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TNT2021

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TNT2021 Foreword

On behalf of the International and Technical Committees, we take great pleasure in welcoming you to Tirana (Albania) for the "Trends in NanoTechnology" International Conference (TNT2021).

TNTconf series will again propose a high-level scientific program addressing key factors for the future of the Nanoscience and Nanotechnology community in Europe.

TNT2021 is being held in large part due to the success of earlier TNT Nanotechnology Conferences. TNT events have demonstrated over the past 20 years that they are particularly effective in transmitting information and promoting interaction and new contacts among workers in this field. Furthermore, this event offers visitors, exhibitors and sponsors an ideal opportunity to interact with each other.

This year, several parallel workshops (Medical doctors meet nanotechnologists / 2nd Cooperation event between Spain, Albania & Japan) and a school on nanoBiosensors will be organised.

We are indebted to the following Government Agencies for their financial support: Academy of Sciences of Albania and MAEC/Embajada de España en Albania.

In addition, thanks must be given to the staff of all the organizing institutions whose hard work has helped planning this conference.

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The Institut Catala de Nanociencia I Nanotecnologia (ICN2) is a flagship research institute within the CERCA network of centres created and supported by the Autonomous Government of Catalonia to raise Catalan science to the premier international level. The patrons of ICN2 are the Government of Catalonia (Generalitat), the Consejo Superior de Investigaciones Científicas (CSIC), and the Autonomous University of Barcelona (UAB). Its core activities are Frontier Basic and Applied Research in Nanoscience and Nanotechnology, Technology Transfer, and Public Outreach. Currently, ICN2 numbers some 200 staff from over 30 countries, of which about 170 are researchers. In addition to the theoretical and experimental groups involved in the project, ICN2´s activities in graphene include thermal management, photovoltaic, biosensors and energy applications, gathering about 40 researchers (permanent staff, postdoc and Ph.D. students). ICN2 achievements were recognised in 2014 with the Severo Ochoa Centre of Excellence accreditation, the most prestigious award targeting research centres in Spain.

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KEYNOTES
contributions

Nanowires (R)Evolution: from VLS vertical nanostructures to SAG Quantum Networks

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The lack of mirror symmetry in binary semiconductor compounds turns them into polar materials, where two opposite orientations of the same crystallographic direction are possible. Interestingly, when semiconductor nanostructures are grown by following the VLS mechanism, their physical properties (e.g.: electronic or photonic) and morphological features (e.g.: shape, growth direction, etc.) strongly depend on the polarity. Tailoring complex free-standing nanostructures by VLS has been used in the last 2 decades as model systems to study basic physics, e.g.: electronic, photonic and quantum phenomena at the nanoscale, with high detail and precision.[1,2,3] However, scaling up this technology has become a nightmare due to the difficulty to design large circuits and networks. Positioning and contacting the different VLS grown nanobuilding blocks (e.g.: nanowires) in a reproducible manner is not an easy task. Fortunately, the development of new growth methodologies such as the guided-growth (GG), selected area growth (SAG) or template-assisted selective epitaxy (TASE) allow the direct growth of horizontal nanowires on top of a selected substrate with high accuracy and the possibility to obtain high quality contacts, enabling the design of complex circuits and networks. This is the case of the newly designed quantum hybrid nanowire networks. [4,5]

We will explore the different growth mechanisms that led to the latest (r)evolution in NWs growth at the atomic scale and understand the related physical properties of the nanostructures. We base our study on a detailed aberration corrected scanning transmission electron microscopy and related spectroscopies methodology. From the structural data obtained we create 3D atomic models that are used as input data for the further electronic/photonic/quantum properties simulations and correlation to the experiments.

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Figures

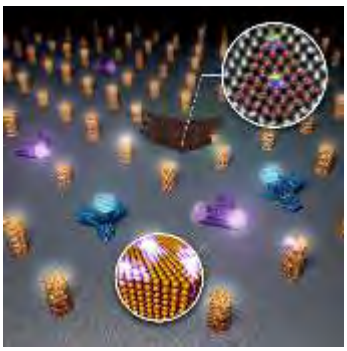

Figure 1. VLS growth

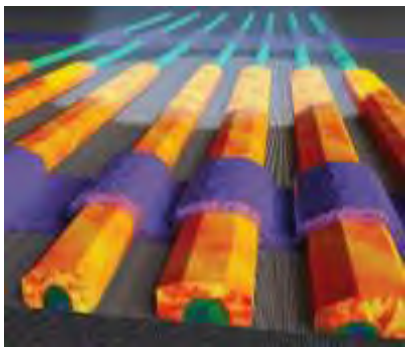

Figure 2. Guided growth

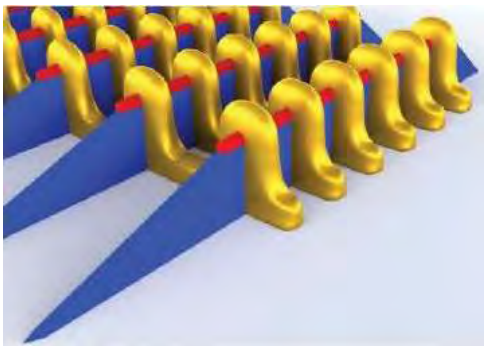

Figure 3. Selected Area Growth

Latest developments in the industrial production of 2D crystals

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The development of industrial-scale, reliable, inexpensive production processes of graphene and related two-dimensional materials (GRMs) is becoming the top priority in this field.[1,2] In fact, this is a key requirement for their widespread use in several application areas,[1-6] providing a balance between ease of fabrication and final product quality. In particular, in the energy sector, the production of GRMs in liquid phase [2,6] represents a simple and cost-effective pathway towards the development of GRMs-based energy devices, presenting huge integration flexibility compared to other production methods.

In this presentation, I will present the strategy of BeDimensional in the production of GRMs by wet-jet milling [7] and the Industrial scale up. Afterward, I will provide a brief overview on some key applications of the as-produced GRMs, for anticorrosion coatings and energy conversion[3,8-11] and storage[8,12-16] devices.

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Translational, multiplexing and multiomics (nano)bioelectroanalytical tools: Taking on gigantic challenges towards precision medicine

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Aware of human diseases evolution involves a highly dynamic and interactive system of multiple layers of molecular markers (e.g. genetics, epigenetics, mRNA transcripts, proteins and metabolites), precision medicine aims to provide a detailed characterization of each disease to customize healthcare. On the other hand, it is now fully accepted that the simultaneous analysis of multiple layers of molecular markers leads to novel strategies for early detection or predisposition to suffer from prevalent and high mortality diseases such as cancer and neurological conditions, thus improving their prevention and treatment. In this sense, features such as versatility to profile multiple biomarkers at different omics levels, simplicity, affordable cost, remarkably shorter analysis time and the smaller sample amount required for the analyses compared to conventional or latest generation methodologies, make electrochemical bioplatforms particularly promising alternatives for this purpose [1].

Bearing this in mind, this lecture will discuss bioelectroanalytical tools recently developed in our research group, implemented both using magnetic microbeads and integrated formats at disposable electrodes, by exploiting advantages of quite current HaloTag and diazonium salt chemistries, new developments and uses of hybrid nanomaterials, latest generation bioreceptors, smart bioassay formats and multiplexed amperometric transduction, for assisting mostly in proteomics and epigenomics. In particular, the most relevant aspects of electroanalytical bioplatforms potentially transferable to the clinic due to their simplicity, cost, testing time, versatility, multiplexing capability and decentralized character, which have shown pioneering applications to decisively assist in personalized early diagnosis of neurological and cancer diseases by targeting dysregulated proteins and autoantibodies, and methylation events in nucleic acids, will be discussed.

The giant strides in the forefront in electrochemical biosensing, of which those to be discussed in this Keynote are a good example, make us expect the birth of new simple, versatile, affordable, and applicable devices even in ambulatory or domestic environments, that will play a leading role both in clinical routine and in our daily life. These biodevices are proved to be ready to validate candidate biomarkers, to manage human diseases, or to face unexpected global health challenges in record time, as occurred with the current coronavirus pandemic, in a personalized and early way. This will entail unprecedented advantages in minimizing the spread of infections, improving both the statistics and the patients' quality of life, also alleviating the cost associated with their treatment by the health systems and the emotional burden on families.

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Smart Nanomaterials for Advanced Biomedical Applications

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The remote control of cellular functions through smart nanomaterials represents a bio-manipulation approach with unprecedented potential applications in many fields of medicine, ranging from cancer therapy to tissue engineering (Figure 1). By actively responding to external stimuli, smart nanomaterials act as real nanotransducers able to mediate and/or convert different forms of energy into both physical and chemical cues, fostering specific cell behaviors [1, 2]. A new paradigm is proposed for nanomedicine, in order to exploit the intrinsic properties of nanomaterials as active devices rather than as passive structural units or carriers for medications.

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Figures

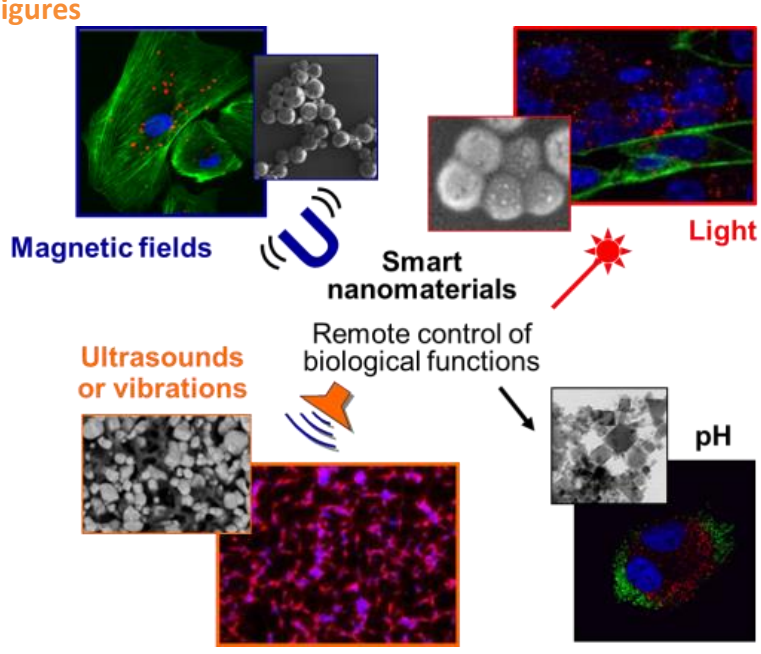

Figure 1. Smart nanomaterials for cell stimulation.

Colloidal Nanoparticles Decorated Graphene based Materials: New Functional Nanocomposites

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Graphene (G) is an extraordinary material for advanced devices, due to its superior electrical conductivity, (electro)catalytic activity and surface chemical reactivity. The last enables the implementation of non-covalent routes for its decoration with inorganic nanostructures, thus resulting in hybrid nanocomposites exhibiting an original ingenious combination of the properties of G and of the inorganic components. Nanoparticles (NPs) prepared via colloidal chemistry approaches possess original size- and shape-dependent properties and are particularly suited for decorating G [1,2], thanks to the possibility to engineer their surface chemistry. Nanocomposites based on graphene based materials and different types of colloidal NPs, PbS, TiO_2 and Au, respectively, [1-3] have been prepared and thoroughly investigated, from a morphological, spectroscopic, electrical and (photo)electrochemical points of view. Distinct decoration approaches have been used, both for immobilizing pre-synthesized inorganic NPs onto the G based structures, and for performing *in situ* synthesis. In both strategies suitable anchoring molecules have represented key element to enable a close interaction between G and NPs and thus direct the chemical and electronic properties of the resulting hybrids. In all the investigated systems a controlled and uniform NP coverage has been obtained. The different obtained materials have been studied and their photoactivity and photoelectrochemical behavior have demonstrated that this class of hybrid nanocomposites hold a great promise for photo conversion, (photo)catalytic and sensing applications [4-6]. Selected examples of nanocomposites will be described and their possible integration in devices presented.

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Figure

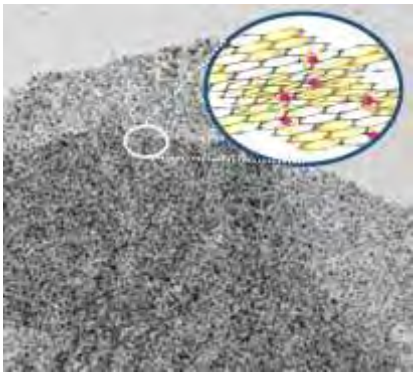

Figure 1: TEM micrograph of a solvent dispersible nanocomposite based on reduced graphene oxide (RGO) *in situ* decorated with Au NPs. In the inset sketch of the anchor molecules mediated interactions between RGO based material and Au NPs.

Implantable and wearable technologies for health monitoring and control

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The combination of genetics, photonics, electronics and micromechanics is enabling completely new micro- and nano-technological approaches for compact and effective tools for diagnostics and therapeutics, which can be disposable, wearable, implantable or tattooable. These new approaches are opening the way to closed loop theranostics, i.e. devices integrating diagnostic capabilities and therapeutic response. In this talk, new technological approaches to produce innovative implantable/wearable devices for optogenetics and fiber photometry, for recording and manipulating brain activity in vivo will be shown. A second technology based on piezoelectric microelectromechanical systems (MEMS) for wearable skin sensing and actuation will be also presented. The possibility to integrate brain technologies with body technologies can enable new solutions for measuring and controlling neurological disorders in closed loop and real time.

Nano delivery systems for imaging and treating pathological disorders overexpressing TSPO

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Decades of studies on the 18-kDa mitochondrial translocator protein (TSPO) have revealed that this protein participates in a variety of cellular functions. As a result of these diverse functions, changes in TSPO expression have been related to different diseases, from cancer to endocrine and neurological diseases as well. TSPO has therefore become an attractive subcellular target for both the early detection of disease states involving its overexpression and the selective mitochondrial drug delivery. Investigation of the functions of this protein, both in vitro and in vivo, has been mainly carried out using high-affinity ligands. Among them, alpidem has been shown to act on both TSPO and the central benzodiazepine receptor, with a preference toward TSPO. In an effort to improve the TSPO-selectivity of alpidem analogs, we have developed many imidazo[1,2-a]pyridine-based compounds and one of them has reached the clinical trial as PET tracer monitoring the neuroinflammation [1]. However, all these diagnostic and therapeutic TSPO ligands have many pharmacokinetics limitations due to their not selective biodistribution and to the subcellular localization of the target protein. Hence, to overcome these limitations nano delivery systems have been explored. In fact, to be effective the nanoparticles have to unload their payloads at the site of disease, more specifically, the encapsulated drug, in some cases, must successfully reach its sub-cellular target [2]. Therefore, the drug loaded nanocarriers have to overcome systemic, extracellular and intracellular barriers to deliver the drug to the specific organelles for effective therapeutic benefit. For example, recently developed nanoparticles, now being investigated for cancer therapy, have been designed with multifunctional capabilities such as long systemic circulation, tumor targeting, cytosolic translocation, organelle-specific targeting for effective cytotoxic effect. The aim of this speech is to describe various strategies that have been adopted so far to enhance the drug's targetability, intracellular drug delivery for nanotherapeutics-based applications.

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CRISPR-powered electrochemical nucleic acid testing

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Nucleic acid testing is decisive for the diagnosis of many diseases as well as for the monitoring of their treatment. In recent years, short non-coding RNAs, like microRNAs (miRNAs), have become more and more important as biomarkers in clinical diagnostics. The presence or dysregulation of specific miRNAs in human body fluids can be associated to various diseases, including Alzheimer or various types of cancer [1]. Besides its wide application in gene editing, CRISPR technology features a powerful tool for the highly sensitive and selective quantification of nucleic acids [2,3]. In this talk, the first CRISPR/Cas13a powered electrochemical microfluidic biosensor (CRISPR-Biosensor) for the on-site RNA detection will be presented [4]. The applicability of the CRISPR-Biosensor is successfully demonstrated by gauging two different miRNAs miR-19b and miR-20a, from very low sample volumes. Without any target amplification, CRISPR-Biosensor offers a low-cost, easily scalable and multiplexed approach for nucleic acid-based diagnostics.

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Figures

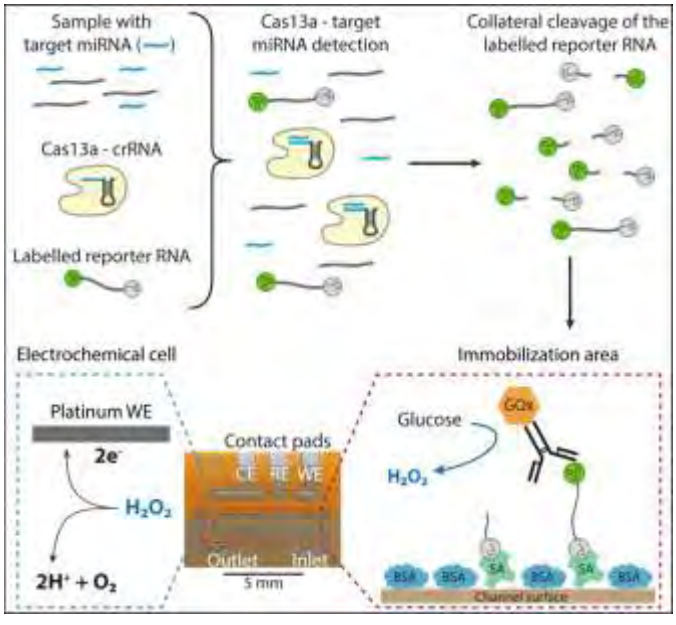

Figure 1. The working principle of the electrochemical CRISPR-Biosensor [4].

From Tissue Engineering to Cybernetics

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Degenerative diseases are spreading rapidly in the world, however, unfortunately, conventional methods are no longer valid for addressing these. Hence, it is the time to manipulate the technology in a way that it serves mankind better. These days, orthopedic diseases are a global pandemic, and there is a need to develop an injectable microenvironment for cells to be guided into bone-like tissue to remedy such conditions. Our primary results indicate that polysaccharide-based hydrogels (i.e., alginate and pectin) in combination with other biomaterials (such as hyaluronic acid and gelatin) and/or nanomaterials can be employed to enhance osteogenesis while they are structurally suitable for injecting into the defect site. The critical element in these studies was taking advantage of a combinatorial approach to screen different parameters in a “high-throughput” manner. Meanwhile, nowadays, various biosensors are trying to find their way into the field of tissue engineering. Along this vein, we have developed a new silk-based composite that is flexible, biocompatible, scalable and conductive. Our findings show that this sensor can transmit light and keeps its functionality at high frequencies. The prepared construction is cheap and scalable, thus, expected to be a building block for future strain-detection sensors and diagnostic devices. The developments in this direction were indeed provocative, and opened a new window at the crossroad of engineering, biology, robotics, chemistry, and medicine. Further research is needed to make the most of these connections and make a platform for diagnosing, treatment, and monitoring patients with different bone-related diseases

Point Defects in Functional Nano-Materials and Their Role in Energy Storage Devices

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Electron paramagnetic resonance (EPR) is a very powerful method due to its enhanced sensitivity to unpaired electrons. In order to understand the defect structure in functional nano-materials we use multi-frequency EPR spectroscopy. In this presentation i) quantum confinement effects in ferroelectric nano-materials ii) EPR and Photoluminescence (PL) investigations of intrinsic defect centers in semiconductor zinc oxide (ZnO) nanoparticles will be given iii) application of metal oxides as electrodes in supercapacitors will be discussed. Starting with the introductory information about EPR spectroscopy; poling, aging, doping and nano-size effects will be discussed for the ferroelectric materials such as, $PbTiO_3$, $BaTiO_3$, $PbZrTiO_3$ (PZT) etc. In the second part of the talk, surface and core defects and their reactivity under temperature and light will be presented for ZnO semiconductor nano-materials. Defect models will be discussed. Finally, in the last part designs of supercapacitor devices will be given and the role of defect structures in the electrochemical performance of supercapacitor devices will be presented.

Figures

Figure 1. Defect evolution of non-stoichiometric ZnO.

Catalytic micromotors for biomedical applications

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Micromotors represent one of the most exciting horizons in micro and nanotechnologies. Micrometer-sized motors can either have a conical tubular or spherical structure. The utilization of self-propelled micromotors in (bio)-chemical assays has led to a fundamentally new approach where their continuous movement around the sample and the mixing associated effect, due to the generated microbubbles tail, greatly enhances the target-receptor contacts and hence the binding efficiency and sensitivity of the assay. This effect is a particularly important aspect to consider when low sample and reagent volumes are available, where other convection approaches are lower efficient to produce adequate interactions.

Catalytic micromotors are constituted by few micro- and nanoscale layers and/or encapsulated components, that confer them self-propulsion, sensing/(bio)-functionalization capabilities, and magnetic properties, among others.

Micromotors technology can integrate nanomaterials in its composition and is highly compatible with optical and electrochemical detection techniques, and microfluidic technology. Point-of-care technology and decentralized analysis can benefit from the inherent advantages of this technology, so that, they are an attractive alternative to perform fast, sensitive, and reliable non-centralized laboratory diagnostic testing, even when extremely low volume of sample is available.

In this talk, selected biomedical applications of different catalytic micromotors will be presented.

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Structure-Function Guided Fabrication of Biodegradable RNA-Binding Polymers

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Development of biodegradable polymers that bind and stabilize RNA is of high importance for various pharmaceutical and biotechnological applications. For instance, the ability to control the degradation rates of RNA is crucial for development of RNA-based vaccines (such as latest developments of coronavirus vaccines). Depsipeptides, which contain both peptide and ester bonds, have been widely studied as biodegradable polymers and as natural products, and are known to synergize from the properties of both peptides and polyesters. While interactions between RNA and positively charged peptides have been previously investigated, no comparable studies on interactions between positively charged depsipeptides and RNA have been reported. To study the structure-function relationship of depsipeptide interactions with RNA, we synthesized a library of positively charged depsipeptides and peptides. The sequences varied in the side chains and in the number and location of ester linkages within the depsipeptide backbone. We demonstrated that positively charged depsipeptides significantly increased the thermal stability of folded RNA structures. In turn, RNA can reduce the rate of hydrolysis of positively charged depsipeptide ester bonds by >30-fold. These results suggest that rational design of positively charged depsipeptides can allow tremendous control over the mode of interaction and stability of RNA-peptide complexes.

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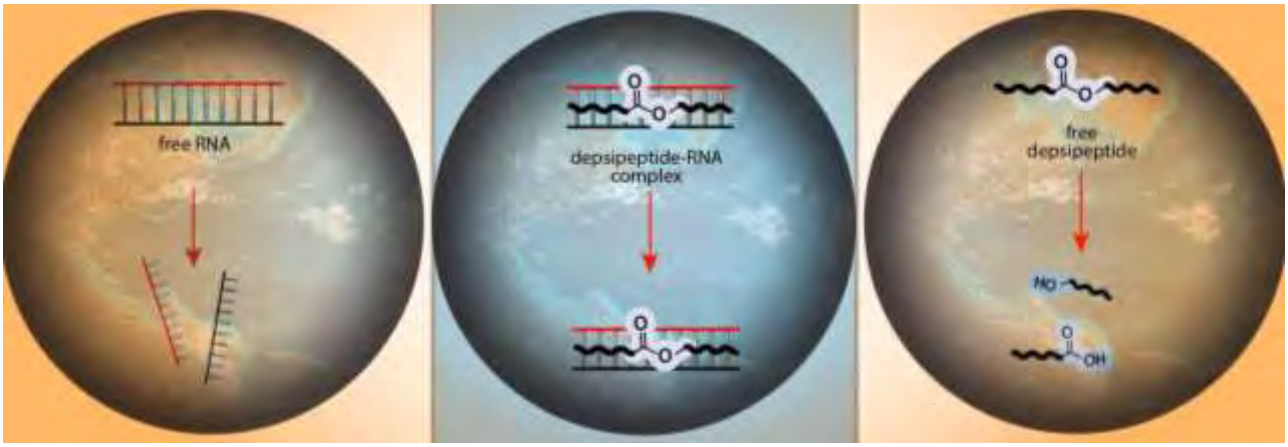

Low-cost Transducers Made of Fabrics

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Woven and non-woven fabrics such as cellulose paper and textiles, are low-cost, flexible, porous and generally biodegradable materials that are ideally suited for the fabrication of disposable sensors and actuators. [1-5] Unlike microfabricated (e.g., PDMS-based) microfluidic systems, printed microfluidics produced using fabrics do not require pumps and other complex components, allowing construction of highly compact, miniaturized devices for rapid, multiplex sensing of various bioanalytes (such as DNA) in the field. The intrinsic properties of cellulose fabrics (cellulose is a highly hygroscopic biopolymer) also enable measuring gaseous analytes in a completely new fashion. This new method of sensing gases allows monitoring respiratory activity in humans and detecting volatiles formed by the degradation of food to measure food freshness. Regardless of the application, devices produced using fabrics only require a series of simple methods of fabrication without the need for specialized facilities such as a cleanroom. In this talk, I will present our latest work on sensors and actuators created using fabrics and how they can enable new classes of low-cost technologies.

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Graphene nanoarchitectonics: building beyond 1D homostructures.

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Bottom-up nanoarchitectonics has demonstrated the capability to control structural parameters of nanomaterials with atomic precision. The surface-assisted synthesis of graphene-based one-dimensional nanostructures à la carte distinctly illustrates the power of this concept. However, despite impressive advances in the synthesis of 1D homostructures, advancing in structural complexity faces major challenges. The functionalization of edges in nanoribbons, an effective strategy to tailor their electronic properties and chemical interactions, is a clear example. The concept of inserting the desired functional groups or dopants in the molecular precursor often fails due to their lack of stability during the reaction path. The fabrication of heterostructures is a second example, where the challenge lies on the control of the size and distribution of their components. A third one is extending the on-surface strategy to two-dimensional structures, where examples of long-range ordered nanoarchitectures are very limited.

I will present different strategies that we developed to overcome each one of this challenges. Regarding edge functionalization, we recently demonstrated the synthesis of amino [1] and fluorine [2] functionalized graphene nanoribbons, both of them showing to be effective for tailoring the electronic band structure. We have also developed a method to synthesize a 2D nanoporous graphene, where the long-range order is achieved by the sequential growth of 1D building blocks and their posterior coupling [3]. Most recently, we have synthesized a similar nanoporous graphene structure that electronically behaves as a 2D superlattice heterostructure [4]. The particular electronic properties of the heterocomponents and the interface structure results in atomically sharp band discontinuities that host subnanometer quantum dipoles, altogether enabling the realization of 1 nm scale superlattice heterojunctions.

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Figures

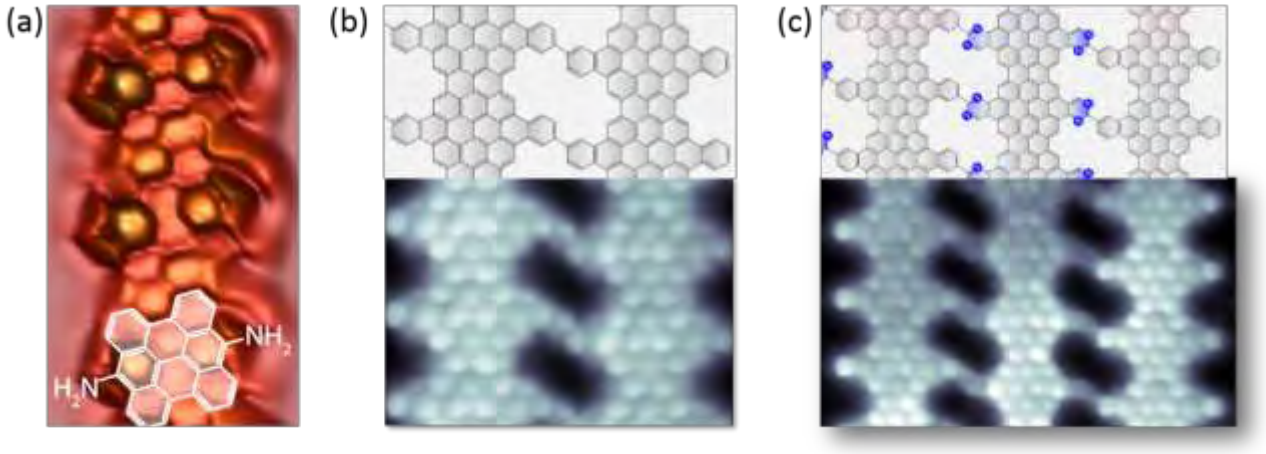

Figure 1. STM images of: (a) Amino functionalized graphene nanoribbon. (b) Nanoporous graphene homostructure. (b) Nanoporous graphene heterostructure.

Multiplexed detection of single nucleotide polymorphisms via solid-phase primer elongation with ferrocene labelled nucleotides

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An approach for the multiplexed detection and identification of single nucleotide polymorphisms exploiting electrode arrays, primer elongation and ferrocene labelled nucleotides is presented. Solid-phase isothermal primer elongation reaction using ferrocene-labelled 2'-deoxyribonucleoside triphosphates (Fc-dNTPs) was exploited for the electrochemical detection of a single nucleotide polymorphism (SNP). Four 5'-thiolated primers, designed to be complementary with the same fragment of the target sequence and differing only in the last base at the 3-OH' end, were self-assembled with 6-mercaptohexanol on individual gold electrodes of an array. Solid phase isothermal primer elongation using Klenow (exo-) polymerase (single stranded DNA targets) for 5 minutes or isothermal recombinase polymerase amplification (double stranded DNA target) for 15 minutes at 37ºC and using an optimised ratio of Fc-dNTPs and natural dNTPs. Square wave voltammetry was used to measure the ferrocene present in the elongated primers. Elongation only occurred with the primer containing the base complementary to the single nucleotide polymorphisms present, with an unequivocal electrochemical signal observed. The platform was applied to the multiplexed detection of SNPs associated with osteoporosis using genomic DNA from a fingerprick blood sample, as well as to the detection of SNPs linked with resistance to the antibiotic rifampicin in *Mycobacterium tuberculosis* again using genomic DNA and results were validated using next generation sequencing. This generic platform has a plethora of potential applications in clinical diagnostics, detection of antibiotic resistance and forensics.

Figures

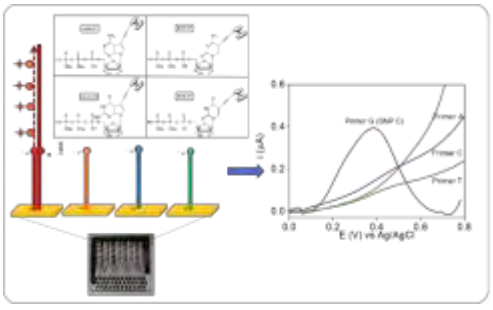

Figure 1: Schematic overview of electrochemical detection and identification of single nucleotide polymorphisms

Towards first-principles electrochemistry: Addressing electrified metal-electrolyte interfaces with DFT-NEGF

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First principles simulations are crucial in many areas of materials science. However, this approach has not been used in the field of electrochemistry, where the complexity of the electrochemical environment and the presence of the external electrode potential have precluded direct application of usual first principles methods like Density Functional Theory (DFT). We aim to overcome these barriers by utilizing recent breakthrough advances in modelling techniques that will allow us to extend the use of DFT to the complexity of the electrochemistry processes.

We demonstrate how Non-Equillibrium Green's Functions techniques can be used to address, from first principles, the atomistic description of metal-electrolyte interfaces in the presence of an external bias applied to the electrodes. The NEGF method allows to deal with open, non-periodic systems driven out of equilibrium by the external applied bias. We use the TranSIESTA method and code [1,2], developed within the SIESTA project [3]) to study problems involving steady-state non-equilibrium situations in nanoscale constrictions, where an external electric bias is applied between the two sides of the constriction, establishing a steady electric current. We show how this computational machinery can be also used to study electrified solid/liquid interfaces [4], where an external bias is applied to the solid electrode. Here, one is not concerned with the quantum electronic transport, but with the effect of the external bias on the structural changes, dynamics and chemical reactions induced at the metal/liquid interface. We will show molecular dynamic simulations of aqueous electrolytes as a proof of concept for future realistic, atomistic first-principles simulations of electrochemical processes.

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Figures

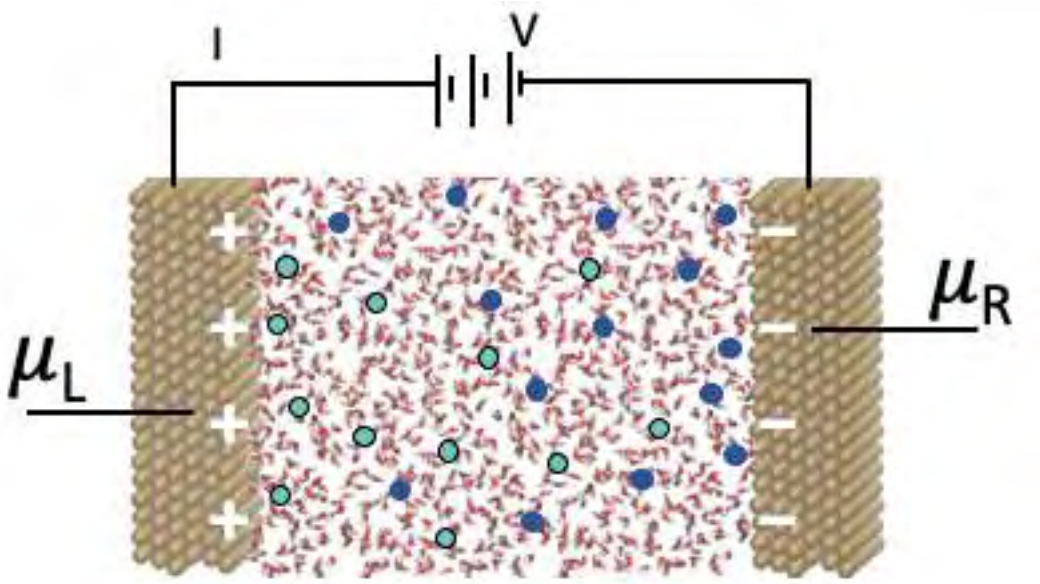

Figure 1. Scheme of the simulation setup for the study of the interface between an electrolyte (water with a salt in solution) and the electrified metallic surface.

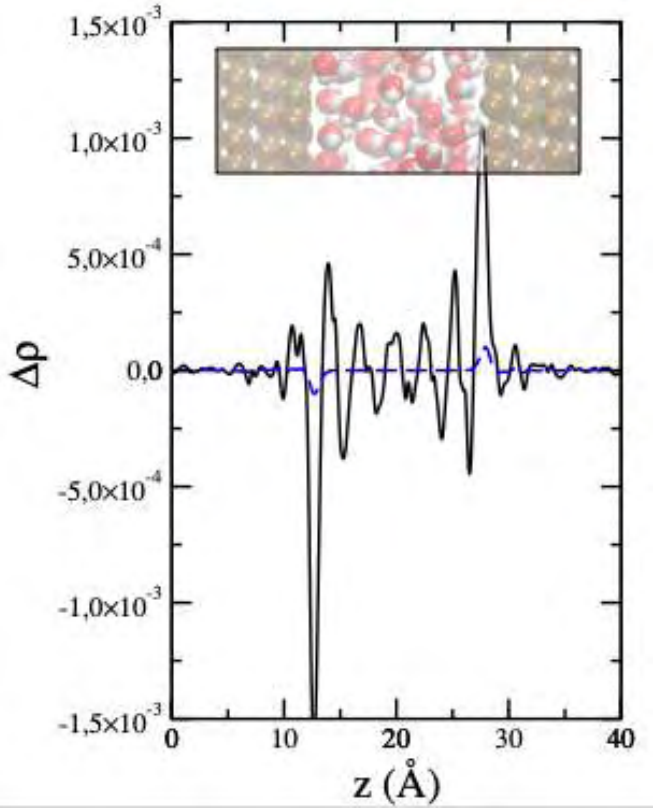

Figure 2. Charges induced by the application of a bias voltage between the two metallic electrodes. Full black and dashed blue lines show the results of the simulation with and without water between the electrodes, respectively. Surface charges accumulate on the metallic surfaces, while the electronic cloud of the water molecules is also polarized, and the water molecules rotate to (partially) align their dipoles along the bias field. The charges induced on the surface are much larger in the presence of water, as the water polarization leads to interface charges that must be screened by free charges in the metallic lead.

