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Scientific Programme

(Scientific Workshop/MC-WG Meeting CA15107),
Prague, September 12th-13th 2019

Thursday, September 12th

08:45 – 09:00	**Registration**	
09:00 – 09:10	**Welcome ceremonial**	
09:10 – 09:55	**Session chair: Silvia Giordani** Invited Keynote Talk I **Aravind Vijayaraghavan** *Graphene-enhanced elastomer composites and their applications*	**SESSION 1**
09:55 – 10:40	**FLASH Presentations (6x5min)** **Zélia Alves** *Characterization of polysaccharide-based films reinforced with well dispersed multi-walled carbon nanotubes using surfactants* **Petr Ashcheulov** *Development of nanocrystalline boron doped diamond electrodes for photoelectrochemical and optoelectronic applications* **Frank Clemens** *Development of piezoresistive elastomer sensors based on nano carbon material for health monitoring and robotic applications* **František Fendrych** *High Temperature Corrosion Testing of Zirconium Nuclear Fuel Rod Cladding Protected with Nanocrystalline Diamond Films Deposited by Microwave Plasma CVD* **Juan P. Fernández-Blázques** *Morphology and thermal behavior of composites of PLA with tunable carbon nanotube fibers* **Miroslav Huskić** *Effect of pre-dispersed and pristine single-walled carbon nanotubes on mechanical properties of low-density polyethylene nanocomposites*	
10:40 – 11:20	**Coffee Break and Posters**	

11:20 – 12:15	**Session chair: Tony Keene** Invited Keynote Talk II **Elena Besley** *Ordering, flexibility and frustration of two dimensional supramolecular arrays on graphene*	**SESSION 2**
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	Jonathan Nitschke *Composites of Carbon Nanotubes with Cages and Metallopolymers* **Michal Novotný** *Zinc phthalocyanine films for chemical gas sensors prepared by pulsed laser deposition*	
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Structuring your Leap from Lab work to Entrepreneurship

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Abstracts

Reduced graphene oxide from industrial tea waste

Gökçen Akgül[1*], Saliha Nur Bıçakçı[1]
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Graphene is considered as the material used for electronic devices of this century. Electronic devices are being developed by utilizing the beneficial properties of graphene, such as electrical conductivity, thermal and chemical stability [1, 2]. However, the applied graphene is mostly originated from fossil sources such as graphite. Since the fossil sources are diminishing, renewable carbon resources having been researched and developed as the substitute to fossil carbon.

Biomass is the single renewable carbon resource which is converted into the carbonized material by pyrolysis. The carbonized material can be considered as graphite/graphene-like carbon resource [3] in the electronic devices.

In this work, industrial tea waste as the renewable carbon resource was carbonized by pyrolysis. The obtained carbonized material was developed to reduced graphene oxide by physical and chemical treatments such catalytic graphitization and modified Hummers method.

The produced reduced graphene oxide was characterized by SEM, XRD, FTIR and optical and electrical properties were determined. The results were compared with the properties of graphene oxide derived from commercial graphite that tea waste biomass would be used as a graphene oxide resource. Much faster and efficient electrical devices would be developed by using renewable and sustainable biomass resources.

Acknowledgement

We gratefully acknowledge the financial support provided by Recep Tayyip Erdoğan University, Scientific Research Projects Coordinator Unit (BAP) (Project No: FYL-2018-970).

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Textile-Reinforced Cement: interface modification

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Cement is by far the most important building material in the industrialized world, used for a wide range of applications in the construction industry. Cementitious elements possess a rather high compressive strength but low tensile strength. The classic solution for that is to reinforce these cementitious elements by heavy steel **re**inforcement **bar** (rebar). However, the rebars suffer from corrosion, especialy in coastal constructions. *Textile reinforced concrete* (TRC) is considered as one of the key alternatives to steel rebars as it is carbon-based and hence non corrosive, light weight, flexible and with extraordinary mechanical properties (stronger than steel, in tension). It can be employed in superior and sophisticated construction and its use lowers the required oxidation protection cement layer (5-8 cm) in rebar-based constructions. The TRC suffers, however, from weak *textile-cement bonding* since the former is hydrophobic and the latter hydrophilic. In the present work, several TRC coating strategies were explored, in which the TRC surface is modified by addition of *graphene oxide* and *cement powder* coating. The *textile-cement bonding* was systematically investigated by conducting pullout measurements of a single yarn from a cement matrix modified by various coatings. Further, the microstructure and interface of the modified textile and the cementitious matrix were imaged by scanning electron microscopy. It is concluded that fresh epoxy-coated textile with further cement powder coating is the optimal interface modification enhancing the *textile-cement bonding* strength by more than two-fold.

Nanostructured iron oxides from MOF and MOF/GRM hybrids decomposition and preliminary electro-catalytic activity evaluation for the oxygen reduction reaction

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Metal Organic Frameworks (MOFs) are crystalline materials made by the self-assembling of inorganic (metallic centers, often transition metals) and organic units (mainly polydentate ligands) through strong coordination bonds. Their morphological features and the chemico-physical versatility are exploited in many fields as gas storage, separation of fluids, catalysis, sensing, biomedicine, fuel purification, etc. Since the inorganic units are metal ions and metal oxides, by properly selecting the metal centers and the organic ligands MOFs can serve as redox active sites during electrochemical processes featuring potential applications as electrode materials for lithium-ion batteries and fuel cells [1]. Many materials have been recently developed exploiting MOFs and their derivatives: one of the most intriguing applications is the use of MOFs as precursors for synthesizing metal oxides with unique nanostructures that can be hardly obtained through other methods. Upon controlled thermal treatment (oxidation or pyrolysis) the metal components, dispersed in MOFs structure as cations (as single ions or, in some cases, as dimers), with a weight ratio of over 40% in most MOFs, provide an intrinsic metal source to produce nanostructures of metals or metal oxides. In this study a Fe-based MOF and its hybrid with a graphene related material (GRM) were produced and further used to build nanostructured metal oxides. The MOF/GRM hybrid was obtained adopting a one-pot synthetic strategy by intercalating the crystalline structure of three 1,3,5-benzenetricarboxylic acid (BTC) Fe-based MOF (MIL100) with a GRM obtained from a nanostructured carbon black through a wet chemical approach [2,3]. The intercalation (5 wt.% of GRM) leads to modifications of the MOF moiety: generation of unpaired metallic sites, pore size distribution tuning. The Fe-based MOFs were thermal treated (up to 500 °C) exploring both oxidative (air, $Fe_yO_x(MIL)_{air}$) and pyrolytic (N_2, $Fe_yO_x(MIL)_{N2}$) treatments and then thoroughly characterized. Both $Fe_yO_x(MIL)_{N2}$ and $Fe_yO_x(MIL)_{air}$ are characterized by macroscopic aggregates of comparable size. While a compact and homogeneous surface is discernible in $Fe_yO_x(MIL)_{N2}$, in $Fe_yO_x(MIL)_{air}$ a fine granularity on the nanometer scale can be observed (side dimensions 10-50 nm). The XRD survey indicates that $Fe_yO_x(MIL)_{N2}$ is composed by elementary Fe with no crystalline character, while $Fe_yO_x(MIL)_{air}$ presents a pattern with intense signals attributable to a-Fe_2O_3 (hematite). The nature of the electric transport was elucidated by impedance spectroscopy measurements and described with the classic Randles equivalent circuit. A general feature arising from these samples concerns the relevant role of intra-grains diffusive phenomena, as well as a strong capacitive behavior of grain boundaries.

The materials were tested as catalysts for the oxygen reduction reaction in alkaline environment showing a promising behavior.

The financial support of PAR 2015-2017 MiSE-CNR under the contract "Sistemi elettrochimici per l’accumulo di energia" was kindly acknowledged.

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Characterization of polysaccharide-based films reinforced with well dispersed multi-walled carbon nanotubes using surfactants

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Nowadays, functional materials based on renewable resources and environmentally friendly processes have attracted considerable attention, particularly the polysaccharides since they represent the most abundant polymers in nature. The use of carbon-based materials is delivering new functional polysaccharide-based materials with an over broad range of application. Multi-walled carbon nanotubes (MWCNTs) have been applied due to their interesting mechanical, thermal and electrical properties. MWCNTs form stable bundles due to van der Waals interactions, making their dispersion and alignment difficult in polymer matrices. The excellent properties of MWCNTs can only be exploited if they are homogeneously dispersed in solution and afterwards in the polysaccharide-based matrices [1].

In this work, MWCNTs were dispersed and stabilized in aqueous media using surfactants with diverse chemical structures, such as sodium dodecyl sulphate (SDS) and cetyl trimethylammonium bromide (CTAB), under well-controlled conditions [2]. Then, polysaccharide-based films were made by dissolving alginate, chitosan or starch with different concentrations of stabilized MWCNTs. Visually, alginate films did not show a good dispersion of the surfactant-MWCNT filler, unlike chitosan-based films which showed better results for both applied surfactants. The films were characterized concerning their crystallographic characteristics by XRD diffraction and the morphology was investigated using scanning electron microscopy (SEM). To confirm the presence of MWCNTs on films, RAMAN spectra were done. The transparency of films was measured by UV-vis spectrophotometry and showed that it was dependent on the amount of filler added. Polysaccharide film exhibited poor electrical properties, but the addition of MWCNTs turned the polysaccharide-based films with higher values of conductivity.

The development of multifunctional MWCNTs-polysaccharide based films can find application in medical, sensor, energy and food packaging fields due to the inherent properties of the polysaccharide together with the filler features.[1]

Acknowledgement: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES. ZA, CN and PF thank FCT for the grants (PD/BD/117457/2016, SFRH/BPD/100627/2014 and IF/00300/2015, respectively). This work was also supported by BIOFOODPACK project (M-ERA.NET2/0019/2016). This work was also funded by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P., in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. COST action 15107, Grant No. 42215 is also acknowledged.

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Development of nanocrystalline boron doped diamond electrodes for photoelectrochemical and optoelectronic applications

Petr Ashcheulov[1], Andrew Taylor[1], Ondrej Hak[1] and Vincent Mortet[1]

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Carbon-based materials are currently under extensive research and development as a promising alternative to highly electrically conductive materials such as indium tin oxide (ITO) and fluorine-doped tin oxide (FTO). Particularly, diamond (sp^3-bonded carbon) is actively studied due its outstanding properties, such as hardness, high thermal conductivity, wide range transparency and corrosion resistance. Synthetic diamond in the form of thin polycrystalline film can be optimized for high optical transparency and metal-like conductivity when doped with boron. Recently, boron-doped diamond (BDD) electrodes were applied in electroanalysis, electrosynthesis and spectroelectrochemistry [l]. The abovementioned properties make BDD electrodes an ideal candidate for implementation in the photoelectrochemical and optoelectronic devices [2-4].

In the present work, we report on the development of inexpensive, optically transparent nanocrystalline boron-doped diamond electrodes. BDD electrodes were integrated into organic photovoltaic devices and studied as a substitution for ITO electrodes. Additionally, we investigate routes towards a direct photoelectrochemical water-splitting via the integration of a silicon solar cell as a light absorber and boron-doped diamond electrodes as a corrision resistant anode material.

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Ordering, flexibility and frustration of two-dimensional supramolecular arrays on graphene

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Two-dimensional (2D) supramolecular arrays provide a route to the spatial control of the chemical functionality of a surface, but their deposition is typically limited to a monolayer termination. We investigate [1] the sequential deposition of one 2D array on another to form a supramolecular heterostructure and realize the growth- normal to the underlying substrate- of distinct ordered layers, each of which is stabilized by in-plane hydrogen bonding. For heterostructures formed by depositing terephthalic acid or trimesic acid on cyanuric acid/melamine, we have determined, using atomic force microscopy under ambient conditions, a clear epitaxial arrangement despite the intrinsically distinct symmetries and/or lattice constants of each layer. Structures calculated using classical molecular dynamics are in excellent agreement with the orientation, registry and dimensions of the epitaxial layers. Calculations confirm that van der Waals interactions provide the dominant contribution to the adsorption energy and registry of the layers.

In a separate study [2], we show that the adsorption of the alkane tetratetracontane (TTC, C44H90) on graphene induces the formation of a curved surface stabilized by a gain in adsorption energy. This effect arises from a curvature-dependent variation of a Moire pattern due to the mismatch of the carbon-carbon separation in the adsorbed molecule and the period of graphene. The effect is observed when graphene is transferred onto a deformable substrate such as water layers adsorbed on mica and an organic solvent, but it is not observed on more rigid substrates such as boron nitride. Our computational studies show that molecular adsorption can be influenced by substrate curvature, provide an example of two-dimensional molecular self-assembly on a soft, responsive interface, and demonstrate that the mechanical properties of graphene may be modified by molecular adsorption, which is of relevance to nanomechanical systems, electronics, and membrane technology.

Finally, through a combined experimental and numerical study [3] of the adsorption of cyclic porphyrin polymers (nanorings) on a graphite surface we conclude that flexible molecules can exhibit a rich and complex packing behaviour. Depending on the number of porphyrin sub- units within the nanoring we observe either a highly ordered hexagonal phase or frustrated packing driven by directional interactions which for some arrangements is combined with the internal deformation of the cyclic polymer. Frustration and deformation occur in arrays of polymers with ten sub-units since close packing and co-alignment of neighbouring groups cannot be simultaneously realized for nanorings with this internal symmetry.

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Synthetic Routes to Polyaniline/CVD Graphene Composites

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Composites of a conducting polymer, polyaniline, and various forms of graphene and graphene oxide have been extensively studied in last decade due to their electrochemical performance as electrode materials in supercapacitors [1-6]. The polyaniline/graphene nanocomposites are often synthesized by *in situ* oxidative polymerization of aniline in a presence of graphene or functionalized graphene. Four types of polyaniline/graphene nanocomposites were reported by Liu *et al.* [7] using graphene oxide, reduced graphene oxide (graphene), aminated graphene, and sulfonated graphene as the basis materials. Graphene, aminated graphene, and sulfonated graphene were prepared by hydrothermal method using graphene oxide as a starting material [7]. Liu *et al.* have shown that the graphene functionalization by amino or sulfonic groups plays an important role in the monomer adsorption on the surfaces and thus affects the polyaniline morphology and the nanocomposite capacitance [7]. Within our contribution, we investigate a role of graphene functionalization in the synthesis of polyaniline/graphene composites using a CVD graphene as a starting material.

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IR CO_2 INDUCED ABLATION OF GRAPHENE IN A PRESENCE OF SULFUR HEXAFLUORIDE

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Abstract
The influence of the sulfur hexafluoride (SF6) gas on the laser deposition of graphene was investigated in our research work. The main advantage of the pulsed laser ablation is its simplicity in implementation. This technique is a vapor deposition process which can be carried out in vacuum or in presence of different gases. For this research, sulfur hexafluoride is used as a background gas for the laser ablation. The laser irradiation at 930 cm^{-1} is strongly absorbed by SF6 and the gas acts as an inert photosensitizer. The ability of SF6 to absorb the laser energy and to convey the energy in a form of heat to the reaction mixture was providing milder conditions for laser ablation. The deposited graphene film was submitted to annealing in order to improve the conductivity of the deposit. The obtained deposits were investigated with Fourier-transform infrared spectroscopy and the obtained spectra indicate successful deposition of graphene onto the substrates, the increased intensity of the C=C peak after the annealing demonstrates positive changes in the structure of the nanomaterial. Scanning electron microscopy was employed for examination of the deposit's morphology and the obtained images demonstrate more homogenous structure with less aggregation and reduced porosity of the deposited films in SF6 atmosphere. The conductivity of the thin films was examined with four point probe resistivity meter. After the annealing the conductivity was significantly increased.

Keywords: annealing, graphene, laser ablation, sulfur hexafluoride.

Deep eutectic solvents/carbon materials interfacial studies for potential energy storage applications

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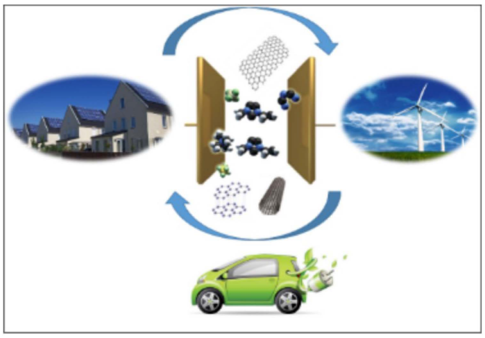
Renewable Energy, coupled with energy efficiency improvements are key elements for the Global Energy Transition Roadmap in bringing a sustainable, safe and smart energy future [1]. Accordingly, supercapacitors are drawing deep attention as high-performance energy storage devices for high energy demand applications. Energy storage is a very challenging topic that may enclose complex mechanisms occurring during the energy harvesting, conversion and storage steps.

In this work, we present recent results that may contribute to a new generation of electrodes based on carbon materials with the potential application on supercapacitors. Being the electrolyte, one of the most important components of an electrochemical device, the effect of the electrolyte was also assessed by using deep eutectic solvents (DES). Specific capacitance was measured for graphene, graphite and carbon nanotubes (MWCNTs)/glassy carbon composite electrodes in contact with choline chloride: ethylene glycol (1:2) DES and the stability was followed by measuring charge/discharge curves at different current densities. BET and Langmuir surface areas were also determined for the different carbon materials.



