



2nd International Conference on Nanotechnologies & Bionanoscience

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ABSTRACT BOOK

The Organizing Committee

Dr. Emmanuel Stratakis

Prof. Emmanuel Kymakis



Monday 11th September

Plenary Session I

Intelligentsia of Nano-Architected Hierarchical Materials

Julia R Greer^{1*}, Seola Lee², Seneca Velling², Kevin Nakahara², and Wenxin Zhang²

¹*Division of Engineering and Applied Sciences, Caltech, Pasadena, CA USA*

²*Kavli Nanoscience Institute, Caltech, Pasadena, CA USA*

* jrgreer@caltech.edu

Abstract:

Creation of reconfigurable and multi-functional materials can be achieved by incorporating architecture into material design. In our research, we design and fabricate three-dimensional (3D) nano-architected materials that can exhibit superior and often tunable thermal, photonic, electrochemical, biochemical, and mechanical properties at extremely low mass densities (lighter than aerogels), which renders them useful and enabling in technological applications. Dominant properties of such meta-materials are driven by their multi-scale hierarchy: from characteristic material microstructure (atoms) to individual constituents (nanometers) to structural components (microns) to overall architectures (millimeters and above).

Our research is focused on fabrication and synthesis of nano- and micro-architected materials using 3D lithography, nanofabrication, and additive manufacturing (AM) techniques, as well as on investigating their mechanical, biochemical, electrochemical, electromechanical, and thermal properties as a function of architecture, constituent materials, and microstructural detail. Additive manufacturing (AM) represents a set of processes that fabricate complex 3D structures using a layer-by-layer approach, with some advanced methods attaining nanometer resolution and the creation of unique, multifunctional materials and shapes derived from a *photoinitiation-based chemical reaction* of custom-synthesized resins and thermal post-processing. A type of AM, vat polymerization, has allowed for using hydrogels as precursors, and exploiting novel material properties, especially those that arise at the nanoscale and do not occur in conventional materials. The focus of this talk is on additive manufacturing via vat polymerization and function-containing chemical synthesis to create 3D nano- and micro-architected metals, ceramics, multifunctional metal oxides (nano-photonics, photocatalytic, piezoelectric, etc.), and metal-containing polymer complexes, etc., as well as demonstrate their potential in some real-use biomedical, protective, and sensing applications. I will describe how the choice of architecture, material, and external stimulus can elicit stimulus-responsive, reconfigurable, and multifunctional response.

[1] Saccone, M. A., et al *Nature* **612**, 685 (2022)

[2] Zhang, W., et al *Nano Letters* (in press, 2023)

[3] Kagias, M., et al *Advanced Materials* **35** (13), 2209153 (2023)

Autophagic mechanisms and cellular homeostasis during ageing

Nektarios Tavernarakis

Institute of Molecular Biology and Biotechnology, Foundation for Research and Technology-Hellas

Medical School, University of Crete, Heraklion, Crete, Greece

Ageing is driven by the inexorable and stochastic accumulation of damage in biomolecules vital for proper cellular function. Although this process is fundamentally haphazard and uncontrollable, senescent decline and ageing is broadly influenced by genetic and extrinsic factors. Numerous gene mutations and treatments have been shown to extend the lifespan of diverse organisms ranging from the unicellular *Saccharomyces cerevisiae* to primates. It is becoming increasingly apparent that most such interventions ultimately interface with cellular stress response mechanisms, suggesting that longevity is intimately related to the ability of the organism to effectively cope with both intrinsic and extrinsic stress. Key determinants of this capacity are the molecular mechanisms that link ageing to main stress response pathways, and mediate age-related changes in the effectiveness of the response to stress. How each pathway contributes to modulate the ageing process is not fully elucidated. A better understanding of the dynamics and reciprocal interplay between stress responses and ageing is critical for the development of novel therapeutic strategies that exploit endogenous stress combat pathways against age-associated pathologies. Mitochondria, the indispensable and highly dynamic, energy-generating organelles in all eukaryotic cells, play essential roles in fundamental cellular processes. Neuronal cells depend, perhaps more than any other cell type, on proper mitochondrial function. Mitochondrial impairment is a major hallmark of several age-related neurodegenerative pathologies, including Alzheimer's disease. Interestingly, accumulation of damaged mitochondria has been observed in post-mortem brain of Alzheimer's disease patients. Mitophagy is a selective type of autophagy mediating elimination of damaged mitochondria, and the major degradation pathway, by which cells regulate mitochondrial number in response to their metabolic state. However, little is known about the role of mitophagy in the pathogenesis of Alzheimer's disease. Although disease-associated tau and amyloid β are known to deregulate mitochondrial function, it remains elusive whether they also directly influence the efficiency of mitophagy. To address this question, we developed an *in vivo* imaging system to monitor mitophagy in neurons. We demonstrated that neuronal mitophagy is impaired in *C. elegans* models of Alzheimer's disease. Urolithin A- and nicotinamide mononucleotide-induced mitophagy ameliorates several pathological features of Alzheimer's disease, including cognitive defects. Mitophagy stimulation restores memory impairment. Age-dependent decline of mitophagy both inhibits removal of dysfunctional or superfluous mitochondria and impairs mitochondrial biogenesis resulting in progressive mitochondrial accretion and consequently, deterioration of cell function. Our findings suggest that impaired removal of damaged mitochondria is a pivotal event in Alzheimer's disease pathogenesis highlighting mitophagy as a potential therapeutic intervention.

Tuesday 12th September

Plenary Session II

“Nanobiotechnology of Intelligent Materials”

Engineering the molecular design of intelligent biomaterials for advanced properties by controlling structure, recognition and specificity, is the first step in coordinating and duplicating complex biological and physiological interactions associated with molecular recognition and targeting. We reexamine and further develop *molecular models* that establish the importance of molecular weight, degree of branching, swelling characteristics, thermodynamic compatibility and presence of “free” binding agents on intelligent materials used on the development of improved cognitive and targeting characteristics. Studies with thermodynamically intelligent biomaterials, branched structures, multi-arm polymers and gels indicate the importance of various molecular structures in biomedical applications for treatment of autoimmune diseases.

**(Plenary) Metallic two dimensional materials for lithium sulphur
batteries**

Manish Chhowalla

University of Cambridge, UK

Inelastic molecular collisions & the gas mean free path in air

Sotiris E. Pratsinis^{1*}, Dimitris G. Tsalikis¹, V.G. Mavrantzas^{1,2}

¹Particle Technology Lab., Dept. of Mech. & Process Engineering ETH Zurich, Switzerland

²Dept. of Chemical Engineering, University of Patras & FORTH-ICE/HT, Patras, Greece

pratsinis@ethz.ch

For over a century, the kinetic theory of gases [1] is used to quantify molecular collisions and transport in gases in atmospheric and industrial processes resulting in also the all-important mean free path (MFP) of the gas, the average distance travelled by molecules between their collisions. The MFP dictates when gas-phase nanoparticle transport takes place in the free molecule or continuum regime. This is crucial in process design of gas phase (laser, plasma, hot wall, ultrasonic. flame) synthesis of films and particles. The kinetic theory of gases assumes elastic collisions between spherical gas molecules. However, is this so with what we know about molecular shape and force fields today? Having reached a state of maturity now, molecular dynamics (MD) elucidate the fundamentals of basic gas-phase processes enhancing understanding of natural phenomena and accelerating process scale-up [2]. Here the mechanics of gas collisions are elucidated for air at room temperature treating O₂ and N₂ as true diatomic molecules accounting for their shape and force field, for the first time to our knowledge.

The MD simulations were conducted for 21/79 mole O₂/N₂ (air) in the NVE ensemble at 300 K & 1 atm [3]. Collisions were identified by the distance between colliding molecules, as in classic kinetic theory. Accounting, however, for the molecular shape and force field, showed that gas molecule trajectories were no longer straight due to the attractive part of the force field and the diatomic shape of N₂ and O₂ as will be shown by the respective videos. There were instances, albeit rare, where even three molecules were involved in the same collision! Moreover, frequently, colliding molecules were split from each other but soon returned to collide again and again without interacting with any other molecule in between. Such collisions are termed spurious and were removed from the analysis to avoid overcounting collisions. These complex collision patterns were never observed when treating O₂ & N₂ as hard spheres! A direct result of the enhanced interactions between air molecules when these are treated as true diatomic ones is that their MFP is considerably smaller than that from the classic kinetic theory. The new value of the MFP for air is 38.5 nm, almost 43% smaller than the currently known and widely used value in textbooks of 67.3 nm at 300 K and 1 atm. Aside from its fundamental value, such a result is significant in description of atmospheric processes and climate effects as well as in gas-phase synthesis of tiny (< 5 nm) nanoparticles where asymptotic (self-preserving) particle size distributions and (fractal-like) structure have not been attained yet to simplify their process design [4].

[1] Maxwell JCMA, *The London, Edinburgh, Dublin Philos. Mag. J. Sci.*, **19**, 19-32 (1860)

[2] Mavrantzas VG & Pratsinis SE, *Curr. Opinion Chem. Eng.*, **23**, 174-183 (2019).

[3] Zambrano H, Walther JH & Jaffe R, *J. Mol. Liq.*, **198**, 107-113 (2014).

[4] Pratsinis SE, *AIChE J.*, **56**, 3028-3035 (2010).

Friday 15th September

Plenary Session III



International Conference on Nanotechnologies and Bionanoscience

**(Plenary) Materials for Eco-Design Strategies for an Innovative
Industry**

Rodrigo Martins

CENIMAT|I3N and CEMOP/UNINOVA, Faculty of Sciences and Technology, NOVA
University Lisbon, Portugal

Thin Film Implants for Bioelectronic Medicine

George Malliaras*

University of Cambridge, Cambridge, UK

** gm603@cam.ac.uk*

Abstract:

Bioelectronic medicine provides a new means of addressing disease via the electrical stimulation of tissues: Deep brain stimulation, for example, has shown exceptional promise in the treatment of neurological and neuropsychiatric disorders, while stimulation of peripheral nerves is being explored to treat autoimmune disorders. The implanted electrodes used in these devices are assembled by hand, using top down techniques that herald from (mechanical) watchmaking! Using the (bottom up) microfabrication techniques of microelectronics promises to revolutionize implantable devices, enabling exceptionally precise stimulation and minimally invasive thin film form factors. I will overview the state-of-the-art in the use of thin film implants and discuss the challenges that lie ahead on the road to deploying this technology to patients at scale.

Monday 11th September

WS1 & WS3 Session II

Biocompatibility and Nanotoxicity of
Nano(bio)Materials I



International Conference on Nanotechnologies and Bionanoscience

**Personalized medicine and predictive health and wellness: Adding the
chemical component**

Anne Milasincic Andrews

*Departments of Chemistry & Biochemistry and Psychiatry & Biobehavioral Health, Semel Institute
for Neuroscience and Human Behavior, Hatos Center for Neuropharmacology, and California
NanoSystems Institute,*

University of California, Los Angeles, USA

Assembly of layer-by-layer PLL-HA nanothick protein reservoirs on poly(glycerol sebacate) microporous implant surface.

Tomasz Urbaniak^{*}, Paweł Piszko², Dana Kubies³, Zuzanna Podgórnika¹, Ognen Pop-Georgievski³, Tomáš Riedel³, Konrad Szustakiewicz², Witold Musiał¹

¹*Department of Physical Chemistry and Biophysics, Faculty of Pharmacy, Wrocław Medical University, Wrocław, Poland*

²*Department of Polymer Engineering and Technology, Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Poland*

³*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic*

^{*} tomasz.urbaniak@umw.edu.pl

Abstract:

Poly(glycerol sebacate) (PGS) is a promising polyester for tissue engineering (TE) applications due to its unique properties, including biocompatibility, biodegradability, and elasticity. However, the hydrophobic nature of PGS surfaces can limit crucial cellular processes such as adhesion and proliferation. Layer-by-Layer (LbL) surface modification has emerged as a promising technique for modifying the surface properties of polyester-based scaffolds, offering mild deposition conditions and the creation of protein reservoirs for controlled release of sensitive biomolecules such as growth factors and cytokines. In this recent study, we aimed to modify the surface of PGS microporous scaffolds using poly-L-lysine (PLL)/hyaluronic acid (HA) nanothick multilayer films as bioactive protein reservoirs while adjusting the surface hydrophilicity of PGS. We evaluated bioactive macromolecules, including VEGF, FGF-2, BMP-2, and CXCL12, as potential cargo for the described LbL system. Specifically, we focused on the characterization of HA/PLL nanofilms containing BMP-2, investigating their thickness, morphology, impact on PGS surface hydrophilicity, and protein loading capacity. Surface plasmon resonance was employed for in situ evaluation of film assembly, providing insights into deposition dynamics and emphasizing the significance of polyanion concentration in preparing PLL/HA systems on PGS via LbL dip coating. The vacuum-assisted LbL coating procedure enabled effective film deposition within the micropores of soft scaffolds, resulting in the sustained release of physiologically and therapeutically significant amounts of protein over several days. These results demonstrate the promise of PLL/HA LbL nanofilms as structures for microporous PGS scaffold modification, offering the potential to significantly enhance the performance of TE devices.

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ESEM and AFM structural characterization of short peptide electrospun fibers

Konstantina Mitropoulou^{1*}, Matteo Bottiglieri¹, Meital Reches², Alexander M. Bittner^{1,3}

¹CIC nanoGUNE, (BRTA) Tolosa Hiribidea 76, 20018 Donostia-San Sebastián, Spain

²Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel ³Ikerbasque

Basque Foundation for Science, Pl. Euskadi 5, 48009 Bilbao, Spain

* k.mitropoulou@nanogune.eu

Abstract:

Electrospinning is a versatile technique, widely used for the production of fibers on the nanoscale, by applying high voltages to polymers in solution. Long nanofibers with controlled diameter can be produced by optimizing different parameters of the experimental set up. [1] Considering that the key factors that indicate the electrospinnability of a solution are the intermolecular interactions, electrospinning of short peptides has recently raised interest. [2] Short peptides [3] are excellent candidates for material fabrication not only because of the potential the different combinations of amino acids offer, but also because of their biocompatibility. [1] Moreover, unlike proteins, they are easier to synthesize and stable in extreme temperatures and pH. In this project the electrospinnability of short peptides by optimizing different parameters is tested. The following structural characterization of the peptide electrospun fibers was performed using two microscopy techniques. Environmental scanning electron microscopy (ESEM) visualises non-conductive peptide fibers in water vapor. Furthermore, the technique also allows to study structural changes in the different peptide fibers (wetting, swelling, dissolution) due to humidity control. Atomic Force Microscopy (AFM) yields the topography of the fibers, as well as force-distance mapping by AFM indentation, which provides useful information on material's stiffness (local Young's Modulus) and local adhesion.

[1] Bucci, R.; Bittner, A.M.; et al.; *Nanomaterials* 11, 1262, (2021)

[2] Nuansing, W.; Bittner, A.M.; et al.; *Faraday Discuss.* 166, 209–221, (2013)

[3] Nikoloudakis, E.; Mitropoulou, K.; et al.; *Chem. Commun.*, 55, 14103-14106 (2019)

First approach on the assessment of laser-synthesized Si nanoparticles: effects on stem cells model for potential tissue engineering application

Clarissa Murru^{1*}, Stefano Testa², Lucas Duvert¹, Adrien Casanova¹, Frederique Magdinier², Anne-Patricia Alloncle¹, Ahmed Al-Kattan¹

1Aix-Marseille University, CNRS, UMR 7341, LP3, Campus de Luminy,

Case 917, 13288, Marseille cedex 9, France

2Aix-Marseille University, INSERM, Marseille Medical Genetics, MMG, 27 Bd Jean moulin

13385 Marseille, France

** clarissa.MURRU@univ-amu.fr*

Abstract:

Stem cells are primitive cells that have the potential to self-renew and develop into different specialized functional cells, they are particularly used for clinical application in cell therapy and tissue engineering depends on the regulation and control of their differentiation into specific cell types¹. It has been studied that nanoscale biomaterials obtained through chemical methodologies showed facilitated capacity for myotube formation and myogenic differentiation which were crucial during skeletal muscle regeneration². However, the bibliography is lacking in works describing nanoparticles (NPs) fabricated through laser ablation method in liquid, especially for tissue engineering applications: laser processing approach offers the possibility to develop innovative NPs with adjustable physicochemical properties exempt of any contaminants for healthcare and wellbeing challenges³. In this work we focused on the fabrication of Si-NPs through ultra-short (femtosecond) laser radiation and systematically studied their effect in the differentiation, proliferation and motility of the cells. In fact, Si-NPs have shown a great interest as functional tools and additives for biomedical applications including tissue engineering³. In this context, this study is conceived as an attempt to clarify not only which aspects of the growth of C2C12 can be improved by NPs, but also the genetic mechanisms that play a fundamental role during the exposure of the cells to different concentrations of Si-NPs, with the aim to take a step forward to expand the use of nanomaterials in tissue engineering and cell regeneration.

[1] Wei, M., et al. *J Nanobiotechnol* 15, 75 (2017)

[2] Poussard, S., et al. *Int J Nanomedicine* 19, 1479-92 (2015)

[3] Al-Kattan A., et al. *Nanomaterials* 11, 712 (2021)

Nano-scale functional analysis of human induced pluripotent stem cell-derived cardiomyocytes

Michal Sarna^{1*}, Anna Dobosz² and Sylwia Bobis-Wozowicz²

¹*Department of Biophysics, Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University, Krakow, Poland*

²*Department of Cell Biology, Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University, Krakow, Poland*

* michal.sarna@uj.edu.pl

Abstract:

Cardiomyocytes (CMs) are the force-generating cells enabling heart muscle contraction thus driving the circulatory system. Dysfunction of CMs is one of the main reasons for heart failure in patients with either inherent conditions or in those after myocardial infarction. It is viewed that heart-related disorders account not only for the majority of premature deaths in western population but are also responsible for deteriorating life condition among elderly. This makes CMs one of the main targets of regenerative medicine. However, due to very limited potential for self-renewal of the cells, researchers are looking for new sources of CMs to replace dysfunctional cells. For obvious reasons, stem cells are of particular interest. Recently, human induced pluripotent stem cell-derived CMs (hiPSC-CMs) have been extensively studied for their potential to restore cardiac function in individuals with either genetic disorders or in patients suffering from a heart attack. Despite significant advancements in hiPSC-CMs culture, quantitative analysis of functional parameters of cell contraction is a challenge. Among the techniques used for functional analysis of hiPSC-CMs, optical microscopy remains a gold standard. Recently, however more sophisticated techniques, such as multielectrode arrays for action potential measurements have been demonstrated whereas special substrates were shown to examine mechanical parameters of cell contraction. Although the above-mentioned techniques allow for fast screening of large population of cells, they lack both resolution and sensitivity that would allow single cell analysis. Here, we demonstrate a unique technique based on a combined atomic force microscopy (AFM) and fluorescence imaging (FI) for quantitative analysis of functional parameters of cell contraction. We show that AFM-FI is capable of simultaneous detection of both mechanical parameters of cell contraction and calcium handling in living cells in real time with high spatiotemporal resolution. During the talk, example applications of the AFM-FI technique in hiPSC-CMs research will be demonstrated, including the effect of ultrastructure of hiPSC-CMs on cell contraction as well as early response of hiPSC-CMs in a model heart attack.

Electrospun, composite-coated endotracheal tubes with controlled siRNA and drug delivery, lubricate and minimize airway injury

Gabriela Gonzales¹, Solaleh Miar^{1,2}, Alisa Isaac¹, Ronit Malka³, Rena Bizios¹, Gregory Dion⁴, Teja Guda¹

¹The University of Texas at San Antonio, San Antonio, TX, USA.

²The University of Hartford, Hartford, CT, USA.

³Brooke Army Medical Center, Ft. Sam Houston, TX, USA

⁴University of Cincinnati, Cincinnati, OH, USA.

*teja.guda@utsa.edu

Abstract:

Endotracheal Tubes (ETTs) maintain and secure a patent airway; however, prolonged intubation often results in unintended injury to the mucosal epithelium and inflammatory sequelae which complicate recovery. ETT design and materials have yet to adapt to address intubation associated complications. In this study, a composite coating of electrospun polycaprolactone (PCL) fibers embedded in a four-arm polyethylene glycol acrylate hydrogel (4APEGA) is developed to transform the ETT from a mechanical device to a dual-purpose device capable of delivering multiple nano-therapeutics. The airway epithelial mucosa is disrupted by contact with stiff electrospun fibers, so the 4APEGA hydrogel was tuned to maintain a smooth lubricating contact surface without significant degradation, and remains resistant under shear because of the adhesion to and integration with electrospun PCL. Further, the composite coating system (PCL-4APEGA) is capable of sustained delivery of dexamethasone (an anti-inflammatory corticosteroid) from the PCL phase over the duration of intubation and polyplexes containing small interfering RNA (siRNA) from the 4APEGA phase. The siRNA is released rapidly and targets *smad3* for immediate reduction in pro-fibrotic transforming growth factor-beta 1 (TGF β 1) signaling in the upper airway mucosa. A bioreactor was used to study mucosal adhesion to the composite PCL-4APEGA coated ETTs and investigate mucus secretory function in *ex vivo* epithelial samples. This study demonstrated that increase in surface lubrication paired with surface stiffness reduction significantly decreased fibrotic behavior while reducing epithelial adhesion and abrasion in an *ex vivo* model. The ETTs as commercially available, PCL fibers with dexamethasone and PCL-dexamethasone+4APEGA-siRNA were all implanted in an injured swine upper airway and observed over a period of 3, 7 and 14 days. The impact on the tissue biomechanics was evaluated by indentation, and histopathological assessment was conducted on the mucosa. PCL only coated ETTs were found to exacerbate the inflammatory response over time, while the tubes coated with the hydrogel composite were found to both reduce inflammatory progression to fibrosis as well as maintain mechanical function of the laryngotracheal tissues over time.

Enhancement of phosphate removal using designed magnetic iron oxide nanostructures

Théo Lucante^{1*}, Philippe Choquet², Manon Kretz¹, Stéphane Le Calvé⁴, Anaïs Becker⁴, Joana Vaz-Ramos^{1,4}, Ariane Zaloszc³, Sylvie Bégin-Colin¹

¹*Institut de Physique et Chimie des Matériaux de Strasbourg, UMR7504, University of Strasbourg, CNRS, 67034 Strasbourg, France*

²*ICUBE, UMR7357, Imagerie Préclinique - Hôpital de Hautepierre, 67412 Illkirch, France*

³*INSERM, UMR1109, Service pédiatrique-Hôpital de Hautepierre, 67000 Strasbourg, France*

⁴*Institut de Chimie et Procédés pour l'Énergie, l'Environnement et la Santé (ICPEES), UMR7515 CNRS-Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, France*

*sylvie.begin@unistra.fr; <https://www.ipcms.fr/>

Abstract:

Chronic kidney disease (CKD) results in the progressive loss of the kidney's purification functions and leads to complications linked to high concentrations of normally useful molecules and to the accumulation of toxins in the body. Among these molecules, phosphates are dangerous as hyperphosphatemia can lead to vascular calcification, cardiac arrest, *etc.*^[1]. In the absence of a transplant, the treatment of CKD involves dialysis techniques. Peritoneal dialysis (PD) is best suited for infants and children and has many advantages over hemodialysis (HD). However, its blood purification efficiency is lower, with a 4-hour cycle allowing 40% of phosphates to be eliminated in PD compared with 50-60% in HD.

To improve the capture of phosphates during PD, a promising approach consists in working on the formulation of the dialysate by incorporating iron oxide nanoparticles (IONs) whose affinity with phosphates has already been demonstrated.^[2,3] Various types of nanostructures satisfying precise specifications (biocompatibility, size, colloidal stability, *etc.*) were synthesized using different synthesis methods leading to different nanosize and shape^[2,3,4] and their capacity in phosphate removal has been evaluated. Analytical protocols have been developed to quantify phosphates and toxins using chemical approaches as well as via a hospital apparatus.

Kinetic and adsorption experiments for phosphates and other toxins were performed on these designed IONs in different media and pH. The kinetics was found very favorable to reduce the PD duration and experiments conducted in dialysate at pH 7 has shown a phosphate adsorption similar to that in water.

We improved further the phosphate capture performance at pH 7 by increasing the surface specific area of IONs. In addition, some functionalized IONs were shown also very efficient to remove other toxins. The most promising systems have been inserted in designed dialysis experimental setup of increasing complexity and of behavior close to dialysis performed in hospital in order to study the diffusion of phosphates through a membrane and their adsorption in the presence of IONs.

[1] Rastogi, A., et al. *Journal of Renal Nutrition* 31, 21–34 (2021)

[2] Daou, T. J., et al. *Chem. Mater.* 19, 4494–4505 (2007)

[3] Ramirez, P. D., et al. *Nanomaterials* 13, 587 (2023)

[4] Gerber, O. et al. *Nanoscale* 9, 305–313 (2017)

Material and size related therapy enhancing effects of metal nanoparticles in proton therapy are ruled by surface chemistry

Christoph Rehbock^{1,}, Sandra Zwiehoff¹, Jacob Johny¹, Astrid Hensel², Carina Behrends^{3,4,5}, Christian Bäumer^{3,4,5,6}, Shirley Knauer², Beate Timmermann^{3,4,6,7}, Stephan Barcikowski¹*

¹University of Duisburg-Essen, Technical Chemistry I and Center for Nanointegration Duisburg-Essen (CENIDE), Universitätsstr. 7, Essen, D-45141, Germany; ²University of Duisburg-Essen, Microbiology II, Universitätsstr. 7, Essen, D-45141, Germany; ³West German Proton Therapy Centre Essen (WPE), 45147 Essen, Germany; ⁴West German Cancer Center (WTZ), 45147 Essen, Germany; ⁵Department of Physics, TU Dortmund University, 44227 Dortmund, Germany; ⁶German Cancer Consortium (DKTK), 45147 Essen, Germany; ⁷Department of Particle Therapy, University Hospital Essen, 45147 Essen, Germany

** Christoph.rehbock@uni-due.de*

Proton therapy (PT) is a modern form of radiation therapy, particularly useful against tumors in sensitive areas like the brain or in developing organs of children. In vitro and in vivo studies already demonstrated that metal nanoparticles (NP) can function as sensitizers in PT, generating reactive oxygen species (ROS) [1]. However, the mechanism of ROS generation during PT in the presence of NP is still underexplored. In this work we studied the effect of colloidal Pt and Au nanoparticles generated by laser ablation in liquids on ROS generation in water phantoms upon irradiation with protons at clinically relevant doses (2-5 Gy). ROS formation was monitored using fluorescent dyes as well as by a DNA breakage assay read out by gel electrophoresis. Here, the size-controlled, initially ligand-free, and sterilizable NP from laser synthesis [2] are particularly useful model materials to pinpoint fundamental mechanisms. We find a linear dependency of the ROS generation on irradiation dose and particle surface concentration [3]. However, we were also able to deduce a higher efficiency of smaller 5 nm AuNP in contrast to their 30 nm counterparts even at the same total surface area, which points at additional surface chemistry effects e.g. structural defects. This is complemented by the fact that PtNP were more active than AuNP, probably linked to the higher catalytic activity of Pt in generation of ROS [3]. In recent experiments we examined the material dependency of ROS generation in proton therapy using PtFe and PtIr alloy NPs and pinpointed the impact of stabilizing surface ligands. In particular, the commonly used sodium citrate, lead to a significant reduction in ROS generation, probably attribute to its radical scavenging properties.

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[3] Zwiehoff, S.; Johny, J.; Behrends, C.; Landmann, A.; Mentzel, F.; Baumer, C.; Kroninger, K.; Rehbock, C.; Timmermann, B.; Barcikowski, S., *Small* **18**, (2022).

Monday 11th September

WS1 & WS3 Session IV

Biocompatibility and Nanotoxicity of
Nano(bio)Materials II

Single-Cell Nanoencapsulation: Past, Present, and Future

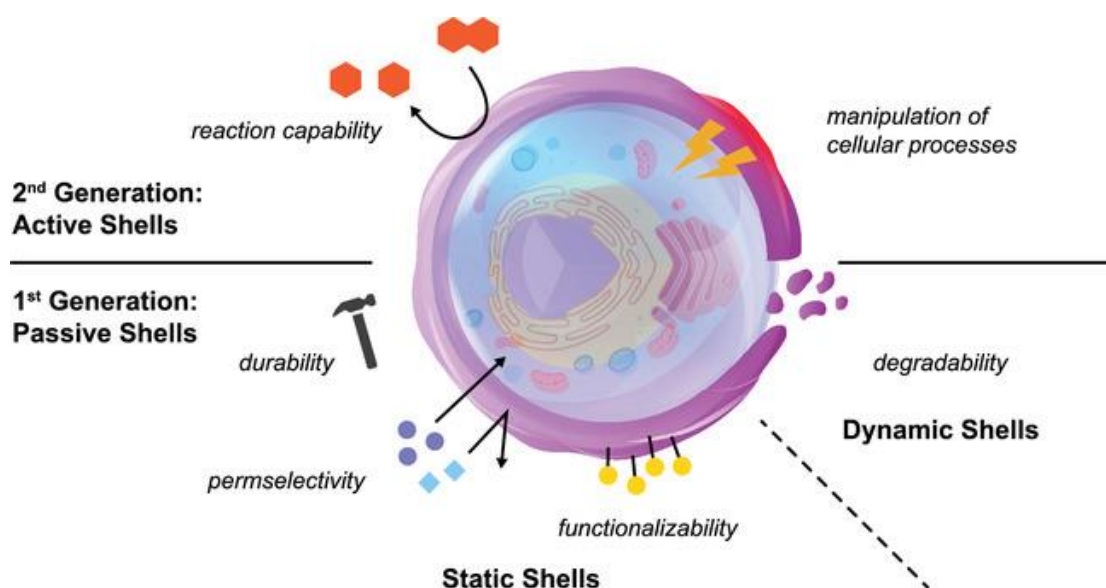
Insung S. Choi

Center for Cell-Encapsulation Research, Department of Chemistry, KAIST, Korea

* ischoi@kaist.ac.kr

Abstract:

Single-cell nanoencapsulation (SCNE) is a cytocompatible chemical strategy that physically confines individual living cells within ultrathin (preferably, < 100 nm), tough shells in three-dimensional space.^[1-3] The cellular nanobiohybrid structures, created by SCNE, have been referred to by various names, such as cell-in-shell structures, artificial spores,^[4,5] micrometric Iron Men,^[6] and micrometric Transformers. Since the concept was first introduced in 2013, the field of SCNE has rapidly grown and recently entered its second stage of development, in which the artificial shells play complementary but active roles in the innate cellular metabolism and activities, beyond merely providing protection against harmful external agents. This talk discusses a concise overview of the past, present, and future of SCNE.



- [1] I. S. Choi, et al. *Adv. Mater.* 32, 1907001 (2020).
- [2] I. S. Choi, et al. *Adv. Mater.* 30, 1706063 (2018).
- [3] I. S. Choi, et al. *Adv. Mater.* 26, 2001 (2014).
- [4] I. S. Choi, et al. *Small* 9, 178 (2013).
- [5] I. S. Choi, et al. *Trends Biotechnol.* 31, 442 (2013).
- [6] I. S. Choi, et al. *Acc. Chem. Res.* 49, 792 (2016).

Biocomposite materials in health protection

Athanassia Athanassiou^{1*}, Marco Contardi¹, Giovanni Perotto¹, Giulia Suarato¹, Martina Lenzuni¹,
Fabrizio Fiorentini¹, Luigino Criante², Maria Summa³, and Rosalia Bertorelli³

¹*Smart Materials, Istituto Italiano di Tecnologia, Genova, Italy*

²*Center for Nano Science and Technology, Istituto Italiano di Tecnologia, Milan, Italy*

³*Translational Pharmacology, Istituto Italiano di Tecnologia, Genova, Italy*

* athanassia.athanassiou@iit.it

Abstract:

Skin wound healing is among the most complex procedures of our body. The four phases that a physiological healing follows, hemostasis, inflammation, proliferation, and remodeling, are often compromised by various conditions. These include the presence of bacteria that colonize wounds causing aggressive infections, aging-related immune deficiency, diabetic hyperglycemia, hypoxia and immobility. Such conditions can obstruct the wound repairing, preventing its closure and leading to chronic wounds, dangerous for the patients and costly in terms of medical treatments.

Commercial passive dressings, such as gauzes and bandages, fail when the aforementioned complications are present. In these cases, functional dressings that can deliver effective therapeutic molecules in a controlled way to the wound, stimulating and accompanying the healing process are essential. Natural polymers are ideal candidates for smart, functional dressings. They provide a biocompatible platform with tunable biodegradability able to deliver timely the therapy, contrasting the onset of adverse events and supporting tissue regeneration. We will present various structures and compositions of bioactive materials based on natural polymers, proteins or polysaccharides, developed for efficient wound management. The presented therapeutic dressings are well-tolerated by the skin, self-adhered and mechanically ductile, while they totally biodegrade by the end of the healing process. The dressings have been evaluated in several *in vitro* models and the best ones have been validated using *in vivo* mice models related to ulcers, diabetic wounds and burns.

Moreover, biocomposite materials based on natural polymers will be presented also as biocompatible, drug-eluting, non-thrombogenic coatings for stents. Stents are routinely used for the treatment of coronary heart disease; nevertheless, complications with restenosis and stent thrombosis are still often. For this reason, the stent research is attracting growing interest regarding the development of stent coatings that controllably deliver drugs to eradicate the causes of such clinical events. We will also present a microfluidic platform that we developed to assess the behavior and hemocompatibility of the proposed biocomposite stent coatings under flow conditions.

Effect of surface topography on mechanotransduction of mesenchymal stem cells

A. Parlanis^{1,2*}, E. Kanakousaki^{1,2}, P. Kavatzikidou¹, A. Manousaki¹, E. Stratakis^{1,3}, A. Ranella¹

¹*Foundation for Research and Technology - Hellas (FORTH), Institute of Electronic Structure and Laser (IESL), Heraklion, Greece*

²*Department of Biology, University of Crete, Heraklion, Greece*

³*Department of Physics, University of Crete, Heraklion, Greece*

** andreasparlanis@yahoo.com*

Introduction: Surface topography properties are crucial for tissue regeneration, as cells make decisions based on stimulation from the extracellular matrix. TAZ and vinculin are proteins that contribute to these cell-ECM interactions. Ultrafast pulsed laser irradiation is a simple microfabrication method capable of producing isotropic or anisotropic discontinuous topographical structures with control over pattern regularity [1, 2]. Also, soft lithography has been successfully used to transfer well-defined micro-sized patterns from silicon masters to polymeric substrates [3, 4]. Mesenchymal stem cells (MSCs) hold great potential for regenerative medicine and tissue engineering as they differentiate along various lineages. The aim of this study is to evaluate the effect of the topography of polymeric replicas on MSCs morphology and osteogenic differentiation.

Experimental Methods: The replicas' topography, wettability, and degradation rate profiles were all examined. Scanning electron microscopy (SEM) was performed for the morphological characterization of the mouse mesenchymal stem cells (mMSCs) C57BL/6, as well as immunocytochemical assays that assessed the ability of mMSCs to sense and convert mechanical stimuli into biochemical signals that result in intracellular changes (mechanotransduction), focusing on vinculin protein activity, TAZ protein translocation, and ALP protein presence.

Results and Discussion: Both the topography and the CNCs gave promising hints for improving the biological performance of MSCs and triggering their differentiation into osteogenic lineages.

ACKNOWLEDGMENTS

The authors would like to thank the European Project NFFA-Europe-Pilot (n. 101007417 from 1/03/2021 to 28/02/2026) for providing financial support to this project. The authors would also like to thank Melodea Ltd, Israel for providing us the free sample of CNCs.

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Breast implants silicon outshell bioinspired multiscale engineering for preventing microbial and fibrosis development

Valentina Dinca^{1*}, Simona Nistorescu¹, Anca Bonciu¹, Andreea Negrescu², Laurentiu Rusen¹, Anisoara Cimpean²

¹ *FOTOPLASMAT center, NILPRP, Magurele, Romania*

² *Faculty of Biology, University of Bucharest, Romania*

** valentina.dinca@inflpr.ro*

Abstract:

The silicone outer shell's characteristics dictate many processes involved in breast implant integration within the body. Although no other biomaterial reveals comparable properties in terms of availability, adaptability and immunogenicity, silicone remains a foreign body that is activating the immune /inflammatory response. As a consequence, the surface of implants will be surrounded with collagen layer, or a "capsule" of scar tissue around the implant as a normal reaction of the body to the foreign materials, leading in time to capsular contracture phenomenon. Within this context, this work focusses on how to design surfaces and materials that can inhibit in vitro biofilm formation, and that can steer the inflammatory reaction by controlling behaviour of various types of cells (i.e. fibroblasts, macrophages). Various multiscaled types of PDMS microreplicated surfaces were obtained and characterized by AFM, SEM, contact angle and surface energy measurements. The surfaces were tested in contact with *Staphylococcus aureus* ATCC 25923 bacterial strain by visualizing the biofilm formation up to 25 days using electron microscopy. The growth of bacteria was compared using various surface textures, from smooth to linear topographies. The results of bacterial attachment on the surfaces showed that the microbial adhesion to the textured substrates is deficient and decreased in time, also numerous cellular remains are found on parallel continuous and interrupted linear patterns, which confirms the anti-biofilm effect of the PDMS microreplicated. Furthermore, fibroblasts and macrophages cells were exposed for 24 and 72 h to PDMS microtopographies to investigate the cell viability, morphology, proliferation and cell adhesion. The influence of the surface characteristics that provide mechanical support, determine cell shape, and allow movement of the cell surface, thereby enabling cells to migrate were investigated. Our preliminary results show that the in vitro assays revealed different fibroblasts and macrophages adherence, from cells alignment to stretching depending on the pattern disposal onto the substrates. As perspective, further molecular analysis is necessary to assess their adherence nature related to the pattern disposal onto the surface.

Calcium Phosphate NanoClay porous scaffolds promote osteogenesis and pore strain induces vascularization of included hydrogel matrix

Mistica Perez¹, Solaleh Miar^{1,2}, Alisa Isaac^{1,3}, Joo Ong^{1,3}, Rena Bizios¹, Akhilesh Gaharwar⁴, Teja Guda^{1,3}

¹The University of Texas at San Antonio, San Antonio, TX, USA.

²The University of Hartford, Hartford, CT, USA.

³University of Texas Health San Antonio, San Antonio, TX, USA

⁴Texas A&M University, College Station, TX, USA.

* teja.guda@utsa.edu

Abstract:

Hydroxyapatite (HA), a biocompatible ceramic, has been widely used in bone tissue engineering to leverage its chemical and physical resemblance to native bone mineral. HA scaffolds have been modified with different materials to improve mechanical properties and osteoconductivity. Laponite is a synthetic nanoclay shown to promote osteogenic differentiation. We developed HA-Laponite nanoclay scaffolds (from 0-50% by volume) by creating colloidal slurries and then sintering template coated polymeric foams to generate highly open, interconnected porous ceramics. Laponite nanoparticles (LNPs) were created by trimethylamine functionalizing 2D nanoclays. Control scaffolds of pure HA and 4 other groups with 5, 10, 25, and 50% of LNPs were generated by sintering. Scanning Electron Microscopy was used to evaluate pore architecture and surface grain size, XRD analysis to characterize crystallinity, elemental analysis using energy dispersive spectroscopy, mechanical testing by compression and porosity and 3D pore structure characterization were assessed using Micro computed tomography. *In vitro* evaluation was conducted by seeding samples with bone marrow human mesenchymal cells and assessing for 21 days (n=4). Immunohistochemistry imaging (Actin, DAPI, and Osteopontin), cell proliferation (Alamar Blue), and alkaline phosphatase assays were performed to evaluate the high doping of calcium phosphates with nanoclays at significant volume fractions. Optimized scaffold mechanical properties and more significantly *in vitro* cell proliferation, and osteogenic commitment were found with nanoclay compositions as high as 25% volume fraction. While there was no significant impact of incorporating nano-clays on the scaffold porosity, the functional grain size changed significantly with increasing silicates and protein adsorption as well as cellular attachment was impacted by the high surface energy of the blended ceramics. The controlled pore and interconnection architectures that can be generated using this template coating process were then demonstrated to significantly improve (at pore interconnections > 350 microns) vascularization of the scaffolds when loaded with micro vascular fragments derived from adipose tissue within fibrin hydrogels in the pores of the scaffolds.

Biodegradability improvement of bacterial cellulose-based materials

Edina Rusen¹, Gabriela Isopencu¹, Gabriela Toader², Aurel Diacon^{1,2}, Adrian Dinescu³
and Alexandra Mocanu^{1,3*},

¹University Politehnica of Bucharest, 1- 7 Gh. Polizu Street, 011061 Bucharest, Romania

²Military Technical Academy “Ferdinand I”, 39-49 George Cosbuc Av., 050141 Bucharest,
Romania

³National Institute for Research and Development in Microtechnologies (IMT-Bucharest), 126 A,
Erou Iancu Nicolae Street, 023573 Bucharest, Romania

* alexandra.mocanu@upb.ro

Abstract:

Bacterial cellulose (BC) is extracellularly produced by different Gram-negative bacterial cultures such as *Gluconacetobacter*, *Acetobacter*, *Agrobacterium* etc. [1] being one of the purest forms of cellulose found in nature. Due on its unique properties like high degree of crystallinity, high water retention (up to 98% wt.), high mechanical strength, and enhanced biocompatibility, BC attracted researchers to develop a wide range of biocompatible and biodegradable materials [2].

The aim of this study was to develop BC-based materials grafted with poly(ethylene glycol) (PEG) derivatives of different molecular weight for biodegradable packaging. The BC based polymer materials were characterized by SEM, FT-IR, contact angle measurements, TGA, tensile tests and DMA analysis.

A new degradation evaluation method was proposed in order to offer quantitative information about the degradation process in contrast with the SEM analysis, primarily used in literature. The degradation rates evidenced that the PEG derivatives of higher molecular weight grafted on the surface of BC led to an acceleration of the degradation process compared with the pristine samples.

Acknowledgement

This work was financially granted by the Ministry of Research, Innovation and Digitalisation (UEFISCDI) through PN-III-P2-2.1-PED-2021– ctr.no. 672PED/2022 and PN-III-P2-2.1-PTE-2021-0514 - contract no. 80PTE/2022.

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Development of Superhydrophobic Flexible Surfaces Utilizing Polymer Nanocomposite Coatings

Kiriaki Chrissopoulou^{1*}, Thaleia-Michaela Chatzaki^{1,2}, Franceska Gojda^{1,3}, Alexandros Thomos^{1,2}, Fanourios Krasanakis¹, Minas Stylianakis^{1,4}, and Spiros H. Anastasiadis^{1,2}

¹*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion, Crete, Greece*

²*Department of Chemistry, University of Crete, Heraklion Crete, Greece*

³*Department of Physics, University of Crete, Heraklion Crete, Greece*

⁴*Department of Nursing, Hellenic Mediterranean University, Heraklion Crete, Greece*

* kiki@iesl.forth.gr

Abstract:

The development of superhydrophobic and/or functional surfaces is attracting the scientific interest due to their broad range of applications [1]. At the same time, polymer materials with optimized properties can be prepared when nanosized inorganic materials are added to a polymer matrix resulting in a nanocomposite [2]. In this work, we report on the development of superhydrophobic and water-repellent polymer nanocomposite coatings deposited either on flexible polymer [3] or hard metal substrates by utilizing nanoadditives of different geometries and sizes, like alumina nanoparticles and/or 2D materials like Mxenes. The coating morphology and effective roughness were investigated with Scanning Electron Microscopy and profilometry, respectively, as a function of the nanoadditive content. The surface properties of the films were investigated by contact angle measurements; the water contact angle depends strongly on both the polymer and the inorganic nanoadditive utilized for the coating as well as on its composition whereas the contact angle hysteresis was significantly affected by the presence of the inorganic nanoadditives. Such coatings may be utilized as antifouling and/or antimicrobial materials.

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Tuesday 12th September

WS1 & WS3 Session II

Subtractive and Additive Manufacturing for
Biofabrication



International Conference on Nanotechnologies and Bionanoscience

Laser Printing

Boris N. Chichkov

Leibniz University Hannover, Institute of Quantum Optics, Welfengarten 1, 30167 Hannover

Abstract:

I will discuss our progress in laser-based printing technology which can be applied for the generation of complex 2D and 3D structures by printing very small and delicate objects like nanoparticles, living cells, and microorganisms. I will consider a few application examples of this technology for printing of metasurfaces, 3D scaffolds for tissue engineering, and biofabrication of biological systems.

From High-Resolution 3D Printing to Bioprinting with Multiphoton Lithography

A. Ovsianikov

*Head of the Research Group 3D Printing and Biofabrication, TU Wien
Chief Scientific Office & Founder UpNano GmbH
Austrian Cluster for Tissue Regeneration
Vienna, Austria
Aleksandr.Ovsianikov@tuwien.ac.at*

Abstract:

Various 3D Printing and Bioprinting approaches have found applications in tissue engineering and regenerative medicine (TERM). The achievable spatial resolution of the most widespread technologies, such as for example extrusion, is usually in the range of hundreds of micrometers, limited by the intrinsic attributes of these methods. However, light-based technologies and in particular multiphoton lithography (MPL) can produce features much smaller than a single mammalian cell, breaking these resolution limits [1]. Among other things, MPL has recently enabled realization of highly porous biodegradable microscaffolds capable of hosting individual cell spheroids [2]. The resulting tissue units can be used for bottom-up self-assembly of larger tissue constructs with very high initial cell density, paving a way for novel TERM approach [3]. Specialized hydrogel materials now allow MPL in the presence of living cells, placing this technology in the domain of bioprinting [4]. Furthermore, MPL is particularly suitable for realization of microstructures directly inside microfluidic devices, enabling advances on the organ-on-a-chip domain [5].

MPL opens exciting perspectives for biomedical application, ranging from production advanced microscaffolds to realization 3D biomimetic cell culture matrices. In this contribution, our recent progress on MPL development will be presented. Current state of the art, challenges and future perspectives will be discussed.

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LASER-ASSISTED CELL BIO-PRINTING AND POLYMER STRUCTURING FOR THE CREATION OF BIO-MODELS

Lucas Duvert^{1*}, Clarissa Muru¹, Stefano Testa², Adrien Casanova¹, Frédérique Magdinier², Anne-Patricia Alloncle¹

¹*Aix-Marseille University, CNRS, UMR 7341, LP3, Campus de Luminy, Case 917, 13288, Marseille cedex 9, France*

²*Aix-Marseille University, INSERM, Marseille Medical Genetics, MMG, 27 Bd Jean moulin 13385 Marseille, France*

*lucas.duvert@univ-amu.fr

Abstract:

Printing techniques applied to biology have begun to develop in the 2000s and have since been greatly improved and perfected. Based on interdisciplinary approaches they make use of cell biology, chemistry, engineering, and a combination of sophisticated protocols to create organized 2D and 3D patterns of a chosen bio-ink.

