Bucharest CA 15107 Fall Meeting on

Multi-Functional Nano-Carbon Composite Materials

Programme and Abstract Book

September 6 – 7, 2018

Bucharest, Romania

This event is organized by the

Center for Surface Science and Nanotechnology –

University Politehnica of Bucharest

in collaboration with the

European Cooperation in Science and Technology

Scientific Programme – CA15107 Fall Meeting

Bucharest, September 6th-7th 2018

Thursday, September 6th	
09h-	**Registration**
09h30- 09h45	**Welcome**
09h45- 11h	**1st FLASH Presentations Session (10 x 6 min talks) – Session Chair Naum Naveh**
	S.1.1. A.Sezai SARAC *Carbon Nanofibers for Electrochemical Capacitors*
	S1.2. Paula Ferreira *Carbonized biomass-based materials for CO_2 adsorption and separation from CH_4*
	S1.3. Hynek Biederman *Nanostructured carbon surfaces prepared by means of C:H nanoparticles combined with PECVD*
	S1.4. Michele Melchionna *Reversible CO2 reduction to formate by carbon nanohorns/Pd@TiO2 nanohybrids*
	S1.5. Gökçen Akgül *Volarization of Industrial Tea Waste Biochar in Energy Storage as Graphitic Carbon Material*
	S1.6. Ana Teresa Brandão *Electrodeposition of Sn and Sn/carbon nanotubes composites using choline chloride-based solvent (ethaline) as electrode materials for Li ion batteries*
	S1.7. Maria K. Rybarczyk *Nitrogen-Doped Carbon from Renewable Resources*
	S1.8. Mariana Silva *Titanium oxide meso-porous materials modified with carbon for photo-catalytic degradation of organic dyes*
	S1.9. Silvia Giordani *Carbon Nano-Onions interfacing with neurons*
	S1.10. Marta d'Amora *Assessment of the toxic potential of carbon nanomaterials*
11h- 11h30	**Coffee Break** **Opportunity to Network and start Discussions at the Posters**
11h30- 12h30	**2nd FLASH Presentations Session (9 x 6 min talks) – Session Chair Paula Ferreira**
	S2.1. Naum Naveh *Compatibilization of thermoplastic alloys with modified GO*
	S2.2. Naoufal Bahlawane *Deposition of CNT-based composite coatings from the gas phase and their implementation for optics and energy storage*
	S2.3. Miroslav Huskić

	The comparison of SWCNT/polyethylene nanocomposites prepared in micro- and laboratory extruder
	S2.4. Mircea Bercu *ELECTRONIC PROPERTIES OF SWCNTs ON DETECTING NO_2 and H_2 MOLECULES*
	S2.5. Claudia Berkmann *Terrylene filled Single Walled Carbon Nanotubes as precursor to n=5 Nanoribbons*
	S2.6. Aleksandra Ivanoska-Dacikj *ESR SPECTROSCOPY AS A NEW METHOD TO ANALYZE THE SYNERGY BETWEEN TWO DIFFERENT NANOFILLERS DISPERSED IN AN ELASTOMER MATRIX*
	S2.7. Helena Oliveira *Cytotoxicity evaluation of graphene nanomaterials*
	S2.8. Poulin Philippe *Graphene oxide polymer composite fibers as torsional shape memory actuators*
	S2.9. Hatem AKBULUT *MnO2 polymorphs/rGO Nanocomposites: Positive Electrode Performance in the Li-ion Batteries*
12h30-13h45	**Lunch Break** **Opportunity for Networking and Discussions at the Posters**
13h45-15h	**3rd FLASH Presentations Session (10 x 6 min talks) – Session Chair Silvia Marchesan**
	S3.1. Professor Oren Regev *Graphite-to-Graphene: Total Conversion*
	S3.2. Cláudia Nunes *Eco-friendly methodology to produce reduced graphene oxide sheets*
	S3.3. Jacek Wychowaniec *Designing peptide / graphene derivatives hybrid hydrogels through fine tuning of molecular interactions*
	S3.4. Michal Bodik *Localization of the graphene oxide in living cells using confocal Raman microscopy*
	S3.5. Grace Morgan *Engineering Spin Switchable Molecules by Assembly on Few Layer Graphene*
	S3.6. Ana Barra *Electrical conductive chitosan - reduced graphene oxide flexible bionanocomposites*
	S3.7. Valentina Gargiulo *Graphene-like layers based inkjet printed chemiresistors*
	S3.8. Michela Alfe' *Embedding graphene-like layers in metal organic frameworks: the effect on gas sorption at high pressure*
	S3.9. Roberto Di Capua *Electrical dc characterizations and impedance spectroscopy on eumelanin and graphene-like/eumelanin hybrids*
	S3.10. Uwe Popp *Graphene in sintered 3D Printed polymer-metal composites?*

