

# SMS / NANOMED / EGF / SENSORS 2022 JOINT INTERNATIONAL CONFERENCES

## 26 - 28 OCTOBER 2022 ATHENS, GREECE

# **BOOK OF ABSTRACTS**

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## SMS / EGF / Sensors / NanoMed 2022

## **Joint International Conferences Program**

26 - 28 October 2022, Athens - Greece

Wed. 26 Oct. 2022		
08:00 - 12:00	Participants registration.	
SMS / EGF / Sensors / NanoMed 2022 Joint Plenary Session I		
	Athenaeum Conference Centre	
	Session's Chairs:	
Dr. Guilla	Dr. Qi Zhang, Basque Center for Materials, Applications and Na nume Lamblin. Luxembourg Institute of Science and Technolog	anostructures, Spain Iv (LIST). Luxembourg
10:00 - 10:30	Ceramic inclusions/polymer matrix nanocomposites, following a route to multifunctional performance <b>G. Psarras</b>	<b>Prof. Georgios C. Psarras</b> , University of Patras, Greece
10:30 - 11:00	2D Nanostructures at Atomic Scale: From Energy an Environmental Applications to Quantum Devices. J. Arbiol	<b>Prof. Jordi Arbiol</b> , ICREA, ICN2, CSIC and BIST, Catalonia, <b>Spain</b>
11:00 - 11:30	In situ monitoring of graphene growth on solid and liquid Cu sub- strates C. Tsakonas, A.C. Manikas, I. Sfougaris and <b>C. Galiotis</b>	<b>Prof. Costas Galiotis</b> , University of Patras, <b>Greece</b>
11:30 - 12:00	Functionalized gold nanorods for the treatment of head and neck cancer L. García-Hevia and M. López-Fanarraga	Dr. Lorena García Hevia, Cantabria-Idival University, Spain
12:00 - 12:30	Miniature power harvesters and solar farms enabled by 2D materials E. Kymakis	Dr. Emmanuel Kymakis, Hellenic Mediterranean University, Greece
12:00 - 14:00	Lunch Break	
SMS / Sensors / NanoMed 2022 Joint Session I. A: Materials synthesis, characterization, and properties Session's Chairs: Prof. Georgios C. Psarras, University of Patras, Greece		
	Dr. Edit Csapó, University of Szeged, Hungary	
14:00 - 14:30	S. Wei, B. Peng, L. Liu and <b>Q. Zhang</b>	<b>Dr. Qi Zhang,</b> Basque Center for Materials, Applications and Nanostructures, <b>Spain</b>
14:30 - 15:00	Bioceramic Surfaces on Metallic Substrate: Synthesis, Characterization and Applications <b>K. Borodianskiy</b>	Prof.KonstantinBorodianskiy,ArielUniversity, Israel
15:00 - 15:30	Copper/nanocarbons composites: ongoing exploration of new multifunctional materials. J. Barbe, A.E. Alves Silva, A. Valéro, J. Crepellière, D. Del Frari, A. Duhain, D. Arl, E. Barbolini, D. Lenoble and <b>G. Lamblin</b>	<b>Dr. Guillaume Lamblin</b> , Luxembourg Institute of Science and Technology (LIST), <b>Luxembourg</b>
15:30 - 15:45	Reduction of Stress Concentration in Notched Composite Laminates - A Finite Element Analysis R. Ramma, <b>B. Murari</b> and A.A Khatibi	Mr. Bill Murari, RMIT University, Melbourne, Australia
15:45 - 16:00	Functionalization of flax fibers with silazanes: Effect on silicone- based composites <b>A. Ishak</b> , R. Sonnier, B. Otazaghine and C. Longuet	<b>Mr. Antoine Ishak</b> , IMT Mines Alès, <b>France</b>
16:00 - 16:30	Afternoon Coffee Break	
Session's Chairs: Prof. Ioannis Papakonstantinou, University College London, UK Dr. Jerome Brunet, Clermont Auvergne, University, France		
16:30 - 17:00	Fluorescent noble metal nanoclusters with tunable optical features: synthesis, characterization and biomedical applications <b>E. Csapó</b> , D. Ungor, G. Gombár, R. Bélteki, Á. Turcsányi and L. Kuklis	<b>Dr. Edit Csapó</b> , University of Szeged, <b>Hungary</b>

17:00 - 17:15	Immobilization of bisacylphosphinoxides and acylgermanes: Formation and application of photoreactive surfaces and particles <b>W. Kern</b> , M. Müller, Ch. Bandl, M. Haas and M. Drusgala	<b>Prof. Wolfgang Kern</b> , University of Leoben, <b>Austria</b>
17:15 - 17:30	Hydrophobic coating encompassing visibility-on-demand for smart and rapid quality control <b>C. Bandl</b> , W. Kern, M.Müller and N. Krempl	Dr. Christine Bandl, University of Leoben, Austria
17:30 - 17:45	<ul> <li>Atmospheric Pressure Plasma Coatings for Corrosion Protection of 3D-Printed Aluminum and Titanium Alloys</li> <li>A. M. Schwan, E. Pycha, S. Augl, D. Heim, A. Hinterer, M. Stummer, J. M. Lackner and W. Waldhauser</li> </ul>	Dr. Alexander M. Schwan, Joanneum Research, Austria
17:45 - 18:00	Adequate TiAlN thin films deposited by sputtering for thermistor sen-sors: the study of conduction mechanisms and the microstructure role on the electrical properties <b>B. Martins</b> , C. Patacas, F. Fernandes, A. Cavaleiro and Pedro M. Faia	<b>Mr. Bruno Martins</b> , Pedro Nunes Institute, <b>Portugal</b>
18:00 - 18:15	Biomimetic Coatings to Regulate Biological Adhesion A. Corozzi, G. Bassi, <b>M. Caruso</b> , F. Furlani, M. Montesi, S. Panseri, M. Raimondo and A. Rossi.	<b>Ms. Maria Caruso</b> , ISTEC CNR, <b>Italy</b>
18:15 - 18:30	Electroconductive, mechanically resistant, IR-reflective, and antibacterial silk fabric covered with AgNWs <b>A.Baranowska-Korczyc</b> , A. Nejman, M. Rosowski and M. Cieślak	<b>Dr. Anna Baranowska- Korczyc</b> , Lodz Institute of Technology, <b>Poland</b>
18:30 - 18:45	Improvement of Thermal Comfort, Antibacterial and Electrical Properties of Aramid Textile Material with Silver Nanowires <b>A. Nejman</b> , A. Baranowska-Korczyc, G. Celichowski and M. Cieślak	Mrs. Alicja Nejman, Lodz Institute of Technology, Poland

	Wed. 26 Oct. 2022		
EGF2022 - Session I. B:			
Graphene and 2D Materials synthesis, characterization, and properties			
	Arcade I Conference Room		
	Session's Chairs: Prof. Michele Merano, University of Padova, Italy Prof. Costas Galiotis, University of Patras, Greece		
14:00 - 14:15	CVD graphene as an effective tool for the protection of artworks <b>G. Gorgolis</b> , M. Kotsidi, M.G. Pastore Carbone, G. Paterakis, G. Anagnostopoulos, G. Trakakis, A. Manikas and C. Galiotis	<b>Dr. Giorgos Gorgolis</b> , University of Patras, <b>Greece</b>	
14:15 - 14:30	Multiple graphene chemical modification strategies for the development of electrical conductive nanocomposite at low percolation threshold <b>T. Lalire</b> , B. Otazaghine, A.Taguet and C.Longuet	<b>Mr. Thibaut Lalire</b> , IMT Mines Ales, <b>France</b>	
14:30 - 14:45	High Optical Response of Room Temperature Graphene Bolometers Fabricated through Various Methods <b>I.J. Agulo</b> , I.M. Verzola, J. Rivera, M. Andalis, J.A. Pasion, and M.A. Madarang	<b>Dr. Ian Jasper Agulo</b> , University of the Philippines Baguio, <b>Philippines</b>	
14:45 - 15:00	Composition and structure of the universal, airborne hydrocarbon contaminant layer on van der Waals material surfaces <b>A. Pálinkás</b> , G. Kálvin, K. Kandrai, M. Szendrő, P. Vancsó, G. Németh, M. Németh, Á. Pekker, J.S. Pap3, P. Petrik, K. Kamarás, L. Tapasztó and P. Nemes-Incze	<b>Dr. András Pálinkás.</b> Centre for Energy Research- Budapest, <b>Hungary</b>	
15:00 - 15:15	In situ Transformation of Graphene to Diamond-Like Carbon for Conductive Coatings <b>R. Gorthy</b> , F. Hou, I. Mardon, D. Tang and C. Goode	Dr. Rukmini Gorthy, Cirrus Materials Science Ltd., New Zealand	
15:15 - 15:30	An Electrochemical Approach for the Surface Modification of 2H- Phase MoS2 nanosheets towards Enhanced Catalysis S. García-Dalí, J.I. Paredes, S. Villar-Rodil, <b>A. Martínez-Jódar</b> , A. Martínez-Alonso and J. M. D. Tascón	<b>Mr. Alberto Martinez Jodar</b> , INCAR-CSIC, <b>Spain</b>	
15:30 - 15:45	Growth and physics-chemical characterization of graphene electrodes synthesized by electrochemical exfoliation J. A. Arevalo, <b>J. E. Alfonso</b> , J. J. Olaya and O. Suarez	<b>Dr. José Edgar Alfonso</b> , National University of Colombia, <b>Colombia</b>	
15:45 - 16:00	Graphene Oxide Reinforced Asphalt Pavements A.P. Chassiakos, <b>P.M. Farmakis</b> , N. Lalioti, L.C. Kontaxis and J. Parthenios	<b>Mr. Panagiotis Farmakis</b> , University of Patras, <b>Greece</b>	
16:00 - 16:30	Afternoon Coffee Break		
	Session's Chairs: Dr. Emmanuel Kymakis, Hellenic Mediterranean University Prof. Costas Galiotis, University of Patras, Greece Prof. Imre Dékány, University of Szeged, Hungary	, Greece	
16:30 - 17:00	Measurement of the out-of-plane optical constants of a two- dimensional crystal <b>M. Merano</b>	<b>Prof. Michele Merano</b> , University of Padova, <b>Italy</b>	
17:00 - 17:15	Novel device engineering strategies for printable photovoltaics <b>G. Kakavelakis</b> , E. Alharbi, T. Baumeler and M. Graetzel	<b>Dr. George Kakavelakis</b> , Swiss Federal Institute of Technology, <b>Switzerland</b>	
17:15 - 17:30	Machine learning integrated with microscale numerical simulation to investigate the thermal conductivity of cementitious composites reinforced by graphene derivatives <b>A. Montazerian</b> , J.A. Overli and S. Goutianos	Mr. Arman Montazerian, Norwegian University of Science and Technology, Norway	
17:30 - 17:45	A leap from non-conductive to conductive states: transformation of multilayered graphene oxide structures to carbon powders and films <b>T. Szabó</b> , A. Talyzin and I. Dekany	<b>Dr. Tamas Szabo</b> , University of Szeged, <b>Hungary</b>	
17:45 - 18:00	Graphene-based composite with high stable dispersion in ethanol. <b>A. Martis</b> , S. Bocchini and F. Pirri.	<b>Mr. Alberto Martis</b> , Polytechnic University of Turin, <b>Italy</b>	
18:00 - 18:15	Semiclassical analysis of tunneling in graphene in the presence of a smoothly inhomogeneous external electromagnetic field <b>M. Perel</b>	<b>Dr. Maria Perel</b> , Eskisehir Technical University, <b>Turkey</b>	

Thu. 27 October 2022			
SMS 2022 Session II. A: Functional / Multifunctional, Composites and Responsive Materials			
Athenaeum Conference Centre			
Session's Chairs: Prof. Grigoris Kaltsas, University of West Attica, Greece Dr. Qi Zhang, Basque Center for Materials, Applications and Nanostructures, Spain Dr. Christos Riziotis, National Hellenic Research Foundation, Greece			
09:00 - 09:30	Functional nanostructures based on smart copolymers <b>S. Pispas</b>	<b>Prof. Stergios Pispas,</b> National Hellenic Research Foundation- Athens, <b>Greece</b>	
09:30 - 10:00	Shape Memory Polymer Composites for Space Sustainability L. Santo	<b>Prof. Loredana Santo</b> , University of Rome Tor Vergata, <b>Italy</b>	
10:00 - 10:15	Facile preparation of MXene/rGO composites with hydrophilic/hydrophobic properties <b>N. Todorova</b> , V. Marinova, D. Dimitrov and C. Trapalis	<b>Dr. Nadia Todorova</b> , Institute of Optical Materials &Technologies-BAS, <b>Bulgaria</b>	
10:15 - 10:30	Patterned and Collective Motion of Densely Packed Tapered Multi-Responsive Liquid Crystal Cilia <b>R.J.H. van Raak,</b> S. J. A. Houben, A.P.H.J. Schenning and D.J. Broer	Mr. Roel J. H. van Raak, Eindhoven University of Technology, The Netherlands	
10:30 - 11:00	Morning Coffee Break		
	Session's Chairs: Prof. Evangelos Hristoforou, National TU of Athens, Greece Prof. Grigoris Kaltsas, University of West Attica, Greece		
11:00 - 11:30	Engineering Optical Structures and Functional Materials towards Photonic Devices Development <b>C. Riziotis</b>	Dr. Christos Riziotis, National Hellenic Research Foundation Theoretical and Physical Chemistry Institute, Greece	
11:30 - 11:45	Nanotextured surfaces based on mixtures of amphiphilic diblock copolymers as bioinspired hybrid materials <b>M. Bina</b> , A. Krywko-Cendrowska, D. Daubian, and C.G. Palivan	Ms. Maryame Bina, University of Basel, Switzerland	
11:45 - 12:00	Optimizing thickness ratio (a-Si:H/AI) during Aluminum induced crystallization (AIC) to obtain higher pressure sensitivity in devices built using AIC-Silicon <b>A. Ratna Arun</b> and R. O Dusane	<b>Mr. Anand Ratna Arun</b> , Indian Institute of Technology Bombay, <b>India.</b>	
12:00 - 12:15	DIC application for damage detection in FRP composite specimens based on an example of a shearing test <b>D. Ziaja</b> , M. Jurek, R. Śliwa, A. Wiater and M. Kulpa	Dr. Dominika Ziaja, Rzeszow University of Technology, Poland	
12:15 - 12:30	L. Vellutini, A. Hachin, T. Buffeteau and E. Boisselier	of Bordeaux, France	
12:00 - 14:00	Lunch Break		
	Sensors 2022 Session II.B: Sensing materials, physical / chemical sensors, optic	al sensors, etc	
	Session's Chairs: Prof. Loredana Santo, University of Rome Tor Verg Dr. Christos Riziotis, National Hellenic Research Found	jata, Italy lation, Greece	
14:00 - 14:30	Overview and Recent Findings on Curcuminoids as Molecular Platforms for Sensors and Electronic Components <b>N. Aliaga-Alcalde</b> , A. González-Campo, D. Herrera-Miranda, R. Zaffino, D. Riba-López, T. Cardona-Lamarca, M. Surós-Román, L. Rodríguez-Cid, R. Díaz-Torres, C. Domingo, M. Soler, D. Dulić, L. Echegoyen, F. Prins, E. Burzuri, H. van der Zant and E. Ruiz	Prof. Nuria Aliaga-Alcalde, ICREA - ICMAB/CSIC, Spain	
14:30 - 14:45	Rapid Ethidium Bromide detection using Ultramicroelectrode Sensors <b>M. Valente</b> , I. Seymour, V. Alessandria, L. Cocolin, K. Meade and A. O'Riordan	Mr Marcello Valente, Tyndall National institute, Ireland	

14:45- 15:00	High sensing potentialities of tetra-tert-butyl- metallophthalocyanines-based acoustic microsensors for xylenes measurement in air at room temperature. <b>J. Brunet</b> , A. Pauly, C. Varenne, A.L. Ndiaye, T. Gueye and A. Kumar	<b>Dr. Jerome Brunet</b> , Clermont Auvergne, University, <b>France</b>	
15:00 - 15:15	Exploring new strategies for vapor explosive detection through solid-state QDs-based sensors <b>F. Mitri</b> , A. De Iacovo, S. De Santis, C. Giansante, G. Sotgiu and L. Colace	<b>Mrs. Federica Mitri</b> , University Roma Tre, <b>Italy</b>	
15:15 - 15:30	Fully optimized waveguide enhanced Raman spectroscopy sensors <b>Z. Liu</b> , M. A. Ettabib, J. S. Wilkinson and M.N. Zervas	<b>Mr. Zhen Liu</b> , University of Southampton, <b>UK</b>	
15:30 - 15:45	Low Power Wearable Sensors for monitoring Knee Joint Instabilities K.S. Prakash, V.C. von Einem, S.K. Muthulagu, P. Agarwal, <b>A.</b> <b>Jamali</b> , P. Woias and L.M. Comella	<b>Mr. Armin Jamali</b> , University of Freiburg, <b>Germany</b>	
15:45 - 16:00	Microfluidics and QCM biosensing – Challenging the Standards M. Forinová, A. Pilipenco, M. Vrabcová, M. Spasovová, P. Yudin, H. Lisalová, <b>N. S. Lynn Jr</b> .	<b>Dr. N. Scott Lynn Jr</b> , Institute of Physics of the Czech Academy of Sciences, <b>Czech</b> <b>Rep.</b>	
16:00 - 16:30	Afternoon Coffee Break		
	Smart Materials and Surfaces - SMS 2022 Session II.C		
Session's Chairs: Prof. Nuria Aliaga-Alcalde, ICREA - ICMAB/CSIC, Spain Dr. Christos Biziotis, National Hellenic Research Foundation, Greece			
	Dr. Christos Riziotis, National Hellenic Research Found	, Spain ation, Greece	
16:30 - 17:00	Prof. Nurla Allaga-Alcalde, ICREA - ICMAB/CSIC, Dr. Christos Riziotis, National Hellenic Research Found Printed sensors and devices on flexible substrates G. Kaltsas	Spain ation, Greece Prof. Grigoris Kaltsas, University of West Attica, Greece	
16:30 - 17:00 17:00 - 17:15	Prof. Nurla Allaga-Alcalde, ICREA - ICMAB/CSIC, Dr. Christos Riziotis, National Hellenic Research Found Printed sensors and devices on flexible substrates G. Kaltsas Accurate dipole radiation model for waveguide grating couplers Z. Liu, M. A. Ettabib, J. S. Wilkinson and M.N. Zervas	Spain ation, Greece Prof. Grigoris Kaltsas, University of West Attica, Greece Mr. Zhen Liu, University of Southampton, UK	
16:30 - 17:00 17:00 - 17:15 17:15 - 17:30	Prof. Nurla Allaga-Alcalde, ICREA - ICMAB/CSIC,         Dr. Christos Riziotis, National Hellenic Research Found         Printed sensors and devices on flexible substrates         G. Kaltsas         Accurate dipole radiation model for waveguide grating couplers         Z. Liu, M. A. Ettabib, J. S. Wilkinson and M.N. Zervas         Curcumin-loaded PCL highly porous composites for rapid amine gas detection         D. Kossyvaki, A. Barbetta, M. Contardi, M. Bustreo, K. Dziza, S. Lauciello, A. Athanassiou and D. Fragouli	Spain ation, Greece Prof. Grigoris Kaltsas, University of West Attica, Greece Mr. Zhen Liu, University of Southampton, UK Ms. Despoina Kossyvaki, Italian Institute of Technology- Genova, Italy	
16:30 - 17:00 17:00 - 17:15 17:15 - 17:30 17:30 - 17:45	Prof. Nurla Allaga-Alcalde, ICREA - ICMAB/CSIC,         Dr. Christos Riziotis, National Hellenic Research Found         Printed sensors and devices on flexible substrates         G. Kaltsas         Accurate dipole radiation model for waveguide grating couplers         Z. Liu, M. A. Ettabib, J. S. Wilkinson and M.N. Zervas         Curcumin-loaded PCL highly porous composites for rapid amine gas detection         D. Kossyvaki, A. Barbetta, M. Contardi, M. Bustreo, K. Dziza,         S. Lauciello, A. Athanassiou and D. Fragouli         Fabrication of biomimetic fibrous substrate with hierarchical micro-structure patterning for reconfigurable soft electronics         Z.V. Soreño, I. Apsite and L. Ionov	Spain ation, Greece Prof. Grigoris Kaltsas, University of West Attica, Greece Mr. Zhen Liu, University of Southampton, UK Ms. Despoina Kossyvaki, Italian Institute of Technology- Genova, Italy Mr. Zhander Vohr Soreño, University of Bayreuth, Germany	

Thu. 27 October 2022		
NanoMed 2022 Session II. A: Nanomaterials for Biomedical / Tissue engineering, drug, and gene delivery		
	Arcade I Conference Room	
Session's Chairs: Prof. Rita Cortesi, University of Ferrara, Italy Dr. Cleofe Palocci, University of Rome "La Sapienza", Italy		
09:00 - 09:30	Overcoming barriers in Nanomedicine: from cancer to Obstetrics <b>B. Godin</b>	Prof. Biana Godin, Houston Methodist Research Institute, USA
09:30 - 10:00	New strategies for the risk evaluation of carotid artery disease patients at the nanoscale F.A. Carvalho, C.S. Lopes, R. Melo, L.M. Pedro and <b>N. C. Santos</b>	Prof. Nuno C. Santos, iMM Lisbon, Portugal
10:00 - 10:15	Amphiphilic block copolymers in hybrid vesicles and micelles to- wards scaffolds for nanoreactors <b>C. Ade</b> , E. Brodszkij, I. N. Westensee and B. Stadler	<b>Dr. Carina Ade</b> , Aarhus University, <b>Denmark</b>
10:15 - 10:30	Computational Assessment of Three-Dimensional Scaffolds for Bone Regeneration <b>O. Ntousi</b> , M. Roumpi, P. Siogkas and D. Fotiadis	Mrs. Ourania Ntousi, University of Ioannina, Greece
10:30 - 11:00	Morning Coffee Break	
11:00 - 11:30	Funtionalization of nanomaterials with proteins to improve biomimetics M. L. Fanarraga	<b>Prof. Monica Lopez</b> <b>Fanarraga</b> , Cantabria-Idival University, <b>Spain</b>
11:30 - 12:00	Nanotechnology for precision medicine and personalized beauty and healthcare <b>M. Colombo</b>	<b>Prof. Miriam Colombo</b> , University of Milano- Bicocca, <b>Italy</b>
12:00 – 12:15	Nanosystems as a therapeutic approach for the treatment of psoriasis J. Castanheira and <b>A.R.T.S Araujo</b>	<b>Dr. André R.T.S. Araujo</b> , Polytechnic Institute of Guarda, <b>Portugal</b>
12:15 - 12:30	Self-assembly of 2D Materials for 3D Tissue Engineering Platforms <b>T. Raicevic</b> , T. Teshima, M. Barbone, F. Stratmann, V. Rincón Montes, K. Müller, A. Bausch and B. Wolfrum	<b>Ms. Teodora Raicevic</b> , Technical University of Munich, <b>Germany</b>
12:00 - 14:00	Lunch Break	
Nai	NanoMed 2022 Session II. B: nomaterials for Biomedical / Tissue engineering, drug, and	gene delivery
	Session's Chairs: Prof. Nuno C. Santos, iMM Lisbon, Portugal Prof. Miriam Colombo, University of Milano-Bicocc Dr. Aleksandra Ellert-Miklaszewska, Nencki Institute- Warsaw	a, Italy ⁄, Poland
14:00 - 14:30	Composition and Functionality Relationship in Dexamethasone loaded Avidin Nucleic Acic NanoAssemblies E. Schiavon, M.B. Violatto, U. Christen, P.Invernizzi, C.Tondello, M. Carbone, S. Bernardotto, A.Mattarei, P.Bigini and <b>M. Morpurgo</b>	Prof. Margherita Morpurgo, University of Padova, Italy
14:30 - 14:45	Design of poly(lactide-co-glycolide) particles: synthesis optimization and controlled drug release <b>N. Varga</b> , A. N. Kovács, Á. Turcsányi, V. Hornok and E. Csapó	Dr. Norbert Varga, University of Szeged, Hungary
14:45 - 15:00	Neuroprotective Peanut Agglutinin-Targeted Nanoparticles for Ocular Drug Delivery Applications <b>P. Colucci</b> , L. Dente, C. Gabellini and V. Raffa	<b>Ms. Patrizia Colucci</b> , University of Siena, <b>Italy</b>
15:00 - 15:15	Using of short peptides attached to the polymer carrier as either anti-microbial, cell-penetrating, or targeting agent of the whole nanotherapeutics <b>E. Grosmanová</b> , R. Pola, M. Pechar, M. Filipová, B. Vokatá, P. Ulbrich, J-L. Coll and T. Etrych	<b>Dr. Eliska Grosmanova</b> , Institute of Macromolecular Chemistry, <b>Czech Rep</b> .
15:15 - 15:30	Peptide conjugation with magneto-polymeric nanoparticles to improve nanomaterials transport across the blood-brain barrier <b>C. I. P. Chaparro</b> , M. Cavaco, M. Castanho, J.P. Borges, V. Neves and P. I. P. Soares	Ms. Catarina Chaparro, NOVA School of Science and Technology- Lisbon, Portugal

15:30 - 15:45	Exploring silicon-nanowire patterned surfaces for yeast transformation L. Gogianu, M. Popescu and M. Simion	<b>Ms. Larisa Gogianu</b> , IMT- Bucharest, <b>Romania</b>
15:45 - 16:00	Interaction of magnetic iron oxide nanoparticles with primary human monocytes and adrenocortical carcinoma cell lines <b>C. Hong</b> , A. Sorushanova, O. Covarrubias-Zambrano, P. Owens, M. O'Halloran, P. Prakash, S. H. Bossmann and M. C. Dennedy	<b>Mr. Cong Hong</b> , National University of Ireland, Gal- way, <b>Ireland</b>
16:00 - 16:15	Nanowire-based electrodes for electrophysiological studies: Fabrication, on-bench characterization and in vitro biocompatibility <b>A. Arché-Núñez</b> , B.L. Rodilla, C. Fernández-González, C. Guillén- Colomer, S. Ruiz-Gómez, J. Camarero, R. Miranda, P. Ocón, L. Pérez, M. Concepción Serrano and M. Teresa González	<b>Ms. Ana Arché Núñez</b> , IMDEA Nanocience- Madrid, <b>Spain</b>
16:00 - 16:30	Afternoon Coffee Break	
	Session's Chairs: Prof. Margherita Morpurgo, University of Padova, Prof. Rita Cortesi, University of Ferrara, Italy	Italy
16:30 - 17:00	Dendrimer nanocarriers as an efficient tool to deliver therapeutic siRNA to glioma-associated microglia and macrophages <b>A. Ellert-Miklaszewska</b> , P. Pilanc-Kudlek, L. Ding, Y. Jiang, AJ. Roura, K. Poleszak, S. Cyranowski, J. Swatler, B. Kaza, S. Giorgio, L. Peng and <b>B. Kaminska</b>	Dr. Aleksandra Ellert- Miklaszewska, Nencki Institute- Warsaw, Poland
17:00 - 17:30	Ratiometric Sensing Systems for Intracellular and Extracellular pH Mapping at Single Cell Level in Tumor Models L.del Mercato	Dr. Loretta del Mercato, CNR- NANOTEC, Italy
17:30 - 17:45	Ultrastructural Visualization of Combinatorial Nanodrug Interaction with Mitochondria of Breast cancer cells <b>S. Raveendran</b> , A. Sen, T. Maekawa and D.S.Kumar	<b>Dr. Sreejith Raveendran</b> , Teesside University, <b>UK</b>
17:45 - 18:00	Anti-tumour/MRI agent loaded LDL for personalized therapy applications <b>S. Rakhshan</b> , D. Alberti, R. Stefania, V. Bitonto, S. Geninatti, A. Deagostino and S. Parisotto	<b>Ms. Sahar Rakhshan</b> , University of Turin, <b>Italy</b>
18:00 - 18:15	Polymer conjugates with anticancer agent cytarabine with increased stability and different speed of hydrolytic release for highly effective antitumor therapy <b>R. Pola</b> , E. Grosmanová, M. Pechar, E. Pokorná, P. Klener and T. Etrych	Dr. Robert Pola, Institute of Macromolecular Chemistry, Czech Rep.
18:15 - 18:30	<ul> <li>Taking advantage of invasive pest species in biotechnology:</li> <li>Spanish slugs (Arion vulgaris) as a potential exosome source for cell delivery applications</li> <li>M. Liegertová, A. Semerádtová, O. Janoušková, M. Kocholatá, M. Průšová, L. Němcová, M. Štofik, L. Kříženecká and J. Malý</li> </ul>	<b>Dr. Michaela Liegertov</b> a, University of Jan Evangelista in Ústí nad Labem (UJEP), <b>Czech Rep.</b>
18:30 - 18:45	Engineered chitosan based nanocarriers for therapeutic miRNAs de-livering to human melanoma cells: in vitro and in vivo studies <b>C. Palocci</b> , L. Chronopoulou , B. Arasi, F. Pedini , F. Felicetti and N. Felli	<b>Dr. Cleofe Palocci</b> , University of Rome "La Sapienza", <b>Italy</b>
18:45 - 19:00	Optimizing Coiled Coil Interactions for Peptide-PAINT Super- Resolution Imaging <b>A.S. Eklund</b> , M. Ganji and R. Jungmann	<b>Ms. Alexandra Eklund</b> , Max Planck Institute of Biochemistry, <b>Germany</b>

Fri. 28 Oct. 2022		
SMS / EGF 2022 Session III.A: Applications for energy and environment		
Athenaeum Conference Centre II		
Session's Chairs: Prof. Georgios C. Psarras, University of Patras, Greece Prof. Loredana Santo, University of Rome Tor Vergata, Italy Prof. Michele Merano, University of Padoya, Italy		
09:00 - 09:30	Luminescent Solar Concentrators: A versatile photonic platform enabled by extreme photon concentration <b>I. Papakonstantinou</b> M. Portnoi, Z. Xu and C. Tummeltshammer	Prof.IoannisPapakonstantinou,UniversityCollegeLondon,UK
09:30 – 10:00	Controlled assembly of liquid phase exfoliated 2D materials for functional materials and devices. <b>A.Dalton</b>	<b>Prof. Alan Dalton</b> , University of Sussex, <b>UK</b>
10:00 - 10:30	Morning Coffee Break	
10:30 - 10:45	Integration of efficient single photon sources into plasmonic devices by two photon polymerization of multifunctional photopolymers D. Ge, A. Issa, A. Abdelaal, A. Broussier, C. Couteau, S. Blaize, R. Bachelot and <b>S. Jradi</b>	<b>Dr. Safi Jradi</b> , University of Technology of Troyes, <b>France</b>
10:45 - 11:00	Phosphate-functionalized graphene obtained by a fast, one-step electrochemical strategy for capacitive energy storage E.H. Ramirez-Soria, S. García-Dalí, J.M. Munuera, <b>D.</b> <b>Fernández-Carrasco</b> , S. Villar-Rodil, J.M.D. Tascón, J.I. Paredes and J. Bonilla-Cruz	Mr. Daniel Fernandez Carrasco, INCAR- CSIC, Spain
11:00 - 11:15	Novel Approach to Enhance Electrochemical Performance of Na0.7CoO2 Layered Cathode and Nitrogen-Sulpher Co-doped Graphene as Anode for Sodium-ion Batteries M. Saquib Khan, N. Bhardwaj, H. Singh Kushwaha, M. K. Banerjee and <b>K. Sachdev</b>	<b>Prof. Kanupriya Sachdev</b> , Malaviya National Institute of Technology, <b>India</b>
11:15 - 11:30	Graphene Aerogel Electrode for Advanced Fuel Cell and CO2 Reduction Electrolyser <b>T.X. Liu</b> , Y. Wang and H. Lei	<b>Mr. Terence Xiaoteng Liu</b> , Northumbria University, <b>UK</b>
11:30 - 11:45	Observation of strongly correlated electronic ground state in rhombohedral graphite <b>P. Vancsó</b> , I. Hagymási, M. Syahid Mohd Isa, Z. Tajkov, K. Márity, L. Oroszlány, J. Koltai, A. Alassaf, P. Kun, K. Kandrai, A. Pálinkás, L. Tapasztó and P. Nemes-Incze	<b>Dr. Peter Vancso</b> , Centre for Energy Research, Institute of Technical Physics and Materials Science- Budapest, <b>Hungary</b>
11:45 - 12:00	Capacitive de-ionization using reduced graphene oxide-based electrodes for desalting synthetic and real saline waters <b>A. Aouni</b> , P. Valerio and H. Hafiane	<b>Dr. Anissa Aouni</b> , CERTE, Tunisia

Fri. 28 Oct. 2022		
NanoMed / Sensors 2022 Session III.B		
Athenaeum Conference Centre III		
Session's Chairs: Dr. N. Scott Lynn Jr, Institute of Physics of the Czech Academy of Sciences, Czech Rep. Dr Toby Hallam, Newcastle University, UK		
09:30 – 10:00	Development of a device for the rapid detection of SARS-CoV-2 based on electrochemical biosensor A. Georgas, S. Angelopoulos, A. Ferraro and <b>E. Hristoforou</b>	Prof. Evangelos Hristoforou, National TU of Athens, Greece
10:00 - 10:30	Morning Coffee Break	
10:30 - 10:45	Bacterial Biosensors that can compute <b>R. Daniel</b>	<b>Prof. Ramez Daniel</b> , Israel Institute of Technology, <b>Israel</b>
10:45 - 11:00	Optical Imaging of Cell Action Potentials via Graphene Based Sensing Devices <b>J. Gorecki</b> and S. Krause	<b>Dr. Jon Gorecki</b> , Queen Mary University of London, <b>UK</b>
11:00 - 11:15	Development of a novel design of Microfluidic Impedance Cytometry for improved sensitivity and cell identification <b>M. Warren</b> , A. Shakouri, V. Pacheco-Peña and T. Hallam	<b>Mr. Michael Warren</b> , Newcastle University, <b>UK</b>
11:15 - 11:30	Development of a Polyanaline/Polystyrene/Au Nanoparticles- based electrochemical biosensor for the detection of SARS-CoV-2 <b>S.Trafela</b> , K. Žagar Soderžnik, A. Korent, A. Krishnamurthy, K. Žužek and S. Šturm	<b>Dr. Spela Trafela</b> , Jožef Stefan Institute, <b>Slovenia</b>

### SMS / EGF/ Sensors/ NanoMed 2022 Joint International Conferences

### **Posters Session**

N.	Poster Title	Author, Affiliation, Country
1.	Convenient synthesis of electro active copolymers of N-vinylcarbazole via emulsion copolymerization. <b>M. Sharifian</b> , W. Kern and G. Riess	Mr. Mohammadhossein Sharifian, University of Leoben, Austria
2.	Immobilization of germanium-based photo-initiators for surface-initiated polymerization. <b>M. Müller</b> , W. Kern, C. Bandl, M. Haas and M. Drusgala	<b>Mr. Matthias Müller</b> , University of Leoben, <b>Austria</b>
3.	Development and characterization of a new cork-based composites produced with plastic wastes. <b>S. Petlitckaia</b> , T. Barboni and P-A. Santoni	<b>Dr. Svetlana Petlitckaia</b> , University of Corsica, <b>France</b>
4.	Investigating flammability properties and smoke prodution of new cork-based composites produced with plastic wastes. <b>T. Barboni</b> S. Petlitckaja and P-A. Santoni	<b>Mr. Toussaint Barboni,</b> University of Corsica, <b>France</b>
5.	Pullout behavior of NiTi crimped SMA fibers made by cold drawing with considering wavelength and height. TH. Park, J. Kang, B. Nhan and <b>E. Choi</b>	<b>Prof. Eunsoo Choi</b> , Hongik University- Seoul, <b>Rep. of</b> <b>Korea</b>
6.	Sol-gel synthesis of transparent and luminescent SiO2@ SrAl2O4 Eu, Dy, B materials V.Vitola and M. Leimane	<b>Dr. Virginija Vitola</b> , University of Latvia, <b>Latvia</b>
7.	Dependence of the Structure and Electronic Properties of Dia-mond-Like a-C Films with Palladium Nanoparticles on Synthesis Conditions. A. P. Ryaguzov, <b>A.R. Assembayeva</b> , R.R. Nemkayeva, N.R. Guseinov and M.M Myrzabekova	Ms. Aliya Assembayeva, Al- Farabi Kazakh National University, Rep. of Kazakhstan
8.	Synthesis and photoluminescence properties of carbon based nanoparticles. I. Dékány, Á. Imre Deák and L. Janovák	Prof. Imre Dékány, University of Szeged, Hungary
9.	Triboelectric Nanogenerator Based on Ferroelectric Composite for Energy Harvesting. K.Malnieks, A.Sutka, L.Lapcinskis and A.Linarts	<b>Dr. Kaspars Malnieks</b> , Riga Technical university, <b>Latvia</b>
10.	Influence of hybrid carbon lignocellulose filler on reduction toxicity of gaseous thermal decomposition products, including dioxins, PAH and smoke during combustion of NR rubber composites <b>P.Rvbiński</b> and A.Głowacki	Prof. Przemysław Rybiński, Jan Kochanowski University, Poland
11.	Synthesis of Graphene oxide/ TiO2-based photoreactive nanocomposite thin films. <b>Á. Deák</b> , L. Janovák and I. Dékány	<b>Ms. Ágota Imre-Deák</b> , University of Szeged, <b>Hungary</b>
12.	Energy Loss Rate in Graphene at Quantizing Magnetic Fields <b>M. Tsaousidou</b> and S. S. Kubakaddi	<b>Dr. Margarita Tsaousidou</b> , University of Patras, <b>Greece</b>
13.	Functionalisation of CVD graphene for gas sensing. <b>A.K. Aladim</b> , C.S. Rigby and T. Hallam	Mr. Abdullah Aaladim, Newcastle University, UK
14.	DNA analogues-directed immobilization in fabrication of microarrays for immunodiagnostics of viral infections. <b>S. Karoń</b> , M. Drozd and E. Malinowska	<b>Ms. Sylwia Karoń</b> , Warsaw University of Technology, <b>Poland</b>
15.	Topologies of synthetic gene circuit for optimal fold change activation. <b>D.Naffaa</b> and R Daniel	<b>Mrs. Doaa Ali-Naffaa</b> , Technion Institute of Technology, <b>Israel</b>
16.	Application of molecular vapour deposited dielectrics for graphene-based biosensor passivation and improvements in graphene device homogeneity and functionality. <b>M. Ali</b> , J. Mitchell, F. Walters, G. Burwell, K. Rejnhard, C. Jenkins, E.Daghigh Ahmadi, S. Sharma and O. Guy	<b>Mr. Muhammad Ali</b> , Swansea University, <b>UK</b>
17.	Photocatalytic Quantum Dot-Armed Bacteriophage for Combating Drug- Resistant Bacterial Infection <b>X. Fan</b> and L. Wang	<b>Mr. Xin Fan</b> , Free University of Berlin, <b>Germany</b>
18.	Synthesis and characterization of smart fluorescent polymers for bio-medical applications. <b>V.Vitale</b> , S. Pragliola, F. Grisi and C. Costabile	<b>Dr. Vissia Vitale</b> , University of Salerno, <b>Italy</b>