Graphene Derivatives for Catalysis and Energy Storage

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Covalent functionalization of graphene leads to graphene derivatives with significantly modulated electronic, magnetic and surface properties with respect to pristine graphene. The graphene derivatives can be applied in various sensing, energy storage and catalytic applications. A wide range of various approaches have been developed for covalent graphene functionalization so far. Despite the progress in direct covalent functionalization of graphene, this approach suffers from a low reactivity of graphene. Recently, we developed alternative route toward graphene derivatives based on chemistry of fluorographene (FG). FG is a stoichiometric graphene derivative (having C_1F_1 composition), which can be prepared by chemical delamination of graphite fluoride in a large scale. FG undergoes various chemical reactions at rather mild conditions [1], which lead to graphene derivatives. FG is susceptible for reductive defluorination, nucleophilic attack, Grignard [2], Bingel-Hirsch [3], photo Diels-Alder [4] and Sonogashira [5] reactions. The reactions result in homogeneously and densely surface functionalized graphene derivatives. Such materials can be utilized in a broad spectrum of applications. Hydroxyfluorographenes bear room-temperature antiferromagnetic or ferromagnetic ordering based on their composition [6, 7]. Cyanographene, i.e., graphene functionalized by nitrile groups, and graphene acid bearing carboxyl groups are well biocompatible materials suitable for further functionalization [8]. Conjugating graphene acid with redox active centers, e.g., ferrocene, leads to redox active heterogenous catalyst for arene CH insertion [9]. Pd nanoparticles with controllable size can be grown on graphene acid. The prepared nanohybrids were highly active catalysts in the Suzuki–Miyaura cross coupling reaction [10]. Anchoring Cu ions to cyanographene resulted in a mixed valence single-atom catalyst (SAC) very active in oxidative amine coupling reactions [11]. Graphene acid was covalently conjugated with dehydrogenase enzymes to a nano-bio catalyst exhibiting good performance in electrocatalytic reduction of CO_2 [12], also due to conductivity of graphene acid. It is worth noting that graphene acid shows metal free catalysis for alcohol oxidation, posing a new limit in carbocatalysis [13]. The high-conductivity and water dispersibility predispose graphene derivatives for electrode materials in supercapacitors [3, 14].

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An Overview of Carbon Based Nanosensors and biosensors and their applications in drug assay and life sciences

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Carbon-based nanomaterials have become very important due to their unique combinations of chemical and physical properties, extensive research efforts are being made to utilize these materials for various industrial applications, such as high-strength materials and electronics. These advantageous properties of carbon-based nanomaterials are also actively investigated in several areas of biomedical and drug assay.

Electrochemical nanosensors have recently found extensive applications in pharmaceutical and biomedical industries with some advantages such as lower detection limits, wider linear response range, sensitivity, good stability and reproducibility when compared with other sensors and techniques. As the demand for smaller, faster, cheaper, and ultrasensitive qualification and quantification of samples rapidly increases, these methods provide a viable path toward the next generation of electrochemical sensors. Carbon-based nanomaterials have been studied extensively in recent decades, with the synthesis of new nano-sized materials being an active trend for the development of assorted applications focused on their interesting electronic properties. In recent years, nanotechnology with its wide applications has become very popular in the biomedical and pharmaceutical area. Electrochemical devices have recently received considerable attention in the development of nanosensors and nanobiosensors. They are devices that intimately couple a pharmaceutical and biological recognition element to an electrode transducer that relies on the conversion of the nanomaterial-drug, nanomaterial-biological compound, antibody–antigen or Watson–Crick base-pair recognition event into a useful electrical signal. Electrochemical devices offer elegant routes for interfacing – at the molecular level–the target recognition and signal transduction elements and are uniquely qualified for meeting the size, cost, low volume, and power requirements of decentralized working diagnostics [1-3].

The high sensitivity of electrochemical nanosensors or nanobiosensors, coupled with their inherent miniaturization, compatibility with modern microfabrication technologies, low-cost and power requirements, and independence of sample turbidity make such devices excellent candidates for centralized and decentralized the related testing. Nowadays, a lot of different analytical methods are used in environmental, pharmaceutical, or clinical laboratories and also a number of the commercial point-of-care devices work using as sensors. As new procedures for the large-scale production of graphene are expected to be developed in the near future, most of such properties – including the electrochemical ones – will be soon experimentally demonstrated, thus permitting the development of the many important technological applications foreseen for this material.

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Magnetic hyperthermia, chemotehrapy and radiotherapy with inorganic nanoplatforms to tackle cancer

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The use of heat to cure cancer is very ancient. Nowadays, many techniques enable to deposit the heat in very specific body regions thus providing more efficient heat treatment with less side effects. Among a variety of novel nanotechnology-based approaches with a remote, spatial and temporal control of temperature increase, magnetic hyperthermia exploits magnetic nanoparticles as heat transducers under alternating magnetic fields (AMF) that are safe for patients, with no limitations on the tissues and body penetration.
This talk aims at providing an overview of our ongoing research efforts to combine magnetic hyperthermia with other clinical accepted therapeutic modalities in particular with chemotherapy or with radiotherapy to treat solid tumors. This presentation is divided into three sections. In the first one, I will report on our progress on preparation of magnetic nanoparticles with optimal heat performance for magnetic hyperthermia.(1)(2) Our goal is to achieve the control on size, size distribution and crystallinity that in turn, enable to control the structural and magnetic properties of the magnetic nanoparticles. Moreover, progress on the synthesis and features of semiconductor-magnetic heterostructures for combining magnetic hyperthermia with radiotherapy, the latter based on cation exchange of Cu64 radioisotopes within the semiconductor domain, will be also reported. (3)
In a second part, I will report on tumor cell studies to determine the magnetic hyperthermia effects, with or without the association of chemotherapeutic drugs, on different subpopulations of patient-derived cancer cells with particular emphasis to the effects on quiescent cancer stem cells.
Finally, in a third part, I will discuss our preclinical results to evaluate the magnetic hyperthermia efficacy of some of our magnetic materials on xenograft murine tumor model focusing on bio-distributions and controlled biodegradation of magnetic nanoparticles at different compositions. (4) (5)

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Surprising Charge Transport in DNA

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Abstract (Calibri 11)
Charge transport through molecular structures is interesting both scientifically and technologically. To date, DNA is the only type of polymer that transports significant current over distances of more than a few nanometers in individual molecules. Nevertheless, and in spite of large efforts to elucidate the charge transport mechanism through DNA a satisfying characterization and mechanistic description has not been provided yet. Measuring the charge transport in DNA was elusive due to great technical difficulties leading to various results. We recently devised an experiment in which double-stranded DNA is well positioned between metal electrodes. Electrical measurements give surprisingly high currents, up to tens of nA, over 100 base-pairs (~30 nm) elevated from the surface. We further found that homogeneous and non-homogeneous sequences transport charge similarly and that at least one continuous backbone is essential to enable transport. The theoretical calculations and the temperature dependence suggest resonant hopping through the backbone as the charge transport mechanism.

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Figures

DNA-based nanodevices for diagnostic and drug-delivery applications

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DNA nanotechnology uses synthetic DNA (or nucleic acids) as a versatile material to rationally engineer tools and molecular devices that can find a multitude of different applications (e.g., in-vivo and in-vitro diagnostics, drug delivery, genetic circuits etc.).

During this presentation I will introduce the field of DNA nanotechnology and I will show how to exploit the "designability" of DNA to fabricate nature-inspired DNA-based nanoswitches and nanodevices that are specifically designed to undergo a conformational change (switch) upon binding to a specific input (i.e. target). This input-triggered conformational change can be used for diagnostic, drug-delivery or synthetic-biology applications.

I will demonstrate how to characterize and recreate in-vitro several mechanisms to control the response of DNA-based nanodevices and how to regulate their activity with different chemical and environmental stimuli including pH, antibodies, enzymes, small molecules and redox inputs.

From bacteria farming to functional nanocellulose materials and devices

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Cellulose is a non-toxic, degradable and almost inexhaustible bioreneweable polymer expected to play a strategic role in replacing petroleum-based polymers and advancing towards a more circular economy. Nanocelluloses combine the properties of cellulose with the high surface area of nanomaterials. Increasing demand for cost-effective sustainable and high-performance materials makes nanocelluloses attractive for innovative applications in many sectors encompassing photonics, food packaging, flexible electronics or biomaterials. In particular, bacterial nanocellulose (BC) produced by microbial fermentation with the same molecular formula as plant-derived cellulose but with higher degree of polymerization, purity and crystallinity has captured the interest of material scientists.

In our group and in collaboration with several labs in Europe, we exploit BC exceptional features to create advanced functional materials. First, I will describe some strategies to control BC topography and microstructuration during its biosynthesis [1]. I will then show an original route to attain a multi-nanoparticle millefeuille for a BC-layered construct (Figure 1) [2]. Finally, I will present some BC potential applications in energy (thermoelectrics [3] and photovoltaics [4]) and in health [5] (corneal bandage [6] and as cell culture supports [7])

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Figures

Figure 1. Bacterial cellulose films with multiple functional nanoparticles in confined spatial distribution

Graphene integration for CMOS multiplexed bioassays

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Graphene is now strongly emerging from the research phase towards industrial applications also in the microelectronics field, including photonics, sensing and electronics. The largest bottleneck in this process has been the scalability and reliability of the graphene fabrication and integration with the microelectronics process flows, in which respect the recent years have provided significant progress.
Most of the applications pioneering the industrialization are related to sensing, driven by the clear benefits of the high electrical responsivity of graphene and the relatively relaxed demands on the graphene quality, especially in terms of charge carrier mobility, with $\mu < 3000$ cm2/Vs already being adequate for most sensing applications. Here the biggest remaining challenges relate to the functionalization and readout strategies, and into the reliability and reproducibility of both the functionalization and graphene properties.
CMOS integration of the graphene sensors provide keys to address all these challenges, and is also the requirement for truly quantitative on-chip bioanalysis by providing the multiplexing for bioassays. In biosensing, the high sensitivity of the graphene transducers is combined with bioreceptors to provide a response specific to the desired bioanalytes, and the quantitativity generally requires both statistics and carefully selected set of receptors for internal calibration and referencing.
I will address our recent progress towards the fabrication of monolithically integrated graphene biosensor assays, from the graphene device fabrication on CMOS to array performance in liquid phase analysis, and give an overview of the future challenges.

Photochemical doping of Graphene and Transition metal Dichalcogenides

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Photochemistry may provide novel ways to covalently modify materials, thus tailoring its electronic and chemical properties. Due to the unique physicochemical processes taking place during the ultrashort pulsed laser-matter interaction, the surface of nanomaterials can be activated, allowing the chemical reaction with different moieties present in the surrounding medium, giving rise to novel materials production. This paper will present our recent work on the application of pulsed laser radiation for the photochemical modification of graphene oxide (GO) and transition metal dichalcogenide (TMD) nanosheets. In particular we report on a present a fast, non-destructive and roll to roll compatible photochemical method for the simultaneous partial reduction and doping of GO nanosheets through ultraviolet laser irradiation in the presence of reactive Cl_2 precursor molecules (Figure 1). By tuning the laser exposure time, it is possible to control the doping and reduction levels and therefore to tailor the work function (WF) of the GO-Cl derivatives from 4.9 eV to a maximum value of 5.23 eV, a WF value that matches the HOMO level of most polymer donors employed in organic photovoltaic devices [1]. It is also found that the same photochemical approach is ideal to sufficiently control the carrier density of a single MX_2 layer by incorporating chlorine atoms on the surface. Photochlorination leads to a controllable reduction of the valley polarization (VP) degree, that is directly related to the decrease of the active defect sites and consequently to the increase of the non-radiative exciton lifetime [2]. The non-linear optical properties of the pristine and photochemically-doped nanosheets are also investigated and discussed.

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Figures

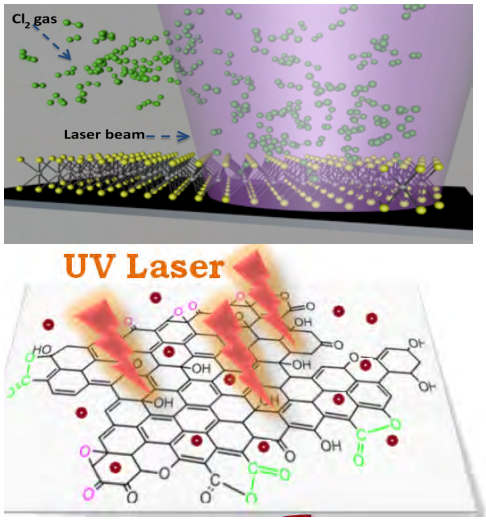

Figure 1. Schematic of the photochlorination of TMDs and GO nanosheets

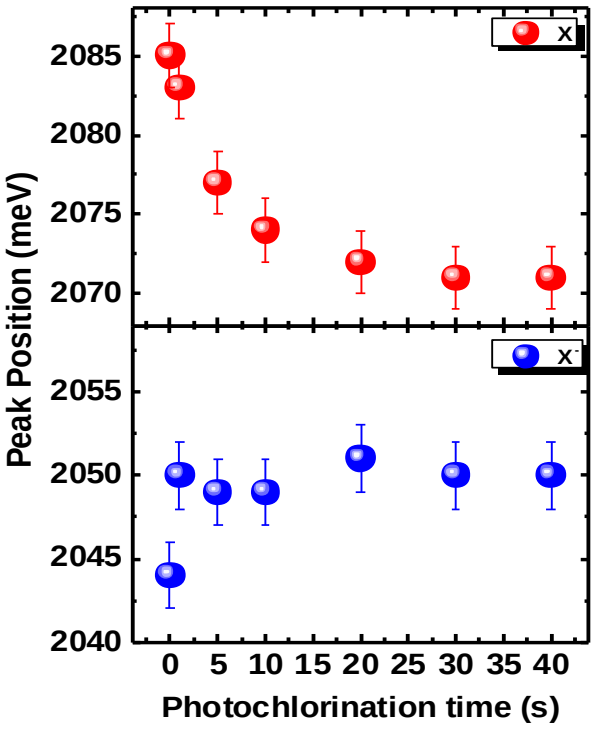

Figure 2. Evolution of the excitonic peaks of a WS_2 monolayer as a function of the photochlorination time

High-speed control of strong emitter-graphene near-field interactions

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The ability to control single-photon emitters through the manipulation of their environment is an important aspect of current nanophotonic research, and highly interesting for many applications, including data communication and quantum technologies. Here we demonstrate that graphene is in many ways an ideal environment, as it enables highly effective and very fast dynamic control of erbium emitters. Erbium emitters are technologically important, as they emit in the C-band of optical communication systems (1.54 microns) and can be used for quantum memories.

We have developed a hybrid erbium-graphene system [1] containing a very thin (~12 nm) layer with erbium emitters having emission properties very similar to emitters in bulk [2]. Graphene is placed directly on top of this thin layer of emitters, and is gate tunable via both a *p*-doped silicon backgate and a polymer electrolyte topgate. In this system, we observe erbium ions with a decay rate that is enhanced by a factor 1,000 and higher, indicating extremely efficient emitter-graphene interaction: 99.9% of the energy of these excited erbium emitters flows to graphene.

Furthermore, we actively and dynamically modulate this interaction using moderate electrical signals (<10 V) that tune the Fermi energy of graphene. The erbium-graphene interactions are thus dynamically modulated between the regime where the emitters lead to interband transitions in graphene, and the regime where they lead to excitation of intraband plasmons. Remarkably, we show modulation frequencies up to 300 kHz, many orders of magnitude faster than the intrinsic decay rate of erbium ions (75 Hz).

This constitutes an enabling platform for integrated quantum technologies, for example opening routes to quantum entanglement generation by collective plasmon emission or photon emission with controlled waveform.

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INVITED SPEAKERS
contributions

Image-based quantification of erythrocyte morphological abnormalities to measure CuO nanoparticle-induced apoptosis

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Abstract

Copper nanoparticles (CuO NPs) are used widely as industrial catalyst, gas sensors or in biomedicines, due to their flexible properties such as large surface área to volume ratio. Their exponentially increased usage has exposed humans to a potential risk of toxicity. However, little is known about the adverse effects of CuO NPs on nontarget organisms. Here, a multiparametric cytotoxicity approach it is used, where CuO nanoparticle posible toxic effects to the crucian carp fish, *Carassius carassius*, were evaluated. The results revealed that both environmentally realistic doses of CuO, 0.5 and 1 mg/L used were toxic to erythrocytes and caused serious cell morphological abnormalities. 96hLC50 value of CuO NPs of 124.9 mg/L provoked generation of oxidative stress. Furthermore, light microscopy image-based quantification of erythrocyte cell and nucleus abnormalities was used to measure the CuO nanoparticle-induced apoptosis. Direct interaction of CuO NPs with erythrocyte membrane was suggested as a possible mechanism of cytotoxicity. The computational method we used here is straightforward, entails only light microscopy field images whose processing can be realised without expensive reagents or specialized instruments, making it applicable by a broad range of researchers and in laboratories where other approaches would be costly.

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Figures

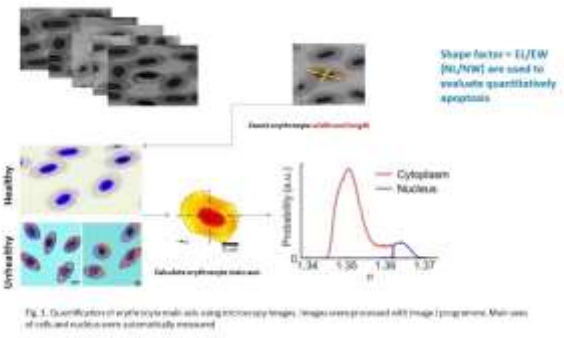

Fig. 1. Quantification of erythrocyte main axis using microscopy images. Images were processed with Image J programme. Main axes of cells and nucleus were automatically measured.

Emerging Amorphous Two-Dimensional Materials

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Formidable progress has been recently achieved in the fabrication and characterization of disordered materials with unprecedented properties. In this context, particular forms of disordered graphene (reduced graphene oxides), obtained by chemical exfoliation techniques, have been found suitable to improve the performances of composite materials for energy applications. Moreover, the recent wafer-scale synthesis of *two-dimensional amorphous carbon monolayers*, structurally dominated by sp2 hybridization has ignited a formidable research of alternative forms of membranes with superior coating properties [1,2]. The uniqueness of 2D amorphous materials derive from the inherent imperfect structural nature which, controlled at the fabrication level, represents the key ingredient for specific target applications. In this respect, new fabrication strategies to modify the degree of disorder and a systematic theoretical characterization of the impact of the material structural quality on the ultimate performance is urgent. Even more importantly, the search for new disordered materials for novel applications appears as an extremely promising way.

In this talk I will present the results of our theoretical investigation on possible strategies to improve the (thermal) reduction process of graphene-oxides and the consequent possibility to recover the quality of pristine graphene [3]. Moreover, we present a systematic analysis of the structural and vibrational properties of amorphous carbon monolayers as a function of the structural quality of the material, showing how disorder results in a tunable thermal conductivity varying by more than one order of magnitude [4]. Finally, one will discuss the newly synthesized thin film of amorphous Boron Nitride showing extremely low dielectric characteristics: high breakdown voltage and likely superior metal barrier properties [5]. The fabricated material has great potential as interconnect insulator in the next-generation of electronic circuits. We discuss the experimental setup and present the results of our calculations which have contributed to the understanding of the structural morphology of the amorphous material as well as explaining the superior dielectric performances.

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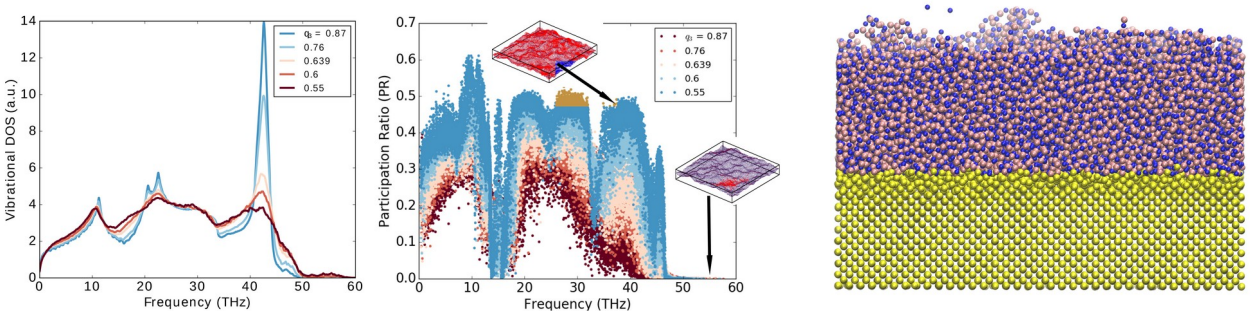

Figure 1. (Left) Vibrational DOS of Amorhous Graphene for different degrees of amorphousness. (Right) Participation Ratio of the samples and atomic displacements (insets) Figure 2. Atomistic sample of Amorphous Boron Nitride

Emerging molecular biology-based applications at department of biotechnology, uot, which may profit from the development of nanobiosensors

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Department of Biotechnology of UOT is researching mainly in agricultural, environmental and aquaculture biotechnologies, which provide economically important products for the country. The methodologies used to explore natural or cultivated capacities of plant species, aquaculture related issues, and environmentally friendly biotechnologies are conventional and advanced ones, however, results prove the need for improvements. Here are presented examples of the emerging molecular-based applications of agrobiotechnology, which may profit from the development of nano-biosensors. The choice of MAS with specific essential oils content is directly related to the TPS regulation, thus isolation and characterization of genes coding for these enzymes from local populations is done through homology-based PCR followed by sequencing. However, a number of disadvantages appear to damage the results: High similarity among genes coding for different monoterpenoids; Difficulties to determine which category of synthases does exactly the gene fragment codes for; High probability that some of the synthases are produced via post-transcriptional modifications; The development of immunosensors, which could detect respective terpene synthases from homogenates of medicinal aromatic plant species of economic importance and allow to measure the quantity per unit of volume of homogenate, would reduce disadvantages. Secondly, the understanding of the regulation of the expression of genes involved in local wheat resistance toward environmental stresses is a research direction strongly related to the emergencies on crop production because of climate changes. Glutathione-S-Transferases (GST) are responsible for degradation of ROS accumulated during stresses. However, the procedure for screening the GST gene expression level is expensive and time-consuming; Stresses (drought, salinity, HT) might induce synthesis of regulatory proteins, which repress the transcription of GST, thus, the detection and measurement of Rubisco activase via immunosensors could be of importance. Third, the early detection of of viral pathogens at in vivo and in vitro fruit-trees is important for the agriculture in Albania. The use of Multiplex-RT-PCR in many cases suffers from the primer pair competition, while single pair RT-PCR is expensive. The development of genosensors for the detection of mixed viral infections at plant material homogenate, based on the hybridization with known viral gene sequences, could serve the issue.

Keywords: UOT-University of Tirana, MAS-medicinal aromatic species, TPS-terpenoid synthases, PCR-polymerase chain reaction, GST-glutathione S transferase, HT-high temperature..

Nanoparticles and the ovary function: the negative effects on the follicular development and ovulation

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The continued increase in the application of nanoparticles (NPs) in many aspects of life is currently raising significant health concerns. Nowadays, NPs can be found not only in drug delivery systems and in clinical therapy but also in various daily used products such as cosmetics, clothes and food. Therefore, in addition to intentional application in medicine, the dermal, pulmonary, and gastrointestinal exposures are considered the three main exposure routes. The negative impact of NPs on human health depends among others from the properties of NPs such as shape, size, structure, dosage, material, surface-coating etc. [1]. It is well known that many types of NPs are able to pass certain biological barriers and exert toxic effects on various organs, such as the brain, liver, kidney and also ovary [2]. The recent evidences show that NP accumulation damages the physiology of the ovary by disrupting follicular development and ovulation process during the ovarian cycle [3]. The ovarian cycle is characterized by regularly repeating patterns of cellular proliferation, differentiation and transformation that accompanies follicular development, maturation and ovulation during the folliculo-luteal transition and corpus lutem formation [4,5]. Therefore any negative effect of NP in each of these physiological stages of ovarian function will cause irreparable damage to the reproductive processes, thus causing temporary or permanent infertility of various species. The possible molecular mechanisms of NTs cytotoxicity in the ovary tissue include inflammation, oxidative stress, apoptosis etc. [2]. There are evidences showing that NPs can enter both follicle cell types (theca and granulosa), affecting their normal function (steroid hormone production), particularly before ovulation [6]. In addition, there are clear evidences that exposure to specific NP can significantly alter levels of gonadotrophins (GnRH, LH, FSH) and steroid hormones (progesterone, testosterone, estradiol), that causes follicle atresia and anovulation, resulting in reduced fertility [7]. In conclusion this contribution will offer a comprehensive overview on the current state of knowledge regarding potential adverse effects of NPs on the ovary function. In addition, an improved understanding of the molecular mechanisms of NT toxicity during follicle development and ovulation has an obviously important implication for the reproductive health and regulation of fertility.

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Electrochemical sensor for monitoring nitrites based on glassy carbon paste electrode modified with electrochemically reduced graphene oxide

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Abstract. Nitrites, known as food additive potassium nitrite (E 249) and sodium nitrite (E 250), have a broader usage in food preserving, especially in meat technology [1,2]. A completely new, sensitive and selective voltametric method is presented as a suitable analytical tool for monitoring of nitrites content in meat products. This highly selective electroanalytical method utilizes a specific reaction of nitrites with ranitidine in an acidic environment to form an electroactive N-nitrosodimethylamine and 2-methylfuran cation with the corresponding side chain in the fifth position [3]. A cathodic reduction at −0.210 V of 2-methyl-2H-furan-3-one at GCE covered with a thin layer of ERGO and adsorbed SDBS surfactant was preferred to anodic oxidation of NDMA at +0.8 V due to the desired selectivity [4]. For evaluation using peak height, two linear ranges from 6.2 to 125 µmol L^{-1} and from 150 to 300 µmol L^{-1} nitrites characterized by R^2 of 0.9991 and 0.9963 with a detection limit of 1.89 µmol L^{-1} nitrites were found, respectively. If the peak-area-based evaluation is preferred, only one linear dependence described by a regression equation Ap^c (µA V) = 0.0079c (µmol L^{-1}) − 0.0442 with the R^2 of 0.9996 will be obtained Results of model samples and meat products shown that this electroanalytical method provides statistically identical values with the commercially available spectrophotometric assay, called as Griess Reagent Kit (G-7921).

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Anisotropic thermal conductivity of layered 2D $SnSe_2$

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Abstract

Thickness, temperature and degree of thermal anisotropy are critical parameters that affect the performance of layered two-dimensional materials in nano-electronics. Here, we systematically study the in-plane and cross-plane thermal conductivity of $SnSe_2$ films of varying thickness (16-190 nm) using two-laser Raman thermometry and frequency domain thermo-reflectance, respectively. We found that both in-plane and cross-plane thermal conductivities monotonically decrease with decreasing film thickness, showing a maximum of 2.5-fold reduction compared to the bulk values. The thermal conductivity anisotropy ratio obtained directly from the experiments was found to be thickness-independent and approximately of ~ 8.4. In addition, we find that the temperature-dependence of the in-plane thermal conductivity gradually decreases as the film thickness decreases. Upon increasing temperature, from 300 K to 473 K, we show that the in-plane thermal conductivity can be reduced more than a factor of 2. Furthermore, using the mean free path reconstruction method, we found that phonons with MFP ranging from 1-53 and 1-30 nm, contribute to 50% of the total in- and cross-plane thermal conductivity, respectively. These calculations are in very good agreement with previous theoretical prediction [1-2]. Our results provide guidelines for the design and thermal management of emerging two-dimensional electronic, optoelectronic, and thermoelectric devices.

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Figures

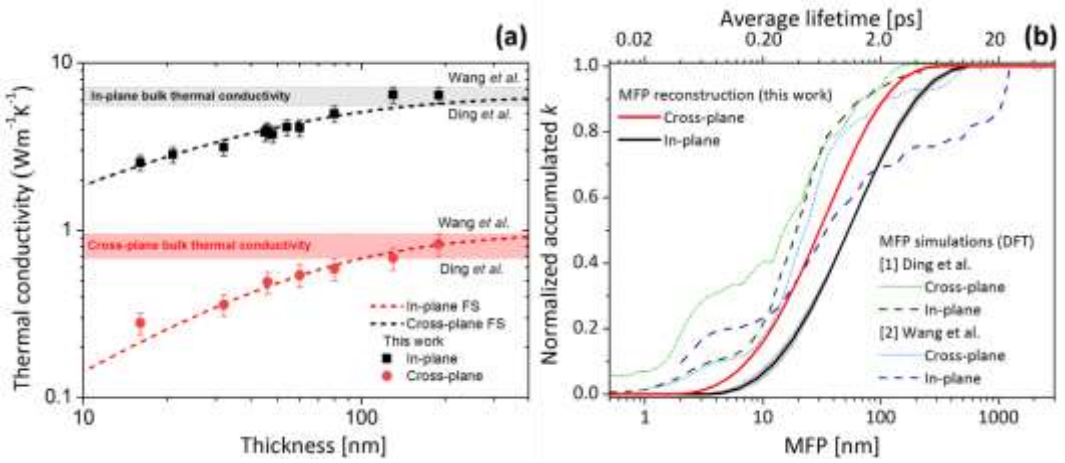

Figure 1. (a) Measured in-plane (black squares) and cross-plane (red circles) thermal conductivities of exfoliated SnSe2 films with thickness between 16 to 190 nm (b) Normalized accumulated in-plane and cross-plane thermal conductivity as a function of the phonon MFP extracted from experimental thermal conductivity.

A wearable sensor platform for sweat analysis

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Abstract

The increasing popularity of sports practice is rising the demand of smart wearable devices to track athlete performance and conditions during training and competition. In case of professionals, real time data concerning sweat composition and muscle fatigue may help coaches to take decisions based on facts rather than guess work and sport clubs to predict outcomes and minimize risks of injury. In addition, wearable sensors represent a possible solution for an enormous number of sports enthusiasts practicing in unsupervised self-training sessions who may be interested to monitor performances with minimal invasiveness and impediment. Here we show a voltammetric sensor platform exploiting laser induced graphene (LIG) electrodes fabricated on a Kapton® foil combined with a paper-based sampler for sweat analysis. LIG electrodes were fabricated using a CO_2 laser on a Kapton foil, and the conductive tracks were protected by an additional kapton layer. The device was used for the analysis for pH, resistance, uric acid, and tyrosine. While tyrosine and uric acid are naturally electroactive, sensor sensitivity to pH was obtained by drop-casting 1 µL of an aqueous solution containing an indoaniline derivative (4-((4-aminophenyl)imino)-2,6-dimethoxycyclohexa-2,5dien-1-one) [1]. A silver/silver chloride reference electrode was integrated in the device by electrodepositing silver on LIG from a silver nitrate solution thanks to the application of a negative voltage (-2 V) and a subsequent treatment with sodium hypochlorite. The reference electrode was finally coated with a Nafion® layer to prevent degradation. The device was calibrated using square wave voltammetry as transduction technique. The reported fabrication technique could be used to develop cheap and conformable pH sensors and may represent an improvement towards wearable sensor systems for personalized healthcare.

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Electroanalysis with metal (nano) film electrodes

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Continuously increasing interest in sensitive, selective and robust chemical sensors pose the need for intensive research aimed at developing novel sensing schemes and approaches. Currently, there is a particular interest in simple, portable, and inexpensive sensing systems that enable decentralized, point-of-care testing, detection at micro-locations, in micro- or nano-volume samples, detection of low/trace concentrations, and measurements without or with a minimal sample (pre)treatment. Among different analytical techniques, electrochemistry meets most of these criteria. It offers unique possibilities for tailoring powerful sensing systems for the detection of numerous inorganic and organic analytes relevant in environmental monitoring, biology, clinical diagnostics, pharmaceutical industry, homeland security, preservation of cultural heritage, etc. Practically unlimited selection of electrode and modification (nano) materials, and unsurpassed possibilities for sensor miniaturization, make the electrochemical sensing even more attractive [1].

In this presentation, the electroanalytical characterization of selected metal film electrodes will be discussed. It is well-known that the electrode surface structure considerably affects the sensors' performance; thus, the development and optimization of preparation protocols yielding different nanostructured modification/sensing coatings still represent a significant challenge. Among others, a nanostructured bismuth film electrode for the detection of trace lead and progesterone will be presented [2-4]. In addition, a copper film electrode will be shown as an interesting sensor for stripping voltammetric detection of trace lead, mercury, and nickel, and for a rather unconventional detection of nitroaromatic compounds [5,6].

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Digital health solutions from conception to clinical practice implementation: pain assessment example

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Digital health solutions are improving patient care across various health disciplines and are quite broad in terms of their scope. They include a variety of categories such as telemedicine, mobile health, wearable devices, personalized medicine, web-based health services and electronic health records.[1,2] The development of digital health solutions which are assisted by Artificial Intelligence (AI) has changed the landscape of how technology is used in healthcare. There are multiple studies demonstrating how AI has mimicked the diagnostic capabilities of health professionals. However, many of these AI supported solutions are in its infancy when it comes to real-world clinical practice implementation.[3]

Pain assessment in people unable to communicate is challenging because of their difficulties in reliably self-reporting their pain. For people with advanced dementia this is a major problem considering that up to 80% of this population group experiences pain and this pain often goes undetected and undertreated.[4,5] Often as a result of their undertreated or undetected pain they experience behavioural and psychological problems. Here we briefly present how a hybrid solution called PainChek® which uses face recognition technology, AI and smart automation was conceptualized, developed and then successfully implemented in clinical practice. Over 600,000 pain assessments have been conducted to date with this digital health solution. Pain assessment is also challenging in infants in whom poor management of procedural pain can have short-term and long-term consequences.[8,9] Here we also discuss a recently developed rapid automated digital solution that assesses procedural pain in infants at point of care.[9] The results of a recent feasibility study evaluating this digital solution supported the use of AI in the assessment of pain in infants, whilst acknowledging that its clinical practice utility requires further research. [9]

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Characterization of nanoparticles deposited on a thin film by using femtosecond pulse laser

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In a homemade vacuumed metallic chamber with Plexiglas windows, is placed a plate containing ZnO. A metallic plate is placed in front of the plate containing ZnO molecules. Femtosecond laser pulses are used in a procedure of the deposition of the ZnO nanoparticles in a thin film. A new procedure, applied at this experiment, made possible a thin film characterized with a homogeneous particle deposition.
Characterization of the film is performed by several techniques. Using an atomic force microscope (AMF) thickness , texture of the surface and roughness were visualized. Scanning electron microscope and–ray diffraction, were used to characterize the thin film layer of nanoparticles. Using the UV-VIS , the bandgap energy of the zinc oxide film was determined.
Keywords: Nanoparticles, Femtosecond laser, Thin film, AMF, ZnO

Nanomolecular structure and phase constituent quantification of multiscale UHPC using 29Si and 27Al MAS NMR, Nanoindentation and XRD techniques

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Abstract: ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (^{29}Si and ^{27}Al MAS NMR) investigations (quantifications) of the C-(A-)S-H nanomolecular structure combined with grid nanoindentation and quantitative X-ray diffraction (QXRD) of multiscale ultra high performance concrete (UHPC) have provided invaluable insights that correlate very well with the macroscopic behavior and properties of this innovative material. The UHPC samples were cured with and without microwave energy. The microwave-cured samples contain in total more hydration products that the one not cured with microwave energy. A nanocomposite (C-S-H/CHnm) that consists of high density (HD) C-(A-)S-H and nanoscale portlandite (CH) is contained, and its amount is more than double for the pressure compacted and microwave-cured sample. There is a higher degree of hydration and of polymerization for samples treated under elevated curing conditions (microwave curing) and especially for the ones that were additionally load-pressed. The incorporation of aluminum (AlIV) in the structure of C-(A-)S-H by substituting silicon leads to an increase in the degree of polymerization of the structure.