In that scope, it has been more than a decade since Laser-Induced Forward Transfer (LIFT) is studied in lab scale for its ability to print biomaterials and more specifically living cells [1]. This technique uses a short laser pulse to transfer tiny amounts of material from a thin film donor to a receptor substrate. Under appropriate conditions, the laser pulse induces the formation of a jet propagating perpendicularly to the donor substrate. The bio-ink previously spread as a thin film (few tens of microns) on this donor substrate is thus deposited as a droplet on the collector slide. In this context, at LP3 and in close collaboration with MMG, we took advantage of our expertise on LIFT process [2] to print bio-inks containing living cells for the creation of in vitro bio-models. This work will be focused on the printing of muscular stem cells and the process optimisation for stem cell differentiation. Our objective is to create a versatile tool for improving differentiation toward the skeletal muscle lineage and formation of neuromuscular junctions (NMJ).

Here, we will present the LIFT process and its optimisation allowing us to achieve a controlled, reliable, precise printing of muscle progenitor cells, ensuring a high postprinting cell survival rate and proliferation. In parallel to the printing process, laser structuration by direct laser ablation of biocompatible polymers was developed. Conditions to obtain microchannel arrays have been determined and effectively promote proliferation, adhesion, and differentiation of the cells. The nature and versatility of our experimental set up allows us to combine both processes, laser printing and laser structuration, in an extremely fast and efficient manner. The cells printed precisely in pre-made microstructured channels shows higher differentiation rate and alignment according to the channels orientations. Besides being able to print living cells, we can reproducibly produce muscle fibres of about 200µm width and several millimetres long from human myoblast cells.

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Flexible 2D and 3D conductive hydrogel platforms for wearable applications

Leonor Aguiar¹, Raquel Pereira¹, Sanjiv Sharma² and Gabriela Martins^{1,3*}

¹*BioMark@ISEP-CEB/LABBELS, School of Engineering, Polytechnic of Porto, R. Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal*

²*Department of Biomedical Engineering, Faculty of Science and Engineering, Swansea University, Swansea SA1 8EN, U.K.*

³*CIETI - LabRISE-School of Engineering, Polytechnic of Porto, R. Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal*

* Email: fym.gabriela@gmail.com

Abstract:

Hydrogels have risen as exceptionally promising support materials in the development of novel wearable electronic devices. Their remarkable biocompatibility coupled with customizable mechanical features make these biomaterials ideal choices for applications involving direct contact with biological tissues.

In this study, a simple and straightforward manufacturing process using bio-sourced polysaccharide chitosan (Chi) was employed for the fabrication of flexible and transparent biopolymeric membranes. Subsequently, this two-dimensional (2D) platform was made conductive, through a one-step process, by utilizing an optimized ratio of chitosan, lactic acid, and silver nanowires (Chi-LaA-AgNWs) dispersion. These electrodes were produced by screen printing technique. Furthermore, a solvent casting technique employing inverse polydimethylsiloxane (PDMS) molds was used to fabricate mechanically stable chitosan microneedles (Chi-MNs). These three-dimensional (3D) structures were enriched with a carbon-based ink during the casting of concentrated Chi hydrogels into the mold while utilizing centrifugal forces.

The electrochemical properties of the fabricated 2D and 3D conductive platforms were evaluated through cyclic voltammetry (CV). Along this study, the water swelling properties of Chi hydrogels were investigated by incorporating natural crosslinkers and plasticizing compounds like citric acid, glycerol, and sorbitol. Optimization of fabrication, physico-chemical and morphological analysis of the membranes and MNs were also performed. Ultimately, the use of Chi combined with environmentally friendly agents enabled the fabrication of flexible conductive platforms holding good stability, uniformity, and desirable electrical attributes.

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4D PRINTED SCAFFOLDS COMPOSED OF NATURAL POLYMERS FOR BONE TISSUE ENGINEERING

P. Daskalakis^{*1,2}, C. Ntoulis¹, E. Kanakousaki^{1,4}, L. Chaniotaki^{1,5}, A. Lamprakis^{1,2}, P. Kavatzikidou¹, A. Manousaki^{1,3}, A. Ranella¹, E. Stratakis^{1,3}

¹Foundation for Research and Technology - Hellas, Heraklion, Greece

²University of Crete, School of Medicine, Heraklion, Greece

³University of Crete, Department of Physics, Heraklion, Greece

⁴University of Crete, Department of Biology, Heraklion, Greece

⁵University of Crete, Department of Materials Science, Heraklion, Greece

* daskalakispanagiotis@iesl.forth.gr

Abstract:

A recent advancement of 3D printing technology is 4D printing. This new technology may not only overcome the general limitations of 3D bioprinting but also mimic the sophisticated dynamics of native tissues and improve the functional responses of constructed tissue. The state-of-the-art 4D fabricated scaffolds possess anisotropic architecture, and thus achieving a maximum, multidirectional 4D transformation. Novel 4D dynamic process using laser-induced graded internal stress characterized as beyond 4D bioprinting will provide great inspiration for not only medical devices. [1] So far, most reported 4D printing studies have disregarded the biocompatibility of the materials, and the external stimuli that has been used, has sometimes been too harsh for tissue engineering applications. [2] In this study, a parametric fluid-deposition-modeling (fluid form) and a fused-deposition-modeling (filament form) (FDM) 4D printing system was developed with the external stimuli to be the laser source, which can print/pattern scaffolds in room temperature in order to i) mimic nature and the topographical micro-environment of native tissue and ii) at the same time develop advance functional materials for tissue engineering applications such as bone/cartilage - mimetic scaffolds. [3] The 4D scaffolds will consist of natural materials such as cellulose and synthetic materials e.g. polycaprolactone with an anisotropic/isotropic architecture in order to be transformed under graded internal stress. The morphological characterization of the 4D scaffolds was performed by Scanning Electron Microscopy (SEM) imaging. Finally, preliminary cell studies were conducted to test the cytocompatibility of the scaffold and the material which constitutes.

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3D printing of polylactic acid/cuttlefish bone biocomposites

Aikaterini Gialouri^{1*} and Nikolaos Bouropoulos^{1,2}

¹ Department of Materials Science, University of Patras, 26504 Rio, Patras, Greece ² Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Chemical Processes, 26504 Patras, Greece

* katerinagialoyri@gmail.com

Abstract:

Marine by-products derived from shrimps, crabs, squids, lobsters, cuttle fishes, etc. create a large number of wastes causing environmental and financial effects. The management of these products leads not only to the reduction of wastes but also to the production of useful materials. For example, shrimp and crab shells are used for chitin production. Cuttlefish bone is a porous material made of aragonite, a calcium carbonate polymorph. Calcium carbonate forms three crystalline polymorphs which are calcite, aragonite and vaterite. Calcite is the thermodynamically most stable form of calcium carbonate and is found in abundance in nature. Aragonite is a common skeletal mineral in marine organisms. Calcium carbonates have been used widely as fillers in polymer biocomposites. The scope of this work is to show the use of cuttlebones on the formation of biocomposites made of the thermoplastic and biodegradable polymer polylactic acid. More specifically, the present work includes a) Purification and characterization of aragonite powder from cuttlefish bones, b) Preparation and characterization of pure PLA and composite PLA/aragonite filaments c) 3D printing and characterization of pure PLA and composite specimens using the fused filament fabrication (FFF) technology. All materials are characterized by DSC, TGA, XRD, SEM and FTIR spectroscopy. Furthermore, water contact angle measurements were performed on flattened filaments, while biodegradability of the PLA biocomposites was studied *in vitro* after immersion of the printed objects in Ringer's solution. It was found that alkaline treatment of cuttle fish bones in boiling NaOH followed by immersion in boiled methanol led to the removal of organic materials and other impurities. Furthermore, filament formulations containing 2.5, 5.0 and 10 % w/w of aragonite were prepared, and finally porous specimens were manufacturing successfully using the 3D FFF method. Water contact angle measurements showed that that PLA/aragonite filaments exhibited more hydrophilic behaviour in comparison with the pure PLA filaments. Finally, *in vitro* biodegradation studies pointed out that all specimens showed a good level of biodegradation after immersion in Ringer's solution. The produced biocomposites need to be further investigated as promising candidates for applications in tissue engineering applications.

Sub-diffractive optical lithography beyond acrylates

Sourav Islam, Georgii Gvindzhiliia, and Thomas A. Klar*

*Institute for Applied Physics, Johannes Kepler University Linz, 4040 Linz, Austria **

thomas.klar@jku.at

Abstract:

Stimulated emission depletion (STED) proved to break the diffraction limit of resolution in fluorescence microscopy. Besides, it was proposed already in 1999 that the STED-confined excitation volume should be applicable to spatially control chemical reactions on the nanometre scale.¹ Meanwhile, this prediction has been experimentally realized using radical polymerization of negative tone resists, most of them (meth)acrylates.²⁻⁴ Recent progress has been made in finding an optically depletable starter which shows only low autofluorescence in the visible spectrum, so that it can be used to construct scaffolds for biomedical applications which do not optically interfere with fluorescent tags.⁵

To the best of our knowledge, this concept has not been transferred to optical nanolithography using cationic polymerization, so far. This is a great pity, because, for instance, epoxy-based resins define today's clean-room standard and, in case of biomedical applications, are less cytotoxic than acrylates. Most recently, we have managed to find a formulation of cationic epoxy resins which allow for STED-inspired optical lithography using visible and near-IR wavelengths.⁶ Besides, we also found a formulation for the class of poly-thiophenes with which we wrote substantially sub-diffractive lines.⁷

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Tuesday 12th September

*WS1 Session IV – **BRIDGE** Session*

Colloidal perovskites and quantum dots



International Conference on Nanotechnologies and Bionanoscience

Halide Perovskite and Perovskite-Related Nanocrystals: Synthesis, Encapsulation, Reactivity

Liberato Manna

Istituto Italiano di Tecnologia, Via Morego 30, 16163, Genova (Italy)

* liberato.manna@iit.it

Abstract:

Halide perovskite semiconductors can merge the highly efficient operational principles of conventional inorganic semiconductors with the low-temperature solution processability of emerging organic and hybrid materials, offering a promising route towards cheaply generating electricity as well as light. Following a surge of interest in this class of materials, research on halide perovskite nanocrystals (NCs) has gathered momentum in the last years. While most of the emphasis has been put on CsPbX₃ perovskite NCs, more recently the so-called double perovskite NCs, having chemical formula A⁺₂B⁺B³⁺X₆, have been identified as possible alternative materials, together with various other metal halides structures and compositions, often doped with different elements. This talk will discuss the synthesis efforts of our group on these materials. The talk will also highlight the techniques developed in our group to encapsulate these materials in various hosts to make them stable for various applications (lighting, biolabeling, etc.) and the reactivity of metal halide nanocrystals in general.

Colloidal Halide Perovskite Nanocrystals: Newly Emerged Sources for Polarized Light Emission

Lakshminarayana Polavarapu

CINBIO, Universidade de Vigo, Materials Chemistry and Physics Group, Department of Physical Chemistry, Campus Universitario Lagoas, Marcosende, 36310 Vigo, Spain E-mail: lakshmi@uvigo.es

Abstract:

Over the last 7-8 years, lead halide perovskite nanocrystals (LHP NCs) have emerged as extremely efficient light sources with color-tunable capability by simple chemistry.¹ LHP NCs exhibit very high photoluminescence quantum yields regardless of the synthesis conditions and the quality of the precursors owing to their defect tolerance nature (especially the Br and I-based). The light emission of LHP NCs is not only tunable by their dimensions and composition² but also through self-assembly into ordered architectures.¹⁻⁴ Interestingly, LHP NCs spontaneously self-assemble into superlattices and exhibit interesting optical properties.⁵ For instance, they emit circularly polarized light when the particles are assembled into chiral architectures.⁵ Similarly, when colloidal perovskite nanoplatelets are assembled into superlattices, they emit linearly polarized emission. This talk will be focused on the self-assembly of LHP NCs to generate interesting optical features ranging from amplified spontaneous emission to linearly- and circularly polarized emission with high dissymmetry factors.

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Colloidal Semiconductor Nanocrystals: From Artificial Atoms to Artificial Molecules

Uri Banin

*Institute of Chemistry and the Center for Nanoscience and Nanotechnology,
The Hebrew University of Jerusalem, Jerusalem 91904, Israel.*

Email: uri.banin@mail.huji.ac.il

<https://openscholar.huji.ac.il/baningroup/home>

Colloidal semiconductor Quantum Dots (CQDs), often considered as artificial atoms, have reached an exquisite level of control, alongside gaining fundamental understanding of their size, composition and surface-controlled properties. Their tuned characteristics and scalable bottom-up synthesis accompanied by the applicability of solution based manipulation, have led to their wide implementation in displays, lasers, light emitting diodes, single photon sources, photodetectors and more.¹

For the next step towards enhancing their functionalities, inspired by molecular chemistry, we introduce the controlled linking and fusion of two core/shell quantum dots creating an artificial molecule manifesting two coupled emitting centers.² The size effect and mechanism of the fusion reaction reveals an interesting behavior of atomic migration allowing to create a crystalline connection between the two emitting centers.³ The nature of the fusion interface between the two emission centers is found to strongly affect the optoelectronic characteristics.⁴ Accordingly, the coupled colloidal quantum dot molecules (CQDMs) present novel behaviors differing than their quantum dot building blocks. Notably, such CQDMs open the path to a novel electric field induced instantaneous color switching effect, allowing color tuning without intensity loss, that is not possible in single quantum dots. All in all, such quantum dot molecules, manifesting two coupled emission centers, may be tailored to emit distinct colors, opening the path for sensitive field sensing and color switchable devices such as a novel pixel design for displays or an electric field color tunable single photon source.

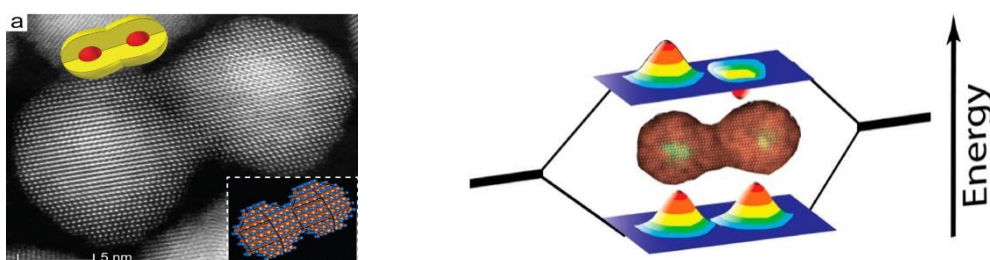


Fig. 1: Coupled homodimer molecule formed by fusing two core/shell colloidal quantum dots. Left: A high resolution electron microscopy image. Right: illustration of the hybridization of the electron wavefunction.

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Laser-assisted Processes on Metal Halide Perovskite Nanocrystals: Shape/Dimensionality Transformations and Conjugation with 2D Materials

K. Brintakis^{1,*}, A. Kostopoulou¹, E. Stratakis^{1,2}

¹ *Institute of Electronic Structure and Laser, Foundation for Research and Technology - Hellas, Heraklion, Crete, Greece*

² *Physics Department, University of Crete, Heraklion, Crete, Greece*

** kbrin@iesl.forth.gr*

Abstract:

It is well-known in our days that the metal halide perovskites are promising materials for various applications due to their tunable optical and electronic properties. In this work, we explore the use of photonic processes in colloids to create and modify metal halide perovskite nanocrystals of different shapes and sizes. These processes include photothermal, photochemical or photophysical effects induced by ultrashort-pulsed laser irradiation. Compared to other materials, metal halide perovskites have received little attention in laser-based nanocrystal fabrication and modification. The existing works mainly involve pulsed laser fragmentation of powders or anion exchange with halides from the solvent. The interactions of laser photons with these materials in nanoscale are poorly understood.

The usual method of chemical synthesis can produce various shapes and structures of perovskite nanocrystals by adjusting the reaction conditions, such as the precursor ratio, the reaction time, the ligand amount and the synthesis temperature. However, this approach requires multiple syntheses to obtain different morphologies for comparison purposes, which is time- and resource-intensive. We present a simple and fast method to alter the shape and dimensionality of perovskite nanocrystals by a single-step laser irradiation of their colloids at room temperature. [1] We also show how to achieve photo-induced conjugation of perovskite nanocrystals with 2D materials by a similar method [2], capable to be used as energy storage materials.

This method offers a unique opportunity for the cost-effective production of single- or multi-phase nanostructures with tunable size, shape, and dimensionality. It also enables new studies on the effects of dimensionality and morphology on the physical properties and the synergy between different materials.

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Acknowledgments

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The role of doping in all-inorganic mixed-halide perovskites for ozone sensing

A. Argyrou^{1,2,*}, K. Brintakis¹, E. Gagaoudakis¹, V. Binas¹, R. Giappa³, I. Remediakis³, A. Kostopoulou¹, E. Stratakis¹

¹ Institute of Electronic Structure and Laser, Foundation for Research & Technology- Hellas, P.O. Box 1527, Vassilika Vouton, 70013 Heraklion, Greece

² University of Crete, Department of Chemistry, Vassilika Vouton, 70013 Heraklion, Greece

³ University of Crete, Department of Material Science and Technology, Vassilika Vouton, 70013 Heraklion, Greece *

kargyrou@iesl.forth.gr

Abstract:

The high demand for detecting and monitoring air pollutants, toxic and explosive gases has led to major advances in gas sensing technologies. Gas sensors exhibit various commercial and industrial applications including air-quality monitoring, medicine and agriculture. Therefore, the development of novel materials that would provide new opportunities in terms of sensitivity, selectivity and stability is essential. However, in order to achieve that, further research into the fundamental principles of the underlying sensing mechanism is required.

Recently, metal halide perovskites have emerged as potential gas sensing elements due to their ability to convert environmental stimulus to electrical or optical signal. In these directions, our group has demonstrated that ligand-free perovskite microcrystals (μ Cs) exhibit enhanced O_3 sensing capability under ultra-low gas concentrations, surpassing the performance of perovskite thin films.¹ Therefore, our current focus is to investigate the underlying sensing mechanism, and particularly the role metal cations and halide anions in O_3 sensing. For this purpose, Mn-doped $CsPbX_3$ mixed halide μ Cs were fabricated under ambient conditions by a cost-effective precipitation-based method. The sensing performance of the μ Cs was explored by electrical measurements at room temperature operating conditions. Interestingly, the sensing behavior was found to be strongly influenced by the nature of halides in the crystal lattice, while significant differences in the performance of μ Cs were observed over time. In addition, to gain deeper insights, we employed a combination of surface analytical techniques and theoretical modeling, which revealed polymorphic transitions of perovskite materials upon time. These structural changes proved the crucial role of metal cations and halogen defects in O_3 sensing. Consequently, this work provides fundamental details about the underlying sensing processes and valuable information about the degradation mechanism of perovskite μ Cs. Moreover, our findings offer new opportunities for developing innovative sensing elements.

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Metal Halide Perovskites as Gas Sensing Elements: From Micro to Nano

Konstantina Alexaki^{1*}, Athanasia Kostopoulou¹, Konstantinos Brintakis¹, Aikaterini Argyrou^{1,2}, and Emmanuel Stratakis^{1,3}

¹*Foundation For Research And Technology Hellas (FORTH), Institute Of Electronic Structure & Laser (IESL), Heraklion, Greece*

²*University of Crete, Department of Chemistry, Heraklion, Greece*

³*University of Crete, Department of Physics, Heraklion, Greece*

* alexaki@iesl.forth.gr

Abstract:

Metal halide perovskite materials have captivated scientific and technological attention due to their intriguing optoelectronic properties. Composition, chemical phases, morphology and size are among the features that heavily influence these properties. Recently, these materials have been explored as potential gas-sensing elements to detect and monitor flammable, toxic and harmful gases due to their ability to change their optical and electronic properties in response to external stimuli [1]. Perovskites in the form of films or microcrystals have been found that can detect ultra-low concentrations of gases such as ozone or hydrogen [2, 3]. Our group reported that ligand-free CsPbBr₃ microcrystals could detect ozone and hydrogen down to 4 ppb and 1 ppm, respectively [3, 4].

Motivated by these results, the use of perovskite nanocrystals can potentially provide more active sites for proton incorporation/gas vacancies at the surfaces due to the increase in their surface area. This could lead to an improvement in gas detection. According to these lines, we present a method towards developing nanosized CsPbBr₃ perovskites free of ligands to improve the sensing capability against ozone. By following a solution-based precipitation method at room temperature it is possible to tune the size of the CsPbBr₃ crystals without the use of ligands. Finally, this work deals with investigating the defects' role by treating the surface of the crystals in the sensing capability. This study could constitute a unique knowledge of how to alter the known materials to improve their sensing properties or even explore new elements.

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Acknowledgments:

This work was funded under the framework of project PeroGaS - ERA-NETS 2019b (MIS 5070514) and EU project BRIDGE (G.A.: 101079421).

Materials modeling for environmental catalysis: from metal nanoparticles to halide perovskites

Rafaela Maria Giappa^{1*}, Apostolos Pantousas¹, Constantinos C. Stoumpos¹, George Kopidakis^{1,2} and Ioannis N. Remediakis^{1,2}

¹*Department of Materials Science and Technology, University of Crete, Heraklion, Greece*

²*Institute of Electronic Structure and Laser, Foundation of Research and Technology (IESL-FORTH), Heraklion, Greece*

* rafaelagiappa@materials.uoc.gr

Abstract:

Two urgent, interconnected problems of our times are the exhaust of conventional energy resources and the need to reduce CO₂ emissions and move towards a sustainable carbon emission free economy. Environmentally-friendly reduction of CO₂ to fuels might serve as a solution to both problems. The use of electrocatalysis or photocatalysis for this reaction will result in green fuel production that could rely on renewable energy sources alone. Up to now, CO₂ reduction is at the forefront of catalysis science and is challenged by selectivity and stability issues in the existing catalytic materials and processes. Aiming to design optimized anode materials for electrochemical CO₂ reduction to fuels, we explore the catalytic properties of two classes of materials, transition metals and perovskite semiconductors, by means of Density Functional Theory (DFT) calculations. Starting with the best-known catalyst for CO oxidation towards CO₂ which is gold nanoparticles [1], we discuss energetics of the reactions and provide insights on how different alloy compositions affect selectivity towards particular reaction products. For the second family of materials, metal halide perovskites can be tailored to the needs of each specific photoelectrocatalytic process [2]. We focus on the optoelectronic properties of their dimensionally reduced 2D homologous series with bulky hydrophobic cations between the sheet-like perovskite layers and comment on their potential uses in environmentally-friendly catalytic processes.

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Wednesday 13th September

WS1 & WS3 Session I

NanoMedicine



International Conference on Nanotechnologies and Bionanoscience

Nanotechnology Approaches for Biology and Medicine

Paul Weiss

University of California Los Angeles

Abstract:

Biology functions at the nanoscale. Thus, there are special opportunities not only to make biological measurements using nanotechnology, but also to interact directly in order to influence biological outcomes. I describe how we fabricate and use nanostructures to advance high-throughput gene editing for cellular therapies targeting genetic diseases and cancer immunotherapy. We also use microfluidics and functionalized nanostructured features in the selective capture, probing, and release of single circulating tumor cells in liquid biopsies in order to diagnose cancers and to assess the efficacy of treatments. We exploit molecular recognition and phase transitions to create molecular treadmills to grow three-dimensional co-cultured organoids efficiently. We exploit supramolecular assembly, acoustofluidics, specific surface functionalization, and plasmonics to enable these processes. Nanoscience and nanotechnology developed from chemistry, physics, biology, engineering, medicine, toxicology, and a host of other fields. Along the way, we taught each other our problems, challenges, and approaches. The interdisciplinary communication skills that were developed and are now part of our training remain unique to the field. As a result, nanoscience contributes to a wide range of other fields, such as neuroscience, the microbiome, oncology, cellular agriculture, and more.

Mapping the protein corona around endocytosed nanoparticles

Wolfgang J. Parak^{1*}, Neus Feliu²

¹*Universität Hamburg, Hamburg, Germany*

²*Zentrum für Angewandte Nanotechnologie CAN, Fraunhofer-Institut für Angewandte Polymerforschung IAP, Hamburg, Germany*

* wolfgang.parak@uni-hamburg.de

Abstract:

When cells internalized nanoparticles via endocytosis this involves also proteins bound to the surface of the nanoparticles. After internalization, the original protein corona may be partly exchanged. In case the proteins bear labels providing contrast for imaging, the in vivo distribution of the originally bound proteins as well as the one of the nanoparticles can be determined. This can be done for example with fluorescence or Xray fluorescence based method. Colocalization analysis then provides information about the degree in which the original protein corona is retained.

Quantitative analysis of the size dependency for cellular entry and excretion of colloidal nanoparticles

Neus Feliu^{1*}, Wolfgang J. Parak²

¹Zentrum für Angewandte Nanotechnologie CAN, Fraunhofer-Institut für Angewandte Polymerforschung IAP, Hamburg, Germany ²Universität Hamburg, Hamburg, Germany

* neus.feliu@physnet.uni-hamburg.de

Abstract:

Most studies about the interaction of nanoparticles (NPs) with cells are focused on how the physicochemical properties of NPs will influence their uptake by cells. However, much less is known about their potential excretion from cells. In order to control and manipulate the number of NPs in a cell however both, cellular uptake and excretion need to be studied quantitatively. Monitoring the intracellular and extracellular amount of NPs over time (after residual non-internalized NPs have been removed), enables to disentangle the influence of cell proliferation and exocytosis, which are the major pathways for the reduction of NPs per cell. Proliferation depends on the type of cells, and exocytosis depends in addition to the type of cells also on the properties of the NPs, such as their size. Examples are given on the role of these two different processes for different cells and NPs.

Cell specific targeting of Lipid Nanoparticles

Panagiota Papadopoulou¹, Gabriela Arias-Alpizar², Rianne van der Pol¹, Niek van Hilten¹, Winant van Os¹, Mohammad-Amin Moradi³, Nico Sommerdijk³, Jordi Llop⁴, Jelger Risselada¹, Agur Sevink¹, Frederick Campbell¹ and Alexander Kros¹

¹*Leiden Institute of Chemistry, Leiden University, the Netherlands*

²*Leiden Academic Center of Drug Research, Leiden University, the Netherlands*

³*Eindhoven University of Technology, the Netherlands*

⁴*CIC biomaGUNE, Basque Research and Technology Alliance, Spain*

p.papadopoulou@lic.leidenuniv.nl

Abstract:

Lipid-based nanoparticles are the most clinically advanced drug delivery systems. However, a persistent and limited understanding of the key nano-bio interactions, has so far stymied progression from empirical discovery towards rational nanoparticle design. Therefore, it becomes clear that there is a need for a deeper understanding of the mechanistic behavior of lipid-based nanoparticles in vivo and for detailed observation of the biological interactions introduced once nanoparticles enter the body. Here, we present the in vivo behavior of a simple, two-component liposome formulation, capable of specifically accumulating in subsets of endothelial cells of embryonic zebrafish.¹ At this developmental stage, these cells highly express enzymes involved in lipoprotein transport and metabolism, namely triglyceride (TG) lipases. A detailed characterization of the nanoparticle using cryo-transmission electron microscopy revealed a unique phase-separated morphology, bearing a single lipid droplet within each phospholipid leaflet, which interacts with the membrane bound TG lipases. This interaction plays a key role on the internalization of these nanoparticles within the TG-lipase rich cells and can be partially inhibited by a lipase inhibitor in zebrafish embryos and mice. When incubated with TG-lipase, we find that the phase separated liposomes undergo selective lipolytic degradation of their lipid droplet while overall nanoparticle integrity remains intact.² We additionally show how the phase-separated morphology can be used in mRNA-LNPs for specific mRNA delivery and transfection of endothelial cells in zebrafish embryos. Overall, in this study we dissect and connect nanoparticle composition, morphology, and protein function to provide a comprehensive picture of a specific nanoparticle-protein communication. Understanding the interface of lipid-based nanoparticles with biologically relevant proteins is essential to comprehend their overall in vivo behavior. This will eventually lead to rational design of such lipid nanoparticles for biomedical applications with an enhanced in vivo function.

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* Equal contribution

Vcam-1 expression screening for therapeutic and diagnostic purposes

Maria Grekioti^{1*}, Lina Papadimitriou¹, Eirini Koutsouroubi¹, Yannis Papaharilaou³ Alexandros Lappas¹ and Anthi Ranella¹

¹ IESL FORTH, Heraklion, Greece

³ IACM FORTH, Heraklion, Greece

* mariagraik@gmail.com

Abstract:

Atherosclerosis is a leading cause of cardiovascular disease. This progressive chronic disease is characterized by the formation of atheromatous plaque in the inner lining of the arterial wall, necessitating the development of non-invasive imaging techniques for early detection and effective management. Several invasive and non-invasive imaging techniques have been developed for the detection and characterization of atherosclerosis in the vessel wall: anatomical/structural imaging, functional imaging and molecular imaging. Vascular cell adhesion molecule-1 (VCAM-1) has emerged as a promising molecular target due to its involvement in leukocyte adhesion and transendothelial migration, key processes in atherosclerotic plaque formation.

In this study, we aimed to investigate the behavior and efficacy of VCAM-1-targeted nanoclusters under conditions of orbital shear stress, mimicking the hemodynamic forces present in the vasculature, to evaluate their potential as theragnostic agents for atherosclerosis. We synthesized biocompatible nanoclusters conjugated with VCAM-1-targeting ligands, which exhibited excellent stability and specific binding to VCAM-1 in vitro. The binding affinity and selectivity of the nanoclusters were assessed using VCAM-1 expressing MSCs. Confocal microscopy demonstrated significant binding of the VCAM-1-targeted nanoclusters to the VCAM-1-expressing cells under orbital shear stress conditions compared to static conditions, suggesting increased targeting efficiency in the presence of shear forces. Moreover, we assessed the internalization and intracellular trafficking of the nanoclusters using confocal microscopy.

Acknowledgements: This work was supported by the LaMIA project funded by “Theodore Papazoglou” FORTH synergy grants.

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Nanocomposite cell culture substrates produced by printed electronics techniques for cell stimulation

Łucja Dybowska-Sarapuk^{1*}, Weronika Sosnowicz¹, Paulina Trzaskowska¹, Anna Grzeczkwicz²,
Małgorzata Jakubowska¹

¹*Centre for Advanced Materials and Technologies Warsaw University of Technology, Warsaw, Poland*

²*Nalecz Institute of Biocybernetics and Biomedical Engineering, Polish*

Academy of Sciences, Warsaw, Poland

** Lucja.Sarapuk@pw.edu.pl*

Abstract:

Nanomaterials, with their special properties such as dimensions, shape, surface area, and potential for functionalization have gained significant attention in the field of biomedical engineering. Carbon nanomaterials, especially graphene, have emerged as a promising area of research in the field of **tissue engineering**. Cell growth stimulation is a crucial aspect of promoting tissue growth outside the human body, and can be often very challenging and expensive. Recently, nanomaterials are studied as specific growth factors stimulating the adhesion and proliferation of cells [1]. In addition, nanomaterials in a substrate are able to support the most important life functions of cells. In this way, these substrates support their most important life functions. By employing **printed electronics techniques** and nanomaterial compositions, it is possible to create specialized layers and substrates **to stimulate cell growth** [2]. Achieving this requires using specially prepared compositions that meet both technical (good ink dispersion, rheology adapted to the printing technique) and biological (cytocompatibility) requirements [3]. Depending on the printing technique, the developed nanocomposite material can be used to produce surfaces – layers/coatings, or special patterns with a resolution in the range of several tens of micrometers. These **surfaces** can be effectively used in cellular **electrostimulation** which is especially important in nerve cell stimulation [4]. According to the literature, **patterns** printed from nanomaterial composites could be a simple way to stimulate stem cell **differentiation** into various cell types [5].

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Evaluation of intra- and extracellular pH detection capabilities of plasmonic nanoprobes

Gail A. Vinnacombe-Willson¹ and Luis M. Liz-Marzán^{1,*}

¹ *BioNanoPlasmonics Laboratory, CIC biomaGUNE, Basque Research and Technology Alliance (BRTA), 20014 Donostia-San Sebastián, Spain* *

gvinnacombe@cicbiomagune.es

Abstract:

Thus far, surface-enhanced Raman scattering (SERS) pH-sensors based on plasmonic gold nanoparticles have been developed and employed in 2D culture and 3D platforms/tissues.^{1,2} These SERS nanoprobes are especially relevant for implementation in cancer cell cultures and tumor models since cancer cells maintain a more alkaline internal pH (pHi) and more acidic external pH (pHe) compared to healthy cells.³ However, recent works identify that inaccuracies in the extrapolated pH may arise depending on the method by which the probes are calibrated and the strength of the Raman background of the sample.^{4,5} Here, we fabricate two varieties of nanoprobes with intense plasmonic responses and evaluate their optimal working range. For each type of pH probe, we identified several SERS peaks that change in intensity with response to pH. We then evaluated and compared different analytical methods (*i.e.*, ratiometric methods, principal component analysis) to estimate pH in biologically relevant systems: within breast cancer cells and in biocompatible hydrogels (commonly utilized for the fabrication of bulk and 3D printed tumor models). Ultimately, improving the precision and accuracy of real-time SERS-based pH measurements can enable cancer cell growth and proliferation tracking in 3D tumor models or facilitate the screening of therapeutics that disrupt pH regulation, for example.³

Acknowledgements:

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Wednesday 13th September

WS1 & WS3 Session III

Advanced Diagnostics and Nanocharacterisation I



International Conference on Nanotechnologies and Bionanoscience

Sustainable nanobiosensors for diagnostics

Arben Merkoçi

Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain.

ICREA - Institutio Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain

e-mail: arben.merkoci@icn2.cat

Abstract:

Health care system as well as environment worldwide are facing several challenges. Aging of the population, chronic disease, spending on health, pandemics, environment pollution request a novel generation of diagnostics platforms. While conventional labs and their clinical analysis instruments are quite important given their sensitivity, information capability including their suitability for basic research they still suffer from issues such as their high costs, being time consuming, requesting sophisticated equipment, trained users, certain facilities etc. Point of care devices (POC) are a great alternative to face overall urgent needs but also for our everyday health care and environment control. The development of POCs is one of the most important R&D in the areas of health diagnostics, environment control, safety/security control of food. The demand to develop innovative, cost effective and sustainable devices and fabrication technologies with interest for health and environment care is increasing day by day. The development of such devices is strongly related to new materials and technologies being nanomaterials and nanotechnology of special role. These devices should be REASSURED: Real-time connectivity, Ease of specimen collection, Affordable, Sensitive, Specific, User-friendly, Rapid, Robust, Equipment-free, Delivered to those who need it. How to design simple plastic/paper-based biosensor architectures including wearables through printing or stamping? How to tune their analytical performance upon demand? How one can couple nanomaterials with paper/plastics and what is the benefit? Which are the perspectives to link these simple platforms and detection technologies with mobile communication? I will try to give responses to these questions through various interesting examples with extreme interest for clinical and environment emergency applications that include important biomarkers (ex. cancer cells, virus etc.) as well as highly toxic compounds in environment (heavy metals, pesticides). These devices and corresponding technologies are related to ubiquitous fabrication methods that would be quite important for democratizing diagnosis and improving healthcare coverage as well as environment monitoring industry.

Graphene oxide electrodes for bio-sensing and bio-stimulation

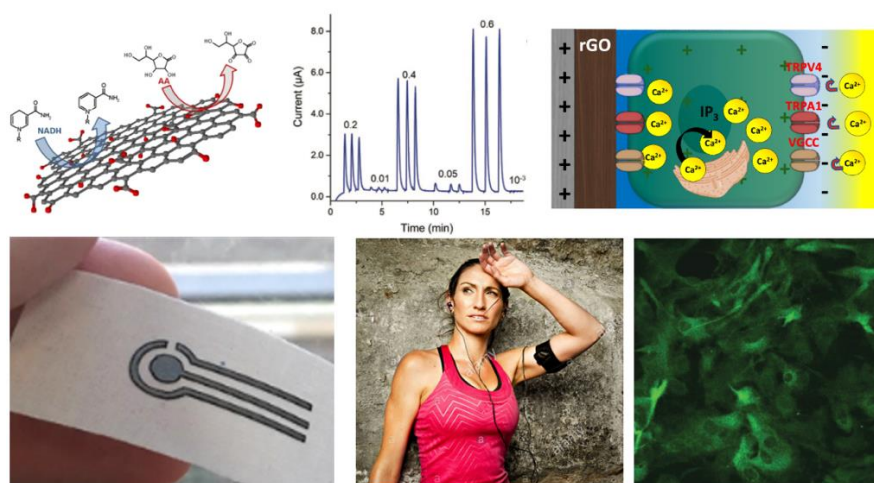
Vincenzo Palermo^{1,2,*}, Roberta Fabbri¹, Alessandro Kovtun¹, Diletta Spennato¹, Giorgia Conte¹, Andrea Candini¹, Filippo Valorosi¹, Emanuela Saracino¹, Katerina Konstantoulaki¹, Chiara Lazzarini¹, Manuela Melucci¹, Emanuele Treossi¹, Chiara Zanardi^{1,3}, Valentina Benfenati

¹ Institute for Organic Synthesis and Photoreactivity (*ISOF*), National Research Council of Italy (CNR), Bologna, Italy. ² Department of Industrial and Materials Science, Chalmers University of Technology, Gothenburg, Sweden. ³ Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Venice, Italy.

* Vincenzo.palermo@isof.cnr.it

Abstract:

Electrodes for bio-sensing or brain stimulation are typically made of conventional materials like metals or conductive carbon inks. Several works published in last years by us and other groups demonstrated how graphene, and in particular graphene oxide (GO), can be used as electrodes for sensing with a greater processability, tunability and efficiency than standard materials. Thanks to their 2-dimensional nature, GO nanosheets are ideal substrates to foster the adsorption of bio-molecules on their surface, allowing the oxidation of the target molecules at low potential values, with a sensitivity much higher with respect to standard, carbon-based electrode materials. GO can be processed in water, coated on different substrates together with other electro-active materials, then reduced to RGO to stabilize it on the substrate. The oxygen-containing defects on the surface of GO can be used to functionalize it with specific molecules, to enhance interaction with specific analytes, and thus maximize sensing selectivity. Besides interaction with single molecules, graphene and GO feature also unique interaction with whole cells, fostering their adhesion and viability for sensing and stimulation. In particular, we recently demonstrated that GO and RGO can trigger selectively different intracellular responses in brain cells called astrocytes, in vitro and in brain slices, depending on the electrical properties of rGO/GO interfaces.



Augmentation of the Standalone Multiplexed Extended-Gate Field-Effect Transistor Immunosensor Response with Gold Nanoparticle/Antibody Bioconjugates

Željko Janićijević^{1*}, Trang-Anh Nguyen-Le¹, Ahmed Alsadig¹, Rugilė Žilėnaitė^{1,2}, Taufhik Hossain Tonmoy¹, Manja Kubeil¹, Michael Bachmann¹ and Larysa Baraban¹

¹*Institute of Radiopharmaceutical Cancer Research, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany*

²*Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Vilnius, Lithuania*

*z.janicijevic@hzdr.de

Abstract:

Electronic biosensors based on the extended-gate field-effect transistor (EGFET) concept show great promise for multiplexed biosensing in clinical screening and monitoring of complex diseases at the point of care. These biosensors offer high sensitivity, simplified integration, and easy interfacing with conventional readout electronics. However, EGFET biosensors face practical limitations that hinder their widespread use, such as the need for complex nanostructuring of extended gates (EGs) and FET transducers to achieve ultra-high sensitivity and operate at low current levels (in the ~nA range).

We present a low-cost, standalone, and multiplexed EGFET immunosensor. Our system consists of a disposable sensing chip with an EG electrode array, a multiplexing module that allows reproducible switching between up to 32 EGs, and a readout module built around a commercial FET transducer using off-the-shelf electronic components. We detect the binding of IgG antibodies by indirectly monitoring the gate surface potential, operating the FET transducer in constant charge mode. To achieve high sensitivity levels (approximately 20 mV/dec) and a low detection limit (around 10 fM), comparable to state-of-the-art nanostructured EGFET biosensors, we employ an innovative assay approach. This involves labeling the analyte antibody through bioconjugation with gold nanoparticles (AuNPs), resulting in a detection limit approximately 10^4 times lower than with the gold-standard optical method for the same antibody. Remarkably, our approach leads to a 5-fold amplification of the potentiometric response compared to direct antibody detection without labeling. To understand the origin of this amplification, we analyze the impedimetric response and find that AuNPs exhibit nanoantennae-like behavior, disrupting charge uniformity within the diffusion barrier layer and producing signal amplification. These findings demonstrate the potential for creating a new cost-effective and highly sensitive potentiometric biosensing format by utilizing customized labeling of analyte biomolecules with metallic nanoparticles.

Nanobiosensor for the Impedimetric Detection of SARS-CoV-2 Antigens and Antibodies Using Interdigitated Gold Nanowires

Diana Isabel Sandoval Bojorquez^{1*}, Željko Jančićević¹, Brenda Palestina Romero¹, Eduardo Sergio Oliveros Mata², Markus Laube¹, Anja Feldmann¹, Alexandra Kegler¹, Laura Drewitz¹, Ciarán Fowley², Jens Pietzsch¹, Jürgen Fassbender², Torsten Tonn³, Michael Bachmann¹, Larysa Baraban¹.

¹*Institute of Radiopharmaceutical Cancer Research, Helmholtz-Zentrum Dresden-Rossendorf e. V. (HZDR), Dresden, Germany*

²*Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf e. V. (HZDR), Dresden, Germany*

³*Department for Experimental Transfusion Medicine, German Red Cross Blood Donation Service North-East, Dresden, Germany.*

* d.sandoval-bojorquez@hzdr.de

Abstract:

The detection of biomolecules is critical for the diagnosis of diseases and for improving our understanding of fundamental processes of life. Detecting different types of molecules, such as proteins, antibodies, and genetic material, can provide information about infection, disease progression, and immunity status. In this regard, the COVID-19 pandemic made it evident that it is not only important to detect these molecules but also to perform the detection at the point-of-care (POC) [1]. Although POC tests are a good alternative to the gold standard techniques, there are challenges regarding their sensitivity and specificity that need to be addressed [2]. One strategy to improve the performance of POC is the integration of nanostructures as sensing elements [3]. In this work, we developed an impedimetric nanobiosensor for the detection of antigens and antibodies related to SARS-CoV-2 [4]. Interdigitated gold nanowires were used in combination with the electrical impedance spectroscopy (EIS) technique to assess the changes in the measured impedance resulting from the molecules binding to the surface of the electrodes. By implementing a standard functionalization strategy, it was possible to detect the molecules of interest in physiological buffer, as well as in human plasma samples. Furthermore, it was possible to perform an on-chip calibration that allowed us to provide an estimation of the level of antibodies present in patient samples. The developed sensing platform could be adapted for the detection of relevant target-analyte pairs in different diseases, making it relevant not only for this but also for future pandemics.

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Plasmonic Bio-Sensing with Photonic Integrated Circuits

D. Tsiokos^{1*}, S. Suckow², A. Manolis¹, C. Eleftheriou¹, M.A. El-Rabiaey¹, G. Tsekenis¹, Sabato D'Auria³, Antonio Varriale⁴, Alessandro Capo⁴, B. Chmielak², O. Bhalerao^{2,5}, A. L. Schall-Giesecke^{2,6}, M. L. Lemme^{2,5}, K. Fotiadis^{7,8}, E. Chatzianagnostou^{7,8}, Dimosthenis Spasopoulos^{7,8}, Stelios Simos^{7,8}, Nikos Pleros^{7,8} and L. Lidorikis^{7,8}

¹ *bialoom Ltd, Nicosia, Cyprus*

² *AMO GmbH, Aachen, Germany*

³ *Department of Biology, Agriculture and Food Science, CNR, Rome, Italy*

⁴ *ISA-CNR, Institute of Food Science, Avellino, Italy.*

⁵ *Chair of Electronic Devices, RWTH Aachen University, Aachen, Germany*

⁶ *Chair of Electronic Components and Circuits, University of Duisburg-Essen, and Fraunhofer IMS, Duisburg-Essen, Germany*

⁷ *Department of Informatics, Aristotle University of Thessaloniki, Greece*

⁸ *Center for Interdisciplinary Research and Innovation (CIRI-AUTH), Thessaloniki, Greece **

dimitristsiokos@gmail.com

Abstract:

In this talk, we report on recent advances of CMOS-compatible plasmonic-augmented, silicon nitride interferometers on photonic integrated circuits targeting biosensing applications. We will report on a plasmophotonic Mach-Zehnder interferometer (MZI) layout for simultaneous detection of multiple heterogeneous biomarkers in fluids within minutes, targeting point of care applications. As a proof-of-concept we combine the detection of *Escherichia coli* (E.coli), one of the most encountered pathogens involved with blood infections, and CRP detection, a disease severity indicator in a single biochip compatible with CMOS semiconductor manufacturing. The sensor chip used in this demonstration can host up to 10 hybrid detection assays. Each biosensor exploits immunoassays on 70 μm long aluminum plasmonic transducers within a silicon nitride waveguide based MZI.

We also show a more compact version of sensors exploiting bimodal interference, reaching optical bulk sensitivities of 4400 nm/RIU while shrinking the sensor footprint, reducing their fabrication cost and removing any need for electrical controls [1].

Acknowledgements: This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreements No 101007448 (GRACED) and 101093166 (AMBROSIA) and from the European Regional Development Fund and Research and Innovation Foundation of Cyprus project MultiCare (SEED/0719/0127).

[1] K. Fotiadis et al., *ACS Photonics* 2023, 10, 8, 2580–2588.



International Conference on Nanotechnologies and Bionanoscience

Thursday 14th September

WS1 & WS3 Session I
Advanced Diagnostics and
Nanocharacterisation II

Sensing polynucleotides with nanomaterials

Antonios G. Kanaras^{a,*}

*^a School of Physics and Astronomy, Institute for Life Sciences, University of Southampton,
Southampton, UK, SO171BJ*

*[*a.kanaras@soton.ac.uk](mailto:a.kanaras@soton.ac.uk)*

Abstract:

The development of new sensors to accurately and selectively detect oligonucleotides of interest in biological environments is of high importance and it will transform diagnosis and prognosis in the years to come.

Recently our group developed a new range of optical sensors based on graphene oxide and upconversion nanoparticles, which allow for the rapid detection of small oligonucleotide sequences of interest at the range of zeptomoles. Our sensors were further developed to detect messenger RNA (mRNA) related to prostate cancer and Alzheimer disease in challenging biological environments such as blood plasma and cell lysate. The technology was also made portable and it was used in crops to detect within minutes the presence of mRNAs related to protein monitoring the development of plants. In this talk I will discuss all recent progress of my group as well as the expansion of our technology to other types of 2D materials.

[1] Alexaki, K.; Kyriazi, M. E.; Greening, J.; Taemaitree, L.; El-Sagheer, A. H.; Brown, T.; Zhang, X.; Muskens, O. L.; Kanaras, A. G. "A SARS-Cov-2 sensor based on upconversion nanoparticles and graphene oxide" RSC Advances 2022, 12(29), 18445-18449.