19.	Exploring the Properties of Anti fouling Nanocoatings for Biosensing <b>M. Spasovovová</b> , F. Dyčka, M. Procházka, J. Štěpánek, I. Barvík, O. Kylián, M. Vrabcová, N. Scott Lynn Jr. and H. Lísalová	Mrs. Monika Spasovová, Charles University, Czech Rep.
20.	<ul> <li>Characteristic of ceramic-polymer materials enhanced with collagen for biomedical applications.</li> <li>B. Tyliszczak, M. Bańkosz, A. Drabczyk, S. Kudłacik-Kramarczyk, A. Tomala, W. Florkiewicz, K. Piętak, D. Słota and A. Sobczak-Kupiec</li> </ul>	<b>Prof. Bozena Tyliszczak</b> , Cracow University of Technology, <b>Poland</b>
21.	<ul><li>Hydroxapatite-reinforced coatings as drug carriers for controlled release of clindamycin.</li><li>A. Sobczak-Kupiec, D. Słota, W. Florkiewicz, K. Piętak and M. Dyląg</li></ul>	<b>Prof. Agnieszka Sobczak- Kupiec</b> , Cracow University of Technology, <b>Poland</b>
22.	Chitosan grafted poly (ethylene glycol) methyl ether acrylate based micro/nanocarriers for biomedical applications <b>C.A. Peptu</b> , C.L. Logigan, C. Delaite, C.E. Tiron, C. Peptu and M. Popa	<b>Dr. Catalina A. Peptu</b> , Gheorghe Asachi Technical University of lasi, <b>Romania</b>
23.	Nanoparticles based on chitosan grafted with PEG derivative as carriers for antibiotics. <b>C.L. Logigan</b> , C. Delaite, C.E. Tiron, C. Peptu, M. Popa and C.A. Peptu	<b>Dr. Corina L. Logigan</b> , Gheorghe Asachi Technical University of lasi, <b>Romania</b>
24.	Nanofabrication of tuneable plasmonic noble metal nanoparticles and their subsequent formation onto cultivation plates used in hotothermal therapy. <b>L. Hochvaldová</b> , L. Válková, K. Simkovičová, K. Plecho, L. Kvítek, H. Kolářová and A. Panáček	Ms. Lucie Hochvaldova, Palacky University, Czech Rep.
25.	Laser-induced In vitro photothermal therapy using noble metal nanolayers <b>L. Válková</b> , L. Hochvaldová, K. Simkovičová, A. Panáček and H. Kolářová	<b>Mrs. Lucie Válková</b> , Palacky University, <b>Czech Rep</b> .
26.	Thymol Self-emulsifying Polysaccharide-based Microbeads Cross-linked by Polyvalent lons: Synthesis, Structure and Dynamics. <b>M. Urbanova</b> , J. Brus, M. Pavelkova and K. Kubova	Dr. Martina Urbanova, Institute of Macromolecular Chemistry CAS. Czech Rep.
27.	How to Describe Microbead Formulations of Active Pharamceutical Ingredients with Micro- and Nanodomain Architecture at Atomic Resolution Level. <b>J. Brus</b> , J. Czernek and M. Urbanova	<b>Dr. Jiri Brus</b> , Institute of Macromolecular Chemistry CAS, <b>Czech Rep</b> .
28.	Gastro-Resistant Self-Emulsifying Pellets as Stable Delivery Systems for Volatile Monoterpene Plant Drug. J. Macku, G. Koutna, <b>K. Kubova</b> , M. Urbanova, E. Maskova, J. Masek, M. Pavelkova, J. Muselik, A. Franc, J. Vyslouzil, D. Vetchy and J. Brus	Dr. Kateřina Kubová, Masaryk University, Czech Rep.
29.	Self-emulsifying System Incorporated in a Polymeric Carrier for Controlled Delivery of Thymol. G. Koutna, <b>M. Pavelkova</b> , K. Kubova, M. Urbanova, J. Muselík, J. Vysloužil, D. Vetchý and J. Brus	Dr. Miroslava Pavelková, Masaryk University, Czech Rep.
30.	Composition and Functionality Relationship in Dexamethasone loaded Avidin Nucleic Acic NanoAssemblies. <b>E. Schiavon</b> , M.B. Violatto, U. Christen, P.Invernizzi, C.Tondello, M. Carbone, S. Bernardotto, A.Mattarei, P.Bigini and M. Morpurgo	<b>Mrs. Elisa Schiavon</b> , University of Padova, <b>Italy</b>
31.	Encapsulation of SerpinB3 Protein in wet Sol-Gel silica /HPMC composite allows its sustained release in a bioactive form. <b>S. Bernardotto</b> , M.Albiero, A.Fullin, E. Franceschinis, P. Pontisso, GP. Fadini and M. Morpurgo	<b>Mr. Simone Bernardotto</b> , University of Padova, <b>Italy</b>
32.	Exploring Nanoformulations for Therapeutic Induction of Necroptosis. <b>T. Chu</b> , C. Rios Luci, C. Maksoudian, A. Sargsian, B.B. Manshian and S. J. Soenen	<b>Ms. Tianjiao Chu</b> , KU Leuven, <b>Belgium</b>
33.	Core-Multishell Nanocarrier Systems for Drug Delivery. <b>K. Rajes</b> , K. A. Walker, S. Hadam, F. Zabihi, J. Ibrahim-Bacha, G. Germer, P. Patoka, B. Wassermann, F. Rancan, E. Rühl, A. Vogt and R. Haag	<b>Ms. Keerthana Rajes</b> , Free University of Berlin, <b>Germany</b>
34.	Using biocompatible polymers for improving the antibody drug conjugate concept. <b>O. Lidický</b> , T. Etrych and P. Klener	Mr. Ondrej Lidicky, Institute of Macromolecular Chemistry, Czech Rep.
35.	Screening DNA condensation properties of multifunctional PAMAM dendrimers with different amine contents for targeted co-delivery of SAHA, 5-FU and TRAIL plasmid <b>B. Bulkurcuoğlu</b> , M.U. Gurbuz, M. Tulu, M. Matuskova, K. Pavlov, S. Tyciakova and S Ercelen	Mr. Bünyamin Bulkurcuoğlu, TUBITAK MRC Genetic Engineering and Biotechnology Institute, Turkey
36.	Positively Charged Mesoporous Silica Nanoparticle as a Medicinal Carrier for Crossing the Blood Brain Barrier in Chicken Embryo. YP. Chen, CK. Lin, YS. Yang and <b>CT. Chen</b>	<b>Prof. Chien-Tsu Chen</b> , Taipei Medical University, <b>Taiwan</b>

37.	Intranasal administration of dexamethasone-loaded nanoparticles improves lung tropism and reduces steroid off-target accumulation in healthy and in pulmonary fibrosis-affected mice <b>A. Morelli,</b> MB. Violatto, A. Passoni, A. Lanno, GY. Moscatiello, M. Corti, E. Schiavon, M. Morpurgo and P. Bigini	Ms. Annalisa Morelli, IRCCS Mario Negri- Milan, Italy
38.	Cholesterol supplementation via intranasal administration as a possible therapeutic strategy in Huntington's disease <b>M. Favagrossa</b> , A. Passoni, R. Camastra, R. Bagnati, G. Birolini, M. Valenza, E. Cattaneo, L. Colombo and M. Salmona	Ms. Monica Favagrossa, IRCCS Mario Negri- Milan, Italy
39.	Recombinase polymerase amplification on silicon nanowires. <b>M.A. Popescu</b> , L. Gogianu and M. Simion	Dr. Melania-Ana Popescu, IMT Bucharest, Romania
40.	Development of surface-enhanced Raman spectroscopy (SERS) based label- free diagnosis of liver and gallbladder injury. <b>S. Lee</b> , J-M. Namgoong and J. Ki Kim	Dr. Sanghwa Lee, Asan Medical Center- Seoul, Rep. of Korea
41.	Negatively charged liposomes for the delivery of manganese derivatives for diagnostic applications. M.Sguizzato, L. Marvelli, M. Drechsler, L. Del Bianco, F. Spizzo, A. Boschi and <b>R. Cortesi</b>	<b>Prof. Rita Cortesi</b> , University of Ferrara, <b>Italy</b>
42.	Functionalization of self-assembled monolayer with gold nanoparticles for protein detection in tear film <b>A. Hachin</b> , G.Raîche-Marcoux, T. Buffeteau, S. Bonhommeau, E. Boisselier and L. Vellutini	Ms. Axelle Hachin, University of Bordeaux, France
43.	The controversial properties of graphene oxide and reduced graphene oxide and impact on microalgae Chlamydomonas reinhardtii. <b>Z. Bytešníková</b> , M. Koláčková, M. Dobešová, P. Švec and L. Richtera	Dr. Zuzana Bytešníková, Mendel University in Brno, Czech Rep.
44.	Fabrication of Nucleus-Free Single-Crystal Graphene-Mesh with Zig-zag Edges in the Wafer Scale <b>B. Tian</b>	Dr. Bo Tian, KAUST, Saudi Arabia
45.	Wafer-scale single-crystal high-crystal-quality monolayer graphene grown on sapphire substrates J. Li	Dr. Junzhu Li, KAUST, Saudi Arabia
46.	Combining Droplet Microfluidics with Magnetoresistive Sensors for Rapid and Specific Detection of Klebsiella pneumoniae <b>C. L. Nogueira</b> , S. Abalde-Cela, P. P. Freitas, S. Cardoso and C. M. Carvalho	Ms. Catarina Nogueira, International Nanotechnology Laboratory (INL), Portugal
47.	Piezoelectric polarization in fluoropolymer obtained via immersion precipitation and low pH exposure <b>V. Khurana</b> and D. Gupta	<b>Mr. Vaibhav Khurana</b> , Indian Institute of Technology Bombay, <b>India</b>
48.	Gold Nanoparticle Formulations for Efficient Delivery of Lupeol: A Promising Therapeutic Approach in the Management of Skin Patholo-gies <b>I. Macasoi</b> , C. Soica, C. Popa, M. Cabuta, I. Marcovici, I. Pinzaru, F. Bociort, A. Motoc, G. Draghici and C. Dehelean	<b>Ms. Ioana Macasoi</b> , "Victor Babes" University of Medicine and Pharmacy, <b>Romania</b>
49.	Pharmacotoxicological Insights Into Supramolecular Complexes With Natural Compounds M. Cabuta, R.C. Racea, I. Macasoi, R. Buzatu, C. Soica, S. Dinu and L. Rusu	<b>Ms. Madalina Cabuta</b> , "Victor Babes" University of Medicine and Pharmacy, <b>Romania</b>





## SMS / EGF / Sensors / NanoMed 2022 Joint Plenary Session I

## Ceramic Inclusions/Polymer Matrix Nanocomposites, following a Route to Multifunctional Performance

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### Abstract:

Ceramic particles/polymer matrix nanocomposites attract enhanced scientific attention because of their properties and the easiness of the fabrication. This type of materials appears as suitable for numerus emerging technologies, which include stationary power systems, cellular phones, wireless personal digital assistants, hybrid electric vehicles etc. Materials or materials' systems exhibiting, at the same time, advanced structural/mechanical, thermal, electrical, and magnetic properties, at low weight, are required in current and future high-tech applications. These materials should be able to respond to various stimuli or signal controls, depending on the application's requirements [1,2]. The key characteristic of these materials is not the nominal value of a specific mechanical/physical property (i.e., Young's modulus, conductivity, magnetic permeability etc.), but their ability to execute functions/operations. Ceramic polar oxides provide tunable polarization, related to their piezoelectric/ferroelectric behaviour, and magnetic nanoparticles induce magnetic properties to the nanocomposites. In addition, these systems exhibit thermal stability and mechanical endurance, which are improving with the ceramic fillers. Ceramic inclusions are considered as a distributed network of capacitors where electric energy can be stored and retrieved [2,3]. Most of the employed particles are semiconductive, but even in the case of conductive inclusions the surrounding insulating matrix and the developed interface leads to a system of nanodevices for storing/retrieving energy. The simultaneous presence of all these responses under the influence of various loading conditions at service, constitute multifunctionality. Multifunctional performance can be defined as the combination of different desirable properties in a materials' system. Certain properties of these systems should be varied in a controllable way, such as stiffness, shape, damping capacity, natural vibration frequency, polarization, conductivity, energy storing efficiency etc. [2]. In this study, ceramic ferro-/piezo-electric polar oxides, ferromagnetic, carbides and carbon allotropes nanoparticles are embedded in a polymer matrix. Morphology, thermal properties, static and dynamic mechanical behaviour, dielectric response,

conductivity, magnetic properties, energy storing/retrieving ability and induced multifunctionality are investigated by means of several experimental techniques. Results are analyzed and discussed targeting to evaluate the optimum behaviour each time.

**Keywords**: hybrid nanocomposites, ceramic inclusions, thermomechanical behaviour, electrical properties, energy storing/retrieving, magnetic response, multifunctionality.



**Figure 1**: Schematic representation of a material's multifunctional performance.

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- Gioti, S., Sanida, A., Mathioudakis, G.N., Patsidis, A.C., Speliotis, T., Psarras, G.C. (2022), Multitasking Performance of Fe<sub>3</sub>O<sub>4</sub>/BaTiO<sub>3</sub>/Epoxy Resin Hybrid Nanocomposites, *Materials*, 15, 1784

### Acknowledgements

The research work was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the "First Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment grant" (Project Number: 2850).

## 2D Nanostructures at Atomic Scale: From Energy an Environmental Applications to Quantum Devices

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### Abstract:

Technology at the nanoscale has become one of the main challenges in science as new physical effects appear and can be modulated at will. As developments in materials science are pushing to the size limits of physics and chemistry, there is a critical need for understanding the origin of these unique properties and relate them to the changes originated at the atomic scale, e.g.: linked to structural changes of the material, many times related to the presence of crystal defects or crystal surface terminations. Especially on 2D materials designed for electrocatalysis in energy and environmental applications, crystallography and distribution of the atomic species are of outmost importance in order to determine the active sites that will improve the reaction performance, including efficiency and selectivity towards certain reactions. In 2D nanomaterials the distribution and coordination of metal species at the surface are determining their final electrocatalytic behavior as the reactions of interest mainly occur at the surface. The presentation will show how pristine and perfect crystalline surfaces may tend to be inert versus particular reactions, while creation of certain types of defects or even a predetermined surface amorphization may highly improve the catalytic activity of these 2D nanomaterials [1-2].

In the present work, a combination of advanced electron microscopy imaging with electron spectroscopy, in an aberration corrected STEM will allow us to probe the elemental composition and structure in a high spatial detail, while determining the growth mechanisms and correlating the structural properties to their electrocatalytic performance.

The first electrocatalyst system to study is based on 2D MoS2 nanoflakes. MoS2 basal plane is not pretty catalytically active, in this sense, we need to find other ways to improve the activity of this material for example for the electrocatalytic hydrogen evolution reaction (HER). The hypothesis of the work considers that the grain boundaries (GBs) created at the interface between nanoflake domains, can be considered as a highly defective perimeter which can certainly improve the density of active sites. Taking this idea in mind, we engineered MoS2 connected nanoflakes at 5nm diameter range, which create a, ultra-high density of GBs (up to ~1012 cm-2). The obtained GBs present a complex bonding coordination that could be studied by atomic resolution aberration corrected (AC) high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). Using the 2D atomic models obtained from our AC HAADF STEM observations we could study the different hydrogen adsorption preferential sites on the different atomic arrangements in MoS2 (including different GBs and Edges). Theoretical DFT calculations of the H2 absorption free energy in these preferential sites in comparison to the MoS2 Basal Plane (BP) were performed, showing that some GB structures show better electrocatalytic activity than edges, and much better than the MoS2 BP [1].

In a second part, we study the way to obtain the maximum utilization of noble metal atoms in our 2D catalysts. We demonstrate the fabrication of a wafer-size amorphous PtSex films on a SiO2 substate via a low-temperature amorphization strategy, which offers single-atom-layer Pt catalysts with high atom-utilization efficiency (~26 wt%). This amorphous PtSex behaves as a fully activated surface, accessible to catalytic reactions, and features a nearly 100% current density relative to a pure Pt surface and reliable production of sustained high-flux hydrogen. Such an amorphization strategy is potentially extendable to other noble metals, including the Pd, Ir, Os, Rh and Ru elements, demonstrating the universality of single-atom-layer catalysts. The study is performed by combining AC HAADF STEM with DFT calculations and precise electrochemical tests [2].

**Keywords**: 2D materials, hydrogen evolution, energy, MoS2, PtSe2, ZnTe, ZnSe, bandgap energy mapping, electrocatalysis, direct to indirect bangap transitions, quantum materials, nanowires.



**Figure 1**: AC HAADF STEM magnified example of a triple grain boundary in MoS2 nanosheets and a detail of the complex bonding coordination [1].

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## In situ monitoring of graphene growth on solid and liquid Cu substrates

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### Abstract:

Graphene is a perfect 2D crystal consisting of covalently bonded carbon atoms and has been established as unique and attractive alternatives to replace current technological materials in a number of applications. Synthesis of large, defectfree graphene is a major challenge toward industrial applications. Chemical Vapour Deposition (CVD), is unquestionably the most well-known technique for thin film synthesis and fulfils all requirements for automated largescale production of graphene. The growth process is rather complex, as it involves numerous of reactions such as hydrocarbon decomposition, carbon adsorption and subsequently diffusion on the catalytic substrate the generation of the nucleation point and finally the growing. Currently most CVD methods employ solid metal catalysts (SMCat) for the growth of graphene however their use has been found to induce structural defects such as wrinkles, fissures, and grain boundaries among others. In contrast to a solid catalytic substrate, graphene growing on Liquid Metal Catalysts (LMCat) might be a solution for the production of defect-free single graphene domain at high synthesis speeds due to the enhanced atomic mobility, homogeneity, and fluidity of a LMCat. Real-time monitoring of such a complex process is of paramount importance for the control of graphene growth and the understanding of growing kinetics. Nevertheless, the lack of in situ techniques enabling direct observation of the growth process has limited our understanding of the process dynamics and primarily led to empirical growth recipes. Herein, we report on the development of real time monitoring of graphene growth via in situ reflectometer for the case of graphene grown on solid and via in situ optical microscopy and Raman spectroscopy for graphene growth on liquid metal substrates

**Keywords**: Chemical Vapour Deposition (CVD), graphene, radiation mode optical microscopy, liquid metal catalysts, Raman spectroscopy.



**Figure 1**: Figure illustrating the different methodologies for in situ monitoring of graphene growth on solid (top) and on liquid (bottom) Cu

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### Functionalized gold nanorods for the treatment of head and neck cancer

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### Abstract:

Head and neck cancer (HNC) is the seventh most common cancer in the world. Currently, HNC is diagnosed by a physical examination followed by an histological biopsy, with surgery being the primary treatment, often followed by adjuvant radiotherapy or chemoradiotherapy<sup>1</sup>. However, unfortunately, local recurrence of HNC squamous cell carcinoma is common<sup>2,3</sup>.

We have shown that preneoplastic and malignant HNC cells and tissues from different origins aberrantly exhibit the glycosphingolipid globotriaosylceramide (known as GB3 or CD77) on their membranes<sup>4</sup>. This receptor specifically binds to the Shiga toxin (ShTxB), which is a high-affinity innocuous natural ligand that, upon binding to the receptor, triggers retrograde receptor internalization through the Golgi network to the endoplasmic reticulum<sup>5,6</sup>.

To mimic natural ligand-specific cell entry mechanisms, we have reproduced the molecular cues found in the Shiga toxin to target nanomaterials into HNC cells bearing the GB3 receptor. We functionalized gold nanordos (AuNRs) with this toxin (AuNRs@ShTxB) and we find that are efficiently retrotranslocated to the cancer cell cytoplasms. After laser radiation with a wavelength resonant with the AuNR longitudinal localized surface plasmon, the death of targeted cancer cells is activated. Both in vitro and in vivo experiments show the noncytotoxic nature of these functionalized nanoparticles and a selective treatment after laser treatment. This functionalization strategy, is a clear example of how some toxin fragments can be used as natural biosensors for the detection of some localized cancers and to target nanomedicines to head and neck lesions.

**Keywords**: gold nanordos, head and neck cancer, natural-ligand, nanoparticle targeting, gly-cosphingolipid, CD77.



**Figure 1**: Post-mortem murine tongues treated and not-treated with laser. These tissues show white swollen lesions. Hematoxylin-eosinstained sections (H&E) show a patent keratosis at the tongue surface (white arrow) that is visibly affected after the irradiation treatment (black arrows). Similar sections immunostained with anti-GB3 antibody (red channel).

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### Graphene-Perovskite photovoltaics take to the field

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### Abstract

During the past decade, there was intensive research on the development of perovskite solar cells (PSCs), which have emerged as an alternative efficient energy harvester for both IoT devices and solar farms. The power conversion efficiency (PCE) of PSCs has rapidly increased and is now approaching the state- of-the-art PCE of 26.1%<sup>1</sup> obtained by crystalline-silicon PVs. However, this impressive PCE obtained on small-area cells and in laboratory conditions should be also valid to largearea PV panels in real outdoor conditions. Interface engineering, using solution processable 2Dmaterials (e.g., graphene and transition metal dichalcogenides) is an effective approach to increase the readiness of this technology for manufacturing. The incorporation of the 2D materials improves the charge dynamics of the interfaces and most importantly protects the perovskite layer against diffusion of external agents, such as oxygen and moisture and the metal ion migration<sup>2</sup>. In this context, the Graphene Flagship partners University Rome Tor Vergata, BeDimensional S.p.A, Greatcell and Hellenic Mediterranean University demonstrated the validity of this technology through the entire value chain, from materials development, perovskite modules and panels fabrication and their integration in an autonomous solar farm, to outdoor field tests, and assessment of the real energy production output. The main validation of the proposed approach is the realization of an autonomous solar farm, consisting of 5m<sup>2</sup> perovskite PV panels in the HMU campus at Crete<sup>3</sup>. A continuous monitoring of the solar farm was performed through in-house developed maximum power point trackers, coupled with a correlation of the environmental conditions, recorded by a weather station, with the outdoor performance of farm. The assembled solar farm delivered peak power exceeding 260W, proving the scalability of the proposed technology. The energy production of the solar farm was monitored for 12 months, demonstrating a remarkable 20% reduction  $(T_{80})$  of the PV performance over 8 months of operation. Moreover, the solar farm's electrical characteristics were monitored as a function of temperature and light intensity. The data analysis demonstrated that the perovskite panels enabled by 2D materials are promising for outdoor operation at elevated temperatures, such as in high-irradiance global locations.

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Figure 1: A photograph of the solar farm

SMS / Sensors / NanoMed 2022 Joint Session I. A: Materials synthesis, characterization, and properties

### Electrocaloric effect in medium entropy-like ceramics

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### Abstract:

Electrocaloric effect of ferroelectric materials has been attracting more and more attentions for more than a decade due to its great potential for next generation EC cooling devices. Bulk ferroelectric ceramics with a large electrocaloric (EC) effect at a very low electric field are very desirable. However, limited to the low pyroelectric coefficient and the low dielectric breakdown strength, there is almost no breakthrough for the EC effect of bulk ceramics for a long time since that the EC effect was found in 1930s. It was observed that the large temperature change ( $\Delta T$ ) could be obtained in some ferroelectric ceramics, but their EC strengths ( $\Delta T/\Delta E$ ) are too small and unappreciable. Therefore, it is urgent to make a large EC effect at a relatively lower electric field based on the greater breakdown risk at higher electric field. In this work, two medium entropylike, Pb(Sc<sub>0.25</sub>In<sub>0.25</sub>Nb<sub>0.25</sub>Ta<sub>0.25</sub>)O<sub>3</sub> (PSINT) ceramics were successfully synthesized by one-step or two-step spark plasma sintering (SPS) processing technology. For the two-step-SPS processed sample, a high EC strength ( $\Delta T/\Delta E \sim$ 0.021 K·cm/kV) and a large EC effect ( $\Delta T \sim 0.85$ K) with around room temperature are obtained at a very low electric field (~40 kV/cm). Moreover, the working temperature range is also very broad  $(\sim 120 \text{ K})$ , which is attributed to the high-degree relaxation of the dielectric peak. It can be believed that the high entropy ceramics can be promising candidates for application in the nextgeneration EC cooling devices.

**Keywords**: Electrocaloric effect, High entropy, Spark plasma sintering.

#### Relaxo



**Figure 1**: a) and b) P-E loops. Insets in the upper-left and lower-right corners: P(T) and  $\partial P/\partial T(T)$  curves, respectively. c) and d):  $\Delta T(T)$  curves based on the Maxwell relationship. Insets:  $\Delta S(T)$  curves. e) Direct measurement of the EC effect of the PSINT-B ceramic.

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## Bioceramic Surfaces on Metallic Substrate: Synthesis, Characterization and Applications

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### Abstract:

Titanium alloys are known for their bioinertness that attractes them in biomedical applications such as dental or orthopedic implants. Enhancement of their bonding with human tissue can be obtained by development of porous surface and incorporation of Ca/P components. Among variety of different surface treatment methods, plasma electrolytic oxidation (PEO) was found to be one of the most promising. PEO is ecofriendly electrochemical method that ensures synthesis of highly adhesive bioceramic surfaces. In current work PEO treatment was applied in electrolyte of nitrate salts that was found to be effective due to the ability to treat large-area surfaces and to confirm their purity [1-3]. TiO<sub>2</sub> surfaces were synthesized by PEO and comprehensively studied. Their morphology and phase composition were revealed by electron microscopy and XRD approaches, respectively. Bioceramic surfaces were examined for biocompatibility by contact angle measurements using Hank's balanced salt solution (HBSS). Finally, their adhesion and bioresponce were analyzed by tensile and in vitro tests. The obtained results showed a successful synthesis of highly adhere bioceremic surfaces that demonstrate enhanced collagen expression and cell viability.

**Keywords**: bioceramic surface, plasma electrolytic oxidation, surface morphology, phase composition, biocompatibility, adhesion, *in vitro* test.



Figure 1: Schematic presentation of PEO process in nitrate salts.

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## Copper/nanocarbons composites: ongoing exploration of new multifunctional materials.

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### Abstract:

In 2013, *Subramaniam et al.*<sup>1</sup> disclosed the fabrication of composite materials based on multiwall carbon nanotubes (MWCNTs) and copper. They proposed to combine the high electrical conductivity of copper with the high ampacity of carbon nanotube (CNTs) to end up with lighter copper/CNTs materials. Their Cu/CNTs, made of aligned MWCNTs trapped into the copper matrix, combined an electrical conductivity close to the one of copper with a 100-fold increase in ampacity. This work triggered a lot of interest and the number of publication about this topics steadily increased.

The talk will provide an overview of the activities related to Cu/nanocarbons composites ongoing at the Luxembourg Institute of Science and Technology. Starting from an original synthesis of Cu-CNTs composites (see figure 1) entirely realized without any electroplating step in organic solvent<sup>2</sup>, several research projects conducted with a major European copper manufacturer has started in 2022. They propose for example to explore the electrical properties (conductivity and ampacity), as well as lightning strike protection (LSP) properties of Copper/CNTs composites. Few results/examples of realizations will be presented to highlight/explain how they can be of interest in several areas like microelectronic, aerospace or energy industry.

**Keywords**: copper, carbon nanotubes, graphene, electroplating, electrical conductivity, ampacity, lighting strike properties, Li-ion battery.



**Figure 1**: Example of a scanning electron microscope image of a Cu/CNTs composite fabricated at the Luxembourg Institute of Science and Technology.

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## Reduction of Stress Concentration in Notched Composite Laminates -A Finite Element Analysis

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### Abstract:

Carbon fibre reinforced polymers (CFRPs) possess highly favourable mechanical properties, including high specific strength and stiffness, excellent fatigue behaviour, and outstanding corrosion resistance. The application of CFRPs is on the rise in the aerospace, automotive and biomedical sectors. As an example, at least 50% of the Boeing 787 Dreamliner is made of composites by weight [1]. Nevertheless, CFRPs exhibit several weaknesses that can degrade the overall structure, preventing it from operating effectively. Composite laminates possess limited stress redistribution capability, leading to easy damage formation around free edges, such as open holes and notches. Since discontinuity in a structure may be present to accommodate necessary joints or form due to damage and manufacturing defects, reducing the resulting Stress Concentration Factor (SCF) could increase the structure's load-bearing capacity.

In this study, carbon nanotubes (CNTs) as nanofillers and interleaving materials were incorporated separately into CFRPs to investigate their effectiveness at reducing SCF around notches using finite element analyses. These reinforcements were centred around the notched area to mitigate stress accumulation. The numerical studies were conducted using COMSOL Multiphysics, and MATLAB was used to generate the models. It was concluded that the CNT reinforcements provided considerable stress concentration reduction around the notches for different hole diameters ranging from 4mm to 20mm. For instance, incorporating 1.5%wt. of CNT around a 4mm diameter open hole resulted in the highest SCF reduction of 19%. A similar result was identified after combining interleaving layers with 1.0%wt. of CNTs to reinforce a 20mm open hole. The developed numerical analysis provides evidence that employing nanofiller reinforcement and interleaving will reduce the SCF in a notched composite laminate.

Moreover, it can be observed that fillers and interleaving have their individual application and advantages. For instance, the CNT fillers effectively reduced the SCF for the smaller holes whereas interleaving was more efficient in larger holes. Adequately dispersing the CNT will prevent agglomeration and provide effective SCF reduction. Both solutions are practical and can be used in designated areas; for example, fillers can be utilised for small holes in aircraft structures, including holes for bolts & rivets. On the other hand, interleaving can be used for larger openings such as cut-outs for pipes or windows in a fuselage of an aircraft.

**Keywords**: stress concentration factor, notch sensitivity, carbon nanotubes, interleaving, carbon fibre polymer



**Figure 1: (a)** Carbon fibre and interleaved plies oriented in a quasi-isotropic configuration. (b) Random arrangement of the homogenised fillers in the carbon epoxy matrix



**Figure 2:** Summary of results of the MWCNT reinforcement solution.



**Figure 3:** Summary of results of the interleaving solution.

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## Functionalization of flax fibers with silazanes: Effect on silicone-based composites

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### **Abstract:**

In recent years, there has been an increase in the use of flax fibers as reinforcement for a variety of matrix in the manufacture of composites. Grafting coupling agents onto flax fibers allows to form a three-dimensional connected network between fibers and matrix by covalent bonds (Figure 1). In this study, Flax fibers were functionalized with vinyl groups using 1,3-divinyltetramethyldisilazane via a chemical reaction to reinforce a silicon rubber matrix. The conditions of reaction have a great effect on the grafting rate, especially the used solvent and the pre-treatment of fibers. The mechanical properties of the composite were characterized via tensile test. It is found that Young's modulus increases up to 40% when the silicone matrix is reinforced with functionalized flax fibers. Indeed, scanning electron microscopy (Figure 2) highlights a highly improved interfacial adhesion between functionalized fibers and silicone matrix.

Keywords: Flax fibers, Silicone matrix, Coupling agents, Fiber/matrix bonding, Silazane.



**Figure 1**: Schematic representation of the formation of the flax/silicone composites with formation of covalent bonds between fibers and polymer matrix



Figure 2: SEM cross-sectional SEM micrographs of prepared composites: with (a) pristine fibers and (b) functionalized fibers.

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## Fluorescent noble metal nanoclusters with tunable optical features: synthesis, characterization and biomedical applications

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### Abstract:

Nanostructured materials, which have unique properties such as high surface area to volume ratio, stability, inertness, easy functionalization, as well as novel optical, electrical, catalytic, and magnetic behaviors, are playing an increasingly important role in a diverse range of fields including but not limited to chemistry, physics, biology, catalytic processes, food processing industries, electronics, energy sectors, optoelectronics, sensing as well as medicine. Several groups can be also distinguished within the inorganic-based nanostructures according to the size: nanoclusters (d < 2 nm or sub-nano sized), nanoparticles (d < 100 nm), colloidal particles (d < 500 nm) and sub-micro sized particles (d < 1000 nm). Here, we exclusively focuses on the interpretation of the preparation possibilities and the structure-dependent optical features of the sub-nanometer sized transition metal-based nanoclusters (mainly noble metals, like gold (Au)). We highlight the possibilities of green chemistry for the production of biocompatible Au NCs using proteins (bovine serum albumin (BSA); lysozyme (LYZ), gamma-globulin ( $\gamma$ G)), nucleotide (adenosine monophosphate (AMP), amino acids (histidine (His); tryptophan (Trp), cysteine (Cys) and small molecules having antioxidant features which result in different nanostructures having tunable blue, green, yellow and orange emissions [1-4]. The main goal of this work was to investigate the spontaneous interactions of AuCl<sub>4</sub><sup>-</sup> and the studied biomolecules as well to optimize the gold/biomolecule ratios and pH on the formation of gold nanosized objects. Moreover, a comprehensive presentation of their possible applications in biomedical fields like selective and sensitive detection of various analytes, and novel possibilities in bioimaging/biolabeling fields will be mentioned.

**Keywords**: noble metal nanoparticles, noble metal nanoclusters, fluorescent nanostructures, preparation possibilities, characterization, biosensors, fluorescent reporters



**Figure 1**: Figure illustrating the generally applied preparation protocols (bottom-up and topdown) of gold nanoclusters (Au NCs)

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Acknowledgement: Project no. TKP2021-EGA-32 has been implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-EGA funding scheme. This research was also supported by the NRDIO through FK131446 project.

## Immobilization of bisacylphosphinoxides and acylgermanes: Formation and application of photoreactive surfaces and particles

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### Abstract:

Immobilized photoinitiators are an interesting approach in surface photochemistry, providing polymerization initiating species which are employed for surface functionalization and the fabrication of nanostructured materials. Typically, photoinitiators are coupled to inorganic surfaces via trialkoxysilyl or thiol anchoring units. Employing photosensitive molecular layers, surface properties such as polarity, chemical reactivity, and optical properties can be adjusted upon light induced irradiation. Moreover, light induced transformations (e.g., isomerizations) are useful to confer new properties on surfaces. In combination with lithographic patterning, 2D structures can be generated.

In addition to planar surfaces, also inorganic particles can be functionalized with photoreactive groups. Selected examples include (i) the addition of photoreactive fillers based on silica nanoparticles modified with Norrish type I photoinitiators (e.g., tri(alkoxy)silyl functionalized acylphosphine oxides) to acrylate and thiol-ene resins as low-migration photoinitiators, and (ii) the generation of inorganic protection layers on inert polymer films and fibers (e.g., PE and PET) by attachment of azidophenyl functionalized silica particles.

The main focus of this presentation is set to recent results on a new class of photoinitiators based on acylgermanes. Group-14 based photoinitiators, in particular triacylhalogermanes (X = Brand I), were prepared and equipped with different coupling units which were subsequently attached to inorganic surfaces such as pre-activated silicon and inorganic particles. The generated light sensitive surfaces were then used for surface initiated polymerization of, e.g., styrene and acrylic monomers. Both the surface composition and the reactivity were studied, using FT-IR and XPS spectroscopy as well as optical techniques and atomic force microscopy (AFM). The high potential and suitable applications of this promising class of photoinitiators are highlighted.

**Keywords**: photoinitiator, photopolymerization, surface activation, surface functionalization, grafting-from, UV light, XPS spectroscopy

### Figure 1:



A surface coupled Ge-based photoinitiator

### Figure 2:



XPS survey spectrum of a functionalized surface

#### Acknowledgment:

M.H. thanks the FWF (Wien, Austria) for financial support (project number P32606-N).

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## Hydrophobic coating encompassing visibility-on-demand for smart and rapid quality control

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### Abstract:

There is a wide application field for hydrophobic coatings ranging from self-cleaning surfaces over anti-graffiti coatings, separation layers for adhesive tapes and labels to demolding aids in the production of polymers. In our previous studies we developed a hydrophobic anti-adhesive coating based on perfluorinated organosilanes, which was proven suitable as a covalently bound/long term demolding aid in the field of polymer processing. [1, 2] Since the coating is transparent and in the nanometer scale, the arising demand for a temporary quality control was answered by the incorporation of a fluorescent marker molecule enabling visibility-on-demand. For this purpose, 1,8-naphthalimide-N-propyltriethoxysilane (NIPTES) was synthesized and deposited together with the silanes of the anti-adhesive formulation in a sol-gel process (hydrolysis and condensation).

The coated substrates were investigated with regard to their surface energy by contact angle measurements, while different spectroscopic techniques such as XPS, FTIR, UV-Vis and fluorescence spectroscopy were used to study their surface composition and optical properties. Furthermore, the surface morphology was determined using AFM. The anti-adhesive effect of the coating was examined by means of injection molding experiments, monitoring the static friction coefficient and the related demolding force over repeated production cycles. Moreover, abrasion and wear of the coating throughout injection molding was followed by UV-induced fluorescence.

The incorporation of NIPTES as a fluorescent marker represents a straightforward and temporary approach for quality control of the applied hydrophobic anti-adhesive coating. Information about the presence and homogeneity of the entire coated area can quickly be assessed by the use of a convenient UV-lamp.

**Keywords**: hydrophobic, anti-adhesive, coating, fluorescence, organosilane, visibility-on-de-mand, naphthalimide



**Figure 1:** Visibility-on-demand property of the hydrophobic organosilane layer utilizing UV-induced fluorescence

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## Atmospheric Pressure Plasma Coatings for Corrosion Protection of 3D-Printed Aluminum and Titanium Alloys

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### Abstract:

Laser powder bed Fusion (L-PBF) allows generating prototypes of complex structures and enables small-series productions on demand. Metallic L-PBF components, however, suffer from rough, microporous surfaces, which increase the risk of corrosion when lattice geometries for lightweight design and metallic inserts have to be considered.

Silicone- and silicate-like coatings formed with plasma-enchanced chemical vapour deposition (PECVD) offer a variety of properties (controllable wetting behaviour, abrasion-resistance, uniform film formation etc.), which makes them well suited for corrosion protection [1,2].

Here, we present our development of fast and environmentally friendly processes for the deposition of anticorrosive cerium-doped SiO<sub>x</sub> coatings on aluminum and titanium alloys with a hot gas atmospheric pressure plasma jet (APPJ).

The APPJ is a powerful and flexible tool, when it comes to plasma polymerization and functionalization of thin and thick films on 3D objects and complex structures (Fig. 1). Precursors such as hexamethyldisiloxane (HMDSO) can be mixed into the plasma jet as vapour or aerosol in combination with dopants or additives, which add desired properties.

Our report will focus on the influence of different process parameters such as plasma energy on the coating properties and the effect of cerium as dopant, which is known to actively protect against corrosion due to its hardly soluble hydroxides and oxides [3,4].

Keywords: Atmospheric pressure plasma, corrosion protection for aluminum and titanium, plasma polymerization, plasma enhanced chemical vapour deposition, organosiliocon coating,  $SiO_x$  coating,.



**Figure 1**: The atmospheric pressure plasma jet for functional coatings with e. g. hexamethyldisiloxane (HMDSO).

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## Adequate TiAlN thin films deposited by sputtering for thermistor sensors: the study of conduction mechanisms and the microstructure role on the electrical properties

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#### Abstract:

A combinatory deposition was carried out by direct current (DC) magnetron sputtering to develop Ti<sub>1-x</sub>Al<sub>x</sub>N thin films with different Ti/Al chemical ratio. The crystal structure as a function of the Ti/Al ratio was studied by X-ray diffraction. Sheet resistance response with temperature was measured up to 200 °C. From x = 0.16 to x =0.56, the film displayed an fcc phase with Al in solid solution in the TiN matrix, whilst from  $x \ge x$ 0.69 showed hexagonal hcp and fcc phases. A negative temperature coefficient (NTC) thermistor behavior was found from x = 0.21 onwards, and a maximum sensitivity  $\beta$  of 1600 °K was observed for x = 0.56 and 0.69. Meanwhile, the highest resistivity of  $2.1 \times 10^4 \ \mu\Omega cm$  was observed for X = 0.69. Two samples with cubic structures (x = 0.46, 0.46) were chosen to analyze the chemical states by X-ray photon spectroscopy, and impedance behavior with temperature variation up to 200°C with electrical spectroscopy. The crystal structure, bond states and impedance analysis were compared with the AlN thin-film deposited by the same technique but in rotation mode. The sheet resistance exceeded the equipment maximum limit due to the high resistive nature of the film. The material presented a highly c-axis oriented single wurtzite structure, strong Al-N bonding and typical-resistive behavior, without imaginary component visible in the Nyquist plots. The conduction mechanism for  $Ti_{1-x}Al_xN$  for x = 0.46 and 0.56 is based upon electron hopping between Ti<sup>3+</sup> and Ti<sup>4+</sup>, and the resistance of the grain boundary is more relevant than the one from the grain at low temperatures. We demonstrate that it is possible to use TiAlN as an NTC-thermistor with different crystal structures and in a broad range of chemical compositions.

**Keywords**: NTC thin-film thermistor, Reactive sputtering, Nitride semiconductors, Impedance spectroscopy, Sheet resistance.



**Figure 1**: Sheet resistance measurement with temperature for each chemical composition, from room temperature to 200 °C in air.

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### Biomimetic Coatings to Regulate Biological Adhesion

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### Abstract:

Surface wettability might be a promising way to regulate biological adhesion on material surfaces in order to have: i) an improvement of biocompatibility, ii) an increase of tissue ingrowth and iii) a de-crease of bacterial adhesion and inflammatory response [1] [2].

Super-hydrophobic surfaces (SHS) have high potential for wide functionality in biomedical and bio-logical sciences due to their availability easy fabrication, and versatility [3] [4].

We present the design of super-hydrophobic hybrid coatings via Lotus leaf-like and Slippery Liquid Infused Porous Surfaces (SLIPS) with an almost negligible wettability (surface free energy 5-50mN/m2) and a low contact angle hysteresis (less than 20°). The inorganic, porous layer is based on ceramic nanoparticles obtained via sol-gel, while the organic layer consists of grafted fluoroalkyl Silanes molecules and trapped polymeric media in the nano-cavities of the solid interface.

The surface morphology and chemistry were investigated both by secondary electrons imaging, EDS analysis, and Atomic Force Microscopy. To assess cell toxicity and biocompatibility, Murine fibroblasts culture was used as *in-vitro* model. MTT as well as PrestoBlue<sup>TM</sup> assay together with morphological analyses were used to access cell vi-ability and proliferation on day 1, 2, 3 and 7 (see Figure 1).

We were able to generate bioinspired superhydrophobic surfaces where samples' hydrophobicity sig-nificantly affects the cell adhesion and viability

**Keywords**: cell adhesive spectra; gradient; nanotopographic interaction; surface wettability; slippery surfaces; biofilm prevention; nonfouling materials.



**Figure 1**: Results of the MTT cell viability assay by coating type.

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## Electroconductive, mechanically resistant, IR-reflective, and antibacterial silk fabric covered with AgNWs

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### Abstract:

Silk materials due to their high biocompatibility, low cytotoxicity, mechanical robustness, biodegradability, and non-inflammatory reaction with skin are an attractive building block for soft bioelectronic [1]. The key issue for their applicability in bio-integrated electronics is the low electrical conductivity of silk.

This study presents electroconductive silk woven fabric functionalized with silver nanowires (AgNWs), obtained in the polyol process [2], using polydopamine (PDA) as a linker. Raman spectroscopy was used to study subsequent stages of the fabric functionalization process. The infrared spectroscopy revealed dominant  $\beta$ -sheets structure of fibroin indicating that silk conformation was retained after PDA and AgNWs coating processes.

