Book of Abstracts Nanoscience & Nanotechnologies 2023

Sessions

MONDAY 29 MAY

Sessions:

One: 9.10 - 11.00

Marco Falzetti, Luisa Riccardi, Nicoletta Amodio

Two: 11.30 – 13.10

Francesco Valle, Pier Gianni Medaglia, Iaroslav Gnilitskyi, Fabrizio Quadrini, Antonio Cricenti

Three 14.50 – 16.10

Round Table on Next project

Four: 16.40 – 18.10

Zeinab Ebrahimpour, Cristian Vacacela Gomez, Marco Menegazzo, Gianlorenzo Bussetti

Horizon Europe, the European Framework Programme for Research and Innovation, and its role in supporting Materials research and innovation.

Marco Falzetti
Direttore APRE - Agenzia per la Promozione della Ricerca Europea, Italy

How has the European Commission Materials context evolved between H2020 and HE, and the new Materials Commission initiatives in light of a program that is strongly oriented towards society, while constrained by the complexities of a geopolitical landscape that influences its interventions on medium-term strategies.

Synergies between European Defence Fund and "civil" Research & Innovation Framework programmes

Luisa Riccardi

Direttore del V Reparto "Innovazione Tecnologica" del Segretariato Generale della Difesa/DNA, Italy

Since its 2023 work programme the European Defence Fund has introduced thematic research action topic calls aimed at spinning-in the results generated in other civil EU-funded programmes to the defence sector with the goal of encouraging cross-fertilisation of the civil-defence innovation landscape.

Moreover respondents to the public consultation on the past, present and future of the European Research & Innovation Framework programmes 2014-2027 have recommended Horizon Europe to strengthening synergies with programmes, such as the European Defence Fund, deemed as crucial to ensure the exploitation of the results of industrial projects

Nanoscience and nanotechnology applications in the defence sector (aerospace, electronics, energy, materials and devices technologies) will definitely benefit in the forthcoming future of this kind civil-defence innovation landscape cross-fertilisation.

Research, Development, Innovation: the Soft Revolution

Nicoletta Amodio

Responsabile Ricerca e Innovazione Confindustria, Italy

How will the National Recovery and Resilience Plan change the way we do R&D in Italy? The NRRP is a potent accelerator but, to be successful, it must be part of a wider national strategy integrated at European level. The mission dedicated to R&D defines a paradigm change - From Research to Business - based on a structural public-private partnership.

Profiling biogenic nanoparticles by nanomechanical characterization

Francesco Valle[1,3], Marco Brucale[1,3], Andrea Ridolfi[1,3], Jacopo Cardellini[2,3], Costanza Montis[2,3], Laura Conti[2], Debora Berti[2,3], Paolo Bergese[2,5], Lucia Paolini[2,5], Andrea Zendrini[2,5], Angelo Musicò[5], Miriam Romano[2,5], Annalisa Radeghieri[5], Lucio Barile[6], Laura Polito[4], Greta Bergamaschi[4], Alessandro Gori[4], Roberto Frigerio[4], Marina Cretich[4].

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Cells are known to produce an important amount of natural nanoparticles, among them Extracellular vesicles (EVs), containing bioactive proteins and RNAs, are newly recognized as the universal agents of intercellular and inter-organismal communication, in both normal and pathological processes.
EVs are reshaping our perspective on life sciences, environment and public health. They are under intensive investigation as early disease multi-biomarkers, while EV-based personalized therapeutic agents and vaccines have produced enticing results in early-phase clinical trials.

However, EV exploitation is not supported by current manufacturing methods, which are inadequate in terms of purity and reproducibility or yield, time and cost.

The purity issue in particular has to deal with another important family of biogenic nanoparticles secreted by the cells: lipoproteins (LPs). The widely overlapping physicochemical properties of lipoproteins (LPs) and extracellular vesicles (EVs) represents one of the main obstacles for the isolation and characterization of these pervasive biogenic lipid nanoparticles from vesicles.

I shall present the application of an atomic force microscopy (AFM)-based quantitative morphometry assay to the rapid nanomechanical screening of mixed LPs and EVs samples [1].

The method that is label-free, single-step and relatively quick to perform can determine the diameter and the mechanical stiffness of hundreds of individual nanometric objects within few hours.

The obtained diameters are in quantitative accord with those measured via cryo-electron microscopy (cryo-EM); the assignment of a specific nanomechanical readout to each object enables the simultaneous discrimination of co-isolated EVs and LPs even if they have overlapping size distributions.

It provides a very useful tool for quickly assessing the purity of EV/LP isolates including plasma- and serum- derived preparations that can be challenging to assess with several established techniques due to ensemble-averaging, low sensibility to small particles.

EVs and all classes of LPs are shown to be characterized by specific combinations of diameter and stiffness [2], thus making it possible to estimate their relative abundance in EV/LP mixed samples in terms of stoichiometric ratio, surface area and volume. Moreover these properties are known to influence their biological function, in terms of, e.g., cellular adhesion, endo/exocytosis, cellular uptake, and mechanosensing.

References.

[1] Compositional profiling of EV-lipoprotein mixtures by AFM nanomechanical imaging. Biorxiv. https://doi.org/10.1101/2022.07.19.500441

[2] AFM-based high-throughput nanomechanical screening of single extracellular vesicles. Anal. Chem. (2020) 92 (15), 10274-10282

Strategies and methodologies to improve performances of electrodes in supercapacitors: nanostructured materials and nano-treatings.

P.G. Medaglia, S. Bellucci, J. Gnilitskyi, C. Leonardi, R. Pezzilli, G. Prestopino,

Many effort have been devoted, in recent years, to the development of energy storage devices, due to the increasing demand for renewable energy. Among these devices, Supercapacitors (SCs) are attracting attention, due to their performances in terms of specific capacity, stored power density, reduced charge/discharge times, but also for other aspects as cheapness, long cycle life, reduced environmental impact, and so on. The electrodes are undoubtedly crucial elements for performances of supercapacitors: the possibility of their optimization are presented, by exploiting nanotechnologies and nanomaterials, or different approaches for the modification of metallic current collectors.

Towards ultrashort lasers and their unique performance to develop functional surfaces

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Today, the issue of surface functionalization of materials is given considerable attention, as super-thin hydrophilic and hydrophobic materials are gaining more and more prospects for use in industrial manufacturing, agricultural field and in everyday life. It is well known that such surfaces demonstrate the effect of self-cleaning from snow, dust and fog, corrosion resistance, transportation of liquids without loss, as well as use in micro-fluid processors, and so on. The analysis of scientific sources shows that to produce functional surfaces (hydrophobic and hydrophilic) various technologies of surface modification are used. The main technologies to keep the template on a thin film of material are various types of lithography, but those technologies are time-consuming, have many technological transitions, require vacuum and expensive equipment [1].

Surface modification by lasers with a pulse duration in the femtosecond range (10^{-15} s), due to non-thermal ablation mechanisms, is an alternative to the above-mentioned methods [2]. One method of such modification is to create on the surface of the material periodic surface structures known as laser-induced periodic surface structures (LIPSS) [3,4]. Adjusting the laser parameters will allow to obtain various configurations of nano- and microstructures, which in turn allows to provide hydrophilic/hydrophobic properties of the surface [5,6]. This technique can implement the orderly integration of hydrophilic and hydrophobic trace elements on one surface.

Thus, the development of new hydrophilic and hydrophobic nanointerfaces as well as the deepening of the understanding of the mechanisms and phenomena under consideration in the surface functionalization, in our opinion, are a promising solution to numerous applications.

[1] Pease, R. F. & Chou, S. Y. Lithography and other patterning techniques for future electronics (2008) Proc. IEEE 96, 248–270
[2] S. Sundaram, E. Mazur, Inducing and probing non-thermal transitions in semiconductors using femtosecond laser pulses (2002) Nat. Mater. 1, 217-224.
[3] I. Gnilitskyi, T. Derrien, Y. Levy, N. M. Bulgakova, T. Mocek and L. Orazi, High-speed manufacturing of highly regular femtosecond laser-induced periodic surface structures: physical origin of regularity (2017) Nature: Scientific Reports, 7, 8485.
[4] M. Shugaev, I. Gnilitskyi, N. M. Bulgakova, and L. Zhigilei, Mechanism of single-pulse ablative generation of laser-induced periodic surface structures (2017) Phys. Rev. B 96, 205429
[5] J. Kisała, I. Gnilitskyi, B. Cieniek, P. Krzemiński, M. Marchewka, A. Barylyak, Y. Bobitski, Synthesis of Micro-Spikes and Herringbones Structures by Femtosecond Laser Pulses on a Titanium Plate − A New Material for Water Organic Pollutants Degradation, (2021) Materials 14, 5556.
[6] G. D. Tsibidis, E. Skoulas, A. Papadopoulos, E. Stratakis, Convection roll-driven generation of supra-wavelength periodic surface structures on dielectrics upon irradiation with femtosecond pulsed lasers (2016) Physical review. B, Condensed matter 94 (8081305.

Optical Nanospectroscopy applied in Material Science and Biomedicine

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Keywords: (Raman, SNOM, IR, Cancer Cells, Heat Transfer)

Carcinomas are complex biochemical systems and in the past their diagnosis was based on morphological differences between malignant cells and their benign counterpart. Recently the paradigm has changed and great interest is focused now on the biochemical profile of tumours in view of the availability of new drugs that specifically target neoplastic cells. This new paradigm requires biochemical analysis of each tumour in order to establish the correct personalized oncological "target therapy". Understanding the mechanism of molecular alterations of a specific tumour is a critical issue to predict the response to personalized therapy. This is important not only for discrimination between healthy and pathological tissues, but also for pre-cancerous tissue state earlier detection and understanding.

The potential of infrared [1] and Raman spectroscopy [2] to characterise cancerous tissues has long been recognised and studies of various cancers by many groups have established that regions of malignant tissue can be easily identified on the basis of its optical spectrum. Early diagnosis of cancer requires an instrument providing specific chemical images at sub-cellular level and the development of diagnostic imaging. Infrared Scanning Near-field Optical Microscopy (IR-SNOM) and micro-Raman set-up meet these requirements provided that SNOM can been coupled with an appropriate infrared light source, that can be based on Free Electron Laser, femtosecond laser or quantum cascade laser.

We present IR-SNOM and micro-Raman in their spectroscopic mode, that is related to the local chemical composition and, thus, to the biological properties of the sample, for tissue imaging and early cancer diagnostics. Applications in the case of Oesophagous [3] and Cervical Cancer [4] as well as in the progression of Amyotrophic Lateral Sclerosis (ALS) [5] will be presented.

Heat transfer at nanoscale is very important in today's nanoelectronic circuits and is dominated by evanescent modes existing only in the near field. We present a method to experimentally image the thermal near-field emitted by a hot sample by use of a home-made scattering SNOM setup. The emission will be in the infrared region and a cold tip will collect the IR light scattered [6].

[1] Cricenti A, Luce M, Tolk NH, Margaritondo G; Nanosci. Nanotechnol. Lett.; 3 (2011) 913;
[2] Çulha M, Bioanalysis, **7**, 2813 (2015)
[3] Smith AD, Siggel-King MRF, Holder GM, Cricenti A, Luce M, Harrison P, Martin DS, Surman M, Craig T, Barrett SD, Wolski A, Dunning DJ, Thompson NR, Saveliev Y, Pritchard DM, Varro A, Chattopadhyay S, Weightman P; Applied Physics Letters; 102 (2013) 053701.
[4] Halliwell Diane E, Morais Camilo LM, Lima Kássio MG, Trevisan Julio, Siggel-King Michele RF, Craig Tim, Ingham James, Martin David S, Heys Kelly A, Kyrgiou Maria, Mitra Anita, Paraskevaidis Evangelos, Theophilou Georgios, Martin-Hirsch Pierre L, Cricenti Antonio, Luce Marco, Weightman Peter, Martin Francis L; Nature Scientific Reports; 6 (2016) 29494.
[5] Picardi Gennaro, Spalloni Alida, Generosi Amanda, Paci Barbara, Mercuri Nicola Biagio, Luce Marco, Longone Patrizia, Cricenti Antonio; Nature Scientific Reports; 8 (2018) 13110.
[6] Becerril D, Cesca T, Mattei G, Noguez C, Pirruccio G, Luce M, and Cricenti A; Review Scientific Instruments 94, (2023) 023704.

Hybrid carbon fiber reinforced laminates with interlaminar nanostructures

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Hybrid carbon fiber reinforced laminates with epoxy matrix can be hybridized by inserting interlaminar nanofibers or nanotubes. The hybrid interlayer between the carbon fiber plies allow increasing the laminate bending strength and the interlaminar shear strength if the optimal interaction between the resin matrix and the nano-structures is achieved. In fact, the reduction of the molecular mobility leads to higher mechanical performances of the interlaminar matrix if an adequate degree of polymerization is reached during laminate curing. Unfortunately, molecular mobility is reduced also during polymerization with possible negative effects in terms of crosslinking degree. Moreover, the use of nano-fillers in composite manufacturing cannot influence the lamination and molding procedures. In this study, nano-fillers in the shape of polyamide nano-fibers and carbon nanotubes have been added during lamination of flat and cylindrical carbon fiber reinforced laminates. Composite molding has been carried out both in nominal conditions by autoclave molding for flat laminates, and by an innovative our-of-autoclave molding procedure for cylindrical composites. Results from mechanical tests show that the laminate ultimate properties may improve up to 10% if the correct interaction is provided by the manufacturing procedure. Nevertheless, the glass transition temperature reduces because of a lower polymerization degree.

Luminescent Sulfophosphate Glass Doped with Plasmonic Nanoparticles: Spectral and Self-cleaning Features

1

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The lanthanide (Ln^{3+}) ions doped sulfophosphate glass systems are promising candidates to be used in different fields, including fiber-optics, waveguide lasers, optical detectors, solar concentrators, and solid-state lasers. The variable and weak interactions between metaphosphate (PO^{3-}) and sulfate (SO_4^{2-}) ions are a great feature for rare earth ion incorporation and give these glasses a high luminescence efficiency with the least non-radiative losses. By adding different modifier oxides, such as alkaline earth oxides, the interaction between PO^{3-} and SO_4^{2-} can be greatly improved. It could result in a disturbance in the glass system and consequently facilitate the creation of non-bridging oxygen (NBO) groups [1].

At an optimum Sm^{3+}/Er^{3+} dopant concentration, emission increases by combining the remarkable properties of rare-earth ions and sulfophosphate glass, such as energy transfer between the erbium and samarium ions. For further improvement of the emission properties, incorporation of plasmonic nanoparticles such as TiO_2 and Ag into the RE-doped glass system has been reported as an effective way to overcome the low emission cross-section of the systems. Spectroscopic techniques represent a unique combination to investigate the structural and optical features concerning the incorporation of Sm^{3+} and Er^{3+} ions in solphophosphate glasses, as well as the role of plasmonic nanoparticle incorporation to modify the optical emission properties of such systems [2–5].

In this contribution, the spectroscopic properties of Sm^{3+}/Er^{3+} doped glass, including titania and silver nanoparticles, are presented. Erbium (Er3+) and samarium (Sm^{3+}) ions doped magnesium zinc sulfophosphate glass systems containing TiO_2 NPs were synthesized using the melt-quenching technique and characterized for the influence of varying TiO_2 ion contents on their spectral properties. UV-Vis-NIR spectra revealed the occurrence of several absorption bands corresponding to the transitions from the ground state to various excited states of the ions. An enhancement in the PL emission intensities in the presence of TiO_2 or Ag NPs were observed. Such enhancement was attributed to the local field effect stimulated by the surface plasmon resonance (SPR) of plasmonic NPs and the energy transfer mechanism among Ln^{3+} ions and the NPs. The self-cleaning characteristics of the glasses were investigated through water contact angle (WCA) and photodegradation rate of methylene blue (MB) measurements. The results revealed that the proposed glass samples may be useful in photonic applications.

References

[1] G. Kaur, M. Kumar, A. Arora, O. Pandey, K. Singh, Influence of Y_2O_3 on structural and optical properties of SiO_2–BaO–ZnO–xB_2O_3–(10-x)Y_2O_3 glasses and glass ceramics, *J. Non-Cryst. Solids* **357** (2011) 858–863.

[2] F. Ahmadi, Z. Ebrahimpour, "Titania nanoparticles embedded Er^{3+}-Sm^{3+} co-doped sulfophosphate glass: Judd-Ofelt parameters and spectroscopic properties enhancement," *J. Alloy. Compd.*, **843**, (2020) 155982.

[3] F. Ahmadi, Z. Ebrahimpour, A. Asgari, and R. El-Mallawany, "Role of silver/titania nanoparticles on optical features of Sm^{3+} doped sulfophosphate glass," *Opt. Mater.*, **105**. (2020).

[4] F. Ahmadi, Z. Ebrahimpour, A. Asgari, and S. K. Ghoshal, "Insights into spectroscopic aspects of Er^{3+} doped sulfophosphate glass embedded with titania nanoparticles," *Opt. Mater.*, **111**, (2020) 110650.

[5] Ebrahimpour, Z., Cabrera, H., Ahmadi, F., Asgari, A., & Niemela, J.. Sulfophosphate Glass Doped with Er3+ and TiO2 Nanoparticles: Thermo-Optical Characterization by Photothermal Spectroscopy. *Photonics* **8** (2021) 115.

Optical and Electrical Properties of Low-Temperature Treated Oxides Graphenes

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Keywords: Graphene Oxide, Optical Bandgap, Electronic Transitions, Absorption Coefficient, Electrical Conductivity

Abstract

The study of the optical properties of graphene oxide (GO) is crucial in designing functionalized GO materials with specific optical properties for various applications such as (bio)sensors, optoelectronics, and energy storage. The present work aims to statistically investigate the electronic transitions, optical bandgap, and absorption coefficient of GO under different conditions. Specifically, the study examines the effects of drying times ranging from 0 to 120 h and low temperatures ranging from 40 ℃ to 100 ℃. Our findings indicate that exposing the GO sample to a drying time of up to 120 hours at 80°C can lead to a reduction in the optical bandgap, decreasing it from 3.6 eV to 3.1 eV. However, for a relatively short drying time (24 h), the temperature does not appear to have a significant impact on the optical bandgap of GO. The $\pi-\pi$ transition was found to be the most affected, shifting from approximately 223 nm at 0 h to 256 nm after 120 h of drying time. In contrast, the $n-\pi$ transition remained unchanged in wavelength, but its intensity decreased with longer drying times, indicating a reduction in the number of oxygen functional groups. At 120 h, the absorption coefficient was measured to be 2344 ml mg−1m−1, a value that closely resembles the absorption coefficients reported for dispersions of exfoliated graphene. Our findings can provide insights into determining the optimal temperature and duration required for transforming GO into its reduced form for a specific application through extrapolation. The study is complemented by analyzing the elemental composition and the surface morphology change.

Investigating the activation of passive metals by a combined in-situ AFM and Raman spectroscopy system: a focus on titanium

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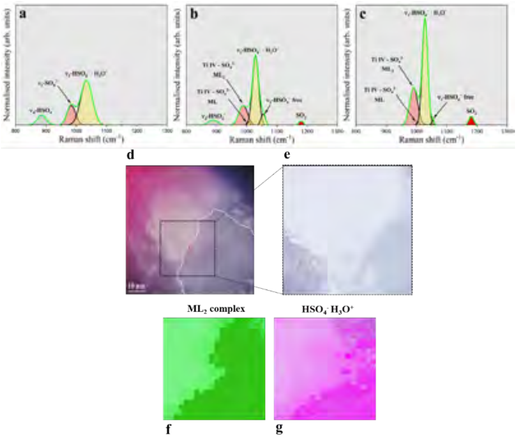
Understanding the main steps involved in the activation of passive metals is an extremely important subject in the mechanical and energy industry and generally in surface science. Here the attack can be very dangerous when the metal is employed, for example, in the construction of fan blades for military engines. This can severely affect the creep resistance and the components capability to sustain the high load condition. Therefore, understanding the main steps leading to titanium activation can be of interest to put the basis for future mitigation strategies involving alloying or surface coatings. The titanium-H_2SO_4 system is particularly useful for this purpose, as the metal can either passivate or corrode depending on potential. Although several studies tried to hypothesise the surface state of the electrode, there is no general consensus about the surface state of Ti in the active-passive transition region. Here by combining in-situ atomic force microscopy (AFM) and Raman spectroscopy, operating in an electrochemical cell, we show that the cathodic electrification of Ti electrodes causes the dissolution of the upper TiO_2 portion of the passive film leaving the electrode covered by only a thin layer of titanium monoxide. Fast anodic reactions involved the acidification of the solution and accumulation of sulphur containing anions. This produces a local increase of the solution turbidity (**Fig.s d** and **e**), allowing to distinguish favourable regions for the precipitation of $TiOSO_4 \cdot 2H_2O$. These results give a rationale about the proton-induced degradation of passive surfaces in presence of sulphur containing species.



a Raman spectrum of the 800-1200 cm^{-1} region collected outside the concentration cell. **b** Raman spectrum of the 800-1200 cm^{-1} region collected at the border of the concentration cell. **c** Raman spectrum of the 800-1200 cm^{-1} region collected at the centre of the concentration cell. **d** Optical image collected in correspondence of a concentration cell delimited by the white dotted profile. **e** enlarged view of image d. **f** Raman map of the intensity of the 991 cm^{-1} component of the ML_2 complex. **g** Raman map of the intensity of the 1029 cm^{-1} component of the $HSO_4^- \cdot H_3O^+$.

Nanoelectrochemistry: mechanisms of sulphate adsorption on Cu (111) electrode surfaces studied by EC-STM and EC-AFM

Gianlorenzo Bussetti
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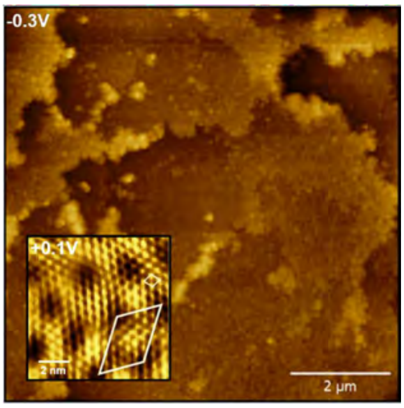
Research in electrochemical processes is usually based on (sub-)millimetric (mesoscopic) description by looking at average charge fluxes and reaction rates. Nonetheless the advent of methods for preparing, studying and interacting with matter of dimensions close to single molecules brings new fundamental insights and experimental potentialities. In addition, there is much to be learned from probing the behavior of single redox molecules, individual catalytic sites, and single-electron-transfer events. Despite these facts, systematic studies on the so-called nanoelectrochemistry (i.e., the influence and even the processes related to nanometric structures) are still missing.

In this talk, we propose an original approach where molecules adsorption (namely, sulphates) on the electrode surface is influenced by the presence of steps, as naturally observed in Cu(111) surface. The electrochemical scanning tunneling microscopy (EC-STM) locally detects the formation of a well-ordered sulphate superstructure (Moiré pattern) in case that the copper terrace size is larger with respect to the Moiré lattice parameter. If the potential applied to the Cu electrode is close to- or within- the anodic corrosion regime, i.e., when copper undergoes a dissolution process that releases copper ions (Cu^{2+}) into solution, EC-STM acquisition becomes difficult, due to the significant detriment of the electrode surface flatness. In the corrosion regime, we successfully exploit the EC-atomic force microscopy (EC-AFM) to prolong the surface characterization towards relatively high anodic potentials. The combined experimental investigation, which is able to follow the electrode morphology on different length scales, highlights the effect of the redox processes and the role of steps during the sulphate molecules adsorption and desorption processes at the Cu surface.



Picture: (8 × 8) μm^2 EC-AFM image of the Cu (111) surface after the dissolution and then the Cu re-deposition process (at 0.15V).

Blow-up: EC-STM image of the Moiré pattern (larger unit cell) and of the sulphate superstructure (smaller unit cell).

TUESDAY 30 MAY

Sessions:

Five: 9.00 - 11.00

Luca Pierantoni, Matteo La Pietra, Eleonara Pavoni, Elahehe Mohebbi, Davide Mencarelli, Joseph Hardly Christopher

Six: 11.30 – 13.10

Francesco Palazzi, Manuel Minnucci, Daniele Mirabile Gattia, Cristiano Albonetti, Matteo Giardino

Seven 14.50 – 16.10

Yosra Toumia, Alessio Truglia, Patrizia Lamberti, Maksim Shundalau

Eight: 16.40 – 18.10

Mustafa Muradov , Aynura Karimova, Gunel Aliyeva,
Habiba Shirinova

Multiphysics modelling of quantum-EM transport in ballistic graphene devices.

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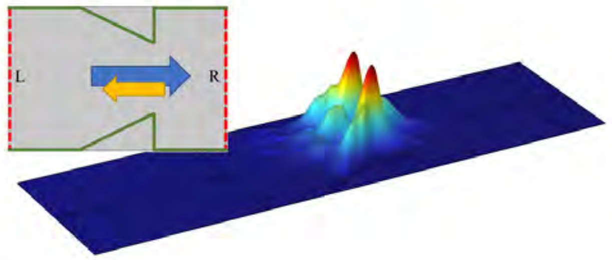
Ballistic graphene device design and modeling can be extremely challenging because it necessitates a rigorous quantum analysis at the nanoscale that is accurate enough to represent the asymmetric behavior of charge transport. Such behavior cannot be modeled using a simple approximation, such as the Kubo-Drude conductivity, since it ignores the ballistic regime. As a result, the quantum behavior of the particles must be considered. Density Functional Theory (DFT) may overcome the problem, however it can only be used for devices made of thousands of atoms. Monte Carlo simulations have also been shown to be a useful tool for the modelling of quasi-ballistic transport, however, are time consuming as they require the computation of many particles.

In this work, we discuss the feasibility to explicitly simulate the transport at the continuum level using a partial differential equation like the Time-Dependent Schrödinger Equation (TDSE) or the Time-Dependent Dirac Equation (TDDE).

In order to model coherent transport in a two-dimensional graphene layer with arbitrary geometry, we provide a full-wave time domain method. Considering a gaussian wave-packet as source, it is shown to be possible to simulate asymmetric transport in closed systems (e.g., in geometric or ballistic diodes).

We present the study of a geometric diode defined by an asymmetric taper of the domain where the charges are confined. The proposed solution clearly shows asymmetric transport and provides a description of the rectification behavior in response to a parametric change.



2D time dependent Schrödinger equation solution in the discontinuity. Asymmetric transport in a geometric diode (inset).

[1] *M. Andelkovic, K. Rakhimov, A. Chaves, G. Berdiyorov, M. Milošević, Wave-packet propagation in a graphene geometric diode, Physica E: Low-dimensional Systems and Nanostructures 147 (2023) 115607.*

[2] *D. Mencarelli, G. M. Zampa, L. Pierantoni, Current-voltage characterization of multi-port graphene based geometric diodes for high-frequency electromagnetic harvesting, IEEE Access 10 (2022) 123251–123258.*

SYNTHESIS AND THERMAL AND MECHANICAL CHARACTERISATION OF NANOCOMPOSITES BASED ON EPOXY RESIN AND GRAPHENE NANOPLATES

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In this work, nanocomposite materials were produced and characterized using epoxy resin as a matrix and graphene as filler. The filler used was synthesized and characterized morphologically with FTIR spectroscopy, Raman spectroscopy and scanning electron microscopy.

In the first part of the work, the process of dispersing the filler in the matrix was studied and optimized using a planetary mixer and a nano mixer. Subsequently, a set of nanocomposites with different filler percentages (weight/weight) was produced, which were characterized morphologically. The cross-linking process of the nanocomposites was then optimized adjusting time and temperature parameters. The nanocomposites were subsequently characterized by dynamic mechanic analysis, differential scanning calorimetry, tensile test, thermogravimetric analysis thermal diffusion test, Raman spectroscopy and scanning electron microscopy to observe the changes made by the filler in the polymer matrix.

Atomistic modeling and simulation of HfO_2 in Metal-Insulator-Metal devices

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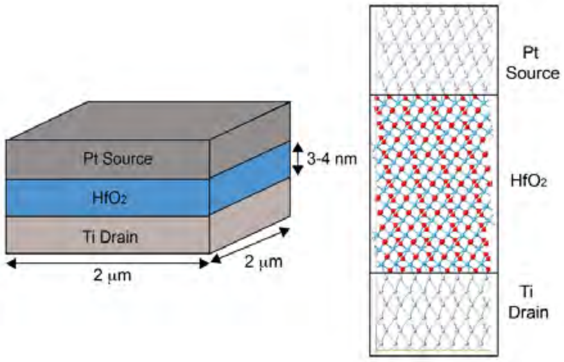
In the present work, nanometric HfO_2 is used as an inorganic dielectric layer inserted between two metallic electrodes to build Metal-Insulator-Metal (MIM) architecture based on the quantum tunneling effect. The metallic portions are made of Pt and Ti, the source and drain electrodes, respectively; while the dielectric layer is composed of 3-4 nm of HfO_2. Three prototypes of MIMs have been fabricated, each one characterized by different contact areas between the layers. The systems consist of 2x2 μm, 3x3 μm, and 3.5x3.5 μm contact areas, and the I-V curves were measured by applying a drain-source bias between -1 and +1 V (to avoid junction burnout).

The same systems were simulated using *ab-initio* Density Functional Theory (DFT) calculations to reproduce and understand the experimental behavior; in particular, QuantumEspresso (QE) and Quantum Atomistic Toolkit (Q-ATK) software packages were used.[1,2]

To atomistic simulate such complex systems, it is of central importance to optimize the interface between the electrodes and the oxide layer; then, the I-V curves can be properly estimated. In detail, Pt and Ti metals, with a Miller Index of 100, were considered separately and the interfaces with monoclinic-HfO_2 were optimized using DFT D3 (using QuantumEspresso). Then, the I-V curves of the complete MIMs were simulated by using the DFT-LCAO based on GGA-PBE density functional and PseudoDojo pseudopotentials (using QuantumATK). To obtain the perfect match with the experimental data, the periodicities were set only for the two axes perpendicular to the layered structures of each MIM (A and B axes), while a Dirichlet boundary condition was applied along the direction parallel to the Pt-HfO_2-Ti layers. The k-point periodicity in the A and B axes was modified to narrowly reproduce the different extents of the contact area.

The results obtained by calculation perfectly matched the findings acquired from the experimental tests, representing one of the first studies of MIM devices characterized by the atomistic point of view.



Schematic representation of the MIM architecture (left) and atomistic structure of Pt-HfO_2-Ti layers (right).

1. P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. de Gironcoli, P. Delugas, R. A. Distasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H. Y. Ko, A. Kokalj, E. Kücükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H. v. Nguyen, A. Otero-De-La-Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu and S. Baroni, Journal of Physics Condensed Matter, 2017, 29, 32.
2. S. Smidstrup, T. Markussen, P. Vancraeyveld, J. Wellendorff, J. Schneider, T. Gunst, B. Verstichel, D. Stradi, P. A. Khomyakov, U. G. Vej-Hansen, M.-E. Lee, S. T. Chill, F. Rasmussen, G. Penazzi, F. Corsetti, A. Ojanperä, K. Jensen, M. L. N. Palsgaard, U. Martinez, A. Blom, M. Brandbyge and K. Stokbro, Journal of Physics: Condensed Matter, 2019, 32, 015901.

Towards new optimization of geometrical graphene ballistic diodes: a atomistic DFTB approach

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Rectenna detectors can be considered ultrahigh frequency radio receivers which have exhibited great applications in energy harvesting of microwave radiations, infrared (IR) and terahertz detectors [1,2]. Moreover, Rectenna has already shown efficient optical frequencies for a solar cell different from traditional semiconductor solar cells [3]. So far, some experimental measurements and theoretical Monte Carlo studies have been reported such of asymmetric graphene ballistic devices (AGBDs) for obtaining the rectification efficiency of nanodevices by evaluating the I(V) characteristics, asymmetry ratio (AR) and Transmittance property (T). However, from the lack of knowledge about the atomistic behavior of ballistic diodes, we persuaded to investigate the electrical and transport properties of AGBDs using self-consistent charge density functional tight-binding (DFTB) approximation, for the first time.

According to our results, among the different proposed AGBDs fabricated based on diverse geometrical dimension of length (L), width (W), neck width (N), edge width (E) and angle (θ) (**Figure 1**), the graphene diode with smallest N of 5 nm and angle of 47° shown the excellent current values of 213 μA along backward direction at voltage 1.5 V, which was higher than other devices. A maximum AR of 2.23 has been achieved at a current of 137 μA for this diode, which is among the highest values for a ballistic device reported to date. This study provides a pathway for optimizing the ballistic graphene diodes to be used as potential applications for energy harvesting devices.

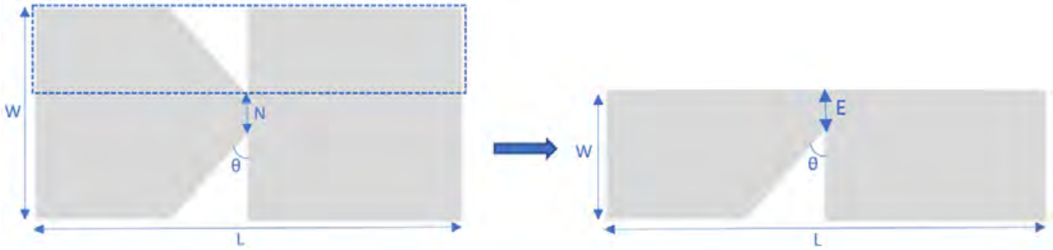

Figure 1 The schematic representation of two different geometrical graphene ballistic diodes (AGBDs). Dimensional parameters: length (L), width (W), neck width (N), edge width (E) and angle (θ).

References

[1] Midrio, M., Pierantoni, L., Boscolo, S., Truccolo, D., & Mencarelli, D. (2022). Nano-antenna array for high efficiency sunlight harvesting. Optics Express, 30(5), 7017-7034.

[2] Zhang, J., Brownless, J., & Song, A. (2019, September). High Performance Graphene Ballistic Rectifiers for THz detection. In 2019 44th International Conference on Infrared, Millimeter, and Terahertz Waves (IRMMW-THz) (pp. 1-2). IEEE.

[3] Zhu, Z., Grover, S., Krueger, K., & Moddel, G. (2011, June). Optical rectenna solar cells using graphene geometric diodes. In 2011 37th IEEE Photovoltaic Specialists Conference (pp. 002120-002122). IEEE.

Nano optical antennas and nonlinear elements for harvesting of light power

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Abstract

The use of fossil fuels, which are not green, is rising steadily, hastening global warming. This trend will become more pronounced in the years to come as the global population rises and modernization-related energy waste rises. The primary objective of the current research effort is to utilize solar energy more effectively and affordably than photovoltaic (PV) solar cell technology. In this work, we demonstrate how to effectively capture solar radiation's electromagnetic spectrum for a potential rectification that might have a higher efficiency than that of single-junction PV cells. Nanoantenna arrays and nanostructured geometric diodes, Fig. 1, [1, 2] have been studied and tested numerically in order to achieve the above target.

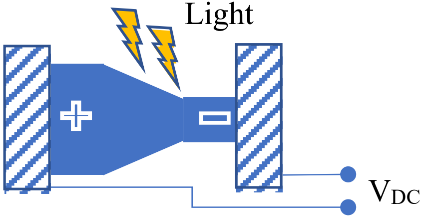

Fig. 1 : Geometric balistic rectifier

References

[1] Midrio M, Pierantoni L, Boscolo S, Truccolo D, Mencarelli D. Nano-antenna array for high efficiency sunlight harvesting. Opt Express. 2022 Feb 28;30(5):7017-7034. doi: 10.1364/OE.450020. PMID: 35299474.

[2] Mencarelli, D. & Zampa, Gian & Pierantoni, Luca. (2022). Current-voltage characterization of multi-port graphene based geometric diodes for high-frequency electromagnetic harvesting. IEEE Access. PP. 1-1. 10.1109/ACCESS.2022.3223134.

Inverted Scanning Microwave Microscopy (iSMM): a novel metrological tool for advanced material characterization

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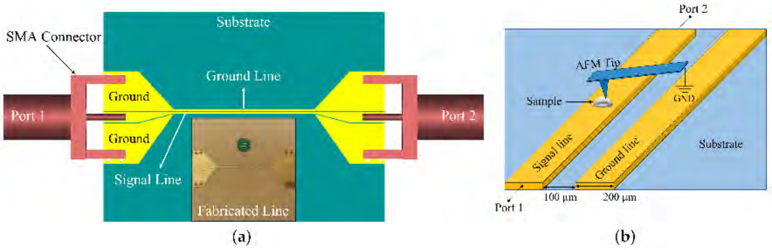
Scanning Microwave Microscopy (SMM) is a technique often integrated/combine with Atomic Force Microscopy (AFM) or Scanning Tunneling Microscopy (STM), enabling the characterization of sub-surface structures and quantitative measurements of electromagnetic parameters (e.g. dielectric constant or conductivity). The use of SMM is limited to very few laboratories, exploring the technique, while just a couple of commercial solutions are currently available. Recently we have introduced a novel technique, inverted Scanning Microwave Microscopy (iSMM), aimed to broaden the application beyond the current focus on surface physics and semiconductor technology.[1,2] The application of the conventional SMM has been limited mainly to surface physics and semiconductor technology because the traditional SMM requires a fragile and expensive probe and is incompatible with saline solution or live cells.

In the iSMM, instead of delivering the signal through the AFM probe, the sample is placed on a planar slot line or coplanar waveguide that is excited by the VNA. The probe just works as a field concentrator; therefore, it is not constrained in its construction or design by the need to carry an RF signal. With a conductive probe, the iSMM can be converted from any existing AFM or STM device, paving the way for using microwave microscopy in a larger number of laboratories and research fields.



The experimental setup of the inverted SMM: (a) The slot-line design (inset shows the fabricated slot line). (b) Schematic description of the grounded metallic AFM tip and the slot line as a sample holder.

Reference:

1. M. Farina, X. Jin, G. Fabi, E. Pavoni, A. Donato, D. Mencarelli, A. Morini, F. Piacenza, R. A. Hadi, Y. Zhao, Y. Ning, T. Pietrangelo, X. Cheng, and J. C. M. Hwang, "Inverted scanning microwave microscope for in vitro imaging and characterization of biological cells", Appl. Phys. Lett. 114, 093703 (2019).
2. M. Farina and J. C. M. Hwang, "Scanning Microwave Microscopy for Biological Applications: Introducing the State of the Art and Inverted SMM," in IEEE Microwave Magazine, vol. 21, no. 10, pp. 52-59, Oct. 2020.

UNIVERSITÀ
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Dipartimento di Scienze Chimiche e Farmaceutiche

Use of lignin in the photochemical iodoalkylation of olefins

Abstract

In this paper we demonstrate how lignin can be used as a radical activator of perfluoroalkyl species leading to the formation of electrophilic radicals by a photochemical process.
The methods by which these perfluoroalkyl radicals are obtained to date can be either wasteful or dangerous. The use of lignin leads to the same result but with advantages, being a natural material and present in very large quantities.
This is due to the structure of lignin, being composed of phenylpropanoic units. It is considered an amorphous biopolymer rich in polyphenols, this structure allows after deprotonation of the carboxyl functional groups and an irradiation that leads to an excited state, thus forming a strongly reducing species, an electronic transfer of an electron to a perfluoroalkyl species.
We have shown how the mechanism can occur via SET single electron transfer from lignin to the perfluoroalkyl species, this electron transfer leads to the breaking of the bond in a mesolytic manner so that an electrophilic radical is obtained.
Once the radical is formed in the presence of a given nucleophilic substrate, in our case a terminal olefin, it can go to addition respecting the steric bulk rules. Adding from the less cluttered side and lead to the formation of alpha-iodoprofluoroalkyl compounds. These compounds can be easily refunctionalized and also the presence of the fluorinated chain can lead to several advantages in many areas.
In addition, the presence of the base, 2,6-lutidine can also serve a dual function. In addition to that of deprotonating the carboxyl sites of lignin and thus initiating the previously mentioned mechanism, also of forming an EDA complex with the perfluorohexyl-hiodide, which can weaken the bond and incentivize this dissociation and thus the formation of the radical.