15h-15h15	**Breathing break** **Opportunity for Networking and Discussions at the Posters**
15h15-16h30	**4th FLASH Presentations Session (10 x 6 min talks) – Session Chair Jacek Wychowaniec**
	S4.1. Jadranka B Gilev *PRODUCTION OF CONDUCTIVE POLYMER BASED COMPOSITE FILMS WITH IR CO2 LASER*
	S4.2. Silvia Marchesan *Nano-catalysts based on N-doped carbon nanomaterials*
	S4.3. Ivan Ristić *Characterization of Reinforced Poly(lactide) Composite Nanofibers*
	S4.4. Frantisek Fendrych *Microwave Plasma CVD Deposited Nanocrystalline Diamond Films for Protection of Zirconium Nuclear Fuel Rod Cladding*
	S4.5. Malamatenia Koklioti *Nitrogen-doped transition metal dichalcogenides decorated with silver nanoparticles for surface-enhanced Raman scattering*
	S4.6. Tőkési Károly *Optical constants obtained from reflection electron energy-loss spectroscopy spectra*
	S4.7. Jan Macutkevic *Synergy effects of triglycine sulphate and graphite nanoplatelets in properties of epoxy resin composites*
	S4.8. Liutauras Marcinauskas *Effect of additive powders on the tribological properties of alumina coatings*
	S4.9. Polina Kuzhir *Additive manufacture for microwave and THz components realization*
	S4.10. Gagik Shmavonyan *RUBBING AS A POWERFUL TOOL FOR MASS PRODUCTION OF TWO-DIMENSIONAL ATOMIC MATERIALS*
16h30-17h	**Coffee break** **Opportunity for Networking and Discussions at the Posters**
17h-17h30	**FLASH Presentation and Short talk – Session Chair Sharali Malik**
	Calin Constantin Moise *Planar perovskite solar cells using coordination fullerene polymers as acceptor layer*
	Edward Goldwyn *Potential use of Video for MultiComp*
17h30-18h30	**Poster session** **Posters:** 1. **Sergejs Gaidukovs**, Casted Bio-based Polyurethanes Nanocomposites Processed by Ultrasonic Dispersion of Ultra-Small Content of Multiwall Carbon Nanotubes Stabilized by Metallic Oxide Nanoparticles 2. **Aleksandras Iljinas**, Deposition of amorphous carbon films and