The best performance for further electronic application revealed the silk fabric covered with 10 g of AgNWs per m<sup>2</sup>. The surface and volume resistance was respectively about 1.0 x  $10^3 \Omega$  and  $6.8 \times 10^2 \Omega$ , and did not change significantly after 12 months of storage. The functionalization process did not harmfully influenced mechanical properties of silk fabric. The elongation at break was slightly improved and high specific strength was retained. The AgNWs presence on silk fabric resulted in obtaining high infra-red reflectance and antibacterial properties against gram-positive Staphylococcus aureus and gram-negative Klebsiella pneumoniae bacteria.

Modification of silk fabric with AgNWs allowed to obtain multimodal material characterized by electrical conductivity, thermal-insulated and antibacterial properties for designing bioelectronic systems and other biological applications.

**Keywords**: silk woven fabric, AgNWs, electrical conductivity, mechanical properties, antibacterial properties, thermal properties, infra-red reflectance



**Figure 1**: SEM image of silk fabric (fibers) functionalized with AgNWs.

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### Acknowledgements:

The study was carried out in the frame of statutory activities (BZT 01 70) of the Lukasiewicz Research Network - Lodz Institute of Technology in 2021 (Ministry of Science and Higher Education). The study of AgNWs synthesis was financially supported by a grant from the National Poland (Opus Science Centre, 15 no. 2018/29/B/ST8/02016). The measurements were carried out on the equipment purchased in POIG.01.03.01-00-004/08 NANOMITEX project, co-financed by the EU, European Regional Development Fund and the National Centre for Research and Development.

## Improvement of Thermal Comfort, Antibacterial and Electrical Properties of Aramid Textile Material with Silver Nanowires

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### Abstract:

Aramid textile materials thanks to their strong mechanical and excellent thermal properties are used in many fields, e.g. ropes, aircraft parts, bulletproof vests, uniforms, etc. Very important aspect in textile industry is ensuring the safety and comfort of using which is need especially in clothing for high-risk professions, e.g. firefighters. Working in dangerous conditions, such as fires, high temperature, thermal radiation, electrostatic discharge, as well as a humid environment which promotes the development of microorganisms, requires to use firefighting clothing with specialproperties. The thermal comfort, resistance to extremely high temperatures, antymicrobial and electrical properties play an important role in functionality of protective textile materials. The nanotechnology development allows to create such multifunctional textile materials. One of the most interesting nanomaterials is silver in the nanowire form, because of its antibacterial [1], electrical, optical, and reflecting the infrared radiation [2] properties.

In our research we modified meta- and para-aramid fabric with silver nanowires (AgNWs) colloid with a dip-coating method, in order to give them antibacterial and conductive propertiesand to improve the thermal comfort. We applied AgNWs colloid by 5 times on the fabrics surface (Figure 1). The effects of the modification were assessed using scanning electron microscopy (SEM/EDS), DSC and TG/DTG analysis and IR thermography, as well as the measurement of electrical surface and volume resistance.

**Keywords**: para-aramid, meta-aramid, silver nanowires, antibacterial properties, electrical surface and volume resistance, SEM/EDS, DSC, TG/DTG, IR thermography.



**Figure 1**: SEM image of meta-aramid fiber with AgNWs coating

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### Acknowledgement

The study has been carried out within the National Science Center project: 2018/29/B/ST8 02016, on the equipment purchased in the Key Project - POIG.01.03.01-00-004/08 Functional nano- and micro textile materials -NANOMITEX and WND-RPLD. 03.01.00-001/09.
# EGF2022 - Session I. B: Graphene and 2D Materials synthesis, characterization, and properties

## CVD graphene as an effective tool for the protection of artworks

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#### Abstract:

All art materials are generally prone to degradation. In particular, the 20th century cultural heritage shows short lifetime expectancy due to the introduction of novel materials and techniques. The exposition of contemporary artworks to UV and visible light, also in addition to oxidizing agents, trigger some degradation effects, such as fading, yellowing and discoloration. The result of these degradation mechanisms is the severe and irreversible alteration of the readability of the artworks, which is an inestimable legacy of mankind. Graphene-related materials have been found to provide considerable ultraviolet shielding as coatings, while a single layer CVD graphene absorbs up to 3 times more in the UV region (190-400 nm), than in the visible range. Additionally, chemical molecules such as water or oxygen cannot penetrate a continuous graphene membrane providing the ultimate shield against degradation. An invisible veil of graphene could provide protection for old and contemporary paintings against all these factors.

According to literature the most effective way of large-scale CVD graphene transfer is the roll-to-roll method (Figure 1). The basic parameters which define the success of the transfer process are the transfer rate, temperature and pressure [1]. In publications it is highlighted that the slower the transfer rate, the more effective is the graphene transfer. Additionally, based on preliminary experiments that have been performed during the micro-rolling procedure, it was observed that mild heating has positive effect on the transfer quality. Regarding the transfer pressure, it is noticed that application of high pressure between the rollers results in homogeneous transferred graphene film [2, 3]. In the frames of ERC-PoC GRAPHENART Project, we covered artworks with graphene using the roll-to-roll method for dry graphene transfer, while an environmental chamber was constructed as well for accelerated environmental aging measurements, in order to observe the protection factor of graphene to the artworks.

**Keywords**: two-dimensional materials, art protection and conservation, dry roll-to-roll graphene transfer



**Figure 1**: Graphene deposition onto artworks: Schematic illustration of the roll-to-roll process used to transfer graphene onto mock-ups and real artworks.

- M. Kotsidi *et al.*, "Preventing colour fading in artworks with graphene veils," *Nat. Nanotechnol.*, pp. 1–7, 2021, doi: 10.1038/s41565-021-00934-z.
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# Multiple graphene chemical modification strategies for the development of electrical conductive nanocomposite at low percolation threshold

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#### Abstract:

Despite numerous advantages of graphene in terms of electrical, mechanical and thermal properties, dispersion of this filler in polymer matrices is still a challenge<sup>1</sup>. Oxidation or functionalization of graphene can improve the dispersion of these nanoparticles but some intrinsic properties like the electrical conductivity are altered. A compromise has to be found between good dispersion in polymer matrices and structure preservation of graphene. Moreover, graphene is expensive in the market. The necessity to reduce the percolation threshold of graphene in polymer matrix is also a challenge<sup>2</sup>. This study discusses the effect of the graphene modifications on its dispersion in immiscible polymethyl methacrylate/ polystyrene (PMMA/PS) polymer blend. A parallel work deals with the development of electrical conductive silicone for flexible electronics application. Polymer blend nanocomposites were produced in two steps: first a masterbatch of graphene or graphene modified (GO-g-PMMA) with the PS matrix was carried out with a solvent cast method, then this masterbatch was meltblending with PMMA. Different graphene structure were synthesized thanks to several chemical modifications strategies (Hummers' oxidation, hydrazine or thermal reduction, P(MMA-co-2hydroxyethyl methacrylate (HEMA)) copolymer functionalization). The goal of those modifications is to control the localization of nanoparticles especially at the interface of the PMMA/PS polymer blend (Figure 1a.b) in order to reduce the percolation threshold <sup>3</sup>. The other interest is to determine parameters that influence the nanoparticles migration during the melt process. For that purpose, impact of graphene chemical treatment, mixing time during the melt-blending, mixing sequence and polymers viscosities on nanoparticles migration were investigated. For silicone matrix, graphene was modified with a polydimethylsiloxane terminated aminopropyl (PDMS-NH<sub>2</sub>). By grafting PDMS agent on graphene (GO-g-PDMS), dispersion of nanoparticles can be improved and electrical conductivity can be reached at low percolation threshold (Figure 1 c.d). Several characterization were carried out on modified graphene to confirm the copolymer grafting and electrical performance (TGA, RAMAN, XRD, FTIR, Py-GC/MS and electrical resistance measurements). Rheological analysis, electrical measurement, STEM images were used for nanocomposites characterization to confirm nanoparticles localization and evaluate the electrical conductivity.

**Keywords**: graphene, functionalization, polymer blend, silicone, electrical conductivity, localization control, nanocomposite, percolation



**Figure 1**: Schematic representation of fillers localization in (a) graphene/PMMA/PS, (b) (GOg-PMMA)/PS/PMMA, (c) graphene/PDMS and (d) GO-g-PDMS/PDMS nanocomposites.

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## High Optical Response of Room Temperature Graphene Bolometers Fabricated through Various Methods

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#### Abstract:

We studied the optical response of room-temperature graphene bolometers fabricated via various methods. The methods employed were drop-casting and ink-jet printing of graphene inks and thermal reduction of graphene oxide. The 2 mm x 2 mm sensors were deposited or placed on 15 mm x 15 mm silicon substrates. Ink-jet printed bolometers were printed with a Sonoplot® Microplotter Proto. The graphene oxide samples were synthesized via modified Hummer's method and were subsequently drop-casted and then thermally-reduced at 200 °C for 2 hours. Raman spectroscopy exhibited the typical peaks corresponding to graphene for both the dropcasted and ink-jet printed inks, and confirms the reduction of the graphene oxide films after thermal treatment.

Since bolometers operate on the principle of changing resistance with respect to temperature changes, we measured the temperature coefficient resistance (TCR) of the samples. We also measured the optical response to power of the samples to an IR laser with a peak wavelength of  $\lambda = 783$  nm. The IR source was turned on and off at varying frequencies from 1 Hz to 10 kHz. This also allowed us to estimate the thermal time constant of the bolometers. Printed graphene bolometers exhibited a TCR of  $-0.6 \, \% K^{-1}$ . On the other hand, drop-casted graphene and thermally reduced graphene oxide (TRGO) exhibited higher TCRs of up to -2.8 %K<sup>-1</sup>. Response times of about 0.5 kVW<sup>-1</sup>, 1 kVW<sup>-1</sup>, and 3.5 kVW<sup>-1</sup> were obtained for the printed, TRGO and drop-casted samples, respectively. From the dependence of the responsivity to the frequency, we obtained thermal time constants of 0.7 ms, 0.2 ms, and 0.4 ms for the printed, TRGO and drop-casted samples, respectively.

We see a noticeable effect on the bolometric properties of ink-jet printing compared to the drop-casted samples, having both came from the same graphene ink. However, it cannot be attributed solely to defects in graphene, as a result of the mechanical forces from the piezoelectric element in the ink-dispenser. The higher optical responsivity and poorer graphene quality of the TRGO compared to the printed sample is inconsistent with such conclusion. Instead, we explore other possible explanations and describe further confirmatory experiments.

**Keywords**: bolometer, graphene, thermally-reduced graphene oxide, responsivity, temperature coefficient of resistance, time constant, ink-jet printing



**Figure 1**: The best optical response of 3,500 VW<sup>-1</sup> was obtained from the drop-casted graphene ink. The thermal time constant of 0.4 ms was estimated from the cut-off frequency of the responsivity vs frequency graph.

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# Composition and structure of the universal, airborne hydrocarbon contaminant layer on van der Waals material surfaces

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#### Abstract:

Layered (van der Waals) materials have gained special interest in the last decade because many of them can be exfoliated down to single unit cell thickness. As the thickness decreases, surface effects become more pronounced; hence, both environmental adsorbates and substrates can substantially influence their properties. Under ambient conditions surface contamination is inevitable, but our knowledge is very limited about its components; usually being described as 'some hydrocarbon and adsorbed water'.

Here we show by complementary, high-resolution AFM and STM microscopy that after a few days under ambient conditions, a self-organized, crystalline lattice of molecules is formed on the surface of van der Waals materials. The molecules self-organize into parallel stripes with 3-4 nm periodicity on several, distinct surfaces: graphene, graphite, hBN, MoS<sub>2</sub>. By low-temperature STM measurements, we have resolved the atomic structure of the molecules on graphite and in combination with infrared spectroscopy, we reveal that the molecules are linear, saturated hydrocarbons with a length of 20-26 carbon atoms, most likely normal alkanes. We show a direct causal link between the self-organized stripe structure of the molecule layer and the wellknown, yet unexplained friction anisotropy domains measured on vdW materials. Additionally, we found that repeated scans along a selected zigzag direction of the host surface in contact mode AFM enables the redrawing or "nano-patterning" of the friction domains. Beyond the manipulation of the molecular lattice, we show details of the growth dynamics and the controlled desorption through annealing. Our work is a major step towards understanding the origin of the ubiquitous hydrocarbon contamination on vdW crystals and its effects on their measured properties. The preprint is available at [1].

**Keywords**: van der Waals materials, 2D materials, contamination, alkane, graphene, hBN, MoS<sub>2</sub>, friction, self-organization, SAMs



**Figure 1**: a) PF AFM topography image of a tripoint boundary of the stripe structure on graphene. b) Contact mode AFM torsion signal on the same area as (a), revealing three distinct friction domains corresponding to the three differently oriented molecule domains.



**Figure 2**: a) Low temperature STM image of the airborne contamination on HOPG revealing the inner structure of the molecules. b) Simulated structure and arrangement of an alkane monolayer on graphite. The blue arrows mark the direction of the lamellas/stripes.

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#### **Acknowledgements:**

The work was conducted within the framework of the Topology in Nanomaterials Lendulet project, Grant No. LP2017-9/2/2017, with support from the European H2020 GrapheneCore3 Project No. 881603. Funding from the National Research, Development, and Innovation Office (NKFIH) in Hungary, through the Grants K-134258, K-131515, FK 125063 and Élvonal KKP 138144 are acknowledged.

# In situ Transformation of Graphene to Diamond-Like Carbon for Conductive Coatings

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#### Abstract:

Diamond-like carbon (DLC) based materials are gaining popularity for tribological applications, biomedical devices, semiconductors, and thermal management systems due to their unique properties such as high hardness, low coefficient of friction, chemical inertness, and low reflectivity(I). DLC is a metastable form of carbon comprising random networks of sp<sup>2</sup> and sp<sup>3</sup> hybrids(2). DLC-based coatings thus possess a combination of graphitic and diamond characteristics. Fabrication of DLC-based materials, unlike diamond, requires lower energies which is a crucial practical advantage for coating applications.

Plasma electrolytic oxidation (PEO) induces the formation of environmentally inert ceramic coatings on light metal surfaces. The process applies a high direct current (DC), pulsed DC or alternating current (AC) between a stable cathode and target substrate in an electrolytic bath. A wear and corrosion resistant oxide coating forms due to micro-arc discharge channels generated on the substrate surface. Traditional PEO processes are energy intensive and require >400 V to produce thick adherent coatings on light metals. Cirrus proprietary PEO technology produces adherent and mechanically robust coatings on light metals (Mg, Al, Ti) using low energy (~160 V) and benign alkaline organo-silicate electrolytes(3, 4). The approach to induce diamond-like behaviour in PEO-modified coatings entailed the addition of graphene dispersed in medical grade polyol, a viscosity modifier, to the electrolyte. Cirrus PEO treatment process occurs at room temperature however the localized temperatures at the arc discharge points can reach 3000 °C. Electrolyte viscosity due to polyol addition aids in increasing the pressure at arc discharge sites thus enabling the transformation of graphene to DLC.

**Keywords**: Diamond-like coatings, environmentally friendly PEO technology, sp<sup>2</sup> to sp<sup>3</sup> transformation, light metal alloys, corrosion-resistant surfaces..



**Figure 1**: Illustration showing the transformation of  $sp^2$  carbon to  $sp^3$  diamond-like carbon during plasma-electrolytic treatment of light metals.

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## An Electrochemical Approach for the Surface Modification of 2H-Phase MoS<sub>2</sub> nanosheets towards Enhanced Catalysis

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#### Abstract:

We describe a novel strategy for the surface functionalization of 2H-phase MoS<sub>2</sub> nanosheets, which affords the grafting of different molecular groups (e.g., acetic acid groups) derived from organoiodides, via an electrochemical strategy [1]. Upon cathodic treatment of a pre-expanded MoS<sub>2</sub> crystal in an electrolyte containing the corresponding organoiodide, water-dispersible nanosheets with a derivatization degree of ~0.10 molecular groups per surface sulfur atom are obtained. This expands the scope of covalent molecular functionalization of two-dimensional MoS<sub>2</sub>, which so far has been mainly restricted to the metastable 1T phase [2]. Functionalization is shown to be driven by the external supply of electrons to the MoS<sub>2</sub> nanosheets provided by the applied cathodic potential although proper reducing agents can be used instead, and to be controlled by the presence of defects (e.g., S vacancies) in the 2H-MoS<sub>2</sub> lattice, where the molecular groups can bind. The functionalized nanosheets were tested as a catalyst for the reduction of nitroarenes and organic dyes with NaBH<sub>4</sub>, which is relevant in environmental remediation and chemical synthesis [3]. The results showed a remarkably enhanced catalytic activity compared to that of non-functionalized 1T- and 2H-phase MoS<sub>2</sub> nanosheets as well as non-noble metal catalysts previously reported for this application. Several concentrations of the organic substrates were also used, and the derivatized 2H-MoS<sub>2</sub> nanosheets retained a good catalytic activity even at realistic (high) reactant concentrations, as well as with binary and ternary mixture of the substrates. The 2Hphase MoS<sub>2</sub> catalyst could also be immobilized on a polymeric scaffold in order to facilitate its manipulation and reutilization for several catalytic cycles. Analysis of the reduction kinetics revealed a correlation between the catalyst activity and the net electric charge of the organic substrates, which was rationalized as arising from the different charge-dependent abilities of the reactants to diffuse to the negatively charged, functionalized  $MoS_2$  surface.

**Keywords**: two-dimensional (2D) materials, transition metal dichalcogenides (TMDs), MoS<sub>2</sub>, electrochemical exfoliation, colloidal dispersion, functionalization, catalytic reduction.



**Figure 1**: Scheme of the electrochemical cathodic strategy used to obtain 2D derivatized, water-procesable dispersions and its potential application to the reduction reaction of several nitroarenes and organic dyes.

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#### Acknowledgements

Funding by MICINN/AEI/FEDER through project RTI2018-100832-B-I00 is gratefully acknowledged. A.M-J. is grateful to MICINN for his predoctoral contract (PRE2019-087583).

# Growth and physics-chemical characterization of graphene electrodes sintherized by electrochemical exfoliation

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#### Abstract:

The growths need in developming of the energy supply devices such as bateries and great capacitors has lead to the improvement and innovation of these devices for that store energy efficiently and aditionally be small, light, with low production costs and friendly to the environment. Therefore, In this work is present the preliminary results of the development of graphene-based electrodes for be used as electrodes of the bateries. The graphene will be synthesized by means of the electrochemical exfoliation technique and deposited as a coating on common glass, silicon and Bakelite by means of the spray technique. The study and characterization of chemical properties will be carried out using Raman spectroscopy and X-ray photoelectron spectroscopy techniques, in addition, the electrical properties in the silicon and Bakelite electrodes and the optical properties in the glass electrode will be evaluated.

Keywords: Grapne, electrochemical exfoliation, electrical properties

### Graphene Oxide Reinforced Asphalt Pavements

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#### Abstract:

The improvement of asphalt pavement performance characteristic through the use of additives is a research and practice goal for a long time, with the consideration of nano-additives to build up in recent years. The aim of this study is to develop, analyze, and test graphene-reinforced asphalt concrete for advancing the stiffness and durability of asphalt pavements. Existing studies have mainly focused on analyzing the effect of the nano-additives on the asphalt binder itself while, in the current study, the performance outcome of the asphalt concrete is sought. Two types of nanomaterials. Graphene Oxide (GO) and reduced Graphene Oxide (rGO), in various mixing proportions were considered while the study has also considered alternative ways of mixing these materials into the asphalt binder. The asphalt concrete specimens that were produced went through several standardized tests to evaluate their mechanical properties (Ring & Ball, Needle Penetration, Elastic Recovery, Marshall Stability and Flow, Stiffness, Cyclic Compression). The test results indicate that the addition of GO/rGO has an effect on pavement performance. In particular, the largest improvement results at a 1% proportion of GO/rGO to the asphalt binder (Figure 1) while lower or higher concentrations exhibit rather moderate performance improvement. The full set of tests and analyses indicate the potential of using GO/rGO for enhancing asphalt pavement performance, in terms of stiffness and rutting resistance, provided that the production cost of such materials becomes more competitive in the future.

**Keywords**: asphalt concrete, bitumen, Graphene Oxide (GO), reduced Graphene Oxide (rGO).





Figure 1: Testing equipment and results of stiffness test (EN 12697-26:2018).

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## Measurement of the out-of-plane optical constants of a two-dimensional crystal

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#### Abstract:

The out-of-plane optical constants of two-dimensional (2D) materials have proven to be experimentally elusive. Therefore, there remains an absence of scientific consensus on how to correctly model these materials. Theoretical descriptions span from isotropic three-dimensional slabs [1] to two-dimensional surface currents with a null out-of-plane surface susceptibility [2, 3]. Here we perform a smoking gun experiment on the optical response of a single-layer two-dimensional crystal that addresses these problems [4]. We determine both the in-plane and the out-of-plane components of the monolayer surface susceptibility tensor. Our results prescribe one clear theoretical model for these crystals.

The main experimental problem in the analysis of the optical response of a 2D crystal is the role of the substrate, that adds a background signal, hiding the small contribution that comes from the out-of-plane optical constants [5]. In a two-step experiment, we measure the in-plane  $(\chi_{\parallel})$  and the out-of-plane ( $\chi_{\perp}$ ) surface susceptibilities, and the in-plane ( $\sigma_{\parallel}$ ) and the out-of-plane ( $\sigma_{\perp}$ ) surface conductivities. First, we extract the ellipsometric data ( $\Psi_s$ ,  $\Delta_s$ ) from a single-layer 2D crystal deposited on a transparent dielectric substrate, namely polydimethylsiloxane (PDMS). Then, the same crystal is completely immersed in PDMS for a second ellipsometric measurement that provides a new set of data ( $\Psi_i$ ,  $\Delta_i$ ). By inverting the fundamental equation of ellipsometry it is possible to extract  $\chi_{\parallel}, \sigma_{\parallel}, \chi_{\perp}, \sigma_{\perp}$  from  $\Psi_s, \Delta_s, \Psi_i$ ,  $\Delta_i$ . The light reflected by the sample in this second step is 2 orders of magnitude less than in the previous one, because there is no more the substrate contribution. For this reason, we set up a manual ellipsometer at the wavelength of 633 nm to measure  $\Psi_i$  and  $\Delta_i$ .

Table 1 resumes our results. The in-plane constants ( $\chi_{\parallel}$ ,  $\sigma_{\parallel}$ ,) that we measure are compatible with those measured by other experimental groups [1, 6]. The out-of-plane constants ( $\chi_{\perp}$ ,  $\sigma_{\perp}$ ) are measured for the first time in this experiment. Their observed value agrees well with ab-initio theoretical predictions ( $\sigma_{\perp}$  for both graphene and MoS<sub>2</sub> is compatible with zero within our experimental error) [7].

Our measurements indicate that a monolayer 2D crystal must be modelled as two surface-electric currents due respectively to the in-plane and the out-of-plane varying surface polarizations [4].

**Table 1**: Optical constants for monolayer graphene and  $MoS_2$  at a wavelength of 633 nm.

	χ <sub>∥</sub> (nm)	σ∥ (10⁻⁵Ω⁻ ¹)	χ⊥ (nm)	σ⊥ (10 <sup>-6</sup> Ω <sup>-</sup> ¹)
Gra- phene	$1.7\pm0.2$	$\textbf{6.8}\pm\textbf{0.3}$	0.6± 0.2	3 ± 3
$MoS_2$	$\textbf{10.8} \pm \textbf{0.5}$	$\textbf{15.0}\pm\textbf{0.4}$	1.1±0.4	$1\pm3$

**Keywords**: 2D materials, birefringence, optical properties.

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### Novel device engineering strategies for printable photovoltaics

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#### Abstract:

There is significant interest in the use of solution processed photovoltaics (PVs) due to their compatibility with large scale, high throughput fabrication processes (ink-jet printing, slot-die coating, doctor blading, etc). However, for the commercialization of solution processed emerging PVs, their efficiency and long-term operational stability should match with the commercial PV standards accompanied with a lower production cost, exploiting high-throughput fabrication processes to cover the rapidly growing energy demands. In this talk, I will discuss how novel material, interfacial and compositional engineering strategies on printed PVs can result in highly efficient and stable photovoltaic devices with a manufacturing cost that is below that of traditional energy sources. Firstly, I will demonstrate the beneficial role of graphene as current collecting electrode in fully printed perovskite solar cells with high efficiency (>15%) and stability (>10000 hours). Additionally, I will present the beneficial role of inorganic passivation agents as a novel strategy to achieve >24% power conversion efficiency. Finally, I will present a novel approach for achieving ~25% power conversion efficiency and >1000 hours operational stability in perovskite solar cells using fine-tuned surface and bulk passivation agents.

**Keywords**: perovskite solar cells, graphene electrodes, interfacial engineering, passivation, solution processing, printed solar cells, carbon electrodes.



**Figure 1**: Figure illustrating the fully printed perovskite solar cells fabricated using the mesoscopic device configuration, employing the mixed cation lead mixed-halide perovskite as the absorber layer, different HTMs and the graphene as the current collecting electrode.

#### Acknowledgements:

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 101024237.

- 1. G. Kakavelakis et al, 2022 (Submited)
- 2. T. Baumeler et al, 2022 (Submited)
- 3. E. Alharbi et al, 2022 (Submited)

# Machine learning integrated with microscale numerical simulation to investigate the thermal conductivity of cementitious composites reinforced by graphene derivatives

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#### Abstract:

Owing to their exceptional conductivity, graphene derivatives are a promising candidate for the development of multifunctional cementitious composites [1]. Graphene derivative reinforced cementitious composites (GDRCCs), possessing high thermal conductivity, can be exploited for diverse applications, including pavements with snow-melting functionality, underfloor heating systems, and deep geothermal exploitation. Furthermore, the optimum amount of graphene derivatives can render cementitious composites with improved thermal conductivity, thereby reducing temperature gradients and minimizing thermal and shrinkage crackings.

It is important to explore the range of thermal conductivity that can be achieved by GDRCCs and how different parameters such as the constituent's properties affect their conductivity.

Even though numerical simulation is a powerful approach to predict the thermal conductivity of GDRCCs, machine learning (ML) techniques can predict composites' conductivity efficiently with minimal computational costs [2]. ML models demand a comprehensive and precise dataset. However, obtaining such a large dataset via experimental studies is demanding. Hence, this study takes advantage of both ML and numerical simulation through a hybrid modelling approach by employing numerical simulations to generate the required dataset to establish the ML models. Accordingly, a representative volume element (RVE) is generated (Fig.1) and the prediction results are validated against limited available experimental data in the literature. The simulations of the thermal conductivity of diverse GDRCCs are implemented by assigning various values for the matrix thermal conductivity, volume fraction, diameter and conductivity of graphene derivatives. Eventually, the hybrid modelling approach presented in this study is capable of capturing the relationships among the thermal conductivity of GDRCCs and varied input variables efficiently.

**Keywords:** numerical simulation, machine learning, thermal conductivity, graphene derivatives, cementitious composites.



Figure 1: Flow chart of RVE generation.

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## A leap from non-conductive to conductive states: transformation of multilayered graphene oxide structures to carbon powders and films

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#### Abstract:

Graphene materials drew initial attention mostly because of their interesting electronic properties and not because of many other special characteristics that have been revealed since the "graphene era" of the early 2010's. While electronic transport properties of single sheets are greatly unique, there has been much les focus on the electronic properties of multilayered assemblies (thin films, particles, membranes) of graphene materials. It is also a rather uncommon knowledge that ultrathin films assembled from the insulating, oxidized sheets of graphene (graphene oxide, GO) and polyionic species are feasible to demonstrate the changes in the electronic properties of carbon sheets associated with the chemical or thermal transformation of graphene oxide to its less oxygenated, "rGO" form.

In this presentation, we will highlight our contributions to the characterization of the sharp transition between conductive and non-conductive states of multilayered graphene based thin films<sup>1</sup>. Also, the exfoliative transformation of powdered, "bulky" graphite oxide to the soot-like black carbon of considerable specific surface area will be investigated and related to the type, composition and purity of graphite oxide particles, as well as the physical parameters such as inert gas pressure used upon the thermal exfoliation procedure<sup>2</sup>. Finally, we devote a great deal to investigate the layer-by-layer formation and structure of multilayered assemblies of graphene oxide/polymer and graphite oxide/polymer composites, including the charge-reversal induced deposition of individual monoparticulate layers and their structural properties<sup>3</sup>. The information presented may be of interest for resaerchers both in academia and industry to fabricate successfully ultrathin graphene derived coatings, and also to fabricate large-area GO-derived solids by chemical or thermal decomposition<sup>4</sup>, which may be of efficient use for contaminant adsorption or as electoactive materials in advanced energy storage devices.

Keywords: graphite oxide, chemical reduction, thermal degradation, ultrathin films. layer-by-

layer build-up, thin film deposition, planar conductivity, deflagration

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## Graphene-based composite with high stable dispersion in ethanol.

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#### Abstract

Graphene is a 2D carbo-material with very particular physical features such as electroconductivity, thermo-conductivity, mechanical stability, and its peculiar aspect ratio with a high surface and a negligible thickness  $(^{1-3})$ . Graphene can be dispersed at high concentration only in polar aprotic solvent such n-methyl-2-pyrrolidone as or dimethyl formamide (<sup>4</sup>) both solvents with a high boiling point and high toxicity for the human and the environment.

For these reasons is preferred to use the oxidised form of graphene, graphene oxide (GO), most easy to disperse, and reduce it to reducer graphene oxide (rGO). However, GO have more defects on the surface than pristine graphene losing a part of the natural performance of the graphene.

Other solutions to solubilise/suspend pristine graphene is the use of molecular surfactant  $\binom{5}{}$  or polar polymer such as the PVP  $\binom{6-8}{}$  to disperse of the material with a good concentration in water.

In this work a new surface modification obtained by reaction with ethyl maleate made graphene easy to disperse in organic polar solvents such as ethanol. Uncontrolled growing of polymer (ethyl maleate derivate) on the surface of the material was performed by microwave reactor that allows the formation of of polymer maleate on the surface of the graphene. This material has good stability in ethanol and maintains that feature after a long time.

This process allows production of graphenebased inks or the deposition on other surfaces by simply removal of the solvent. At the same time the polyethylmaleate can be removed by simply ablation originated from heating of the material in an inert atmosphere to obtain pristine graphene with a low number of defects.



Graphene with poly maleate stability in ethanol

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# Semiclassical analysis of tunneling in graphene in the presence of a smoothly inhomogeneous external electromagnetic field

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#### Abstract:

Wave functions of electrons and holes in the monolayer graphene immersed in external static electric and magnetic fields satisfy the 2D Dirac equation. The orientation of fields is shown on Fig. 1a, both fields are smoothly inhomogeneous and depend only on x coordinate. Let electrostatic potential vary in a monotone way. We study the influence of a magnetic field, which assumed to be not very large, on the process of tunneling of electrons and holes incident on the potential barrier under different angles. If the magnetic field is absent, the particles incident on the potential barrier along x axis transmit without reflection for any energy. It is the wellknown Klein tunneling phenomenon. For the case of not normal incidence, the wave is reflected: reflection and transmission for the case of arbitrary smooth monotone electrostatic potential were studied asymptotically in [1],[2].

Here, we take into account the magnetic field and study its influence on the Klein tunneling. The dependence of wave function on y coordinate is given by the factor  $exp(ik_yy)$ . We apply a semiclassical approximation. The problem is reduced to the system of ordinary differential equations with a small parameter at the derivatives. Detailed asymptotic description requires considering vicinities of the degeneracy (turning) points.

Outside vicinities of the degeneracy points solutions can be found in the WKB approximation. We show that in the presence of magnetic field two degeneracy points occur, see Fig. 1b. Let WKB solutions  $\Psi$  of the Dirac equation in the classically allowed regions read

 $\Psi \approx k_e^- \Psi_{e^-} + k_e^+ \Psi_{e^+}, \quad \Psi \approx k_h^- \Psi_{h^-} + k_h^+ \Psi_{h^+},$ where  $\Psi_{e^-}$  and  $\Psi_{e^+}$  are WKB solutions running in the electron zone in the positive and negative *x* directions, respectively, WKB solutions  $\Psi_{h^-}$  and  $\Psi_{h^+}$  are determined analogously. The transfer matrix **T** is defined as follows

$$\binom{k_h^-}{k_h^+} = T\binom{k_e^-}{k_e^+}$$

The problem with two turning points was studied in the general case in [3], where the transfer matrix, and reflection (R) and transmission (T) coefficients for particles incident on the barrier were found. Applying results of [3], we found not only modules of R and T but also their phases which can be useful for studying the n-p-n junction.

The qualitative analysis for this case was given in [4] in assumption that the magnetic field does not influence the tunneling on distinct e-n or n-e transitions.

The influence of the small mass term also discussed.

**Keywords**: semiclassical approximation, Dirac fermions, p-n junction, reflection coefficient, transition coefficient, transfer matrix.



**Figure 1 a)** Geometry of the problem. The electric field **E** is in the plane of graphene, the magnetic induction **B** is perpendicular to the sheet of graphene; **b**)  $\mathcal{E}$  is an energy of the particle, U(x) is an electrostatic potential. A degeneracy (turning) point  $x_{\mathcal{E}}$  splits into two turning points of the first order  $x_e$  and  $x_h$ . Grey region x is a classically forbidden zone, orange regions x are classically allowed zones.

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#### Acknowledgment:

This work was supported by RFBR grant no. 20-02-00490.

# SMS 2022 Session II. A: Functional / Multifunctional, Composites and Responsive Materials

### Functional nanostructures based on smart copolymers

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#### Abstract:

Amphiphilic and water-soluble copolymers present a number of interesting stimuli responsive self-assembly properties in aqueous solutions forming nanosized structures through self-assembly or co-assembly with other entities (e.g. polyelectrolytes, proteins, nucleic acids, inorganic nanoparticles). These gives them high application potential as smart materials in drug and gene delivery, functional interfaces and surfaces, antimicrobial protocols. Reversible addition-fragmentation chain transfer (RAFT) polymerization has been proven to be an effective and flexible synthesis methodology for the preparation of different copolymer architectures using a gamut of functional monomers. Here we present the synthesis of novel linear diblock copolymers, random-diblock terpolymers, triblock terpolymers and hyperbranched copolymers utilizing functional monomers through RAFT polymerization schemes. The copolymers present stimuli responsive self-assembly behavior in aqueous media as a function of copolymer molecular characteristics, architecture and solution pH, temperature and ionic strength. Their co-assembly with linear DNAs, globular proteins, hydrophobic drugs and magnetic nanoparticles provides proof of concept for the development of functional (bio)hybrid nanostructures with potential applications to nanomedicine (drug, gene and protein delivery), water purification and bio-imaging.

**Keywords**: smart copolymers, complex macromolecular structures, polymer synthesis, responsive nanostructures, self-assembly, co-assembly, nanoparticles, drug delivery, biomedical applications. Amphiphilic block polyelectrolyte micelles PH, LCST pH and thermo-responsive nanoassemblies

**Figure 1**: Figure illustrating the variety of block copolymer self-assembled and co-assembled nanostructures we study with potential nanotechnology applications in nanomedicine, agriculture and water purification

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Polymer self- and co-assembly

## Shape Memory Polymer Composites for Space Sustainability

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#### Abstract:

Shape memory polymer composites (SMPCs) are smart materials that combine structural properties of fiber reinforced laminates with functional behavior of shape memory polymers. They can change their configuration reacting to specific external stimulus, mostly heat-induced, and remember the original shape.

SMPCs are optimal candidates to develop new concept structures for space applications from deployable systems (such as solar sails, panels, shields, booms, and antennas) to grabbing devices.

SMPCs are also sustainable materials not for their chemical nature, but for their functionalities. In fact, they can clean Space by removing space debris and allow the use of solar energy by deploying solar panels and solar sails. Moreover, as tested, they are low weight and durable in the Space environment.

Commercial CFR prepregs have been used for samples fabrication (HexPly/M49/42%/ CHS-3 K by Hexcel). These prepregs are 0/90 fabrics with high performance epoxy matrix. The functional SM behavior is added to the composite laminates by using an uncured epoxy resin in the form of fine powder (Scotchkote 206 N by 3 M). Differential scanning calorimetry and dynamic mechanical analysis have been used to evaluate the thermo-mechanical behavior of the SMPC laminate in comparison with the CFR laminate and the SM epoxy resin of the interlayer. Recovery tests have been carried out for evaluating the shape memory behavior.

SMPCs have also been tested in different space missions, in microgravity condition inside and outside the International Space Station. Figure 1 shows the sample of the Materials International Space Station Experiment- MISSE-9.

In this work, the achievement in SMPC design and testing in Space and on ground is discussed, considering the new concept of Space sustainability.

**Keywords**: shape memory polymer composites, space sustainability.



**Figure 1**: Figure illustrating the sample of the Materials in Open Space (M.in.O.S.) project: Polymers and Composites Experiments during the MISSE-9 space mission.

This experiment aims to evaluate on-orbit sample recovery due to solar heating, and the aging effect of space exposure on shape memory behavior, mass loss & material degradation (crosslinking, chain polymer break, delamination, and embrittlement).

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## Facile preparation of MXene/rGO composites with hydrophilic/hydrophobic properties

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#### Abstract:

Currently, a new family of 2D nanomaterials, i.e. MXene are receiving huge interest from the scientific society. The natural hydrophylicity of the MXenes is an important advantage for their functionalization and incorporation in different matrices. However, the decrease of their conductivity due to formation of TiO<sub>2</sub> is a serious drawback. Coupling with graphene has been reported to protect MXenes against oxidation and to enhance their conductivity [1, 2]. In the present work, MXene/reduced Graphene Oxide (M/rGO) composites were synthesized via facile one-pot hydrothermal or solvothermal processing. Initially,  $Ti_3C_2T_x$  type MXene was prepared by etching of Ti<sub>3</sub>AlC<sub>2</sub> MAX phase with LiF/HCl and consequent delamination under Argon flow, while graphite oxide (GtO) was manufactured via oxidation of natural graphite by modified Hummers' method. Then, MXene/GtO mixtures with 3:1 weight ratio were dispersed in water and isopropanol and treated in autoclaves at 180 °C for 16 h resulting in w-M/rGO and i-M/rGO composites, respectively. The XRD analysis revealed the characteristic MXene peak at  $2\theta \sim 6^{\circ}$  as well as some peaks originating from the parent MAX phase. Diffraction peak corresponding to the GtO component was not observed due to its delamination and reduction to rGO during the treatment. For the composite prepared in water medium, formation of TiO<sub>2</sub> in the form of anatase and rutile was found. On the contrary, these titania peaks were not observed for composite prepared in isopropanol medium. The SEM analysis also evidenced the presence of TiO<sub>2</sub> in the w-M/rGO composite. In addition, it was found that hydrophilic MXene/rGO composite was produced when water was used as solvent, while the treatment in isopropanol resulted in MXene/GtO composite with strong hydrophobic behaviour. This outcome was related with: (i) the initial MXene/GtO ratio used and (ii) the influence of the water and isopropanol media on the processes of MXene oxidation and Graphene Oxide reduction which occur simultaneously during the thermal treatment. The results can be utilized for MXene protection during processing, but also for functionalization of MXene/rGO composites in order to be incorporated in hydrophilic/hydro-phobic formulations.

**Keywords**: 2D nanocomposites; MXene; reduced graphene oxide; hydrothermal; hydrophylicity; hydrophobicity.



**Figure 1**: XRD patterns and SEM images of the MXene/reduced Graphene Oxide (M/rGO) illustrating the influence of the solvent i.e. water (w) and isopropanol (i) on the composition and the morphology of the nanocomposites.

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#### Acknowledgements:

The support from National Scientific Program "Petar Beron i NIE" contract number K $\Pi$ -06- $\chi$ E/3 and "2D-NanoSMART" is highly appreciated.

## Patterned and Collective Motion of Densely Packed Tapered Multi-Responsive Liquid Crystal Cilia

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#### Abstract:

Cilia are of vital importance for myriad of natural functions such as the propulsion of microorganisms or the cleaning of the mammalian respiratory system.<sup>[1]</sup> These cilia often show coupled shape changes such as waves to perform their function. In recent years, there have been many attempts to artificially mimic natural cilia, for instance by magnetically doped elastomers or liquid crystal polymers.<sup>[2]</sup> Unfortunately, most of these attempts have been lacking in either size, versatility in bending patterns, or dense surface coverage. Here, we present a new versatile platform of responsive azobenzene-doped liquid crystal polymer microcilia obtained through a replica-moulding process, by using a commercially available track-etched membrane as a template.<sup>[3]</sup>

Our cilia are tunable in size and show excellent homogeneity over large areas. Symmetry inside the cilia is broken by electrically aligning the liquid crystal monomers during polymerisation. This process programs an actuation direction into the individual cilia. Due to the built-in alignment, the cilia actuate out-of-plane in response to a temperature increase. In addition, the incorporated azobenzene derivative provides light responsivity. The bending speed and tip displacement of the cilia are modulated through careful adjustment of the actuating stimulus. Illuminating the cilia with a constant blue light source and a pulsed UV light source gives back and forth oscillation with a predetermined frequency. We anticipate that our versatile platform to cover surfaces with active cilia could find a wide range of applications, such as transporting loads in confined spaces, self-cleaning surfaces, or haptics.