This work proceeds toward an optimization of the procedure by adjusting parameters and using appropriate compounds such as choosing the best base and solvent for this procedure. A generalization of the obtainable products is also carried out so as to make the reaction potentially applicable in more contexts.

Autori:
Francesco Palazzi
Prof. Maurizio Prato
Prof. Giacomo Filippini

Abstract n&n2023:

PORPHYRIN-BASED DYES FOR ADVANCED APPLICATIONS

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The energy transition from fossil fuels to renewables is already ongoing, but it will be a long and difficult process because the energy system is a gigantic and complex machine. The production of clean energy and the transformation of CO_2 into valuable chemicals are nowadays central topics and are both considered fundamental to fight climate change and global warming.[1]

The **SunLab group** is mainly focused on the rational design and the judiciously tailored synthesis of porphyrin-based advanced materials as sensitizers for the conversion of solar energy into electricity (*Dye-Sensitized Solar Cells*, *DSSCs*, for third generation photovoltaics) (Figure 1)[2][3] and into chemical energy (*Dye-Sensitized Photoelectrochemical Cells*, *DSPECs*, for artificial photosynthesis) (Figure 2).[2][4]

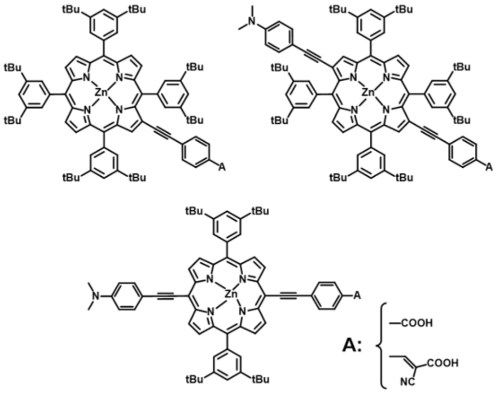

Figure 1: *Some examples of β-pyrrolic and meso substituted Zn(II) porphyrins synthesized by the* ***SunLab group*** *for DSSCs*

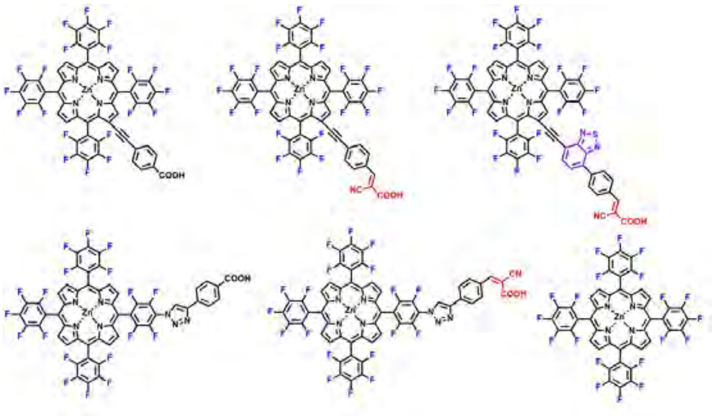

Figure 2: *Some examples of β-pyrrolic and meso substituted Zn(II) porphyrins synthesized by the* ***SunLab group*** *for DSPECs.*

Moreover, recent research interests involve the investigation of suitably-functionalized Fe(III)-porphyrins as homogeneous catalysts for photo- and electrochemical CO_2-to-CO conversion,[5] and the application of perfluorinated porphyrins for the assembly of nano-heterojunctions with metal semiconductor oxides, to be used as chemoresistors for the detection of volatile organic compounds (VOC) in biomedical applications.[6] Finally, the **Sunlab group** has a well-established experience in the investigation of the second order nonlinear optical properties of variously substituted push-pull Zn(II)-porphyrins.

The present contribution aims thus to provide the audience with a synopsis of the main results achieved so far in all these research fields.[7–10]

References

(1) Armaroli, N.; Balzani, V. Solar Electricity and Solar Fuels: Status and Perspectives in the Context of the Energy Transition. *Chem. Eur. J.* **2016**, *22* (1), 32–57. https://doi.org/10.1002/chem.201503580.

(2) Di Carlo, G.; Orbelli Biroli, A.; Pizzotti, M.; Tessore, F. Efficient Sunlight Harvesting by A4 β-Pyrrolic Substituted ZnII Porphyrins: A Mini-Review. *Front. Chem.* **2019**, *7*, 177. https://doi.org/10.3389/fchem.2019.00177.

(3) Di Carlo, G.; Biroli, A. O.; Tessore, F.; Caramori, S.; Pizzotti, M. β-Substituted ZnII Porphyrins as Dyes for DSSC: A Possible Approach to Photovoltaic Windows. *Coordination Chemistry Reviews* **2018**, *358*, 153–177. https://doi.org/10.1016/j.ccr.2017.12.012.

(4) Orbelli Biroli, A.; Tessore, F.; Di Carlo, G.; Pizzotti, M.; Benazzi, E.; Gentile, F.; Berardi, S.; Bignozzi, C. A.; Argazzi, R.; Natali, M.; Sartorel, A.; Caramori, S. Fluorinated Zn ^{II} Porphyrins for Dye-Sensitized Aqueous Photoelectrosynthetic Cells. *ACS Appl. Mater. Interfaces* **2019**, *11* (36), 32895–32908. https://doi.org/10.1021/acsami.9b08042.

(5) Rao, H.; Lim, C.-H.; Bonin, J.; Miyake, G. M.; Robert, M. Visible-Light-Driven Conversion of CO_2 to CH_4 with an Organic Sensitizer and an Iron Porphyrin Catalyst. *J. Am. Chem. Soc.* **2018**, *140* (51), 17830–17834. https://doi.org/10.1021/jacs.8b09740.

(6) Pargoletti, E.; Hossain, U. H.; Di Bernardo, I.; Chen, H.; Tran-Phu, T.; Chiarello, G. L.; Lipton-Duffin, J.; Pifferi, V.; Tricoli, A.; Cappelletti, G. Engineering of SnO_2 –Graphene Oxide Nanoheterojunctions for Selective Room-Temperature Chemical Sensing and Optoelectronic Devices. *ACS Appl. Mater. Interfaces* **2020**, *12* (35), 39549–39560. https://doi.org/10.1021/acsami.0c09178.

(7) Tessore, F.; Biroli, A. O.; Di Carlo, G.; Pizzotti, M. Porphyrins for Second Order Nonlinear Optics (NLO): An Intriguing History. *Inorganics* **2018**, *6* (3), 81. https://doi.org/10.3390/inorganics6030081.

(8) Di Carlo, G.; Pizzotti, M.; Righetto, S.; Forni, A.; Tessore, F. Electric-Field-Induced Second Harmonic Generation Nonlinear Optic Response of A_4 β-Pyrrolic-Substituted Zn ^{II} Porphyrins: When Cubic Contributions Cannot Be Neglected. *Inorg. Chem.* **2020**, *59* (11), 7561–7570. https://doi.org/10.1021/acs.inorgchem.0c00451.

(9) Tessore, F.; Di Carlo, G.; Forni, A.; Righetto, S.; Limosani, F.; Orbelli Biroli, A. Second Order Nonlinear Optical Properties of 4-Styrylpyridines Axially Coordinated to A4 ZnII Porphyrins: A Comparative Experimental and Theoretical Investigation. *Inorganics* **2020**, *8* (8), 45. https://doi.org/10.3390/inorganics8080045.

(10) Limosani, F.; Tessore, F.; Di Carlo, G.; Forni, A.; Tagliatesta, P. Nonlinear Optical Properties of Porphyrin, Fullerene and Ferrocene Hybrid Materials. *Materials* **2021**, *14* (16), 4404. https://doi.org/10.3390/ma14164404.

Innovative materials and additive technologies for the energy sector

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Keywords: Additive Manufacturing, LPBF, Heat Exchange, Ferritic Steel, precipitates

INTRODUCTION

Additive manufacturing is a range of technologies developed since the 1980s. The widespread use that these technologies have had in recent years can be ascribed to the enormous increase in the computing speed of computers and the implementation of automated systems. The potential of these technologies is considerable:

- rapid prototyping;
- the ability to produce components with complex geometries and lightweight;
- potential reduction of energy demand for production;
- reduction of the amount of waste materials and optimization of raw material utilization;
- reduction of the number of components to be assembled.

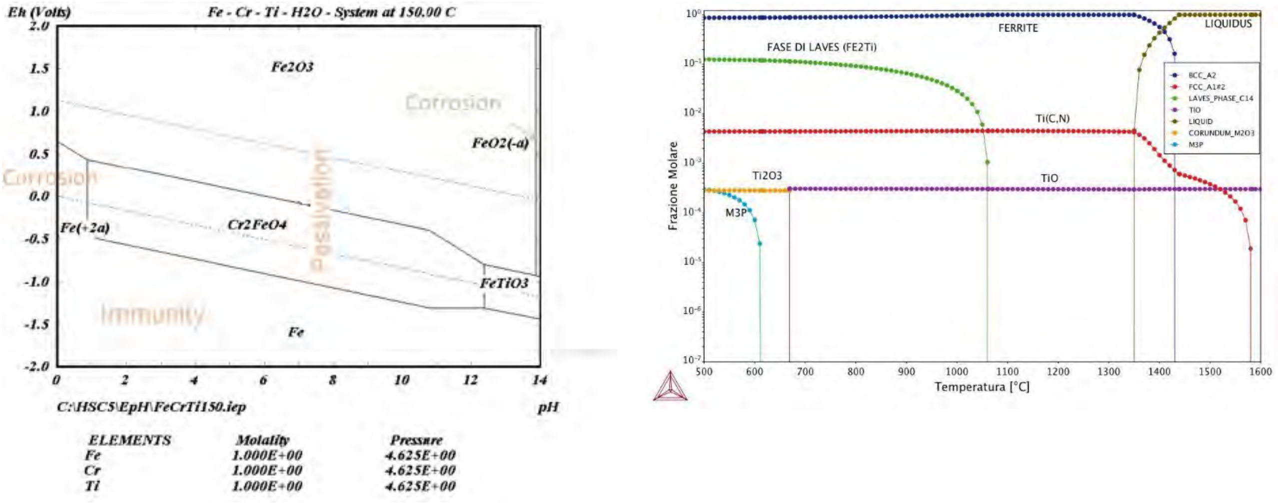
One of the main limitations of these technologies is represented by the materials as well as by the printing rate [1]. In fact, depending on the type of technology used, there are a limited number of materials available for the additive processes, thus limiting the number of possible applications [2, 3, 4]. Heat exchange is one of the energy sectors where 3D printing can bring out its advantages by allowing components to be made with internal channels. In fact, this work focuses on the realization of a ferritic alloy for heat exchangers for particularly harsh environments such as corrosive alkaline solution. This is the case of absorption machines, used for air-conditioning, with ammonia water cycle. In the case of refrigeration, for example, the system is based on the principle that in the liquid-gas transition, substances absorb heat. These systems are particularly interesting because they can be coupled with renewable energy sources. In absorption machines, therefore, heat exchangers are among the main components.

AIM

In order to realize heat exchangers for absorption machines in a single block, which do not require assembly or gaskets, the possibility of realizing them by means of additive processes, in particular powder bed ones, was considered. Using an alloy design approach, a ferritic alloy has been specifically designed for these processes.

RESULTS AND DISCUSSIONS

Considering corrosion of Ni and Cu in presence of ammonia, even at room temperature, due to the formation of complexes, a stainless steel, with Cr content higher than 13wt%, and without Ni has been investigated. Titanium is known to have good corrosion resistance even in ammonia environment [5]. Pourbaix diagrams, obtained with code HSC_5 [6] show a large passivity region in the case of Titanium (figure 1a). One of the critical points in titanium and titanium alloys in presence of ammonia is related to the uptake of hydrogen in case of molecule dissociation. However, this phenomenon could take place at temperatures higher than 300°C and with high pressures, due to the formation of a thicker passivation layer which can fracture due to thermal mismatches and offer metallic surface to hydrogen. In the case of absorption machines the temperatures are largely lower respect these conditions. In this scenario a ferritic Fe-Cr alloy with Ti content has been considered. Ti can also stabilize chromium oxide with increasing temperature.



a) b)

Figure 1: Pourbaix diagram obtaing with code HSC_5, for a composition of Fe-Cr-Ti (a); stepped calculation (Thermocalc®) for a ferritic steel with 14% Cr and 4wt% of Ti (b)

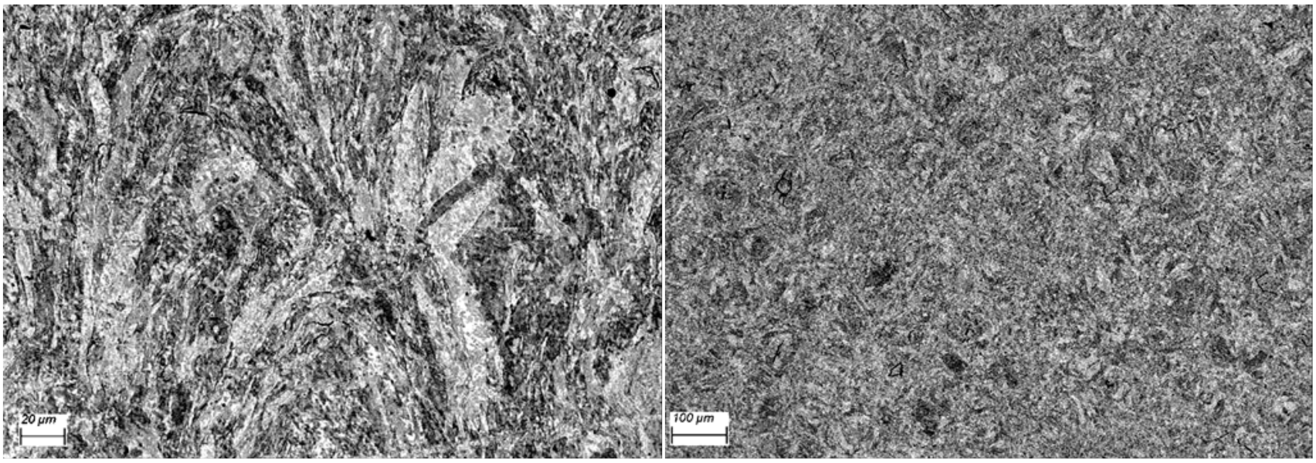
With the aim of thermodynamic software, Thermocalc® for material properties investigations, the phase diagram has been obtained for ferritic alloys with modified composition. In figure 1b, right, the stepped calculation graph for an alloy with composition 14% Cr and 4% Ti is reported. Low content of C and N has been considered in order to keep as lower as possible the content of Ti(C,N) and TiO_2. During AM processes rapid cooling is expected and the content of intermetallic phases should be hindered respect to the content reported in figure 1b.

After defining the ferritic steel composition, the alloy has been produced by Vacuum Induction Melting (VIM), in the form of a bar and successively gas atomized by an Electrode Induction Melting Inert Gas Atomization (EIGA).

The base material demonstrated a thermal conductivity more than two times higher respect to that of AISI316 and a smaller coefficient of thermal expansion.

A laser-bed powder bed process (LPBF) has been used to produce samples for microstructural characterization and corrosion resistance tests.

Figure 2 shows the microstructure in the parallel (a) and in the perpendicular (b) direction, respect to the sample growing direction, revealing the presence of oblongs and fine grains respectively in the first and in the second case. X-Ray diffraction, not showed, revealed the α-iron BCC crystal structure and, within the resolution of the technique, the absence of other relevant phases.



a) b)

Figure 2: SEM images reporting the microstructure in the parallel (a) and in the perpendicular (b) direction, respect to the growing direction, for the sample printed by LBPF process.

SEM observations on sectioned and etched samples, from material produced by VIM, revealed the presence of a very fine form of precipitates, even smaller than 10 nm.

CONCLUSIONS

A ferritic alloy with higher thermal conductivity, lower coefficient of thermal expansion respect to AISI316 and good resistance to harsh alkaline ammonia-water solutions has been produced by VIM and EIGA processes with the aim of realizing heat exchangers for absorption machines with ammonia-water cycle. Samples have been produced also by additive manufacturing with LPBF process. Even if the alloy is promising as substitute of conventional stainless steels, for these specific applications, further investigations are needed in order to ascertain the nature of very fine precipitates in the matrix.

ACKNOWLEDGEMENTS

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[1] Kelbassa I, Wohlers T, Caffrey T (2012) Quo vadis, laser additive manufacturing? Journal of laser applications 24(5):050101
[2] Simons, M. Additive manufacturing—a revolution in progress? Insights from a multiple case study. Int J Adv Manuf Technol 96, 735–749 (2018)
[3] Yoon, H., Lee, J., Kim, H. et al. A comparison of energy consumption in bulk forming, subtractive, and additive processes: Review and case study. Int. J. of Precis. Eng. and Manuf.-Green Tech. 1, 261–279 (2014)
[4] T. Gutowski et al., Note on the Rate and Energy Efficiency Limits for Additive Manufacturing, Journal of Industrial Ecology, 21 (2017) S69-79
[5] Royer, R. & Collings, E.(1993). Materials Properties Handbook: Titanium Alloys, ASM International
[6] HSC-Chemistry (Version 5) by Chemistry Software, Suite #829, 1321 Upland Drive, Houston, TX 77043, USA

Identification of ultra-thin molecular layers atop monolayer terraces in sub-monolayer organic films with scanning probe microscopy

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The morphology of sub-monolayer organic films has been investigated *in situ* and *ex situ* as a function of the substrate temperature of deposition. In this thickness range, monolayer terraces formed of edge-on molecules, i.e. nearly upright, are typically nucleated. Herein, the terrace height is found to be correlated to both the film morphology and the substrate surface energy. In particular, the presence of a layer of variable thickness with molecules lying face-on or side-on can be identified atop the terraces when the deposition is carried out on inert substrates. This phenomenon can be evidenced thanks to accurate height measurements made with atomic force microscopy and further data obtained with advanced scanning probe microscopy techniques operating in different environments, *viz.* liquid, air and vacuum. An upward displacement of molecules from the substrate to the top of the terraces is considered to be responsible for this layer formation, whose molecules weakly interact with the underlying terraces.

Nanostructured glass substrate for SERS detection and characterization of micro and nanoplastics

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Microplastics are defined as plastic particle fragments whose size is below 5 mm, whereas nanoplastics have dimensions laying in the range between 1um and 1nm.

Characterization of nanoplastics by traditional Raman microscopy is a tedious task due to the small size and low concentration in real samples, and therefore thedue to their weak scattering intensity, of these samples.

Surface Enhanced Raman Spectroscopy (SERS) is a variant of the Raman spectroscopy in which a metallic nanostructure is exploited to obtain a local enhancement of the electromagnetic field resulting in a sensible increase of the Raman cross-section.

It represents an interesting approach for detecting analytes in low and ultra-low concentrations, and recentlythe detection of analytes in low and ultra-low concentrations and, recently, it has also been applied to the study of micro and nano plastics.

We hereby propose a new type of SERS sensor based on a pillar nanostructured glass coated with a thin film of metals exhibiting plasmonic properties, such as gold and silver.

The pillar nanostructures are obtained by deposition of a copper nanoparticles shadow mask on the glass substrate, and its subsequent processing by reactive ion etching (RIE) in a CF_4 and Ar atmosphere.

The glass is finally coated with a gold or silver layer of thickness in the range between 20 and 60nm by means of RF sputtering.

Polystyrene micro and nano beads were chosen as an analytical model of micro and nano plastics, and the sensitivity of the different sensors showed promising results for the detection in a Raman microscope at different excitation wavelength.

Radiation-Sensitive Phase-Change Nanodroplets for Hadron Therapy Dosimetry and Range Verification Assessed by Ultrasound Imaging

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Radiotherapy is one of the most adopted medical treatments for different types of cancer. Ad hoc strategies allowing for in-situ dosimetry and range verification are essential in charged-particle radiation therapy to reduce the safety margins applied to account for uncertainties introduced in the entire treatment workflow and to assess the radiation dose imparted on the target volume and surrounding healthy tissues. We recently developed a novel non-invasive dosimetry concept for carbon-ion and proton therapies based on a new biocompatible formulation of phase-change ultrasound contrast agents. Injectable nanodroplets (NDs), made of a superheated perfluorobutane (C4F10, boiling point.-2°C) liquid core, encapsulated with a crosslinked poly(vinyl alcohol) shell (PVA/PFB NDs), are vaporized when exposed to hadron beams at physiological temperature and clinically relevant doses. The in vitro evaluation of the contrast enhancement at the Bragg peak via ultrasound (US) imaging can be correlated to the absorbed dose and enables range verification with sub-millimeter accuracy. We demonstrated the first nanodroplets' proton response, achieved in vivo, in healthy rats, within the FET-Open EU project AMPHORA. These early findings underline the ground-breaking potential of phase-change nanodroplets for radiotherapy dosimetry and range verification. This contribution will discuss the concept from the initial demonstration of radiation-induced NDs' vaporization in phantoms to their first in vivo application and highlight the challenges for this promising technology.

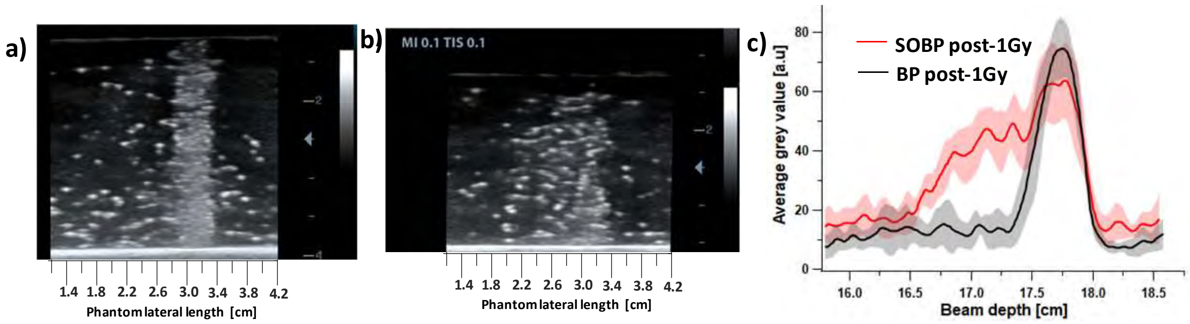

Figure1. PVA/PFB NDs triggered vaporization by carbon ion beam @37°C: a) and b) US images of NDs in tissue-mimicking phantom post-exposure to 1Gy Bragg peak (BP) and spread-out Bragg peak (SOBP) irradiation, respectively. The bright area shows the generated NDs' vaporization occurring at the BP. c) Quantification of generated US contrast profiles upon the BP and SOPB irradiations.

References

1. Heymans SV *et al. Med. Phys. 48*: 1983-1995, (**2021**).
2. Collado-Lara G., et al. *Ultrasound Med. Biol. 48*, 149–156, (**2022**)
3. Toumia Y *et al. Sci Rep 12*, 8012 (**2022**).

Synthesis and characterization of oxidized alginate-doxorubicin nanoparticles for the treatment of breast cancer

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In recent years, doxorubicin has been one of the most effective anticancer agents for the treatment of leukemia and a wide range of solid tumors, and several prodrugs have been developed that use anthracycline as the active molecule. The efficacy of current chemotherapy is mainly limited by the toxicity associated with anticancer drugs to healthy tissue.

This limitation arises from the fact that currently used drugs lack efficient selectivity towards cancer cells. In order to realize a nanostructured system suitable for the transport of chemotherapeutic drugs, showing selectivity for diseased cells compared to healthy cells, the oxidized alginate-doxorubicin conjugate was synthesized and characterized.

Alginate requires partial oxidation which makes it easily degradable under physiological conditions. This first synthesis favors the degradation in aqueous solvents and a reduction of the molecular weight. The oxidized polymer was subsequently functionalized with doxorubicin through the formation of a Schiff base, which can favor the release of the drug, once subjected to pH variations. Exploiting the compound's amphiphilicity characteristic, the prodrug was self-assembled into nanoparticles that can be able to respond to the acidic environment of cancer cells and selectively release the chemotherapeutic. Nanostructures offer advantages over the chemical species from which they are generated as they possess greater strength and electrical conductivity and, potentially, increased biological activity. These properties, combined with the possibility of functionalizing their surface or modifying their core, make nanoparticles promising for drug delivery. They can also be taken through all the classic routes of administration and thanks to their structure, they can protect the drug from enzymatic degradation, increasing its residence time in the body until it reaches the target site.

Sensitivity analysis of a THz graphene-based passive device

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1. Summary

A FEM model of THz passive component will be presented and used to assess the effect on the whole device performance of the uncertainties affecting geometrical and physical parameters of the component by means of sensitivity analysis. Moreover, with the aim of support the experimental validation, the overbounding and underbounding of the performance will be derived ranging the actual behaviour of the designed component.

2. Description of the problem and proposed approaches

The performance f of an electromagnetic system is the output that the designer looks for: several efforts have to be applied in order to ensure the satisfaction of the customer constraints. Usually, the designed parameters are considered fixed and well know, i.e. the vector $\underline{x}_0 = (x_{10}, x_{20}, \ldots, x_{n0})$ of the n design parameters, and it corresponds to a point in the parameter space $D = [x_{1L}, x_{1U}] \times \cdots \times [x_{nL}, x_{nU}]$ with x_{iL} and x_{iU} the min and max values of x_i parameter respectively. Nevertheless, there are actually several sources of uncertainty leading to unavoidable Δ_i variation in the parameters. It means that each component of the design parameter vector becomes "interval value", given by $x_{i0} \pm \Delta_i$, and the point $\underline{x}_0$ becomes the hyper-rectangle $U(\underline{x}_0) = [x_{10} - \Delta_1, x_{10} + \Delta_1] \times \ldots \times [x_{n0} - \Delta_n, x_{n0} + \Delta_n]$ (fig. 1 for n=3) [1]. As a consequence, also the performance will be an "interval function" that could be mismatched with respect to the desired design. This is especially true when the technology is not well established or the material behaviour and its physics is still understudies such as the case of nanocarbon-based device [2]. In this case, bounding of the performance function and sensitivity analysis can help to identify the more effective parameter and the results of such analysis can be used as a support in the experimental validation [3]. To this aim, A FEM model of THz passive component will be presented [4] and used to assess the effect on the whole device performance of the uncertainties affecting geometrical and physical parameters of the device [5]. In particular a 3-level full factorial approach will be considered and used to support Vertex Analysis in order to define the bounding of the assumed PF. Moreover, the scattered data numerically obtained from the simulation of the device (modelled with a commercial software Comsol Multiphysics), will be used to assess the relevance of the considered design parameters, with the aim of select the most influencing one [6]. Moreover, simulated scattered data will be used to evaluate the sensitivity of the performance due to the assumed variability in discrete way [6].

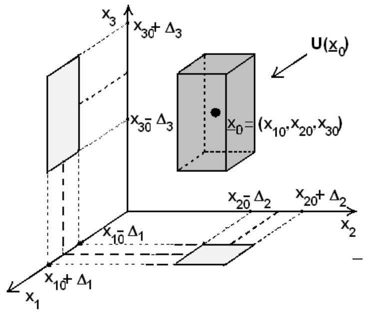

Figure 1 Hyper-rectangle $U(x_0)$ representing all the possible values assumed by the vector $\underline{x}$ when each component is affected by a variation Δi

3. Acknowledgement.

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4. References

[1] Egiziano, L., Lamberti, P., Spinelli, G., Tucci, V., Kuzhir, P.P. "Sensitivity analysis of a multilayer shielding device based on graphene" (2017). Int. Conf. ETCMOS 2017 Emerging Technologies: Communications, Microsystems, Optoelectronics, Sensors, Warsaw, Poland - May 28 – 30, 2017.

[2] La Mura, M., Lamberti, P., Tucci, V. "Numerical evaluation of the effect of geometric tolerances on the high-frequency performance of graphene field-effect transistors" (2021) Nanomaterials, 11 (11), art. no. 3121. doi: 10.3390/nano11113121

[3] P. Kuzhir, et al. "Main principles of passive devices based on graphene and carbon films in microwave - THz frequency range" JOURNAL OF NANOPHOTONICS. Vol. 11. (2017) 03250401 (19pp), doi: http://dx.doi.org/10.1117/1.JNP.11.032504

[4] Kuzhir, P., et al. "FEM Approach to the Robust Design of a Graphene-Based 3D Structure for THz Devices" (2021) 2021 IEEE 16th Nanotechnology Materials and Devices Conference, NMDC 2021. doi: 10.1109/NMDC50713.2021.9677563

[5] Lamberti, P.; La Mura, M.; Tucci, V.; Nkyalu, E.; Khan, A.; Yakovleva, M.; Valynets, N.; Paddubskaya, A.; Saushin, A.; Vanyukov, V.; Baah, M.; Urbanowicz, A.; Svirko, Y.; Kuzhir, P. The Performance of Graphene-Enhanced THz Grating: Impact of the Gold Layer Imperfectness. Materials 2022, 15, 786. https://doi.org/10.3390/ma15030786

[6] Y. Jin, B. Sendhoff: "Trade-off between performance and robustness: an evolutionary multiobjective approach", Lecture Notes in Computer Science, Springer-Verlag Heidelberg, Vol. 2632, August 2003, pp. 237-251.

Quantum chemical analysis of structures and THz spectra of hexagonal boron-nitride quantum dots

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Two-dimensional hexagonal boron-nitride is a material structurally similar to graphene, wherein it has very different electronic, optical, and chemical properties. In its turn, boron-nitride quantum dots (BNQDs) are characterized by properties that differ from the two-dimensional analogs due to their nanoscale. They have unique photophysical properties and are biocompatible, which determines their promising application in biomedicine for bioimaging and as the boron delivery agents for neutron capture therapy. The geometry and structure of BNQDs, and hence their properties, depend on the synthesis method. It is assumed that the hydrothermal method is preferred for the reproducible synthesis of BNQDs of definite size, functionalized (or decorated) with functional groups of boron and nitrogen atom precursors used in the synthesis process.

The most common spectral characterization of BNQDs includes analysis of IR, Raman, UV/Vis, and luminescence spectra. Nevertheless, the THz region (up to 300 cm^{-1}) has unique features due to the spectral manifestations in this region characterize low-frequency deformation vibrations and weak interactions between fragments of a system including its layers.

In this study the structural, spectral, and other characteristics of BNQDs were calculated using quantum chemical methods based on density functional theory (B3LYP and BPW91 functionals) and all-electron (cc-pVnZ) Gaussian basis sets. Nowadays, these methods allow the prediction of structural parameters with high accuracy that is a prerequisite for an adequate simulation of spectral and other properties. We have considered single-, double-, and triple-layer models of BNQDs, which include up to 50 boron and 50 nitrogen atoms, and different functional groups on the edges. Two of considered structures are shown in Fig. 1.

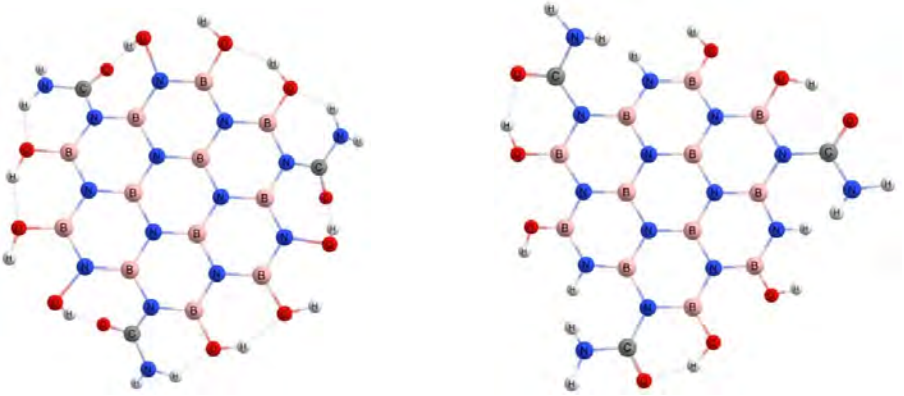

Fig. 1. Structures of BNQDs with hydroxyl and amide groups.

For all considered models the calculated structural and energy parameters, including inter-layer distance and HOMO–LUMO gap, agree with experimental ones. For each model structure the vibrational spectra, including the THz region, were also calculated and analysed. Some regularities between the number of boron and nitrogen atoms, the number of layers, the presence of different functional groups and their chemical composition, and THz spectra were established.

This work was supported by Horizon 2020 RISE DiSeTCom Project (GA 823728).

EFFECT OF MAGNETIC NANOPARTICLES ON THE PERFORMANCE OF TRIBOELECTRIC NANOGENERATOR

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Triboelectric nanogenerators (TENGs) are systems that can convert mechanical energy into electrical energy from various mechanical energy sources such as walking, running, and jumping due to the triboelectric effect in daily life. The TENG is a system with a new type of energy harvesting strategy and there are various ways to increase the output performance of TENGs such as by changing the surface morphology of triboelectric films[1], by increasing the external force and its frequency[2] and by enhancing the surface charge density[3]. Among ways to improve the performance of TENGs, the introduction of magnetic nanoparticles into the triboelectric film can affect the electric field and the output performance of TENGs in several ways. First of all, magnetic nanoparticles can increase the charge density on the surface of the triboelectric film[4]. Consequently, when the TENG is subjected to mechanical deformation, the magnetic nanoparticles can influence the separation and accumulation of charge carriers on the surface of the triboelectric film. This effect can lead to an increase in the output voltage and power of the device. Also, magnetic nanoparticles can change the surface morphology and contact area of the triboelectric film. Thus, the formation of rough surfaces in the film leads to an increase in the contact area between two triboelectric materials and to the strengthening of the triboelectric effect. Finally, the incorporation of magnetic nanoparticles into the triboelectric film can also affect the mechanical and electrical properties of the TENG. Magnetic nanoparticles can increase the mechanical strength and stability of the film, which makes the TENG more durable and reliable.

In this study, the mechanism of the effect of magnetic nanoparticles on the output performance of the triboelectric nanogenerator was investigated. Magnetite nanoparticles were obtained via the co-precipitation method[5]. In this synthesis, $FeCl_3 \cdot 6H_2O$, and $FeCl_2 \cdot 4H_2O$, with a 2:1 mole ratio were each dissolved in 50 mL of deionized water. Then the two solutions were mixed into a 250 mL beaker glass and then stirred and heated until 70°C for 30 min under the nitrogen atmosphere. For coating with polyethylene glycol (PEG) an appropriate amount of polymer was slowly added to the solution, and stirring was continuing about 1h. After it, 10-15 mL NH_4OH 23-25% was added drop-wise until the pH was 10 and the temperature was increased to 90°C, and the solution was vigorously stirred for about 1h. Further liquid and precipitate separated using a NdFeB magnet and washed with deionized water and ethanol several times. Then, PEG-coated Fe_3O_4 magnetic nanoparticles were put in an oven and subsequently dried for 4h at 80°C. In order to investigate the effect of Fe_3O_4 magnetic nanoparticles on the performance of TENG, a nanocomposite material is obtained using Nylon (nylon socks, nylon 100%) as a polymer matrix. Firstly, a 0.5wt% solution of Fe_3O_4 magnetic nanoparticles was prepared in ethanol. Then the obtained solution is dispersed by the sonochemical method within 2 minutes. The dispersed solution is sprayed on the surface of the Nylon material, which is previously attached to the aluminum foil by means of double-sided adhesive, through the spray coating method. The samples were dried at room temperature for one day, and the next day a 5x6 cm section was cut, and a TENG was fabricated using polysiloxane film as another triboelectric material. The value of open-circuit voltage and short-circuit current of TENG made with conventional Nylon was measured as U_{OC}=30 V and I_{SC}=2 μA, respectively. The output voltage and current of the nanocomposite-based triboelectric nanogenerator increased and showed values of U_{OC}=45 V and I_{SC}=2.8 μA, respectively. Tests on a triboelectric nanogenerator based on polysiloxane and nylon materials were performed using a digital multimeter (DMM6500 6-1 / 2 digit multimeter, Keithley). Temperature and relative humidity during the analysis was 12 ° C, and 78%, respectively. During the experiments, it is clear that the Nylon/Fe_3O_4 nanocomposite-based TENG performed better than the conventional Nylon film-based TENG.

References:

1. *Cui, Shengnan, Linglin Zhou, Di Liu, Shaoxin Li, Li Liu, Shengyang Chen, Zhihao Zhao, Wei Yuan, Zhong Lin Wang, and Jie Wang. "Improving performance of triboelectric nanogenerators by dielectric enhancement effect." Matter 5, no. 1 (2022): 180-193.*
2. *Huang, Junjun, Wangping Wu, Ruxia Zhang, Guoqing Lu, Bing Chen, Zhenming Chen, and Chengmei Gui. "Novel electrode material using electroless nickel plating for triboelectric nanogenerator: Study of the relationship between electrostatic-charge density and strain in dielectric material." Nano Energy 92 (2022): 106734.*
3. *Kang, Xiaofang, Chongxiang Pan, Yanghui Chen, and Xiong Pu. "Boosting performances of triboelectric nanogenerators by optimizing dielectric properties and thickness of electrification layer." RSC advances 10, no. 30 (2020): 17752-17759.*
4. *Sun, Ruixue, Lingxiao Gao, Mengjie Shou, Bing Li, Xin Chen, Fayang Wang, Xiaojing Mu, Lei Xie, and Changrong Liao. "Tribo-material based on a magnetic polymeric composite for enhancing the performance of triboelectric nanogenerator." Nano Energy 78 (2020): 105402.*
5. *D. Serantes, K. Simeonidis, M. Angelakeris, O. Chubykalo-Fesenko, M. Marciello, M.d.P. Morales, D. Baldomir, C. Martinez-Boubeta, Multiplying Magnetic Hyperthermia Response by Nanoparticle Assembling, The Journal of Physical Chemistry C. 2014, 118, 5927-5934.*

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INFLUENCE OF THERMAL ANNEALING AND GAMMA IRRADIATION ON STRUCTURE AND OPTICAL PROPERTIES OF GO/PVA NANOCOMPOSITES

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Introduction: The fact that GO and PVA are easily soluble in water and that GO can be dispersed in the PVA polymer matrix makes the application of GO/PVA nanocomposites relevant. GO/PVA is one of the most widely used composites for the fabrication of Schottky diodes and electronic devices as an interfacial material with properties such as conductivity and high dielectric constant. Modification of materials by gamma irradiation attracts the attention of researchers not only as an environmentally friendly method but also because it is cost-effective and can be performed at room temperature. Irradiation of materials with γ -rays produce free radicals by the process of excitation and ionization, which leads to the modification process involving physical, chemical, and biological changes in the substance [1]. These property changes can vary depending on the type of substance, concentration, environment, radiation source, and dose, and other factors. In the literature, there are results on the degradation of the PVA polymer chain under the influence of gamma radiation, and a change in the optical properties and band gap value of PVA was observed with the increase of the dose. There are also results such as the reduction of GO under the influence of gamma rays in various works of literature. This method is considered a cleaner and easier method in the synthesis of rGO.