[2] Alexaki, K.; Giust, D.; Kyriazi, M. E.; El-Sagheer, A. H.; Brown, T.; Muskens, O. L.; Kanaras, A. G. "A DNA Sensor Based on Upconversion Nanoparticles and Two-Dimensional Dichalcogenide Materials" Front. Chem. Sci. Eng. 2021, 15(4), 935-943.

[3] Giust, D.; Lucio, M. I.; El-Sagheer, A. H.; Brown, T.; Williams, L. E.; Muskens, O.L.; Kanaras, A. G. "Graphene Oxide–Upconversion Nanoparticle Based Portable Sensors for Assessing Nutritional Deficiencies in Crops." ACS Nano, 2018, 12 (6), pp 6273–6279 DOI: 10.1021/acsnano.8b03261

[4] Vilela, P.; El-Sagheer, A. H.; Millar T. M.; Brown, T.; Muskens, O. L.; Kanaras, A. G. "Graphene oxide-upconversion nanoparticle based optical sensors for targeted detection of mRNA biomarkers present in Alzheimer's disease and prostate cancer" ACS Sensors 2017, 2 (1), 52-56 DOI: 10.1021/acssensors.6b00651

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A Nanotransducer Mediated Approach to Genome Editing

F. Tantussi^{1*}, S. Konstantinidou², A. De Carli³, D. Witt⁴, A. Lindstaedt⁴, M. D'Amora^{1,2}, M. Lai³, A. Everhardt⁵, F. Fuso⁶, P. Barski⁴, V. Raffa², F. de Angelis¹

¹*Plasmon Nanotechnologies, Istituto Italiano di Tecnologia, Genova, Italy;*

²*Department of Biology, University of Pisa, Pisa, Italy;*

³*Department of Medicine, University of Pisa, Pisa, Italy;*

⁴*ProChimia Surfaces, Gdynia, Poland;*

⁵*LioniX International, Enschede AL, The Netherlands*

⁶*Department of Physics, University of Pisa, Pisa, Italy*

[*francesco.tantussi@iit.it](mailto:francesco.tantussi@iit.it)

Abstract:

Starting from the famous CRISPR/Cas 9 genome editing technique, we exploit plasmonic nanoparticles and their resonant laser radiation to activate controlled DNA break and reduce off-target events.

The most popular and significant tool for genome editing is represented by the CRISPR/Cas9 technology. This system consists of molecular scissors for cutting the DNA and leading to a gene knockout or gene knock-in. Unfortunately, this technology is not considered safe for clinical applications in humans, because CRISPR/Cas 9 can cause undesirable unspecific, and unwanted cuts (off-target events) in the genome. Here we propose a novel concept of genome editing to make a safer tool, by combining a nano transducer (NT) with Boolean logic operator “AND” only when multiple events are satisfied does the cutoff occur.

The nano transducer is composed of a DNA sensor and a gold nanoparticle activated by light. This activation triggers a thermo-inducible DNA break. Through this approach, the DNA double-strand break (DSB) is induced by the activation of nanoparticles and not by the Cas9 activity reducing the current limitation of off-targets. The energy released is the result of the resonant excitation of the plasmonic resonances of the particle used. The so generated heat by the nanoparticles upon irradiation can lead either to the activation of a thermophilic domain which cleaves the DNA (single nanoparticle approach) or to a direct DSB upon coupling of nanoparticles (dimer approach). Finally, it is shown that the presented nanoformulation can serve as an efficient delivery vehicle in cells.

The project I-GENE has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 862714.

Synthesis, detection, and actuation of self-assembling DNA nanostructures

Ibon Santiago^{1,*}

¹*CIC nanoGUNE BRTA, Donostia-San Sebastián 20018, Spain*

[*i.santiago@nanogune.eu](mailto:i.santiago@nanogune.eu)

Abstract:

DNA provides a unique platform for constructing supramolecular structures of nearly any geometry from the bottom up, enhancing precision in the rational design of self-assembled nanostructures. This talk will focus on recent advancements in the detection, control, and activation of DNA self-assembled nanostructures.

I will describe the development of a novel collision electrochemistry platform. This approach enables the detection of single-particle collisions in solution, offering new insights into the behavior of enzymes [1] and DNA origami [2] at a single-particle level. Further, I will present the measurement and regulation of the 2D diffusion dynamics of DNA nanostructures interacting with lipid membranes, thereby providing control over a biomimetic signaling model system. [3]

Finally, I will discuss the actuation of DNA-based nanodevices under the influence of external fields. By drawing from single-molecule biophysics and employing a forcespectroscopy approach, our recent findings give insights into the parameter space influencing the electrical actuation of DNA-based nanorobots.

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- [2] Pensa, E., Bogawat, Y., Simmel, F. C. & Santiago, I. Single DNA Origami Detection by Nanoimpact Electrochemistry. *ChemElectroChem* **9**, e202101696 (2022).
- [3] Bogawat, Y., Krishnan, S., Simmel, F. C. & Santiago, I. Tunable 2D diffusion of DNA nanostructures on lipid membranes. *Biophysical Journal* **121**, 4810-4818 (2022).

Biomimetic nano-vesicles for intelligent RNA delivery

Miriam Colombo^{1,*}, Stefania Garbujo¹ and Davide Prospero¹

¹*NanoBioLab, University of Milano-Bicocca, Dep. Of Biotechnology and Biosciences, Milano Italy.*

*miriam.colombo@unimib.it

Abstract:

Gene therapy success in cancer treatment relies not only on a good molecular strategy but also on the need of a safe, efficient, and target-selective gene delivery system. Despite the great clinical achievement of lipid nanoparticles (LNPs) as non-viral gene therapy vectors, they suffer from lack of tumor targeting capability, which is a prerequisite for effective and selective cancer therapy. In this regard, the cell membrane coating technology is becoming a prospective tool for targeting specific cells. This top-down approach makes use of cell membrane-derived vesicles to camouflage nanoparticles as “self” and bestow them with inherent capabilities of the source cells. Specifically, the coating with cancer cell membranes has been widely investigated for selective tumor targeting, owing to the homotypic self-recognition ability of cancer cells.

We explored the natural composition of tumor cell membranes to achieve a heterotypic targeting, relying on the intrinsic interaction of cancer cells with heterotypic cells in tumor microenvironment (TME). In particular, we focused on desmoplastic cancers, which exhibit hardly accessible tumor stroma. Herein, rather than acting directly on hardly accessible cancer cells, we reasoned that it could be more convenient to develop an innovative gene therapy vector suitable to deliver RNA-based anticancer agents specifically to the more readily available cancer associated fibroblasts (CAFs). After the establishment of a CAF cellular model, a systematic biochemical characterization of the peculiar features of CAFs was accomplished, including the metabolic phenotype profile disclosure and identification of selective biomarker expression (i.e., α -SMA). Next, we focused on the fabrication of a core-shell system, whereby siRNA encapsulating LNPs (core) were wrapped by cancer cell membrane derived nano-vesicles (CCM-NVs) (shell). First, we developed a reproducible protocol to produce labeled CCM-NVs derived from murine 4T1 cancer cells. Secondly, we optimized a protocol to produce Cy5-labeled siRNA-encapsulating LNPs by means of microfluidic technology. Finally, we developed a protocol for LNPs coating with CCM-NVs. Flow cytometry was selected as a characterization method for evaluating the their co-localization inside target cells.

Controlling the Synthesis of Iron Oxide Based Nanomaterials and Nanocomposites with Advantageous Features for Biomedical Applications

Liudmyla Storozhuk^{1,2,*} and Rachel A. McKendry^{1,3}

¹London Centre for Nanotechnology, University College London, 17-19 Gordon Street, London, WC1H 0AH, UK

²Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK

³Division of Medicine, University College London, London WC1E 6BT, UK

*l.storozhuk@ucl.ac.uk

The unique remarkable properties, such as superparamagnetism, size, non-toxicity and biocompatibility, of iron oxide based nanomaterials and their derivatives have made them widely used materials for various applications including biomedical ones. These include diagnosis and therapy of cancer, targeted drug delivery, bio-sensing, cell and tissue imaging and regenerative medicine. However, when IONPs (Fe_3O_4 (magnetite) or $\gamma\text{-Fe}_2\text{O}_3$ (maghemite)) reach smaller sizes (about 10–20 nm for iron oxide), superparamagnetic properties become evident, so that the particles achieve a better performance for most of the aforementioned applications.

Using different synthesis methods, iron precursor types, solvents, etc., one can control the properties, size and shape of IONPs, rendering them suitable for several medical applications. For example, the current interest for novel positive (T_1) contrast agents for magnetic resonance imaging (MRI) arises from the health risks entailed by the current clinical gadolinium complexes. Iron oxide nanoparticles (IONPs) with ultra-small size (≤ 5 nm) synthesised via reproducible, scalable and non-toxic synthesis routes are a potential substitute for this purpose [1].

Bigger IONP (≥ 30 nm) show excellent heating ability under alternative magnetic field and can be employed for magnetically induced hyperthermia (MIH). The heating ability is considered a critical factor in MIH and is usually prioritised when developing synthesis of IONPs destined for this application [2].

The fabrication of novel hybrid materials based on IONP and plasmonic materials will allow us to combine luminescent properties with the ability to "fish out" and concentrate targets, thus obtaining attractive theranostic materials with excellent magnetic and optical properties. Such hybrid NPs are deemed as particularly promising for sensing, high contrast imaging and targeted delivery applications.

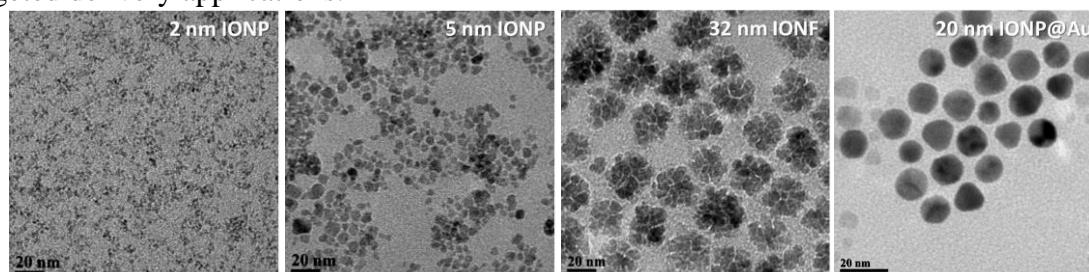


Figure 1. TEM images of IONP with different shapes and sizes for a range of biomedical applications

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[2] L. Storozhuk, et al. *Journal of Applied Materials and Interface*. 13: 45870–45880 (2021)

A comprehensive orthogonal study on the interaction of nanoparticles with mucin

Matteo Tollemeto^{1*}, Isidro Badillo Ramirez¹, Lasse Højlund Eklund Thamdrup¹, Yudong Li², Tania Patiño Padial², Jan van Hest², Anja Boisen¹

¹*The Danish National Research Foundation and Villum Foundation's Center IDUN, Department of Health Technology, Technical University of Denmark, Kgs. Lyngby, Denmark*

²*Laboratory of Chemical Biology, Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, The Netherlands*

*matoll@dtu.dk

Abstract:

Oral delivery of drugs is often the most preferred method of administration. Also in this respect nanomedicine could play an important role, as was for example demonstrated by Ould-Ouali and colleagues, who described that PEG-p(CL-g-TMC) micelles composed of poly(ethylene glycol)-poly(caprolactone-trimethylene carbonate) block copolymers increased solubilization of risperidone, a poorly water-soluble drug¹. However, especially in the case of nanomedicine, efficacy is affected by the ease of particle distribution, which can be hampered by interaction with the protective mucus layer. Although this has been recognized, until now remarkable few studies have investigated systematically how nanoparticles interact with mucus. Here, we report a comprehensive study on the interaction between polymeric micelles and mucin. We initially screened for the interaction using the classical approach using dynamic light scattering (DLS). Although DLS has been the standard method for mucoadhesion studies: i) it can be affected by the presence of larger aggregates, and ii) does not give any information on the kind and strength of interaction. We, therefore, focused on complementing DLS with a range of different techniques. Interaction was determined using quartz crystal microbalance with dissipation (QCM-D). By using Surface-enhanced Raman spectroscopy (SERS), we showed that the interaction between polymeric micelles and mucin is mostly due to the interaction with the hydrophilic, sugar moieties of the protein, shown by the broadening of the peak representing the OH and COOH groups. Further, using isothermal calorimetry (ITC), we learnt how the interaction is thermodynamically controlled. Lastly, by using the Periodic Acid Schiff (PAS) assay, we quantified the amount of bound mucin to the nanoparticles.

These results provide a better insight in how polymeric micelles would interact with mucus, which is valuable information to further develop nanomedicine formulations for oral drug delivery.

[1] Ould-Ouali, Louisa, et al. *Journal of Controlled Release* 102, 657–68 (2005)

Ultrathin water layers on viruses

A.M. Bittner^{1*}, M.A. Iriarte-Alonso¹, J.H. Melillo², S. Cervený², S. Chiantia³

¹CIC nanoGUNE (BRTA)/Ikerbasque, San Sebastián/Bilbao, Spain; ²Donostia. Intl. Phys. Center and Centro Fís. Mat., San Sebastián, Spain; ³Potsdam University, Germany

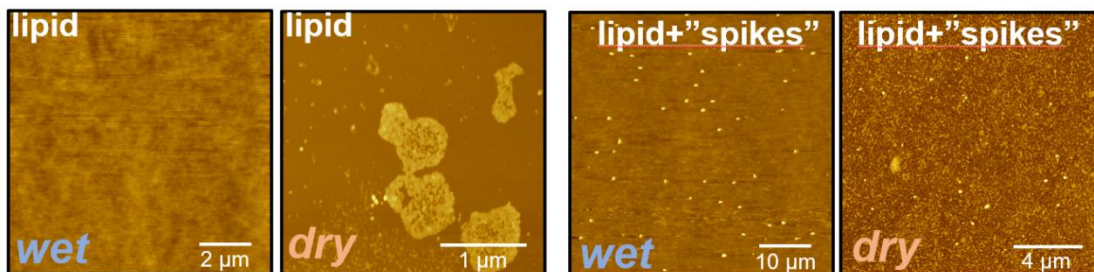
*a.bittner@nanoqune.eu

Abstract:

For many viruses, transmission requires "survival" in dry conditions, specifically for the airborne route [1,2,3]. Simple plant viruses survive complete dehydration and exhibit an ultrathin water layer in ambient conditions [3,4]. For the complex enveloped viruses, the lipid bilayers must persist. How is this possible?

We first modelled the influenza A virus surface by hemagglutinin trimer "spikes" in supported lipid bilayers and investigated it by AFM and fluorescence correlation spectroscopy. We found that - in dry conditions - the spikes effectively block nano- and microscale restructuring, and slow lipid diffusion [1].

We proceeded by modelling the (glycosylated) spikes themselves by mannosylated gold particles, adsorbed on hydrophobic and on hydrophilic silane layers. AFM with hydrophobic and hydrophilic tips proves that glycosylation allows to retain ultrathin water layers (ca. 1 nm) even at low air humidity.



Lipid bilayers withstand drying in presence of the viral HA "spikes" (AFM)

[1] M.A. Iriarte-Alonso, A.M. Bittner, S. Chiantia, "Influenza A virus hemagglutinin prevents extensive membrane damage upon dehydration", *Biochem. Biophys. Acta Adv.* 2 (2022) 100048

[2] J.H. Melillo, E. Nikulina, M.A. Iriarte-Alonso, S. Cervený, A.M. Bittner, "Electron microscopy and calorimetry of proteins in supercooled water", *Sci. Rep.* 12 (2022) 16512

[3] A. Calò, A. Eleta-Lopez, T. Ondarçuhu, A. Verdagner, A.M. Bittner, "Nanoscale Wetting of Single Viruses", *Molecules* 26 (2021) 5184

[4] J.M. Alonso, T. Ondarçuhu, C. Parrens, N. Górzny, A.M. Bittner, "Nanoscale wetting of viruses by ionic liquids", *J. Molec. Liq.* 276 (2019) 667

Thursday 14th September

WS1 & WS3 Session III
Micro and Nanofabrication

Densified Collagen Conduits for Vascular Grafts

Alexander W. Justin¹, Federico Cammarata¹, Kouros Saeb-Parsy², Athina E. Markaki^{1,*}

¹ *Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB2 1PZ, UK*

² *Department of Surgery, University of Cambridge, and NIHR Cambridge Biomedical Research Centre, Cambridge, CB2 0QQ, UK*

[*am253@cam.ac.uk](mailto:am253@cam.ac.uk)

Abstract:

We have developed and patented a fabrication method for tubular grafts with true off-the-shelf capability. The method employs “densified” collagen hydrogel, so overcomes limitations of collagen’s mechanical strength, whilst exhibiting the potential for tissue regeneration. The grafts are customisable in terms of tube diameter and wall thickness, yielding tubes for both small animal and human-sized tissues. Our fabrication method is fully materials-based (i.e. not dependent on cell seeding, bioreactor culture, decellularisation), reducing significantly manufacturing costs and time. We are targeting vascular access grafts for haemodialysis as a first indication and are currently evaluating our bioengineered grafts as a replacement artery (artery-to-artery) before transitioning to a vascular access setting (artery-to-vein). The talk will focus on *ex vivo* and *in vivo* testing of our bioengineered grafts as a replacement artery. The testing validates that the densified collagen grafts have sufficient mechanical strength for surgical implantation and function, whilst also exhibiting the potential for tissue regeneration (re-endothelialisation).

Bottom-up engineering of 3D microtissues using cell-instructive micro biomaterials as tissue matrix-mimicking building blocks

Zeinab Niloofar Tahmasebi Birgani

Department of Instructive Biomaterials Engineering, MERLN Institute for Technology-Inspired Regenerative Medicine, Maastricht University, Universiteitssingel 40, 6229 ER Maastricht, The Netherlands

*z.tahmasebibirgani@maastrichtuniversity.nl

Abstract:

Bottom-up tissue engineering (TE) relies on self- or directed assembly of heterogeneous building blocks from cells alone, embedded in hydrogels, or aggregated with microscale biomaterials in a hybrid assembly. Using bottom-up TE, tissues can be engineered *in vitro* in a modular way, with a microstructural definition and hierarchical complexity resembling that of their native counterparts. In a recent paradigm, a bottom-up TE approach based on cell-guided aggregation of explicitly designed and engineered micro biomaterials made from relatively stiff biomaterials has been introduced. The engineered micro biomaterials can be tuned in terms of overall size and shape, bulk stiffness, (surface) chemistry, and micro- or nano-topographies, all of which present powerful tools in controlling (stem) cell fate. The resulting three-dimensional (3D) hybrid cell-biomaterial assemblies enable the micro biomaterials' use in a wider range of applications, for example in establishing a standard pipeline for biological screening of biomaterials in a 3D microenvironment or in regenerative therapies for hard tissues. The current work is focused on the engineering of cell-instructive micro biomaterials using various microfabrication technologies, their enrichment with physical, chemical and biological information, and their use in biomaterials development and as matrixmimicking building blocks for developing new bottom-up regeneration therapies.

Adipose-derived extracellular matrix foams with integrated reduced graphene oxide as implantable scaffolds for neural regeneration

Papadimitriou Lina^{1*}, Paula Marques², Beatriz Olalde³, Emmanuel Stratakis¹ and Anthi Ranella¹

¹ *Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (FORTH), Heraklion, Greece*

² *TEMA - Centre for Mechanical Technology and Automation, Department of Mechanical Engineering, University of Aveiro, 3810-193 Aveiro, Portugal*

³ *TECNALIA, Basque Research and Technology Alliance (BRTA), E20009 Donostia-San Sebastian, Spain*

*lpapadim@iesl.forth.gr

Abstract:

Spinal cord injury (SCI) is a devastating condition that affects the life of millions of patients and their families worldwide. The development of an effective SCI treatment is still an unmet clinical need as the current therapeutic interventions aim to reduce the pressure at the site of the injury and to prevent or delay further nerve damage. The main issue in SCI repair is the limited self-healing ability of the Central nervous system (CNS) that despite some signs of adaptive remodeling of the neural circuits after injury the severed axons ultimately fail to regenerate beyond the site of the lesion. In this study, we are proposing the use of adipose-derived extracellular matrix foams with integrated reduced graphene oxide (adECM/rGO foams) as implantable scaffolds to drive neuronal regeneration. These adECM/rGO foams possess tunable biophysical and mechanical properties that promote neural stem cells (NSCs) differentiation towards neurons^{[1],[2]} and enhance axonogenesis and synaptogenesis while they reduce glial formation which present a major hurdle for successful axon regeneration. The adhesion and the mechanoresponse of NSCs on adECM/rGO foams are studied in order to elucidate the underlying mechanisms that regulate NSCs fate. The expression of key molecules of the mechanotransduction machinery such as integrins, vinculin, FAK and YAP/TAZ are analyzed in relation to the mechanical properties of the foams. Understanding CNS mechanotransduction pathways in tissue engineering scaffolds may lead to the development of new or improved therapeutic targets and strategies for CNS repair.

Acknowledgements: This work was supported by the EU funded NeuroStimSpinal project, Grant agreement ID: 829060

[1] N. Barroca, et al, *Biomaterials advances* volume 148 (2023)

[2] M. Cicuéndez et al, *Int. J. Mol. Sci.*, 22(8), 3847 (2021)

Study of *in vitro* differentiation of NE-4C cells encapsulated in 3D adipose derived-ECM hydrogels

Kyriaki Stampouli^{1*}, Lina Papadimitriou¹ and Andrea García-Lizarribar², Beatriz Olalde², Anthi Ranella¹

¹ *Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (FORTH), Heraklion, Greece*

² *TECNALIA, Basque Research and Technology Alliance (BRTA), E20009 Donostia-San Sebastian, Spain*

[*kyriakise@iesl.forth.gr](mailto:kyriakise@iesl.forth.gr)

Abstract:

The interaction between extracellular matrix (ECM) and cells influences several cellular functions such as survival, proliferation, differentiation, and migration. Cell growth within 3D scaffolds resembling cellular microenvironments provides better insights into tissue development than traditional 2D culture systems. Hydrogels, a type of polymeric material, not only offer physical and chemical properties that support cell development, but their 3D microarchitecture creates a more physiologically relevant environment, favoring tissue regeneration and mechanosensing, particularly in neural regeneration studies^{1,2}. Among different studies, *in vitro* systems with cells encapsulated in 3D hydrogels seems to reproduce better the neural tissue microenvironment to investigate the viability and differentiation process of neural stem cells (NSCs)³. In this study, we aimed to investigate the viability and differentiation process of NSCs by employing *in vitro* systems with neuroectodermal NE-4C cells encapsulated in 3D hydrogels derived from adipose tissue ECM (adECM). By varying the concentration of the adECM in the hydrogels, the impact on cell behavior and differentiation pathways was examined. Results showed that even though hydrogel concentration did not significantly affect cell survival, it did influence the differentiation process as revealed by the relative expression of neuronal lineage specific markers such as tubulin β III, synaptophysin, and gfap. Understanding the *in vitro* differentiation of NE-4C cells encapsulated in 3D adECM hydrogels has the potential to advance *in vitro* models for neural tissue engineering and regenerative medicine.

Acknowledgments: This work was supported by the NeuroStimSpinal project, Grant agreement ID: 829060

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Controlling Aerosol-Jet Printed MXene Flakes Morphology For Neural Applications

Javier Gutierrez-Gonzalez^{1,2,3*}, Dahnna Spurling², Tara McGuire¹, Ian Woods^{1,3}, Adrian Dervan¹, Fergal J. O'Brien^{1,3} and Valeria Nicolosi^{2,3}.

1. Tissue Engineering Research Group, Dept. of Anatomy & Regenerative Medicine, Royal College of Surgeons in Ireland (RCSI), Dublin, Ireland.

2. School of Chemistry, Trinity College Dublin (TCD), Dublin 2, Ireland.

3. Advanced Materials Bio-Engineering Research Centre (AMBE, RCSI and TCD).

*jgutierr@tcd.ie

Abstract:

MXenes are 2D layered nanomaterials consisting of carbides and nitrides of transition metals with excellent electrical conductivity, charge storage and biocompatibility. Mainly used as aligned flakes, under certain processing conditions these 2D flakes can also fold in crumpled 3D structures. Despite being occasionally associated with faulty deposition, crumpled MXenes hold untapped potential, harboring intriguing properties that remain largely unexplored. Thus, the main goal of this study was to investigate the impact of MXene flake morphology on neuronal biocompatibility for the development of future neural interfaces.

In this work, the production of crumpled and aligned MXene ($Ti_3C_2T_x$) flake morphologies (Fig 1) was systematically studied by using high-resolution Aerosol Jet 3D printing, while assessing their novel physical properties, such as roughness, conductivity, or optical properties. Furthermore, cell line - derived and primary neurons were plated on either morphology to examine the ability of both forms to support neuronal growth and development.

By modifying several 3D printing parameters, MXene flakes could both align and crumple at specific mass and sheath flow regimes, depending on the nozzle size, speed and solvent mixture, while flake morphology was rapidly monitored using the in-built camera.

To assess biocompatibility, mouse neurons were seeded on printed crumpled and aligned MXene films, revealing distinct behavior depending on the flake morphology: crumpled MXene facilitated higher cell adhesion (as indicated by DNA count and immunostained cells) whereas neurons grown on aligned MXene films possessed longer neurite outgrowth. Further analysis using mouse primary neurons, resulted in healthy neuronal growth on both types of MXene for 8 days, while crumpled surfaces elicited decreased expression of GFAP via imaging quantification, suggesting a reduced astrocytic reactivity¹. Taken together, these results demonstrate that both crumpled and aligned MXenes, can be easily 3D printed with Aerosol Jet printing, while exhibiting unique characteristics when supporting neuronal growth. This study highlights the need for precise management of MXene deposition and customized flake design, encouraging researchers to intensify the study of crumpled MXenes and other 2D materials, and their application in multiple fields including biomedicine, electronics and energy storage.

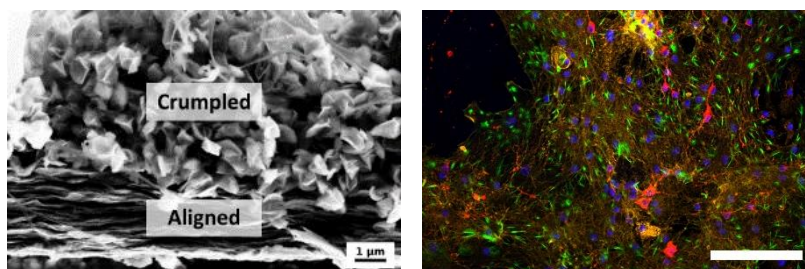


Figure 1. Left) SEM image of a cross-section of crumpled and aligned MXene. Right) Immunostained cortical primary neurons seeded on crumpled MXene. (red β -III tubulin; green GFAP; orange Phalloidin; blue DAPI)

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Funded by the Engineering and Physical Sciences Research Council and Science Foundation Ireland (EPSRC-SFI) Centre for Doctoral Training in Advanced Characterisation of Materials.

Statin-loaded biodegradable micropatterned polymeric replicas on osteogenic differentiation

Eleni Kanakousaki^{1,2*}, Paraskevi Kavatzikidou¹, Despoina Angelaki^{1,3}, Alexandra Manousaki¹, Emmanuel Stratakis^{1,3} and Anthi Ranella¹

¹*Foundation for Research and Technology-Hellas (FORTH), Institute of Electronic Structure and Laser (IESL), Heraklion, Greece*

²*Department of Biology, University of Crete, Heraklion, Greece*

³*Department of Physics, University of Crete, Heraklion, Greece*

*ekanakousaki@iesl.forth.gr

Abstract:

Biofabricated microenvironments are offering mechanistic insights into how the extracellular matrix (ECM) regulates self-renewal, proliferation and differentiation potentials of the stem cells. YAP/TAZ are considered as master regulators of cell-ECM interactions. Statins, which are potent inhibitors of cholesterol biosynthesis, are demonstrated to stimulate the new bone formation.[1] Ultrafast pulsed laser irradiation is a simple microfabrication technique to produce substrates by controlling the topographical geometry and pattern regularity.[2,3] Such structures with an anisotropy discontinuous topographical nature, could manipulate cellular growth and alignment (e.g., neuronal [4,5]). Soft lithography has been used to transfer well-defined micro-sized patterns from silicon to polymeric surfaces allowing the in-depth study of cellular behavior.[6] The aim of this study is the development of biomimetic scaffolds with incorporated statins, for inducing osteogenic differentiation.

In this study, a series of micro-patterned silicon structures were fabricated by ultrafast laser irradiation. This resulted in different anisotropic discontinuous patterns at micro-nano scale. Positive replicas of natural polymers (e.g., Cellulose Acetate and their composites) have been successfully reproduced from the Si structures via soft lithography. Statin-loaded replicas were then produced. The morphological characterization of the replicas was performed by Scanning Electron Microscopy (SEM) and their wetting properties were determined by water contact angle. Finally, the cytotoxicity of the statin-loaded replicas with mouse Mesenchymal Stem Cells (MSCs) C57BL/6 was evaluated, as well as, the cellular responses of MSCs cultured on the replicas. Cell mechanotransduction was analyzed via the cytoskeleton organization and YAP localization. The effect of the replicas on MSCs fate was also studied. The surface roughness and chemical composition influenced the cell morphology, as well as, they had an effect on the MSCs mechanotransduction and differentiation.

The authors would like to thank the European Project NFFA-Europe-Pilot (n. 101007417 from 1/03/2021 to 28/02/2026) for providing financial support to this project.

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Thursday 14th September

WS1 Session V

Nanomaterials for catalysis, energy storage and sensing

Densely and Selectively Functionalized Graphenes for Energy Storage and Catalysis

Aristides Bakandritsos

Regional Centre of Advanced Technologies and Materials, Czech Advanced Technology and Research Institute (CATRIN), Palacký University Olomouc and

Nanotechnology Centre; Centre of Energy and Environmental Technologies, VŠB–Technical University of Ostrava

[*a.bakandritsos@upol.cz](mailto:a.bakandritsos@upol.cz)

Abstract:

Selective and dense functionalization of graphene with redox-active, bioinspired, discrete molecular species or single metal atom ions can mitigate its tendency for restacking and can boost the interactions with molecules of interest. Such properties are pre-requisites for sustainable electrode materials for energy storage and heterogeneous catalysis. By leveraging the reactivity of fluorographene with nucleophiles, advanced and tailored graphene derivatives are obtained for the targeted applications. Graphene acid (GA), cyanographene (G-CN), superdoped graphene are indicative examples. GA, in particular, bears carboxyls which are strong metal-coordination sites and handles to immobilize aminoacids for development of catalysts for fuel production. As a Li-ion battery anode, GA offers high redox capacity stemming from its abundant carboxyl groups, and high conductivity. The nitrile groups of G-CN mediate electronic communication between the graphene and metal ions, affording mixed valence Cu(I)-Cu(II) undercoordinated catalytic centres, enabling the effective production of pharmaceutical synthons via cooperative single-atom catalysis. Nitrogen superdoping affords dense conductive electrodes with superior electroactivity and energy density in supercapacitors. Such graphene derivatives lay the ground for the development of the next generation materials for energy storage, and catalysis but also for sorption, environmental monitoring and biomedical applications.

Acknowledgements: All co-authors are acknowledged for their key contribution in all related works. The support from the Czech Science Foundation is acknowledged (EXPRO No19-27454X and 22-27973K), and from Horizon-WIDERA-2022-TALENTS, "APROACH" No 101120397.

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Nanostructures of graphitic carbon nitride (g-C₃N₄) for optosensing applications

Spyros Kokkotos^{1,2}, Evangelia Vasilaki^{1,3}, Maria Vamvakaki^{1,3}, Argyro Klini¹

¹IESL/FORTH, N. Plastira 100, GR 700 13, Heraklion, Crete, Greece

²Department of Physics, University of Crete, GR 700 13, Heraklion, Crete, Greece

³Department of Materials Science and Technology, University of Crete, GR 700 13, Heraklion, Crete, Greece

Graphitic carbon nitride (g-C₃N₄) is a graphene-analog, which has been extensively investigated in the recent years [1]. Owing to its novel mechanical, physicochemical and optoelectronic properties [2], it has gained enormous interest for its potential use in a wide range of applications, such as in energy conversion [3], photocatalysis [4], photoelectric conversion [2], hydrogen production [5], and more recently in sensing technologies [6].

Herein we report on the synthesis and characterization of graphitic carbon nitride (g-C₃N₄) allotropes (bulk, exfoliated sheets and quantum dots) of tunable fluorescence emission, by applying thermal polymerization of nitrogen rich precursors.

The as-synthesized g-C₃N₄ allotropes were fully characterized in terms of their morphological, structural and optical properties by Field Emission Scanning Electron Microscopy (FE-SEM) (Fig. 1a), X Ray Diffraction (XRD) and Diffuse Reflectance UV-Vis and Fourier transform infrared (FT-IR) spectroscopies.

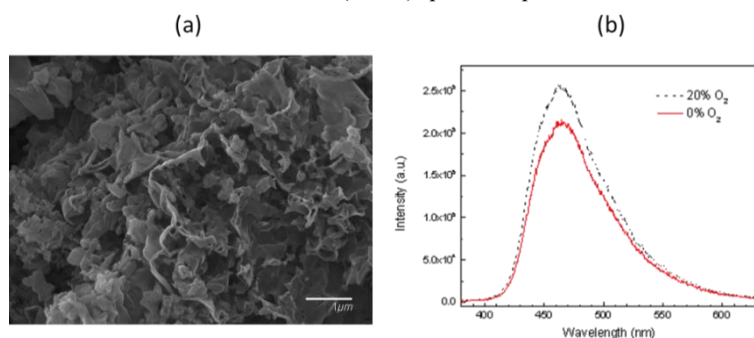


Fig. 1: (a) SEM image of bulk g-C₃N₄ and (b) room-temperature PL emission spectra of g-C₃N₄ in air (black dotted line) and in low vacuum (7.5×10^{-2} Torr) atmosphere (red solid line), upon excitation at $\lambda_{exc} = 355$ nm and $F_{exc} = 0.6$ mJ/cm²

Moreover, the ability of these materials to exhibit sensing behavior towards oxygen exposure is demonstrated by monitoring the variations of their laser (Nd:YAG, $\lambda_{exc} = 355$ nm and $F_{exc} = 0.6$ mJ/cm²) induced photoluminescence emission at 460 nm (Fig. 1b) [7].

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Monitoring Volatile Signatures in Food, Health and Environment Applications

Jonathan Beauchamp*

Fraunhofer IVV, Freising, Germany

[*jonathan.beauchamp@ivv.fraunhofer.de](mailto:jonathan.beauchamp@ivv.fraunhofer.de)

Abstract:

Volatile organic compounds (VOCs) are ubiquitous in everyday life. The air is replete with volatiles of varying nature arising from diverse sources. Despite the complex mixtures relating to their different origins, individual volatiles or their specific classes might be indicative of deleterious conditions. This represents an opportunity to exploit their presence to flag such situations by detecting and/or monitoring these compounds.

Specific cases of scenarios in which volatiles might be exploitable include the microbial spoilage of food, especially fresh products such as meat or dairy, whereby the abundance of volatile degradation by-products correlates with the degree of spoilage [1,2]. Similarly, the presence of certain volatiles in human exhaled breath has been associated with disease and/or infections or can relate to therapeutic intervention [3]. A further example is air quality, both in indoor and outdoor environments, which can be ascertained by the presence of individual gas-phase molecules arising from pollution or unwanted emissions sources [4].

Exploring the associations of volatiles with specific scenarios is typically undertaken using comprehensive analytical technologies, primarily through use of mass spectrometry. Once the associated compounds have been identified and characterized, however, low-cost and compact sensor-based systems can be utilized to monitor individual compounds or classes. This represents an immediate opportunity for such emerging technologies to find both niche and widespread applications.

This talk will review how volatiles associated with different scenarios might be exploited by monitoring their presence and abundance to indicate undesirable situations.

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Chitosan-Modified Polyethyleneimine Nanoparticles for Enhancing the Carboxylation Reaction and Plants' CO₂ Uptake

Cyril Routier^{1*}, Lorenzo Vallan², Yohann Daguerre³, Marta Juvany³, Emin Istif², Daniele Mantione^{2,4}, Cyril Brochon², Georges Hadziioannou², Åsa Strand⁵, Torgny Näsholm³, Eric Cloutet², Eleni Pavlopoulou^{2,6}, and Eleni Stavrinidou^{1,3}

¹ *Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, SE-60174, Norrköping, Sweden.*

² *Laboratoire de Chimie des Polymères Organiques (LCPO–UMR 5629), Université de Bordeaux, Bordeaux INP, CNRS, F-33607 Pessac, France.*

³ *Umeå Plant Science Centre, Department of Forest Genetics and Plant Physiology, Swedish University of Agricultural Sciences, SE-90183 Umeå, Sweden.*

⁴ *POLYMAT, University of the Basque Country UPV/EHU, 20018 San Sebastián, Spain*

⁵ *Umeå Plant Science Centre, Department of Plant Physiology, Umeå University, SE 901-87 Umeå, Sweden.*

⁶ *Institute of Electronic Structure and Laser, Foundation for Research and Technology— Hellas, P.O. Box 1527, 71110 Heraklion Crete, Greece.*

[*Cyril.Routier@liu.se](mailto:Cyril.Routier@liu.se)

Abstract:

Increasing plants' photosynthetic efficiency is a major challenge that must be addressed in order to cover the food demands of the growing population in the changing climate. Photosynthesis is greatly limited at the initial carboxylation reaction, where CO₂ is converted to the organic acid 3-PGA, catalyzed by the RuBisCO enzyme. RuBisCO has poor affinity for CO₂, but also the CO₂ concentration at the RuBisCO site is limited by the diffusion of atmospheric CO₂ through the various leaf compartments to the reaction site. Beyond genetic engineering, nanotechnology can offer a materials-based approach for enhancing photosynthesis, and yet, it has mostly been explored for the light-dependent reactions. In this work, we developed polyethyleneimine-based nanoparticles for enhancing the carboxylation reaction. We demonstrate that the nanoparticles can capture CO₂ in the form of bicarbonate and increase the CO₂ that reacts with the RuBisCO enzyme, enhancing the 3-PGA production in *in vitro* assays by 20%. The nanoparticles can be introduced to the plant via leaf infiltration and, because of the functionalization with chitosan oligomers, they do not induce any toxic effect to the plant. In the leaves, the nanoparticles localize in the apoplastic space but also spontaneously reach the chloroplasts where photosynthetic activity takes place. Their CO₂ loading-dependent fluorescence verifies that, *in vivo*, they maintain their ability to capture CO₂ and can be therefore reloaded with atmospheric CO₂ while in planta. Our results contribute to the development of a nanomaterials-based CO₂-concentrating mechanism in plants that can potentially increase photosynthetic efficiency and overall plants' CO₂ storage.

Nano-sized Co-Ce catalysts for the preferential CO oxidation in hydrogen rich gases -influence of the support and preparation method

Silviya Zh. Todorova^{1*}, Bozhidar K. Grahovski, Diana G. Filkova, Iliyana Hristova, Hristo G. Kolev, Daniela B. Karashanova

¹ *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria*

² *Institute of Optical Materials and Technologies "Acad. Jordan Malinowski", Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 109, 1113 Sofia, Bulgaria*

[*todorova@ic.bas.bg](mailto:todorova@ic.bas.bg)

Abstract:

The preferential CO oxidation (PROX) is a simple, efficient, and economic method for CO removal. Due to high price of precious metals, non-precious metal catalysts have been considered as a potential alternative for the CO PROX reaction. Co-based catalysts have shown promising catalytic performance for the CO PROX reaction. The main drawback of the bulk cobalt oxide appears to be the reduction to the metallic Co under the excess H₂, which lead to deactivation.

Co₃O₄ nano-sized particles were supported on the silica or alumina by two methods-hydrothermal method (HT) and impregnation (I). The cobalt samples supported on SiO₂ was additionally modified with cerium and sequence of ceria introduction was investigated. The as prepared samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR), HRTEM, Uv-vis spectroscopy. Finely divided weakly interacting cobalt oxide particles are formed on the surface of the silica supported catalyst prepared by hydrothermal method. In addition to the phase of Co₃O₄, a superficial Co-Al spinel-like phase is formed on the surface of alumina supported sample as these phases predominate when the sample is obtained by impregnation.

The most active sample in the PROX reaction is the one supported on Co-Al₂O₃-HT. This could be related to the presence of finely divided Co₃O₄ strongly interacting with the support and the presence of Co²⁺ ions which could be sites for oxygen adsorption and formation of active oxygen species. Catalytic tests showed that cerium modified the catalytic behaviour of cobalt in PROX reaction. The homogeneous distribution of Co₃O₄ and CeO₂ and good contact between them are key factors controlling the activity.

Acknowledgements

The authors kindly acknowledge the financial support of project № BG05M2OP001-1.002-0014 „Center of competence HITMOBIL – Technologies and systems for generation, storage and consumption of clean energy”, funded by Operational Programme “Science and Education For Smart Growth” 2014-2020, co-funded by the EU from European Regional Development Fund.

Cork based sensing platform for an inflammatory biomarker detection in Point-of-Care

Bárbara Correia^a Daniela Oliveiraa^b, Georgeta Vulpe^c, Ana P.M. Tavares^d, M. Goreti, F. Sales^d, Abel J. Duarte^e, Sanjiv Sharma^c and Felismina T.C. Moreira^{a,b,*}

^a *BioMark@ISEP-CEB/LABBELS, School of Engineering, Polytechnic of Porto, R. Dr. António Bernardino de Almeida, 431, 4249-015 Porto,*

^b *LabRISE-CIETI - School of Engineering, Polytechnic of Porto, R. Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal*

^c *Department of Biomedical Engineering, Faculty of Science and Engineering, Swansea University, Swansea SA1 8EN (UK)*

^d *BioMark@UC-CEB/LABBELS, Faculty of Sciences and Technology, University of Coimbra, R. Sílvio Lima, Pólo II, 3030-790 Coimbra, Portugal*

^e *REQUIMTE, School of Engineering, Polytechnic Institute of Porto, Porto, 4200-072, Portugal*

Synthesis and characterization of cationic polymer-capped AuNPs for application in molecular diagnostics

Stylianos Grammatikos^{1,2*}, Ioannis Svoliantopoulos^{1,3} and Electra Gizeli^{1,2}

¹*Institute of Molecular Biology and Biotechnology, Foundation for Research and Technology-Hellas, 100 N. Plastira Str., 70013 Heraklion, Greece*

²*Department of Biology, University of Crete, 70013 Voutes, Heraklion, Greece*

³*Department of Chemistry, University of Crete, 70013 Voutes, Heraklion, Greece*

[*s.grammatikos@imbb.forth.gr](mailto:s.grammatikos@imbb.forth.gr)

Abstract:

Loop-mediated isothermal amplification (LAMP) is a robust and versatile molecular diagnostics technique that provides rapid results with high sensitivity and specificity, under isothermal conditions. However, achieving sensitive naked-eye detection of the amplified target in a crude sample is challenging. Herein, we report a simple, yet highly efficient and sensitive methodology for the colorimetric visualization of a single target copy in saliva, using cationic polymer-capped AuNPs (cAuNPs), synthesized via a green chemistry approach. The role of free cationic polymer in the cAuNPs solution was investigated and the mechanism of cAuNPs stabilization/aggregation was revealed, in a complex solution including saliva. Specifically, it was attributed to electrostatic and depletion effects exerted between the cAuNPs, free cationic polymer and the solution components. The naked-eye detection of <10 copies in 20% saliva with AuNPs has never been shown before, and combined with the simplicity and flexibility of the method, presents a significant advancement towards global point-of-care (POC) diagnostics.[1]

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Thursday 14th September

WS1 & WS3 Session VI

Tissue Platforms for disease modelling and drug testing

Human Nanomedicine: Human Clinical Results with Nanomaterials

Thomas J. Webster^{1,2}

¹Hebei University of Technology, Tianjin, China

²Interstellar Therapeutics, Mansfield, MA, USA

*websterthomas02@gmail.com

Abstract:

Nanomaterials have been widely tested in vitro and in small order animal studies for decades. Results have shown greater tissue growth, decreased bacteria growth, and inhibited inflammation compared to conventional materials [1-3]. However, few studies exist examining human responses to nanomaterials. This invited presentation presents a cohort study of nano implants inserted into humans. In particular, one study includes the implantation of nanotextured spinal implants (Figure 1) into over 14,000 patients over the past 5 years. Results demonstrated no cases of infections or other implant failures which is significantly better than statistics on conventional spinal implants which have up to 20% failure rates [1-3]. This study will further explain that nano implants mimic the natural nano texture of bone and tissue itself and possess surface energy that can competitively increase the adsorption of proteins known to promote osteoblast (bone forming cells) functions, decrease bacteria functions, and limit inflammatory cell functions. Additional examples will be given implanting nanomaterials into humans including into bone, cancerous tissues, infected tissues, and the heart. As such, this unique presentation will cover the few human clinical studies that exist on implanting nano implants into humans showing improved human health.

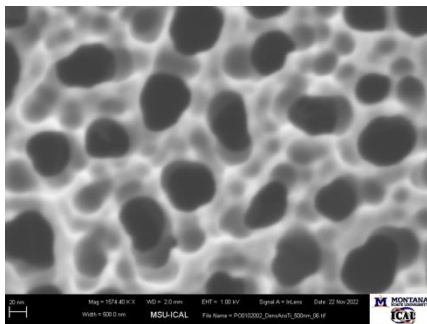


Figure 1: Titanium implants modified to have nanoscale surface features.

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Cytotoxicity effect of zinc oxide (ZnO) nanoparticles under static and dynamic culture conditions

Eleftheria Babaliari^{1*}, Dionysios Xydias^{1,2}, Maria Kefalogianni^{1,3}, Anna Pantelaiou^{1,4,5}, Sotiris Psilodimitrakopoulos¹, Paraskevi Kavatzikidou¹, Anthi Ranella¹ and Emmanuel Stratakis^{1,3}

¹*Foundation for Research and Technology – Hellas (F.O.R.T.H.), Institute of Electronic Structure and Laser (I.E.S.L.), Heraklion, Crete, Greece*

²*Department of Materials Science and Technology, University of Crete, Heraklion, Crete, Greece*

³*Department of Physics, University of Crete, Heraklion, Crete, Greece*

⁴*University of Crete, Heraklion, Crete, Greece*

⁵*Technical University of Crete, Heraklion, Crete, Greece*

*ebabaliari@iesl.forth.gr

Abstract:

In the past few years, the widespread use of nanomaterials raises concerns over the acute and long-term impact of nanomaterials on human health. Nanomaterials can pose health risks depending on the dose, frequency and duration of exposure [1]. However, there is a gap between nanomaterials application and unknown risks which could have a negative impact on potential future commercialization. Additionally, the current nanotoxicology platforms which are based on cell culture plates result in improper control of cell exposure to nanomaterials due to aggregation and sedimentation resulting in very different exposure profiles and thus misleading data [2]. As a consequence, it is urgent to find new methodologies to address these issues. To overcome the ongoing challenges faced by traditional nanotoxicology platforms, we developed a more physiologically-realistic microfluidic platform incorporating polymeric microgrooved substrates that could be inserted to a non-linear microscope for live imaging observation. The effect of zinc oxide (ZnO) nanoparticles on NIH 3T3 cells was examined in terms of survival and proliferation both under static and dynamic conditions.

