activity.

Keywords: apricot pomace, extraction, phenolic content, free radical-scavenging

I. Introduction

Several plants are rich in useful phytochemicals/"green" organic compounds which can be present in different parts of the plant such as leaves, crust, peels, flowers, fruits and seeds. Apricot pomace represents the portion of the fruit with the highest concentration of chemical active molecules so that their waste represents a double loss for agri-food industry that has to face the cost of disposal and the loss of profits for their re-use and valorization. In the present work we report the physicochemical properties of apricot pomace of an agroindustrial waste of Apricot fruit. The field of application of plant extracts is very diverse. Phytochemicals/"green" organic compounds can be used for the green synthesis of nanomaterials [1], as corrosion inhibitors [2], to create nanoemulsions [3]. The stability of different extracts from the same material depends on the extraction solvent used for removal of the polyphenolic compounds, and it is apparent that extracts from the same plant material may vary widely with respect to their antioxidant concentrations and activities. Different extraction solvents have been investigated for the extraction of green organic compounds from wastes. The solvent properties present, undoubtedly the key role in the extraction of green organic compounds. Our work is the first approach for studying each group to secondary metabolites separately and investigating if there is a correlation between the composition of the extracts and the AgNPs synthesis features [4-6]. Our hypothesis is that different morphologies and properties of nanoparticles can be obtained using chemical fractions of the plant extract. The most suitable solvents for the extraction of «green» active compounds, from the point towards safety for the environment, are water, ethanol and 2-propanol or mixtures thereof. At the same time there is a lack of information to compare, the effects of different solvents on the composition profiles and physicochemical properties of the apricot pomace.

II. Experimental Set-up and Procedure

The object of research is crushed dried of apricot pomace. One apricot (*Prunus armeniaca* L.) cultivar known under local name "Favorite" was harvested (during July 2019) in two geographical regions of Ukraine (Kherson, Nikolaev). Dried root powder (20 g) was packed into a Soxhlet apparatus and extracted with 300 mL solvent at 60–65 °C for 3–4 h. Three frequently used solvent systems; including ethanol (EtOH) C₂H₅O; 99.8%, CAS 64-17-5), PubChem CID: 702), 2-propanol ((C₃H₈O; CAS 67-63-0; PubChem CID: 3776),) and solution of 2-propanol/ethanol were selected for comparisons. The final extract was then filtered in Whatman filter paper No. 1. DPPH• and ABTS• methods were selected to evaluate the in vitro antioxidant capacities of extracts.

III. Analysis

The extracts of apricot pomace (APE) were analyzed by gas phase chromatography-mass spectrometry (GC-MS) tech-

nique as described in our previous work [4]. The components were identified by comparing the peak retention times in the chromatogram and the complete mass-spectra of individual components with the corresponding results for pure compounds in the NIST-5 Mass Spectral Library. Voltammetric experiments were carried out with a potentiostat/galvanostat.

IV. Results and discussions

GC-MS analysis gives an idea about the phytochemical constituents present in extracts of apricot cakes. According to the obtained chromatographic-mass spectral analysis data, the composition of propan-2-ol extract of dry pomace of apricot contains 38 individual components present in an amount of more than 0.54 %. All of them are known compounds and are easily identified by mass spectrum and linear retention indices. The main components are aldehydes: hexanal (1.32 %), (E)-2-hexanal (3.10 %), (Z)-2-heptenal (3.65 %), heptanal (2.18 %), 2-phenylacetaldehyde (1.29 %), β -cyclocitral (5.17 %), (E,E)-2,4-decadienal (3.65 %), also ketones: 2-hexanone (1.03 %), 3-hexanone (0.54 %). The class of alcohols is presented by (Z)-3-hexenol (0.76 %), (E)-2-hexenol (1.87 %), hexanol (5.67 %). In a minor amount, the extract contains esters, such as (E)-2-hexenyl acetate (2.78 %), (Z)-3-hexenyl butanoate (1.51 %), hexyl hexanoate (2.12 %). Also, the kernel of the fruit contains many acids, this class is represented by octadecanoic acid (6.02 %), (9Z,12Z)-octadeca-9,12-dienoic acid (4.2 %), hexadecanoic acid (5.4 %), (9Z)-octadec-9-enoic acid (6.1 %), (9Z,12Z,15Z)-9,12,15-octadecatrienoic acid (0.63 %). The extract of apricot pomace contains an increased content of terpene alcohols: linalool (3.06 %), α -terpineol (5.98 %), nerol (3.02 %), geraniol (8.54 %), isoborneol (1.03 %), nerolidol (8.54 %), farnesol (1.38 %) and others. These compounds represented over 18 % of the total volatiles in apricot pomace.

The mixture of solvents displays a higher capacity of phenolics extract than the isolated solvents. The 2-propanol - EtOH mixture extracted more phenolic compounds. The results obtained are in agreement with the studies reported, which related that the mixture of solvents is more favorable for the extraction of phenolic compounds in vegetable samples than the mono-solvent systems.

TPC of the apricot pomace extracts ranged from 33.1 GAE/100 g (fw) to 51.3 GAE/100 g (fw). The amounts of phenolic compounds in the ethanol extract were highest. The total flavonoid (TFC) content of these extracts was determined. The EtOH/2-propanol APE also had the highest TF content, followed by EtOH APE and 2-propanol APE (Table 2). No linear correlation was observed between solvent polarity and TPC. The total antioxidant activity of EtOH /2-propanol APE is 440.86 ± 2.63 mg of AsA/g of the extract.

The oxidation behavior of apricot pomace extracts was investigated by CV. Electrochemical methods such as cyclic voltammetric studies can be used to obtain the redox potential, which can be used to estimate the reducing power of an antioxidant, a key factor governing its antioxidant ability. During a cyclic voltammogram of an apricot pomace extract, the phenolics present will be oxidised as the electrode potential is scanned in a positive direction. The overall response will be the sum of the various species present. While any other oxidisable components present in the extracts also contribute at some potential, it is only the phenolics that are expected to produce a current at potentials less than 400 mV. The cyclic voltammogram for the extract showed no clear reversible peaks but only gave a shoulder and a monotonously increasing peak. For comparison, current-voltage curves are obtained on model substances. Ascorbic acid shows a reversible peak at 0.303 V. Gallic acid shows two peaks at 0.3 and 0.42V. Since the voltammogram does not show any clear reversibility, it was not possible to calculate the area of the voltammogram, which in turn could be used to estimate the total antioxidant capacity of the extract.

The antioxidant potential determined by this method followed the same tendency observed for the total phenolic compounds, in which the extracts obtained with the binary mixtures were more efficient in the extraction of compounds with antioxidant activity than the mono-component solvent systems. These results can indicate that the phenolic compounds present in the apricot pomace display a moderately polar character.