Materials and methods [2]: GO used in the mentioned work was synthesized by a modified Hummers method. The synthesized GO was added to distilled water (DW), sonicated, centrifuged, filtered, and air-dried at room temperature. At the initial stage, PVA is completely dissolved in DW. In the next step, GO was added at these different weight concentrations. The solution was subjected to ultrasound for 2 minutes. Finally, the solution is filtered into containers and air-dried at room temperature. Thus, GO/PVA nanocomposites were prepared at 1, 2, 3, 5, and 20% weight concentrations. Part of the prepared nanocomposites was thermally annealed at 40, 70, and 110°C, while other samples were exposed to 1, 50, and 150 Mrad radiation.

X-ray Diffraction (XRD) analysis: Figure 1 shows the XRD results of pure PVA and GO/PVA nanocomposites with different concentrations (2%, 3%, and 20%) obtained at room temperature. Figure 1.(1) shows the diffraction peaks of pure PVA. Figures 1.(2), (3), and (4) show the diffraction patterns of 2%, 3%, and 20% GO/PVA-based nanocomposites, respectively. It is clear from the results that the intensity of the peaks decreased with the increase in the amount of GO in the composite. Increasing the amount of GO within the composite may cause disorder in the polymer matrix and weaken the packing of the polymer chain, which results in a decrease in the crystallinity of the nanocomposite. Additional peaks observed at small angles are attributed to the PVA matrix.

Figure 2a shows the XRD results of 2% GO/PVA nanocomposite samples thermally annealed for 2 h at different temperatures. Peaks observed around 2θ=19° are characteristic of PVA. The characteristic peak of GO is not visible in the XRD spectrum of these composites. The absence of the characteristic peak of GO in the diffraction pattern of GO/PVA nanocomposite indicates the good distribution of GO as a result of dispersion within the PVA matrix. The low concentration of GO is another factor contributing to the non-appearance of the characteristic peak associated with GO. The observation of additional peaks depending on the temperature is associated with the softening of the polymer and the formation of new oriented structures entering between its GO sheets.

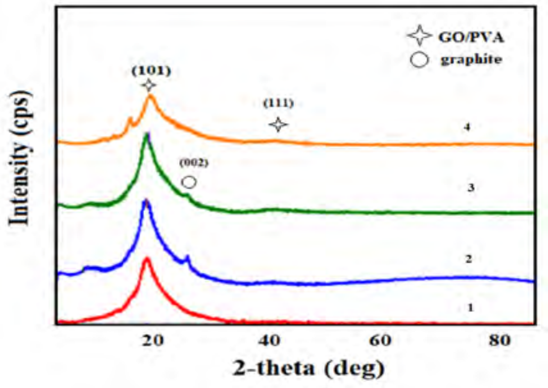

Figure 1. XRD results of GO/PVA nanocomposites with different concentrations of graphene oxide: 1 – PVS; 2 – 2% GO/PVS; 3 – 3% GO/PVS; 4 - 20% GO/PVS.

As can be seen from Figure 2b, shifts in the XRD peak are observed depending on the dose of gamma radiation. The calculations show that the distance between the layers has increased due to the effect of radiation. Also, the additional peak related to graphite disappeared under the influence of radiation. This is due to compression of Van der Waals interaction due to radiation, increase in the distance between graphite layers, and disruption of the structure. Under irradiation, the separated graphite layers are oxidized to form GO and coalesce into larger GO particles. Depending on the radiation dose, additional peaks are observed, which are related to the breaking of hydrogen bonds between GO and PVA, softening of the polymer, formation of new cross-links, and wrinkling of GO sheets [3].

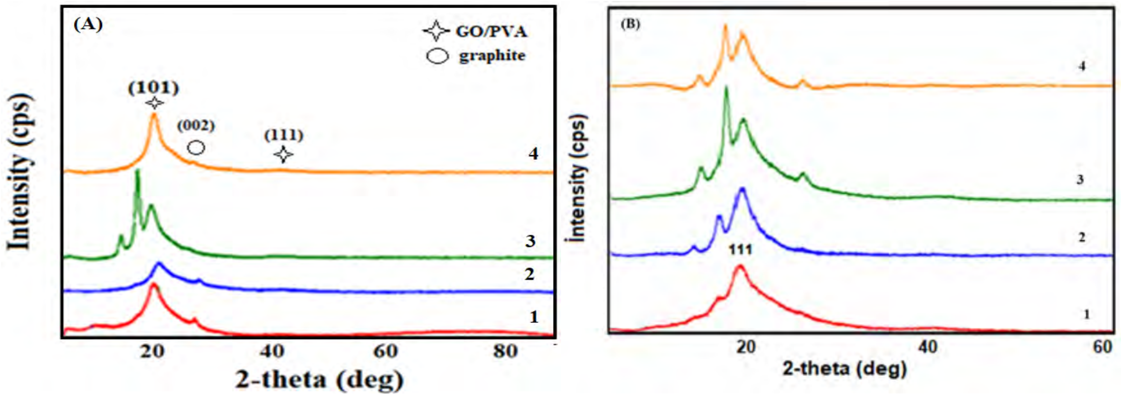

Figure 2. (A)-XRD results of thermally processed 2%GO/PVA nanocomposites atdifferent temperatures: 1 – T=25°C; 2 - T=40°C; 3 – T=70°C; 4 – T=110°C. (**B**)-XRD

results of 5%GO/PVA nanocomposites exposed to radiation at different doses: 1 – T=0 Mrad; 2 - T=1 Mrad; 3 – T=50 Mrad; 4 – T=150 Mrad.

Optical properties: The band gap decreases as the wt% of GO in the composite increases. Thus, when GO concentration increases from 1 to 5, the band gap decreases from 2.65 eV to 1.80 eV. It can be observed from Table 1 that the band gap decreases with increasing temperature. The decrease of the band gap with increasing temperature may be due to the softening of the polymer and the growth of GO particles. Calculations show that the band gap decreases with increasing gamma radiation (Table 2). This is due to the presence of free radicals caused by gamma radiation, as well as the formation of new chemical bonds and localized states between energy bands. However, the value of the band gap does not only depend on the radiation dose. Thus, the value of the band gap depends on the size of the particles, their interaction with the environment, and many other factors.

Table 1. Dependence of the band gap on thermal annealing for 2% GO/ PVA composite

Composite	25 °C	40 °C	70 °C	110 °C
2% GO / PVA	2.40 eV	2.35 eV	2.30 eV	2.20 eV

Table 2. The band gap values for samples depend on the dose of gamma radiation.

Samples	Band gap value (eV)			
	0 Mrad	1 Mrad	50 Mrad	150 Mrad
5% GO/PVA	1.88 eV	1.63 eV	1.44 eV	1.20 eV

Conclusion: The result of our experiments shows that the structure and optical properties of composites GO/PVA depends on the concentration of NPs, temperature of annealing and irradiation dose. These changes are connected with changing crystalline and chemical structures of nanocomposites.

Reference:

1. Chieng, B.W., Ibrahim, N.A., Daud, N.A., Talib, Z.A., 2019. Functionalization of graphene oxide via gamma-ray irradiation for hydrophobic materials. In: Synthesis, Technology and Applications of Carbon Nanomaterials. Elsevier, Synthesis, Technology, pp. 177–203.

2. Hurayra–Lizu, K.A., Bari, M.W., Gulshan, F., Islam, M.R., 2021. GO based PVA nanocomposites: tailoring of optical and structural properties of PVA with low percentage of GO nanofillers. Heliyon 7 (5), e06983.

3. Muradov, M., Baghirov, M. B., Eyvazova, G., Gahramanli, L., Mammadyarova, S., Aliyeva, G., ... & Abdullayev, M. (2023). Influence of gamma radiation on structure, morphology, and optical properties of GO and GO/PVA nanocomposite. Radiation Physics and Chemistry, 208, 110926.

FeCu bimetallic nanoparticles for nitrate reduction

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In recent years, industrial and agricultural activities such as fertilization of agricultural land, irrigation with sewage, as well as an increasing amount of nitrogen-containing municipal and industrial wastewater, have made nitrate pollution of water more and more serious. The content of nitrates and nitrites exceeds the norm and not only worsens the quality of water, but also poses a serious danger to human and animal health. In the human body, nitrates can be reduced to nitrites, which can react with hemoglobin in the blood to form methemoglobin, thereby preventing oxygen from being transported to body tissues. Based on this, it is very important to study methods for effectively removing nitrates from water. Nitrates have a high solubility in water, which makes them difficult to co-precipitate or adsorb. Currently, nitrate removal methods include physicochemical methods such as ion exchange, reverse osmosis, electrodialysis, biological denitrification, and chemical reduction. These methods can remove nitrates to varying degrees. However, they all have certain disadvantages. In fact, physicochemical methods don’t completely remove nitrates, but only transfer or concentrate them. Meanwhile, they produce a large amount of highly concentrated regeneration waste water and need further purification. Based on this, this method is not economically viable. Currently, chemical reduction methods are widely used, which use certain chemical reducing agents to remove nitrates.

Zero-valent iron is widely used for nitrate reduction due to its advantages of large specific surface area and high reactivity. However, studies have shown that iron nanoparticles tend to agglomerate and oxidize, which leads to a decrease in reactivity and limits their wide application. In recent decades, much attention has been paid to bimetallic catalysts due to their catalytic properties. The synergistic effects between the two metals provide increased activity, selectivity and stability compared to their monometallic analogues. The addition of other metals as a catalyst to iron nanoparticles has become another effective and novel way to increase the reactivity of iron. Research on bimetallic nanoparticles to reduce nitrate in wastewater has not been sufficiently studied.

This work investigated the effectiveness of FeCu bimetallic nanoparticles for nitrate reduction. The aim of this investigation is production and application of bimetallic nanoparticles that can be used for the high nitrate concentrated remediation. FeCu based bimetallic nanoparticles were synthesized freshly and used for nitrate removal. Synthesis of bimetallic nanoparticles was carried out in the presence of sodium oleate as stabilizing agent by chemical reduction method. Batch experiments were performed on nitrate contaminated (300 ppm) water samples. The parameters investigated were the FeCu dosage (0.05, 0.1, 0.2, 0.3, and 0.4 g L^{-1}), the reaction pH (unbuffered; buffered at pH = 3; initial pH = 3, 5, and 10), temperature (283, 298, 303, and 313 K) and nitrates concentration after their reusing. It was determined that almost complete elimination of nitrates was always observed after 15 min at a concentration of bimetallic nanoparticles above 0.4 g L^{-1}. The concentration of bimetallic nanoparticles was optimized at a fixed pH value. After nitrates reduction the same nanoparticles were repeatedly used. This experiment was conducted three times to determine the effectiveness of the bimetallic nanoparticles after every use. Have been determined that the efficiency of nitrate removal decreases after repeated use.

Polymeric Nanoparticles – Tool in a Drug Delivery Systems

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Abstract

Nanocarriers provide the multipurpose platform for the delivery of different therapeutic agents. Comprehension the advances in nanostructure-based drug delivery up till now and the boundaries that still need to be diminished provide a perspective for future research. In this paper, a brief overview of the advances and characteristics of the polymer nanoparticles for drug delivery are described. In addition, the opportunities and challenges of the main issues regarding nano-based drug delivery are also discussed.

Keywords: *nanocarriers, polymeric nanoparticles, drug-delivery systems, cancer drug-delivery systems*

One of the challenges of modern medicine and pharmacy is low drug selectivity. Therapeutic agents are introduced into the body through traditional ways of penetrating various organs and tissues and are distributed relatively evenly. Intravascularly administered therapeutics experience biological barriers sequentially before reaching the target sites. Therefore, only a small amount of the administered drug dose reaches the target cells that required therapeutic one [1]. Hence, the remaining amount of the drug that has delivered non-target organs and tissues often causes adverse effects. A more promising approach to solving this problem is the creation of targeted drug delivery systems [2]. The realization of a targeted concentration of therapeutic agents primarily in the area of the pathological focus can dramatically reduce the organism's undesirable reactions to drug exposure. Moreover, this approach can decrease the drug's therapeutic dosage and the frequency of its administration.

Therapeutic agents provided with a delivery system include the following advantages over free drugs: (1) the solubility of hydrophobic drugs increases; (2) their penetration into cells improves; (3) drugs appear the ability to overcome membrane and blood-brain barriers; (4) the effects of drugs prolong; (5) their biocompatibility and protection against premature degradation increases; (6) their directed transport and controlled release carry out, etc. [3].

Great opportunities open the door for using various nanostructures (liposomes, micelles, microspheres, dendrimers, fullerenes, polymer nanoparticles, etc.) for targeted drug delivery. Amongst nanostructures, polymeric nanoparticles (PNPs) play a noticeable role since they can bring therapeutics to the intended position in the human body with efficiency. PNPs are solid-state and colloidal particles, the core of which can consist of natural (albumin, collagen, gelatin) or synthetic (poly (methyl methacrylate), polyacrylamide, polystyrene, polyglycolide, polyglutamic acid) polymers with the sizes varying from a few nanometers to 1 μm. Due to their small sizes, biocompatibility, higher permeation, and retention (EPR) effect PNPs are considered the potential materials not only for drug [4] and gene [5] delivery but also tissue engineering [6], vaccination strategies [7], antimicrobial activity [8], etc.

Depending on the preparation method and purpose, the active substance can be (1) encapsulated inside the core, (2) adsorbed on its surface, or (3) attached to the surface by a covalent bond [9-12]. Moreover, depending on the therapeutics' chemical and physical characteristics it can be either conjugated with nanoparticles during the polymerization process or coupled after their formation [13, 14]. Besides, the chosen technology should allow the achievement of an efficient loading amount of the drug and maximize its pharmacological activity.

In addition to high stability and capacity characteristics, PNPs can bind both hydrophobic and hydrophilic substances. Another advantage includes their suitability for injection of the organism in various ways, including oral and inhalation. In the organism, therapeutic agents are released from PNPs by diffusion or desorption. Their release is facilitated via the polymer matrix swelling, its erosion, and degradation, as well. Since the polymer degradation rate varies over a wide range (from hours to several months), using the PNPs as transport systems makes it possible to control the active substance release. In the bloodstream, PNPs rapidly adsorb plasma proteins (opsonization). These nanoparticles are recognized by the system of mononuclear phagocytes, which realize the purpose of blood cleaning from "unknown" particles. The capture of nanoparticles by macrophages (liver, spleen, bone marrow) occurs through endocytosis, then these particles enter lysosomes, where they are destroyed and drug release occurs.

A significant part of the research is devoted to the studies of PNPs as drug delivery systems are related to the chemotherapy of cancerous tumors. These studies' results are summarized in several reviews [14-16]. PNPs for targeted drug delivery are being tested in other areas of medicine, as well [17-19]. Along with passive drug delivery, which occurs as a result of the natural biodistribution of the carrier and depends on its physicochemical properties and the state of the target, PNPs can also be employed for the active transport of therapeutics [20]. Active delivery is realized due to the specific interaction of the ligand on the surface of the nanoparticles with the corresponding receptors located on the surface of the target cell. As ligands for PNPs usually are used apolipoproteins, transferrin, folates, integrins, etc. [21-24].

Nanotechnology provides us with a new perspective to exploit the unique properties of a material by manipulating them at the nanoscale. Fabricating nanoscale polymeric particles for drug delivery opens up new methods to target tumors. To successfully obtain PNPs for biomedical applications, a wide range of physical, chemical, biological, and physiological aspects must be considered. Nevertheless, by adjusting the properties of the core, shell, and ligands, these factors can be taken benefit of to provide the required, bifunctionality and biocompatibility, making PNPs suitable for targeted drug delivery applications.

References

1. Zongmin, Z.; Anvay, U.; Jayoung, K.; Samir M. Targeting Strategies for Tissue-Specific Drug Delivery. *Cell* **2020**, 181(1):151-167, doi: 10.1016/j.cell.2020.02.001.
2. Chong, L.; Jiancheng W.; Yiguang W.; et al. Recent progress in drug delivery, *Acta Pharmaceutica Sinica B* **2019**, 9 (6), doi.org/10.1016/j.apsb.2019.08.003.
3. Calzoni, E.; Cesaretti, A.; Polchi, A.; Di Michele, A.; Tancini, B.; Emiliani, C. Biocompatible polymer nanoparticles for drug delivery applications in cancer and neurodegenerative disorder therapies. *Journal of Functional Biomaterials* **2019**, 10, 1-15, doi:10.3390/jfb10010004.
4. Rai, R.; Alwani, S.; Badea, I. Polymeric nanoparticles in gene therapy: New avenues of design and optimization for delivery applications. *Polymers* **2019**, *11*, doi:10.3390/polym11040745.
5. Fathi-Achachelouei, M.; Knopf-Marques, H.; Ribeiro da Silva, C.E.; Barthès, J.; Bat, E.; Tezcaner, A.; Vrana, N.E. Use of Nanoparticles in Tissue Engineering and Regenerative Medicine. *Frontiers in Bioengineering and Biotechnology* **2019**, 7, 1-22, doi:10.3389/fbioe.2019.00113.
6. Liu, B.; Wu, Z.; Liu, T.; Qian, R.; Wu, T.; Liu; Aizong Shen, Q. Polymeric Nanoparticles Engineered as a Vaccine Adjuvant-Delivery System. *Immunization - Vaccine Adjuvant Delivery System and Strategies* **2018**, doi:10.5772/intechopen.81084.
7. Lam, S.J.; Wong, E.H.H.; Boyer, C.; Qiao, G.G. Antimicrobial polymeric nanoparticles. *Progress in Polymer Science* **2018**, 76, 40-64, doi:10.1016/j.progpolymsci.2017.07.007.
8. Jia, L.; Wang, R.; Fan, Y. Encapsulation and release of drug nanoparticles in functional polymeric vesicles. *Soft Matter* **2020**, *16*, 3088-3095, doi:10.1039/d0sm00069h.
9. 63. Wang, J.; Liu, W.; Tu, Q.; Wang, J.; Song, N.; Zhang, Y.; Nie, N.; Wang, J. Folate-decorated hybrid polymeric nanoparticles for chemically and physically combined paclitaxel loading and targeted delivery. *Biomacromolecules* **2011**, *12*, 228-234, doi:10.1021/bm101206g.

10. Yousefpour, P.; Atyabi, F.; Vasheghani-Farahani, E.; Movahedi, A.A.M.; Dinarvand, R. Targeted delivery of doxorubicin-utilizing chitosan nanoparticles surface-functionalized with anti-Her2 trastuzumab. *International journal of nanomedicine* **2011**, *6*, 1977-1990, doi:10.2147/ijn.s21523.
11. 65. Zhang, W.J.; Hong, C.Y.; Pan, C.Y. Fabrication of Reductive-Responsive Prodrug Nanoparticles with Superior Structural Stability by Polymerization-Induced Self-Assembly and Functional Nanoscopic Platform for Drug Delivery. *Biomacromolecules* **2016**, *17*, 2992-2999, doi:10.1021/acs.biomac.6b00819.
12. Couvreur, P.; Barratt, G.; Fattal, E.; Legrand, P.; Vauthier, C. Nanocapsule technology: a review. *Crit Rev Ther Drug Carrier Syst* **2002**, *19*, 99-134, doi:10.1615/critrevtherdrugcarriersyst.v19.i2.10.
13. Pinto Reis, C.; Neufeld, R.J.; Ribeiro, A.J.; Veiga, F. Nanoencapsulation I. Methods for preparation of drug-loaded polymeric nanoparticles. *Nanomedicine: Nanotechnology, Biology, and Medicine* **2006**, *2*, 8-21, doi:10.1016/j.nano.2005.12.003.
14. Yao, Y.; Zhou, Y.; Liu, L.; et al. Nanoparticle-Based Drug Delivery in Cancer Therapy and Its Role in Overcoming Drug Resistance. *Front Mol Biosci.* **2020**, 7, 193, doi: 10.3389/fmolb.2020.00193.
15. Liu, G.; Yang, L.; Chen, G.; et al. A Review on Drug Delivery System for Tumor Therapy. *Front Pharmacol.* **2021**, 4, 12, 735446. doi: 10.3389/fphar.2021.735446.
16. Nader, S.; Farahnaz, F.; Fatemeh M.; et al. Polymer-based drug delivery systems for anticancer drugs: A systematic review. *Cancer Treatment and Research Communications*, **2022**, 32, 100605, doi.org/10.1016/j.ctarc.2022.100605.
17. Nasiruddin, M.; Neyaz, M.K.; Das, S. Nanotechnology-Based Approach in Tuberculosis Treatment. *Tuberc Res Treat.* **2017**, 2017, 4920209. doi: 10.1155/2017/4920209.
18. Yudaev, P.; Chuev, V.; Klyukin, B.; Kuskov. A.; Mezhuev, Y.; Chistyakov E. Polymeric Dental Nanomaterials: Antimicrobial Action. *Polymers (Basel).* **2022**, 14(5), 864. doi: 10.3390/polym14050864.
19. Zolnik, B.S.; González-Fernández, A.; Sadrieh, N.; Dobrovolskaia, M.A. Nanoparticles and the immune system. *Endocrinology* **2010**, 151(2), 458-65. doi: 10.1210/en.2009-1082.
20. Nahar, M.; Dutta, T.; Murugesan, S.; Asthana, A.; Mishra, D.; Rajkumar, V.; Tare, M.; Saraf, S.; Jain, N.K. Functional polymeric nanoparticles: an efficient and promising tool for active delivery of bioactives. *Crit Rev Ther Drug Carrier Syst.* **2006**, 23(4), 259-318. doi: 10.1615/critrevtherdrugcarriersyst.v23.i4.10.
21. Hartl, N.; Adams, F.; Merkel, O.M. From adsorption to covalent bonding: Apolipoprotein E functionalization of polymeric nanoparticles for drug delivery across the blood-brain barrier. *Adv Ther (Weinh).* **2020**, 4(1), 2000092. doi: 10.1002/adtp.202000092.
22. Lopes, A.M.; Chen, K.Y.; Kamei, D.T. A transferrin variant as the targeting ligand for polymeric nanoparticles incorporated in 3-D PLGA porous scaffolds. *Mater Sci Eng C Mater Biol Appl.* **2017**, 73, 373-380, doi: 10.1016/j.msec.2016.12.091.
23. Gong, Y.C.; Xiong, X.Y.; Ge, X.J.; Li, Z.L.; Li, Y.P. Effect of the Folate Ligand Density on the Targeting Property of Folated-Conjugated Polymeric Nanoparticles. *Macromol Biosci.* **2019**, 19(2), e1800348, doi: 10.1002/mabi.201800348.
24. Wu, P.H.; Opadele, A.E.; Onodera, Y.; Nam, J.M. Targeting Integrins in Cancer Nanomedicine: Applications in Cancer Diagnosis and Therapy. *Cancers (Basel).* **2019**,11(11), 1783. doi: 10.3390/cancers11111783.

Surface functionalization of graphene oxide nanolayers with Schiff bases based on covalent and non-covalent approaches

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Graphene oxide (GO) is a two-dimensional carbon-based nanomaterial that holds various functional groups on its surface and has excellent chemical properties, among other properties [1]. Due to this property, GO nanolayers and their functionalized forms have been widely used in sensor applications, photothermal therapy, and drug delivery [2]. Among these application areas, it has gained significant attention in the field of drug delivery due to the abundance of functional groups on the basal plane and edges that facilitate drug loading. It is possible to connect different organic molecules to the surface of GO by creating covalent bonds as a result of the functional groups on the surface [3]. GO can interact with drugs through π-π stacking, hydrogen bonding, and electrostatic interaction. Through the use of non-covalent interactions, it is possible to create supramolecular structures using organic molecules based on these phenomena [4]. Considering these features, the surface functionalization of GO by covalent and non-covalent approaches was carried out in the presented paper, and Schiff bases were used for functionalization.

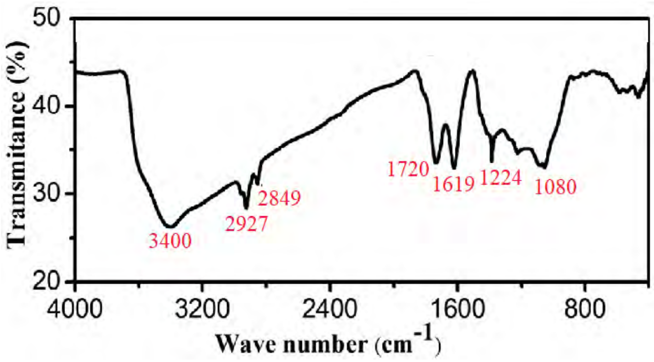

Fig 1.FTIR Analysis of Graphene Oxide – GO

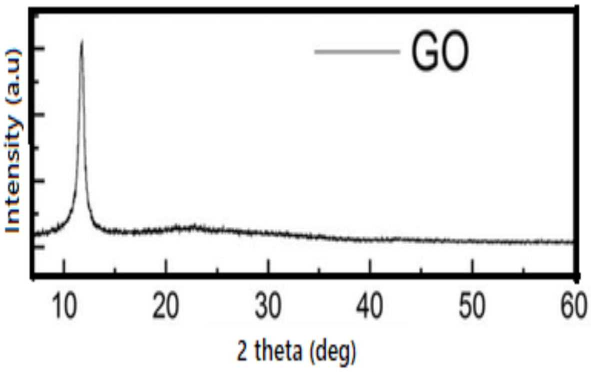

Fig 2. XRD analysis of GO

GO was synthesized by a modified Hummer method. Finally, H_2O_2 is added to the graphite mixture mixed with H_2SO_4, and $KMnO_4$. The obtained GO was washed with pure water and dried under a vacuum. X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Fourier-transform infrared spectroscopy (FTIR) analyses of the synthesized GO were performed (Fig1,Fig2). Then, Schiff bases were synthesized for surface functionalization.

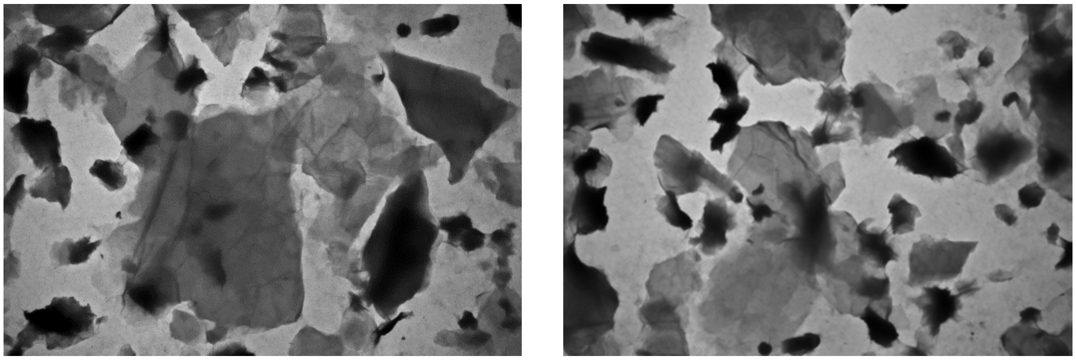

Fig 2. TEM images of GO

The Schiff bases are absolutely new and not randomly selected. Schiff bases, used for surface functionalization of graphene oxide nanolayers based on covalent and non-covalent approaches, were obtained by condensation of a primary amine group with an aldehyde group. In the synthesis of Schiff's bases, the antibiotic ampicillin used for the prevention and treatment of endocarditis, urinary tract infection, meningitis, salmonellosis, and respiratory tract infections was used. The reaction was carried out in methanol with stirring using a magnetic stirrer for 24 hours at room temperature. It was then separated from the solvent in a vacuum evaporator and purified by the recrystallization method. The purity of the compounds was checked by thin-layer chromatography (TLC) and the structures were confirmed by Nuclear Magnetic Resonance (NMR) spectroscopy.

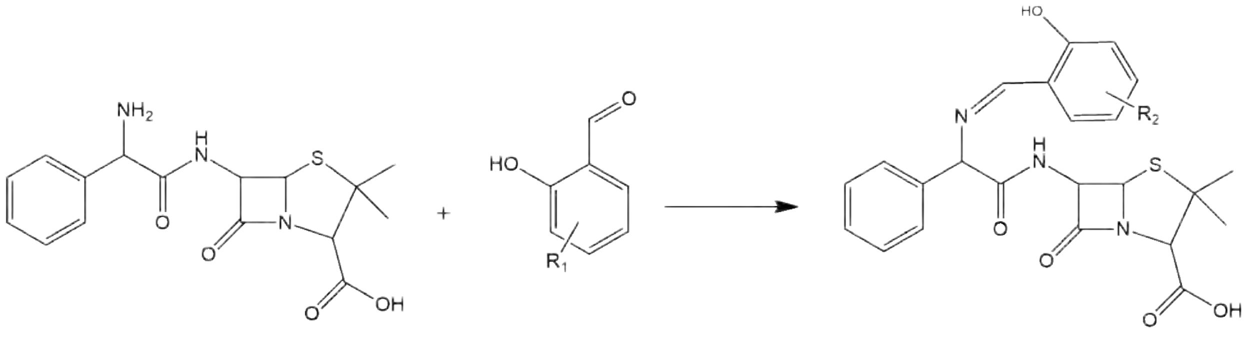

Fig 3. General scheme of synthesis of Schiff base

The non-covalent modification was carried out by dropwise addition of sonicated GO to a Schiff base solution prepared in a slightly basic medium and stirred for 24 h. The resulting mixture was filtered through a PTFE membrane filter and then washed thoroughly with ultrapure water. The GO-Siff base was thoroughly washed with ethanol and finally dried under a vacuum overnight. An illustration of the non-covalent functionalization route is illustrated in Scheme 1, showing H-bonding interactions between the oxygenated functional groups of GO and the hydroxyl groups of the Schiff base, as well as p-p stacking interactions between their aromatic rings.

In order to covalently attach organic molecules to the surface of GO, it is first necessary to convert the carboxyl group (COOH) on the surface of GO into acyl chloride (COCl). For this, the dispersed GO was reacted with $SOCl_2$ at 80°C for three days. Acyl chloride-functionalized GO was separated by centrifugation, washed with anhydrous THF, and dried under a vacuum. Then, an esterification reaction takes place between the hydroxyl (-OH) group of the organic molecule and GO-CO-Cl. This completes the covalent bond. The degree of grafting is determined by FTIR analysis.

References

1. Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J. W., Potts, J. R., & Ruoff, R. S. (2010). Graphene and graphene oxide: synthesis, properties, and applications. Advanced materials, 22(35), 3906-3924.
2. Chung, C., Kim, Y. K., Shin, D., Ryoo, S. R., Hong, B. H., & Min, D. H. (2013). Biomedical applications of graphene and graphene oxide. Accounts of chemical research, 46(10), 2211-2224.
3. Yang, Q., Pan, X., Clarke, K., & Li, K. (2012). Covalent functionalization of graphene with polysaccharides. Industrial & engineering chemistry research, 51(1), 310-317.
4. Sainz-Urruela, C., Vera-López, S., San Andres, M. P., & Díez-Pascual, A. M. (2022). Surface functionalization of graphene oxide with tannic acid: Covalent vs non-covalent approaches. Journal of Molecular Liquids, 357, 119104.

WENESDAY 31 MAY

Sessions:

Nine: 9.30 - 11.00

Elias Fattal, Maddalena Grieco, Simone Dinarelli

Ten 11.30 – 13.15

Vadim Krivitski, Iolanda Francolini, Vincenzo Taresco, Alessia Mariano

Eleven 14.45 – 16.15

Silvia Arpicco, Nicole Zoratto, Ilaria Andreana

Twelve: 16.40 – 17.00

Enrico Dainese, Sergio Ammendola, Marco Girasole, Giovanni Longo

Nanotechnologies for the delivery of nucleic acids and glucocorticoids in inflammatory diseases

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Nanomedicines are today considered for drug delivery in inflammatory diseases since they can cross leaky endothelium and release their payload at the target site. Approaches of passive targeting in inflammatory diseases were performed to illustrate such potential. For this purpose, we have designed novel dexamethasone nanoparticles (NPs). They were obtained using dexamethasone palmitate and DSPE-PEG2000 and characterized for their physicochemical and biopharmaceutical properties. Their therapeutic efficacy and joint targeting were evaluated on collagen-induced arthritis (CIA) mice model. NPs exhibited a diameter of 130nm, a negative zeta potential (-45mV), and a very high DXP encapsulation efficiency of 98%, corresponding to a DXM drug loading of 49% (w/w). Three NPs IV injections at 1mg/kg (eq.DXM) significantly improved CIA symptoms compared to saline or free drug. Fluorescent NPs proved their specific accumulation into inflamed joints. We then developed a delivery approach to target the anti-tumor necrosis factor α (TNF-α) since it is a critical cytokine overexpressed in many inflammatory diseases, including lung injury and rheumatoid arthritis. We developed a cationic phosphorus dendrons and dendrimers platform to deliver TNF-α siRNA in mice models of LPS-induced lung injury and the CIA model. The most efficient dendrimers to complex siRNA are from generation 3 and possess pyrrolidinium as terminal protonated amino end-groups. Dendrons with the same end groups attached to a C18 fatty-acid chain displayed the same properties as the dendriplexes. Both types of dendriplexes made of dendrimer or dendron demonstrated the ability to protect siRNA from nuclease degradation and promote cellular uptake. Moreover, they both led to a good inhibition of TNF-α in the lipopolysaccharide (LPS)-activated mouse macrophage cell line RAW264.7. The highest TNF-α silencing effect (80%) was confirmed in vivo in a murine model of acute lung inflammation induced by LPS after nasal delivery of dendriplexes made of dendrimers (v/s free siRNA). Besides, a significant anti-inflammatory effect in the collagen-induced arthritis mice model has also been observed with dendriplexes consisting of dendrons carrying the TNF-α siRNA. These results suggest that nanoparticles made of lipid prodrugs of glucocorticoids and dendriplexes have attractive properties for passively targeting inflammatory diseases.

Modulation of hyaluronic acid hydrogels enables their use as 3D cell culture model.

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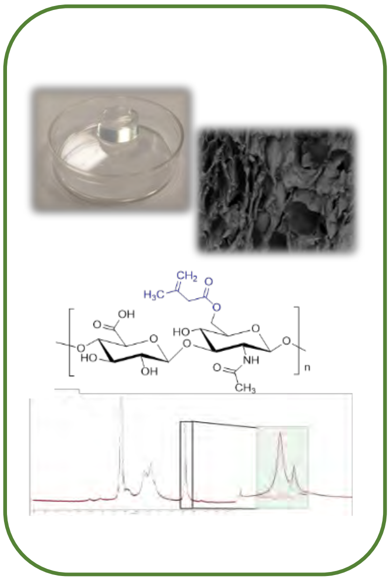
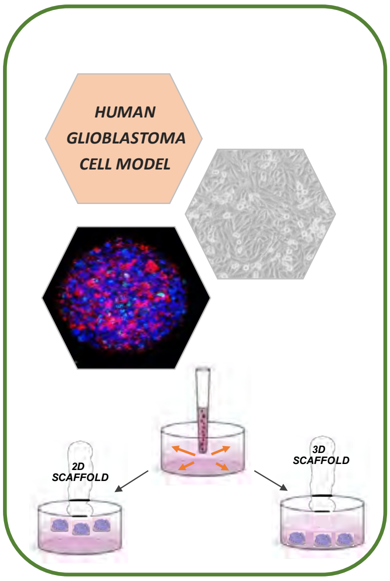
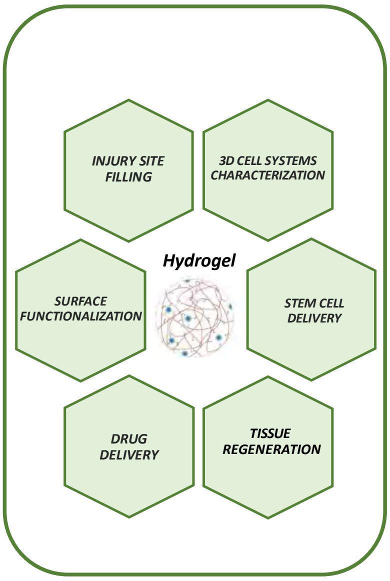
Abstract

Bioengineered hydrogels represent physiologically relevant culture platforms for studies of cell behaviour in the fields of tissue engineering and regenerative medicine as well as in in vitro disease models. Hyaluronic acid (HA) is an ideal platform being a natural biocompatible polymer widely used to study cellular crosstalk, cell adhesion and cell proliferation and one of the major components of the extracellular matrix (ECM). In our work, we realised chemically modified HA with photo-crosslinkable methacrylated groups synthesized in aqueous solutions and in strictly monitored pH and temperature conditions to obtain hydrogels with controlled bulk properties. The methacrylation substitution degree (DM) of hyaluronic acid methacrylate (HA-MA) conjugated polymers was investigated by NMR analysis, while the physical and chemical properties of the different HA-MA hydrogels were investigated through rheological studies, mechanical testing and scanning electron microscopy (SEM) imaging. The correlation between the physico-chemical properties of the HA-MA hydrogels allowed us to determine the optimal bio-mechanical properties, developing biocompatible scaffold. We thus evaluated the morphological processes and proliferation rates of glioblastoma cells (U251-MG) cultured spheroids on HA-MA hydrogel surfaces comparing 2D to 3D microenvironments, showing that changes in dimensionality impact cellular functions and interactions. Cell viability assays and evaluation of mitochondrial metabolism showed that hydrogels do not interfere with cell survival. In addition, morphological studies provided evidence of cell-matrix interactions that promote cell budding from the spheroids and the invasiveness in the surrounding environment. Our studies represent an improvement in the development and design of in vitro culture platforms with the most optimal characteristics required within 3D in vitro cancer models.







Human erythrocytes and beta-amyloid, what we can learn from a combined AFM and biochemical study.

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Abstract

The erythrocytes' (RBCs) aging is a fundamental physiological phenomenon that, in vivo, regulates the cells' turnover and is responsible for the maintenance of the blood homeostasis. Investigation of RBCs' aging allows to understand basic aspects of the mechanisms that regulate the function of these cells for senescence is associated to changes of the erythrocyte's structural properties and behaviour. The in vitro aging of RBCs can be monitored by following the evolution of different biochemical and morphological factors and environmental conditions or external effectors can be important and can strongly influence the observed aging pattern. The 1-42 beta-amyloid (Aβ) peptide is the major constituent of the amyloid plaques observed in Alzheimer disease (AD). The peptide arises from a transmembrane precursor activated after hydrolytic cuts by sectatases (a,b,g), and can occur in a monomeric (protective) or in an oligomeric (toxic) form. Beside AD, the amyloid is involved in other severe pathologies: some kind of cancers (hepatic, lung, colorectal) and the Down syndrome. The Aβ peptide interacts in the blood with RBCs, at least in pathological conditions, but the consequences of the interaction are still largely unknown. In this work we study, along the RBC's in-vitro aging, the ultra-morphological and biochemical cell alterations that are induced by three acting stimuli: the temperature (20 vs 37 ^{o}C), the presence of the 1-42 Aβ peptide and the absence (starvation condition) or presence of glucose in the solution. The morphological pattern has been monitored using Atomic Force Microscopy (AFM) imaging and measuring the RBCs' plasma membrane roughness employed as a morphological parameter capable to provide information on the structure and integrity of the membrane-skeleton. Results evidence that Aβ boosts the development of crenatures and proto-spicules simultaneously to acceleration in the weakening of the cell cytoskeleton contacts and to the induction of peculiar nanoscale features on the cell membrane. Incubation in the presence of glucose can remove all but the latter Aβ-induced effects. Biochemical data demonstrate that contemporaneously to morphological and structural alterations, Aβ and glucose depletion trigger a complex signalling pathway involving caspase 3, protein kinase C (PKC) and nitric oxide derived metabolites. As a whole, the collected data revealed that, the damaging path induced by Aβ in RBC provide a sequence of morphological and functional intermediates following one another along RBC life span, including: (i) an acceleration in the development of shape alteration typically observed along the RBC's aging; (ii) the development of characteristic membrane features on the plasma membrane and (iii) triggering a complex signalling pathway involving caspase 3, PKC and nitric oxide derived metabolites. In this frame, a raise of temperature determines a huge acceleration of the aging pattern; yet it doesn't change the phenomenon itself (same sequence of morphological alterations and roughness trend). Probably, it just increases the consumption of resources. We found that the Aβ peptide has much lesser morphological effects; yet the

presence of Aβ is capable to change the aging paradigm as it influences specific biochemical cascades that determine accelerations of cellular degradation. Overall, Aβ has weak effect at 20°C, but is very stressful at 37°C. Our study provides a comprehensive picture in which Aβ treatment of RBC induces changes in specific cell signalling events and/or metabolic pathways, in turns affecting the membrane–cytoskeleton interaction and the membrane integrity.