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Acknowledgments

This work was supported by NFFA EUROPE Pilot (EU 2020 framework programme) under grant agreement no.101007417 from 1/03/2021 to 28/02/2026.

Viscosity influence on human hepatoma tumor spheroids formation in core-shell alginate-carboxymethylcellulose microcapsules

Xuan Peng,^{1*} Željko Jančićević,¹ Sandy Lemm,¹ Markus Laube,¹ Jens Pietzsch,¹ Michael Bachmann,¹ Larysa Baraban¹

¹Helmholtz-Zentrum Dresden-Rossendorf, Institute of Radiopharmaceutical Cancer Research, 01328 Dresden, Germany

*x.peng@hzdr.de

Abstract:

Biomolecular and physical stimuli, such as stiffness and stress, of the extracellular environment, regulate collective cell dynamics and tissue patterning.^[1, 2] The viscosity in the tumor microenvironment can increase due to the accumulation of macromolecules over time.^[3] Islands of rigid tumors are surrounded by soft cells that are more deformable than their healthy counterparts.^[4] Nonetheless, how the viscosities of the tumor microenvironment regulate collective cell spatial and temporal organization is not fully understood. Here, we used the human hepatoma (HepG2) cancer cells, the basic structural component of the liver, as an example to study the influence of viscosity (range from 0.8 cP to 15 cP) on cancer cell collective behavior in 3D microcapsules reactors. Alginate/Alginate-carboxymethylcellulose microcapsules (AL/AL-CMC MCs) with HepG2 cells were generated using a home-made high-throughput droplet-based microfluidic platform.^[5] Cell distribution, cell proliferation, spheroids growth, morphology change, and cytoskeleton difference were observed and quantified, showing a significant effect on viscosity change. Importantly, F-actin and keratin 8 intensity and distribution results can be a cue that viscosity increases enhancing the ability of cancer cells to squeeze through dense tissue. The results thus demonstrate that extracellular viscosity as an important physical cue regulates tumor development relevance to cancer biology.

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[2] K. Bera, et al. *Nature*, 365-373 (2022)

[3] R.J. Ellis, et al. *Biochem. Sci.*, 597-604 (2001)

[4] T. Fuhs, et al. *Nat. Phys.*, 1510-1519 (2022)

[5] X. Peng, et al. *Biotechnol. J.*, e2200365 (2023)

***In vitro* cytotoxicity of polymeric-based theranostic nanocarriers for drug delivery in central nervous system disorders**

Magdalena Procner^{1*}, Marta Szczęch², Magdalena Regulska¹, Monika Leśkiewicz¹, Krzysztof Szczepanowicz², Władysław Lason¹, Agnieszka Basta-Kaim¹ and Piotr Warszyński²

¹*Maj Institute of Pharmacology, Polish Academy of Sciences, Krakow, Poland*

²*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland*

[*procner@if-pan.krakow.pl](mailto:procner@if-pan.krakow.pl)

Abstract:

One of the major limitations in treatments of neurodegenerative diseases is an inefficient delivery of neuroprotective drugs through the blood-brain barrier (BBB). The very poor water solubility of most promising neuroprotectants limits their delivery to the affected part of the brain. Nowadays, nanoparticles (NPs) have attracted much attention as promising drug carriers that could deliver therapeutics to their specific molecular targets. Moreover, the multifunctional theranostic NPs are suitable for both diagnosis and therapy.

Herein, we present a novel methodology for delivering selected neuroprotective substances using multifunctional nanocarriers based on polymeric nanoparticles. The drug-loaded NPs were prepared from nanoemulsion template methods, i.e., the spontaneous emulsification solvent evaporation method [1]. For further studies two types of nanocarriers were prepared - with a liquid core and solid core (made of docusate sodium salt (AOT)/poly L-lysine (PLL) complex or polycaprolactone (PCL)) in which selected neuroprotectant (cyclosporine A or tacrolimus) was encapsulated. Subsequently, NPs were modified using the layer-by-layer approach by creating multifunctional polyelectrolytes shells made of poly-L-glutamic acid (PGA) and poly L-lysine (PLL) or gadolinium-labeled poly L-lysine (PLL-Gd), and PEGylated-PGA. The obtained NCs were characterized by determination of their size distribution and zeta potential. Human neuroblastoma SH-SY5Y cell line was used to estimate the biocompatibility of the theranostic nanocarriers loaded with selected drug in cell viability and toxicity assays. Next, we examined the neuroprotective potential of encapsulated drugs against oxidative stress-induced cytotoxicity. Obtained results indicate, the developed polymeric-based NPs seem to be promising carriers for drug delivery and diagnosis in CNS therapies.

Acknowledgements: The authors thank the National Science Centre in Poland for financial support (Grant no. 2020/39/B/NZ7/01913).

[1] M. Szczęch, et al. *Nanomaterials* 10, 496-511 (2020)

Cytotoxicity and Drug Release Assessment of the reduced graphene oxide films and ocular patches

Paraskevi Kavatzikidou^{1*}, Phanee Manganas¹, Katerina Anagnostou², Evangelos Skoulas¹, Stella Maragkaki¹, Alexandra Manousaki¹, Minas M. Stylianakis^{1,2}, Dimitrios M. Kosmidis², Vasileios Selimis⁴, Ilias Maragkos⁴, Ioannis M. Aslanides⁴, Emmanuel Kymakis², Anthi Ranella¹, Emmanuel Stratakis¹

¹ *Institute of Electronic Structure and Laser, Foundation for Research and Technology – Hellas (FORTH-IESL), Heraklion, Crete, Greece*

² *Electrical & Computer Engineering Department, Hellenic Mediterranean University, Heraklion, Crete, Greece*

⁴ *Emmetropia Mediterranean Eye Institute, Heraklion, Crete, Greece*

*ekavatz@iesl.forth.gr

Abstract:

Glaucoma is the second most common cause of blindness worldwide. It is estimated that in 2010, 60.5 million people worldwide had some form of glaucoma and this figure will reach 79.6 million by 2020^{1,2}. Glaucoma is a group of ophthalmic diseases that lead to progressive damage of the optical nerve responsible for the transfer of information in the brain. If it is not treated immediately, the vision loss is irreversible. The reduction of intraocular pressure (IOP) is associated with slowing down to a great extent the risk of the disease progression. The thickness and the mechanical properties of the cornea are the main parameters influencing the IOP measurement. Nowadays, the majority of people with glaucoma will have to use eye drops to tackle the problem. The biggest hurdle is that many patients do not comply with their treatment. Various drug delivery systems have been developed limiting the incidence, but have failed to overcome significant limitations such as the delivery of hydrophobic drugs and their high cost.

In this context, EOF project envisaged the development of innovative devices known as "Alternative Smart Ocular Patches with Controlled Ophthalmic Pharmacokinetics" to improve the treatment of glaucoma. The main features of the ocular patches studied and presented in this work were: The cytotoxicity of the graphene nanostructures of graphene oxide and the binding of desirable drugs on films and on the ocular patches, as well as the controlled drug release mechanism from the ocular patch.

Acknowledgments: This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-02024).

[1] H.A. Quigley, A.T., Broman, *Br J Ophthalmol*, 90(3):262-7 (2006)

[2] C. Cook, P. Foster, *Can J Ophthalmol.*, 47(3):223-6 (2012)

Development of a nano drug delivery system based on MCM-48 and polyoxometalates for poorly soluble drug, Glipizide

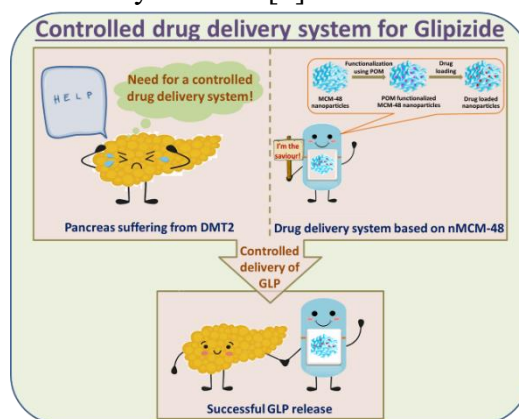
Debatrayee Dasgupta^{1*} and Anjali Patel¹

¹Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat-390 002, India

*depuja79@gmail.com

Abstract:

Diabetes mellitus (DMT2) is a heterogeneous disease associated with variety of medical conditions. Glipizide (GLP), a poorly soluble second generation sulphonyl urea, is prescribed widely for the treatment of DMT2 [1]. However, it has a short half life and causes dose-dependent hypoglycemia. Therefore, a controlled drug delivery system (DDS) for GLP is expected to maintain a more stable plasma glucose levels, lower dosing frequency, and reduce the incidence of hypoglycemia. In this direction, developing a nano DDS for GLP as a pharmaceutical application of nanotechnology, would demonstrate potential advantages in enhancing drug solubility and availability, controlling drug release, minimising therapeutic side effects, and overcoming human body barriers [2].



In the present work, a DDS based on 12-tungstosilicic acid (TSA) functionalized MCM-48 nanoparticles (nMCM-48) was synthesized and characterized by various techniques. *In vitro* release study of GLP/TSA/nMCM-48 was carried out in simulated body fluid (pH-7.4, 37 °C) under stirring conditions followed by the evaluation of the release kinetics and mechanism. Further, the developed nano DDS was compared to that of commercially available formulation, Glynase using dissolution apparatus. The release study demonstrates that GLP/TSA/nMCM-48 exhibits more controlled release than Glynase. Furthermore, taking into account the anti-cancer activity of GLP, this work demonstrates that GLP has potential of inhibiting cancer to some extent.

[1] Y. V. Simos, et al. *Asian Journal of Pharmaceutical Sciences*, 16, 62–76 (2021)

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International Conference on Nanotechnologies and Bionanoscience

Structural, Electrical, and Optical Properties of Organic-Inorganic Thin Films Based on Natural Alkaloids and Halometallates(II)

Lidija Androš Dubraja^{1,*}, Mia Mesić¹ and Marko Dunatov¹

¹*Ruđer Bošković Institute, Zagreb, Croatia*

Friday 15th September

WS1 & WS3 Session II

Theranostics, Drug Delivery, Magnetic hyperthermia

Overcoming resistance to nano-immunotherapy in solid tumors

Triantafyllos Stylianopoulos*

Cancer Biophysics Laboratory, University of Cyprus, Nicosia, Cyprus

*[*tstylian@ucy.ac.cy](mailto:tstylian@ucy.ac.cy)*

Abstract:

Compromised therapeutic outcomes in solid tumors are caused in large part by abnormalities in the tumor microenvironment (TME) that inhibit the delivery of nanomedicines and antibodies and induce hypoxia and thus, immunosuppression. These conditions, in turn, fuel tumor progression, metastasis and drug resistance. TME abnormalities in fibrotic cancers, such as subtypes of breast, pancreatic and colorectal cancers and sarcomas, include the dense tumor stroma, which is abundant in cancer-associated fibroblasts (CAFs), collagen and hyaluronan. These structural components of the TME cause stiffening of the tumor and accumulation of mechanical forces, leading to tumor vessel compression and thus, the formation of a dysfunctional vasculature that limits oxygenation supply and drug delivery. To restore these abnormalities, an effective therapeutic strategy is the normalization of the structural components of the TME. A new class of drugs being used to induce TME normalization is the “mechanotherapeutics”. These therapeutic agents modulate tumor mechanics to alleviate stiffness and intratumoral mechanical forces in order to decompress tumor vessels and restore perfusion.

In my talk, I will summarize the physiological barriers to drug delivery to solid tumors and discuss strategies for overcoming them. I will further present preclinical data providing evidence of how normalizing the TME with different families of mechanotherapeutics can significantly improve the delivery and efficacy of nano-immunotherapy, leading to complete cure and immunological memory. Finally, I will discuss the use of ultrasound imaging methods to monitor changes in tumor stiffness and perfusion for the development of biomarkers predictive of tumor response to therapy.

Hybrid Silver Iron Oxide Nanoflowers: Synthesis, characterization and their theranostic ability against glioblastoma

Sofia G. Nikolopoulou^{a,b,*}, Beata Kalska-Szostko, Anna Basa, Eleni K. Efthimiadou^{a,b}

^a *Inorganic Chemistry Laboratory, Chemistry Department, National and Kapodistrian University of Athens, Panepistimiopolis, Zografou 157 71, Greece*

^b *Sol-Gel Lab, Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", 153 41 Aghia Paraskevi Attikis, Greece*

*sophiagnik@chem.uoa.gr

Abstract:

Inorganic nanoparticles have been studied thoroughly in recent years to evaluate their potential in different applications due to their unique properties. By combining the characteristics of different metal nanoparticles hybrid nanoparticles are synthesized combining different desired properties. Among this category are silver – iron oxide nanoparticles, which can combine magnetic properties due to iron and plasmonic properties due to silver¹.

In our work, we investigate the synthesis of hybrid silver – iron oxide nanoflowers that can be used as a theranostic tool in the treatment of glioblastoma. Hybrid nanoflowers are characterized fully morphologically and structurally, while their synthesis is being tested by varying synthetic parameters to give conclusions on the factors affecting the formation of this unique morphology. Different nanoflowers are obtained when the reaction time and/or Ag/Fe ratio is changed, and the results are compared. Moreover, nanoflowers are evaluated for their cytotoxicity, their hemocompatibility and their ability to internalize into cells monitored by two different protocols².

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[2] Das, Raja, et al. "Boosted hyperthermia therapy by combined AC magnetic and photothermal exposures in Ag/Fe₃O₄ nanoflowers" *ACS applied materials & interfaces* 8.38 (2016): 25162-25169

Functional nanomaterials for combined tumor therapy

Mikhail V. Zyuzin*

School of Physics and Engineering, ITMO University, St. Petersburg, Russian Federation

**mikhail.zyuzin@metalab.ifmo.ru*

Abstract:

The limitations of traditional cancer treatments stem from the non-specific targeting of cancer drugs, which can lead to significant harm to healthy cells and an increased risk of cancer recurrence. To overcome these issues, combining different therapies can enhance the therapeutic effect [1]. Recent advances in the design and application of various nanostructured materials have led to some progress in combined cancer therapy. It allows the fabrication of nanostructures, which enable multimodal treatment against cancer. This report reviews the use of different nanostructured materials for combined therapy of various types of cancer. In particular, we present the successful inhibition of melanoma cancer tumors through the combination of radiotherapy, photothermal therapy (PTT), and chemotherapy using gold nanorods (Au NRs) as nanocarriers. The synthesized nanocarriers have a high labeling efficiency (94-98%) and radiochemical stability (>95%) suitable for radionuclide therapy. By injecting ^{188}Re -labeled Au NRs into the tumor and applying PTT with near-infrared laser radiation, dual photothermal and radionuclide therapy was achieved. Furthermore, combining ^{188}Re -labeled Au NRs with paclitaxel (PTX) significantly improved the treatment efficacy compared to monotherapy [2].

Another study explores the use of combined chemo- and radionuclide therapy for lung metastatic cancer using radionuclide carriers (^{177}Lu -labeled core-shell particles) and the chemotherapeutic drug cisplatin (CDDP). The core-shell particles can be loaded with ^{177}Lu therapeutic radionuclide effectively and exhibit good radiochemical stability over an extended period. In vivo biodistribution experiments reveal that the developed carriers accumulate primarily in the lungs without increased radiation absorption by healthy organs. Mono-regime radionuclide therapy with radiolabeled particles inhibits the number of metastatic nodules [3]. Combining chemo- and radionuclide therapy further enhances therapeutic efficacy. This work provides systematic research on the potential application of combined therapies for cancer treatment.

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[2] O. Peltek, et al. *ACS Appl. Mater. Interfaces*, 15, 13460–13471 (2023)

[3] A. Timin, et al. *J. Controlled Release*, 344, 1-11 (2022)

HF_n-mAb nanoconjugates-mediated anticancer activity in 3D tumor models

Davide Prosperi*, Linda Barbieri and Miriam Colombo

NanoBioLab, Department of Biotechnology and Biosciences, University of Milano- Bicocca, Piazza della Scienza 2, 20126 Milan, Italy

*[*davide.prosperi@unimib.it](mailto:davide.prosperi@unimib.it)*

Abstract:

During the last decades, immunotherapy has significantly developed as an alternative modality to treat cancer malignancies. In contrast to the other therapeutic concepts, immunotherapy aims to eliminate the primary mass of cancer and relevant peripheral metastases by re-educating the host immune system to recognize the cancer cells as “non-self” and consequently react against them. Monoclonal antibodies (mAbs) can promote tumor killing both by immune cell activation through a mechanism known as antibody-dependent cellular cytotoxicity (ADCC) and by the direct inhibition of tumor proliferation and survival pathways. However, the therapeutic efficacy of mAbs is still limited by poor pharmacokinetics and low penetration across biological barriers. The use of nanocarriers proved to be a promising strategy to overcome mAbs limitations, because they can be both functionalized on the surface with specific ligands and exploited as vehicles for drug delivery. H-ferritin (HF_n), a recombinant form of human apoferritin, has been extensively studied due to its biocompatibility, easy loading with drugs and effectiveness in tumor targeting thanks to the selective recognition by TfR1, overexpressed in most solid cancers. We demonstrated that HF_n is an efficient mAb carrier across the blood-brain barrier (BBB) without loss of antitumoral activity. Next, we developed 3D cellular models using spheroids of human breast and brain cancers, resembling their spatial architecture, cellular layered assembly, physiological responses, and nutrient gradients. Experiments were carried out to evaluate the internalization of HF_n-mAbs by flow cytometry. In addition, we investigated the ability of HF_n-mAb nanoconjugates to trigger the ADCC by Operetta live imaging system monitoring over time the increase in mortality resulting from the activation of the apoptosis mechanism. To further confirm the ability of our nanoconjugates to initiate ADCC, we also studied the activation of natural killer (NK) cells, which, after binding to the Fc portion of mAbs, release cytotoxic granules that kill cancer cells. Moreover, we also performed a preliminary *in vivo* experiment which showed a preferential accumulation of the nanoconjugate at the tumor site. The data obtained so far with 3D models demonstrated the efficacy of HF_n-mAbs to trigger an anticancer effect and activate the immune system.

[1] M.A. Rizzuto, et al. *Biomaterials Sci.* 9, 2032-2042 (2021)

Design of versatile graphene oxide-based nanoconstructs with immunomodulatory activity

Despoina Despotopoulou^{1*}, Maria Stylianou², Thomas Kisby², Neus Lozano¹, Kostas Kostarelos^{1,2,3}

¹ Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain

² Nanomedicine Lab, Faculty of Biology, Medicine, and Health, The University of Manchester, Manchester, M13 9PT, U.K.

³ National Graphene Institute, The University of Manchester, Booth Street East, Manchester, M13 9PL, U.K

*despoina.despotopoulou@icn2.cat

Abstract:

Current immunotherapeutic strategies have proven to be effective only in a fraction of patients. Variable response rates may arise from the heterogeneity of immune mechanisms between different individuals [1]. A potential approach to overcome this reality introduces novel nanoscale-based immunomodulation platforms attempting to offer tissue specificity and durability of the therapy [2]. Towards this aim, 2D materials characterized by a large available surface area can offer increased loading of biologically-active molecules. Graphene oxide (GO) nanoconstructs are one such platform system for medical use, utilizing also their colloidal stability in biological fluids, biocompatibility and biodegradability [3,4]. In the present study, GO was complexed non-covalently with a small immunomodulatory molecule (a synthetic TLR7/8 agonist) resulting in colloiddally and chemically stable nanoplatforms (**Figure 1**). A simple and highly reproducible protocol for the preparation of the nanoplatforms will be presented. Moreover, the successful complexation has been indicated through a series of physicochemical characterizations along with *in vitro* and *in vivo* studies demonstrating its immunomodulatory activity. Collectively, this study proves that GO can serve as a viable platform for the non-covalent decoration with immune system-activating molecules. The described system is being exploited for *in vivo* immunotherapeutic applications against different cancer types.

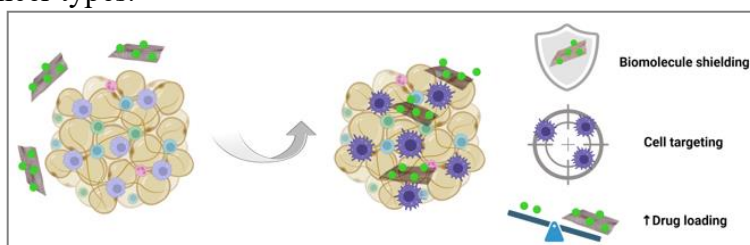


Figure 1: Schematic depiction of a GO-based immunomodulation platform

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Bio-Nanomachine Interfaces in Externally Controllable Nanonetworks for Brain Tumour Management

Andreani D. Odysseos^{1*}, Maria Kokonou¹, Theodoulakis Christofi¹, Abdul Quddious², Asif Bilal², Stavros Iezekiel², Costas Pitris²

¹*EPOS-Iasis, R&D, Nicosia, Cyprus*

²*University of Cyprus, Nicosia,, Cyprus*

[*andreani@epos-iasis.com](mailto:andreani@epos-iasis.com)

Abstract:

Glioblastoma Multiforme (GBM) is the most frequent and morbid brain tumour. Despite the recent flurry of molecular and immunologic therapies, GBM patients have not yet benefited unlike other tumours. This is greatly attributed to (i) the large genetic and phenotypic spatiotemporal heterogeneity, (ii) lack of successful delivery across the Blood-Brain-Barrier (BBB) and the Tumour Microenvironment (TME), including the extracellular matrix (ECM), (iii) ineffective quantification of therapeutics uptake within the tumour bulk and ultimately, (iv) insufficiency of direct evaluation of the effectiveness of targeted therapies. Advanced nanosystems have been extensively explored as potential solutions in overcoming both biological and mechanical barriers but have not as of yet made it effectively to the clinic. Induced Neural Stem Cells (iNSC) engineered to produce and deliver therapeutic genetic material sequences such as non-encoding nucleic acids encapsulated in exosomes, epitomised by micro-RNAs (miRNA) have a high potential to home tumour niches and inhibit progression and are emerging as highly promising advanced biological therapeutics in GBM.

Molecular Communications define a supra-discipline at the interface of Molecular Medicine with Information and Communication Technologies where cellular and sub-cellular units, such as engineered stem cells and exosomes function as information sender and receiver bio-nanomachines propagating through biological and mechanical barriers [1]. Encapsulation of bio-nanomachines in implantable organoids confer a precision attribute to the therapeutic scheme. An ambitious paradigm shift is emerging in Oncology Research, where real-time monitoring of tumour initiation, progression and response to personalized therapy enables the supra-discipline of “bio-nanomachine diagnostics” ushering the emergence of the “Externally Controllable Nanonetwork Therapeutics” field, interfacing the tumour and the therapeutic organoids with actuating nanodevices embodied by wearable metamaterial antennas and multifunctional and implantable multimodal smart biosensors, functioning autonomously in a close-loop Externally Controllable Molecular Communication (ECMC) system.

Acknowledgements: This work has been supported by Grant Agreement number: 828837 — GLADIATOR — H2020-FETOPEN-2018-2020

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Monday 11th September

WS2 Session III

Organic and Perovskite Photovoltaics

Indoor, outdoor and in-situ characterization strategies for Perovskite Solar Cells

Kenedy Tabah Tanko,¹ Fanny Baumann¹, Ashitha Paingott Parambil¹, Masoud Karimipour¹,

Sonia Ruiz Raga¹, Monica Lira-Cantu^{1,*}

¹ Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and the Barcelona Institute of Science and Technology (BIST). Building ICN2, Campus UAB E-08193, Bellaterra,

Barcelona, Spain. E-Mail: monica.lira@icn2.cat

Abstract

Halide perovskite solar cells (PSCs) have already achieved a certified power conversion efficiency (PCE) above 25 %, making them one of the most promising emerging photovoltaic technologies. One of the main bottlenecks towards their commercialization is their long-term stability, which should exceed the 20-year mark. Many are the strategies applied to extend device lifetime, among them are the use of additives, the optimization of the fabrication process of perovskite thin films or the replacement of unstable organic transport layers such as Spiro-OMeTAD. Although most of these approaches can effectively improve device efficiency, they frequently fail at providing stable PSCs as defined as those able to display less than 10 % degradation after 1000 h of continuous illumination under 1 sun. In this work we present our most recent work regarding the analysis of PSC stability. We carried out the fabrication of PSCs applying different strategies, such as additive engineering, interface modification employing MXenes, among others. We demonstrate that adding organic additives and 2D interfacial modifiers to the PSC allows for the passivation of shallow or deep defects, having a tremendous impact on the device stability. We analyse our solar cell following ISOS protocols (ISOS-D, ISOS-L and ISOS-O), as well as in-situ characterization. We expect that our work will have important implications for the current understanding and advancement of operational PSCs.

Hybrid Materials for Energy Conversion Toward Smart Photovoltaics

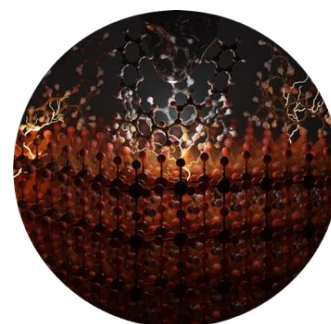
Jovana V. Milić

jovana.milic@unifr.ch

Adolphe Merkle Institute, University of Fribourg, CH-1700 Fribourg, Switzerland

Abstract

Hybrid organic-inorganic materials are increasingly relevant for emerging energy technologies. In particular, metal halide perovskites have become one of the leading semiconductors for solar-to-electric energy conversion in photovoltaics.¹⁻² However, their operational instability hinders practical applications. While this can, to an extent, be overcome by incorporating organic moieties within hybrid perovskite frameworks that form low-dimensional architectures with superior operational stabilities, their electronically insulating character often compromises the resulting photovoltaic performances.²⁻³ This has been addressed by relying on the supramolecular engineering in the design of adaptive bioinspired materials and (photo)electroactive organic species to enhance the functionality of hybrid perovskites by enabling control in response to external stimuli,³ such as voltage bias,⁴ light,⁵ and pressure,⁶ opening a path toward multifunctional materials and smart photovoltaics.



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- [3] J. V. Milić*, *J. Mater. Chem. C* 2021, 9, 11428–11443.
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Wednesday 13th September

WS2 Session II

Organic and Perovskite
Photovoltaics

Efficient Structures And Processes for Upscaling of Perovskite Modules and Tandems

Tom Aernouts^{1*,2,3}

¹*Imec, imo-imomec, Thin Film PV Technology, Thor Park 8320, 3600 Genk, Belgium*

²*Hasselt University, imo-imomec, Martelarenlaan 42, 3500 Hasselt, Belgium*

³*EnergyVille, imo-imomec, Thor Park 8320, 3600 Genk, Belgium*

* tom.aernouts@imec.be

Abstract:

The unprecedented fast rise of power conversion efficiency (PCE) of perovskite-based solar cells (PSC) in recent years has created a vast worldwide research activity in this material class for photovoltaic and other opto-electronic applications. Several materials compositions and device architectures have been described and best reported PCE's yield recently more than 25%. Also improved stability under specific conditions has been shown for specific architectures. Whereas all these results indicate a high potential for this novel solar technology, further steps must be taken to convince industry and even the whole PV community that perovskite-based photovoltaics can really emerge from the lab into industrially applicable solar module processing. Our R&D program works actively on the upscaling of perovskite solar modules with scalable processes up to sizes of 35x35 cm².

Similarly, the perovskite PV technology has boosted tandem research whereby perovskite cells and modules are placed on top of other PV devices like Si or CIGS solar cells. Impressive lab scale results exceeding 30% PCE have been reported. New challenges arise when this needs to be upscaled to full wafer or module size. It will be discussed how we approach these challenges.

Mesoscale ordered two-dimensional semiconductor polymers with Dirac cones and flat bands by on-surface synthesis

Giorgio Contini^{1,2}

¹ Istituto di Struttura della Materia-CNR (ISM-CNR), Via Fosso del Cavaliere 100, 00133
Roma, Italy

² Department of Physics, University Tor Vergata, Via della Ricerca Scientifica 1, 00133
Roma, Italy

Dirac cones, present in the band structure of graphene, are responsible of its remarkable charge-transport properties. However, they are not exclusive to graphene but require that the material presents specific symmetry and delocalized electrons. Efforts have been devoted to identifying 2D materials beyond graphene that offer a greater degree of tunability and a nonzero band gap while retaining high carrier mobility.¹ On-surface synthesis represents an opportunity to manipulate the electronic band structure of the material by varying the molecular building blocks (e.g. by the change of constituent atoms and symmetry). By using a class of heteroatom substituted triangulene monomers we synthesized mesoscale ordered 2D π -conjugated polymers on Au(111) with semiconducting properties arranged in a kagome lattice showing Dirac cone structures and flat bands, theoretically predicted.²⁻³ We demonstrate that it is possible to tune the Dirac cone structures and flat bands energy positions by changing the bridging atoms in the triangulene monomers.⁴ These results overcome the major barriers to the application of 2D π -conjugated polymers due small domain size and high defect density attained so far. Although the 2D polymers have been obtained on a metal surface, they can be detached and transferred to other substrates to be used in devices.

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Probing single molecules in active molecular layers of devices

Shadi Fatayer^{1*}

¹*King Abdullah University of Science and Technology, Thuwal, Saudi Arabia*

** shadi.fatayer@kaust.edu.sa*

Abstract:

Organic electronics enable the fabrication of devices with unique properties and low manufacturing costs. Self-assembled monolayers (SAMs) of electronically active materials placed between the conducting electrode and photoactive layer have a significant impact on device performance. They extract charge, passivate defects, and alter interfaces, ultimately increasing the efficiency of organic devices.

Experimental imaging techniques with sub-molecular resolution play a crucial role in studying the influence of SAMs on interfaces. These techniques surpass the limitations of traditional experimental methods, allowing for detailed examination of molecular properties and establishing robust correlations between device performance and molecular characteristics.

Here, we will discuss the contributions that can be achieved by employing scanning tunneling microscopy (STM) and atomic force microscopy (AFM) in the context of SAMs on conductive interfaces. We will focus on key information, including molecular packing, adsorption orientation, and assembling properties. Additionally, we will demonstrate how these properties vary depending on the preparation conditions of the devices.

Nanophotonics for thin-film perovskite solar cells

Aleksandra Furasova^{1*}, Sergey Makarov^{1,2,3}

¹*School of Physics and Engineering, ITMO University, 197101, St. Petersburg, Russia*

²*Harbin Engineering University, Harbin 150001, Heilongjiang, China*

³*Qingdao Innovation and Development Center of Harbin Engineering University, Qingdao 266000, Shandong, China*

* aleksandra.furasova@metalab.ifmo.ru

Abstract:

Thin film perovskite solar cells (PSCs) present one of the most promising tools to get fast, cheap and environment friendly electricity source for charge generation in Space, IoT applications or for household supply. Despite their rapid efficiency growth due to the careful selection of perovskite chemical composition and engineering of a cell design there are several unsolved problems with the charge generation and light management inside the perovskite thin layer.

In our work we consider dielectric photonic nanostructures (A_3B_5 [1], Si [2-4] and SiO_2 [5,6] nanoparticles) as a powerful tool for improvement of thin-film optoelectronic devices because of their low optical losses, a light antenna effect, and chemical resistance to halide perovskites. Based on multi-physical calculations, concerning doping (for A_3B_5 and Mie-resonant Si nanoparticles), size, location, and concentration of optical nanoantennas, we selected and created n-i-p perovskite solar cells with different designs. The inclusion of Si resonant nanoparticles into mesoporous TiO_2 layer helps to improve light absorption by a perovskite layer without reduction of the active material. The management of Si nanoantennas concentration provides to reach a power conversion efficiency of 21.1% for $MAPbI_3$ SCs and 18.9% when adding of GaP nanowires by increasing all main device parameters (when the bare cells can reach only 17.7% of power conversion efficiency). Moreover, we are working on SiO_2 microparticles (900 nm in size) array incorporated into a gold perforated top electrode to create a bifacial perovskite solar cells [6] with light trapping function. According to our metaphysical calculations, bifacial PSCs with the light trapping electrode can achieve efficiency close to 33% when $MAPbI_3$ perovskite is used as an absorber layer. To introduce photonic nanostructures in PSCs spin-coating, blade-coating are used as large-scale and low-cost approaches to develop large-scale devices and modules in future.

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Monday 11th September

WS4 Session III

Emerging Printed Electronics and
Bioelectronics

Printed electronics enabled by 2d materials: Emerging energy harvesters beyond photovoltaics and multi-functional sensors

Konstantinos Rogdakis,^{1,2} Christos Polyzoidis,¹ Katerina Anagnostou,¹ George Veisakis,¹ Ioannis Kalogerakis,¹ Dimitris Tsikritzis,¹ George Viskadourous¹ and Emmanuel Kymakis^{1,2}

¹*Department of Electrical & Computer Engineering, Hellenic Mediterranean University, Heraklion, Crete, Greece.*

²*Institute of Emerging Technologies (i-EMERGE) of HMU Research Center, 71410 Heraklion, Greece*

An aggressive technological deployment will soon affect the planet's energy landscape, demanding a swift transformation from the predominant use of fossil fuels to that of renewable energy installations. With its concurrent arrival, the Internet-of-Things (IoT) deployment promises to create a largely distributed global network of wireless sensors and wearables connected to the "cloud": Humankind is exploiting new technological platforms able to impact sustainable development and prosperity toward Industry 4.0 revolution. These platforms will create a robust demand of energy for their power supply, making a battery-free operation mandatory together with the need of a low manufacturing cost and reduced environmental impact. 2D-material enabled "harvesters" span across a wide range of scales. The demonstrated prototypes include self-powered miniaturized IoT devices, to large scale renewable energy infrastructures.¹

Hereby, as an example of emerging energy harvesters enabled by 2d materials, we formulate water-based graphene oxide (GO) inks to fabricate moisture energy generators (MEGs) while a two-fold geometric tuning is proposed to encourage enhanced performance.² Two GO-based structures with distinctly different thicknesses were prepared as the moisture absorbing layer: a GO-pellet (GOP) and a thinner GO-film (GOF). The effect of electrical contacts' configuration on the MEG's output voltage (V_o) was evaluated as a second geometric tuning approach by varying the surface area of the contacts and their orientation with respect to the GO plane, i.e., horizontal or vertical. GOF-based devices that employed a horizontal contacts' configuration demonstrated champion V_o values (~350 mV) and the fastest response to humidity.

2D-material-based devices could also open the path for novel concepts enabled by emerging multi-functionalities. We use a facile, ultra-low-cost, and up-scalable printable manufacturing process to fabricate flexible multi-functional sensors that respond simultaneously to light illumination and mechanical strain.³ The active layer of the device is based on defect-free In_2Se_3 flakes with inherent piezo-phototronic properties formed by using an in-house spray coating system. Using the same material stack, we demonstrate efficient photodetectors and force sensors. Overall, by applying industrially compatible materials for the underlying flexible substrate and electrodes, combined with spray coating, removes manufacturing complexities that engage costly and energy intensive fabrication.

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Localized laser sintering as a comprehensive additive manufacturing technology for sensing applications

M. Pervolaraki^{1*}, E. Gagaoudakis¹, L. Zouridi^{1,2}, K. Tsimvrakidis¹, E. Mantsiou¹, V. Binas^{1,3},
E. Stratakis^{1,2}

¹*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas,
Heraklion Crete 71110, Greece*

²*Department of Materials Science and Technology, University of Crete, Heraklion Crete 71003,
Greece*

³*Department of Physics, University of Crete, Heraklion Crete 71003, Greece **

pervolaraki@iesl.forth.gr

Abstract:

In modern times, food industries play vital roles in the global economy, encompassing resourcing, production, processing, packaging, and marketing of edible goods. Food waste poses a significant challenge globally, leading to water depletion and energy waste. Global efforts to enhance food safety and security have resulted in an increased interest in smart food packaging. Our focus lies in developing intelligent food packaging capable of monitoring gases released during food shelf life.

Specifically, during the catabolism process of products like fresh meat, chicken, fish, fruits, and vegetables, CO₂ gases and nitrogenous compounds (such as trimethylamine, dimethylamine ethylamine, and ammonia) are released. Hence, we present the fabrication of CO₂ gas sensors for food monitoring applications, using newly developed metallic and metal oxide nanoparticle inks. These inks are printed on rigid and flexible substrates using low-cost technologies and locally laser sintered. The inkjet printing method is utilized to fabricate both the conducting inter-digitated electrodes and the semiconducting zinc oxide nanoparticle-based sensing layer of the device. We employed a homemade prototype laser sintering station emitting at 808 nm with continuous wave emission. This talk will demonstrate the structural, electrical, and gas sensing properties of intelligent food sensors created through state-of-the-art, photonic processing.

The electrical response of the newly developed Ag nanoparticle structures revealed a resistivity (ρ) of approximately $11 \times 10^{-8} \Omega\text{m}$ and a conductivity of around $9 \times 10^6 \text{ S/m}$, corresponding to 7 times the resistivity of bulk silver ($\rho_{\text{Ag bulk}}$). Finally, the all-printed and all-laser sintered ZnO sensor can detect CO₂ gas concentrations as low as 10% at room temperature.

Acknowledgements: SMARTPACK project, T2EDK-02373 co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation.

Inkjet printing of nanobiosensors: what's next?

Giulio Rosati^{1*}, Massimo Urban¹, Gabriel Maroli^{1,2}, Gustavo Dalkiranis^{1,3}
and Arben Merkoçi^{1,4}

¹*Institut Català de Nanociència i Nanotecnologia (ICN2), Edifici ICN2, Campus UAB - 08193
Bellaterra (Barcelona) Spain*

²*Instituto de Investigaciones en Ingeniería Eléctrica Alfredo Desages (IIIE), Universidad Nacional
del Sur – CONICET, San Andrés 800 Bahía Blanca-B8000CPB, Argentina*

³*Instituto de Física de São Carlos (IFSC), Universidade de São Paulo (USP), Av. Trab. São Carlense,
400 - Parque Arnold Schimidt, São Carlos, SP, 13566-590 Brazil*

⁴*ICREA Passeig Lluís Companys 23 08010 Barcelona, Spain*

*giulio.rosati@icn2.cat **Abstract:**

Electrochemical sensors, biosensors, and nanobiosensors are fundamentally composed of basic electronic components such as electrodes, conducting lines, contacts, and insulators. Therefore, it should not be surprising if the most advanced nanobiosensors are typically fabricated by standard microelectronic methods (also known as clean room based methods) such as photolithography and others. If on one hand these methods allow for reproducible and ultra-high resolution 3D structures with a wide variety of materials, on the other hand they are very expensive. In fact, they require keeping the working environment completely dust free (possible only in specific spaces called clean rooms) and using high profile equipment. Inkjet printing emerged in the past years as a promising alternative to both clean room and other printing methods for the fabrication of electrochemical nanobiosensors. This method, combined with nanomaterials-based inks (nanoparticles, 2D flakes, etc.) allows the fabrication of thin-film metal electrodes (100 nm – 1 µm) with a XY resolution in the micrometer range on both rigid and flexible substrates. The drop-on-demand strategy permits saving ink without the need of any mask and allowing for an ultra-short concept to prototype time. In our group, we have proved that consumer (low-cost) inkjet printer can be successfully used for the fabrication of electrochemical biosensors on flexible plastic substrates without any post-printing treatment using metal nanoparticles-based inks, even with multi-material real-time printing. Furthermore, we have introduced a simple heater that can facilitate the printing on different substrates improving the ink adhesion and that can be printed itself with the same printer. The design of the biosensors is extremely easy and can be performed on any drawing software, including MS Paint. The loading of the ink and printing are simple and straightforward as well. The perspective of our work is to be able to take not the biosensor but it's fabrication at the point of care, replacing the current paradigm of centralized fabrication to a more distributed one that we call ubiquitous printing. This will allow our society to be more resilient to supply chain disruptions (as during the COVID19 pandemic).

Combinatorial nanomaterial inkjet printing for next-generation electrochemical transducers and devices

Massimo Urban^{1*}, Giulio Rosati¹, Arben Merkoçi^{1,2}

¹*Catalan Institute of Nanoscience and Nanotechnology (ICN2), Edifici ICN2, Campus UAB, 08193 Bellaterra, Barcelona, Spain*

²*Catalan Institution for Research and Advanced Studies (ICREA), Passeig de Lluís Companys, 23, 08010 Barcelona, Spain*

*massimo.urban@icn2.cat (M. Urban) and arben.merkoci@icn2.cat (A. Merkoçi)

Abstract:

Inkjet printing has gained its popularity for the precise deposition of functional materials for the fabrication of electronic devices and biomedical applications. [1] Metal nanoparticles, 2D-materials and polymers can all be used and deposited by inkjet printing, giving a huge variety of materials and combinations possible. [2-4]

Although not intended for research purposes, consumer printers have been studied over the years as a cheaper alternative for the fabrication and fast prototyping of sensor and devices. [5] A key feature of these equipment is the multiple ink slots available (typically up to 6), meaning that six different nanofunctional inks can be loaded and used at the same time. Thus, it is possible to combine these nanomaterials together, by simultaneous or layer-by-layer deposition, obtaining cooperative interactions and properties rising from the combination of the materials.

Here we present our perspective about combinatorial inkjet printing for development of next-generation electrochemical transducer and devices. Metal nanoparticles and graphene derivatives, between others, can be combined to create structures and devices with multiple functionalities. An even broader library of functional materials couple with fast and simple fabrication with consumer inkjet printers can be the next step for true decentralize ubiquitous fabrication of devices for biomedical and electronic applications.

Stable and Efficient Perovskite Solar Modules and Panel for Terrestrial and Space Applications

Narges Yaghoobi Nia^{1,2*}

¹ School of Aerospace Engineering, University of Rome Sapienza, Via Salaria, 851 - 00138 Rome, Italy

² Laboratory of Photonics and Interfaces, École Polytechnique Fédérale de Lausanne, Lausanne, 1015, Switzerland

* *Email address of the presenting author:* narges.yaghoobinia@uniroma1.it;
narges.yaghoobinia@epfl.ch

Abstract:

The modern space economy is rapidly advancing due to private ventures and increased global access. Space technology is progressing, including the development of durable and affordable power systems. Photovoltaics (PVs) are crucial for power generation on earth and in space. Perovskite photovoltaics, with their efficiency, quick energy return, and resilience to harsh conditions, are gaining attention for aerospace applications¹. These features make them competitive with traditional PV systems in the space economy.

Hybrid organic-inorganic perovskite structures exhibit significant promise as effective light absorbers, particularly for integration into emerging thin film photovoltaic (PV) technologies. Renowned for their exceptional photoconversion efficiency and impressive specific power-to-weight ratio, perovskite solar cells (PSCs) also boast cost-effectiveness in terms of production. Notably, their exceptional resilience to radiation is emerging as a standout quality, positioning them as a viable option for next-generation space photovoltaics.

In light of this context, the P4SPACE project (EU project) aims to advance and upscale flexible PSCs modules and panel, ensuring robust performance and longevity even in the demanding conditions of space environments. This endeavor seeks to establish enduring PV solutions applicable to the full spectrum of current and future space applications.

In my talk, I will introduce P4SPACE project including some key concepts and guidelines for scale production of high-performance perovskite PVs for terrestrial and space applications including cell/module and panel design, laser proceeding, impact of the terrestrial and space stressors on various perovskite layers², effect of composition and encapsulation and packaging methods. In particular, I will present some of our innovative approaches toward fabrication and test results of high stable and efficient perovskite solar modules (single junction and tandem configurations) with outstanding tolerance and stability against terrestrial and space stressors^{3,4}. I also will present high stable efficient tandem solar large module (perovskite/silicon) and high stable single junction module reaching above 20% photoconversion efficiency and stability above 3000 hours in against different stressor⁵.

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- [4] Zendehtdel M, Yaghoobi Nia N, Paci B, Generosi A, Di Carlo A. Zero- Waste Scalable Blade- Spin Coating as Universal Approach for Layer- By- Layer Deposition of 3D/2D Perovskite Films in High Efficiency Perovskite Solar Modules. Sol RRL 2021. doi:10.1002/solr.202100637.
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Integration of two-dimensional materials-based perovskite solar panels into a stand-alone solar farm

George Viskadouros, Konstantinos Rogdakis, Ioannis Kalogerakis, Emmanuel Spiliarotis, Emmanuel Kymakis

viskadouros@hmu.gr

** Email address of the presenting author*

Abstract:

As a vital step towards the industrialization of perovskite solar cells, outdoor field tests of large-scale perovskite modules and panels represent a mandatory step to be accomplished. Here we demonstrate the manufacturing of large-area (0.5 m²) perovskite solar panels, each containing 40 modules whose interfaces are engineered with twodimensional materials (GRAphene-PErovskite (GRAPE) panels). We further integrate nine GRAPE panels for a total panel area of 4.5 m² in a standalone solar farm infrastructure with peak power exceeding 250 W, proving the scalability of this technology. We provide insights on the system operation by analysing the panel characteristics as a function of temperature and light intensity. The analysis, carried out over a monthslong timescale, highlights the key role of the lamination process of the panels on the entire system degradation.

Pescetelli, S., Agresti, A., Viskadouros, G. *et al.* Integration of two-dimensional materials-based perovskite solar panels into a stand-alone solar farm. *Nat Energy* **7**, 597–607 (2022).

Tuesday 12th September

WS4 Session V

Emerging Printed Electronics and
Bioelectronics

Can we move from inorganic to carbon nanoallotrope thermoelectrics? 2D and 3D printing of highly efficient TEG devices

Lazaros Tzounis^{*1,2,3}, Fivos Simopoulos¹, Emmanouil Porfyrakis¹, Kampourakis George¹, Papadakis Nikolaos¹ and Emmanuel Kymakis^{3,4}

¹*Mechanical Engineering Department, Hellenic Mediterranean University, Heraklion, Greece*

²*Printed Electronic Devices of Things P.C., Volos, Greece*

³*Institute of Emerging Technologies (i-EMERGE) of HMU Research Center, Heraklion, Greece*

⁴*Department of Electrical & Computer Engineering, Hellenic Mediterranean University, Heraklion, Greece*

* tzounis@hmu.gr

Abstract:

Thermal energy is one of the many forms of renewable energy sources; yet, > 60% of the above energy is wasted, involving temperatures below 100°C. Since direct conversion of heat to electricity is feasible without hazardous environmental impacts, thermoelectric power generation (TE) has been acknowledged as a reliable method for recovering waste heat. Thermoelectric Generators (TEGs) could be an emerging and promising renewable energy technology leading to a wide range of applications, such as energy harvesting, while efforts are also being made towards applying this technology in the soft robotics and wearable electronics. In addition to the material development process, there is currently a huge trend to move from inorganic thermoelectrics which are typically based on toxic and low abundance elements, non-flexible etc., to organic and carbon nanoallotrope thermoelectrics that have recently reached thermoelectric figure of merits in the range of ~0.5 and power conversion efficiency $\eta = 3-5\%$ [1].