The results clearly indicated that the apricot extracts significantly inhibited free radicals generation based on concentrations and assays used. The highest values of DPPH radical inhibition were observed in standard compound ascorbic acid (87.65 %), whereas the lowest inhibition value was recorded for 2-propanol extracts (13.55 %) at the initial concentration (0.05 mg/ml). Standard solution (ascorbic acid) exhibited the highest inhibition (98.50 %), followed by EtOH /2-propanol APE (95.71 %), EtOH (92.02 %), and 2-propanol (57.78 %) extracts at a concentration of 0.30 mg/ml. The analysis of DPPH• scavenging activity results indicated that EtOH /2-propanol APE were the most effective DPPH radical scavengers among two other extracts (2-propanol and EtOH). In addition, the results of the DPPH and ABTS radical scavenging activities indicated that apricot pomace possessed strong antioxidant activities, which compared well with the synthetic antioxi-

dants. This fact is of great economic interest owing to several applications of apricot pomace in the cosmetic and medicinal industries, in chemical material science.

V. Conclusions

With the increasing interest in circular economy and zero waste, there has been intense effort to revalorise food by-products. The apricot pomace contains a considerable amount of phenolic compounds with antioxidant potential, which can be extracted using organic solvents. However, this extraction depends on the interaction between the phenolic compounds present and the type of solvent. Moderately polar solvent mixtures such as 2-propanol and EtOH, were highly efficient to extract the phenolic antioxidant compounds of the studied sample. Thus, the extracts obtained from apricot pomace have the potential to become a promising phytochemicals/"green" organic compounds, with varied applications in the cosmetics, pharmacy and food industries. The apricot pomace extracts contained more phenolic compounds with substantial antioxidant potentials. The antioxidant potentials of apricot pomace extracts may be attributed to other compounds, such as organic acids, along with the phenolics.

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P-11

Effective Liquid Coagulants from Secondary Raw Materials

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Abstract

Acid-thermal activation liquid complex coagulants were characterized by the following chemical composition (by major components): coagulant LCCL Fe - 82,87%, Al - 5,12%, Ti - 0,98%, Ca - 1,78%. Synthesis of effective coagulants was carried out by acid-thermal treatment of alumina waste. Liquid complex action coagulants, obtained in a simple way from alumina waste, have shown high efficiency (up to 99.7%) against dyes of different nature. The efficiency of using synthesized liquid coagulants was tested on model waters containing cationic dyes (methylene blue), anionic dyes (Congo chevrons), and mixture thereof. The synthesized liquid coagulant are dominated by compounds of iron, aluminum and titanium, which make it more efficient than commercial FeCl₃. The results obtained for the synthesized coagulants were compared with those for the FeCl₃ product coagulant. It was found that for synthesized coagulant with a dose of 10 mg/l the efficiency was 99,7%, while for FeCl₃ with a dose more than 2,5 times only 95,4%. Due to the acceleration of the stage of formation, integration and deposition of particles, the duration of coagulation purification by synthesized coagulants is 3 times less than when using commercial FeCl₃.

Keywords: Effective coagulant, coagulation, wastewater treatment, red mud, dyes

I. Introduction

In recent years, despite the improvement of existing technologies in the chemical industry, man-made load on the biosphere is increasing, which is reflected in the amount of waste and wastewater volume. The textile industry is no exception and the quantity of sewage polluted by pollutants of different nature (dyes, surfactants, salts of different nature) is constantly increasing. Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light. Therefore, to achieve a satisfactory degree of purification of such wastewater, it is necessary to carry out a complex of technological methods such as coagulation, filtration, adsorption on activated carbon and the like.

Among the many methods of water treatment, today in practice (both on municipal treatment plants and in industry), the coagulation method is most often used, which allows to remove contaminants of different origin. This method is simple, provides for use of different coagulants and is quite effective (Nabibidhendi G.R. et al. 2007).

Consequently, the traditional wastewater treatment of textile industries is usually realized by combining the use of iron-containing coagulants with sorption purification on activated carbon. However, the high cost of activated carbon and the complexity of its regeneration make it necessary to find ways to modify it to improve performance. Therefore, it is relevant for wastewater treatment without the use of activated carbon is the need to develop new highly efficient and inexpensive coagulants. For such coagulation reagents, cost reductions are possible, for example, when replacing raw materials for waste from different productions containing iron and aluminum compounds. Such wastes in large quantities are waste from alumina production - red mud. Due to the high content of iron oxides (up to 55%) and aluminum (up to 30%), red mud can be used in water purification technology as coagulants or adsorbents after their synthesis processes (Kyrii S.O. et al. 2018).

II. Experimental Set-up and Procedure

The synthesis of the coagulant was carried out by treating the red mud with 15% HCl in a mass ratio 1: 1 and boiled at 100 °C for 1 hour. The resulting suspension was filtered and the filtrate was used as a liquid coagulant (LC). The elemental composition of the synthesized coagulants by major components was determined by the X-ray fluorescence method on an

Oxford X Supreme instrumentation device. For coagulation experiments jar-test was used.

III. Analysis

Acid-thermal activation liquid complex coagulants were characterized by the following chemical composition (by major components): coagulant LC Fe - 82,87%, Al - 5,12%, Ti - 0,98%, Ca - 1,78%.

The efficiency of using synthesized liquid coagulants was tested on model waters containing cationic dyes (methylene blue), anionic dyes (Congo red), and mixture thereof. The results obtained for the synthesized coagulants were compared with those for the FeCl_3 product coagulant.

IV. Results and discussions

The coagulation was examined using a pH-adjusted jar test. For the synthesized coagulants the pH was adjusted to 7, for the commercial FeCl_3 coagulant - to 9 (at the beginning of the flocs formation).

As a result of the research, the optimal conditions for carrying out the coagulation process for different types of dyes were determined. It is established that for the treatment of water contaminated with one type of dye, the optimal doses are the same for both coagulants and equal to 10 mg/l. For the treatment of model water with a mixture of dyes, the optimal dose of the standard FeCl_3 coagulant is in 2.5 times higher (25 mg/l) than for the synthesized coagulant LC (11 mg/l). In this case, the removal efficiency of dyes ranges from 94% to 99.7% depending on the type of dye and coagulant obtained by the liquid coagulation reagents (Fig. 1).

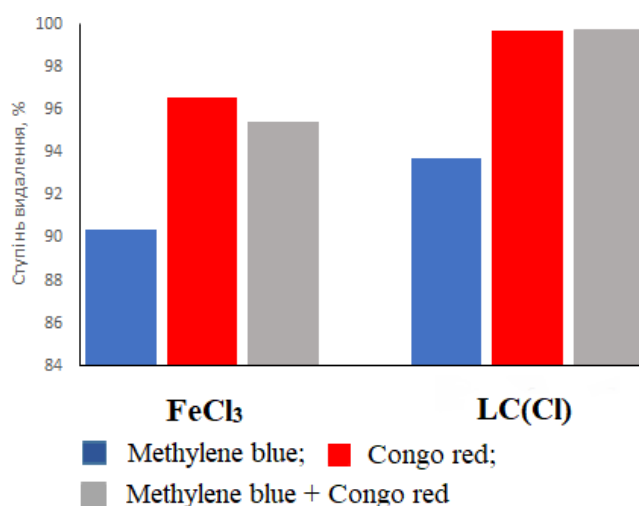


Fig. 1: Comparison of the effectiveness of using FeCl_3 and LC for different pollutants at optimal doses

V. Conclusions

A new effective liquid coagulant was synthesized from wastes of alumina production. It was found that in the case of removal of a mixture of dyes (anionic and cationic) from aqueous solutions, the dose of synthesized coagulant is 2 times lower than the commercial coagulant FeCl_3 . The difference in efficiency between the commercial FeCl_3 and the synthesized LC is explained by its complex effect, since in the LC, in addition to the iron compounds, has also aluminum and titanium compounds.