Acknowledgements

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Polymerized electrodes based on poly(neutral red) for active pharmaceutical ingredient detection

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This work is focused on the electrochemical preparation of poly(neutral red) (PNR) onto glassy carbon (GC) electrodes in order to determine optimal electropolymerization conditions for the detection of drug substances, especially heparin. Functional conductive polymers are particularly interesting materials for the construction of electrochemical sensors aimed at detection of important analytes. The preparation of electroactive films is mostly performed by electropolymerization, during which the film thickness, its permeability and charge transfer can be controlled. PNR belongs to poly(phenazine dyes) and is used as an electron transfer mediator for electrochemical sensors and biosensors or as a sensitive selective layer of these sensors [1]. The electrochemical polymerization of PNR can be controlled by changing the pH, selecting the salt in the electrolyte and the applied potential range, as well as the number of cycles and the potential scanning rate [2]. An important advantage of PNR is that it is electrochemically active at physiological pH. Nowadays, studies concerned with the detection of heparin gain a lot of interest, because of its use in medicine, where it plays an important role in binding to biological proteins. Due to the presence of sulfate and carboxyl groups, it has a high anionic charge density so that it can react with basic dyes to form supramolecular heparin dye complexes [3, 4]. Polymeric PNR films were prepared using cyclic voltammetry (CV) during twenty-five cycles in the potential window from -0.65 to 1.25 V (vs. Ag/AgCl) at scan rate of 50 mV.s^{-1} in 0.1 M H_2SO_4 solution containing 0.001 M NR. Electrochemical (CV and EIS) and spectroscopic (IR and MS) methods of characterization of PNR layers confirmed the presence of polymer on the electrode surface, it was also found out that the polymerization process runs through an amino group and an aromatic ring. PNR electrodes were used to detect heparin by using electrochemical CV and EIS methods. Measurement of the peak current intensity of the PNR-modified electrode during CV was more sensitive to changes in heparin concentration comparing to changes in resistance (impedance response). The PNR-modified GC electrode showed clearly defined A1/K1 oxidation-reduction peaks at -0.083/-0.242 V (vs. Ag/AgCl), and its height decreased continuously in the concentration range of 2–30 μg.mL^{-1} after heparin addition with detection limit 0.8 μg.mL^{-1}. The PNR electrode allowed a relatively accurate determination of heparin in real injection samples.

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Development of piezoresistive elastomer sensors based on nano carbon material for health monitoring and robotic applications

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Piezoresistive elastomer based materials are interested for health monitoring, prosthesis and robotic applications. This talk will give an overview on the development and evaluation of extrinsic conductive thermoplastic elastomers and natural rubber sensor composites made in in the last years to develop a reliable soft matter sensor material. To achieve electrical conductivity, different kind of nano carbon materials like carbon black, graphene and carbon nanotubes have been investigated over the last years. Quasi static and dynamic strain measurements have been performed to investigate drift and relaxation behavior of the sensor composites and the results show that matrix and carbon source strongly affects the electrical resistivity behavior of composite materials. Selected piezoresistive composite material was successfully integrated into different demonstrator designs: into an industrially woven elastic band and into a 3D printed auxetic design structure. Finally, the piezoresistive sensor designs have been tested for health monitoring, natural user interface and exercise monitoring of robots. The soft matter piezoresitive sensor material shows very promising for the analysis of the breathing and pulse of a human. A wrist sensor device for drone and robot control has been successfully tested, and the robots can be easily steered by natural human movements.

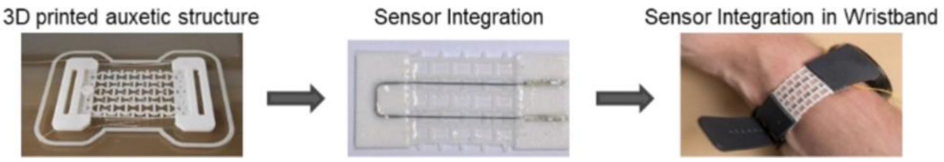

Figure 1: Integration of a piezoresistive soft matter sensor composite into an 3D printed auxetic design structure.

Figure 2: Natural user interface to control a drone flight.

Hyaluronic acid functionalized carbon nano-onions for drug delivery in cancer cells

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Carbon nano-onions (CNOs) are promising materials for biomedical applications, thanks to their low cytotoxicity and good biocompatibility. They can be used as drug carriers for targeted drug delivery, thanks to their supramolecular functionalization with biocompatible polymers. In this study, we selected the hyaluronic acid (HA), as hydrophilic targeting agent with the double purpose of enhancing the solubility of these carbon nanomaterials and of obtaining a targeted delivery to CD44 overexpressing cancer cells. We assessed the *in vitro* toxicity of the functionalized CNOs on different cancer cell lines and the potential *in vivo* effects in zebrafish during the development. Zebrafish represent alternative and complementary model organisms, with several peculiarities, making them established systems for toxicity screening, in comparison to other species [1]. Moreover, we evaluated the cellular uptake and cellular localization of the functionalized CNOs in cancer cells and their biodistribution in zebrafish larvae once they are completed developed. Our results will open new perspectives in the application of carbon nano-onions for specific drug delivery in cancer cells.

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Electrons localization on the edges of graphene and graphene – like materials

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Quantum – mechanical single – electron states localized at the surfaces of metals and semiconductors is a well – studied topic of solid – state physics. On the other hand, little is known about the nature of edge states of two – dimensional materials, such as graphene and transition metal dichalcogenides (TMDs), despite the extensive research both theoretically and experimentally.

Previous study on quasi 1D TMD nanoribbons, has shown that regardless of edge composition all structures consist of a semiconducting bulk bounded be metallic edges [1,2]. According to W. Shockley [3] electron wavefunctions can present a maximum at the surface of a material (resonance states) solely due to the fact that the structure periodicity is broken.

In this study, we perform theoretical calculations using Density – Functional Theory (DFT) as implemented by the open – source GPAW package [4] and we locate true surface states on graphene nanoribbons and the four most common TMDs nanoribbons (MoS_2, WS_2, $MoSe_2$, WSe_2). For each structure we use a (1x6) supercell, which consists of one unit cell in the periodic x direction and six in the finite direction y, and we calculate the electrostatic potential and the electron probability density as a function of the atoms positions throughout the structures. We find that the localization of electrons on the edges of quasi 1D graphene – like materials is in excellent agreement with the Shockley theory and we conclude on the width of the metallic region. The electron probability density for MoS_2 and graphene nanoribbons is shown in figure 1.

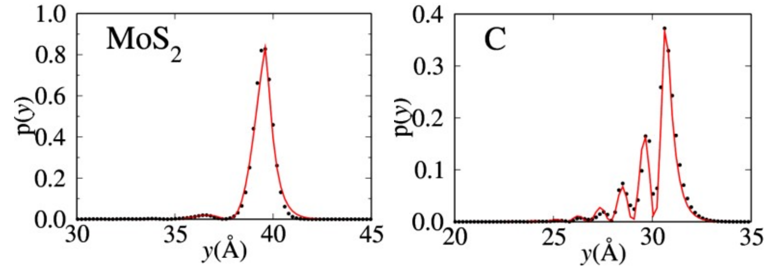

Figure 1: Electron probability density for MoS_2 (left) and graphene nanoribbons (right) as a function of atoms position in the finite y direction. In both figures for the atoms positions, we present a range close to the edge of the nanoribbons. The direct calculation and the non – linear curve fit according to Shockley theory, are presented with black dots and red curves respectively.

Acknowledgements
This project was supported by the Research Committee of University of Crete, the Greek G.S.R.T and H.F.I.R., the Cy-Tera Project, Bibliotheca Alexandrina and finally the Greek Research & Technology Network (GRNET) in the National HPC facility – ARIS.

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A Comparative Study of Glucose Adsorption and electrooxidation on the metal- graphene/ITO Electrodes

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ABSTRACT

At present, the graphene is coated on Cu foil with the 5 sccm hexane (C_6H_{14}) flow rate, 50 sccm hydrogen (H_2) flow rate, and 20 min deposition time parameters by the CVD method. The graphene on the Cu foil is then coated onto few-layer the ITO electrode. Furthermore, the Pt and Au metals are electrodeposited on graphene/ITO electrode with electrochemical method. These electrodes are characterized by Raman spectroscopy and Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis (SEM-EDX). The graphene structure is confirmed by Raman analysis. The Au, Pt, and graphene network are clearly visible from SEM images. In addition, glucose ($C_6H_{12}O_6$) electrooxidation is investigated with cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) measurements. As a result, Pt-graphene/ITO indicates the best $C_6H_{12}O_6$ electrooxidation activity with 9.21 $mA.cm^{-2}$ specific activity (highly above the values reported in the literature). In all electrochemical measurements, the Pt-graphene/ITO exhibits best electrocatalytic activity, stability, and resistance compared to other electrodes. The adsorption of the $C_6H_{12}O_6$ molecule is examined theoretically over metal atom-(gold and platinum) doped graphene surfaces using the density functional theory (DFT) method. The interaction between $C_6H_{12}O_6$ molecule and OH adsorbed Pt-doped surface is stronger than that of OH adsorbed Au-doped graphene surface thermodinamically according to the reaction energy values.

Keywords: Au, Pt, graphene, Chemical vapour deposition, glucose electrooxidation, density functional theory

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Structural, transport and spectroscopic characterization of metal-organic framework / graphene-like composites

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Metal Organic Frameworks (MOFs) attracted in the last years a great attention due to their high surface area and the possibility to tune their chemico-physical and textural properties, by either varying the metallic centers or acting on organic functionalities. Their peculiar properties as well as this flexibility make them very interesting for a large range of potential applications. In this work, we performed a study on composite materials obtained by a Cu-based MOF (known in literature as HKUST-1), by embedding, in its structure, graphene-like layers (GL) prepared by a simple and unexpensive two-steps oxidation/reduction treatment of carbon black [1,2]. Different MOF-GL composites (MGL) were synthesized, having different GL amount [3]. Electrical conductivity dramatically increases with the GL relative amount (up to five order of magnitude for a GL content ranging from 5wt.% to 40 wt.%, where the HKUST-1 precursor is an insulator), showing signature of percolation phenomena due to the filling of GL in the MOF matrix. Structural characterizations indicate that the presence of GL modifies the structure of HKUST-1: distortion of the porosity of the material and the disappearing of the typical octahedral crystals of HKUST are observed. Advanced spectroscopic techniques measurements, namely Nuclear Magnetic Resonances (NMR) spectroscopy, X-rays Photoemission Spectroscopy (XPS), X-rays Absorption Spectroscopy (XAS), and Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy, were performed on precursors and MGL composites. Preliminary analysis of the collected data allows first hypothesis on the role of GL inclusion on electronic, geometrical and chemical properties on the investigated materials.

The authors acknowledge the financial support of CERIC-ERIC Consortium under proposal 20142029 for the access to experimental facilities at Materials Science Beamline (MSB), Elettra Synchrotron in Trieste and at the Slovenian NMR Center of Lubjiana. This work has received support also from the project Electrical and Spectroscopic Properties of Eumelanin for Related Innovative Applications (ESPERIA) funded by the University of Naples Federico II inside the 2016 call for Finanziamento della Ricerca di Ateneo and from Piano Annuale della Ricerca Mise-CNR 2015–2017 "Sistemi elettrochimici per l'accumulo di energia".

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Polycaprolactone as graphene transfer medium

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Single layer graphene of high-quality is synthesized on copper metal foils in chemical vapor deposition (CVD) process. After deposition, graphene is usually transferred from metal foil to versatile dielectric substrates. The most popular transfer method uses poly(methyl methacrylate) (PMMA) dissolved in acetone which is sprayed over graphene surface [1,2]. After solvent evaporation, PMMA layer is formed on top of graphene and protects it from mechanical cracking while metal substrate is chemically etched in next step of transfer process. Finally, graphene-PMMA composite is mechanically aligned with dielectric substrate and washed with acetone which removes PMMA layer and results with graphene-on-dielectric. This process is usable only for dielectrics resistant to acetone. In this work polycaprolactone is used instead of PMMA to achieve universal transfer of graphene to any kind of dielectric material. Polycaprolactone is dissolved in toluene and sprayed over graphene. At room temperature evaporation of solvent is adequate for spin-coating. Copper-graphene-polymer composite is thermally transferred to dielectric substrate with use of hot-iron. After cooling to room temperature copper substrate is removed in ferric-chloride bath resulting in graphene-polymer-dielectric composite suitable for electric measurements. Polycaprolactone melting point is at 60 degrees Celsium so this process is also suitable for dielectrics with low melting point such as polyethylene and polypropylene.

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3-Dimensional $LiMn_2O_4$ Positive Electrode for Solid-State Lithium-Ion Batteries

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Lithium-ion batteries (LIB) are one of the most attractive battery systems for future applications due to its high energy density. However, safety and toxicity problems still remain in commercial LIB with organic liquid electrolyte. By replacing the conventional electrolyte with a solid-state lithium-ion conducting polymer or ceramic these issues may be resolved and result in an increased energy density. These all-solid-state lithium-ion battery (SSB) system have been extensively studied with regards to the ionic conductivity of the electrolytes and the interfacial issues between the electrodes and the electrolyte.

One of the most remarkable advantages of the SSB is the potential usage of metallic lithium as anode, which has a ten times higher specific capacity than graphite. However, to fully leverage this advantage the cathode needs to contain large amounts of lithium intercalating material. Unfortunately, these oxide materials are poor electric and ionic conductors which limit the useable thickness of the cathode. To solve this problem, three-dimensional (3D) positive electrode need to be created. Here, relatively thin layers of active material are directly contacted with the electric and ionic conducting material.

In this work we describe the fabrication of such positive electrodes containing $LiMn_2O_4$ (LMO) as active material and polyethylene oxide/LiTFSI (PEO) as the polymer-type solid electrolyte directly inside of a carbon-based electric conductive matrix via sol-gel synthesis. We avoid the usage of nitrates during the synthesis which would create nitrous gases during the preparation process. The 3D positive electrodes are then tested in a self-built battery setup demonstrating the viability of our battery concept.

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Polybutylene Succinate Reinforced with Hybrid Nanoparticles

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The polybutylene succinate / nanocellulose / graphene composites have been fabricated using several loadings of different ratios of mixed hybrid nanoparticles. Processing conditions were chosen to be as compounding in solution and melt. Finally, 8 different materials combinations and neat polymer reference were prepared. Composites were process by solution casting, compounding above melting temperature, electrospinning. Mechanical properties, dynamic mechanical analysis, differential scanning calorimetry, thermal gravimetric analysis and structural analysis of the obtained polybutylene succinate composites were performed. In all cases, the composites containing hybrid fillers exhibited the best properties. Respectively 50% improvement in tensile strength and modulus were obtained. Moreover, 2-fold improvement in the storage modulus were observed due to the incorporation of nanocellulose/graphene hybrid reinforcement into the polymer system. Microstructure reveal good dispersion of nanoparticles inside polymer matrix.

Acknowledgement: This research is funded by the Latvian Council of Science, Project No. lzp-2018/1-0136

High Temperature Corrosion Testing of Zirconium Nuclear Fuel Rod Cladding Protected with Nanocrystalline Diamond Films Deposited by Microwave Plasma CVD

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Nanocrystaline diamond (NCD) film can be utilized as a protective coating for zirconium alloy (Zircaloy2) nuclear fuel cladding (NFC) of nuclear reactors. One big disadvantage of Zircaloy2 is that it reacts with water steam and during this (oxidative) reaction releases hydrogen gas, which partly diffuses into the alloy forming zirconium hydrides. Moreover, the large production of hydrogen gas can result into catastrophic hydrogen-air explosions (as occurred in the recent Fukushima accident, March 11, 2011). We have successfully demonstrated the possibility to cover a cylindrical rod-shaped Zircaloy2 nuclear fuel cladding by a 300 nm thick protective NCD layer using the microwave linear antennas plasma enhanced CVD [1], (Figure 1). NCD coated Zircaloy2 rods underwent a set of corrosion tests, namely a reactor irradiation test and hot steam oxidation. SEM, Raman, XRD, XPS were employed [2], [3] confirming that a thin NCD layer can serve as a anticorrosion protective coating on NFCs in the harsh environment of a nuclear reactor at substantially elevated temperatures (Figure 2).

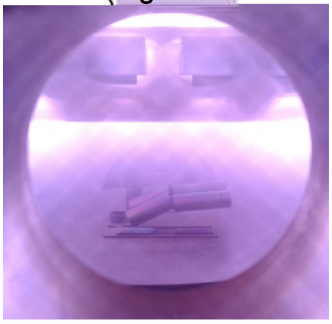

Figure 1 Deposition of NCD film on Zircaloy2 by MW linear antennas plasma.