Keywords: Nanomolecular structure, phase constituent, multiscale UHPC, 29Si and 27Al MAS NMR, Nanoindentation, quantitative XRD

An autonomous perovskite solar park enabled by 2D materials interface engineering

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Organic–inorganic hybrid perovskite solar cells (PSCs) have revealed their potential as excellent solar energy conversion devices, reaching a power conversion efficiency (PCE) of 25.2%. However, their operational long-term stability, especially at outdoor conditions, remains the main obstacle impeding their commercialization. Engineering approaches to tackle these issues include the incorporation of two-dimensional (2D) interlayers (e.g., graphene and transition metal dichalcogenides) a process applicable also in large-area modules, the optimization of the doping and surface functionalization of 2D interlayers, as well the possibility of integrating passivation layers such as 2D insulators. On top of that, their compatibility with large-scale, solution-processable methods such as sheet-to-sheet and roll-to-roll lay the ground for their direct integration in pilot manufacturing lines, significantly improves the capital expenditure of this technology. In this context, a wide range of 2D materials have been used as replacements for conventional charge transport layers and interlayers not only to improve the charge dynamics of the devices but also to protect the perovskite layer against diffusion of external agents, such as oxygen and moisture and the metal ion migration.
In this talk, I will give an overview of our recent activities on the realization of highly efficient and stable perovskite solar cells and modules. I will give a holistic insight on how the hierarchical placement of 2D materials in all the perovskite device can tune the transport layers work-function, passivate the interface/surface traps and most importantly protect the interfaces, resulting in a simultaneously improvement of the triangle of performance, stability and scalability of the perovskite PVs. Furthermore, I will discuss the implementation of a Solar Park consisting of 2D enabled perovskite 0.5 sqm panels at the Hellenic Mediterranean University campus at Crete, developed under the Graphene Flagship initiative by the Hellenic Mediterranean University, University of Tor Vergata, Bedimensional and GreatCell Solar, in which outdoor field tests are currently performed. The continuous monitoring of the 2D -enabled solar park's performance is providing a better understanding of single panels reliability issues, while the concurrent benchmarking process against commercial PV technologies such as Si, CdTe and CIGS is allowing the assessment of their possible application in future PV system for on-grid electricity generation. I will also directly correlate the electrical measurements of the solar farm with environmental parameters, while at the same time, benchmark their outdoor performance against commercial PV panels installed at the same site. This study is a pivotal information on the commercialization potential of this technology.

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Modification of material surfaces with nanometric organic layers derived from aryl diazonium salts

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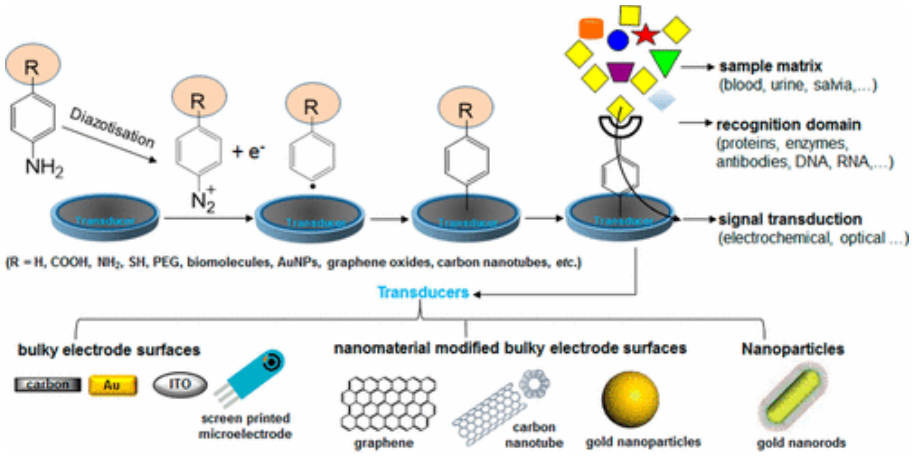
Abstract

Tethering material surfaces with very thin aryl films derived from aryl diazonium salts during their electro-chemical reduction is now a very common approach, Scheme 1. [1-4] The success of this method lies i) in the high reactivity of aryl radicals that attack surfaces of carbon (all types including graphene), metals and metal oxides and their nanoparticles, semiconductors including metal dichalcogenides MX_2, ii) the stability of covalently anchored layer and iii) the fast reaction that is performed under mild conditions.. [3-5] The attached organic layer improves the resistance of the materials toward their environment but it may serve also as a platform for further modification due to the presence of substituents in the benzene ring or for the attachment of nano-objects. This approach has found a lot of applications such as molecular junctions, optoelectronics, biosensors, click chemistry, composite materials, etc. [6-7]



Scheme 1. Aryl radicals are prone to attach to many materials surfaces. [4]

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Generation of nanoparticles by spark discharge: In-situ tailoring of the electrode surface with a 3D positioning device

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One of the most promising physical techniques for the generation of various types (metal, semiconductor, alloy or carbon) nanomaterials in the gas phase is spark discharge. The sparking process is conducted in the absence of any electrolyte, or template and relies on the application of an electric field capable of producing an electric discharge when the two conductors, being connected with an external power supply, are brought into close proximity (Fig. 1). The ensuing dielectric breakdown produces free electrons and ions originating from ionized molecules of air constituents, which in turn, bombard the sparked electrodes. Heat, introduced due to the flow of electricity leads to the formation of air plasma and vaporized (nano)particles by each electrode material at the closest points between the conductors.
In a straightforward electrode-to-pin approach between a low-cost graphite electrode and a metal, alloy or carbon tip (Fig. 1), the vaporized electrodes' material, eventually transformed by the reactions with the environment, e.g. oxidation in the presence of air, is positioned in the space between the two electrodes and upon the termination of the discharge, solidifies and deposited on the surface of the electrodes.
Results demonstrated an extremely simple technique for the generation of template-free nanoparticles of high purity that enables the in-situ tailoring of low-cost screen-printed electrodes while offering sensors with enhanced detection capabilities and a wide-scope of applicability. Sparked (single or mixed) metal or graphite nanomaterial-modified SPEs can be prepared on-demand, even on-site, within a few minutes or even seconds, through a totally green and solution-free methodology that requires only the respective metal/alloy/carbon wire and a power supply. Data on the generation of bismuth [1,2], copper, nickel and alloyed copper/nickel [3], tin [4], gold [5,6], iron [7], molybdenum [8] and carbon [9] nanomaterials as well as on the analytical utility of the resulting sensors will be presented.

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Figure

Figure 1. Setup for the in-situ tailoring of electrode surface with spark-generated nanoparticles

Rare diseases but common problems: Shwachman Diamond Syndrome from genetics to therapy through the combination of nanoscale techniques

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Shwachman-Diamond Syndrome (SDS) is a ribosomopathy with a wide spectrum of clinical presentations [1] associated with the loss of function of Shwachman-Bodian-Diamond Syndrome (SBDS) protein [2] and as we described for the first time [3], the Elongation Factor-Like 1 (EFL1).Together, these proteins remove the anti-associationfactor eIF6 from the surface of the pre-60S ribosomal subunit to promote the formation of mature ribosomes. Due to the lack of knowledge of the molecular mechanisms responsible for SDS pathogenesis, current therapy is nonspecific and focuses only at alleviating the symptoms. For that reason, we studied [4] the interaction mechanism of the proteins in solution and demonstrated that binding SBDS*EFL1 consists of two independent and cooperative events, with domains 2–3 of SBDS directing the initial interaction with EFL1, followed by docking of domain 1. In solution, both proteins exhibited large flexibility and consisted of an ensemble of conformations, as demonstrated by Small Angle X-ray Scattering (SAXS) experiments [4, 5]. SAXS is a powerful technique for structural investigation of macromolecules in solution as for nanoparticles in solution or in solid state. Building on the recent observation that EFL1 single-point mutations clinically manifest as SDS-like phenotype, we carried out comparative Molecular Dynamics (MD) simulations on three mutants, T127A, M882K and R1095Q and wild type EFL1 [6] combining with SAXS experiments. This study supports the notion that EFL1 function is governed by an allosteric mechanism involving the concerted action of GTPase domains and can help point towards new approaches to SDS treatment.

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Use of Nanoparticles in Biosensor Systems, Integration with Smartphones, Applications on Different Platforms

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Healthcare technology has recently been converting from centralized medical laboratories or hospitals to point-of-care (POC) diagnostic devices together with the advancements in micro and nano technologies as well as cloud computing. The need for a continuous, real-time monitoring of specific health conditions motivates the reduction of the gap between the available healthcare facilities and the demand, particularly in developing countries due to inadequate healthcare budgets [1, 2]. POC diagnostic platforms have the following properties: affordable, sensitive and specific, user-friendly, rapid and robust, equipment-free, and deliverable to those in need, namely 'ASSURRED' technologies [3]. Compared to controlled laboratory-based techniques, POC gives rapid and accurate results without being costly, thus, it is preferable especially in resource-limited areas [4]. Nanoparticles are easily synthesized and biocompatible, they can be surface-modified and mostly colored, due to surface plasmon resonance properties, to provide visibility, practicality, and efficiency in colorimetric analysis [5]. They also can be used as a signal enhancer molecule in electrochemical measurements [6]. With a surface modification, they can become carriers, targeting agents, or detection interfaces on different sensing platforms [7]. Due to the lack of integration and automation of the designs, most of the POC designs has either not been commercialized or widely established in the market. Both to automate and integrate the POC diagnostics to medical world, smartphone technology emerges as the obvious choice. There emerges a term 'mobile health (mHealth)' which aims to provide an immediate resource for clinical decision by the healthcare professionals, prescription information and other medical treatments for a better personalized healthcare [8, 9].

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Tailored Growth of 1D Carbon Nanostructures via Chemical Vapour Deposition and their Application in Advanced Nanocomposite Materials

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Carbon nanostructures and specifically nanotubes and/or nanofibres, are important materials in nanotechnology as a prime example of one-dimensional structures. Further development of this technology, as well as the use of these nanomaterials in a wide range of applications, depends on the availability of these nanomaterials at reasonable prices and feasible quantities. The aim of this study is the synthesis, modification and use of nanotubes and/or nanofibres in a range of demanding applications that are mainly used in the construction sector, exploiting their unique properties. The growth of the carbon nanostructures, their proper chemical modification which has been selected according to the application, and finally the evaluation of the properties of the final nanocomposite material in which the nanomaterials are used, have been considered.
For the tailored growth of the fibrous carbon nanostructures, thermal chemical vapor deposition technique (T-CVD) has been chosen, which is preferable for the synthesis of large amounts of carbon nanotubes, as it allows easy control of parameters and is accompanied by lower energy requirements [1]. Two main routes of developing one-dimensional structures have been considered: the supported catalyst approach where, acetylene is used as carbon source, and catalysts are synthesized in house with transition metals and porous substrates, as well as the floating catalyst approach, in which both the precursor compound and the carbon source are simultaneously introduced into the reactor in vapour form [2]. The results from the use of the produced nanostructures in a range of applications are presented. In particular, nanotubes and/or nanofibers are first tested in polymer nanocomposites [3], such as epoxy resins [4] and organic coatings [5], in cement mortars [6], and finally in electronic applications (e.g. supercapacitors) [7].

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Characterisations of raw material derived from natural sand of albanian coastline-possible applications

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Abstract

In this work the natural material derived from sand of Albanian coastline is studied. The raw material is obtained from the quartz sand processing plant (the former called coastal sand enrichment department). The structural characterization of the material is performed using SEM and XRPD analysis. From the results it can be concluded that the raw material represents a conglomerate of several minerals[1]. The presence of rutile is identified, although in small quantities. The main mineral is magnesium ferrite followed by quartz and titanium magnetite. The others are in minimal quantities. Based on the chemical analysis with ICP-MS, the chemical composition of the material was determined confirming the presence of TiO_2 (2.50%), Fe_2O_3 (24.07%) and Cr_2O_3 (2.65%). The effect of TiO_2 has been proven in many studies for different applications[2]. We have tried to study two applications of this titanium magnetite containing material: i) the adsorption capacity to Cu by means of adsorption kinetic models [3]and ii) the analytical performance of modified carbon paste sensor using redox couple Fe(III)/Fe(II) and determination of b-blockers in environmental water systems.

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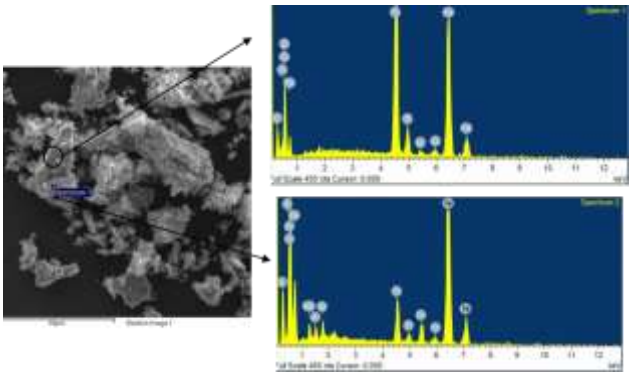

Figure 1. SEM analyses of mechanical activated material

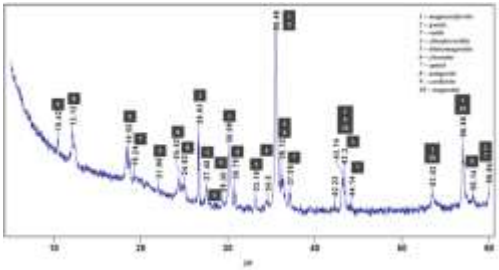

Figure 2. X-ray diffractogram of the raw material

The influence of order/disorder phenomena and nanoscopic defects on the thermoelectric properties of In_5Ch_5X (Ch = S, Se; X = Cl, Br)

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Abstract

The mixed-valence compounds In_5S_5Br, $In_5S_3Se_2Br$, In5SSe$_4$Br, and In_5Se_5Br crystallize in the orthorhombic SG *P*mn2$_1$ and reveal real structures with no anomalies while consisting of 3:3 arrangements. Interestingly they show thermoelectric properties. As the selenium content in the structure of In_5S_5Br increases, the Seebeck potential increases. In_5S_5Br exhibits low Seebeck potentials within the studied range (ΔT = 0–80 K) and a maximum value of 0.34 mV for ΔT = 80 K. It behaves as a *p*-type semiconductor. The substitution of two sulphur species by selenium, as in $In_5S_3Se_2Br$, shows *n*-type conductivity and approx.−16.00 mV for the same ΔT. Further substitutions of sulphur in the structure maintain the *n*-type conductivity and increase dramatically the Seebeck potential to -225.26 mV (ΔT = 80 K). Repeating cycles of Seebeck potential variation over time for In_5Se_5Br and In_5SSe_4Br, show differences in their potentials, shape of maxima as well as in their recovery time. Electrical conductivities from 0.3 pS for In_5S_5Br up to 13 pS for In_5Se_5Br, strongly influence their thermoelectricity. In contrast to In_5Ch_5Br (Ch = S, Se), the non isotypic sibling compounds In_5Ch_5Cl obtained by full substitution of bromine with clorine, presented a variety of anomalies in their real structure. Beside the existence of the 4:2 and 2:4 arrangements (observed from the average structure) the HRTEM images and the SAED patterns evidenced the existence of layers with 3:3 arrangements within the structure. In addition, their real structures reveal the presence of polymorphic intergrowth of layers with different arrangements, the polysynthetic twinning and the intergrowth of large separated domains containing In_6S_7. Similarly to In_5Ch_5Br (Ch = S, Se) they behave as *p*- and *n*-type semiconductors but show no thermoelectric properties. The extinction of the thermoelectric properties of In_5Ch_5Br (Ch = S, Se) is merely atributed to its structural anomalies.

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Carbon-based nanomaterials in electrochemical sensing: the role of oxidized functional groups

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Non-invasive sensors, which accurately measure biomarkers of physiological interest in biological fluids, can allow a more personalized approach to fitness goals and to health monitoring. As an example, important analytes such as glucose and lactate, present in sweat, can be monitored by enzymatic biosensors exploiting an electrochemical transduction. In addition, some drugs of abuse can be detected in urine and saliva samples by exploiting their direct electrochemical oxidation on a conducting substrate [1]. In all these cases, the use of carbon-nanosized materials as the sensing element can strongly improve the efficiency of the electrochemical detection.

This presentation will discuss the role played by different oxygenated functional groups spontaneously present on carbon-based nanomaterials in the performance of the resulting sensor system [2]. Their direct interaction with target analytes and their role in stably fixing suitable bioreceptors will be addressed trying to find a correlation between the chemical composition of the material and the analytical performance finally obtained. Results coming from electrochemical, spectroscopic and morphologic analyses are combined to obtain new insights on the role played by different moieties in electrochemical sensing. This approach allowed us to direct the synthesis of the material acting as the sensing element in order to obtain sensors working at best for the specific application sought. Examples discussed in this presentation will include sensors exploiting graphene oxide, carbon nanotubes and carbon black (Figure 1), finding common behaviour among these nanosized materials.

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Figures

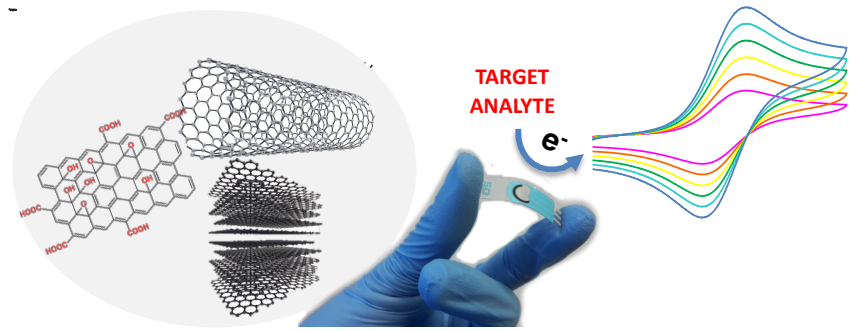

Figure 1. Approach to electrochemical sensing by carbon nanosized materials

Low energy ion beam induced pattern formation on Si and Ge surfaces

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Abstract
The fabrication of regular nanostructures on the nanometer length scale builds the basis for many technological applications in variety of fields, from optics to optoelectronics, to biological optics, to templates for the deposition of functional thin films, and to data storage industry. One effective method is the low-energy ion beam erosion of solid surfaces that is a widespread technique used in many surface processing applications. For particular sputtering conditions, due to self-organization processes, the surface erosion process can lead into well ordered nanostructures on the surface like ripples or dots.
Typically, during ion sputtering, the surface of the solid is far from equilibrium and a variety of atomistic surface processes and mechanisms become effective. It is the complex interplay of these processes that either tends to roughen (e. g., by curvature dependent sputtering or incorporation of surface contaminations) or smoothen (e. g., by surface diffusion or viscous flow of surface atoms) the surface, which, finally, can result in a rich variety of surface topographies.
In this talk the current status of self-organized pattern formation by low-energy ion beam erosion is summarized. In detail it will be shown that a multitude of patterns can evolve on the surface with a periodicity from 30 nm to 100 nm.[1,2] Furthermore a successful combination of conventional lithographically nanostructuring techniques with the ion induced self-organization processes that leads to hierarchical nanostructuring will be presented.

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Figures

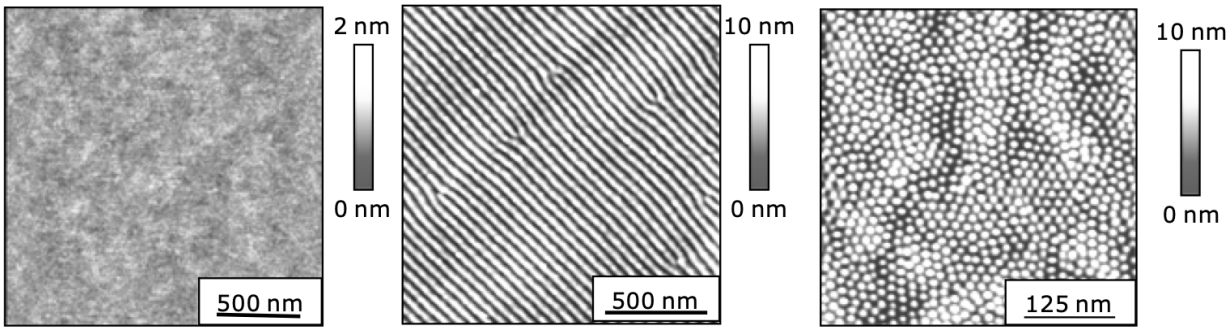

Figure 1. AFM images of Si surfaces after low energy ion beam erosion.

A novel technology for automatic testing of the screen printed electrodes

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Screen printed electrodes (SPEs) have been serving as a platform combining electrochemistry and nanotechnology in area of sensors and biosensor for couple of decades. When the current application requires to use miniaturized analyzing system the using of the SPEs is often the choice. Many different concepts and constructs with different materials have been reported [1], however, one may ask a question what is the real potential of this platform? Each analytical method needs to meet one parameter before we can call it "analytical method" and further we can start to compare in between. This parameter is called repeatability. Does the use of the SPEs as a platform suffer from the lack of repeatability? How can we easily estimate the repeatability of SPEs? Manual testing means to carry out hundreds of measurements. This brings many types of unavoidable errors [2].
Since we believe in the future of the SPEs as a platform for sensing and further for robust point of care testing (POCT) and other applications, as environmental or emergency, we designed and successfully tested automatic bench top device for SPEs testing, which is shown below. This platform will be discussed including advantages and further steps in development of this instrument.

References

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Figures

Figure 1. Fully automatic bench-top device for testing of SPEs driven by a tablet PC with user friendly SW (on left). SPEs in specially designed container preventing scratching of the active side and pins of the SPEs (on right).

ORALS
contributions

Controling the orientation of single fluorescent dyes using the DNA origami technique

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Abstract
Over the last decade, DNA nanotechnology has been increasingly used to self-assemble functional nanostructures. One of the main advantages of this approach is that different species including high quality colloidal nanoparticles and single photon emitters such as fluorophores can be positioned with nm precision and stoichiometric control [1]. In order to fully manipulate the interaction between these species, a key factor for mthe development of nanophotonic devices, it is necessary to not only control their relative position but also their relative orientation. We have recently shown that fluorophore incorporation to DNA origami structures by a covalently bond to the single stranded DNA (DNA Staple) using a single anchoring point leads to a broad distribution of orientations [2]. Alternatively, some fluorophores such as Cy5 can be covalently incorporated to the DNA staples through two anchoring points at the ends. Therefore, fluorophores incorporated in this way could be "stretched" by "pulling" from the ends and thus deterministically oriented along the main DNA double helix. In this work, we study the orientation of Cy5 fluorophores incorporated in this way using two independent measurements carried out in a standard wide-field fluorescence microscope [2]. First, the orientation of the absorption transition dipole of the molecule is determined through a polarization-resolved excitation measurement. Second, the orientation of the DNA origami structure is obtained from a DNA-PAINT nanoscopy measurement (Figure 1). Our results show that single fluorophores attached with two anchoring points can adopt different orientations on a DNA-origami, from perpendicular to aligned with the double-helix depending on the number of bases removed from the complimentary sequence (Figure 2). We consider that this work is a first step towards the orientation control of single fluorophores in DNA origami structures, that will enable the development of more efficient and reproducible self-assembled nanophotonic devices.

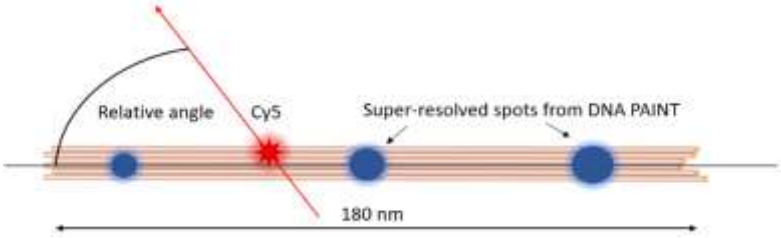

Figure 1. DNA origami sketch with incorporated fluorophore and 3 super-resolved spots from the DNA PAINT measurements. The relative angle is an angle between the DNA origami structure and the transition dipole moment of the Cy5.

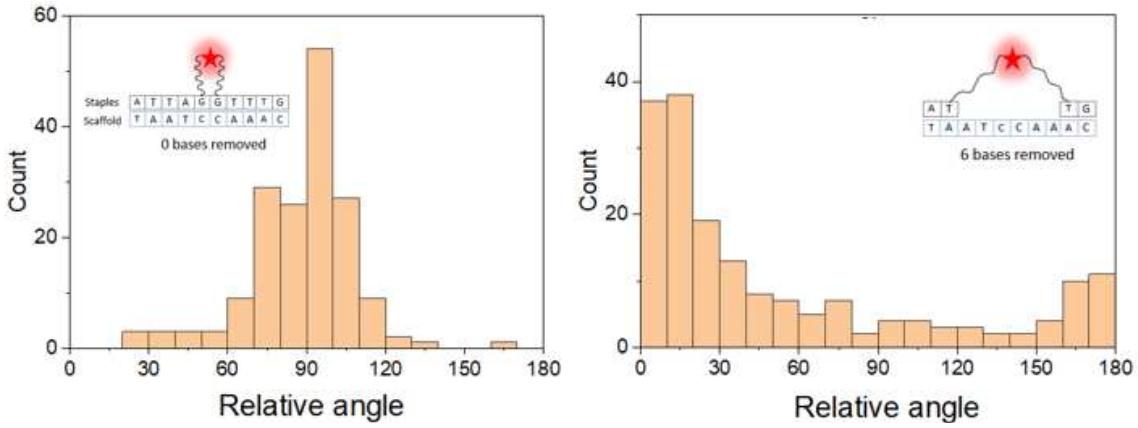

Figure 2. In plane orientation of the excitation transition dipole moment of Cy5 with respect to the DNA origami structure for two different samples where no bases (left) or 6 bases (right) were removed from the sequence and a fluorophore was attached covalently with two anchoring points.

References

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The influence of “Edge efefct” on determining the diffusion constant of Helium gas in ULE glass

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In recent years, new methods of calibrating gas pressure measurements are being developed, toward replacing primary standard of the SI unit of pressure, Pascal, by the quantum-based standard definition of it. In this context, many electromagnetic and thermodynamic properties of gases are expected to be more accurately measured and/or calculated. In this paper, we present a method, which we used to determine the diffusion constant of Helium in ULE glass, by means of outgassing rate dependence on time. We have used experimental data [1] for the dependence of the outgassing rate on time for three different ULE glass plates, with different geometrical dimensions. Instead of considering the plates semi-infinite, as it is usually done in most of the literature, we took into account all three dimensions of the plates by considering them rectangular shaped parallelepipeds and worked out the mathematical model of outgassing rate vs. time. Then, we found optimal value of the diffusion constant D, for which the mathematical model best fitted the data. Optimal value was obtained by least square method of fitting. From the computed values, we found the mean and uncertainty related values of D. Then we compare this result with the result of the semi-infinite model, and by this comparison, we can calculate the effect of the edge of the plate in determination of diffusion coefficient.

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Resistive Memories for automotive applications

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Abstract

Emerging memories are gaining a lot of interest from academia and industry mainly by the increase of market of electronic components such as smartphones, tablets, automotive and applications such as VR, IOT, edge computing etc. With the increase of data volumes to Tbit and beyond, there is a constant research to find alternative solutions to Flash and DRAM which dominate the memory market. These technologies begin to face scaling and cost/bit limitations when applied to high volume manufacturing [1,2]. Among different alternatives proposed in the literature, Random-Access Memory (RAM) is a promising candidate. RRAM is a non-volatile memory technology, where the resistance of the memory element is modulated from conductive to insulating state by an electric field as shown in Fig. 1. In order to overcome the endurance-retention trade-off [2,3], bilayer RRAM device with resistive bilayer are proposed in literature, allowing to improve the memory performances with respect to monolayer reference technology. In reference [3,4], Al_2O_3 is studied because of the lower reset current, possibly due to a large band gap (8.9 eV) and its low power/energy consumption is attractive for memory applications. Thermal stability up to 250°C for a baking time 10^5s is shown in Fig. 2a. The high resistive state (HRS) increase is due to a longer insulating gap in the resistive layer after the RESET operation. Endurance of 10^5 cycles (compared to 10^4 cycles for the reference monolayer sample) maintaining a memory window of 1 decade is shown in Fig.2a. This improvement is due to the reduced stack degradation and the mitigated defect generation in the resistive layer during cycling [3, 4]. These properties make the technology as one of the most promising candidates among emerging memories for automotive applications. Considering the low power and cost/bit, RRAM technology is also suitable for machine learning and neuromorphic applications.

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Figures

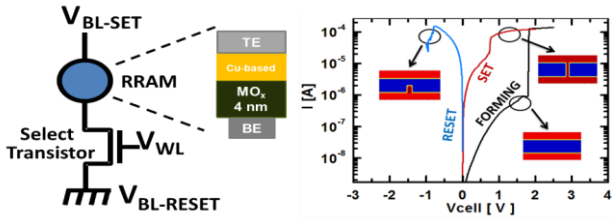
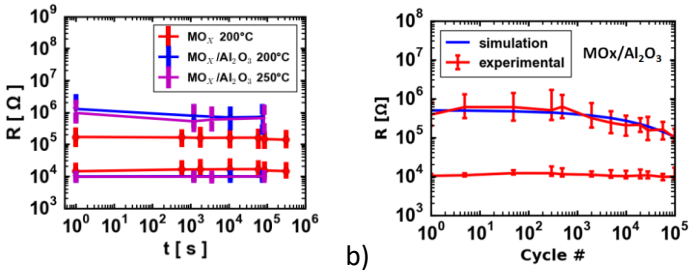


Figure 1. RRAM integrated in 1T1R configuration and its DC IV cell characteristics during SET/RESET [3].



a) b)

Figure 2. Reliability study of 1T1R array in terms of a) Endurance up to 1E5 cycles and b) Retention up to 250°C/24hrs [4].

Nanoscaled control of VO_2 insulator-to-metal transition by plasmonic single-nanoantenna

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It is well-established that, when illuminated at the right wavelength, gold single nanoantennas feature plasmon excitation [1]. This plasmon excitation gives rise to, among other effects, electromagnetic field concentration close to the antenna surface, which allows to manipulate light at the nanoscale by strengthening the light-matter interaction and the nonlinear response. Active materials, i.e., materials whose properties change under the application of an external stimulus, are often combined to plasmonic antennas to obtain metasurfaces with enhanced optical properties [2,3]. Among these materials, the VO_2 phase transition material is one of the most studied owing to its insulator-to-metal transition, induced by heating, occurring at relatively low critical temperature (68°C) [4].
Here, we exploit a laser-induced pumping effect, obtained by placing a single gold nanoantenna on top of a VO_2 film, to steer the phase transition in the VO_2 thermochromic material. In this combined experimental-theoretical study, we show how the size and permittivity of the nanometer-scale VO_2 regions where phase transition occurs is affected by the geometry of the single nanoantenna under different pumping conditions. It turns out that a higher VO_2 phase transition effect is obtained for pumping of the longitudinal or transversal localized surface plasmon depending on the antenna length. Moreover, we demonstrate that the antenna-VO_2 hybrid is characterized by a picosecond dynamics, useful for the realization of fast nano-switches.
The determination of the key parameters underlying the antenna capability of inducing the phase change and producing a hybrid nonlinear optical response is desirable for the design and realization of optimized nanostructures, such as nanoscale nonlinear optical devices and switches.

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Figures

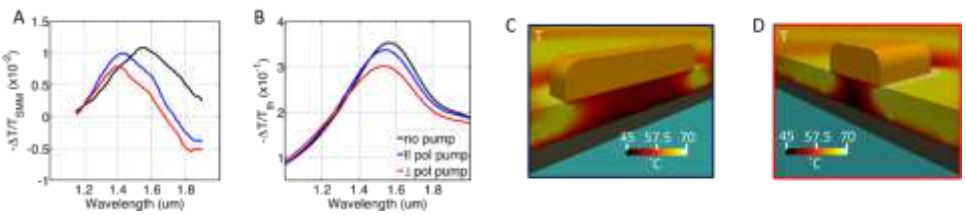

Figure 1. Measured normalized spatial modulation transmission and (B) simulated normalized differential transmission of the system as a function of the probe wavelength. (C, D) Colormap of the simulated temperature in the system under pumping (C) parallel and (D) perpendicular to antenna length.

Binding of alkyl radicals onto graphene - a DFT study

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Grafting alkyl groups onto graphene remains an open question in terms of their geometry, binding strength, the type of the created bond, and the activation energy required for such a process to occur. To further understand the grafting process, we used Density Functional Theory (DFT). A 5x5 armchair hydrogen-passivated graphene monolayer was used as a study model for this purpose (Figure 1). The surface concentration and distance between the attached alkyl groups provided critical information about their influence on the interaction strengthening caused by the cooperative actions of the first grafted group on the second [2].

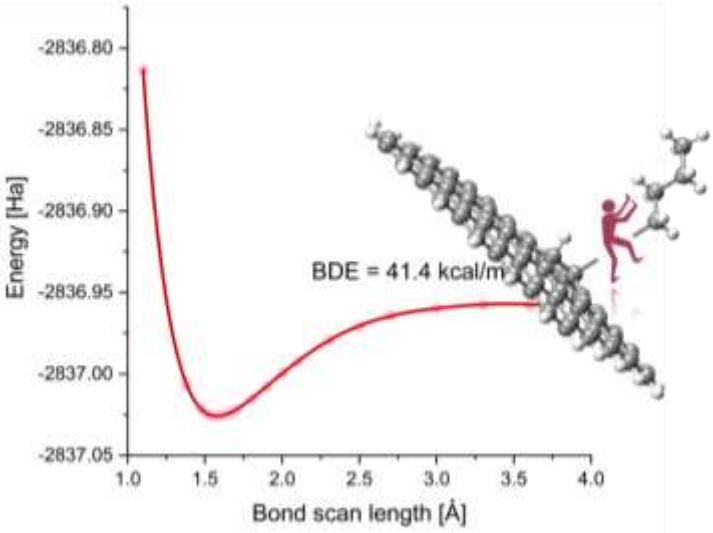

Figure 1. Bond Dissociation Energy (BDE) of the grafted graphene surface (5x5 ZigZag hydrogen passivated model).

When the bonded alkyl moieties possess functional groups, as demonstrated by Molecular Dynamics, this provides an easy way to alter graphene's dispersion properties. The Density Overlap Zones Indicator (DORI) analysis was used to visualize both covalent and noncovalent interaction regions simultaneously using a real space function. The two-dimensional electron localization function plot and three-dimensional DORI surface demonstrate unequivocally the covalent bonding between the alkyl radical and the graphene surface. The same conclusion is drawn from the computed Laplacian Bond Order (LBO), certainly proving once again the bond's covalent nature.

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A Label-free impedance biosensing assay based on CRISPR/Cas12a collateral activity for bacterial DNA detection

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The rapid and selective identification in the clinical setting of pathogenic bacteria causing healthcare associated infections (HAIs) is a major challenge, as the number of people affected worldwide and the associated mortality are on the rise. In fact, traditional laboratory techniques such culture and polymerase chain reaction (PCR)-based methodologies are often associated to high response times and are not able to response of this issue. Recently, a new class of programmable endonuclease enzymes called Cas proteins associated to clustered regularly interspaced short palindromic repeat loci (CRISPR) has revolutionized molecular diagnostics and biosensors field [1]. In this study, we present an electrochemical label-free biosensing assay based CRISPR/Cas12a to detect *Escherichia coli* (*E. coli*) and *Staphylococcus aureus (S. aureus)*. The programmable Cas12a endonuclease activity, induced by a specific guide RNA (gRNA), and the triggered collateral activity were assessed in in vitro restriction analyses (Figure1 a,b), and evaluated thanks to electrochemical impedance spectroscopy measurements using a modified electrode (Figure1c) [2]. The Cas12a/gRNA system was able to specifically recognize amplicons from different clinical isolates of *E. coli* and *S. aureus* with a limit of detection of 3nM and a response time approximately of 80 minutes.