Additive Manufacturing (AM) technologies could aid in this notion as a cost-effective means for TEG fabrication using thermoelectric material inks and pastes. In this presentation/ talk, a focus will be given on the fabrication of TEGs using 2D printing technologies (screen printing) as well as 3D printing- fused filament fabrication (FFF) combined with paste deposition. Mainly, SWCNT p- and n-type legs, will be discussed in detail regarding i.e. the SWCNT ink formulations, the 2D and 3D printing parameters, the TEG device characterization, as well as practical applications powered-up by the TEG device, with SWCNT Power factors of $>150 \mu\text{W}/\text{mK}^2$ and $100 \mu\text{W}/\text{mK}^2$, for p-, n- type SWCNT thermoelements, respectively, at $\Delta T=100\text{K}$.

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2D Materials for energy applications

Francesco Bonaccorso

*BeDimensional SpA, Via Lungotorrente Secca 30r, 16163 Genova
Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova*

* f.bonaccorso@bedimensional.it

Abstract:



International Conference on Nanotechnologies and Bionanoscience

Thursday 14th September

WS4 Session

Emerging Printed Electronics and
Bioelectronics

Scalable NanoManufacturing of Sustainable Large-Area Electronics

Prof. Thomas D. Anthopoulos

*King Abdullah University of Science and Technology (KAUST)
Division of Physical Sciences and Engineering,
Kingdom of Saudi Arabia*

Abstract:

Our ability to continuously downscale critical dimensions of the silicon transistor has proven extremely successful over the past sixty years in increasing the computational power of modern-day microelectronics. The extraordinary developments were accomplished through a virtuous cycle of scientific and engineering breakthroughs, leading to various electronic technologies with extraordinary impacts on our society and personal lives. However, adopting silicon's approach of size-downscaling to emerging technologies, such as large-area electronics and their implementation in the ever-expanding range of emerging applications, has proven challenging regarding technology and economics. In this talk, I will discuss recent work from our laboratory in downscaling emerging forms of large-area electronics and their use in various applications, including sensing, energy harvesting and telecommunication. I will emphasize the use of advanced materials and innovative and highly scalable nanomanufacturing paradigms.

Metabolite-induced *in vivo* fabrication of substrate-free organic bioelectronics

Daniel T. Simon^{1*}, Tobias Abrahamsson¹, Magnus Berggren¹, Hanne Biesmans¹, Jennifer Y. Gerasimov¹, Roger Olsson², and Xenofon Strakosas^{1,2}

¹ *Laboratory of Organic Electronics, Dept. of Science and Technology, Linköping University, Norrköping, Sweden*

² *Chemical Biology and Therapeutics, Dept. of Experimental Medical Science, Lund University, Lund, Sweden*

* daniel.simon@liu.se

Abstract:

Interfacing electronics with neural tissue is crucial for understanding complex biological functions, but conventional bioelectronics consist of rigid electrodes fundamentally incompatible with living systems. The difference between static solid-state electronics and dynamic biological matter makes seamless integration of the two challenging. To address this incompatibility, we developed a method to dynamically create soft substrate-free conducting materials within living biological environments. We demonstrate *in vivo* electrode formation in tissue and live animal models using endogenous metabolites to trigger enzymatic polymerization of organic precursors within an injectable gel, thereby forming conducting polymer gels with long-range conductivity [1]. This approach can be used to target specific biological substructures and is suitable for nerve stimulation, paving the way for fully integrated, *in vivo*-fabricated electronics within the nervous system.

In this presentation, we will discuss the developmental path that led us to this point, our results, our ongoing experiments, and implications for the future.

[1] X. Strakosas, H. Biesmans, et al. *Science* 379, 795–802 (2023)

Organic electrochemical neurons and synapses with ion-mediated spiking

Simone Fabiano

*Laboratory of Organic Electronics, Department of Science and Technology, Linköping
University, Norrköping SE-60174, Sweden E-mail: simone.fabiano@liu.se*

Abstract:

Biointegrated neuromorphic hardware holds promise for developing new protocols to record, process, and regulate signaling in biological systems. Traditional silicon-based neuromorphic systems have limited potential for bio-integration due to their poor biocompatibility, high circuit complexity, and low energy efficiency. Organic mixed ionic-electronic conductors (OMIECs) offer a potential solution to overcome these limitations. Thanks to their structural similarity to biomolecules and their ability to facilitate ionic-electronic transport, OMIECs are an excellent choice for bridging the gap between electronics and biology, enabling energy-efficient signal transduction. This presentation will explore the use of OMIECs to develop organic electrochemical neurons and synapses that possess ion-modulated spiking capabilities. We will discuss the ease of their integration with biological nerves and demonstrate neurosynaptic circuits that can modulate spiking through neurotransmitters, amino acids, and ions. These soft, flexible organic electrochemical neurons and synapses operate at low energy and respond to multiple stimuli, signaling a new era for organic bioelectronics.

Bioelectronic devices and Therapeutic applications: The selective Vagus Nerve Stimulation as a paradigm of the new Bioelectronic Medicine era

Dimitrios A. Koutsouras

Imec-NL, Eindhoven, The Netherlands

dimitrios.koutsouras@imec.nl

Abstract:

Bioelectronic Medicine (BEM) is the emerging field that promises to revolutionize the way clinicians detect and cure diseases by replacing drugs with electrical impulses. The approach involves switching the focus of therapeutic intervention from the vascular system, and the delivery of medications through it, to the nervous system, and the use of electrical currents to treat pathologies. The motivation stems from the fact that every organ in the body is controlled by neuronal circuits which utilize electrical signals to manage the organ's functions. Since these circuits consist of discrete, but interconnected, neuron cells, fiber tracts and nerve bundles, they provide a unique opportunity for targeted, and with reduced side effects, therapies through the modulation of the action potential patterns which regulate them. Especially, the Peripheral Nervous System (PNS) offers numerous opportunities for therapeutic neuromodulation archetypes due to its role to connect the brain and the spinal cord to the rest of the body. The Vagus Nerve (VN), as the main parasympathetic nerve of the PNS, is responsible for innervating multiple organs throughout the torso, and therefore it manages a variety of sensory, motor, and physiological functions. Thus, it is believed to hold the key to alleviating many ailments, including several chronic ones. However, the selective Vagus Nerve Stimulation (VNS), and the resulting functionally specific effects, remain to date a challenging endeavor, even though the need for establishing effective ways to achieve it is imperative. Medical devices play an essential role in the task as they are the means to deliver BEM therapies. In this context, and especially during the last couple of decades, organic bioelectronic devices have gained great attention as a way of establishing seamless communication pathways, between the worlds of biology and electronics. Our work focuses on developing novel implantable BEM devices for selective VNS paradigms. By designing geometry and material optimized electrodes, we deliver sophisticated VN stimulating impulses on large animal models to achieve spatially selective nerve activation and reduced off-target effects. Our findings pave new routes towards innovative and personalized drug-free treatments.

Functionalized carbon fiber yarns for application in 1D supercapacitors and triboelectric devices

José Tiago Carvalho¹, Raquel Barras¹, Ines Cunha¹, Diana Gaspar², Elvira Fortunato¹, Rodrigo Martins¹, Pedro Barquinha¹, Luís Pereira^{1,2*}

¹*CENIMAT/i3N, Department of Materials Science, NOVA School of Science and Technology,*

NOVA University Lisbon and CEMOP/UNINOVA, Campus da Caparica, Caparica

2829-516, Portugal

²*AlmaScience Colab, Campus da Caparica, Caparica 2829-516*

** lmnp@fct.unl.pt*

Abstract:

Carbon fibers (CFs) are versatile materials for energy harvesting and storage applications, particularly when focusing on wearable device applications. They present a combination of some unique properties such as suitable electrical conductivity, and mechanical strength, being also lightweight.

Stretch-broken carbon fiber yarns (SBCFYs) can be used as current collectors to fabricate 1D fiber-shaped supercapacitors (FSCs). The areal-specific capacitance reaches $433.02 \mu\text{F}\cdot\text{cm}^{-2}$ at $5 \mu\text{A}\cdot\text{cm}^{-2}$. The maximum achieved specific power density is $0.5 \text{ mW}\cdot\text{cm}^{-2}$, at $1 \text{ mA}\cdot\text{cm}^{-2}$. The 1D FSCs possess a long-life cycle, 92% capacitance retention after 10000 charge/discharge cycles. The specific capacitance can be improved through functionalization of CFs with MoS_2 nanosheets, reaching $58.6 \text{ F}\cdot\text{g}^{-1}$ at $1 \text{ mV}\cdot\text{s}^{-1}$ with a power density of $15.17 \text{ W}\cdot\text{g}^{-1}$ and energy density of $0.5 \text{ mWh}\cdot\text{g}^{-1}$.

Functionalization of CF by introducing functional groups or nanoparticles onto the fiber surface is also crucial in optimizing power conversion efficiency in energy harvesting devices, such as triboelectric ones. We propose triboelectric generator yarns (TEG yarns) with axially grown ZnO nanorods using a new method for depositing PDMS directly onto conductive carbon yarns. The in-situ PDMS curing method allows the fast formation of a uniformly thick coating over functionalized CFs. Single-electrode configuration TEG yarns were developed, and their electrical output was optimized by precisely adjusting the PDMS layer thickness and by changing the chemical and physical nature of the SBCFYs surface, reaching a power density of $74.1 \mu\text{W cm}^{-2}$. We demonstrate that electrodeposited cellulose nanocrystals layers can replace ZnO nanorods in improving local polarization, which results in an increase of 100% of the TEGs electrical output to around $142.7 \mu\text{W cm}^{-2}$.

Both SBCFYs supercapacitors and triboelectric devices can be hand-stitched onto fabrics showcasing the practicality and versatility of the prepared 1D CFs energy harvesting and storage devices to power the future generation of wearables electronics.

Oxide thin-film transistors as enablers of innovative flexible electronics: the examples of e-textiles and ionizing radiation detectors

Pedro Barquinha^{1*}

¹*CENIMAT/i3N, Department of Materials Science, NOVA School of Science and Technology (FCT-NOVA) and CEMOP/UNINOVA, NOVA University Lisbon, Campus de Caparica, 2829-516 Caparica, Portugal*

** Email: pmcb@fct.unl.pt*

Abstract:

Thin-film transistors (TFTs) have been fueling flat panel display industry for the last 3 decades, and with oxide semiconductors enabling a combination of good electrical performance, low-temperature/large area fabrication and even optical transparency, academics and industry are pushing the boundaries for these devices and taking them to applications far from conventional displays. This presentation addresses two of the areas that have been explored at CENIMAT|i3N over the last years regarding radically new applications of oxide TFTs:

- Electronic and multifunctional textiles, where oxide transistors are developed on fiber-like shape, with a low thermal budget (sub-200 °C) and with mechanical reliability to assure that they could withstand textile weaving processes, while assuring similar electrical performance compared to oxide TFTs on glass. Integration with other fiber-based electronic components enables smart textile lighting/display systems, targeting revolutionary applications on smart homes and internet of things (IoT). [1, 2]
- Flexible ionizing radiation detectors, where oxide semiconductors exhibit impressive radiation hardness, allowing to have a stable basis for direct detectors. The radiation is stopped in a high X-ray absorbing dielectric and creates e-h pairs. The holes, trapped in the dielectric, create a charge accumulation inducing a shift of threshold voltage (V_T), proportional to the total absorbed dose [3, 4]. These oxide TFT detectors can then find application in passive, programmable, wireless tags reporting in real time the excess of critical radiation doses and have the potential for seamless integration of sensors and associated electronics in the same flexible platform.

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Friday 15th September

WS4 Session III

Emerging Printed Electronics and
Bioelectronics

PyzoFlex[®] matrix: How to combine printed ferroelectric sensors and organic transistors for vital parameter, tactile pressure and proximity sensing

Barbara Stadlober¹, Andreas Petritz¹, Esther Karner-Petritz¹, Herbert Gold¹, Andreas Tschepp¹, Martin Zirkl¹, Manfred Adler¹, Takafumi Uemura^{2,3}, Teppei Araki^{2,3}, Micael Charbonneau⁴, Romain Coppard⁴, Marco Fattori⁵, Eugenio Cantatore⁵, and Tsuyoshi Sekitani^{2,3}

¹ *Joanneum Research, Institute for Sensor, Photonics and Manufacturing Technologies, Weiz, Austria*

² *The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, Japan*

³ *AIST Advanced Photo-Bio Lab, Photonics Center Osaka University, Suita, Osaka, Japan*

⁴ *CEA-LITEN, Grenoble, France*

⁵ *Eindhoven University of Technology, Department of Electrical Engineering, Eindhoven, The Netherlands*

Takafumi Uemura, Osaka University, uemura-t@sanken.osaka-u.ac.jp

Teppei Araki, araki@sanken.osaka-u.ac.jp

Tsuyoshi Sekitani, sekitani@sanken.osaka-u.ac.jp

Micael Charbonneau, CEA-LITEN, micael.charbonneau@cea.fr

Romain Coppard, CEA-LITEN, romain.coppard@cea.fr

Marco Fattori, Eindhoven University of Technology, M.Fattori@tue.nl

Eugenio Cantatore, Eindhoven University of Technology, E.Cantatore@tue.nl

Flexible sensors impress with their outstanding properties; as they allow cost-effective and environmentally friendly production of large-area, flexible and, when fabricated on ultrathin, highly conformable or even stretchable substrates. These special properties enable an unprecedented integration possibility of sensor technology on complex-shaped objects, and pave the way for multi-stimuli responsive electronic skins used in human machine interfaces, soft robotics, prosthetics, implantable, wearable and physiological sensors, and sensor networks for the internet of things or structural health monitoring.

One transducer material that has proven to be very effective in many of the above-mentioned applications is the ferroelectric co-polymer P(VDF-TrFE). It can be printed at high resolution on various substrates in different form factors and is sensitive to pressure / force, strain, vibration / structure-borne sound as well as proximity / MIR radiation owing to its piezo- and pyroelectric nature ^[1].

An area where ferroelectric e-skins with low weight and high wearing comfort are of particular interest is the monitoring of human vital parameters such as pulse rate, blood pressure, tactile pressure or proximity signals at the point of care/living. Since vital parameter transducers should be highly conformable to the human body and provide a high spatial and temporal resolution, active addressing of the pixels in the ferroelectric transducer matrix in real time is inevitable. Such active addressing in e-skins is best achieved with organic thin film transistors, which, due to their compatibility with flexible, ultrathin or stretchable substrates, are the ideal counterparts for flexible ferroelectric transducers.

Here I will demonstrate several combinations of ferroelectric polymer transducers with organic thin film transistors on flexible substrates for tactile pressure sensing, proximity detection, pulse rate as well as blood pressure monitoring.

First, the basics of our printed ferroelectric sensor technology PyzoFlex[®] highlighting its scalable manufacturing and versatile application scenarios focussing on biosignal monitoring via the human pulse wave are presented ^[2]. Then I will show an ultra-compliant active-matrix tactile pressure sensor, where organic transistors are monolithically integrated with the ferroelectric transducers on a just 1 μm thin polymer substrate. More than 100 pixels at a pitch of ≈ 3 mm are addressed in this way. Advanced shadow-mask processes allow for a transistor channel length of < 20 μm and overlays < 100 μm , enabling operating frequencies in the 10 kHz regime and frame rates > 100 Hz ^[3].

Finally, I will demonstrate an in-pixel amplified actively addressed flexible proximity-sensing surface for process control, work security and robotics based on the integration of an allprinted organic thin film transistor backplane with an all-printed pyroelectric sensor frontplane. The system can detect a human hand approaching from different directions and track the position of a movable heat source up to a distance of around 0.4 m at a readout speed of 100 frames per second ^[4].

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Aerosol jet-printed ion-selective electrodes for sweat monitoring.

Jakub Krzemiński^{1*}, Jan Dominiczak¹ and Dominik Baraniecki¹

¹*Centre for Advance Materials and Technologies, Warsaw University of Technology, Polezki 19 street
02-822, Warsaw, Poland*

** jakub.krzeminski@pw.edu.pl*

Abstract:

This presentation highlights the development of skin patches using the Aerosol-Jet Printing (AJP) method on flexible substrates for potentiometric measurements of human body parameters. These patches offer significant potential for athletes to effectively monitor various life parameters.

The research process began with the manual printing of membranes and ink depositions, leading to the adoption of AJP for miniaturization and automation. Consequently, a fully printed skin patch with AJP printed ion-selective electrode was successfully fabricated.

The integration of ion-selective electrodes within the skin patch enables accurate and real-time potentiometric measurements of essential body parameters. Athletes can utilize these patches to monitor parameters such as electrolyte levels, pH balance, and other relevant indicators. The non-invasive nature of the skin patches ensures ease of use, comfort, and continuous monitoring without interfering with an individual's physical activities.

The presentation will delve into the fabrication process of the AJP-printed skin patches, emphasizing the advantages they offer over traditional manual methods. Furthermore, the implementation of ion-selective electrodes and their impact on enhancing measurement accuracy will be discussed. Finally, the potential applications and benefits of these skin patches for athletes will be highlighted, showcasing their role in optimizing performance, recovery, and overall well-being.

Overall, this presentation demonstrates the innovative use of AJP technology to create skin patches with ion-selective electrodes, catering specifically to the needs of athletes. These patches offer a promising solution for improved monitoring of human body parameters, allowing athletes to gain valuable insights into their physiological state and optimize their performance.

Metal oxide transistors with unconventional tri-channel geometry for various sensing applications

Wejdan S. Alghamdi^{1*}, Abhinav Sharma¹, and Thomas D. Anthopoulos¹

¹King Abdullah University for Science and Technology, Thuwal, Saudi Arabia

* Wejdan.ghamdi@kaust.edu.sa

Abstract:

Utilizing field effect transistors (FETs) as sensors is a highly attractive approach for biosensing due to the potential for direct electrical reading and simultaneous signal amplification.^[1] Moreover, the variety of advanced fabrication processes for FETs makes the technology easy to scale, which can, in turn, help enhance the electrical properties of the devices and lead to improved sensitivity and faster response times for numerous emerging biosensing applications.

Interfacing biological elements with electronics using advanced FET platforms often relies on developing new materials and advanced or unconventional device architectures. Here, we describe the development of a multi-layer metal oxide FET and its application as a novel sensor platform. The large area (2 mm by 2 mm) device combines a novel heterostructure metal oxide channel that forms a quasi-2-dimensional electron gas (q2DEG), leading to significantly higher electron mobility and a higher signal-to-noise ratio.^[2] Because of the buried nature of the conducting channel, exceptional electron transport can be sustained even after the surface of the heterojunction is functionalized with a suitable molecular receptor and while the sensing area of the device is exposed to the aqueous analyte-containing solution during biochemical sensing. The unique combination of superior electron transport and the proximity of the q2DEG to the sensing area leads to FET biosensors with ultra-high sensitivity and capability for various sensing applications such as DNA intercalation, SARS- CoV- 2 Spike Protein, and glucose detection. This level of performance compares favourably with the current state-of-the-art sensors and paves the way towards advanced, yet simple to manufacture, FET biosensors.

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Leaf electronics: Nature-based substrates and electrodes for organic electronic applications

Rakesh Rajendran Nair¹, Laura Teuerle¹, Jakob Wolansky¹, Hans Kleemann¹, and Karl Leo¹
¹*Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP) and Institute of Applied Physics, Technische Universität Dresden, Nothnitzer Str. 61, 01187 Dresden, Germany*

rakesh_rajendran.nair@tu-dresden.de

Abstract:

The need to reduce the environmental impact of inorganic electronic systems is pressing. Although the field of organic electronics provides a potential solution to this issue, research and optimization is still majorly carried out on glass or plastic substrates. Additionally, the fabrication of organic devices requiring transparent electrodes is fraught with complex techniques and expensive materials which limit widespread implementation and sustainability goals. Here, we show that the quasi-fractal lignocellulose structures extracted from natural leaves can be successfully modified to be used as biodegradable substrates as well as electrodes for optoelectronic applications. Chemically coating the microstructures of these leaf skeletons with metals results in quasitransparent, flexible electrodes having sheet resistances below $1 \Omega/\square$ and a concomitant current carrying capacity as high as 6 A over a $2.5 \times 2.5 \text{ cm}^2$ leaf electrode, all while maintaining broadband optical transmittance values of around 80%.

Organic electronics is a field poised for ubiquitous implementation in broad walks of life. It is also one touted to be much more environmentally friendly compared to current, commercial inorganic electronics. However, some pertinent issues remain. Foremost is the fact that most research into organic device fabrication is currently being carried out on glass or plastic substrates which are energy-intensive in terms of recycling. For a truly environmentally friendly organics domain, more research efforts need to be directed towards the development and optimization of devices on inexpensive and environmentally friendly/biodegradable substrates. Another issue is the need for transparent or quasi-transparent electrodes. Currently, the fabrication of highly conducting layers with high light transmittance is rife with processing and cost related issues that are slowly being mitigated with research.¹

Here we propose a solution based on naturally occurring tree leaves which may allow biomaterials based on lignocellulose to offer a potential solution to these two bottlenecks while maintaining the environmental sustainability goal that underlies organic electronics research.

Unlike biodegradable polymers such as poly(glycolic acid) (PGA), poly(lactic acid) (PLA) etc.², or biodegradable substrates such as paper,³ biopolymers are naturally occurring and are produced by living organisms. Among such materials, cellulose, and lignin (commonly found together and hence termed ‘lignocellulose’) constitute the most abundant biopolymers on

Earth^{4,5} and in combination with hemicellulose, they constitute the major components of a leaf's vasculature. These porous, quasi-fractal structures when combined further with non-toxic, biocompatible and biodegradable polymers such as ethyl cellulose⁶⁻⁸ for example, can result in flexible sheets implementable as substrates.

Lignocellulosic polymers if effectively implemented as replacements of pollution-causing units of mass-produced technology (such as substrates) can provide an advantage within the purview of circular economic principles. This is especially so considering the millions of tons of leaf waste incinerated or put into major greenhouse gas emitting landfills annually.⁹

Another application of lignocellulose leaf skeletons is in utilizing them as free-standing, metallized flexible electrodes in sensors/transducers, or as quasi-transparent electrodes for photon flux applications such as solar cells, OLEDs etc.¹⁰⁻¹³ This is possible owing to their high transparency and flexibility even when embedded with thin layers of metals such as Cu or Ag. This opens doors for the ingress of naturally occurring, partially treated materials as potential replacements of expensive and process-intensive ones like Indium Tin Oxide (ITO) without reducing the state-of-the-art performance metrics or efficiencies in some applications.^{14, 15}

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Biohybrid plants with self-assembled electronics as a platform for glucose sensing

Gwennaél Dufil^{1*}, Daniele Mantione² and Eleni Stavrinidou¹

¹*Linköping University, Norrköping, Sweden*

²*Polymat, San Sebastián, Spain*

gwennael.dufil@liu.se

Abstract:

The extensive labor of modern agriculture is causing dramatic issues with the quality of the microbiome found in the soil and the induced fertility of the land. This decreasing availability of agricultural lands after a historical peak in 2000 has to be placed in parallel with an increasing human population projected to reach 9.7 billion individuals by 2050.

The concept of smart agriculture aims to sense multiple physiological and environmental parameters of the plants and deliver chemicals to the soil in a more controlled manner. In the past years, our group developed a method to create conducting biohybrid tissues in plants utilizing a terthiophene oligomer called ETE-S. This molecule polymerizes at the plant cell wall due to the presence of enzymes resulting in a seamlessly integrated conducting polymer (p(ETE-S)). Plant roots are very interesting organs for p(ETE-S) interfaces as roots are responsible for nutrient uptake and release of exudates such as glucose, a metabolite playing a great role in symbiosis with the microbiome.

We, therefore, aim to develop a root bioelectronic platform to sense glucose from root exudates. Two different pathways to create biohybrid roots for glucose sensing were developed. The sensors reach a sensitivity of 0.1 mM with a stability up to 1 week. We also developed a conformable electrode to establish electrical contact with the biohybrid root without physical stress.

This work presents a new innovative way to sense metabolites relevant to plant physiological aspects. With these plant sensors, we aim to have live sensing of plant health and associate this with more precise and targeted chemical treatments in agricultural lands.

Tuesday 12th September

WS5 Session III

Nanophotonics and Biophotonics

Nanoscale laser writing for biomimetic photonics

Min Gu

Centre for Artificial-Intelligence Nanophotonics

School of Optical-Electrical and Computer Engineering,

University of Shanghai for Science and Technology, Shanghai, China

Biomimetics that imitates the functionality of nature becomes increasingly important as it can give rise to a sustainable solution to environmental and energy challenges but also provide a new technology platform for artificial innovations that do not exist in nature. Biomimetic photonics is inspired by nature's ability to self-assemble complex nanostructured materials with superior optical properties to that of conventional materials. Artificial construction of bio-inspired photonic devices ultimately requires three-dimensional 3D printing with nanometre resolution. In this sense, super-resolution photoinduction-inhibition nanolithography (SPIN) is advantageous in developing bioinspired nanophotonic devices. It has been discovered that the circular birefringence in a 3D nanostructures inspired by butterfly wings (*Callophrys rubi*) can be revealed with a feature exceeding their natural origins. More intriguingly, these nano-engineered nanostructures can support the topologic state of light if the parity symmetry is broken. Recently, we have also fabricated neuron-inspired 3D Steiner tree structures with an ultra-low density and a topologic photonic feature. These unprecedented 3D nanotechnology platforms allow for the accelerating development of biomimetic neural networks for optical artificial intelligence.

Attosecond Field Emission

Eleftherios Goulielmakis¹

¹*Institute of Physics, University of Rostock, Albert-Einstein-Str. 23, D-18059 Rostock, Germany*

e.goulielmakis@uni-rostock.de

Abstract:

Field emission of electrons underlies great advances in science and technology, ranging from signal processing at ever higher frequencies to imaging of the atomic-scale structure of matter. The advancing of electron microscopy techniques to enable the complete visualization of matter on the native spatial (picometre) and temporal (attosecond) scales of electron dynamics calls for techniques that can confine and examine the field emission on sub-femtosecond time intervals. We used intense, sub-cycle light [1][2] transients to induce optical field emission of electron pulses from tungsten nanotips and a weak replica of the same transient to directly investigate the emission dynamics in real time [3]. Access to the temporal properties of the electron pulses rescattering off the tip surface, including the duration $\tau = (53 \text{ as} \pm 5 \text{ as})$ and chirp, and the direct exploration of nanoscale near fields open new prospects for research and applications at the interface of attosecond physics and nano-optics.

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Post-Melting Encapsulation of Glass Microwires for the Development of Advanced Waveguides

Ioannis Konidakis^{1*}, Foteini Dragosli¹, Aby Cheruvathoor Poulouse², Josef Kašlík², Aristeidis Bakandristos^{2,3}, Radek Zboril^{2,3} and Emmanuel Stratakis¹

¹*Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology - Hellas (FORTH), Heraklion-Crete, Greece*

²*Regional Centre of Advanced Technologies and Materials, Czech Advanced Technology and Research Institute (CATRIN), Palacký University, Šlechtitelů 27, 783 71, Olomouc, Czech Republic*

³*Nanotechnology Centre, Centre of Energy and Environmental Technologies, VŠB-Technical University of Ostrava, Ostrava-Poruba, Czech Republic*

*ikonid@iesl.forth.gr

Abstract:

In recent studies we have shown the excellent feasibility of a post-melting encapsulation procedure towards the development of ultrastable and highly luminescent perovskite glasses [1], composite two-dimensional (2D) materials glass nanoheterojunctions [2], and superior photochromic glasses [3]. Herein we exploit the post-melting protocol for the development of advanced all-glass waveguides without the need for laser processing or chemical procedures. Namely, at first silver iodide phosphate glass microwires (MWs) are drawn from typical splat quenched samples. Following the drawing, the glass MWs are incorporated in a controlled manner within previously prepared silver phosphate glass rectangular prisms. The composition of the employed glasses is chosen so that the host phosphate glass has a lower refractive index than the embedded MWs. In such case, the waveguide mechanism relies on the propagation of light inside the encapsulated higher refractive index MWs. Moreover, the presence of silver nanoparticles within the MWs enhances the light transmission due to scattering effects. Waveguide devices with either one or two incorporated MWs were fabricated. Remarkably, in the latter case, the transmission of light of two different colors and in multipath direction is possible, rendering the developed waveguides outstanding candidates for various photonic, optoelectronic, and smart sign glass applications.

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Impact of plasmonic modes and metal thermophysical properties on the formation of self-organised nano-patterns in thin films

George D. Tsididis^{1,3}, Panagiotis Lingos¹, George Perrakis¹, Odysseas Tsilipakos^{2,1}, Emmanuel Stratakis^{1,4}

1. Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology (FORTH), Vassilika Vouton, 70013, Heraklion, Crete, Greece

2. Theoretical and Physical Chemistry Institute National Hellenic Research Foundation, GR-11635 Athens Greece

3. Department of Materials Science and Technology, University of Crete, 71003, Heraklion, Greece

4. Department of Physics, University of Crete, 71003, Heraklion, Greece

Nanoscale laser-induced periodic surface structures in thin metal films (of the size of the optical penetration depth) is a yet unexplored area that is expected to open new routes for laser patterning and a wealth of exciting applications in optics, photonics, and sensing. In contrast to the common belief that excitation of Surface Plasmon Polaritons (SPPs) on the air/metal interface plays the dominant role in the features of the induced topographies, in this work, we demonstrate that the excitation of coupled SPPs in both air/metal and metal/substrate interfaces (Fig.1a), along with other parameters such as the thickness of the material, the photon energy, and the substrate refractive index, dictate the spatial modulation of the absorbed energy. Results are shown for Au while the methodology can be followed for any metal. A detailed theoretical analysis of the excited plasmonic waves and a multiscale modelling of laser-induced physical phenomena manifests that depending on the laser conditions and thickness of the irradiated solid, topographies with periodic features of diverse sizes (ranging from $\lambda_L/3$ to λ_L , where λ_L stands for the laser wavelength) and different orientation can be realized (Fig.1b) [1].

Furthermore, to illustrate the role of thermophysical properties of the irradiated solids on the features of the produced periodic topographies, the formation of periodic patterns on two materials of different electron-phonon coupling and electron heat conductivity (Au, Stainless Steel) is analysed in detail (Fig.1c,d). Results demonstrate the pronounced role of these parameters [2]. The capability to control and tune the characteristics

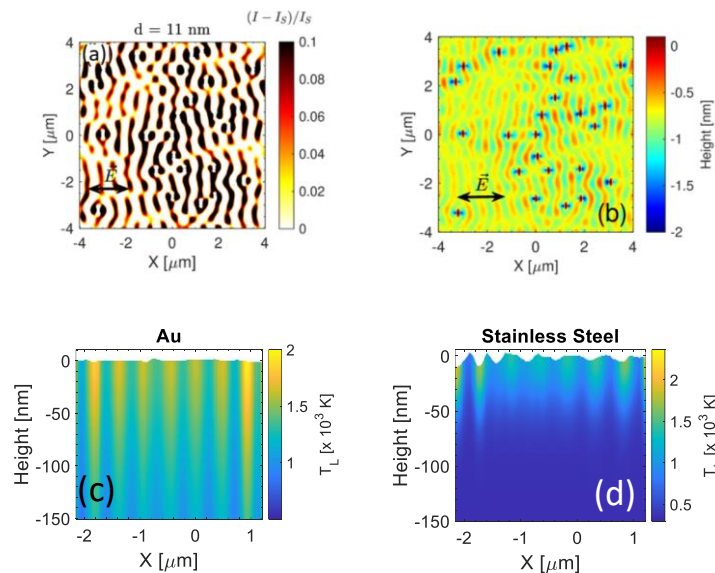


Fig. 1 (a) Scattering by randomly distributed nano-defects of radius $r = 50 \text{ nm}$ and average spacing $l \approx 1.6 \mu\text{m}$ for film thickness $d = 11 \text{ nm}$ (air/Au/SiO₂ structure). Intensity distribution in the xy plane just below the top air/Au interface for $\lambda = 1026 \text{ nm}$. (b) LIPSS patterns on Au for thickness $d = 11 \text{ nm}$. (c) Lattice temperature spatial profile at time $t = 20 \text{ ps}$ for (c) Au, (d) Stainless steel. Produced corrugation is shown in (c), (d) after 5 pulses.

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Tailoring surface topographies on solids with Mid-IR femtosecond laser pulses

Stella Maragkaki¹, George D. Tsididis², Ludovit Haizer³, Zsuzsanna Pápa³, Roland Flender³, Bálint Kiss³, Zsuzsanna Márton³ and Emmanuel Stratakis^{1,4}

1. Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology (FORTH), Vassilika Vouton, 70013, Heraklion, Crete, Greece
2. Department of Materials Science and Technology, University of Crete, 71003, Heraklion, Greece
3. ELI-ALPS, ELI-HU Non-Profit Ltd., Wolfgang Sandner utca 3., Szeged, H-6728, Hungary
4. Department of Physics, University of Crete, 71003, Heraklion, Greece

Irradiation of solids with ultrashort pulses using laser sources in the mid-infrared (mid-IR) spectral region is a yet predominantly unexplored field that opens broad possibilities for efficient and precise surface texturing for a wide range of applications. In the present work, we investigate both experimentally and theoretically the impact of laser sources on the generation of surface modification related effects and on the subsequent surface patterning of metallic and semiconducting materials. Through a parametric study we correlate the mid-IR pulsed laser parameters with the onset of material damage and the formation of a variety of periodic surface structures at a laser wavelength of $\lambda_L=3200$ nm and a pulse duration of $\tau_p=45$ fs. Results for nickel and silicon indicate that the produced topographies comprise both high and low spatial frequency induced periodic structures, similar to those observed at lower wavelengths, while groove formation is absent (Fig. 1a,b). The investigation of the damage thresholds suggests the incorporation of nonlinear effects generated from three-photon-assisted excitation (for silicon) (Fig. 1c) and the consideration of the role of the non-thermal excited electron population (for nickel) at very short pulse durations (Fig. 1d). The results demonstrate the potential of surface structuring with mid-IR pulses, which can constitute a systematic novel engineering approach with strong fields at long-wavelength spectral regions that can be used for advanced industrial laser applications [1].

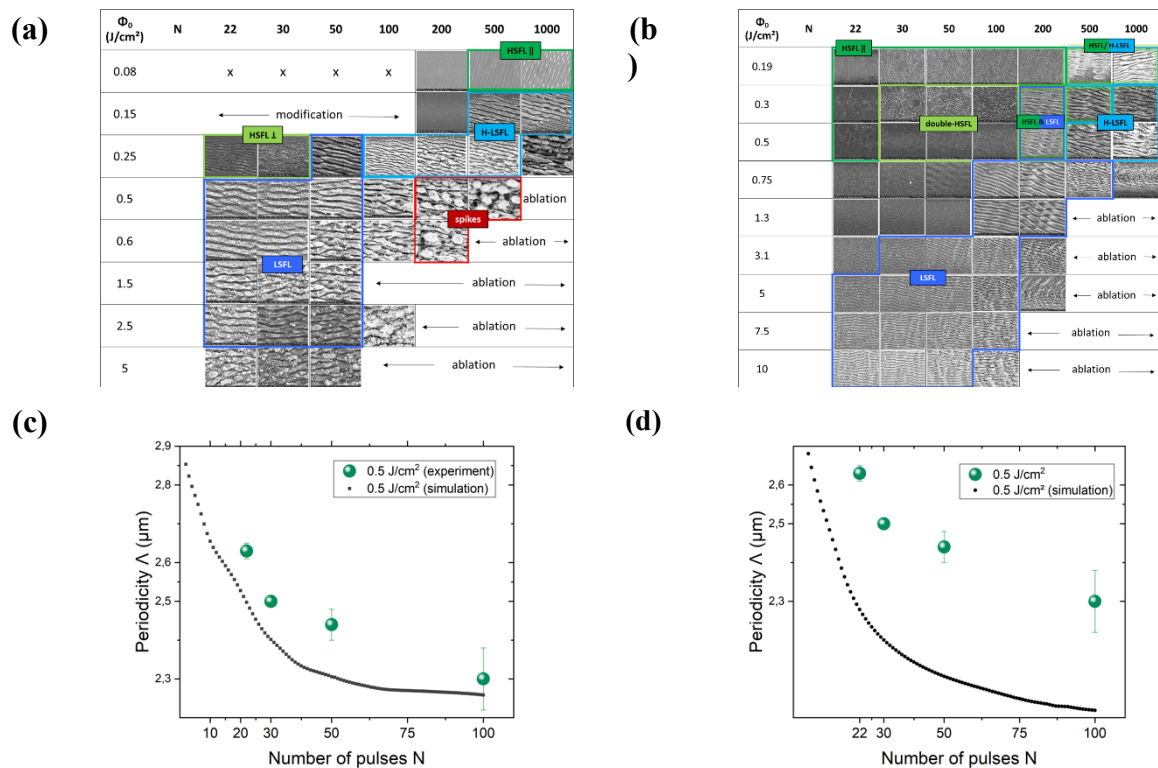


Fig. 1 Map of morphologies for Silicon (a) and Nickel (b). Periodicity of LIPSS for 22 pulses for Silicon (c) and Nickel (d).

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Vector optical field laser micro/nano-fabrication for nonlinear materials

Fang Yao, Wang Qinsong, Chen Lianwei, Ma Xiaoliang, Li Xiong*, Pu Mingbo, and Luo Xiangang*

State Key Laboratory of Optical Technologies on Nano-Fabrication and Micro-Engineering, Institute of Optics and Electronics, Chinese Academy of Sciences, Chengdu 610209, China.

Research Center on Vector Optical Fields, Institute of Optics and Electronics, Chinese Academy of Sciences, Chengdu 610209, China

* qiling006@163.com, lxg@ioe.ac.cn

Abstract:

Nonlinear optics is the study of nonlinear responses from the interaction of intense light with matter. A nonlinear optical effect typically describes a process in which the optical properties of a material change nonlinearly as a consequence of the strong irradiation of incident light.[1] For most nonlinear optical effects, an intensified incident light is required to trigger the nonlinear effects that can be observed. The study of nonlinear optics started when Franken and coworkers firstly observed the second-harmonic generation in 1961, right after the demonstration of a functional laser system by Maiman one year before. Since then, various nonlinear optical effects have been discovered and this field has grown continuously into an important branch of modern optics. After many years of development, nonlinear optics has become the pillars for many frontier research and widely used systems, including laser fabrication, optical imaging, information processing & communications, as well as nanoscale lithography.[2]–[6]

Nonlinear material is the basis for nonlinear optics. In this presentation, the latest progresses and future directions to fabricate micro/nano-nonlinear optical materials with vector optical field technology is summarized. It is demonstrated that vector optical field technology is a feasible approach to achieve results beyond the capabilities of the conventional laser ablation methods.

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Transparent and Resilient 3D Microoptics

Karolis Galvanauskas¹, Darija Astrauskytė², Arūnas Čiburys¹, Darius Gailevičius¹,
Andrius Melninkaitis³, Lina Grinevičiūtė², and Mangirdas Malinauskas^{1*}

¹*Laser Research Center, Physics Faculty, Vilnius, Lithuania*

²*Center for Physical Sciences and Technology, Vilnius, Lithuania*

³*LIDARIS Ltd, Vilnius, Lithuania*

[*mangirdas.malinauskas@ff.vu.lt](mailto:mangirdas.malinauskas@ff.vu.lt)

Multi-photon lithography dramatically extends additive manufacturing of free-form 3D microoptics. It is already established for rapid prototyping and production of miniature optical elements and stacked compound components: diffractive, refractive, guiding, filtering, polarizing, as many optical functions can be merged into monolith devices with sub-wavelength features. Yet currently made optics are limited to polymer materials which are low grade in context of optical materials [1].

Here we present major advancement of the 3D printed microoptics: improving their transparency and increasing their laser induced damage threshold (LIDT). High transmission can be achieved by functionalizing them with anti-reflective (AR) coating employing atomic layer deposition (ALD) method [2]. In contrast to previously reported work by Giessen et al. [2], our applied material is hybrid organic-inorganic SZ2080™ substance, which can be calcinated [3] and turn the objects into transparent glass-ceramics [4]. The achieved transparency after ALD reaches more than 99% for single, doublet, and triplet micro-lenses at 633 nm. The calcination and morphing to purely inorganic substance results into improvement of LIDT for the micro-lenses by 1.5-3 times increase at 1030 nm and 3-6 times increase for the 515 nm exposure wavelengths, measured by S-on-1 tests in respect to pristine photopolymer [5]. Latest benchmarking results of ALD coated triplet glass-ceramic microlenses with improved LIDT will be presented during the talk. It is an important breakthrough for excellent and heavy-duty performance of micro-optical and nano-photonic devices which can be laser 3D printed via route of multi-photon lithography without suffering limitations inherited from plastic (organic) materials [6].

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Femtosecond-Laser-Induced All-Silicon Dielectric Metasurfaces Assisted by Wet Chemical Etching

Ioanna Sakellari^{1*}, Sotiris Droulias², Andreas Lemonis³ and Emmanuel I. Stratakis¹

¹ *Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, Heraklion, Crete, 71110 Greece.*

² *University of Piraeus, Piraeus, 18534 Greece.*

³ *Biomimetic, Science and Technology Park of Crete, Heraklion, Crete, 70013 Greece.*

** isakel@iesl.forth.gr*

Abstract:

All-dielectric metasurfaces offer low material loss and strong field localization and are, therefore, well-suited for ultrathin and compact optical devices for electromagnetic wave manipulation at the nanoscale. All-silicon dielectric metasurfaces, in particular, may additionally offer the desired compatibility with CMOS technology and, hence, are ideal candidates for large-scale monolithic integration on a photonic chip. However, in conventional silicon microfabrication approaches, the combination of mask photolithography with reactive ion etching usually involves expensive masks and multiple pre-processing stages leading to increased cost and fabrication times. In this work, a single-step lithographical approach is proposed for the realization of all-silicon dielectric resonant metasurfaces that involves femtosecond (fs) laser processing of silicon below ablation threshold in combination with subsequent wet chemical etching. The method exploits the different etching rate between laser-modified and untreated regions, enabling large-area fabrication of patterned silicon surfaces in a facile and cost-efficient manufacturing approach. It is presented how 2D silicon micro/nanostructures with controllable features, such as nanocones, can be effectively generated and, as a proof of concept, an all-silicon dielectric metasurface device supporting antiferromagnetic order is experimentally demonstrated.

Wednesday 13th September

WS5 Session IV

Nanophotonics and Biophotonics

Ultracompact perovskite lasers integrated with waveguiding systems

Sergey Makarov^{1*}

¹ *School of Physics and Engineering, ITMO University, Lomonosova, 9, Saint-Petersburg 191002, Russia*

[* s.makarov@metalab.ifmo.ru](mailto:s.makarov@metalab.ifmo.ru)

Abstract:

Recently, the study of halide perovskites has attracted enormous attention due to their exceptional optical and electrical properties. As a result, this family of materials can provide a prospective platform for modern nanophotonics [1] and metaphotonics [2,3], allowing us to overcome many obstacles associated with the use of conventional semiconductor materials. Resonant halide perovskite micro- and nanocrystals is a rapidly developing research area driven by its potential applications for lasers, nanophotonics, and optoelectronic devices. Here, we overview the recent progress in the field of halide perovskite nano- and microlasers starting from record-small single-particle light-emitting microcrystals supporting lasing generation [4,10] to the larger designs where the perovskite microlasers [5, 6] are coupled with waveguiding systems [7,8,9].

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Colloidal quantum dot infrared optoelectronics: LEDs, Lasers and Photodetectors

Gerasimos Konstantatos^{1,2*}

¹ICFO-Institut de Ciències Fotoniques, The Barcelona Institute of Science and Technology, Castelldefels, 08860 Barcelona, Spain.

²ICREA-Institució Catalana de Recerca i Estudis Avançats, Lluís Companys 23, 08010 Barcelona, Spain.

** Gerasimos.Konstantatos@icfo.eu*

Abstract:

In this talk I will discuss recent progress of my group on developing low-cost, solution-processed and CMOS compatible optoelectronics in the short-wave infrared based on colloidal quantum dots.

I will first present our approach on high quantum efficiency light emitting diodes enabled by engineering the energetic potential landscape at the suprananocrystalline level and the leverages we have in boosting quantum efficiency, stability and radiance. I will then present results on CQD Pb-chalcogenide QD as a gain medium for accessing the telecom wavelengths and the demonstration of optically pumped lasers operating at room temperature. I will further elaborate on the use of robust doping as a mechanism to reduce gain threshold in such systems and the engineering of dots at the single dot level to suppress Auger and drastically increase the gain coefficient. I will conclude this part by showing recent results on stimulated emission above 2 μm for the first time using solution processed QDs with compelling performance characteristics. In the last part of my talk I will present recent results on development of heavy metal free colloidal quantum dots in the short wave infrared that open the way for the deployment of this technology in consumer electronics markets.

Polarization-Resolved Optical Second Harmonic Generation microscopy in 2D Materials

S. Psilodimitrakopoulos^{1*}, L. Mouchliadis¹, G. M. Maragkakis^{1,2}, G. Kourmoulakis^{1,3}, I. Demeridou¹, A. Lemonis¹, G. Kioseoglou^{1,3} and E. Stratakis¹

¹ Institute of Electronic Structure and Laser-Foundation for Research and Technology-Hellas, GR-711 10, Heraklion, Greece

² Department of Physics, University of Crete, 71003 Heraklion, Greece

³ Department of Materials Science, University of Crete, 71003 Heraklion, Greece

* sopsilo@iesl.forth.gr

Abstract:

The emerging family of two-dimensional (2D) materials has provided researchers with fertile ground for exploring fundamental physical phenomena and developing innovative technological solutions. Lately, nonlinear optical measurements, including optical second-harmonic generation (SHG) have created new opportunities for improving the image resolution of 2D crystals [1,2]. At the same time, the polarization of the SHG field depends on the 2D crystal symmetry and orientation. Based on such SHG signal dependencies, the crystal quality of TMDs can be evaluated using polarization-resolved SHG (P-SHG) optical microscopy [1,2]. Moreover, 2D TMDs can be assembled in vertical stacks. This creates new physical properties that depend on the relative orientation (twist angle) between the TMD monolayers. P-SHG optical imaging provides precise and real-time measurement of the twist angle, which is of utmost importance for characterizing a twisted 2D TMD heterostructure [3]. Additionally, degenerate minima in momentum space –valleys– in 2D materials provide an additional degree of freedom that can be used for information transport and storage. P-SHG imaging reveals that the temperature-induced changes of the P-SHG, is a unique fingerprint of valley population imbalance (VPI) [4]. We envisage the optical P-SHG imaging microscopy as a powerful tool for the characterization of 2D TMD heterostructures and the engineering of their physical properties for emerging applications.