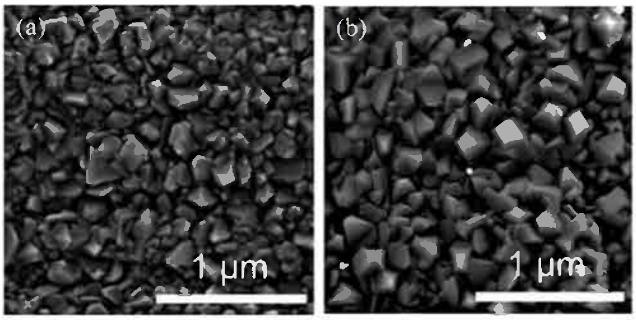

Figure 2 (**a**) Initial surface of a Zr alloy sample covered with 300 nm thick NCD, (**b**) the surface after 30 days of exposure to 360 °C hot water.

Acknowledgement
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Morphology and thermal behavior of composites of PLA with tunable carbon nanotube fibers.

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The use of nonpetroleum and biodegradable polymers is a need due to the increase of pollution and plastic waste. In this contest, polylactic acid (PLA) plays an interesting role because is a biodegradable polymer synthesized from starch. PLA can be processed by the common techniques as injection, extrusion or compression molding.[1] Otherwise, one of the main handicap of PLA is its brittleness and low impact resistance,[2] which can be improved by different strategies, being one of the most interesting the use of PLA as a matrix in composites. One of the main limitation in nanocomposites, mainly nanocarbon as graphene or carbon nanotubes (CNTs), is the preparation of high loading nanocomposites, because the good dispersion of these nanocarbons is problematical. However, if these CNTs are assembled into a macroscopic fiber, prior the fabrication of the composites, the axial properties of CNT, which are excellent, can be extrapolated to the macroscopic fiber.[3] Therefore, PLA/CNTf composites seems a good option to fabricate composites with high CNT concentration.

The aim of this work will be the preparation of PLA/CNT fiber composites by immersion in polymer solution followed by drying, with CNT concentration from 3.5 to 35 wt%. The morphological, thermal, and crystallization properties were studied. This processing method ensure full impregnation and the formation of a huge interphase of CNT/polymer due to the high porosity of the fibers. The good interaction of both materials is confirmed by the formation of an oriented transcrystalline (TC) layer of PLA on the fiber surface. This TC is associated to an improve in thermal stability, higher crystallization and faster nucleation, which are be probed by Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and 2D Wide and Small Angle X-Ray diffraction (WAXS/SAXS) experiments.[4]

Acknowledgement
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Improvement of Quartz Crystal Microbalance Gas Sensors by Nanostructured Thin Films

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Focused Laser beam is a widely used for deposition, localized annealing and patterning of various materials (eg. metals, oxides, organic substances). Our work is focused to possibilities of usage of continuous wave (CW) lasers for local deposition and patterning of black metal and organic semiconductors on the QCM sensor substrates. Our method is based on laser direct write to sensing layer on the active electrode and laser induced forward transfer of sensing material to sensing substrates. For our test we used QCM substrates based on circular (d=8.65 mm) quartz AT cuts with chrome + gold electrode with base working frequency at 10.880 MHz. As the sensing layer we used black gold ,black palladium, Zinc Phthalocyanine. The direct write/ deposition apparatus includes micro CNC machine (minimal step adjustable to 300 nm) equipped with the semiconductor laser (lambda = 405 nm, power of 50 mW, spot size 6 microns) in CW mode and focusing optics. Deposition process was held in an inert gas (Argon, Nitrogen) at atmospheric pressure. Morphology and microstructure of modified and deposited layers were studied by optical, electron microscopy and AFM. Chemical composition of deposited Phthalocyanine was studied by FTIR and compared with the source substances. It was proved that chemical structure of all chosen substances is not affected by this deposition technique. Employing our technique we are able to achieve precise and reproducible laser transfer of organic semiconductors to the target sensor substrate with lateral resolution of 14 microns. Our sensors were tested for detection of NOx, VOCs and the results shown significant improvement of sensitivity caused by enhanced surface morphology.

Acknowledgement
This work was supported by Czech Science Foundation (GACR), Project No. 18-09347S and also by Ministry of Education, Youth and Sports within the projects LTC17058 and 8J18FR011 and by COST Action CA15107 MultiComp.

Polybutylene Succinate Reinforced with Hybrid Nanoparticles

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The polybutylene succinate / nanocellulose / graphene composites have been fabricated using several loadings of different ratios of mixed hybrid nanoparticles. Processing conditions were chosen to be as compounding in solution and melt. Finally, 8 different materials combinations and neat polymer reference were prepared. Composites were process by solution casting, compounding above melting temperature, electrospinning. Mechanical properties, dynamic mechanical analysis, differential scanning calorimetry, thermal gravimetric analysis and structural analysis of the obtained polybutylene succinate composites were performed. In all cases, the composites containing hybrid fillers exhibited the best properties. Respectively 50% improvement in tensile strength and modulus were obtained. Moreover, 2-fold improvement in the storage modulus were observed due to the incorporation of nanocellulose/graphene hybrid reinforcement into the polymer system. Microstructure reveal good dispersion of nanoparticles inside polymer matrix.

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Hydrophilic carbonaceous nanoparticles for water remediation applications: an experimental study on heavy and rare earth metals adsorption

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The interest toward carbonaceous materials bearing oxygen containing functional groups in heavy metals capture relies in their well-known binding activity to form a metal complex. Heavy metals are widely considered as the most toxic water pollutants and their removal through adsorption over carbonaceous materials is one of the most successful and largely studied option [1]. In the present work adsorption complexation properties of Cd^{2+}, Zn^{2+}, Pb^{2+}, Ln^{3+} over hydrophilic carbonaceous nanoparticles (HNPs) have been investigated by using X-ray fluorescence and differential pulse voltammetry. HNPs with uniform dimensions and a good grade of dispersion in water, were obtained through the oxidation of a carbon black with nitric acid at 100°C, for different reaction times (2-24 hours). The characterization results showed that the oxidative treatment did not affect CB micro and nanotexture and a variable number of oxygen functional groups (mainly carboxylic) were introduced. An increase of both microporosity and mesoporosity was also observed [2]. The experimental data collected in the 2.0 to 7.0 pH range suggested that the sorption of metal ions on HNPs particles is controlled by chemical adsorption involving a strong surface complexation of metal ions with the carboxylic groups on the surface of HNPs. In particular, this study reveals that the surface complexation of the lanthanide Eu^{3+} ions is comparable to that of Pb^{2+} ions, and higher than that of Zn^{2+} and Cd^{2+} ions. The promising results on the adsorption of Ln^{3+} ions open the exploitation of HNPs for solid phase extraction applications aimed to preconcentration, separation and determination of rare earth elements and actinides. The HNPs were also tested for the Cd^{2+}, Ni^{2+}, Pb^{2+} ions removal in practical configurations. To this aim the HNPs were supported over silica beads to enhance their separation from treated water through sedimentation. The use of silica beads as a mechanical support eliminates the constraints posed by the colloidal nature of HNPs, allowing a better exploitation of HNPs adsorbing properties. Adsorption tests were performed in batch exploring the effect of the most relevant process parameters (temperature, pH, initial concentration of the target metal, HNPs oxidation degree, HNP loading over the silica support).The supported HNPs exhibit high removal efficiencies for the three metals at neutral pH and low temperature (10°C), a condition that commonly occurs for natural water remediation applications and for some types of industrial wastewater. The sorbents capture Ni^{2+} ions with the highest selectivity, while Pb^{2+} ions are adsorbed at a lowest efficiency. The sorbents exhibited high adsorption capacities per gram of active phase (up to 0.54 mg/g for cadmium, 13.48 mg/g for nickel and 8.87 mg/g for lead at the corresponding quality limit admitted by Italian regulations on wastewater), which makes them likely to be used for water cleaning purposes.

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Carbon nano-onions as non-cytotoxic carriers for cellular uptake of glycopeptides and proteins

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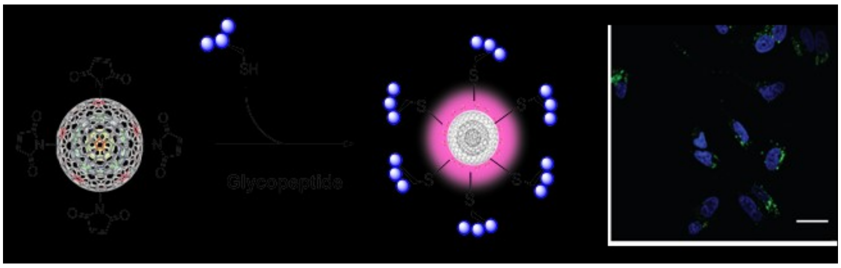
Carbon nano-onions (CNOs) possess favorable properties that make them suitable for biomedical applications, including small size, ready surface modification and good biocompatibility. Here, we report the covalent immobilization of a synthetic glycopeptide and the protein bovine serum albumin (BSA), onto the surface of carbon nano-onions using the maleimide -thiol-"addition reaction". The glycopeptide and BSA are readily transported inside different cell lines, together with carbon nano-onions, through the endocytosis pathway. Our results show that carbon nano-onions are excellent scaffolds for glycopeptides and proteins immobilization and intracellular carriers for these biomolecules. These findings open new perspectives in the application of carbon nano-onions as intracellular transporter in diverse biomedical applications.



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Synthesis of Graphene Quantum Dots: from Small Molecules to Biomaterials

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In the last few decades, significant advances were achieved in the research of carbon nanomaterials. Nowadays, the nanocarbon family spans from fullerene, the first member, to graphene quantum dots (GQDs), the last to join. GQDs are a fascinating class of nanocarbons that comprise quasi-spherical nanoparticles with sizes below 10 nm. They typically display excitation wavelength dependence, excellent photostability and chemical stability, good biocompatibility, high-water solubility, low toxicity. Furthermore, they can be easily functionalized with biomolecules. Due to these unique properties, GQDs have attracted tremendous interests for their potential in a lot of applications, especially in the biomedical field.

In this work, the main objective was to obtain GQDs through a bottom-up approach: microwave-assisted pyrolysis method using glucose and ethylenediamine as molecular precursors. The as-prepared nanoparticles showed excitation-dependent visible and near-ultraviolet emission. Moreover, they have shown near-infrared emission, one of the research millstones of fluorescent carbon nanoparticles. The synthesized GQDs were nitrogen-doped and presented amine groups on their surface. The as-prepared GQDs exhibited a high-water solubility due to the high nitrogen content. The morphology and size were studied by atomic force microscopy (AFM) and transmission electron microscopy (TEM), and the quasi-spherical crystalline nanoparticles of 2-5 nm were found. Finally, based on the *in vitro* analysis, the synthesized GQDs showed excellent biocompatibility.

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Towards a Tuneable Thermal Conductivity Material via Low Voltage Ordering of CNT Networks

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Traditionally we seal our devices and insulate our houses with static materials that possess no ability to change their insulation value. This inevitably leads to increased energy consumption due to thermal management needs: a device may be required to be cooler or warmer, and an insulating material, of static thermal conductivity, doesn't help in this regard. Here we examine the real-time tuneable thermal conductivity properties of a low-voltage device, consisting of a Carbon Nanotube Network embedded in a gel matrix and sandwiched between custom made electrodes. The operating principle is that the thermal conductivities of disordered networks tend to be insulating, while highly aligned networks become metallic. The thermal conductivity, durability, power consumption and extensibility properties of the device are examined.

Fig 1. depicts a cross-section of the experimental device, showing the counter electrodes, which have attached to them highly aligned SWNT arrays, while in between is situated the CNT network in its suspension matrix. Displayed is the fully metallic (aligned) state and the insulating, disordered state (bottom).

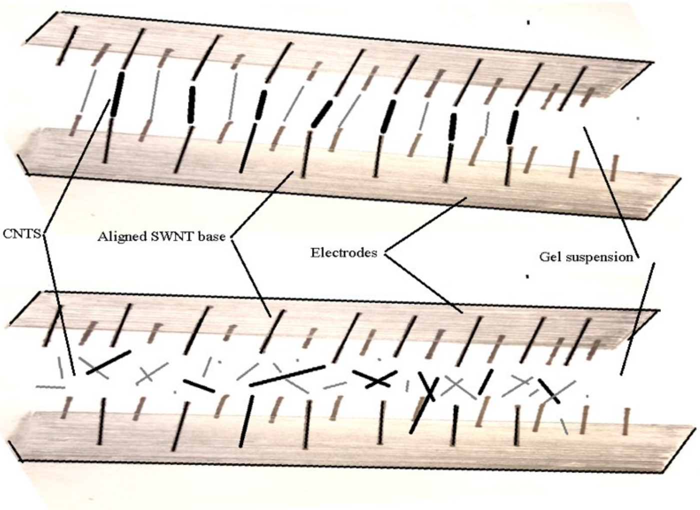

Fig. 1. Cartoon of the experimental apparatus, showing the ordered (top) and disordered states (bottom).

Enhanced light-matter interaction in layered 2D heterostructure

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Abstract

Two-dimensional materials (2D) have attracted substantial attention in nano-optoelectronic and electronic industries owing to their unique physical and structural properties. A great deal of research has been done in the past few years exploring the optoelectronic properties of semi-metallic, semiconducting, and insulating 2D materials, etc. However, significant development is still required to achieve practical applications, which can be adopted by the industries. For instance, the semiconducting 2D materials, in particular, transition metal dichalcogenides (TMDCs) show unique properties of light-matter interaction. The TMDCs have direct bandgap in monolayer showing strong light-matter interaction, but in bulk, they show indirect bandgap, which reacts less significantly compared to its monolayer counterpart. Meanwhile, owing to the lack of materials in monolayer, the carrier density of states responsible for absorption or emission is limited. In this work, we adopt a new strategy to circumvent the issue. We have designed vertical stakes of the monolayer (1L) TMDCs separated by few-layer hexagonal boron nitrides (hBN), an insulating 2D material, which separates the 1L TMDCs, MoS_2 keeping the monolayer properties intact in the heterostructure, MoS_2/hBN/MoS_2, see Figure 1a. The optical microscopy image of the device is shown in Figure 1b. Interestingly, the emission spectra of such heterostructure show much stronger radiation density at the heterojunction compared to its monolayer counterpart, see Figure 2a. Depending upon the hBN thickness, we also found that the enhancement can be tuned. We interpret such enhancement of emission is due to the exciton coupling at the heterojunction. We further map the excited state carrier lifetime, which shows a much shorter lifetime at the heterojunction confirming the coupling induced emission at the junction, see Figure 2b, that make the emission intensity stronger. Our work, therefore, should be beneficial and timely for the development of high-performance nano-optoelectronic devices.

Porphyrin Thin Films for Gas Sensing Application

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Porphyrins and porphyrinoids represent a significant group of materials that have found a wide application in the field of chemical sensors. Thanks to their chemical structures and physicochemical properties (e.g. they have a large π-aromatic system, they are natural chromophores and are able to form complexes with metal ions), they can be used as receptors of various kinds of chemical sensors with different transducer mechanisms. [1-2]

In this work, we prepared thin films of free base tetraphenylporphyrin (TPP) and metal tetraphenylporphyrins (MTPP; M = Co, Cu, Ni, Zn) to investigate their use for optical and chemiresistive detection of vapors of nerve chemical warfare agent simulants. The films were deposited on fused silica (for spectrophotometry) and silicon substrates (for photoluminescence) at room temperature by vacuum thermal evaporation.

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Photoregeneration and improvement of chemical sensors

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Photoregeneration is a soft and economic method for desorption of adsorbed analytes from thin gas sensor layers (= for sensor regeneration). It is based on the illumination of the sensor by specific light at a precise wavelength and intensity [1]. This method of regeneration is appropriate especially for thin organic or inorganic layers that suffer from long recovery times and baseline shifts. Or there where temperature regeneration is undesirable due to possible morphological changes of the active layer.

The main aim of our work is focused on the optimization of photoregeneration method for phthalocyanine chemiresistors and quartz crystal microbalance (QCM) sensors sensitive to NO_2.

Part of our work also focuses on the improvement of sensing properties of QCM sensors by the use of metal-blacks (MBs) MBs are highly nanoporous and nanostructured materials that have a large specific surface area. This large surface provides more binding sites for analytes and, hence, increase the response of the QCM sensor.

In the future, we would like to combine these two principles together and prepare high-sensitive and simply regenerable QCM sensors sensitive to NO_2 or other analytes depending on the used active layer.

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Effect of pre-dispersed and pristine single-walled carbon nanotubes on mechanical properties of low-density polyethylene nanocomposites

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Carbon nanotubes (CNT) presents a revolution in the field of nanocomposites. Due to their geometrical configuration, which forms a large interfacial area with host material, they profoundly improve material's mechanical properties [1]. In recent years a demand and production of these nanofillers significantly increased, which consequently lowered their prices to more affordable levels [2]. These products are now on the market in a variety of forms; from pre-dispersed CNTs in a specific host medium, to pristine CNTs, which are difficult to transport and process, since they occupy a great deal of space and present a health risk. Within the scope of our research, we determined the mechanical properties of polyethylene (PE) nanocomposites with pre-dispersed and pristine single-walled carbon nanotubes (SWCNTs).