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Figures

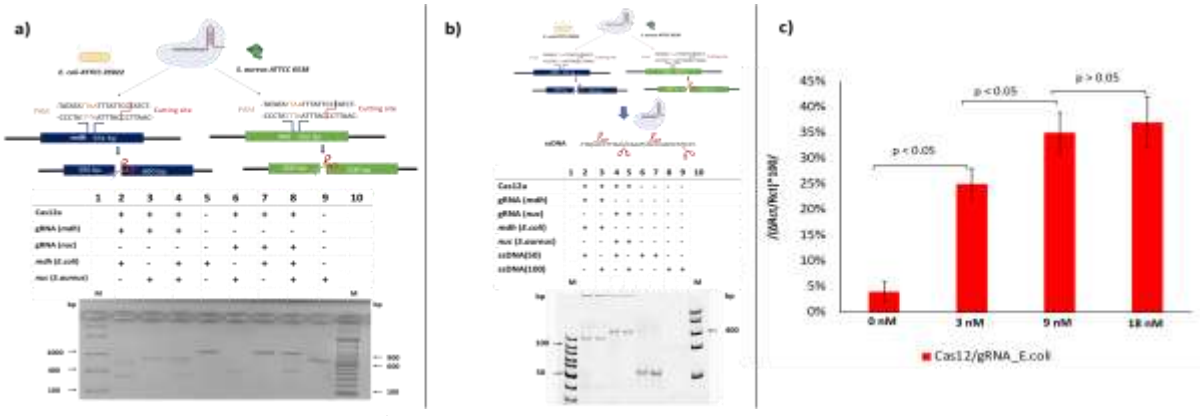

Figure 1. a) Visualization of the CRISPR/Cas12a cleavage specificity on a 1% agarose gel; b) 10% PAGE in TBE 1X. The gel shows Cas12a collateral activity upon cleavage of a ssDNA reporter; c) EIS Biosensing assay calibration response of Cas12/gRNA Vs E. coli target in the range from 3nM to 18nM .

Ceramics for Supercapacitors: B_4C and ZnO

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The problem of energy storage will be one of the most urgent scientific and technological challenges of the 21st century due to increasing demand for the use of renewable energy sources. Supercapacitors (SCs) can deliver considerable amount of energy at high power in a very short time owing to their much higher power density, considerably faster response times and much longer cycling life when compared to batteries. The main drawback of SCs is their low energy density. Hence, the development of new device configurations and novel nanostructured electrode materials is necessary because the working mechanism of SCs is highly dependent on the device design, the type of electrode materials, morphology, crystal size and defect structures.

In this work, a novel SC design comprising boron carbide (B_4C) and zinc oxide (ZnO) based electrode materials will be presented. Recent studies showed that semiconductor ZnO nanocrystals exhibit hybrid supercapacitor mechanism due to their intrinsic defects [1]. On the other hand, in addition to its superior thermal and chemical properties, B_4C is known as the hardest material produced in tonnage quantities for commercial applications [2]. Although there are a few studies in literature on its use in electronics and energy applications, there is very limited information regarding its use as an electrode material for SCs. It is reported that both B_4C and ZnO are semiconductors and have interesting defective and capacitive properties [1, 3]. In this study, B_4C powder was synthesized via modified sol-gel process at low temperatures (≤1500°C). The defective properties of the B_4C and ZnO were investigated using state-of-art Electron Paramagnetic Resonance (EPR) and optical techniques such as photoluminescence (PL) and UV-Visible spectroscopies. Electrical measurements of SCs were performed via potentiostatic electrochemical impedance spectroscopy (PEIS), cyclic voltammetry (CV) and galvanostatic cycling with potential limitation (GCPL) techniques. The electrochemical performance of the SCs will be discussed.

Acknowledgement

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Selection and characterization of bioreceptors to develop nanoparticle-based lateral-flow immunoassays under COVID-19 pandemic

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The ongoing COVID-19 pandemic has shown the importance of developing reliable yet easy-to-use, cheap, fast, and portable diagnostic devices to support mass-testing. [1-3] As suggested by World Health Organization (WHO), in order to meet such a high demand of testing, countries have been relying on Lateral Flow Assays (LFAs), due to their inherent features, *e.g.* fast, low-cost, user-friendly.
The selection of a suitable bioreceptor is not an automatic step in the development of LFA. Detailed information on binding affinity and association kinetics is not always found in commercial antibodies, thus creating a scenario in which new antibodies have to be tested in a trial and error fashion. With the motivation to develop a LFA to detect SARS-CoV-2 nucleoprotein, we implemented a two-step methodology to screen antibodies for their suitability as bioreceptors in LFA, consisting in: (1) enzyme-linked immunosorbent assays (ELISA), to quickly check antibody binding performance; and (2) half-stick format LFA, to check their compatibility with the conditions encountered in a LFA (*i.e.*, under a constant flow in a nitrocellulose membrane). Up to 80 antibody couples have been tested, of which only 4 were deemed suitable to be used on the final half-stick LFA format. The entire selection process required over 10 months and ~25,000 €. Herein we raise the issue as to whether antibody producers should implement more extensive characterization of their products, which in turn would definitely help the research community in their purchases.

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ZnO nanoparticle-assisted synthesis of porous interface molecularly imprinted polymeric nanofilm for electrochemical antidepressant sensor

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Abstract
Increasing population and economic activities lead to the release of anthropogenic contaminants, including pharmaceuticals, into the environment. Additionally, antidepressants, especially Fluoxetin (FLX), can undergo 26 transformation products (TPs) which causing a non-negligible impact on human health and ecosystems [1]. This study designed a new strategy to fabricate molecularly imprinted electrochemicals sensors for a novel aspect of molecular imprinting technique, utilizing sacrificial metal oxide nanoparticles [2]. In the first step, the molecularly imprinted polymeric film was fabricated on the glassy carbon electrode (GCE) using 2-hydroxyethyl methacrylate (HEMA)/N-methacryloyl-L-Phenylalanine (MAPA) as basic monomer/functional monomer in the presence of ethylene glycol dimethacrylate (EGDMA) as a cross-linking agent by photopolymerization to produce selective fluoxetine detection. Then, a series of molecularly imprinted polymeric films were synthesized using different template/functional monomer/cross-linking monomer ratios. The ratio of HEMA/EGDMA and MAPA/FLX in the monomer mixture was varied as 5:1, 4:1, 3:1, 2:1, and 1:1. The surface morphology of membranes was studied by scanning electron microscopy (SEM) with diameters ranging from 10 nm to 200 nm. The etching of sacrificial materials, zinc oxide particles were completed in only 15 min by applying 10 mM HCl solution, which also facilitated easy removal of the template and reversible binding during later use. This novel design with multiple recognition sites is quite simple and suitable for detecting antidepressants even at very low levels.

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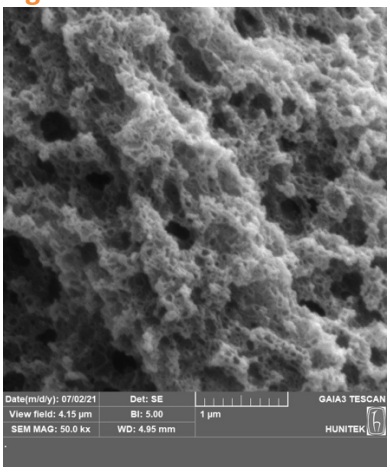

Figure 1. SEM images of the porous molecularly imprinted polymeric nanofilm surface

Laser carbonization of Carbon composite for flexible electronics

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Laser-fabrication methods have been investigated as fast, energy-saving, low-cost, and precise material processing techniques in both science and industry recently and thus direct laser-induced materials synthesis has become an active field of research. As it allows for high-precision materials modifications with unprecedented accuracy, suggests the use for manufacturing several electronic and photonic products. In most cases, graphene is produced by laser-induced reduction of graphene oxide (GO). GO, a 2D nanomaterials with sp^2 hybridized thick sheet bears abundant oxygen-containing groups, such as hydroxyl and epoxy groups on the basal planes of GO and carboxyl groups at the edges of GO. Carbon nanotubes (CNTs) with one dimensional (1D) structure, possess excellent mechanical strength, extraordinary heat transfer capability and electrical conductivity. These properties make them promising materials for wide range of applications in nanotechnology. However, due to strong Van der Waals force applications in CNTs causes hydrophobicity and chemical inertness. They usually entangle with each other, as a result difficult for dispersion which limits their commercial applications. To solve this technical problem, the CNTs are tailored with surface modifications using chemical reactions. Various acid treatments are introduced to modify the CNTs surface structure, mild oxidation with acids yielded higher concentrations of carbonyl and hydroxyl functional groups while more aggressive oxidation form higher fractional concentration of carboxyl groups. These kind of approach are based on CH–π, hydrogen bonding or electrostatic interaction to adsorb functional groups on CNTs surface without any impairment of the original tube structure of CNTs. Thus, GO can be used with functionalized CNT to construct 3D GO/CNT hybrids through π-stacking interaction formed between the π-conjugated multiple aromatic regions of GO sheets and walls of CNTs. There may present another interaction in between the functional groups present in GO with oxygenated surface groups of modified CNTs. Due to this synergistic effect, this composite become an improved material for laser treatment. In this study, the electrochemistry of this hybrid structure is investigated as electrodes in bend form. R-GO/CNTs composite is initially characterize with FTIR and Raman spectroscopy and significant shifting in peaks with peak ratio from precursors indicates the presence of the composite further supported by XRD and XPS analysis. SEM and STEM were performed to investigate the dispersion and morphology of the composite. Carbon nanodots (0D) having amine and carboxyl group outside, can anchor with functionalized CNT to having two different kinds of sp^2 domain inside the lattice. In another hand metal enriched CNDs have great application in electrocatalysis, CO_2 reduction. Possible advantages of the changes induced by the metal embedded in the CND include increased photo stability, fluorescence enhancement. These hybrid material is useful as EDLC in terms of capacitance and improved stability make this composite a better material for the future applications.

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MoS_2-Based SERS sandwich immunoassay for liver cancer biomarker detection

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In 2020, there have been 19.3 million new cases of cancer detected worldwide and 9.9 million cases leading to death. Early detection of cancers with highly sensitive diagnostics is highly necessary to reduce the amount of cancer related deaths. With the current diagnostics tools, the cancers are generally detected only when the cancer biomarker levels are relatively high in biological samples, and the treatment is not anymore that effective. In particular, liver cancer is one of the most common and highly dangerous cancer types in the world.[1] There are no effective therapeutic options if an early liver cancer diagnosis is not achieved. Among various analytical techniques, Surface-Enhanced Raman Scattering (SERS) technique is one of the most promising methods in detecting trace amounts of molecules owing to its high molecular specificity and high sensitivity.[2]

In this work, we developed a sandwich SERS-based immunosensor using gold-silver core-shell nanoparticles modified MoS_2 nanosheets for the ultrasensitive detection of liver cancer biomarker, which is typically present in human serum and utilized for the monitoring of early stages of hepatocellular carcinoma.[3] The sandwiched immunosensor exhibited an extraordinary SERS activity and analytical performance with a low detection limit at as good as fM level towards the cancer biomarker. The proposed immunosensor has promising potential to be used as an alternative analytical platform for the detection of early-stage cancer biomarkers in clinical applications.

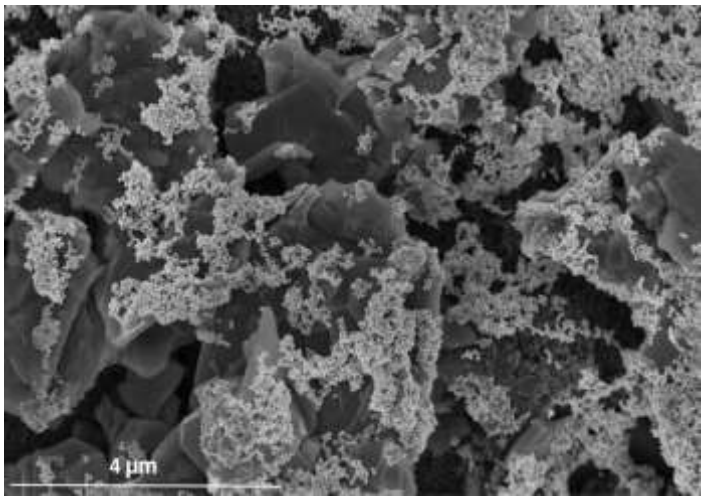

Figure 1. Au-Ag core-shell nanoparticles decorated MoS_2 nanosheets

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Inkjet-printed Two-Dimentional Material Biosensors on Flexible Substrates

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Point-of-care (PoC) diagnostic technology is poised to be a key tool for addressing some of the complex healthcare challenges faced by a growing and ageing global population. Without the utilization of diagnostic tests, patient diagnoses are little more than educated guesses based on anecdotal descriptions, regularly resulting in misdiagnosis and mistreatment.[1] By moving sensing devices away from the lab, PoC devices offer rapid, cheaper, patient centred care.[2] In the myriad of proposed sensor technologies, two-dimensional materials (2DMs) have risen as promising candidates owing to their unique combination of characteristics.[3] Graphene for example, is a stable biocompatible, semi-metal with high mobility which is well suited for sensing of biologically relevant analytes.[4] Moreover, 2DMs can be dispersed as inks – combining conducting, insulating and semiconducting inks together offers a route for economical, flexible printed electronics devices on a wearable platform. However, there persist challenges in producing stable, high-concentration inks for scalable production of such printed electronic devices made using 2DMs.[5]

In this work, we demonstrate inkjet-printed field-effect transistors on rigid and flexible form factors for wearable applications. In our work, transistor structures were printed by utilizing graphene inks as the active channel area, h-BN inks as the dielectric material and MXene and silver inks as the electrodes. A systematic analysis of alcohol-polyvinylpyrrolidone (PVP) based 2DM inks was carried out to improve stability and achieve concentrations ranging from 0.1 mg mL^{-1} to > 10 mg mL^{-1}. Raman spectroscopy indicated that the inks comprised of electronically decoupled layers of graphene. The lateral flake size was characterized by AFM, SEM and TEM, with a likely modal average of 0.4 – 0.5 µm within a range of flakes extending between 0.2 µm and 5 µm and flake thicknesses of up to 30 nm. The synthesized inks were then inkjet-printed and characterised as solution-gated and back-gated structures and their field-effect mobilities measured. Finally, we also demonstrate how the transistor performance can be modulated as a function of the analyte of interest, establishing their viability for printed large-scale biosensors.

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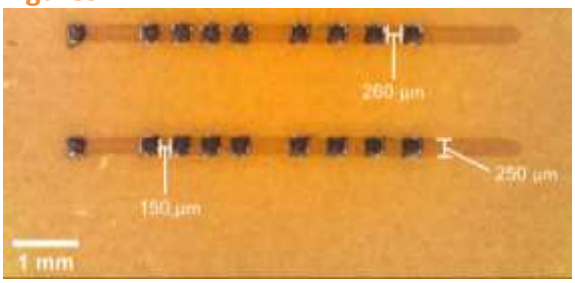

Figure 1: Inkjet-printed graphene field effect transistors with silver electrodes.

Photocatalytic activity Enhancement: a New Vision

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Abstract (Calibri 11)

Semiconductor photocatalysis has received much attention as a potential solution to the worldwide energy shortage and counteracting environmental degradation. The role of photocatalysis is to initiate or accelerate specific reduction and oxidation (redox) reactions in the presence of irradiated semiconductors. This reaction occurs when the energy of the incident photons matches or exceeds the bandgap. The potential applications of photocatalysis are found mainly in the following fields: (i) photolysis of water to yield hydrogen fuel; (ii) photo-decomposition or photo-oxidization of hazardous substances; (iii) artificial photosynthesis. Significant progress has been made in the development of novel nanomaterials in recent years. Nevertheless, the efficiency of nanomaterials, especially in solar photocatalysis, must be improved to meet engineering requirements. Therefore, another critical issue influencing the photocatalytic capability will be discussed in present work, like surface/interface chemistry. The surface energy, chemisorption properties play crucial roles in the transfer of electrons, the energy between substances at the interface, in governing the selectivity, carrier density of the electrons, and in determining the susceptibility of the photocatalyst toward photo-corrosion.

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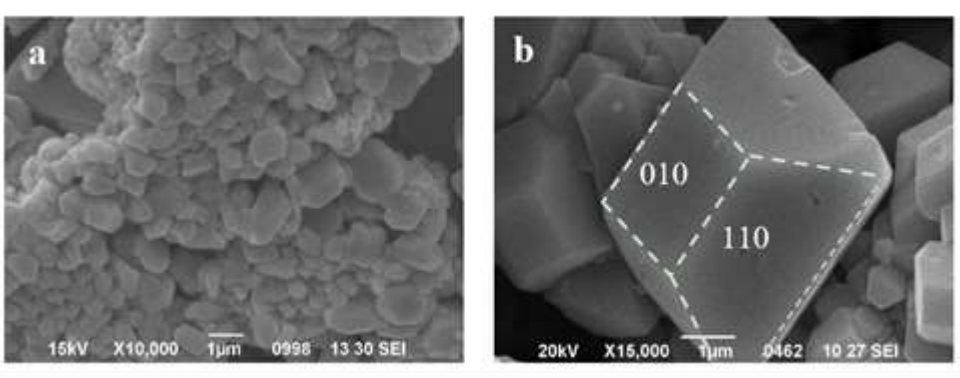

Figure 1. SEM image of (a) BiVO4 without PVP, (b) after adding 0.40 mmol PVP with different orientation faces.

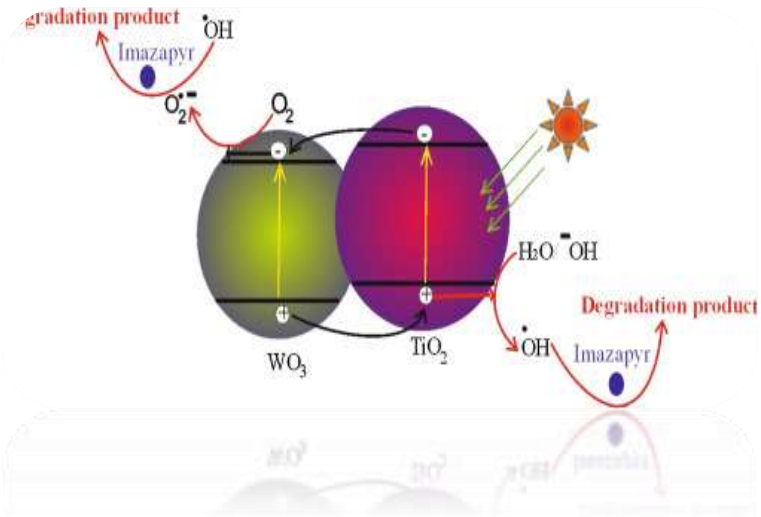

Figure 2. Schematic illustration of the proposed mechanism of the charge separation

Graphene-based electrically conductive coatings for wearable microneedle biosensors

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Microneedle-based biosensing provides an attractive path towards continuous health monitoring - the use of microneedles causes substantially lower pain to the user than traditional hypodermic needles while providing accurate sensing information [1]. Due their small footprint and ease of application, such biosensors are easily worn with minimal nuisance to the user, enabling wearable health sensing anywhere and at any time. Electrochemical microneedle biosensors typically require the microneedles to be electrically conductive - a task which has previously been accomplished using vacuum-deposited gold coatings [2]. As gold is an expensive material and the process requires deposition under high vacuum, it is desirable to replace the gold evaporation with a low-cost and scalable process.

Graphene and related materials such as graphene oxide (GO) and reduced GO (rGO) have emerged as suitable materials for electrochemical biosensors [3]. In this work, novel rGO coatings are developed to provide the electrical conductivity required for the microneedle sensing. The coatings can be deposited in a scalable manner using spray-coating, they can be easily functionalised due to their carbon-based chemistry and form ultra-thin conformable conducting films which are non-toxic. Here, GO is synthesised using well-established methods and it is deposited using a customised automatic spray-coating instrument. Several different methods for the subsequent reduction to rGO are compared to determine their suitability for the microneedle substrates. The glucose sensing enzyme is then immobilised using different protocols, and finally, the suitability of the coatings for electrochemical biosensing is demonstrated by sensing glucose in solution. The coatings do not rely on metal layers or metal nanoparticles, reducing the costs and complexity of the sensors. The developed needle substrate can be seen in Figure 1.

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Figures

Figure 1. Graphene-based conductive coating on polymer microneedles

NH_3 and PH_3 Identification Using Graphene based Gas Sensor

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Abstract
Both NH_3 and PH_3 are widely used in industrial processes, and yet they are noxious and exhibit detrimental effects on human health. [1] A variety of gas sensors have been developed to detect and monitor the NH_3/PH_3 gas in an industrial environment. [2-4] Despite the remarkable progress of sensors development, there are still some limitations, for instance, the requirement of high working temperature, and the dedication to solely individual gas monitoring. [5] Here we develop an ultrasensitive, highly discriminative platform for the detection and identification of NH_3 and PH_3 at room temperature using a graphene nanosensor. Graphene is exfoliated and successfully functionalized by a copper phthalocyanine derivate (CuPc). In combination with efficient machine learning techniques, the developed graphene nanosensor demonstrates an excellent gas identification performance even at ultralow concentration, 100 ppb NH_3 (accuracy-100%, sensitivity-100%, specificity-100%) and 100 ppb PH_3 (accuracy-77.8%, sensitivity-75%, and specificity-78.6%), as shown in Figure 1. Molecular dynamics simulation results reveal that the attachment of CuPc on the graphene surface facilitates the adsorption of NH_3 owing to hydrogen bonding interactions. This smart-sensor prototype paves a path to design highly discriminative, ultrasensitive, miniaturized, non-dedicated gas sensors towards a wide spectrum of industrious gases.

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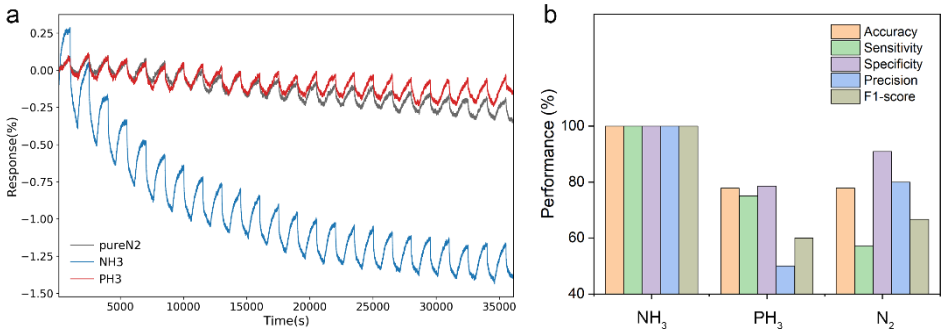

Figure 1. (a) Sensor response towards 100 ppb analyte gas (NH_3, PH_3 and N_2). (b) Sensor performance metrics towards analyte gas at their 100 ppb concentration using hold-out cross-validation method.

Metal nanoparticles-based electrochemical immunosensors for sensitive detection of protein biomarkers

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Currently, immunosensors have taken a lot of attention for their rapid responses, low-cost, simple, and most important integrable on point-of-care technology for detecting proteins [1-3]. Hence, an electrochemical immunosensor has been developed for simultaneous determination of selected protein biomarkers with clinical significance. For this immunoassay, the sandwich arrangement of immunocomplex formation has been preferred, which is composed of immunosorbent and bioconjugate. The immunosorbent consists of magnetic beads immobilized with primary antibodies, helped to concentrate protein, reduce purification steps, and nonspecific sorption. Whereas the bioconjugate include secondary antibodies, labelled with electroactive metal nanoparticles, and combined with mesoporous silica nanoparticles.

Nanoparticles are tiny materials classified depending on their properties. Owing to increased surface area enabling the conjugation with ligands, e.g., specific antibodies, together with metal nanomaterials, the nanoparticles are able to interact with corresponding proteins to be determined [4]. Selection of proper combination of several metal nanoparticles was the key step of developed immunosensor. These nanoparticles are electrochemically readable and were chosen with different oxidation in order to get simultaneous electrochemical detection, without overlapping, thus making this assay more practice and accurate. The outcome signals are measured electrochemically, using square wave voltammetry, which is known for trace analysis with low detection (10^{-12} M).

The selection of specific antibodies of high quality, ensuring the functionality of the system, has been another key step of developed immunosensor. Using the immunochemical dot-blot assay, suitable antibodies for each protein were found. SDS-PAGE was used for evaluation of the binding efficiency in immunosorbent and bioconjugate preparation.

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Hybrid functional nano-assemblies of fluorescent silver nanoclusters

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Combining atomically precise silver nanoclusters (AgNC) with nucleic acid (NA) nanotechnology provides large prospects for creating novel hybrid functional nanomaterials with unique properties. Nucleic acids can serve as both templates for silver nanocluster (AgNC) formation and building blocks for large nano-assemblies. Herein, we create various types of NA-AgNC hybrid nanomaterials which are more photostable, biocompatible and exhibit novel functional properties. The formation of AgNCs on single stranded cytosine rich DNA promotes unique optical properties defined by the sequences and conformation of the DNA templates. The size and shape of AgNCs are regulated by rationally designed and chemically synthesized short DNAs with different numbers of single-stranded cytosines embedded in secondary and tertiary DNA structures such as hairpin loops. Hairpin loops of various sizes (C6-C14) template similar size – Ag10 – nanoclusters while the optical properties of DNA-AgNCs are dictated by the loop size. We combine experimental and theoretical studies to understand the influence of cluster shape, loop conformation, and metal-to-ligand charge transfer on optical behavior of NA-AgNCs. Our observations point to the complexity of the electronic structure of the nanoclusters and the abundance of possibilities of de-excitation processes. This allows for fine-tuning of fluorescent properties of AgNCs. Furthermore, we demonstrate that tuning of the optical properties and red-ox stability of the AgNCs is possible by controlling the position of templating sequence within RNA-nanoring assemblies. These properties beget the use of DNA-AgNCs in a variety of nanophotonics and biosensing applications. We further apply the rational design of hybrid NA-AgNCs to create: 1) biosensors targeting specific sequences of micro RNA (mRNA-21) and heavy metals (Hg2+), 2) novel stable imaging probes active in near-IR portion of the spectrum, 3) effective anti-bacterial agents which are potent to combat multi-drug resistant bacteria.

Measurements of Helium Permeation in Zerodur glass used for the realisation of quantum pascal

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In the new optical pressure standard Ultra-Low Expansion glass (ULE) cavities were proposed to measure helium refractivity for a new realisation of the unit of pressure, pascal. However, it was noticed that the use of this type of material causes some difficulties. One of the main problems of ULE glass is the pumping effect for Helium [1]. Therefore, instead of ULE, Zerodur glass was proposed as a material for the cavity. This proposal was given by the Vacuum Metrology team of the Physikalisch-Technische Bundesanstalt - PTB in the QuantumPascal project. In order to calculate the flow of helium gas through Zerodur glass one has to know the permeation constant K. Moreover, the modelling of time dependency of the flow requires the knowledge of diffusion constant D as well. The relation between them is given by $K = S \cdot D$, where S is solubility of Helium in glass. In our research work we measured permeation of helium gas in Zerodur. The measurements were performed in the temperature range 27 – 120 °C. Based on our results, we consider that the Zerodur material has the potential to be used as cavity material for the new quantum standard of pressure.

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Utilization of semiconducting bismuthene, antimonene and V_2O_5 2D nanosheets in electrochemical sensing

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Abstract: 2D inorganic layered materials have been on the forefront of energy related applications for almost two decades. However, their impact on electroanalysis should not be underestimated, since they have undoubtedly invigorated the field due to their enhanced electrocatalytic properties, great surface to volume ratio and direct electron transfer between the modified electrode surface and the redox centers of biomolecules [1]. Our research fixes upon the implementation of 2D inorganic nanosheets, produced via various top-down approaches, and their use, as electrocatalysts, for the determination of heavy metal ions, explosive and highly toxic compounds or pharmaceutical compounds. It should be stressed out that the majority of inorganic nanosheets are low to wide band gap semiconductors with some exceptions illustrating metallic properties [such as 1T polymorph of dichalcogenides, MXene-core (not taking into consideration electronic state deviations originating from various etching procedures), etc.]. This leads to the necessity of creating conjugated or composite forms of those materials with more conducting phases to ameliorate sensor sensitivity. Our first endeavor is the production shear-force exfoliated bismuthene which is a low band gap semiconductor (bilayer bismuthene ranges from 0.18 to 0.23 eV) and its conjugation with similarly produced few-layer graphene for the anodic stripping voltammetric determination of Cd(II) and Pb(II) at the sub-ppb level (LODs of 0.33 ppb). Our second effort was the production of few-layer antimonene, which is a wide band gap semiconductor with an indirect band gap of 2.28 eV (predicted for monolayer β-Sb), with probe sonication and the in-situ formation of a semi-conducting heterostructure with poly(3,4ethylenedioxy thiophene):poly(styrene sulfonate) for the nanomolar cathodic determination of 4-nitrotoluene (LOD 16.7 nM) and 2,4-dinitrotoluene (LOD 33.3 nM). Finally, we have successfully utilized few-layer V_2O_5 nanosheets, which have a very wide band gap, predicted to be 4 eV for a monolayer, via a simple bath sonication procedure. Admittedly, while this great a band gap partially hampers electronic transfer, it can provide a great electroanalytical platform through the intercalation/deintercalation of ionic species which can enhance proton related redox reactions. This is proven by the nanomolar determination of diclofenac (a widely administered non-steroidal anti-inflammatory drug), via the quantification of its electrochemically active oxidation product, thus reaching an LOD of 6.6 nM. The analytical utility of the respective screen-printed sensors was evaluated in real-world samples, in which excellent recovery values were obtained.

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Fibre based capacitors for wearable biosensing applications

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Current medical and health diagnostic technology rely on mature biosensor technology that can provide a rapid and accurate diagnosis[1]. However, traditional sensors produced from rigid materials are inflexible and hard-to-wear[2], which is inconvenient for diagnostics at the point-of-care (PoC)[3]. A flexible fibre device as a basement for e-textile and wearable PoC devices[4] to achieve wearable diagnostics. Graphene and two-dimensional materials are used due to their, large surface area, chemical stability, and excellent electrical conductivity[5]. In this work we report a wearable fibre-based capacitors produced in a core-shell architecture using reduced graphene oxide (rGO) and hexagonal boron nitride (h-BN). Wet spined rGO fibre exhibiting a conductivity of ~ 8,000 S m^{-1} and young's modulus of 17200 MPa was used as the core that further dip-coated with h-BN as an insulating layer, and another rGO layer as another electrode. This structure represents a key enabling step for wearable fibre-based transistor that can be integrated into textile platforms, paving the way to truly wearable biosensors.

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Figures

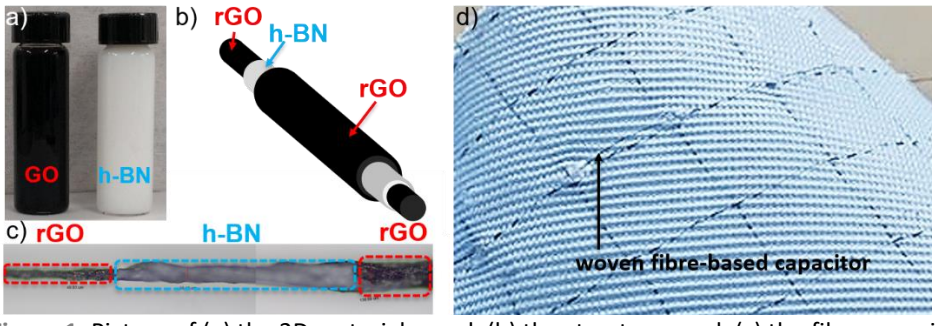

Figure 1. Picture of (a) the 2D materials used, (b) the structure used, (c) the fibre capacitor, and (d) its woven example.

NFC technology for data transmission in wearables. Can graphene be the technological solution for flexible antennas?

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Printed electronics have opened a plethora of new opportunities in the world of wearables and point of care devices. These devices present two major challenges, how to transmit the data to the user and how to power the device. In this context, NFC technology can be the solution, not only transmitting the results to the user's smartphone but also powering our wearable device.

One of the main issues of the implementation of this technology on printed flexible devices is that antennas printed with silver nanoparticles-based ink (the most widespread commercial ink for inkjet printing) typically have a high electrical resistance. Consequently, these antennas have high losses and, in consequence, it is necessary to place the smartphone very close to the device.

In the case of environmental sensors, it is often necessary to obtain the information through a glass or acrylic wall; therefore, it is required to have a larger reading distance. Therefore, with the aim to face this issue, there are two possibilities: designing antennas with wider tracks (limiting the miniaturization of the device), or exploring new nanomaterials with higher electrical conductivity, giving the possibility to transmit at a greater distance.

In this work, we will evaluate and compare silver nanoparticles printed antennas with flexible antennas obtained from high conductivity sheets of graphene with a very simple and fast fabrication method.

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Inkjet-printed-based Electrochemical Approaches for Testing of SARS-CoV-2

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COVID 19 pandemic, initially blindly thought of as a flu-like disease, has reshaped our entire lives. Nowadays, 216 countries are being struck down by the disease, reaching up to 123.419.065 people infected, with 2.719.163 reported deaths globally [1]. Current diagnostic technologies, such as PCR, antigen-, and serological tests are not sufficient to outweigh the incidence of the disease [2]. Their main drawbacks are case-to-case variations, specimen-/sample-collection dependence, high cost, required trained personnel, and generation of false-positive results, along with a lack of sensitivity of the rapid serological and antigen tests at the initial stages of the disease [3]. Considering the current limitations in infrastructure and resources, there is an important need to significantly increase the speed of production and testing, as well as the availability and accessibility of cost-effective, reliable, and rapid Point-of-Care (POC) devices, especially in low-income countries.

In this work, we propose a highly scalable fabrication procedure for a nanomaterial-based impedimetric biosensor using only office equipment, such as inkjet printers, and commercially available materials, as well as a low-cost smartphone readout [4]. The silver nanoparticles ink-based electrodes were successfully functionalized with aptamers binding the SARS-CoV-2 spike protein (SP) [5], and able to detect it at very low concentrations, reaching a LOD of 10 nM in synthetic buffer. The biosensor specificity was studied using SARS-CoV-2 nucleoprotein (NP) and bovine serum albumin (BSA). Further studies encompass an adaptation for its use in more complex media. In comparison to the currently available technologies, the ease and scalability of the proposed biosensing technology could allow for a distributed out-of-the-lab fabrication, maximizing and making the biosensors distribution rapid, equal, and capillary for this and future pandemics.

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Production of electrospun zeolite-incorporated nano-microfibers from recycled PET

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Various research groups have studied the physical, mechanical and thermal properties of PET, and due to some of its advantageous properties such as non-toxicity, strength, lightweight, safety, flexibility, PET became very important and a useful raw material globally recognized as 100% recyclable. Moreover, the structure of PET has polar groups like oxygen, which seems to develop a highly selective membrane in coupling with specific chemical or biochemical reagents for contaminant removal. Furthermore, an advantage of application of PET waste materials instead of pure samples is due to the fact that there are no significant physical or chemical properties [1] between pure/virgin and recycled PET samples. So by using recycled PET one can reduce the environmental pollution and achieve low cost nanofibrous membranes. In this study, PET has been recycled from plastic bottles and then used as a material to produce a nano/microfibrous mesh by electrospinning process. The aim of the study was to produce a membrane that could serve for water filtration applications. For such an application, researchers have made certain modifications by adding nanoparticles to the fibrous structure to improve water purification properties [2, 3]. Zeolites are nanoporous crystalline alumino-silicates with a rich variety of interesting properties and industrial applications. The novelty in this work is the incorporation of zeolites into the fibrous structure, which are expected to increase the antibacterial properties of the membrane. Optimization of the fibrous structure was done by playing with various electrospinning parameters such as voltage applied, polymer concentration, flow rate and the size of zeolites added to the polymeric solution [Fig. 1] in terms of fiber structure properties.

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Figures

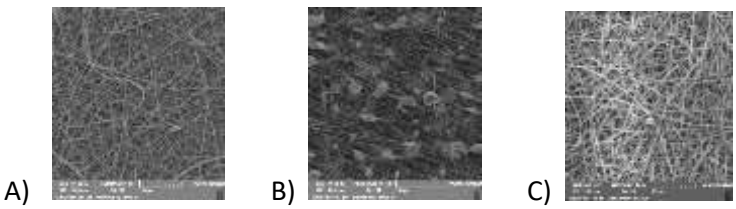

Figure 1. Scanning electron microscope image of PET-based nano-microfibers. A) Recycled PET and B) Commercial PET and C) Zeolite-incorporated PET.