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Polarization-resolved third harmonic generation (P-THG) of myelin inside optic nerves

Maria Kefalogianni^{1,2*}, Leonidas Mouchliadis¹, Niki Ktena^{3,4}, Stefanos Kaplanis^{3,4}, Ilias Kalafatakis^{3,4}, Sotiris Psilodimitrakopoulos¹, Domna Karagogeos⁴, Emmanuel Stratakis^{1,2}

¹*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete, 71110, Greece*

²*Department of Physics, University of Crete, Heraklion Crete, 71003, Greece*

³*Department of Basic Sciences, Faculty of Medicine, University of Crete, Heraklion Crete, 71003, Greece*

⁴*Institute of Molecular Biology and Biotechnology, Foundation for Research and Technology-Hellas, Heraklion Crete, 71003, Greece*

*mkefalogianni@physics.uoc.gr

Abstract:

Myelin wraps and insulates neurons, constituting a key component of nervous tissue development, aging and neurological diseases [1]. The need of understanding myelin biology requires a suitable high-resolution label-free minimally invasive imaging technique. That still remains a challenge [2]. Here, we utilize the endogenous third-harmonic generation (THG) from myelin [3] and we resolve its polarization pattern in order to identify the structure of myelin in normal and abnormal nervous tissues.

Polarization-resolved THG (P-THG) imaging comprises a rotating half - waveplate retarder (HWP) in the excitation path and an analyzer in detection right in front of the photomultiplier tube (PMT), using three different experimental conditions either without or with analyzer in two perpendicular directions. By fitting experimental data with equations describing the THG intensity, we can derive the ratios of the third order susceptibility components, A, B, D, E and the angle between the myelin axis and the lab X-coordinate, φ . Experimental observations determine A as a quantification factor of myelin content and φ as an indicator of myelin's axons orientation differentiation indicate different myelin type. The absolute value of A ratio is much larger in the control optic nerve than in the mutant one for each respective condition, verifying the reduced amount of myelin in the latter.

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Thermally-induced mechanical switching of the second harmonic generation in pNIPAM hydrogels-linked Au and Si nanoparticles

E. N. Gerasimova^{*}, V. V. Yaroshenko¹, L. V. Mikhailova¹, D. M. Dolgintsev¹, A. S. Timin¹,
M. V. Zyuzin¹, D. A. Zuev¹

¹*Department of Physics, ITMO University, Kronverksky Pr. 49, bldg. A, 197101 St.
Petersburg, Russian Federation*

** elena.gerasimova@metalab.ifmo.ru*

Abstract:

Nanostructures enabling of optical properties tuning in response to external stimuli are widely used in different optomechanical systems. Their functionality originates from the design; therefore, its rapid reconfiguration modulates optical signals. The process can be automated via the integration of stimuli-responsive materials in such nanoscale systems. These materials undergo reversible phase transitions, such as shrinking or swelling, at specific temperatures, typically around 32-33°C. The shrunk state is hydrophobic and has a reduced volume, while the swollen state is hydrophilic and has a larger diameter. This work observes a thermally sensitive pNIPAM microspheres modified with silicon (pNIPAM@Si) and both silicon and gold nanoparticles (pNIPAM@Si@Au) to probe the temperature-dependent reversible mechanical transformations through the second harmonic generation signal switching. The second-harmonic generation process is investigated theoretically and experimentally depending on the applied temperature and pNIPAM phase. The enhancement of second harmonic generation is shown for both systems in the shrunk state. For the pNIPAM@Si, the second harmonic amplification equals 7 times, whereas for the pNIPAM@Si@Au, the enhancement exceeds 32 times. These changes are totally reversible and reproducible during several cycles. The reason of this phenomena is electrical-field-induced second harmonic (E-FISH) contribution and hot spot reconfiguration. Therefore, developed nanostructured platforms are perspective for the motion probing in optical nano- and micromechanical systems controlled by surrounding temperature. [1]

This work was supported by the Russian Science Foundation (project No. 21-72-30018)

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Monday 11th September

WS6 Session V

2D materials and devices

Exciton complexes in Transition Metal Dichalcogenide Monolayers

Xavier MARIE

*Université de Toulouse, INSA-CNRS-UPS,
Laboratoire de Physique et Chimie des Nano-Objets,
135 Avenue de Rangueil, 31077 Toulouse, France
marie@insa-toulouse.fr*

Optical properties of Transition Metal Dichalcogenides (TMD) are governed by very robust excitons with binding energies of a few hundreds of meV. Encapsulation of these TMD monolayers in hexagonal Boron Nitride (hBN) yields narrow optical transitions approaching the homogeneous exciton linewidth [1-3]. The neutral exciton radiative rate in these van der Waals heterostructures can be tailored by a simple change of the hBN encapsulation layer thickness as a consequence of the Purcell effect [4,5].

I will present recent results on the investigation of charge tunable devices based on WSe₂ and WS₂ monolayers encapsulated in hexagonal boron nitride. In addition to the well-known radiative recombination of neutral and charged excitons, stationary photoluminescence measurements highlight weaker-intensity optical transitions. We show that these lines correspond to impurity-assisted radiative recombination of indirect exciton and charged excitons [6,7].

These results demonstrate the importance of second-order exciton recombination processes in transition-metal dichalcogenide structures.

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Nonlinear generation and detection of valleys in atomically thin semiconductors

P. Herrmann¹, S. Klimmer², T. Lettau², M. Monfared³, I. Staude¹, I. Paradisanos³, U. Peschel²,
G. Soavi^{1,*}

¹*Institute of Solid State Physics, Friedrich Schiller University Jena, Germany*

²*Institute of Condensed Matter Theory and Optics, Friedrich Schiller University Jena, Germany*

³*Country Institute of Electronic Structure and Laser, Foundation for Research and Technology, Crete, Greece*

* giancarlo.soavi@uni-jena.de

Abstract:

Light is the ideal candidate to realize devices operating with high speed and low consumption thanks to all-optical operations [1]. A promising approach in this direction is based on valleytronics using two-dimensional transition metal dichalcogenides (TMDs): TMD monolayers are direct gap semiconductors with two energetically degenerate but non-equivalent valleys in the K and K' points of the Brillouin zone. The valleys can be selectively excited (write) in an all-optical fashion using light of opposite helicity, while their detection (read) was so far mostly based on polarization-resolved photoluminescence (PL). However, steady-state PL has two main drawbacks: (1) it detects an averaged light emission over a time-scale that is much longer compared to the valley and spin lifetimes; (2) it is intrinsically a destructive method, which measures the valley polarization (VP) only after light emission. Nonlinear optics [2], and in particular second harmonic generation (SHG), overcomes these disadvantages and provides an ultrafast and non-destructive method for the detection of the VP in TMDs [3]. In this seminar, I will discuss our recent results [4], where we simultaneously pump (write) and probe (read) the VP in WSe₂ with one single elliptically polarized ultra-short pulse. We probe the VP using polarization dependent SHG measurements at different values of the fundamental wavelength and find that resonant SHG at the 1s exciton state is the most sensitive probe of the VP. In addition, we show that, in the case of below gap excitation, the VP is generated by ultrafast coherent optical Stark-shift, which is valley selective in TMDs. This work provides direct evidence of ultrafast and all-optical coherent generation and detection of valleys in atomically thin semiconductors.

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Biaxial strain tuning of exciton energy and polarization in monolayer WS₂

George Kourmoulakis^{1,2,*}, Antonios Michail^{3,4}, I. Paradisanos¹, Xavier Marie⁵, M.M. Glazov⁶, J. Parthenios⁴, K. Papagelis^{4,5}, E. Stratakis^{1,8}, and G. Kioseoglou^{1,2}

¹Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion, 70013, Greece

²Department of Materials Science and Technology, University of Crete, Heraklion, 70013, Greece

³Department of Physics, University of Patras, Patras, 26504, Greece

⁴Institute of Chemical Engineering Sciences, Foundation for Research and Technology-Hellas, Stadiou str Platani, Patras, 26504, Greece

⁵Universite de Toulouse, INSA-CNRS-UPS, LPCNO, 135 Av. Ranguel, 31077, Toulouse, France

⁶Toffe Institute, St.-Petersburg, 194021, Russia

⁷School of Physics, Dept. of Solid-State Physics, Aristotle University of Thessaloniki, Thessaloniki, 54124, Greece

⁸Department of Physics, University of Crete, Heraklion Crete 71003, Greece

*geokourm@iesl.forth.gr

Abstract:

Single layers of transition metal dichalcogenides, MX₂ (M = Mo, W and X = S, Se) have been the focus of intense research because they are direct gap semiconductors with inequivalent K-points making them prime candidates for valleytronics, a concept where the valley index is a potential new degree of freedom to store, manipulate and read out information [1,2]. Owing to their significant mechanical flexibility, these two-dimensional materials provide an ideal platform for strain engineering [3], enabling versatile modulation of their optical properties and specifically spin-valley polarization [4-6].

In this work, we perform micro-photoluminescence and Raman experiments to examine the impact of isotropic, biaxial strain in the optical properties of WS₂ monolayers. A strong shift on the order of ~130 meV per % of strain is observed in the neutral exciton emission at room temperature. Under near-resonant excitation, we measure a linear decrease in the circular polarization degree as a function of applied isotropic biaxial strain. We experimentally distinguish contributions from the energy detuning, and we evaluate the net effect from biaxial strain. Variations in the optical matrix elements, as well as modifications in the scattering channels result in a suppression of the circular polarization degree.

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Electron density control in WSe₂ monolayers via photochlorination

Eirini Katsipoulaki^{1,2,*}, George Vailakis^{1,3}, I. Demeridou¹, D. Karfaridis⁴, P. Patsalas⁴, K. Watanabe⁵, T. Taniguchi⁶, I. Paradisanos¹, G. Kopidakis^{1,3}, G. Kioseoglou^{1,3}, and E. Stratakis^{1,2}

¹Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion, 70013, Greece

²Department of Physics, University of Crete, Heraklion, 70013, Greece

³Department of Materials Science and Technology, University of Crete, Heraklion, 70013, Greece

⁴Department of Physics, Aristotle University of Thessaloniki, Thessaloniki, 54124, Greece

⁵ Research Center for Electronic and Optical Materials, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

⁶ Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

* ekatsip@physics.uoc.gr

Abstract:

Transition Metal Dichalcogenides (TMDs) of the form MX₂ (where M=Mo or W and X=S, Se, Te), are a special class of 2D-layered materials [1]. Unlike their 3D-counterparts that are indirect gap semiconductors, single layers of MX₂ have a direct-gap, with tremendous consequences in the PL quantum yield [2].

Modulation of the Fermi level using an ultraviolet (UV)-assisted photochemical method [3,4] is demonstrated in tungsten diselenide monolayers. Systematic shifts and relative intensities between charged and neutral exciton species indicate a progressive and controllable decrease of the electron density and switch tungsten diselenide from n-type to a p-type semiconductor. The presence of chlorine in the 2D crystal shifts the Fermi level closer to the valence band while the effect can be only partially reversible via continuous wave laser rastering process. Chlorine species in the lattice are validated by X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) [5] calculations predict that adsorption of chlorine on the selenium vacancy sites leads to p-type doping. The results of our study indicate that photochemical techniques have the potential to enhance the performance of various 2D materials, making them suitable for potential applications in optoelectronics.

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Exploring the optical near-field interaction of Mie nanoresonators with a monolayer semiconductor

D. Katrasioti^{1, 2, *}, P. R. Wiecha³, G. Larrieu³, J. Müller³,

J.-M. Poumirol⁴, A. Cuche⁴, G. Agez⁴, V. Paillard⁴,

X. Marie⁵, B. Urbaszek⁶, E. Stratakis^{1, 7}, G. Kioseoglou^{1, 2} and I. Paradisanos^{1, 5}

¹ *Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology (FORTH), Heraklion, Crete, Greece*

² *Department of Materials Science and Technology, University of Crete, Heraklion, Greece*

³ *LAAS-CNRS, Université de Toulouse, Toulouse, France*

⁴ *CEMES-CNRS, Université de Toulouse, Toulouse, France*

⁵ *Université de Toulouse, INSA-CNRS-UPS, LPCNO, Toulouse, France*

⁶ *Institute of Condensed Matter Physics, Technische Universität Darmstadt, Darmstadt, Germany*

⁷ *Department of Physics, University of Crete, Heraklion, Greece*

**E-mail: danaekatrasioti@iesl.forth.gr*

Abstract:

Transition metal dichalcogenide (TMD) monolayers are atomically thin direct bandgap semiconductors hosting strongly bound electron-hole pairs (excitons) with unique optical selection rules [1]. The unique characteristics of TMD monolayers, including strong spin-orbit interaction and broken inversion symmetry, make them highly appealing for linear and nonlinear optics [2-3]. Potential applications in future optoelectronics require approaches to enhance the light-matter interaction in these materials. One approach involves Mie resonances using dielectric nanostructures with unique opportunities for large resonant enhancement of both electric and magnetic near-field interactions [4].

In this study, monolayers of molybdenum disulfide (MoS₂) are positioned in close proximity to dielectric nanoantennas composed of silicon nanopillars and investigated using photoluminescence (PL), Raman spectroscopy as well as Atomic Force Microscopy. The excellent mechanical properties of TMD monolayers allows their direct placement in the near-field of dielectric nanoantennas where the local electric field response can be strongly modified and enhance interactions between light and monolayers. Photoluminescence excitation spectroscopy (PLE) experiments reveal that the MoS₂ absorption is enhanced via the near-field of nanoantennas at resonant energies away from the material's intrinsic states. Our results suggest that the optical properties of TMD monolayers can be tailored using the optical near-field of photonic nanostructures, which is compatible with silicon technology.

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Probing valley population imbalance in transition metal dichalcogenides with temperature-dependent second harmonic generation imaging

Leonidas Mouchliadis^{1*}, Sotiris Psilodimitrakopoulos¹, George Miltos Maragkakis^{1,2}, Ioanna Demeridou^{1,2}, George Kourmoulakis^{1,3}, Andreas Lemonis¹, George Kioseoglou^{1,3}, and Emmanuel Stratakis¹

¹ *Institute of Electronic Structure and Laser-Foundation for Research and Technology-Hellas, 70013, Heraklion, Greece*

² *Physics Department, University of Crete, 71003, Heraklion, Greece*

³ *Department of Materials Science and Technology, University of Crete, 71003, Heraklion, Greece*

* mouhliad@physics.uoc.gr

Abstract:

Degenerate minima in momentum space—valleys—provide an additional degree of freedom that can be used for information transport and storage. Two such minima naturally exist in the bandstructure of two-dimensional (2D) transition metal dichalcogenides (TMDs). When these atomically thin crystals interact with intense laser light, the emerging second harmonic generation (SHG) inherits special characteristics that reflect not only the broken inversion symmetry in real space but also the valley anisotropy in reciprocal space [1]. The latter is present whenever there exists a valley population imbalance (VPI) between the two valleys and affects the polarization state of the produced SHG. In this work, it is shown that the temperature-induced changes of the SHG intensity dependence on the excitation field polarization is a fingerprint of VPI in TMDs [2]. In particular, pixel-by-pixel VPI mapping based on polarization-resolved raster-scanning imaging microscopy was performed in TMD flakes inside a cryostat. The generated SHG contrast is marked by rotation of the intensity polar diagrams with varying temperature and it is attributed to the VPI-induced SHG. Control over the population of TMD electronic states with light paves the way for future advancements in the field of valleytronics.

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Second harmonic generation spectroscopy in van der Waals homo- and heterobilayers

I. Paradisanos^{1*}, D. Lagarde¹, A.M.S. Raven¹, T. Amand¹, S. Shree¹, L. Lombez¹, P. Renucci¹, C. Robert¹, K. Watanabe², T. Taniguchi³, A. Balocchi¹, I. C. Gerber¹, L. Golub⁴, M. M. Glazov⁴, B. Urbaszek¹, X. Marie¹

¹Université de Toulouse, INSA-CNRS-UPS, LPCNO, Toulouse France

²Research Center for Electronic and Optical Materials, NIMS, Tsukuba, Japan

³Research Center for Materials Nanoarchitectonics, NIMS, Tsukuba, Japan

⁴Ioffe Institute, St. Petersburg, Russia

* paradeis@insa-toulouse.fr

Abstract:

The twist angle in transition metal dichalcogenide bilayers is a compelling degree of freedom that determines electron correlations and the period of lateral confinement of moiré excitons. We perform polarization-resolved second harmonic generation (SHG) spectroscopy in MoS₂/WSe₂ heterostructures. We demonstrate that by choosing suitable laser energies the twist angle between two monolayers can be measured directly on the assembled heterostructure[1]. We show that the amplitude and polarization of the SHG signal from the heterostructure are determined by the twist angle between the layers and exciton resonances at the SH energy[1]. For heterostructures with close to zero twist angle, we observe changes of exciton resonance energies and the appearance of new resonances in the linear and nonlinear susceptibilities[1]. In inversion symmetric MoS₂ homobilayers we demonstrate tuning of non-linear optical processes with a strong enhancement of the SHG signal in applied electric fields for pump energies resonant with interlayer exciton states[2].

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Tuesday 12th September

WS4 & WS6 Session V

Emerging printed electronics and bioelectronics & 2D
materials and devices

Can we move from inorganic to carbon nanoallotrope thermoelectrics? 2D and 3D printing of highly efficient TEG devices

Lazaros Tzounis^{*1,2,3}, Fivos Simopoulos¹, Emmanouil Porfyarakis¹, Kampourakis George¹, Papadakis Nikolaos¹ and Emmanuel Kymakis^{3,4}

¹*Mechanical Engineering Department, Hellenic Mediterranean University, Heraklion, Greece*

²*Printed Electronic Devices of Things P.C., Volos, Greece*

³*Institute of Emerging Technologies (i-EMERGE) of HMU Research Center, Heraklion, Greece*

⁴*Department of Electrical & Computer Engineering, Hellenic Mediterranean University, Heraklion, Greece*

** tzounis@hmu.gr*

Abstract:

Thermal energy is one of the many forms of renewable energy sources; yet, > 60% of the above energy is wasted, involving temperatures below 100°C. Since direct conversion of heat to electricity is feasible without hazardous environmental impacts, thermoelectric power generation (TE) has been acknowledged as a reliable method for recovering waste heat. Thermoelectric Generators (TEGs) could be an emerging and promising renewable energy technology leading to a wide range of applications, such as energy harvesting, while efforts are also being made towards applying this technology in the soft robotics and wearable electronics. In addition to the material development process, there is currently a huge trend to move from inorganic thermoelectrics which are typically based on toxic and low abundance elements, non-flexible etc., to organic and carbon nanoallotrope thermoelectrics that have recently reached thermoelectric figure of merits in the range of ~0.5 and power conversion efficiency $\eta = 3-5\%$ [1].

Additive Manufacturing (AM) technologies could aid in this notion as a cost-effective means for TEG fabrication using thermoelectric material inks and pastes. In this presentation/ talk, a focus will be given on the fabrication of TEGs using 2D printing technologies (screen printing) as well as 3D printing- fused filament fabrication (FFF) combined with paste deposition. Mainly, SWCNT p- and n-type legs, will be discussed in detail regarding i.e. the SWCNT ink formulations, the 2D and 3D printing parameters, the TEG device characterization, as well as practical applications powered-up by the TEG device, with SWCNT Power factors of $>150 \mu\text{W}/\text{mK}^2$ and $100 \mu\text{W}/\text{mK}^2$, for p-, n- type SWCNT thermoelements, respectively, at $\Delta T=100\text{K}$.

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2D Materials for energy applications

Francesco Bonaccorso

BeDimensional SpA, Via Lungotorrente Secca 30r, 16163 Genova

Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova

*f.bonaccorso@bedimensional.it

Abstract:

Studying the interfacial interactions in polymer/GO nanocomposite materials

Ioannis Karnis^{1,2}, Fanourios Krasanakis¹, Kiriaki Chrissopoulou¹

¹*Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, GR-70013 Heraklion, Crete, Greece*

²*Department of Chemistry, University of Crete, Heraklion Crete, Greece*

Presenting author's e-mail: gkarnis@iesl.forth.gr

Abstract: Polymer nanocomposites have been the aim of study of the research community due to their improved properties compared to the respective ones of the pure polymers. In this work, nanohybrids consisting of hyperbranched polymers of different generations and graphene oxides (GO) with varying degrees of oxidation were developed at different concentrations to cover the whole regime from pure polymer to pure graphene oxide; the aim was to investigate the effect of the varying polymer / surface interactions on the nanocomposite structure and properties. Initially, the GO samples were synthesized either by altering the oxidation time or the amount of oxidizing agent to achieve different degrees of oxidation. Weakly to fully oxidized graphene oxides were synthesized by changing the amount of the oxidizing agent while the oxidation time did not seem to have any significant effect on the samples. Subsequently, nanohybrids were prepared using hyperbranched polyester polyols of three different generations and the GO samples with increasing oxidation degree. Differences were observed in the structure of the nanocomposites with X-ray Diffraction indicating the existence of either a phase-separated structure or an intercalated one, depending on the degree of oxidation of GO. The thermal properties were also influenced by the observed structure of the nanohybrids whereas there was a significant effect of the presence of GO on the thermal stability of the polymer and of the presence of the polymer on the reduction temperature of GO.

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Single and double pulse UV- femtosecond laser-induced breakdown spectroscopy (LIBS) for depth-resolved characterization of nano-scaled films

N. Giannakaris¹, P. Siozos², V. Pinon², S.P. Banerjee³, M. Sentis³, D. Anglos^{2,4}

¹*Institute of Applied Physics, Johannes Kepler University Linz, A-4040 Linz, Austria*

²*Institute of Electronic Structure and Laser (IESL), FORTH, Heraklion, Crete, Greece*

³*LP3 Laboratory, Case 917, 163 Avenue de Luminy, Marseille, France*

⁴*Department of Chemistry, University of Crete, Heraklion, Crete, Greece*

* psiozos@iesl.forth.gr

Abstract:

The distribution, analysis, and profiling of 2D materials in multi-layered samples are crucial for the semiconductor industry. However, the implementation of an analytical technique into an industrial environment for online in-situ measurements is challenging. Laser-induced breakdown spectroscopy (LIBS) is a non-contact quantitative analysis tool that identifies the elemental composition of a target material. Therefore, LIBS can be potentially used to diagnose in real time the elemental composition of different layers of a multi-layered material during laser scribing [1].

In this work, we managed to distinguish different material layers with thicknesses in the range of a few tens of nanometers using UV femtosecond LIBS. Laser pulses produced by a femtosecond laser are employed for different thin film structures (stacks) to obtain a single-shot LIBS spectrum after the successful laser ablation of layers with thicknesses down to 10 nm.

Double-pulse femtosecond LIBS method enhances the plasma emission while reducing the ablation rate. An increase in the emission enhancement factor value is observed by decreasing the fluence of the laser beam.

The results reveal a minimum average ablation rate (AAR) of approximately 60 and 40 nm for the single-pulse and double-pulse modes respectively, on ITO films. These ablation rates were obtained from laser shots at a fluence of 420 mJ/cm² and 250 mJ/cm² for the single-pulse and double-pulse modes, respectively.

Finally, carbon nitrate emission is recorded in the LIBS spectra produced from a nanometer-thickness layer. The molecular carbon emission can therefore be used to detect organic layers overcoming the limitation of the detection of organic nanolayers using LIBS due to weak emission of atomic carbon emission.

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2D Bismuthene as a Functional Interlayer for Enhanced Oxygen-Evolution BiVO₄ Photoanodes

Salvador Eslava^{1*}, Junyi Cui¹, Matyas Daboczi¹, Sixto Gimenez², and Ji-Seon Kim³

¹ Department of Chemical Engineering and Centre for Processable Electronics, Imperial College London, London, United Kingdom

² Institute of Advanced Materials (INAM), Universitat Jaume I, Castelló, Spain

³ Department of Physics and Centre for Processable Electronics, Imperial College London, London, United Kingdom

* s.eslava@imperial.ac.uk

Abstract:

Photoelectrochemical and photocatalytic conversion of water and carbon dioxide using solar energy offers a clean solution to the world energy requirements of a sustainable future. Achieving its full potential depends on developing inexpensive photoelectrodes and photocatalysts that can efficiently absorb solar light and drive photoinduced charges to react with water and carbon dioxide. In this talk, I will present recent developments we have achieved in the preparation of inexpensive BiVO₄ photoanodes functionalized with 2D bismuthene. Partially oxidized two-dimensional (2D) bismuthene is prepared by reduction of BiCl₃ and demonstrated to be an effective, stable, functional interlayer between BiVO₄ and the archetypal NiFeOOH co-catalyst. Comprehensive (photo)electrochemical and surface photovoltage characterizations show that NiFeOOH passivates hole trap states of BiVO₄; however, it is limited in influencing electron trap states related to oxygen vacancies (V_O). Loading bismuthene on BiVO₄ photoanodes fills the V_O-related electron traps, leading to more efficient charge extraction. This is confirmed by kelvin probe measurements. Moreover, bismuthene increases adsorption sites for reaction intermediates and increases interfacial band bending boosting hole charge flux to the electrolyte. With the synergistic interaction of bismuthene and NiFeOOH on BiVO₄, this composite photoanode achieves a 5.8-fold increase in photocurrent compared to bare BiVO₄ reaching a stable 3.4 (±0.2) mA cm⁻² at a low bias of +0.8 V_{RHE} or 4.7(±0.2) mA cm⁻² at +1.23 V_{RHE}. The use of 2D bismuthene also boosts other photoanodes such as hematite, demonstrating its wide potential to boost the performance of photoelectrodes for energy conversion applications.

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PANI/MoS₂ based NH₃ sensor

Aakanksha Jain^{1,2*}, Ajithkumar MP² and Siddhartha Panda^{1,2}

¹*Department of Chemical Engineering, Kanpur, India*

²*National Centre for Flexible Electronics, Kanpur, India*

** aajain@iitk.ac.in*

Abstract:

Researchers have used PANI/MoS₂ composite in various applications, but its use in gas sensing studies is limited. The need for gas detection in the sub-ppm range with good response and selectivity always has importance as it can open the door for non-invasive disease detection in humans. In this research work, PANI-MoS₂ nanocomposite-based flexible gas sensors for NH₃ detection in the sub-ppm range, operating at room temperature, have been investigated. Two different synthesis routes were explored to study morphology's effect on sensing. The synthesized samples were characterized using RAMAN, FESEM, TEM, XRD, and other spectroscopic characterizations. All characterizations confirmed the formation of a combination of MoS₂ and PANI nanofibers. The novelty lies in identifying the best synthesis route for PANI/MoS₂ composite to get the best sensing response. In addition, using flexible substrates, i.e., PET substrates, provides potential applications for these sensors in wearable and portable electronic products. The devices were subjected to mechanical deformations to check their flexible stability.

Acknowledgements

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Electrical and Magnetic Features of Heterometallic Oxalate Coordination Polymers with 2D Layers: Oxide-Related Use

Marijana Jurić^{1*}, Ana Lozančić¹, Lidija Molčanov¹, Sanja Renka¹, Damir Pajić²,
Dario Barišić², Martina Vrankić¹ and Sanja Burazer¹

¹*Ruđer Bošković Institute, 10000 Zagreb, Croatia*

²*Department of Physics, Faculty of Science, University of Zagreb, 10000 Zagreb, Croatia*

*Marijana.Juric@irb.hr

Design of new materials with targeted physical properties is a very attractive field of research nowadays. In recent years, the structural diversity of metal-organic coordination systems has paved the way for the development of multifunctional materials that combine two or more different properties, especially magnetic and electrical. A very important role in the design and synthesis of these materials is played by the oxalate anion, $C_2O_4^{2-}$, due to its various ways of coordination to metal centres and its potential to mediate electronic effects between paramagnetic metal ions. Through the "building block chemistry" approach, in which a molecular anionic ligand such as the tris(oxalato)metalate anion, $[M^{III}(C_2O_4)_3]^{3-}$, is used as ligand in reaction with other metal cations, many (hetero)polynuclear species, in particular two-dimensional (2D) and three-dimensional (3D), exhibiting different magnetic ordering, have been obtained.

Two polymorphs of the 3D coordination polymer $[Cu^{II}Fe^{II}_2(H_2O)(terpy)(C_2O_4)_3]_n$, formed hydrothermally using $[Fe(C_2O_4)_3]^{3-}$, consist of antiferromagnetically ordered 2D honeycomb layers $[Fe^{II}_2(C_2O_4)_3]_n^{2n-}$, bridged by $[Cu(H_2O)(terpy)]^{2+}$ cations. These compounds exhibit a strong increase of the electrical conductivity with the increase in relative humidity. However, the proton conductivity appears to be relatively low [2]. Therefore, we focused on preparing novel oxalate-bridged compounds that would exhibit proton conductivity as a new functionality by incorporating different alkyl ammonium components as counterions. A procedure was employed using an aqueous solution of $[Cr(C_2O_4)_3]^{3-}$ as a precursor containing $(CH_3)_2(C_2H_5)NH^+$ or $(CH_3)(C_2H_5)_2NH^+$ as counterions instead of the more common NH_4^+ or K^+ . Magnetically ordered isostructural compounds comprising an irregular 2D layers $[Mn_4Cl_4Cr_4(C_2O_4)_{12}]_n^{\delta n-}$ interleaved by the hydrogen-bonded templating cations were prepared. They exhibit remarkable humidity-sensing properties and very high proton conductivity [2].

Moreover, due to appropriate ratio of metal ions, these heterometallic compounds were used as single-source precursors for the preparation of spinel mixed-metal oxides by a simplified synthetic route through one-step thermal decomposition.

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Establishing Polydioxanone as a flexible resorbable sensor platform

Finn Jaekel^{1*}, Sarah Spitzner¹, Hans Kleemann¹, Dennis Wahl², Daniel Bockler², Eberhard Grambow², Sebastian Hinz², Clemens Schafmayer², Jochen Hampe³ and Karl Leo¹

¹*Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP), Dresden, Germany*

²*Department of General, Visceral, Thoracic, Vascular and Transplantation Surgery, Rostock University Medical Center, Rostock, Germany*

³*University Hospital Carl Gustav Carus at the Technical University of Dresden, Dresden, Germany*

**finn.jaekel@tu-dresden.de*

Abstract:

Polydioxanone is a well established medically licensed material typically used for resorbable medical structures. Hence, it could provide an ideal substrate for in-vivo electronic sensors in order to monitor post-surgery healing of wounds. However, the thermal budget and chemical robustness represents a significant challenge for the integration of electronic components – in particular, when aiming for a bioresorbable sensor. Here, we demonstrate a biodegradable electronic sensor on extruded Polydioxanone sheets as a flexible resorbable substrate. We pioneered the processed for the integration of resistive temperature sensors and pH-sensors based on organic electrochemical transistors, utilizing a combination of various techniques such as physical vapor deposition, inkjet printing, and screen printing. The variety of established processes opens up several possibilities to integrate further functionalities into the sensor platform.

This technology/sensor platform is tested in context of the DFG project FAVORS (Rapid alert system for anastomosis failure using organic resorbable sensors) [1] in which experiments on pigs are performed for in-vivo testing. Preliminary data of in-vivo measurements, as well as results on biocompatibility and influence of the substrate on wound healing are presented.

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Thursday 14th September

WS4 & WS6 Session III

Emerging Printed Electronics and Bioelectronics & 2D
materials and devices

Recent advances on graphene grown on liquid metal catalysts: synthesis, in situ monitoring and direct separation

Anastasios C. Manikas¹, Christos Tsakonas¹, Irene Groot², Marc de Voogd³, Gertjan van Baarle³ and Costas Galiotis^{1,4*}

¹*Institution A, City, Country* University of Patras, Chemical Engineering Department, 26504 Patras, Greece

²*Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

³*Leiden Probe Microscopy (LPM), Kenauweg 21, 2331 BA Leiden, The Netherlands*

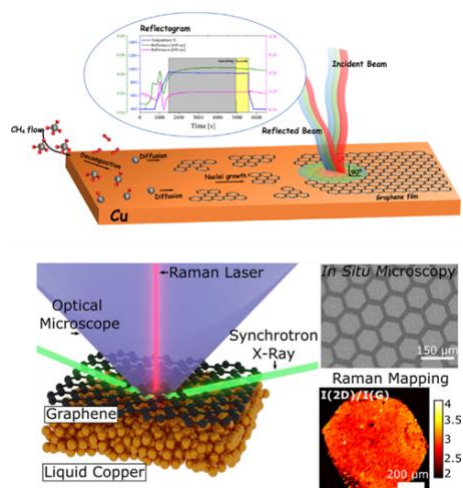
⁴*Institute of Chemical Engineering Sciences, Foundation for Research and Technology Hellas*

* c.galiotis@iceht.forth.gr

Abstract:

Graphene is a perfect 2D crystal consisting of covalently bonded carbon atoms and has been established as a promising candidate to replace current technological materials in a number of applications. Synthesis of large, defect-free 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. 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. The quality of LMCat graphene has been also investigated conforming its superior properties in terms of electrical and mechanical response. Finally, a novel platform for the direct separation of Gr from the liquid Cu substrate will be presented aiming towards the synthesis of wafer scale single crystal Gr of pristine quality.



Chemical and physical sensing with two-dimensional materials

Paolo Samorì

ISIS, University of Strasbourg & CNRS, Strasbourg, France

samori@unistra.fr

Physical and chemical sensors bear a direct societal impact on well-being, which includes, among others, the monitoring of human's health, the quality and composition of the air we breathe, the water we drink, and the food we eat.

Physical sensors are essential components for the fabrication of devices for medical diagnosis and health monitoring, upon use of active materials with sensitivities in the low-pressure or medium-pressure range, respectively. In this framework, flexible piezoresistive pressure sensors are compatible with wearable technologies for digital healthcare, human-machine interfaces and robotics. Among active materials for pressure sensing, graphene-based materials are extremely promising because of their outstanding physical characteristics. Currently, a key challenge in pressure sensing is the sensitivity enhancement through the fine tuning of the active material's electro-mechanical properties. We have achieved this by combining chemically reduced graphene oxide (rGO) with (macro)molecular materials with controlled mechanical properties. [1]

In chemical sensing higher sensitivity, faster response time and recovery time can be achieved by using 2D materials as active components. Instead, selectivity can be attained either through the optimization of the energy levels of the analyte with respect to those of the active material, as demonstrated via the fabrication of sensors of heavy metals[2] or polyaromatic molecules[3], or through the functionalization of the latter with supramolecular receptors ensuring a high discrimination of ions and small molecules in the sensing event.[4]

Strategies for simple integration of working devices with electrical read-outs will be presented.

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Wednesday 13th September

WS1 Poster Session

Nanomaterials and Nanomedicine

Three SiO₂ layered approach for stable and PL active CsPbBr₃@SiO₂ nanocrystals biological agents

Markella Splinaki^{1*}, Konstantina Alexaki¹, Konstantinos Brintakis¹, Paraskevi Kavatzikidou¹, Anthi Ranella¹, Athanasia Kostopoulou¹ and Emmanuel Stratakis^{1,2}

¹ Institute of Electronic Structure & Laser (IESL)

Foundation For Research And Technology Hellas (FORTH), Heraklion, Greece

² University of Crete, Department of Physics, Heraklion, Greece

*msplinaki@iesl.forth.gr

Abstract:

Metal halide perovskites nanocrystals (ABX₃), present unique optical properties, making them advantageous compared to conventional quantum dots used in biomedical applications [1]. These nanocrystals (NCs) are able to provide personalized diagnosis and therapy. However, their limited stability and cytotoxicity issues hinder their bio-applications. To overcome these limitations, we propose a new three-layered silica approach for encapsulating CsPbBr₃ NCs within a protective silica shell preserving at the same time the optical properties of the core [2,3]. This three-layered silica approach is suggested to improve the dispersibility and the stability of the perovskite-SiO₂ particles in aqueous environment. In the shell formation process, tetramethyl orthosilicate (TMOS) was selected for its ability to form quickly a thick SiO₂ due to its small carbon chain and the (3-Mercaptopropyl) trimethoxysilane (MPTMS) which is proved to bond tightly on the Pb atom of the perovskite. The stability of the NCs aqueous dispersions of this approach was also compared with those of a single layer or a double layer. Additionally, the effect on the PL stability of the order of the TMOS or MPTMS additions was investigated. The optimum CsPbBr₃@SiO₂ NCs with the three-layered silica coverage exhibited homogenous dispersions, highly fluorescent green emission, and a narrow size distribution in aqueous environments and biological media. We also evaluated the cytotoxicity and internalization behavior of CsPbBr₃@SiO₂ NCs using *in vitro* experiments. Low cytotoxicity was demonstrated, indicating the biocompatibility of these NCs. Furthermore, the successful delivery of CsPbBr₃@SiO₂ was proved by experiments investigated the dose- and time-dependent internalization of the NCs in HeLa and NIH 3T3 cells highlighting their potential for diagnostic applications.

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Electrospinning of short peptides and characterization through Hyperspectral Raman spectroscopy

Matteo Bottiglieri¹, Konstantina Mitropoulou¹, Maria L. Gelmi² and Alexander M. Bittner^{1,3}

¹ CIC nanoGUNE, (BRTA) Tolosa Hiribidea 76, 20018 Donostia-San Sebastián, Spain

²Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano, Via Mangiagalli 25, 20131 Milano (Italy)

³Ikerbasque Basque Foundation for Science, Pl. Euskadi 5, 48009 Bilbao, Spain

*m.bottiglieri@nanogune.eu

Abstract:

Electrospinning is a well-established technique for the preparation of fibers from micro to nanoscale through uniaxial stretching of a viscoelastic solution due to the application of a high voltage. Application of this technique on pure/polymer-free peptides and peptidomimetics is a field still in his infancy, but thanks to their wide biochemical relevance and their ability to self-assemble [1] they are promising candidates [2].

The mechanism of fiber production by electrospinning leads to the formation of fibers with a high degree of molecular orientation and this affects the characteristics of the material produced. Electrospinning process presents a complex fluids behavior, so the final fibers have a wide distribution of properties. Classic characterization methods of large bundles of fibers provide an average of the characteristics of the fibers and not much information about uniformity of orientation [3].

Raman spectroscopy is a non-invasive method that at first instance, provides a vibrational spectrum of the chemical composition of samples. It allows the interpretation and identification of the compounds from the characteristic vibrations of the functional groups [4]. Combining Raman with a confocal microscope, we could obtain a **hyperspectral imaging** of the fibers, that consists in mapping the spectral and spatial features of single and multiple fibers [5]. Furthermore, in a system of uniaxial symmetry (fibers), intensity ratios of **polarized Raman spectra** allow to determinate order parameters of the orientation distribution function. With these data, we can determine the qualitative and quantitative orientation of the molecules that form the fibers [6].

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Photoactive singlet oxygen generating nanofibrous membrane for biomedical applications

Petra Křtěnová^{1*}, Vojtěch Liška¹, Robert Willimetz¹ and Jiří Mosinger¹

¹Faculty of Science, Charles University, Hlavova 2030, 128 43, Prague 2, Czech Republic

*krtenovp@natur.cuni.cz

Abstract:

Polycaprolactone (PCL) is an attractive polymer commonly used in regenerative medicine and tissue engineering. It is biocompatible, biodegradable and can be easily electrospun to produce nanofibrous membranes with excellent diffusion for oxygen. PCL nanomembranes can be easily surface functionalized to modify their wettability, enhance cellular attachment or allow binding of wide range of compounds including drugs or antimicrobials. In our study, several nanofibrous membranes from polycaprolactone were prepared. Doping with photosensitizers, light-absorbing compounds generating singlet oxygen, resulted in development of photoactive self-sterilizing material. The membranes exhibit great antimicrobial activity against *Escherichia coli* and are highly suitable for various biomedical applications where mitigating bacterial contamination is needed, e.g. wound dressings, filters, or scaffolds for *in vitro* cell culturing.

In Vitro And Ex Vivo Examinations Of The Antiplatelets And Antimicrobial Properties Of Functionalized Silver Nanoparticles As A Potential Coating For Cardiovascular Devices

Iwona Inkielewicz-Stepniak^{1*}, Anna Supernat¹ and Elzbieta Megiel²

¹*Medical University of Gdansk, Gdansk, Poland*

²*University of Warsaw, Warsaw, Poland*

[*iwona.inkielewicz-stepniak@gumed.edu.pl](mailto:iwona.inkielewicz-stepniak@gumed.edu.pl)

Abstract:

Thrombus formation and bacterial infection are two common problems that lead to complications of blood-contacting medical devices such as catheters, vascular grafts and heart valves [1]. Developing antithrombotic and antimicrobial coatings is of paramount importance to sustain the functionality of such biomedical devices, and thereby reduce the mortality rate and medical costs due to complications. Incorporating antiplatelets and antimicrobial agents into the surface coating has proven to be an effective strategy to reduce thrombus formation or bacterial infection related complications [2-3].

In this work, functionalized with ticagrelor and tirofiban silver nanoparticles were synthesized for modifying the surface of PVC device. We investigated its physio-chemical characteristics using Field Emission- Scanning Electron Microscopy and Energy dispersive X-Ray analysis, X-Ray Diffraction (XRD), UV-Visible and Diffuse Reflectance spectroscopy, and Dynamic Light Scattering characterization methods.

The coated catheter was able to reduce protein adhesion, blood platelets adhesion and activation, and prevent microbial surface attachment for a broad spectrum of bacteria, including clinical strains more significantly when compared to unmodified one.

This type of coating materials, exhibiting the potential for both antithrombotic and antimicrobial properties, may be useful to help resolve complications due to thrombus formation and bacterial infection associated with a wide range of biomedical devices.

This work was supported by grant HARMONIA (2017/26/M/NZ7/01030) from the Polish National Science Center (NCN).

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Conformational Effects of Gold Nanoparticle Exposure on Enzyme Creatine Phosphokinase

Taneeka Anand^{1*}, Mahima Unnikrishnan² and Catherine J. Murphy²

¹*University of California, Los Angeles, California, United States*

²*University of Illinois, Urbana-Champaign, Illinois, United States*

[*anandtaneeka@gmail.com](mailto:anandtaneeka@gmail.com)

Abstract:

Understanding the implications of the interaction between nanoparticles (NPs) and biomolecules is essential to improve emerging technologies that involve the release of nanomaterials into the environment. Research at The NSF Center for Sustainable Nanotechnology places an emphasis on how relatively little is known about this phenomenon and aims to delve deeper into the impact of NPs on our environment and the organisms in it. Biomolecules such as proteins are especially relevant to study in the context of nanomedicine, given their abundance and importance in the functioning of the human body. Creatine phosphokinase (CPK) is one such protein that is the oldest marker to identify myocardial infarctions, which makes it interesting to study at the nano-bio interface. A possible consequence of the interaction between CPK and nanoparticles is a conformational change observed in the protein structure, which could dictate changes in the functions carried out by the protein. In the physiological environment, changes to protein function could lead to downstream effects that are detrimental to cellular function. Cationic nanoparticles, in particular, have been known to undergo cellular uptake and cause cytotoxicity in the literature. In this study, the secondary structure of the CPK enzyme is analyzed using circular dichroism spectroscopy after exposure to positively charged gold nanoparticles to determine any deviations from the original conformation of CPK. Secondary structure data from studies performed under different in vitro incubation conditions will be discussed in this work. This study can be extended to future investigations of the effects of NPs on CPK enzymatic activity, or to proteins with similar properties.

Biological evaluation of TiO₂-based photocatalytic nanoparticles

Evangelia Tsitsou^{1,2}, Athina Papadopoulou^{1,2}, Maria Theodosiou^{1,2}, Elena Charalampous¹, Maria Kourmoussi¹, Panagiotis Tzevelekidis¹, Christina-Anna Mitsopoulou¹ and Eleni K. Efthimiadou^{1,2*}

¹Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

²Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Athens, Greece #

*tsitsoueva@chem.uoa.gr

Abstract:

In our lab we work on the synthesis of innovative modified nanoparticles based on titanium with increased antipollutant and antimicrobial activity in visible light. Although titanium and titanium alloys are characterized by adequate stability and biocompatibility, their materials lack of intrinsic antibacterial activity.[1] Titanium dioxide (TiO₂, titania) is a compound with risen scientific interest due to its ability of producing ROS under UV light (photoactivity) and inducing cell death.[2] Efforts have been made to conjugate metal nanoparticles with enhanced antibacterial activity to titanium. The different types of photocatalytic nanoparticles synthesized in our lab are constituted of TiO₂@Ag, TiO₂@ZnO, TiO₂@QDs and TiO₂@Cu. Their crystallinity was characterized by PXRD analysis and their morphology and size were studied with SEM and TEM analyses. The present work is focused on the biological evaluation of these nanoparticles. All the biological experiments are carried out using a healthy cell line, HaCaT, which is a human epidermal keratinocyte line. First of all, cytotoxicity is studied following the MTT assay. Then, the mechanism of nanoparticles' interaction with the cells is deepened. More particularly, the degree of apoptosis and necrosis caused by the administration of the nanoparticles to the cells is studied, as well as the percentage of the produced ROS. Finally, gel electrophoresis is used in order to identify, characterize and quantify the interaction of nanoparticles with plasmid PUC-19.

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Biomimetic Lipid Nanoparticles for Tumor-Targeted RNA Delivery

S.Garbujo^{1*}, C.Baioni¹, F.Magni², M.Colombo¹, D.Peer³ and D.Prosperti¹

¹ *Department of Biotechnology and Bioscience, University of Milano-Bicocca, Milan, Italy*

² *School of Medicine and Surgery, University of Milano-Bicocca, Veduggio al Lambro, Italy*

³ *The Shmunis School of Biomedicine and Cancer Research, Tel Aviv University, Tel Aviv, Israel*

*[*stefania.garbujo@unimib.it](mailto:stefania.garbujo@unimib.it)*

Abstract:

Despite the great clinical success of lipid nanoparticles (LNPs) as non-viral gene therapy vectors, they suffer from lack of tumor targeting capability, which is a prerequisite for selective cancer therapy [1]. Cell membrane coating technology offers appreciable means for imparting several advantageous functions to nanoparticles, including targeting capability [2]. In this work, the natural composition of tumor cell membranes is explored to achieve both homotypic and heterotypic targeting, relying on the intrinsic self-interaction of cancer cells and on their crosstalk with heterotypic cells in tumor microenvironment, respectively. A core-shell system, whereby RNA-loaded LNPs (core) were wrapped by cancer cell membrane derived nanoghosts (CCM-NGs, shell), derived from murine 4T1 breast cancer cells, was synthesized. CCM-NGs were dye-labeled and characterized in terms of size, surface charge, protein content, membrane sidedness and fluorescence properties, and their potential in promoting homotypic (with 4T1 cells) and heterotypic (with cancer associated fibroblasts) interactions was tested in culture. Cy5-labeled LNPs encapsulating small interfering RNA prepared by microfluidic technology were incorporated into CCM-NGs resulting in biomimetic LNPs. The results of this work provide a proof of principle that LNPs loaded with RNA can be readily incorporated into biomimetic nanoparticles with obvious advantages in terms of target selectivity, bioavailability and safety.

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[2] L. Liu, et al. *Nature Communications* 13, 1–15 (2022)

Evaluation of HF_n-mAb nanoconjugates-mediated anticancer activity in 3D tumor models

Barbieri L., Rizzuto MA., Pellicchia F., Andreotti C., Colombo M., Prospero D.