As a host material low-density polyethylene, i.e. LDPE (DOW LDPE 780 E NATURAL, Dow Chemicals Company, USA) was used, while two types of single-walled carbon nanotubes were used as a filler: i.) Tuball 801 masterbatch (denoted as 801m) consisting of 10 wt.% of pre-dispersed SWCNTs in low molecular weight polyethylene wax and ii.) Tuball 801 (denoted as 801s), which were pure SWCNTs. Solution compounding was applied to 801s, using LDPE as a host material to create a masterbatch for easier further processing. Nanocomposites were prepared by melt mixing using Haake Minilab twin-screw compounder with the SWCNT content from 0 to 1 wt%, and immediately reprocessed into samples for mechanical properties determination, by Minijet injection moulding maschine..

Results, obtained from determination of mechanical properties, i.e. Young's modulus, effective reinforcement modulus, etc. showed no distinctive difference between both types of prepared nanocomposites. Although fairly high content of low-molecular weight polyethylene wax, i.e. 9%, was used, it has no impact on mechanical reinforcement within observed SWCNT content. However, nanocomposites prepared with 801m were more brittle as determined from the smaller strain at break.

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Formation of amorphous carbon films using argon-acetylene and argon-acetylene-hydrogen plasma

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Amorphous carbon films were formed on nickel/silicon (100) substrates by plasma jet chemical vapor deposition (PJCVD). The carbon films were deposited at atmospheric pressure using an argon-acetylene and argon-hydrogen-acetylene plasma. The plasma composition was analyzed by optical emission spectroscopy (OES). The results indicated that the dominant species in the argon-acetylene and argon-hydrogen-acetylene plasmas were the CH radical and C_2 particles. The emission intensities of CH and C_2 lines depended on the hydrogen amount in plasma and the distance. Scanning electron microscopy analysis demonstrated that the surface roughness of the coatings decreased with the addition of hydrogen and the increase of distance from 5 mm to 7 mm. The oxygen concentration increased with the increase of the deposition distance. The Raman spectroscopy results indicated that the addition of the hydrogen in the argon-acetylene plasma lead to the formation of nano-crystalline graphite films at 5 mm distance. The increase of the distance from 5 mm up to 7 mm stipulated the formation of multiphase SiC/carbon films when the argon-hydrogen-acetylene ratios were 100:2.4:1 and 100:1.2:1.

Biodegradable Polyurethane/Graphene Oxide Scaffolds for Soft Tissue Engineering: *In Vivo* Behavior Assessment

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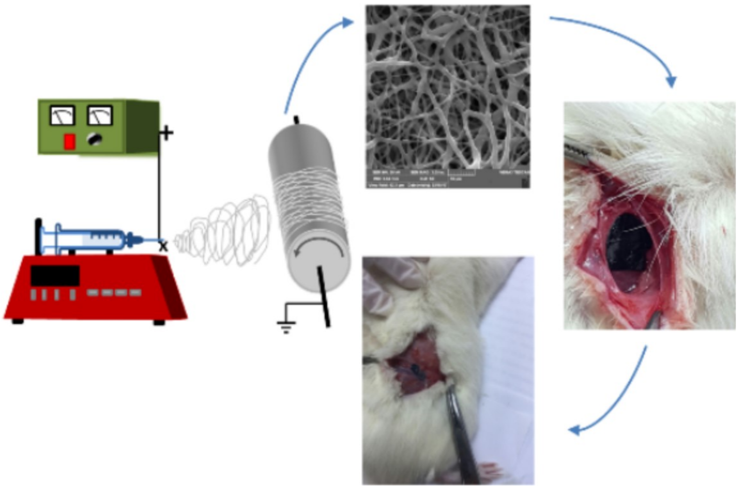
In this work, the already obtained 3D porous electrospun scaffolds based on DegraPol® (DP), a polyester urethane, with different concentrations of graphene oxide (GO) (0.0–2.0 wt%) were assessed for their *in vivo* behavior .



To enable proper sterilization of the scaffolds without their degradation and/or morphological degeneration, the aqueous solution of colloidal silver was proposed as a novel way to serialize polymer scaffolds. In order to assess biocompatibility and biodegradability of the scaffold and the suitability of the sterilization method, *in vivo* study was performed on albino Wistar rat according to the procedures for the use of experimental animals for scientific purposes. Since the potential of this material for reparation of soft tissue was assessed, one of the obtained porous scaffolds was used to heal an artificial lesion of subcutaneous tissue (the innermost layer of skin), an injury that cannot heal only by reepithelialisation alone. The histological tissue analysis was performed 3 months after the application of the scaffold. The results of the *in vivo* analysis, showed scaffold degradation, absence of an inflammatory process and penetration of tissue cells in the scaffold.

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Carbon nanofiller type and size effects on the thermal conductivity of PLA-based nanocomposites

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This study investigates the influence of nanofillers like carbon nanotubes, graphene and their mixture, as well as their size on the thermal conductivity of PLA nanocomposites prepared using the melt mixing method by means of a twin-screw extruder. The polymer matrix used in this study was Ingeo™ Biopolymer PLA-3D850 (Nature Works) grade, developed especially for manufacturing 3D printer monofilament. Four types of carbon nanofillers were used: 1) industrial graphene TNIGNP (Number of Layers: < 30; Thickness: < 30 nm; Aspect Ratio: ~230 /165); 2) industrial MWCNTs – TNIMH4 (OH-2.48% content; size: outer D=10-30 nm, Length=10-30 µm; Aspect Ratio: ~1000); 3) graphene – TNGNP (length > 5-10 µm, thickness 4-20 nm, aspect ratio AR~500) and 4) MWCNTs – NANOCYL® NC7000™ (diameter 9.5 nm, length 1.5 µm, aspect ratio AR=150). A Hot Disk 2500 thermal analyzer was used to measure the thermal conductivity of hot-pressed specimens of composites. The results have shown that the industrial TNIGNP (with higher number of layers and thickness and smaller AR) has highest thermal conductivity (with ~ 380% improvement at maximum filler content of 12wt%), compared with the higher quality of graphene and both types of MWCNTs. On the other hand, the NANOCYL MWCNTs (with the smaller diameter, length and AR), shows better thermal conductivity results, compared with the industrial MWCNTs.

Acknowledgement

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Conductive Polyamide Made by Water-Based Layer-by-Layer Multilayer Nanocoatings

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Conductive multilayered nano-coating composed of multi-walled carbon nanotubes (MWCNT) stabilized by sodium deoxycholate (DOC) and poly(diallyldimethylammonium chloride) (PDDA) was deposited via layer-by-layer assembly on the surface of enzymatic modified polyamide 6.6 (PA6.6) [1, 2].

The increased hydrophilicity after enzymatic modification, due to introduced carboxyl and amino groups and larger zeta potential, improve surface functionality of PA6.6 which became able to accept more electro-conductive nano-coating. Multilayer nanocoating of PDDA/MWCNT-DOC bilayers reduced the sheet resistance of modified fabric at a greater rate than the unmodified polyamide. The conductive network on the surface of the modified fabric has a better morphology from that of the unmodified sample. The nano-coating covers each modified fiber conformally with more MWCNT present that creates interfiber bridges. This mild and environmentally friendly treatment could likely be used to impart the functionality of a variety of hydrophobic synthetic fabrics.

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The effects of concentration of reactants on the kinetics of polyhydroxylation of fullerene

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Due to specific physico-chemical properties: solubility in water, ability of free radical scavenging, antioxidant properties, photo-toxic, photo-catalytic and anti-microbial activity it could be expected that fullerol find applications in various fields of chemistry, biochemistry, pharmacy and medicine [1]. In this work, the effects of concentrations of: fullerene, phase transfer catalyst (cetyltrimethylammonium bromide (CTABr), hydrogenperoxide (H_20_2) and sodium hydroxide (NaOH), on isothermal kinetics of polyhydroxylation of fullerene have been thoroughly investigated.

The fullerol preparation by the method of fullerene polyhydroxilation in the presence of phase transfer catalyst is described in details [2]. The concentration of fullerenes in organic phase of reaction mixture was monitored by spectrophotometric method [2]. The elemental content (C,O,H) of the synthesised products was determined using Elemental Analyzer type EA 1108, Carlo Erba, Italy. The reaction order of the fullerene polyhydroxilation against the particular reactant was determined by the method of initial rates.

The effects of: fullerene concentration (within range 0.2 - 1.0 g/L), CTABr concentration under the conditions of changing CTABr concentration (range 0.08 - 0.25 g/L), H_20_2 concentration (range 0.25 - 0.8 g /L), NaOH (range 5 - 30 g /L) on the kinetics of fullerole formation were investigated under constant values of the other reaction parameters. Based on the experimentally determined kinetics curves of fullerol formation, it was concluded that: kinetics of fullerol formation under the different concentrations of fullerene, CTABr and H_20_2 is kinetically controlled reaction which can be described with the kinetics model of first order chemical reaction against to the particular reactant. The changes in concentration of fullerene, CTABr and H_20_2 don't have influence on the chemical composition of the final product - $C_{60}(OH)_{24}$. The kinetics of fullerol formation under different NaOH concentrations presents a reaction controlled with diffusion. The changes in NaOH concentration has effect on the chemical composition of the final product.

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Optimization of Graphene functionalization process for applications

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Control of the electronic structure of graphene is important for its application in new nanoelectronic devices, sensors or in energy conversion. Chemical functionalization represents an attractive way to achieve this task. However, for proper function of the modified graphene it is necessary to be able to carefully optimize the functionalization process. This can be a very challenging task if chemically exfoliated graphene is used. Here, I will briefly introduce possible strategy and tools for graphene modification enabling control of this process on model sample of CVD graphene and discuss how the obtained knowledge can be transferred to functionalization of chemically exfoliated samples.

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Thermoresponsive PS/PNIPAM blend films with switchable wettability and micromorphology

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Wettability is an important property of solid surfaces and it is governed by surface chemistry and topographic structure. There are several applications, that require control of the wettability, but much of the attention attract applications of smart materials, that have the ability to switch their wettability between hydrophilicity to hydrophobicity by an external stimulus, such as temperature. PNIPAM is a thermoresponsive polymer, which switches between hydrophilicity and hydrophobicity at 32°C[1]. Wettability is also affected by the surface topography and it can be enhanced, inducing roughness in the surface[2]. The combination of thermoresponsive polymer systems with switchable wettability and micro-patterned surfaces can develop carbon composites with advanced properties, suitable for novel applications and the development of smart materials.

We develop spin-casted films of blends of PNIPAM with PS (PS/PNIPAM) on laser-microstructured Si substrates, and we study their thermoresponsive wetting behavior. Silicon surfaces are microstructured via laser processing and spin-casted with PS/PNIPAM blend of two blend ratios. Also, films are casted onto flat and microstructured Si substrates with their native SiO_2 and without it in order to study the effect of microstructuring and the SiO_2 removal on the film wettability. The film morphology was characterized by SEM, their chemical homogeneity and wetting properties were characterized by EDS, Raman spectroscopy, and XPS techniques, and water contact angle measurements.

All films respond to the stimulus of temperature, but films casted on microstructured substrates show the highest thermoresponsivity,switching between hydrophilicity and hydrophobicity. Microstructuring provides large specific area that extend the contact of PNIPAM chains with water molecules, enhancing film thermoresponsivity. Although the absence of the native SiO_2 from silicon substrates results in films with higher water contact angles below and above 32°C, films casted on Si substrates with the native SiO_2 show higher thermoresponsivity than that casted on Si substrates without the native SiO_2. The presence of the native SiO_2 generates the PNIPAM arrangement in the upper layers of the film, enriching the interaction of PNIPAM chains with water molecules, and thus film thermoresponsivity. Developing microstructures with switchable wettability provides carbon composite systems suitable for novel applications such as self-cleaning surfaces, industrial surface coatings, tissue engineering, cell encapsulation, sensing, and microfluidics[3].

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Characterization of hydrogenated amorphous carbon thin films growth by ECR-MPCVD

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Abstract: Electron cyclotron microwave plasma chemical vapor deposition (ECR-MPCVD) was employed to growth hydrogenated amorphous carbon thin films (a-C:H) on glass and silicon substrates. High purity methane (CH_4) gas was used as a precursor. The effect growth parameters on the optical, electrical, structural and morphological properties were investigated. Amorphous carbon thin films reveal high optical transmittance in the near infrared and visible regions. The optical band gap energy (E_g) of the films increased with increasing processing pressure. Hall measurement was performed to determine the carrier type and resistivity. Amorphous carbon thin films exhibit p-type conductivity and electrical resistivity was in the order of 10^4-10^5 Ωcm. Three main peaks were observed at photoluminescence (PL) spectra at 405 nm (3.06 eV), 533 nm (2.32 eV) and 671 nm (1.84 eV). Fourier transforms infrared spectroscopy (FT-IR) and Raman spectroscopy measurements were used to obtain information about the bonding structures. Surface morphology and the roughness of the films were determined by atomic force microscopy (AFM) measurement.

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Towards Graphene- and Graphite-Supported Ullmann Catalysts

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Ullmann coupling is one of the earliest types of metal-mediated catalysis.[1] Common reactions include aryl C−C coupling from aryl iodides, usually over copper powder. This traditional route requires large catalyst loadings and is often difficult to remove form the reactant solution. A more modern approach is to use a Cu(I) or Cu(II) ion chelated into a multidentate ligand, reducing the amount of catalyst required. However, this can lead to difficulties in separating soluble Cu(ligand) species from solution.

We are investigating the use of a new potential catalyst, [Cu(**SB-1**)][2,3] (where **SB-1** = 4-hydroxybenzylsalicylidine) for use as a standard solution-phase catalyst and also as a heterogeneous graphene- or graphte-supported version. [Cu(**SB-1**)] is a highly planar molecule containing π-rings, making it a good candidate for strong π-π interactions with graphene and thus immobilising it on the substrate surface.

Multiple deposition routes have been attempted (precipitation through vapour soprtion; evaporation from pyridine solution and; mechanochemical embedding in graphite), resulting in different catalyst loadings and particle morphologies.

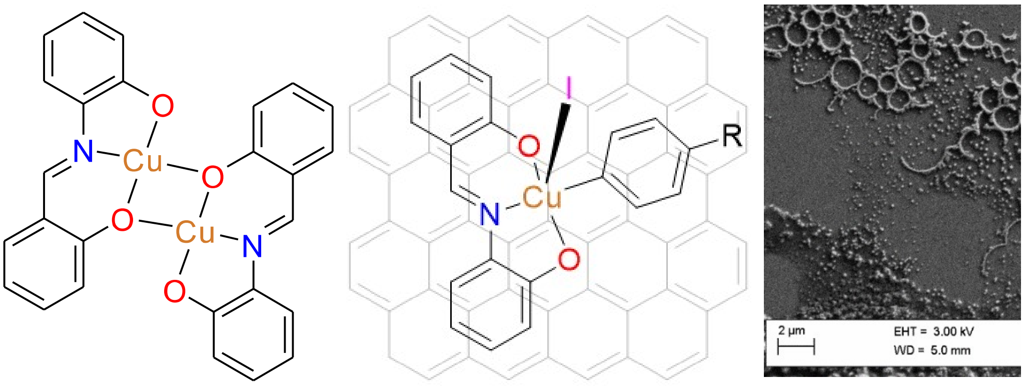

Figure 1: left: $[Cu(SB\text{-}1)]_2$ dimer; centre: proposed [Cu(**SB-1**)] monomer immobilised on graphene after oxidative addition across an aryl-I bond during Ullman coupling; right: [Cu(**SB-1**)] evaporated onto few-layer graphene from pyridine solution.

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Poly(3-hexylthiophene-2,5-diyl) Nanoparticles Immobilised on Graphene Oxide - A Spectroelectrochemical Study

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Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a regioregular semiconducting polymer. It has been thoroughly studied in bulk-heterojunction (BHJ) organic solar cells[1] and as a hole- transporting/electron-blocking material in hybrid organic photovoltaic (HOPV) devices.[2] Graphene oxide (GO) is obtained by an exfoliation of graphite down to atomic layers. The main difference between GO and pristine graphene lies in the number of defects and the presence of heteroatoms (such as oxygen) in the structure. However, these defects give the GO different properties in respect to pristine graphene, for instance GO can be dispersed in aqueous solutions and the heteroatoms can act as anchoring group for other molecules.[3]

In this work, we investigate a composite consisting of P3HT nanoparticles immobilized on GO flakes and we study the electrochemical behaviour of this system. The material exhibits a strong photoluminescence (PL) which is efficiently quenched by an application of relatively low positive potential of +300 mV. In negative mode, PL quenching requires higher potential of at least -1000 mV. Natural Raman signals of P3HT with a shift of around 1450 cm^{-1} are well observable after applying a weak positive potential, since at zero or negative potentials said signals are covered by the abovementioned strong PL. Potentials higher than ±1000 mV lead to an efficient suppression of the Raman signals. Additionally, electrochromic properties of the polymer have been observed. Originally red P3HT nanoparticles become colourless at relatively low positive potentials of +400 mV. This change is reversible and in the negative mode, the material keeps its red colour to up to -1000 mV. When voltages of ±1500 mV and higher are applied, the polymer undergoes unspecified irreversible changes and practically degrades, since the material loses both its PL and electrochromic properties and shows only weak Raman signals whose intensities do not respond to applied voltage anymore.