Ex-vivo antioxidant yttrium oxide nanoagents

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Reactive oxygen species (ROS) portray highly oxidant components generated in biological or natural environment, implying a myriad of physiological and pathological processes, leading to inflammation, cell signal transduction, and neurodegenerative diseases.[1] Among these species, highly active hydroxyl radicals (●OH), exhibits strong oxidizing properties, inducing potential DNA damage, protein carbonylation, and lipid peroxidation, causing a variety of health problems, including cancer, aging and chronic inflammations.[2,3] Thus, preventing the generation of ●OH radicals is vital. Ceria nanoparticles are widely explored as antioxidants for preventing ●OH radicals due to their unique redox properties and general biocompatibility.[4] Therefore, here we provide a novel choice for antioxidant agent based on yttrium oxide nanocrystals with cubic structure and $Ia\bar{3}$ spatial group. Performing wet chemical methodologies, yttrium oxide nanocrystals with sizes <50 nm in the shape of nanotriangles, nanohearts and self-assembled nanodiscs, were synthesized. We highlight the influence of their shapes on the antioxidant properties, along with *ex-vivo* trials. Additionally, the doping of yttrium oxide nanocrystals with lanthanide ions (Er^{3+}, Yb^{3+}), was investigated as a route towards the generation of a more efficient antioxidant agent. The performance of these yttrium oxide agents are comparable with those of highly explored ceria nanoparticles.[4]

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Figures

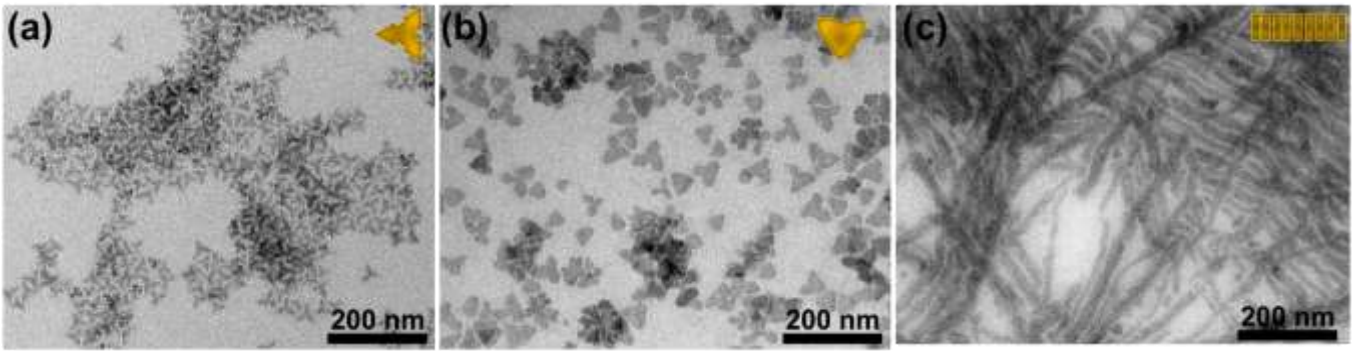

Figure 1. Transmission electron microscopy images of different shapes of yttrium oxide nanocrystals: (a) nanotriangles, (b) nanohearts, and (c) self-assembled nanodiscs, synthesized via wet chemical methodologies.

Breath-level detection of H_2S in humid air by selective carbon-nanotube sensor arrays

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The potential of exhaled breath analysis as a cost-effective and non-invasive approach for the precise identification of diseases has been intensively studied in the past years [1]. However, addressing the selective detection of specific molecules in highly complex media like human breath remains a great challenge. To tackle this problem, emerging gas sensing technologies are taking advantage of the special properties of nanostructured materials as a promising alternative to reach the selectivity and sensitivity needed for such application [2,3].

In this context, we present the selective detection of low parts per billion (ppb) concentrations of H_2S gas in humid air and at room temperature by a multichannel chemiresistive gas sensing platform based on semiconducting single-walled carbon nanotubes (sc-SWCNTs) functionalized with gold nanoparticles (AuNP). The multichannel device, consisting of 64 individual sensors (Figure 1a), was fabricated using standard UV-lithography and metal deposition techniques, and the sc-SWCNTs were deposited by a controlled dielectrophoretic process. The sensing area was then functionalized with gold nanoparticles by potentiostatic electrodeposition achieving an optimal average particle diameter of 60 nm and separation distances of around 100 nm along single tube agglomerations (Figure 1b). AuNP-functionalized sensors showed an increased sensitivity to all tested concentrations compared to non-functionalized tubes of 0.122 %/ppb and a calculated limit of detection (LOD) of 3 ppb (Figure 1c). Moreover, the sensors demonstrated low cross-sensitivity to relevant breath concentrations of NH_3 and NO, and higher sensitivity compared to commercial electrochemical-based gas sensors (AlphaSense, UK). These results suggest the potential application of our sensing platform in the field of exhaled breath analysis.

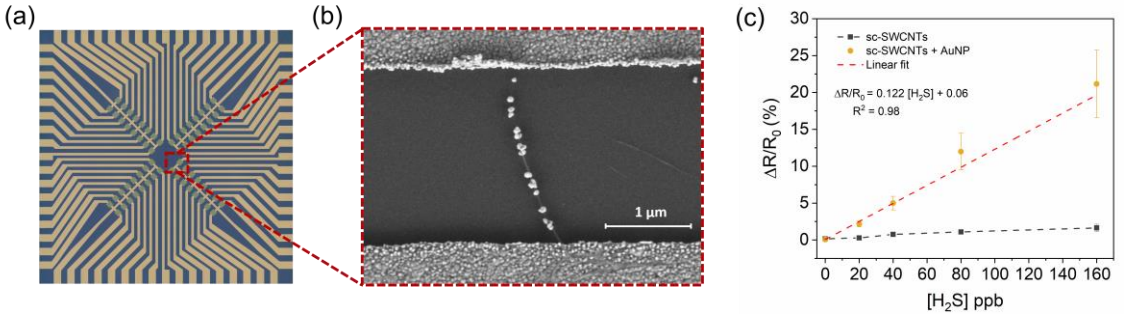

Figure 1. Multichannel gas sensing platform and exposure experiments to H_2S gas. (a) Optical image of the multichannel device comprising 64 individual sensors. (b) Scanning electron micrography of AuNP-functionalized sc-SWCNT. (c) Sensing response ($\Delta R/R_0$) of AuNP-functionalized and non-functionalized sensors to low ppb concentrations of H_2S.

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Flexible graphene-based electrodes for biosensing in wearable devices

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Non-invasive, wearable devices for continuous detection of biomarkers in biological fluids are nowadays possible thanks to the presence on the market of disposable electrodes, which employ low amounts of solution and allow a simple, fast, and reproducible analyte detection. To impart best performance to the sensor response, various nanomaterials can be included in the printed ink or added as a coating afterwards: graphene derivatives are increasingly exploited in electrochemical biosensing, since specific oxidized moieties are well exposed to the surrounding environment and they are responsible for the activation of electrocatalytic processes toward several species, i.e. a decrease of the oxidation or reduction potentials of the analyte with respect to pristine carbon electrodes [1]. We report the advantages in the use of graphene paper (G-paper) for the realization of unfunctionalized, ready-to-use electrodes on flexible plastic and textile supports, as well as their application as wearable (bio)sensing platforms (Figure 1). G-paper is a flexible, electrically conductive, paper-like material which has a large surface area and can be shaped in different ways; it features a high electrical conductivity ($1x10^5$ Sm^{-1}), mechanical and chemical stability even after one million bending times [2]. We demonstrate that G-paper electrodes can be successfully employed in wearable biosensing platforms: a comparison with graphite-based commercial electrodes demonstrates that our novel, unfunctionalized devices outperform them in sensing of nicotinamide adenine dinucleotide (NADH), a key molecule for enzymatic biosensing; in addition, thanks to the stable deposition of lactate dehydrogenase for enzymatic detection of lactate, we also demonstrate the possible advantages in the use of these new devices with respect to those present on the market, opening new possibilities for comprehensive smart fabrics in wearable electronic applications.

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Figures

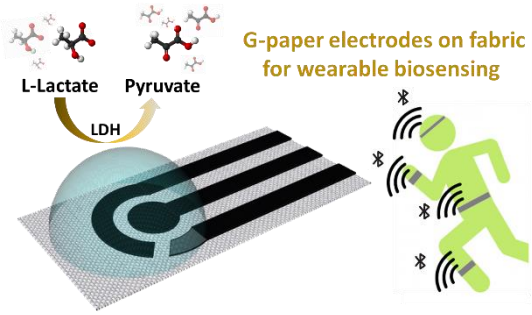

Figure 1. G-paper electrode on cotton fabric and exemplificative application for biomarkers detection during training.

Electrochemical MIP sensor based on pure Graphene electrode. Detection of Isoproturon

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Abstract

A new method for exfoliation of graphite rod electrode in organic media with a single stage of exfoliation is developed. It is based on cathodic electrochemical exfoliation of graphite rod electrode which enables the production of graphene flakes via intercalation of tetrabutylammonium cations in the presence 1-methyl-2-pyrrolidone (NMP) as solvent in a three-electrode cell. Chronoamperometry has been used as electrochemical method for the exfoliation of graphite rod electrode and the best results are obtained -2.5 V /SCE for a time 6h. XPS, Raman, IR spectroscopy results confirms the formation of a high-quality graphene that contains a low quantity of sp^3 carbon atoms (Figure 1) and oxygenated functional groups on its structure. This graphene is used for the fabrication of pure graphene on polystyrene (PS) electrodes with different geometrical area. The electrodes have shown good electrochemical properties and were used for the preparation of electrochemical molecular imprinted polymer (MIP) sensor for isoproturon detection.[1] The Graphene-MIP sensor was able to detect isoproturon in nano-molar concentration with good reproducibility and repeatability and shows good robustness during the 7 successive analyzes. Low limits of detections (LOD) and quantifications (LOQ) have been reached in water samples contaminated with isoproturon,

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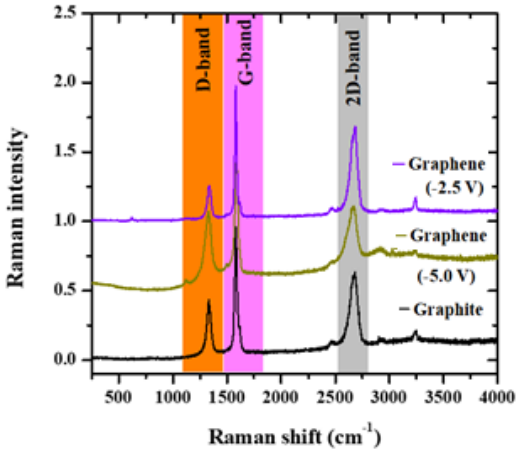

Figure 1. Raman spectra of graphite, graphene -5V, and graphene -2.5V

Novel aptamer development for tetrodoxin detection in puffer fish

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Tetrodotoxin (TTX) is a paralytic marine neurotoxin [1] causing seafood poisoning after the consumption of contaminated marine species such as puffer fish and shellfish [2]. Liquid chromatography-mass spectroscopy is routinely used for laboratory-based analysis of field samples [3]. Competitive immunoassays have also been developed and are available in the market for TTX detection. Aptamers are attractive alternatives to antibodies and have great potential in analytical applications [4]. They are artificial synthetic nucleic acids (RNA/DNA) that bind specifically to their target and they are selected through an in vitro iterative process called Systematic Evolution of Ligands by Exponential enrichment (SELEX) [5]. In this work we sought to develop novel aptamers binding to TTX and exploit them for TTX detection in puffer fish. Using a variation of SELEX suitable for small molecules (Capture-SELEX) in combination with high-throughput Next Generation Sequencing, TTX aptamers were identified, and their binding properties were characterized. Finally, a highly sensitive and user-friendly hybrid antibody-aptamer sandwich assay was developed with superior performance compared to several assays reported in the literature and commercial immunoassay kits. The assay exhibited excellent recoveries for the detection of TTX spiked in fish extracts and it was also successfully applied for the quantification of TTX in puffer fish extracts. Ongoing work is focused on the development of a lateral flow assay which would allow the rapid and facile analysis of field samples.

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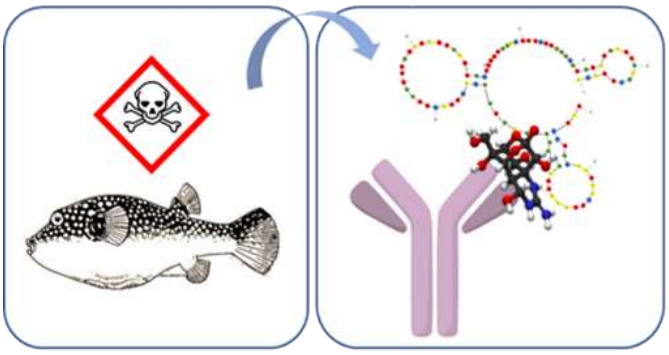

Figure 1. Hybrid antibody-aptamer assay for TTX detection

Acknowledgements: This work is funded by King Abdulaziz University, under the financing of a collaborative project with URV entitled "Cost-effective tools for mycotoxin testing".

New Approaches in Nanotechnology in Pharmaceutical Forms

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Nowadays, nanotechnology is used more and more frequently in formulation of pharmaceutical forms, thus improving in its delivery by resulting the maximum of plasma concentration of active ingredients. This approach improves the pharmaceutical forms such as suspension, granules, ointments, tablets.
The aim of this study is to bring awareness that well-known active ingredients with well-known pharmaceutical forms may have clinical significance.
Materials and methods: Well-known formulations were taken and substituted with excipients through a new method of technology. The chemical results are improved according to USP Pharmacopeas Standards.
Results: The pharmaceutical forms have given stability, purity, disintegration and disolution of study forms and are under the process to be in formulation for registration for the final products.
Conclusion: Nanotechnology methods improve the stability of the forms and clinical efficiency by reducing toxicity that is the goal of pharma industry.

Keywords: Nanotechnology, efficiency, stability, excipients.

On the road to the control and overseeing of COVID-19 diagnosis and monitoring through versatile and efficient multiplexed electrochemical biosensing tools

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Control and management of infectious diseases have gained tremendous importance since COVID-19 was officially declared as a global pandemic. Currently, and especially with the introduction of COVID-19 vaccination protocols as well as with the emergent SARS-CoV-2 variants, immune response tracking to SARS-CoV-2, critically required for a deeper understanding of the extent of the infection, represents the basis for an 'immunity passport' enabling individuals to return to normal life [1]. However, assuming vaccines are not 100 % effective, a breakthrough infection could be expected. Since people who get vaccine breakthrough infections can be contagious [2], interrogation of a broad spectrum of COVID-19 related markers for discriminating infectious, vulnerable, and/or immune-population, either vaccine-protected or unvaccinated, continues to be of paramount demand.

Inspired by the willingness to cooperate for this purpose, we present two simple and effective interrelated electrochemical biosensing devices based on both laser-engraved graphene-[3] and magnetic beads-coupled screen-printed electrodes for the sensitive, fast, and reliable multiplexed interrogation of viral antigen (nucleocapsid protein, NP), SARS-CoV-2 specific immunoglobulins (IgGs and IgMs), and the inflammatory biomarker C-reactive protein, as well as total and specific-isotypes SARS-CoV-2 immunoglobulins (IgGs, IgMs, and IgAs) against the most antigenic viral receptors: spike (S) and nucleocapsid (NP)-antigens, respectively.

The factual applicability of both biosensing tools has been extensively demonstrated by analyzing RT-PCR confirmed COVID-19-positive and -negative blood and saliva samples from healthy and SARS-CoV-2 infected subjects. Results provided by both multiplexed bioplatforms agree admirably with those proffered by other methodologies that require more effort, knowledge, and application in centralized environments, thus corroborating the reliable and suitable performance of the established methodologies.

All this proves beyond doubt that electrochemical biosensors continue to demonstrate their exceptional capabilities in the fight against one of the most dramatic health and economic crisis of the modern era, paving the way to the implementation of affordable and easily accessible diagnostic devices for the entire population.

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Application of nanotechnology to inhibit cancer cell proliferation

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Abstract

Cancer represents one of the most unpredictable diseases that not only affects the quality of life but can lead to death in case of inappropriate treatment. The key feature of all cancer cells is related to their uncontrolled proliferation by repeatedly overlooking cell cycle checkpoints. The introduction and development of nanotechnology in cancer research has proven to be extremely useful in several aspects. It has shown promising results for efficient diagnosis, targeted drug delivery, and personalised treatment. One of the most prominent oncogenes found hyperactivated in approximately 30% of all human cancer, is Ras. It has been established that Ras is a crucial player in the induction and control of cell cycle progression. Due to its continuous and high-speed activity as a GTP-ase bound protein, targeting Ras has been an incredible challenge for researchers over the years. We present here a novel technology able to selectively and specifically target endogeneous Ras, diminish its activity and consequently interfere with cell cycle progression. Our approach consists in the direct inhibition of native Ras via manipulation of NF1.

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Figure

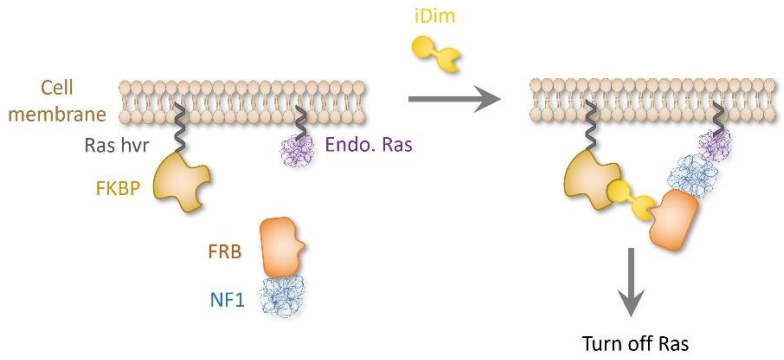

Figure 1. An inducible nanotechnological switch.

Inkjet-printed electrochemically reduced graphene oxide microelectrode as a platform for HT-2 mycotoxin immunoenzymatic biosensing

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The design and application of an inkjet-printed electrochemically reduced graphene oxide microelectrode for HT-2 mycotoxin immunoenzymatic biosensing is reported. A water-based graphene oxide ink was first formulated and single-drop line working microelectrodes were inkjet-printed onto poly(ethylene 2,6-naphthalate) substrates, with dimensions of 78 µm in width and 30 nm in height after solvent evaporation. The printed graphene oxide microelectrodes were electrochemically reduced and characterized by Raman and X-ray photoelectron spectroscopy spectroscopies in addition to microscopies. Through optimization of the electrochemical reduction parameters, differential pulse voltammetry was performed to examine the sensing of 1-naphthol (1-N), where it was revealed that reduction times had significant effects on electrode performance. The developed microelectrodes were then used as an immunoenzymatic biosensor for the detection of HT-2 mycotoxin based on carbodiimide linking of the microelectrode surface and HT-2 toxin antigen binding fragment of antibody (anti-HT2 (10) Fab). The HT-2 toxin and anti-HT2 (10) Fab reaction was reported by anti-HT2 immune complex single-chain variable fragment of antibody fused with alkaline phosphatase (anti-IC-HT2 scFv-ALP) which is able to produce an electroactive reporter – 1-N. The biosensor showed detection limits of 1.6 ng · mL^{-1} and a linear dynamic range of 6.3 – 100.0 ng · mL^{-1} within a 5 min incubation with 1-naphthyl phosphate (1-NP) substrate.

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NANOBIOSENSORS SCHOOL
contributions

Demonstration of different portable nanosensing platforms with optical and electrochemical readout

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Inexpensive, fast and easy-to-use point-of-care detection systems are in demand for application in different fields. We will demonstrate that graphene and other nanomaterials can be used in combination with a smartphone to develop this kind of devices. Different sensing platforms will be shown; for example, a screening device with a smartphone readout, a screen-printed electroluminescent lamp modified with graphene oxide, a paper-based electrophoretic bioassay, a portable ELISA plate reader and a new method of transferring laser-scribed conductive rGO films onto almost any substrate.

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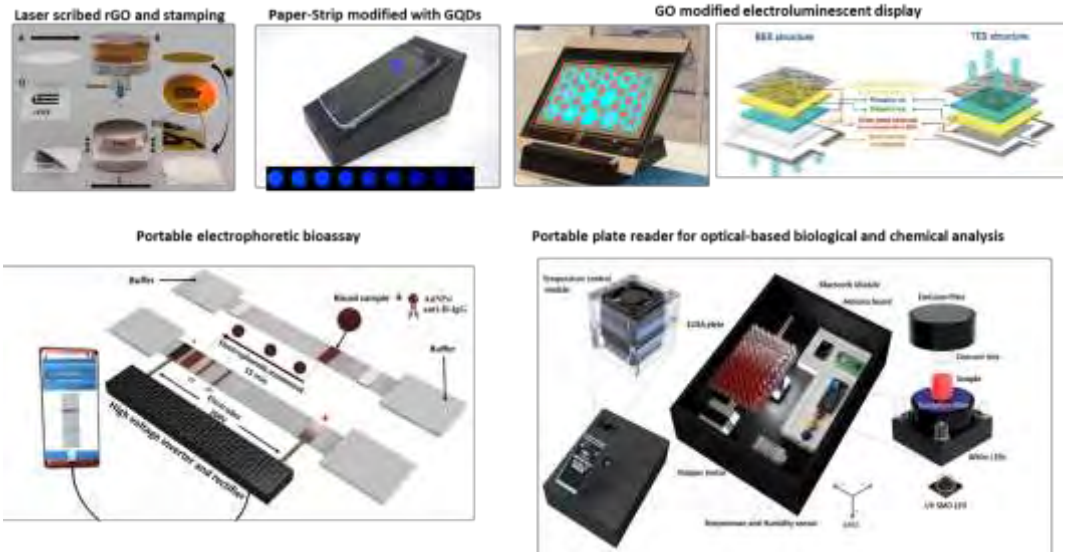
Figures



Carbon black as an outstanding and affordable nanomaterial for electrochemical (bio)sensor design

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Carbon is present in several allotropic forms ranging from graphite to diamond, till the most recently discovered fullerene, nanotubes, and graphene. The latter ones hold a leading role in the current electrochemical sensor scenario, thanks to their unique properties. The presence of carbon nanotubes or graphene on the surface of the working electrodes can improve the electroanalytical performances by enhancing the electron transfer at the surface of modified electrodes. In recent years, another interesting carbonaceous nanomaterial is becoming utterly interesting, due to its excellent conductive and electrocatalytic properties: Carbon Black (CB). CB is a form of amorphous carbon that has an extremely high surface area to volume ratio, and it has been one of the first nanomaterials for common use. In fact 70% of CB is used as a pigment and reinforcing phase in automobile tires. Few applications are reported in literature until 2010 using CB as sensing element for analyte detection in solution [1]. Herein, we present our results obtained in the last eight years with more than 20 publications on the use of CB as modifier for screen-printed electrodes towards several analytes including thiocholine, cysteine, NADH, hydrogen peroxide, free chlorine, tyrosine, and phenolic compounds. The high sensitivity of this nanomaterial for thiocholine was exploited to develop a chemosensor for Hg(II) and a biosensor for organophosphorus pesticide detection. The fouling resistance of CB was demonstrated for thiocholine as well as for the phophomolybdate complex. Moreover, the suitability of CB in electroanalysis was also explored preparing hybrid nanocomposites with gold nanoparticles for glucose, As(III) and Hg(II) detection, thionine for bisphenol A, cobalt(II) phthalocyanine for thiocholine and Prussian Blue nanoparticles for hydrogen peroxide. Furthermore, a direct comparison with SPE modified different types of carbon black as well as with graphene and carbon nanotubes, showed the advantages of CB for its electrochemical properties, cost-effectiveness, capability to easily obtain a stable and homogenous dispersion, demonstrating that CB can be widely employed in the development of nanomodified electrochemical sensors. Recently, we have successfully also used CB to assemble novel paper based electroanalytical tools for phosphate, ascorbic acid, buryrylcholinesterase, ethanol, glutathione, mustard chemical warfare agents, pesticides, and sodium ions.

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Paper-based electrochemical (bio)sensors: how?

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Despite substantial advances in sensing technologies, the development, preparation, and use of self-testing devices is still confined to specialist laboratories and users. Decentralized analytical devices will enormously impact daily lives, enabling people to analyze diverse clinical, environmental, and food samples, evaluate them and make predictions to improve quality of life, particularly in remote, resource-scarce areas. In recent years, paper-based analytical tools have attracted a great deal of attention; the well-known properties of paper, such as abundance, affordability, lightness, and biodegradability, combined with features of printed electrochemical sensors, have enabled the development of sustainable devices that drive (bio)sensors beyond the state of the art. Their blindness toward colored/turbid matrices (i.e., blood, soil), their portability, and the capacity of paper to autonomously filter/purge/react with target species make such devices powerful in establishing point-of-need tools for use by non-specialists. Depending on analytical requisites, different types of paper (filter, office) and configurations (1D, 2D, 3D) can be adopted. A wide overview regarding application ranging from DNA to heavy metals, through pesticides detection will be provided, with the aim in showing the potentialities of paper-based electrochemical biosensors for improving society involvement in monitoring.
The talk is aimed to provide general basis regarding the development of paper-based electrochemical strips for multiple applications. However, it should be noted that the term "paper" is too general: chromatographic paper, office paper and nanocellulose are only some of the paper-based substrates that can be exploited. The main question from non-experts is: which kind of paper should I use? The best answer is "it depends"! Answers depend on the application and the analytical need.

Research interests

Biosensors, point-of-care, nanomaterials, nanoengineering, lab on chip, microfluidics

Real-time, continuous monitoring of clinically relevant molecules via electrochemical aptamer-based sensors

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Abstract

The development of biosensors able to measure clinically and physiologically relevant molecular targets in-situ in the body could revolutionize health care. Real-time monitoring of drug or metabolite levels in the blood, for example, would support the high-precision measurements of patient-specific pharmacokinetics and, ultimately, even closed-loop feedback-controlled drug delivery. Such personalization of drug dosing would maximize drug efficacy while minimizing side effects. Electrochemical aptamer-based (EAB) sensors can achieve this goal in a modular way, so far supporting the multi-hour in vivo monitoring of several relevant targets without relying on their specific chemical properties [1-3]. The modularity of EAB sensors relies on the use of nucleic acid aptamers as recognition elements, which can be selected to reversibly and selectively bind any kind of molecular target supporting their detection in untreated biological fluids such as whole blood. However, the development of EAB sensors from in vitro settings to relevant in vivo clinical applications displays some technical challenges. This tutorial will describe the general concepts behind the fabrication and the characterization of electrochemical aptamer-based (EAB) sensors, and their next adaptation to achieve real-time measurements of clinically relevant targets directly in living animals.

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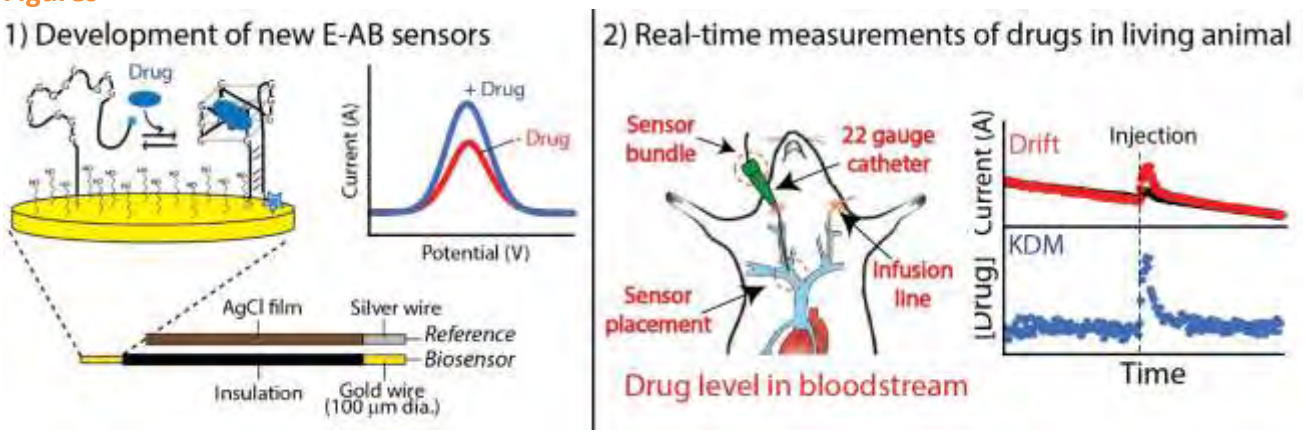
Figures



The Collaboration Between Developers and Clinicians

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The COVID-19 pandemic further encouraged the design of multidisciplinary projects that aim to solve complex medical problems by combining expertise coming from different fields of research. Soon it became obvious how the establishment of an effective collaboration between developers/technologists and clinicians is paramount to successfully and rapidly carry out such projects, besides being mutually beneficial for both the individuals and their institutions.[1] In this talk, taking inspiration from my recent professional change (from technical to clinical research), I will present how it is possible to maximize such collaborations. In particular, I will present who are the main players involved and the timeframes to carry out the main tasks of the collaboration. Finally, I'll briefly present preliminary results of my current research project on the development of a point-of-care diagnostic device for the diagnosis of malaria in international travelers.

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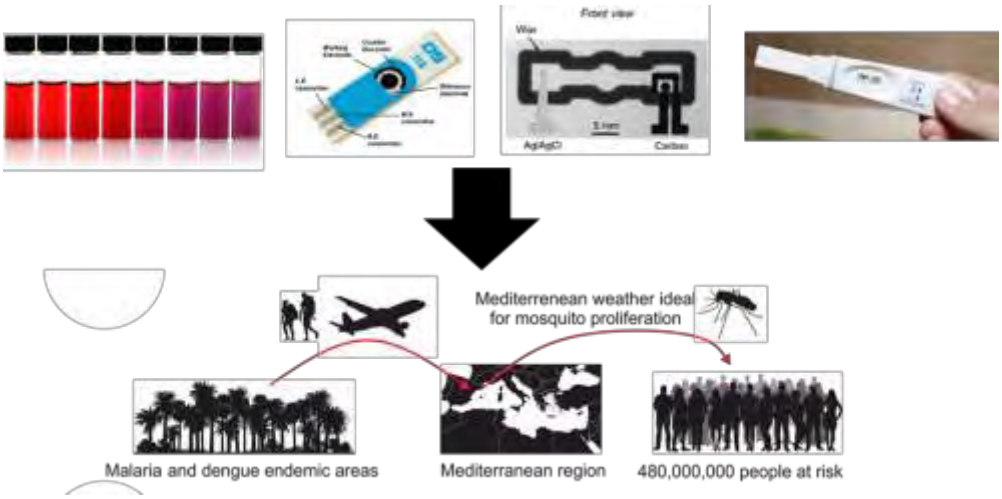

Figure 1. We will discuss why an effective collaboration between developers and clinicians is essential and how to establish it. As example, I will present my current work on the development of a point-of-care sensor for the diagnosis of malaria in international travelers.

A look through Rapid Diagnostics Tests (lateral flow tests)

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Lateral flow tests are the most popular type of rapid diagnostic tests, being widely used in point-of-care[1] applications such as pregnancy tests or for the detection or SARS-CoV-2 infection. Lateral flow tests stand out for their inexpensiveness, portability, ease of use and for being battery/equipment-free. To highlight that the inclusion of nanomaterials in lateral flow tests[2-4] can boost the capability of these devices allowing even to quantify the response at naked-eye or with a smartphone[5]. The objective of this tutorial talk is to introduce the concept of how do lateral flow tests work and the different components of a lateral flow paper strip (figure 1).

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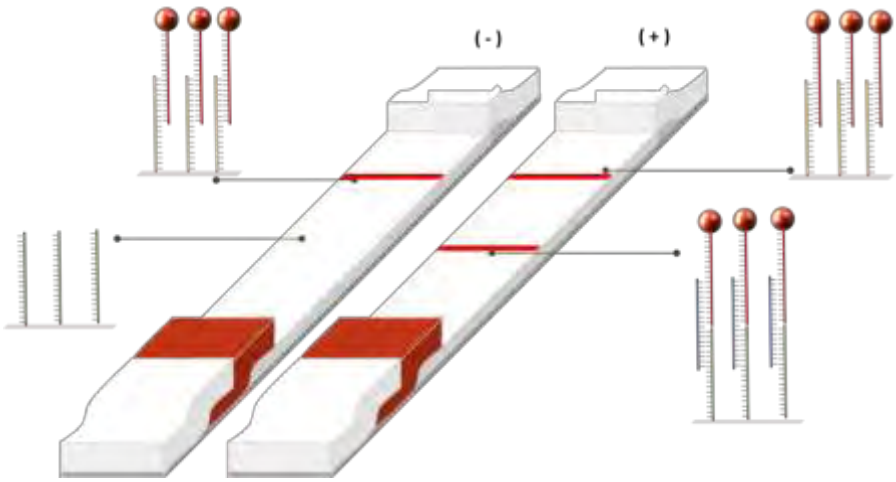

Figure 1. Components of a lateral flow strip

Nanobiosensors school: Inkjet printing for ubiquitous ultra-fast and low cost electrochemical biosensors fabrication

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Biosensors fabrication should guarantee high performances and reliability, low variable costs and possibly low investment. Furthermore, the recent pandemic showed us the increasing need of decentralized (virtually ubiquitous) production.

Inkjet printing with nanofunctional inks and office-like equipment have these characteristics, as will be showed in the tutorial which will be presented at the school on nanobiosensors.

Indeed, inkjet printing of metallic nanoparticles-based inks with consumer printers on flexible semipermeable substrates offers the opportunity for easy, one step, and affordable production of flexible electronic devices with a nice control in resolution and on the electrical properties of the printed structures.
The addition of hydrophobic layers, for example by wax printing, can effectively passivate the semipermeable layer for electrochemical measurements in contact with electrolyte solutions (avoiding imbibition and parasitic currents between the printed electrodes).
Finally, the encapsulation of the obtained devices with patterned lamination pouches or biadhesive sheets permit obtaining complete electrochemical flexible sensors even with microfluidic channels.

Functionalization of these devices can space between standard approaches such as using antibodies and thiolated aptamers, and more advanced nanobiotechnological approaches such as using nanoswitching labelled aptamers or CRISPR/Cas enzymes.

Last but not least, the readout of these devices can be performed with portable and wireless systems, including but not limited to smartphone sensing through the audio and microphone channels, low-energy Bluetooth modules connected to integrated potentiostat chips, and RFID capacitive, resistive and electrochemical biosensing systems.

Synthetic cell-based and cell-free biosensors for water contamination in resource limited settings

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Abstract

This tutorial will introduce the principles, latest progress and challenges in developing synthetic biology enabled cell-based and cell-free biosensors for environmental toxins and pathogens. It will bring opportunities to developing new generation low-cost, portable and robust biosensors for use in resource limited settings. Cell-based biosensors have great potential to detect various toxic and pathogenic contaminants in aqueous environments. However, frequently they cannot meet practical requirements due to insufficient sensing performance. Here, we investigated a modular, cascaded signal amplifying methodology to address this issue. We first tuned intracellular receptor densities of the sensory module to increase sensitivity, and then engineered ultrasensitive activator-based multi-layered transcriptional amplifiers to sequentially amplify the transduced sensor signal and boost output expression level. We demonstrated these strategies by engineering ultrasensitive bacterial cell-based sensors for arsenic and mercury contamination. We next developed an encapsulated microbial sensor cell array for low-cost, portable and precise field monitoring, where the analyte concentration can be readily visualized via displaying an easy-to-interpret volume bar-like pattern. The ultrasensitive signal amplifying methodology along with the sensing platform will be widely applicable to many other cell-based sensors, paving the way for their real world applications in the environment and healthcare. Further, new low cost cell-free paper-based biosensors that produce visible outputs and can be freeze-dried for long-term storage are being developed to facilitate their reliable performance and ultra-portability in the field.