**Keywords**: Liquid crystal polymer, Active cilia, Replica moulding, Azobenzene, Biomimetic, Heat-response, Light-response, Oscillation



Figure 1: SEM micrograph of our active liquid crystal cilia, packed on a glass substrate. The cilia are approximately 8  $\mu$ m high and 1  $\mu$ m in diameter at their base. The schematic overlay indicates the asymmetric motion of our cilia in response to either heat or light as a stimulus.

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## Engineering Optical Structures and Functional Materials towards Photonic Devices Development

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#### Abstract:

Photonics engineering has been widely recognised as a Key Enabling Technology-KET with applications in many technological areas. Advances in materials research have driven the development of new exotic optical material platforms such as multicomponent or nanostructured glasses and polymers with customizable properties that could enable in turn the further development of tailored photonic devices. However, further to the fundamental research on those platforms the applicability in real applications is still rather limited as is required considerable amount of research for the development of reliable components required to follow strict operational specifications and standards. In parallel the need for low cost customizable photonic devices, structures and sensors for specific applications requires the efficient exploitation of well established platforms. Employment of efficient material processing techniques and use of specially designed functional materials provides a route that allows the rapid prototyping of customized devices. Within this frame we present recent and characteristic activities of photonics engineering (at NHRF) towards the development of customized structures and devices for a wide range of demanding and emerging applications. Theoretical design & modeling issues together with experimental implementations of structures by direct laser writing, micromachining, and thermal processing will be covered. Photonic platforms such as polymer optical fibers, silica or specialty hybrid fibers, silica-based integrated optics, plasmonic and resonating structures, will be considered towards smart sensors development. A broad range of customized solutions covering application areas from Structural Health Monitoring-SHM, industrial monitoring & predictive maintenance, to defence systems, biomedical applications and finally quantum computing based on integrated optics will be presented.

**Keywords**: photonics, optical fibers, optical materials, Laser, micropatterning, devices, physical sensing, chemical sensing, structural health monitoring, biomedical applications.

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## Nanotextured surfaces based on mixtures of amphiphilic diblock copolymers as bioinspired hybrid materials

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#### Abstract:

Naturally occurring materials can display a variety of stimuli-responsive properties, such as extraordinary adhesion to adapt to the environment, superhydrophobicity, bacteria repellence, or structural coloration. The smart behavior of such materials often originates from the texturization of their surfaces on a nanoscale. Typical methods to obtain such surfaces are physical or chemical patterning such as laser ablation or chemical vapor deposition, which are expensive to use, require specialized equipment and do not equip the materials with biomimetic properties. Here, we present how to obtain a hybrid patterned surface via a direct self-assembly of its components. The subsequent fully synthetic planar membrane undergoes phase separation into domains upon transfer onto a solid support, resulting in nanotextured morphology. The obtained mono- and bilayer membranes are composed of two amphiphilic diblock copolymers (PEO-b-PEHOx and PMOXA-b-PDMS) as direct synthetic analogues of lipid molecules, with distinct properties and mixed at various concentrations. The molar ratio of the copolymers in the mixture and the nature of the solid support were the key parameters to induce nanoscale phase separation of the hybrid planar membranes. Our bioinspired approach to fabricate biomimetic nanopatterned surfaces was performed via Langmuir-Blodgett and Langmuir-Schaefer, i.e. mechanically assisted transfer, which leads to formation of membranes with a biomimetic structure across. The fabricated soft nanotextured membranes taking inspiration from the phase separation within cellular membranes open new avenues in the development of multifunctional surfaces of increased complexity, controlled combination with multiple active compounds and active platforms for dual sensing or cascade reactions.

**Keywords:** multifunctional surfaces, textured surfaces, biosensor, amphiphilic diblock copolymer, self-assembly



**Figure 1:** Schematic illustration of the polymers studied, PEO-*b*-PEHOx and PMOXA-*b*-PDMS, and the resulting domain formation after their transfer onto a solid support. Side chains on the PEHOx block are shown to represent steric hinderance.<sup>1</sup>

#### **Reference:**

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# Optimizing thickness ratio (a-Si:H/Al) during Aluminum induced crystallization (AIC) to obtain higher pressure sensitivity in devices built using AIC-Silicon

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#### Abstract:

Several applications in industry and healthcare sector exist where pressure measurements are required. Diabetic neuropathy is a medical condition for which flexible foot plantar pressure measurement system can be employed to detect abnormal pressure points on foot of the patient to detect neuropathy. AIC-Silicon has been explored as a viable piezoresistive material by various researchers. The capability to deposit it at lower temperatures make it suitable for flexible substrates which can be used to build flexible foot plantar pressure sensor system. In this paper, Aluminum induced crystallization was performed by depositing hydrogenated amorphous silicon (around 115 nm) on Kapton and Corning glass substrates. Five different Aluminum thicknesses (34 nm to 137 nm) were deposited over this and the configuration was then annealed at a constant temperature of  $380^{\circ}$ C for a duration of two hours in Nitrogen environment. AIC-Si obtained after wet-etching of Aluminum on top at 600C was then viewed under optical microscope and SEM. An increase in the thickness ratio (a-Si:H/Al) led to an increase in size/density of micro-pits over the surface of AIC-Si as visualized through SEM images. This consequently led to a decrease in electrical mobility of the film from 14.2 to 3.12 cm<sup>2</sup>/Vs. Piezoresistive property of AIC-Si was measured in terms of gauge factor which was found to be directly dependent on electrical mobility and hence decreased from 50.5 to 10.3 with the increase of thickness ratio. By employing a physical mask, Wheatstone bridge circuit-based pressure sensing devices were built using AIC-Si for different thickness ratios. Static load-based pressure responses in terms of output voltage were found to be non-linear with the initial application of load and nearly linear for pressure beyond 7kPa with the maximum pressure sensitivity measured to be 148.4 mV/V/MPa for the smallest thickness ratio 0.84.

**Keywords**: Aluminum induced crystallization, piezo-resistivity, flexible pressure sensor, gauge factor, pressure sensitivity, Wheatstone bridge circuit

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## DIC application for damage detection in FRP composite specimens based on an example of a shearing test

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#### Abstract:

Fiber Reinforced Polymer (FRP) composite materials are widely used in many areas of life from aerospace, through automotive, boatbuilding, mechanical and civil engineering even to art. Thanks to their lightweight, high strength, and ease of shaping are very attractive materials [1]. The main disadvantage of FRP composites is the possibility of defects in their structures which influence on proper work of material. These defects can appear in the production phase as well as caused by impact. The defects/damages are especially dangerous in the responsible application like aerospace structures. In this paper the application of DIC to tracking the development of strain field in FRP composites with different types of fibres is proposed (Figure 1).



**Figure 1**: The development of the strain field in the GFRP sample subjected to the shear test. The colour maps present the fields of effective strain according to the von Mises formula. Application of DIC helps to predict the area where the damage can appear.

The DIC is vision-based, non-contact, full-field measurement technique, so the finding of areas where the strain distribution (caused by loads) is different than in surroundings is possible. In authors opinion, this method with combination to the other non-destructive testing is potentially applicable in damage detection of the aircraft sheathing. However, its application to the online monitoring requires further research, especially considering minimisation of equipment, supply of energy and wireless data transmission [2].

**Keywords**: Digital Image Correlation (DIC), FRP composites, damage detection

#### Acknowledgment:

This article/publication is based upon work from COST Action CA18203 (ODIN – <u>www.odin-cost.com</u>) supported by COST ( European Cooperation in Science and Technology).



Authors would like to thanks for providing measurement data obtained as part grant Preludium project no. 2019/35/N/ST8/01086 founded by National Science Centre (NCN), Poland.

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## Reactivity of Azide-Terminated Self-Assembled Monolayers

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#### Abstract:

In the field of biotechnology and nanotechnology, the control of surface properties represents an important parameter for their development. Self-Assembled Monolayers (SAMs) have attracted significant attention since their introduction in 1980 by Sagiv.<sup>1</sup> SAMs based on the chemistry of the organosilanes<sup>2</sup> provide molecularly defined platforms for chemical derivatization and control surface properties such as biocompatibility, wetting and adhesion...

The biomolecule's immobilization (conjugation reaction) strategies often use non-selective methods involving either physisorption or random covalent bonds on functionalized SAMs which can induce a lack of bioactivity. The regioselective and bioorthogonale copper-catalyzed alkyne-azide cycloaddition reaction (CuAAC) constitutes an interesting way to covalently immobilize, via a specific ligation site, biomolecule species, and thus control their orientation onto the surface.<sup>3</sup>

Azide-terminated SAMs have been prepared successfully by using three different deposition methods (postfunctionalization and direct grafting by immersion as well as spin coating).<sup>4</sup>

Strikingly, our study shows that the reactivity of the azido group on the surface with the alkyne in solution is not trivial and seems to be closely related to the orientation of the azide. Indeed, more the azide is vertically oriented more it is accessible and reactive. The orientation of azido dipoles at the surface depends strongly on the method used to prepare the monolayer. The post-functionalization method allows to have a homogeneous population of the azide groups on the surface with a better vertical orientation than that obtained using direct grafting by immersion or spin coating processes. Whatever the type of azideterminated SAMs, the reactivity of the accessible vertical azido groups is complete.

**Keywords**: Self-Assembled Monolayers, Click chemistry, PM-IRRAS, X-ray Photoelectron Spectroscopy, Atomic Force Microscopy



**Figure 1**: Schematic representation of the molecular organization inside the azide-terminated-SAMs.

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# Sensors 2022 - Session II.B: Sensing materials, physical / chemical sensors, optical sensors, etc

## Overview and Recent Findings on Curcuminoids as Molecular Platforms for Sensors and Electronic Components

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#### Abstract:

The widespread application of molecular systems is still in its early stages. The study of molecular properties is a necessary step, with the aim of identifying and redesigning efficient, low-cost, environmentally friendly and high-performance molecular systems at the nano- and micro-scale. Considering that there is "plenty of room at the bottom", the best molecular models should encompass the above-mentioned features.

My group works with curcuminoids (CCMoids), a family of molecules that are well known in biomedicine-related fields and have gradually found their way into other research areas as useful molecular platforms for the creation of multifunctional systems, which can be coupled with all kinds of materials, creating bio-inspired and hybrid systems. In particular, this work aims to highlight our role in the design of molecular nanowires based on CCMoids inserted into Au and graphene electrodes. Also how molecular design can help us to organise our molecules on different surfaces and their function as small molecule sensors.[1-4] Our most relevant findings, emphasising the structure-function correlation, will be discussed in order to give an overview and future vision of the use of CCMoids in nanoscience and nanotechnology.

**Keywords**: curcumin derivatives, curcuminoids, multifunctional molecules, molecular platform, bioinspired material, molecular-based nanowires, graphene-based nanoFETs, functionalized surfaces, 2D-CPs, sensing and electronic applications, luminescence, coordination, microcontact priting, sublimation.



**Figure 1**: General scheme showing the diversity of topics in which my group, FunNanoSurf, is using CCMoids as active components with different functions.

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### Rapid Ethidium Bromide detection using Ultramicroelectrode Sensors

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#### Abstract:

Ethidium bromide is one of the most used and efficient fluorescent marker for double stranded structures of nucleic acids. At the same time, it's also a molecule that presents a high risk for the user due to its ability to enter the nuclear membrane and binding to cellular DNA, potentially causing changes on a genetic and chromosomic level; thereby increasing the risk of tumorigenic mutations.

Over the last decade ethidium bromide has been also studied for its electrochemical properties, due to its specificity for double strand DNA, which can improve accuracy and precision of electrochemistry-based biosensors. (1)(2) Square wave voltammetry (SWV) has been employed to facilitate highly sensitive electrochemical measurements. SWV is typically used to minimize the background electrochemical noise; which results in detection limits for ethidium bromide at the nano-molar scale. This level of detection can be employed to measure the degree of contamination for surfaces in environments where ethidium bromide has been used. This can help prevent accidental exposure, minimizing adverse health effects.

Pre-fabricated ultramicroelectrodes were gold modified with through chronopotentiometric deposition using a AuCl bath, (3) which enabled the development of an ethidium bromide sensor with a detection limit on the picomolar scale. This shows an improvement over the previous literature, which shows detection at the micromolar level, potentially also inducing a denaturation of the toxic substance itself (4).Keywords: ethidium bromide. electrochemical sensors. chronopotentiometry, interdigitated Working electrodes



**Figure 1**: (a) SEM analysis of the working electrode interdigitated structure after the AuCl deposition. Gold is deposited in a more coherent way and without the over deposition in the complementary interdigitated structure. (b) Typical chronopotentiometric profile related to gold deposition (Vs Ag/AgCl). (c) Square wave voltammogram of ethidium bromide (Vs on chip Pt reference electrode). (d) Square wave voltammogram of a ethidium bromide contaminated surface

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## High sensing potentialities of tetra-tert-butyl-metallophthalocyaninesbased acoustic microsensors for xylenes measurement in air at room temperature.

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#### Abstract:

Xylenes, classified as Volatil Organic Compounds, is a very harmful pollutant for human health that can be absorbed into the body via all exposures routes: inhalation, ingestion, or dermal. As defined by the US Environmental Protection Agency, the occupational exposure limites are set to 100 ppm while the guidelines in non-occupational context are fixed to 50 ppm. For the concentration measurements in the atmosphere, authorities commonly used sampling methods with post-exposure chemical titration or chromatography. A strong interest remains on the development of low cost, low power consumption and easy implemented microsensors able to deliver real-time indicative measurements in the ppm concentration range.

Most of microsensors aimed to the quantification of xylene concentration in air implement doped MOx [1,2], MOx nanocomposites [3,4] or Metallic Oxide Frameworks [5]. Despite their suitability for xylene detection into the ppm concentration range, the main drawback remains the high required operating temperature (>250 °C). During this lecture, the high potentialities of acoustic microsensors with tetra-tert-butyl metallophthalocyanine as sensing materials for xylene monitoring will be highlighted. If neither the nature of the metallic layer used as an electrode on quartz, nor the nature of the central metal atom in the phthalocyanine macrocycle have no impact on the sensor responses, the sensing enhancement provided by butyl groups is established. Experimental results revealed that ttb-CuPc based OCM sensors are suitable for accurate measurements of xylene concentration from 50 to 500 ppm, without any hysteresis effect, at room temperature. The response and recovery times were assessed close to 3min, while the LOD to a few ppm, and a good repeatability is manifest. The cross-sensitivities were determined towards various VOCs and NO<sub>2</sub>, with higher responses obtained for xylenes (Fig.1). The influence of relative humidity of gas mixture on response was investigated and will be discussed.

Keywords: Substituted phthalocyanines, Organic semi-conductor, Quartz Crystal Microbalance, acoustic sensors, Xylenes, Volatiles Organic Compounds, gas microsensors, pollutant monitoring.



**Figure 1**: Intercomparison of ttb-CuPc-based QCM responses towards NO<sub>2</sub> and Volatils Organic Compounds at room temperature. The stabilized responses were obtained after 3 minutes of pollutant exposure and a temperature drift compensation was applied to each measured frequency.

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## Exploring new strategies for vapor explosive detection through solidstate QDs-based sensors

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#### Abstract:

Fluorescentbased methods have been extensively employed in recent years for the detection of nitroaromatic explosives since they accomplish most of the criteria required in field for an effective sensing, including high sensitivity and selectivity <sup>1</sup>. When interacting with explosives, fluorophore species, such as metal-organic frameworks, quantum dots (QDs) and conjugated polymers, can change their fluorescence intensity, usually by photoinduced electron transfer  $^2$ . However, many of these materials require complicated and long-term synthetic routes, bulky and expensive optical instruments to quantify the fluorescence change and suffer from being often limited to the aqueous medium. Furthermore, the typical detection procedure with QDs, that involves the dispersion of both the QDs and the target analyte in the same solution, does not produce actual sensors and it is not amenable for the instant onsite identification of explosives. To promote the use of this technology also in operating environments, we have been working on the development of portable, easy-to-use and lowcost devices based on PbS QDs for vapor detection of nitrobenzene (NB), chose as a representative nitroaromatic compound (NACs). To reach this goal, we propose three different devices. Firstly, we designed a chemiresistive sensor, demonstrating that the change in conductivity of an ethylenediamine-capped QDs sensor can be successfully used for explosive detection. The sensor showed high sensitivity to NB, with the lowest detectable concentration of 65 ppb and a theoretical detection limit of 2 ppb. Then, we developed an optical system based on the photoluminescence quenching of solid-state QDs cast on a silicon substrate for which a detection limit of 10 ppb was estimated. The system was assembled with low-cost and lowpower components including a blue LED pump and a NIR photodetector. Figure 1 shows a comparative plot of the sensor response vs NB concentration of these two sensors in the 455 ppb -16 ppm range. Sensor response is the relative change of the sensor output signal. Finally, we reported on a novel architecture for gas sensing applications based on the integration of a solidstate ODs photoluminescent probe with a ODs photodetector on the same silicon substrate. The device was highly selective towards NB gas, with excellent repeatability in response to multiple cycles of the same NB concentration and no ageing effect was observed over a 70-day period. All devices were fabricated through simple, rapid and low-cost methods based on spin-coating or drop-casting of colloidal QDs onto a silicon substrate, followed by an in-situ ligand exchange procedure to functionalize the nanocrystals surface with specific ligands, thus enabling the selective detection of the target analyte. The results demonstrate that QDs are very promising not only for laboratory-scale testing but also to develop sensors suitable for practical applications on the field.

**Keywords**: quantum dots, nitroaromatic compounds, explosive detection, solid-state photoluminescence, chemiresistive device, photodetectors.



**Figure 1**: Sensor response vs. NB concentration of the chemiresistive (in purple) and optical (in pink) PbS QDs sensors.

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### Fully optimized waveguide enhanced Raman spectroscopy sensors

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#### Abstract:

Waveguide enhanced Raman spectroscopy (WERS) is emerging a powerful tool for biochemical sensing. Maximizing a figure of merit (FOM) for optimum WERS signal collection has attracted much attention. The conventional FOM is written as a product of the pump and signal surface modal-field-squared [1], while the scattering loss, which is usually relatively strong in WERS, has been oversimplified to a constant independent of the waveguide dimensions. Schmid's theoretical approach [2] and our experimental results, shown in Figure 1, have shown that the scattering loss that dominates the propagation loss in WERS is impacted by the waveguide parameters (e.g. core thickness for planar waveguides) to a great extent. Furthermore, another omission when studying WERS is the inclusion of the signal orthogonal to the pump polarization. Novotny's theoretical approach [3] infers that the radiation from a dipole on a waveguide could be captured back to the waveguide in polarization and spatial modes different from the pump, provided the waveguide can support them.

In this work, we verified experimentally the theoretically predicted dependence of the scattering loss on the waveguide thickness and introduced a new FOM that takes this dependence into account. In addition, the cross-polarized signal excitation and capture are also incorporated in our new FOM, based on Novotny's theory [3]. Planar waveguides working at 785nm wavelength with Ta<sub>2</sub>O<sub>5</sub> core, SiO<sub>2</sub> substrate and water superstrate are studied. Our initial WERS experimental results confirmed both co-polarized (TE) and cross-polarized (TM) signal collection from a TE pumped waveguide, and the ratio of the observed power in different polarizations agrees well with our theory. Our new FOM suggests that once the core thickness increases beyond 81nm, which is the optimum value given by traditional FOM for a  $TE_0$  waveguide, the signal power will increase significantly due to the reduced scattering loss and higher number of modes supported by waveguide, as shown in table 1. It is shown that in comparison with the conventional optimization, our optimized larger-core waveguides result in a WERS signal collection efficiency increase by a factor of ~2.6 when using TE pumping and a factor of  $\sim$ 7.5-8 when using TM pumping. It is also

shown that the highest improvement is observed with the higher-order  $TM_1$ -polarized pump.

Keywords: waveguide enhanced Raman spectroscopy, scattering loss, slab waveguide, tantalum pentoxide



**Figure 1**: Surface modal field square (solid line) of  $TE_0$  (red) and  $TM_0$  (blue) and their corresponding scattering loss (dash line), which results from the 1nm root-mean-square roughness, as a function of the thickness of the waveguide core. Experimental results (normalized to the mean square of the roughness) are presented by dots, with error bars in the corresponding color.

Pump	rFOM	Thickness (µm)	Length (cm)
TE <sub>0</sub>	2.601	0.123	2.39
TE <sub>1</sub>	2.580	0.334	3.39
TM <sub>0</sub>	7.645	0.332	8.67
$TM_1$	8.111	0.469	6.16

**Table 1.** The optimal new relative FOM (rFOM, normalized to conventional FOM) for different pump modes and their corresponding waveguide core thickness and sensing length.

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### Low Power Wearable Sensors for monitoring Knee Joint Instabilities

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#### Abstract:

The anterior cruciate ligament tear causes instability of the knee joint, and it is very common among young adults. [1] However, reliable examination methods for an objective assessment of the injuries are rare. The diagnosis in many cases exclusively is based on the physical examination methods of the attending physician. The results are, accordingly, subjective. Certified instruments exist. However, they only allow static measurements for the quantification of knee joint instability, they are bulky and uncomfortable for the patient. [2,3] For this reason, a flexible, Polydimethylsiloxane (PDMS) capacitive sensor has been developed along with the front-end system. [4] Both the stretchable sensor and the flexible board adhere to the leg like a patch, being comfortable to wear and light to carry. The measured data are transmitted to the computer wirelessly, making the device comfortable to use for the physician, who can conduct the measurement without cables limiting the physician's interaction with the patient. Low power software and hardware design guarantee the use of the device for several days without recharging. The whole sensor unit has been tested with a knee simulator by subjecting the sensor to 3 cycles of motion mimicking the internal medial rotation. This movement is characterized for 3 different cycles of rotation. As a result, a good correspondence is observed and is fitted with a second-order polynomial equation. There is a slight deviation in the curve of one of the cycles towards larger angles and this is due to the slight slippage of the aluminum socket during the test when rotated. The R-square value of 0.993 is close to 1 which also proves the correspondence. This validation of data of the sensor with the knee simulator setup facilitates further clinical trials on patients with ligament instabilities.

#### Keywords:

Strain gauge, PDMS, microcontroller, low power electronic, Bluetooth, wearable sensors, ACL rupture diagnosis.



**Figure 1** (a) nee Simulator setup wi...(b) battery-powered ASIC/MCU connected to the capacitive sensor pinned to the ACL ligament position of the knee. (b) Knee simulator data analysis curve with the characterization data in the table.

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## Microfluidics and QCM biosensing - Challenging the Standards

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#### Abstract:

In recent decades the use of microfluidic flow cells has become ubiquitous in affinity-based biosensing applications, including those based on nearly all transduction mechanimsms. For almost every sensor, and especially for sensors based on the quartz crystal microbalance (QCM), each fluidic architecture follows the same simple principle: a single inlet/outlet system is used to deliver fluid to a sensing chamber situated over the sensing surface. Often little attention, if any at all, is given to the geometries describing the sensing chamber. In this format, the detection of most biologically relevant analytes leads to diffusionlimited conditions, under which the height of the sensing chamber has a large impact on the performance of the biosensor itself. Hence, small changes in the sensing chamber height can lead to changes in the sensor's limit of detection (LOD) by a factor of  $4 \times$  or more.<sup>1</sup> Thin sensing chambers (<50µm), however, can be somewhat problematic, specifically due to either clogging or by negative effects related to high fluid pressures.

Nevertheless, diffusion limitations lead to another aspect of biosensing that frequently goes unnoticed: the capture of target analyte to the sensor surface has a non-homogenous distribution that is heavily balanced towards the fluidic inlet. For QCM sensing this is disadvantageous because, due to the inlet position, the bulk of analyte is deposited near the edges of the biochip, in positions where the QCM crystal has limited sensitivity. It thus makes sense to place a fluidic inlet directly over the crystal surface, where the crystal's mass sensitivity is at its maximum.

In this presentation we will demonstrate that the performance of QCM sensing devices can be drastically improved through both modern 3D printing methods as well as the use of simple changes to the flow cell design. We will show that flow cells with optimal design can increase sensitivity by up to  $7 \times$  or more over what is available commercially, depending on the target analyte and specific affinity interaction. We will show that simple 3D printed flow cells can be used to add a variety of functionalities to commercially available QCM instruments, where

these flow cells not only increase the sensor's sensitivity, but also reduce the sensing noise, remove effects from fluidic dispersion and furthermore, increase the sensor useability. We will present both numerical and experimental data, where the latter concerns a variety of target analytes, mainly based on pathogenic material present in simple (PBS) as well as in complex media (food and human derived solutions). Through these simple examples we will present guidelines as to how one might redesign their experimental flow cells.



**Figure 1**: (top) Comparison of QCM sensing using a commercial and a 3D printed flow cell for the detection of E.Coli in PBS. (bottom) Numerical simulation contrasting the difference in diffusion-limited analyte capture for two flow cells, one with a standard inlet (commercial design) and one with a center inlet (3D printed).

**Keywords**: QCM, biosensor, microfluidics, sensitivity, 3D printing

#### **References:**

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## Smart Materials & Surfaces SMS 2022 Session II.C

### Printed Sensors and Devices on Flexible Substrates

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#### Abstract:

Traditionally, complex electrical-electronic and electromechanical devices are based on IC/MEMS technology, which requires high-cost infrastructure and specialized human resources. In recent years, printed electronics technology has been developed, which has great potential and appears to be complementary to established integrated circuit manufacturing technology and, in several cases, provides significant alternatives. This specific technology provides the possibility of developing electronic devices with a maskless approach (inkjet) and the use of inks whose basic properties can be adjusted according to the application (conductive, insulating, photo-thermoelectrochromic, stress-strain sensitive, temperature dependent etc). In addition, devices can be developed on flexible substrates of different materials and properties (plastic, paper, metal, etc). In this specific paper, the development of printed devices with inkjet and screen-printing technologies on various substrates (paper, Kapton, PET) will be presented. Specifically, the fabrication of custom printed sensor devices (namely: temperature, humidity and stress-strain sensors) will be presented in detail, as well as their characterization, which showed excellent performances (figure 1). Additionally, we will refer to the development and characterization of printed 2D flow sensors with screen-printing technology. Basic layouts of printed resistors and micro-heaters utilizing a custom functionalized reduced graphene oxide ink (f-rGO) will also be presented, as the relevant study proved that very high Thermal Coefficient of Resistance (TCR) values can be achieved, which leads to highly efficient heaters. In the framework of this work, the development of flexible pressure sensors will be demonstrated, which were fabricated in array form so that they can extract the pressure field on a surface. The same devices can also be used as distance sensors as they are based on capacitive structures.

**Keywords**: Printed devices, Flexible electronics, inkjet, screen-printing, sensors, functional inks.



**Figure 1**: Paper-based inkjet-printed humidity (a), temperature (b) and strain (c) sensors.

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### Accurate dipole radiation model for waveguide grating couplers

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#### Abstract:

The waveguide grating coupler (WGC) provides a robust method to couple light into waveguides, which are essential to optical chips and on-chip optical sensors. A number of methods have been proposed to design efficient WGCs. However, designs based on widely used approaches, such as coupled-mode theory, lack accurate analytical solutions. Sychugov et al. developed a model to calculate the input coupling efficiency of a WGC from the reciprocal problem, i.e. the scattering outcoupling of a waveguide grating [1]. However, due to the weak grating assumption, our numerical simulations show that Sychugov's approach is not accurate in practice, although it is the only simple approach that can calculate the coupling efficiency directly. So far, the design and optimization of the WGC are done mainly by time-consuming numerical simulations, using software packages such as Lumerical and Comsol. Exploring the full parameter space, including grating depth, period, grating length etc., for optimizing the WGC proves quite lengthy using numerical methods. Moreover, we have shown that optimizing the WGC is not a convex optimization problem. Therefore, the typical numerical optimization could be iterating within a local optimum, consuming huge computing power and rendering partially optimized parameters. To understand the mechanism of and fully optimize the WGC, a theoretical model is built on the theory of dipole radiation in optical layers [2]. The grating tooth is treated as a special optical layer that is filled with dipoles. The assumed dipole is excited by the electric field of the guided mode, and the radiation is modulated by interference between the optical layers of the whole structure. Thus, the scattering pattern can be calculated, and the input coupling efficiency of a WGC can be obtained. This model has bypassed the weakgrating assumption and has shown a good agreement with numerical simulation for a practical grating, as shown in figure 1. The non-monotonic dependence of the CE on the core thickeness is due to multilayer interference effects and described accurately by the new dipole-based model. The new model is extremely fast and can be used for accurate optimization of WGCs.

**Keywords**: waveguide grating coupler, coupling efficiency, interface dipole radiation, multilayer interference



**Figure 1**: Theoretical results and comparison with numerical results. The cladding, core and substrate of the WGC are air, Si and SiO<sub>2</sub>, respectively, working at 1300nm. (a) The optimal WGC parameters, grating depth and period, for different core thickness. Numerical and theoretical results are presented by dash-dot line and solid line, respectively. (b) The optimal coupling efficiency of analytical and numerical results. The analytical result calculated with the parameters obtained from numerical optimization is plotted with a dash-cross line.

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## Curcumin-loaded PCL highly porous composites for rapid amine gas detection

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#### Abstract:

In the field of smart materials, and more specifically of the colorimetric indicators, several challenges still need to be tackled, such as their detection limit and real-time monitoring capability. Most of the existing indicators are fabricated in the form of films,<sup>1</sup> something that cannot give them the accuracy needed, due to lack of porosity and low surface to volume ratio. Furthermore, the evaluation of their pH-induced color changes in the presence of vapors is scarcely reported,<sup>2,3</sup> something that may lead to false estimations about the condition of the studied environment.

To overcome these challenges, fibrous materials have been fabricated for use as pH indicators in various applications.<sup>4,5</sup> These materials present high active surface area allowing their better interaction with various substances, and thus, their faster response with respect to films.<sup>6</sup> However, the responsive capability of such materials can be adjusted not only by the porosity induced by the fibers, but also by the existence of pores on each fiber, which further enhance their active surface area.

In this study, curcumin-loaded polymeric porous fibrous mats were fabricated by combining nonsolvent induced phase separation and electrospinning and their use as colorimetric indicators for the rapid detection of amine vapors was explored.<sup>7</sup> Their color change capacity was explored and compared to the one of their non-porous equivalents. We prove that the ultra-porous system presents significantly higher surface area and consequently higher responsivity to dimethylamine vapors, showing a distinct color change within the first seconds of exposure, even in the presence of very low vapor concentrations. We also demonstrate that the color change of the indicator after interaction with various types of amine vapors are visually perceivable and in some of the cases reversible, enabling its use for several times (Figure 1). This, combined with its antioxidant activity induced by curcumin, make it a sustainable colorimetric indicator that can be used in various applications.

**Keywords**: porous electrospun fibers, gas sensing, antioxidant activity, pH indicators, amines, CIELAB color space analysis, smart materials



**Figure 1**: Figure illustrating the use of the curcumin-loaded colorimetric indicator.

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## Fabrication of biomimetic fibrous substrate with hierarchical microstructure patterning for reconfigurable soft electronics

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#### Abstract:

Despite significant efforts to improve the performance of flexible electronics and sensors, as evidenced by recent advances in the development of innovative material and structure concepts, the development of a substrate that overcomes critical issues such as compliance, breathability, conformability, and lightweight is still ongoing. Recent studies describing synthetic film-forming polymers like polyethylene terephthalate (PET), polyurethane (PU), polydimethylsiloxane (PDMS), and polyimide (PI) show good mechanical properties that are similar to human skin mechanical properties, but important aforementioned aspects are underrepresented. Electrospun nanofiber-based flexible materials have lately gained a lot of interest due to their unique features such as breathability, large surface area, and Elastomeric substrates are conformability. widely explored among common soft polymer candidates due to their potential to be designed with geometric morphologies for improved stretchability. Due to their unique mechanical response, microstructured hierarchical lattice materials have recently emerged as exciting materials for improving stretchability, flexibility, and sensitivity. Surprisingly, these morphologies reflect comparable stress-strain behaviors of natural biological tissues' nonlinear J-shaped stress-strain profile. We present an integrated simple fabrication of a highly-porous fibrous-based flexible composite fibrous substrate with tailored geometric morphologies via the printing of a stiff melt electrowritten (MEW) geometric microstructure on an elastic electrospun (ES) film. Several patterns may be printed via melt-electrowriting, which allows unique highly controlled fiber production using computer-aided direct-writing of melted polymer. A promising morphology and surface design of a composite film fabricated in an ES-MEW-ES approach demonstrated a synergistic effect. In comparison to pristine nanofiber film, the stress-strain profile of the composite material showed elaborated J-shaped behavior using tensile testing. Using a combination of MEW and ES, we developed a straightforward technique for fabricating biomimetic fibrous substrates for soft electronics applications.

**Keywords**: melt-eletrowriting, electrospinning, flexible substrate, fibrous substrate, stress-strain curves, network design.



Figure 1: Schematic illustration of the fabrication method of inherently high porous fibrous substrate: ES (pink) – MEW (blue) – ES approach (pink) (left) and its cross-sectional view illustrating sandwich strategy of soft elastomer (pink) and stiff polymer (blue) that exhibit wavy and wrinkled surface morphology (right).

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## Development of Sensors for Detection of Bisphenols in Water

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#### Abstract:

Persistent and mobile chemicals (PMCs) are found in tens of thousands of everyday products as well as in all relevant media of our natural environment, and their severe negative impacts on human health and global ecology is only now starting to be understood. Our aim is to create new types of electrochemical sensors customised for PMC detection in on-site environments, strategically placed to disambiguate impacts from possible sources (Figure 1).<sup>1</sup> Within thousands of PMCs we selected four with their chemical groupings as main targets for new electrochemical sensor development: melamine, benzotriazole, bisphenol S and benzothiazolinone.

In the present work we focus on the development of receptor element for detection of three bisphenols, namely bisphenol S (BPS)<sup>2</sup>, bisphenol A (BPA) and bisphenol F (BPF). To guide sensor development and the sensor evaluation process, conventional chemical analysis of selected bisphenols was needed. Indicative samples from sites were taken from defined Slovenian sites and analysed within the laboratory for concentrations of bisphenols to establish baselines and sensitivities for sensing, and to check for any substances that may obfuscate or compromise sensing devices, or determine the types of sensors or hardware sampling methods needed. The chemical or electrochemical processing of receptor elements was performed on commercial screen-printed electrodes (SPE), with carbon as a working electrode, platinum as counter electrode and silver as reference electrode. The working electrode was modified using a powerful electrocatalyst (Augroup metals) with a material that provides a large surface area (carbon black or SWCNT's) to produce a nanohybrid that exhibits efficient redox characteristics for a given analyte at low potential. Characterized and fully understood receptor elements were integrated into proof of concept system and exposed to target analytes in water. For detection of bisphenols in water solutions electrochemical measurements, e.g. cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CA) were applied. CA was used to calculate the calibration curve to obtain the sensitivity and limit of detection (LOD) for certain experimental conditions. Finally, the sensor was tested for selectivity. Selective detection of BPS, BPA and BPF was observed by using DPV on the same SPE working electrode with a solution containing all three isomers.

**Keywords:** sensor, electrochemistry, SPE electrode, persistent and mobile chemicals, bisphenols.



**Figure 1**: Detection points and working principle of sensor platforms and integration.

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## NanoMed 2022 - Session II. A: Nanomaterials for Biomedical, Tissue engineering, drug, and gene delivery

### Overcoming Barriers in Nanomedicine: from Cancer to Obstetrics

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#### Abstract:

Organ microenvironment represents the first frontier and an efficient barrier for delivery of nanotherapeutics to the cells were these should act. Thus organ microenvironment should be considered when developing the strategies for drug delivery to an ailment.

As an example, in the primary breast tumors, the lesions are angiogenic and are characterized by developed and permeable vasculature. However, in conditions such as liver metastasis the lesions from the same origin are less vascularized than the surrounding normal tissue, thus, the structure of the organ itself conjures with cancer-specific behavior to impair drug transport and uptake by cancer cells. Thus, strategies to enhance the accumulation of the medicines in the liver lesions, while preventing the wash out should be pursued. On the other hand, in the field of obstetrics, the main goal is to deliver the required medicine to the mother, while preventing placental transport and associate fetal toxicities.

Fetal toxicities of medications commonly given during pregnancy complications are frequently a concern and can be dose- and time- of- exposure limiting factors. Nanomedicine can prevent placental passage of medications. Important design factors of nanomedicines to be able to target maternal tissues, while not crossing the placental barrier to the fetus will be discussed. In the case of indomethacin, one of the most frequently used tocolytic agents for prevention of preterm labor, the dose-limiting factors are renal and cardiac fetal toxicities. We developed and studied uterus targeted indomethacin delivery system, which was able to significantly enhance the concentration of the drug in the uterus, the target tissue. and reduce fetal exposure and toxicities.

There is a great need to anchor the therapeutics in the maternal compartment. Based on the specific cues in the maternal and fetal compartments, nanomedicines can be designed to attain this goal. Cells and elements in the organ microenvironment that play a key role in the process of delivery and retention of therapeutics by nanocarriers, as well as ways to personalize nanotherapy based on the organ's features using cell culture models and computational modeling will be discussed.

**Keywords**: breast cancer, liver metastasis, nanomedicine, obstetrics, tocolytics, indomethacin.

## New strategies for the risk evaluation of carotid artery disease patients at the nanoscale

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#### Abstract:

Cardiovascular diseases are the leading cause of death worldwide. The development of cardiovascular diseases emerging from atherosclerosis is partially a consequence of a severe inflammatory process. Erythrocyte hyperaggregation, due to high fibrinogen levels, has been recognized as a cardiovascular risk factor.

The main goals of this study were to evaluate changes in fibrinogen-erythrocyte and erythrocyte-erythrocyte interactions in carotid artery disease (CAD) patients, and to characterise the biomechanical properties of carotid atherosclerotic plaques from CAD patients.

Blood samples collected from CAD patients, before and after endarterectomy surgery, were analysed and compared to the control group. These studies comprised the analysis of haemorheological parameters and atomic force microscopy (AFM) based force spectroscopy measurements of fibrinogen-erythrocyte and erythrocyte-erythrocyte interactions, as well of cell elasticity / stiffness.

CAD patients before surgery presented stiffer and less deformable erythrocytes than the control group of healthy blood donors. Furthermore, erythrocyte-erythrocyte adhesion was found to be stronger in these patients. Plasma total and  $\gamma$ ' fibrinogen levels were also increased. All these results can be associated with increased cardiovascular risk. Six months after surgery, patients presented improvements, particularly at the level of the erythrocyte deformability and cell-cell adhesion. Twelve months after surgery, patients had decreased erythrocyte aggregation, deformability and stiffness, as well as decreased  $\gamma$ ' fibrinogen levels, revealing an improvement in the inflammatory process.

Atherosclerotic plaque elasticity was also evaluated in different regions of the plaque, using AFM. It was observed that calcified regions present significantly higher stiffness than the other regions of the plaque.

Keywords: nanosensing, atomic force spectroscopy, force spectroscopy, clinical prognosis, cardiovascular diseases, carotid artery disease, atherosclerosis, fibrinogen, cell stiffness, cell-cell adhesion.



**Figure 1**: Schematic representations of the experimental strategy used to probe at the nanoscale cell elasticity fibrinogen-cell binding and cell-cell adhesion with erythrocytes from carotid artery disease patients (before and after endarterectomy) and control healthy blood donors.

## Amphiphilic block copolymers in hybrid vesicles and micelles towards scaffolds for nanoreactors

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#### Abstract:

Amphiphilic block copolymers can play a versatile role in the self-assembly of micelles or polymer-lipid hybrid vesicles (HVs). Their broad tunability and possibilities of varying the chemical composition make them interesting for applications that require specific characteristics suitable for the environment as well as potential cargo as in artificial organelles. Here, we outline various functional carriers with distinct (membrane) properties by adjusting the chemical composition of the hydrophilic or hydrophobic block of the block copolymer involved in micelle or HV formation. The pH-responsive poly(carboxyethyl acrylate) (PCEA)<sup>1</sup> served as the hydrophilic block, while cholesteryl methacrylate (CMA), butyl methacrylate (BuMA), or 2-hydroxyethyl methacrylate (HEMA), or a combination of CMA and BuMA, or CMA and HEMA were employed as the hydrophobic blocks. Small and giant HVs were assembled with soybean L-a-phosphatidylcholine resulting in differing extents of accompanying micellar populations. Membrane packing and permeability of the assemblies were compared by using the fluorescent probes Laurdan and 5(6)-carboxy-X-rhodamine or carboxvfluorescein, respectively (Figure 1a). The membrane composition was thereby influencing the permeability or suitability for an enzymatic reaction forming potential nano/microreactors. Specifically, HEMA-containing membranes exhibited higher permeability for small molecules than others and the association of  $\beta$ -galactosidase showed more efficient substrate conversion in membranes with BuMA.<sup>2</sup> Alternatively, the lipid building block was exchanged by either 1,2-dioleoyl-sn-glycero-3-phosphocholine or 1,2dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE) and HVs made with PCMA-PCEA or polymeric micelles thereof were characterized. Furthermore, their interaction with RAW 264.7 cells was evaluated in terms of cytotoxicity, cellular uptake, and lysosomal escape capabilities (Figure 1b). The conjugation of the pH-sensitive peptide GALA or DOPE-containing assemblies allowed thereby for lysosomal escape and high uptake efficiencies.<sup>3</sup>

Taken together, the morphology, membrane permeability, eligibility as potential nano/microreactor supporting enzymatic reactions, and the interaction with mammalian cells can be controlled by the composition of the block copolymer or lipid content used in micelle or HV assemblies. The gained insight offers new opportunities for the assembly of artificial organelles with potentially cytosolic placement in mammalian cells.