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A rare Mn(III) Low-Spin Compound Attached to Few-Layer Graphene

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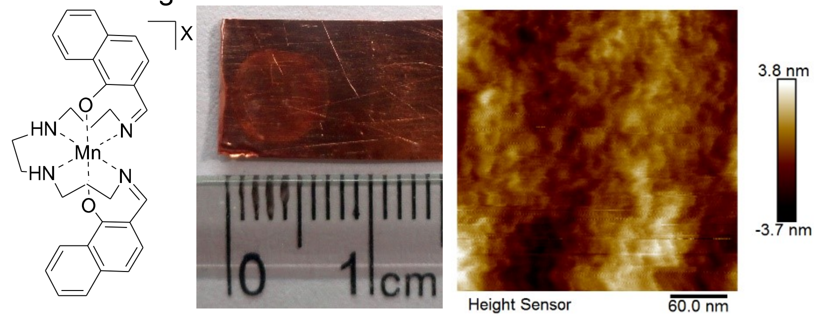
The phenomenon of spin crossover in metal complexes is known since the early 1930s,[1] and has attracted a lot of interest due to potential applications of these molecules for use as molecular switches in data storage and in displays.[2] The transition between a low spin state and a high spin state in an octahedral metal complex can be achieved by application of an external stimulus, like heat, light, pressure or applied magnetic field.[3]

We have synthesized coordination complexes based on Mn(III) and a Schiff base ligand with a conjugated π-system (see Figure) and have its magnetic behavior, showing the start of a spin transition. This compound was used in combination with Few-Layered Graphene (FLG) bulk, to investigate the bond behaviour towards graphene. The bulk material was afterwards characterized by IR spectroscopy, to proof that the metal containing complex is still intact. Additionally, graphene film (CVD graphene on Cu) was used to attach a thin layer of metal complexes on the surface. The used complex contains a bulky naphthaldehyde, which is supposed to form π–π bonds between the layer and the ligand around the metal centre which allowed the synthesis of new materials. The synthesized materials were analysed by Raman Spectroscopy, AFM and high-resolution SEM.



(a) (b) (c)

Figure 1. (a) Schematic structure of Mn(III) complex with X = BPh4 (1). (b) surface attachment of the complex on to graphene coated Copper. (c) AFM image of the surface, including the height.

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Investigations of dielectric and thermal properties of layered EVA composites with carbon and Fe_3O_4 nanoparticles

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Polymeric composites with electrically conductive fillers are widely used as materials which not only have the desired properties of polymers such as flexibility, lightness, resistance to fractures but can also be enhanced with high electrical or thermal conductance. Such materials are for example widely used as electromagnetic interference (EMI) shielding materials in the microwave frequency range. Compared to conventional filled composite that are single layer systems, specially designed multi- layered composites are rapidly gaining attention as a single layer absorber might not be efficient enough for use as an EMI shielding material. If layered structure modifications of a bulk material are performed, it is expected the transmittance will be lowered in microwave frequency owing to the repeated reflectance effect, independently of what kind particles are used. A gradient of filler concentration inside a single layer was also revealed to decrease transmission. Properties of layered composites with carbon nanotubes (CNT), graphitic nanoplates (GnP), Fe_30_4 nanoinclusions and hybrid composites with these nanoinclusions were investigated in wide frequency range (from 20 Hz to 2 THz). All investigated composites (except with single Fe_30_4 inclusions) are above percolation threshold. The strong enhancement of microwave and terahertz radiation absorption is observed in hybrid composites in comparison with composites with single inclusions. At low temperatures (below 200 K) the electrical conductivity of all hybrid composites follows the tunnelling law model and lowest potential barrier was estimated for composites with CNT inclusions. The best thermal properties are also observed for composites with CNT inclusions. This effect can be explained by strong synergy effects between different nanoparticles in hybrid composites. The network of CNT inclusions plays a bridge role for rapid transfer of electrons between various types of other nanoparticles.

Graphene composites with dental and biomedical applicability

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Pure graphene in the form of few-layer graphene (FLG) - 1 to 6 layers is biocompatible and non-cytotoxic. This makes FLG an ideal material to incorporate into dental polymers to increase their strength and durability. It is well known that graphene has high mechanical strength and has been shown to enhance the mechanical, physical and chemical properties of biomaterials. However, for commercial applicability, methods to produce larger than lab-scale quantities of defect-free graphene are required. Here, we present a simple method to make large quantities of FLG starting with commercially available multi-layer graphene (MLG). This FLG material was then used to fabricate graphene dental-polymer composites. The resultant graphene-modified composites show that low concentrations of graphene can lead to very significant performance improvement in physio-mechanical properties. Herein we report a new, cheap and simple method to make large quantities of defect-free few-layer graphene which was then incorporated into a common dental polymer to fabricate graphene-composites which shows very promising mechanical properties [1].

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In search of customized nanoarchitectures for increasing the efficacy of anti-tumor therapies

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Background Radiotherapy and the newly implemented photodynamic therapy (PDT) [1] are valuable therapeutic tools for fighting against cancer. They rely on massive and sudden generation of reactive oxygen species (ROS) which trigger oxidative stress and a profound disturbance of signaling networks. It is expected that oxidative stress will generate antioxidant responses in treated tumor cells, which may reduce therapy efficacy. Therefore, pharmacologic down-regulation of the transcription factor NRF2, which controls the expression of more than 250 cytoprotective genes, including antioxidant ones [1], might represent a valuable co-therapy to conventional anti-tumor therapies.

Aim To assess the molecular networks underlining the *in vitro* exposure of human colon adenocarcinoma cells to PDT and to identify the molecular signature of NRF2.

Experimental design Human colon carcinoma HT-29 cells were loaded with a porphyrinic photosensitizer and were subjected *in vitro* to PDT (10 J/cm2, considered mild PDT settings). The evolution of cell viability was monitored using the MTs assay in conjunction with the LDH release test. At various time points after PDT cells were harvested for RNA extraction. The gene expression profile was evaluated by pathway-focused PCR array addressing 84 genes that are critically involved in oxidative stress, hypoxia signaling, DNA damage and repair, osmotic stress, inflammatory response, as well as cell death by apoptosis, necrosis and autophagy.

Results Cell death in HT-29 cultures exposed *in vitro* to mild PDT settings started to occure at 6-7 hrs post-PDT and at 24 hrs almost ½ of cells were dead. Cells developed a strong antioxidant response mediated by the transcription factor NRF2, which sustained the survival of HT-29 tumor cells, along with several other cytoprotective mechanisms related to hypoxia responses.

Conclusion Pharmacologic down-regulation of NRF2 in cancer cells may increase the efficacy of anti-tumor therapies based on oxidative stress. Nevertheless, such therapies should be targeted towards tumor cells, considering that redox signaling has a key role in maintaining homeostasis in normal tissues. Therefore, our group is in high need of biocompatible nanostructures to be coated with tumor-targeting molecules and inhibitors of NRF2.

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Carbon nanostructure templates composites for phosphoproteomics

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Protein phosphorylation regulates numerous pathological processes, however, their characterization is challenging due to their low abundance and transient nature. Therefore, nanomaterials are being developed to address this demanding task [1]. In particular, carbon nanostructures are attracting interest as scaffolds for functional nanocomposites [2], yet only isolated studies exist on the topic of phosphoproteomics, and little is known on the effect of nanocarbon morphology on templating nanocomposites. However, their nanomorphology has shown to play a key role in the development of composites, hybrid, and biomaterials in general [3,4]. In this work, we compared oxidized carbon nanotubes, graphene oxide, oxidized carbon nanohorns and graphitized carbon black, as scaffolds for magnetized nanocomposites with titania and magnetite nanoparticles. The nanomaterials were extensively characterized with experimental and *in silico* techniques. Next, they were applied to phosphopeptide enrichment [5] from cancer cell lysates for NanoHPLC-MS/MS. Overall, new insights emerged for the understanding and the design of nanocomposites for phosphoproteomics, with selectivity as high as 90% and several-thousand identification hits.

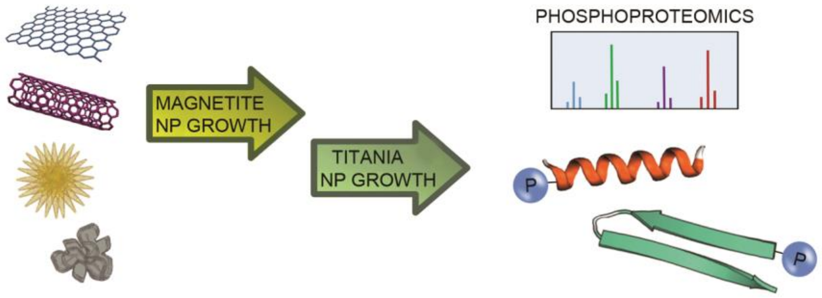

Figure 1. Carbon nanostructures are used as templates for the nucleation and growth of magnetite and titania nanoparticles to obtain composites applied in phosphoproteomics.

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Tribological properties of plasma sprayed alumina-graphite coatings

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Al_2O_3 and Al_2O_3-graphite coatings were formed at atmospheric pressure using air-hydrogen plasma. The influence of graphite concentration and spraying parameters on the tribological properties of coatings were investigated. Energy dispersive X-ray spectroscopy measurements revealed that the graphite fraction in the as-sprayed coatings was lower than in the initial feedstock powder. The X-ray diffraction investigations indicated that the increase in spraying power resulted in decreased concentration of alpha-Al_2O_3 phase in the composite coatings. Scanning electron microscopy and profilometry were used to determine the surface morphology and roughness of coatings. It was obtained that Al_2O_3 and Al_2O_3-graphite coatings demonstrated lamellar structure. Meanwhile the surface roughness varied in the range of 2-3 μm, depending on the graphite concentration in feedstock powders and spraying parameters. Friction coefficients and wear rates were investigated using ball-on-disk tribometer at dry sliding conditions. It was obtained that Al_2O_3-graphite coatings had up to 25 % lower friction coefficient values compared to the steel substrate. Al_2O_3-graphite coatings proved to be wear resistant under low loads (up to 4 N) as only plastic deformations were observed after the dry sliding tests.

Functionalisation of Plasma Exfoliated Graphite using Aryl Radicals

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Commercially produced multi-layer graphene (MLG) can be produced via plasma-processing of natural graphite, within a multi-electrode dielectric barrier discharge (DBD) plasma reactor. Such MLG often suffers from decreased reactivity as a result of the large stacks of graphene present, and thus, functionalisation becomes elusive.[1] As a result, reactive reagents are required to covalently attach moieties to the graphene surface. Traditionally, diazonium salts are heavily exploited as a method to functionalise graphene, due to their high reactivity, and ease to form radicals upon nitrogen cleavage.[2] Unfortunately, these compounds are notoriously dangerous, due to their explosive nature.[3] In fact, several historical incidents report explosions resulting from exploitation of diazonium salts. Subsequently, it may be argued that diazonium salts are un-attractive precursors for large-scale use within industry. As a result, access to such aromatic radicals through utilisation of alternate precursors is heavily desirable, to meet the demand for industrial production of functionalised graphitic material. Herein, aryl radicals are produced from alternate sources to diazonium salts, and their reaction with MLG is investigated. Various analytical techniques are applied to characterise the functionalised MLG, including XPS, Raman, SEM, TEM, EDX and XRD.

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The $MnFe_2O_4$ nanoparticles effect on dielectric properties of multiwall carbon nanotube based epoxy resin composites

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In present work, the dielectric properties of epoxy resin composites materials based on multiwall carbon nanotubes (MWCNT) and manganese ferrite ($MnFe_2O_4$) nanopowder were studied in order to detect any synergy effects.

The synergy effect means the percolation presence in hybrid composites (two or more filler types) at concentrations that do not lead to DC conductivity in the corresponding series of samples with a single filler [1].

Commercial Epikote 828 epoxy resin was used as a polymer matrix. The MWCNT grown by the CVD method [2] and commercially available manganese ferrite ($MnFe_2O_4$) nanopowder with 28 nm spherical particle size [3] were used as fillers. To prepare the composites the standard procedure for filler particles dispersing in a polymer matrix was used [4]. The hybrid MWCNT/$MnFe_2O_4$/epoxy resin composites under study had a fixed MWCNT volume concentration of 0.35%, while $MnFe_2O_4$ concentration varied: 0, 0.025, 0.05, 0.35, 0.65 vol.%. The selected fixed MWCNT concentration is just below the percolation threshold in order to reach the pre-percolation state inside the composite.

The complex dielectric permittivity of the samples was measured using an HP4284A LCR meter in the frequency range from 20 Hz to 1 MHz and in the temperature range from 30 to 500 K. For low-temperature measurements (30-300 K), the samples were placed in the closed-cycle cryostat. Measurements at high-temperature (300-500 K) were performed in a home-made furnace. Silver paste was used for contacting.

The frequency and temperature dependencies of dielectric permittivity and electrical conductivity are presented.

Results observed reveal that certain small amounts of $MnFe_2O_4$ particles improve the dielectric properties of MWCNT/epoxy resin composites in wide frequency range due to the better MWCNT dispersion inside polymer matrix.

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MULTI-WALLED CARBON NANOTUBES / POLYPYRROLE COMPOSITES WITH DIFFERENT SURFACTANTS

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In our work multi-walled carbon nanotubes/polypyrrole (MWCNT/PPy) counter electrodes (CE) were prepared in the presence of different surfactants. Electrochemical deposition of PPy layer onto the MWCNT decorated FTO glasses was performed. For the improvement of MWCNT dispersion and for improving the PPy morphology we have used different kind of surfactants. Surfactants play important role during MWCN suspension preparation and also during pyrrole polymerization.

These composites will be tested in promising hybrid solar cell technologies, in the dye-sensitized solar cells (DSSC). As alternatives to standard Pt counter electrode (CE) carbon-based materials modified with conducting polymers have been studied intensively. Catalytic activity of PPy/MWCNT layers prepared onto FTO glasses (FTO) were evaluated by CV and photovoltaic properties of DSSCs with PPy/MWCNT counter electrodes were characterized by I-V measurements. In the next step MWCNT/PPy electrode will be used in perovskite type of solar cells [1].

Acknowledgement. The work was supported by project COST CA15107 and project MVTS PLL.

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Clicked magnetite-graphene oxide nanocomposite as a new support for immobilization of catalyst

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Abstract

Graphene oxide (GO) is a single layer of graphite oxide with various reactive functional groups on its basal planes and edges, high and stable dispersibility in various solvents as well as high surface area which is an ideal support for the heterogenization of homogeneous catalysts [1,2]. GO/magnetite nanocomposites, due to their potential applications have attracted many attentions in many different research fields such as energy storage, water treatment and catalytic applications [3,4]. Employing magnetic nanoparticles to GO facilitates quick separation using an external magnet due to the isolation of GO from the reaction mixture with traditional methods like filtration and centrifugation is difficult. These nanocomposites show increased effective surface area and less aggregation of graphene oxide sheets. Thiol-ene click reaction as a new approach with mild reaction conditions, simplicity, absence of by-products as well as high efficiency has been employed for modification and functionalization of nanocomposites in recent years [5]. In this work, clicked graphene oxide/magnetite as support was synthesized via thiol-ene click reaction to immobilize peroxophosphotungstate (PW). The stepwise preparation of the GO/MNPs/PW catalyst is shown in Fig.1. This heterogeneous catalyst was investigated on the epoxidation of olefins in the presence of H_2O_2 as oxidant. The prepared heterogenous catalyst indicated high catalytic activity and can be easily reused by an external magnet from the liquid phase for the next run. With our recent development of a safe, cheap and scalable production method for GO we see this and similar catalysts as relevant candidates for industrial use.

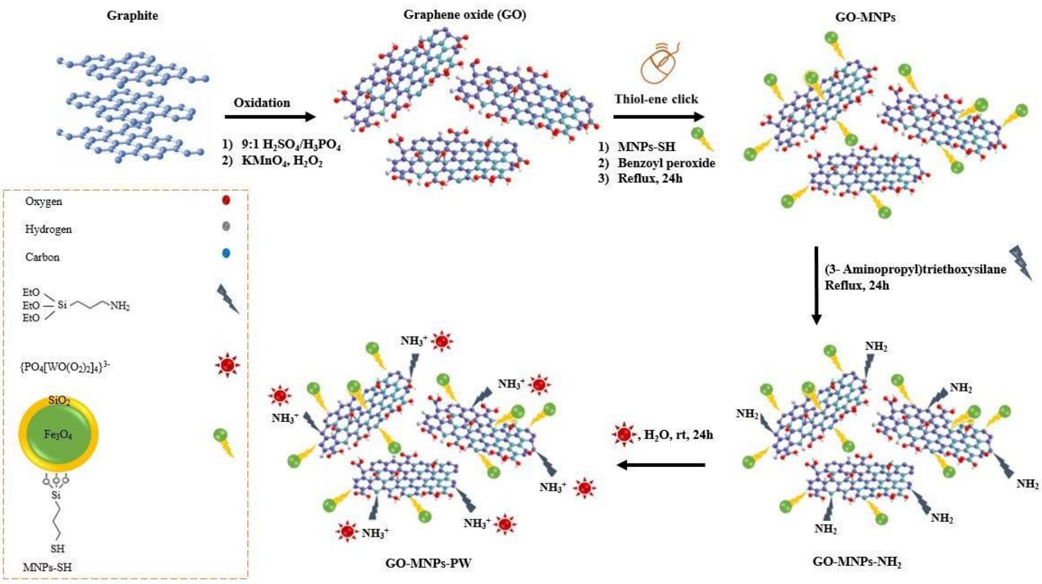

Figure 1. Preparation steps of the GO/MNPs/PW catalyst

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Development of nano-structured interphases in carbon-epoxy composites

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Carbon fiber reinforced polymers (CFRP's) for high performance applications demand the highest specific mechanical properties. Yet in practice, these properties do not reach their full potential. This is most prominent in the direction transverse to the fibers due to a lack of stress transfer between the matrix and the fibers. Stress transfer is related to the interphase as a constituent, the immediate and adjacent region of matrix to the fiber interface. The mechanical properties of the composite at the macro-scale are strongly dependent on the characteristics of the interphase at the nano-to-micro scale, which include the surface energies from a thermodynamic viewpoint, as well as chemical interactions and the dynamic/viscosity effects during processing.