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The common equipment for the lateral flow production at different stages and the commercial operations to maximise the business success

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Abstract
The lateral flow production stages can be divided into a few stages according to the purpose and the scale of the production. Different devices are recommended to meet the budgets and the production outputs of individual researchers and manufacturers.

1. R&D
2. Small Scale
3. Medium Scale
4. Large Scale

After resigned from Kinbio in 2016 and before made the decision to move to Portugal, I spoke with all the principal suppliers of Rapid test equipment in China, including Biodot. The problems which I found prevented from getting more market share in Kinbio weren't unique. In 2017 to 2020, more conversations and meetings were made with the local business entities in Portugal. The problems are universal, many business entities are operating without a careful business analysis and a solid mid to long term planning. In 2020 and 2021, the certain commercial operation measures were placed into business practice for the first time and have had brought million dollars businesses, the target territory become the leading foreign market in Kinbio, obtained above 50% market share in 2021 by now(Average market share in the past 5 years is about 10% - 15%).

Figures

SATELLITE WORKSHOP
contributions

Comprehensive Understanding of Bio-nano Interactions-A challenge for future applications of nanoparticles in medicine

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Abstract

In addition to the great contribution that large scale production and remarkable progress in developing newer nanomaterials, the field of nanotechnology holds great promise for revolutionizing biomedicine. The uniqueness of nanoparticle physico-chemical properties suggests that their interactions with cells and tissues may be unpredictable. Having comparable dimensions, man-made nanoparticles and cellular molecular machines, a possible direct interactions and/or interference of nanoparticles with cellular vital mechanisms can be revealed. In order to design intelligently and use safely and effectively nanomaterials, a holistic understanding of bio-nano interactions is needed. Here, a review of our research in designing a battery of reliable, low cost and specific biomarkers of nanotoxic effects to unearth the mechanisms of bio-nano interactions, is shown. Furthermore, potential opportunities and challenges in applying of these biomarkers in the study of bio-nano interfaces are also provided.

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Figures

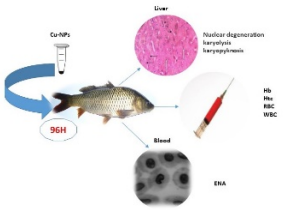

Figure 1. Battery of biomarkers of effects to assess toxic effects of nanoparticles.

Electrochemical Application of Boron-doped Diamond Electrodes

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Boron-doped diamond (BDD) electrodes are very attractive material, because of their wide potential window, low background current, chemical inertness, and mechanical durability.[1] In these years, we have reported several examples for electrochemical sensor applications.[2] Here, novel microsensing systems for in vivo real time detection of local drug kinetics are reported. Furthermore, applications for electrochemical organic synthesis[3] including CO_2 reduction[4], and electrochemiluminescence (ECL) systems[5] are also reported.

Microsensing system for in vivo real time detection of local drug kinetics[2b]
We have developed a microsensing system for in vivo real time detection of local drug kinetics and its physiological relevance. The system consists of two different sensors of both a micro-sensor composed of BDD microelectrodes with tip diameter ~40 µm and a glass microelectrode. By using the system, we have first tested bumetanide, a diuretic that is ototoxic but applicable to epilepsy treatment.
CO_2 reduction[4]
We investigated the electrochemical reduction of CO2 to HCOOH in a flow cell using BDD electrodes. The faradaic efficiency (FE) for the production of HCOOH was as high as 94.7%. The selectivity for the production of HCOOH was more than 99%. Furthermore, recently, by optimizing certain parameters and conditions used in the electrochemical process with BDD electrodes, such as the electrolyte, the boron concentration of the BDD electrode, and the applied potential, we were able to control the selectivity and efficiency with which carbon monoxide is produced.[4c]
Electrochemiluminescence (ECL)[5]
A novel coreactant-free electrogenerated chemiluminescence (ECL) system is developed where $Ru(bpy)_3^{2+}$ emission is obtained on BDD electrodes. The method exploits the unique ability of BDD to operate at very high oxidation potential in aqueous solutions and to promote the conversion of inert SO_4^{2-} into the reactive coreactant $S_2O_8^{2-}$. This novel procedure is rather straightforward, not requiring any particular electrode geometry, and, since the coreactant is only generated in situ the interference with biological samples is minimized. The underlying mechanism is similar to that of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system. Furthermore, recently, another ECL system is presented. The system takes advantage of the unique properties of BDD to promote oxidation of carbonate (CO_3^{2-}) into peroxydicarbonate ($C_2O_6^{2-}$), which further reacts with water to form hydrogen peroxide (H_2O_2), which acts as a coreactant for $Ru(bpy)_3^{2+}$ ECL.

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Electrochemiluminescence application of boron-doped diamond electrodes

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Electrogenerated chemiluminescence, or electrochemiluminescence (ECL), is a luminescent phenomenon triggered by electrochemical reactions. Radicals produced at electrode undergo a high energetic electron transfer to generate the excited state, which later emits light.[1]
The combination of electrochemical and spectroscopic methods give ECL several advantages such as: temporal and spatial control on light emission, intrinsically very low background, then high sensitivity (pM), broad dynamic range (i.e. more than six order of magnitude) and rapid measurement (i.e. few seconds) in low volume (μl).
Applications of ECL mainly concern sensor and biosensor for a variety of analytes (e.g., metals ions, organic molecules, proteins, immunoglobulins, and DNA), as well as ECL imaging for the characterization of nanomaterials or cell mapping.[2]
Because ECL is primary triggered by an electrochemical reaction, the electrode material plays a major role in the signal generation, where the most common are Pt, Au, glassy carbon and carbon nanomaterials.[3]
We investigated the use of boron-doped diamond (BDD) electrodes for the ECL of the coreactants tri-n-propylamine (TPrA) and peroxydisulfate ($S_2O_8^{2-}$),[4] and a special method of coreactant generation directly in situ that can be achieved thanks to the particular characteristics of BDD. The oxidation of inorganic salts which later act as coreactants can be achieved by the wide potential window and the generation of hydroxyl radical from water oxidation.[6-7]
A peculiarity of BDD is the possibility to select the amount of boron doping level which affects the electrochemical behaviors, and this aspect has been investigated for the ECL emission.[8]
ECL at BDD is still in its infancy and needs proper investigation, furthermore the ECL by coreactant generation directly in situ might offer new opportunities for sensors development.

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Emerging applications that solve health related challenges: a focus on medication adherence and pain assessment

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The number of digital health technologies has boomed lately and the field has considerably evolved in the last two decades.[1] It is recognized that these technologies are also becoming major drivers towards improved quality of healthcare.[3] Digital health solutions have benefited from increased capabilities of more specific areas such as artificial intelligence (AI)Whilst the type of AI can vary and is subject to ongoing innovations, most health-related interventions use a form of signal processing or machine learning.[4] In terms of scope of application, these solutions address various health related problems in therapeutics, diagnostics, education and health promotion. Here we focus on two health-related challenges that can be assisted by use of digital health technologies and supported by artificial intelligence. Finding better ways of detecting and therefore improving medication adherence is one challenge that currently has a number of health consequences. Over half of people with chronic conditions are non-adherent to their medications and this results in increased hospitalizations, mortality and healthcare cost. [5,6] Much of this non-adherence relates to issues with medication self-administration. In this regard, we used an AI-driven system to wirelessly detect and evaluate the technique of inhaler and insulin self-administration.[6] Secondly, use of digital health technologies supported by AI can also be demonstrated in the area of pain assessment in people unable to communicate. Population groups such as infants and people living with advanced dementia are unable to self-report their pain.[7,8] People with dementia often experience behavioural and psychological symptoms whilst the underlying cause of that may be undertreated or undetected pain. There are other multiple health related challenges that can be assisted by use of digital health solutions and continuous advancements in AI techniques will further facilitate development and clinical deployment of these solutions.

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Functionalized, nanostructured multiscale cementitious materials

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The developement of sustainable multifunctional materials requires to move away from the linear economic model of take-make-use-dispose and to replace this with a higher efficiency and viability of using resources according to the “cradle to cradle principle“. A model for this can be nature. The transfer of structural principles from biological systems to new materials (bioinspired materials) with the help of nanotechnology is the key to develop such materials. The high strength, performance and durability of these materials alone is not sufficient. They should additionally bear other properties (functionalities) In addition, they should have “intelligent“ properties, multi-functionality, sustainability and economy. Hence it is imperative not only to have materials with the highest possible performance but also sustainable “intelligent“ ones with multi-functionality and cheap to produce.

Comprehensive basic research has been carried out using different methods of micro- and nanoanalytics on model systems in order to analyze the reaction mechanisms of the micro and nanoparticles. Self Compacting and Ultra High Performance Concrete with improved and new properties have been produced based on nanotechnology. On this basis, Ultra High Performance Concrete was also produced as a porous material by innovative foaming. The foam concretes can be used for heat and sound insulation. Multiscale Ultra High Performance Concrete (MSUHPC), a material on the front-edge of performance with extreme 2 hours strength (more than 400 MPa) was developed and its main properties characterized.

Alternative cement-free binders based on industrial by-products such as blastfurnace slag and fly ash have been developed to be used for the development of cement-free Self Compacting and Ultra High Performance Concrete. On top of that the the surface functionalisation of Ultra High Performance Concrete (MSUHPC) is carried with the aim is to develop multifunctional concrete that is not only very resilient, strong and durable but it has additional surface properties.

Keywords: functionalized, sustainable nanostructured cementitious materials, multiscale Ultra High Performance Concrete.

Tailoring electronic and magnetic properties with molecular strategies: from ligand chemistry to covalent nanoarchitectures.

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The flexibility of synthetic chemistry can be exploited in various ways for tailoring electronic and magnetic properties of nanomaterials. One can use ligand chemistry to tune the properties of single magnetic ions and their interaction with the underlying surface. This interaction can be finely tuned by weak intermolecular interactions in self-assembled structures. A different strategy aims at using coordinate or covalent bonding to build nanoarchitectures out of molecular building blocks. Here the stronger coupling leads to the emergence of properties that are not related with those of the building blocks, such as highly delocalized bands or magnetic exchange.
Here I will present different strategies studied in our group to: i) tune interactions between magnetic molecules and metallic [1] and topological insulator surfaces [2], ii) combine Dirac and flat bands in a single metal-organic framework [3], and iii) build graphene-based nanoarchitectures with atomic precision [4].

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Figures

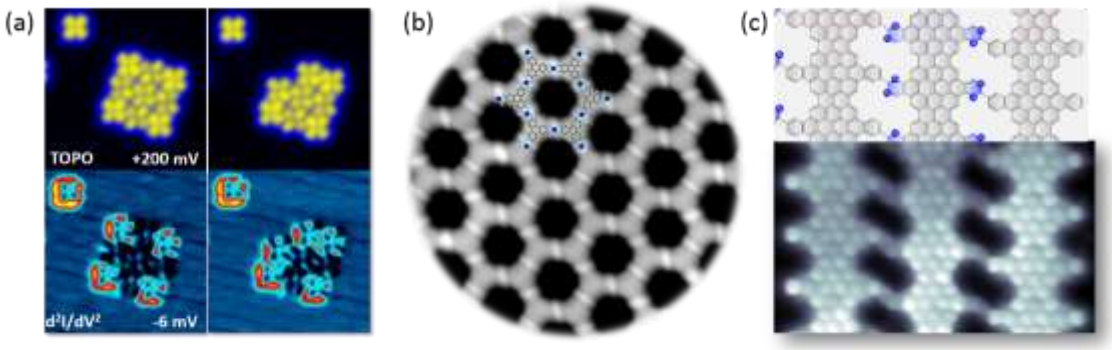

Figure 1. (a) STM topographic and spectroscopic maps of a self-assembled cluster of CuPc molecules, before and after removal of one corner molecule, demonstrating how weak intermolecular interactions can dramatically affect the electronic and magnetic properties of neighbor molecules. (b) Example of an on-surface synthesized metal-organic framework with honeycomb structure, where Dirac and flat bands coexist. (c) Example of an on-surface synthesized, graphene-based lateral superlattice heterostructure.

Photocatalytic Generation of Solar Chemicals

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Photocatalysts as photo-functional materials are able to convert photo energy to chemical one, thus the property gives wide range applications for environmental cleaning and resource production, such as air and water purification, sterilization, hydrogen evolution, and photoelectrochemical conversion. In this presentation, photocatalytic production of bio-related chemicals are reported.

1) Production of rare sugars using photocatalysis. Rare sugars have much attention because of their potential candidates for new foods and drags. For example, D-allose has strong suppressive effect against cancer cell proliferation, and D-psicose shows much sweetness, high solubility, water-holding property, spreadability, resiliency and antioxidation. However, it is very hard to obtain those sugars, thus a common and facile new method to produce rare sugars is strongly requested. Our group recently reported that arabinose could be produced from the oxidative decomposition of glucose by titanium dioxide (TiO_2) photocatalysis under ultra-violet (UV) light illumination. In this work, we examined decomposition of monosaccharides to produce rare sugars by using the TiO_2 photocatalyst. Photocatalytic decomposition of galactose was performed with the TiO_2 photocatalyst under UV illumination, resulting in production of lyxose which is a rare sugar. From the comparison of molecular structure between garactose and lyxose, α-carbon was selectively released. We further performed photocatalytic oxidative decomposition of mannose, gulose, and allose, which allows production of arabinose, xylose and ribose, respectively. Those reaction also showed regular molecular conversion by release of α-carbon. Those results suggested that photocatalytic oxidative decomposition is able to produce rare sugars.

2) Spore inactivation with visible light responsive photocatalyst WO_3. Bacteria that cause serious food poisoning are known to sporulate under conditions of nutrient and water shortage. The resulting spores have much greater resistance to common sterilization methods, such as heating at 100 °C and exposure to various chemical agents. Since such bacteria cannot be inactivated with typical alcohol disinfectants, peroxyacetic acid (PAA) often is used, but PAA is a harmful agent that can seriously damage human health. Furthermore, concentrated hydrogen peroxide, which is also dangerous, must be used to prepare PAA. Thus, the development of a facile and safe sporicidal disinfectant is strongly required. In this study, we have developed an innovative sporicidal disinfection method that employs the combination of an aqueous ethanol solution, visible light irradiation, and a photocatalyst. We successfully produced a sporicidal disinfectant one hundred times as effective as commercially available PAA, while also resolving the hazards and odor problems associated with PAA.

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Polymer-based Nano/microfibers for Hard Tissue Engineering Applications

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Polymers, both natural and synthetic ones, have found a wide range of applications in the last decades. They are mostly used as biomaterials, which have the aim of tissue regeneration, as they can serve as scaffolds/support for cells during their growth and replace the function of the damaged tissue until a neo-tissue is formed. Dependant on the aim of application, these polymeric scaffolds undergo certain fabrication techniques such as foaming, freeze-drying, 3D printing and electrospinning. Electrospining is a technique that produces various nano/microfibers by means of a high voltage. This work, focuses on preparation of electrospun biodegradable nano/microfibers for hard tissue engineering purposes such as bone and meniscus tissue. In a previous study, a microbial polyester, poly(3-hydroxybutyrate-co-3- hydroxyvalerate) (PHBV) blended with lactide-based polymers were electrospun into fibrous scaffolds for bone tissue engineering use. Process parameters were optimized (Fig. 1A) and the influence of fiber diameter on cell performance was studied. In vitro studies with human osteosarcoma cells revealed that electrospun scaffolds promote cell growth and penetration (Fig. 1B). To increase surface hydropfilicity, surface was modified with oxygen plasma treatment which improved the cell proliferation rates. Consequently, all scaffolds prepared by electrospinning revealed a significant potential for use in bone tissue engineering applications; PHBV-PLLA blend appeared to yield the best results [1]. In another study, collagen type I isolated from rat tails, was used as a support to mimic the 3D structure of a meniscus tissue. Coll-PLGA blend increased the mechanical properties of the fibrous mesh, which was incorporated inside a 3D multilayered structure (Figs. 1C and 1D) [2]. The last research shows electrospun polyethylene terephthalate (PET), recycled from pastic bottles, to be studied for its antibacterial properties due to zeolite incorporation inside the fibrous structure.

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Figures

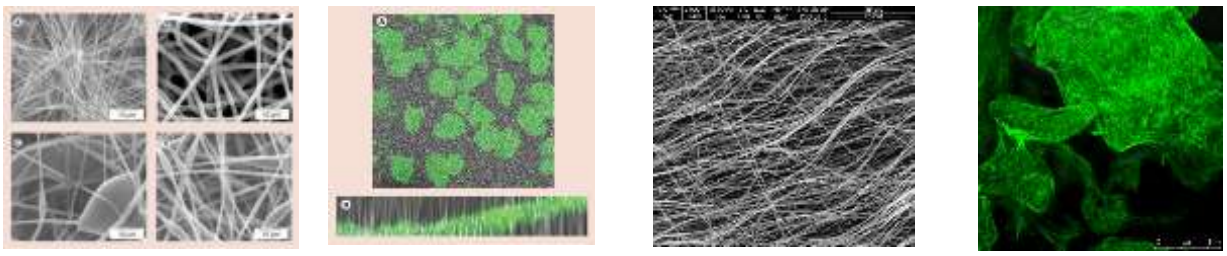

Figure 1. (A) PHBV-lactide based fibers; (B) Interaction of SaOs-2 cells with fibers; (3) Coll-PLGA nanofibers; (4) Interaction of human meniscus cells with collagen-based 3D structure (from left to right).

Chemical and electrochemical exfoliation of graphite in a large scale

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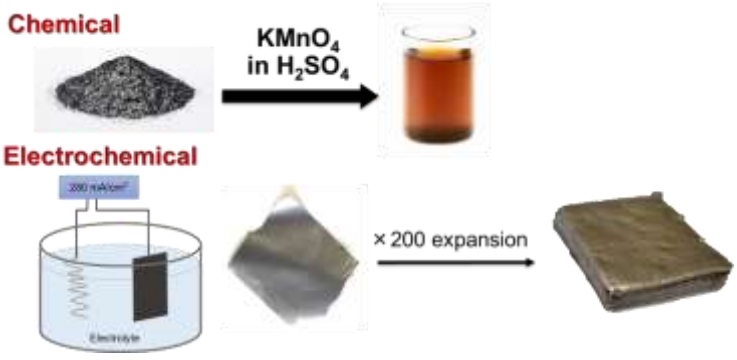
Graphene is the ultimate two-dimensional material with the thickness of a single carbon atom and is expected to be a next-generation material because it has excellent various physical properties required for functional materials such as electrical conductivity, specific surface area, and strength. However, many obstacles must be overcome for practical use. The biggest challenge is to establish a method for producing high-quality graphene on a large scale and with good reproducibility at a low cost. The production methods of graphene include a bottom-up method (chemical vapor deposition method, arc discharge, organic synthesis, etc.) and a top-down method (graphite exfoliation method). Currently, there is a trade-off between cost and physical properties, thus we are required to select an optimum preparation method of graphene depending on the application. For polymer composite materials, lubricating additives, conductive coatings, inks, catalysts, and supercapacitors, ultra-high purity graphene is not necessary. These applications require large amounts of graphene at a reasonable cost. For this reason, two-dimensional nanocarbons similar to graphene have been attracting attention by a top-down method capable of large-scale production using low-cost and easily available graphite as a raw material.

Graphene oxide (GO) obtained by oxidizing and exfoliating graphite will be introduced as an example. We have achieved a 500 g scale production of GO in the laboratory, and 10 kg production in a prototype plant by optimized oxidation method using $KMnO_4$ in H_2SO_4. These large-scale productions were achieved by the mechanistic study of the oxidation process using in situ analyses, such as XRD and XANES [1]. Our optimized GO production processes enabled the control of the size, oxidation degree, and functional group distribution on GO [2]. The conventional oxidation of graphite uses a strong oxidant in concentrated sulfuric acid; thus, there are environmental and safety issues. In contrast, the electrochemical oxidation of a graphite electrode has recently attracted considerable attention because it does not require any oxidant or concentrated sulfuric acid [3]. GO produced through the existing electrochemical method is generally lacking in quality, due to the non-uniform destruction of the intermediately oxidized graphite. We developed a method for the non-destructive oxidation of graphite using a specially designed electrolyte [4]. Compared to chemically generated GO, the electrochemically generated GO exhibits similar or better physical and chemical properties toward lithium-ion battery electrodes and water purification membranes. This electrochemical method is also applicable to a continuous flow system, thus promising the mass production of GO for future industrialization [5].



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Layered conjugated polymers with stimuli-responsive color-change properties

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Layered inorganic compounds have attracted much interest for their Intercalation and exfoliation properties. In contrast to these "rigid" layered structures, exfoliation and intercalation chemistry of soft layered materials have not been fully studied toward exploration of the dynamic functions. Our group focuses on "soft" layered materials. Soft layered composites are efficiently exfoliated into the nanosheets.[1,2] Recently, the designed organic layered materials are synthesized and applied to a superior electrocatalyst for hydrogen evolution reaction and active material of aqueous supercapacitor.[3,4] In this symposium, I focus on a soft layered conjugated polymer, namely layered polydiacetylene (PDA), exhibiting the structure flexibility and dynamic properties (Figure 1).[2,5-13] Intercalation of the guests controls flexibility of the layered conjugate polymer leading to the dynamic color-change properties. The stimuli-responsive color-change properties are controlled by the types of the intercalated guests. A variety of external stimuli, such as heat,[5–8] light,[9,10] and force,[11–13] are not only visualized but also quantified using the new layered composites based on PDA and their devices.

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Figure

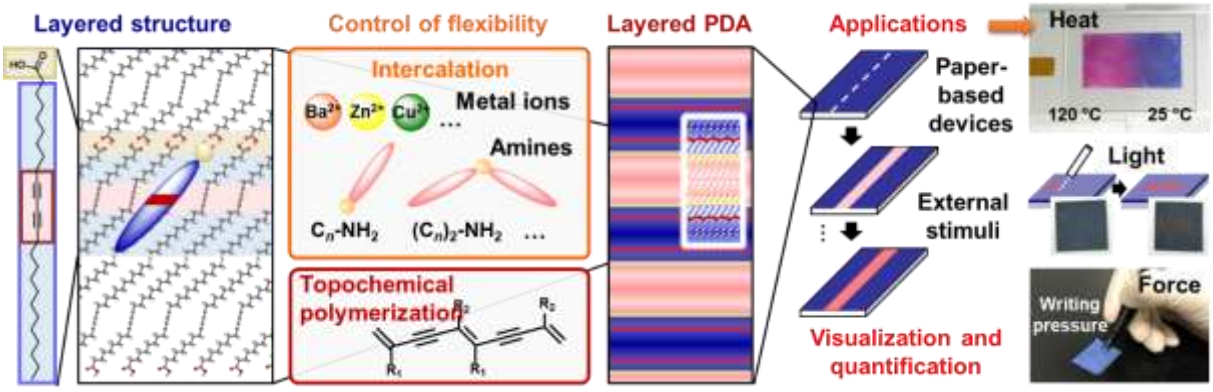

Figure 1. Schematic illustrations of layered polydiacetylene (PDA) with tunable stimuli-responsive color-change properties and applications to visualization and quantification of external stimuli, such as heat, light, and force.[5–13]

Research and Innovation at the Catalan Institute of Nanoscience and Nanotechnology

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The talk will provide a broad view of the model of the Catalan Institute of Nanoscience and Nanotechnology - ICN2, one of the centres belonging to the CERCA system in Catalonia. ICN2 focuses its activities in all the aspects of Nanoscience and Nanotechonology, from basic, blue skies research, to the development of technologies devoted to solving societal and industrial challenges, all the way into the establishment of start-up companies. I will give the main principles that govern the functioning of the Institute, and examples of specific activities. I will also provide a view of the plans for future expansion of the ICN2, focused on collaborative projects in the areas of Energy and Health research.

Modification of the surfaces of materials with functional organic layers

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Abstract

Tethering carbon (all types), metal, semiconductor and polymer surfaces with organic moieties ensuing the electrochemical reduction of vinylics, aryl diazonium salts and the oxidation of primary alkyl amines, carboxylates has shown the tremendous potential of different organic molecules to create thin organic coatings that change drastically the properties of the material. [1,2] Among these reagents, aryl diazonium salts are widely used due to wide substrate compatibility, strong adhesión to substrate surface and the modification is performed in organic and aqueous solvents. In most of the cases, the organic moieties bear different functional groups that serve as coupling agents for further post modification of the attached layer through many different ways, Figure 1.[3] This strategy has permitted to prepare new entities that are used for many applications like chemical and biosensors, catalysis, optoelectronics, molecular electronics, drug delivery etc.

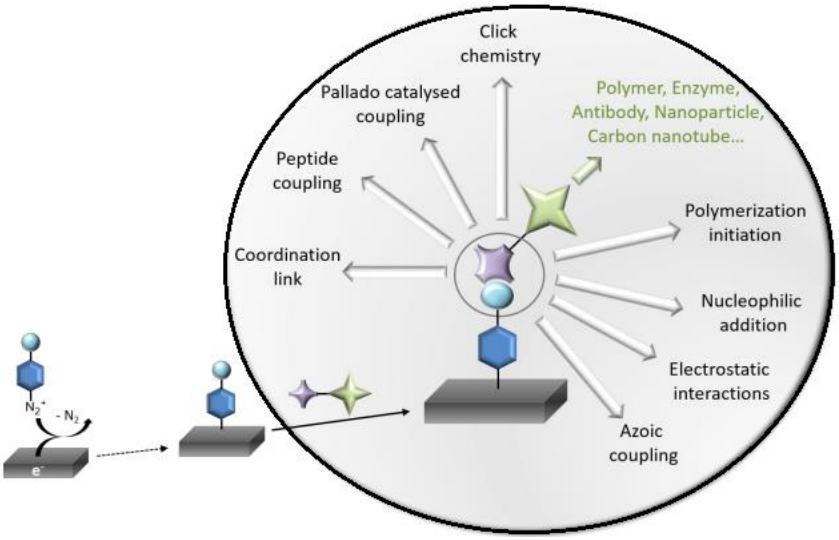

Fig. 1. Modification of material surfaces with functional organic moieties that unable further post-modification through different ways. [3]

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Electrochemical Sensing of Dissolved Hydrogen Sulfide on Boron Doped Diamond Electrodes

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Hydrogen sulfide (H_2S) is a flammable, water soluble and colorless gas with a strong smell of rotten eggs. It is also harmful when emitted into the air[1]. Electrochemical sensors have some advantages for H_2S detection. The sensitivity, selectivity, and stability are high, and detection is in real time, with a low-detection limit (LOD) and good reproducibility[2]. Thus, many methods require a redox mediator to prevent sulfur from being deposited on the surface. An electron is received from H_2S or HS^- and is regenerated on the working electrode and a measurable current can be observed[3]. In this work, we attempted to study the electrochemical oxidation reaction of dissolved hydrogen sulfide using BDD electrodes and to detect H_2S or HS^- without using a mediator or modifying the surface. Especially, the pH of the electrolyte and the scan rate of the CV measurement were varied to investigate the electrochemical reaction. Then, the performance was examined, and an interference test was conducted. The performance was compared with that of two other commonly used electrodes for hydrogen sulfide sensing: glassy carbon and platinum electrodes.

Here, we report detection of dissolved hydrogen sulfide using boron doped diamond (BDD) electrodes and 0.1 mol L^{-1} $KClO_4$ as an electrolyte. Oxidation of H_2S and HS^- started at potentials of +1.7 V and +0.5 V (*vs*. Ag/AgCl), respectively. We varied the pH to confirm the oxidation behavior. The electrolyte pH was adjusted to 1.6 and 10.2 in order to individually characterize the CVs for H_2S and HS^-. H_2S is the dominant species at pH 1.6 and HS^- at 10.25[4]. In order to study the oxidation mechanism, CVs at various scan rates were conducted. In this regard, the oxidation current increased linearly with the square root of the scan rate over the range 0.01 – 0.06 V s^{-1}, indicating that the process is transport controlled with little or no fouling of the electrode[5]. At pH=1.6, the slope as diffusion coefficient was 0.0019 (R = 0.998) and the calculated value for n was about ~7 electrons[6]. Next, at pH=10.2, the potential range from 0 V to 0.8 V (*vs*. Ag/AgCl) was used in order to avoid overlapping of the oxidation peak at +1.3 V (*vs*. Ag/AgCl). The slope as diffusion coefficient was 0.01 (R= 0.96) and the value of n was ~4 electrons. A linear calibration curve was observed in the concentration range of 0.08 – 2.34 mg L^{-1} (R = 0.99) with a detection limit of 0.82 µg L^{-1} (S/N = 3).

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Development of electrochemical imunosensors based on CPE modification

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Ferritin is a major intracellular iron storage protein present in all cells, tissues and tissue fluids of the organism. Low ferritin levels result in lower iron concentrations which is directly involved with anemia. Elevated levels of ferritin, or hyperferritinemia, indicate the presence of viruses and bacteria into the body. Clinical observations on Covid-19 patients have reported cases accompanied by elevated levels of ferritin in blood [1]. An attempt is made to develop a new voltametric immunosensor for determination of ferritin based on the principles of biological recognition, antibody-antigen reaction combined with nanotechnology and the advantages of electrochemical detection strategies. Carbon Paste Electrode modified with grain natural material, characterized as titanium magnetite is used as substrate for immunosensor. The immobilization of ferritine antibody (FeAb) can be effectively improved by using a thin film of surfactant [2], trimethyl-tetradecylammonium chloride (TTDC), onto the CPE substrate. The modification procedure of the immunosensor is characterized by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The effect of FeAb incubation time and the FeAb-ferritine reaction kinetic are explored to provide optimum analytical performance. The quantitative determination of ferritine is based on the change in DPV response before and after antibody-antigen reaction [3]. The linear range resulted within the interval 0.05 – 0.5 mg/l ferritine (R^2=0.9947). The recovery of ferritine addition in real sample matrix resulted from 87% to 125%. The specificity of FeAb-ferritin reaction evaluated in terms of binding constant, resulted in the order of 10^{-9} l/mol. All measurements are done in pH=7 phosphate buffer saline (PBS) at room temperature.

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Figures

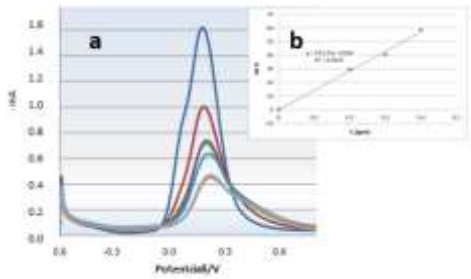

Figure 1. (a) DPVs of FeAb/CPE in different concentrations (0.1-0.5mg/L) of ferritin solutions in PBS; (b)calibration graph.

Influence of the pH on the stability of CdTe QDs investigated by fluorescence and particle size analyses

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Abstract

CdTe quantum dots are mainly used as biological markers (labels). Compared to the usual biomarkers they reveal size and composition tunable emissions, narrow emission spectra, wide excitation profiles, and long luminescence lifetimes. The environment around the tumor cells often shows decreased pH values compared to healthy cells. CdTe QDs were prepared from the mixture of two main solutions: a) $Cd(CH_3COO)_2$, mercaptosuccinic acid in slightly basic solution and b) Na_2TeO_3 + $NaBH_4$. The obtained CdTe QDs are stabilised by mercaptosuccinate ions. Their behavior and stability was tested in buffer solutions within the pH range 3-8. Their stability was tested by fluorescent spectra for each pH at different times and tracking of particle size changes through Malvern zetasizer. Shifting from the initial position of the fluorescence emission maxima were observed for the low and high pH values.
In the acidic pH range (3-3.5) the carboxyl groups are not dissociated and as a consequence their particles increase over time from 0.5 µm to 1.5 µm. The increase of particle size leads to enhancement of fluorescence intensity, peak broadening and shifting of intensity maxima toward greater wavelengths. Through maxima shifting in fluorescence spectra and particle size analysis could be proved the increase of the CdTe QDs system stability near neutral pH values. At pH values > 7 particle size increases slightly due to surface modifications, leading to slight shifting of intensity maxima toward smaller wavelengths. The increase of pH slows down the process of coagulation and sedimentation. In alkaline pHs there a slight increase of the particle size is observed.

Figures

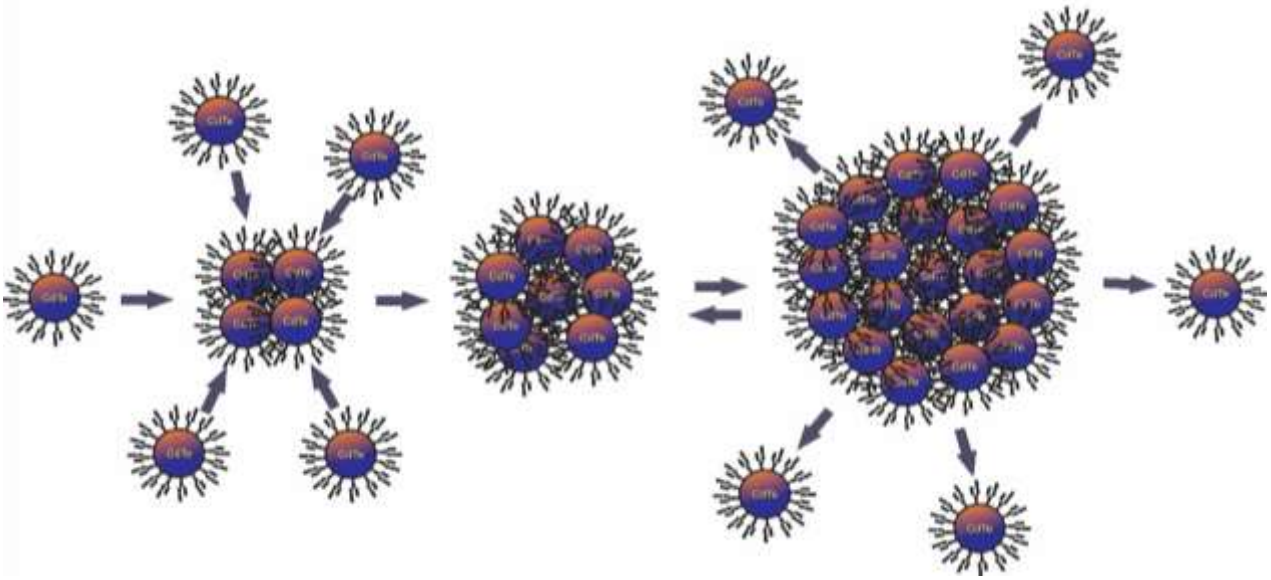

Figure 1. Dynamics of CdTe particle size particles increase at low pH values.

POSTERS

Experimental and theoretical determination of Heliums diffusion coeficient in Kapton®

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Kapton (poly-oxydiphenylene-pyromellitimide) is a polyimide film that is stable throughout a large temperature range of -269 to +400 degrees. This polymer is utilized in a variety of applications, including flexible printed circuits, in spacecraft (aluminized foils to provide thermal insulation), aircraft (for insulated electrical wiring), satellites, as an insulator in ultra-high vacuum environments, as a material for windows used with all kinds of X-ray sources, 3D printing and cryogenics. Since this material is widely employed as an insulator in ultra-high vacuum conditions, it is necessary to investigate gas diffusion/permeation properties. The evaluation of helium diffusion on this material is explored both experimentally and by Molecular Mechanic calculations. The throughput method is used to measure diffusion, permeation and solubility coefficient. The throughput method uses an orifice with known dimensions. Measurements were performed for different temperature in the region from 23 -150 ^{0}C.

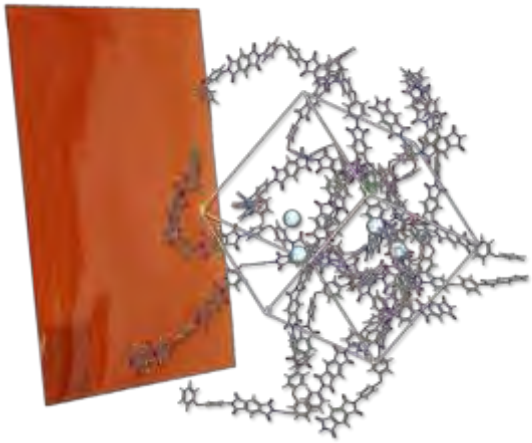

Figure 1. Kapton® film and the PBC model used in theoretical calculations.