<table>
<tr><td></td><td colspan="2">nanostructures at atmospheric pressure
3. **Polona Umek**, Carbon/Molybdenum Carbide Based New Hybrid Inorganic Nanomaterials
4. **Jelena Tanasić**, The influence of multi-walled carbon nanotubes on crystallization behavior of poly(lactide)
5. **Amra Bratovcic**, associate professor, Synthesis of titanium dioxide – carbon xerogel composites
6. **Martin Vrňata**, Polymerized Ionic Liquids as Sensitive Layers of Chemiresistors
7. **Oskars Platnieks**, Preparation and characterization of bio-based polybutylene succinate / graphene biodegradable composites
8. **Jan Vlcek**, Poly-Ionic Liquids With Fullerenes Nanocomposite Materials for Gas Chemiresistors: Synthesis and Characterization
9. **Premysl Fitl**, Laser Patterning of Fullerene Thin Films
10. **Ivan Radovic**, Research Professor, Wake effect in the interaction of an external charged particle with a graphene-sapphire-graphene structure due to excitation of plasmon-phonon hybrid modes
11. **Valentina Veselinović**, Evaluation of the Optical Properties of Acrylic Resin Denture Base Material (PMMA) Modified with Gold Nanoparticles
12. **Matti Knaapila**, Crystal growth of conjugated oligomers on graphene
13. **Konstantinos S. Triantafyllidis**, Reinforcement of Glassy and Rubbery Epoxy Polymers with 1-D, 2-D and 3-D Carbon Nanostructures
14. **Carla Bittencourt,** Low-Kinetic Energy Nitrogen Ion Irradiation of Vertically-aligned Carbon Nanotubes
15. **Carla Bittencourt,** Gas Sensing Properties of Fluorinated Carbon Nanotubes
16. **Tutu Sebastian**, Novel approach to increase the electrical conductivity of polymer composite fibers
17. **Cristina Ciobota,** Functionalization of carbon based materials for applications in filtering membranes
18. **Nelly Maria Rosas Laverde,** Graphene oxide-modified electrodeposited ZnO / Cu2O heterojunction solar cells
19. **Sabrina Rosoiu**, Morphological and structural investigations of electrodeposited Ni-Sn alloy/reduced graphene oxide composites from deep eutectic solvents
20. **Aida Pantazi**, Multiwalled carbon nanotubes-silver nanocomposite coatings from ionic liquids analogues – morphological and structural analysis
21. **Geanina Mihai**, Manufacturing and dispersion of SWCNTs as a prerequisite for nanodevice building using Electron Beam Lithography
22. **Stefania Marin,** Antimicrobial activity of collagen matrices loaded with SWCNTs and essential oil
23. **Oana Lazar**, Platinum decorated reduced graphene oxide for PEM fuel cells applications</td></tr>
<tr><td>19h30-</td><td colspan="2">**Conference Dinner**</td></tr>
<tr><td colspan="3">**Friday, September 7th**</td></tr>
<tr><td>09h30-10h45</td><td>MC Meeting</td><td rowspan="2">Parallel session:-
Other meeting Participants with Mr. Edward Goldwyn.</td></tr>
<tr><td>10h45-11h15</td><td>**Coffee Break**</td></tr>
</table>

11h15-12h30	MC Meeting concluded	Opportunity for Networking and Discussions at the Posters.
12h30-14h	**Lunch Break**	
14h-15h15	WGs Meetings	
15h15-15h30	**Breathing Break**	
15h30-16h30	WGs Meetings	
16h30-17h	**Coffee Break**	
17h-18h30	WGs Leaders/Representatives Reporting	

Abstract Book

Oral Presentations

Carbon Nanofibers for Electrochemical Capacitors

A.Sezai Sarac

Istanbul Technical University, Polymer Science and Technology, Nanoscience & Nanoengineering ,Istanbul, Maslak, 34469, Turkey

sarac@itu.edu.tr

Supercapacitors are preferable, where the amount of energy stored per surface area is more significant than energy per mass; they have various areas of applications due to instantaneous energy demand such as hybrid energy systems in vehicles, digital telecommunication systems, and laser techniques. Carbon derivatives such as carbon nanofibers (CNFs) and carbon nanotubes (CNTs) can be good alternatives due to their high energy and power densities. These nanomaterials for supercapacitor applications have been widely investigated due to their high surface areas and efficient ion diffusion pathways.

Polyacrylonitrile(PAN)-based CNFs and PAN /Graphen Oxide CNFs were successfully obtained via electrospinning technique [1,2] , and fabrication was followed by oxidation and low temperature (950 C) carbonization [3,4]. Rotating collector was used as a collector to improve the fiber alignment and enhance the CNF electrochemical applications. The D and G Raman peaks were observed, which are well known peaks for carbon materials, and (I_D/I_G) ratio was recorded as 0.87. Aqueous and organic electrolytes are used due to their different properties, i.e., dipole moment, dielectric constant, and molecular weight. The combination of all parameters affects electrolytes' physical properties, which is directly related with the capacitive behavior of electrode. Aqueous electrolytes have narrower electrochemical stability window, with higher ion conductivity, and frequently cause to rise higher capacitance due to smaller ions by fast ion transport, resulting in high rate capability compared to organic electrolytes.Ionic liquids (ILs) in propylene carbonate (PC) or acetonitrile (ACN) are used as electrolyte due to their larger electrochemical stability window.