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P-12

Effects of Diisocyanate Compatibilizers on the Properties of Star-Shaped Poly(ϵ -caprolactone) / Poly(lactic acid) Blends

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Poly (lactic acid) (PLA) is linear aliphatic thermoplastic polyester, known as one of the most popular biodegradable polymers which can be produced from renewable resources. It has a relatively high tensile strength, rigidity, stiffness and high modulus, but its brittleness and low toughness confine its potential applications (Drumright, 2000; Noroozi, 2012; Piorkowska, 2006;) [1-3]. In order to be used effectively PLA is needed to be toughened and its brittleness should be reduced (Deokar, 2016; Drumright, 2000). So, it is generally blended with other flexible and biodegradable polymers. Poly (ϵ - caprolactone) (PCL) is one of the widely used biodegradable polymer which is used for the improvement of toughness as well as enhancing its features (Deokar, 2016). But PLA and PCL blends display immiscible (phase-separated) morphology which causes a disadvantage. The commercial compatibilizers such as diisocyanates (methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), phenylene diisocyanate (PDI)) are generally added to the mixtures in order to increase the compatibility between two immiscible polymers. In this study, the effects of amount of diisocyanate compatibilizers which is added to the selected compositions were investigated to the thermal, mechanical and morphological behaviors of the star-shaped PCL/PLA blends.

Keywords: Diisocyanate, star-shaped, PLA, PCL

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P-13

Water Harmony Projects: Impact on Water Related Education

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Abstract

Water resources, as well as sources of fresh water are distributed in the world unevenly. Thus, the issues of development, management and rational use of water resources, the formation of water policy at the international, regional and national levels affects all aspects of sustainable development - social, environmental, integral - and are the focus of attention of water related education. Water Harmony Projects gave a great opportunity to improve scientific component of masters and post-graduate programmes in partner universities, to create sustainable and dynamic network of water professionals.

Keywords: water related education, Water Harmony Project, teaching approach

I. Introduction

Generally, education is one of the most effective ways of sharing experience. Implanting the philosophy of sustainable development in terms of legislative, scientific and practical aspects in the institutions of higher education, the universities integrate this knowledge into other areas through their graduates – into production, society; they influence politics and involve more and more participants.

Water Harmony Projects allow using international experience in the field of water resources to involve an increasing number of participants: students, scientists, representatives of environmental and other public organizations. First Water Harmony Project has been established in 2011 and involved eight universities from five countries: Belarus, Kazakhstan, Tajikistan, Ukraine and Norway. Water Harmony II is the second stage that develops a successful initiative to harmonize water related higher education. The second stage of the project unites 10 universities from Belarus, Moldova, Kazakhstan, Kyrgyzstan, Tajikistan, Ukraine and Norway.

II. Overall objectives of the Water Harmony Projects and results

Main aim of the Projects is to harmonize teaching approaches and strategies on water related graduate education. Development and harmonization of the graduate programs, dissemination of best practices among partners, strengthen entrepreneurship skills for both students and teachers, upgrading laboratories, development e-learning modules, involving students, teachers and professionals into joint events such as international conferences, exhibitions, workshops, dissemination of project results and success stories are the overall objectives of the Water Harmony Projects.

The results of the Projects are achieved through the Interaction with enterprises, NGOs, employers, a large number of student and staff mobility across countries, and joint research, lectures and publications.

III. Added value of the Water Harmony Projects

The most significant benefit of the Projects is related to students, administrative/teaching staff and interaction with future employers. For instance, students' understanding of the importance of foreign language skills and experience in the chosen field has been improved. Students also improved their transversal skills: market mobility, professional development facilitating transformation into a new role. Additionally, the understanding of administrative staff and teachers about the use of Internet technologies to intensify collaboration with entrepreneurs has improved. Teachers have gained experience in organizing international meetings, learned best practices, IT skills, transversal skills, and improved language skills.

IV. Conclusions

Water Harmony Projects have great impact on water related graduate education in countries involved in the project. The water problem, which is the main topic of the Projects, is not only of a local or national, but also of global scope. Project

graduates are able to see water problems, the ways of its solution and new opportunities to sustainably solve the problems connected with water. Larger quantity of participants in the Water Harmony II Project allows to share experience and best practices widely.

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P-14

Selective Metal-Free Aerobic Oxidations of Toluene to Benzaldehyde with *N*-Hydroxyphthalimide in Trifluoroacetic Acid

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Abstract

Despite enormous efforts, the synthesis of aldehydes by direct aerobic oxidations of methylaromatics, in particular toluene conversion to benzaldehyde, still is problematic preparatively even with such remarkable catalyst as NHPI. Herein we first study the aerobic oxidation of toluene with and without NHPI experimentally utilizing trifluoroacetic acid as highly polar reaction media. The potential of highly polar trifluoroacetic acid (TFA) for the PINO-propagated aerobic oxidations was demonstrated experimentally utilizing *N*-hydroxyphthalimide (NHPI) with catalytic (NaNO₂) amounts of initiators. The oxidations of toluene gave benzaldehyde with >90% selectivities under high conversions of starting hydrocarbon.

Keywords: Metal-free oxidations, *N*-hydroxyphthalimide, highly polarized radical, toluene

I. Introduction

Partial oxidation of toluene to benzaldehyde represents a formidable challenge both for laboratory and industrial chemistries as even at moderate conversions over-oxidations to benzoic acid dominate. Here, we propose to utilize powerful "green" organocatalyst *N*-hydroxyphthalimide (NHPI, Scheme 1) for corresponding selective transformation. NHPI occupies an outstanding position in aerobic oxidations (Melone, 2013) as it useful for hydrocarbons ranging from nonactivated saturated to activated alkylaromatics and is effective both in presence of transition metals (Opeida, 2011) and under metal-free conditions (Sakaguchi, 2001). At the initiation step (typically with the metal-peroxo species or with NO₂-radical, **A**, Scheme 1) NHPI generates highly electrophilic phthalimide *N*-oxyl (PINO) radical, which is involved into the CH-abstraction step (**B**) from hydrocarbon (RCH₃). This recovers the catalyst NHPI³⁵ and thus formed hydrocarbon radicals RCH₂• are trapped (**C**) with molecular oxygen to form peroxy-radicals RCH₂OO• that propagates the oxidation by generating PINO from NHPI (**D**). Hydroperoxides RCH₂OOH thus formed undergo dehydrations/exchanges/oxidations typical for hydrocarbon aerobic chemistry (**E**).