Helium's self-diffusion coefficient in Kapton was theoretically determined through the use of Molecular Dynamic simulations. The amorphous cell module was used to build a periodic model consisting of ten chains of poly-oxydiphenylene-pyromellitimide units and five He atoms (Figure 1). This model is geometrically optimized in the first stage (using the COMPASSII forcefield), then exposed to NPT at 0.1MPa (1000 ps), and finally to NVT (3000ps). D=MSD(t)/6 was used to compute the self-diffusion coefficient D (cm^2/s) from the Mean-Square Displacement (MSD) of the helium molecules.

Origanum vulgaris essential oil-loaded nanosystems: preparation, characterization and stability studies

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Introduction
In recent years, there has been a growing interest in the therapeutic properties of natural herbal essential oils. Origanum vulgaris essential oil (OEO) has shown a wide range of medicinal applications. However, therapeutic applications of EO in general are limited since it's proven that they possess high volatility and poor stability, water solubility and bioavailability, leading to decline/loss of efficiency. In that regard, nano-encapsulation of OEO is a promising approach to overcome these disadvantages.
Purpose
Preparation and evaluation of the encapsulation efficiency and stability of OEO nanosystems.
Methods
Preparation and characterization of different nanocarriers, liposomes and nanoemulsions, was done by using the ethanol injection method (Lipoid S100, Phospholipon 85G, and 90H) and homogenization process (MCT, lecithin, and surfactant), respectively. Their particle size, polydispersity index, Zeta potential, encapsulation efficiency were compared and evaluated at t0 and after 2 months.
Results
Stability results for 2 months at 25°C showed that nanoemulsions produced similar results to Phospholipon 90H based liposomes, exhibiting the average particle size of the smallest of all studied formulations. Compared to Ph 85G/Lipoid S100 loaded liposomes, Ph 90H loaded liposomes and nanoemulsions improved the loading rate of OEO.
Conclusion
According to our findings, developing OEO nano delivery systems has the potential to solve the major shortcomings of its free unencapsulated form while also enhancing encapsulation efficiency, making it a prospective choice for a more efficient therapeutic strategy.

This project was financially supported by the Kosovo Ministry of Education, Science, Technology and Innovation.

Mimoza Basholli-Salihu, Aida Shala and Toskë L. Kryeziu are members of NANOALB research group.

A DFT study of the binding of aryl and alkyl radicals to the B12N12 nanocage cluster

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The interaction, electronic and optical properties of octahedral B12N12 nanocage cluster covalently modified from the attachment of alkyl and aryl radicals[1] were analyzed using Density Functional Theory calculations. At T = 298.15 K in the vacuum and solvent, the measured adsorption and binding energies of aryl (Figure 1) and alkyl radicals with the B12N12 fullerene are also evaluated. In order to classify the most significant changes occurring as a result of interactions between B12N12 fullerene and radicals, UV absorption and IR spectra were computed and analyzed.

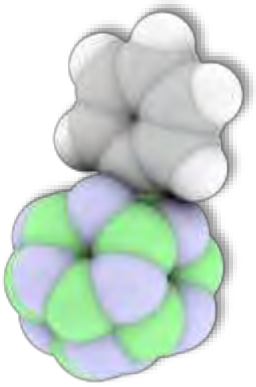

Figure 1. The optimized geometry of grafted B12N12 nanocage cluster by a phenyl group.

The adsorption of the aryl or alkyl diazoniums onto the B12N12 surface, where van Der Waals interactions play a major role, is a first step prior to grafting reaction. Furthermore, the transition state indicates that the interaction of aryl and alkyl radicals indicates that the modification steps is spontaneous.

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Voltametric detection of β-lactam antibiotics based on modified nanocomposite carbon paste electrode

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Abstract

β-Lactams, a group of widely prescribed antibiotics, are often detected in wastewater effluent and in the natural aquatic environment. In this work, a simple voltammetric sensor was developed for the sensitive detection of the β-lactam antibiotic penicillin, using nanocomposite electrodes modified with rutile natural mineral (CPE-TiO_2). The electrochemical behavior of penicillin at modified nanocomposite sensors CPE-TiO_2 was investigated using voltammetric techniques SWV in acetate buffer solution pH=4. The effect of nanomodifiers at CPES response was estimated by comparing the electroanalytical signal of modified sensor with the bare electrode. The enhanced oxidation peak current of penicillin at modified sensors can be attributed to the catalytic effect of rutile natural mineral incorporated into carbon paste electrode. Under optimize condition, a good linear calibration curve, were obtained ranging from 0.18 mM to 0.65 mM, with detection limits of 4.28 µM. The nanocomposite modified sensor showed good reproducibility (RSD 3.6 %), and high sensitivity for the detection of penicillin with a very high stability in its electrochemical response. The proposed method was successfully applied in real samples, pharmaceutical formulations.

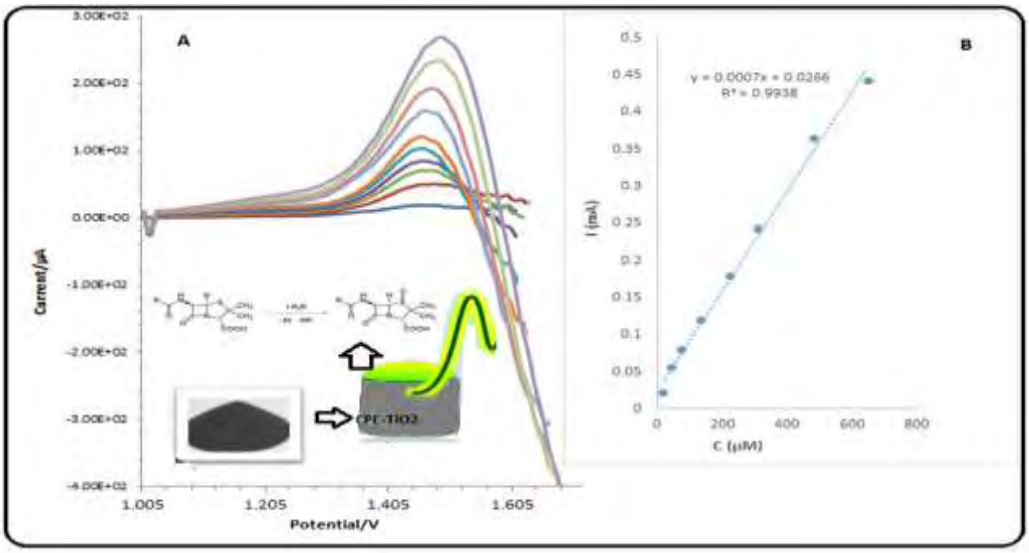

Figure 1. A) Square wave voltammograms for CPE-TiO_2 Sensor for different concentration of penicillin. Frequency 30 HZ, amplitude 50 mV and step potential 5 mV.B) Corresponding Calibration curves.

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An electrochemical sensor for leflunomide determination and detection in tablet forms and biological fluids based on a molecularly imprinted copolymer

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Leflunomide (LEF) is a disease-modifying anti-rheumatic medication (DMARD) that is used to treat rheumatoid arthritis (RA), psoriatic arthritis (PA), and multiple sclerosis [1].

The aim of this research is to create a quick, sensitive, and selective technique for detecting LEF in biological fluids and tablet forms at low concentrations. A new molecularly imprinted polymer (MIP)-based electrochemical sensor was created for this purpose, utilizing cyclic voltammetry (CV) to electropolymerize a copolymer of aniline (ANI) and o-phenylendiamine (o-PD) on glassy carbon electrode (GCE). In addition, for the optimization and characterization investigations, as well as the assessment of the performance of the newly designed MIP-based sensor, differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) techniques were utilized.

Electrochemical techniques are preferred over other analytical methods because they are more cost-effective, shorter analysis time, and environmentally friendly. Electrochemical methods also have the advantages of simplicity, a wide linear range, high precision, good stability, and repeatability. Recently, the number of studies on MIPs has increased. Reusability, physicochemical and long-term stability, high sensitivity, and selectivity at extremely low concentrations are only a few of the advantages of MIP-based electrochemical sensors. In this study, MIP-based electrochemical sensors were developed by the copolymerization of two functional monomers, ANI and o-PD, for the selective and sensitive determination of LEF in pharmaceutical dosage form and synthetic human serum samples.

This new sensor demonstrates a highly effective alternative for LEF analysis without extensive steps such as derivatization or sample preparation. Furthermore, because of its low cost, ease of production, excellent selectivity, and sensitivity, the produced sensor is a potential alternative approach. To monitor each phase of manufacturing utilizing DPV and CV methods, the MIP@ANI-co-o-PD/GCE sensor was tested using the indirect method, $Fe[(CN)_6]^{-3/-4}$ redox marker. The proposed method was achieved in a linear working concentration range of 1.0 fM-10.0 fM with a detection limit of 0.291 fM under optimal conditions for LEF. The recoveries were found as 99.15% and 99.46%, and relative standard deviation (RSD) was calculated as 1.39% and 1.22% in synthetic serum samples and pharmaceutical dosage form.

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27Al MAS NMR key for nanomolecular structure modification of C-(A-)S-H of multiscale UHPC concrete

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Abstract

The present paper reports an investigation of six Ultra-High-Performance Concrete (UHPC) modified with pyrogenic oxides (represented by Aerosil and AluC) and treated under different temperature and pressure conditions by using the NMR method [1].
^{27}Al MAS NMR utilization as a complementary method has been useful to study the nanomolecular structure of UHPC's main phase, C-A-S-H. On analyzing different sites of the C-S-H, spectral deconvolution is shown to be a valuable tool [2]. The nanomolecular investigation of this new UHPS leads us to a better understanding and improvement of the properties of the material on a macro-scale.

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Figures

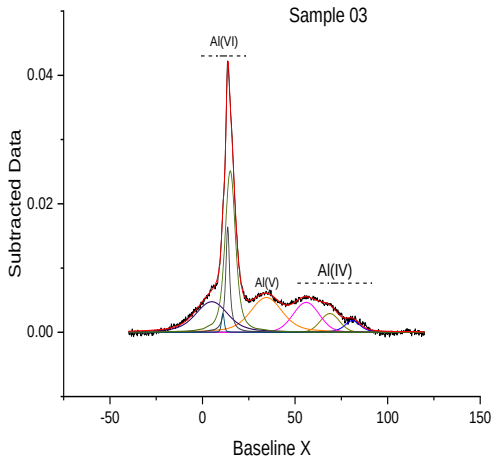

Figure 1. ^{27}Al MAS NMR Analysis

A new electroanalytical method for determination of nitrites in water sample using surface response methodology

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A new selective electroanalytical method has been developed and optimized for the determination of nitrites in water samples. This electroanalytical method is based in a specific reaction of nitrites with ranitidine in 0.1 M Britton Robinson buffer (pH 2.0) to form an electroactive nitrosamine and 2-methylfuran cation. Electrochemical reduction of the 2-methyl-2H-furan-3-one with side chain derived from ranitidine at the unmodified screen-printed electrodes was observed at -0.413 V using square wave voltammetry. Working conditions (such as temperature, time, pH, concentration of the buffer and ranitidine) as well as electroanalytical parameters (frequency, step potential and amplitude) necessary for quantitative nitrites reaction and subsequent electrochemical detection using square wave voltammetry had to be optimized using surface response methodology. Two linear ranges from 2.0×10^{-6} to 5.0×10^{-4} mol L^{-1} and from 5.0×10^{-4} mol L^{-1} to 1.0×10^{-3} mol L^{-1} of nitrites characterized by correlation coefficients 0.9996 and 0.9975, limits of quantification 3.2×10^{-6} mol L^{-1} and detection limit of 6.9×10^{-7} mol L^{-1} were achieved. The recovery results for different concentration have shown that SWV is sensitive method for determination of nitrite ions in water and wastewater samples being comparable to spectrophotometric method.

Keywords: nitrite ions; ranitidine; screen-printed electrode; square wave voltammetry.

Preleminary data on removal of ammonia from wastewater using metal oxide material derived from the quartz sand enrichment process

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Ammoniacal nitrogen (ammonia and ammonium) in agricultural wastewaters can promote eutrophication of receiving waters and be potentially toxic to fish and other aquatic life. Natural material (NM), metal oxide material derived from the quartz sand enrichment process have been successfully utilized for their ammonia removal efficiency.

The effect of contact time, pH and initial concentrations on the adsorption capacity of the adsorbent has also been investigated. It can be observed that as the size of sorbents particles gets lower, the adsorption capacity, as well as removal efficiency, gets higher. After pretreatment with 1 mol/L NaCl solution, maximum efficiency increments were observed 60.3 %. A comparison of mathematical model applied to the adsorption of ammoniacal nitrogen was evaluated for the Langmuir and Freundlich adsorption models.

The Freundlich adsorption isotherm corresponds well with the equilibrium adsorption data (R^2 varied from 0.98 to 0.99), while the Langmuir model was found to be mismatched.

Keywords: ammonia, natural material, adsorption, efficiency, wastewater.

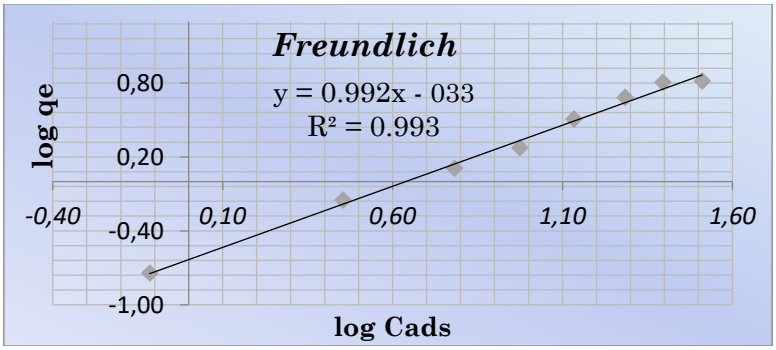

Figure 1. The linear Freundlich adsorption isotherm

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ELECTROCHEMICAL CHARACTERIZATION OF SCREEN-PRINTED CARBON ELECTRODE MODIFIED WITH GRAPHENE AND TYROSINASE FOR DIRECT DETERMINATION OF PARACETAMOL

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Abstract
The aim of this study was to develop an amperometric biosensor utilizing mushroom (Agaricus bisporus) tyrosinase (EC 1.14.18.1) suitable for the selective determination of acetaminophen in human urine. The presented biological device was based on a commercial screen-printed carbon electrode covered with a thin graphene layer (transducer) with an enzyme (bioreceptor) immobilized with glutaraldehyde and Nafion.
Owing to the use of tyrosinase and presence of NFG, the developed analytical instrument is able to measure even at potentials of 0 V. Linear ranges differ according to choose of detection potential, namely up to 130 µmol L^{-1} at 0 V, up to 90 µmol L^{-1} at −0.1 V, and up to 70 µmol L^{-1} at −0.15 V. The first mentioned linear range is described by the equation Ip [µA] = 0.236 − 0.1984c [µmol L^{-1}] and correlation coefficient r = 0.9987. The limit of detection of APAP was estimated to be 1.1 µmol L^{-1}. A recovery of 96.8% (c = 25 µmol L^{-1}, n = 5 measurements) was calculated. Best flow rate in flow injection analysis was 0.6 mL·min^{-1}. It can be stated that this biosensor can be used to detect paracetamol in very complex samples such as urine, for the possibility of operation at potential 0V.

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Figures

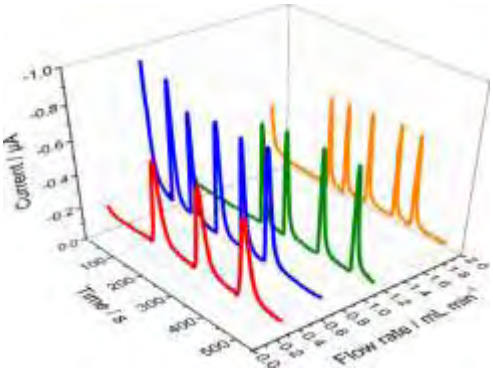

Figure 1. Effect of flow rate

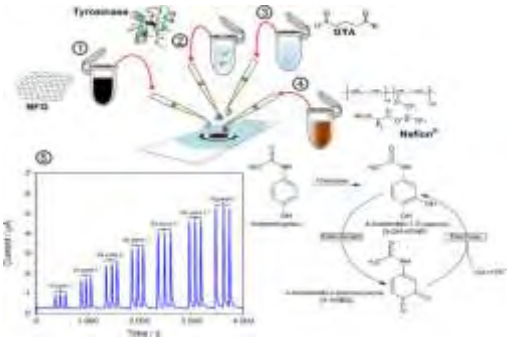

Figure 2. Preparation process of Tirosinase biosensor

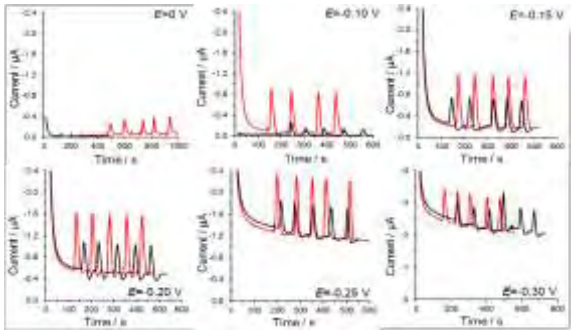

Figure 3. Dependence of the amperometric response of pure human urine (blue) and that with an admixture of 50 µmol L^{-1} APAP (yellow column). Supporting electrolyte: non deaerated 0.1 mol L^{-1} PBS of pH 7.0; injection volume: 100 µL, flow rate: 0.6 mL min^{-1} and temperature: 25°C.

Antibody conjugated magnetic nanoparticles in agglutination assay for dengue biomarker detection

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Dengue fever is a mosquito borne viral infection affecting billions living in the tropical parts of the world [1]. To tackle the spread of dengue at the community level, proper course of testing and treatment is necessary. Early diagnosis for the disease can be of important clinical care, surveillance of an outbreak, academic research etc. [2]. Rapid Diagnostic Tests (RDT) have been instrumental regarding speed of testing and usability. However, RDTs have drawbacks in terms of sensitivity, and it does not provide information about the previous infections [3]. There is a need for developing a test, with speed of a RDT or screening test and high accuracy of a laboratory test like ELISA. We present, a novel agglutination based optomagnetic assay for the detection of Dengue fever biomarkers [5]. Magnetic nanoparticles (MNPs) are conjugated with a ligand specific to dengue virus, and agglutinate in the presence of Dengue virus like particles (DVLPs). The MNPs bind to the analyte and enable formation of MNP chains. A homogenous magnetic field is applied to speed up reaction kinetics o the agglutination. The chains rotate and align under a magnetic field, and in an alternating magnetic field the chains repeatedly align and modulate the intensity of the transmitted light (Figure 1A). MNPs were conjugated with Dengue antibody using carbodiimide reaction to demonstrate the detection of dengue fever biomarkers in solution. These conjugates were characterized using BCA assay to estimate the amount of ligand conjugated on the MNPs, DLS and tested in agglutination assay using DVLPs, to determine the limit of detection in the agglutination assay (Figure 1B). The conjugates demonstrate a dose-response behavior with increasing concentration of DVLPs and show a potential to be implemented in an assay with patient samples.

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Figures

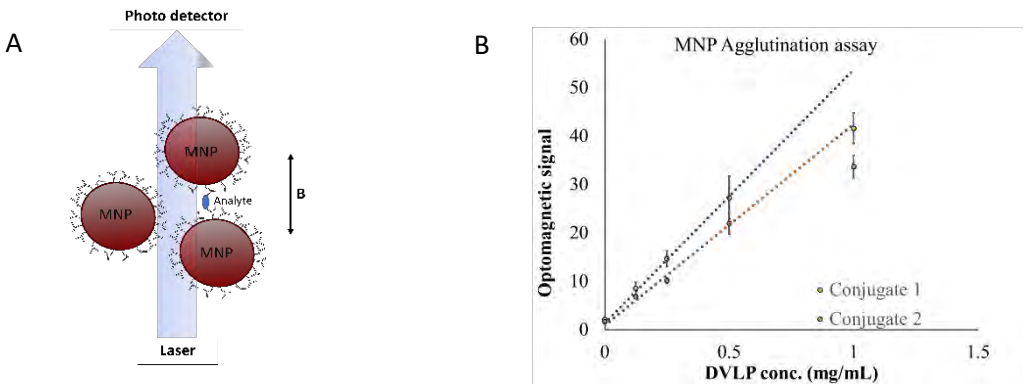

Figure 1. A) Sketch of optomagnetic detection of MNPs in a magnetic field and formation of MNPs chain in the presence of an analyte. **B**) optomagnetic signal versus DLVP concentration for two different conjugates. Error bars are calculated from 3 replicates. Lines are linear fit for concentrations below 1 mg/ml. Further DLS was performed to obtain hydrodynamic size. The conjugate -1 has a hydrodynamic size of 186.8 ± 1.5 nm and conjugate – 2 169.2 ± 0.3 nm.

Acid-activated bentonites of Kosovo to be used for oil regeneration

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Abstract

Bentonite soils are the most widely used bentonites due to their physicochemical properties, the ability to increase the space between the layers after undergoing the activation process (acid, alkaline, thermal or mix. This paper presents a summary of the results of activation of two Kosovo bentonites mainly in the Goshica area and the Karaqeva area. The two bentonites have been modified by introducing optimal bentonite processing methods including acid activation, in order for them to be used as bleaching agents. They have been compared with each other and with the untreated natural bentonites. It was found out that the activation of bentonites brings about significant changes in their structure and physicochemical properties. The specific surface area and cationic exchange capacity correlate well with the amount of activator. Acid activated Kosovo bentonites show promising results to be used for industrial processing, bleaching agents and UMO recycling at industrial scale.

Catalytic mechanism of phenol alkylation with diethylcarbonate using a nanostructured synthetic zeolite

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Abstract

In this study, type X zeolites were synthesized from fly ash by pre-fusion method followed by hydrothermal treatment. The synthesis was performed by a pretreated with hydrochloric acid, with low crystallization temperature (60 °C) using both seawater and distilled water [1]. The synthetic zeolites from fly ash were employed as substrates for developing catalysts with improved performance [2]. They were tested via the base-catalyzed gas-phase alkylation of phenol using diethyl carbonate as an innovative alkylating agent, thus obtaining phenol conversions up to 95% with a selectivity of more than 85% in phenetole. Moreover, the results show that the zeolites formed from fly ash have a greater catalytic activity than that shown by commercial NaY and synthetic MgO, which were chosen as basic reference catalysts [3]. The catalytic activity of the zeolites synthesized from fly ash gives high yields, is clean, cost effective, environmentally friendly which make the fly ash-based zeolites efficient catalysts and alternatives for industrial applications.

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Figures

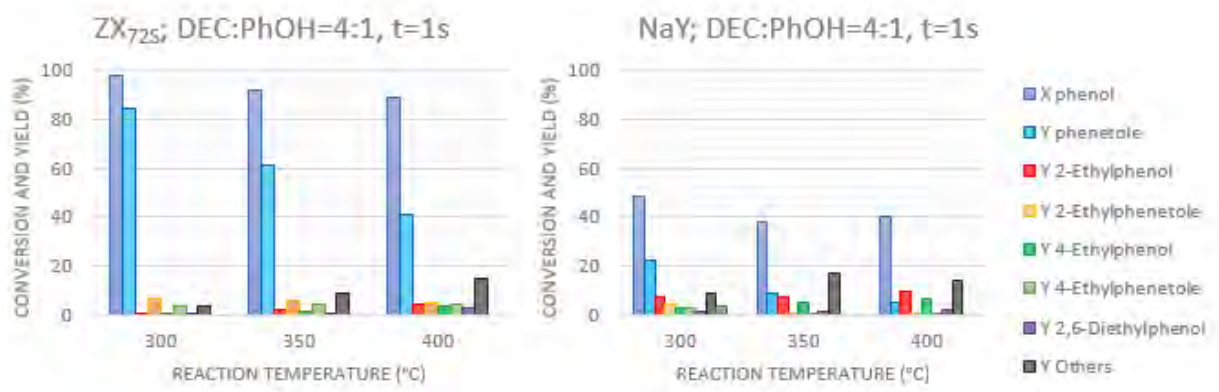

Figure 1. Catalytic results obtained from zeolite synthesis ZA_{72S} (left) and commercial NaY (right) based on reaction temperature. Reaction condition: DEC:phenol molar ratio 4, τ=1s.

Microencapsulation of some essential oils, and their antimicrobial activity properties.

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This study is extended in many years, from 2010 and continues to be one of our main research line in nanotechnology impact in herbal drugs. We have taken into consideration, essential oils obtained from medicinal and aromatic plants, because they are often applied for their antimicrobial, antinflammatory and skin whitening properties. Current topical applications of these volatile compounds turn out to be complicated because of their chemical and physical properties, which are major problems for their therapeutic uses; Therefore, we have studied their microencapsulation in polymers such as β-cyclodextrine and hydroxy-propyl β-cyclodextrine which could be the solution to the problems of stability, evaporation and controlled release.
Herbal plants are collected from different zones of Albania. The essential oils from albanian medicinal plants, such as *Satureja montana*, *Thymus vulgaris*, *Origanum vulgare*, *Myrtus communis*, *Rosmarinus officinalis*, *Thymus capitatus* and *Salvia officinalis,* are obtained by hydrodistillation in a Clevenger type apparatus. Chemical composition of isolated essential oils is determined by gas GC/MS and GC/FID methods.
Complexes of β-cyclodextrine and essential oils are prepared by co-precipitation method with the four ratios oil: β-cyclodextrine as follows 5:95, 10:90, 15:85 and 20:80 (w/w) in order to determine the effect of the ratio on the inclusion efficiency of β-cyclodextrin for encapsulating oil. The essential oils were tested for antimicrobial activity before and after microencapsulation. The antimicrobial test is done by the disc diffusion method using suspension of *P. vulgaris, E. coli, S. aureus, C. albicans* and dermatophytes such as *M. gypseum*, *M. canis, A. cajetani, T. violaceum, T. mentagrophytes, E. floccosum, T. r ubrum, T. tonsurans, B. cinerea and P. oryzae* . Negative controls were set up with equivalent quantities of DMSO. In addition, positive controls discs such as Cefuroxime, Ciprofloxacine, Tetracycline and Nystatin were used for comparison.
Encapsulation of essential was found to be more efficient to ratios oil:β-cyclodextrine 20:80 and the retention oil in ratio 15:85. Evaluation of biological activity after encapsulation lead to the conclusion that the antibacterial and antifungal activity are almost at the same range, even higher because of the slow releasing of essential oil from the complex. This fact was observed in some ratios, 10:90 and 20:80 (oil:β-cyclodextrine)
In conclusion these essential oils can be complexed in β-cyclodextrine in optimal ratios and can be applied in dermatological formulations due to their low risk of skin sensitizing and high antibacterial and antifungal activity they demonstrated after encapsulation. Further investigation is going on with systemic formulation with complexed essential oils which can be a very useful solution in many patients.

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Natural ageing in polyvinyl alcohol films

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Abstract (Calibri 11)

We make a study on the differences that undergo the physicochemical properties of polymeric membranes of polyvinyl alcohol (PVA) stored for 10 years after they have been prepared. This in context of the special significance of this widely used polymeric material and especially for use of biomedical and pharmaceutical sciences.
The aim of this study is to evaluate the stability of thermal properties and the degree of interaction with water. Positively, we will use thermal analysis to determine the thermal parameters (crystallinity and Tg) of the polymer matrix and water absorption experiments to determine the degree of swelling and the percentage of dissolution. Events on the molecular level lead to change in the morphology and macroscopic physical properties
Comparison of the properties indícate that: Qualitatively, with age, it turns out that we have an increase in the value of Tg and a decrease in the percentage of crystallinity. Quantitatively, membranes in 2020 absorb less water and swell much less
In summary, we can say that after 10 years the material does not fully retain its physico-chemical properties, but we also do not have substantial changes as the membranes are partly amorphous and partly crystalline (only the ratio changes). Also the attitude towards water does not change much with time aging. PVA membranes are similar in appearance but less relaxing

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Insights from SECM and DFT calculations regarding the interaction of oxygen bubbles onto bare and modified gold surfaces

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Abstract

The utilization of aryl radicals generated during the de-diazotization of aryldiazonium salts to modify/functionalize a variety of surfaces is seen as a straightforward and versatile technique[1]. In comparison to other methods of surface modification [2], it remains one of the most efficient methods of surface modification. The diazonium salts have been considered as simple and efficient coupling agents between surface and functional species in the majority of research studies. Another significant point that makes this approach attractive for surface modification processes is the extraordinary stability of the covalently bonded multilayer structure formed once the aryl moieties are attached to the electrode surface.

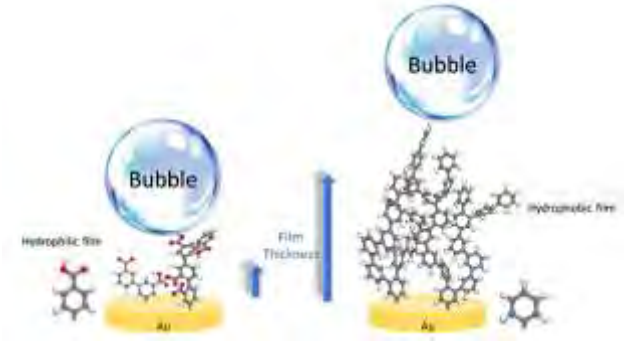

Figure 1. Schematics representing the oxygen bubble on top of the gold surface by phenyl or carboxyphenyl layers.

The covalently grafted 2D Carboxyphenyl (CP) or phenyl layers on the gold Surface (Figure 1), derived from their corresponding diazonium salts, were investigated in this study as a tunable gateway for ion exchange between gas bubble and the modified surfaces. Bubbles and microbubbles are attractive possibilities for future practical applications because they enable the exploration of the electrical properties of the gas–water interface using a variety of measurement techniques. Gas bubbles may play a role in a variety of biogeochemical cycles and in renewable energy studies since they are formed by electrochemical reactions. They are involved in different processes including photo-assisted water splitting reactions[3] , in the fabrication of gas sensing electrodes, foam fractionation, food processing, and purification processes.

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Microscopy resolution analysis when Fourier Ptychography is combined with laser illumination

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Fourier Ptychography is a computational imaging technique which makes use of a matrix array illumination to acquire a set of low-resolution images, that are used to reconstruct a complex image, resulting in a high space-bandwidth product. When utilizing the LED matrix in experimental settings that requires the acquisition of a large number of images, different LEDs encounter different optical paths, thus producing an image that is out of focus. In order to improve the quality of the separate images we implement autofocus algorithms. A second improvement is done by substituting the LED illumination with laser illumination. Good quality of the images were successfully acquire while using a rotating diffuser. Once all the acquired images are adjusted for the variance of the working distance, the overall reconstructed image shows a better spatial resolution. Also, we report successful Fourier ptychography employing laser illumination.

Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 760921 (PANBioRA).

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Figures

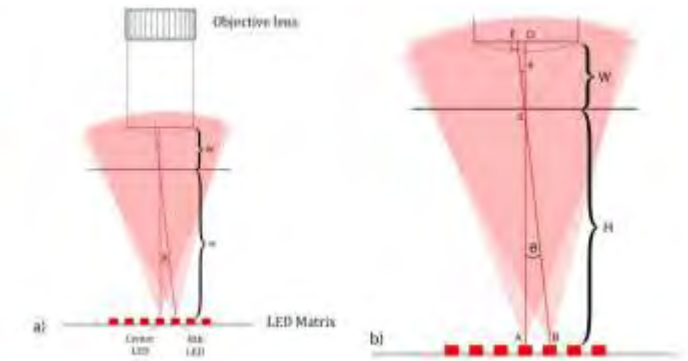

Figure 1. a) Representation of the angular illumination intensity shift when different LEDs are used b) closer view of the similar triangles that form above and below the sample

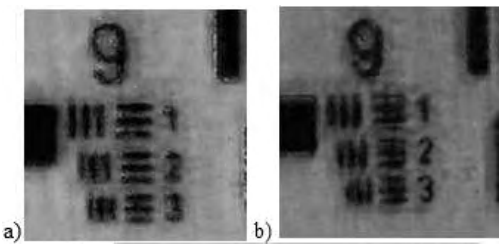

Figure 2. a) Without refocusing b) With refocusing

Silver nanoparticles as potential antiplatelet, antibacterial and hemocompatibile agents

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Abstract
Background: Among metal nanoparticles, silver nanoparticles (AgNPs) are emerging as an attractive tool for many nanomedical applications. We hypothesized that AgNPs, a known antimicrobial agent, can be used as blood-compatible, "ideal material'' in medical devices or as a drug delivery system. Therefore, the aim of the current study was to investigate if functionalized AgNPs affect platelet function and platelets as well as endothelial cell and red blood cells viability *in vitro*. Methods: AgNPs, functionalized with reduced glutathione (GSH), polyethylene glycol (PEG) and lipoic acid (LA) were synthesized. Quartz crystal microbalance with dissipation was used to measure the effect of AgNPs on platelet aggregation. Platelet aggregation was measured by changes in frequency and dissipation, and the presence of platelets on the sensor surface was confirmed and imaged by phase contrast microscopy. Flow cytometry was used to detect surface abundance of platelet receptors. Lactate dehydrogenase test was used to assess the potential cytotoxicity of AgNPs on human blood platelets, endothelial cells, and red blood cells. Commercially available ELISA tests were used to measure the levels of thromboxane B2 and metalloproteinases (MMP-1, MMP-2) released by platelets as markers of platelet activation. Antimicrobial activity was assessed by the minimal inhibitory concentrations (MIC). Results: 2 nm AgNPs-GSH, 3.7 nm AgNPs-PEG both at 50 and 100 µg/mL, and 2.5 nm AgNPs-LA at 100 µg/mL reduced platelet aggregation, inhibited collagen-mediated increase in total P-selectin and GPIIb/IIIa, TXB2 formation, MMP-1, and MMP-2 release. The tested AgNPs concentrations were not cytotoxic as they did not affect, platelet, red blood cell or endothelial cell viability. Conclusion: All tested functionalized AgNPs inhibited platelet aggregation at nontoxic concentrations. AgNPs have antimicrobial properties against pathogens commonly associated with the placement of the biomaterial into the vessel. Therefore, functionalized AgNPs can be used as an antiplatelet agent or in design and manufacturing of blood-facing medical devices, such as vascular grafts, stents, heart valves, and catheters.
This work is funded by the National Science Centre of Poland HARMONIA grant: 2017/26/M/NZ7/01030.

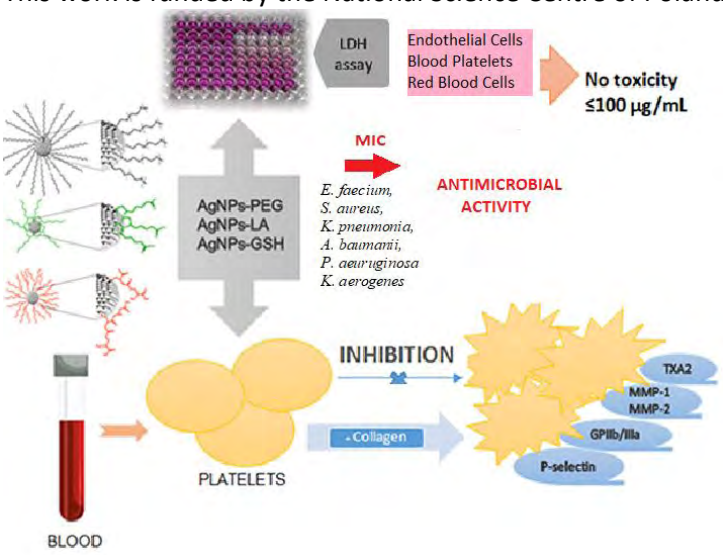

Figure 1. Antiplatelets and antimicrobial properties of hemocompatible AgNPs.

Thermoplastic nanocomposites with magnetic nanoparticles for bonding and debonding on demand applications by local induction heating

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Induction heating is a convenient and flexible method to deliver high-strength magnetic fields to ferromagnetic nanoparticles, which act as susceptors, generating heat in nanocomposite materials by hysteresis [1]. Taking advantage of the induction heating mechanism, nanocomposite materials embedded with magnetic nanoparticles (MNPs) constitute promising materials for adhesive joining systems, enabling reversible joining procedures, providing easy-to-disassembly operations by induction disassembly [2].