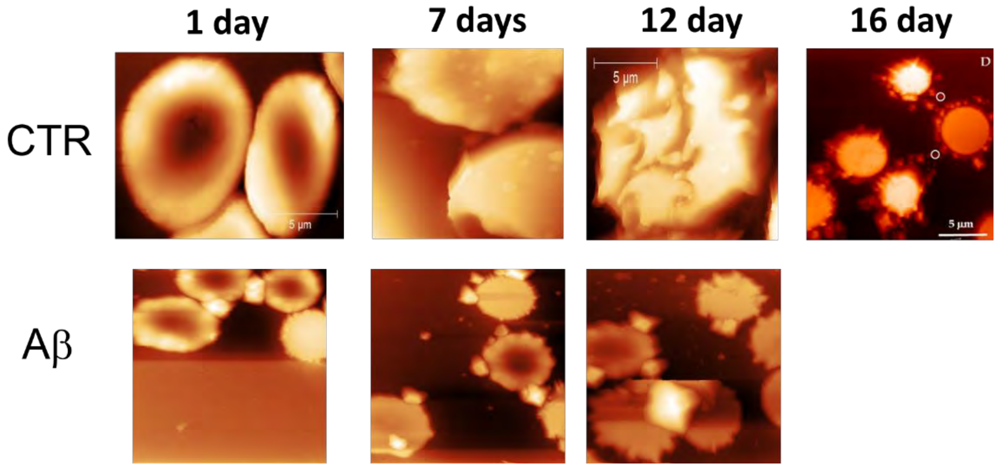


Figure 1: AFM images showing the morphological changes induced by the exposure to Aβ during the in vitro ageing of RBCs in starvation conditions at 20°C

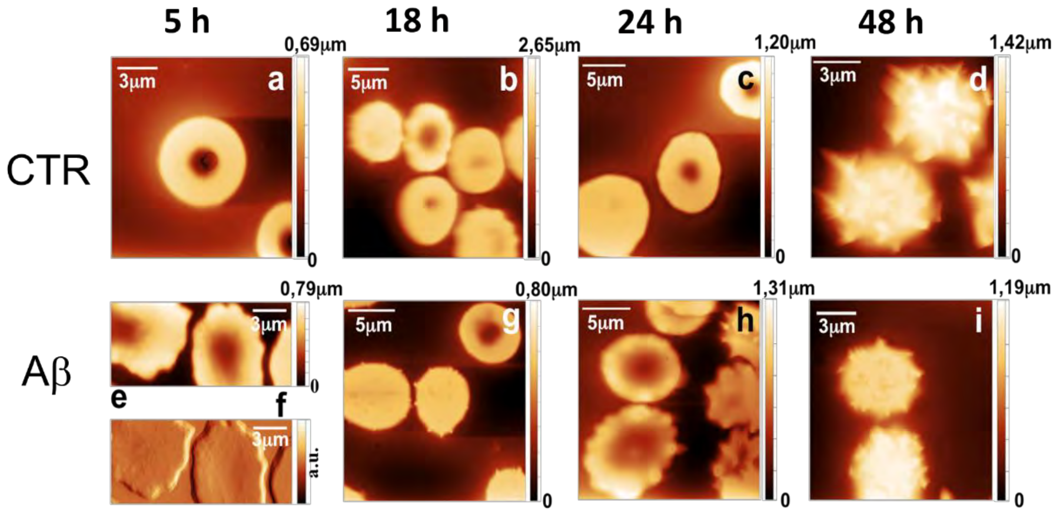


Figure2: AFM images showing the morphological changes induced by the exposure to Aβ during the in vitro ageing of RBCs in starvation conditions at 37°C

References:

Dinarelli, S, Girasole, M, & Misiti, F (2019). Amyloid β peptide affects erythrocyte morphology: Role of intracellular signaling pathways. Clinical Hemorheology and Microcirculation, 71(4), 437-449

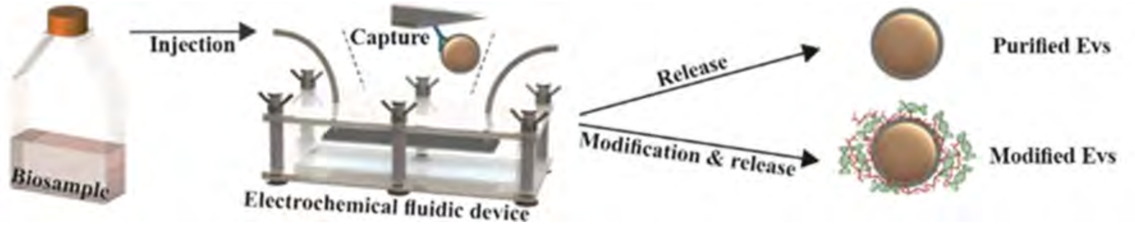
Carelli-Alinovi, C, Dinarelli, S, Sampaolese, B, Misiti, F, & Girasole, M (2019). Morphological changes induced in erythrocyte by amyloid beta peptide and glucose depletion: A combined atomic force microscopy and biochemical study. Biochimica et Biophysica Acta (BBA)-Biomembranes, 1861(1), 236-244

Carelli-Alinovi, C, Dinarelli, S, Girasole, M, & Misiti, F (2016). Vascular dysfunction-associated with Alzheimer’s disease. Clinical Hemorheology and Microcirculation, 64(4), 679-687

Ultra-fast separation of extracellular vesicles from physiological fluids by a portable microstructured electrochemical device

Due to their safety, inherent bioactivity, and low immunogenicity, extracellular vesicles (EVs) have emerged as versatile therapeutic agents, non-invasively collectable biomarkers, and potential drug carriers. They are found in various biological fluids (e.g., blood, urine, saliva, cerebrospinal fluid, breast milk, bile, and ascites), and participate in a wide range of physiological functions. EVs gain ever-growing attention from the biomedical research community, as reflected by increased number of publications (<10 in 2000 to >16,000 in 2021) and clinical trials. Nonetheless, current progress in EVs research and application is, in part, limited by inefficient isolation techniques. The separation of EVs from raw physiological fluids is a challenging task that often requires sample pretreatment and multiple steps, specialized laboratory equipment and skilled operators. Still, the process may result in insufficient yield, low purity, and compromised integrity.

To overcome the various challenges associated with the isolation of EVs from native physiological fluids, we have designed a state-of-the-art electrochemically controlled device enabling the rapid purification of EVs from various biofluids with a high level of purity. The separating unit consists of a fluidic channel confined within antibody-coated microstructured electrodes. EVs purification steps are performed as follows: i) The µCF surface of the fluidic channel is modified with antibodies against the surface proteins of EVs. ii) The biofluid is injected into the fluidic channel, where the EVs are specifically adsorbed by immunoaffinity interactions. iii) The EVs are then washed and released in a buffer of choice or deionized water by applying negative potential on the working electrode. An optional loading step could be added following to EVs attachment, by injecting the loading solution and removing unbound reagent in a subsequent wash before the release of the loaded EVs.



The principle operation of the device.

Compared to conventional EVs isolation methods, the developed device allows the processing of larger sample volumes of various physiological fluids, in a significantly shorter time, without the bulky equipment, at a low cost and with a high level of purity. Furthermore, sample handling, reagent mixing, separation, and detection are simplified.

Self-assembled chitosan-sodium usnate nano drug delivery systems against osteosarcoma 143B cells

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Osteosarcoma (OS) is the most common primary malignant bone sarcoma in pediatric and adolescent patients [1]. Chemotherapy remains the main therapeutic strategy against OS. In order to mitigate common inconvenience associated with toxic active ingredients, including poor solubility and systemic toxicity, in this study, chitosan (CS) was investigated as nanocarrier for the anticancer drug sodium usnate (NaU). Sodium usnate is the sodium salt of usnic acid, a bioactive compound extracted from different species of lichens. It has several biological activities but is hepatotoxic [2]. In this study, we confirmed the NaU hepatotoxicity against HepG2 cells at final concentration of 1.5, 0.75 and 0.375 mg/mL, decreasing the percentage of living cells under 50% after all analyzed times (24, 48 and 72 h). It showed a sub-hepatotoxic effect at 0.187 mg/mL, mainly after 48 h and 72 h of treatment, while at final concentration of 0.093 and 0.047 mg/mL no significant cell viability decrease was reported after any analyzed time. The three NaU concentrations with lower hepatotoxic effect were also tested on osteosarcoma 143B cells. NaU at 0.187 mg/mL) significantly decreased 143B cell viability already at 24 h. In order to decrease NaU hepatotoxicity, NaU was loaded into CS nanoparticles (NPs) obtained by ionotropic gelation. NaU loading was performed without the use of organic solvents or surfactants.

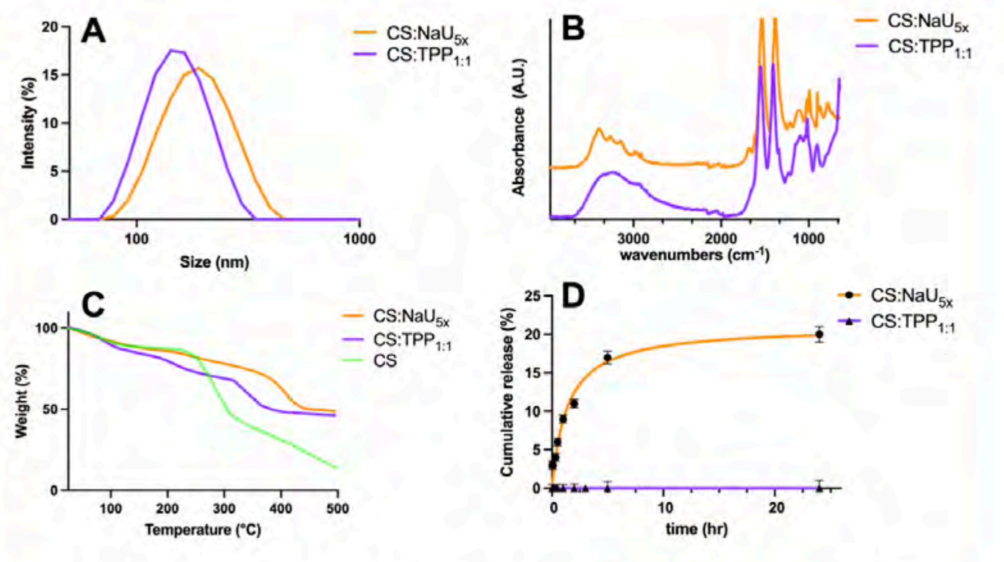

Figure 1. Size distribution (A), ATR-FTIR spectra (B), thermogravimetric analysis (C) and cumulative NaU release (D) for CS:TPP$_{1:1}$ and CS:NaU$_{5x}$.

Three concentrations, 5x, 10x and 20x of the NaU toxic concentration (0.187 mg/mL), were used in the encapsulation experiments. Only, when 5x NaU concentration was used, a stable suspension with 188 nm in-size NPs (Figure 1A) was obtained. A high drug encapsulation efficiency was achieved thanks to the establishment of drug/polymer ionic interactions, as evidenced by Fourier Transformed Infrared spectroscopy (Figure 1B) and thermogravimetric analysis (Figure 1C). *In vitro* drug release study, performed in PBS pH 7.4 at room temperature, showed that only ca. 20% of the entrapped drug was released in 24 h (Figure 1D). This finding reflects a drug adsorption throughout specific physico-chemical drug/polymer interactions, which limited drug release.

A significant reduction in NaU hepatotoxicity when encapsulated in CS NPs compared to free NaU was evidenced and, for the first time, a relevant synergistic activity of CS and NaU in promoting Maspin stimulation in 143B cells was found (Figure 2). Maspin is a non-inhibitory member of the serine protease family (SerpinB5), which has been described as a tumor suppressor molecule in many types of cancer, among them the osteosarcoma.

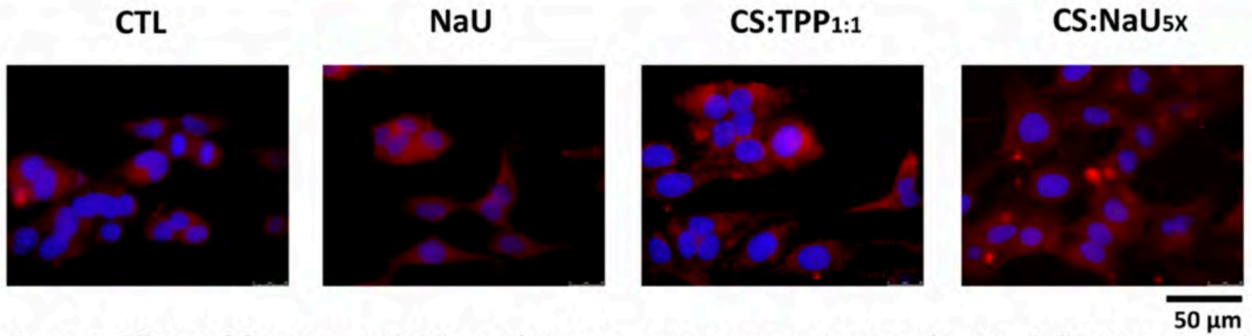

Figure 2. Effects of free NaU, CS:TPP$_{1:1}$ and CS:NaU$_{5x}$ on Maspin protein production. Cells were treated with 1:3 dilutions of CS:TPP$_{1:1}$ and CS:NaU$_{5x}$ suspension and free NaU, for 24 h and then, analyzed by immunofluorescence using anti-Maspin primary antibody and Alexa Fluor 568 (red) secondary antibody. Nuclei were stained in blue with DAPI (original magnification 63X).

The safety of NaU-loaded CS NPs observed in *in vivo* biocompatibility tests on nematodes (Figure 3) further validates these systems as suitable nano-formulations to deliver toxic anticancer agents.

References

[1] Li, S., Zhang, H., Liu, J., & Shang, G. (2023). Targeted therapy for osteosarcoma: a review. *Journal of cancer research and clinical oncology*, 10.1007/s00432-023-04614-4.

[2] Ingólfsdóttir K. (2002). Usnic acid. *Phytochemistry*, *61*(7), 729–736. https://doi.org/10.1016/s0031-9422(02)00383-7

Enhanced Functionalised Carriers for Drug Delivery Applications – Novel Glycerol and Diglycerol Derived Polyesters

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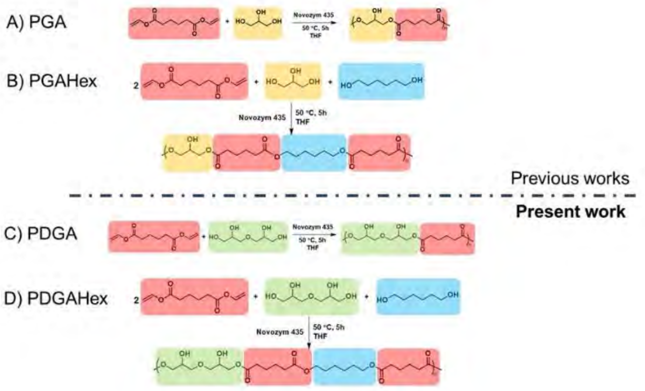

Scheme1. Enzymatic synthesis of A) PGA, B) PGAHex C) PDGA D) PDGAHex in THF. The different monomers have been colour coded to facilitate the detection of the composition of the final repeating unit .

Sustainably derived poly(glycerol-adipate) (PGA) (**Scheme1 A**) delivers all the desirable features expected in a polymer for drug-delivery, including biodegradability, biocompatibility, self-assembly into nanoparticles (NPs) and functionalisable pendant groups.[1] Despite showing these advantages over commercial alkyl polyesters, PGA suffers from a series of key drawbacks caused by poor amphiphilic balance. This leads to weak drug-polymer interactions and subsequent low drug-loading in NPs, as well as low NPs stability. To address these limitations, PGA derivatives are usually obtained by functionalising the glyceryl side hydroxyl group present along the main polymer scaffold.[2,3] However, if the synthetic pathways are not finely tuned, the self-assembling ability of these new polymeric modifications might be hampered by the poor amphiphilic balance.

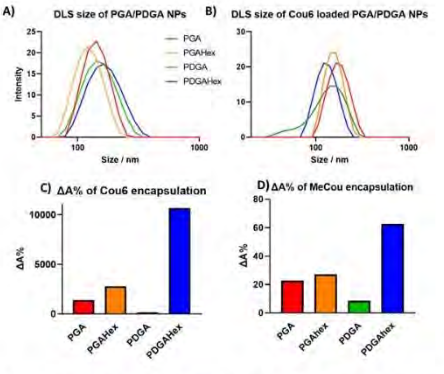

Figure 1 – **A)** Polymer NPs sizes by DLS. **B)** Cou6 loaded NPs sizes by DLS. **C)** ΔA% of Cou6 (hydrophobic model molecule) against PGA, PDGA and modifications. **D)** ΔA% of MeCou (amphiphilic model molecule) against PGA, PDGA and modifications.

To tackle these further drawbacks, previously, we have shown as new functionalities can be introduced directly in the one-pot PGA enzymatic polymerisation without the need of further synthetic steps.[4] For instance, by introducing 1,6-n-hexanediol (Hex) (**Scheme1 A and**

B), as hydrophobic diol, we tuned the amphiphilic balance of the new repetitive unit with consequent enhanced drug encapsulation.

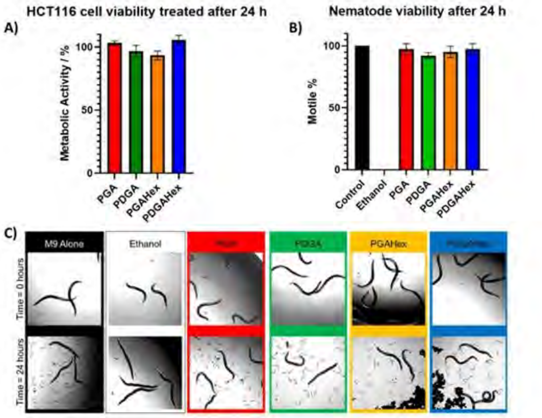

Figure 2 – **A)** Cell viability after 48 h, tested on HCT116 human carcinoma colon epithelial cells. **B)** *C. elegans* viability, as a function of motiloity, after completion of 24 hour challenge with polymers; experiments were conducted in triplicate per polymner with >10 nematodes per experiment, no significant differences in viability were observed ($p>0.05$). **C)** Microscope images of nematodes before and after exposure to polymer NPs. Nematode progeny can be seen in control maintenance M9 alone and polymer treated suspensions after 24 h of exposure, indicative of nematode viability.

Inspired by this, in the present work, we further investigated the effect of amphiphilic balance variation upon physical properties and drug interactions as well as self-assembly.[5] We replaced glycerol with the more hydrophilic diglycerol, also, we adjusted the final amphiphilic balance of the repetitive units by incorporating Hex (**Scheme1 C and D**). The produced materials were extensively physically and chemically characterised, NPs were produced and tested for their stability and for their ability to encode enhanced drug loading (**Figure1**). Finally, the novel materials showed good biocompatibility *in vitro* experiments and did not exhibit significant changes in *C. elegans* viability, motility and progeny production (**Figure2**). We demonstrated that through the selection of starting polyols, both hydrophobic and hydrophilic, the enzymatic synthetic pathway was exploited as a sustainable, one-pot tool to produce new functional polyesters.

References

1 S. M. E. Swainson, I. D. Styliari, V. Taresco and M. C. Garnett, *Polymers (Basel).*, , DOI:10.3390/polym11101561.

2 R. K. Animasawun, V. Taresco, S. M. E. Swainson, J. Suksiriworapong, D. A. Walker and M. C. Garnett, *Mol. Pharm.*, 2020, **17**, 2083–2098.

3 K. Damrongrak, K. Kloysawat, S. Bunsupa, K. Sakchasri, A. Wongrakpanich, V. Taresco, V. Cuzzucoli Crucitti, M. C. Garnett and J. Suksiriworapong, *Int. J. Pharm.*, 2022, **618**, 121636.

4 P. L. Jacob, L. A. Ruiz Cantu, A. K. Pearce, Y. He, J. C. Lentz, J. C. Moore, F. Machado, G. Rivers, E. Apebende, M. R. Fernandez, I. Francolini, R. Wildman, S. M. Howdle and V. Taresco, *Polymer (Guildf).*, 2021, **228**, 123912.

5. P. L. Jacob; B. Brugnoli; A. Del Giudice; H. Phan; V. M. Chauhan; L. Beckett; R. B. Gillis; C. Moloney; R. J. Cavanagh; E. Krumins; M. Reynolds-Green; J. C. Lentz; C. Conte; V. Cuzzucoli Crucitti; B. Couturaud; L. Galantini; I.Francolini; S. M. Howdle and V. Taresco, *J. Colloid Interface Sci.,* 2023, Accepted

N-Acetylglucosamine in nanoform as an antiviral and anti-inflammatory alternative against respiratory viral infections.

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Background

Respiratory viral infections are very frequent in the world population of all age groups and are responsible for a variety of symptoms from common colds to severe respiratory syndromes. In particular, the latter have often been associated with strong inflammation, mediated by a storm of cytokines, responsible for acute respiratory distress syndrome (ARDS) and lung failure. The worldwide impact of SARS-CoV-2 has highlighted that few treatment options are available and that research in the field of antivirals is an open challenge. In these years of the health emergency, considering the long times that a new molecule development requires, the repositioning or reproposing of existing drugs has been considered as a valid alternative. Natural molecules have proven to be excellent candidates in the repositioning process as they are often easier to obtain, have fewer side effects still showing good pharmacological properties against different pathologies, from inflammatory to infectious disease. In this perspective, N-acetylglucosamine (GlcNAc), a derivative of glucosamine (GlcN), known as an immunomodulatory and anti-inflammatory drug to treat autoimmune diseases as well as osteoarthritis and other inflammatory diseases, has been "repurposed" to counteract the cytokine storms in respiratory virus infections. However, its greatest limitation is the low bioavailability, which makes it necessary to increase the administered doses. In this regard, the use of nanoparticle formulations represents an excellent tool to improve the effectiveness of GlcNAc improving its bioavailability and pharmacokinetic properties, finally increasing its therapeutic effect. In the last years, we studied the anti-inflammatory and antiviral effect of GlcNAc in an *in vitro* model of infected pulmonary cells. In particular, the GlcNAc effect in both bulk and nanoform was compared to evaluate whether, through the production of nanoparticles, the molecule biological effect could be optimized. In this study, influenza A/H1N1 virus (IAV) and human adenovirus type 2 (AdV2) were used. Since infection with both viruses can trigger severe lung inflammation and induce acute lung injury, limiting viral replication and relieving inflammation are two important therapeutic strategies in the fight against these infections.

Results

GlcNAc nanoparticles (NPs) were synthetized using a wet mixture of GlcNAc and PVP in a planetary ball miller at room temperature. After the process, the wet mixture was dried under a vacuum oven, and the composition of dry powder was tested performing DLS analysis. Results from three independent preparations, providing three overlaying curves, showed that the distribution of GlcNAc NPs is monomodal and the Z-Average resulted around 267 nm with a Polydispersity index (PI) of 0.383 ± 0.055.

The *in vitro* cytotoxic effect of both GlcNAc and GlcNAc NPs, was evaluated at different concentrations in MDCK and A549 cells performing MTT assays. These experiments revealed that while GlcNAc and GlcNAc NPs up to 16 mM were not able to affect the MDCK cell viability, they were found to be non-toxic in A549 cells only up to a concentration of 2 mM and 4 mM, respectively. Consequently, to determine the concentration necessary to inhibit viral infection by 50% (effective concentration 50%, EC_{50}) the ability of serial dilutions of GlcNAc and GlcNAc-NPs, were tested both in IAV-infected MDCK cells and in AdV2-infected A549 cells.

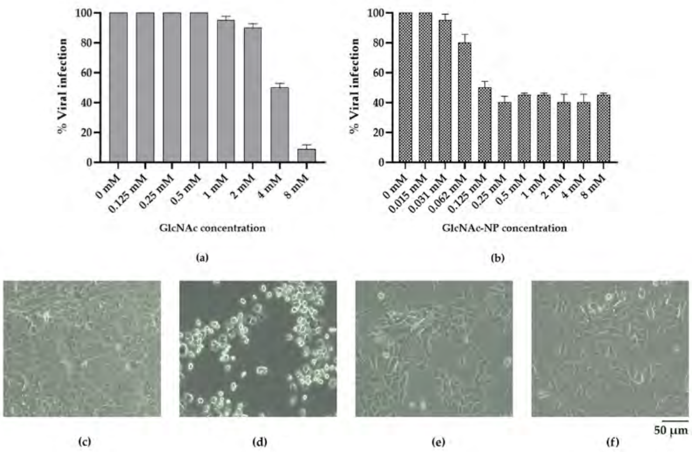

Figure 1. Activities of the GlcNAc formulations against IAV infection

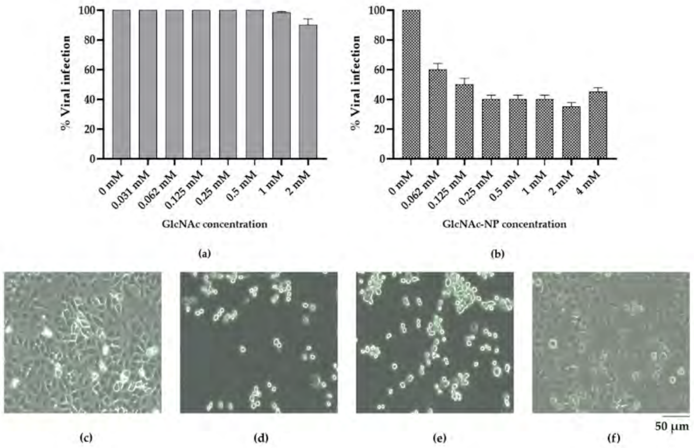

Figure 2. Activities of the GlcNAc formulations against AdV2 infection

Under these experimental conditions, GlcNAc showed a dose-dependent inhibitory activity, being able prevent 50% IAV cytopatic effect in MDCK cells at 4 mM whereas GlcNAc-NPs prevent 50% of infection at 0.125 mM (Fig.1).

On the other hand, as regards AdV2 infection in A549 cells, GlcNAc treatment was unable to prevent viral replication. Conversely, the concentration of GlcNAc-NPs required to inhibit viral replication by 50% also in this virus-cell system was 0.125 mM (Fig.2).

Finally, the effect of the two forms of GlcNAc on inflammatory process induced by viral infection was investigated. The infected cells were treated with the EC_{50} of GlcNAc and GlcNAc-NP determined in MTT assays. The production of Tumor Necrosis Factor alpha (TNF-α), Interleukin-6 (IL-6) and Interleukin-8 (IL-8) was determined in the supernatants of MDCK and A549 cells after IAV and AdV2 infection, respectively. In both cell lines, at 24 and 48 h the cytokines were not detectable whereas, at 72 h post infection, IAV and AdV2 induced a statistically significant stimulation of all three analyzed cytokines. Interestingly, in IAV-infected MDCK cells both 4 mM GlcNAc and 0.125 mM GlcNAc-NPs were able to bring back cytokine secretion to mock- infected cell level (CTL).

In AdV2-infected A549 cells, 2 mM GlcNAc was not able to counteract the inflammation stimulated by AdV2 infection, while 0.125 mM GlcNAc in nanoformulation was able to bring back IL-6 and TNF-α production to mock-infected cell level and to reduce IL-8 secretion partially but significantly.

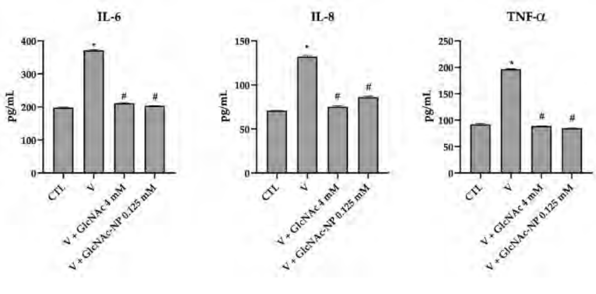

Figure 3. Effects of GlcNAc and GlcNAc-NP on IL-6, IL-8 and TNF-α production in MDCK cells

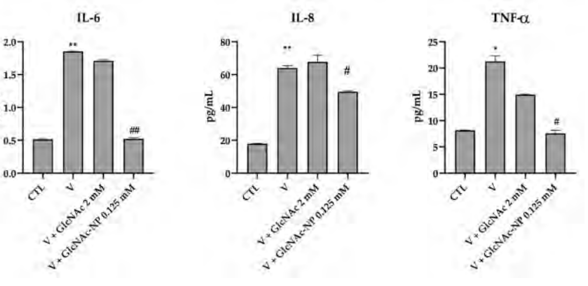

Figure 4. Effects of GlcNAc and GlcNAc-NP on IL-6, IL-8 and TNF-α production in A549 cells

Conclusion

In conclusion, we demonstrated that GlcNAc-NPs had better antiviral activity than the bulk form. In particular, while in IAV infected cells, the two formulations resulted effective, only the nanoform was able to inhibit the cytopathic effect of AdV2 in A549 cells, where the bulk GlcNAc resulted completely inactive. GlcNAc NPs also proved to be much more effective in inhibiting the inflammatory activity of both viruses than the bulk form.

STRATEGIES AND CHALLENGES TO IMPROVE THE TARGETING ABILITY OF ANTICANCER NANOMEDICINES

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The side effects of drugs used in the therapy of some diseases, like cancer, would be reduced by selectively delivering them into those cells or tissues where their action is required.

Ideally, a drug designed for clinical use should have a high therapeutic index, which is the ratio between the drug efficacy (therapeutic effect) and its toxicity (side effects). A drug with a low therapeutic index but high activity should be delivered in a higher concentration to the target cells (thereby increasing efficacy) avoiding non-target cells (thereby reducing toxicity). This delivery approach, called drug targeting, provides a mean to increase the therapeutic index of the drugs and achieving more effective therapy, with possible economic benefit.

Many different systems have been explored to selectively target antineoplastic agents to cancer cells or tissues. One of the most general approaches is the linkage to a carrier molecule (such as protein, polysaccharide, natural or synthetic macromolecule, lectin or antibody, small molecules) by a covalent bond to an active moiety, such as an antitumoral drug or a cytotoxic protein (1).

A useful alternative approach to target antineoplastic drugs to tumor cells is the use of vesicular or particulate systems, such as liposomes and nanoparticles, to improve the drug concentration at the target by altering both tissue distribution and the drug pharmacokinetics. To further enhance the cytotoxic effect, selective delivery of drugs to target cells can be achieved by conjugating vesicles to various targeting ligands; in this way, the conjugated nanovescicles are potentially able to bind to a specific receptor on target cell membranes, triggering their own internalization by the mechanism of endocytosis.

Different targeting agents and drug delivery systems designed for the smart delivery of antitumoral drugs will be illustrated and discussed (2-4).

1. H. Maeda, Seymour, Miyamoto Y. (1992) “Conjugates of anticancer agents and polymers: advantages of macromolecular therapeutics in vivo” *Bioconjugate Chemistry* 3, 351-62.
2. F. Dosio, S. Arpicco, B. Stella, E. Fattal (2016) “Hyaluronic acid for anticancer drug and nucleic acid delivery” *Advanced Drug Delivery Reviews*, 97, 204-236.
3. E. Gazzano, B. Rolando, K. Chegaev, (..), S. Arpicco, C. Riganti (2018) “Folate-targeted liposomal nitrooxy-doxorubicin: an effective tool against P-glycoprotein-positive and folate receptor-positive tumors” *Journal of Controlled Release*, 270, 37–52.
4. S. Arpicco, M. Bartkowski, A. Barge, D. Zonari, L. Serpe, P. Milla, F. Dosio, B. Stella, S. Giordani (2020) “Effects of the molecular weight of hyaluronic acid in a carbon nanotube drug delivery conjugate” *Frontiers in Chemistry*, 8, 578008.

Hyaluronan-cholesterol nanogels for enhancing the ocular delivery of therapeutics

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INTRODUCTION

Topical drug delivery is an easy, self-administrable and non-invasive procedure widely used to treat both anterior and posterior segment diseases affecting the ocular tissues and eye drops are the most common method for ocular drug administration [1,2]. Although topical instillation is characterised by high patient acceptability, the anatomy and physiology of the eye strongly limit the bioavailability of locally administered drugs [3]. Specifically, the cornea, with its sandwich-like structure, represents the main mechanical and chemical barrier preventing the permeation of hydrophilic and most hydrophobic drugs into the anterior camera of the eye [4]. Hence, less than 5% of topically applied therapeutics can successfully reach the intraocular tissues [5]. Thus, nanocarriers able to efficiently load therapeutics and interact with the ocular surface components, represent an appealing platform for facilitating drug permeation across eye barriers and enhancing ocular drug delivery [6].

AIM

In this work, we aim at investigating the capability of hyaluronan-cholesterol nanogel-based formulations (HA-CH NHs) to adhere to the cornea surface and interact with its components, enhancing drug permeation through the cornea [7].

RESULTS AND DISCUSSION

In order to prepare HA-CH NHs, the carboxyl groups of HA were covalently linked to cholesterol moieties, leading to an amphiphilic HA-CH polymer, which is able to form self-assembled nano-sized structures after a suitable autoclave treatment (121 °C, 20 min) [8]. Such NHs successfully entrapped both poorly water-soluble drugs, such as dexamethasone (DEX) and piroxicam (PIR), and hydrophilic drugs, such as tobramycin (TOB) and diclofenac (DCF), leading to systems that showed small hydrodynamic diameters, suitable ζ-potential and PDI values and good stability under physiological conditions (pH 7.4, 290 mOsmol).

Thereafter, to assess the bioadhesive properties of HA-CH NHs both *ex-vivo* studies by fluorescence microscopy and *in-tube* analyses with mucin were performed, suggesting that NHs were able to interact with corneal components, being retained on porcine corneas. Despite these bioadhesive properties, HA-CH NHs were not able to cross the corneal stroma. Finally, ex-vivo permeation experiments were performed on porcine corneas with DEX-, PIR-, TOB- and DCF-based NHs formulations, showing that HA-CH NHs play an active role in the permeation process of both hydrophobic and hydrophilic drugs through the porcine cornea. Specifically, the permeation of the hydrophilic TOB and DCF was highly enhanced by NHs compared to the free drug solutions, whereas the permeation of hydrophobic DEX and PIR was strongly dependent on the water solubility of the entrapped molecules. These results confirmed that NHs may act as permeation enhancers increasing drug diffusion through the corneal tissue.

CONCLUSION

In this project work, we demonstrate the capability of NHs formulations to improve the ocular bioavailability of the instilled drugs by increasing their preocular retention time (hydrophobic drugs) or facilitating their permeation (hydrophilic drugs), thus opening the route for the application of HA-based NHs in the treatment of both anterior and posterior eye segment diseases.

REFERENCES

[1] G. A. Rodrigues, et al., *Pharmaceutical Research*, 35 (**2018**) 1-5.

[2] D. R. Janagam, et al., *Advanced Drug Delivery Reviews,* 122 (**2017**) 31-64.

[3] N. Omerović, et al., *Health and Technology (Berl.)*, (**2020**).

[4] D. Huang, et al., *Advanced Drug Delivery Reviews*, 126 (**2018**) 96-112.

[5] A. Patel, et al., *World Journal of Pharmacology*, 2 (**2013**) 47.

[6] J. C. Cuggino, et al., *Journal of Controlled Release*, 307 (**2019**) 221-246.

[7] N. Zoratto, et al., *Pharmaceutics*, 13 (**2021**) 1781.

[8] E. Montanari, et al., *Journal of Materials Science: Materials in Medicine*, 26 (**2015**) 32.

Targeting muscular tissue by polymer nanoparticles

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Muscular dystrophies (MDs) are a group of rare genetic pathologies, encompassing a variety of clinical phenotypes and mechanisms of disease. Several compounds have been proposed to treat compromised muscles. However, drawbacks related to the instability of therapeutics or the unreached global distribution to all compromised tissues limit the clinical applicability of many active molecules [1,2]. To solve these issues, it has been suggested that nanomedicine could be used to allow controlled and targeted drug release. Currently, novel nanomedicines are optimized for the treatment of skeletal muscle pathologies like MDs. However, multiple biological and pharmaceutical barriers challenge nanomedicine delivery to skeletal muscles [3].

In this context, we selected a biodegradable and biocompatible polymer, namely poly-(lactic-*co*-glycolic) acid (PLGA) to prepare self-assembled nanoparticles (NPs). Fluorescently-labeled PLGA NPs were prepared to assess the myofibres distribution and the potential applicability of biodegradable NPs as a strategy to reach and treat compromised tissues. PLGA NPs were characterized by a size below 120 nm and a negative zeta potential around -45 mV. However, skeletal muscle is a composite organ made up of muscle cells, but also of connective tissue, blood vessels, and nerves, meaning that the NPs intended for intramuscular delivery are required to move through this complex environment before finally entering the myofibres. We have therefore set up an *ex vivo* experimental system to monitor the biodistribution of fluorescently-labeled PLGA NPs injected into an explanted murine skeletal muscle. To preserve its integrity, immediately after the injection of PLGA NPs, the skeletal muscle was maintained in a bioreactor under dynamic conditions. Fluorescence microscopy observations showed that after 1 h from the administration, the nanocarriers were found close to the site of injection. After 3 h incubation, PLGA NPs accumulated in the connective tissue, and at longer incubation times, from 6 h to 24 h, PLGA NPs progressively accumulated inside the myofibres. These results demonstrated how PLGA NPs progressively crossed the plasmalemma through endocytosis and escaped endosomes to accumulate in the cytoplasm.