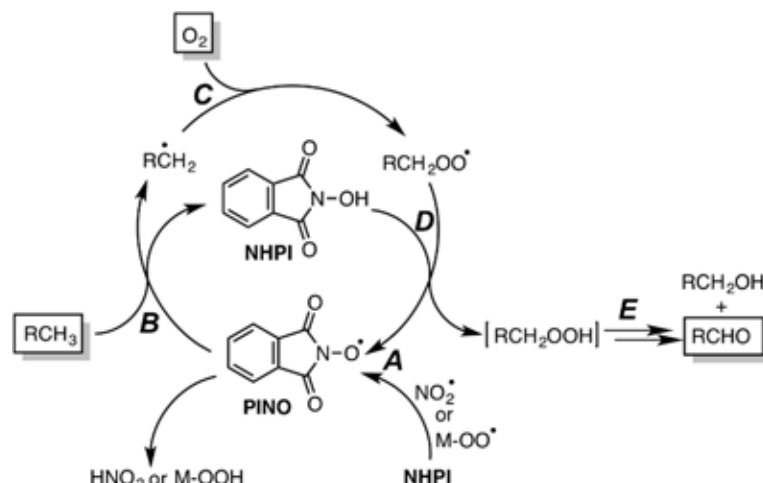


Fig. 1. The aerobic oxidations of the methyl group carried by the phthalimide *N*-oxyl (PINO) radical generated from *N*-hydroxyphthalimide (NHPI) and initiated by the NO₂- or metal-peroxo-radicals.

II. Experimental Procedure

Toluene (1) oxidation to benzaldehyde (3), Method A. Under oxygen atmosphere 6 mL of TFA is slowly added in portions to a stirred mixture of 2 mL (18.9 mmol) of toluene (**1**), 750 mg (4.6 mmol) of NHPI, 525 mg (7.6 mmol) of NaNO₂ in 6 mL of co-solvent (*n*-hexane or CH₂Cl₂) of at 0 °C. The reaction mixture stirred at room temperature for 13 h, quenched by water (5 mL). Organic layer was separated and water part was extracted with *n*-hexane (2x5 mL). Combined extracts were washed with 10%-NaHCO₃ solution (3x5 mL), water (2x5 mL), shaken with saturated solution of NaHSO₃ (10 mL) for 2 h and diluted with water to dissolve the precipitate. Water layer was separated, washed with *n*-hexane (2x5 mL) and 10 mL of 20%-NaOH water solution was added. A free aldehyde was extracted by pentane (3x5 mL), combined extracts washed with water (2x5 mL), dried over MgSO₄ and evaporated to give 0.7 g (35 %) of benzaldehyde (**3**) identical to the standard sample.




Toluene (1) oxidation to benzaldehyde (3), Method B. The same as **Method A**, but without a co-solvent gave 0.76 g (38 %) of benzaldehyde (**3**) isolated as above.

Toluene (1) oxidation to benzaldehyde (3), Method C. A solution of 525 mg (7.6 mmol) of NaNO₂ in 1 mL of water was added in portions to a stirred under oxygen atmosphere mixture of 2 mL (18.9 mmol) of toluene (**1**), 750 mg (4.6 mmol) of NHPI, 6 mL of TFA at room temperature over 1 h. Reaction mixture stirred at room temperature for 3.5 h resulting in 0.74 g, (37 %) of benzaldehyde (**3**) as above.

III. Results and discussions

In order to avoid undesired electrophilic aromatic substitutions we replace the traditional source of NO₂-radical, namely nitric acid by alternative source. Sodium nitrite (NaNO₂) is an environmentally friendly inexpensive transition-metal-free “green” catalyst (Su, 2013), produces NO under mild acidic conditions. We first tested the acetic acid as a media for the oxidations of **1** with NaNO₂/NHPI and found a negligible conversion even at prolonged reaction times (Table 1, Entry 1). In contrast, in TFA at room temperature in presence of *catalytic amounts* of NaNO₂ the reaction proceeds smoothly displaying high conversions rates of **1**. To our surprise even at 80% conversion of **1** benzaldehyde **3** still dominates in the reaction mixture and benzoic acid (**14**) is formed only in trace amounts (Table 1). We compared two different procedures, namely the addition of solid NaNO₂ with (Method A, Table 1, Entries 1- 3 and 7-9) and without co-solvent *n*-hexane (Method B, Entries 4 and 5) and did not find any substantial differences. As some previous NHPI-oxidations in biphasic systems^{83,84} or in aqueous organic solvents⁸⁵ were successful, we also used NaNO₂ as saturated water solution (Method C, Entry 6). All three procedures (A-C) gave benzaldehyde **3** in 35-38 % preparative yield.

Table 1. The oxidations of toluene (**1**) in trifluoroacetic acid (TFA)

#	Method	Temp.	Time, h	Conv. of 1 , %	CH ₂ OH  (2), %	CHO  (3), %	COOH  (4), %	Isolated yield of 3 , %
1	A ^{a,b}	RT	25	4	traces	0.1	0.3	-
2	A	RT	13	83	2	38	0	35
3	A	10 °C	4.5	12	0.5	0.6	0	-
4	B ^c	35 °C	13	98	7	48	5	38
5	B	45 °C	2	90	4	31	11	-
6	C ^d	RT	4.5	89	3	42	3	37
7 ^e	A	RT	22	18	traces	1.4	3	-
8 ^f	A	RT	20	0	0	0	0	-
9 ^g	A	RT	13	7	traces	1.1	0	-

aMethod A: 18.8 mmol of toluene, 4.6 mmol of NHPI, 6.2 mmol of NaNO₂, 6 mL of hexane, 6 mL of TFA; b acetic acid used instead of TFA; c Method B: Same as Method A, but without *n*-hexane; d Method C: Same as Method B but NaNO₂ was added in 1 mL of water dropwise over 1 h; e without NHPI; f without NaNO₂; g under argon atmosphere.

The signs of the over-oxidation were observed only under slight heating, which substantially accelerates but lowers the selectivity of the reaction (Table 1, Entries 4 and 5). Only very slow reaction was observed in the absence of NHPI (Table 1, Entry 7), where benzoic acid dominates over **3**. The reaction is completely suppressed in absence of initiator NaNO₂ (Table 1, Entry 8) and only traces of oxidation products form under argon atmosphere (Table 1, Entry 9) demonstrating the true

aerobic nature of the reaction.

IV. Conclusions

Trifluoroacetic acid demonstrates its high efficiency as a solvent for the metal-free aerobic NHPI-catalyzed oxidations of toluene. Utilization of the catalytic amounts of sodium nitrite NaNO_2 instead of HNO_3 allows achieving the unprecedentedly high selectivities for toluene conversions to benzaldehyde almost completely avoiding over-oxidations.

Acknowledgements

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P-15

Silver Complexons as Anti-Microbial Additives to Cosmetic Products

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Abstract

The synthesis and investigation of silver complexants on the basis of ethylenediaminetetraacetic and ethylenediaminedisuccinic acids are presented. Using the physicochemical methods of analysis, the composition and structure of the synthesized compounds were determined, and the stability constants of the complexes were calculated. Using the method of dynamic light scattering and electron microscopy, it is shown that the obtained systems are nanoscale one-dimensional objects. Dispersion systems are monodisperse, with a predominant particle size of 50 nm. The introduction of silver in the composition of biologically active complexes promotes the antibacterial properties of silver complexants in comparison with free ligands

Keywords: argentum, complexons, complexants, antibacterial properties

I. Introduction

Drugs based on silver interfere with the reproduction of fungi, parasites, viruses and block their entry into cells, are effective against hundreds of species of bacteria, whose resistance to silver is very low (Martinez-Andrade 2018). Despite such effective resistance to microorganisms, silver does not show any toxic effect on the skin's own flora. The effectiveness of silver is due to the ability to inhibit the activity of enzymes that help oxygen exchange in simpler organisms. In this regard, foreign microorganisms die in the presence of silver ions due to impaired oxygen supply (Ignacio Azócar 2014). The specific properties of complex silver compounds create the preconditions for synthesis and research, because they are used in medicine, pharmacology, cosmetics and are in demand among the population, who is aware of the unique properties of silver, long ago. The use of nanosilver in cosmetic products is a new trend in modern research. It is known that depending on the dispersion of silver nanoparticles may exhibit different properties. Therefore, it is of interest to synthesize and investigate the coordination compounds of silver in which the biologically active compounds, in particular complexes, will act as ligands.