CNFs were evaluated on the basis of Electrochemical Impedance Spectroscopy (EIS). Variations on the electrolyte type have dramatically effect on the capacitance values; the ideal capacitance is obtained for 0.5 M H_2SO_4 electrolyte solution which can be chosen as an electrolyte for CNF capacitance applications. Maximum specific capacitance was recorded as C_{sp} 204 F g^{-1} and specific capacitance values vary between C_{sp} 149–204 F g^{-1} for different electrolyte types (Fig 1). Cyclic Voltammetric (CV) cycle life tests proves that produced CNF webs have a good stability range, after 500 CV cycles, performance lost in the CNF varies between 2 and 28% according to electrolyte type, indicating that CNF webs can be efficiently used for capacitance applications.

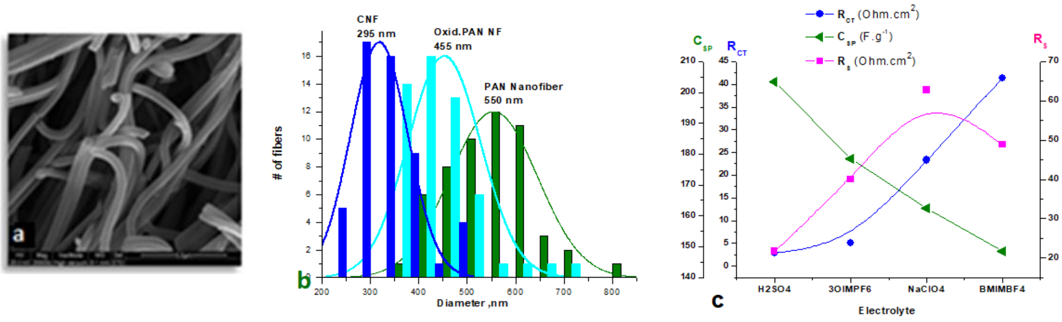


Figure 1. Carbonized PAN nanofibers (a) fiber diameter distribution (b) and Comparison of C_{sp}, R_{ct}, and R_s with electrolyte type(c); values of C_{sp} is taken at scan rate of 5 mV s^{-1}

[1] I.Gergin ,E. Ismar , A.S.Sarac ,Oxidative Stabilization of Polyacrylonitrile Nanofibers and Graphene oxide (GO) Containing Carbon Nanofibers: Spectroscopic & Electrochemical Study, Beilstein J. Nanotechnol. 8, 1616–1628 (2017)

[2] A. Sezai Sarac, Nanofibers of Conjugated Polymers (Pan Stanford Publishing) 2016

[3] E.Ismar.,T.Karazehir ,M.Ates,A.S.Sarac ,Electrospun Carbon Nanofiber Web Electrode: Supercapacitor Behavior in Various Electrolytes,J.Apl.Polym.Sci.135,4,45723(2018)

[4] E. Ismar ,A.S.Sarac, Oxidation of polyacrylonitrile nanofiber webs as a precursor for carbon nanofiber: aligned and non-aligned nanofibers,Polymer Bulletin 75 , 2 ,485-499 (2018)

Carbonized biomass-based materials for CO_2 adsorption and separation from CH_4

M.A.O. Lourenço[1], C. Nunes[1], J.R.B. Gomes[1], J. Pires[2], M.L. Pinto[3], P. Ferreira[1]

1- CICECO, University of Aveiro, 3810-193 Aveiro, Portugal.