**Keywords**: block copolymer, hybrid vesicle, membrane composition, micelle, nanoreactor, artificial organelle, lysosomal escape, RAW 264.7.



**Figure 1**: Schematic illustrating the assembly of block copolymers and lipids into hybrid vesicles (HVs). a) HVs with varying membrane compositions resulting in different morphologies and membrane permeabilities. b) Interaction of HVs assembled with varying lipid content or polymeric micelles with mammalian cells.

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## Computational Assessment of Three Dimensional Scaffolds for Bone Regeneration

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#### Abstract:

During the past few years, tissue engineering has been qualified as a solid surrogate of autografts in the stimulation of bone tissue regeneration, through the development of three dimensional (3D) porous matrices, commonly known as scaffolds. Polycaprolactone based scaffolds have attracted worldwide attention as promising biodegradable implants in bone tissue engineering. Finite Element Analysis (FEA) is used in tissue engineering to evaluate the mechanical behavior and to simulate the processes inside the scaffold. In this work, we analyzed two regular polycaprolactone scaffold structures (with sharp edges and with rounded edges, Figure 1) by performing computational fluid dynamics simulations, as well as structural analyses to compare velocity and pressure distributions for the two scaffolds. A sensitivity analysis was performed for the two different scaffold geometries and the element size that was used was 0.07mm. A laminar flow of 1 mm/s was used as an inlet boundary condition at the top of the scaffolds and the fluid was treated as Newtonian [1, 2]. Regarding the structural analyses, the bottom layer of the scaffolds was set as a fixed support and a steady pressure was applied at the top layer as a loading boundary condition. Our results indicate that the scaffold with sharp edges depicted a better flow velocity distribution within the pores of the scaffold for all layers and a lower speed, compared to the scaffold with rounded edges. The pressure gradually decreases from the inlet to the outlet, with no substantial differences between the two geometries, with a uniform pressure distribution along the height of the scaffolds. From the structural analysis there are no significant differences from the parameters that were calculated in both geometries, thus not allowing us to draw concrete conclusions on which geometry is better. Based solely on the CFD-derived results, the sharp edges geometry produced more appealing velocity distribution results which makes it superior compared to the rounded edges scaffold.

**Keywords**: Scaffold, modeling, fluid flow, polycaprolactone, sensitivity analysis, structural analysis, three dimensional.



Figure 1: (a) Geometry with sharp edges, (b) geometry with rounded edges respectively. The scaffold is a cube 12x12x12mm. The pores have dimensions 1.029x0.8mm and the strut 0.6x0.8mm.

#### Acknowledgement

This work is supported by the BIOBON3D project that has received funding from the Operational Programme EPAnEK 2014-2020 and is co-financed by Greece and the European Union.

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## Funtionalization of nanomaterials with proteins to improve biomimetics

#### M. L. Fanarraga<sup>1</sup>

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#### Abstract:

Engineering the 'bio' identity of man-made nanomaterials is central for most biological/ therapeutic applications. The low success in the 'bench-to-bed' translation is the result of our lack of understanding of the bio-synthetic interactions occurring upon nanoparticle exposure to biological media.[1] Controlling these interactions is a key issue for producing nano-surfaces with a specific function, improving their efficacy in the biological context.

To circumvent this issue, nanomaterials destined for *in vivo* applications are coupled to targeting ligands and are typically protected with chemical agents such as poly(ethylene glycol) (PEG) and are attached to targeting moieties, such as antibodies or (poly)peptides. However, despite these solutions, less than 1 % of the nanotherapies administered reach their destination.

In our laboratory, we design mimetic nanomaterials endowed with a custom-designed biological identity. We assemble nanostructures that externally "look like" viruses and behave like them in terms of specificity, receptor affinity, cell recognition mechanisms, entry routes, etc. while internally they are synthetic and innocuous, and can be designed for use in different strategies, for example, introducing drugs, genes or nanoparticles into cells.

To do this, we use genetically modified high-affinity targeted proteins copied from natural ligands (mainly toxins).[2] These proteins are genetically modified by keeping the domains that interact with target receptors but removing the catalytic parts to render them harmless. These engineered ligand-proteins are fused with nanomaterial interaction domains [3] for precise and stable binding to the nanosurface in an "as designed" orientation, thus preventing protein inactivation, biofouling, or disorientation upon exposure to the biological medium.



**Figure 1**: Figure illustrating the design of natural ligands using a toxin. The figure shows the design of a natural ligand based on Shiga toxin. The ShTxA domain, which is the catalytic domain, is removed, and the ShTxB domain, the receptor recognition domain, is modified and fused to a nanomaterial binding domain to be used in functionalization.

**Keywords**: natural ligads, ligand-protein, toxin, viral ligands, biotechnology, nanomedicine, bio-functionalization

Acknowledgments: Instituto de Salud CarlosIII, the European Union FEDER funds under Projects ref. PI19/00349 (AES 2019), INNVAL 21/19.

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## Nanotechnology for precision medicine and personalized beauty and healthcare

#### M. Colombo<sup>1</sup>

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#### Abstract:

The new millennium is increasingly oriented towards a medicine in which the therapies of pathological states and the cure of the person have been recapitulate in a holistic approach: the treatments are no longer intended exclusively to the surgical intervention and/or drug administration, but therapeutic strategies involve all aspects including diet, physical activity and beauty treatments, in order to improve life style and quality, fundamental for the well-being of the person. Within the context of Life Science the pharmaceuticalcosmetic sector plays a primary role.

Taking advantage of a new infrastructure, called NanoCosPha, we developed innovative nanostructured systems and formulations useful for clinical translation of nanodrugs and for the designed of new innovative materials for cosmetics. The aim of this infrastructure is to network several skills and technologies to:

 bridge the gap between academic research and the productive network by ensuring development of innovative processes and products capable of addressing current issues such as prevention and treatment of diseases and the well-being of man;
define the lead compounds (natural and synthetic molecules) and nano-drugs to be inserted in customizable pharmaceutical products;

3) develop innovative systems with synergistic action that combine nanocarriers with fine formulations designed to improve absorption and enhance the controlled release performance while carrying several active ingredients simultaneously;

4) exploit nanotechnologies to optimise cosmetic formulations with a particular focus on skin care and anti-age and anti-inflammatory treatments.

Thanks to this platform we obtained promising results in particular using a customized 3D binder jetting printer for solid formulations for oral administration. The resulting printlets exhibit optimal properties compared to the well-known tablets for specific applications, which proved to be favourable in view of a personalized medicine.

**Keywords**: nanoparticles administration; solid formulation; semi-solid formulation; 3D binder jetting printer; personalized medicine; prototyping.



Figure 1: NanoCosPha fields of action

https://nanocospha.it

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### Nanosystems as a therapeutic approach for the treatment of psoriasis

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#### Abstract:

Psoriasis is a chronic, inflammatory skin disease that affects approximately 2% to 5% of the global population (1) with a strong genetic predisposition and autoimmune pathogenic characteristics, which are manifested by epidermal proliferation, abnormal keratinization and increased dermal vascularity (2). Currently, there is still no effective treatment, conventional therapies used have adverse effects, and there is low adherence. Considering these limitations, the area of nanotechnology emerges as a promising alternative in the development of nanosystems with therapeutic action in the inflammatory process associated with psoriasis. Thus, the main objective of this work was to review the different nanosystems developed more recently with possible applications in the treatment of this disease.

After analyzing the articles, it was possible to verify that the most representative developed nanosystems can be subdivided into: i) lipid nanoparticles; ii) vesicular systems; iii) micro and nanoemulsions; iv) polymeric nanoparticles, and v) metallic nanoparticles. Different drugs used in conventional treatment were incorporated, such as calcipotriol and cyclosporine, clobetasol, dithranol, etanercept and methotrexate, tacrolimus and tazarotene, as well as other molecules. In addition, and in general, all these nanosystems after being characterized and compared with conventional therapies showed better therapeutic effects. Such results were achieved since nanosystems have excellent stability, act as a system that incorporates drugs/bioactive molecules and allows their more sustained release, thus constituting a more targeted tool for the target site, minimizing adverse effects.

It is thus possible to conclude that nanotechnology will continue to represent a promising area with a tendency to evolve in the sense of developing new therapeutic systems that are more effective in the treatment of psoriasis. **Keywords**: psoriasis, topical treatment, nanotechnology, nanoparticles.

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## Self-assembly of 2D Materials for 3D Tissue Engineering Platforms

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#### Abstract:

Two-dimensional layered materials (2DLMs) have been extensively studied due to their tunable characteristics for applications in electronics<sup>1</sup> and optoelectronics.<sup>2</sup> Their high transparency, flexibility, and biocompatibility make them promising candidates for the integration of functional materials with tissue engineering. To mimic the human body environment accurately, there is a need for creating three-dimensional (3D) tissue engineering platforms. However, to create 3D structures containing 2DLMs has been technically limited due to challenges in the microfabrication process. In this study, we propose a self-folding mechanism to transform 2DLMs to 3D structures using polymeric thin films based on parylene-C. After dissolving a sacrificial hydrogel layer, a strain in the 2DLM leads to the formation of microroll structures whose diameters directly correspond to the parylene thickness. By using this method, we were able to induce 3D microrolls from graphene, MoS<sub>2</sub> and hBN.

All of the 2DLMs experienced strain during selffolding. Raman spectroscopy revealed a blue shift of G ( $\sim 8 \text{ cm}^{-1}$ ) and 2D peaks ( $\sim 16 \text{ cm}^{-1}$ ) in graphene, while MoS<sub>2</sub> exhibited a smaller peak shift (~2 cm<sup>-1</sup>) in  $A_{1g}$  mode. In a previous study our method was used for the self-folding of graphene and encapsulating neural cells.<sup>3</sup> In this study, we extended the variety of cell types and 2DLMs (MoS<sub>2</sub>-Figure 1a, hBN-Figure 1b) and analyzed their behavior in self-assembled structures. We observed proliferation and elongation of cardiomyocytes (HL-1 cell line) along the graphene-laden microrolls (Figure 1c). As shown in previous studies,<sup>3,4</sup> the microrolls enabled encapsulated cells to migrate and proliferate, allowing formation of tissue-like structures. Since the shape of microrolls has a relevance in the human body, this method is applicable for mimicking muscles, blood vessels, and nerve-like tissues.

We believe that our method could allow simple integration of single and stacked 2DLMs in 3D



**Figure 1**: Self-folded rectangular bilayers with dimensions of  $600 \times 300 \ \mu\text{m}^2$  made from a) MoS<sub>2</sub>, b) hBN. c) Time-lapse observation of HL-1 cell behavior inside graphene-laden microrolls after 0 h, 27 h and 54 h. Scale bar: 100  $\mu$ m.

multifunctional devices for studying cellular processes and tissue formation.

**Keywords**: self-folding, 2D materials, graphene, MoS<sub>2</sub>, hBN, 3D microscaffold, cell-interface

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## NanoMed 2022 - Session II. B: Nanomaterials for Biomedical, Tissue engineering, drug, and gene delivery

### Composition and Functionality Relashionship in Dexamethasone loaded Avidin Nucleic Acic NanoAssemblies

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#### Abstract:

The natural high affinity of egg white avidin for the nucleic acids is exploited to obtain highly defined buffer stable poly-avidin nanoassemblies (Avidin-Nucleic-Acid-NanoASemblies-

ANANAS). These soft biocompatible nanoparticles can be considered as avidin analogues with improved performance with a number of applications in biomedicine, among which drug delivery<sup>1,2</sup>. Each nanoparticle possesses a large number of biotin binding sites (BBS) which are available for docking about 1000 functional elements (drugs, fluorophores and/or targeting elements), provided these are linked to a biotin moiety. The high affinity of biotin for avidin (Kd~10<sup>-15</sup>M) permits to exploit the available BBS to obtain functional NPs with stoichiometric control of composition by simply mixing core NPs with the desired biotinylated moieties. Functional NPs are thus obtained in "one pot" solution and, as long as the number of available BBS or the available NP surface (about 6000 nm<sup>2</sup>) are not exceeded, they can be used without the need of purification. Therefore, the ANANAS platform is a convenient tool in nanomedicine to identify relationships between NP surface compostion and functionality, which potentially may be of value also for other NP geometries.

When injected parenterally, ANANAS show strong tropism for the liver. In recent years, we investigated the use of ANANAS functionalized with the antiflmammatory drug dexamethasone (dex) as candidates for treating liver inflamatory diseases.<sup>3,4</sup> Along the years, a number of biotindex conjugates have been developed for ANANAS drug loading and used for generating a number of ANANAS-dex assemblies (Figure 1). Through a combinantion of in vitro and in vivo experiments, we showed that both the chemistry used for acid reversible dex tethering, the length and nature of the linker between the drug and the biotin moiety and the mode of NP surface decoration affect the NP colloidal stability, the kinetics of drug release and the biodistribution pattern in animal models.



**Figure 1:** ANANAS-dex formulation design and a selection of the assemblies investigated.

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## Design of poly(lactide-co-glycolide) particles: synthesis optimization and controlled drug release

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#### Abstract:

Nowadays, the polymer-based nanostructured drug carriers play a key role in the field of nanomedicine. By using them, we can prolong and increase the efficacy of the drugs. Due to the excellent biocompatibility and good material properties, the poly(lactide-co-glycolide) (PLGA) copolymers is one of the most popularly used biopolymers in the development of new type of colloidal drug delivery systems. The degradation and hydrophilicity properties of PLGA are excellently controllable with the changing of the monomer ratios, which is advantageous in the application of these carriers. Our aim was to prepare drug-containing nanoparticles (NPs) by using poly(lactide) (PLA) and PLGA and to determine the effect of the synthesis parameters (e.g concentration, solvent and stabilizing agents) on the structure of the NPs. Nanoprecipitation method was used for the preparation of these systems (Figure 1), where the NPs have been characterized by DSC, FT-IR spectroscopy, DLS, TEM, SEM and UV-Vis measurements. During the synthesis of the PLGA NPs, it has been proved that the hydrodinamic diameter and the size distribution of the particles can be controlled with the changing of the initial parameters. The drugs having different hydrophilicity (e.g. ketoprofen (KP), D-α-tocopherol polyethylene glycol 1000 succinate (TPGS) and  $(\pm)$ - $\alpha$ -tocopherol (TP)) have been encapsulated, where the highest entrapment efficiency (%) is obtained for the most lipophilic ( $\pm$ )- $\alpha$ -tocopherol (~90%). Moreover, we found that the release of the active substance can be changed by the lactide:glycolide ratio.

**Keywords**: PLGA, nanoparticles, biomedical application, drug delivery, controlled drug release, tocopherol (vitamin E), ketoprofen

Acknowledgements: Project no. TKP2021-EGA-32 has been implemented with the support provided by the Ministry of Innvation and Technology of Hungary from the National Research, Development and Innovation Fund. This research was also supported by the NRDIH through FK131446 project. Csapó thanks the financial support of the "Momentum" Program of the Hungarian Academy of Sciences (LP2021-5). The research was supported by the ÚNKP-19-4-SZTE New National Excellence Program of the Ministry for Innovation and Technology (N. Varga).



**Figure 1**: Schematic representation of the preparation of the PLGA NPs by nanoprecipitation method and TEM images of different drug-containing PLGA NPs

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## Neuroprotective Peanut Agglutinin-Targeted Nanoparticles for Ocular Drug Delivery Applications

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#### Abstract:

Ocular posterior segment diseases represent a debilitating and increasingly frequent health problem worldwide. In fact, endogenous and exogenous stress stimuli may lead to the degeneration of the retina, causing partial or total blindness. The complex anatomical structure and the physiological mechanisms that protect the eye make the delivery of drugs a challenging goal. Indeed, several compounds, as neurotrophins, which are known to play a protective role against retinal degeneration, fail in clinical trials owning to difficulties in crossing the biological barriers and their short half-life. Our work has been focused on the synthesis and optimization of polyacrylamide nanoparticles (ANP), which have been functionalized with Peanut Agglutinin (PNA) as ocular-targeted molecule, and Nerve Growth Factor (NGF) to implement an organic polymerbased ocular carrier (Figure 1). The nanoformulation (ANP:PNA:NGF) has been characterised in terms of hydrodynamic diameter and proteinbinding efficiency. The biological activity of the ANP-conjugated NGF has been then validated in vitro on PC12 cells. Using zebrafish as an in vivo model, it has been demonstrated that the ANP spontaneously migrate through the retinal lavers after intravitreal (IVT) injection, but the presence of PNA, that specifically recognise cone photoreceptors, is crucial to stably retain the carrier in the eye and prevent it from spreading over time. Most importantly, only the ANP:PNAconjugated NGF has been proven to protect the retina from the oxidative damage induced by the IVT injection of hydrogen peroxide, as revealed by both behavioural and functional assessments in zebrafish larvae. Specifically, the optokinetic response assay has been shown that only the ANP:PNA:NGF, but not the ANP:NGF (without PNA) or the free NGF, are able to prevent the strong decrease of the visual functions induced by the oxidative damage. These data have been also confirmed through the evaluation of active caspase 3 expression, revealing that the number of the apoptotic cells is significantly reduced in the ANP:PNA:NGF group, but not in the free NGF one, compared to the hydrogen peroxidetreated larvae.

**Keywords**: organic nanoparticles, drug delivey, ocular posterior segment, nerve growth factor, peanut agglutinin, zebrafish.



**Figure 1**: Figure illustrating the distribution of nanoparticles (ANP:PNA:NGF) in the posterior segment of the eye after intravitreal injection. Our ocular-targeted polymer-based nanocarrier represent a smart drug delivery system for neuroprotective applications in retina.

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## Using of short peptides attached to the polymer carrier as either antimicrobial, cell-penetrating, or targeting agent of the whole nanotherapeutics

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#### Abstract:

The microbial resistance is a one of the main problems of the nowadays medicine. Recently, the antimicrobial peptides were recognized as novel pipeline for the overcoming the microbial resistance issue, nevertheless their low stability in biological media and potential immunogenic response of the organism somehow limit their use in human medicine. It has been repeatedly reported that attachment of a low-molecularweight drug to a biocompatible polymer drugcarriers often leads to improved pharmacokinetics, lower non-specific toxicity and better therapeutic efficacy. Polymer therapeutics can be also targeted using peptides to specific organs or tissues, e.g. to tumors. Other peptides called cellpenetrating peptides can improve the enhanced penetration of the polymer nanotherapeutics. Here, we present the design, synthesis and preliminary biological evaluation of such polymerpeptide conjugates.

First, novel biocompatible N-(2-hydroxypropyl)methacrylamide based polymer nanocarriers with antimicrobial effect or enhanced tumor-accumulation and/or penetration were designed and successfully synthetized. Subsequently, prepared fluorescently-labeled polymer-peptide nanosystems were evaluated in vitro using microbiological methods. The affinity of the polymer conjugates to bacterial or cellular membranes and receptors was studied depending on the particular structure of attached peptides. Prepared polymerpeptide nanosystems showed increased tumor cell uptake due to presence of respective peptides. Moreover, selected polymer-peptide conjugates were evaluated in vivo. Results indicate that these multifunctional systems would serve for further preclinical evaluation as candidates for tumor visualization or treatment.

**Keywords**: antimicrobial peptides; tumor targeting peptides; cell-penetrating peptides; HPMA copolymers; drug delivery; nanotherapeutics.



**Figure 1**: Schematic description of polymerbased nanotherapeutic decored with various peptides for targeting or cell-penetrating.

#### **Acknowledgement:**

The work was supported by the Czech Science Foundation (project No. 20-04790S and 22-12483S).

## Peptide conjugation with magneto-polymeric nanoparticles to improve nanomaterials transport across the blood-brain barrier

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#### Abstract:

Poly(lactic-co-glycolic) acid (PLGA) nanoparticles enhance drug pharmacodynamics and bioavailability, and when loaded with superparamagnetic iron oxide nanoparticles (SPIONs) they can act as contrast agents for magnetic resonance image (MRI) [1]. These characteristics make them attractive for brain imaging and therapy. However, the application of nanoparticles (NPs) for brain drug delivery is hindered by the presence of the blood-brain barrier (BBB). The BBB is a natural defense against circulating toxic and infection agents that also prevents most therapeutic compounds from reaching the brain. BBB peptide shuttle (BBBpS), are small peptides that engage adsorptive mediated transport (AMT) across the BBB and allow brain uptake [2]. In this work, we propose SPIONs-loaded PLGA nanoparticles functionalized with a BBBpS, as a platform for brain drug delivery. We produced SPI-ONs-loaded PLGA NPs (Figure 1 (A)) through simple-emulsion solvent evaporation technique with a size range of 120-170 nm and iron content of SPIONs in NPs of 80%. In the functionalization step 30% of fluorescently labeled BBBpS was conjugated to NPs surface (BBBpS-NPs), resulting in alteration of size. The size increasing in 30 nm but zeta potential does not change significantly due to the low net charge of the BBBpS, ranging from -33.2±0.6 before functionalization, to -31.2±1.2 after functionalization. To test activity of NP we first investigated the interaction with human brain endothelial cells (BEC) that make up the BBB. NP internalization in BEC was evaluated through flow cytometry and fluorescence microscopy (Figure 1 (B)). The results reveal that BBBpS promotes internalization, with an increase of 4-fold in BBBpS modified NP, in comparison with naked NP, at 24h. Also, timecourse evaluation of NP internalization reveals a plateau at 12 h, suggesting an equilibrium between endocytosis and exocytosis. We will further test these NPs in in vitro models of the BBB and in vivo brain uptake with the purpose of supporting those novel hybrid nanoparticles as a new strategy for brain drug delivery.

**Keywords**: Magnetic nanoparticles, polymeric nanoparticles, cell-particles interactions, bloodbrain-barrier, neurodegenerative disorders, biomedical applications.



Figure 1: (A) TEM image of SPIONs-loaded PLGA NPs. Scale bar = 100 nm. (B) confocal microscopy of NPs conjugated with BBBpS and internalized in BEC. Blue is Hoechst 33342 (nucleus) and in yellow are the BBBpS-NPs. Scale bar =  $50 \mu m$ .

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### Exploring silicon-nanowire patterned surfaces for yeast transformation

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#### Abstract:

Silicon nanowires (SiNWs) have been recently explored for their potential to deliver large molecules inside cells by mechanical force. The principle of the method is that SiNWs coated with the molecules to be delivered can penetrate the cells without disrupting them, thus introducing the desired molecules inside the cells<sup>1,2,3,4</sup>. Alternatively, SiNWs might possess antimicrobial properties, since the penetration of cells could facilitate cell lysis<sup>5</sup>. While the results repored so far focused on bacterial or mammalian cells, our current study explore the biomaterial interface between SiNWs and the yeast model organism Saccharomyces cerevisiae. Scanning electron microscopy imagin of S. cerevisiae incubated on SiNWs showed that the nanowires sporadically penetrate the cells without causing lysis, dehydration and death. Fluorescent microscopy techniques were employed to show that yeast cells continue to grow and proliferate on SiNWs. These preliminary results suggested that SiNWs are compaptible with yeast cultivation and that they might facilitate molecule delivery. As such, we attempted to mechanically transform the leucine auxotroph yeast strain W303-1A by incubating it on SiNWs previously functionalized with (3-Aminopropyl)triethoxysilane (APTES) and coated with a pRS415 plasmid carrying the LEU2 gene. The transformation with pRS415 was considered successful if yeast cells recuperated from the SiNW surface generated colonies on selective SD-leucine medium. Different time parameters were explored, with one successful transformation after 4 hours SiNWs. incubation However, on the experimental repeatability was low, mainly due to bacterial contamination occurring while manevrating the SiNWs. To solve this problem, we devised a platform containing localized SiNWs at the bottom of PDMS wells. This platform will allow us to better control the incubation conditions on SiNWs, to easily recuperate cells from the SiNWs and eventually to optimize the molecular delivery of DNA inside the yeast cells. Should our proposal prove successful, it will not only constitute an alternative yeast transformation method, but a

less complex and less expensive method to transform multiple strains with various plasmids at once, on a reusable nanostructured platform.

**Keywords**: silicon nanowires, biocompatibility, *S. cerevisiae*, yeast transformation



**Figure 1**: (1<sup>st</sup> row) SEM imaging showed SiNWs penetrating the yeast cells. (2<sup>nd</sup> row) Fluorescent microscopy imaging showed that yeast cells expressing a green fluorescent protein continued to grow and proliferate on a SiNW surface for 52 hours.

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## Interaction of magnetic iron oxide nanoparticles with primary human monocytes and adrenocortical carcinoma cell lines

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#### Abstract:

Magnetic iron oxide nanoparticles (MIO-NPs) have become a strong candidate for the use in a variety of applications ranging from drug and hyperthermia delivery, clinical therapy and other bio-applications (1). Adrenocortical carcinoma is a rare cancer that carries a poor prognosis with limited treatment options (2). MIO-NPs may represent a material of interest for the treatment of ACC, to deliver hyperthermia and/or improve the efficacy of chemotherapy. However, high immune and endothelial cell uptake of nanoparticles may interfere with the ability to specifically target ACC using systemic injection. In this study, we aimed to evaluate the relative uptake of MIO-NPs into monocytes and ACC cells with the purpose of developing a strategy to maximise ACCspecific MIO-NP uptake. MIO-NPs uptake was evaluated using a transwell system consisting of primary human monocytes (upper chamber) and ACC cells (lower chamber). The transwell insert was coated with fibronectin or a HUVEC endothelial cell layer. We hypothesised that monocytes (and HUVEC layer) exhibit high MIO-NPs uptake upon exposure, with limited quantites of MIO-NPs reaching ACC cells in the bottom chamber.

MIO-NPs were manufactured at University of Kansas (SB). ACC cell-lines (H295R, MUC1 and HAC15) and Endothelial cell-line (HUVEC) were used. Primary monocytes were isolated, using negative selection (MACS®-system) from PBMCs isolated by gradient centrifugation (Fi-COLL®) from the blood of healthy volunteers. MIO-NPs were added at an optimised concentration of 10 µg/ml and incubated for 24 hours. MIO-NPs uptake, rate of uptake and cellular toxicity was assessed using Flow Cytometry. Confocal Microscopy and Live Imaging were used to evaluate time-dependent MIO-NP uptake. Intracellular location of MIO-NPs within monocytes assessed was by transmission electron microscopy (TEM). Uptake efficiency of MIO-NPs into ACC cells was evaluated in the presence and absence of monocytes. Monocyte migration through fibronectin and HUVEC layer was also assessed.

MIO-NPs were taken up monocytes in a concentration and time-dependent manner (Figure 1A). MIO-NPs taken up by monocytes were predominantly located intracellularly within vesicles and the nucleus (Figure 1B). In the presence of monocytes, MIO-NP uptake by ACC across all three cell lines was reduced (Figure 2A). This was demonstrated in the presence and absence of an endothelial cell layer. The endothelial barrier further reduced the uptake of MIO-NPs into ACC cells (Figure 2B).

In conclusion, we characterise the uptake of MIO-NPs into ACC cells in the presence and absence of monocytes and endothelium. Non-specific MIO-NPs uptake by monocytes and HUVEC cells reduces ACC uptake of these NPs and therefore strategies towards more specific uptake must be undertaken.

**Keywords:** Nanoparticles, monocytes, adrenocortical carcinoma, MUC1, HAC15, H295R, HUVEC.



Figure 1: (A) demonstrates concentration and time-dependent uptake of MIO-NP by human monocytes and (B) demonstrates the

intracellular location (white arrows) of MIO-NP within vesicles and the nucleus.



**Figure 2**: (A) reduced MIO-NP uptake was demonstrated in all three cell lines in the presence of monocytes and (B) this uptake was further reduced in the presence of a HUVEC endothelial barrier.

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### Nanowire-based electrodes for electrophysiological studies: Fabrication, on-bench characterization and *in vitro* biocompatibility

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#### Abstract:

Neuronal information is transmitted from neuron to neuron through electrical impulses. These impulses, which travel through the synapses, can be either measured or stimulated artificially using electrodes. Depending on the number of neurons involved, electrodes can be extracellular, when interacting with a bunch of neurons, and intracellular, when addressing a single neurons. Regarding the first, planar microelectrodes arrays are mostly used [1]. However, these may affect cell survival as a consequence of electrodes rigidity, chemical composition and degradation. For the intracellular ones, patch clump techniques are commonly used [2], although cell content exchange and membrane perforation reduce cell survival.

To overcome these limitations, we design nanostructured electrodes based on metallic nanowires. These electrodes were fabricated by a combination of metal anodization and templateassisted electrodeposition technique [3]. Next, we characterized the electrode morphology and electrochemical properties. Additionally, their morphological and functional interactions with embryonic neural progenitor cells at 14 days was analysed. In the context of intracellular measurements, tip-based electrodes are being explored by applying the fabrication techniques of planar electrodes for extracellular measurements.

Trial outcomes by cyclic voltammetries and electrochemical impedance spectroscopy confirmed that, in contrast to their flat counterparts, vertical metallic nanowires-based electrodes increased the effective area, while impedance values were reduced. Equally important, there were a superior neural cell development and more efficient contacts with the nanostructured electrode, and both spontaneous activity and ability of neuronal synchronization were increased. Based on these electrical and biological findings, the use of our nanostructured electrodes is expected to increase cell survival when measuring or stimulating neural cells and tissues, obtaining a high signal to noise ratio on the measurements.

This project was funded by the European Union's Horizon 2020 research and innovation programme under grant agreement No 737116 (ByAxon), the I+D+I projects DPI2017-90058-R (BiSURE) and PID2020-120202RB-I00 (REGINNA) from Spanish MICINN, as well as the 'Severo Ochoa' Programme for Centres of Excellence in R&D (SEV-2016-0686).

Keywords: nanowires, electrodes, anodization, electrodeposition, cyclic voltamogram, electrochemical impedance spectroscopy, biocompati-



bility, neural cells.

**Figure 1**: Neural cell culture on a vertical metallic nanowires-based planar electrode.

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## Dendrimer nanocarriers as an efficient tool to deliver therapeutic siRNA to glioma-associated microglia and macrophages

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#### Abstract:

Malignant gliomas are the most common and aggressive primary brain tumors in adults with a median survival time of 15 months. Microglia brain resident myeloid cells, which participate in immune defense andantitumor responses in benign brain tumors, support tumor progression in malignant gliomas. Together with peripheral monocytes, microglia are recruited to the tumor and contribute to glioma invasion, immunosuppression and angiogenesis. Due to their critical role as instigators of inflammatory or pro-tumorigenic events, microglia are considered to be a promising therapeutic target. Genetic manipulation of microglia in diseases using small interfering RNA (siRNA) is however hampered by the lack of safe and efficient siRNA delivery methods. We assessed the use of the amphiphilic dendrimer nanovectors (AD) for functional siRNA delivery and gene knockdown in primary microglia cultures. AD protected the siRNA from degradation, facilitated its cellular uptake and enabled endosomal release. AD effectively delivered Id1-targeting siRNA to primary microglia cultures and decreased target gene and protein expression. Id1 is a negative regulator of myeloid cell differentiation and is upregulated in gliomastimulated microglia. Global gene expression analysis (RNAseq) revealed that Id1 knockdown led to attenuation of the pro-invasive reprograming of microglia stimulated by glioma cells. AD complexes were also effective as in vivo siRNAnanocarriers in an orthotopic glioma model in mice. The AD dendrimer constitutes a promising innocuous carrier for siRNA delivery into microglia and opens up new perspectives on functional genomic studies and therapeutic targeting of microglia in brain tumors and other CNS diseases. The study supported by National Science Centre Poland (2017/25/B/NZ3/02483), National Centre for Research and Development in Poland and French National Research Agency under the frame of Era-Net EURONANOMED projects "Nanoglio" and "iNanoGun".

Keywords: amphiphilic dendrimers, glioma, microglia, siRNA

## Ratiometric Sensing Systems for Intracellular and Extracellular pH Mapping at Single Cell Level in Tumor Models

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#### Abstract:

The tumor microenvironment is characterized by an elevated hydrogen ion concentration, which is the result of increased cellular metabolic demand and altered perfusion, e.g., oxygen availability or acidic metabolic waste products.<sup>1</sup> The acidity of the tumour microenvironment, which is spatially and temporally heterogeneous,<sup>2</sup> affects cancer initiation and progression, but also the efficacy of anti-cancer drugs treatments.<sup>3</sup> Therefore, monitoring the local pH metabolic fluctuations is critical in understanding the basic biology of the tumour, and can also be used as a valid metabolic readout for cancer diagnosis and treatment. Importantly, the complexity of the tumour microenvironment, which includes cell-cell interactions and extracellular matrix composition, coupled with the fast diffusion and mobility of extracellular protons, makes the extracellular pH mapping extremely challenging.<sup>4</sup>

Herein, the synthesis and application of nanostructured micro- and nanomaterials will be described with a special focus on the properties they could offer for sensing applications (**Figure 1**). Examples will be given in which particles-based sensors are applied (i) for automated and precise quantification of organelle acidification in single tumor cells,<sup>5</sup> (ii) for mapping extracellulat pH metabolic variations in the local environment of 3D cell-seeded scaffolds.<sup>6</sup>

**Keywords**: Ratiometric optical pH-sensors; silica micrpartcles; hydrogels; fluorescence; pH sensing, organelle acidification; microparticle tracking; cancer; cell metabolism; tumour microenvironment data compression, automated cluster analysis.



**Figure 1**: Optical sensing systems for pH sensing in tumor cell cultures, based on either fluorescent ratiometric microparticles, hydrogels, electrospun nanofibers and additive manufactured scaffolds.

#### Acknowledgments

The research leading to these results received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No [759959], "INTERCELLMED").

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## Ultrastructural Visualization of Combinatorial Nanodrug Interaction with Mitochondria of Breast cancer cells

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#### Abstract:

Novel strategies are required to stop the proliferation and progression of highly malignant tumors and cancers irrespective of their subtypes. Current therapeutic and diagnostic strategies are based on the availability of one or the other biomarkers for specific targeting. This limits the development of a powerful generalized therapeutic strategy for cancers. However, identification and development of combo-theranostic modules can offer a common platform to target them as well as trace their existence after personalized therapies. More over, ultrastructural visualization of targeted nanomodules against its interactions with subcellular organelles through electron microscopy and its 3D rendering is always challenging. Mechanistic and conformational understandings of specific subcellular connections of novel smart nanocarriers with various intrinsic receptors of breast cancer cells are critical for the design and delivery of novel cancer therapeutics. Toxicological effects of gold nanocages, passivated with extremophilic polysaccharide, Mauran functionalized with 4hydroxytamoxifen and monoclonal antibody Pr1E11 result in downright decimation of subcellular organelles in breast cancer MCF7 cells resulting in parallel type I and type II cell deaths. Herein, the deleterious repercussions of the therapeutic gold nanocages (TANs) on the subcellular organelles of MCF7 cells are studied. Together, this data fortifies the benefit of subcellular cancer targeting and multiple parallel damage explained through advanced electron microscopic visualization.

**Keywords**: Breast cancer, 3D-TEM imaging, combination therapeutics, nanocages, drug targeting, apoptosis, autophagy, nanotoxicology, cancer therapy, nanomedicine.



**Figure 1**: Figure illustrates the segmented 3D reconstructed TEM micrograph of mitochondria in breast cancer cells, infested witht the TAN particles. Images shows the damaged outer and inner membrane of mitochondria by nanoparticles.

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### Anti-tumour/MRI agent loaded LDL for personalized therapy applications

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#### Abstract:

The combination of imaging and therapeutic agents in the same smart nanoparticle is a promising option to perform a minimally invasive imaging guided therapy.

Low density lipoproteins (LDL)<sup>1</sup>, one of the most attractive biodegradable and biocompatible nanoparticles, were used for the simultaneous delivery of Paclitaxel (PTX), a hydrophobic antitumour drug and an amphiphilic contrast agent, Gd-AAZTA-C17, in B16-F10 melanoma cell line. These cells overexpress LDL receptors, as assessed by flow cytometry analysis. PTX and Gd-AAZTA-C17 loaded LDLs (LDL-PTX-Gd) have been prepared, characterized and their stability was assessed.

The anti-tumour drug loaded into LDLs showed a significantly higher toxicity on B16-F10 cells with respect to the commercially available formulation Paclitaxel kabi (PTX Kabi) used in clinical applications.

Therefore, the treatment with PTX loaded LDL on B16-F10 tumour bearing mice resulted in a marked reduction of tumour growth compared to the administration of PTX Kabi alone.

Moreover, LDL have been proposed for the treatment of mesothelioma cells overexpressing LDL receptor as well. Due to the high dissemination of these tumours, of any significant therapies and the median survival after diagnosis is less than

9–12 months we decided to try to treat them with an alternative radiotherapy named Boron Neutron Capture Therapy (BNCT)

BNCT is an example of targeted therapy with good efficacy and low toxicity that provides a tumor selective cell death. More specifically, this therapy is able to combine low energy thermal neutron irradiation with the presence of boron containing agents at the targeted pathological tissues successfully applied to primary brain tumours and recurrent head and neck cancer<sup>2</sup>. Therefore, for this application, LDL were loaded with a boron containing molecule specifically delivered to mesotelioma cells. **Keywords**: drug delivery, Low Density Lipoprotein, Paclitaxel, Gadolinium, Boron contained comound, Boron Neutron Capture therapy(BNCT).



**Figure 1:** Schematic representation of LDL as a carrier for both PTX and Gd-AAZTA-C17.

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## Polymer conjugates with anticancer agent cytarabine with increased stability and different speed of hydrolytic release for highly effective antitumor therapy

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#### Abstract:

Mantle cell lymphoma (MCL) is a rare subtype of B-cell non-Hodgkin lymphoma (B-NHL) with chronically relapsing clinical course. Implementation of anticancer drug cytarabine (araC) into induction and salvage regimen became standard of care for majority of MCL patients. In this study, water soluble polymer conjugates based on N-(2-hydroxypropyl)methacrylamide (HPMA) polymer containing covalently bound araC (araC copolymers) were designed, synthesized and evaluated for their anti-lymphoma efficacy in vivo. Prepared conjugates have different velocity of hydrolytic release of drug from polymer backbone based on type of spacer between the drug and polymer carrier. Based on the structure of used spacers we can influence the hydrolytic release of araC from conjugates at pH 7.4, which seems to be crucial in in vivo experiments. Although the polymer conjugates differ in the velocity of releasing the drug, in comparison with free araC all conjugates are more effective in eliminating mantle cell lymphoma cells on a patient-derived xenograft murine model. The polymer conjugates have no observed toxicity compared to free araC and so these conjugates seem to be ideal for using of treatment of non-Hodgkin lymphomas.

**Keywords**: HPMA copolymer, drug delivery, cytarabine, mantle cell lymphoma, nanotherapeutics.



**Figure 1**: Schematic description of the mode of action of polymer-araC nanomedicines Abbreviations: araC = cytosine arabinoside, araU = uracil arabinoside.

#### Acknowledgement:

The work was supported by the Czech Science Foundation (project No. 22-12483S).

# Taking advantage of invasive pest species in biotechnology: Spanish slugs (*Arion vulgaris*) as a potential exosome source for cell delivery applications

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#### Abstract:

Many studies show that exosomes could be used as a delivery system of various types of cargo into the target cells, making them a valuable tool for the delivery of therapeutics for human treatment (1). Up to day mostly human- or mammalderived exosomes are used for this purpose, however there are many potentially interesting sources of exosomes found within the animal kingdom. Here we examine the potential of exosomes collected from the widely spread invasive pest species of garden slugs as an accessible and cheap alternative to mammalderived exosomes for cell delivery in humans.

We developed methods for the slug mucus collection, used classical methods for isolation (ultra-centrifugation) and characterisation (DLS, NTA analysis, TEM, confocal microscopy figure 1, BCA assays) of slug exosomes and proved their ability to deliver loaded cargo (dyes, doxorubicin) into mammalian as well as plant cells.

**Keywords**: exosomes, cell delivery, slugs, mucus.



**Figure 1**: Figure obtained by confocal microscopy illustrating the successful entry of slug exosomes labeled with ceramide bodipy TR dye into U87 human glioblastoma cell line.

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doi: 10.3389/fmolb.2022.846650 PMID: 35586196

#### Acknowledgements:

The author acknowledges the assistance provided by the ERDF/ESF project "UniQSurf – Centre of Biointerfaces and Hybrid Functional Materials" (No. CZ.02.1.01/0.0/0.0/17 048/0007411).