II. Experimental Set-up and Procedure

The silver complexes with Ethylenediaminetetraacetic (Agedta) and Ethylenediaminedisuccinic acid (Agedds) were synthesized. Ethylenediaminedisuccinic acid was obtained by reacting ethylenediamine with maleic acid. The reaction time is 8-9 h pH = 9; t = 105 °C, 90% yield of complexon. The synthesis of the complexes was carried out in aqueous solution at an initial ratio of components 1: 1, pH = 7-8. The complexes were planted with ethanol in a ratio of 1: 3 aqueous solution: alcohol, respectively. The yield of the final product was 90-95% depending on the complexon. Elemental analysis is used to determine the composition of synthesized compounds. The hydrated composition of the compounds and their thermal characteristics were determined by the differential thermal analysis (DTA) method. The IR spectroscopy method is used to determine the method of coordination of metals with functional groups of ligands in complexes. Electron absorption spectroscopy (ESA) and diffuse reflection spectroscopy (DRS) methods were used to determine the structure of the resulting complexes and surface-plasmon resonance band registration. The method of dynamic light scattering was used to determine the dimension of systems.

III. Analysis

Determination of the contents of the elements (C, H) was carried out on the Perkin-Elmer CHN 2400 analyzer. Elemental analysis on the metal content was carried out on the atomic emission spectrometer ICPE 9000 of the Shimadzu company. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Q-1500°D type derivatograph (F.

Paulik, J. Paulik, L. Erdey system) in the temperature range from 20 to 500 °C (heating rate 5 °C/min) in a platinum crucible in the presence of anhydrous carrier Al_2O_3 in a static air atmosphere. IR spectra were recorded on a Spectrum BX II FT-IR spectrophotometer (Perkin-Elmer) in a KBr tablet. ESA and DRS were recorded on a spectrophotometer UV-VIS-IR Shimadzu UV-3600 in the region of 10000-50000 cm^{-1} . Particle size determination was performed by dynamic light scattering on a ZetaSizer Malvern device system at 25 °C in water. The microphotographs were recorded on a Tescan Mira 3 LMU scanning electron microscope (SEM).

IV. Results and discussions

The results of elemental DT analysis correspond to the compounds Agedds and Agedta. The method of coordination of the central ion with functional groups of ligands is established by the method of IR spectroscopy. In the IR spectra there are bands at 1722 and 1710 cm^{-1} , respectively, corresponding to ν vibrations of uncoordinated (COOH) groups. In the spectra of both the complexes of the nas (COO-) and ns (COO-) bands in the region of 1310-1400 cm^{-1} and 1500-1600 cm^{-1} are significantly shifted to the low frequency region by a relatively pure ligand, which indicates the formation of a bond of metal ions with dissociated carboxyl groups (Fig.1).

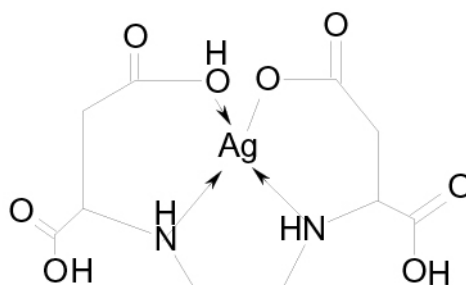


Figure 1. Structure of Agedds

In the ESP at 32400 cm^{-1} there is an intense band characteristic of $p \rightarrow \pi^*$ transition. The surface-plasmon resonance band could only be captured in the Agedds synthesis process, prior to deposition of the system. The bandwidth of 435 nm corresponds to particles with a size of about 30 nm. The band is quite wide, that is, there is a possibility of particles of different size in the system of particles, which is obviously because different types of complexes can be present in the system prior to deposition. Investigations of the dispersion of synthesized complexons in aqueous solution by the method of dynamic light scattering and the analysis of microphotographs (Fig. 2) showed that, depending on the ligand environment, the size of nanoparticles in the system is from 30-40 nm. The particles have a spherical shape.

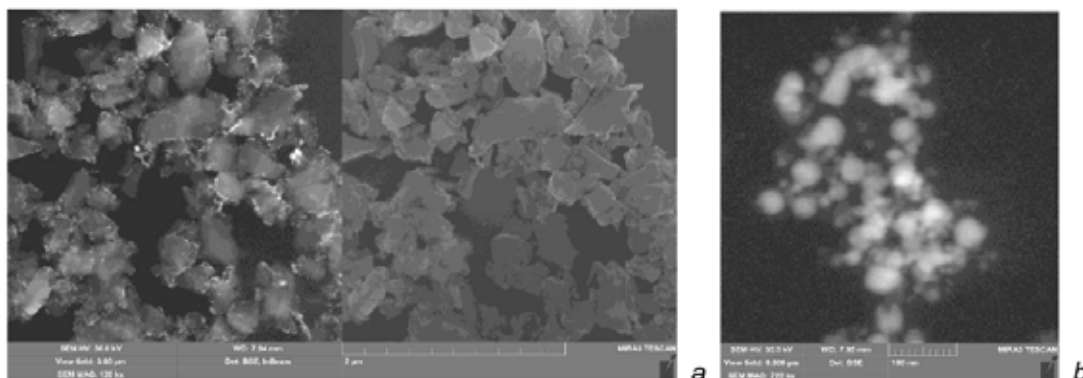


Figure 2. SEM image of Agedds system, scale marc 2 mm (a) and 100nm (b).

V. Conclusions

Agedds and Agedta silver complexes were synthesized and investigated in solid state and in solution. The lower values of the stability constants of Agedds compared to Agedta are obviously due to the asymmetric structure of the acid and as a consequence of the closure of the complex into the cycle. The difference in the position of the bands $\nu_s(COO^-)$ and $\nu_{as}(COO^-)$

($\Delta n \sim 200 \text{ cm}^{-1}$) in the IR spectra indicates their monodentate coordination in the complexes. The absence of a band of surface plasmon resonance in the study of solutions after their precipitation with alcohol indicates a small size of cluster particles up to 10 nm. The introduction of such nanosystems into cosmetics will increase the permeability and effectiveness of the agent and will probably avoid the toxic effects of silver nanoparticles.

Acknowledgements

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P-16

Polymer-Based Coatings with Self-Activating Temperature-Dependent Antibacterial Properties

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Abstract

Temperature-responsive polymer brushes consist of surface grafted polymer chains which are able to change their properties sharply upon relatively small temperature changes. The polymeric coatings of two types of poly(4-vinylpyridine) (P4VP), poly(oligo(ethylene glycol)ethyl ether methacrylate246) (POEGMA246), poly(4-vinylpyridine-co-oligo(ethylene glycol)ethyl ether methacrylate246) (P(4VP-co-OEGMA246)), poly(di(ethylene glycol)methyl ether methacrylate188) - (POEGMA188) attached to glass were successfully fabricated and then silver ions were immobilized in coatings. Recorded amount, size and shape of NPs depend on the chemical nature of brushes. Shape of NPs plays the crucial role in their antibacterial, catalytic and optical properties.