2 - CQB – Center of Chemistry and Biochemistry, Faculty of Sciences, University of Lisbon, 1749-016 Lisboa, Portugal

3 - CERENA, Instituto Superior Técnico, University of Lisbon, Av. Rovisco Pais, n°1, 1049-001 Lisboa, Portugal
pcferreira@ua.pt

Abstract: Affordable materials for CO_2 removal from gas mixtures with CH_4, as for example from biogas, are still highly required. Activated carbons are extremely good adsorbents but usually have low selectivity. To prepare efficient adsorbents for CO_2/CH_4 adsorption-separation, the materials must hold high specific surface areas, microporosity and nitrogen content.

Herewith, it is described the development of chitosan spheres which were dried using different methodologies (room temperature, 40 °C in conventional oven and supercritical CO_2) and pyrolysed under nitrogen atmosphere. The materials are tested for CO_2/CH_4 adsorption/separation. It is hypothesized that the spheres drying method may play an important role on the features of the materials obtained by pyrolysis, namely, on the final pore size and pore curvature, which will directly affect the diffusion of the reagents or gas molecules inside the pores.

From the CO_2 adsorption capacities and selectivities determined in our study, the usage of supercritical CO_2 to dry the chitosan spheres was found to be the most interesting drying methodology when compared either with drying the chitosan spheres under air at 25 °C for 30 days or in an oven at 40 °C during 24 h. The adsorbent with the best physical and chemical features to adsorb CO_2 has a Henry constant of 7.73×10^{-2} $mol\cdot kg^{-1}\cdot kPa^{-1}$ at 25 ºC (Table 1). Additionally, the corresponding Henry constant for CH_4 is extremely low (0.02×10^{-2} $mol\cdot kg^{-1}\cdot kPa^{-1}$). The best adsorbent material showed the highest selectivity value (95 at 500 kPa) in the CO_2/CH_4 separation and adsorbs pure carbon dioxide (0.99 molar composition) under these conditions. Furthermore, this material could be reused during at least three adsorption-desorption cycles without any losses on its adsorption capacity for CO_2. This indicates the possible regeneration of the material and its application in cyclic separation processes.

Table 1. Virial coefficients (C_1 and C_2) and Henry's constants (K) for the adsorption of CH_4 and CO_2 at 25 °C on the pyrolysed materials

Gas	Pyrolysed material	K $(mol\cdot kg^{-1}\cdot kPa^{-1}) \times 10^{-2}$	C_1 $kg\cdot mol^{-1}$	C_2 $(kg\cdot mol^{-1})^2$	CO_2/CH_4 ratio
CH_4	Chitosan dried in air				
	Chitosan dried at 40 °C				
	Chitosan dried with supercritical CO_2	0.02	0		
CO_2	Chitosan dried in air	0.19	8.32	0.04	-
	Chitosan dried at 40 °C	2.12	2.65	-0.48	-
	Chitosan dried with supercritical CO_2	7.73	1.35	-0.03	434

Acknowledgement: CICECO-Aveiro Institute of Materials POCI-01-0145-FEDER-007679 (Ref. FCT UID/CTM/50011/2013), CERENA (Ref. FCT UID/ECI/04028/2013), and Smart Green Homes Project POCI-01-0247-FEDER-007678. These projects are financed by Portugal 2020 under the Competitiveness and Internationalization Operational Program and by the European Regional Development Fund (FEDER). FCT is acknowledged by the Investigator FCT program (PC, MLP and JRBG) and the grants ref. SFRH/BD/80883/2011 (MAOL) and SFRH/BPD/100627/2014 (CN).

Nanostructured carbon surfaces prepared by means of C:H nanoparticles combined with PECVD

A. Shelemin, P. Pleskunov, D. Nikitin, R. Tafiichuk, A. Choukourov and H.Biederman

Charles University, Faculty of Mathematics and Physics, Department of Macromolecular Physics, Prague, Czech Republic

Gas aggregation cluster sources (GAS) equipped with DC planar magnetrons are usually used for the production of metal (e.g. Pt, Ag, Cu, Ti) and metal oxide (e.g. TiO_x, Al_xO_y) nanoparticles (NPs) as was first described by Haberland et al. [1]. However, plasma polymer or hybrid NPs may be also obtained by this approach if RF magnetrons with graphite targets and n-hexane or Ar/HMDSO/O_2 are used. In addition, RF magnetron sputtering of nylon or PTFE targets can be performed in the configuration of the GAS to synthesize NPs of corresponding plasma polymer.