One of the main hurdles for the delivery to skeletal muscles lies in the presence of the dense extracellular matrix (ECM), which accounts for 1 to 10% of the muscle mass [4]. For years, the enhanced permeation and retention (EPR) effect was the chosen strategy for passive targeting [5]. However, models used to study the EPR effect are often not sufficiently accurate to describe the nanocarrier behavior in the human body; moreover, sometimes EPR effect alone is not sufficient to allow the drug therapeutic concentration to be reached in the target site. In this context, a second potential approach involving PLGA NPs has been proposed. Surface-engineered nanosystems have been designed to actively promote muscle cell targeting thanks to specific molecules anchored on the nanocarrier surface. We identified the Na^+-coupled organic cation/carnitine transporter (OCTN) as a potential target for drug delivery at the muscular level. In particular, the class OCTN2 has a high affinity for L-carnitine, which is a small zwitterion molecule endogenously synthesized by liver, kidney, and brain [6]. On these bases, we selected a derivative of L-carnitine, namely stearoyl-L-carnitine (SC), to promote the association of L-carnitine to the surface of PLGA NPs. Furthermore, the recent understanding of the pathogenic mechanism of MDs has opened new possibilities for innovative strategies. Within the frame of drug repurposing, pentamidine (PTM), an aromatic diamine approved as antiparasitic drug, has been investigated as an experimental MD treatment. Empty and loaded SC-associated PLGA NPs were prepared between 5% and 10% w/w of SC. All the NP formulations showed a mean diameter of about 100 nm. The incorporation of the free base form of PTM (PTM-B) led to an increased mean size of up to 130 nm and a polydispersity index (PDI) of about 0.2. 5% SC-NPs were characterized in terms of encapsulation efficiency (65%) and drug release. The cytotoxic assay was performed on empty NPs to evaluate the potential toxicity of the targeting agent. The metabolic activity of C2C12 myoblasts decreased significantly after 24 h incubation in a dose-dependent manner, exerting slight toxicity. Observation of fluorescent NPs at confocal microscopy and TEM demonstrated that 5% SC-NPs rapidly enter myoblasts and myotubes and accumulate in the cytoplasm, but never penetrate the cell nucleus. Although 5% SC-NPs proved to enter both myoblasts and myotubes, morphometric analysis revealed that these nanocarriers were better internalized in myotubes than in myoblasts. This phenomenon is probably due to the higher amount of OCTN2 receptors on myotubes in comparison to myoblasts. These results pave the way to the use of active targeting strategy to improve muscular uptake, challenging its biological complex structure by enhancing the permeation and therapeutic efficacy of drugs.

References

1. Markati, T.; Oskoui, M.; Farrar, M.A.; Duong, T.; Goemans, N.; Servais, L. Emerging Therapies for Duchenne Muscular Dystrophy. Lancet Neurol ***2022****, 21, 814–829, doi:10.1016/S1474-4422(22)00125-9.*

2. Andreana, I.; Repellin, M.; Carton, F.; Kryza, D.; Briançon, S.; Chazaud, B.; Mounier, R.; Arpicco, S.; Malatesta, M.; Stella, B.; et al. Nanomedicine for Gene Delivery and Drug Repurposing in the Treatment of Muscular Dystrophies. Pharmaceutics ***2021****, 13, doi:10.3390/pharmaceutics13020278.*

3. Engin, A.B.; Nikitovic, D.; Neagu, M.; Henrich-Noack, P.; Docea, A.O.; Shtilman, M.I.; Golokhvast, K.; Tsatsakis, A.M. Mechanistic Understanding of Nanoparticles' Interactions with Extracellular Matrix: The Cell and Immune System. Part Fibre Toxicol ***2017****, 14, 22, doi:10.1186/s12989-017-0199-z.*

4. Gillies, A.R.; Lieber, R.L. Structure and Function of the Skeletal Muscle Extracellular Matrix. Muscle Nerve ***2011****, 44, 318–331, doi:10.1002/mus.22094.*

5. Shi, Y.; van der Meel, R.; Chen, X.; Lammers, T. The EPR Effect and beyond: Strategies to Improve Tumor Targeting and Cancer Nanomedicine Treatment Efficacy. Theranostics ***2020****, 10, 7921–7924, doi:10.7150/thno.49577.*

6. Juraszek, B.; Nałęcz, K.A. SLC22A5 (OCTN2) Carnitine Transporter-Indispensable for Cell Metabolism, a Jekyll and Hyde of Human Cancer. Molecules ***2020****, 25, doi:10.3390/molecules25010014.*

Role of membrane lipids in the development of biosensors based on engineered ion channels

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The classical fluid-mosaic model of the biological membrane organization has been significantly modified in recent years. Membrane proteins are no longer figured as simply floating in a two-dimensional oriented solution, and their solvent is not only a simply viscous phospholipid bilayer. In fact, lateral compartmentalization and membrane asymmetry impose specific constraints to diffusion and partition between the two monolayers of specific hydrophobic molecules, thus affecting structure, and hence function, of membrane-bound proteins

The main objectives and results of the BioInspireSensing (BIS) trans-national network are focused on investigating, building, and producing a new generation of bioinspired implantable sensors of pressure, temperature and acidity. The BIS project will apply the state-of-the-art in ion channel proteins, cell membrane transport, unilamellar vesicles, tethered planar lipid bilayers, synthetic biochemistry, and biodegradable and flexible conducting polymers to obtain the novel biosensors.

In the framework of BIS project we developed strategies for production of a minimal functional protein channel construct for temperature sensing. Regarding the channel stabilization into bilayers, protein affinity for different lipid compositions were analyzed by FRET using mutant and liposomes with different compositions.

In parallel, cholesterol-sensitive peptides based on Cholesterol recognition aminoacid consensus (CRAC) sequences and on newly cholesterol-binding peptides designed by us have been selected to its implementation as novel cholesterol biosensors. In this project, different peptide sequences sensitive to cholesterol have been designed, evaluated by docking analysis and experimentally chosen for developing novel cholesterol biosensors and for in vitro cell-live imaging.

The BIS project is an example of a unique multi-sectorial and multi-field environment to further teach early-stage researchers (ESR) to apply the gained knowledge in analyzing and designing/engineering complex biological nanosensors of medical importance.

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Organic Nanoparticles: Synthesis and Applications.

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Nanoscale was described by physicists who studied the optical properties of thin films, in the mid-nineteenth century. A century later, Feynman formalized the nanotechnology as field of research to miniaturize electronic components. In 1979 Ekimov discovered the use of quantum mechanics to produce nanoparticles with innovative properties of semiconductors, opening the race for nanoparticle synthesis to find new applications in all disciplines.

Nanoparticles (NPs) are grouped in three main type: inorganic, hybrid inorganic-organic, organic. The first particles, deliberately synthesized for electronic applications, were gold and silver NPs. They were also applied in the biomedical field, where the silver NPs showed a great antibiotic power.

The methods of synthesis can be Bottom-up or Top-down. In the first case the bulk material is atomized and atoms are assembled in to NPs. In the second case the bulk material, on the basis of its granulometry, must be progressively crushed until to comminute the material at the nanoscale. Usually, the choice of the methods depends on starting materials and the putative future applications.

The idea of exploiting metal NPs has gradually given the possibility of increasing the applications and for this reason it has been decided to functionalize the particles by combining them with other substances also of organic type. The metal-organic hybrid NPs found applications in diagnostics and sensors or even allowed to solubilize otherwise insoluble active ingredients and changed the bioavailability of some drugs. Cancer research currently uses nanoparticles to convey substances as specifically as possible. During the last twenty years research has also moved towards the synthesis of completely organic particles with the aim of reducing the use of inorganic substances harmful to the environment. Currently, the frontier of research on NPs is the green synthesis that seeks to learn from nature and exploit the living world to produce all type of nanomaterials.

In our laboratory we are interested in studying NPs from nutraceuticals, working in water solvent and minimizing the use of inorganic materials. Moreover, the aim of the study is to set up a productive process on pilot scale. For these reasons, we choose the planetary ball miller, that is considered scalable and with low impact on costs of production.

In so far we have synthesized the NPs from three different sources: Boswellia serrata, N-Acetyl-Glucosamine and N-Acetyl-Carnitine.

In all cases we obtained NPs with a size ranging from 200 nm to 400 nm

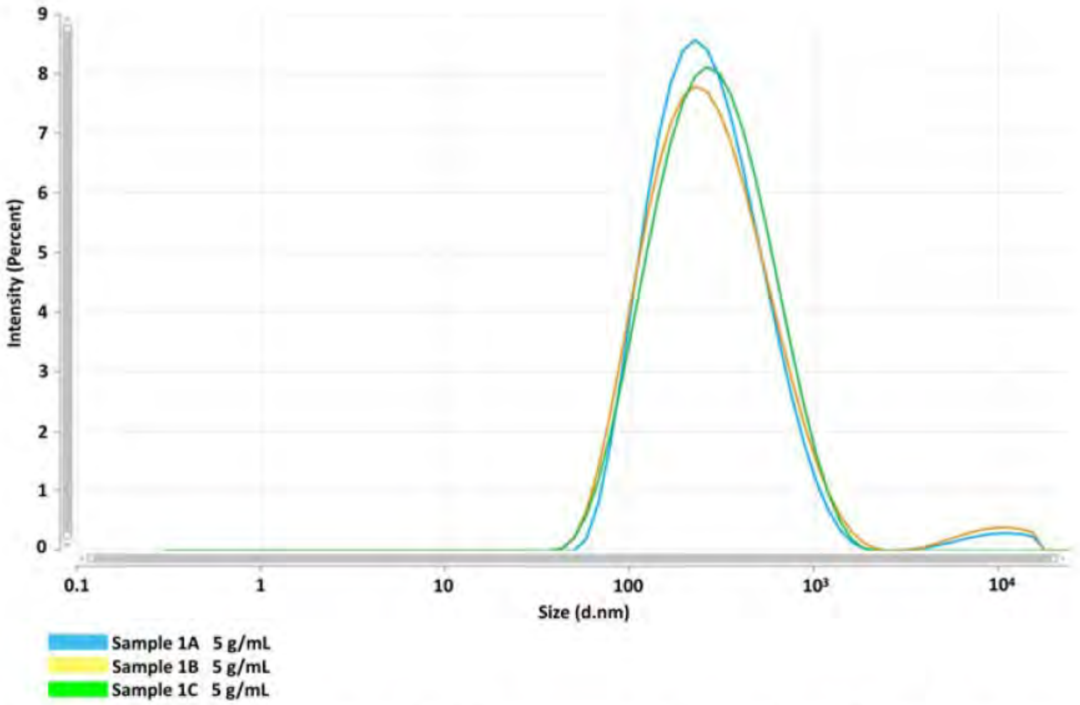

Figure 1. Size distribution of GlcNAc NP suspension at 5 g/mL by DLS at a fixed angle of scattering, expressed as Z-average (d.nm). Three independent preparations were carried out to analyse the size and distribution of NPs. Sample 1A (blue line), Sample 1B (yellow line), and Sample 1C (green line).

Conclusion:

The physical technique to mill the millimetric raw powder from different source can be used to synthesize NPs with a purity greater than 95%. The study of their biological activities showed that NPs exhibited a increased potency of about 10^3 folds respect to native molecules (no-NPs). Our NPs can find different application as novel foods, nowadays, the absence of toxic effects and their biological activity are under study in rats.

Evidences of a different metabolic regulation in favism erythrocytes and consequences on the cells aging process

Marco Girasole – Istituto di Struttura della Materia - CNR

Favism uniquely arises from a genetic defect of the Glucose-6 Phosphate Dehydrogenase (G6PD) enzyme and results in a severe reduction of erythrocytes' (RBCs) reducing power that impairs the cells' ability to respond to oxidative stresses. After exposure to fava beans or a few other drugs, the patients experience acute hemolytic anemia due to RBCs' lysis.

Here we compare selected biochemical, biophysical, and ultra-morphological properties of normal RBCs and cells from favism patients measured along cellular aging. Along the aging path, the cells' characteristics change, and their structural and functional properties degrade. However, the analysis revealed differences in the membrane arrangement on the nanoscale and distinct metabolic regulation in G6DP-deficient cells that result in important differences in the cell properties and ultra-morphology during aging.

In particular, the initial higher fragility and higher presence of structural/morphological alterations of favism cells develop, at long aging times, into a stronger resistance to external stresses and into a higher general resilience to lysis. This surprisingly higher endurance against cell aging has been related to a metabolic regulation that permits, to G6PD defective cells, a lower energy consumption in environmental stress conditions. Our results provided a direct and coherent link between the RBCs' metabolic regulation and the cell properties that would not have been possible to establish without an investigation performed during aging.

Atomic Force Cantilevers as nanosensors for real-time investigations in biomedicine

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Movement is connected to life. Studying living biological systems and their nanoscale movements we can achieve a novel insight in their metabolic status and in how they react to external stimuli.

To investigate these movements, we exploited the sensitivity of AFM cantilevers to develop a novel nanoscale sensor, called the nanomotion sensor, which we applied to characterize the innate correlation between life and movement.

Due to its sensitivity, the nanomotion sensor can be used to study bacterial species [1,2], yeasts and fungi and their response to drugs as well as to chemical or physical stimuli.

We will show how the fast response of the sensor, leads to exciting applications in the medical practice, with evident advantages for patients care. For instance, by combining it with rapid isolation of bacteria from clinical samples, we have optimized a protocol to produce a complete characterization of a bacterial infection directly from a clinical source in few hours. [3]

Finally, we will present the latest results in the nanomotion characterization of single mammalian cells. As an example, we will present our nanomotion investigation of neurons exposed to amyloid proteins [4], Red Blood Cells aged in starving conditions and the oxidative stress response of a cell model system for Friedrich's ataxia.

In very general terms, all these pioneering results indicate that a sensor capable of transducing metabolically-related movements can deliver a new point of view in the analysis of living systems and allow a new means to characterize the metabolic activity. This has also led us to propose this nanomotion sensor as an innovative technique to detect life in extreme environments. [5]

[1.] Longo et al., Nat. Nanotech., 8, 522-526, (2013)
[2.] Mustazzolu et al., Antim Ag Chem, 63 (3), e02194-18 (2019)
[3.] Longo et al. Clin. Microbiol. Infect., 23, 400-405, (2017)
[4.] Ruggeri et al. Cell Death Disc., 3, 17053 (2017)
[5.] Kasas et al., PNAS, 112 (2), 378–381 (2015).


NN 23

NANOSCIENCE & NANOTECHNOLOGY

INFN | LABORATORI NAZIONALI DI FRASCATI
VIA E. FERMI 54, FRASCATI ITALY
29TH MAY - 1ST JUNE 2023

THURSDAY 1 JUNE

Sessions:

Thirteen: 9.10 - 11.00

Nicola Cioffi , Lala Gahramanli, Faycal Bensouici , Tahar Tata , Said Boukerche

Fourteen: 11.30 – 13.10

Adriana Trapani, Giorgia Natalia Iaconisi, Rosanna Mallamaci, Antonello Caponio, Stefano Castellani

Fifteen 14.50 – 16.10

Maurizia Palummo, Roberto Flammini, Antonio Maffucci, Francesca Arcudi

Sixteen: 16.40 – 18.10

Michele Pisarra , Antonello Sindona, Enrico Perfetto , Paola Gori

Nanoantimicrobials for active food packaging applications

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In 2012, the term "Nanoantimicrobials" (NAMs) appeared for the first time in the title of one of the most diffused textbooks in the field of antimicrobial nanomaterials.[1] Since then, the number of papers combining the keywords "nano" and "antimicrobial" has progressively increased (Fig. 1); the vast majority of this scientific production being focused on the development of nanomaterials with enhanced nanoparticle properties, and/or antibacterial functionalities.

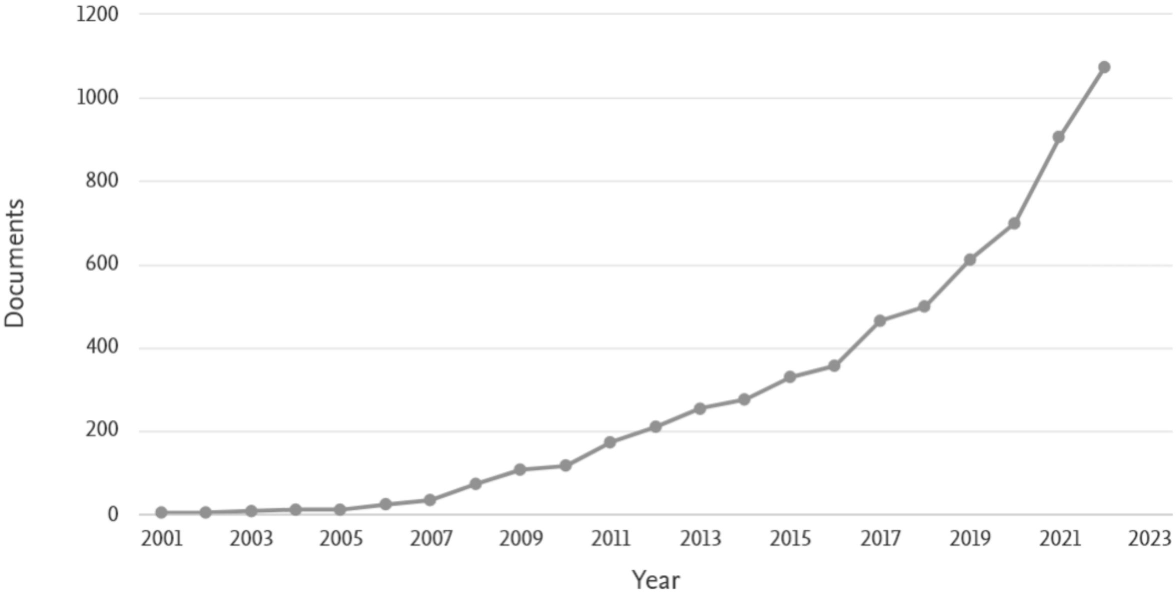

Fig. 1. Publication trends in the field of nanoantimicrobials. Source Scopus® database, searched on May 15th 2023 with the keywords "nano" and "antimicrobial"; time interval: 2001-2022; distribution shows more than 6200 documents.

After the outbreak of the severe acute respiratory syndrome coronavirus (SARS-CoV-2), several groups working on NAMs re-oriented their activities towards the development of antivirals [2]. This has not been the first, nor the last pandemic, as recently demonstrated by the additional outbreak of the monkeypox virus.
Microbial infections are a major issue worldwide. Among them, healthcare- and food-related infections are the most abundant ones. They are frequently associated to the occurrence of biofilms and or AntiMicrobial Resistance (AMR) phenomena. Biofilms have the ability to tolerate antibiotics, host defense systems and other external stresses. [3] AM resistant bacterial strains are able to resist antimicrobial treatments, especially antibiotics, and have a direct impact on human and animal health, along with a great economic impact.[4]
The nanomaterials community is offering several technological solutions to challenge the ongoing and future global health emergencies. Most of the proposed materials are proven to be highly effective in the removal of individual biothreats, including virus, antibiotic-resistant bacterial strains, biofilms of industrial and biomedical concern. However, an increasing concern is being risen about (nano)safety The question is how our research on antimicrobial agents may match the increasing demand for green and chemically safe technologies: do we really investigate nanotechnologies that will help us to solve the future biothreats?

Our most recent experimental efforts are being devoted to the development of green and scalable routes to broad spectrum antimicrobials with *non-nano characteristics:* bulk metal alloys, ionic exchangers, coordination polymers, submicron particles, intrinsically insoluble salts, biomass-related organic active components, etc.

This presentation will focus on our most recent results on the development of smart additives for active food-packaging applications.
In this field, our preferred technological solutions involve the dispersion of smart nanoantimicrobials into suitable (biodegradable) dispersing matrices, such as poly-lactic acid, polyethylene-oxide, chitosan. AMR issues are prevented by the combination of multiple functionalities in the same antimicrobial agent, by means of synergistic bioactivity.

An overview will be presented on these active compounds and materials, proposed as non-conventional tools for the fight against biothreats.
Some key aspects of the roadmap to novel and enhanced (non-nano-)antimicrobials of industrial value will be concisely discussed.

[1] "Nanoantimicrobials. Progress and Prospects", Springer-Verlag Publisher, N. Cioffi, M. Rai Eds., 1st Edition, 504 pp, ISBN 978-3-642-24427-8, 2012.
[2] Sportelli, M.C.; Izzi, M.; Kukushkina, E.A.; Hossain, S.I.; Picca, R.A.; Ditaranto, N.; Cioffi, N. "Can Nanotechnology and Materials Science Help the Fight against SARS-CoV-2?" Nanomaterials 2020, 10(4), 802
[3] Sharma, D., Misba, L. & Khan, A. U. Antibiotics versus biofilm: an emerging battleground in microbial communities. Antimicrobial Resistance & Infection Control 8, 76, 2019.
[4] EU One Health Action Plan against AMR, https://health.ec.europa.eu/antimicrobial-resistance/eu-action-antimicrobial-resistance_en

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Utilization of novel $Ag-Ag_2S-CdS$ nanocatalysts for photocatalytic dye degradation

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In this paper, to create $Ag-Ag_2S-CdS$ hybrid nanocatalysts polyol synthesis method and the combined cation exchange and photo-reduction method were used. These materials were investigated in the photodegradation process in the example of Methylene blue (MB) dye. Here, we selected 3 ambiances to determine degradation efficiency under influence of the sunlight at different hours.

For to determine crystal structure, the obtained $Ag-Ag_2S-CdS$ nanowires were investigated by XRD, and are shown in Fig 1.

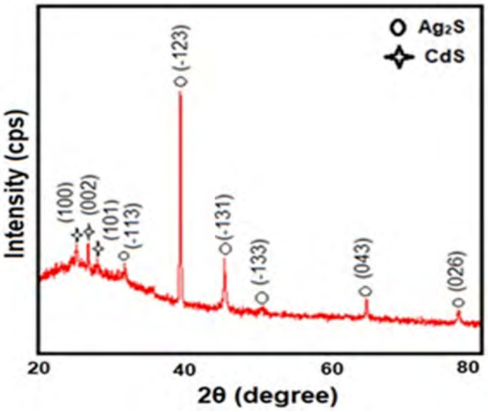

Figure 1. The XRD pattern of the $Ag-Ag_2S-CdS$ hybrid nanocatalysts.

According to the XRD results, the peaks observed in the diffraction pattern at $2\theta=23.53°$, $25.18°$, and $26.78°$ correspond to CdS with card number ICDD 01-079-3167 and are labeled as (100), (002), and (101), respectively. According to card number ICDD 01-074-3322, the peaks observed at $2\theta = 38.14°$, $44.32°$, $51.28°$, $64.43°$, and $77.40°$ angles confirm the formation of alpha-Ag_2S. These peaks are also indexed with the Miller indices (-123), (-131), (-133), (043), and (026), respectively.

To utilize these materials in the photocatalysis purpose, we used MB dye in 3 ambiances such as neutral, alkaline, and acidic. By adding the synthesized $Ag-Ag_2S-CdS$ nanocatalysts to each environment, their photodegradation processes were carried out at 1-5 hours intervals under the influence of sunlight. After repeating this process for every 3 mediums, the samples were studied by UV-Visible spectroscopy to determine the degradation efficiency. The absorption spectra of the samples in the different ambiances of MB dye as a function of time is given in Fig. 2 (a,b,c).

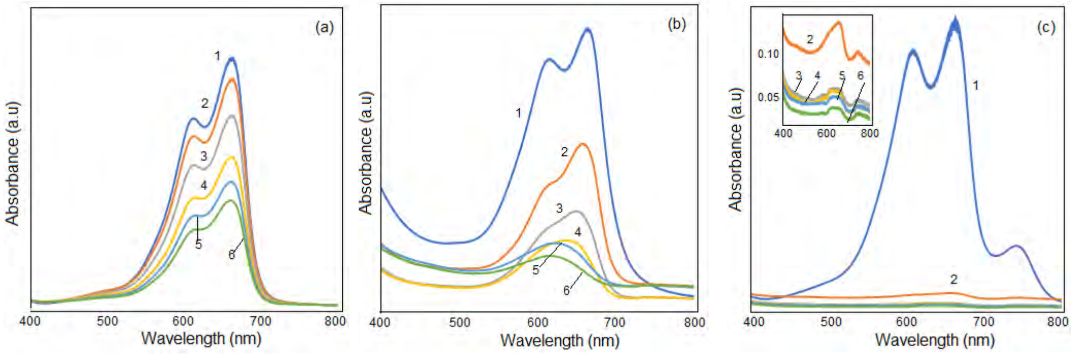

Figure 2. Absorption spectral changes of MB dye with different pH degrees (a) neutral solution; b) alkaline solution; c) acidic solution) with Ag-Ag_2S-CdS NWs under the influence of sunlight at a different time

The absorption spectra of samples taken every hour were recorded with a UV-Vis spectrometer to measure the degradation performance of MB dye through Ag-Ag_2S-CdS hybrid nanocatalysts under the influence of sunlight at different hours (1-5 hours). Fig. 2 depicts the absorption spectra of the neutral (Fig.2.a), alkaline (Fig.2.b), and acidic (Fig.2.c) environments. The efficiency of photodegradation processes can be determined during photocatalysis processes carried out at different pH degrees. The process of intensity decrease in the absorption spectrum is observed as exposure time increases.

Fig.3 reflects the degradation efficiency of three different pH degrees as the chart form and Table 1 displays the calculated results as the percent value.

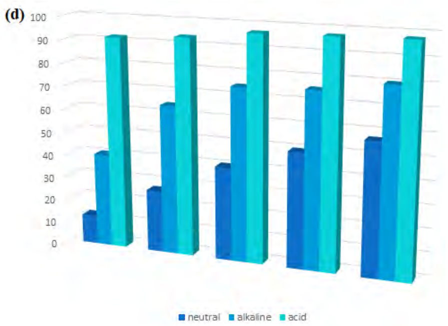

Figure 3. The degradation efficiency in different pH degrees

Table 1. Degradation efficiency (%) for MB of 3 different ambiances with Ag-Ag_2S-CdS hybrid nanocatalysts with exposure time

Time (hours)	**ambiances**		
	neutral	**alkaline**	**acid**
1	12.47	40.58	91.87
2	26.91	64.54	93.56
3	40.41	74.67	96.93
4	49.76	75.68	97.36
5	57.02	80.08	97.92

As shown in the table, the effectiveness of Ag-Ag_2S-CdS hybrid nanocatalysts in degrading the MB dye increased as the exposure time to sunlight increased. According to the degradation efficiency, the decomposition process in the acid environment is quick. At the same time, it should be noted that the decomposition process can be carried out effectively in all three environments. Based on the findings, it is possible to conclude that Ag-Ag_2S-CdS hybrid nanocatalysts can be effectively used in the treatment of dyes, organic pollutants, and wastewater and that they are a material of significant industrial importance.

As can be seen from the results, the highest decomposition efficiency occurred in an acidic environment, then in an alkaline environment, and the least in a neutral environment. In the first hour of the degradation process, the maximum decomposition was related to an acidic environment. This shows that the degradation kinetics is higher in an acidic ambiance than in another ambiance.

The photodegradation kinetics of the different environments is determined by the absorbance spectrum from the UV-Vis spectrum. According to the calculations, the rate constants of Ag-Ag_2S-CdS hybrid nanocatalysts in the neutral medium, have increased uniformly from 0.0876 to 0.8292. This dependence in an acidic environment can be seen as initially increasing sharply from 0.6835 to 1.1948 (between 1 h and 2 h), and then gradually increasing from 1.1948 to 1.4850 in later hours (between 2 h to 5 h). It increased sharply from 0.3712 to 1.2234 (between 1 h and 3 h) in the alkaline environment, and then gradually increased from 1.2234 to 1.3380 in the following hours (between 3 h to 5 h). The rate of photodegradation in a neutral environment, according to the results, is 0.0029. Because photodegradation occurs with varying intensities in alkaline and acidic environments, the degradation rate is not uniform. Thus, in an acidic environment, the rate of photodegradation is 0.0085 in the first 1-2 hours and 0.0016 in the following hours. The photodegradation rate in the alkaline environment was 0.0071 in the 1-3 hours interval and 0.001 in the 3-5 hours interval. According to the findings, the acidic environment experienced the fastest decomposition.

Based on the obtained results, it can be noted that the pH level has a significant effect on the photocatalytic decomposition process. Thus, in the scientific literature, there are many works on the effect of pH on the decomposition of dyes [1,2]. At the same time, depending on the pH level of the surface charges of the catalyst, the process of absorption of the dye substance on their surface also varies. The properties of the surface charges of the catalysts will also change depending on the pH level at this time [3].

References

[1] Reddy, M.; Venugopal, A. Hydroxyapatite photocatalytic degradation of calmagite (an azo dye) in aqueous suspension, *Appl. Catal. B: Environ.* **2007**, *69 (3– 4)*, p.164-170.
DOI: 10.1016/j.apcatb.2006.07.003

[2]_Sun. J.; Qiao, L. Photocatalytic degradation of Orange G on nitrogen-doped TiO2 catalysts under visible light and sunlight irradiation, *J. Hazard. Mater.***2008**, *155 (1–2)*, p. 312-319.
DOI: 10.1016/j.jhazmat.2007.11.062

[3]_Sampa, Ch.; Binay, K. Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, *J. of Hazar. Mat.***2004**, *112 (3)*, p.269-278.
DOI:10.1016/j.jhazmat.2004.05.013

Effect of grain size on the electrons mobility and photocatalysis activity of TiO_2 thin films

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Abstract

In this work, we have successfully fabricated bare titanium oxide (TiO_2) and fluorine (F) doped TiO_2 thin films via the sol-gel dip-coating technique on the soda lime glass substrates. The effect of fluoric acid (HF) concentration on the structural, optical, photocurrent and photocatalytic properties of TiO_2 thin films is investigated. The films are characterized by X-ray diffraction (XRD) technique, Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy, and UV-visible spectrophotometer. The XRD patterns show the presence of highly crystalline anatase phase TiO_2 and the decrease of grain size whith increasing the molar ratio of HF. The SEM images reveal some cracked surfaces, while the EDX reveal the absence of fluorine in all samples. The AFM images exhibit a decrease in roughness with the increase in HF concentration. UV-visible spectrometry reveals high transparency in the visible region (about 85%) and the shift in absorption edge toward the higher energy side. The photocatalytic activities and the electron mobilities test shows a decrease in the degradation rate of MB and the electron mobilities with the decease of grain size. This work will trigger the development of highly efficient acid-modified photocatalysts for environmental remediation.

Keywords: Fluorine, titanium oxide, organic dye, thin films, photocatalysis.

CHEMICAL COMPOSITION AND EVALUATION OF THE BIOLOGICAL ACTIVITIES OF THE ESSENTIAL OIL OF CYMBOPOGON CITRATUS MILL

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Abstract

The routine use of synthetic antioxidants and anti-inflammatories is being questioned due to negative effects on consumer health that have recently been attributed to them. Thus, new natural substances of plant origin with antioxidant and anti-inflammatory properties are being sought. This study aims to evaluate the chemical composition, antioxidant and anti-inflammatory properties of the essential oil of lemongrass (Cymbopogon citratus). The essential oil was extracted by hydrodistillation and its chemical composition was analysed by gas chromatography-mass spectrometry. The antioxidant activity was evaluated by two methods, DPPH (2,2-diphenyl-1-picrylhydrazyl), phenanthroline assay, the anti-inflammatory activity was estimated by the protein denaturation method. The essential oil of C, citratus has Geranial (28.93%), Neral (24.30%) and β -Myrcene (23.92%) as majority compounds. This study revealed moderate antiradical activity of C, citratus (IC50 = 163.12 % µg/ml) compared to those of reference antioxidants. While, phenanthroline activity showed a significant EC50 (7.80 ± 1.42). In addition, C, citratus has a very high anti-inflammatory activity with percentage of inhibition of 78.15% compared to Diclofenac sodium (96.42 %).

Key words: *Cymbopogon citratus*, essential oil, GC/MS, antioxidant activity, anti-inflammatory activity

Phytochemical screening and antimicrobial activity of *Calotropis Procera*

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Abstract

The present work focused on the valorization of a medicinal plant known by their traditional use in the south-western region of Algeria; calotropis procera by phytochemical screening, identification of some bioactive compounds and evaluation of the antimicrobial activity of leaves and stems of calotropis procera.

The extraction of polyphenols showed that the macerated aqueous extract of the leaves recorded high yields (22.13 ± 0.43%) compared to the other extracts. The qualitative phytochemical tests showed a richness of the extracts in bioactive compounds by the presence of total and gall tannins. Whereas the tests for flavonoids and were minimal or negative. Quantitative determination reveals that the decocted aqueous extract of the leaves is the richest polyphenol (553 µg EAG/g). For flavonoid determination, the decocted aqueous extract of leaves was found to be the richest (255 µg EQ/ dry g) followed by the decocted aqueous extract of stems (225 µg EQ/ dry g). The antimicrobial activity of the extracts on E. coli, S. aureus, Lactobacillus sp. and Candida albicans determined that the extracts are more active on Gram+ and Gram- bacteria with an inhibition diameter of 32 mm and with a lower MIC (8mg/ml).

Key words: *Calotropis procera*, Phytochemical, Polyphenols, Antimicrobial effect

Multilayered TiO_2 and Cr-Doped TiO_2 Nanostructured coatings for the Improvement of Stainless Steel 304 Corrosion Behaviour

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ABSTRACT

Multilayer coatings based on TiO_2 and Cr-doped TiO_2 nanoparticles are deposited on 304 stainless steel substrates and on transparent glass using the sol-gel dip coating technique, followed by annealing at 450°C for 1h. XRD analysis reveals nanocrystalline TiO_2 phases for all multilayer films, and for all added percentages of Cr. All the observed diffraction peaks were indexed by anatase TiO2. Moreover, no additional diffraction peaks belonging to Cr species are observed. The optical microscopy images show the presence of some stripes, holes and microtraces, besides, the obtained coatings reveal different colors, from blue, to yellowish. The analysis by UV-Visible spectroscopy indicates that the band gap of all samples has approximately the same value, around 3.67eV.
Corrosion tests were performed, including potentiostatic (EIS) and potentiodynamic (Tafel plot). EIS shows two capacitive loops, the first loop is related to oxygen reduction and the second loop is related to metal dissolution. The diameter of the loops for SS 304 stainless steel coated with 0.2% and 0.6% Cr doped/TiO_2 layers is larger than that of the bare metal loop revealing the stability and compactness of these layers, ensure to these coatings a better protection in a saline solution. An equivalent electrical circuit model representative of each of the curves has been proposed to model the S.I.E. data.
The corrosion protection performance of 304 stainless steel (304 SS) was evaluated in a 3% NaCl solution. The obtained results reveal that multilayer thin films in the chromium doping range (from 0.2% to 1.0%) show a remarkable improvement in corrosion protection performance, reaching a protection efficiency about 84% for 0.6% Cr-doped TiO_2 coating.

Keywords: *sol-gel coatings; nanoparticles; corrosion; Cr-doped/TiO_2 ; corrosion.*

Nose-to-Brain delivery of dopamine via nanocarriers or polymer conjugates: a comparative study

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Among neurological disorders, Parkinson's disease (PD) is one of the most common pathologies affecting over 60-year-old patients in Western Countries. As known, the death of neurons producing the neurotransmitter dopamine (DA) in the *Substantia Nigra* of the brain is the primary hallmark of the appearance of this disorder. Therefore, much research is devoted to identify strategies for brain DA supply as innovative PD treatment. To overcome this drawback, an interesting option is represented by the development of DA-loaded nanocarriers, which may be able to be administered via nose to brain delivery in order to bypass the Blood Brain Barrier and achieving a higher patient compliance [1-4]. In this communication, we report our preliminary results of a comparative study on DA loaded- Solid Lipid Nanoparticles (SLN) adsorbing a natural antioxidant agent and, precisely, SLN were formed according to the melt homogenization method using Gelucire® 50/13, a self-emulsifying lipid [5,6]. Additionally, herein we have also evaluated the option of a chemical link between the neurotransmitter and a polymeric backbone, leading to a polymer conjugate, to limit the mentioned drawbacks. In this context, some carboxylate chitosan-DA conjugates were synthesized and their potential for improving the brain delivery of the neurotransmitter DA was investigated.

References

1. Rodríguez-Nogales C. et al., Brain aging and Parkinson's disease: new therapeutic approaches using drug delivery systems. Maturitas, 2016, 84, 25-31.
2. Saraiva C. et al., Nanoparticle-mediated brain drug delivery: Overcoming blood-brain barrier to treat neurodegenerative diseases. J. Control. Release 2016, 235, 34-47.
3. Bourganis V. et al., Recent advances in carrier mediated nose-to-brain delivery of pharmaceutics. Eur. J. Pharm. Biopharm. 2018, 128, 337–362.
4. Cassano, R.. et al., Synthesis and characterization of novel chitosan-dopamine or chitosan-tyrosine conjugates for potential nose-to-brain delivery. Int J Pharm 2020, 589, 119829.
5. Trapani A. et al., Protection of dopamine towards autoxidation reaction by encapsulation into non-coated- or chitosan- or thiolated chitosan-coated-liposomes. Colloids Surf B Biointerfaces. 2018, 170, 11-19.
6. Trapani A. et al., Glutathione-loaded solid lipid nanoparticles based on Gelucire® 50/13: Spectroscopic characterization and interactions with fish cells. J. Drug Deliv. Sci. Tec. 2018, 47, 359–366.

BIOTECHNOLOGICAL PRODUCTION OF HYALURONIC ACID: INNOVATION AND FUTURE FOR BIOMEDICAL APPLICATIONS

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Hyaluronic acid (HA) is a glycosaminoglycan polymer with repeating units of β-(1,4)-glucuronic acid and β-(1,3)-N-acetylglucosamine linked together (1).

This molecule is present in many bacterial strains and in all vertebrates. HA functions in human body include lubrication, water homeostasis, macromolecular filtering, growth of epithelial cells, eosinophils and macrophages. HA is commercially produced today for both pharmaceutical and cosmetic applications, in particular for the treatment of osteoarthritis, wound healing and drug delivery (2). In recent years, several possible strategies for the industrial production of HA have been developed, in fact HA has been gaining an exponential interest due to the increased number of its applications, so the market share tends to grow over the years. Therefore, there is a growing attention to the optimization of HA production processes in order to obtain a product ensuring high quality standards, along with high efficiency and affordable costs.

In our studies *E. coli* BL21 RIL (Thermofisher®) cells were used to achieve the biotechnological production of hyaluronic acid by fermentation. The cells were co-transformed with two recombinant plasmids of new generation: pET duet and pRSF duet plasmids (3). Each of them contains two of the most important genes involved in the biosynthetic pathway of HA cloned in tandem: *hasA* and *hasE* in pET plasmid, *hasB* and *hasC* in pRSF plasmid.

After having co-transformed the bacterial cells, all the induction parameters were optimized. The obtained results suggested that the optimal IPTG concentration necessary for a good expression of genes of interest and for an optimal cellular growth was 0.5 mM. Hence, the gene expression was evaluated and then the microbial fermentation was performed. The process was taken overnight, so the hyaluronic acid was extracted from the fermentation broth. Then it was tested by carbazole assay and its identity was demonstrated by FT-IR.

At this point the obtained hyaluronic acid will be applied for biomedical purpose. In particular, it will be used to functionalize nanoparticles and to administer antiseptics and antibiotics, which require frequent administration to preserve their activity.

References

1. Gallo, N., Nasser, H., Salvatore, L., Natali, ML., Campa, L., Mahmoud, M., Capobianco, L., Sannino, A., Madaghiele, M. (2019). Hyaluronic acid for advanced therapies: Promises and challenges, *European Polymer Journal*, 134-137.

2. Vasvani, S., Kulkarni, P., Rawtani, D. (2020). Hyaluronic acid: A review on its biology, aspects of drug delivery, route of administrations and a special emphasis on its approved marketed products and recent clinical studies. *International journal of biological macromolecules*, 151, 1012-1029.

3. Lai, Z. W., Rahim, R. A., Ariff, A. B., Mohamad, R. (2021). Comparison of hyaluronic acid biosynthesis by the recombinant Escherichia coli strains in different mode of bioreactor operation. *Journal of Microbiology, Biotechnology and Food Sciences*, 2021, 905-910.

Combined Dopamine and Grape Seed Extract-Loaded Solid Lipid Nanoparticles: Biological Evaluation.