Thermo-responsive antibacterial properties of the POEGMA188 and P4VP brush coatings based on silver nanoparticles (AgNPs) embedded in, activated spontaneously above their transition temperature and leading to the elimination of two model bacteria (*Escherichia coli* ATCC 25922 and *Staphylococcus aureus* ATCC 25923) at 37 °C, were demonstrated.

Antibacterial glass is an extremely prospective material, which can find numerous applications as display cover glass for wall panels, doors, windows and touch surfaces (e.g., in smartphones), medical equipment, food packaging, where the strengthened growth of bacteria at elevated temperatures is a natural but unwanted tendency.

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P-17

Green Pathway of Plant Oil-based Polymers Synthesis via Enzymatic Polymerization

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Abstract

The enzymatic polymerization is considered as more environmental friendly pathway for the synthesis of polymeric materials compared to other conventional polymerization methods. However, this process has not been fully studied yet and needs more attention. In this study, the free-radical polymerization of high oleic soybean oil-based (HOSBM) initiated by redox system (hydrogen peroxide/ acetylacetone (ACAC)) catalyzed by horseradish peroxidase (HRP) is studied with emphasis on using greener pathway for biobased polymer synthesis and control of the molecular weight of the resulting polymers. Enzymatic assay shows that H₂O₂ loading accelerates the reaction, with a critical concentration of ACAC that is needed to effectively generate polymerization. Moreover, the concentration of H₂O₂ in the system has a noticeable impact on conversion and molecular weight of polymers whereas the amount of enzyme loaded in the system has not influenced the polymerization process. In this research study, we varied the ratio between enzyme, H₂O₂ and ACAC concentrations in order to achieve the highest conversion and molecular weight of plant oil-based polymer. The promising results obtained in our study provide an opportunity to move towards greener processes in the synthesis of polymeric materials derived from renewable resources.

Keywords : horseradish peroxidase, free-radical polymerization, high oleic soybean oil (HOSBM), enzymatic polymerization.

P-18

NH_4^+ -Templated and Co-doped with Fe^{2+} and Co^{2+} at Electrodeposition OMS-2 Hollandite

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Abstract

Manganese(IV) oxides were electrodeposited on Pt anode from fluorine-containing electrolytes at the presence of 1.5M $(\text{NH}_4)_2\text{SO}_4$ and FeSO_4 with CoSO_4 at different ratios of metal-ions (1 : 10, 1 : 1, 10 : 1). Samples were studied by chemical analysis, XRD, FTIR, electron microscopy. Ammonium-ions are the template of hollandite structure order as shown by XRD- and FTIR-studies. Hollandite framework was simultaneously co-doped with ions of Fe and Co to supply matrix with electrocatalytically active sites for ORR and OER bifunctional catalyst.

Keywords: OMS-2, hollandite, manganese dioxide, bifunctional catalyst

I. Introduction

The family of Mn(IV) oxide polymorphs found wide application as battery electrode materials, active catalysts for eco-applications including degradation of volatile organic compounds (VOC). The advantages of their use are abundance in nature, low price and variety of so-called tunnel structures of Octahedral Molecular Sieves (OMS) that display high catalytic activity and adsorption selectivity. The interest to OMS-materials of manganese has increased significantly after pioneering work of P. Bruce who proposed the use of $\alpha\text{-MnO}_2$ as a rechargeable Li-air battery (LAB) air-electrode (Bruce, 2005). Despite the significant efforts, the cathode electrocatalyst for LAB has had low efficiency since must possess high activity in both oxygen reduction and oxygen evolution reactions (ORR & OER). As shown earlier (Ivanova, Boldyrev, 1998), composition and properties of manganese oxide compounds obtained from fluoride-containing electrolytes can be easily controlled. Electrolytic doping by ions of metals expands the limits of OMS phases available by traditional electrodeposition (Sokolsky, Ivanov et al, 2012). The aim of this work was to use combined opportunities of electrodeposition, fluoride electrolytes, and electrolytic doping to realise bifunctional OMS for LAB.

II & III. Experimental Set-up, Procedure, and Analysis

Manganese(IV) oxide samples were electrodeposited galvanostatically ($i = 10 \text{ [A/dm}^2\text{]}$) at the platinum anode and platinum plate as an auxiliary electrode. The pristine fluorine-containing electrolyte consisted of 0.1 M HF + 0.7 M MnSO_4 . Dopant additives were sulfates of the following concentration in the electrolyte: 1.5 M $(\text{NH}_4)_2\text{SO}_4$, and 0.01M or 0.1M FeSO_4 with CoSO_4 at different ratios of metal-ions (1 : 10, 1 : 1, 10 : 1). The electrodeposition duration was 1 — 3 hours. Precipitates of doped electrolytically manganese dioxide were filtered, rinsed with distilled water till the negative reaction on BaSO_4 , dried 3 hours at 120 °C. Manganese dioxide nanodispersed samples were studied by XRD, FTIR, AAS, TGA, SEM, TEM, Mossbauer spectroscopy methods.

IV. Results and discussions

According to XRD, FTIR spectroscopy results, such factors as temperature rise up to 70 °C or increase of electrolysis time make hollandite phase component contribution more pronounced in electrodeposition product whereas the growth of dopant additives of Co and Fe favours to distorted or defect ramsdellite component (the ramsdellite phase is isostructural with goethite, $\alpha\text{-FeOOH}$ and heterogenite, CoOOH). The substitution by dopants into Mn oxide framework in the dopant con-

concentrations range studied is suggested because of absence of individual dopant phase components and significant broadening of some peaks of XRD-patterns (Suib, 2000). Ammonium ions template effect of hollandite structure tunnels stabilization expresses itself most clearly at longer electrolysis time. The semiamorphous ramsdellite-like deposits are typical for the first hour of electrodeposition disappearing and transforming into hollandite phase further, whereas chemical redox interaction with $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox pairs nivelate template effect probably due to decrease of hollandite crystallites growth lifetime. $\beta\text{-MnO}_2$ as an individual pyrolusite phase is not typical for electrolytic manganese (IV) oxide. The pyrolusite coherent scattering areas appear and grow in size together with the growth of Fe^{2+} additive.

V. Conclusions

New NH_4^+ -templated and co-doped with Fe^{2+} and Co^{2+} at electrodeposition OMS-2 hollandite samples allow to modify phase and chemical composition in broader limits than conventional methods, display prospective structure behaviour for application in LAB since individual Co^{2+} or Fe^{2+} dopant incorporation displayed the best performance in ORR (Sokolsky, Ivanov et al, 2018).