Nanocomposite filaments for Additive Manufacturing, reinforced with MNPs were used to investigate the heating capacity, using induction heating technology. Thermoplastic (TP) matrices of polypropylene (PP), polyurethane (TPU), polyamide (PA12) and polyetherketoneketone (PEKK) were compounded with 2.5, 5, 7.5, and 10 % wt. iron oxide nanoparticles (Fe_3O_4). MNPs were introduced to the polymers matrices by a twin-screw extrusion system, following appropriate temperature profiles. After the extrusion, nanocomposite specimens were prepared either by thermo-pressing in molds or by 3D printing. Heating capacity of specimens was examined as a function of time in a radiofrequency (RF) generator with a solenoid inductor coil, varying the working parameters (i.e., maximum power, frequency, time).

All nanocomposite specimens presented temperature increase proportional to the MNPs concentration as a function of exposure time in magnetic field. Specifically, specimens with higher concentration of MNPs showed more rapid temperature increase, resulting in melting state in the most of trials. Nanocomposites of PP, TPU, and PA12 with 10% wt. MNPs reached their melting temperature in less than 2 minutes of exposure in a magnetic field of 585 kHz frequency. In case of PEKK, a lower concentration of MNPs is preferable, since PEKK is more demanding during the extrusion process. Specimens of PEKK with 2 % wt. presented an increase of temperature after 5 minutes of exposure in magnetic field. However, the heating capacity was not sufficient to melt PEKK nanocomposite. The working parameters of the RF generator, such as frequency and input power, significantly affect the heating capacity of MNPs [3]. Using a coil with solenoid geometry, higher input power and frequencies promote the rapid increase of temperature of all nanocomposites. Developing innovative TP nanocomposites will allow a faster and leaner integration and repair of 3D printed structures, compared to thermoset repair processes, promoting advanced applications in many fields of Nanotechnology.

This work is funded by the European Union's Horizon 2020 research and innovation programs entitled: 'Recycling and Repurposing of Plastic Waste for Advanced 3D Printing Applications' (Repair3D) under GA No 814588, and 'Digital method for improved manufacturing of next-generation multifunctional airframe parts' (DOMMINIO) under GA No 101007022.

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Waste sponge derived carbon-Co_3O_4 nanoparticle based nanosensor for the sensitive determination of ruxolitinib from its dosage form and biological samples

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In the last decade, the use of carbon materials obtained through green synthesis from agricultural, animal, domestic, and industrial wastes in electrochemical sensing applications has increased dramatically. Carbon materials obtained from wastes have many fascinating properties such as high surface area, good pore size distribution, high electrical conductivity, chemical stability, good mechanical strength, superior electrocatalytic performance, and great active site. Cobalt oxide nanoparticles (Co_3O_4 NPs) are indispensable for electrochemical sensor applications due to their excellent reversible redox ability, superior magnetic properties, relatively high surface area, excellent semiconductivity, high catalytic performance, good chemical stability, and high corrosion resistance.

Compared to other techniques, electroanalytical-based techniques are thoroughly used for the detection of a wide variety of drug compounds due to their economic, limited chemical consumption, good selectivity, excellent sensitivity, and rapid analysis time; furthermore, there is no need for complicated sample preparation procedures. Surface modification strategies are critical in the field of electrochemical applications. Therefore, the main feature of electrodes modified with nanomaterials, which are widely used in electroanalysis, is their ability to reduce overpotential and prevent contamination for many electrochemical processes of analytical importance [1].

Janus kinases (JAKs) are inhibitors of four (JAK1, JAK2, JAK3, and 2 TYK2)cytoplasmic tyrosine kinases that play a critical role in hematopoiesis. Ruxolitinib (RUX) is one of the most selective inhibitors belonging to the JAK1-JAK2 group, which is found in the signaling pathway of various cytokines and growth agents.

The purpose of this study is to investigate and discuss the detailed voltammetric behavior and sensitive analysis of RUX by means of waste sponge-cobalt oxide nanoparticles modified GCE (WS-Co_3O_4-GCE) using cyclic voltammetry (CV) and adsorptive stripping differential pulse voltammetry (AdSDPV). The developed nanosensor exhibits high sensitivity, fast response and good reproducibility. This nanosensor can be used for sensitive and selective analysis of RUX in pharmaceutical dosage forms. The originality of this study is that for the first time, functional carbon materials obtained from waste sponges are used together with Co_3O_4 nanoparticles as electrode modification and the modification properties of each material are elucidated through various characterization techniques. This study will provide a more environmentally friendly and green perspective to the studies in the field of electrode modification.

Under optimum experimental conditions, calibration curves for RUX were obtained as 20uM – 80 nM with a limit of detection (LOD) of 6.7 nM by the WS-Co_3O_4-GCE using AdSDPV. The proposed method is validated and successfully performed to analyze the RUX in tablet dosage forms and human serum samples with great accuracy, recovery, and precision. There are no interferences from the excipients and endogenous substances obtained in the tablet dosage forms and human serum samples.

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A Molecularly Imprinted Polymer Sensor Developed by using an Amino acid Based Functional Monomer for the Sensitive Determination of Bisphenol S

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The trace-level concentration of endocrine disruptors contained in complex sample matrices requires highly sensitive platforms with good stability and reproducibility. This study reports the molecularly imprinted polymer which is an ideal surface-sensitive technique that creates recognition sites on the electrochemical sensor with high sensitivity and selectivity.
In line with this, the porous polymeric film was synthesized using N-methacryloyl-L-tyrosine (MA-Tyr) as the functional monomer in the presence of ethylene glycol dimethacrylate (EGDMA) as the cross-linker by photopolymerization. After the characterization of the developed sensor (MA-Tyr@MIP/GCE), the experimental conditions affecting MIP (dropping volume, monomer:template ratio, removal process of the template, rebinding process of the template) was optimized and then the evaluation of the analytical performance cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) methods were carried out by utilizing 5 mM ferri/ferro cyanide solution as the redox probe. Under the optimum experimental conditions, the calibration graph of MA-Tyr@MIP/GCE showed a linear response in the concentration range of BPA between 1×10^{-15} M and 1×10^{-14} M. The limit of detection (LOD) and limit of quantification (LOQ) values were found as 0.171 fM and 0.569 fM, respectively.
The applicability of the MA-Tyr@MIP/GCE was assessed by applying it to human serum and plastic bottled water samples. The LOD and LOQ values were calculated as 0.229 fM and 0.762 fM for the serum sample, respectively. Imprinting factor and interference studies were also carried out using similarly structured compounds (bisphenol A, bisphenol B, bisphenol F, and 4-aminophenol) and the most common interfering agents (ascorbic acid, dopamine, NaCl, etc.) showing the selectivity of the MA-Tyr@MIP/GCE sensor. Finally, the non-imprinted polymer (NIP)-based sensor was prepared to control the MA-Tyr@MIP/GCE performance.

Oregano essential oil-loaded liposomes: Cytotoxic and Antioxidant studies

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Introduction
Drug resistance, adverse effects, and high costs are frequently connected with current breast cancer treatment regimens, indicating the need for more effective and less harmful medicines. A growing number of researchers are looking into the potential of oregano essential oils (OEOs) to help with these problems. OEO loading into nanosystems is becoming a successful strategy due to the oil's poor bioavailability and stability. While there have been indications of improved bioactivity, no data on the cytotoxicity of EO encapsulated in various nanoformulations have been published.

Purpose
Preparation, characterization, and assessment of OEO nanosystems' efficacy in increasing antioxidant and cytotoxic activity.

Methods
MTT assay was used to examine the cytotoxic activity of the prepared and characterized OEO nanoformulations in human cancer cells MCF-7. DPPH scavenging activity was used to measure antioxidant activity. To improve the properties of oregano essential oil, suitable formulations of natural soybean phospholipid vesicles were created in this research. Saturated (Phospholipon 90H) and unsaturated (Lipoid S100, Phospholipon 85G) phospholipids, in combination with cholesterol, were used to prepare oregano essential oil loaded liposomes using the ethanol injection method.

Results
Based on the findings, it appears that OEO nanoformulations may be more exhibits significant cytotoxic activity in breast cancer cell lines in comparison to free form of the essential oil.

Conclusion
The successful development of OEO nanosystems that significantly enhance OEO's cytotoxic and antioxidant properties demonstrates a viable technique for a promising successful therapeutic approach.

This project was financially supported by the Kosovo Ministry of Education, Science, Technology and Innovation.

Mimoza Basholli-Salihu, Aida Shala and Toskë L. Kryeziu are members of NANOALB research group.

Automation of screen-printed electrodes modification with molecularly imprinted polymer

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The design and application of semi-automatic electrochemical analyzer are reported. The analyzer is based on 3-axis positioning system, which moves unique head designed to mount and dismount electrochemical sensors (screen-printed electrodes). The head mounts electrode in tray and move it to desired wells of multi-well plate filled with modifying and/or analyzed solutions, where electrochemical methods are performed.
There are several field of analytical chemistry, where automation is desired. The reported benchtop device enables to perform electrochemical procedures without significant attention of operator in a high throughput mode and decreases the influence of human errors on the results. Using the reported analyzer, we optimized design of electrochemical sensor for detection of histamine. At first, screen printed electrodes were modified with gold particles using cyclic voltammetry to increase electrode sensitivity towards $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ reporter. The nonconductive layer of molecularly imprinted polymer on electrodes were created by electroplymerizing of a mixture of histamine (analyte) and 3-aminophenol (monomer). The developed sensors were characterized by electroanalytical methods (cyclic voltammetry and electrochemical impedance spectrocopy) and scanning electron microscope.

Acknowledgements
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Molecularly Imprinted Polymer-Based Electrochemical Sensor For The Determination of A Growth Hormone Inhibitor Octreotide

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Abstract

In this study, a new electropolymerized molecular imprinted polymer (MIP) film was synthesized by using cylic voltemetry (CV) in the presence of aniline, which is used as a functional monomer and template molecule octreotide (OC) on a glassy carbon electrode (GCE). The expression of MIP was optimized using $[Fe(CN)_6]^{3/4-}$ as a redox probe.

Removal and rebinding processes were performed with differential-pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) techniques. The analytical performance of MIP/aniline/GCE were investigated by comparing the electrochemical reaction of MIP with non-imprinted polymer (NIP).

The calibration curve of OC on MIP/aniline/GCE was found to be linear in the range of 1×10^{-14} M and 8×10^{-14} M. Limit of detection (LOD) and limit of determination (quantification) (LOQ) were determined 1.16×10^{-15} M and 3.85×10^{-15} M, respectively. The feasibility and validity of the developed sensor was proved by applying it to the artifical serum and pharmaceutical preparation. The selectivity of the sensor was compared by examining the binding of samotostatin from the same growth hormone family. The developed MIP@aniline/GCE sensor shows high sensitivity and selectivity for OC determination in serum. This is the first study in which OC determination was performed by electrochemical analysis.

Deep Learning Techniques in Evaluating Microscopy Images

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Abstract

Cell imaging and analysis is a noninvasive technique that provides essential quantitative data in medical field and that has been gradually passed from medical practitioners to computing units. Imaging is the primary choice when multiparameteric chambers are used and is a good substitute for chemical based techniques that measure cell metabolic activity. Cells may undergo several changes that are directly exhibited in the morphological parameters (area, perimeter, eccentricity, elongation etc). After a microscope image is acquired, the first step is to implement computational microscopy algorithms that can be used to improve the resolution, to remove the noise, and to enhance it. Some of these tasks are conducted using Deep learning techniques which directly enables a faster evaluation of the cell condition in cell culture media. Afterwards the quantitative analysis including classification, detection and segmentation is conducted. Here we will report the cell segmentation accuracy for three different neural netowrk architectures (u-net, u^2-net and u^3-net) in unstained brightfield images.

Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 760921 (PANBioRA).

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Figures

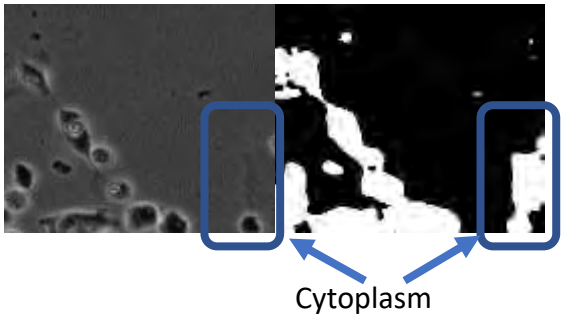

Figure 1. Cell components detection using U-net architecture

A SIM Card-Type Biosensor for the Point-of-Care Determination of Creatinine in Urine

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Abstract: The development of medical diagnostic devices for point-of-care (POC) applications is of immense interest towards the establishment of decentralized health-care systems. The cost of miniaturized transducers, the need for elaborated modification of the sensing surface and the complexity of the assay workflow impede the widespread use of current biosensing technologies to POC applications. Herein, we report on the synthesis and characterization of pH responsive copolymers of methacrylic acid (MAA) and methylmethacrylate (MMA) at different MAA/MMA ratios and molecular weights, and their use in the development of a sim card-type responsive copolymer-modified paper-based biosensor for the point-of-care, drop volume determination of creatinine in urine. A vertical microfluidic channel was fabricated on a paper strip by wax printing. The channel was blocked by depositing PMAA/PMMA copolymer. Atop of the dry copolymer/paper surface, creatinine deiminase was immobilized by physical adsorption. The functionalized paper strip was sandwiched between two conductive tapes from which the top one was hole patterned to serve as a dosing well for the microfluidic channel. Data demonstrated, on the one hand, infinity resistance to vertical flow of the urine sample though the enzyme-free biosensor, and on the other hand, in the presence of immobilized creatinine deiminase, a creatinine concentration dependent flow rate due to the degradation of the pH responsive PMAA/PMMA copolymer by the enzymatically produced ammonia, as a result of the action of creatinine deiminase on creatinine. Under selected experimental variables, the detection range of the device was tuned [1] over 3-30 mM creatinine that covers the normal range of creatinine (5-17 mM) in urine. The biosensor was assembled on a SIM card holder incorporating a third conductive strip, which in combination with a low-cost reading unit offers an automatic on/off (addition of the sample/degradation of the membrane) function for the measuring of the degradation time, and a screen for displaying the determined concentration. The device was applied to the drop-volume determination of creatinine in 1+1 diluted urine sample (adjusted to pH 6.5). The relative error (%) with respect to a hospital method was <7.1%.

Acknowledgment: This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-03341).

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Comparison of alkali versus acid activation of Kosovo bentonites to be used for oil regeneration

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Abstract

Clay minerals are natural products with very high absorbent, ion-exchange and catalytic properties; chemical nature and pore structure have an important impact on these properties. In this paper, it is proposed to modify the Bentonite clay of Kosovo (Goshica region) by acid and alkali activation to be used for oil recycling. Acid and alkali activation was performed in ratios (10, 30 and 50%) in order to see the effect of acid and alkali treatment on the properties of Goshica Bentonite. The samples were characterized using X-ray powder diffraction (XRD), Fourier transform infrared (FTIR), structural and chemical analysis. Physio-chemical analysis was performed to find out the best activation treatment in order to increase the bentonite´s adsorption and ions exchange capacity. Significant changes were observed in the original pore structure. All the conclusions drawn correlate well with the amount of activator used. This study will provide valuable data on the effect of acid and alkali activated bentonite for the treatment and recyclability of UMO, which is essential for local industry.

Preliminary data on the absorption of Cr (III) and Cr (VI) ions in the metal oxide-based material derived from the quartz sand enrichment process.

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Abstract
In present study, a metal oxide based material, derived from the enrichment process of quartz coastal sand was used as adsorbent for the removal of chromium (III) and (VI) ions from solution. Following additional modification of the adsorbent, the effect of operational parameters including pH, adsorbent dosage, contact time and Cr (III, VI) concentration were studied according to one-factor-at-a-time procedure. Obtained results revealed that selected material exhibited higher adsorption efficacy of trivalent chromium in alkaline solution (pH = 6-9) while adsorption of hexavalent chromium was best performed in strong acidic solution (pH = 1-2). The maximum removal efficacy of tri and hexavalent chromium ions (>93%) was achieved after 180 and 30 minutes of contact time, respectively, for the adsorbent dosage of 0.05 g/L and initial chromium concentration of 20 mg/L. The adsorption isotherms were better described by the Freundlich equation for both tri and hexavalent chromium ions (R^2 = 0.934 and R^2 = 0.995, respectively). Adsorption of trivalent and hexavalent chromium ions onto selected material followed the pseudo second order model (R^2 = 0.996 and R^2=0.991). Hence, the residual materials derived from the enrichment processes of quartz sand can be used as adsorbent for the removal of tri and hexavalent chromium ions from aqueous solutions.

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Figures

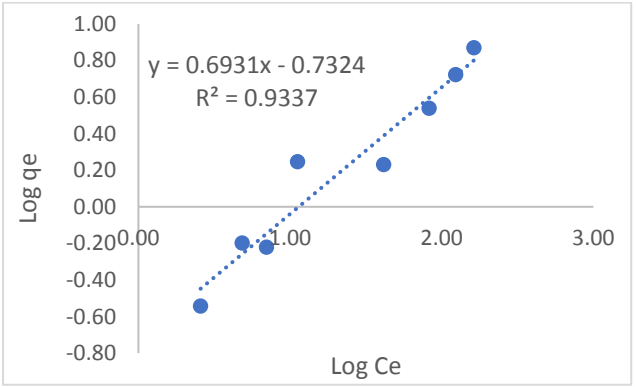

Figure 1. Freundlih adsorption isotherm for Cr (III) ions.

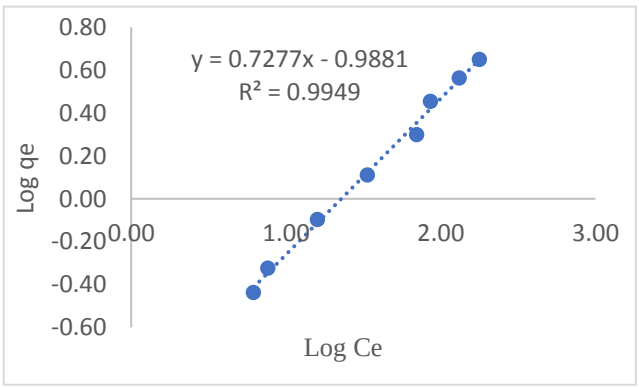

Figure 2. Freundlih adsorption isotherm for Cr (VI) ions.

Electrical characterization of low-dimensional structures by nanoprobe based approach

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Ongoing downscaling of electronic devices requires deep understanding of electronic properties of low-dimensional materials and nanostructures. Among the investigative approaches for electrical characterization of the nanostructures, the nanoprobe-based approach receives particular attention of the researches nowadays. The nanoprobe-based approach to contact the individual nanostructure is the most straightforward way to study their electronic properties, as far as it does not require wet lithographic process for the contact preposition, time-consuming transfers procedures, etc.

Recently, our research group develop advanced technique for in-situ electrical characterization of the individual nanostructures using the tips of the nanomanipulators mounted in the chamber of scanning electron microscope (SEM). Additionally, the SEM was equipped with the focused ion beam tool, employed to tune the properties of the nanoscale contacts. We successfully employ developed technique to study in detail the electronic properties of the single nanorod based ZnO/GaN [1, 2] heterostructures, GaN/AlGaN nanowire light emitting diodes [3], and graphene/ZnO nanorods junctions (Figure 1).

This work provides a useful reference for the in-situ electrical characterization of the low dimensional structures in the SEM with emphasis on the ion beam assisted approaches for better reliability of obtained experimental results.

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Figures

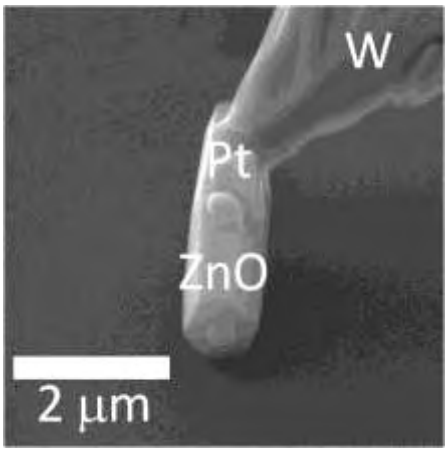

Figure 1. Tungsten nanoprobe in contact with ZnO (nanorod)/graphene structure.

An innovative biomimetic sensing platform as a promising nano-device for gonadorelin detection

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Ongoing improvements in the pharmaceutical industry have expanded the list of potential doping agents regulated and annually reviewed by the World Anti-Doping Agency (WADA) [1].
Low molecular weight peptide hormones (<2000 Da), holding a well-defined structural characteristic, represent a new frontier in antidoping research as these peptides (e.g. gonadorelin, buserelin, deslorelin, leuproprelin etc.) have been included in the S2 section of the WADA's List of Prohibited Substances [2, 3].
In this framework, we focused our attention on gonadorelin misuse in sports competitions.
Gonadorelin is a synthetic decapeptide (peptide sequence: pGlu-His-Trp-Ser-Tyr-Gly-Leu-Arg-Pro-Gly-NH_2, MW 1182.33 Da) that has the same chemical structure as the endogenous neuro-peptide gonadotropin-releasing hormone (GnRH) [4]. It is available as clinical and veterinary drugs (e.g. for the treatment of hypogonadism, cancer, etc.) and is improperly used by male athletes to enhance their physicals performances by stimulating the pulsatile endogenous secretion of testosterone in the bloodstream via the hypothalamic-pituitary-gonadal (HPG) axis, eventually with impact on the athlete's biological passport.
Our study aimed to develop an efficient and selective molecularly imprinted polymer (MIP)-based assay to detect gonadorelin levels in biological fluids, such as urine and plasma. The process of molecular imprinting involves the synthesis of a 3-D poly(norepinephrine) matrix with binding sites complementary in shape, size, and functional groups to the template molecules [5,6]. The interaction between gonadorelin and "tailor-made" synthetic biopolymer was preliminarily characterized by a surface plasmon resonance (SPR) sensing platform. Afterward, a competitive inhibition biomimetic assay was designed employing a biotinylated gonadorelin as competitor molecule. This type of assay is appropriate for the detection of small molecules which lack multiple epitopes. Encouraging results were recorded for gonadorelin in buffer and synthetic urine samples by using a simple biotin-streptavidin signal amplification strategy. Moreover, we intend to provide a strategy to detect gonadorelin which can be easily miniaturized, by tuning different amplification strategy embedded with nano-MIPs, to set-up a point-of-care (POC) sensing device for in-situ athletes' monitoring.

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Miniaturized Electrochemical Sensing Unit for Cell Cultures

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Abstract
The need to gather data at a high rate in biomaterial science or medical field has become an essential element and this is facilitated once microfluidic chambers are employed. Multiparametric biosensing platform embedded microfluidic chambers require the miniaturization of several electrodes on a small volume. The measurement strategy should limit interfering and cross-talk signals. The obtained electrochemical data that include low-level voltages and/or currents is one of the important sources of data in evaluating the condition of the cell cultures. Monitoring of these signals requires large and expensive data acquisition modules. Nowadays, a significant number of experiments make use of these signals to monitor the changes in the structure, composition, metabolism and the health state of biological samples. The medical practitioners need to monitor the behavior of these signals in time as generally the biological signals have some transient components. For this reason, the data should be stored in a computing unit by means of data acquisition cards. In this work, we present the design of portable potentiometric and chronoamperometric circuits on PCB that utilize myDaq and NI Labview for the measurement of the potential difference and current values as a function of time. The components used are all portable units, cost-effective, the data acquired and analyzed, and an excellent match is observed with the data acquired using benchtop commercial products.

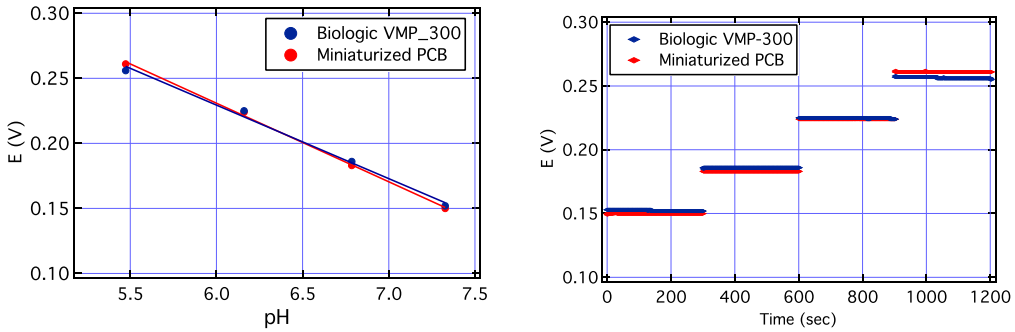

Figure 1. The results obtained from the commercial unit and the homemade miniaturized PCB

Acknowledgement
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Detection of a protein biomarker with an inkjet-printed nanobiosensor

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The importance of novel protein biomarkers for monitoring and early-diagnosis of the associated diseases is a critical point in the biomedical field [1]. The evolution of some of these diseases is rapid, and they can lead to severe conditions if not adequately monitored [2]. For this reason, an efficient, reliable Point-of-Care (PoC) device for homecare detection and preventive diagnosis is needed [3]. Inkjet printing has been investigated as an alternative for mass-production of PoC biosensors, due to its versatility and excellent performances [4]. This technique allows the production of low-cost, high-performance nanobiosensors, that can be tailored toward the specific application needed. In this work, we present a fabrication method for disposable, inkjet-printed nanobiosensor with smartphone readout. Electrochemical impedance spectroscopy (EIS) has been used to characterize the general performance of the device and to optimize its fabrication. The system has been tested for the detection of a protein biomarker in different media showing the potentiality of this technique in the biosensing field and opens the doors to multiple other applications using inkjet technology for diagnosis at the PoC.

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Acknowledgements

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REMOVAL OF PHENOLIC COMPOUNDS FROM WASTEWATER USING NATURAL ADSORBENT

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Abstract

The present study was conducted in order to investigate the capability of sawdust used as an adsorbent for phenol removal in industrial wastewater. The obtained results demonstrate that activated sawdust could be used as an efficient and low-cost adsorbent for phenol removal from industrial effluents discharge. The use of low cost absorbent may also contribute to the sustainability of the surrounding environmental. The optimum conditions for the removal of phenol within the experimental range of variables studies were; 140 mg/l of initial phenol concentration, 0.4 g-0.5 g of adsorbent dose, pH value of 4 and 140 min of contact time. Under these conditions the maximum removal efficiency was 83 %. The results of isotherm data showed that the adsorption of phenol followed Freundlich isotherm. Adsorption of phenols from carbonized sawdust fits well with the pseudo-second order kinetics equation.

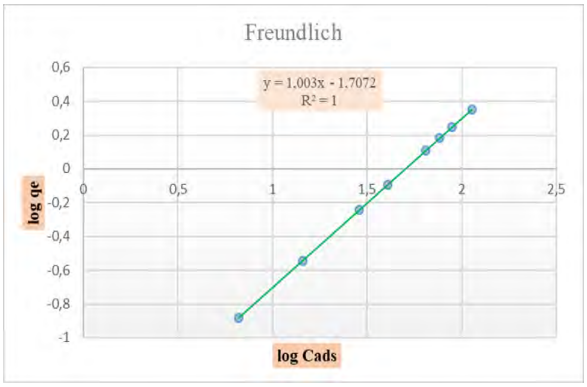

Figure 1. The linear Freudlich adsorption isotherm

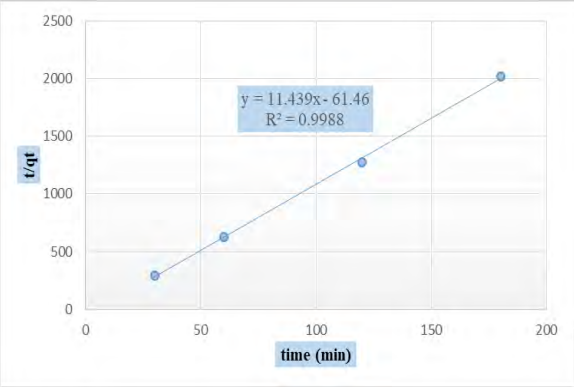

Figure 2. Pseudo-second order graph

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A new Electrochemical Sensor based on Nano-sized Carbon Materials for the detection of Azithromycin in the Environmental and Biological Samples

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A simple and highly sensitive electrochemical sensor, for the detection of Azithromycin (AZT) in the environmental and biological samples was developed using carbon paste electrode modified with graphene nanoplatelets (GNPls). Optimization of the amount of the modifier was done and best results are obtained with the presence of 5 % (m:m) of the modifier. With the prepared electrode, the analyte showed the oxidation peak at a working potential of 0.8 V. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were applied as suitable electrochemical methods using Britton-Robinson buffer solution at pH 9.00. Additional, experiments will be carried out in order to find the best analytical parameters and also for testing the electrode linearity, the limit of detection, interference studies, repeatability, reproducibility before applying the sensor in real samples.

Keywords: Azithromycin, Graphene Nanoplatelets, Carbon paste electrode

A low- cost Raspberry Pi- based optical sensor (PiSENS) for continuous monitoring of NO_2 as indicator for air quality in Prishtina

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Nitrogen dioxide (NO_2) is produced mostly from combustion processes and it is a significant indicator of air pollution. In Kosovo, this gas is often present at undesirable levels and monitoring is required under a variety of different conditions. For the continuous determination of NO_2 in Prishtina an optical sensor (PiSENS) has been used, which consists of a low-cost processing unit (Raspberry Pi) and its imaging camera. The NO_2 concentration was determined by monitoring the Saltzman colourimetric reaction for capturing NO_2 from the air that results in color development upon contact with the suitable absorbing solution, where the gas was collected by active sampling (portable pump). Digital images were captured by the camera inside a box under controlled lighting conditions. The images were analyzed without any extraction procedures, using a dedicated python application developed by our research group. PiSENS was thoroughly calibrated in the range that corresponds to the air quality index scale for an hourly concentration of NO_2.

Mock samples of different concentrations have been analyzed using PiSENS and the obtained results were evaluated with the UV-VIS method resultng 95.0-99.07 % as recovery values. Air samples were analyzed in heavy traffic conditions in Prishtina city and the concentration of NO_2 was found to be 21.58 µg/ m^3. The obtained result correlates very well with data from the IHMK (Institute for Hydrometeorology of Kosovo) with a recovery percentage of 96.76 % confirming the presented method as valide method for determination of NO_2 in air samples.

Keywords: Raspberry Pi, Python, Air quality, Nitrogen dioxide

A sensor to monitor the growth of bacterial biofilms

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Abstract

Health care systems in Western countries are requiring increasing resources and this creates concerns about sustainability of a universal health care. The present pandemic once again highlights an unmet need for technologies providing prompt measurements of physical, chemical and biological parameters. In this view, sensors and wearable sensors are expected to be the core of point of care devices and telemedicine systems that will play a key role in the near future.
Here, we describe the use of a potentiometric sensor based on functionalized reduced graphene oxide for monitoring the formation and growth of biofilms from three bacterial species (*Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*) in liquid and semisolid culture media [1]. The Open Circuit Potential (OCP) between an Ag/AgCl pseudo reference electrode and a working electrode, both screen-printed on a flexible polyethylene terephthalate film, was measured during the growth of biofilm-forming bacteria. The OCP decreased over time as bacteria grew on the sensor surface, exhibiting a negative correlation between the optical density of the liquid broth and number of bacteria. Since we have used a similar device in previous studies for the monitoring of pH in chronic wounds [2], the possible application of this technology and its limitations for this specific purpose will also be discussed.

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Figure

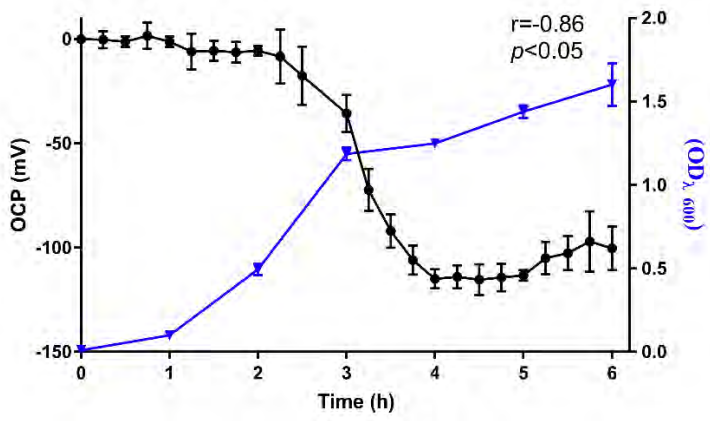

Figure 1. OCP and optical density values during bacterial growth in Luria Bertani liquid culture for *E. coli* ATCC 25922.

Characterization of Graphene/ZnO Schottky Barriers Formed on Polar and Nonpolar ZnO Surfaces

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Unique properties of graphene-semiconductor junctions offer a great opportunity to investigate new fundamental phenomena taking place at the interface between a two-dimensional (2D) semimetal and a three-dimensional (3D) bulk semiconductor, and make this junction extremely attractive for a new generation of graphene-based devices. One of the key issues in these junctions is to understand the charge transport mechanisms. In the last few years we focused on the preparation of graphite/semiconductor junctions by simple drop casting of graphite colloidal solution with the aim to describe charge transport mechanism in such junctions [1-4]. We showed that the interaction between graphite and polar surfaces of ZnO affects electrical properties of graphite/ZnO Schottky junctions. A strong interaction of the Zn-face with the graphite contact causes interface imperfections and results in the formation of laterally inhomogeneous Schottky contacts. On the contrary, high quality Schottky junctions form on the O-face, where the interaction is significantly weaker. Moreover, we observed that the electrical properties of graphite/ZnO Schottky junctions strongly depend on the crystallographic orientation of the ZnO substrate. The current-voltage, capacitance-voltage, and impedance measurements indicate that near-ideal Schottky junctions form on c-plane, while on a- and m-plane the junctions are laterally inhomogeneous. Now we focus on a systematic analysis of charge transport mechanisms in the junctions formed by a 3D oxide semiconductor (ZnO) and 2D graphene [5]. We further attempt to deeply understand how the interaction between graphene and different crystallographic planes of oxide semiconductor affect the charge transport.

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Parallelized Quantitative Electrochemical Isothermal Amplification

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The human papillomaviruses (HPV) are globally distributed, heterogeneous, small double-stranded DNA that infect epithelial tissues at a variety of anatomic sites.[1] HPV genotypes have different oncogenic capacities and are classified as high and low-risk genotypes.[2] Infection by low-risk types, such as HPV6, HPV11, HPV42, etc., have a negligible risk of malignant progression,[3] whereas as high-risk HPV DNA such as HPV16, HPV18, HPV33 is found to be present in 99.7% cervical cancer worldwide.[4] Cervical cancer, on the global scale, is the third most common cancer-related death in women.[5] Therefore, HPV detection is a crucial step in the early diagnosis of cervical cancer. Whilst PCR is the most commonly used method to detect HPV, applying solid-phase bridge amplification on an electrochemical biosensor can surpass PCR's limitations and increase the sensitivity of the assay by achieving parallelized quantitative detection of multiple targets. We are currently developing a generic platform for the parallelized quantitative electrochemical isothermal amplification of nucleic acids which can be used at the point-of-need. Recombinase Polymerase Amplification (RPA) is an isothermal amplification technique that has several advantages over other isothermal techniques due to its simplicity, sensitivity and rapid amplification at a constant temperature (between 25 and 42°C), without the need for tight temperature control.[6] In solid-phase, at least one primer is linked to a surface and amplification may occur simultaneously both in the liquid and at the solid-phase, whereas in bridge amplification both 5'-primers are immobilised eliminating the primer-dimer problem. In our approach, we exploit the use of ferrocene modified dNTPs and 5'-thiolated primers, which are immobilised on the surface of gold electrodes of an array. The RPA amplicons are measured electrochemically using square wave voltammetry. To date we have optimized the reaction time and temperature for the simultaneous detection of HPV16 and β-globin and the platform will be expanded to the quantitative detection of multiple HPVs.

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