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Parkinson's disease (PD) is a common brain disorder affecting millions of people worldwide. The precise mechanisms that cause this disease remain to be identified but oxidative stress is one of the contributors to dopaminergic neuron loss in Parkinson's disease. In the present study formulated solid lipid nanoparticles (SLNs) were investigated combining the neurotransmitter dopamine (DA) and the antioxidant grape seed-derived pro-anthocyanidins (grape seed extract, GSE) with the aim reduce the PD-related oxidative stress due to the synergic effect with DA to enhance its brain bioavailability. Three types of nanoparticles were used: DA SLNs co-encapsulating GSE, GSE adsorbing DA-SLNs and DA-FITC-SLNs co-encapsulating GSE. The particle size, PDI and zeta potential were measured in each sample and Transmission electron microscopy (TEM) was adopted to investigate the nanoparticle morphology at the dried state. In vitro studies were carried to cytotoxicity assessment in Olfactory Ensheathing cells (OECs) and in SH-SY5Y and flow cytometry studies evidencing higher uptake when GSE was co-encapsulated rather than adsorbed onto the particles. *Ex vivo* permeation studies were carried out through excised nasal porcine mucosa using a vertical Franz cell confirmed the permeation of DA from both SLNs.

In vitro model to study different nanoformulations in human nasal epithelial cell line (RPMI2650)

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Parkinson's disease (PD) is a progressive neurological disorder that affects movements and is characterized by symptoms such as tremors, rigidity, and slowness of movement and it is caused by the degeneration of dopaminergic neurons in the brain. The idea behind this study is to use the nasal route as access to the Central Nervous System to deliver the neurotransmitter dopamine (DA) in order to bypass the blood-brain barrier. In this perspective, the first barrier that a drug has to cross is the nasal epithelium; therefore, in this study, we decided to use the RPMI2650 human cell line, which is often chosen as a model of the nasal epithelial barrier and for this reason has been shown to be suitable for use in drug permeation studies. On this cell line, we conducted *in vitro* viability tests using drug delivery systems composed of solid lipid nanoparticles (SLNs) loaded with DA and grape seed extract (GSE)[1] with antioxidant function, synthesized with the aim of reducing oxidative stress and finding a remedy for neurotransmitter deficiency in dopaminergic neurons of PD patients. Cell viability assays were conducted using two different methods, Resazurin and MTT. Resazurin is a blue dye commonly used in cell biology experiments to monitor the growth or viability of cells. MTT, or 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide, is another commonly used dye in biological assays; it is a yellow dye that is reduced by living cells to form a purple formazan product and is often used as a measure of cell viability, metabolic activity, or proliferation. Some different formulations of SLNs containing DA and GSE have been synthesized and used: DA-SLNs co-encapsulating (CO) GSE, DA-SLNs adsorbing (ADS) GSE, DA-SLNs CO and ADS GSE in gel Poloxamer/Carbopol and AlgOx/Hydroxypropyl Methylcellulose, DA-SLNs CO and ADS GSE in cryoprotectant sucrose and methyl beta cyclodextrin, DA-FITC-SLNs CO and ADS GSE, DA-SLNs without GSE. After treatment for 6, 12, 24 hours with various nanoformulations, no significant decrease in viable cells number was observed as compared to control condition.

1. Trapani A. et al., Glutathione-loaded solid lipid nanoparticles based on Gelucire® 50/13: Spectroscopic characterization and interactions with fish cells. J. Drug Deliv. Sci. Tec. 2018, 47, 359–366.

Mucopenetration properties and interaction with airway epithelial cells of solid lipid nanoparticles containing magneto sensitive iron oxide

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Chronic respiratory diseases, whose hallmarks are oxidative stress and persistent inflammation, need novel therapeutic tools and pharmaceutical agents. We have previously demonstrated the ability in reducing oxidative stress and inflammation by natural substances obtainable from the red grape seed (polyphenols) encapsulated in solid lipid nanoparticles (SLNs), in airway epithelial cells *in vitro* [1]. These studies revealed that SLN were taken up in a dose-dependent fashion and persisted into cells at detectable levels up to 16 days.

Since in most chronic respiratory diseases excessive viscous airway secretions oppose a formidable permeation barrier to drug delivery systems limiting their therapeutic efficacy *in vivo*, one of the possible strategies pursued to overcome mucus clearance is based on nanoparticles with magnetic cores pulled by external magnetic forces through the mucosal barrier. Thus, we evaluated whether penetration of SLNs through airway sputum may be improved using a magnetic field.

For this purpose, we tested magneto-sensitive iron oxide containing SLNs (mSLNs) based on Gelucire® 50/13 [2] on mucus samples derived from three different sources: i) a sputum obtained from chronic obstructive pulmonary disease (COPD) outpatients and ii-iii) aspirates from high and low airways of COPD patients, respectively, during their admission in the intensive care unit (ICU). Based on the FEV1/FVC ratio (Tiffenau index) >0.7, COPD oupatients were in mild condition, whereas COPD patients in ICU required mechanical ventilation for severe traumatic brain injury and acute respiratory insufficiency.

Briefly, fluorescent mSLNs were prepared with the melt-emulsification method in presence of magnetic iron oxide (II, III) and an ethanolic solution of 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine-N-(lissamine rhodamine B sulfonyl) ammonium salt (Liss Rhod PE). As control, plain fluorescent SLN (pSLNs) were produced in absence of magnetic iron oxide. The resulting SLNs were characterized for their size, zeta potential and polydispersion index (PDI). SLNs characterization revealed that incorporation of iron oxide induced a significant increase in mean diameter value (313 ±14 nm for mSLNs vs 141 ± 11 nm for pSLNs). In general, Liss Rhod PE adsorption resulted in a shrinking of mean diameter for both SLNs. Concerning zeta potential values, all SLNs resulted negatively charged (with and without Liss Rhod PE), indicating a good colloidal stability which should prevent their aggregation. Moreover SLNs exhibited wide PDI values, particularly for both mSLNs and pSLNs adsorbing Liss Rhod PE.

Sputum diffusion studies were performed as previously described [3]. Briefly, one-hundred µL of pooled mucus/sputum was stratified on the upper chamber of a semipermeable filter (Transwell, 0.33 cm^2, porosity 3 µm), while 600 µL of PBS were placed on the bottom chamber. Either fluorescently-labelled magnetic SLNs (mSLNs) or plain SLNs (pSLNs) diluted in 100 µL PBS at a final concentration of 16 µg/mL were placed onto the mucus/sputum layer or in PBS in absence of mucus/sputum as control, the transwells were placed on top of a magnetic plate at 37°C, and the fluorescence in the basolateral medium was measured at different times, up to 30 hours. The results of mucopenetration in presence of a magnetic field, show that mSLNs are more permeable in COPD sputum than pSLNs, while high and low secretions are still difficult to overcome. Moreover, in order to study mSLNs interaction with differentiated airway epithelial cells in presence of magnetic field, primary bronchial epithelial cells were grown on transwells in air-liquid interface (ALI) conditions for two weeks producing mucins and expressing cilia. We observed a dose-dependent rate of adhesion with a strong effect of the magnetic field both after 2 h and 4 h of incubation. Moreover, mSLNs did not affect the organization of tight junctions.

The results highlight that mSLNs can achieve mucopenetration properties in the presence of a magnetic field, depending essentially on the viscoelastic features of the mucus/sputum sample, suggesting that the delivery of therapeutic agents with this strategy might be more successful when the patients are considered in a milder condition.

References

1. Castellani, S., et al., *Nanoparticle delivery of grape seed-derived proanthocyanidins to airway epithelial cells dampens oxidative stress and inflammation.* J Transl Med, 2018. **16**(1): p. 140.
2. Trapani, A., et al., *Protection of dopamine towards autoxidation reaction by encapsulation into non-coated- or chitosan- or thiolated chitosan-coated-liposomes.* Colloids Surf B Biointerfaces, 2018. **170**: p. 11-19.
3. De Leo, V., et al., *Preparation of drug-loaded small unilamellar liposomes and evaluation of their potential for the treatment of chronic respiratory diseases.* Int J Pharm, 2018. **545**(1-2): p. 378-388.

"Novel materials for energy applications: insight by ab-initio ground and excited state simulations"

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The use of novel materials in energy applications presupposes a detailed microscopic understanding of their electronic and optical properties which can be nowadays obtained by means of GW and BSE approaches on top of DFT simulations.

Several examples of application of these ab-initio methodologies to novel materials from bulk inorganic perovskites to layered and 2D materials of interest for energy production, solar harvesting and light-emitting devices will be discussed.

A spatially-resolved XPS study of graphitic channels in diamond

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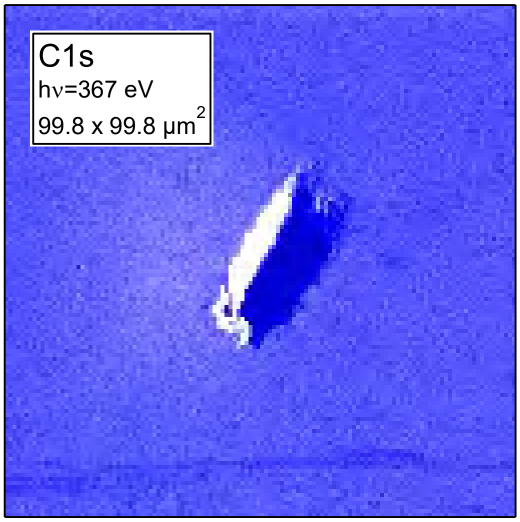
Abstract:



Diamond is a wide band-gap semiconductor with extraordinary thermo-electronic properties, such as high carriers' mobility, large diffusion length, and low work function, identifying this material as promising platform to act as photon-enhanced electron emission (PETE) cathode if a defect-engineering strategy is applied [1]. Apart from the different strategies to shift the Fermi level towards the minimum of the conduction band such as hydrogenation [2,3] or n-doping [4], the formation of bulk graphitic micro-channels can reduce the diamond series resistance by several orders of magnitude, avoiding the bottleneck of the refilling of the surface thermal electrons sustaining efficiently the emitted current [5]. In this talk, recent results on the characterization of such channels by means of spatially-resolved XPS, will be presented. The measurements have been carried out at the Elettra Synchrotron Radiation Source (ESCA Microscopy beamline). The evolution of the spectra as a function of the distance from the channel is discussed in terms of the ability of the sample to avoid charging due to the photoemission process.

[1] A. Bellucci, P. Calvani, M. Girolami, D.M. Trucchi, 2015 IEEE 15th International Conference on Environment and Electrical Engineering, EEEIC 2015 -Conference Proceedings2015, pp. 1616-1619.

[2] R. Flammini, M. Satta, A. Bellucci, M. Girolami, F. Wiame, D.M. Trucchi, Applied Surface Science, 512 (2020).

[3] V. Serpente, A. Bellucci, M. Girolami, M. Mastellone, S. Iacobucci, A. Ruocco, D.M. Trucchi, Diamond and Related Materials, 114 (2021).

[4] D.M. Trucchi, A. Bellucci, M. Girolami, P. Calvani, E. Cappelli, S. Orlando, R. Polini, L. Silvestroni, D. Sciti, A. Kribus, Advanced Energy Materials, 8 (2018).

[5] M. Girolami, L. Criante, F. Di Fonzo, S. Lo Turco, A. Mezzetti, A. Notargiacomo, M. Pea, A. Bellucci, P. Calvani, V. Valentini, D.M. Trucchi, Carbon, 111 (2017) 48-53.

Advanced sensing solutions with nanomaterials and machine learning

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Summary

Reliable real-time monitoring pollutants is a major need in industrial and residential areas, to ensure health and safety [1]. Traditional techniques, such as chromatography [2], are not suitable for a real time in-situ detection, hence effort is currently addressed to assess monitoring and sensing technologies suitable for: i) in-situ monitoring (through compact sensing platforms); ii) smart distributed systems (collective data processing).

The first concept is addressed through alternative electrical and electrochemical techniques, such as Voltammetry, VA [3-4] or Electrical Impedance Spectroscopy, EIS [5-7]. Indeed, both techniques can be implemented by means of compact systems with hand-held sensing platforms connected to portable instrumentation. For instance, disposable Screen-Printed Electrodes (SPEs) can be used as sensing platforms. However, the limits of conventional SPEs (i.e., made by graphite, carbon, etc.) related to their sluggish surface kinetics severely affect the sensor performance indicators (such as sensitivity, selectivity, responsivity, etc.. [4]).

To overcome these limits, the SPEs can be modified by enhanced materials, such as the promising Carbon Nano-Materials (CNMs), that can improve surface kinetics and enhance electroactive surface area [4-5]. More in general, CNMs are abundant and span a wide range of physical and chemical properties that can be tailored according to the purposes. Graphene, Carbon Nanotubes (CNTs), Nano-Diamond (ND) and their derivates have been widely employed for electrochemical sensing in recent years [8-9].

Despite the high improvement in SPEs' performance after their modification, a reliable technology for in-situ real-time monitoring based on these platforms and the above-mentioned techniques is still far to be assessed. Indeed, major limits still need to be overcome: (i) high sensitivity of the platforms to uncertainties of the fabrication process, environmental conditions, and ageing effects; (ii) complicated time- and resource-consuming calibration procedures, needed for in-situ measurements; (iii) difficult classification of substances with similar electrical and electrochemical footprint.

Many of the above issues can be faced by moving from conventional solutions to IoT paradigms [10]. This is the second concept mentioned above: the sensing platforms becomes nodes of a smart distributed sensing system, where the data are processed both locally and collectively (e.g., in Cloud), eventually by means of Artificial Intelligence (AI) algorithms. This approach can strongly improve the monitoring performance also in presence of the above-mentioned uncertainties, see for instance [11], where IoT-based real-time frameworks are proposed to perform water quality monitoring, by using machine learning approaches and cloud computing.

The talk will present some recent results related to the detection and classification of organic pollutants (quinones) in water performed by means of EIS and VA techniques. Improved sensing platforms will be shown, where the sensing membranes for EIS and working electrodes for VA are modified by means of 2D nanomaterials. Examples of AI-based post-process will be also discussed, with the possibility of classifying the pollutants starting from VA results, transformed into equivalent images via GAF transformations and finally processed by pre-trained convolutional neural networks.

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References

[1] H. Nakamura (2010) Anal. Methods, 2, 430-444
[2] A. M. Meyer, et al. (2019) Science of the Total Environment, 651, 2323-2333.
[3] N.-B. Mincu, et al. (2020) Diagnostics, 10, 517
[4] R. Cancelliere, A.D. Tinno, et al., (2021) Biosensors, 12, 2.
[5] M. Baah, et al., (2022) Nanotechnology, 33, 075207.
[6] G. Miele, et al. (2021) IEEE Trans. on Instrum. and Measur., 70, 503912.
[7] L. Ferrigno, et al. (2020), Nanotechnology, 31, 075701
[8] H. Beitollahi, et al., (2020) Anal. Methods, 12, 1547–1560.
[9] R. Kour, et al., (2020) J. Electrochem. Soc., 167, 037555
[10] G. Mois, S. Folea, and T. Sanislav (2017) IEEE Trans. Instrum. Meas., 66, 2056–2064
[11] A. Bhardwaj, et al. (2022) Environ Sci Pollut Res (DOI: 10.1007/s11356-022-19014-3).

Photocatalytic Generation of Solar Fuels and Commodity Chemicals

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This talk will describe two separate strategies to photocatalytically produce (i) CO from CO_2,[1] and (ii) polymer-grade ethylene from an ethylene feed with acetylene contaminant.[2] CO_2 reduction is accomplished in pure water with an unprecedented combination of performance parameters: turnover number (TON(CO)) >80,000, quantum yield (QY) >3% and selectivity >99%, using $CuInS_2$ colloidal quantum dots (QDs) as photosensitizer and a Co-porphyrin catalyst. The amine/ammonium-terminated ligand shells of the QDs are responsible for the exception performance of this system by establishing (i) an electrostatic assembly with Co-porphyrin, which allow the colocalization of protons, CO_2, and catalyst at the QD core that serves at the source of the electrons; (ii) a dynamic equilibrium between carbamic acid and free CO_2 that increases the local concentration of available CO_2; and (iii) "second-sphere" effects that improve the efficiency of the Co-porphyrin catalyst. Our room-temperature capture‒conversion approach is possible because of the nanoconfined environment of the QD surface, which enables the reactivity of the carbamic acid as a labile sequestration agent (Figure 1A).[1] In a separate system based on a Co-porphyrin catalyst, acetylene is reduced to ethylene, an intermediate in the production of ~50-60% of all plastics. The semi-hydrogenation of acetylene impurity to ethylene usually requires energy-intensive thermochemical routes. Our selective photocatalytic strategy is a major step toward the production of ethylene from acetylene with the lowest energy footprint possible. Our system reduces acetylene into ethylene with several advantages over the present hydrogenation technology, including (i) operation with near 100% conversion in an ethylene-rich gas feed and ≥99% selectivity under both non-competitive (no ethylene co-feed) and competitive (ethylene co-feed) conditions, the latter being industrially relevant; (ii) operation at room temperature using light and water in place of high temperature and an external H_2 feed, and (iii) use of earth-abundant cobalt in the catalyst, which works not only in combination with the benchmark photosensitizer $[Ru(bpy)_3]^{2+}$, but also with inexpensive and organic semiconductor (carbon nitride) (Figure 1B). These features offer substantial advantages over current hydrogenation technologies with respect to selectivity and sustainability.[2]

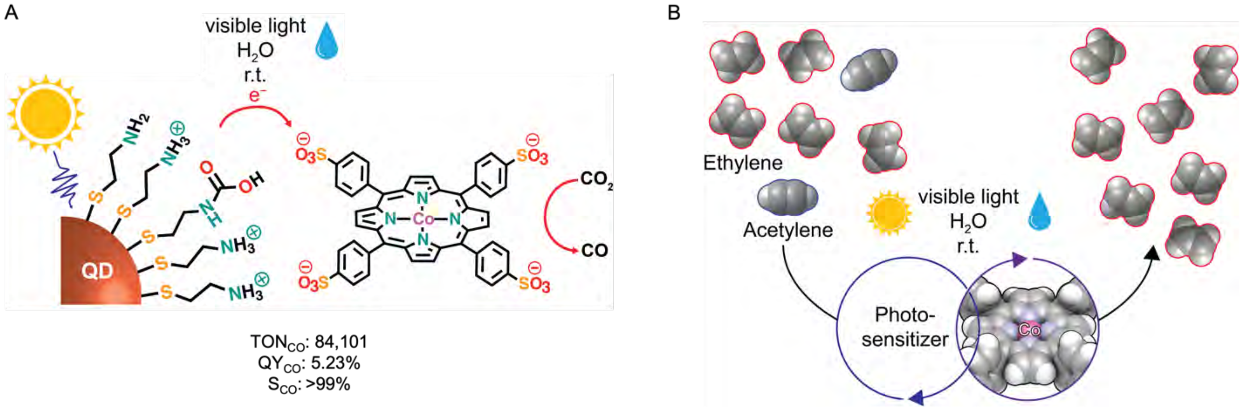

Figure 1. Photocatalytic reduction of (A) CO_2 to CO and (B) C_2H_2 to C_2H_4.

REFERENCES
1. Arcudi F. et all "Quantum Dot-Sensitized Photoreduction of CO_2 in Water with Turnover Number > 80,000" *Journal of the American Chemical Society* **2021**, 143 (43), 18131–18138 (2021).
2. Arcudi F. et all "Selective Catalytic Conversion of Acetylene to Ethylene Powered by Water and Visible Light." *Nature Chemistry* **2022**, DOI: 10.21203/rs.3.rs-932017/v1.

Real Space-Time sub femtosecond imaging of electronic motion in molecules

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'Seeing' electron motion at both its natural length and time scales is a long-awaited dream of natural sciences. Reaching such spatial or temporal resolutions is nowadays possible, but not simultaneously. Current attosecond science techniques allows to generate and track electronic motion in real time with incredible time resolution (200 attoseconds to few femtoseconds) in ever larger systems, but not in real space. Scanning tunneling microscopy (STM), on the other hand, can locally probe the electron density in molecules and solids with the necessary (picometer) resolution, but cannot provide by itself the dynamical information at the ultrafast time scale that is inherent to electronic motion.

In this work [1], we break this space-time limitation by combining STM and attosecond technologies (Fig1a). We show that the coherent electronic motion generated by < 6 fs CEP-stable near-infrared pulses can be locally and non-invasively probed with both picometer and 300 attosecond resolution, thus allowing for a direct visualization of electron dynamics without the need for any additional reconstruction. We apply our technique to self-assemblies of PCTDA molecules deposited on a Au(111) surface. Thanks to state of the art DFT calculations we are able to correctly identify the specific electronic states, which participate in the coherent oscillations (Fig.1b). Finally, through an effective two state model and dipole couplings, calculated ab-initio, we are able to correctly predict the population of each state as function of the laser pulse delays (Fig.1c).

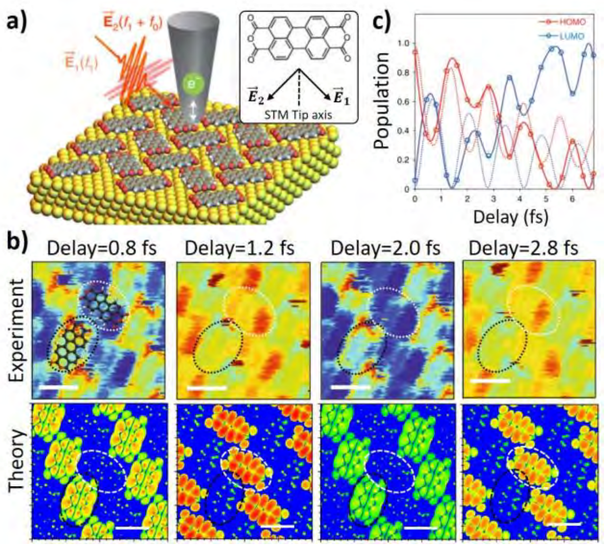

Figure 1. a) C Simplified model of the experiments: Two ultrashort laser pulses impinge on a self-assembly of PTCDA molecules deposited on a gold surface, in tunnel contact with an STM. **b)** Comparison between the experimental and calculated STM images for different laser pulse delays for a 4-Layer PCTDA self assembly on Au(111): depending on the delay between the laser pulses either the HOMO or the LUMO in different molecules are visualized [1]. **c)** Experimental (solid lines and dots) and computed (dashed lines) populations for the HOMO and LUMO as function of the laser pulse delay.

References

[1] M. Garg, A. Martin-Jimenez, M. Pisarra, Y. Luo, F. Martin, K. Kern, *Nature Photonics* **16** 196 (2022)

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Massive and massless plasmons in flat hexagonal nanosheets

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The search for connections between electronic and structural features is a key factor in the synthesis of artificial materials for on-demand applications, with graphene and analogous elemental semimetals playing a distinguished role as building blocks of photonic and plasmonic systems.

A diversity of arrangements and electronic-state dispersions is offered by currently synthesized two-dimensional allotropes of silicon and germanium, respectively known as silicene and germanene. These monolayers make the ideal playground to understand how their collective and single-particle electronic states, excited by electron or light beams, may be controlled by geometry rather than doping or gating.

Here, we provide such a study using time-dependent density-functional theory, under several levels of increasing accuracy, from the random-phase approximation to the Bethe-Salpeter equation formalism, to identify the structural dependent properties of charge-density plasmon oscillations and optical absorption in flat to buckled silicene and germanene lattices.

We further single out flat germanene as an unprecedented two-dimensional conductor, hosting Dirac cone fermions in parallel with metal-like charge carriers, which contribute to strong intraband plasmon modes and one-electron excitations in the far-infrared limit. Indeed, this rare coexistence of linear and parabolic dispersions yields correlated charge density modes exploitable for nanometric light confinement.

We show that both freestanding and some supported germenene monolayers can sustain infrared massless modes, resolved into an out-of-phase (optical) and an in-phase (acoustic) component.

We also indicate precise experimental geometries that naturally host infrared massive modes, involving two different families of parabolic charge carriers.

The interplay of the massless and massive plasmons can be finetuned by applied extrinsic conditions or geometry deformations, which constitutes the core mechanism of germanene-based optoelectronic and plasmonic applications.

References

[1] Plasmon modes of graphene nanoribbons with periodic planar arrangement.
C. Vacacela Gomez, M. Pisarra, M. Gravina, J. M. Pitarke, and A. Sindona
Phys. Rev. Lett. 117, 116801 (2016)

[2] Plasmon oscillations in two-dimensional arrays of ultranarrow graphene nanoribbons.
A. Sindona, M. Pisarra, S. Bellucci, T. Tene, M. Guevara, and C. Vacacela Gomez.
Phys. Rev. B B 100, 235422 (2019).

[3] Dielectric screening versus geometry deformation in two-dimensional allotropes of silicon and germanium. A. Sindona, C. Vacacela Gomez and M. Pisarra. Sci Rep 12, 15107 (2022). https://doi.org/10.1038/s41598-022-19260-y

[4] Massive and massless plasmons in germanene nanosheets. M. Pisarra, C. V. Gomez and A. Sindona. Sci Rep 12, 18624 (2022). https://doi.org/10.1038/s41598-022-23058-3

Figures

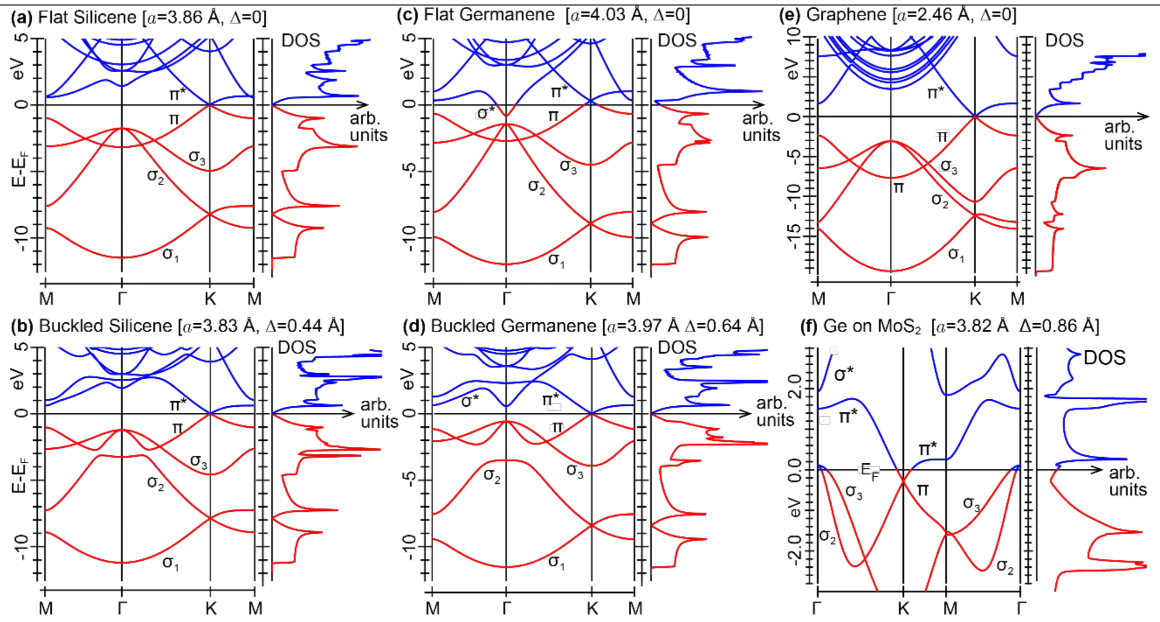

Figure 1: Computed Band energies and densities of states (DOS) of: (a) flat silicene, (b) buckled silicene, (c) flat germanene, (d) buckled germanene, (e) graphene, (f) Ge grown on MoS2. In (c) and (f) the monolayers exhibit parabolic and linear dispersing bands at the Fermi level (EF), which are proved to host massless and massive plasmon modes.

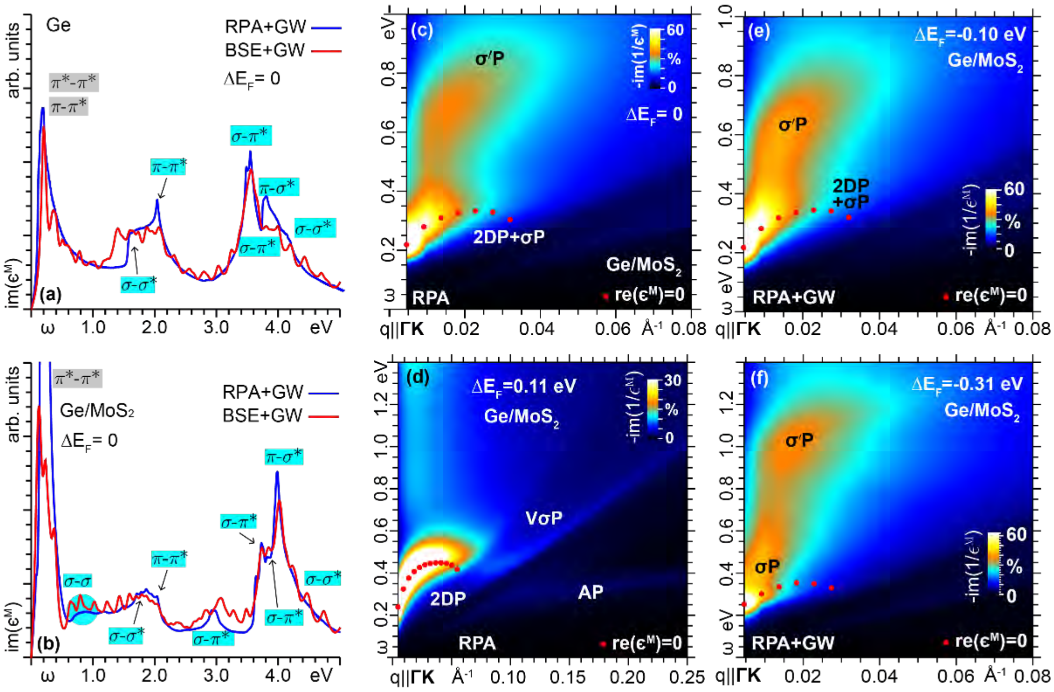

Figure 2: Imaginary macroscopic permittivity of (a) free standing germanene (Ge) and (b) Ge grown on MoS2 in intrinsic conditions (ΔE_F= 0), as obtained within the RPA+GW approximation and the BSE+GW formalisms. The low energy end (<0.8 eV) of the Ge/MoS2 spectrum (b) shows signatures of optical excitations around the Dirac cone (π*-π*) and the parabolic bands (σ-σ). Instrinsic (c) and extrinsic (d)-(f) energy loss spectra of MoS2 computed within the RPA and RPA+GW approximations. Two massless two-dimensional plasmon modes (2DP,AP) appear superimposed to massive, parabolic plasmon modes (σP,σ'P,VσP). The relative intensity of these modes is finetuned by doping.

Coherent-to-incoherent crossover of photoexcited electron-phonon dynamics in 2D materials

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We present a first principles nonequilibrium Green’s function approach to describe the carrier and nuclear dynamics of 2D materials. Our scheme is based on the simultaneous propagation of the electronic and phononic degrees of freedom and includes the GW, Ehrenfest, and Fan-Migdal self-energies. The method scales linearly with the propagation time, and allows to describe in a conserving fashion the retarded Coulomb screening and the cooling dynamics of hot carriers via phonon emission. Numerical results are provided for a monolayer MoS2 photoexcited above the gap. The intra-valley scattering is responsible for an ultrafast carriers migration toward the band edges already during pumping. Intervalley scattering occurs on a longer timescale, of the order of a few hundreds of femtoseconds. At high carrier density the energy exchange between electrons and phonons is very efficient, leading to a sizable increase of the lattice temperature within one picosecond. During this processes the electronic coherence is lost. The lattice coherence, instead, survives for much longer. Several hundreds of femtoseconds after the dephasing of the electronic polarization the nuclear displacements still exhibit undamped oscillations.

Are Xenes excitonic insulators? How screening, band dispersion and external electric field affect the prediction

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Excitonic insulators (EIs) arise from the spontaneous formation of bound electron-hole pairs when their binding energy E_b is larger than the fundamental gap E_g. Among 2D systems the existence of the EI phase should be more likely, because of the reduced screening in two dimensions and the consequent large exciton binding energy [1]. The quest for an EI phase in 2D materials is currently widely pursued, as witnessed by the numerous recent publications on this subject [2].

The graphene-like but buckled 2D allotropes of group-IV elements, the Xenes silicene, germanene, stanene and plumbene, with a small SOC-induced fundamental gap, should be outstanding candidates for the observation of the EI phase. Using a variational approach, the binding energies E_b of the lowest bound excitons in Xenes under varying electric field are investigated. The internal exciton motion is described both by Dirac electron dispersion and in effective-mass approximation (EMA), while the screened electron-hole attraction is modeled by a Rytova-Keldysh potential with a 2D electronic polarizability α_{2D}. Moreover, a simple and convenient way to estimate the screening is introduced, bypassing the need of heavy calculations.

The relation of E_b and E_g is shown to be ruled by the screening. The existence of an EI phase with $E_b > E_g$ sensitively depends on the chosen 2D electronic polarizability α_{2D} (see Fig. 1). The values of E_g and α_{2D} are strongly modified by a vertical external electric bias, which defines a transition from the topological into a trivial insulator. But gating does not change the results about the occurence of an EI phase: the prediction done at zero electric field is confirmed when a vertical electric field is applied.

Finally, as a proof of concept, fully ab-initio Many-Body perturbation theory calculations are presented, based on the Green's function method (GW, Bethe Salpeter), applied to stanene, which validate the results obtained by ab initio and model calculations of α_{2D}. It is shown that, at odd with published literature [3], Xenes do not turn out to be EIs. However, a convenient recipe to model 2D excitons for Dirac materials is provided, that only requires the knowledge of the electronic gap and of the effective masses, together with a simple modeling of the polarizability α_{2D}.

[1] O. Pulci, P. Gori, M. Marsili, V. Garbuio, R. D. Sole, and F. Bechstedt, Strong excitons in novel two-dimensional crystals: Silicane and germanane, Europhysics Letters 98, 37004 (2012); M. S. Prete, D. Grassano, O. Pulci, I.

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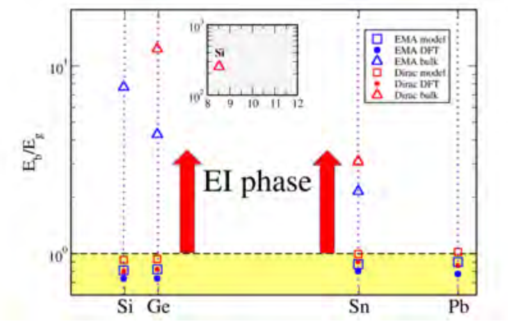

FIG. 1. Ratio of exciton binding energy E_b to the gap E_g for Xenes. The symbols refer to different electronic polarizabilities.

Kupchak, V. Olevano, and F. Bechstedt, Giant excitonic absorption and emission in two-dimensional group-III nitrides, Scientific Reports 10, 10719 (2020).

[2] D. Varsano, M. Palummo, E. Molinari, and M. Rontani, A monolayer transition-metal dichalcogenide as a topological excitonic insulator, Nature Nanotechnology 15, 367 (2020); Y. Jia et al., Evidence for a monolayer excitonic insulator, Nature Physics 18, 87 (2022); B. Sun et al., Evidence for equilibrium exciton condensation in monolayer WTe_2, Nature Physics 18, 94 (2022).

[3] M. N. Brunetti, O. L. Berman, and R. Y. Kezerashvili, Optical properties of excitons in buckled two-dimensional materials in an external electric field, Phys. Rev. B 98, 125406 (2018); M. N. Brunetti, O. L. Berman, and R. Y. Kezerashvili, Can freestanding Xene monolayers behave as excitonic insulators?, Physics Letters A 383, 482 (2019).

STEFANO BELLUCCI - CONCLUDING REMARKS

End of conference

Book of Abstracts
Nanoscience & Nanotechnologies 2023
Poster Session

Sonochemical synthesis of Cu-doped Co_3O_4 nanoparticles for photocatalytic degradation of methylene blue

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Cobalt oxide (Co_3O_4) nanoparticles are one of interesting metal oxides because it has uncommon physical and chemical properties. These nanoparticles are widely used as a gas sensor, catalyst, anode material in Li-ion rechargeable batteries, supercapacitors, electrochemical sensors, solar absorbing and electrochromic material. Metal doping is an efficient technique to enhance electrical conductivity and catalytic activity. Up to date, several dopants were used to modify the Co_3O_4 nanoparticles including transition metals (Fe, Mn, Cu, Ni, Mo, Cr), noble metals (Ag, Pd, Au), rare earth metals (La, Nd, Gd, Sm), non-metals (N, B, C, S) and metal oxide (PdO).

In the presented study, the degradation abilities of pure and different concentrations of (2%, 4%, 6%, 10%) Cu-doped Co_3O_4 nanoparticles with methylene blue (MB) under visible light irradiation were investigated. MB is an organic contaminant in wastewater, so the removal of this dye from water can prevent environmental and health problems. The synthesis of nanoparticles was carried out by the sonochemical method and subsequent calcination at 500ºC temperature. The synthesized nanoparticles were further characterized using X-ray diffraction and UV-vis spectroscopy. According to the XRD results, no impurity peaks associated with copper or copper oxide phases were observed in the diffractograms of doped samples. The crystallite size was calculated using Debye-Scherrer formula and the values were given in Table 1. For photocatalytic measurements, the dye concentration used in the reaction was 10 ppm and 10 mg catalyst was added to the dye solution. The stirring was performed in the dark for 45 min to get an adsorption-desorption equilibrium between the dye and catalyst. Then 0.4 ml of 450 mM hydrogen peroxide (H_2O_2) solution as an oxidant was added to the solution and the solution was exposed to visible light irradiation. 116W halogen lamp was used as a source of visible light. UV-vis absorbance spectrums were measured in the range of 400 nm-800 nm at pre-determined time intervals. The degradation efficiency for MB dye in the presence of pure Co_3O_4 nanoparticles and H_2O_2 was calculated using the Beer-Lambert equation and was 79.20% after 330 min. Very weak degradation occurred in the dye in the absence of a catalyst and degradation efficiency was 2.72% after 330 min. The degradation efficiency of MB dye in the presence of $Cu_{0.02}Co_{2.98}O_4$ nanoparticles increased from 46.77% to 87.51% for 90-330 min irradiation time. In the presence of $Cu_{0.04}Co_{2.96}O_4$, $Cu_{0.06}Co_{2.94}O_4$ and $Cu_{0.1}Co_{2.9}O_4$ nanoparticles, the degradation efficiency of MB dye increased from 38.76% to 74.66%, 44.95% to 85% and 31.47% to 65.60% for 90-330 min irradiation time, respectively. As can be seen from the results, the highest degradation was observed in the presence of 2% Cu-doped Co_3O_4 nanoparticles and the weak degradation was observed in the presence of 10% Cu-doped Co_3O_4 nanoparticles. When $Cu_{0.04}Co_{2.96}O_4$ and $Cu_{0.1}Co_{2.9}O_4$ nanoparticles are used, the degradation efficiency is lower as compared to undoped Co_3O_4 nanoparticles. As shown in Table 1, $Cu_{0.02}Co_{2.98}O_4$ nanoparticles have a wide band gap. Thus, when these nanoparticles are used as a catalyst, the decrease of electron-hole pair recombination and the generation of free electrons and holes for the formation of radicals leads to an increase in the degradation efficiency. The decrease of photocatalytic activity at high concentrations of copper can be attributed to the excessive oxygen vacancies and the high amount of the dopant acting as recombination centers of photoinduced electrons and holes [1]. Photocatalytic reactions kinetics was calculated using Langmuir–Hinshelwood (L–H) model and the high rate constant was observed for $Cu_{0.02}Co_{2.98}O_4$ nanoparticles (0.0062 min^{-1}). Figure 1a) reveals the pseudo-first-order kinetic study of photocatalytic degradation curves for MB with $Cu_xCo_{3-x}O_4$ nanoparticles. The rate constant values for other nanoparticles were given in Table 1 along with degradation efficiency values and correlation coefficients (R^2).