The aim of this work was to design nanostructured (porous) hydrogenated carbon (a-C:H) surfaces of different architecture with controlled wettability. For this purpose, a GAS has been used to synthesize and deposit hard plasma polymer (C:H) NPs on solid supports. The nanoparticles were prepared in the 5 vol. % mixture of n-hexane and Ar at the pressure of 50 Pa and at the RF power of 50 W. Under these conditions, the NPs with the mean size of about 300 nm were produced. Beams of the NPs were directed onto the glass substrates where they were deposited (soft landed) with an average flux of $2.1 \pm 0.8 \cdot 10^{10}\ m^{-2} \cdot s^{-1}$. The layers with different amount of the NPs were produced by changing the deposition time. The NP layers were subsequently overcoated by layers of hard a-C:H using a PECVD process in the n-hexane/Ar mixture at the pressure of 5.5 Pa, the RF power of 60 W and the sample bias of -330 V (Figure 1a). The thickness of the overcoat could be varied from 50 to 150 nm. Finally, the samples were ultrasonicated in H_2O for 20 min. Ultrasonication triggered the relaxation of the compressive stress in the hard coatings and resulted in the ejection of the NPs from them. Thus, nanoporous a-C:H structure was produced (Figure 1b). The size and the number of pores were controlled by the size and the number of the NPs as well as by the thickness of the a-C:H overcoat. Control over the resultant architecture allowed to influence the wettability of the surface since the pores served as closed air pockets under the water droplet. Such nanostructured carbon surfaces are expected to be attractive for tunable protein adsorption and cell adhesion.

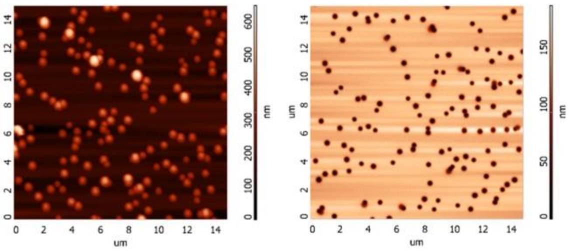


Figure 1. AFM images of: a) C:H NPs overcoated by hard a-C:H film; b) nanoporous structure created after ultrasonication.

Acknowledgement

The authors would like to acknowledge the contribution of the COST Action CA15107 (MultiComp) and support by the grant LTC17062 from the Ministry of Education, Youth and Sports of the Czech Republic

References

[1] Haberland, H.; Mall, M.; Mosseler, M.; Qiang, Y.; Rainers, T.; Turner, Y. J. Vac. Sci. Technol. A 1994, 12, 2925.

Reversible CO_2 reduction to formate by carbon nanohorns/Pd@TiO_2 nanohybrids

M. Melchionna[1], P. Fornasiero[1], M. Bonchio[2], M. Prato[1,3]

1- Department of Chemical and Pharmaceutical Sciences, INSTM. University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy
2- ITM-CNR and Department of Chemical Sciences, University of Padova, Via F. Marzolo 1, 35131 Padova, Italy
3- Carbon Nanobiotechnology Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20009 Donostia-San Sebastian, Spain