Nano-structured interphases are developed to attain both strength and toughness, by applying nano-structured surface treatments to the carbon fibers before impregnation. Typical treatments include oxidation, plasma treatment, and introduction of carbon-related nanoparticles (graphene, graphene oxide) and nanotubes (CNT). Surface free energies (dispersive and polar components) of the fibers are evaluated using contact angle measurements of a droplet on a single fiber followed by a numerical solution for the Carol's equation.

CNTs were applied onto the fibers or fabric from a CNT/acetone dispersion at various concentrations, or deposited by pulsed laser deposition (PLD) on a cold finger stage (collaboration with CSSNT UPB Bucharest, Prof. M . Enachescu). HRSEM micrographs from PLD show even, well dispersed coating of segregated CNTs.

Microdroplet pull-out tests were performed with a custom made micro-vise jig. The droplet was cured on a single carbon filament in a three-step curing cycle from 80 to 160°C. The shear strength increases by either oxidation of the fibers or plasma treatment . Results will be shown.

A lot of effort was spent to develop fragmentation tests of carbon/epoxy single filaments. Preliminary results will be presented.

Latest AFM results indicate that response is correlative to elastic moduli and interphase width. Surface treated fibers show a different modulus gradient, which may turn beneficial and mitigate stress concentration.

Composites of Carbon Nanotubes with Cages and Metallopolymers

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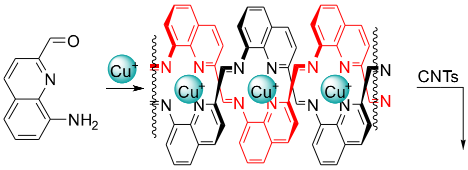
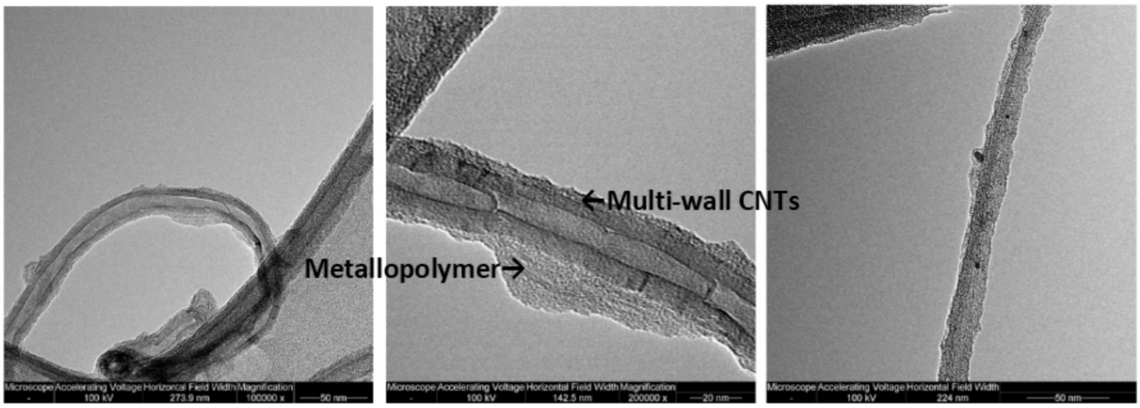
Carbon nanotubes (CNTs) have unique physicochemical properties that make them highly attractive for a number of applications, especially for energy, catalysis, and the preparation of conductive materials. However, a key issue of CNTs is their poor dispersibility in polar solvents, which is typically addressed by means of chemical modification, typically at the expense of their electronic properties. This step is crucial to achieve an intimate interface with other chemical components in order to create synergy between the two.[1] In particular, the combination of nanostructured metal-containing architectures and CNTs has mainly focussed, thus far, on metal oxides, and has shown great improvement in catalytic performance when an interface between CNTs and the metal is achieved, and aggregates of either species are avoided.[2]

This work explores the interaction between supramolecular metal-organic architectures[3-5] and pristine CNTs (shown below) and demonstrates that homogeneous dispersions are obtained for both multi-wall and single-wall CNTs, in appropriate solvents dictated by the metal-organic architecture solubility, including water. Unique properties of such architectures range from luminescence to molecular transport across solvents. We envisage that such fine control over molecular organization and its intimate interaction with CNTs can be exploited to achieve materials with new and improved properties, and opens new avenues in areas spanning from catalysis to electroactive materials.





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Zinc phthalocyanine films for chemical gas sensors prepared by pulsed laser deposition

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Phthalocyanines are promising candidates for several optoelectronic devices, small molecular organic solar cells or chemiresistive gas sensors. Optical properties and electrical conductivity of phthalocyanine films are significantly influenced by redox reactions induced by particular gases in atmosphere (O_2, NO_x, ...). Structural and microstructural properties as well as morphology play important role in tuning gas sensor properties. Phthalocyanine thin films are most commonly fabricated by vacuum evaporation technique. Pulsed Laser Deposition (PLD) is well known as a versatile PVD technique to deposition of nanostructured thin films of inorganic materials. PLD was also shown as successful in fabrication of some kind of organic thin films.

Zinc Phthalocyanine (ZnPc) thin films were fabricated by PLD in vacuum on fused silica substrates at room temperature. PLD used a KrF laser (λ=248 nm, τ=5 ns), where laser fluence was varied in the region from 10 mJ.cm^{-2} to 100 mJ.cm^{-2} and frequency in the interval from 50 Hz to 200 Hz. The growth of the thin films was in-situ monitored using transmission measurement in the UV-VIS spectral range.

Optical properties were characterized by optical spectroscopy, spectrophotometric measurement and spectral ellipsometry. The electrical properties were analyzed by van der Pauw method. Morphology was studied by AFM and SEM. FTIR was used to examine deterioration of the deposited ZnPc films.

The optical properties suggested the growth of the film in β-phase. We show that PLD could produce ZnPc thin films of competing quality with respect to evaporation technique. Moreover PLD profits from its simplicity, modesty and flexibility that could provide also important results toward development of functional materials and devices for chemical gas sensors or organics electronics.

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Biocomposites of chitosan and reduced graphene oxide-magnetite particles for magnetic hyperthermia treatment of melanoma

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Magnetic hyperthermia is a promising cancer therapy. Typically, magnetic nanoparticles vectorized to the tumor area generate heat when exposed to an alternating magnetic field. The heat induces a temperature increase up to 40-45 °C and promotes cancer cells death without damage of normal cells.[1] However, this approach is challenged by the difficulty in constrain the area of heat delivery and potential nanoparticle agglomeration, which may produce hot spots that can be harmful to healthy cells.[2] The development of magnetic composites can stabilize the nanoparticles and allow an easy manipulation of the bulk material, since it can be implanteddirectly on the tumour location or be used topically. Herein, bionanocomposites were prepared using chitosan biopolymer as matrix and reduced graphene oxide-magnetite nanoparticles as fillers[3] A good dispersion of fillers throughout the matrix was observed, with a consequent homogeneous electrical and magnetic response. The cell viability evaluated through the 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyltetrazolium bromide (MTT) assay showed no toxicity of bionanocomposites to both human melanoma cells (MNT-1 cell line) and to the nontumorigenic human keratinocyte cells (HaCat cell line). The magnetic hyperthermia response of bulk materials and its effect on MNT-1 cells viability were studied. The flexibility, non-toxicity and hyperthermia performance of these bionanocomposites are highly desired features to allow the magnetic hyperthermia cancer therapy. Moreover, the electrical conductivity conferred by reduced graphene oxide can be used to develop an associated electrical controlled drug delivery system.

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Preparation of Gas Sensors Based on Conductive Polymers in Combination with Nanofibrous Structures – part 1

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Conductive polymers are polymeric compounds that can behave as conductors due to the presence of conjugated double bonds. By using suitable dopants, their conductivity can be varied within a wide range. Such activated conductive polymers can significantly change their conductivity even when exposed to toxic vapors or gases and can therefore be used as a detection layer of gas sensors. The overview of basic types of conductive polymers is presented. Furthermore, their conductivity is compared, principle of function of gas sensors with conductive polymer detection layer and methods of their doping are described. Various types of platform gas sensor platforms suitable for the application of a conductive polymer detection layer have been prepared and examples of their response when exposed to a toxic gas phase are given.

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Preparation of Gas Sensors Based on Conductive Polymers in Combination with Nanofibrous Structures – part 2

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Conductive polymers are polymeric compounds that can behave as conductors due to the presence of conjugated double bonds. By using suitable dopants, their conductivity can be varied within a wide range. Such activated conductive polymers can significantly change their conductivity even when exposed to toxic vapors or gases and can therefore be used as a detection layer of gas sensors. Basic methods of preparation of conductive polymers from monomers are described and their morphology and microstructure are characterized. Possibilities of application of conductive polymers to comb platforms in combination with a suitable substrate and nanofibrous structures are presented. The results of sensory experiments show that gas CP based nanofibers show a much higher sensitivity and faster response to target gases than flat film-based sensors. Reversibility and low selectivity are general features of CP sensors.

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Preparation of Gas Sensors Based on Conductive Polymers in Combination with Nanofibrous Structures – part 3

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Conductive polymers are polymeric compounds that can behave as conductors due to the presence of conjugated double bonds. By using suitable dopants, their conductivity can be varied within a wide range. Such activated conductive polymers can significantly change their conductivity even when exposed to toxic vapors or gases and can therefore be used as a detection layer of gas sensors. The conductive polymer detection layer can also be applied to other types of gas sensors. A SORPTEST device with a QCM resonant sensor is currently available to monitor the response of the conductive polymer detection layer based on the QCM sensor frequency change. A similar device with a resonant SAW sensor is being prepared. Examples of application of these sensors for some toxic gases and vapors are given and the principle of their function is described.

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Structuring your Leap from Lab work to Entrepreneurship

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The possibilities for transition of innovative "products" from the level of lab work to an entrepreneurial level has never been so pronounced as in the past 20 years. In this period, our identification of innovative ideas and successfully coupling them to transformational aspects of our business processes has made it possible for better health care services, effective educational tools, improved transportation, greater social networking, efficient use of materials, the development of early warning systems in weather monitoring and a lot more, to be at our disposal. Whilst such life changing achievements emanate often from diligent research work, their adoption at the commercial level come with a lot of constraints which leave researchers discouraged to make the effort needed to venture into the entrepreneurialspace.

At the European level, there are lots of possibilities and programs set-up to assist researchers raise intellectual properties and to engage societies with their findings. These programs do indeed foster commercialization of research findings but the quota of success is still meager largely because the motivation for entrepreneurial risk-taking is insufficient

Most researchers do not have the capacity to raise venture capital. On average it requires at least €1 Million of seed capital to reasonably prepare a proven lab success for the marketplace . Insufficient funding can easily starve a proven lab success to business-death within the first business year. In fact there is data showing that about 80% of start-up companies suffer terminal defeat by marketplace challenges within the first
2 years of business hence are forced toclose-down.

In this presentation, I will give a personal account of my journey from Lab work to Entrepreneurship, especially highlighting the role of "grit"; the ability to exhibit perseverance and passion over a long time, and the role of so-called "growth-mindset". These attributes together with access to a network that supports talent accumulation and market visibility are key.

In vivo investigations on the pulmonary toxicity of inhaled graphene-based nanoplatelets

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Graphene-based nanomaterials (GBNs) hold excellent physicochemical properties that confer them numerous applications[1-3]. Nonetheless, GFNs potentially widespread use is raising considerable concerns about their toxic potential towards the environment and human health. This is particular relevant in a scenario of occupational and environmental exposures where pulmonary toxicity may occur[4]. On the scope of the FP7-ERA-NET SIINN project PLATOX we aimed to screen *in vitro* the toxicity of selected GBNs and to validate *the vitro* results by performing a 28-day *in vivo* inhalation toxicity study. In the present study part, we performed an *in vivo* based study, in which we investigated the pulmonary toxicity of single layered graphene (SLG), graphene nanoplatelets (GNPs) and carbon black (CB). Wistar rats were exposed by nose-only inhalation for 4 weeks to different concentrations of GFNs and sacrificed after 3 and 28 days of recovery. Bronchoalveolar lavage fluid (BALF) cells were collected and cell cycle dynamics profile was analysed. Furthermore, Nuclear Magnetic Resonance (NMR) metabolomics was applied to disclose pulmonary metabolic variations. The results showed that all materials induced alterations in the cell cycle of BALF cells. SLG and CB induced an increase in the sub G0/G1 subpopulation, which may indicate DNA damage. Furthermore, SLG induced a dose dependent decrease in the percentage of cells at G0/G1 and an increase in the percentage of cells in S-phase, which was mostly maintained after the 28-days recovery period. On the other hand, GNP exposure did not induced changes in the cell cycle dynamics of BALF cells. NMR metabolomics of intact lung tissues revealed that both SLG, GNP and CB exposures induced alterations to the normal metabolic profile of the rat lungs, mostly related to antioxidant pathways.

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Construction of SORPTEST Device for Testing Resistance of Porous and Non-porous Barrier Materials against Permeation of Volatile Toxic Compounds – part 1

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The mobile device SORPTEST designated for testing resistivity of porous and non-porous barrier materials used in anti-gas protection against the permeation of volatile toxic compound in static and dynamic conditions has been developed. The rate of permeation in continually observed with the help of high sensitive QCM sensor with a polymeric detection layer. This one is inbuilt in a heated PVDF permeation cell of a new construction. A modular form of SORPTEST device enables a simple change of a character of tested samples (porous, non-porous) and even conditions of measurement. Used software equipment enables observation and evaluation of achieved permeation data in the real time (on-line). Setting and duration of the permeation measurement are automatically displayed and controlled with the help of a computer with original software equipment. After entering tested materials into 3 permeation cells and setting of needed parameters the calibration, resetting and even measurement including processing of permeation data run automatically. Permeation data is immediately available after measurement finishing in the form of the protocol from measurement. As the carrier gases the air (mini pump) or nitrogen (pressure cylinder) are used within measurement in dynamic conditions. This devise has been developed in cooperation with GRYF HB, limited company which is also its producer. Both the permeation cell construction and the permeation device construction are protected as an industrial design. The principle of permeation of gases and vapors by various types of barrier materials, theoretical course of permeation and design of used permeation cells are presented. Individual parts of the SORPTEST device, principle of QCM sensor function, wiring diagram and realization of permeation cells of own construction is described. A method for adjusting the concentration of a test chemical, a method of calibration, and an example of a sorption and desorption curve for a real test chemical within permeation through a porous barrier material are described.

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Construction of SORPTEST Device for Testing Resistance of Porous and Non-porous Barrier Materials against Permeation of Volatile Toxic Compounds – part 2

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The mobile device SORPTEST designated for testing resistivity of porous and non-porous barrier materials used in anti-gas protection against the permeation of volatile toxic compound in static and dynamic conditions has been developed. The rate of permeation in continually observed with the help of high sensitive QCM sensor with a polymeric detection layer. This one is inbuilt in a heated PVDF permeation cell of a new construction. A modular form of SORPTEST device enables a simple change of a character of tested samples (porous, non-porous) and even conditions of measurement. Used software equipment enables observation and evaluation of achieved permeation data in the real time (on-line). Setting and duration of the permeation measurement are automatically displayed and controlled with the help of a computer with original software equipment. After entering tested materials into 3 permeation cells and setting of needed parameters the calibration, resetting and even measurement including processing of permeation data run automatically. Permeation data is immediately available after measurement finishing in the form of the protocol from measurement. As the carrier gases the air (mini pump) or nitrogen (pressure cylinder) are used within measurement in dynamic conditions. This devise has been developed in cooperation with GRYF HB, limited company which is also its producer. Both the permeation cell construction and the permeation device construction are protected as an industrial design. A complete set of SORPTEST equipment is presented as well as an overview of barrier materials for protective equipment that can be tested on this equipment for protective properties. The course of permeation is monitored using the original software and some of the steps necessary for setting the measurement conditions are shown. There is also a shortened version of the automatically generated measurement protocol and an example of permeation data processing in Excel and a model of the permeation curve.