Table 1. The crystallite size, band gap, degradation efficiency, rate constant values and correlation coefficients for $Cu_xCo_{3-x}O_4$ nanoparticles.

Sample	**Crystallite size (nm)**	**The band gap (eV)**	**Degradation efficiency (%)**	**Rate constant (k, min^{-1})**	**Correlation coefficient (R^2)**
Undoped Co_3O_4	22.55	1.58 and 3.33	79.20	0.0047	0.9984
$Cu_{0.02}Co_{2.98}O_4$	29.17	1.70 and 3.43	87.51	0.0062	0.9927
$Cu_{0.04}Co_{2.96}O_4$	21.87	1.45 and 3.26	74.66	0.0039	0.9861
$Cu_{0.06}Co_{2.94}O_4$	34.19	1.44 and 3.21	85	0.0061	0.9743
$Cu_{0.1}Co_{2.9}O_4$	31.26	1.26 and 3.08	65.60	0.0029	0.9432

To determine the main active species in the photocatalytic process, trapping experiments were carried out for the degradation of MB in the presence of $Cu_{0.02}Co_{2.98}O_4$ nanoparticles. For this purpose, isopropanol alcohol (IPA, as OH· scavenger), L-ascorbic acid (as $\bullet O_2^{-}$ scavenger) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, as hole scavenger) were used [2]. A certain amount (4 mmol/L) was added to the MB solution and the rest of the experiment is the same. The photocatalytic activity of $Cu_{0.02}Co_{2.98}O_4$ nanoparticles decreased to 80.65%, 63.75% and 66.53% in the presence of IPA, L-ascorbic acid and EDTA-2Na, respectively. These results suggest that holes and superoxide radicals are the main active species in the photodegradation process of MB.

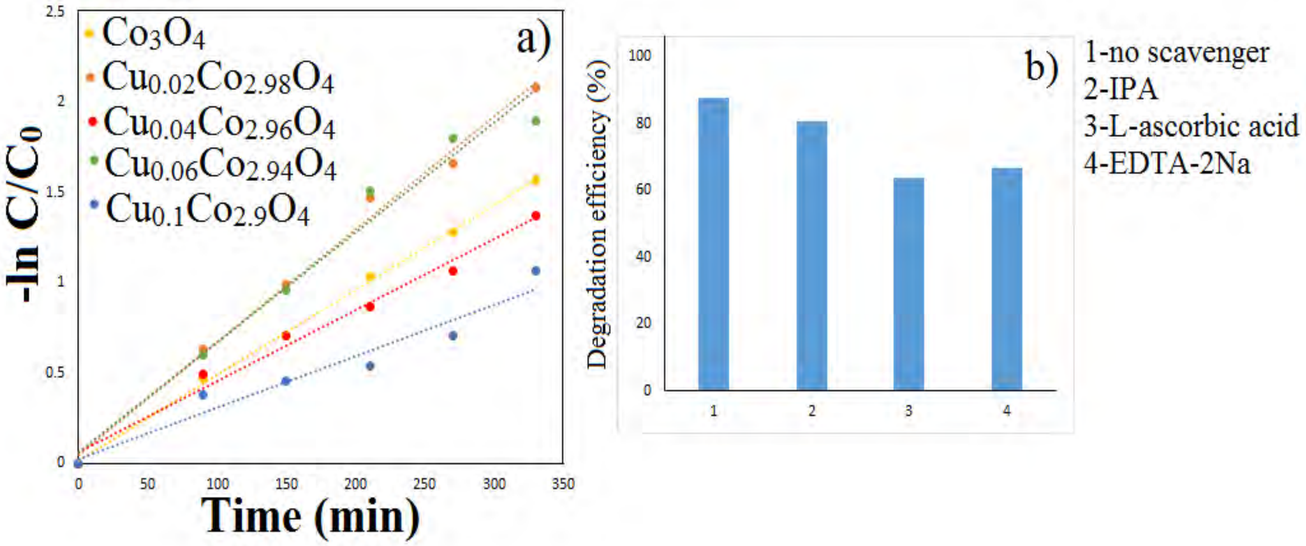

Figure 1. a) The plots of pseudo-first-order kinetics for degradation of MB with Cu$_x$Co$_{3-x}$O$_4$ nanoparticles, b) the degradation efficiency of MB after 330 min in the presence of Cu$_{0.02}$Co$_{2.98}$O$_4$ nanoparticles using different scavengers.

References

[1] B. Hameeda, A. Mushtaq, M. Saeed, A. Munir, U. Jabeen & A. Waseem, Development of Cu-doped NiO nanoscale material as efficient photocatalyst for visible light dye degradation, Toxin Reviews. 40 (2021) 1396-1406. https://doi.org/10.1080/15569543.2020.1725578

[2] H. Ait Ahsaine, A. El jaouhari, A. Slassi, M. Ezahri, A. Benlhachemi, B. Bakiz, F. Guinneton, J-R. Gavarri, Electronic band structure and visible-light photocatalytic activity of Bi2WO6: Elucidating the effect of lutetium doping, RSC Advances, 6(103), 101105–101114. doi:10.1039/c6ra22669h

HYALURONAN-ESTRADIOL NANOGELS AS POTENTIAL DRUG CARRIERS TO TARGET ER+ BREAST CANCER CELL LINE

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The delivery of bioactive molecules to the target site has attracted increasing attention over the past three decades as a turning point in the treatment of several diseases [1]. In this regard, polysaccharide-based nanoparticles offer benefits in terms of high loading efficiency, rapid drug release rates and good targeting ability through the easy functionalization of the polymeric backbones [2,3]. Finally, small molecules, peptides, proteins, and nucleic acids can be loaded into nanoparticle systems, which can be functionalized on the surface to actively deliver the cargo to cells that have receptors capable of selectively recognizing the ligand [4].

In this light, an innovative hyaluronan-based nano-delivery system is proposed for the active targeting towards ER+ breast cancer. Hyaluronic acid (HA), an endogenous and bioactive anionic polysaccharide, was functionalized with estradiol (ES), a sexual hormone involved in the development of some hormone-dependent tumors, to give an amphiphilic derivative (HA-ES) able to spontaneously self-assemble in water to form soft nanoparticles or nanogels (ES-NHs). ES-NHs ability to entrap hydrophobic molecules was also investigated, by loading curcumin (CUR) and docetaxel (DTX), both able to inhibit the growth of ER+ breast cancer. The formulations were studied for their capability to inhibit the growth of the MCF-7 cell line, thus evaluating their efficacy and potential as a selective drug delivery system, and internalization assays were performed to follow the cell distribution of the nanosystems.

Ours results demonstrate that both ES-NHs/CUR and ES-NHs/DTX inhibit MCF-7 cell growth, with ES-NHs/DTX effect higher than that of free DTX. Internalization of fluorescent-labeled ES-NHs shows a rapid intracellular uptake, assuming a receptor-dependent targeting.

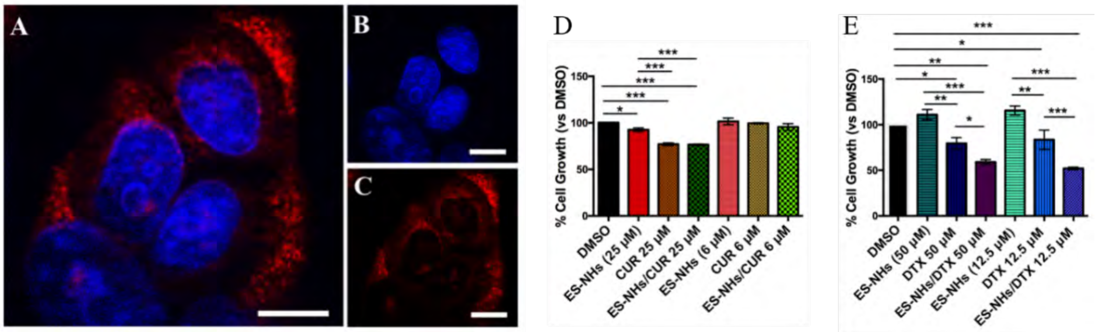

Figure 1 : Internalization analysis of MCF-7 cells incubated with fluorescent ES-NHs : A) merge, B) DAPI, C) ES-NHs ; Effect of D) ES-NHs/CUR and E) ES-NHs/DTX formulation on MCF-7 cell line.

[1] Mazdaei M. et al., *British Journal of Pharmacy*, 7(1), 1-13, 2022
[2] Plucinski A. et al. *Journal of Materials Chemistry B,* 9(35), 7030-62, 2021
[3] Zoratto N. et al. *Pharmaceutics*, 13(11), 1781, 2021
[4] Sanità G. et al. *Frontiers in Molecular Biosciences,* 7, 587012, 2020

Peptide-conjugated Gold Nanoparticles for Localized Doxorubicin Chemotherapeutic Treatment of Glioblastoma: Antitumoral Effects in Human Cellular Model

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Abstract

Glioblastoma (GBM) is the most common and aggressive of primary central nervous system tumors, characterized by high recurrence rates and a poor outcome. Still today, surgery, chemotherapy and radiotherapy are the gold standard treatments but its heterogeneity, along with an immunosuppressive tumor microenvironment (TME) and the blood–brain barrier (BBB) prevents therapeutic success. Chemotherapeutic agents such as doxorubicin (DOX), have the superior ability to kill cancer cells, but on other hand, can determine systemic toxicity and cardiomyocytes damage as well as having poor bioavailability, short half-life and the inability to cross the BBB. For this reason, a selective DOX drug-delivery nanotechnological system constitutes a major goal in precision nanomedicine for the treatment of GBM.

Gold bioconjugates nanoparticles, have attracted great interest as they can be employed in many different biomedical applications in conjunction with specific molecules.

The aim of this work is to present a highly novel and effective strategy to target GBM by 1) improving the selectivity of cancer chemotherapeutic agents; 2) lowering the cytotoxicity of anticancer drugs to normal tissues, and thus reduce their toxic side effects. Therefore we investigated the effects of innovative synthetized PEG-Au(III) nanoparticles conjugated with both DOX and biotinylated NFL-TBS.40-63 peptide (BIOT-NFL), known to enter specifically in glioma cancer cells destroying microtubule network and inhibiting cell growth, on a human cell model of GBM constituted by U87-MG cell line.

We observed the antitumoral activity of nanoparticles (NPs) on U87-MG cells along with a decreased proliferation, increase of cell death and apoptosis in relation to the nanoparticles concentration.

These results are an outset for a new area of research and to develop new tools to study intracellular interaction of NPs which can enhance both the therapeutic efficiency and efficacy in cancer treatment.

Surface Treatment of TiO_2 Thin Films by Nitrogen Plasma Deposited by Spin Coating Sol-Gel Technique

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Abstract

In this study, TiO_2 thin films were prepared on a glass substrate via the spin-coating sol-gel technique using Tetraethyl-orthotitanate $Ti(OC_2H_5)_4$ as a precursor source of TiO_2. Following brief annealing, the obtained TiO_2 thin films are treated with nitrogen RF discharge under controlled conditions of nitrogen gas pressure and fixed plasma exposure duration. X-ray diffraction analysis showed typical peaks of the TiO_2 anatase phase. UV visible analysis exhibit transparency in the range of 75–90%, and by increasing nitrogen gas flow the energy band gap slightly decrease from 3.4 to 3.2 eV. The four-probe measurements show a decrease in electrical sheet resistivity from 35 to 17Ω.cm. The wettability test shows a super-hydrophilicity of TiO_2 thin films treated by plasma. Negligible effect on the photocatalytic activity of nitrogen plasma-treated TiO_2 thin films was observed. However, after 1 hour a significant effect of the films has been noticed.

Key-Words: TiO_2 thin films, Sol-gel processes, Plasma treatment, Photocatalysis.

Hyaluronan-cholesterol nanogels for the enhancement of the ocular delivery of therapeutics

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The anatomy and physiology of the eye have always been a limit to the local delivery of therapeutics; cornea represents the main mechanical and chemical barrier limiting the diffusion of both hydrophilic and hydrophobic drugs into the anterior camera of the eye. Thus, the use of nanocarriers able to efficiently encapsulate therapeutics appears as an attractive strategy to facilitate the permeation and enhance ocular drug delivery [1-2].
Among all the polymeric nanocarriers that have been formulated to improve the bioavailability of ophthalmic drugs, polysaccharide-based nanogels (NHs) offer several advantages, such as biocompatibility, biodegradability and mucoadhesive property [3-4]. Since its abundance in the eyes, hyaluronic acid (HA) represents a good candidate for the preparation of NHs [5].

On this basis, an HA's amphiphilic derivative, obtained by grafting the polymeric backbone with cholesterol moieties (HA-CH), was used to load both hydrophobic (dexamethasone DEX and piroxicam PIR) and hydrophilic (tobramycin TOB and diclofenac DCF) drugs and ex vivo transcorneal permeation experiments were performed to assess the capability of such NHs to behave as permeation enhancers. It has been shown that the polymeric chains of HA-CH are able to spontaneously self-assemble in aqueous environment thus forming NHs by an easy-fast preparation procedure. Ex vivo studies by fluorescence microscopy and in-tube analyses with mucin showed that HA-CH NHs can interact with corneal components, being retained on porcine corneas, but they weren't able to penetrate the stroma.

Furthermore, DEX and PIR were successfully loaded into NHs with an encapsulation efficiency (%EE) of 57% and 37% respectively, thanks to the interactions with the internal hydrophobic cholesterol domains. The encapsulation of TOB was excellent (77% EE), due to the formation of electrostatic interactions between the positively charged drug and the negatively charged HA-CH NHs, whereas very low for DCF, which is negatively charged at physiological pH (14% EE).

Finally, ex vivo permeation experiments performed on porcine corneas showed that the permeation of the hydrophilic drugs is highly enhanced by NHs compared to the free drug solutions, whereas the permeation of the hydrophobic ones is strongly dependent on the water solubility of the entrapped molecules.

In conclusion, results suggest that NHs formulations can improve the ocular bioavailability of the instilled drugs by increasing their preocular retention time (hydrophobic drugs) or facilitating their permeation (hydrophilic drugs), thus opening the route to the application of HA-based NHs in the treatment of anterior eye segment diseases.

[1] E. A. Mun et al – *Mol. Pharmaceutics* 2014, 11, 10, 3556
[2] J. C. Cuggino et al – *J. of Controlled Release*, 2019, 307, 221
[3] R. Ilka et al – *Int. J. of Biol. Macromol.*, 2018, 109, 955
[4] M. A. Grimaudo – *Int. J. of Pharm.*, 2020, 576, 118986
[5] N. Zoratto et al – *Pharmaceutics*, 2021, 13, 1781

Researcher: Ana Lia Bernardo Leonardi

Presentation Title: Novel peptide-based cholesterol biosensors

University: University of Teramo (Italy)

Presentation Type: Poster presentation

ABTRACT

Novel peptide-based cholesterol biosensors.

Ana Lia Bernardo Leonardi, University of Teramo, Fondazione Santa Lucia

Cholesterol is an amphiphilic lipid sterol-type ubiquitous in eukaryotic cells involved in controlling the activity of a wide range of membrane signaling proteins, including neurotransmitter and hormone receptors and ion channels specifically by interactions through direct binding to its transmembrane-spanning domains (TMDs). Furthermore, cholesterol homeostasis is a vital cellular process pointed as a hallmark of chronic inflammatory diseases including cancer atherosclerosis and cardiovascular diseases; neurodegenerative and neuroinflammatory diseases as Alzheimer or Parkinson, as well as fertility and obesity disorders. Thus, for understanding signaling receptors function and cholesterol trafficking and effect, is critical to identify cholesterol recognition motifs on its structures.

The goal of this study was to develop a miniaturized electrochemical biosensor based on a novel cholesterol recognition peptide. Screen-printed carbon electrode (SPCEs) modified with a biocompatible Poly-lactic acid (PLA) porous nanomembranes (NMs) were used as support for the covalent immobilization of the peptide into PLA porous. Data obtained by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) has demonstrated the effective binding affinity of the novel peptide towards cholesterol leading open the way of the implementation.

These results lead to an alternative method for cholesterol sensing by combining biorecognition motifs with biocompatible polymeric materials presumably used on living organisms.

Influence of synthesis method on structural properties and antibacterial effect of silver nanoparticles

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Abstract

This work consists of the synthesis of pure silver nanoparticles (Ag NPs) by two methods; the first is by using chemical compounds (chemical synthesis) and the second consist of use green leaves extract of *Lentisk Pistachio* plant (biosynthesis). The main objective is to replace chemical, toxic, and expensive reducing agents by 'green' products which are plant extracts or essential oils which are ecological, non-toxic, and abundant.

The results obtained showed that the nanoparticles prepared by biosynthesis method are extremely pure than the nanoparticles prepared by chemical method. While the crystallites size was to find 21 nm in the case of biosynthesized silver nanoparticles which is lower than that prepared by chemical process (34 nm).

The study of the antibacterial effect showed that the silver nanoparticles have very good antibacterial activity on all the strains tested, especially for those synthesized by green leaves extract, where the zone of inhibition reaches 18.04 mm for the concentration of 100 µg /ml. Which is going to have a promising new antibacterial strategy at the nanoscale.

Keywords : *nanoparticles, silver nanoparticles, biosynthesis, X-ray diffraction, antibacterial effect.*

Nanostructured AZO thin films deposited by confocal RF magnetron sputtering: Effect of substrate and heat treatment on physical properties

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Abstract

In the last few decades, aluminum-doped zinc oxide (AZO) thin films have been extensively studied due to their very promising electrical and optical properties. A variety of deposition methods are used for the preparation of AZO thin films. Among these deposition techniques, radiofrequency (RF) magnetron sputtering is considered to be the most widely used techniques to deposit AZO films with high crystallinity at low processing temperature and with a good control of the deposition rate on different types of substrate surfaces. In this work, RF magnetron sputtering technique in confocal configuration was used to fabricate AZO thin films with a deposition time of 1 hour 30 minutes on glass, and quartz substrates. The effects of substrate and heat treatment at 400°C for 60 min on the structural, morphological, optical and luminescence properties are studied by using various characterization techniques. X-ray diffraction patterns reveal that all the AZO thin films are polycristalline and exhibit a hexagonal wurtzite structure with a preferential orientation along the (002) plane. The crystallinity, (002) peak intensity, grain size and surface roughness of the films are found to be dependent on substrate and heat treatment. According to Ultraviolet-Visible-Near Infrared spectrophotometry measurements, as-deposited and annealed AZO thin films grown on glass substrates demonstrate a better average transparency in the visible region. Moreover, for both substrates, the annealing in air causes an enhancement in the optical transmittance and a reduction in the band gap of AZO films. Room temperature photoluminescence investigations put into evidence that emission spectra are depending on the substrate type and heat treatment. In particular an intense violet emission is observed for the AZO film deposited on quartz substrate at room temperature. The annealing at 400°C leads to the enhancement of the UV emission, the quenching of the violet emission and the improvement of the green and yellow-red bands.

Keywords: *AZO thin films, Confocal sputtering, Substrate type, Heat treatment, Physical properties*

Synthesis, characterization and physical properties of sol-gel Ag doped ZnO thin films

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Abstract

Zinc oxide (ZnO) thin films with moderate Ag doping (Ag/Zn<10%) were deposited by sol-gel dip-coating process on glass substrates. Microstructure, surface topography and optical properties of such films were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM), UV-Visible (UV-Vis) spectrophotometry and photoluminescence (PL) spectroscopy, respectively. XRD analysis shows that all the films have a polycrystalline wurtzite structure with a preferential orientation along the c-axis and exhibit a minimum residual stress. AFM results reveal that root mean square roughness of the thin films decreases from 2.58 nm to 1.62 nm with increasing Ag concentrations. According to UV-vis. measurements, the undoped ZnO thin film is highly transparent in the visible region with an average transmittance of about 83%. As the concentration of the doped Ag increases the transmission slightly decreases. Moreover, the direct optical band gap is found to increase with increasing Ag doping concentration. Room temperature PL spectra put into evidence that emission is found to be influenced by Ag content. The UV emission initially increased with increasing Ag doping up to 6% and then decreased, whereas the intensity of the visible emission decreased with the increase in the Ag concentration from 0 to 3% and then increased for higher concentrations. The high quality of Ag doped ZnO thin films with interesting optical properties suggests that these films may have good applications in optoelectronics.

Keywords: ZnO:Ag thin films, Sol-gel process, Microstructure, Optical properties, optoelectronic applications.

Hyaluronan-Cholesterol Nanogels: Novel Nano-delivery Systems for Topical Transdermal Delivery of Betamethasone in Potential Psoriasis Treatment

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Background: Psoriasis is an inflammatory skin disease affecting about 2~4% of the worldwide population, and betamethasone (BM) is commonly used glucocorticoid in its treatment [1]. However, the current treatment options are limited due to the inherent skin barriers and poor bioavailability of BM in conventional formulations. Polymeric nanogels (NHs) is a promising strategy in the improvement of cutaneous drug delivery [2]. Among various polymeric carriers, cholesterol (CH) grafted hyaluronic acid (HA) is an excellent candidate as both components occur naturally in the skin [3].

Aim: Developing HA-CH NHs based formulation for BM encapsulation. Evaluating the skin permeability both *in vitro* and *ex vivo*, as well as the potential advantages for psoriasis therapy.

Methods: Amphiphilic HA-CH was synthesized by grafting the CH moieties onto polymeric backbone, giving spontaneously self-assembly ability in aqueous environment. BM-loaded NHs were incorporated into Carbopol based hydrogel to improve rheological properties for topical applications. The properties of nano-systems, such as size, ζ potential, encapsulation efficiency (EE%), rheological properties, and *in vitro* drug release profiles were investigated. Both *in vitro* (Strat-M® membrane) and *ex vivo* (pig ear skin) permeation capacities were evaluated by Franz diffusion cells. Further skin permeation and deposition was studied by confocal fluorescence microscope.

Results and conclusion: HA-CH NHs showed high EE% (apparent solubility of BM improved up to 9-fold), small size (~190 nm) and good stability. Besides, Carbopol based gel system exhibited excellent rheological properties for skin application. The *in vitro* sustained drug release lasted for over 8 hours. The obtained results revealed that the NHs system can effectively promote skin permeation and retention in the deeper layers of epidermis and dermis, making it advantageous for topical BM delivery. Overall, we have developed a novel HA-CH NHs system for effective BM loading and skin delivery, which shows promise in the psoriatic topical treatment.

[1] A. Rendon et al. Int. J. Mol. Sci. 2019, 20, 1475.
[2] J.C. Cuggino et al. J. of Controlled Release 2019, 307, 221-246.
[3] N. Zoratto et al. Pharmaceutics 2021, 13, 1781.

Effect of Substrate Nature on the Microstructural, Morphological and Optical Properties of Nanostructured TiO_2 Thin Films Deposited by RF Magnetron Sputtering

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ABSTRACT

Titanium dioxide (TiO_2) thin films were successfully fabricated on three different substrates (glass, quartz and silicon (Si(100))) at room temperature with a deposition time of 90 min using the RF magnetron sputtering technique. The TiO_2 thin films are then air annealed at 400 °C for one hour and the effect of the substrate type on the microstructure, morphology, surface topography, transmission and optical band gap of these films was studied by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), Atomic force microscopy (AFM) and UV-Visible (UV-Vis) spectrophotometry. XRD analysis showed that all thin films are polycrystalline and only crystallize in the anatase tetragonal structure of TiO_2 with a preferred orientation along the (101) plane. Crystallinity, peak intensity and crystallite growth were found to be dependent on substrate type. The observed Raman peaks confirmed the presence of anatase phase in all samples in good agreement with XRD data. SEM and AFM images showed that TiO_2 thin films have different surface topography, which seems to be influenced by substrate type, as expressed by the average grain size and surface roughness. Transmission spectra demonstrated that the TiO_2 thin films grown on quartz show a higher average transmission in the visible range than that deposited on a glass substrate. In addition, the obtained values of band gap and refractive index for TiO_2 thin films deposited on glass and quartz substrates were found to be 3.615 and 3.512 eV and 2.248 and 2.271 eV, respectively.

Keywords: TiO_2 thin films, RF sputtering; Substrate nature; Transmittance and bandgap; Optoelectronic applications.

METAL-ORGANIC-FRAMEWORKS COMPOSITES FOR INNOVATIVE SEPARATION TECHNOLOGY

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Keywords: magnetic nanoparticles, MISA, metal-organic frameworks composites

This work aims to develop innovative materials for the implementation of a new technology called MISA (Magnetic Induction Swing Adsorption) to improve the separation efficiency of CO_2/N_2 mixtures in the industrial sector. MISA is based on the use of composite materials consisting of a porous organic component and magnetic nanoparticles. The heating generated under the action of a magnetic field by the nanoparticles determines the release of the gas adsorbed on the organic material, allowing the sorbent regeneration. The advantages of this technology are fast regeneration, indirect heating and high energy transfer efficiency. MISA efficiency is related to the material properties. We have developed the synthesis of a novel composite consisting of magnetite nanoparticles embedded into the HKUST-1 metal organic framework. The latter was selected due to its high carbon dioxide uptake capacity and selectivity. The composite is synthesized at room temperature by a simple and fast mechanochemical process which involves two steps: functionalization of magnetite nanoparticles (previously synthesized by thermal decomposition method) with trimesic acid and growth of organic framework on the nanoparticles surface. Produced composites were characterized by structural, chemical, thermal and morphological analyses. CO_2/N_2 adsorption/desorption properties were evaluated by both static and dynamic measurements.

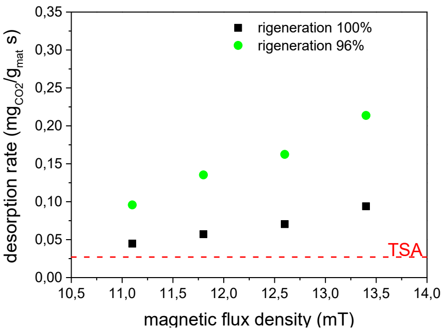

Figure 1. Productivity of the composite material as a function of the applied field. The figure also shows the value determined by conventional heating (TSA-Thermal Swing Adsorption).

MOLECULAR CHARACTERISTICS OF SUCROSE AQUEOUS SOLUTION

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The study of structural features and molecular characteristics in aqueous solutions is one of the most actual problems facing modern biophysics and molecular biology [1-4]. The aqueous solution of sucrose has both scientific and practical importance due to its unique physicochemical properties and wide range of practical applications. Also, the study of the physicochemical properties of sucrose aqueous solutions is very important for providing fundamental theories of water-soluble carbohydrates. In a number of cases, sucrose affects various processes, and the study of the molecular mechanism of this effect stimulates a wider study of sucrose-aqueous solutions. It should be noted that most of the functional activity of sucrose is related to the water environment. Therefore, the comparative study of the molecular characteristics of sucrose aqueous solutions by different methods is quite necessary.

In this work, the dynamic viscosity and density of the sucrose aqueous solutions have been measured in the temperature range of 20-50^{0}C and the mass fraction concentration of sucrose in the range of 0-60%, as well as the absorption spectra of the solutions in the IR region, has been recorded. Based on the analysis of viscous flow properties and IR absorption spectra of the considered system, structural properties have been investigated. Based on experimental results Gibbs energy (ΔG_η), activation enthalpy of viscous flow (ΔH_η), activation entropy of viscous flow (ΔH_η), structural temperature (T_0), hydrogen bond energy (E_H) and length (R_H) of water molecules in solution has been determined (table).

Table. Gibbs energy of activation of viscous flow (ΔG_η), activation enthalpy of viscous flow (ΔH_η), activation entropy of viscous flow (ΔS_η), structural temperature (T_0), frequency of valence oscillations of OH groups of water molecules (ν), the hydrogen bond energy between water molecules in solution (E_H) and length (R_H) (t=20^{0}C) in different concentrations of sucrose aqueous solution.

C, %	ΔG_η, C/mol	ΔH_η, C/mol	ΔS_η, C/(K·mol)	T_0, K	ν, sm^{-1}	$-E_H$, kC/mol	R_H, Å
0	9292	17397	27.65	146	6862.00	16.3	1.86
10	10112	19265	31.22	148			
20	11230	21090	33.64	151	6857.08	16.7	1.85
30	12640	23027	35.43	154			
40	14484	26398	40.64	159	6847.07	17.1	1.84
50	17010	33526	56.34	165			
60	20630	43036	76.43	170	6833.77	18.0	1.82

As can be seen from the table, the values of ΔG_η, ΔH_η, ΔS_η, T_0, and E_H quantities increase, while the values of ν and R_H quantities decrease with the increase in concentration for the sucrose aqueous solution at a given temperature. We assume that the obtained results are related to the structuring effect of sucrose on water and the further strengthening of this effect depending on the concentration. We assume that the obtained results are due to the structuring effect of sucrose on water and it is related to the strengthening of this effect depending on the concentration.

REFERENCES

1. Masimov E.A., Hasanov H.Sh., Pashayev B.G. // Russian Journal of Physical Chemistry, 2013, vol. 87, №6, p. 948.
2. Almasy L., Artykulnyi O.P. Petrenko V.I., Ivankov O.I., Bulavin L.A., Yan M., Haramus V.M. // J. Molecules. 2022. V. 27. p. 2573.
3. Pashayev B.G. // Conference Proceedings, Modern Trends In Physics Baku, 01-03 May 2019, p. 170.
4. Masimov E.A., Pashayev B.G., Rajabov M.R. // Russian Journal of Physical Chemistry, 2020, vol. 94, № 12, p. 2574.

Dielectric response of atomically precise nanoribbons: band-gap effect vs low-dimensional confinement

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Nanoribbon based structures are promising prototypes for high-performance, atomically-compact and ultra-low power devices, whose functioning is controlled by charge density waves induced at the interface of the materials with the external dielectric environment. The associated plasmon modes are here scrutinized by looking at the frequency-dependent permittivity of a class of graphene, silicene, and germanene, nanoribbons, being 5 atoms wide, over the whole optical range, from the far-infrared to the near-ultraviolet.
Time-dependent density functional theory is used, with a specifically developed tool on the random phase approximation, which provides the diverse dielectric response of isolated (purely one-dimensional) nanoribbons and correlated (two-dimensional) nanoribbon arrays. Many-electron correlations are taken into account, at the level of the Bethe-Salpeter equation formalism.
The main technological interest is on the bulk plasmon, whose propagation and interplay with the edge plasmons are comprehensively analyzed down to the terahertz domain, which is expected to guide the implementation of novel graphene nanoribbon architectures.

References

[1] Plasmon modes of graphene nanoribbons with periodic planar arrangement. C. Vacacela Gomez, M. Pisarra, M. Gravina, J. M. Pitarke, and A. Sindona Phys. Rev. Lett. 117, 116801 (2016)

[2] Plasmon oscillations in two-dimensional arrays of ultranarrow graphene nanoribbons. A. Sindona, M. Pisarra, S. Bellucci, T. Tene, M. Guevara, and C. Vacacela Gomez. Phys. Rev. B B 100, 235422 (2019).

[3] Dielectric screening versus geometry deformation in two-dimensional allotropes of silicon and germanium. A. Sindona, C. Vacacela Gomez and M. Pisarra. Sci Rep 12, 15107 (2022). https://doi.org/10.1038/s41598-022-19260-y

[4] Massive and massless plasmons in germanene nanosheets. M. Pisarra, C. V. Gomez and A. Sindona. Sci Rep 12, 18624 (2022). https://doi.org/10.1038/s41598-022-23058-3

Figures

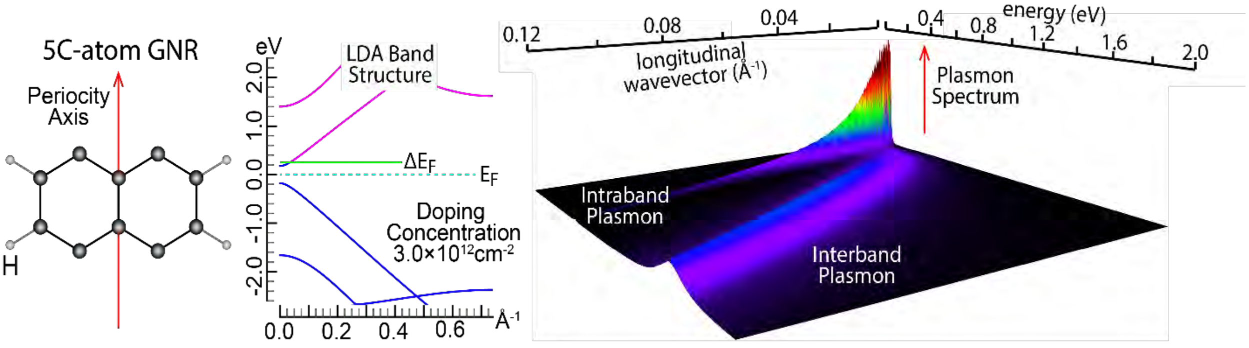

Figure 1: Geometry, Band Structure, and Plasmon Spectrum of a 5-carbon-atom-wide graphene nanoribbon with an induced Fermi energy shift of 0.25 eV (due to doping or gating)

$Ni_{60}Co_{40}$ NANOPARTICLES SUPPORTED ON γ-Al_2O_3 AS MAGNETIC CATALYST FOR INDUCTION HEATED REFORMING REACTIONS

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Keywords: Induction heating, Magnetic catalysis, Steam reforming, Ferromagnetic nanoparticles

Reforming reactions are presently the main route to hydrogen production. Due to thermodynamic constraints, temperatures higher than 750°C are commonly utilized to achieve high equilibrium conversions. It follows that the productivity of reforming plants is very dependent on how efficiently heat can be transferred to the catalytic bed. Among the different energy transfer options, induction heating is a technology well known for its high efficiency. Energy is supplied directly to a suitably responding magnetic material by a radiofrequency alternating magnetic field, in a fast and efficient way.

In this work, we report our experimental results on the catalytic activation of steam reforming of methane powered by induction. At the scope, a catalyst composed by $Ni_{60}Co_{40}$ nanoparticles supported on commercial γ-Al_2O_3 pellets was developed. The metallic nanoparticles act at the same time as heating agents and catalysts for the steam reforming reaction[1]. In such a way the heat of reaction is provided instantaneously and remotely on the chemically active site avoiding dissipation due to inefficient transfer from outside the reactor. Depending on the metal content and the adopted synthesis procedure, temperatures in the range 600°C-750°C have been reached showing promising equilibrium methane conversion values.

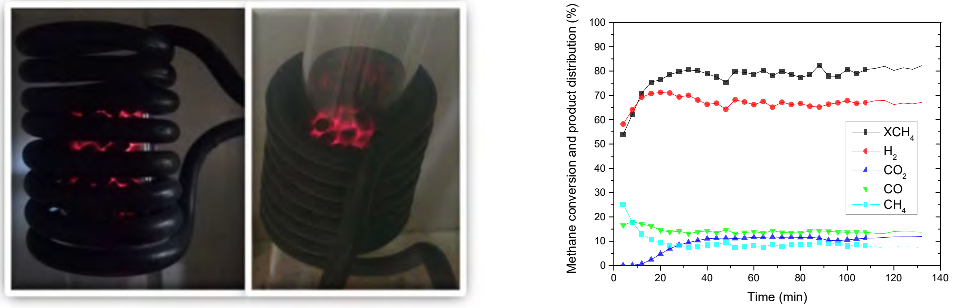

Fig. 1. (a) Induction heated $Ni_{60}Co_{40}$ on γ-Al_2O_3 (180 pellets) inside a tubular quartz reactor. (b) Methane conversion and product distribution (Volumetric inlet flow: N_2 = 90 mL min^{-1}, CH_4 =50 mL min^{-1}, H_2O = 100 mL min^{-1}) upon the application of Ip=130A (B=23.1mT) to the coil.

[1] C. Scarfiello, M. Bellusci, L. Pilloni, D. Pietrogiacomi, A. La Barbera, F. Varsano, Int. J. Hydrogen Energy 46, 2021, 134-145

EVALUATION OF STIFFNESS INFLUENCE IN A 3D BIOMIMETIC MICROENVIRONMENT OF GLIOBLASTOMA.

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Abstract

Glioblastomas (GBM) are the most common and malignant of brain tumors, with a poor survival rate after diagnosis, and represent the IV grade of Glioma, according to WHO classification. The prognosis for patients is poor, showing a median survival of 1,5 years, depending on tumor invasiveness and radio-chemoresistance. One alternative for better clinical outcome is to identify targets with essential roles in the microenvironment survival signal. The uncontrolled proliferation of tumors limits the availability of oxygen, inducing a hypoxic state, giving a typical characteristic to microenvironment feature in mostly of solid tumors. During GBM development the extracellular matrix has variations to increase the fibrosis, affecting the extracellular stiffness. These changes could activate different pathways related to improve cell survival, one of these is the YAP/TAZ pathway. This activation is regulated by mechanical cues, as stiffness and actin remodelation. To understand the GBM cells response to physical cues of the microenvironment we have developed different platforms using mixes of Agar-Pluronic (F125) with varying concentrations in order to obtain different stiffnesses. *The main aim of this work* was to characterize the effect of stiffness on GBM survival and to evaluate effectors involved of YAP/TAZ pathway as metalloproteinase 2 (MMP2), Oct-4, and SOX-2 related to invasiveness and cell division. To test these parameters, we used U87 cell line derivates from glioblastoma and Glioma Stem Cells. We show that our mixes are stable using swelling and degradation tests until day 7. In agreement with these results, the glioblastoma cells are able to survive using our platforms and we were also able to observe growth of U87 spheroids after 7 days of incubation. These results demonstrate that our scaffolds represent a good tool to mimic the extracellular tumor microenvironmental.

HYDROGEN SULFIDE DELIVERY NANOTECHNOLOGIES IN WOUND HEALING: THE SULFUROUS THERMAL SPRING WATER POTENTIAL ON A DRESSING

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Abstract

The multiple positive effects of hydrogen sulfide (H_2S) on several pathologies and health threating conditions are well established. The efficacy of an exogenous supply of this gas-transmitter is related to the advantages represented by its pre-existing endogenous synthesis by enzymes present in all human tissues, skin included. These chemical patterns represent the main support to the medical effectiveness of sulfurous thermal spring waters in different health pathologies and skin ailments. Hard to heal-chronic wounds represent an increasing economic and social burden. Several studies analyzed the advantages of H_2S delivery on wounds despite their etiologies. Being a volatile molecule, H_2S is difficultly delivered by conventional dressings whereas Nano technology and nano-carriers may represent the perfect example of translational application. Here, we present a systematic review of available H_2S nano-dressings for wound healing purposes aimed at evaluating the effectiveness of this extremely technological dressing miming the natural healing effect of sulfurous spring thermal water.

Methods:

We reviewed all articles concerning the effectiveness of nano-technologies dressing delivery H_2S for wound healing purposes interrogating the following bibliographic, citational databases and search engine: PubMed (Medline), Scopus, Web of Science (Science and Social Science Citation Index), Cochrane Library and Scholar Google. The research has been performed using the keywords and MeSH terms: “H_2S”, “nano”, “dressing”, “wound”, “delivery”, “releasing”. The research considered all the articles published up to the 1st May 2023. Results were independently examined by 3 main investigators.