## Engineered chitosan based nanocarriers for therapeutic miRNAs delivering to human melanoma cells: in vitro and in vivo studies

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#### Abstract:

As well known chemotherapeutic agents have certain limitations when it comes to treating cancer, the most important being severe side effects along with multidrug resistance developed against them. Tumor cells exhibits drug resistance due to activation of various cellular level processes viz. activation of drug efflux pumps, anti-apoptotic defense mechanisms etc. Recently the application of nanotechnologies in the field of biomedical research has recently led to significant progress and developments of technologies for the transport of nucleic acids with antitumor activity by using taylor made nanocarriers (1,2). Currently, RNA interference (RNAi) based therapeutic approaches are under vibrant scrutinization to seek cancer cure. Especially small interfering RNA (siRNA) and micro RNA (miRNA), are able to knock down the carcinogenic genes by targeting the mRNA expression. Among the various nanostructured vectors, polymeric nanoparticles proved to be particularly advantageous and safer than viral vectors, being characterized by important properties such as biocompatibility, biodegradability and non-toxicity. In the present study, chitosan nanoparticles were synthesized for therapeutic miRNA delivering within cancer cells. This microRNA is able to induce tumor regression in melanoma cells especially when combined with the administration of other anticancer drugs (3). The choice of chitosan lies in its chemical-physical properties and its biocompatibility(4). The positive charge exhibited by the polymer guarantees a strong interaction with the negatively charged oligonucleotides to be conveyed, leading to the formation of stable complexes in which the nucleic acid is shielded in terms of charge and protected from the action of nucleases. The internalization tests with the cells were carried out by using CS-miRNA nanoparticles conjugated with a specific antibody for melanoma cells to favor targeting. The optimization of the amount of trapped miRNA and the chemical-physical characteristics by means of the ionotropic gelation method have been carried out. Dynamic Light Scattering (DLS), Nanosight, and morphological analysis by using scanning electron microscopy (SEM) were performed.

We finally demonstrated the *in vivo* antitumoral effects of the nanocarriers above-described. To this end, we developed a reproducible mouse model of liver and lung metastases via intra-splenic injection of melanoma cell lines. The mice were then treated with CS-miRNA obtaining a strong reduction of cancer dissemination.





**Figure 1**: Figure illustrating the in vitro and in vivo targeting of human cancer cells by using Cs based engineered Nps

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## Optimizing Coiled Coil Interactions for Peptide-PAINT Super-Resolution Imaging

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#### Abstract:

Super-resolution microscopy is transforming research in the life sciences by enabling the visualization of structures and interactions on the nanoscale. DNA-points accumulation for imaging in nanoscale topography (PAINT) is a relatively easy-to-implement single-molecule based technique, which relies on the transient interaction of dye-labeled oligonucleotides binding to their complementary docking strands for super-resolution imaging [1]. However, similar to many imaging approaches, it is still hampered by the subpar performance of labeling probes in terms of their large size, availability and limited labeling efficiency. To overcome this, we here translate the programmability and transient binding nature of DNA-PAINT to coiled coil interactions of short peptides, and call this new method: Peptide-PAINT [2]. In a single-molecule assay where tens of thousands of molecules can bind, we analyze the binding kinetics of multiple variations of one coiled coil pair and directly compare it to classical DNA-PAINT. We observe that Peptide-PAINT outperforms classical DNA-PAINT in terms of imaging speed and efficiency. In addition, the speed of Peptide-PAINT is further increased by changing the salt concentration of the buffer, similarly to DNA-PAINT. We then demonstrate the super-resolution capabilities of Peptide-PAINT using self-assembled DNA origami structures. Peptide-PAINT can be used to successfully reconstruct DNA origami with docking sites spaced 20 nm apart. Finally, in a proof-of-principle experiment, we show the applicability of Peptide-PAINT for cellular imaging by targeting the microtubule and vimentin network using primary and peptide-conjugated secondary antibodies in fixed U2OS cells.

**Keywords**: super-resolution, coiled coil interactions, transient binding, Peptide-PAINT, DNA-PAINT, single-molecule imaging, DNA origami



Figure 1: Figure illustrating the principles and applications of Peptide-PAINT. A dye-labelled imager coil repetitively binds to its complementary docking coil, generating the blinking pattern required for super-resolution imaging. The binding kinetics of a coiled coil pair for Peptide-PAINT was derived from a single-molecule assay (top). Peptide-PAINT and DNA-PAINT imaging of a 20-nm DNA origami structure were performed for direct comparison of both superresolution methods (bottom left). Peptide-PAINT can also be applied for super-resolution imaging in fixed cells. A zoom-in of microtubules from U2OS cells imaged with Peptide-PAINT are presented here, as an example (bottom right).

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- Eklund\*, A.S., Ganji\*, M., Gavins, G.; Seitz, O., Jungmann, R. (2020) Peptide-PAINT super-resolution imaging using transient coiled coil interactions, *Nano Lett.*, 20, 9, 6732-6737.
## SMS / EGF 2022 - Session III.A: Applications for energy and environment

## Luminescent Solar Concentrators: A versatile photonic platform enabled by extreme photon concentration

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#### Abstract:

The luminescent solar concentrator, or LSC, is an emerging technology for building integrated photovoltaic (PV), [1]. In general, it constitutes of a transparent host matrix (polymer or glass) dopped with fluorophores (quantum dots or fluorescent dyes). Incident solar photons falling onto the device are absorbed, down-shifted in wavelengths due to the Stokes effect and then re-emitted. The majority of these photons are then trapped by total internal reflection (TIR) within the higher refractive index lightguide and directed to the edges of the device where they can be converted into electrical current via attached photovoltaic (PV) cells (see Fig. 1). LSCs come in different forms and can comprise both rigid and flexible devices, making them applicable for a wide range of applications, from semi-transparent windows that can generate electricity to powering up consumer electronics, [2].

At its core, the LSC is an extremely versatile and powerful photonic technology platform, owing to its highly desirable inherent ability to efficiently concentrate incident light, even if diffuse, [3]. Conventionally, optical systems are limited by the principle of conservation of étendue, meaning that there is a tradeoff between the acceptance angle and maximum concentration gain that can be achieved. However, in the presence of a Stokes shift étendue needs not to be conserved in the same way: both broad acceptance angles and high concentration gains that grow exponentially with  $\Delta \omega$  can be achieved, whilst still adhering to the second law of thermodynamics. As an example, the predicted concentration gain for an LSC device operating in the visible region with a 0.25 eV Stokes shift (typical for fluorescent dyes used in LSC research) can exceed 104, a value which is nearly four orders of magnitude larger than what can be achieved with a device that does not shift frequency. Such extreme concentration gains captivated researchers' imagination, who have come up with numerous innovative ways to put LSCs into use. Overall, LSC-based devices can be designed to collect, control and manipulate the spectra and spatial distribution of emitted light, with the exciting possibility for their response to evolve dynamically as a function of time.

In this presentation, I will review the recent work in the photonic innovations lab covering both rigid and flexible LSCs, LSCs for high data rate free space communications, [4] and even LSCs that can improve crop yield in greenhouses, [5].



**Figure 1**. Diagram depicting the principle of operation of a Luminescent Solar Concentrator (LSC) when employed for use in harvesting solar energy.

**Keywords**: luminescent solar concentrators, fluorescence, quantum dots, micropatterning, building integrated PV, horticulture, high speed free space communications.

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## Integration of efficient single photon sources into plasmonic devices by two photon polymerization of multifunctional photopolymers

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#### Abstract:

The integration of nano-emitters into plasmonic and photonic devices with spatial control and nanometer precision has become a great challenge. In this work, we report on the use of a hybrid and functionalized photopolymers [1, 2] to selectively integrate nano-emitters on specific preselected sites of plasmonic nano-antennas and optical waveguides. For this, two approaches were developed to integrate the nano-emitters (See Figure 1). The first one consists of using a photosensitive formulation containing quantum dots (QDs) where acrylic monomers are grated on Blue, Green and Red emitting QDs before adding Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Irg. 819) as photoinitiator. This hybrid photopolymer is then used to integrate the nanoemitters by 2-photon polymerization (TPP) in the near field of a single gold nano-cube [3, 4]. The second approach uses functionalized photopolymers making it possible to attach negatively charged nanoparticles right at the preselected polymerized sites, which subsequently recognize the nano-emitters to be attached [2]. Since the resulting active medium is a spatial memory of specific plasmonic modes, it is anisotropic, making the hybrid nanosources sensitive to light polarization [4, 5]. The ability to adjust their statistical average lifetime by controlling the volume of the nanopolymer is demonstrated on two kinds of nano-emitters coupled to GNCs: doped polystyrene nanospheres and semiconductor colloidal quantum dots. These 2 approaches are currently under investigation to integrated single photons sources in a specially controlled manner into photonic and plasmonic nanostructures.

**Keywords**: Quantum dots, single photon sources, plasmonic nanoantennas, Two photon polymerization, Photopolymers, polymer surface functionalization, Quantum technologies.





**Figure 1**: Figure illustrating our integration approachs for the creation of efficient photon sources. Top: integration of QDs in a sapatially controlled manner by local near field TPP of a QDs-containing photopolymer in the vicinity of a single gold nanocube. Bottom: fabrication of a hybrid photon source after integration of a smart functionalized polymer by local near field TPP and electrostatic immobilization of QDs.

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### Phosphate-functionalized graphene obtained by a fast, one-step electrochemical strategy for capacitive energy storage

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#### Abstract:

graphene In recent years. materials functionalized with heteroatoms or molecular groups have become highly relevant as an electrode material for electrochemical energy storage, as they provide a number of benefits that can include improved wettability by the electrolyte, enhanced electrical conductivity and/or extra redox activity. Phosphate groups have particularly shown their attraction in this regard (Tanguy et al., 2020). In this work, we the preparation of phosphatereport functionalized graphene nanosheets by a straightforward method based on the electrochemical exfoliation of graphite. Using phosphoric acid or sodium phosphate as the electrolyte in aqueous medium, functionalized nanosheets can be obtained at room temperature in a single step upon anodic treatment of the precursor graphite (Figure 1). Compared to previous methodologies that make use of, e.g., graphene oxide and high the temperatures, present strategy is considerably less timeand resourceconsuming and, thus, more sustainable (Ramírez-Soria et al., 2021). Upon optimization of the electrolytic treatment conditions, functionalized graphenes with phosphorus contents around 2 at.% were obtained. A discussion of the graphene functionalization mechanisms under the electrolytic conditions is provided. The phosphate-functionalized graphenes were tested as electrodes for supercapacitors in acidic electrolyte. In a three-electrode configuration, capacitance values up to  $\sim 375$ F/g (540 F/cm3) were obtained. When tested in a two-electrode configuration (symmetric cell), these graphenes afforded energy densities up to 17.6 Wh/kg (25.3 Wh/L) and power densitiesup to 10.2 kW/Kg, with capacitance retention values around 98-99 % after 10,000 cycles.

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#### Acknowledgements

Funding by MICINN/AEI/FEDER through project RTI2018-100832-B-I00 is gratefully acknowledged.





**Figure 1.** Schematic representation of the green process to prepare phosphate-functionalized graphene (denoted as PFG-acid and PFG-salt) via one-step anodic exfoliation/functionalization of graphite using  $H_3PO_4$  or  $Na_3PO_4$  as electrolyte/phosphate source, and its use as an electrode material for capacitive energy storage.

## Novel Approach to Enhance Electrochemical Performance of Na<sub>0.7</sub>CoO<sub>2</sub> Layered Cathode and Nitrogen-Sulpher Co-doped Graphene as Anode for Sodium-ion Batteries

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#### Abstract:

P2-type Na<sub>0.7</sub>CoO<sub>2</sub>, an eminent layered transition metal oxide (LTMO), owing to this capability of high ionic diffusivity, has been studied on a big scale for future practical applications of sodium-ion batteries as cathode. However, its poor conductivity and poor structure stability have sharply obstructed its practical applicability in sodium-ion battery (SIB). Herein, a stable P2- Na<sub>0.7</sub>Ag<sub>0.11</sub>Cu<sub>0.33</sub>Co<sub>0.56</sub>O<sub>2</sub> layered cathode with simultaneous silver and copper doping and hierarchical spherical nanostructures originated from nanoparticles subunits assemblage is reported. Due to Ag ion doping and Cu ion substitution, interdiction of the phase transition during charge and discharge tests is revealed by using X-ray diffraction measurement and diffusion kinetics analysis. In addition, the hierarchical spherical nanostructure is shown to hold a robust structure, which increases the capacity retention from 70% to 85% over 100 cycles when compared to its bulk counterpart. For anode material nitrogen-sulphur co-doped graphene is utilized due to the enhanced electrical conductivity originating from nitrogen doping. However, sulphur doping in graphene is introduced to expand the interlayer spacing for high capacity and long cycle life. The novel material demonstrates marvellous electrochemical performance with a high capacity retention of 85% over 100 cycles at 1C current rate and delivers a specific capacity of 115mAh g<sup>-1</sup>.

**Keywords**: nitrogen-sulphur co-doped graphene, layered transition metal oxide (LTMO), structure stability, phase transition, diffusion kinetics.



Figure 1: Schematic interpretation of the elementary working mechanism of sodium ion transfer in SIB during the charging and discharging process.

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## Graphene Aerogel Electrode for Advanced Fuel Cell and CO<sub>2</sub> Reduction Electrolyser

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#### Abstract:

Super lightweight, multifunctional graphene aerogel (GA) monolith has been prepared as electrode material for electrochemical energy and environmental remedy devices. In this presentation, we will discuss its application in a direct methanol fuel cell (DMFC), which is demonstrated for the first time. A new GADMFC design is proposed by using GA to replace two main components within the DMFC-the gas-diffusion layer and the flow field plate. The results indicate a 24.95 mW cm<sup>-2</sup> maximum power density of air polarization is obtained at 25 °C. The membrane electrolyte assembly has a 63.8% mass reduction compared to an ordinary one, which induced 3 times higher mass power density<sup>1</sup>. Electrochemical reduction of CO2 (eCO2RR) to low carbon organic compounds has been considered as a promising method to mitigate the greenhouse effect and produce useful energy carrying chemicals. However, from the commercialization points of view, numbers of challenges in the eCO<sub>2</sub>RR remain to be tackled: 1. Low energy efficiency. e.g., inertness and low solubility of CO<sub>2</sub>, low selectivity and activity of catalysts, which requires high energy input with low fuel production. We will also discuss its application in electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR) electrolyser for alternating the structural design of cells led to massively increased mass transfer and overall performance. A hybrid gas diffusion electrode-based reaction cell is demonstrated using highly porous carbon paper (CP) and graphene aerogels (GAs), which is expected to offer directional diffusion of gas molecules onto the catalyst bed, to achieve an increase in the Faraday efficiency (FE) from  $\approx 60\%$  to over 94% toward carbon monoxide (CO) and formate production compared with a CP only cell with Cu<sub>2</sub>O as the catalyst. It also suppresses the undesirable side reaction-hydrogen evolution over 65 times than the conventional H-type cells<sup>2</sup>.

**Keywords**: graphene aerogel, fuel cell, CO<sub>2</sub> reduction reaction, electrolyser, mass transfer, porosity



**Figure 1**: Graphene aerogel's application in (a) direction methanol fuel cell and (b) CO<sub>2</sub> reduction electrolyser

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## Capacitive de-ionization using reduced graphene oxide-based electrodes for desalting synthetic and real saline waters

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#### Abstract

Capacitive deionization is an emerging electrochemical technology for water desalination with low energy consumption. According to the CDI Process, the electrode material is crucial for the performance of the CDI.

The ideal electrode for CDI should have a large specific surface area with a pore structure offering high ion mobility, high conductivity, good wettability, and be composed of inexpensive, scalable, and easy-to-process material.

Among the many electrode materials, graphene-based nanomaterials are remarkable and play an essential role during the deionization process due to their fascinating characteristics. Graphite, which is the basic material for the synthesis of reduced graphene oxide will be taken as the main substrate or support.

The main objective of this work was to study a new technique for reducing salts by capacitive de-ionization (CDI) based on reduced graphene oxide electrodes under the effect of an electric field for saline water treatment (Figure 1).

In this study, a nanocarbon material (reduced graphene oxide) was synthesized by the Hummers method to obtain graphene oxide, which was then chemically reduced to form reduced graphene oxide (rGO). Subsequently, graphite substrate electrodes was spread by rGO for capacitive deionization (CDI).

Experimental results showed that the rGO synthesized material has a porous structure with a specific surface area equal to 17.85  $m^2.g^{-1}$  and a microporosity of 13.0202  $m^2.g^{-1}$ . Its conductivity is equal to 862.06 S.m<sup>-1</sup>. The electrochemical characteristics (cyclovoltammetry analysis) obtained from rGO-based electrode indicate a specific capacitance of 0.125 F.g<sup>-1</sup> at a scanning speed of 10 mV/s.

CDI electrosorption performance using different electrodes (graphite, rGO and rGO +

graphite) was evaluated. The lab-scale tests for desalinating four types of saline water, two synthetic (NaCl, Na<sub>2</sub>SO<sub>4</sub>) and two real (tap water and well water) show a decrease in conductivity during CDI treatment time, with important desalination rates (%) equal to 61.5%, 52.5%, 40% and 41.05%, respectively.

The experimental results confirmed that the electrochemical potential of rGO, produced by oxidation and chemical reduction, can be further improved by incorporating a minor amount of graphite. The resulting rGO has proven to be a promising and highly efficient electrode material for good cost-effectiveness in CDI technology, which appears to be a high-performance electrochemical technique for saline water desalination.



Figure 1: Schema of capacitive deionization set-up

**Keywords:** capacitive deionization, nanomaterial, reduced graphene oxide, graphites electrodes, hummer method, desalination, brackish water, saline water.

## NanoMed / Sensors 2022 Session III.B

## Development of a device for the rapid detection of SARS-CoV-2 based on electrochemical biosensor

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#### Abstract:

The devastating consequences of the spread of COVID-19 have necessitated the development of new technological tools to combat the virus. Particular emphasis is given to the development of diagnostic methods that monitor the spread of the virus rapidly and effectively. This paper presents an electrochemical biosensor for the rapid detection of SARS-CoV-2 in biological samples.

Initially, the sensing element is developed, based on the immobilization of the natural receptor of the virus, the enzyme ACE2, on the surface of interdigitated electrode capacitors. The results of the biosensor measurements are correlated with the real-time PCR results for the same samples.

After the sensor has been verified to function properly, the sensor is integrated into a lab-developed portable device. This device consists of a custom precision electronic circuit that performs impedance measurements. Also, using Bluetooth, the device wirelessly transmits the measurement results to an android mobile application.

The final stage concerns the packaging of the biosensor and the electronic device, but also the construction of the connector between the two. The packaging of the device and the manufacturing of the connector are done using 3D printing. The packaging of the biosensor is carried out using a photosensitive film, ORDYL SY 300, which is processed by the method of optical lithography.

**Keywords**: biosensor, SARS-CoV-2, capacitance, electronic readout circuit, microcontroller, packaging, interdigitated electrodes

### Bacterial Biosensors that can compute

#### R. Daniel

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#### Abstract:

Over the past decade, whole-cell biosensors have gained widespread attention, owing to its potential in providing low-cost analytical tools for environmental monitoring, e.g., detection of toxic chemicals in the air, water, and food [1] and biomedical applications. e.g., detection of blood in the gastrointestinal tract [2]. Whole-cell biosensors often consist of: (1) genetically engineered bacteria that can recognize different analytes. The bacterial cells convert the biological response to electrical signals and (2) electronic detectors that record the measured signals.

Advantages of using bacterial biosensors are: first, they contain many highly evolved biochemical pathways providing sensitivity to a vast range of chemicals and analytes, in contrast to chemical biosensors. Second, Bacteria have high versatility and can survive in various complex settings, such as extreme temperatures and broad ranges of salinity and pH. Third, living cells, tissues, and organs can be integrated with low-cost electronic detectors. For example, using a singlephoton avalanche diode, we have built a bioluminescent biosensor that can detect toxins in water [3] and blood markers in urine [4]. Finally, recent DNA assembly advancements showed that bacteria biosensors could be reprogrammed, including large-scale synthetic genetic networks.

This study shows the implementation of several bio-designs into bacterial biosensors in order to improve their performance (Figure 1). Synthetic biological regulatory networks in bacterial cells comprise feedforward and feedback loops, which allow cells to perform sophisticated tasks [5]. We started with the implementation of a 2-bit analog-to-digital converter (ADC), which divides the dynamic range of a single input into four ranges (low, low-moderate, moderate-high, high) encoded in two discrete-binary outputs {00, 01, 10, 11}. Bacterial biosensors that include ADC can report on the level of the measured signal and not only on its presence.

Then, we implemented a new genetic regulatory network, namely an indirect coherent feedforward (ICF) loop [6], into *Escherichia coli* cells to improve ON/OFF ratio of biological sensor. We experimentally demonstrated that such a network could reduce the basal level (leak-iness) while maintaining the maximum activity at

high levels. We applied ICF loop for six other different specific and responsive promoters into *Escherichia coli biosensors*, starting with synthetic promoters as a proof-of-principle. We examined native promoters that are either functionally specific (e.g., Arsenic and Heme-sensitive promoters) or systemically involved in complex pathways, such as oxidative stress and SOS response. Such biological systems are widely used for biosensing applications. Using our designs, we improved the ON/OFF ratio of specific/stress promoters sensitive for Arsenic substance ten times, for Heme (blood) molecule nine times, for Nalidixic Acid twice, and for hydrogen peroxide twelve times.



Figure 1: Describes advanced bacterial biosensors that can detect multi-markers for signal processing.

**Keywords**: bacterial biosensors, whole-cell biosensors synthetic biology, gene circuit design.

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## Optical Imaging of Cell Action Potentials via Graphene Based Sensing Devices

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#### Abstract:

All cells within our body have an inherent electrostatic potential which influences the cells activity, however specific cells such as neurons and cardio myocytes have the unique ability to change their electrostatic properties through depolarizing ion currents, creating an 'action potential' in which there is a sudden change in their extracellular potential. Current methods to investigate action potentials in a spatially resolved manner have limitations such as slow speeds, cytotoxicity, or low sensitivity [1]. To overcome these issues it is advantageous to find optical measurement techniques which are sensitive to electrostatic fields. Monolayer graphene is extremely sensitive to local electrostatic fields due to its two-dimensional nature, where a small change in external field can result in a large change in graphene's electronic properties which makes it perfectly suited for biological sensing applications. Biological cells can exhibit voltages in the order of 10-100 mV, which is capable of changing graphene Fermi energy by ~100 meV. This effect has been utilized recently in a critically coupled graphene waveguide device to optically measure changes in electrostatic potential of nerve cells [2], which highlights the opportunities for future biosensing devices. In the visible / NIR regions the change in the transmission and reflection coefficients of graphene due to Fermi energy changes are extremely small, and therefore it is helpful to find methods to amplify the small changes in Fresnel coefficients.

Here we utilize a graphene on glass device (Fig. 1a) where the thickness of the glass causes an anti-reflection effect due to destructive interference, which is sensitive to phase rotation effect upon reflection on the glass / graphene interface, resulting in a high sensitivity over a large Fermi energy range. The device consists of a slab of glass (n = 2, d = 430 nm), covered with monolayer graphene, and illuminated by a 1560 nm laser source. Fig. 1b shows the change in reflected power at the glass / graphene for a range of incident wavelengths, which shows a sharp step feature which is caused by the Pauli blocking effect in graphene. Although this effect creates a large response at a specific Fermi energy it is not suitable for sensing continuous or smooth changes in Fermi energy. Fig. 1c plots the reflected power from the devices (which is calculated numerically from summing multiple internal reflections) as a function of graphene Fermi energy. Around 0.4 eV there is a sharp jump in reflected power, however most importantly the region from  $\sim 0.45$ - 0.8 eV displays a near linear change in reflection. Fig. 1d displays the reflected power (minus the reflection at low Fermi energy) to highlight the improvement to sensitivity which is achieved by the device as compared to the graphene. The graphene / glass interface (red) shows the characteristic step profile, however the device (blue) reveals a sensitivity over a much larger Fermi energy range, which is ideal for sensing applications. We propose that by monitoring such a device with a photodiode array we will be able to measure changes in Fermi energy created by electrostatic doping of biological cells on the surface. This device is advantageous as it requires no patterning of the surface, and as it is an optical effect it will allow for spatially resolved measurements with extremely fast acquisition times.

**Keywords**: biological sensing, action potential, graphene,



Figure 1: (a) Schematic of device (b) Reflected power of graphene / glass interface c) Reflection of anti-reflective stack. (d) Reflected power (minus  $R_0$ ) of glass/graphene (red) and the anti-reflective device (blue).

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## Development of a novel design of Microfluidic Impedance Cytometry for improved sensitivity and cell identification

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#### Abstract:

Microfluidic Impedance Cytometry has been developed as a label-free method which is capable of carrying out rapid, single cell measurements in order to allow medical diagnostic tests to be carried out in challenging or resourcescarce environments. A long-standing issue for these devices is the accuracy in determining the size of cells during counting and measurements. This is due to inhomogeneity of the electric field in the sensing region, which induces errors as the cell position and size information becomes conflated. Traditional approaches have sought to address this issue through the addition of more ornate device designs [1], or the use of sophisticated signal processing [2].

We report a novel design of cytometer that produces a more homogenous electric field in the sensing region than that of existing designs, based on a ground-up approach to electrode integration which also lends itself to simplified manufacturing techniques. It is shown that this device demonstrates higher accuracy in cell counting and sizing, reducing the reliance on cell focusing and signal post-processing techniques, allowing device size and complexity to be minimised.

The concept is validated and the increased accuracy of the device over traditional designs is demonstrated through the use of finite element simulations to generate data sets for particle trajectories and model expected signal variations for existing and novel device designs. We demonstrate that our device has an inherently higher sensitivity and is less susceptible to cell sizing measurement error in two-electrode configuration and an optomised three-electrode configuration that further improves sensitivity while maintaining increased accuracy.

**Keywords**: microfluidics, impedance cytometry, cell counting, biomedical applications, blood count, micropatterning, biomedical applications.

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## Development of a Polyanaline/Polystyrene/Au Nanoparticles-based electrochemical biosensor for the detection of SARS-CoV-2

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#### Abstract:

COVID-19 is an ongoing pandemic that has resulted in more than 500 million confirmed cases and 6 million deaths worldwide, as of June 2022, according to the World Health Organization (WHO) reports [1]. Therefore, there is a demand for new assays (e.g., biosensors) that provide cost-effective, portable, and rapid diagnostics of COVID-19 [2-4]. We have developed a new type of testing strategy based on the electrochemical biosensing aspect for rapid and portable detection of SARS-CoV-2. The detection platform (Figure 1) is based on a highly conductive matrix (fabricated polystyrene/polyaniline-Au nanocomposite) which enables immobilization of representative receptor elements (antibodies/Ab) i.e., specific to the SARS-CoV-2 spike (S)-protein. The concept of a detection system is to translate specific covalent interaction between Ab and its corresponding binding viral S-protein, into a measurable, concentration-dependent electrochemical signal. The biosensor is able to monitor the electrochemical response in PBS, without using hazardous  $[Fe(CN)]_6^{3-/4-}$  redox couple. By creating an electrochemical readout (CV, EIS, and DPV), data enables qualitative and quantitative analysis. Additionally, it exploits outstanding conductivity and biocompatibility, thus resulting in high analytical sensitivity and a low detection limit of 15.6  $\mu$ g/mL, which is within the physiologically relevant concentration range. Hence, the proposed feasible design of the biosensor platform represents an excellent starting point for practical and low-cost testing of asymptomatic patients or people before symptom onset.

**Keywords**: electrochemical biosensors, nanostructured material, SARS-CoV-2.



**Figure 1**: Schematics of SARS-CoV-2 electrochemical biosensor detection platform.

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## **Posters Abstracts**

## Convenient synthesis of electro active copolymers of N-vinylcarbazole via emulsion copolymerization

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#### Abstract:

The demand for electrically active polymers, e.g. for light-emitting diodes, capacitators, and memory devices, has resulted in a renewed interest in carbazole-based materials, such as polyvinylcarbazole.[1] Among various methods reported for polymerization of N-vinylcarbazole (NVCz), a straightforward and environmentalfriendly polymerization method which could diminish the risk of carbazole oxidation during the process remains a challenge.[2] Recently, attention has also been focused on carbazole-based polymers for bioapplications. Through the regular method, it is not possible to prepare biocompatible polyvinylcarbazole derivatives. The demand is to prepare a biocompatible polymerization method which will not alter their electrical properties.[3]

In this contribution, we report a facile technique for copolymerizing carbazole-based monomers via a batch emulsion polymerization. Under mild conditions, carbazole copolymer latices containing butylacrylate as comonomer were synthesized by emulsion copolymerization of N-vinylcarbazole in the presence of varying amounts of butylacrylate. We studied the effects of the comonomer composition on emulsion copolymerization as well as the properties of the copolymer latices. In order to obtain homogeneous spheres, the vinylcarbazole content was regulated from 100 to 50 wt% in the copolymer latex. The copolymers were characterized by FT-IR, NMR and GPC. The morphology of particles was determined by microscopic analysis (e.g., SEM) and by dynamic light scattering.

**Keywords**: Poly(vinylcarbazole), emulsion polymerization, electric active materials, photo-conductive polymers.

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## Immobilization of germanium based photoinitiators for surface-initiated polymerization

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#### Abstract:

Since surface initiated polymerization gained increasing interest in the last decades, the coupling of photoinitiators to surfaces and particles has become an important research topic in polymer photochemistry. To give some examples, immobilized photoinitiators are employed for surface modification, including the adjustment of surface polarity, its optical properties and reactivity as well as the fabrication of nanostructured materials by lithographic patterning. Moreover, photoactively functionalized particles are applied as low-migration photoinitiators, and for the generation of inorganic protective layers on inert polymer films and fibers. An example is the reaction of azidophenyl functionalized silica particles with polyethylene and poly(ethylene terephthalate).

In a recent study, the potential of selected acylgermanium components as photoinitiators was demonstrated. The group-14-based compounds formed germyl radicals upon irradiation with UV light ( $\lambda = 355$  nm), which added to double bonds of acrylic and vinylic monomers. This new class of photoinitiators showed high photoreactivity even at low concentrations as well as considerable photobleaching, which makes them promising for high performance applications. [1]

In the present work, selected Ge-based photoinitiators were immobilized to inorganic surfaces utilizing different routes. Firstly, the direct attachment of triacylhalogermanes (X = Br and I) to oxidized surfaces by reaction of the Ge-halogen unit with superficial hydroxyl groups of the substrate was investigated. In a second approach the Ge-based photoinitiators were modified with functional silanes, introducing trialkoxy groups which act as coupling units in the subsequent immoblization reaction. The photoreactive surfaces were then employed in surface initiated polymerization reactions. Thin layers of polystyrene and acrylic polymers were generated on the modified substrates. Moreover, structured polymer films were prepared, proving the high photoreactivity and efficiency of the immobilized germanium based photoinitiators in spatially resolved grafting-from reactions. The functionalized samples were investigated with regard to surface composition, using UV-Vis and fluorescence spectroscopy as well as XPS spectroscopy and atomic force microscopy.

Future prospects encompass the immobilization of the germanium based photoinitiators onto inorganic particles such as silica nanoparticles in order to prepare high performance low-migration photoinitiators, which are required in the field of UV-curable printing inks for example.

**Keywords**: immobilized photoinitiator; germanium based photoinitiator; surface initiated photopolymerization; grafting from; surface coupled initiator



**Figure 1**: Schematic representation of a surface coupled Ge-based photoinitiator (left) initiating the polymerization of styrene (right)

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#### Acknowledgments

M.H. thanks the FWF (Wien, Austria) for financial support within project number P32606-N.

## Development and characterization of a new cork-based composites produced with plastic wastes

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#### **Abstract:**

The use of the waste materials as filler and as matrix for the composite materials is receiving increasing attention as an approach to increasing the economic value of streams.

In this study, new composite material based on polymer waste (PP or PEHD caps) and cork powder from unused cork (male cork) was developed (figure 1). The composite based on polymer waste and modificated cork powed used as flame retardant was also tested. The interest the use of cork is a high capacity for thermal insulation.

The composite materials were obtained by twinscrew extrusion and by injection molding. The maximum incorporation of cork on the matrix was 20 % in weight. These composites were investigated in term of mechanical, structural and thermal properties. Evaluation of the flammability of the composites was performed using cone colorimeter. Results show, for example, that the peak HRR value for composites based on PP an PEHD with 10 % of cork is 534 kW/m<sup>2</sup> and 686 kW/m<sup>2</sup> respectively. The value of thermal conductivity for composites for composites PP/cork and PEHD/cork is about 0.170 W/mK and 0.230 W/mk respectively.

The feasibility of the composites based on cork and PP or PEHD wastes opening new ways of valorization of male cork and plastic wastes. The thermal insulation and fire resistant properties will be optimized.

**Keywords**: composite materials, polymer and cork wast, polypropylene and high density polyethylene, modificated cork powed, flame retardant, flammability of the composites, thermal insulation.



**Figure 1**: Figure illustrating the raw materials such as cork wast and caps and new cork –based composites for thermal insulation.

# Investigating flammability properties and smoke prodution of new cork-based composites produced with plastic wastes T. Barboni, S. Petlitckaia, P-A. Santoni

SPE CNRS UMR 6134, University of Corsica, Corté, France

#### Abstract:

The use of the waste materials as filler and as a matrix for the composite materials is receiving increasing attention as an approach to increasing the economic value of streams.

In this study, a new composite material based on polymer waste (PP or PEHD caps) and cork powder from unused cork (male cork) was developed and flammability properties of new material were estimated.

The combustion test was performed on a cone calorimeter coupled to an Antaris IGS FTIR Spectrometer (Thermo Fisher Scientific). Each specimen was explised to a 40 kW/m<sup>2</sup> external heat flux. The emission of gas was measured by IRTF spectrometer, COV were analysed by GC/MS and aerosols were measured with to the use of a He-Ne-laser in order to assess the aerosols mass concentration

Many parameters as the heat release rate (HRR), total heat release (THR), specific extinction area (SEA), smoke production rate (SPR), total smoke release (TSR) and carbon monoxide production (COP) were estimated.

The results show that gas measured during the analysis was principally  $H_2O$ ,  $CO_2$ , CO,  $CH_4$  and  $NO_x$  (Fig.1). Aerosols are produced in large quantities by the fuel while VOCs are produced in small quantities but are very toxic. The composites based on PP are more flammable and less combustible that the composites based on HDPE. The data shows that the increasing the cork contant induces an increase of flammability of samples. The combustibility is not affected by the cork contante for the composites based on PP.

However, increase the cork content decrease the combustibility of materals for the HDPE composites.

It seems that the toxicity is lower for the corkbased composites with 0 - 10 % wt. of cork. Howeher the toxicity is more important for 15 and 20 % wt of cork. **Keywords**: composite materials, polymer and cork wast, polypropylene and high density polyethylene, flammability, combustibility, smoke, gas emission, toxicity



**Figure 1**: Figure illustrating the test performed on a cone calorimeter and the results of characterization of gas emission by IRTF.

## Pullout behavior of NiTi crimped SMA fibers made by cold drawing with considering wave length and height

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#### Abstract:

Shape memory alloys (SMAs)are considered as an smart materials in civil engineering. Thus, The SMA is used for various types and several applications. The SMA fiber is rising to be used for smart composite materials of cementitious materials. The SMA fiber can provide crack-closing, prestressing, re-centering capacities in cementitious materials. Thus, in this study, NiTi crimped SMA fibers made by cold drawing are investigated in pullout action with considering wave length and height. For the crimped fiber, wave's length and height are corelated, and, thus, smaller wave length should have smaller wave height, while number of waves in unit length becomes larger. Thus, this study prepares four types of wave lengths and four types of wave heights for each wave length. In the test, monotonic and cyclic pulling out tests are conducted. Monotonic test investigates bond behavior and pullout resistacne, while the cyclic test examines re-centering capacity during unloading phase.

The results show that small wave length with large wave height fiber shows the largest pullout resistance. Moreover, the fuluctuation behavior during pulling out decreases with smaller wave length. Thus, it can be said that smaller wave length and large number of waves is more beneficial in pullout action.

**Keywords**: shape memory alloy, reinforcing fiber, cold drawing, crimping,



Figure 1: Variable of Crimped Fiber.



Figure 2: Pullout Test Set Up.



Figure 3: Pullout Force-Displacement Curve

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## Sol-gel synthesis of transparent and luminescent SiO2@ SrAl2O4 Eu, Dy, B materials

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#### Abstract:

Persistent luminescence is light emission from excited material that can last for several minutes or even hours after the termination of the excitation. SrAl2O4:Eu,Dy is one of the most efficient persistent luminophores that have been discovered up-to-date [1, 2]. The afterglow can be observed for up to 30 hours after removing the excitation. This material is widely used in many applications - emergency signs, luminous paints, luminescent coatings, in vivo imaging [1-2]. The possibility to obtain transparent luminescent glass is widening the range of possible applications even more. In this work we present glass based SiO2@ SrAl2O4 Eu, Dy, B materials that have been synthesised using sol-gel synthesis (Figure 1). This work presents a working method for persistent luminescent glass and deals with the composition control, luminescent and afterglow properties of these materials.

We acknowledge the financial support of ERDF PostDoc project No. 1.1.1.2/VIAA/3/19/440 (University of Latvia Institute of Solid State Physics, Latvia).

**Keywords**: persistent luminescence, glass materials, afterglow



**Figure 1**: Schematic representation of the sample synthesis process

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## Dependence of the Structure and Electronic Properties of Diamond-Like a-C Films with Palladium Nanoparticles on Synthesis Conditions.

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#### Abstract:

It is known that diamond-like carbon (DLC) films are characterized by exceptionally high mechanical and tribological characteristics, as well as chemical inertness. All of the above causes a high interest in the development of technologies for creating wear-resistant and corrosion-resistant protective coatings on various materials on their basis [1]. Recently, special interest has been given to the control of the electronic properties of a-C films by nanoparticles of various chemical nature. Of particular interest are metal nanoparticles that do not form a chemical bond with carbon [2, 3]. Non-carbideforming substances include atoms of the platinum group. This work considers the issue of modifying the structure and properties of a-C films with palladium nanoparticles at different power density of DC ion-plasma discharge

For the deposition of DLC a-C<Pd> films, the method of magnetron ion-plasma co-sputtering of a combined target in an argon gas atmosphere was used. The pressure in the working chamber was 0.7 Pa. Quartz and silicon (100) wafers were used as substrates.

Studies have been carried out to reveal the effect of palladium nanoparticles on the structure and electronic properties depending on the concentration of palladium and the power of the DC discharge. The elemental composition of the samples was studied by the EDS method on a Quanta 200i 3D setup (FEI Company, USA). The surface structure was studied by the methods of electron and atomic force microscopy. Raman spectroscopy revealed the effect of synthesis conditions and palladium concentration on the sp2/sp3 bond hybridization ratios in DLC films. It has been found that with an increase in the Pd concentration in DLC films, the optical band gap decreases. At a palladium concentration of more than 0.5 at.% a-C<Pdx>, the films can be classified as graphite-like with a band gap Eg<1.0 eV. In addition, it was found that an increase in the discharge power leads to an additional decrease in  $E_g$ . From the temperature dependence of the conductivity, the values of the specific conductivity of the DLC a-C<Pdx> films at room temperature ( $\sigma_{\kappa}$ ) were determined. It was found that in films with palladium nanoparticles, a percolation mechanism of conduction is observed. At a concentration of palladium <2 at.%, a significant increase in the value of  $\sigma_{\kappa}$  is observed.

It can be concluded that palladium nanoparticles significantly affect the amount and ratio of diamond-like and graphite-like structure components in a–C films and, as a consequence, their electronic properties.

**Keywords**: diamond-like carbon films, magnetron sputtering, Raman spectroscopy, electronic properties, percolation mechanism of conduction

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## Synthesis and photoluminescence properties of carbon based nanoparticles

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#### Abstract:

Nowadays the research activity on fluorescent carbon nanoparticles (CNDs) is receiving increasing attention because their excitation and emission wavelengths are highly tunable, biocompatible, have high photostability, and do not harm the environment. In this work we mainly deal with the production and qualification of carbon nanoparticles synthesized by hydrothermal process, for which we used chitosan, starch and cellulose as well as carbohydrates as carbon sources.

In our work, a comparison of carbon nanoparticles produced from different carbon sources reveals a strong correlation between particle size and photoluminescence (PL) intensity, which means that a decrease in size increases PL intensity.

Binding of the CNP fluorescent sensor (CNPDot) was investigated on SiO2 (Aerosil® - 200) and Optigel (layered silicate) supports. Due to the electrostatic interactions between oppositely charged surfaces, CNPDot binds well to both the Optigel and SiO2 surfaces. The amount of CNPDot bound to the support increased with increasing sensor-to-carrier ratio. The layered graphite oxide (GO) sensor can be

used as a carrier, but can also be used as a fluorescent label alone, as it exhibits a maximum emission at 585 nm upon excitation at 395 nm.

Carbon nanodots were prepared from the citric acid feedstock in an autoclave (DotA) by a onestep hydrothermal process as well. Their structural and optical properties were examined by fluorescence and UV-Vis spectroscopy, X-ray diffraction and thermoanalytical measurements, and IR spectroscopy. When excited with a 365nm light emitting lamp, DotA is visibly fluorescent and fluorescent units are clearly visible under a fluorescence microscope. The sensor CND binds strongly to the silicate-based support and a stable aqueous colloidal dispersion can be produced.

**Keywords**: carbon nanoparticles, photoluminescence, graphite oxide, graphene, hydrothermal synthesis, sensors, support materials, colloidal dispersions

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## Triboelectric Nanogenerator Based on Ferroelectric Composite for Energy Harvesting

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#### Abstract:

Triboelectric nanogenerators (TENGs) are intriguing mechanical energy-harvesting devices that could power small portable devices and detectors or charge batteries.<sup>1</sup> TENGs can also act as selfpowered sensor elements for mechanical displacement, chemical or acoustic sensors, and biomedical monitors. The working principles of TENG are based on friction-related contact electrification. Most commonly, a TENG consists of two connected conductive electrode layers from which at least one is covered with a polymer insulator. These two surfaces from distinct materials are then contacted and separated, creating opposite sign net charges on the surfaces, which in turn induce charges on underlying conductive electrodes. During separation the electric potential difference is established, and electrons are driven to flow between the two electrodes in order to balance the electric potential difference<sup>2</sup>.