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Fullerene/Phthalocyanine Composites for Gas Sensing

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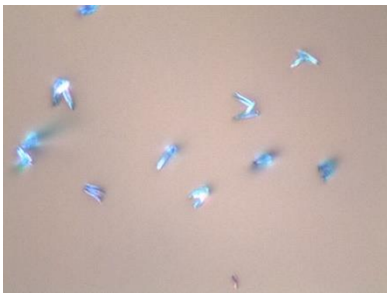
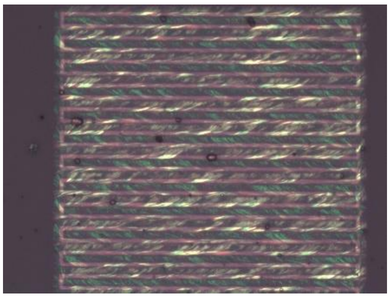
Nanocomposite organic semiconductor/fullerene thin films are used with success in the field of solar cells technology as a bulk heterojunction film structures[1]. We propose this kind of thin films as an active layer for chemiresistive gas sensors with a great potential. Analogically to solar cells we use (i) phthalocyanines (zinc, copper, etc.), which exhibit with detection abilities of nitrogen oxides (NO_x) and VOCs[2] and (ii) fullerenes (C_{60} and C_{70}). In our case fullerenes play the role of dopant. Nanocarbons (fullerenes, CNTs) are known to be useful in an inorganic nanocomposite sensor films for enhancement of selectivity and sensitivity of basic oxide materials[3].

In our case we have prepared nanocomposite films and microcrystals by a unique technique of Continous-Wave Laser Induced Forward Transfer (CW-LIFT) from source multilayers of phthalocyanine and fullerenes with sacrificial layer of sputtered gold. We used continuous wave laser (wavelength of 405 nm), laser spot had a spatial resolution of less than 5 µm. Source thin films were deposited by an organic molecular evaporation in high vacuum with base pressure of 10^{-5} Pa. Portion of fullerene was up to 50% of volume. Laser processed films were deposited to Si(100) and fused silica substrates for characterization of morphology by AFM and SEM. Investigation of sensing properties was done by using fused silica sensor substrates with 4 pairs of interdigitated gold electrodes with area of 10^{-4} cm^2. Sensing abilities were studied as DC-responses for basic gas analytes (NO_2, hydrocarbons, alcohol vapours, etc.).





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Pd_{NPs} / graphene and Pd_{NPs} / MoS_2 ensembles for the electrocatalysis of molecular oxygen reduction reaction

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Boosting the oxygen reduction sluggish kinetics is a decisive step for improving the efficiency of environmental friendly energy conversion devices, including fuel cells. Graphene (G), due to its outstanding conductive network, high specific surface area and excellent chemical stability, is widely considered as a unique substrate for the immobilization of metal nanoparticles (MNPs), aiming at the construction of highly efficient hybrid electrocatalysts. In this frame, graphene-related 2D nanostructures, such as layered transition metal dichalcogenides have similarly generated significant research interest as they can effectively adsorb MNPs, due to their high surface area and the plethora of d electrons, leading to hybrids with remarkable high electrocatalytic performance. Moreover, they present inherent electrocatalytic activities attributed to the exposed prismatic edges that are active towards oxygen reduction and/or hydrogen evolution reaction.[1-3]

Herein[4], the ORR electrocatalytic behavior of the hybrid material based on Pd nanoparticles and covalently modified MoS_2 sheets (Pd_{NPs}/f-MoS_2) was critically compared with that of graphene-based one (Pd_{NPs}/f-G). Electrochemical studies unveiled an enhanced performance for the Pd_{NPs}/f-MoS_2 hybrid, suggesting the use of transition metal dichalcogenide nanosheets as alternative platforms for the construction of innovative hybrid electrocatalysts. Overall, these results pave the way for the design of platinum-free and high-performance electrocatalysts toward energy conversion applications, including fuel cells.

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Soft dielectric materials for sensing and energy harvesting applications

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High permittivity and efficient electromechanical coupling are critical to perform energy storage or conversion between mechanical and electrical energy for various applications of electrostrictive polymers. We report a giant electrostriction effect in liquid crystalline graphene doped elastomers. The materials are formulated by graphene oxide functionalization, and by a phase transfer method which allows the solubilization of graphene oxide monolayers in non-polar solvents. It is shown in particular that a liquid crystal transition leads to an increased percolation threshold. Because of their unique liquid crystal structure, the resultant composites show a giant electrostriction coefficient (M~10^{-14} m^2/V^2 at 0.1 Hz) coupled with good reproducibility during cycles at high deformation rates. This work offers a promising pathway to design novel high performance soft dielectric materials for sensing or energy harvesting applications. We will also discuss recent developments concerning dielectric foams and multilayers systems that allow ultra-low pressure sensing via piezo-capacitive effects.

Analytical modeling of experimental EELS data for free-standing graphene

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We present an analytical modeling of the experimental electron energy loss (EEL) spectroscopy data for free-standing graphene obtained by scanning transmission electron microscope using a two-dimensional, two-fluid extended hydrodynamic (eHD) model and an *ab initio* method [1]. An analytical expression for the probability density for energy loss of fast electrons traversing graphene under normal incidence is derived in the long wavelength limit in terms of an arbitrary form of the conductivity of graphene given in the local, i.e., frequency-dependent form. The calculated probability density from both theoretical models is directly compared with the EEL spectra from three independent experiments [2-4] and we find very good agreement, especially in the case of the eHD model. Furthermore, we point out that the method of subtraction of the zero-loss peak from the experimental EEL spectra may strongly affect agreement with analytical models.

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Synthesis of silicone biobased conductive materials

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Abstract

Conductive silicone elastomeric materials with tailored properties are under development recent years. Unique mechanical properties in combination with conductivity made silicone materials interesting for a broad range of application. This paper reports the preparation of elastomeric conductive materials, based on polydimetilslixane/multi-walled carbon nanotube (MWCNT). For this purpose MWCNT were surface-modified by hydrochloric acid. MWCNT with different contents (0,5; 1; and 5 wt%) were loaded to study its influence on the properties of silicone elastomers. FTIR analysis confirmed the structure of obtained samples and absence of the chemical interaction between polymer matrix and MWCNT nanofiller. DSC analysis shows that a MWCNT had a significant influence on the thermal properties of obtained nanocomposites, raising the Tm values. Thermo-gravimetric analysis estimated that degradation onset temperature of composites with chemically modified MWCNT was much higher than degradation temperature of pure silicone. Conductivity of obtained hybrid materials increases with increased of MWCNT nanofiller contents.

Keywords: silicone elastomer; conductive polymers; thermal properties; MWCNT.

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Sustainable and renewable carbonaceous materials

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Exploring new materials, including carbonaceous electrocatalysts with enhanced catalytic activity towards oxygen reduction reaction (ORR) is a prerequisite for the sustainable commercialization of fuel cell devices [1-4].

In our studies, N-doping (~3%mas.) has been successfully introduced into carbon structure in order to receive a metal-free catalyst. Our results confirm that the type of nitrogen group (pyridinic or graphitic) and the surface roughness strongly influence the ORR activity. Further, these materials exhibit efficient electrocatalytic activity (the onset potential of 0.76V vs. RHE) for oxygen reduction reaction (ORR) in alkaline media.

Using the similar protocol the amino-functionalized, luminescent carbon nanodots (CNDs) have been synthesized from chitosan via simple and green hydrothermal carbonization. After the preparation of liquid phase - CNDs various techniques including XPS, FTIR fluorescence, atomic force microscopy (AFM) and transmission electron microscopy (TEM) have been used to characterize carbon nanodots. These functionalized carbon nanodots that consist carbon core and various surface groups were used to modify the commercial membrane to check their anti-biofouling properties. Experimental data proved that amino-rich CNDs can inhibit the growth of two Gram-negative bacterial colonies.

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Graphene Oxide/ PEDOT Nanofibers and Nanocomposites

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In this work, conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) was synthesized in the presence of graphene oxide (GO) and reduced graphene oxide (rGO) via in- microemulsion polymerization process to obtain GO-PEDOT and rGO-PEDOT nanocomposites. Nanofibers of PEDOT, GO-PEDOT, rGO-PEDOT and GO on poly(acrylonitrile-co-styrene) (P(AN-co-St)) matrice have also been fabricated due to their high potential in using as electrodes for flexible supercapacitors.
SEM and AFM results indicated that nanofibers have beadless structure with a diameter range less than 300 nm. The electrochemical capacitive properties of the nanofibers were determined by electrochemical impedance spectroscopy(Fig.1).
The electrochemical impedance measurements reveal that GO enhance capacitive behavior of P(AN-co-St) nanofiber more than rGO and both GO and rGO improve electrochemical performance of the nanofibers.
High surface to volume ratio and as a result of high charge storage capacity allows to use this system as a potential electrode for further implantable electronic devices[1-3].

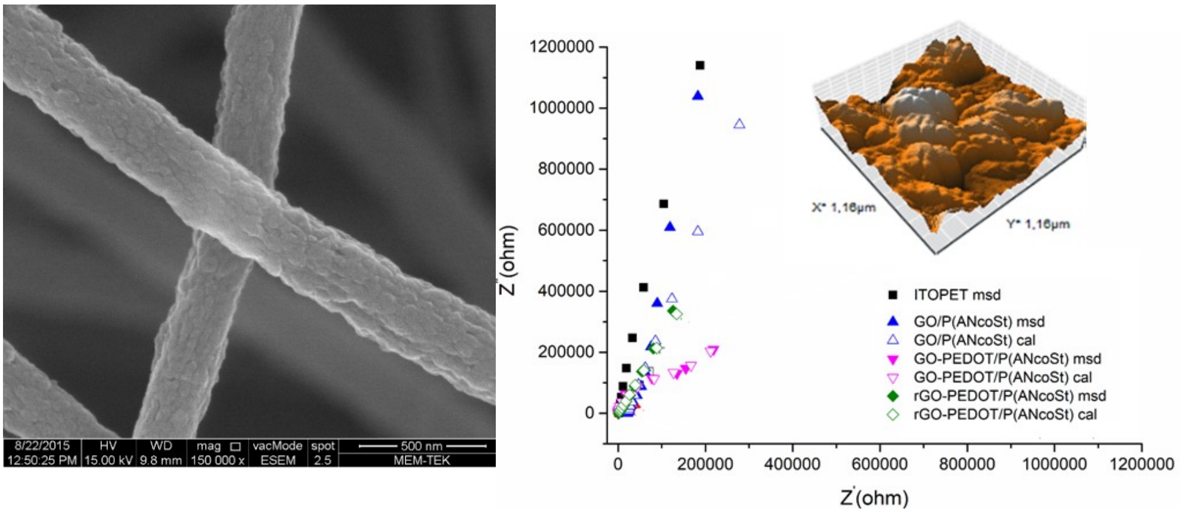

Fig 1.GO PEDOT P(AN-co-Sty] composite nanofiber and Nyquist Plots of bare ITOPET and different nanofibers composites (inset GO/PEDOT composite before electrospinning)

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Crysrtalline Nano Cellulose (CNC) and Carbon Nanotubes (CNT) based composites films and coatings

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ABSTRACT

Crysrtalline Nano Cellulose (CNCs) and commercial multi-walled carbon nanotubes (CNTs) are used to prepare CNC-CNT films at various CNT weight ratio via an aqueous suspension casting method. with the purpose of studying potential synergistic effects between the CNTs and the CNCs in hybrid nanoparticle networks. CNCs is one of the most exciting new bio materials recently available in commercial scale. Nano Cellulose can be produced from cell walls of trees, plants and waste effluent such as that of paper mills and municipal sewage system sludge. In its almost-pure form, CNC has a tiny crystalline molecular structure with 100-400 nm length and 5-10 nm width and is as strong as Kevlar (150-200Gpa). This substance has intriguing properties and many potential applications. CNC may be present as liquid crystal solution in water or organic solvents (in its surface modified form) and self-assemble to macro scale highly transparent ordered films having a thickness at the nano-scale and layered structure that can pack active ingredients and nano particals (NPs). CNCs suspension is known to have exceptional ability to form highly stable aqueous dispersions of NPs. depending on the formulation, the film may be hydrophilic or hyrophobic, a gass barrier or transparent.

The MWCNTs are well dispersed and homogeneously distributed in CNCs aqueous suspension, the nanotubes are densely packed in each multilayer, forming a random network.

The CNCs aqueous suspensions even at very low concentrations help to disperse and stabilize the CN Ts. The hybrid films show superior tensile and promising electrical properties by comparison with the CNC film. CNT enhanced CNC films prepared with micro-size CNT aggregates in the absence of surfactant exhibit improved tensile properties by comparison with the CNC films A maximum in tensile properties is obtained at a CNT concentration of around 1-2 wt.% with 4 GPa modulus and 130 MPa strength. Moreover, the hybrid films are more ductile than the CNC film, resulting in improved tensile toughness. The surface electrical resistivity for the hybrid films can be tuned within a range from 25 to 1000 O/sq by manipulating the CNT weight fraction.

The obtained films can be employed for the design of transparent and biocompatible carbon nanostructured based electrodes or as transparent conductive and gas barrier coating for smart food packaging and more, future research should combine disciplines from different fields of biology, materials engineering and polymers engineering in order to further improve and adjust the mechanical properties of such composites according to the required applications in the biomedical fields as well as other industrial fields such as sports, automotive, construction and more as bio-based replacement for synthetic materials.

Substrates Rubbed Two-Dimensional Material Nanostripes for Advanced Device Fabrication

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2D atomic material unique nanostripes and sheets are obtained by substrates rubbing technology suggested by us [1, 2]. This technology for mass production of high quality and large-size mono- and few layer 2D materials has advantages over the similar technologies:

- simple (one step), can be obtained even by hand, without using complicated nanotechnology equipment, hazardous toxic chemicals and high temperatures,
- short-lasting (lasts a few tens of seconds),
- cost-efficient (a few times, as no complicated nanotechnology equipment, hazardous toxic chemicals and high temperatures needed),
- highly productive (production yield is almost 100 % after optimization and production rate is a few g/h or a few tens of tons/year as the rubbing process is extremely fast),
- ecologically clean (no contamination, chemicals, surface doping, contact with any other material),
- universal and unique (any 2D material can be obtained by rubbing technology).

The substrates rubbed nanostripes are mono-, few- and multiple atomic layers of exfoliated flakes organized in self-assembled narrow bands of nano-sized quantum dots, which are reported for the first time. The nanostripes consist of arrays of quantum dots, while sheets consist of nanostripes, and 2D atomic devices consist of sheets with nanostripes. 2D material nanostripes are obtained by rubbing both graphite or other layered bulk materials and carbon nanotubes and hydrogenated fullerene (opening them) on dielectric, semiconducting and metallic substrates at atmospheric pressure conditions. The size, shape and density-controlled nanostripes, embedded in different devices as well as other factors greatly affect the device (solar cells, etc.) performance.

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Hydrocarbon plasma polymer particles for versatile oil/water separation

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Modification of porous non-woven viscose fabric and carbon cloth membranes was performed by utilizing the sequential deposition of plasma polymerized hexane particles and thin films of plasma polymerized hexamethyldisiloxane (HMDSO). The method resulted in the independent control of the surface roughness and the chemical composition of the functional nanocomposite coatings. As a consequence, membranes with a wide range of wettability were produced. Super-hydrophobic membranes were utilized for the selective absorption of non-polar organic solvents from water. Super-amphiphilic membranes were used for the gravity-driven separation of water from light oil as well as for the separation of heavy oil from water. The separation efficiency above 99.99% and 99.97% was achieved for the water-removing and oil-removing regimes.

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Nanoscale biosensor for VOCs detection

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Nanoscale sensing elements offer promise for single-molecule detection in physically or biologically constrained environments. Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Their advantage compared to other nanomaterials is due to a unique combination of electrical, optical, mechanical and chemical properties which are valuable for a wide range of applications, including biosensing [1]. CNTs have a large surface area and tunable near-infrared emission that responds to changes in the local environment while remaining stable to permanent photo-bleaching. Single-walled carbon nanotubes emit near-infrared (NIR) bandgap photoluminescence (PL), which is highly responsive to its physical and chemical environment [2]. SWCNT are unique among nanoscale sensor platforms in their ability to detect the adsorption of a single molecule [3]. Non-covalently bound polymers could be used to achieve specificity to the certain analyte that upon binding to the polymer will change the properties of the nanotube-polymer, resulting in a change in the PL of SWCNTs. We aim towards the development of novel SWCNT biosensor standoff detection technology platform to identify volatile organic compounds. It made of peptide encapsulated SWCNTs [3], able to bind and react differently to specific volatile molecules.
We successfully developed a sensor that could distinguish between pyridine, butyl acetate, ethyl acetate, and ethanol.

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Photoactive nanoarchitectures based on heterofullerene $C_{59}N$ carrying a pentafluorophenylquinoline derivative.