NanoBioLab, Department of Biotechnology and Biosciences, University of Milano-Bicocca, Piazza della Scienza 2, 20126, Milan, Italy

**linda.barbieri@unimib.it*

Abstract:

During the last decades, immunotherapy has significantly developed as an alternative modality to treat cancer malignancies. In contrast to the other therapeutic concepts, immunotherapy aims to eliminate the primary mass of cancer and relevant peripheral metastases by re-educating the host immune system to recognize the cancer cells as “non-self” and consequently react against them. Many different strategies have been reported in the literature and, among these, antibody-based therapy is one of the most successful for the treatment of highly aggressive cancer subsets. Indeed, monoclonal antibodies (mAbs) can promote tumor killing both by immune cells activation through a mechanism known as antibody-dependent cellular cytotoxicity (ADCC) and by the direct inhibition of tumor proliferation and survival pathways. However, the therapeutic efficiency of mAbs is still limited by problems related to their poor pharmacokinetics and crossing of biological barriers. Nanoparticles proved to be a promising strategy to overcome mAbs’ limitations because they can be both functionalized on the surface with specific ligands and exploited as vehicles for drug delivery. Among them, H-ferritin (HF_n), a recombinant form of human apoferritin, has been extensively studied because it is biocompatible, can be loaded with drugs and exhibits tumor targeting by recognition of transferrin receptor 1 (TfR1), overexpressed in 98% of human cancers. After demonstrating that HF_n is an efficient carrier to enhance the blood-brain barrier (BBB) crossing of mAbs without the loss of their antitumoral activity on 2D tumor models, we focused on the evaluation of the activity of HF_n-mAb nanoconjugates on 3D cellular models. As a three-dimensional model we chose to use spheroids because they are able to closely mimic the main features of human solid tumors. First experiments were carried out to optimize the formation of cancer spheroids of glioblastoma and breast cancer cell lines, to produce a recombinant form of human apoferritin with a reduced endotoxin content and to optimize the conjugation reaction between HF_n and the monoclonal antibody Cetuximab (CTX). Then we evaluated the internalization of HF_n-CTX by flow cytometry and confocal microscopy and we investigated the ability of HF_n-mAb nanoconjugates to trigger the ADCC monitoring over time the increase in mortality resulting from the activation of the apoptosis mechanism. To further confirm the ability of our nanoconjugates to initiate ADCC, we also studied the activation of natural killer (NK) cells which, after the binding to the Fc portion of mAbs, release cytotoxic granules that kill cancer cells. The data obtained so far with 3D models demonstrated the efficacy of HF_n-mAbs to trigger an anticancer effect and activate the immune system. In the future, we’ll try to co-administer our HF_n-mAb with doxorubicin or cisplatin-loaded ferritin to combine the immune system activation with the chemotherapeutic activity of these drugs and then proceed with the in vivo administration of our nanoconjugates.

Transdermal electrochemical sensing: combining microneedles with molecularly imprinted polymers for point-of-care testing

Daniela Oliveira^{1, 2, 3, 4*}, Bárbara P. Correia^{1, 2}, Sanjiv Sharma³ and Felismina T. C. Moreira^{1, 2*}

¹*BioMark@ISEP-CEB/LABELS, School of Engineering, Polytechnic of Porto, R. Dr. António Bernardino de Almeida, 431, 4249-015 Porto*

²*CIETI - LabRISE-School of Engineering, Polytechnic of Porto, R. Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal*

³*Faculty of Sciences and Technology, University of Coimbra, R. Silvío Lima, Pólo II, 3030-790 Coimbra, Portugal*

⁴*Department of Biomedical Engineering, Faculty of Science and Engineering, Swansea University, Swansea SA1 8EN, U.K.*

**ddsol@isep.ipp.pt, ftm@isep.ipp.pt*

Abstract

Biomarkers from interstitial skin fluid (ISF) complement conventional biofluids for point-of-care testing and real-time monitoring. In this study, we propose a new approach that combines microneedle technology with molecularly imprinted polymers to improve transdermal electrochemical sensing. The molecularly imprinted polymer, which acts like a plastic antibody, is easy to synthesis and scalable, offering a low detection limit and rapid measurement (20 minutes). It detects IL -6, a proinflammatory cytokine associated with several clinical conditions, including neurological disease and pneumonia caused by SARS-CoV-2. The transdermal sensors successfully identified IL -6 in simulated skin ISF at very low concentrations (1 pg/mL). This breakthrough enables affordable and bloodless testing, facilitating access to point-of-care testing worldwide. The integration of molecularly imprinted polymers and microneedle arrays is very promising for efficient transdermal electrochemical sensing that could find application in various clinical scenarios.

Keywords: Microneedles; Interstitial skin fluid; Electrochemistry; Biosensor

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Redox-Active Enzyme Conjugates on DNA Origami Nanoscaffolds for Bioelectrochemistry

Diana Soukarie¹, Jokin Yeregui^{1,2}, Alexander Bittner¹ and Ibon Santiago*¹

¹ CIC nanoGUNE BRTA, Donostia-San Sebastián 20018, Spain

²KTH Royal Institute of Technology, Stockholm, Sweden

[*d.soukarie@nanogune.eu](mailto:d.soukarie@nanogune.eu), i.santiago@nanogune.eu

Abstract:

Interrogating the catalytic activity of single nanoentities using nanoscopic tools deepens our understanding of confined electron transfer reactions. Recently, the "nano-impact" method has garnered attention due to its capability to detect individual particles and biomolecules (1, 2) that collide with or adsorb onto ultramicroelectrodes. Although time-resolved detection is achievable, probing the catalytic activity of spatially heterogeneous enzyme distributions remains a scientific challenge. This often necessitates the immobilization of enzymes in favorable microenvironments.

We have previously tethered DNA aptamers to detect thrombin on a microchip (3). In this work we leverage the advantages and potential applications of DNA as nanoscaffolds for enzyme immobilization and interrogation. Thanks to its programmable self-assembly properties, DNA can form robust, precise, and predictable nanostructures. This makes it an ideal platform for the spatial positioning of redox moieties and enzymes. We employed a quinoprotein with a high reaction rate and functionalized it onto a self-assembled DNA origami scaffold. We examined the chemical stability and catalytic activity of the conjugated enzymes, characterizing the resulting structures using Atomic Force Microscopy in a liquid environment.

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- [2] L. Jiang, I. Santiago, J. Foord, Observation of nanoimpact events of catalase on diamond ultramicroelectrodes by direct electron transfer. *Chemical Communications* **53**, 8332 (2017).
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Sustainable Recycling Of Spent Automotive Catalysts

S. Todorova^{1*}, Z. Cherkezova-Zheleva¹, D. Paneva¹, I. Yakoumis² and K. Sakkas³

¹*Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria*

²*MONOLITHOS Catalysts and Recycling Ltd, Athens, Greece*

³*YS Cypriot Catalysts Ltd., Psevdas, Cyprus*

*todorova@ic.bas.bg

Abstract:

Spent auto-catalysts are considered as a promising future source of platinum group metals (PGMs), based on their rapidly increasing demand along with the underlying uncertainty of the sustainability and long-term availability of PGMs. Currently, the main consumption of PGMs is for production of automotive catalytic converters, estimated that above 360t/y are needed for the fabrication of automotive catalysts [1]. The green transition will additionally increase the PGM demand for production of fuel cell vehicles and other new applications. Thus, the research investigations are concentrated on PGM recycling opportunities, as well as on their sustainable and environmentally friendly reuse. Recycling methodology presents attractive advantages for the conservation of primary raw materials and reduction of negative environmental impact due to exploitation. PGM recovery is the major aim of recycling operations despite their minor concentration in spent autocatalysts, which implies that the remaining materials are disposed of as unwanted solid waste after the extraction process. Thus, the development of recycling processes for spent auto-catalysts have to be oriented on the recovery of all valuable metals, while moderating environmental pollution and global warming. This work paper presents a series of laboratory scale experiments toward optimization and greening the recycling technology of PGMs from spent automotive catalysts by application of mechanochemical approach. Mechanochemically recovered PGMs are used for preparation of catalysts which were characterized by different physicochemical methods and tested in the reaction of CO oxidation.

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[1] IPA fact sheets 2022, <https://ipa-news.de/index/platinum-group-metals/pgm-fact-sheets.html> .

New polymeric nanoparticles as platform in drug delivery field

Giustra M.D.^{1*}, Bolis L¹, Barbieri L.¹, Baioni C., Spena F.¹, Prosperi D¹, Colombo M.¹

¹ NanoBioLab, Department of Biotechnology and Bioscience, University of Milano Bicocca, Milan, Italy

*marco.giustra@unimib.it

Abstract:

Currently, the production of new cutting-edge platforms for RNA delivery is one of the topics under the spotlight, especially with the introduction of vaccines against SARS-CoV-19.

Considerably research has gone into the development of lipid nanoparticles (LNPs), although the resulting disadvantages are not entirely obvious. For example, colloidal stability and manufacturing costs. Here we present an easy way to produce two forms of biocompatible nanoparticles (NPs) based on poly (isobutylene-alt-maleic anhydride), named PMA.

This polymer can easily react with primary amines, thanks to 39 monomeric units of succinic anhydride per polymer chain. In this work, polymer backbones were functionalized with D-glucosamine (GlycoPMA) to create one NPs type.

PMA and GlycoPMA NPs were obtained through the nanoprecipitation technique - polymer dissolved in the organic phase is added to an aqueous solution allowing the formation of monodisperse colloidal dispersion with a diameter of ~55 nm by TEM.

These NPs were employed to evaluate the encapsulation capability of various cargos. We selected five molecules and one of the molecules is Manganese (II) phthalocyanine, a paramagnetic macrocycle, useful to be exploited as a contrast agent to be used in biomedical imaging.

Moreover, cell viability and penetration in NIH-3T3 fibroblast and U87 glioblastoma cell lines were evaluated noticing no toxicity effects and high cell-uptake levels in both lines.

The data open the way for the creation of a new cheap and scalable drug delivery system based on RNA delivery. RNA encapsulation and delivery will be the next steps supporting the *in vivo* studies work in progress.

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Structural polymorphism research of alverine citrate

Magdalena Janczura^{1,2}, Natalia Rosiak² and Judyta Cielecka-Piontek^{2*}

¹ *Synteza sp. z o.o., Poznan, Poland*

² *Department of Pharmacognosy and Biomaterials, Faculty of Pharmacy, Poznań University of Medical Sciences, Poznan, Poland*

**jpiontek@ump.edu.pl*

Abstract:

Alverine citrate is a spasmolytic, which has a specific action on the smooth muscle of the alimentary tract and the uterus. Alverine, as a free base is a liquid practically insoluble in water ($0.00096 \text{ mg}\cdot\text{mL}^{-1}$), while commercial active pharmaceutical ingredient - alverine citrate, is a white solid that can form different crystalline forms or polymorphs, and its solubility in water reaches $12 \text{ mg}\cdot\text{mL}^{-1}$. Despite the fact that alverine citrate has been on the market for several decades, only few crystallographic studies are characterizing alverine citrate polymorphism by XRPD. Recent reports describe except form I of alverine citrate also form II, which does not contain crystal water and form B as alverine citrate monohydrate. The study compares the active substance alverine citrate from three commercial sources in order to demonstrate polymorphic forms using the XRPD, SEM, and IR techniques.

XRPD and FT-IR analysis shows that all alverine citrate samples (despite differences in the synthesis process eg. solvents used in the synthesis process, crystallization temperature) are in the same polymorphic Form I. Scanning electron micrographs of alverine citrate from each manufacturer show differences in morphology (texture). The solubility studies confirmed the complete solubility of the highest dose of alverine citrate in media with a pH of 1.2-6.8. Based on the solubility tests of alverine citrate, a hard capsule was prepared with the highest possible dose of the active substance. The release studies show that the release of the active substance, regardless of the manufacturer type, meets the immediate release requirement. Accelerated stability studies confirm the stability of the alverine citrate from selected manufacturers.

The improvement of suitable crystalline forms to some drugs character of alverine citrate is found to be significant in view of solubleness, stability and immense impact on to drug effect performance. Our study confirmed that alverine citrate from producers is in the same polymorphic Form I, despite differences in the synthesis process. As a result, the manufacturer of the final medicinal product may allow their interchangeability during production without compromising the safety or efficacy of the medicinal product.

Design of Experiment approach to design space designating of the Hot Melt Extrusion process

Magdalena Paczkowska-Walendowska^{1*}, Anna Stasiłowicz-Krzemień¹, Natalia Rosiak¹, Judyta Cielecka-Piontek¹

¹ Department of Pharmacognosy and Biomaterials, Faculty of Pharmacy, Poznan University of Medical Sciences, Poznan, Poland

*mpaczkowska@ump.edu.pl

Abstract:

In the pharmaceutical manufacturing industry, oral ingestion is the most favored mode of administration among other drug delivery routes. However, most active pharmaceutical ingredients have low water solubility, which limits their oral bioavailability. In recent decades, hot extrusion (HME) technology as a thermal treatment has attracted much attention as an approach to increase solubility and permeability and improve the bioavailability of poorly soluble drugs to achieve optimal therapeutic efficacy.

The purpose of this work was to develop an experience matrix in accordance with the Design Experiment (DoE) approach to determine the design space of the Hot Melt Extrusion process for compound X (project confidential data). Soluplus® was added as an excipient (BASF Pharma). Statistica 13.3 software (TIBCO Software Inc., Palo Alto, CA, USA) was used to prepare the central composition plan and analyze the results (with $\alpha = 1$). As input parameters to the model, critical for the extrusion process, the process temperature ($130 \pm 5^\circ\text{C}$) and screw rotation speed (120 ± 10 rpm) were determined. The following parameters were determined as the output parameters: torque, true density, active substance content, the rate of release of active substance in 45 minutes. Regardless of the model, the amorphism of the obtained extrudates was confirmed.

It was shown that changing the process temperature in the range of 125 - 135°C and the screw rotation speed in the range of 110 - 130 rpm did not affect the quality of the produced extrudates.



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Application of electrospun nanofibers to increase the solubility and permeability of resveratrol-rich extracts from red vine leaves

Magdalena Paczkowska-Walendowska^{1*}, Andrzej Miklaszewski², Judyta Cielecka-Piontek¹

¹ *Department of Pharmacognosy and Biomaterials, Faculty of Pharmacy, Poznan University of Medical Sciences, Poznan, Poland*

² *Faculty of Mechanical Engineering and Management, Institute of Materials Science and Engineering, Poznan University of Technology, Poznan, Poland*

[*mpaczkowska@ump.edu.pl](mailto:mpaczkowska@ump.edu.pl)

Abstract:

Red vine leaves extract is a herbal medicine containing several polyphenols, with resveratrol and polydatin as the main compounds exhibiting antioxidant and anti-inflammatory properties. The low oral bioavailability of the resveratrol and polydatin limits their health-promoting effect and forces the search for new technological solutions. In the first stage of the work, using the Design of Experiment (DoE) approach, the red vine leaves extract (50% of methanol, temperature 70 °C, and 3 cycles per 60 minutes) was chosen, which showed the best antioxidant and anti-inflammatory properties.

The second part focuses on optimizing the electrospun synthesis process of polyvinylpyrrolidone (PVP) and hydroxypropyl- β -cyclodextrin (HP β CD) nanofibers loaded with optimized resveratrol-rich red vine leaves extract. The optimization of the process concerned the time of system mixing before electrospinning, the mixture flow rate, and the rotation speed of the collector. The identification of nanofibers was confirmed based by using XRPD diffractograms, SEM pictures, and FTIR-ATR spectra. Dissolution studies of resveratrol from nanofibers showed improved its solubility (over five-fold). Additionally during the PAMPA-GIT assay was confirmed significantly better buccal penetration of resveratrol (over ten-fold).

The proposed strategy for the electrospun nanofibers production with red vine leaves extract is an innovative approach to better use the synergy of biological action of active compounds present in extracts, especially during nutraceutical development.

Funding: This research was funded by National Science Center (Poland), under Sonata grant (number 2020/39/D/NZ7/01824)

Cobalt catalysts supported on Al₂O₃ and SiO₂ VOC oxidation and PROX process-influence of the support

S. Todorova¹, I. Yordanova^{1*}, A. Naydenov², D. Filkova¹, B. Grahovski¹, H. Kolev¹

¹ *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., bl. 11, 1113 Sofia, Bulgaria*

² *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., bl. 11, 1113 Sofia, Bulgaria*

*yordanova@ic.bas.bg

Abstract:

The design of a catalytic system for complete oxidation of hydrocarbons and CO is an important problem of the environmental catalysis. Cobalt oxide is reported to be quite promising among the metal oxides used for preparation of supported catalysts for the removal of VOC. Cobalt oxide is quite promising among the metal oxides used for preparation of supported catalysts for the elimination of the above mentioned compounds.

Co₃O₄ nano particles were supported on the silica or alumina by hydrothermal method and characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR). The catalytic performance was examined in the complete *n*-hexane and methane oxidation.

Finally divided cobalt oxide particles and cobalt silicate are formed on the surface of the silica supported catalyst. In addition to the phase of cobalt oxide, a phase of surface Co²⁺ ions is formed on the surface of alumina supported catalyst.

It was confirmed that cobalt oxide catalysts supported on SiO₂ and Al₂O₃ can be prepared by one step hydrothermal method. The Co₃O₄/SiO₂ catalyst possesses the appropriate characteristics for the reaction of the total *n*-hexane oxidation, namely, a high dispersion of the oxide phase and the weak interaction with the support. The small crystallite size gives rise to more easily accessible active sites, the formation of more active oxygen species and easy reduction. The lower activity of the alumina supported catalyst could be related to the formation of the inactive surface spinel-like phases.

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pH responsive biohybrid BSA-poly(DPA) nanoparticles for interlysosomal drug delivery

Maria Papageorgiou^{1*}, Lina Papadimitriou¹, Alexis Theodorou², Errika Voutyritsa², Argryi Papagiannaki², Kelly Velonia² and Anthi Ranella¹.

¹*Institute of Electronic Structure and Laser (IESL), Foundation of Research and Technology-Hellas(FORTH), Heraklion, Crete, Greece*

²*Department of Materials Science and Technology, University of Crete, Heraklion, Crete, Greece*

[*mpapag19@gmail.com](mailto:mpapag19@gmail.com)

Abstract:

In the last decades, diseases such as cancer and neurodegenerative disorders have been treated through various conventional drug administration, which suffers from limited bioavailability and off-target toxicity, leading to adverse effects. Nanoparticle-based drug delivery systems offer advantages like controlled release, increased circulation time, and selective targeting of tissues. pH-responsive nanoparticles are particularly promising for drug delivery, as they can release drugs at specific target sites like tumor microenvironments or intracellular compartments, which could be beneficial for treating Lysosomal Storage Diseases (LSDs). This study highlights the potential of a specific pH-responsive protein-polymer nanocarrier, bovine serum albumin-poly(2-(diisopropylamino)ethyl methacrylate) (BSA-poly(DPA)), for targeted drug release and its potential application in treating LSDs, where conventional therapies face limitations due to the blood-brain barrier. The nanoparticles were synthesized using a grafting-from controlled radical polymerization approach, and their physicochemical properties were studied using various techniques. The encapsulation efficiency of acridine orange (AO) and 5-amino fluorescein (5AF) in the nanoparticles was determined, and their pH-responsive drug release behavior was evaluated. In addition, the nanoparticles' uptake by HeLa cells was investigated using metabolic activity assays, confocal microscopy, and lysosomal staining. The metabolic activity assay showed that low concentrations of BSA-poly(DPA) NPs up to 2 $\mu\text{g/ml}$ did not affect cell metabolism, but higher concentrations (above 8 $\mu\text{g/ml}$) reduced cellular metabolic activity by half after 48 hours. The nanoparticles were found to effectively release their cargo at the acidic pH of late endosomes and lysosomes. The use of BSA in the nanocarrier system is expected to increase its circulation half-life, making it a promising candidate for in vivo drug delivery applications. Internalization studies revealed that BSA-poly(DPA) NPs are endocytosed using an energy consumption-based mechanism, and they successfully delivered their cargo to lysosomes. Though further research is needed, this study showed that the BSA-poly(DPA) nanoparticles hold potential for personalized drug delivery with programmable multiple therapeutics release.

Revelation of tooth structural integrity at the microcrack site by combining X-ray tomography with photoluminescence and machine learning

Irma Dumbryte^{1*}, Maria Androulidaki², Donatas Narbutis³, Elena Jasiuniene⁴,
Arturas Vailionis⁵, Saulius Juodkazis⁶, and Mangirdas Malinauskas⁷

¹*Institute of Odontology, Vilnius University, Vilnius, Lithuania*

²*Microelectronics Research Group, Institute of Electronic Structure & Laser, Foundation for Research and Technology FORTH-Hellas, Heraklion, Crete, Greece*

³*Institute of Theoretical Physics and Astronomy, Vilnius University, Vilnius, Lithuania*

⁴*Ultrasound Research Institute, Kaunas University of Technology, Kaunas, Lithuania*

⁵*Stanford Nano Shared Facilities, Stanford University, Stanford, USA*

⁶*Optical Sciences Centre and ARC Training Centre in Surface Engineering for Advanced Materials (SEAM), School of Science, Swinburne University of Technology, Hawthorn, Australia*

⁷*Laser Research Center, Vilnius University, Vilnius, Lithuania*

*irma.dumbryte@mf.vu.lt

Abstract:

Although teeth microcracks (MCs) were recently characterized in three-dimensions (3D), it is still unknown whether there are changes in the tooth material within the MC compared to the enamel areas that are without cracks^{1,2}. The aim of the study was to combine an X-ray micro-computed tomography (μ CT) with photoluminescence (PL) and convolutional neural network (CNN) assisted voxel classification and volume segmentation for tooth structural integrity assessment at the MC site and verify this approach with extracted human teeth. The samples were first examined using an X-ray μ CT and segmented with CNN to identify enamel, dentin, and cracks. A new CNN image segmentation model was trained based on “Multiclass semantic segmentation using DeepLabV3+” example and was implemented with “TensorFlow”. Secondly, buccal and palatal teeth surfaces with MCs and sound areas were used to obtain fluorescence spectra illuminated with wavelengths of 325nm and 266nm. X-ray μ CT technique which was employed allowed the recognition, detection, and 3D characterization of all tooth MCs, precisely identifying those cracks that were analyzed using PL. With both excitation wavelengths, the fluorescence signal intensity associated with the crack was significantly (30–50%) reduced, while it was higher in the region of the sound tooth spectrum around the MC. The ability to assess the spectral changes in the tooth MC and compare them with the spectrum of the sound enamel revealed differences in the material along the crack line, with a variation in the hydroxyapatite crystals at the cracked versus sound area, suggesting a possible loss of structural integrity at the MC site. The proposed approach – using X-ray μ CT in combination with PL and CNN assisted segmentation – reveals the possibilities for tooth structural integrity assessment at the crack area with distinct precision and versatility and can be applied for all the teeth microstructure and surface mapping analysis.

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Nanotechnology patenting activity in Greece

K. Glynou^{1*}, C. Andrikopoulou¹, A. Thymiopoulos¹

¹ *Hellenic Industrial Property Organization (OBI), Athens, Greece*

*kglyn@obi.gr

Abstract:

Industrial property, especially patents, are an indicator of technological innovation. Since innovation plays a crucial role in a nation's progress, it is essential to analyze patents in national level, in order to provide researchers and policy makers with useful information. Nanotechnology is a rapidly developing field since the 1980s, nevertheless the most significant period of nanotechnology development begins at 2000 [1].

In this work, we have identified, collected and analyzed published patent applications relevant to nanotechnology, filed in the Hellenic Industrial Property Organization (OBI), since 2000. It should be noted that patent applications are published after a period of 18 months from the earliest priority or filing date, therefore explaining the low data retrieved after 2021 and the focus of the present study in the period 2000-2021. During this process, we excluded applications by foreign applicants, so that conclusions are based on the Greek R&D activity and innovation.

In our search queries, we used a combination of keywords and classification codes in order to minimize background noise and retrieve as accurate results as possible. The queries were performed in the internal database of OBI as well as in the EPO database Espacenet and the documents retrieved were 175 in total.

Results indicate that patenting activity in the field of nanotechnology in Greece has been following an increasing trend over the years. However, a decreasing tendency is observed in the years 2020-2021, which could be attributed to delays in R&D projects due to the coronavirus pandemic. The patent output regarding the applicant affiliations suggests that 38,3% of the patent activity is coming from universities and institutes, while- individual applicants account for the 37,1% of the activity, followed by 22,3% coming from companies and 2,3% from collaborations between universities/institutes and companies. Patents are classified in one or more technical fields according to their content. Most nanotechnology patent applications in Greece are classified in fields related to medicinal preparations.

As the number of patent applications seemed limited, we have performed an indicative comparison between applications classified in the fields of medical science and scientific publishing retrieved from the database Pubmed. Results revealed an important number of scientific articles contrary to that of patent applications, suggesting that there is still room for patenting in the field of nanotechnology in Greece.

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Lead-free metal halide perovskites for gas detection

A. Argyrou^{1,2,*}, K. Brintakis¹, E. Gagaoudakis¹, V. Binas¹, A. Kostopoulou¹, E. Stratakis^{1,3}

¹ *Institute of Electronic Structure and Laser, Foundation for Research & Technology-Hellas, P.O. Box 1527, Vassilika Vouton, 70013 Heraklion, Greece*

² *University of Crete, Department of Chemistry, Vassilika Vouton, 70013 Heraklion, Greece*

³ *University of Crete, Department of Physics, Vassilika Vouton, 70013 Heraklion, Greece*

* kargyrou@iesl.forth.gr

Abstract:

The increasing demand for the accurate detection and monitoring of air pollutants, toxic gases, and explosive compounds has driven remarkable advancements in gas sensing technologies. With applications encompassing air quality assessment, medical diagnostics, and safety assurance, the demand for novel sensor materials offering heightened sensitivity and selectivity has intensified.

In recent years, metal halide perovskites, with the chemical formula ABX_3 , (A: organic or inorganic cation, B: divalent metal, X: halide ion) have gained attention as promising candidates for gas sensing elements. However, despite the great effort for ultra-sensitive gas sensors, challenges concerning the toxicity of lead (Pb) hinders the further exploitation of these materials in gas sensing devices. Herein, the aim of this research is the fabrication of environmental- friendly Pb-free halide perovskites and the evaluation of their ozone (O_3) sensing capability.

To achieve this, $Cs_2AgBiBr_6$ microcrystals (μCs) were fabricated under ambient conditions using a facile, cost-effective solution-based method. The sensing performance of the μCs was explored by electrical measurements at room temperature operating conditions. Notably, the sensor was able to operate under the ultra-low power of 0.1 V and exhibited a significant response, even down to 160 ppb. Additionally, the response and recovery times of less than 50 s, reinforces its suitability for real-time detection applications. Interestingly, the sensor demonstrated remarkable selectivity for O_3 detection compared to other target gases, including NO , H_2 and CH_4 . Moreover, the influence of relative humidity (RH%) was investigated, revealing an unexpected enhancement in sensor performance with increasing humidity levels. Finally, the effect of working temperature was also investigated, revealing the ability of the sensor to operate even at temperatures as high as 200°C.

Acknowledgements

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International Conference on Nanotechnologies and Bionanoscience

Wednesday 14th September

WS3 Poster Session

Tissue Engineering & Regenerative Medicine

PDMS hydrophobicity tailoring by surface modifications based on zwitterionic coatings

Nicoleta Dumitrescu*, Anca Bonciu, Simona Nistorescu, Laurentiu Rusen and Valentina Dinca

National Institute for Lasers, Plasma and Radiation Physics

[*nicoleta.dumitrescu@inflpr.ro](mailto:nicoleta.dumitrescu@inflpr.ro)

Abstract:

Within the area of biomedical applications, the use of PDMS is restricted due to its hydrophobicity, and the surface modification is required. The use of zwitterionic phosphorylcholine-based polymers can raise interest due to their high hydrophilic profile, implying as well decreasing proteins and bacterial adhesion. In this work, the Matrix-Assisted Laser Evaporation (MAPLE) technique was investigated as a new approach for functionalising Polydimethylsiloxane (PDMS) surfaces with zwitterionic poly(2-Methacryloyloxyethyl-Phosphorylcholine) (pMPC) polymer. Evaluation of the physical–chemical properties of the new coatings revealed that the technique proposed has the advantage of achieving uniform and homogeneous stable moderate hydrophilic pMPC thin layers onto hydrophobic PDMS without any pre-treatment, therefore avoiding the major disadvantage of hydrophobicity recovery. The capacity of modified PDMS surfaces to reduce bacterial adhesion and biofilm formation was tested for Gram-positive bacteria, *Staphylococcus aureus* (*S. aureus*), and Gram-negative bacteria, *Escherichia coli* (*E. coli*). Cell adhesion, proliferation and morphology of human THP-1 differentiated macrophages and human normal CCD-1070Sk fibroblasts on the different surfaces were also assessed. Biological in vitro investigation revealed a significantly reduced adherence on PDMS–pMPC of both *E. coli* (from 29×10^6 to 3×10^2 CFU/mL) and *S. aureus* (from 29×10^6 to 3×10^2 CFU/mL) bacterial strains. Additionally, coated surfaces induced a significant inhibition of biofilm formation, an effect observed mainly for *E. coli*. All these highlighted the potential for the new PDMS–pMPC interfaces obtained by MAPLE to be used in the biomedical field to design new PDMS-based implants exhibiting long-term hydrophilic profile stability and better mitigating microbial infection.

Mesenchymal stem cells interaction with hierarchical textured surfaces obtained by laser processing

Valentina Dinca^{1*}, Livia Elena Sima², Icriverzi Madalina², Laurentiu Rusen¹, Anca Bonciu¹, Anca Roseanu²

¹National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor, 077125, Magurele, Romania

²Institute of Biochemistry of the Romanian Academy, Bucharest, Romania

*valentina.dinca@inflpr.ro

Abstract:

The potential of Mesenchymal stem cells (MSC) for implantology and cell-based therapy represents one of the ongoing research subjects within the last decades. In bone regeneration applications, the various environmental factors including bioactive compounds such growth factors, chemicals and physical characteristics of biointerfaces are the key factors in controlling and regulating osteogenic differentiation from MSCs. In our study we have investigated the influence of nano and micro hierarchical biointerfaces based on ceramics laser textured on the osteogenic fate of MSCs. The complex interfaces were created *via* a fs laser texturing technique. Scanning Electron Microscopy, EDAX, contact angle and surface energy of the analyzed coatings were correlated to biological response on both short and longer term (72h, respectively 28 days). Human MSC were cultured on the developed coatings and viability, proliferation and morphology were evaluated. All surfaces were shown not to exhibit toxicity, as confirmed by LIVE/DEAD assay. Micro and nanotextured ceramic interfaces exhibited an increase in osteogenic differentiation of hMSC cells, results supported by ALP and mineralization assays. This is the first report about nano and micro hierarchical biointerfaces directing osteogenic differentiation from hMSCs indicating potential for application in bone regeneration.

Mechanosensitivity of Aged Mesenchymal Stem Cells (MSCs)

Anna Maria Kapetanaki^{1*}, Monica P Tsimbouri², Matthew Dalby² and Massimo Vassalli¹

¹Centre of Cellular Microenvironment, James Watt School of Engineering, University of Glasgow, UK

²Centre for Cell Engineering, Institute for Molecular, Cell and Synthesis Biology, College of Medical, Veterinary and Life Sciences, University of Glasgow, UK

*2454721K@student.gla.ac.uk

Abstract:

Cells are dynamic units able to feel their surrounding environment (mechanosensitivity) and adapt to it (mechanotransduction) [1-2], by triggering their cytoskeleton remodelling and activating different signalling pathways resulting in the alteration of their gene expression. This activity controls physiological processes such as proliferation, differentiation, migration, and apoptosis [3].

MSCs are mesoderm-derived progenitor cells with fibroblast-like morphology which can be differentiated into osteocytes, adipocytes, and chondrocytes [4]. The decision towards a specific cell lineage is determined by the way that MSCs sense their microenvironment. Soft and thick like fat cell matrices or substrates are adipogenic, whilst stiff like bone matrices are osteogenic [5].

Dysregulation of cell, and in particular MSCs, mechanosensitivity results in cell dysfunctions and eventually various pathologies, such as cardiovascular disease, osteoporosis, and intestinal problems [6-8]. Aging is a crucial factor that deteriorates cell mechanosensitivity and in the case of MSCs leads to impaired cell renewal [9–10].

Here we will present data on MSCs' mechanosensitivity related to aging. The ultimate goal of this project is to use mechanosensitivity as a physical biomarker for MSCs characterisation.

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Moving towards UFP – Chemical and Toxicological Characterization of Brake Wear Particles below PM₁

Bozhena Tsyupa^{1,3*}, Chiara Emma Campiglio², Alessandro Mancini³, Andrea Bonfanti³,
Manuela Teresa Raimondi¹, Andrea Remuzzi²

¹*Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Italy*

²*Department of Biomedical Engineering, Istituto di Ricerche Farmacologiche Mario Negri IRCCS, Bergamo, Italy*

³*Materials Engineering & Laboratories, GCF Research & Development, Brembo S.p.A, Stezzano, Italy*

*bozhena.tsyupa@polimi.it

Abstract:

Over last decades the presence of nanoparticles in human environment is continuously growing. This trend can be observed in several fields, ranging from industrial sector to medicine, thus reflecting on the environment. Lingering on the last one, the continuous increase of nanoparticles in the environment is mostly related to anthropogenic activities. Among contributors, transport sector is well known to be a relevant source to the diffusion of nanoparticles in the environment [1]. In particular, particular matters (PMs) are known to be hazardous and poorly affected by countermeasures. As far as toxicological hazard of environmental PMs is concerned, it is well known that sub-micrometric and nanometric fractions exhibit stronger effects [2]. However, few investigations are currently available in literature looking specifically at nano-particles generated by brakes. For this reason, nanometric PMs generated by the brake wear of passenger cars components were collected at the dynamometric bench, simulating standard driving and braking conditions. Filters with particulate matter in the range between 400 – 450 nm coming from three different brake wears emissions, namely M1, M2 and M3, were collected. Their chemical composition was assessed through SEM/EDXS and Raman Spectroscopy measurements. The main difference between emissions is related to the presence of Copper in the M2 emission. Following to chemical characterization, toxicological test, such as cells viability was conducted on A549 alveolar cells and on monocytic leukemia THP-1 cells, both in submerged conditions. Cell viability of A549 cells is less sensitive compared to the THP-1 cells, which is variable over a wider range.

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3D printing of polylactic acid/cuttlefish bone biocomposites

Aikaterini Gialouri^{1*} and Nikolaos Bouropoulos^{1,2}

¹ *Department of Materials Science, University of Patras, 26504 Rio, Patras, Greece*

² *Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Chemical Processes, 26504 Patras, Greece*

** katerinagialoyri@gmail.com*

Abstract:

Marine by-products derived from shrimps, crabs, squids, lobsters, cuttle fishes, etc. create a large number of wastes causing environmental and financial effects. The management of these products leads not only to the reduction of wastes but also to the production of useful materials. For example, shrimp and crab shells are used for chitin production. Cuttlefish bone is a porous material made of aragonite, a calcium carbonate polymorph. Calcium carbonate forms three crystalline polymorphs which are calcite, aragonite and vaterite. Calcite is the thermodynamically most stable form of calcium carbonate and is found in abundance in nature. Aragonite is a common skeletal mineral in marine organisms. Calcium carbonates have been used widely as fillers in polymer biocomposites. The scope of this work is to show the use of cuttlebones on the formation of biocomposites made of the thermoplastic and biodegradable polymer polyactic acid. More specifically, the present work includes a) Purification and characterization of aragonite powder from cuttlefish bones, b) Preparation and characterization of pure PLA and composite PLA/aragonite filaments c) 3D printing and characterization of pure PLA and composite specimens using the fused filament fabrication (FFF) technology. All materials are characterized by DSC, TGA, XRD, SEM and FTIR spectroscopy. Furthermore, water contact angle measurements were performed on flattened filaments, while biodegradability of the PLA biocomposites was studied *in vitro* after immersion of the printed objects in Ringer's solution. It was found that alkaline treatment of cuttle fish bones in boiling NaOH followed by immersion in boiled methanol led to the removal of organic materials and other impurities. Furthermore, filament formulations containing 2.5, 5.0 and 10 % w/w of aragonite were prepared, and finally porous specimens were manufacturing successfully using the 3D FFF method. Water contact angle measurements showed that that PLA/aragonite filaments exhibited more hydrophilic behaviour in comparison with the pure PLA filaments. Finally, *in vitro* biodegradation studies pointed out that all specimens showed a good level of biodegradation after immersion in Ringer's solution. The produced biocomposites need to be further investigated as promising candidates for applications in tissue engineering applications.

Studies of cells behavior on printed graphene layers and patterns with variable composition, morphology and macrogeometry

Weronika Sosnowicz

Centre for Advanced Materials and Technologies CEZAMAT, Warsaw, Poland

weronika.sosnowicz.dokt@pw.edu.pl

Abstract:

The presented study examines the effects of graphene layers on the behavior of eucaryotic cells. Composites based on graphene nanoplatelets were utilized in printed electronics techniques: spray coating and inkjet printing to produce coatings and patterns [1]. The main goal was to understand the fundamental behavior of cells cultured on layers and patterns e.g., adhesion, formulation of cell connections and differentiation. Numerous scientific studies have demonstrated the effectiveness of graphene-based materials in cell stimulation, including human mesenchymal stem cells, human fibroblasts, osteoblasts, and nerve cells. However, there is still limited research focusing on the fundamental material-cell interactions. Creating scaffolds and microenvironments that mimic the properties of the extracellular matrix (ECM) allows cells to properly adhere, proliferate, and differentiate, which are crucial processes in tissue regeneration. The research included the characterization of inks, considering their properties such as dispersion, rheological features influencing the printing process and print quality, as well as the analysis of the layers in terms of microstructure, conductivity, and elemental composition. The authors anticipated a series of experiments to determine the cytotoxicity of the prints, as well as the adhesion, growth, and morphology of cells on the surface of the printed films (glass, polystyrene, TPU foil). The proposed utilization of GNP layers and patterns allowed for the mimicry of physiological microenvironments using graphene materials to successfully promote cell adhesion, proliferation, differentiation, and control of intercellular interactions necessary for tissue regeneration [2].

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Modeling PML-mediated Glioblastoma Growth Dynamics: Insights from Spheroid-Based Studies and Brain Tissue Slice Implantation

*E. Makrigiannaki^{1,2}, M. Tampakaki^{1,3,4}, E. Tzamali¹, G. Zacharakis³, K. Sidiropoulou^{5,6}, V. Sakkalis¹, J. Papamatheakis^{5,6}

¹Foundation for Research and Technology Hellas, ICS, Heraklion, Greece

²University of Crete, School of Medicine, Heraklion Crete, Greece

³Foundation For Research and Technology-Hellas, IESL, Heraklion Crete, Greece

⁴ University of Zurich, Faculty of Science, Zurich, Switzerland

⁵Department of Biology, University of Crete, Heraklion, Greece

⁶Foundation for Research and Technology-Hellas, IMBB, Heraklion, Greece

*eirini@ics.forth.gr

Glioblastoma (GB) is the most aggressive brain tumor among adults and its malignancy and recurrence are closely related to its excessive proliferation and infiltration within the brain. The Promyelocytic Leukemia protein (PML) is a cell regulator, expressed in all tissues and has been implicated in various ways to cancer biology. However, its specific effects are not yet clear, since it can have either tumor suppressing or tumor promoting effects, depending on the type of cancer involved [1]. In brain, PML participates in the physiological migration of the neural progenitors and it has been shown to decelerate the cell cycle and proliferation of the GB cells [4]. Here, we studied further the PML-mediated effects regarding the tumor growth capacity using 2D / 3D *in vitro* biological models. Furthermore, to monitor the progression of the tumor in conditions that better mimic the natural microenvironment of GB, we have cultured *ex vivo* murine brain slices engrafted with GB U87MG spheroids.

The U87MG-GB cell line was used in this work, wherein two distinct variants were generated: U87MG-shPML, featuring downregulated PML expression, and U87MG-PML OE, characterized by conditional PML overexpression upon doxycycline (DOXY) presence. Moreover, the control cell lines were the U87MG-PML transfected cells in absence of DOXY along with the wild type non-transfected U87MG-wt cell line. The doubling time and cell viability of all cell lines was estimated in 2D cultures using the trypan blue exclusion viability assay. 3D spheroids were generated and cultured in ULA-plates and their radial expansion was monitored over time using wide-field microscopy. Spheroids of day 2 in culture, labelled with the cytosolic probe DRAQ9, were also implanted in the cortex and hippocampus of murine brain slices of 350um thickness, acquired from 8-week-old C57Bl/6 wild-type mice. The brain slice-spheroid *ex vivo* culture was imaged using confocal microscopy.

U87MG-PML OE cells exhibited significant differences compared to the control U87MG cell lines regarding their growth dynamics. The U87MG-PML OE cells exhibited lower proliferation rate compared to the control cell lines, as indicated by doubling time/trypan blue viability assay experiments. Furthermore, they generated smaller spheroids, also indicating lower proliferative rate, while the U87MG-shPML cell line variant sustained its proliferative capacity, similar to the control cells. By taking advantage of the brain tissue auto-fluorescence we have also visualized the engraftment of the spheroids within the brain tissue.

The growth and invasive capacity of GB spheroids in their microenvironment of origin is anticipated. By taking advantage of the brain tissue auto-fluorescence we have also visualized the engraftment of the spheroids within the brain tissue. In the future, we aim to define the brain slice viability in long-term *ex vivo* cultures and study the invasive capacity of GB cells in conditions that better mimic the microenvironment of origin of GB. Unravelling further the role of PML in GB invasion could set PML as a therapeutic target to eliminate multiple sub-clones based on their proliferative /invasive phenotypes in the tumor.

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Wednesday 13th September

WS2 Poster Session

Organic and Perovskite Photovoltaics

Functionalized MXenes for Stable Halide Perovskite Solar Cells

Ashitha Paingott Parambil¹, Masoud Karimipour¹, Kenedy Tabah Tanko¹, Sonia Ruiz Raga¹, Monica Lira-Cantu^{1,*}

¹ Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and the Barcelona Institute of Science and Technology (BIST). Building ICN2, Campus UAB E-08193, Bellaterra, Barcelona, Spain. E-Mail: monica.lira@icn2.cat

Abstract

Perovskite solar cells (PSCs) with an accredited power conversion efficiency (PCE) above 25% demonstrate a great potential towards commercialization. Currently, PSCs are largely susceptible to poor stability and durability issues which restricts their utility in practical applications. Despite the performance improvement observed in perovskite solar cells (PSCs) when MXenes are employed as transport layers, studies on device stability are still missing. Especially under real outdoor conditions where devices are subjected to the synergy of multiple stressors. In this work, functionalized 2D Ti_3C_2 MXene is employed in a normal PSC configuration and placed at the interface between the halide perovskite (HP) and the hole transport layer (HTL). The functionalization of the Ti_3C_2 MXene was made utilizing the same organic additive chosen for the halide perovskite layer. Our strategy permits us to create an improved and continuous link between the MXene and the halide perovskite layer. Champion MXene-based PSCs with ~22 % efficiency were obtained, in comparison with the 20.56 % obtained for the control device. Stability analyses under any analyzed condition (dark, continuous light irradiation and real outdoor analysis) demonstrates that the enhancement of the PSCs lifespan is always observed when the MXene layer is employed. Analysis under continuous light irradiation (ISOS-L) revealed an almost 100% retention of device performance, while outdoor testing (ISOS-O) for > 600 h revealed a T_{80} of \square 600 h. To our knowledge, this is the first report of the stability analysis of MXene-based PSCs carried out under real outdoor (ISOS-O) conditions and indicates that MXene can pave the way to a highly stable PSC required for the commercialization of the technology.

Bulk and Micro-Photoluminescence Studies of Perovskites

Georgios N. Arvanitakis^{1*}, Stuart A. J. Thomson¹

¹*Edinburgh Instruments, Livingston, United Kingdom*

* georgios.arvanitakis@edinst.com

Abstract:

Perovskite-based solar cells are the subject of intense research interest due to the attractive properties of perovskite; high carrier mobilities, large absorption coefficients, tuneable bandgaps, and long carrier diffusion lengths. One of the challenges in any solar cell design is getting the charge carriers out of the device efficiently. To aid charge extraction, electron and hole extraction layers are routinely incorporated into the device stack.

One promising material investigated as a hole extraction layer is vertically aligned carbon nanotubes (VACNTs). The VACNTs can be grown in a grid pattern of ‘towers’ atop the ITO electrode to achieve improved charge extraction while maintaining high optical transmission through the ITO/VACNTs.

Photoluminescence response from perovskite materials is proportional to the number of charge carriers in the layer and, therefore, sensitive to charge extraction into adjacent layers. This makes photoluminescence-based techniques invaluable for investigating the performance of new extraction layers. In this work, steady-state and time-resolved confocal photoluminescence microscopy and photoluminescence quantum yield studies were used to quantify hole transfer efficiency into the VACNT towers.

A thiol-based salt for surface passivation in perovskite solar cells

Spyros Orfanoudakis^{1,3}, Filippos Harlaftis¹, Konstantina Gkini¹, Lazaros Theofylaktos¹, Apostolos Kalafatis¹, Georgia Basina¹, Lida Givalou¹, Maria Konstantakou¹, Athanasios G. Kontos², Thomas Stergiopoulos^{1*}

¹*Institute of Nanoscience and Nanotechnology, NCSR Demokritos, 15341, Aghia Paraskevi, Athens, Greece*

²*Department of Physics, National Technical University of Athens, 15780, Zografou, Athens, Greece*

*e-mail: t.stergiopoulos@inn.demokritos.gr

Perovskite solar cells (PSCs) have drawn significant attention in recent years due to their high photovoltaic efficiencies and potential for low-cost, large-scale manufacturing. However, despite these benefits, the commercialization of these materials faces significant obstacles due to their instability in ambient conditions and susceptibility to degradation.¹ Surface passivation with organic molecules is a promising approach to enhance the stability of PSCs.² Thiols are known to passivate the surface defects of perovskite, which can lead to improved device performance and stability.³ The -SH group of thiols can bind to the surface of the perovskite crystals and effectively reduce surface recombination.⁴ In this context, 2Diethylaminoethanethiol hydrochloride (DEAET) has been investigated as a surface passivator for PSCs. For this, various concentrations and solvents have been tested in order to effectively cover the FAPbI₃ perovskite film with DEAET. The optical and morphological properties of the resulted perovskite films were characterized using UVvis spectroscopy, steady-state photoluminescence, scanning electron microscopy (SEM), and atomic force microscopy (AFM). Finally, planar devices were fabricated based on perovskite's film post treatment with DEAET. This treatment was found to effectively passivate the surface defects, thereby improving the charge carrier lifetime and increasing the Voc. These effects also helped significantly the long-term stability of the device. The results of this work pave the way for the use of thiol-based salts as efficient agents for interface engineering in optoelectronic devices.

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An efficient approach for controlling the crystallization, strain, and defects of the perovskite film in hybrid perovskite solar cells through antisolvent engineering.