Ferroelectric contacting electrodes for a TENG device were prepared from a PVDF solution in dimethylformamide (DMF) by spin-coating in combination with immersion-precipitation. BaTiO<sub>3</sub> nanoparticles in a wide compositional range (0–35 vol %) were ultrasonically dispersed in PVDF solution and spin-coated on an indium-tin oxide (ITO) substrate. In the next step, the freshly spin-coated films were immersed in antisolvent (methanol), thus triggering the polymer precipitation and formation of porous structures.

In this work highly porous piezoelectric nanocomposites based on BaTiO<sub>3</sub>/PVDF were successfully prepared by immersion-precipitation. It was observed that the piezo-electric response rises with increasing BaTiO<sub>3</sub> loading until 25 vol % content is reached. Sample films were further used in TENG devices as contacting layers on electrodes, and a clear correlation was observed between piezoelectric response and TENG performance. The PVDF/BaTiO<sub>3</sub> nanocomposite with optimal composition shows 47.9 pC  $\hat{N}^{-1}$  as the piezoelectric coefficient, higher than that usually reported for such composites, and in TENG mode a record high 2.7 kV Voc value is achieved (Figure 1). However, our results also indicate that piezoelectric charges cannot be solely responsible for great TENG performance; thus, a "double capacitor model" has been introduced. The mechanism involves interaction between two charged ferroelectric layers during contact-separation, and contacted inversely polarized layers can be considered as capacitors connected in series. Air gap formation during separation rapidly decreases the total capacitance while the potential difference increases. The induced charge redistribution in the external circuit is registered as a current. Predictions of our model also hold true when experimentally obtained charge density  $(6.55 \text{ nC cm}^{-2})$  values are compared with ones obtained from model calculations ( $6.60 \text{ nC cm}^{-2}$ ). As triboelectric research continues to thrive and expand, we anticipate that our work will help the TENG community to further improve the performance of ferroelectric-based triboelectric devices.

**Keywords**: energy harvesting, nanogenerators, triboelectricity, piezoelectricity, ferroelectricity, poly(vinylidene fluoride).



**Figure 1**: Figure illustrating PVDF BaTiO<sub>3</sub>(25% vol) triboelectric performance from 5 cm<sup>2</sup>

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Influence of hybrid carbon lignocellulose filler on reduction toxicity of gaseous thermal decomposition products, including dioxins, PAH and smoke during combustion of NR rubber composites

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#### Abstract:

In recent years, the market demand for polymer composite materials with reduced flammability, smoke emissivity and toxicity of gaseous products of its thermal decomposition has been increasing.

It is widely known that between 65 and 80% of the fatalities in fires are the result of poisoning with toxic gases and smoke. Epidemiological studies carried out in the United States clearly indicate that poisoning only with carbon monoxide, hydrogen cyanide or hydrogen chloride is often the cause of fatal accidents resulting from suffocation, as a consequence of a fire.

During thermal decomposition of most polymers and polymer composites many organic compounds are being released. Most of them absorbing on black carbon particles easily penetrate into living organisms through the respiratory tract. Such compounds include, e.g. polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), as well as polycyclic aromatic hydrocarbons (PAHs).

Dioxins have a hormone-like effect due to their chemical structure, which is similar to the steroid hormones. In addition, the negative effect of dioxins on the human immune system was proven. Delaying immune resistance may lead to an increase in susceptibility to various types of infections, psychomotor disorders in children, thyroid disease, to an increase in cancer risk, decreased fertility in men, ovarian cystic disease or neurodegenerative changes that affect the ability to learn and memorizing. The carcinogenic effects of PAHs, especially benzo(a)pyrene, have been proven and are currently beyond doubt.

In the work, the innovative, hybrid carbon black- lignocellulose filler has been obtained. Laboratory analysis which have been made, clearly indicated that developed hybrid filler decrease fire hazard of natural rubber composites. Fire hazard should be understood not only as flammability but also smoke density and in the consequence amount of PCDD/Fs which can penetrate into living organism. The obtaining studying data indicate that hybrid fillers reduce amount emitted non organic compound such as HCN, HCl, NO, NO<sub>2</sub>, SO<sub>2</sub>, CO and CO<sub>2</sub>, what is very important from the point of toxicometric indexes.

**Keywords**: Natural rubber composites, fire hazards, PCDD/Fs, PAH



Figure 1: Structure of PCDD.

Founding: The work was founded by the National Centre for Research and Development POIR 04.01.04-00-0131/19.

## Synthesis of Graphene oxide/ TiO<sub>2</sub>-based photoreactive nanocomposite thin films

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#### Abstract:

One type of self-cleaning surfaces is the photocatalytic coating which can chemically degrade organic materials when exposed to light [1-3]. During the photocatalytic process the irradiated photocatalyst particles produce highly reactive oxygen species and due to these formed reactive radicals the photocatalyst particles can degrade many organic compounds.

The main goal of our present work was to synthetized graphene-oxid/ $TiO_2$ /polymer thin films with photoreactive and superhydrophobic property.

The photocatalyst particles (like TiO<sub>2</sub>, ZnO) were shown photocatalytic properties under UV and LED-light irradiation and the use of poly(perfluorodecyl acrylate) (PPFDA) fluoropolymer binder material increase the mechanical durability of the photoreactive composites.

The structure and morphology of the synthesised photocatalyst/polymer coatings were examined by SEM- measurements. According to our experiments the structure of the thin films becomes more and more structured and roughened with the increasing of nanoparticles in the nanocomposite content. Mechanical profilometer was used to examine the surface roughness of the nanocomposite layers (Form Talysurf Series 2 from Taylor Hobson Ltd., Leicester, Great Britain).

The hydrophobicity of the composite layers was determined by water contact angle ( $\theta_w$ ). We used an EasyDrop drop shape analysis device (Krüss GmbH, Hamburg, Germany) with a Peltier temperature chamber and a 0.5 mm diameter syringe steel needle. From the obtained angles the total apparent surface free energy ( $\gamma_s^{tot}$ ) of the layers was calculated. Increasing the graphene-oxid/TiO<sub>2</sub> content in the composite layers resulted greater surface roughness and contact angle values.

The photocatalytic activity of the prepared hybrid thin films were verified via ethanol photodegradation tests by gas chromatography (Shimadzu GC-14B) under UV-Vis light illumination at S/G interface. The surface roughness and wetting properties of the layers could be finely adjusted by the graphene-oxid/TiO<sub>2</sub>/fluoropolymer ratio. It was found that the superhydrophobic behaviour (>  $150^{\circ}$ ) and the satisfactory photocatalytic properties of the thin film occurred at 80–90 wt% graphene-oxid/TiO<sub>2</sub> content.

**Keywords**: graphene oxide/ TiO<sub>2</sub>, fluoropolymer, nanocomposite, photoreactive and superhydrophobic property.



**Figure 1**: The photo and SEM micrograph of the photoreactive superhydrophobic, nanocomposite surface.

#### Acknowledgement:

This project was supported by the ÚNKP-22-4 (Á.D.) and ÚNKP-22-5 (L. J.) New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund to Ágota Deák, László Janovák and by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences granted to László Janovák. The authors are grateful for the financial assistance from the National Research, Development and Innovation Office (GINOP-2020-1.1.2-PIACI-KFI-2021-00193 and GINOP-2019-1.1.1-PIACI-KFI-2019-00334).

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### Energy Loss Rate in Graphene at Quantizing Magnetic Fields

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#### Abstract:

We present a theoretical model for the calculation of the energy loss rate F(T) of hot electrons in graphene due to their scattering by acoustic phonons in the presence of a perpendicular magnetic field. Numerical simulations of F(T)are presented as a function of magnetic field for various values of the electron temperature and the Landau level (LL) width. At high magnetic fields the Landau quantization of the electron energy spectrum leads to oscillations of F(T)analogous to Shubnikov-de Haas oscillations in resistivity. We consider electron coupling to both transverse and longitudinal acoustic phonons [1,2,3]. Screening effects are taken into account and it is found that they result to a significant reduction of F(T) at low temperatures. Our model provides a good quantitative interpretation of the experimental data by Baker et al. [4] as it is shown in Figure 1.

Finally, we predict strong magnetophonon oscillations of F(T) due to inter-Landau level transitions. The oscillations exhibit a very similar structure with those reported recently in resistivity in extra-large graphene [1,2]. The magnitude of the peaks increases with temperature and as the width of the LL decreases.

**Keywords**: energy loss rate, electron-phonon coupling, acoustic phonons, Landau levels, magnetophonon oscillations, graphene.



Figure 1: Electron energy loss rate as a function of electron temperature in graphene with carrier density 143 x  $10^{15}$  m<sup>-2</sup> at filling factor  $\nu = 34$ . The filled symbols are the experimental data [4] and the solid line is the theoreti-

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### Functionalisation of CVD graphene for gas sensing

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#### Abstract:

Graphene is well capable to use within gas sensing devices, due to its ultimately large surface-tovolume ratio [1] and thinness [2]. In particular, graphene's atomic thickness means that any adsorbate on the graphene will have the effect of doping of the entire graphene channel thickness [1-6]. In addition, graphene typically presents high carrier mobilities and a low density of states close to its Dirac point [3]. Evaluated in combination, these factors have given rise to graphene as an ideal candidate for gas sensing, even at the modest charge exchange, interaction between the graphene sheet and adsorbates should produce a measurable variation in the graphene's conductivity [7, 8] and shift in the Dirac point of the graphene channel [7-9]. In this work, oxygen moieties are introduced to chemical vapour deposition (CVD) graphene gas sensors to enhance the sensitivity of nitrogen dioxide (NO<sub>2</sub>).

We will present results where even for a relatively low concentration of introduced oxygen groups  $(\sim 5 \times 10^{10} \ cm^{-2})$  the resistance of the oxygen functionalised CVD graphene sensors show a sensor response of up to 600x that of the nonfunctionalised sensor. The response time for oxidised CVD graphene and pristine CVD graphene sensors are 70s and 100s, respectively. We have characterised sensor response using a first order rate equation that shows the adsorption rate increases after the oxidation as the sensitivity of sensors improved.

**Keywords:** chemoresistors gas sensors, graphene field effect transistor gas sensors, CVD graphene gas sensors, functionalized CVD graphene NO<sub>2</sub> gas sensors.

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## DNA analogues-directed immobilization in fabrication of microarrays for immunodiagnostics of viral infections

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#### Abstract:

It will be still essential to develop decent immunodiagnostic tools of viral infections and immunological methods that allow for rapid fabrication and adjustment of receptor layers for the detection of specific biomarkers.

The proper immobilization of the antibody on the surface is a critical aspect of the design of immunosensors and antibody arrays. The difficulty of the challenge is the obligation to consider several factors, such as an appropriate immobilization efficiency and retention of the antibody's biological activity while keeping the process simple and as low in cost as possible. The use of so-called DNA-directed immobilization is an intriguing approach. Proteins labeled with short oligonucleotide sequences (so called conjugates) enable the rapid development of immunosensor platforms based on DNA hybridization reaction. In this approach, the advantages of spontaneous self-assembly of oligonucleotide probes on various surfaces are combined with the simplicity of formation and regeneration of obtained receptor layers.

Layers based on DNA probes or their analogs (PNA – peptide nucleic acid and ZNA- zip nucleic acid) will be developed as part of the work (Fig. 1), allowing for the immobilization of proteins conjugated with nucleic acids. The layers on gold or polymer/silica substrates will be optimized to maximize the sensitivity of biomarkers detection and provide resistance to non-specific adsorption. Surface plasmon resonance and immunoenzymatic methods with optical detection will be used for interaction studies.

**Keywords**: immunodiagnostics, DNA-directed immobilization, biosensor, viral biomarkers, surface plasmon resonance, DNA analogs



**Figure 1**: Figure illustrates a golden chip for SPR measurements covered with DNA/PNA/ZNA oligos. Conjugates of complementary DNA anchor and specific protein (a viral antigen or an antibody) hybridize with the probes forming receptor layer for further detection

Acknowledgement: This work has been financially supported by the National Centre for Research and Development in Poland (grant no. POIR.01.01.01-00-0638/20 - ImGen) and Warsaw University of Technology.

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## Topologies of synthetic gene circuit for optimal fold change activation

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#### Abstract:

Natural regulatory networks encompass feedforward and feedback loops. These are responsible for allowing cells to carry out complex tasks. The computational complexity of synthetic gene circuits has been scaled up by using feedforward and feedback loops in living cells.

Recently, an integral feedback controller and an incoherent feedforward loop were used to achieve robust adaptation in Escherichia coli cells.

Here we use new feedforward and feedback loops to improve the fold change level of target promoters (ON/OFF ratio), we implemented new genetic regulatory networks into prokaryotic and eukaryotic cells, namely ICF, and double negative feedback (DNF) loops. In E. coli, such networks show reduction in the basal level ("leakiness") while keeping the maximum activity high. Specially, we applied ICF loop and mutual inhibition, formed by a DNF loop design, for six different synthetic and native promoters into E. coli. By using our designs, ON/OFF ratio has been improved nine times plus.

Additionally, the model-guided approach shows similar behavior in mammalian ICF and DNF gene networks. Initially, we explored several different DNF gene circuit models with inducible activator-dependent promoter activation. The models all contain an activator-dependent promoter, followed by GOIs (genes of interest). An inherent small hairpin RNA (shRNA) represses GOI signaling. Under an activator-dependent promoter like the GOI, a second gene is expressed - either beneath a duplicate promoter or beneath the same promoter with an internal ribosome entry site (IRES) between them. By repressing the expression of shRNA, this gene effectively mitigates the effect of repression on the GOI. ShRNA reduced the basal expression of the GOI at low

activator levels. However, at high activator levels, a second gene under the activator-dependent promoter is used to reduce the repression, so that expression is maintained at high levels.



**Figure 1**. Antisense transcription is combined with inverting switch to get double negative feedback (DNF) circuit.

The behaviour of the circuit will be controlled by AHL, aTc and an inducer.

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## Application of molecular vapour deposited dielectrics for graphenebased biosensor passivation and improvements in graphene device homogeneity and functionality

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#### Abstract:

Graphene-based sensors can be fabricated using photolithographic processes at wafer-scale. However, these approaches are known to leave polymer residues on the surface. Additionally, graphene may have intrinsic transfer-induced defects. Both defects and resist contamination can affect the homogeneity of graphene-based sensors. leading to inconsistent device performance and unreliable sensing. Selectivity is a critical aspect of graphene-based sensing devices, and the chemical modification of graphene and subsequent electrochemical testing often involves harsh chemicals, which can potentially damage the sensors. Therefore, a reliable, wafer-scale method of device passivation must be devised, which exposes the graphene active area, but protects the more sensitive device materials, such as metal interconnects. Molecular vapour deposition technology is a novel low temperature process which creates dielectric films that can be used graphene-based to passivate biosensing devices. We utilise the MVD<sup>®</sup> growth process and previously reported "healing" effects of dielectric deposition on graphene to reduce photoresist residue and repair graphene defect sites, improving graphene device homogeneity. The effective passivation has been investigated XPS and Raman Spectroscopy, using The passivation allows for respectively. protection of the graphene devices from harsh chemicals and allows for selective real-time sensing applications in liquid mediums. The improvement in device consistency allows for more reliable, homogeneous graphene devices, that can be fabricated at wafer-scale for biosensing applications. The passivated devices have been used to detect biomarkers related to hepatitis.

**Keywords:** graphene, passivation, molecular vapour deposition, biosensors, hepatitis



**Figure 1:** (A) Cross-section of a passivated graphene device sensing with a liquid medium; (B) passivated device inserted into a graphene device connector for selective real-time sensing

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## Photocatalytic Quantum Dot-Armed Bacteriophage for Combating Drug-Resistant Bacterial Infection

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#### Abstract:

Multidrug-resistant (MDR) bacterial assosiated infection is one of the greatest threats to public health, a crisis demanding the novel highly effective antibacterial agents to specifically target MDR bacteria. Herein, a novel photocatalytic quantum dots functionalized bacteriophage (QD@Phage) is synthesized for combating *Pseudomonas aeruginosa* (*P. aeruginosa*) infections, which caused globally millions of deaths every year.<sup>[1]</sup> With the infectivity of the phage itself, the proposed QD@Phage nanosystem can specifically bind to the host *P. aeruginosa*. Also, the system shows an excellent bactericidal efficacy from the synergistic effect of phage and the photocatalytic localized reactive oxygen species (ROS) generated from anchored QD components. Notably, this highly targeted QD@Phage nanosystem achieves robust *in vitro* antibacterial elimination for both planktonic andbiofilm modes of growth. Moreover, the biosafety and *in vivo* antibacterial performance of the system are evaluated in mouse wound infection models. The result confirmed the highly efficient wound disinfection and good biocompatibility of the system. Overall, we anticipate that the novel QD@Phage nanosystem can not only diversify the existing pool of antibacterial agents but also inspire the development of promising therapeutic strategies against MDR bacterial infection.

**Keywords**: bacteriophage therapy, biofilm-associated infection, functional antibacterial nanosystem, photocatalytic therapy, reactive oxygen species (ROS)



Figure 1: Schematic illustration of phage-assisted photocataytic therapy against P.aeruginosa.

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## Synthesis and characterization of smart fluorescent polymers for biomedical applications

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#### Abstract:

In the last 15 years, the smart materials have aroused considerable interest in the field of biomedicine and in particular in drug delivery because they have the ability to respond to external stimuli. The central goal of drug delivery is to maximize therapeutic activity while minimizing side effects. (1) After administration of the drug, it is important to deliver the drug selectively to a target organ or tissue so it is essential to follow the path of the drug in our body by chemically binding a fluorescent probe to the polymeric carrier. (2) For this purpose a promising fluorescent probe is represented by coumarin. It is an oxygen-containing heterocycle belonging to the lactone family. Although this natural compound occurs in various parts of different plants, its highest concentration can be found in fruits, roots, stems, and leaves. Apart from plants, microorganisms are also a natural source of coumarins. The isolated coumarins are mostly biologically active and show antimicrobial, antibacterial, antifungal and antiviral activity. (3) We report the polymerization by ATRP (atomic transfer radical polymerization) using a molar ratio of monomer 7-methacryloyl oxycoumarin) (MAOC) and initiator of 10 to 1, 20 to 1 and 40 to 1. To obtain a copolymer, the homopolymer (PMAOC) was first synthesized by ATRP and then 2-dimethyl amino ethylmethacrylate (DMAEMA) was added. A sequential polymerization was then followed by operating with a molar ratio between the two monomers (MAOC and DMAEMA) of 1 to 10. The block copolymers have a different length of the fluorescent block chain where the fluorescent part (PMAOC) has only the role of tracing the path of the drug, while DMAEMA is the carrier with cytotoxic activity.

**Keywords**: smart materials, drug delivery, polymeric carrier, fluorescent probe, biomedical applications.



**Figure 1**: Figure illustrating the several kinds of carriers for drug delivery. They can be polymeric or inorganic and they can have different architecture (nanoparticles, micelle, nanotubes). After an external stimulus, the carrier releases the drug and being tied to a fluorescent probe, it is possible to follow its path.

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## Exploring the Properties of Anti fouling Nanocoantings for Biosensing

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#### Abstract:

Thanks to their usability and versatility, label-free affinity-based biosensors represent a promising tool for point of care diagnostics. However, their performance is strongly influenced by non-specific interactions occurring on the biochip surface (biofouling), which hinder data analysis and lead to loss of sensing performance. Therefore, the surface of a biochip is often modified with an anti-fouling nanolayer coating, the state of the art of which are currently represented by zwitterionic polymer brush (PB) coatings. The development of these nanocoatings is partially held back by the fact that biofouling from complex biological samples (e.g. blood plasma) is not a fully understood process. There are currently no coatings that completely suppress biofouling; an elucidation of the relevant mechanisms of biomolecular fouling offers a path to create coatings that exceed the current state of the art.

In this work we aim to elucidate the process of biofouling of proteins from human plasma on PB-coated biochips by the means of mass spectrometry (MS), surface-enhanced Raman spectroscopy (SERS), and molecular dynamics simulations (MDS). We investigate a series of copolymer brushes composed of different monomeric ratios of N-(2-hydroxypropyl) methacrylamide (HPMAA) and carboxybetaine methacrylamide (CBMAA). MS allows us to qualitatively and quantitatively characterize the proteins fouled from both real-world fluids (blood plasma) as well as model samples. Through comparison of SERS data obtained different surfaces we estimate the permeability of PB for different molecules, and the combination with MDS brings a novel approach in study of the interaction of biomolecules on PB surfaces.

Our results will help in the future design of nanocoatings for biochips used for a variety of applications.

**Keywords**: polymer brush, anti-fouling, fouling, nanocoating, biosensing, biosensor, mass spectrometry, SERS, molecular dynamics

#### Acknowledgement

This work was supported by the Charles University Grant Agency (grant no. 288822) and the Czech Science foundation (contract no. P205/21/19779S)

## Characteristic of ceramic-polymer materials enhanced with collagen for biomedical applications

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#### Abstract:

In recent years, the increase in human life expectancy resulting from the significant growth of medical sciences has been observed. This phenomenon is considered an undoubted success, however, it constitutes also a challenge in the treatment of diseases developing with age, including skeletal diseases. The main purpose of the study was to develop ceramic-polymer materials for bone tissue regeneration. The composite materials based on polyvinylpyrrolidone (PVP) and poly(vinyl alcohol) (PVA) have been prepared via the UV-induced polymerization. As a ceramic phase, a synthetic hydroxyapatite synthesized via the wet precipitation method has been selected while as a natural protein collagen of bovine or fish origin (30 wt.%) has been used. Obtained materials have been characterized by means of FT-IR (Fourier transform infrared) spectroscopy. Next, incubation studies in simulated physiological liquids have been performed. Importantly, sorption properties of the composites have been investigated as well as their roughness profiles via the contact profilometer, and their wetting angles (thus their wettability). Additionally, tribological studies aimed at verifying the friction coefficient of the composites and the mechanical analyses aimed at determining their tensile strength and maximum percentage elongation have also been conducted. In Fig. 1. example images of the composites are presented.



Figure 1: Ceramic-polymer composites containing collagen of bovine origin.

Keywords: ceramic-polymer composites, hydroxyapatite, bovine collagen, fish collagen, skeletal diseases, bone tissue regeneration, photopolymerization, biomedical applications. Based on performed investigations the preparation of the composites containing both the ceramic and polymer phase as well as collagen (the absorption bands characteristic for this protein on obtained FT-IR spectra) have been demonstrated. All tested composite materials showed sorption properties while the greatest ones have been reported for samples analyzed in distilled water. Next, during the 14-day incubation any rapid pH changes which could testify to the samples' degradation have not been observed. Considering such advantages as quick and simple synthesis methodology, the possibility of the preparation of the composites with various shapes and sizes and properties desirable in terms of their application for bone tissue regeneration it is considered that developed materials showed a great application potential and need to be subjected to next, more advanced investigations.

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#### Acknowledgement:

The "Multifunctional biologically active composites for applications in regenerative bone system medicine" project is carried out within the TEAM-NET program of the Foundation for Polish Science financed by the European Union under the European Regional Development Fund. POIR.04.04.00-00-16D7/18
## Hydroxapatite-reinforced coatingsas as drug carriers for controlled release of clindamycin

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Abstract:

A major challenge of tissue engineering and materials science is the development of bioactive, multifunctional biomaterials. The coating technique involves covering a certain implant (e.g., metallic or polymeric) with an additional layer of material. In this way, it is possible to provide additional properties without changing the base material. One of them is the use of such a coating as a controlled drug delivery system (DDS). DDS can provide transport of active compounds directly to the target site and minimize undesirable side effects of conventional drug intake. It is also one strategy for prolonging their distribution and enhancing therapeutic efficacy by maintaining an optimal concentration of the active ingredient at the local target site throughout the treatment period.

In our study, we focused on the preparation and characterization of coating materials based on two synthetic, bio-safe polymers (polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG)), collagen (COL), and hydroxyapatite (HAp). Materials were enriched with clindamycin and applied to 3D printed polylactide plates. The materials were obtained by UV light crosslinking.

In the present study, we focused on the relationship between material composition and the amount of drug released. Incubation studies were conducted, including the sorption capacity of the coatings. Clindamycin release studies from the materials were carried out by HPLC chromatography. The amount of released drug depended on the sorption capacity of the composites.

### Acknowledgement:

The "Multifunctional biologically active composites for applications in regenerative bone system medicine" project is carried out within the TEAM-NET program of the Foundation for Polish Science financed by the European Union under the European Regional Development Fund. POIR.04.04.00-00-16D7/18.

**Keywords**: drug delivery systems, clindamycin, composites coatings, hydroxyapatite, polymers,, collagen, biomedical applications.



**Figure 1**: The obtained clindamycin-modified coatings: A - PVP/PEG; B - PVP/PEG/COL; C and D PVP/PEG/COL with increasing HAp content.

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## Chitosan grafted poly (ethylene glycol) methyl ether acrylate based micro/nanocarriers for biomedical applications

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### Abstract:

Nanotechnology is already used in different biomedical applications through the use of liposomes, nanoparticles, and nanotubes, which are currently interesting and promising alternatives. Chitosan (CS) is a natural polysaccharide that has been thoroughly investigated, but its water solubility poses problems and difficulties when working in higher pH media, therefore, limiting chitosan processability. The current study highlights the obtaining of micro/nanoparticles (NPs) based on CS chemically grafted with synthetic poly (ethylene glycol) methyl ether acrylate (PEGA) via Michael's addition, a mild reaction [1]. The preparation of modified chitosan-based nanocarriers has been performed by a double crosslinking, ionic and covalent, in water/oil emulsion [2]. The studied reaction parameters are CS-PEGA concentration, stirring speed, and quantity of ionic crosslinker (Na<sub>2</sub>SO<sub>4</sub>). The NPs were structurally and morphologically (figure 1) characterized through infrared spectroscopy, scanning electron microscopy, light scattering granulometry, and zeta potential, showing that modified CS allows better control of dimensional properties and morphology as compared with neat CS. NPs swelling properties were studied in acidic and neutral pH media, and the results showed a similar pH-dependent behavior as crude CS, after grafting and double crosslinking.

All particles with optimal characteristics (in terms of morphology, water swelling degree, etc.) have been analyzed and tested from the point of view of their capacity of inclusion/release of levofloxacin (LEV) and ciprofloxacin (CP), showing an excellent capacity. Moreover, the particles were found to be cytocompatible and hemocompatible, recommending them for use as a controlled release system for biomedical applications.

**Keywords**: Chitosan, poly (ethylene glycol) methyl ether acrylate, micro/nanocarriers, double crosslink-ing; levofloxacin; ciprofloxacin, biomedical applications



**Figure 1**: Micrographs SEM of NPs (sample P4) (magnification graphical bar length:10 μm)

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Acknowledgments: This work was supported by a grant from the Ministry of Research, Innovation and Digitization, CNCS—UEFISCDI, project number PN-III-P4-PCE-2021-1365, within PNCDI III, (contract number PCE 115/2022)

# Nanoparticles based on chitosan grafted with PEG derivative as carriers for antibiotics

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### Abstract:

The nanotechnology field is dedicated to designing materials with nanometric dimensions by using different devices, structures, and systems that are inspired constantly by nature. Chitosan (CS) crosslinking has been thoroughly investigated, but the chemical reactions leading to submicronic hydrogel formulations pose problems due to various physical/chemical interactions that limit chitosan processability. The current study employs the chemical modification of chitosan by Michael's addition of poly (ethylene glycol) methyl ether acrylate (PEGA) to the amine groups [1] to further prepare chitosan particulate hydrogels (CPH). Thus, modified CS is subjected to a double crosslinking, ionic and covalent, in water/oil emulsion [2]. The studied process parameters are polymer concentration, stirring speed, and quantity of ionic crosslinker (Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>).

The CPH were structurally and morphologically (figure 1) characterized through infrared spectroscopy, scanning electron microscopy, light scattering granulometry, and zeta potential, showing that modified CS allows better control of dimensional properties and morphology as compared with neat CS. Swelling properties were studied in acidic and neutral pH conditions, showing that pH-dependent behavior was maintained after grafting and double crosslinking.

The applicability of the prepared materials was further tested for drug loading and in vitro delivery of levofloxacin (LEV), showing excellent capacity. CPH were found to be cyto- and hemocompatible demonstrating their potential for effective use as a controlled release system for different biomedical applications.

**Keywords**: Chitosan particulate hydrogels; poly (ethylene glycol) methyl ether acrylate; double

crosslink-ing; levofloxacin; biomedical applications



Figure 1: Micrographs SEM of CPH (sample A9, Amagnification graphical bar length: $10 \mu m$ )

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### Acknowledgments

This work was supported by a grant from the Ministry of Research, Innovation and Digitization, CNCS—UEFISCDI, project number PN-III-P4-PCE-2021-1365, within PNCDI III, (contract number PCE 115/2022).

## Nanofabrication of tuneable plasmonic noble metal nanoparticles and their subsequent formation onto cultivation plates used in photothermal therapy

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### Abstract:

Two noble metal nanoparticles (silver and gold) were chosen for their strong plasmonic properties and the ability to tune their localized surface plasmon. Both nanoparticles were nanofabricated by bottom-up approach via wet reduction method, where the final size, shape, therefore optical properties were tuned within the synthesis. Part of the research is focused on the deposition of the nanoparticles on plastic and glass surfaces (cultivation plates, medical devices), where 2D films are electrostatically deposited by layer-bylayer assembly and can be used in many biomedical applications. Optical properties and the plasmon of the nanoparticles can be easily tuned within the synthesis for instance by changing the ratio between the reducing and stabilizing agent or via adjusting the concentration of reducing agent. The proposed application of those materials in this research is related to the tuneable photothermal properties, which are associated with the position of the localized surface plasmone. If it is in resonance with the frequency of the used laser, absorption properties are enhanced, and the energy can be easily converted to the heat. This phenomenon can be used in light-assisted therapeutic methods as photothermal and photodynamic therapy, which transform the energy of light to heat and cause hyperthermia and damage to the cells, which can be used in antibacterial and anticancer therapy and in the treatment of other diseases.

This work was supported by the students grant DSGC-2021-0120 "Light-assisted in vitro therapy using plasmonic materials" funded under the OPIE project "Improvement of Doctoral Student Grant Competition Schemes and their Pilot Implementation",

reg. no. CZ.02.2.69/0.0/0.0/19 073/0016713.

**Keywords**: photothermal therapy, plasmonics, silver and gold, nanoparticles, synthesis, deposition, hyperthermia.



**Figure 1**: Water dispersion of silver nanoparticles of various sizes and shapes changing their optical and plasmonic properties.

- Z. Mala et al. The application of antimicrobial photodynamic inactivation on methicillin-resistant S. aureus and ESBL-producing K. pneumoniae using porphyrin photosensitizer in combination with silver nanoparticles. Photodiagnosis and Photodynamic Therapy 2021;33.
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## Laser-induced In vitro photothermal therapy using noble metal nanolayers

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### Abstract:

Photothermal therapy (PTT) is a promising method in cancer treatment utilizing a light-toheat conversion. The phenomenon photothermal effect is based on the surface plasmon resonance of noble metal nanoparticles and their ability to strongly absorb light in UV/VIS and/or NIR spectral regions. Irradiation of such particles with a suitable wavelength leads to the absorption of electromagnetic radiation which results in the local production of heat and causes irreversible damage to cancer cells.<sup>1</sup>

For this purpose, silver and gold nanoparticles with tunable optical properties were synthesized and deposited on a 96-well plate using the layerby-layer technique to evaluate the antitumor efficacy of in vitro photothermal therapy. As a model cancer cell line, the human cervical carcinoma cells (HeLa) were utilized for in vitro experiments. Colloidal particles were characterized by UV-VIS absorption spectroscopy and transmission electron microscopy. To induce the photothermal effect, lasers with two different wavelengths (660 and 730 nm) both corresponding to the plasmon band of the metal were used. Temperature increase after irradiation of the silver and gold-coated cultivation plates was evaluated by a thermographic camera. An important part of the study was the determination of the influence of irradiation on the HeLa cells cultivated on normal plates (without noble metal nanolayer). Biophysical methods such as spectroscopic determination of cell viability were used to determine the photothermal efficacy. A significant decrease in cell viability was observed in HeLa cells cultivated on both Ag and Au-coated plates subjected to irradiation of various irradiation energy doses (exposure time), while the maximal photothermal effect was induced on Au-coated plates using 660 nm laser (100 mW) where the irradiation energy was 10 J and cell viability decreased under 35%. However, the viability of the cells cultivated on normal plates and subjected to the same energy doses remained unchanged.

Based on the results we can conclude, that this relatively non-invasive and novel technique based on the physicochemical properties of plasmonic noble metal nanoparticles is offered as an effective and promising tool in the fight against cancer diseases.

**Keywords**: photothermal therapy, noble metal nanolayers, In vitro methods, Hela cells



**Figure 1**: Scheme of layer-by-layer deposition of noble metal nanoparticles on the surface of the polystyrene cultivation plates and subsequent In vitro photothermal therapy in CO<sub>2</sub> incubator

### **References:**

1 M. Mistrik., Z. Skrott, P. Muller, et al. Microthermal-induced subcellular-targeted protein damage in cells on plasmonic nanosilver-modified surfaces evokes a two-phase HSP-p97/VCP response, Nat. Commun. 12 (2021)

## Thymol Self-emulsifying Polysaccharide-based Microbeads Crosslinked by Polyvalent Ions: Synthesis, Structure and Dynamics

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### Abstract:

Polysaccharides are natural biopolymers with unique properties which make them attractive as excipients for a wide spectrum of pharmaceutical dosage forms. One of the most promising area of the pharmaceutical research are particulate drugdelivery systems.

Gastrointestinal (GI) diseases and digestive disorders are widespread. Usually, the gold standard therapies are antibiotics and corticosteroids. Unfortunately, the use of these compounds is usually associated with many side effects and possible resistance or tolerance.

An interest in finding new alternatives for "gold standard" therapies of gastrointestinal diseases is thus growing. Due to the broad scale of biological activities, thymol, the phenolic terpene derived from Lamiaceae sp., is a promising candidate for topical treatment of intestinal mucosa. Its limitations such as volatility, lipophilic character, and partial absorption in the stomach, could be overcome by its incorporation into the solid selfemulsifying gastro microbeads.

Specifically, thymol as a part of the self-emulsifying system (SES) consisting of triglycerides, Labrasol® and propylene glycol was incorporated into the polysaccharides microbeads. The synthesized microbeads were continuously tested for qualitative properties, molecular structure and dynamics, thymol *in vitro* release and *ex-vivo* tissue penetration as demonstrated in Scheme 1.

The presented contribution thus brings a comprehensive insight into the synthesis and atomic-resolution structure and dynamics of alginate-pectin gels crosslinked by polyvalent ions ( $Ca^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$  and their mutual combination) in microbeads formulations. By applying a range of advanced techniques of solid-state NMR spectroscopy we verified distribution of crosslinking ions in alginate – pectins gels and a high extend of ion exchange. We also found out a multi-component character of polysaccharides gels caused by the concentration fluctuations of residual water molecules, which are preferentially localized along the polymer chains containing high amounts of manuronic residues (for alginates). The resulting co-existence of different types of polysaccharides chains differing in segmental dynamics was revealed by the analysis of <sup>1</sup>H-<sup>13</sup>C dipolar profiles. The <sup>13</sup>C CP/MAS NMR spectra then displayed a strong dependence of the microstructure of polysaccharides polymers on the type of crosslinking ions. The <sup>13</sup>C MAS NMR spectra confirmed the presence of dissolved of thymol in prepared systems. The demonstrated experimental strategy thus allowed us to gain a new perspective on the structure and dynamics of crosslinked polysaccharides gels for which the high-quality diffraction data at atomic level-resolution are inherently unavailable.



**Scheme 1**: The proposed rational design of polysaccharide-based particulate systems.

**Keywords**: polysaccharides, alginates, pectin, solid-state NMR, structure, thymol

### Acknowledgments:

This work was supported by Czech Science Foundation (Grant No. GA 22-03187S).

## How to Describe Microbead Formulations of Active Pharamceutical Ingredients with Micro- and Nanodomain Architecture at Atomic Resolution Level

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### Abstract:

An increasing number of compounds with desirable biological activity may never reveal their true potential due to their unfavorable physicochemical properties. In the field of nanomedicine, recent efforts to optimize the therapeutic efficacy of these substances have led to the development of a range original supramolecular systems. Progress in the development of these materials requires their accurate structural analysis, but this is a stringent requirement because these systems exist at the borderline between crystalline and amorphous solids for which the highquality diffraction data are unavailable.

This paper brings an efficient approach for gaining insight into the structure of complex particlebased drug delivery systems with micro- and nanodomain architectures. This strategy is based on the combination of domain-selective solidstate NMR spectroscopy (ss-NMR), crystal structure prediction (CSP), and density functional theory (DFT)-based calculations.

The potential of this analytical approach is demonstrated on the recently developed biodegradable, injectable polyanhydride microbead formulation of decitabine (DAC), an archetypal DNA methyltransferase inhibitor used as an efficient therapeutic for epigenetic cancer therapy.

It has been found out, that in this innovative drug-delivery formulation a mixture of microcrystalline domains of decitabine and nanodomains of sebacic acid (SA) is embedded in the semicrystalline matrix of poly(sebacic acid) carrier. Despite this complicated architecture, however, the atomic-resolution structure of each component, was unambiguously determined (Figure 1). Based on the same principle, denuovo determination of the crystal structure of chemotactic N-formyl-L-Met-L-Leu-L-Phe-OH tripeptide is also presented.

This paper thus demonstrates the synergistic effect of the combination of experimental and computational approaches, which significantly extends the NMR crystallography approach into the area of structure determination of complex nanostructured particle-based systems for drug delivery.

**Keywords**: microbead formulations, drug-delivery systems, polymer-based biomaterials, solidstate NMR spectroscopy, NMR crystallography.



Figure 1: Figure illustrating the structure of microbead formulations of decitabine with microand nanodomain architecture at atomic resolution level.

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### Acknowledgments:

This work was supported by Czech Science Foundation (Grant No. GA 22-03187S and GA 20-01233S).

## Gastro-Resistant Self-Emulsifying Pellets as Stable Delivery Systems for Volatile Monoterpene Plant Drug

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### Abstract:

To avoid standard therapies for gastrointestinal inflammatory diseases, an interest in finding new alternatives is rising. Plant monoterpene substances, such as thymol, carvacrol, eugenol, etc., exhibit many valuable biological activities in treating intestinal inflammation. The basic problem is that monoterpenes are volatile hydrophobic substances with poor oral bioavailability. Thymol is only partially absorbed mainly from the stomach, resulting in a 16% bioavailability. It is cumulated in a higher amount of intestinal mucosa (1). Thymol could be incorporated into solid self-emulsifying pellets with gastro-resistant properties to overcome drawbacks and support intestinal wall cumulation. During pellets formulation by extrusion/spheronisation, liquid and solid phases are in a temporary or permanent contact. It opens the scope for interactions, instabilities, and components transfer within the dosage form. Therefore, a deep investigation of such a system by solid-state nuclear magnetic resonance spectroscopy (ss-NMR) is also necessary.

As a part of the self-emulsifying system (SES) consisting of triglycerides, Labrasol<sup>®</sup>, and propylene glycol, thymol was adsorbed into Neusiline<sup>®</sup>US2, blended with chitosan and microcrystalline cellulose, and formulated to pellets. Consequently, final pellets were coated (Eudragit<sup>®</sup> L30 D55) in a Wurster-type fluid bed. Pellets were tested for physicochemical properties, structure, *thymol in vitro* release, and *ex-vivo* tissue penetration.

Innovative gastro-resistant self-emulsifying pellets showed excellent mechanical characteristics (low friability, porosity) and stable thymol incorporation into Neusilin<sup>®</sup>'s structure, proved by solid-state NMR. *In-vitro* dissolution behaviour showed the potential to avoid unwanted stomach systemic absorption (pH 1.2 - 9.2% after 3 hours, followed by *burst effect* and prolonged thymol release for the next six hours at pH 6.8). Moreover, the preparation process of extrusion/spheronisation was optimized, and processing time was reduced to a minimum. *Ex-vivo* tissue penetration was confirmed on the rabbit animal model intestinal wall (Figure 1). The first results also suggest the long-term stability of the developed system.

**Keywords**: Self-Emulsifying System, Pellets, Thymol, Gastro-resistant, ss-NMR



**Figure 1**: A cross-section of thymol gastro-resistant self-emulsifying pellet and *ex-vivo* thymol penetration into the intestine rabbit wall

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### Acknowledgments

This work was supported by Czech Science Foundation (Grant No. GA 22-03187S) and by Masaryk University (Grant no. MUNI/A/1251/2021)

## Self-emulsifying System Incorporated in a Polymeric Carrier for Controlled Delivery of Thymol

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### Abstract:

The biocompatibility and biodegradability of natural polymers make them an object of interest for many applications in biomedicine and pharmacy. Their ability to control drug release makes them very significant pharmaceutical excipients for formulating dosage forms, especially particulate dosage forms. These advantages, together with encapsulation of natural active agents and the use of some soft method for their preparation, an "eco-friendly" drug dosage form could provide. Many natural active ingredients today are experiencing a comeback. However, most of them have low solubility, leading to low bioavailability and ultimately low therapeutic efficacy. Therefore, a way of their modification and incorporation into the dosage form plays a crucial role in their therapeutic effectiveness.