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Azafullerene $C_{59}N$ is the most explored heterofullerene[1] participating in light harvesting nanoarchitectures.[2] Starting from the parent azafullerene dimer $(C_{59}N)_2$ a series of monoadducts can be synthesized via the $C_{59}N^+$ intermediate.[3] In this respect, a series of $C_{59}N$-dyads have been prepared by the covalent incorporation of planar and parabolic arenes, ferrocene, phthalocyanine, corole, perylene and oligophenylenevinylene derivatives on the $C_{59}N$ cage. Apart from the monoadducts, $C_{59}N$ has also a rich chemistry towards multi-addition patterns and we recently proposed a tether-directed approach for the synthesis of highly regioselective bis-adducts.[4]

In contrast to chemical functionalization, the supramolecular chemistry of $C_{59}N$ is poor and mostly focused on $C_{59}N$ derivatives carrying monodentate nitrogen ligands for coordination to the metal center of light harvesting molecules likewise phthalocyanines and porphyrins. Recent advances on the chemistry of carbon nanobelts empowered supramolecular assemblies driven by the molecular recognition of the $C_{59}N$ cage by [10]-cycloparaphenylene nanohoops through π-π interactions at the concave-convex interface.[5,6]

In this work, we explore two photoactive nanoarchitectures based on a $C_{59}N$ cage carrying a pentafluorophenylquinoline derivative (FQ). Pentafluorophenyl-quinolines have been proposed as candidates improving the energy level matching between organic polymer donors and electron acceptors in solar cell devices. In general, quinoline derivatives are versatile building blocks since: (a) they are capable to form dimer complexes via axial coordination to metal centers and (b) the protonation of their N-atom enables their implementation to supramolecular architectures based on electrostatic interactions. Such $C_{59}N$-based nanoarchitectures are yet unexplored. Collectively, coordination and protonation revealed strong electronic interactions in the ground and excited states of the examined supramolecular nanoarchitectures.

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Synthesis of acrylate based hybrid nanocomposite

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ABSTRACT

In order to design binders for use in printed electronics, polyacrylate were synthesized by emulsion polymerization of methyl methacrylate and 2-ethylhexyl acrylate with the initiator concentration ranged from 0.1-0.5%, and in the temperature range of 55-75 °C. These emulsions gave films that are uniform in structure, resistant to water, and act as a suitable binder for conductive films. In order to obtain conductive films, zinc oxide nanoparticles and carbon nanotubes were used as filler. The nanoparticle concentration ranged from 0.5% to 2% by weight of the polymer. In our work we used two principles of preparation of conducive emulsions for application in printed electronics: the addition of nano fillers to already prepared emulsions and in situ modification of emulsions with nano fillers during synthesis. FTIR spectroscopy was used to confirm the structure of obtained acrylate films. The influence of the concentration of nano fillers on the thermal properties and conductivity of obtained acrylate base films were investigated. Conductivity measurements confirmed that addition of the fillers increasing conductivity of emulsion, which made it suitable for using as binder in printing electronics. Thermal properties were increased with the addition of nano fillers, while higher increasing was observed for the acrylate films filled with carbon nanotubes.

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Revision of optical property of silicon by a reverse Monte Carlo analysis of reflection electron energy loss spectroscopy spectra

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In recent years a well-established technique based on the reflection electron energy loss spectroscopy (REELS) has been developed to obtain optical constants in a wide range of electron energy loss. The REELS method does not require a complicated process for preparation of samples and the incident electron energy is usually around a few keV. However, the REELS spectrum usually contains not only bulk excitation but also surface excitation. To remove the surface excitation effect and multiple scattering effect from the REELS spectrum in data analysis, Da et al. [1] developed a reverse Monte Carlo (RMC) method for the derivation of the energy loss function (ELF) and thereby the dielectric function and optical constants of solids in a much wider photon energy range than that of the usual optical measurements [2,3]. The RMC method combines a Monte Carlo modelling of electron transportation for REELS spectrum simulation with a Markov chain Monte Carlo calculation of parameterized ELF. During the Monte Carlo simulations we used the Mott cross section with Thomas–Fermi–Dirac atomic potential to describe the electron elastic scattering, and the dielectric function theory for the description of the electron inelastic scattering processes [2]. The REELS spectra of Si were measured with primary electron energies at 3000, 4000 and 5000 eV in an energy-loss range of 0-200 eV. Then the RMC technique was applied to extract the ELF of Si. The reliability of the obtained data has been confirmed by applying the Thomas-Ritchie-Kuhn and the perfect-screening sum rules. We found that the agreement between the final simulated REELS spectra and experimental REELS spectra on the absolute intensity scale is excellent, covering the energy loss range from the elastic peak down to an energy loss of 100 eV, for the primary energy of 4000 eV.

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Tailoring Interfacial Interactions in Fiber Reinforced Polymeric Composites by the Electrospray Deposition of Waterborne Carbon Nanotubes

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The use of fiber reinforced polymeric composites (FRPCs) have been significantly broadening in aerospace, automotive and marine industries, sporting goods and many other applications demanding high performance such as enhanced thermal, mechanical, electrical properties. The ultimate performance of the FRPCs can be improved by enhancing the fiber-matrix interfacial interactions, which can be tailored using nanoscale reinforcements.

In this study, single-walled carbon nanotubes (SWCNTs) were deposited onto carbon fabric (CF) surface via an in-house developed electrospray deposition or airbrush coating. SWCNTs were deposited from a waterborne suspension, eliminating any solvent use or other complex processes and enabling larger scale fabrications. The surface morphology of SWCNT coated CFs was characterized using scanning electron microscopy (SEM) to verify the homogeneous coverage of CNTs on fiber surfaces. The hybrid CF-SWCNT structures were then used in a vacuum infusion process (VIP) to manufacture high-performance FRPCs to assess the influence of SWCNTs on the stress transfer between the fiber-matrix interface and to compare the two deposition methods. SWCNTs located at the fiber-matrix interface are presumed to serve as stress transfer bridges between the fiber and polymer matrix and contribute to the enhancement of interlaminar shear strength and flexural properties. Mode I and Mode II interlaminar fracture testing experiments showed that SWCNTs significantly strengthens the adhesion of the laminate plies.

Two dimensional graphene composites – physics meets chemistry

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Rational design of graphene-based composites requires deep understanding of mutual chemical and physical interactions of all components. Consequently, the bilateral communication of the nanocarbons and the surroundings, through highly efficient channels - the interfaces and the covalent links - must be promoted and rationalized. To build up a material with coveted properties, one must explore the principles of the coupling on the bottommost level. The graphene's willingness to undergo chemical reactions is strongly influenced by doping and mechanical strain as well as by the presence of edges, defects and plethora of functional groups introduced mainly due to liquid exfoliation processes [1]. To understand the role of doping and strain in chemistry of graphene, we fabricated two dimensional (2D) graphene composites with intentionally introduced topographic corrugations. The strategies include transfer of the graphene on substrates decorated with nanoparticles [3], fullerenes [4] and nanopillars [5], or count on different thermal expansion of the graphene and the supporting substrate [6]. Consequently, we achieved spatial modulation of the strain and doping on scale of few nanometers and we were able to explore the impact of curvature and position of the Fermi level on the local reactivity. We will demonstrate how the hydrogenation and fluorination can be carried on graphene with nanometer resolution giving rise to 2D nanocomposites with spatially modulated conductivity and optical properties.

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APPLICATION OF BODY COOLING SYSTEMS IN THE CBRN HAZARDOUS ENVIRONMENT

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The present study was conducted in order to evaluate efficiency of a personal body cooling system based on different technologies and its effects on test subjects and their psycho-physiological suitability during exertional heat stress in hazardous environment. Performed results are based on conducted tests in climatic chamber in the Military Medical Academy Institute of Hygiene in Belgrade. Ten male test subjects were subjected to exertional heat stress test consisted of walking on motorized treadmill at a speed of 5 km/h in hot environment. Tests were performed with and without cooling system. As a physiological strain indicator the following parameters have been determined: mean skin temperature, tympanic temperature, heart rate and sweat rate. Results confirmed that cooling vest worn over the clothes was able to attenuate the physiological strain levels during exercise, when compared to identical exposure without the cooling system.

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MECHANICAL PROPERTIES OF NEW PMMA DENTURE BASE MATERIAL MODIFIED WITH GOLD NANOPARTICLES

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INTRODUCTION: One of the most widely used materials in prosthetic dentistry is polymethyl methacrylate (PMMA). Since its introduction to dentistry, it has been successfully used for denture bases because of its ease of processing, low cost, light weight, and color-matching ability. However, acrylic resin denture base materials have poor strength, including flexural strength. A numerous studies showed that 68% of acrylic resin dentures break within a few years after fabrication.

AIM:

The aim of this study was to investigate the effect of addition of gold nanoparticles (AuNPs) produced through Ultrasonic Spray Pyrolysis (USP) on the mechanical properties of heat-polymerized polymethyl methacrylate (PMMA).

MATERIAL AND METHOD:

Experimental samples that containing different concentration of gold nanoparticles were evaluated. Speciment without filler served as control. The flexural strength were determineted using a three-point bending test with Zwick/Roell Z010 testing machine. We compared flexural strength of gold nanomodified acrylic denture base material with conventional one. Testing were performed in accordance to ISO 20795-1:2013. For statistical analysis, one-way ANOVA test were performed. Statistical significance was set at $p < 0.05$.

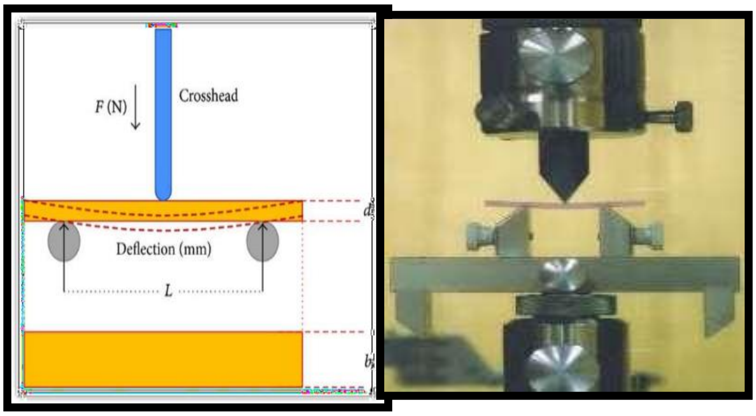

Figure 1. Three-point bending test to determinate the flexural strength: L-support span (40 mm), b-speciemen width (10 mm), d-speciemen thickness (3±0,5 mm), crosshead speed 1,0 mm/min and F-force

Graphene-enhanced elastomers and their applications

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Elastomers, particularly natural rubber, are widely used in applications such as tires, gloves, clothing, medical devices, etc. We demonstrate that the mechanical properties of elastomers can be improved by the incorporation of graphene fillers. Elastomers are compounded either an aqueous formulation called a latex, or as a solid. In order to maximize the impact on mechanical properties by the addition of a small volume fraction of graphene, it is essential to ensure uniform dispersion of the graphene flakes in the elastomer matrix. Upon optimization, it is possible to improve an elastomer by making it simultaneously 50% stronger, 50% more elastic and 50% more hard wearing.

A graphene-modified elastomer can then be formed into a number of shapes using, most popularly, dip-molding of latex or compression molding of solid rubber. I will discuss the fabrication and testing of dip-molded elastomer-graphene composite products such as condoms and gloves, as well as compression molded products such as shoe soles.

I will present the specific case of athletic footwear, where the rubber-graphene composite gives markedly improved grip on tough terrains while simultaneously improving durability. The graphene-enhanced athletic shoes from Inov-8 Ltd. have been available for purchase, worldwide, since July 2018. I will also talk about the future potential of graphene-enhanced elastomers, and a new spin-out company Grafine Ltd. for this purpose.

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Chemical Gas Sensors Based on Poly-Ionic Liquid/Fullerene Nanocomposite

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Poly-ionic liquids (PILs) are the promising class of materials with unique features for sensor devices[1,2]. PILs exhibit ion conductivity and they can be effectively used as chemiresistors device, in which resistance depends mainly on mobility of ions. Gas analyte permeating into PILs material can affect this ion mobility by filling of their free space and also by direct chemical interaction with ionic species. We found that addition of nanocarbons into the PILs can also modify selectivity and sensitivity.

We present gas sensing by nanocomposites consisting of PILs matrix (Tetrabutylphosphonium sulfopropylacrylate as a copolymer) and dispersed nanocarbons - fullerenes (C_{60}, C_{70}). We also demonstrate the effect of phosphonium ion size by Tetrabutylphosphonium and Tributyloctylphosphonium. We describe synthesis and preparation process from dispersing of nanocarbons in PILs precursors to photopolymerization. Nanocomposites in form of thin films are polymerized on glass sensor substrate with a pair of gold sputtered electrodes. Sensor behavior was measured as an impedance changes (in range of 1 Hz - 1 MHz) to selected gas analytes (H_2, CO_2, NO_2, ethanol) in concentrations from 10 ppm in synthetic air. Material behaviour was fitted by Randles-circuit and sensitivity is then determined from the Warburg impedance as an ion mobility change. We present characterization of prepared nanocomposites by SEM, UV-Visible and electrochemical impedance spectroscopy.

Acknowledgement
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From electrostatically-assembled magnetic graphene oxide-based dispersions to 3D printable magnetic hydrogels

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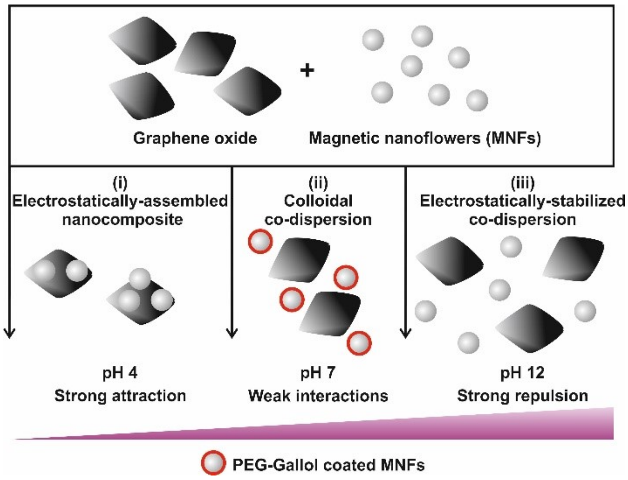

Figure 1: *Selection of controllable magnetically-responsive graphene oxide dispersions.*

Magnetic nanoparticles (MNPs) and their clusters are used in the biomedical field for a wide range of applications from cancer treatment to MRI imaging [1]. Graphene and graphene oxide (GO) continue to be extensively explored for fields spanning from nano-composites [2] to biomaterials [3]. In this project we designed facile routes for fabricating functional colloidal dispersions of magnetic nanoflowers (MNFs) with graphene oxide. In particular, we were able to control electrostatic forces between the two components by varying pH and surface chemistry of the MNFs leading to 3 discrete regimes of colloidal dispersions (***Figure 1***). We then encapsulated these in thermoresponsive Pluronic F127 polymers to form thermally responsive (and reversible) nanocomposite hydrogels and evaluated their hyperthermic responses for heat-responsive applications. We finally showed that bulk properties of our hybrid hydrogels could be engineered (through precise physicochemical modifications) across multiple length scales to modulate their response to applied magnetic fields and that they can be spatially patterned using our in-house 3D printing technologies. These advantages will contribute to the goal of textured multifunctional and stimuli-sensitive nanocomposites delivery systems with precise heat/dosage-control.

Acknowledgements

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Carbon Nanotubes Coated by Plasma Enhaced CVD and Atomic Layer Deposition for Gas Sensing Applications

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Carbon nanotube (CNTs) as well as other nanostructure carbon materials provide excellent base material for chemiresistive or electrochemical sensing applications because of their conductivity and high surface-to-volume ratio [1-3]. In order to utilize fully their potential it is advantageous to modify their surface by other materials aiming to improve the analyte adsorption and create heterojunctions [4,5]. The CNTs-metal oxide semiconductor (MOS) composites can provide a new pathway for room temperature chemiresistive gas sensors due to combined properties of both the materials and the creation of heterojunctions between CNTs and MOS.

In this recently published work [5], multi-walled carbon nanotubes (MWCNTs) were grown by catalytic chemical vapor deposition (CCVD) on Si substrates coated with SiO_2 layer. The MWCNTs were coated by TiO_2 films of different nominal thicknesses, 5, 10 and 20 nm, using atomic layer deposition (ALD). ALD is a self-limiting surface process providing highly uniform and conformal coatings if reactive sites exist on the surface. Since the CNT surface is quite inert and the modification of MWCNTs by carboxyl plasma polymer (PP) film prepared by Plasma enhaced chemical vapor deposition (PECVD) was applied prior to the ALD of TiO_2. The carboxyl PPs improved film uniformity, even though the thinnest TiO_2 film still formed an island-like structure. Raman spectroscopy revealed that coating by TiO_2 or carboxyl PP increased structural disorder of sp^2 carbon in the MWCNTs and the thinnest TiO_2 coatings induced the lowest disorder. The thinnest coatings also resulted in the highest sensor response to NH_3. Nevertheless, for all thicknesses the sensors coated with carboxyl PP/TiO_2 double layer showed higher response as compared to the pristine CNTs and those without the carboxyl PP film.

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