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P-19

FTIR Study of Non-Enzymatic Collagen Cross-Links Formation Induced by Aminoacid Copper Coordination Compound

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Abstract

FTIR study on denaturated collagen solution as a model of epidermis collagen was performed to confirm the anti-aging effect of non-enzymatic collagen cross-linking induced by coordination compound of L-lysine with copper(II). $\text{Cu}(\text{L-Lys})_2(\text{SO}_4) \cdot 3\text{H}_2\text{O}$ (CLLS) was synthesized, characterised by XRD, FTIR, Karl Fischer Titration and LC-MS methods. Denaturated collagen solution contacted with $\text{Cu}(\text{L-Lys})_2(\text{SO}_4) \cdot 3\text{H}_2\text{O}$ (1 : 100 ratio by mass) was dried and FTIR-studied to detect cross-linking induced by Cu coordination compound. Changes in collagen solution after short contact with coordination compound involve amide $\text{C}=\text{O}$ and N-H bonds and opposite to collagen FTIR spectra effects after UV irradiation where intensities of amide peaks were decreased.

Keywords: FTIR, collagen, cross-links, copper coordination compound, L-lysine.

I. Introduction

The solar radiation has profound effect on premature skin aging where the collagen and elastine fibres are the most abundant components of extracellular matrix connective tissues. Collagen and its cross-linking play also an important role and/or applied in tissue engineering, bone regeneration, wound healing, drug delivery agents (Riaz, 2018).

It has been shown recently that copper(II) and zinc malonates can be the active components of anti-aging cosmological formulations with main function to facilitate epidermis collagen cross-linking (Mahoney J., 2008). In our opinion, Cu, Zn — L-Lysine coordination compounds could be better suppliers with building blocks of collagen cross-links. This hypothesis was recently supported by our developed formulations of anti-ageing cream with an active Cu^{2+} — Zn^{2+} — L-Lysine complex and its testing on middle-age volunteers (Sokolsky, 2018, 2019).

The Fourier spectroscopy (FTIR) method was recently used to show lower fibril organization level and structure change after exposure to ultraviolet light, i.e. decomposition of aggregated collagen fibrils and thermal break up of H-bonds and etc. It was observed that integral absorbance of collagen amide bands (A, I, and II) decreased after UV irradiation (Riaz, 2018). The aim of this work is to study by FTIR the influence of copper (II) coordination compound with the amino acid ligand L-lysine on denaturated collagen solutions as a model of the possible anti-aging effects for human skin collagen.

II & III. Experimental Set-up, Procedure, and Analysis

Synthesis of Cu-Lys coordination compound: L-lysine (1.0 g) was dissolved in distilled water (20 mL). Sodium acetate (0.7 g) added as a buffer above liquid until the pH rose to 7. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.85 g) was dissolved in distilled water (10 mL). A few drops of H_2SO_4 were added to prevent hydrolysis. The reaction solution was kept at 80 °C for 2 h with further evaporation.

Collagen: 100 ml of 0.3M CH_3COOH was added to 100 mg of collagen and the obtained gel-like translucent mass was kept for 7–8 days at room temperature (25 °C) and weak stirring. Under these conditions, collagen passes into solution and dissolves almost without residue.

Collagen and complex: to 10 mg of collagen dissolved in 20 ml of 0.3 M acetic acid were added certain amounts (from 0.1 to 100%) of the coordination compound dissolved in distilled water (0.1 to 50 ml) with/without solution of urotropin

(20%) as a buffer. The reaction was carried out under normal conditions for 30 days under gentle stirring (300rpm) on a magnetic stirrer type IKA RCT basic. Then the solution was evaporated on a rotary evaporator type RV-05 Basic 1-B connected to a diaphragm vacuum pump type MP 601 E, to obtain an average vacuum, at 37 °C.

Coordination compound and collagen, their interaction products were characterised by XRD (DRON-4), FTIR (FSM-2101(Russia)), Fisher method (Metrohm 716 DMS Titrimo) and LC-MS methods(CLBQ14).

IV. Results and discussions

The complexes were synthesized from copper sulfate and copper chloride solutions. Unlike conventional procedures, the evaporation under vacuum conditions ($P = 15\text{-}20$ mm of Hg) and vacuum drying allowed to obtain crystalline coordination compounds. Their composition was evaluated after Fisher analysis of water content as follows: $[\text{Cu}(\text{L-Lysine})_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$; $[\text{Cu}(\text{L-Lysine})_2 \cdot \text{SO}_4] \cdot 5\text{H}_2\text{O}$. LC-MS spectra, XRD- and FTIR analyses confirmed mentioned individual phases formation known from literature.

FTIR spectra of initial collagen and pure $[\text{Cu}(\text{L-Lysine})_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$; $[\text{Cu}(\text{L-Lysine})_2 \cdot \text{SO}_4] \cdot 5\text{H}_2\text{O}$ were registered and the series of theoretical spectra with ratio of components identical to further experimental one was calculated. The comparison was made with experimental spectra of collagen with different ratios of components. For instance, the FTIR spectrum with $[\text{Cu}(\text{L-Lysine})_2 \cdot \text{SO}_4] \cdot 5\text{H}_2\text{O}$: collagen ratio 1 : 100 by mass is shown in Figure (Spectrum 1) in comparison with spectra of pure collagen (2) and complex (3). The observations and their discussion for these FTIR spectra after collagen and CLLS contact (Figure) are described below. The peak at 3500 cm^{-1} downshifted to 3370 cm^{-1} (amide A & O-H stretching bands) although some disturbance of intermolecular H-bonds of O-H broad stretching vibration at 3500 cm^{-1} with simultaneous growth of amide A band intensity as H-bonded N-H is the more relevant alternative explanation when compared with initial collagen spectrum 2 (Figure). C-H asymmetrical stretch also displays growth at 2960 cm^{-1} for amide B. The very weak peak at 3078 cm^{-1} (all curves) can be attributed to the Fermi resonance overtone of the band at 1539 cm^{-1} . The peak at 1750 cm^{-1} disappears. Peaks at 1620 (amide I stretching vibrations), 1260 (C-N amine stretching vibrations), and also at 1100 and 810 cm^{-1} demonstrate larger intensity than expected comparing with theoretical spectra of collagen and CLLS in ratio 1 : 100 by mass. Aforementioned effects are evidences of the structure changes in collagen including cross-linking after relatively short contact of collagen with CLLS. The observed changes are opposite to FTIR spectra effects after UV irradiation when intensities of Amide peaks were decreased (Riaz, 2018).

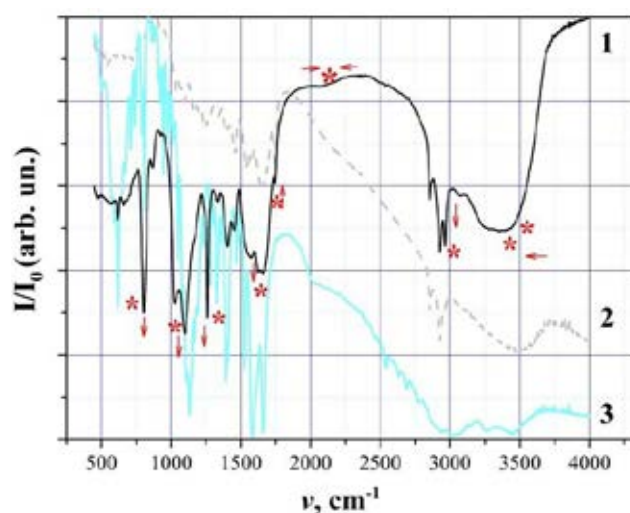


Figure. FTIR spectrum of collagen and $\text{Cu}(\text{L-Lys})_2(\text{SO}_4) \cdot 3\text{H}_2\text{O}$ mixture in ratio 1 : 100 by mass obtained without buffer after short contact (1) and pure initial collagen (2) and $\text{Cu}(\text{L-Lys})_2(\text{SO}_4) \cdot 3\text{H}_2\text{O}$ (3) displaying changes in 3 shown by asterisk (*).