There are many methods to increase the bioavailability of poorly soluble drugs after oral administration. The formation of a self-emulsifying system (SES) ensures the dissolving of lipophilic active substance and, after its reconstitution, the shape of o/w emulsion, which is necessary for drug absorption either in the systemic circulation or inflamed mucosa. This systemic or local effect depends on the drop size of the internal phase of the emulsion, whether the nanoemulsion, microemulsion, or macroemulsion is created (1).

Thus, this paper discusses a dosage form of pectin/alginate particles as a carrier of SES with dissolved monoterpene thymol. It is a drug with a wide range of biological effects (antimicrobial, antiviral, antifungal, anti-inflammatory, antioxidant, antineoplastic, etc.) with potential usage in nonspecific intestinal inflammations (NSZ). Nowadays, the treatment of NSZ includes mostly corticosteroids and antibiotics administration, so that this new approach could become an alternative to this treatment. Thymol's incorporation into the SES containing triacylglycerols, Labrasol<sup>®</sup>, and propylene glycol in ratio 2:7:1 and their subsequent solidification in pectin/alginate particles lead to the final solid drug form formation. The evaluation of the morphological parameters

using optical and electron microscopes, evaluation of swelling capacity and dissolution profiles, and finally, the assessment of the formed emulsion after SES reconstitution in a phosphate buffer pH 6 are integral parts of this experiment.

**Keywords**: pectin, alginate, hydrogel particles, self-emulsifying system, thymol, controlled release of drug, nonspecific intestinal inflammations



**Figure 1**: Figure showing the polymeric carrier of the self-emulsifying system containing thymol, providing prolonged thymol release and o/w emulsion formation after SES reconstitution in a pH 6 environment

### **References:**

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### Acknowledgments

This work was supported by Czech Science Foundation (Grant No. GA 22-03187S)

### Composition and Functionality Relashionship in Dexamethasone loaded Avidin Nucleic Acic NanoAssemblies

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#### Abstract:

The natural high affinity of egg white avidin for the nucleic acids is exploited to obtain highly defined buffer stable poly-avidin nanoassemblies (Avidin-Nucleic-Acid-NanoASemblies-

ANANAS). These soft biocompatible nanoparticles can be considered as avidin analogues with improved performance with a number of applications in biomedicine, among which drug delivery<sup>1,2</sup>. Each nanoparticle possesses a large number of biotin binding sites (BBS) which are available for docking about 1000 functional elements (drugs, fluorophores and/or targeting elements), provided these are linked to a biotin moiety. The high affinity of biotin for avidin (Kd~10<sup>-15</sup>M) permits to exploit the available BBS to obtain functional NPs with stoichiometric control of composition by simply mixing core NPs with the desired biotinylated moieties. Functional NPs are thus obtained in "one pot" solution and, as long as the number of available BBS or the available NP surface (about 6000  $\text{nm}^2$ ) are not exceeded, they can be used without the need of purification. Therefore, the ANANAS platform is a convenient tool in nanomedicine to identify relationships between NP surface compostion and functionality, which potentially may be of value also for other NP geometries.

When injected parenterally, ANANAS show strong tropism for the liver. In recent years, we investigated the use of ANANAS functionalized with the antiflmammatory drug dexamethasone (dex) as candidates for treating liver inflamatory diseases.<sup>3,4</sup> Along the years, a number of biotindex conjugates have been developed for ANANAS drug loading and used for generating a number of ANANAS-dex assemblies (Figure 1). Through a combinantion of in vitro and in vivo experiments, we showed that both the chemistry used for acid reversible dex tethering, the length and nature of the linker between the drug and the biotin moiety and the mode of NP surface decoration affect the NP colloidal stability, the kinetics of drug release and the biodistribution pattern in animal models.



**Figure 1:** ANANAS-dex formulation design and a selection of the assemblies investigated.

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## Encapsulation of SerpinB3 Protein in wet Sol-Gel silica /HPMC compostite allows its sustained release in a bioactive form

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### Abstract:

Topical administration of protein drugs is challenging due to their instrinsic instability. Physical entrapment in wet sol-gel silica polymer network can stabilize proteins' conformation and permit their sustained delivery[1]. However, irreversible syneresis and poor viscoelastic properties hamper wet-sol-gel silica application as a semisolid vehicle.

The SB3 protein SB3 was identified as a positive biomarker of successful diabetic wound healing, therefore, its exogenous administration may promote healing[2].

In this work, a sol-gel silica/hydroxypropylmethylcellulose (HPMC) hydrogel blend (Figure 1) was investigated to overcome the limits of wet sol-gel silica, and applied for the development of a formulation for topical administration of SB3.



Figure 1: SB3-SiO<sub>2</sub>/HPMC formulation concept.

We showed that SB3 entrapped into 8% (w/v) SiO<sub>2</sub> wet-sol-gel silica preserves its structure, is stabilized against denaturation and protease attack, and it is slowly released for at least one day(Figure 2).

Silica gel blending with a HPMC-glycerol hydrogel permits spreadability without affecting the protein release kinetics.

This formulation was capable to promote wound healing in a SB3 Knock out mice, which suffer from impared wound healing.

**Keywords**: Sol-gel Silica; Protein stability; SerpinB3; Diabetic ulcer; Chronic Ulcer; wound healing.



**Figure 2**: A) SB3 thermal stabilization upon Solgel silica entrapment; B) SB3 stabilization against proteolysis upon silica embedment; C) Sustained release of functionally active SB3 from sol-gel silica; D) in vivo efficacy of SB3-SiO<sub>2</sub>/HPMC blend in SB3-Knock Out mice.

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## Exploring Nanoformulations for Therapeutic Induction of Necroptosis

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### Abstract:

Nanomaterials have gained high interest in their use as potent anticancer agents. Apart from delivering chemotherapeutic agents in order to reduce off-target effects, molecular agents have also been widely explored. The advances in our understanding of cell biology and cell death mechanisms<sup>1</sup> has generated a broad library of potential therapeutic targets by siRNA, mRNA or pDNA complexes. In the present study, we explore the ability of pDNA-polyplexes to induce tumor-specific necroptosis. This results in a cascade of effects, where immunogenic cell death potentiates anti-tumor immune responses, and results in an influx of dendritic cells and cytotoxic T cells, rendering the tumor more amenable to immune checkpoint inhibition. This study aims to explore whether the induction of necroptosis in a subpopulation of tumor cells can be used to potentiate immune checkpoint inhibition studies

**Keywords**: protein folding, nanoporous sol-gel glasses, silica-based biomaterials, circular dichroism spectroscopy, surface hydration, crowding effects, micropatterning, biomedical applications.



**Figure 1**: Figure illustrating the mechanism that our nanopartle complexes tragers necroptosis inside cell.

### **References:**

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### Core-Multishell Nanocarrier Systems for Drug Delivery

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### Abstract:

Various skin deseases can be treated through drug delivery ranging from conventional dermatological therapy of inflammatory skin diseases, such as atopic dermatitis or psoriasis, and skin tumour therapy, such as topical chemotherapy and photodynamic therapy, to transcutaneous drug delivery and vaccination. Despite the uprise in novel systems, only few innovative molecules made it into new topical formulations due to poor skin uptake.

Dermal drug delivery can host problems due to various reasons such as a drug's lipophilicity or size affecting its permeability through the skin barrier. Skin is characterised by different redox environments changing over the different skin layers. Those redox environments also vary in healthy and inflamed skin, thus offering the usage of redox dependent drug delivery.

Polymeric drug delivery systems aim at overcoming the solubility issue by entrapping the drug in a solubility-enhancing polymeric environment. Among the vast diversity of polymeric drug delivery systems, dendritic nanocarriers are considered as universal systems, as their defined core-shell architecture offers many benefits.

The skin harbours mainly glutathione (GSH) / glutathione disulphide (GSSG) buffers maintaining the redox systems. Oxidative environments host among increased GSSG levels also reactive oxygen species (ROS). Carrier systems can utilise those redox environments by incorporating reduction as well as oxidation sensitive components. Hydrophobicity changes of thioether moieties upon oxidation can thereby lead to a controlled drug release in the skin while reduction of sulphide bonds can lead to its cleavage and subsequently drug release.

An *ex vivo* skin-based inflammatory model enabled to study both drug dermal delivery and antiinflammatory efficacy. Rapamycin formulated in CMS nanocarriers thereby efficiently reduced the expression of inflammatory cytokines IL-2 in Jurkat T cells. Additionally, various smart polymers were tested regarding the anti-inflammatory response of their respective drug formulations.

Keywords: drug delivery, nanocarriers, coremultishell systems, redox-responsiveness, inflammation, dermal drug uptake, rapamycin, biomedical applications.



**Figure 1**: Figure illustrating the structure of core-multishell nanocarrier systems with a hydrophilic core and outer shell while the hydrophobic inner shell contains the drug that can be released upon redox-stimulation.

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## Screening DNA condensation properties of multifunctional PAMAM dendrimers with different amine contents for targeted co-delivery of SAHA, 5-FU and TRAIL plasmid

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### Abstract:

The aim of this study is to synthesize four types of dendrimer and their conjugates with increasing number of amine groups via different acetylation levels to screen their ability to compact DNA. A multifunctional PAMAM dendrimer, containing folate (FA) as the targeting molecule, 5-Fluorouracil (5-FU) as the chemotherapeutic drug, Suberoylanilide hydroxamic acid (SAHA) as an epigenetic factor and an expression plasmid for TNF-related apoptosis-inducing ligand (TRAIL) has been designed and synthesized for the targeted and synergistic therapy of colorectal cancer (CRC). The primary amino groups on the surface of the generation 4 and 5 poly(amidoamine) (PAMAM) dendrimer (G4 and G5 dendrimer) were partially acetylated to reduce the toxicity of dendrimer<sup>1</sup>. FA and SAHA were conjugated to the remaining primary amino groups on the dendrimer through amide and ester linkage and 5-FU loaded to internal cavities of dendrimer. TRAIL plasmid is expected to interact with remaining cationic amine groups of dendrimer conjugates<sup>2</sup>. Fourth and fifth generation PAMAM dendrimers were purified via liquid phase retention technique (LPR)<sup>3</sup>. Characterization of the PAMAM dendrimers has been determined by multiple analytical methods such as Attenuated Total Reflectance Spectroscopy (ATR), Nuclear Magnetic Resonance Spectroscopy (NMR), and Ultra-Violet spectroscopy (UV). DNA condensation properties of dendrimer conjugates were performed via fluorescence spectroscopy and agarose gel electrophoresis techniques, which was later correlated with particle size and zeta potential measurements. Finally multifunctional dendrimer conjugates have been tested in vitro for their transfection ability depending on amine contents and cytoxicity on HCT116 cells.

**Keywords**: Dendrimer, drug delivery, gene delivery, DNA condensation, targeted delivery, colon cancer thrapy.



**Figure 1**: Schematic illustration of DNA condensation by PAMAM dendrimer conjugate

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## Positively Charged Mesoporous Silica Nanoparticle as a Medicinal Carrier for Crossing the Blood Brain Barrier in Chicken Embryo

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### Abstract:

We previously demonstrated that the bridging size and charge effects of mesoporous silica nanoparticles (MSN) for crossing the blood-brain barrier (BBB) may be due to protein corona influence with negatively charged THPMP in larval zebrafish. Herein, we further investigated the MSN as a carrier for crossing the BBB, in regard to a therapeutic purpose for brain diseases. We synthesized two kinds of positively charged MSN in two different zeta potentials, namely MSN-PEG/TMAC (2:1): 9.10±1.08 mV and MSN-PEG/TMAC (1:2): 18.10±1.10 mV; both were 40 nm in diameter by DLS and with uniform, mesoporous structures by TEM. The chicken chorioallantoic membrane (CAM) was employed as an alternative model for BBB penetration evaluation. Administration of RITC conjugated MSN-PEG/TMAC demonstrated the ability of BBB penetration, showing distribution outside of the cerebral blood vessels of brain after intravenous injection on the 15th day after chicken embryo was fertilized using the IVIS Imaging System. The silicon content of brain treated with RMSN-PEG/TMAC (1:2) was higher than that of RMSN-PEG/TMAC (2:1) quantified by ICP-MS analysis. Furthermore, doxorubicin (Dox) loaded MSN-PEG/TMAC could promote the delivery of Dox across the BBB, followed by the release of the Dox. We validated the therapeutic potential of MSN with positively charged TMAC, which enables the drug loading and BBB penetration in the brain (Figure 1).

**Keywords**: mesoporous silica nanoparticles, blood-brain barrier, chicken chorioallantoic membrane, doxorubicin, brain disease.



**Figure 1**: Figure illustrating the chicken chorioallantoic membrane employed as an alternative model for BBB penetration in which MSN-PEG/TMAC acts as a drug carrier crossing the BBB toward the therapeutic purpose for brain diseases.

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## Intranasal administration of dexamethasone-loaded nanoparticles improves lung tropism and reduces steroid off-target accumulation in healthy and in pulmonary fibrosis-affected mice

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### Abstract:

Pulmonary fibrosis is a chronic disorder involving lung parenchyma. In patients, a paradoxical tissue repair response leads to irreversible scarring and lung remodelling due to an excessive deposition of extracellular matrix (ECM). This alteration impairs respiratory function and, in idiopathic forms is fatal. Fibroblasts are key cells responsible for ECM deposition and upon different stimuli they can hyperproliferate at sites of injury and differentiate into myofibroblasts supporting the fibrotic process. These activated cells are highly responsive to growth factors and cytokines, indicating that both inflammation and immune mechanisms contribute to fibrogenesis. Therapeutic approaches to arrest or at least reduce fibrosis still lack due to the difficulty of reaching the target. To this aim, it has been evaluated the targeting of intranasally-injected steroid-loaded nanoparticles (Avidin-Nucleic Acid Nanoassemblies - ANANAS) in healthy mice and in a murine model of pulmonary fibrosis. The biodistribution and pharmacokinetics of free and ANANAS-linked dexamethasone were investigated both in vivo and ex vivo. After a single intranasal instillation, an intense and protracted signal was detected in lungs; nanoparticles were able to penetrate rapidly and segregate inside lysosomes of pulmonary macrophages (Figure 1), which are closely involved in inflammatory disease onset and progression. These cells also have a strong ability to ingest foreign materials, and can thus capture circulating nanoparticles, making these systems the ideal carriers. Lastly, dexamethasone level measurement shows an efficient drug release from ANANAS in lungs, avoiding blood circulation and off-target accumulation. These data suggest that this formulation can be a promising tool for the treatment of lung fibrosis and other autoimmune disorders.

**Keywords**: nanomedicine, lung fibrosis, inflammation, nanocarriers, histopathology, corticosteroids, drug delivery, biomedical applications.



**Figure 1**: ANANAS nanoparticles as a novel drug delivery system for the treatment of lung disorders. Alveolar macrophages are able to uptake the dexamethasone-loaded nanoparticles and release the drug avoiding off-target accumulation.

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## Cholesterol supplementation via intranasal administration as a possible therapeutic strategy in Huntington's disease

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### Abstract:

Huntington's disease (HD) is a dominant neurodegenerative disorder characterized by neuronal dysfunction and cell loss. One of the affected pathways implicates brain cholesterol (chol) metabolism, and exogenous chol administration to HD mice ameliorates their phenotype, indicating chol as a good candidate for HD treatment. Considering that the strategies used are invasive and not easily transferable to the patients, we decided to combine the safety of the intranasal (IN) technique with the administration of liposome-loaded cholesterol-D6 (chol-D6), whose formulation has already been used for commercial drugs. We have already demonstrated the efficacy of the nose-to-brain delivery in WT mice. Here, we performed an acute trial, and the LC-MS analysis confirmed the delivery of chol-D6 to the whole brain through IN route independently from the genotype by reaching a stable concentration until ten days after IN treatment (0.4 ng/mg). Chol-D6 rose in the first 24 hours in the peripheral tissues and declined ten days after IN treatment. At 42 days after IN treatment, chol-D6 level in the striatum of R6/2 mice was statistically reduced than in WT mice, suggesting that exogenous chol supplied the lack of chol in R6/2 mice. Following this, we performed a chronic trial. The LC-MS analysis confirmed the chol-D6 accumulation after IN repeated treatments in the brain areas (about 4.0 ng/mg). R6/2 mice treated with liposomes rescued cognitive decline, while their strength was statistically improved compared to R6/2 treated with PBS. Analysis of chol precursors and metabolites is ongoing. In conclusion, this result highlights the distribution of chol-D6 in the whole brain independently from the genotypes. In addition, the data obtained after 42 days suggest that R6/2 mice supplied the lack of endogenous cholesterol with the exogenous one. Moreover, repeated IN treatments rescued cognitive functions completely and counteracted the muscular strength defect.

**Keywords**: Huntington's disease, liposome, cholesterol, intranasal administration, nose-to-brain route, R6/2 animal model.



**Figure 1**: Schematic representation of nose-tobrain routes. Through the olfactory nerve pathway (green), the drug can reach the anterior part of the brain. Through the trigeminal nerve pathway (red), the drug can reach the caudal and the deeper part of the brain.

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### Recombinase polymerase amplification on silicon nanowires

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### Abstract:

Recombinase polymerase amplification (RPA) represents an equipment-free, fast and facile isothermal amplification method. It employs two primers and an operating temperature range between 37-42 °C. The reaction time is between 20-40 min and the amplification capacity is of 10<sup>11</sup> [1], [2].

This method is easily adaptable for solid-phase amplification, and in this respect, research papers regarding solid-phase RPA[3], [4] already exist. However, the research based on solid-phase isothermal amplification did not tackle the issues related to the use of a solid support, which reduces the reaction efficacy. In solid-phase PCR, a low amplification efficiency was observed due to the masking effects (the amplicons mask adjacent primers), molecular crowding effects (the high density of surface primers inhibits the attachment of template DNA) and neighboring DNA interactions (the DNA template likely to hybridize with an adjacent amplicon in preference to the primer) [5]. Thus, the impetus for using a nano-structured substrate is to increase the surface area available for binding the probes in order to increase the solid-phase amplification reaction. The nanostructured substrate based on silicon nanowires (SiNWs) can be easily configured using metal assisted chemical etching. Metal assisted chemical etching (MACE) of Si was reported in 1997 and represents a low cost and versatile method for manufacturing SiNWs [6], [7].

Thus, the present paper proposes a nanostructured substrate based on localised etched SiNWs for the implementation of solid-phase isothermal amplification with application in clinical detection of microbial strains involved in endophthalmitis.

**Keywords**: recombinase polymerase amplification, silicon nanowires, biomedical applications.



**Figure 1**: (a) Image of the configured nanowires; (b) PDMS cavities defined the active areas; (c) represents the solid-phase RPA result.

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## Development of surface-enhanced Raman spectroscopy (SERS) based label-free diagnosis of liver and gallbladder injury

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### Abstract:

During living donor liver transplantation, a number of blood vessels and bile ducts are anastomosed while the liver and gallbladder are resected in the donor and recipient. If the patency of these blood vessels is not smooth after surgery, liver function deteriorates. On the other hand, biliary tract complications, such as bile leakage around the biliary anastomosis or biliary narrowing, are common concern in liver transplantation. Since the patient is exposed to the risk of infection with a bile drainage tube after surgery, it is important to track the recovery of the bili-ary tract so that the drainage tube can be re-moved as soon as recovery of the biliary injury. A technique capable of monitoring prognosis in bile from a patient with a tube for bile drainage is a minimally invasive approach. In this study, a biosensing chip that can monitor the patient's health status from the bile excreted during the recovery process has been developed using a surface-enhanced Raman sensing chip. It is necessary to utilize a highly sensitive and reproducible prior detection technology [1,2] targeting the nano biomarkers in bile. As in the orange arrow progress in Figure 1, Surface-enhanced Raman spectroscopy signals of bile obtained from normal, bile duct ligation (BDL), and gallbladder damage mouse models using a cautery device were identified and analyzed. Also, as in the green arrow progress in Figure 1, the surface-enhanced Raman chip with a nanometer-level porous structure can selectively separate the nanometer biomarkers and measure the Raman signal. Through the detection of nanometer biomarkers in bile and comparative analysis of histopathology, the Raman signal in the damaged gallbladder was compared with that caused by BDL liver damage, showing that it becomes a biosensing chip for monitoring recovery.

**Keywords**: Bile duct ligation (BDL), Gallbladder cauterization, Surface enhanced Raman spectroscopy (SERS), Nano-biomarker, Principle component analysis (PCA).



**Figure 1**: Figure illustrating Nano-biomarker based surface-enhanced Raman spectroscopy for selective diagnosis of gallbladder and liver injury

Acknowledgements: This work was supported by the NRF of Korea (2018R1D1A1B07048562, 2019R1A2C2084122, 2020R1A2C2102137) and MRC grant of Korea (2018R1A5A2020732), by the MSIT and the MOTIE (20000843) of Republic of Korea.

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## Negatively charged liposomes for the delivery of manganese derivatives for diagnostic applications

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### Abstract:

The development of multimodal imaging techniques such as positron emission tomography (PET) and magnetic resonance imaging (MRI) allows the contemporary obtaining of metabolic and morphological information. To fully exploit the complementarity of the two imaging modalities, the design of probes displaying radioactive and magnetic properties at the same time could be very beneficial. In this regard, transition metals offer appealing options, with manganese representing an ideal candidate. As nanosized imaging probes have demonstrated great value for designing advanced diagnostic/theranostic procedures, this work focuses on the potential of liposomal formulations loaded with a new synthesized paramagnetic Mn(II) chelates. As manganese(II/III) complexes, [Mn(II)(PTA)(Cl)<sub>2</sub>  $(H_2O)_2$ ] (MP) Mn(II)(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub> (R=Et, MDE2; CH<sub>2</sub>CH<sub>2</sub>OEt, MDB), and Mn(III)(S2CNEt2)3 (MDE3) were considered due to their different water solubility. In particular, two different surfactant were used to prepare anionic liposomes, namely N-Lauroylsarcosin sodium salt (NLS) and sodium lauroyl lactylate (SLL).

Negatively charged liposomes were produced by thin-layer hydration method and extrusion. The obtained formulations were characterized in terms of size, surface charge, efficiency of encapsulation, stability over time, effective magnetic moment, and in vitro antiproliferative effect on human cells by means of the MTT assay. The produced anionic paramagnetic liposomes were monodisperse, with an average hydrodynamic diameter not exceeding 200 nm, and they displayed good stability and no cytotoxicity.

As determined by optical emission spectroscopy, manganese complexes were loaded almost completely on liposomes maintaining their paramagnetic properties.

This study enabled the selection of liposomes based on SLL (LS) as the best in terms of size, encapsulation, retention, physical stability over time, safety toward cells and ability to cross the cell membrane. Moreover, LS did not show differences in loading hydrophilic or lipophilic manganese compounds, resulting in a suitable system to convey all the synthesized complexes. The encouraging results obtained concerning the magnetic properties after LS encapsulation allowed to select MBD as the manganese compound to be further investigated for a potential application in diagnostic imaging. The preliminary data shown in this study strongly support further preclinical studies aimed at understanding the potential applicability of these formulations for diagnostic purposes.

**Keywords**: lipid-based nanosystems, liposomes, manganese, PET/MRI, magnetic susceptibility, biomedical applications.



**Figure 1**: Cryo-TEM images of extruded negatively charged liposomes. LS-MP (a), LS-MDE2 (b), LS-MDB (c), LN-MP (d), LN-MDE2 (e), and LN-MDB (f). Bar corresponds to 500 nm.

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## Functionalization of self-assembled monolayer with gold nanoparticles for protein detection in tear film

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### Abstract:

Currently, more than 90% of ophthalmic medications are administered by eye drops. However, the passage of drugs through the cornea is the main obstacle to their therapeutic action in the eye. The percentage of active products available in the anterior chamber of the eye, behind the cornea, is less than 0.02%. Much research is underway to develop mucoadhesive drug carriers for these diseases to improve drug delivery in eye drops. However, each individual has a different ocular mucin composition and some ocular pathologies also modify the ocular mucosa. Therefore, the development of a molecular platform for the sensitive and selective determination of mucins present on the ocular surface (figure 1) would allow for an efficient improvement of the diagnosis in certain cases, as well as the treatment of ocular diseases by proposing the most suitable drug vector for each individual. Indeed, gold nanoparticles (AuNPs) have the ability to bind bioreceptors on their surface which allows them to interact with target molecules. In this way, it is possible to specifically and selectively detect mucins according to the biomarker, here an aptamer. The covalent immobilization of AuNPs on a planar substrate via a self-assembled monolayer (SAM) will allow on the one hand to detect mucins by taking advantage of the properties of the AuNPs, to exalt the RAMAN signal by SERS effect and on the other hand will ensure the stability of the interface and thus the detection. This functionalization could lead to a tool for the SERS assay of different mucins.

**Keywords**: Self-Assembled Monolayers, Click chemistry, Phase Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS), Atomic Force Microscopy (AFM), Protein, Nanoparticles, Biodetection, Surface-enhanced Raman spectroscopy (SERS)



**Figure 1**: Illustration of the biosensor with the example of mucin 1 (MUC1). Self-assembled monolayers (SAMs) functionalized with gold nanoparticles that have been previously functionalized with MUC1 specific aptamers. Detection will be by surface enhanced Raman scattering (SERS).

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## The controversial properties of graphene oxide and reduced graphene oxide and impact on microalgae *Chlamydomonas reinhardtii*.

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### Abstract:

Although graphene-based nanomaterials could be applied in the wide field of bioapplication the wrong terminology, low quality of tested graphene-based nanomaterials, and insufficient characterization in multidisciplinary articles slow their actual applications. Graphene, reduced graphene oxide, and graphene oxide are three different nanomaterials with different properties, and it is impossible to swap them. As well as their characteristics (e.g. number of layers) ensure their proclaimed properties.

Therefore graphene-based nanomaterials have misrepresented positive or negative properties like biocompatibility and toxicity. We reported the synthesis of graphene oxides synthesized by two differently modified Hummer's methods to obtain graphene oxide with different sizes of sheets and different degrees of oxidation. Both graphene oxides were further reduced with two different reducing agents to obtain two differently reduced graphene oxides and resulting in six nanomaterials that differ by sizes of sheets and degree of reduction. All nanomaterials were tested on microalgae Chlamydomonas reinhardtii as an aquatic model organism. Our work divided tested materials into toxic and biocompatible with supporting the characterization of all tested nanomaterials. Highly reduced graphene oxides were the most toxic against Chlamydomonas while the most biocompatible material was graphene oxide with the largest sheets and the highest degree of oxidation. This study will also permit us to discuss graphene oxide as a material with a positive hormetic effect and its application in biomass power plants.

**Keywords**:graphene oxide, reduction, biocompatibility, toxicity, microalgae, *Chlamydomonas reinhardtii*.

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## Fabrication of Nucleus-Free Single-Crystal Graphene-Mesh with Zigzag Edges in the Wafer Scale

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### Abstract:

In addition to conventional monolayer or bilayer graphene films, graphene-mesh metamaterials have attracted considerable research attention within the scientific community owing to their unique physical and optical properties. Currently, most graphene-mesh metamaterials are fabricated using common lithography techniques on exfoliated graphene flakes, which require the deposition and removal of chemicals during fabrication. This process may introduce contamination or doping, thereby limiting their production size and application in nanodevices. Herein, we demonstrate the controlled production of waferscale high-quality single-crystal nucleus-free graphene-mesh metamaterial films with zigzag edges. We utilize the <sup>13</sup>C-isotopic labelling graphene-growth approach, large-area Raman mapping techniques, and a uniquely designed highvoltage localized-space air-ionization etching method to directly remove the graphene nuclei. Subsequently, a hydrogen-assisted anisotropic etching process is employed for transforming irregular edges into the zigzag edges within the hexagonal-shaped holes, producing a large-scale high-quality single-crystal graphene-mesh metmaterial film on a Cu(111) substrate. The carrier mobilities of the fabricated field-effect transistors on the as-produced films are measured. The findings of this study enable the large-scale production of high-quality low-dimensional graphene-mesh metamaterials and provide insights for the application of integrated circuits based on graphene and other two-dimensional metamaterials.

**Keywords**: Graphene; isotopic labelling; Cu(111) substrate; large-scale; two-dimensional metamaterials.



**Figure 1**: Figure illustrating of a controllable production approach of wafer-scale high-quality single-crystal nucleus-free graphene-mesh metamaterials with zigzag edges.

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 Tian, B., Li, J., Samad, A., Schwingenschlögl, U., Lanza, M., & Zhang, X. (2022). Production of Large-Area Nucleus-Free Single-Crystal Graphene-Mesh Metamaterials with Zigzag Edges. Advanced Materials, 2201253.

## Wafer-scale single-crystal high-crystal-quality monolayer graphene grown on sapphire substrates

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### Abstract:

The growth of inch-scale high-quality graphene on insulating substrates is desirable for electronic and optoelectronic applications, but remains challenging due to the lack of metal catalysis. Here we demonstrate the wafer-scale synthesis of adlayer-free ultra-flat single-crystal monolayer graphene on sapphire substrates.

We converted polycrystalline Cu foil placed on Al<sub>2</sub>O<sub>3</sub>(0001) into single-crystal Cu(111) film via annealing, and then achieved epitaxial growth of graphene at the interface between Cu(111) and Al<sub>2</sub>O<sub>3</sub>(0001) by multi-cycle plasma etching-assisted-chemical vapour deposition. Immersion in liquid nitrogen followed by rapid heating causes the Cu(111) film to bulge and peel off easily, while the graphene film remains on the sapphire substrate without degradation. Field-effect transistors fabricated on as-grown graphene exhibited good electronic transport properties with high carrier mobilities. This work breaks a bottleneck of synthesizing wafer-scale single-crystal monolayer graphene on insulating substrates and could contribute to next-generation graphenebased nanodevices.

**Keywords**: Wafer-scale; Graphene; Single-crystal; high-crystal-quality; adlayer-free; CVD growth; Sapphire substrates



**Figure 1**: Figure illustrating of a schematic of the graphene growing during MPE–CVD.



**Figure 2**: Figure illustrating of a schematic of the transformation process from a commercial polycrystalline Cu foil into a single-crystal Cu(111) film on Al2O3(0001).

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## Combining Droplet Microfluidics with Magnetoresistive Sensors for Rapid and Specific Detection of *Klebsiella pneumoniae*

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### Abstract:

*Klebsiella pneumoniae* has been issued as one of the most common pathogens associated with healthcare-associated infections <sup>1,2</sup>. Moreover, the World Health Organization (WHO) reported multiple antibiotic resistance in more than 50 % of *K. pneumoniae* isolated strains <sup>3</sup>.

However, the current methods for pathogen detection are time-consuming, labor intensive, and present low specificity and/or sensitivity <sup>4</sup>. Diagnostic tools that rapidly identify the causative agent would greatly benefit the containment of such infections and provide oriented treatment options.

Herein we present a novel method for the detection of *K. pneumoniae* relying on the combined use of a droplet-based microfluidics with magnetoresistive sensors. Microdroplet generators assisted in the high-throughput production of highly monodispersed emulsions with encapsulated bacteria and magnetic nanoparticles (MNPs).

The specific magnetic labeling of *K. pneumoniae* in the droplets was achieved by the functionalization of 130nm MNPs with a receptor binding protein (RBP) from a *Klebsiella* bacteriophage. These proteins offer great stability, sensitivity, and present innate high specificity <sup>5,6</sup>.

Magnetic signals of the encapsulated bacteria-MNPs conjugates revealed a significant decrease in the number of false positives (due to particle aggregation) when compared to non-encapsulated bacterial samples and allowed the specific identification of *K. pneumoniae* in less than one hour with clinically relevant limits of detection  $(10^3 \text{ CFU/mL})$ .

By coupling the specificity of phages' RBPs with the sensitivity of MR sensors<sup>7</sup> in an integrated droplet-based microfluidic channel network, we provide an effective diagnostic tool with potential for use at the point-of-care for the fast diagnosis of *K. pneumoniae* infections. **Keywords**: *Klebsiella pneumoniae*, diagnostics, magnetic nanoparticles, functionalization, droplet microfluidics, bacteriophages, receptor binding proteins, magnetoresistive sensors.

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Tool for Rapid Detection of Hospital Bacterial Infections: Clinical Study with Klebsiella Pneumoniae Cells. *Biosens. Bioelectron. X* 2022, *11* (December 2021),

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**Figure 1**: Detection of *Klebsiella pneumoniae* by combining a droplet-based strategy with the use of a bacteriophage receptor binding protein functionalized in magnetic nanoparticles for magnetic detection in magnetoresistive sensors

## Piezoelectric polarization in fluoropolymer obtained via immersion precipitation and low pH exposure

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### Abstract:

Piezoelectric fluoropolymers are capable of converting mechanical stimuli into a useful electrical output thus making them ideal for powering electronic devices. To perform this operation a net polarization must be induced in the polymer, currently which is achieved via the electrical poling. The solution-processed films difficult to pole owing to their porosity are crystallized via immersion precipitation followed by low pH exposure. This, effectively circumvents the electrical poling. Here, by combining the X-ray diffractometry, Raman spectroscopy and piezoelectric force microscopy (PFM) results we reveal an unseen polarization locking in the polyvinylidene fluoride (PVDF) matrix increasing anomalously with the time of acidic aqueous solution exposure. The electrostatic interaction of PVDF chains with high polar solvents along with highly concentrated H<sub>3</sub>O<sup>+</sup> solution (low pH) results in the polarization locking. In addition, the anomalous behavior is observed which is attributed to the formation of a more thermodynamically non-polar  $\alpha$ phase with longer time of acidic aqueous solution exposure thus reducing the polarized state of the polymer. The induced polarization, driven via  $H_3O^+$  ion exposure facilitates high energy harvesting capacity, with a measured piezoelectric coefficient( $d_{33}$ ) of -57.0±9.3 picometers per volt which is significantly higher than the unexposed samples (approximately  $-11.4\pm3.0$  picometers per volt). This study provides a simple approach towards developing highly polarized fluoropolymer solution processed films, which enables the development of energy harvesters with improved performance.

**Keywords**: piezoelectric fluoropolymers, pH exposure, energy harvesters, polarization locking, piezoresponse force microscopy



**Figure 1:** (a)Schematic of electrostatic interaction of PVDF chains with hydronium ions present in low pH solution. (b) Polarization locking after evaporation of solvent owing to the orientation of dipole along one direction providing net dipole moment to the polymer.

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## Gold Nanoparticle Formulations for Efficient Delivery of Lupeol: A Promising Therapeutic Approach in the Management of Skin Pathologies

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#### Abstract:

Globally, skin cancer represents a major public health challenge, with the incidence of this type of cancer reaching epidemic proportions. The various types of skin cancer can be divided into two main categories, namely melanoma (resulting from dysfunction of the melanocytes) and non-melanoma skin cancers (arising from epidermal derived cells). The incidence of melanoma is less than 1% of all skin cancers, but it is responsible for over 90% of skin cancer-related mortality. The treatment of cancer remains unsatisfactory, and the survival rate among patients with cancer is low despite the remarkable progress made in the fields of cancer genomics, biology, and proteomics. As a result of the disadvantages, limitations and challenges associated with conventional oncological treatments, as well as those derived from natural compounds, gold nanoparticles have demonstrated tremendous potential to improve the bioavailability of active substances, prolong circulation times, control release, and increase the selectivity of their action. The use of natural compounds remains a viable option for the management and treatment of melanoma. Among these, lupeol has attracted the interest of researchers in the field due to its wide range of therapeutic effects (antioxidant, anti-inflammatory, as well as antitumor). The present study was designed to modulate and enhance the therapeutic action of lupeol by creating gold nanoparticles capable of incorporating and transporting the compound to the tumor cells in a targeted manner. In order to examine cell viability, cell morphology, as well as the appearance of signs of cell apoptosis, two human melanoma cell lines SK-MEL-28 and RPMI-7951 and a human keratinocyte cell line HaCaT were selected. The results indicated that the gold nanoparticles with lupeol showed antiproliferative activity depending on

concentration, reducing tumor cell viability significantly. Furthermore, changes characteristic of the apoptosis process were observed at the levels of cellular morphology and nuclei and actin fibers. Meanwhile, no cytotoxic effects were observed at the level of healthy cells, the viability of the cells not being significantly lower than that of control cells. All of these results indicate that gold nanoparticles with lupeol exhibit an apoptotic-like effect on tumor cells, suggesting that they could be considered potential therapeutic approaches for the treatment of melanoma.

**Keywords**: gold nanoparticle, lupeol, apoptoticlike effect, nuclei condensation, selective cytotoxicity



**Figure 1**: Graphic representation of the main effects of gold nanoparticles with lupeol on melanoma cells observed in the present study.

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### Acknowledgement

Funding. This research was funded by UMFVBT, grant number 1EXP/1233/30.01.2020.

## Pharmacotoxicological Insights Into Supramolecular Complexes With Natural Compounds

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### Abstract:

Medicinal plants serve as a source of traditional remedies as well as the basis of modern medicine. Despite its many advantages (low toxicity, good tolerance, etc.), the natural compound is prone to metabolism problems and lacks a targeted action. Therefore, in recent years, researchers in this field have focused on developing new supramolecular formulations based on natural products. Eugenol is the major constituent of the volatile oil of cloves, Eugenia caryophyllata Thunb. As a therapeutic agent, eugenol is known primarily for its antiseptic and analgesic properties, and is currently used in dentistry. Eugenol, however, has gained a great deal of attention due to its antitumor properties. A useful strategy for improving eugenol's pharmacokinetic properties and facilitating its cell penetration is the use of nanocarriers. Thus, in the present study, encapsulated forms of eugenol were prepared, which underwent extensive pharmacotoxicological evaluation in vitro regarding cell morphology, cell viability, and the impact on cell organelles with a major role in tumorigenesis. In order to achieve this objective, two cell lines were selected: one of healthy cells - the human gingival fibroblast (HGFa) and an other of cancerous cells - tongue squamous carcinoma (SCC4). According to the results of the study, the cytotoxic effect of the compound was concentration-dependent in SCC4 cells, while no significant reduction in cell viability was observed in HGFa cells. Further, at the level of morphology and at the level of nuclei and actin fibers, changes characteristic of apoptosis were observed, including the condensation of nuclei and the presence of apoptotic bodies. It is noteworthy that both morphological changes and changes in the nucleus and actin fibers were observed predominantly in the tumor cell line. It is concluded that eugenol in its supramolecular form has a marked cytotoxic effect on oral squamous cancer cells, which will be investigated further in terms of the biological mechanisms involved.

**Keywords**: natural compounds, supramolecular chemistry, pharmacotoxicological evaluation, antitumor activity



**Figure 1**: Figure 1 summarizes the steps performed in the in vitro evaluation of Eugenol incorporated in nanoparticles for the modulation of antitumor activity.

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Acknowledgement Funding. This research was funded by grant UMFVBT, g 1EXP/1233/30.01.2020. number

### Green synthesis of reduced graphene oxide aerogels

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### Abstract:

Graphene aerogels are three-dimensional lightweight scaffold materials which thanks to their remarkable properties like high mechanical strength and electrical conductivity, thermal resistance and adsorption capacity, have been immensely enriched [1]. The main routes for obtaining such materials are the hydrothermal reduction/self-assembly, chemical reduction, template-directed reduction, cross-linking and solgel processes while the main application fields regard water desalination and filtration/purification, energy storage [2] and environmental protection. But the main drawback for these materials which can slow down their widespread application is their high cost. The cost for synthesizing such materials is mainly increased from the carbon source which is graphene oxide (GO). At the same time, there are plenty of carbonaceous sources to be exploited in order to assist in the synthesis of graphene-related (GRMs) materials. In that direction, NANOGRAPHENE, a spin off company of Sabanci University (SU), with production capacity of 500kg/month, starting from waste carbon black coming from the pyrolysis of waste-tires, are able to supply with Graphene-NanoPlatelets (GNPs) powder. In this study, the successful synthesis of graphene aerogels using as carbon source the GO which has been obtained from the oxidation of the previously-mentioned GNPs powder and conventionally prepared GO, is reported. In the frames of the SOLAR-ERA.NET 'GO-FOR-WATER' project, Scanning Electron Microscopy, Raman microscopy and X-ray diffraction are used to characterize the produced graphene aerogels in University of Patras and FORTH, while the mechanical behaviour (i.e. static and dynamic compression) are going also to be investigated by using micro-testing facilities already available at both institutions [3].

**Keywords**: two-dimensional materials, organic waste, reduction, macro-porosity



**Figure 1**: Characterization of the graphene aerogels. (A) Deconvoluted C1s XPS spectrum of the GNPs powder. (B) SEM photo of the as-obtained graphene aerogel showing the macro-porosity of the material. (C) XRD diagram of the aerogel. The as-made graphene aerogel exhibits a weak broad peak, characteristic of an amorphous material, at  $2\theta = 26^{\circ}$ , which corresponds to the (002) plane of graphite structure . (D) Raman spectrum of the aerogel showing the characteristic G and D peaks of graphene.

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