Nikolaos Tzoganakis^{1*}, Konstantinos Chatzimanolis¹, Emmanuel Spiliarotis¹, George Veisakis¹, Dimitris Tsikritzis^{1,2} and Emmanuel Kymakis^{1,2}

¹*Department of Electrical & Computer Engineering, Hellenic Mediterranean University (HMU), Heraklion 71410, Crete, Greece*

²*Institute of Emerging Technologies (i-EMERGE) of HMU Research Center, Heraklion 71410, Crete, Greece*

* ntzoganakis@hmu.gr

Abstract:

The efficiency and stability of perovskite solar cells are regulated by defects at the grain boundaries and at the surface of organic–inorganic halide perovskite films. Various methods have been proposed to improve the quality of the perovskite film, but most of these approaches complicate the fabrication procedure. Here, we show an efficient and simple engineering approach for regulating the crystallization, strain, and defects of the perovskite film by adding the organic salt octylammonium bromide (OABr) in the antisolvent solution. The proposed treatment improves the crystallization of the perovskite film, controls the strain in the film, and efficiently passivates defects of the hybrid quadruple cation perovskite, reducing the charge trap density and non-radiative recombination. Consequently, the non-radiative losses in the optimized OABr treated devices were considerably mitigated by 43.6%, allowing a V_{oc} of 1.16 V and efficiency up to 20.4% to be achieved. In addition, the stability of the OABr treated devices was improved, retaining 80% of their initial performance under ambient conditions for more than 1400 hours.

[1] Tzoganakis, et al. *Sustainable Energy Fuels*,7, 4136-4149 (2023)

Incorporating TDMs and NFAs into printable indoor Organic Photovoltaics – The IntoPV Project

Marinos Tountas^{1,2}, Christos Polyzoidis^{1,2} and Emmanuel Kymakis^{1,2}

¹*Department of Electrical & Computer Engineering, Hellenic Mediterranean University,*

²*Institute of Emerging Technologies (i-EMERGE) of HMU Research Center*

** tountasm@hmu.gr*

Abstract:

So far, State-of-the-art NFA-based OPVs have only been demonstrated for outdoor usage and mostly for AM1.5G sunlight on a laboratory scale, while only few studies use different light sources combined with active areas larger than 1cm². In contrast, PCBM-based OPVs have been produced in large areas but their stability is moderate. In order to be considered relevant by the OPV industry, the most promising combination of Donor:NFA and Donor:PCBM have to be identified.

The IntoPV project aims to develop OPV cells and modules that suit indoor applications, while exhibiting enhanced efficiency at different indoor lighting scenarios and increased stability. To that direction, Transitional Metal Dichalcogenide (TMD) materials are exploited for use as buffer layers or as compound constituents for buffer layers, while the Donor:Acceptor-type active layer will contain fullerene- and non-fullerene acceptors (NFAs). The IntoPV research adopts State-of-the-Art materials and synthetic procedures. Characterization of materials and resulting films aims to lead to the fabrication of functional cells that contain TMDs as well as NFA or fullerene-based acceptors in an effort to find optimum film parameters towards upscaling. ISOS stability characterization for both small and large area samples is applied with respect to the lighting peculiarities and atmosphere conditions of indoor environment.

Emerging Sb₂S₃ absorber for planar chalcogenide solar cells via optimized SbAc₃*TU*DMF route

L. Theofilaktos^{1,2*}, L. Gkivalou¹, K. Gkini¹, S. Orfanoudakis¹, A. Kalafatis¹, G. Basina¹, P. Dallas¹, P. Tsipas¹, V. Psycharis¹ and T. Stergiopoulos¹

¹*Institute of Nanoscience and Nanotechnology, National Centre for Scientific Research "Demokritos", 15310 Ag. Paraskevi, Athens, Greece*

²*Department of Chemistry, School of Natural Sciences, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece.*

* l.theofilaktos@inn.demokritos.gr

Abstract:

In a world of ever growing energy demand, solar energy is an excellent complementary candidate for covering energy needs in a variety of places worldwide. Despite the fact that for the past 20 years the main scientific focus was concentrated on Perovskite Solar Cells, during the last 5-10 years an increasing number of emerging photovoltaic technologies have been under the investigation spotlight, mainly tackling the toxicity problems of the Lead (Pb) containing perovskite solar cell technology.

Antimony sulfide is an excellent candidate material for solar light absorption owing to its suitable bandgap (1,7-1,8eV), its high absorption coefficient ($\sim 10^5 \text{cm}^{-1}$), its excellent environmental stability, its earth abundance and its constituents' relative non-toxicity^[1]. The state of the art champion modified PCE is at 8%, albeit the Shockley-Queisser theoretical limit sitting above 28% efficiency for solar devices based on Sb₂S₃, mainly hindered by internal crystallization-orientation issues (recombination) arising from the Quasi-1D nature of the material.

Herein, an optimized, novel, simple 1 day procedure is presented, showcasing a reproducible way of fabricating efficient Sb₂S₃ solar cell devices, by exploiting the SbAc₃*TU in DMF complex.

A champion efficiency of 6% under AM 1,5G illumination is achieved in our lab, with a J_{sc} of 16.9 mAcm⁻², a V_{oc} of 621mV and a FF of 57%.

The exhibited optoelectronic figures of merit are some of the highest reported in literature among all fabrication routines for an unmodified Sb₂S₃ solar cell. The reported procedure paves the way for reliable, reproducible and modifiable-tunable experiments, aiming to the proliferation of scientific work on this emerging new PV technology.

[1] J. Tang, et al. *Joule* 2, 857-878 (2018)

Acknowledgements

We acknowledge the financial support from the European Research Council (ERC) through Consolidator Grant (818615-MIX2FIX).

Improving stability of α -FAPbI₃ solar cells by tailoring SnO₂/perovskite interface with 2D g-C₃N₄

Konstantina Gkini^{1*}, Spiros Orfanoudakis^{1,2} and Thomas Stergiopoulos¹

¹*Institute of Nanoscience and Nanotechnology, NCSR Demokritos, Athens, Greece*

²*School of Applied Mathematical and Physical Sciences, NTUA, Athens, Greece*

* k.gkini@inn.demokritos.gr

Abstract:

Perovskite solar cells (PSCs) based on formamidinium lead triiodide (FAPbI₃), used as the absorber, hold the record efficiency among other perovskite-based photovoltaics. Although its suitable bandgap, long-term stability issues of FAPbI₃ are still under intense investigation as the photoactive black phase (α -FAPbI₃) is easily converted to the non-active yellow phase (δ -FAPbI₃) under ambient conditions [1]. Apart from the absorber's internal stability, the nature of electron transport layer is also a significant factor that affects the overall stability of PSCs since it acts as a crystallization substrate in a n-i-p perovskite solar cell. Tin dioxide (SnO₂) is commonly used in FAPbI₃-based PSCs but it is characterized by high defect density leading to charge extraction and energy level alignment issues [2,3]. In this work, a way to tackle these issues is proposed by which 2D π -conjugated graphitic carbon nitride (g-C₃N₄ - gCN) is utilized to tailor the SnO₂/FAPbI₃ interface. The fabricated films and devices were optically and electrically characterized. The results showed that the insertion of a 2D material, which exhibits excellent thermal and chemical stability, does improve the photovoltaic performance of the PSCs but most notably it enhances the stability of the perovskite film and the corresponding devices.

[1] S. Masi, et al. *ACS Energy Lett.*, 5, 2, 418–427 (2020)

[2] Y. Zhang, et al. *ACS Energy Lett.*, 7, 929–938 (2022)

[3] J. Zhuang, et al. *Adv. Funct. Mater.*, 31, 2010385 (2021)

Acknowledgements:

The research project was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “1st Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment” (Project Number: 1027). We acknowledge the financial support from the European Research Council (ERC) through Consolidator Grant (818615-MIX2FIX).

Two-step ligand exchange strategy for AgBiS₂ conductive thin-films for photovoltaic applications

A. Kalafatis^{1,2*}, L. Theofylaktos¹, S. Orfanoudakis^{1,3}, L. Gkivalou¹,

K. Gkini¹, G. Basina¹, M. Konstantakou¹, P. Dallas¹, T. Stergiopoulos¹

¹*Institute of Nanoscience & Nanotechnology, National Centre of Scientific Research "Demokritos", 15310 Agia Paraskevi, Greece*

²*Université de Bordeaux, F-33405 Talence Cedex, France*

* apostolos.kalafatis@etu.u-bordeaux.fr; t.stergiopoulos@inn.demokritos.gr;

Abstract:

AgBiS₂ nanocrystals are actively investigated for their photovoltaic applications because of their spectral tunability, eco-friendly synthetic route and broad absorption range extending to the infrared.¹ These sulfides exhibit an exceptionally high absorption coefficient reaching 10⁶ M⁻¹·cm⁻¹. As a result, they are an ideal choice for ultrathin film solar cells that can maintain high power conversion efficiency while minimizing material consumption and production cost. The nanocrystalline nature of the absorber is crucial with respect to the bandgap tunability and optimized energy levels. AgBiS₂ nanocrystals have suitable conduction and valence bands which can form an ideal energy alignment with typical hole transport and electron transport materials.² The synthesis involves the addition of capping agents that functionalize the surface of the nanoparticles to prevent agglomeration and achieve a proper dispersion in common organic solvents. Surfactants like oleylamine and oleic acid restrain the carrier mobility, induce recombination and trap states and interfere with the formation of ohmic contacts, all of which inhibit the photovoltaic performance³. This study focuses on combining both solid-state and wet-chemistry ligand exchange processes with the latter being conveniently integrated into the nanoparticle synthesis. Using this two-step strategy we have achieved a more efficient replacement of the bulky ligands with smaller and less electrically resistive moieties. The synthesis is ultimately refined to prioritize cost-effectiveness and scalability by using less expensive reagents under atmospheric conditions without the need for inert gas flow.

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3. Liu, M. *et al.*, *Nat. Mater.* **16**, 258–263 (2017).

We acknowledge the financial support from the European Research Council (ERC) through Consolidator Grant (818615-MIX2FIX).

Integrated system for finding installation places and inspection the performance of large photovoltaic parks in real time with IR-image processing by autonomous aerial vehicle (drone) with the help of mini weather station

G. Viskadourous^{1*}, E. Astrakianakis², Z. Sarris³ and E. Kymakis⁴

^{1,4} *NANO Research Group, Hellenic Mediterranean University*

¹ *E-Synergy PCC*

² *Entec Green Economy Consultants (E. Astrakianakis & SIA EE)*

³ *ALTUS LSA*

[*g.viskadourous@e-synrg.com](mailto:g.viskadourous@e-synrg.com)

Abstract:

The photovoltaic parks are the most popular systems of energy production from renewable sources, not only in Greece but globally and will be a basic element of the upcoming smart energy grids. Currently the investing opportunities in the field have brought in the foreground the need of a system that will help the investors as the network managers as well in the search of the proper installation place. In addition, the basic condition of the healthy function of the photovoltaic park is the control of the performance and check functional problems of the photovoltaic components. Target of this work is to show a complete system, finding an installation place and control the performance of photovoltaic parks in real time with processing IR images from an unmanned aerial vehicle with the help of a mini weather station. This vehicle (a) achieves an easily preliminary study for the installation of photovoltaic parks, (b) achieve an automatic control of photovoltaic systems, (c) upgrade the quality and speed control of the embedded weather station on the drone and (d) achieve a real time estimation of damages of photovoltaic panels for better and optimal energy performance of the park. The complete system consists of :

- The drone with sensors of geolocation and transmission system of data
- Thermal camera embodied in the flying vehicle and mini meteorological station
- Software for the takeoff, flight, landing and charging of drone.

Development of the software for searching available installation places for photovoltaic parks, processing software of real time of thermal images which are collected by drone and detects the faulty photovoltaic panels are realized. In the end, the system check through remote monitoring and control software, with secure data communication and be inspects photovoltaic park,

The system give to user the opportunity to choose if he will use it for the (a) preliminary study of the installation place or (b) the inspection of the photovoltaic park.

If (a) create a flight plan and the system after the processing of images from the area will produce a report according to the morphology of the ground, the optimal dimensioning of the photovoltaic park and an estimation of the produced energy.

In (b) create the flight plan and the system based on the meteorological conditions in the area and the information gathered from thermal imaging, will produce a report that will inspect the faulty photovoltaic panels.

The user receive the safe reports in real time and introduce the functional parameters of the system through the internet. The processing of the thermal images realized locally so that big amount of data is not transmitted through the web.

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- [3] Singh R, Sharma M, Sastry OS, et al. Non-destructive in-situ performance monitoring of high efficiency SPV modules using infrared thermography in composite climate of India. *MOJ Solar Photoen Sys.* 2018;2(2):54–60. DOI: 10.15406/mojsp.2018.02.00024.
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Wednesday 13th September

WS4 Poster Session

Emerging Printed Electronics and
Bioelectronics

Challenges in Printing Ion-Selective Sensors on Skin-Compatible Films

Izabela Wojciechowska^{1*}, Filip Budny¹, Andrzej Peplowski¹ and Małgorzata Jakubowska¹

¹*Warsaw University of Technology, Warsaw, Poland*

** izabela.wojciechowska2.dokt@pw.edu.pl*

Abstract:

The market of electronic skin patches is a developing area, increasing its revenue annually. Its representatives are sensors dedicated to exercise monitoring, which, thanks to the use of ion-selective layers, enable the measurement and analysis of various biomarkers contained in human sweat.

The poster will highlight the challenges in printing ion-selective sensors on skin-compatible films. Based on research with direct ink writing on thermoplastic polyurethane substrate (TPU), phenomena present during the ink distribution process will be discussed.

The high compatibility of the ink's solvent and the TPU substrate affects the occurrence of phenomena such as uneven ink distribution and bubble formation in a membrane. During the distribution of the membrane ink on the TPU substrate, the ink spreads and forms a too-thin membrane layer, which affects the sensors' signal quality.

Another phenomenon is bubble formation in membrane ink. Due to high compatibility, the solvent dissolves the TPU film, which releases gas bubbles from the film to the membrane structure. In addition, if the ion-selective layer is applied to a printed electrode, gas releases may also take place, due to printed structure's porosity.

The results from measurements with the sensors affected by the above phenomena will be presented.

The control sample was the ion-selective layer applied to the PET substrate, on which the above phenomena do not occur. Due to surface tension, a drop is formed, and the layer dries, forming an even surface.

This research aims to contribute to advancing electronics integrated into wearable devices, showcasing their potential for accurate and non-invasive health monitoring, mainly through sweat analysis.

New Methylpyridine Dyes with Benzyl Bromides and Methyl Iodides for Fluorescent Labels

Stela Minkovska^{1*} and Georgi B. Hadjichristov²

¹*Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria*

²*Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria*

* *Email: stelamin@ic.bas.bg*

Abstract:

Nowadays, the fluorescent dyes are widely used in modern technologies of fluorometry in biochemical, biophysical and biomedical research. Highly-emissive organic dye molecules have found applications as sensitive fluorescent nano-probes, ranging from sensing of bioactive objects, *in vitro* analytical systems, to in *cellulo* or *in vivo* optical sensing and imaging for fluorescent staining and visualization of biological structures and tissues, as well as in clinical diagnostics, e.g. in fluoro-bioanalytical systems for highly sensitive and selective determination of substances and objects of biological and pharmacological interest, such as specific antibodies, antigens, hormones, DNA components. Efforts in various high-tech and innovation areas are necessary for this purpose. The tasks related to the synthesis of such dyes and the optimization of their fluorescent properties is also innovative. Their design is no trivial. Recently, we have successfully synthesized and characterized the emission properties of a series of yellow-fluorescent styryl dyes, intended to be applied as efficient fluorescent markers and bio-labels.

The optical absorbance and the photo-excited emission from diluted aqueous solutions (10^{-6} M – 10^{-5} M) of the produced dyes were characterized. They exhibit a large Stokes shift towards the visible spectrum. The results obtained on the photo-physical characteristics of the synthesized fluorescent dyes show that they are appropriate for investigations of live cells and other bio-objects by use of the optical sensing and imaging techniques.

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[2] K. Supabowornsathit, K. Faikhruea, B. Ditmangklo, T. Jaroenchuensiri, S. Wongsuwan, S.Junpra-ob, I. Choopara, T. Palaga, C. Aonbangkhen, N. Somboonna, J. Taechalertpaisarn, T.Vilaivan, Sci Rep. 2022; 12: 14250.

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Photoswitchable photochromic spirooxazines for optical sensing

Stela Minkovska^{1*} and Georgi B. Hadjichristov²

¹*Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria*

²*Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria*

* *Email: stelamin@ic.bas.bg*

Abstract:

Spirooxazines (SOs) are an important class of photochromic dyes having intense photocoloration, high coloration contrast, reversibility, and good photo fatigue resistance. With the progress in the synthesis of SOs, their potential for application as multifunctional materials has greatly increased. Nowadays, SO derivatives and modifications have advanced application for optical sensing. The optical sensing by such photochromic molecular switches can be greatly extended by proper substituents in their chemical structure and functionalization. Thus, sensitive fluorescent nanoprobe photoswitchable upon UV and visible light, were developed [1,2].

Here we report novel SOs bearing different substituents in their naphthoxazine and indoline ring molecular systems. The design of these compounds aims their application for bio-labelling and for photoswitchable fluorescence imaging of bio-objects, for research in biology, molecular biology, biochemistry, and biomedical diagnostics. The key property of SOs is their photoswitching ability: upon UV light their closed form transforms into an open merocyanine form having very different optical properties, and vice-versa by visible light. We studied the effects of both the molecular structure of the synthesized SOs and their solvation in various solvents (organic and inorganic) on the optical absorption properties and photoswitching of the SOs, as well as on their fluorescence induced by UV light.

The obtained results on the photo-physical characteristics and photo-transformations of the synthesized SOs are useful since they can be applied in the highly sensitive and selective analytic techniques for optical sensing and imaging.

[1] S. Rahimi, et al. *Biomacromolecules* 21, 3620-3630 (2020)

[2] A.T. Frawley et al. *ChemPhysChem* 24, e202300125 (2023)

Acknowledgements: This research was supported by the European Regional Development Fund, as a part of the Operational Programme „Science and Education for Smart Growth 2014-2020”, Project: CoE „National Center of Mechatronics and Clean Technologies“, BG05M2OP001-1.001-0008-C01).

3D/2D Heterostructure mixed halide perovskite resistance memories enabled by perfluorinated spacer cations with enhanced retention and endurance characteristics

Michalis Loizos¹, Konstantinos Rogdakis^{1,2*}, Weifan Luo³, Patricia A. Gaina³, Jovana V. Milić^{3*}, and Emmanuel Kymakis^{1,2*}

¹ Department of Electrical Computer Engineering, Hellenic Mediterranean University (HMU), Heraklion, Greece

² Institute of Emerging Technologies (i-EMERGE) of HMU Research Center, Heraklion, Greece

³ Adolphe Merkle Institute, University of Fribourg, Switzerland.

Email: mloizos@hmu.gr

Metal halide perovskites are high-quality semiconductors with outstanding opto(electro)ionic properties originating in their mixed ionic-electronic conductivity. These characteristics broaden the range of their applications in optoelectronic devices, particularly solar cells, where most research efforts are focused due to their remarkable performance in solar energy harvesting. However, hysteresis in current-voltage characteristics is a feature of perovskite solar cells responsible for causing losses in performance¹, which has been associated with ion migration, charge trapping, and ferroelectricity as some of the contributing factors². Contrary to solar cells, hysteresis effects are desired traits for applying halide perovskites in resistive switching memories³. To this end, perovskite materials have been implemented for information storage, logic operations, artificial synapses, and crossbar arrays, with the advantage of their low-cost, low-temperature, and solution-processed fabrication, in contrast to the techniques required for conventional oxide-based memristors⁴. Devices with high ON/OFF ratios, fast switching speed, and good retention have been demonstrated⁵; however, the relatively low cycling endurance ($\sim 10^4$ cycles) limits their potential use for practical applications^{6,7,8}. In this work, we address these operational stability issues of halide perovskite-based resistive switching memories by assembling 2D/3D heterostructures based on perfluorinated spacer cations⁹. We compare the effect of Ruddlesden-Popper and Dion-Jacobson phases in the 2D/3D heterostructure on the performance of the halide perovskite memory. As a result, we show that devices with 2D/3D heterostructures outperform reference cells by extending their cycling endurance and retention, offering a versatile strategy for advancing halide perovskite-based memory elements.

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Enhancing Aqueous Dispersibility and Stability of Electrochemically Exfoliated Graphene Using Porphyrin-Based Surfactants: A New Approach against Graphene's Hydrophobicity

Evangelos Sotiropoulos^{1*}, Katerina Anagnostou^{1*}, Konstantinos Rogdakis¹, Athanasios Coutsoulelos², Emmanuel Kymakis¹

¹Department of Electrical & Computer Engineering, Hellenic Mediterranean University (HMU), Heraklion 71410, Crete, Greece

² Laboratory of Bioinorganic Chemistry, Department of Chemistry, University of Crete (UoC), Voutes University Campus, Heraklion 70013, Crete, Greece

*Email: mtk53@edu.hmu.gr; katerinanag@hmu.gr

Abstract:

Graphene is a two-dimensional carbon-based nanomaterial that displays exceptionally high electrical and thermal conductivity, enhanced tensile strength, as well as high flexibility, and transparency, making it a material suitable for electronics, energy devices, and biomedical applications. However, the intrinsic hydrophobicity of graphene has long been a significant barrier to its efficient dispersion in water and aqueous media. Instead, the liquid-based processability of graphene is generally achieved in toxic and non-environmentally friendly solvents such as N, N-Dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP). This study investigates the use of a hydrophilic porphyrin-based compound, specifically 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin ($H_2TCPP4Na^+$), to address this problem by enhancing the dispersion and stability of electrochemically exfoliated graphene (EEG) in water. Firstly, EEG was prepared via electrochemical exfoliation of pure graphite foil. Subsequently, a series of EEG dispersions were formulated via ultrasonication in $H_2TCPP4Na^+$ aqueous solutions with varying EEG to $H_2TCPP4Na^+$ ratio. EEG dispersions in DMF and ultrapure water were also prepared as reference samples. To evaluate the ability of $H_2TCPP4Na^+$ to successfully disperse EEG in water and offer stability over time, UV-Vis Absorption Spectra of all prepared dispersions were recorded immediately after preparation and after multiple days. All samples were further characterized using Attenuated Total Reflectance Infrared (ATR-IR) and Raman spectroscopy. It is reported that the porphyrin-based solutions outperformed DMF as a medium for successful EEG dispersions, both in terms of dispersibility and stability. Not only higher EEG concentrations were achieved in the $H_2TCPP4Na^+$ solutions, but these concentrations diminished only slightly after a period of 24, 48 and 96 hours, whereas the stability of EEG in DMF began to decline significantly after the 24 hour mark. To support these findings, the following mechanism is proposed: the aromatic rings of the porphyrin structure interact with the graphene flakes via π - π stacking, while the carboxyl groups interact with the water molecules, thus keeping the exfoliated graphene flakes suspended. These results demonstrate the potential of porphyrin-based surfactants in overcoming the intrinsic hydrophobicity of graphene-based dispersions constituting a significant advancement in graphene-based nanotechnologies.

Printed Graphene-based Moisture Energy Generators and Humidity Sensors

Katerina Anagnostou^{1*}, Massimo Urban², George Veisakis¹, Ioannis Kalogerakis¹, George Viskadourous¹, Konstantinos Rogdakis¹, Giulio Rosati², Arben Merkoçi^{2,3}, Emmanuel Kymakis¹

¹Department of Electrical & Computer Engineering, Hellenic Mediterranean University (HMU), Heraklion 71410, Crete, Greece

²Catalan Institute of Nanoscience and Nanotechnology, BIST, and CSIC, Edifici ICN2 Campus UAB, 08193 Bellaterra, Barcelona, Spain

³ICREA, Passeig Lluís Companys 23 08010 Barcelona, Spain

*Email: katerinanag@hmu.gr

Smart generators that convert untapped ambient energy into electrical power are an innovative approach toward developing wearable, self-powering technologies, such as sensors and IoT devices, that do not require batteries, and therefore reduce the inevitable battery waste. Clean energy can be generated through the spontaneous absorption and evaporation cycles of water molecules and exploited through moisture-energy-harvesting technologies or hydrovoltaics [1]. Notably, water in the form of atmospheric moisture is abundant and omnipresent, making it an excellent source of clean, renewable, and cost-effective energy. In this context, aqueous graphene oxide (GO) dispersions were formulated to fabricate simple moisture energy generators (MEGs), which generate electrical current via a chemical mechanism that involves the generation and diffusion of protons (H^+) upon water molecule absorption [2]. The effects of the GO moisture absorbing layer's structure and the electrical contacts configuration were explored, in terms of achievable output voltage (V_o) and response time to relative humidity (RH) variations. The thickness of the GO layer, the surface area and position of the silver contacts as well as the distance between them were varied, and the resulting device performances were compared. These geometric tuning techniques allowed for the investigation of the optimum device configuration towards efficient moisture-based energy generation with a quick response. We now strive to progress this work by a) fabricating flexible and light-weight GO-based MEGs b) achieving up-scalability by introducing a sophisticated, large scale printing method c) enhancing the efficiency of the moisture-absorbing layer by formulating GO-polymer hybrid inks and d) exploiting a second inherent function of the device, i.e., humidity sensing. To this end, GO-based inks are deposited on flexible PET substrates via inkjet printing [3], allowing for simultaneous streamlined fabrication of multiple MEG devices. Through these studies, we seek to achieve facile and environmentally safe fabrication methods to develop wearable, self-powering technologies that harness ambient, waste-free water energy.

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Wednesday 13th September

WS5 Poster Session

Nanophotonics and Biophotonics

Non-linear optical microscopy correlates the age-dependent nuclear lipid droplets deposition with cellular aging in *Caenorhabditis elegans*

Meropi Mari* and George Filippidis

Institute of Electronic Structure and Laser, Foundation for Research and Technology,
Heraklion 71110, Crete, Greece

Konstantinos Palikaras

Department of Physiology, Medical School, National and Kapodistrian University of Athens,
Athens 11527, Athens, Greece

Christina Ploumi, Andrea Princz and Nektarios Tavernarakis

Institute of Molecular Biology and Biotechnology Foundation for Research and Technology,
Heraklion 71110, Crete, Greece

* mmari@iesl.forth.gr

Abstract:

The development of non-invasive microscopic techniques used as new tools in biomedical research for aging studies is of great importance. We implemented non-linear imaging modalities to monitor and quantify age-dependent nuclear lipid deposition in *Caenorhabditis elegans*. Age-dependent deterioration of nuclear morphology is a common feature in evolutionarily divergent organisms. Lipid droplets localize in most nuclear compartments, where they impinge on genome architecture and integrity. However, the significance of progressive nuclear lipid accumulation and its impact on organismal homeostasis remain obscure. By employing Third Harmonic Generation (THG) technique as a diagnostic tool is feasible to obtain high resolution label free images and increased biological sample penetration depth. Lipid bodies are the main intracellular sources for the high THG signals [1]. We found that nuclear lipid droplets become increasingly accumulated in nuclear envelope during aging of the animal. Longevity promoting interventions, such as low insulin signalling and caloric restriction, abolish the rate of nuclear lipid accrual and decrease the size of lipid droplets. Suppression of lipotoxic lipid accumulation in hypodermal and intestinal nuclei is dependent on the transcription factor HLH-30/TFEB and the triglyceride lipase ATGL-1. HLH-30 regulates the expression of ATGL-1 to reduce nuclear lipid droplet abundance in response to lifespan-extending conditions. Notably, ATGL-1 localizes to the nuclear envelope and moderates lipid content in long-lived mutant nematodes during aging. Our findings indicate that the reduced ATGL-1 activity leads to excessive nuclear lipid accumulation. Thus, THG allows the monitoring of cellular lipid metabolism in live organisms and uncovers the molecular mechanism that preserves nuclear lipid homeostasis and organismal physiology during aging [2].

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[2] K. Palikaras et al. Aging Cell 2023, 22 e13788

Fabrication of laser-induced periodic structures on polycarbonate by UV ultrashort pulses

Matina Vlahou^{1,2*}, Nektaria Protopapa^{1,3}, Stella Maragkaki¹, George D. Tsididis¹ and Emmanuel Stratakis^{1,3}

¹ Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology (FORTH), N. Plastira 100, Vassilika Vouton, 70013, Heraklion, Crete, Greece

² Department of Materials Science and Technology, University of Crete, 71003 Heraklion, Crete, Greece

³ Department of Physics, University of Crete, 71003 Heraklion, Crete, Greece

* matinav@iesl.forth.gr

Abstract:

In this work, we report on the fabrication of laser-induced periodic surface structures (LIPSS) on bulk polycarbonate (PC) with femtosecond laser pulses at 258 nm where PC exhibits high absorptivity and significantly large ($\sim 10^{-2}$) extinction coefficient. A systematic approach was pursued to demonstrate the influence of laser parameters such as fluence, energy dose and polarisation on the LIPSS size and orientation. Results revealed that the employment of linearly polarised beams led to the formation of parallel (Fig. 1a) or perpendicular (Fig. 1b) to the laser polarisation periodic structures depending on the excitation level attained similarly to LIPSS produced on dielectrics. Furthermore, observations shown that low excitation levels can lead to the generation of remarkably more uniform LIPSS. By contrast, circularly polarised beams resulted into the development of topographies covered with protruded nanodot-like structures (Fig. 1c) of sizes depending on the laser conditions. The impact of the features of the fabricated patterns were evaluated by analysing the wetting and optical properties that manifested a more hydrophilic behaviour over time and a slight increase of optical absorbance retaining their absorbance peak resonances.

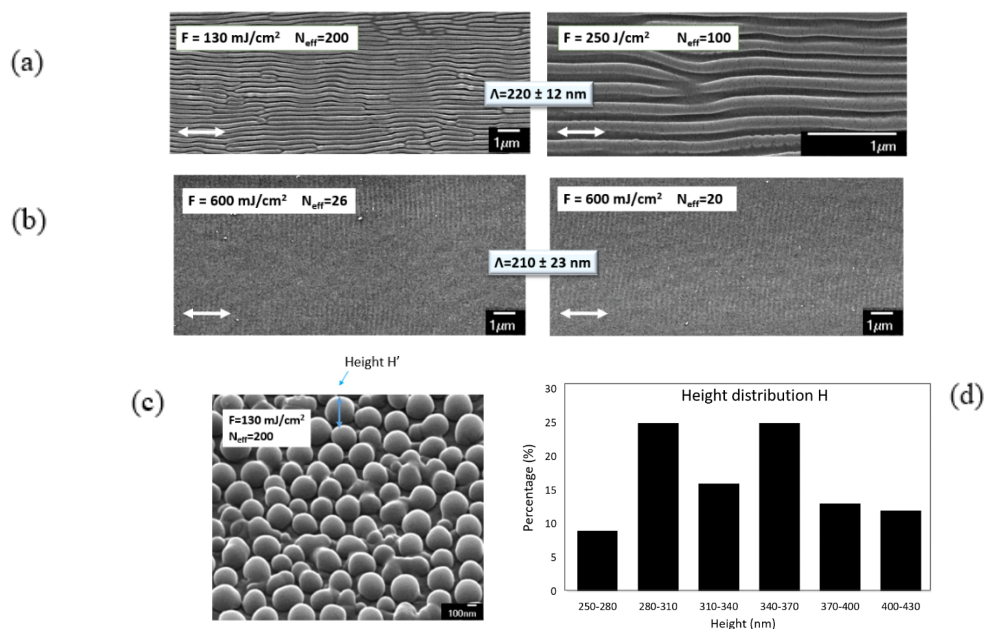


Figure 1: LIPSS on PC by employing linearly and circularly polarized UV laser pulses (a) SEM image of LSFL-II structures and (b) LSFL-I structures. The white double-headed arrow indicates polarisation direction (c) SEM image of nanoprotrusions (tilted by 45°) (d) Height distribution of protrusions.

A low-cost, label-free microfluidic scanning flow cytometer system for the characterization of different particles

Maryamsadat Ghoreishi^{1,2*}, Riccardo Reale¹, Giancarlo Ruocco^{1,2}, and Marco Leonetti^{1,3}

¹Center for Life Nano- & Neuro-Science, Italian Institute of Technology, Rome, Italy

²Sapienza University of Rome, Rome, Italy

³Institute of Nanotechnology, Consiglio Nazionale delle Ricerche, Rome, Italy

*Maryamsadat.ghoreishi@iit.it

Abstract:

High-throughput biological analysis at the single-cell level is a key tool for several research fields, including immunology, molecular biology, bacteriology, cancer biology, and infectious disease monitoring. In particular, the label-free analysis of cells, i.e. their characterization without any immune-specific labelling, holds significant potential for diagnostic and point-of-care (POC) applications. Flow cytometers represent the gold standard single-cell analysis, but their usefulness for label-free applications is limited by the unreliability of forward and side scatter measurements [1]. Scanning flow cytometers represent an appealing alternative, as they exploit measurements of the angle-resolved scattered light to provide accurate and quantitative estimates of cellular properties, but the requirements of current setups are unsuitable for integration with other lab-on-chip technologies or for point-of-care applications.

We recently presented the first microfluidic scanning flow cytometer (μ SFC), able to achieve accurate angle-resolved scattering measurements within a standard polydimethylsiloxane microfluidic chip [2]. The μ SFC can collect the angle-resolved scattered light using a single photoreceiver. The optical apparatus of the system was formed by a microscope objective (40x) which collected the scattered light and a lens to focus the light onto a slit placed in front of a photoreceiver. The microfluidic channel was 400 μ m out-of-focus allowing different scattering angles to reach the detector at different times. A filter with linearly variable optical density was placed in the back-focal plane of the objective, leading to a reduction in the dynamic range of the signal and a higher signal-to-noise-ratio.

The system exploits a low-cost linearly variable optical density (OD) filter to reduce the dynamic range of the signal and to increase its signal-to-noise ratio. We present a performance comparison between the μ SFC and commercial machines for the label-free characterization of polymeric beads with different diameters and refractive indices. In contrast to FCM and FACS, the μ SFC yields size estimates linearly correlated with nominal particle sizes ($R^2 = 0.99$) and quantitative estimates of particle refractive indices.

Thanks to its simplicity, the system can be easily integrated within other lab-on-chip systems and other point-of-care diagnostic applications to achieve a multi-parametric cell analysis.

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Wednesday 13th September

WS6 Poster Session

2D materials and devices

Anisotropic Third Harmonic Generation in Two-Dimensional SnS

George Miltos Maragkakis^{1,2}, Sotiris Psilodimitrakopoulos¹, Leonidas Mouchliadis¹, Abdus Salam Sarkar¹, Andreas Lemonis¹, George Kioseoglou^{1,3} and Emmanuel Stratakis^{1,2}*

¹*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete 71110, Greece.*

²*Department of Physics, University of Crete, Heraklion Crete 71003, Greece.*

³*Department of Materials Science and Technology, University of Crete, Heraklion Crete 71003, Greece.*

** gmaragkakis@physics.uoc.gr*

Abstract:

The in-plane structural anisotropy of two-dimensional (2D) monochalcogenides, provides an additional degree of freedom that enables the manipulation of their physical properties, which is important for future optoelectronic devices. Here, we report that third harmonic generation (THG) from tin (II) sulfide (SnS) crystals is anisotropic along the armchair and zigzag crystallographic directions. Polarization-resolved THG (P-THG) imaging allows the simultaneous recording of the intensity of two orthogonal components of the third harmonic field. Then, upon simultaneous fitting with a theoretical nonlinear optical model, which accounts for the orthorhombic crystal structure of SnS, we are able to determine the relative magnitudes of the $\chi^{(3)}$ tensor components, for several 2D SnS flakes belonging in the same field of view. For these $\chi^{(3)}$ ratios and the introduced THG anisotropy ratio, mean values based on a statistical analysis are registered, quantifying the anisotropic nature of the THG process. The demonstrated technique is all-optical, minimally invasive and rapid and can be useful as a powerful characterization technique in future devices exploiting the in-plane anisotropy.

Surface modification of Ti-6Al-4V for medical applications

M. Benčina^{1,2,3} N. Rawat,² A. Iglič,^{2,3} V. Kralj-Iglič,³ A. Vesel,¹ I. Junkar¹

1 Department of Surface Engineering, Jožef Stefan Institute, Ljubljana, Slovenia;

2 Laboratory of Physics, Faculty of Electrical Engineering, University of Ljubljana, Ljubljana, Slovenia;

3 Laboratory for Clinical Biophysics, Faculty of Health Sciences, University of Ljubljana, Ljubljana, Slovenia.

** metka.bencina@ijs.si*

Abstract:

Ti-6Al-4V alloy, known for its excellent bio-compatibility and mechanical properties, is widely used in orthopaedic and dental implants. However, its inherent surface properties can limit its osseointegration and long-term stability within the body. Common surface modification methods of Ti-based surfaces include physical vapour deposition, plasma spraying, anodization, and hydro-thermal treatments [1]. One significant issue with medical implants is the occurrence of bacterial infections, which can lead to severe complications and implant failure. Despite the remarkable properties of Ti-6Al-4V alloy, its surface can serve as a potential breeding ground for bacteria, compromising the success of implantation procedures. The present contribution will present the effect of non-thermal plasma treatment on the surface properties of Ti-6Al-4V alloy. Morphology, surface chemistry and wettability of the Ti-6Al-4V treated with different plasma parameters (gas, power, time, etc.) have been examined by Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX), X-ray photoelectron spectroscopy (XPS) and Water contact angle (WCA) analysis. The analyses showed that nano-structured surfaces with improved wettability had been prepared by non-thermal plasma treatment. The analysis of the surface elemental composition showed that plasma-treated surfaces possess a higher concentration of O₂ than untreated surfaces, which can influence bio-response of Ti-6Al-4V. In addition, antibacterial tests with Gram-negative *E. coli* and Gram-positive *S. aureus* have been performed. The results indicate that plasma-treated surfaces have improved anti-bacterial efficiency compared to untreated Ti-6Al-4V. The presence of nano-features on plasma-treated surfaces of Ti-6Al-4V alloy has the potential to rupture bacterial membranes, indicating a possible mechanism for inhibiting bacterial adhesion. Also, improved wettability of plasma-treated surfaces can exert an influence on bacterial adhesion.

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Electrodeposited Graphene Oxide- Cu electrodes for Aqueous Zinc-energy storage devices

N. Kavousanos^{1,2*}, M. Apostolopoulou¹, K. Brintakis², A. Kostopoulou², E. Stratakis², D. Vernardou¹

¹*Hellenic Mediterranean University (H.M.U.), Heraklion, Greece*

²*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (FORTH), Heraklion, Greece*

** nikoskabousanos@gmail.com*

Abstract:

Improving energy storage and more specifically increasing the capacity and life-time of the batteries is considered a major issue of the modern world. Exploring sustainable ways to enhance batteries' performance has been a standing goal for the researchers. Considering zinc's abundancy, energy storage systems that incorporated non-lithium-based electrolytes, such as aqueous zinc-based electrolytes, have been reported in the last years.[1]

In these directions, Graphene Oxide- Copper (GO-Cu) electrodes have been fabricated through an electrodeposition method [2] to be used in Zn-based storage systems. Specifically, the GO was dispersed in deionized water and then deposited on a 10 mm×10 mm×1 mm Cu substrate through a Cyclic Voltammetry (CV) set up using a three-way electrode system (graphite counter electrode, AgCl reference electrode, Cu working electrode). Various characterization techniques such as scanning electron microscopy (SEM), Raman-IR and X-ray diffractometry (XRD) have been utilized to find out the optimum parameters for the electrodeposition process. The thickness, morphology and crystal structure of the deposited films have been determined by these techniques verifying the successful deposition. Then, the capacity, stability and life-time of the GO-Cu electrodes in a ZnSO₄/MnSO₄ aqueous electrolyte solution were measured in the same CV system. The capacity of the electrodes was calculated at 95.6 mAh/g even after 100 cycles.

These electrodes will be used in the future in Zn-based energy storage systems, including Pb-based and Pb-free perovskites as energy storage materials.

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Wednesday 13th September

Poster Session

VARIOUS WORKSHOPS

Establishing Polydioxanone as a flexible resorbable sensor platform

Finn Jaekel^{1*}, Sarah Spitzner¹, Hans Kleemann¹, Dennis Wahl², Daniel Bockler², Eberhard Grambow², Sebastian Hinz², Clemens Schafmayer², Jochen Hampe³ and Karl Leo¹

¹*Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP), Dresden, Germany*

²*Department of General, Visceral, Thoracic, Vascular and Transplantation Surgery, Rostock University Medical Center, Rostock, Germany*

³*University Hospital Carl Gustav Carus at the Technical University of Dresden, Dresden, Germany*

* finn.jaekel@tu-dresden.de

Abstract:

Polydioxanone is a well established medically licensed material typically used for resorbable medical structures. Hence, it could provide an ideal substrate for in-vivo electronic sensors in order to monitor post-surgery healing of wounds. However, the thermal budget and chemical robustness represents a significant challenge for the integration of electronic components – in particular, when aiming for a bioresorbable sensor. Here, we demonstrate a biodegradable electronic sensor on extruded Polydioxanone sheets as a flexible resorbable substrate. We pioneered the processed for the integration of resistive temperature sensors and pH-sensors based on organic electrochemical transistors, utilizing a combination of various techniques such as physical vapor deposition, inkjet printing, and screen printing. The variety of established processes opens up several possibilities to integrate further functionalities into the sensor platform.

This technology/sensor platform is tested in context of the DFG project FAVORS (Rapid alert system for anastomosis failure using organic resorbable sensors)¹ in which experiments on pigs are performed for in-vivo testing. Preliminary data of in vivo measurements, as well as results on biocompatibility and influence of the substrate on wound healing are presented.

[1] FAVORS - Frühwarnsystem vor Anastomosen-Versagen durch Organische Resorbierbare Sensorik, K.Leo and C. Schafmayer, DFG Project Number 461264398, 2021

Ozone decomposition over manganese-based catalysts in gas phase

Petya Karakashkova^{1*}, Katerina Zaharieva², Silvia Dimova³

¹*Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria “Acad. G. Bonchev” St., Block 11, 1113 Sofia, Bulgaria*

²*Institute of Mineralogy and Crystallography “Acad. I. Kostov” Bulgarian Academy of Sciences, “Acad. G. Bonchev” St. Block 107, 1113 Sofia, Bulgaria*

³*Institute of Polymers, Bulgarian Academy of Sciences, “Acad. G. Bonchev” St., Block 103A, 1113 Sofia, Bulgaria*

**Email: petya.karakashkova@gmail.com*

Abstract:

Ground-level ozone pollution has become an increasingly serious environmental problem worldwide. Ozone (O₃) is toxic gas used in industrial and environmental processes and can have a deleterious effect on human health. Catalytic decomposition is the most promising method for purification of toxic gases containing ozone, especially at room temperature [1]. The catalytic decomposition of ozone to molecular oxygen was investigated over a range of manganese-based catalysts. Catalytic samples containing the copper manganese oxide materials were prepared using co-precipitation followed by calcination at 500°C. The copper manganese oxide/clinoptilolite composites were also synthesized by co-precipitation and then thermal treatment at 500°C. CeO₂-Mn₂O₃ oxides catalyst was prepared using Pluronic-assisted co-precipitation [2]. The catalytic activity of the metal oxide catalysts in the reaction of ozone decomposition was measured by monitoring the inlet and outlet ozone concentrations and calculating the conversion of ozone to molecular oxygen. It was found out that all tested catalyst samples have activity in ozone decomposition. A maximum conversion degree of about 73% was observed with the catalyst sample CeO₂-Mn₂O₃ oxides catalyst. The prepared samples were investigated using powder X-ray diffraction, Fourier-transform infrared spectroscopy and scanning electron microscope.

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Printed Microelectrode Arrays: Advancing Electrophysiological Research with Aerosol-Jet Printing Technology

Dominik Baraniecki^{1*}, Jakub Krzemiński¹, Jan Dominiczak¹ and Małgorzata Jakubowska¹

¹*Warsaw University of Technology, Warsaw, Poland* *dominik.baraniecki@pw.edu.pl

Abstract:

Electrophysiological research plays a crucial role in understanding the complexities of brain function and neurological disorders. To meet the ever-growing demand for precise and scalable tools, our project focuses on developing innovative microelectrode arrays (MEAs), "neutrodes", using advanced printed electronics techniques, specifically aerosol printing.

The project leverages aerosol-jet printing's unique capabilities to fabricate microscale neutrodes suitable for studying small organisms like rodents while paving the way for upscaling to human-sized devices. Aerosol printing offers the flexibility to produce customized measurement systems tailored to individual anatomies, ensuring minimal tissue damage and precise placement within the cerebral cortex grooves. Neutrodes will find applications in both in vitro and in vivo studies, enabling simultaneous exploration of multiple brain regions and enhancing electrophysiological data collection.

This work presents the first steps towards the fabrication of microelectrode arrays with the novel approach of using aerosol-jet printing, highlighting its advantages in achieving personalized and precise brain research tools. It emphasizes the potential impact of this technology on advancing our understanding of brain function and addressing neurological challenges.

Keywords:

Electrophysiology, Microelectrode Arrays, Aerosol Printing, Brain Research, Neurological Disorders, Biocompatibility, Proof of Concept

MOFs as a key to safer agriculture: Sensing and Remediation for Pesticide Health Management

Marianna I. Kotzabasaki^{1*}, Giasemi K. Angeli², Chrysanthos Maraveas¹ and Thomas Bartzanas¹

¹*Agricultural University of Athens, Department of Natural Resources and Agricultural Engineering, Athens, Greece*

²*National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute*

*[*mariannakotz@aau.gr](mailto:mariannakotz@aau.gr)*

Abstract:

Contemporary agriculture is currently experiencing a consistent surge in the utilization of agrochemicals, including fungicides, insecticides, herbicides, plant growth regulators, and fertilizers, all aimed at optimizing crop yields. However, the extensive application of these agrochemicals has led to significant environmental and human health risks, resulting in substantial losses. Consequently, there is a pressing need to innovate and establish effective management systems for agrochemicals that facilitate their sustainable detection and remediation. This is essential to mitigate potential human health issues stemming from their widespread use [1-4].

To effectively address this emerging challenge, environmentally friendly agrochemical nanoformulations based on advanced porous materials have been employed to provide sustainable and efficient solutions. Among the wide array of materials investigated, Metal-Organic Frameworks (MOFs) due to their physicochemical characteristics (e.g., high pore volume, enhanced chemical stability, abundant open metal sites with the potential to act as catalytic sites as well as the plethora of functional groups which can be grafted on their organic building units), have emerged as highly promising candidates, offering versatile applications as both remediation agents and chemical sensors. MOFs, are hybrid porous materials constructed from inorganic and organic building units, are uniquely suited for tailored synthesis, enabling their adaptation for specific applications [5,6]

This study focuses on the utilization of highly stable MOFs based on Zr(IV) and rare earth elements (REs), exploring their efficacy in catalytic decomposition of selected agrochemicals and their potential as sensors in aquatic environments. We present a comprehensive review of pertinent literature and experimental findings, along with insights into future directions aimed at enhancing performance and sustainability in agrochemicals management for improved public and environmental health.

Acknowledgements

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