V. Conclusions

L-Lysine coordination compounds with Cu and/or Zn were synthesized and used as non-enzymatic agents for study of capability of collagen to form cross-links. Changes in collagen solution after short contact with CLLS (1 : 100 ratio by mass) at moderate acidic environment were detected by FTIR method. These changes involve amide $=\text{C}=\text{O}$ and N-H bonds

and opposite to FTIR spectra effects after UV irradiation where intensities of amide peaks were decreased. It is concluded that these bonds are responsible for effects that are under control in skin anti-aging cosmetics. The developed experimental procedure and obtained preliminary results will be further verified on other collagen and coordination compound samples.

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P-20

Superhydrophobic Titania-based Hybrid Nanocomposites for Cultural Heritage Protection

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Abstract:

Current research is putting relevant effort into the preparation and investigation of novel composites combining in a single material appealing macroscopic features, chemical stability, and low-cost synthetic strategies.

Among several application fields, cultural heritage protection could benefit of "smart" composites, possessing elevate hydrophobicity (i.e. protection towards humidity), tunable rheology (consolidants and/or protective material), and colour profile compatible with the underlying cultural asset (e.g. a fresco, a marble architectural element, etc.). Thus, an interesting combination could result in merging polysiloxanes and titania (TiO₂) chemistry. Polysiloxanes (PSs) are organic polymers characterized by: i) simple and scalable preparation protocols; ii) inertia under prolonged UV-light irradiation; iii) tunable rheology (Abe, 2004). On the other side, doped TiO₂ nanoparticles (TiNPs) are produced using cheap precursors, possess elevate surface area/volume ratio and efficiently photocatalyze the decomposition of environment pollutants (Gupta, 2011).

Herein, we report the last results regarding the investigation of fluorinated PSs/TiNPs coatings. The preparation methodology has been established combining already-reported protocols (Ding, 2011) and using commercially available precursors. Depending on the nature of the precursors, two different matrices were isolated and exhaustively characterized by means of NMR, FT-IR, SEM and XPS. Then, the polymeric matrices were combined with TiNPs at different wt. percentages, and the modification hydrophobicity was monitored by measuring contact angle values.

Subsequently, photodegradation tests were carried out using a model compound, methylene blue, as a benchmark of the photocatalytic activity. Spectroscopic measurements pointed out the persistent photocatalytic activity by TiNPs, even when embedded by the polymer network, without being released in solution. A correlation between apparent kinetic profile and TiNPs wt. percentage was found.

By employing doped TiO₂, the photocatalytic process can be activated by visible light, thus offering an effective strategy for self-cleaning consolidant and protective smart nanocomposites for cultural heritage applications, such as natural lipidic materials.

Keywords: Cultural heritage, hybrid composites, methylene blue, photodegradation, titania nanoparticles.

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P-21

Impact of Inkjet Printed Oil Droplets onto Immiscible Water Interfaces: Fragmentation and Electrical Characterization

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Abstract

The impact of droplets onto immiscible liquids is known to trigger a complex dynamic (Che et al.) which can be leveraged for the production of oil-in-water capsules with ultrathin polymeric sheets, (Kumar et al.) or drop fragmentation into smaller daughter drops (Lhuissier et al.). In this regard, it is very important to extend these concepts from macroscale droplets to printing technologies, which allow automated droplet generation at smaller scales (from nano- to femto-liter) at ease. In this work, picoliter-scale oil droplets are generated by conventional inkjet printing technologies. The droplets are printed onto surfactant-laden water interfaces leading to the spontaneous fragmentation into smaller sized oil femtoliter-scale droplets in the receiving water interface (Arrabito et al.). Under the moderately high Weber number (101) impact conditions, the oil droplet is subjected to spreading and capillary instabilities at the water/air interface, which lead to rupture in smaller droplets, in accord with the reported models for macroscale droplets (Lhuissier et al.). The femtoliter-scale droplets are characterized by a microfluidic chip with integrated microelectrodes, permitting to extract number, velocities and diameter distribution (about 3 μm) by means of electrical impedance measurements. This work permits to shed light on the effects of downscaling for fragmentation phenomena at immiscible interfaces, leading to a knowledge platform for a tailored oil droplets fabrication applicable for drug encapsulation, pharmaceutical preparations, and thin-film wrapping around droplets.

Keywords: Inkjet Printing, Fragmentation, Impedance Characterization, Oil-in-water emulsions

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P-22

Vibrational Spectroscopy as a Tool to Diagnose Psychiatric and Neurodevelopmental Disorders, Through Chemometrics Analysis of Spectral Data of Blood Plasma Samples

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It is well known that neurodegenerative illnesses like Alzheimer's, which are associated with loss of cognitive functions, have been amplifying their impact on society with the increase of the lifetime expectation achieved in the last few decades. But also in the case of psychiatric and neurodevelopmental disorders for which aging is not a dominant factor (like, for example, autism, schizophrenia and bipolar diseases), the demands of the modern life have augmented their societal importance. Unfortunately, most of these types of diseases are of difficult clinical diagnosis due to the heterogeneity of their symptoms, what leads to errors in the initial diagnosis, for example of the bipolar disorder, close to 70%, with more than 30% of patients remaining misdiagnosed for at least 10 years. Alternative/complementary strategies that may help clinicians to improve these numbers are then of great relevance, in particular when they rely in fast and cheap analytical procedures having a molecular basis. Use of spectroscopic methods for accomplishment of this goal, through analysis of body fluids and identification of biomarker-related spectroscopic features, appears as a promising approach to this problem. In fact, this approach has been shown to be appropriate for helping diagnosis of other types of diseases, like cancer and infectious diseases, for example.

In this investigation, vibrational spectroscopy (both infrared absorption – IR – and Raman scattering), has been selected as analytical technique for trial diagnosis of a series of disorders affecting the cognitive functions. Vibrational spectroscopy is a very sensitive analytical method to sample composition and variability; it allows fast and cheap analyses and, when the object of analysis is a body fluid, the tests can be performed without requiring patients' multiple visits to the health units (in contrast with the clinical traditional methods).

The present program of studies focusses on the analysis of blood plasma samples of patients clinically diagnosed as bearing psychiatric or neurodevelopmental disorders, in order to find proper biomarker-related spectroscopic features that can help a correct diagnosis. Chemometrics is used to perform the analysis of the spectroscopic data obtained by IR or Raman spectroscopies, in the search for a reliable statistical model to discriminate and classify the patients according to their disease.

In this poster, the results obtained for the case of autism will be presented, together with the plan designed for the ongoing studies focusing on other types of illnesses, in particular, schizophrenia and bipolar diseases (including subgroups: bipolar depressive episode, manic episode and otimic), as well the relevant information about the research consortium established to undertake these studies. It will be shown that the information contained in the infrared spectra of blood samples of autistic patients allowed for their correct classification against the control group, thus testifying the potential of the used methodology for the aimed purposes.

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