Results:

From a first research 4670 articles were found, after abstract reading and duplicates removal, 56 abstract were eligible to full text reading. Finally, 25 articles met the inclusion criteria, 9 focused on diabetic wounds. All articles reported positive outcomes expressed in term of cell proliferation, migration, wound healing promotion and re-epithelization.

Conclusion:

By date, H_2S-releasing nano engineered dressings showed a great, still unexplored, potential in wound healing.

References:

1. Pinto RV, Carvalho S, Antunes F, Pires J, Pinto ML. Emerging Nitric Oxide and Hydrogen Sulfide Releasing Carriers for Skin Wound Healing Therapy. ChemMedChem. 2022 Jan 5;17(1):e202100429.
2. Fan J, Pung E, Lin Y, Wang Q. Recent development of hydrogen sulfide-releasing biomaterials as novel therapies: a narrative review. Biomater Transl. 2022 Dec 28;3(4):250-263

REVIEW: OPPORTUNITIES AND CHALLENGES OF GAS SENSORS BASED ON GRAPHENE NANOMATERIALS

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A single-layer allotropic type of carbon known as graphene is flexible, light, and very resistant. There are numerous uses for graphene and nanomaterials based on it, mostly in the fields of medication delivery, electronics, energy, and the military. The possibility of graphene as a gas sensor is one of the material's intriguing uses. The exceptionally high surface-to-volume ratio of graphene, an atom-thick carbon material, makes it an attractive candidate for the detection of gaseous molecules. The scientific literature was studied for this purpose and the benefits and drawbacks of utilizing graphene as a gas sensor were examined. Even though solid-state gas sensors possess advantages such as small size, low power, high sensitivity, and low cost for detecting very low concentrations of a wide range of gases in the range of parts per million, they suffer from problems associated with long-term stability and limited measurement accuracy [1].

The main issue in the creation of such sensors is the large surface-to-volume ratio, which plays an important role in the determination of very small amounts of gases, which so far have been difficult for traditional sensors to determine, and so the corresponding materials developed in the nanometer range overcome the existing deficiency in this field as well. allows to lift. Since graphene has high electrical conductivity and sensitivity, it also has very high effects on changing the chemical environment. It was shown in [2] that the two-dimensional structure of graphene makes the electron transport through graphene highly sensitive to the adsorption of gas molecules. Some of the advantages of these graphene-based sensors have been their easy operating principle, high robustness, excellent durability, and efficient performance in terms of sensitivity and longevity [3,4]. Additionally, using graphene as a gas sensor has some drawbacks. The band gap does not exist in the basic case of graphene. Different additives are doped into grapevine to increase its sensitivity as a gas sensor. When the sensors react with the gases, the presence of noble metals enhances the change in signals. Through weak hybridization at the graphene's surface, the adsorption of the gaseous absorbents contributes holes or electrons to the material. While electron-withdrawing gases like NO_2 increase the final conductance of the prototypes, electron-donating gases like NH_3 decrease the overall conductance [5,6]. Porous microstructures are created when nanocomposites made of polymers are formed, hastening the migration of gaseous molecules into the sensing layers. The total response is also influenced by the presence of water molecules on the sensing surface of these graphene sensors. As demonstrated above, a great amount of work has been put into creating graphene-based sensors and utilizing them for gas-sensing applications. There are still certain limitations in the current situation despite the fact that a lot of work has been put into fabricating and implementing graphene-based gas sensors. To determine the robustness and longevity of the gas sensors created in the controlled environment, measurement of the sensors must be done. The production of graphene is still a problem from a fabrication standpoint.

References:

[1] *S. Capone, A. Forleo, L. Francioso, R. Rella, P. Siciliano, J. Spadavecchia, et al., Solid state gas sensors: State of the art and future activities, Journal of Optoelectronics and Advanced Materials 5 ,2003, 1335-1348.*

[2] *G.H. Lu, L.E. Ocola, J.H. Chen, Reduced graphene oxide for room-temperature gas sensors, Nanotechnology 20,2009, 445502-4455011.*

[3] *Wang, T.; Ouyang, Z.; Wang, F.; Liu, Y. A review on graphene strain sensors based on fiber assemblies.* SN Appl. Sci. *2020,* 2*, 862.*

[4] *Vasseghian, Y.; Dragoi, E.-N.; Moradi, M.; Khaneghah, A.M. A review on graphene-based electrochemical sensor for mycotoxins detection.* Food Chem. Toxicol. *2021,* 148*, 111931.*

[5] *Singh, E.; Meyyappan, M.; Nalwa, H.S. Flexible graphene-based wearable gas and chemical sensors.* ACS Appl. Mater. Interfaces *2017,* 9*, 34544–34586.*

[6] *Yuan, W.; Shi, G. Graphene-based gas sensors.* J. Mater. Chem. A *2013,* 1*, 10078–10091*

Non-adiabatic time evolutions and irreversible entropy production

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In recent decades, thanks to the advancements in experimental quantum physics, it has become possible to prepare and control increasingly complex quantum systems. The field of quantum thermodynamics aims to study the energetics of such systems, taking into account their quantum nature and related phenomena such as the generation of coherences or correlations. It seeks to understand whether these phenomena represent a barrier or an advantage.

In our work, we focused on studying the role of non-adiabatic evolutions in the production of irreversible entropy in a closed quantum system that is taken out of equilibrium through a time evolution generated by a time dependent Hamiltonian. In general, taking a system out of equilibrium is always accompanied by the production of a certain amount of irreversible entropy.

As a general result, we have shown that the produced irreversible entropy can be divided into two contributions: an adiabatic contribution, which is related to the variations in the energy gaps in the spectrum of the Hamiltonian under consideration, and a non-adiabatic contribution that depends strictly on the rotation speed of the eigenspaces in Hilbert space.

Subsequently, we applied this decomposition to two physical models. The first one involved a qubit taken out of equilibrium, with a time-dependent Hamiltonian causing changes in energy gaps and rotations of eigenspaces. By studying the production of irreversible entropy in this system as a function of the process duration, as expected from the general results, we observed that the longer the process duration, the more the system evolves adiabatically. Consequently, the only contribution to the production of irreversible entropy is the adiabatic one, which represents a lower bound for the thermodynamic quantity under examination.

As a second example, we examined a qubit whose temporal evolution is generated by a Landau-Zener Hamiltonian. In this case, we demonstrated that the produced irreversible entropy strongly depends on the presence of an avoided crossing between the eigen-energies.
It is Known that when a quantum system initially prepared in its ground state is driven across a quantum critical point (QCP), the dynamics fails to be adiabatic however slow the rate of change in the parameters of the Hamiltonian may be. So our purpose was studying the irreversible entropy production in systems that exhibit a quantum phase transition (QPT).
So, we considered the transverse Ising model and studied irreversible entropy production in the case of instantaneous quench of the external field (infinitesimal and non) by studying its low and high-temperature limits. Next, we studied the case in which the quantum phase transition is induced by a linear ramp of the external field. In the latter case, we used the results obtained for the Landau- Zener model, showing that the diabatic term appearing in the expression of irreversible entropy production has the same scaling, with respect to the quench velocity, as predicted by the Kibble-Zurek theory for the density of topological defect. Again, studying low and high temperatures limits we have reached the conclusion that the higher the temperature, the more the system behaves adiabatically.

Coating and intercalation of h-BN nanoparticles with Fe and Fe_3O_4

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Hexagonal boron nitride h-BN matrix magnetic nanopowder composites are synthesized chemically by coating and/or intercalation of h-BN nanoparticles with ferromagnetic iron Fe and/or its ferrimagnetic oxide Fe_3O_4 (magnetite). Studying of room-temperature magnetization curves confirms their potential to be effectively applied in BNCT (Boron Neutron Capture Therapy) as agents of external magnetic field controlled delivery of neutron-capturing boron isotope ^{10}B to target cancer cells.

RADIATION CROSSLINKING OF BUTADIENE NITRILE COPOLYMER COMPOSITES WITH ZINC OXIDE NANOPARTICLES: ENHANCING PHYSICOCHEMICAL PROPERTIES

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Introduction. The topic of this scientific research is highly relevant due to the increasing applications of elastomers based on nitrile rubbers. These elastomers possess desirable properties such as resistance to gasoline and oils, wide temperature range, low gas permeability, and resistance to radiation and thermal aging. As a result, they are extensively used in industries such as electrical, mechanical, and petrochemical, where products and parts come into contact with aggressive media.

With the emergence of new applications for nitrile elastomers and the tightening of requirements for their performance, the need to develop new elastomer materials has gained significant research attention. A primary concern in the rubber industry is environmental pollution caused by the use of various chemicals in production processes. The European Union (EU) has reported that the rubber industry consumes approximately 100 thousand tons of zinc oxide (ZnO) and other zinc-containing additives annually as activators. To address this, the EU has developed the Eco Zinc concept to reduce the use of zinc in products. However, the small specific surface area of finely dispersed ZnO results in a limited reaction with accelerators, leading to a significant amount of this compound remaining in the vulcanizate. The release of such compounds into the environment is considered toxic to the body.

Numerous studies have focused on investigating the structure, thermomechanical properties, and the molecular and supramolecular level transformations of polymers induced by ionization effects. These investigations contribute to a deeper understanding of the behavior and characteristics of polymer systems when subjected to radiation, enabling the development of tailored materials with desired properties [1]. The utilization of radiation methods in nanotechnology presents an excellent opportunity for the development of novel functional polymeric materials with enhanced properties. It offers the advantage of controlling the size and distribution of nanoparticles within the polymer matrix. In nanosystems composed of filled polymers, the application of ionizing radiation leads to the formation of a three-dimensional network not only within the matrix but also between the elastomer macromolecules and the filler particles. The presence of nanoparticles in this system serves as centers for energy absorption and facilitates the activation of the polymer crosslinking process. The issues of the influence of nanosized oxide fillers on the process of structure formation during radiation vulcanization and on the physicomechanical and operational properties of compositions based on nitrile butadiene rubbers have received little attention, both theoretically and practically.

The aim is to reduce the use of zinc oxide powders while achieving enhanced elastomeric material performance. This research addresses the need for improved elastomer materials, considering environmental concerns and the industry's demand for higher quality and performance. By exploring alternative methods of rubber compound preparation, this study aims to contribute to the development of elastomers with improved properties for various. Applications [2].

Materials and methods. The research focused on investigating the properties of nitrile butadiene rubber (NBR), which is a copolymer synthesized from butadiene and acrylonitrile. In this study, metal oxide nanoparticles of ZnO (specifically, 20-25 nm particles obtained from Sigma Aldrich) were employed as an activator. Additionally, low-molecular chlorine-containing compounds, triazine compounds, and carbon black were utilized as accelerators, crosslinking agents, sensitizers, and fillers in the radiation-chemical processes.

The γ-radiation (Co^{60}) source was employed to activate the radiation-chemical vulcanization process. This was carried out using the MRX-γ-25M installation, which facilitated the controlled application of γ-radiation to induce the desired crosslinking reactions in the NBR-based composites.The mechanical properties of the vulcanizates, as well as their resistance to aging in different aggressive media, were evaluated using a universal testing machine. The testing procedures followed established standards ASTM D573 and ASTM D412to ensure accurate and reliable measurements.

Result and discussion. These radiation (D=250 kGy) and thermoradiation (T=423K x 5 min, D=250 kGy) vulcanization methods were compared with a model mixture obtained through thermal (sulfur) (T=423Kx40 min.) vulcanization. Sulfur vulcanization is a widely used method in rubber industry, where sulfur and accelerators are added to initiate crosslinking. By comparing the properties of the rubber compounds prepared using different methods, the study aimed to determine the effectiveness of thermal and thermoradiation methods in improving the physical and mechanical properties of the elastomeric materials.

Table 1. Mechanical properties of vulcanizates based on nitrile-butadiene rubber obtained by different methods

Mechanical parameters	Type of vulcanization		
	Sulphur	Irradiation	Thermo-radiation
Stress at 300%, MPa	10	8	12
Tensile Strength (σ), MPa	25	18	26
Elongation at break (ε_b), %	480	600	460
Hardness (Shore A)	65	60	65
Compression set resistance *(20%, 150˚C, 72 h.)*	62	57	52
Dynamic endurance during cyclic stretching (N) (150%, 500 cyc/min)	20	20	23
Aging coefficient, K, % (150˚C, 150 h.)			
by tensile strength (σ)	0,70	0,82	0,85
by elongation at break (ε)	0,52	0,62	0,64
by dynamic endurance (N)	0,75	0,77	0,77
Change of mass after swelling in mix of benzyl-benzene (3:1) (353K, 24h), %	38	30	27

The composition of the mixture - 100 wt.h. NBR: ZnO - 4.0; DSHB - 4.0; DAFST - 3.0, fuel oil: bitumen - 3.0, carbon black P324 - 50.0.

Note: During thermal vulcanization, in addition to mixture 2.0, with thermal radiation 0.2 kb.h. sulfur is included.

The study's results indicate that vulcanizates obtained with C-C cross-links exhibit superior resistance to aromatic hydrocarbons compared to polysulfide bonds ($C\text{-}S_x\text{-}C$). This was observed, for example, when gasoline-benzene (3:1) was tested on radiation vulcanizates made from NBR elastomer (Table 1). Additionally, the strength and elastic properties of thermoradiation vulcanizates were found to be higher than those of radiation and sulfur vulcanizates.

To assess the performance of elastomeric materials (specifically seals) used in sealing applications on drilling rigs, comparative tests were conducted in aggressive environments. These tests aimed to determine the impact of temperature and operating conditions on the performance of the elastomeric materials. By subjecting the materials to these conditions, their resistance and suitability for such applications could be evaluated and compared.

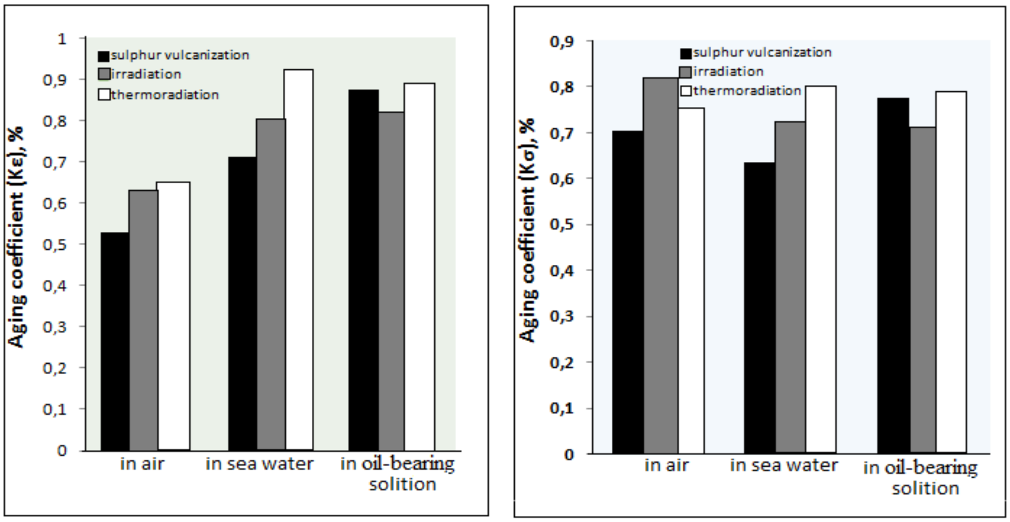

Figure 1. Dependence of ageing coefficients on tensile strength and elongation at break in different coditions

The obtained data suggest that sulfur seals exhibit less swelling and residual compressive strain accumulation compared to sulfur elastomers. On the other hand, sulfur seals demonstrate a higher coefficient of thermal aging in sea water and oil-bearing solutions compared to sulfur elastomers (Fig. 1.). Additionally, radiation vulcanizates showed lower tensile strength after contact with the medium compared to sulfur and thermoradiation vulcanizates.

The observed differences in behavior can be attributed to the distribution of cross-link lengths between neighboring nodes in the vulcanization network [3] It is believed that in the presence of energetically weak bonds like C-Sx-C, molecular chains tend to break when stretched. Consequently, the presence of a significant number of such bonds in the vulcanizate structure can lead to decreased thermal stability and reversion resistance. In contrast, the presence of heat-resistant C-C bonds help to irreversibly fix stresses, while the presence of easily rearranged polysulfide bonds promotes relaxation processes. This results in a network structure without strong internal stresses.

Conclusion. The results of the study on radiation-chemical vulcanization utilizing a nanoparticle activator, cross-linking agent, sensitizer, plasticizer, and filler have demonstrated the ability to produce elastomeric materials surpassing sulfur-based materials in terms of their physical and mechanical properties. Based on these findings, a specific composition for an elastomeric sealing material was determined, showcasing resistance to wear in sea water and oil solutions within a temperature range of 80-120ºC. Additionally, the material exhibited durability against numerous deformations and dynamic loads.

References

1. Wu J, Xu Z, Zhai M, Zou M, Guo Z. Effect of gamma radiation on the mechanical properties of nitrile butadiene rubber. Radiation Physics and Chemistry. 2008;77(3):251-254.
2. Thakur S, Singha NR, Das A, Jha S, Kumar A, Pradhan D. Influence of gamma radiation on the thermal and mechanical properties of butadiene acrylonitrile rubber–silica composite. Radiation Physics and Chemistry. 2017;130:457-465.
3. R. F. Khankishiyeva, The improvement of physical and mechanical properties of sealers based on nitrile-butadiene rubber and combination of nano metal oxides // SOCAR Proceedings, – 2020, vol.3, – p. 164–172.

Structural evaluation and thermal properties of nanocrystalline $Ti_{50}Ni_{43}Cu_7$ prepared via Mechanical Alloying

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Abstract

The process of mechanical alloying and annealing has been employed to produce a nanocrystalline NiTiCu shape memory alloy. A high-purity mixture of the elements Ni, Ti, and Cu with a nominal composition of $Ti_{50}Ni_{43}Cu_7$ was exposed to intensive mechanical alloying in a energy ball mill under various milling conditions .The fabricated alloys were characterized byX-ray diffraction and scanning electron microscopy.
Experimental results demonstrated that after an optimum milling time of 48h,NiTiCu(B_{19}) phase with the crystallite size of less than 20 nm was achieved.Milled powders were annealed at 1491 K for 900 seconds to produce a nanometric NiTiCu (B_{19}) phase, relieve internal strain, and promote grain development.
The results of the investigations demonstrated that high-energy milling, followed by annealing, produced nanocrystalline NiTi alloy with the required shape and homogeneous structure.

It was also discovered that the milling duration has a significant impact on the thermal behavior of alloyed powders

Keywords : nanocrystalline $Ti_{50}Ni_{43}Cu_7$, Thermal analysis, Mechanical Alloying

Optical and Photoluminescent Properties of Polypropylene/ZnO based Nanocomposites

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Abstract

Nanocomposite materials were obtained by incorporating ZnO NPs into a polypropylene matrix using solution blending and hot pressing methods. UV-Vis and photoluminescence spectroscopic methods were used for investigation. According to UV-vis spectroscopic analysis, a characteristic absorption peak of ZnO NPs at 373 nm wavelength appeared, which is related to the internal absorption of the ZnO band gap characteristics. Furthermore, the photoluminescence (PL) spectrum of PP/ZnO nanocomposites was investigated depending on weight percent of NPs. The intensity of the PL spectrums increases with the increase of the weight percent of NPs that is explained by the raising of the luminescence centers in the nanocomposite material. These luminescence centers are the emission of deep-level defects, such as interstitial defects of zinc atoms and oxygen vacancies.

Keywords: *nanocomposite, polypropylene, zinc oxide,absorbtion, photoluminescence*

Polymer nanocomposite materials based on ZnO nanoparticles (NPs) attracted attention due to their optical, mechanical, and electrical characteristics [1-3]. Inorganic NPs incorporation into thermoplastic polypropylene (PP) matrix generated significant characteristics improvements and founds industrial applications in many aspects of technology. It is possible to take advantage of both materials' functional properties like good structural flexibility, optical transparency [4-6], mechanical and optoelectronic characteristics of PP, and high transparency, electron mobility, and electrical properties of ZnO NPs.

In this research, polymer nanocomposite samples were obtained through incorporation of 1, 3, 5, 7, and 10 wt% ZnO NPs into PP matrix. Solution blending and hot pressing methods were used for the preparation of the polymer nanocomposites [7]. Firstly, PP was added to toluene (PP/toluene), and was mixed at 100°C in a magnetic stirrer for 20-30 min. Secondly, a certain weight percent of ZnO NPs (10-30 nm) and toluene mixture (ZnO/toluene) was prepared and dispersed by ultrasonic cavitation for uniform distribution. Then ZnO/toluene was added to the PP/toluene solution and stirred for 30 min. The obtained solution was filtered into a petri dish and dried in a vacuum oven at 60°C within 3 hours. After solvent evaporation white cracks texture of the nanocomposite was obtained. Finally, dried sample was compressed under 100 kPa pressure at 160°C and thin film was obtained. Polymer nanocomposite thin film samples were produced in a followed way for various weight percent of the NPs (namely 1%, 3%,5%,7%, and 10%).

Fig. 1 shows the absorption spectra of the pure PP matrix and PP/ZnO nanocomposites prepared with different weight percent of NPs.

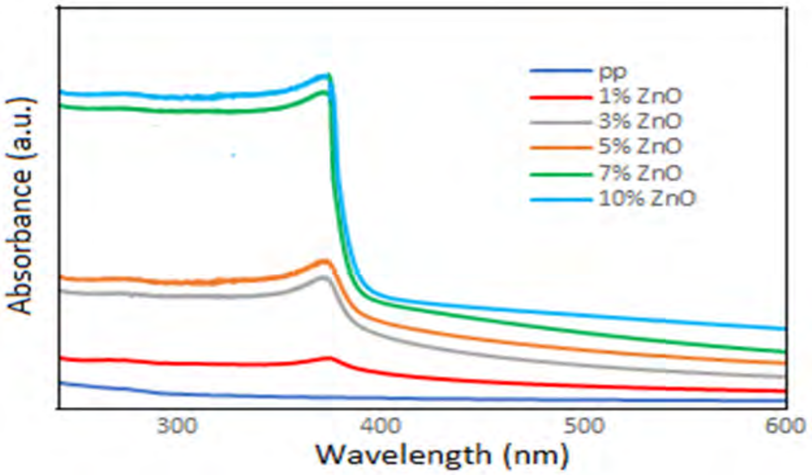

Fig. 1 Absorption spectra of PP and PP/ZnO polymer nanocomposites

A characteristic absorption peak of inorganic phase at 373 nm wavelength appeared due to the transition of electrons from the valence band to the conduction band, which may be related to the internal absorption of the ZnO band gap characteristics [8]. Furthermore, the samples' spectra did not include any shifts, although their intensity increased by increasing the weight percent of ZnO NPs in the polymer matrix. It was revealed that ZnO NPs were not agglomerated during nanocomposite formation and were homogeneously distributed in the polymer matrix, as well.

Fig. 2 shows the photoluminescence (PL) spectra of ZnO NPs and PP/ZnO nanocomposites with various weight percent of NPs. The spectra were recorded using an excitation wavelength of 325 nm.

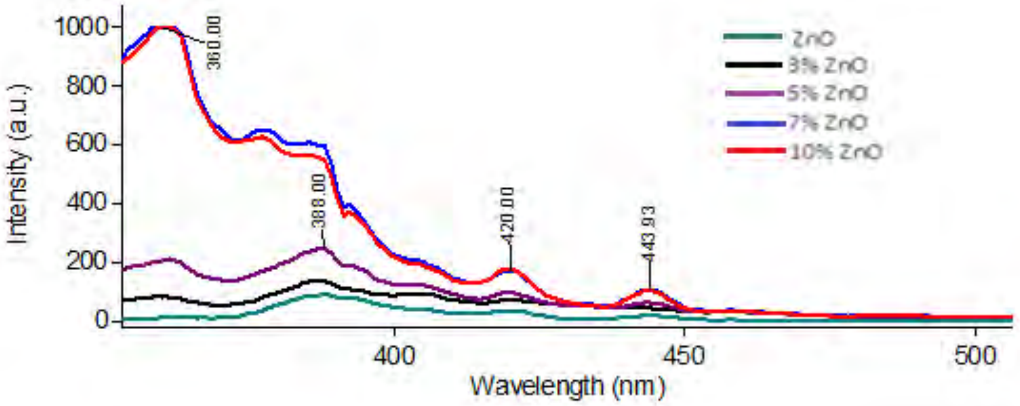

Fig. 2 PL measurements of ZnO NPs and PP/ZnO polymer nanocomposites

PL spectra of samples exhibited similar emission peaks at 388 nm. This occurs due to the UV edge emission that is related to the recombination of free excitons in exciton-exciton collisions. Moreover, some differences in spectra are also observed. The luminescence of ZnO NPs in the visible wavelength range from 400 to 500 nm is mainly associated with the emission of deep-level defects, such as interstitial defects of zinc atoms and oxygen vacancies. The blue emission peak observed at 445 nm corresponded the presence of oxygen vacancies [9]. A new peak at a wavelength of 359 nm in the polymer nanocomposite samples relates to the presence of PP alkene groups (alkenes or olefins - C_nH_{2n}) [10-11]. The intensity of all samples increased with an increasing amount of ZnO NPs. This can be explained by an increase in the number of luminescence centers with an increase of the ZnO NPs weight percent in the polymer matrix.

References

1. Shanshool, H. M., Yahaya, M., Yunus, W. M., & Abdullah, I. Y. (2016). Investigation of energy band gap in polymer/ZnO nanocomposites. *Journal of Materials Science: Materials in Electronics*, *27*(9), 9804-9811. https://doi.org/10.1007/s10854-016-5046-8
2. Ambrosio, R., Carrillo, A., Mota, M., De la Torre, K., Torrealba, R., Moreno, M., Vazquez, H., Flores, J., & Vivaldo, I. (2018). Polymeric Nanocomposites membranes with high permittivity based on PVA-zno nanoparticles for potential applications in flexible electronics. *Polymers*, *10*(12), 1370. https://doi.org/10.3390/polym10121370
3. Viswanath, V., Nair, S. S., G., S., & Muneera, C. (2019). Zinc oxide encapsulated poly (vinyl alcohol) nanocomposite films as an efficient third-order nonlinear optical material: Structure, microstructure, emission and intense low threshold optical limiting properties. *Materials Research Bulletin*, *112*, 281-291. https://doi.org/10.1016/j.materresbull.2018.12.022
4. Lin, O. H., Md Akil, H., & Ishak, Z. M. (2009). Characterization and properties of activated nanosilica/polypropylene composites with coupling agents. *Polymer Composites*, *30*(11), 1693-1700. https://doi.org/10.1002/pc.20744
5. Papageorgiou, G. Z., Achilias, D. S., Bikiaris, D. N., & Karayannidis, G. P. (2005). Crystallization kinetics and nucleation activity of filler in polypropylene/surface-treated SiO2 nanocomposites. *Thermochimica Acta*, *427*(1-2), 117-128. https://doi.org/10.1016/j.tca.2004.09.001
6. Srinivasa Reddy, C., & Kumar Das, C. (2006). Polypropylene–nanosilica-filled composites: Effects of epoxy-resin-grafted nanosilica on the structural, thermal, and dynamic mechanical properties. *Journal of Applied Polymer Science*, *102*(3), 2117-2124. https://doi.org/10.1002/app.24131
7. Ramazanov, M., Shirinova, H., Nuriyeva, S., Jafarov, M., & Hasanova, M. (2021). Structure and optic properties of the nanocomposites based on polypropylene and amorphous silica nanoparticles. *Journal of Thermoplastic Composite Materials*, *36*(4), 1762-1774. https://doi.org/10.1177/08927057211028890
8. Rauf, M. A., Owais, M., Rajpoot, R., Ahmad, F., Khan, N., & Zubair, S. (2017). Biomimetically synthesized ZnO nanoparticles attain potent antibacterial activity against less susceptible S. aureus skin infection in experimental animals. *RSC Advances*, *7*(58), 36361-36373. https://doi.org/10.1039/c7ra05040b
9. Estrada-Urbina, J., Cruz-Alonso, A., Santander-González, M., Méndez-Albores, A., & Vázquez-Durán, A. (2018). Nanoscale zinc oxide particles for improving the physiological and sanitary quality of a Mexican landrace of red maize. *Nanomaterials*, *8*(4), 247. https://doi.org/10.3390/nano8040247
10. Ambid, M., Teyssedre, G., Mary, D., Laurent, C., & Montanari, G. C. (2006). Optical properties and luminescence behaviour of PP/Clay Nanocomposites. *IEEJ Transactions on Fundamentals and Materials*, *126*(11), 1097-1104. https://doi.org/10.1541/ieejfms.126.1097
11. Jacques, P., & Poller, R. (1993). Fluorescence of polyolefins—2. Use of model compounds to identify fluorescent species in thermally degraded polymers. *European Polymer Journal*, *29*(1), 83-89. https://doi.org/10.1016/0014-3057(93)90276-I

Adsorption of heavy metal ions from an aqueous medium on thermochemically processed porous carbon materials from cellulose-containing wastes and micro- to nanoscale transition effect on their adsorption attributes

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We present an investigation of polydisperse carbon materials, obtained by our methodology, - their physicochemical characteristics and its application in the field of surface chemistry, particularly, in adsorption processes.

Among modern methods of water purification for decontamination of water from heavy metal ions, sorption treatment has great importance, the effectiveness of which is determined by the qualities of the sorbent. Carbon-based polydisperse powders are widely used in this regard. These materials are characterized by high porosity, developed surface, mechanical strength, chemical stability, and electrical properties. However, the industrial scale of derivatives of carbon nanomaterials are quite expensive sorbents due to the high price of raw materials and high energy costs for production, thereafter their use to treat large volumes of water is not feasible. Currently, many research studies are underway to find cheap carbon-based sorbents.

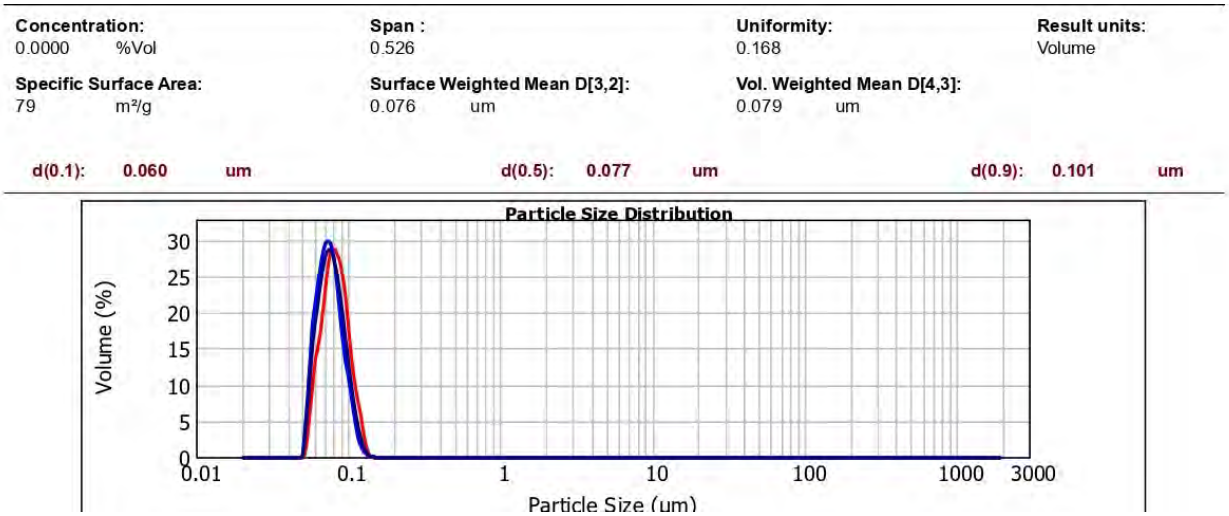
At the R. Agladze Institute of Inorganic Chemistry and Electrochemistry of TSU was developed thermochemical method to obtain defined carbon materials with unique properties, high textural characteristics and decent adsorption capacities from cellulose-contained secondary raw materials (hazelnut/walnut shell and nectarine kernel) [1]. Produced carbon materials are characterized by large specific surface, high mechanical strength, developed porous structure, and low ash. Prepared carbon material can be attributed to the so-called transitional forms of carbon, which have crystalline and amorphous area in their structure as well as carbon nanotubes and fullerenes, graphite, carbon black; carbon-carbon composite materials have such a structure. The high value of the total pore volume and specific surface area, the ability to control the pore size distribution during synthesis make these materials highly promising for their use as sorbents.

Obtained carbon sorbents were tested for the extraction of heavy metal ions Pb2+, Cu2+, Fe2+, Co2+, Cd2+ from model solution [2-4]. Studies have shown that carbon materials obtained from hazelnut and walnut shells were characterized by the best adsorption capacity.

Next, we focused our investigations mainly on carbon nanopowders obtained from hazelnut shell by grinding them in a nanomill (Fritsch Pulverisette 7) and studying their selectivity with respect to Pb^{2+}, Cu^{2+}, Fe^{2+} ions. As the size of carbon particles decreases to nanoscale, their adsorption capacity can be increased of their large surface areas and the ability to establish electrostatic interactions.

The physical characteristics of the obtained materials were studied by Micrometrics the GEMINI VII 2390T surface area analyzer and the Mastersizer 3000 MALVERN particle size analyzer; Morphology and chemical composition was determined by the Scanning Electron Microscope (SEM) HITACHI TM 3030 Plus and integrated with them the BRUKER QUANTAX EDS Analyzer. Results of the measurements are shown in Tables 1, 2 and Figures 1, 2.

Fig. 1 Particle size of carbonaceous material obtained from hazelnut shell



Concentration: 0.0000 %Vol	**Span :** 0.526	**Uniformity:** 0.168	**Result units:** Volume
Specific Surface Area: 79 m²/g	**Surface Weighted Mean D[3,2]:** 0.076 um	**Vol. Weighted Mean D[4,3]:** 0.079 um	

d(0.1): 0.060 um **d(0.5): 0.077 um** **d(0.9): 0.101 um**

Table 1. Textural parameters of carbonaceous material

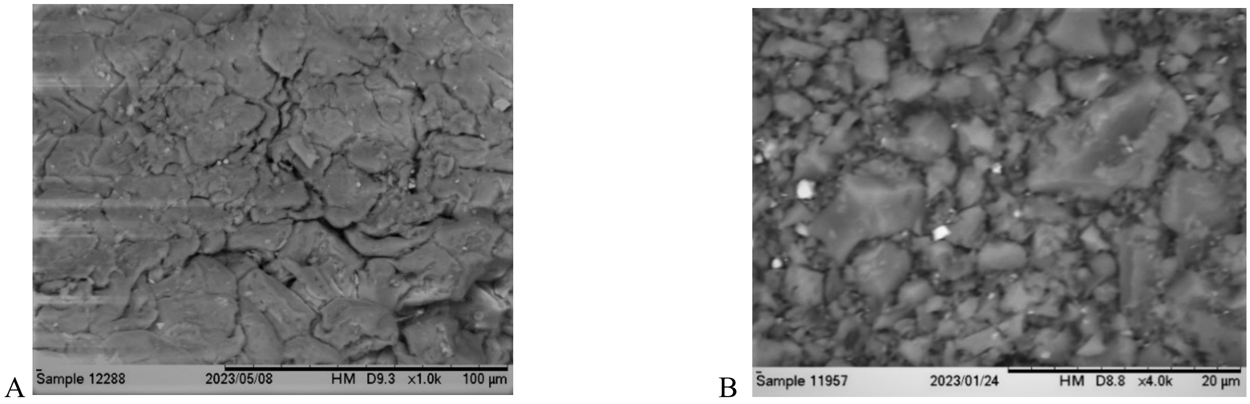
Sample	**BET** (m^2 g^{-1})	**Micropore area** (m^2 g^{-1})	**Mesopore area** (m^2 g^{-1})
Hazelnuts hell	469.37	314.94	0.15

Table 2. Chemical composition of untreated nectarine kernel and produced/prepared carbon material

Sample	**Chemical composition of samples % (averaged)**												
	C	O	Ca	K	Si	S	Fe	Ni	Cu	Zn	Al	Pb	Cr
Pure Hazelnut shell	44	53	0.89	1.18	0.12	0.1	0.3	0.06	_	0.06	0.29	_	_
Carbon nanomaterial obtained from hazelnut shell	95.0	4.0	0.20	0.6	_	0.1	0.1	_	_	_	_	_	_

The Scanning Electron Microscopy (SEM) images of untreated hazelnut shell and produced carbon nanomaterial are shown in Fig. 2 A and B, respectively. Before activation, the hazelnut shell shows a bulk structure with thick and large sheets as shown in Fig. 2A. After thermal treatment and grinding produced nano powder shows discrete sheets and nano carbon structures with enhanced surface area (Fig. 2B).

Fig. 2 Structure of (A) untreated nutshell and (B) carbon nanomaterial prepared from nutshell



In order to assess the adsorptive properties of carbon nanomaterial, it was applied for Pb2+, Cu2+, Fe2+ removal. Studies have shown that, when using nano materials (particle size 60-100 nm) while all the other parameters are constant (mads. – 1g, C_0 – 0.01M; Time – 90min; $V_{sol.}$ – 100ml, temperature - 25°C) adsorption and removal of heavy metals increased 1.5-2 times compared to micro-sized particles (40 µm) used in previous studies. The results are shown in Table 3.

Table 3. Heavy Metal Ions Adsorption and Removal

Heavy metal ions	**A (adsorption), mg g^{-1}**	**R (removal), %**
Carbon nanomaterial (~ 70 nm) obtained from hazelnut shell		
Pb^{2+}	148	70
Cu^{2+}	49.5	78
Fe^{2+}	53	96
Carbon material (~40µm) obtained from hazelnut shell		
Pb^{2+}	87	41
Cu^{2+}	33	52
Fe^{2+}	30	54

It was established that produced carbon nanomaterial show an efficient adsorbent capacities (without additional activation and modification) for removing heavy metals from aqueous solutions.

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References

1. Method For Receiving Sorbents from Waste of Plastics and Cellulose. The National Intellectual Property Center of Georgia - "Sakpatenti" Patent P 2021 7309 B. https://www.sakpatenti.gov.ge/media/publication_pdf/BL202021_eng.pdf
2. T. Marsagishvili, G. Tatishvili, N. Ananiashvili, N. Giorgadze, E. Tskhakaia, J. Metreveli, M. Gachechiladze, M. Machavariani. (2020). Adsorption of Lead Ions on Carbonaceous Sorbents of Nutshell Obtained from Secondary Raw Material. In: Tiginyanu, I., Sontea, V., Railean, S. (eds) 4th International Conference on Nanotechnologies and Biomedical Engineering. ICNBME 2019. IFMBE Proceedings, vol 77. Springer, Cham. https://doi.org/10.1007/978-3-030-31866-6_21
3. N. Ananiashvili, N. Giorgadze and E. Tskhakaia. Adsorption of Iron(II) and Cadmium(II) Ions Separately using Carbon Materials from Hazelnuts and Walnuts Waste Shells. Asian Journal of Chemistry; Vol. 34, No. 12 (2022), 3100-3104, https://doi.org/10.14233/ajchem.2022.23838
4. T. Marsagishvili, G. Tatishvili, N. Ananiashvili, E. Tskhakaia, N. Giorgadze, M. Gachechiladze, M. Matchavariani, and L. Kvinikadze. (2022). Sorbents Obtained from Cellulose-Containing Waste for Water Purification. In: Tiginyanu, I., Sontea, V., Railean, S. (eds) 5th International Conference on Nanotechnologies and Biomedical Engineering. ICNBME 2021. IFMBE Proceedings, vol 87. Springer, Cham. https://doi.org/10.1007/978-3-030-92328-0_61