Corresponding author email address: prato@units.it

Abstract: The selective electrochemical reduction of CO_2 is a formidable challenge, achieved in nature by enzymatic catalysts such as Formate Dehydrogenase enzymes (FDH). From an energy point of view, this catalytic process allows the recycling of the greenhouse gas CO_2 to produce carbon based fuels, implying carbon neutral energy schemes.[1] Artificial replicas of the FDH, namely bio-inspired multi-component hybrids, are highly desirable, although the vast majority of systems are plagued by poor product selectivity, too high overpotentials to trigger the reduction and poor stability, plaguing their practical use.[2] We have constructed a bio-inspired ternary nanohybrid consisting of carbon nanohorns enveloped within a shell of hydrated TiO_2 embedding Pd nanoparticles. This hierarchical catalyst exploits the synergy oft he three components, enabling selective CO_2 reduction to formic acid at very small applied potentials (~ -0.2 V vs RHE) overriding the competitive reduction of water to hydrogen. Moreover, we observed that the catalyst works reversibly, as the continuous evolution of hydrogen is observed over time, derived from the cascade dehydrogenation of the as formed formic acid once a steady concentration is reached.[3] This peculiar behaviour is achieved thanks to the interplay of the three components, with in situ formed Pd hydrides being the catalytically active species, while TiO_2 serves to favour water adsorption needed to hydrogenate the CO_2 and the carbon nanohorns surface to guarantee efficient electron conductivity (Figure 1). The net result hints at a unique CO_2 "circular catalysis" where formic acid versus H_2 selectivity is adressable by flow-reactor technology.

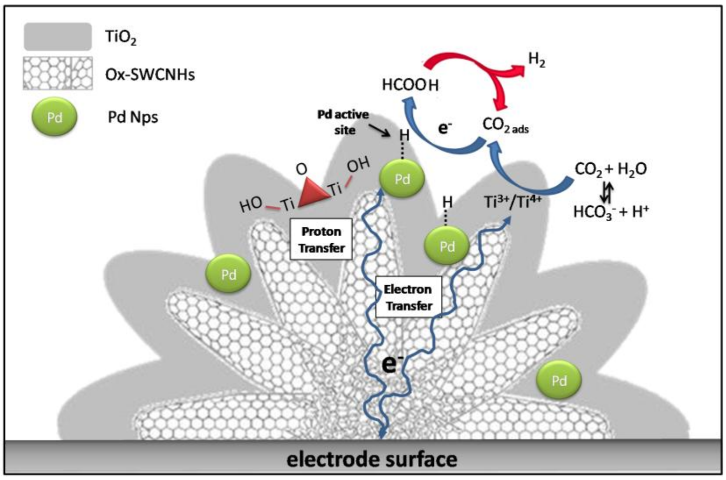


Figure 1 Scheme of the electrocatalytic hydrogenation mechanism envisaged for the conversion of CO_2 to formic acid (blue arrows) and its dehydrogenation (red arrows) at the Pd@TiO_2/ox-SWCNHs triple functional interface (-0.2 V vs RHE)

[1] M. Aresta, A. Dibenedetto and A. Angelini, Chem. Rev., 3, 1709-1742 (2014)
[2] D. D. Zhu, J. L. Liu and S. Z. Qiao, Adv. Mater. 28, 3423-3452 (2016)
[3] M. Melchionna, M. V. Bracamonte, A. Giuliani, L. Nasi, T. Montini, C. Tavagnacco, M. Bonchio, P. Fornasiero and M. Prato, Energy Environ. Sci., 11, 1571-1580 (2018).

Volarization of Industrial Tea Waste Biochar in Energy Storage as Graphitic Carbon Material

Gökçen Akgül[1], **Daniel Iglesias Asperilla**[2], **Pilar Ocon**[3], **Eduardo Moreno Jiménez**[4], **Silvia Marchesan**[2]

[1]*Recep Tayyip Erdogan University, Engineering Faculty, Department of Energy Systems Engineering, 53100, Rize, Turkey*

[2]*University of Trieste, Chemical & Pharmaceutics Science Department, 34127, Trieste, Italy*

[3]*Universidad Autonoma de Madrid, Faculty of Sciences, Department of Chemical Physical Applications, 28049 Madrid, Spain*

[4]*Universidad Autonoma de Madrid, Faculty of Sciences, Department of Agricultural and Food Chemistry, 28049 Madrid, Spain*

Corresponding author email address: gokcen.akgul@erdogan.edu.tr

Abstract: Carbon as the main skeleton element of the world life, is a fascinating material that being found many industrial and scientific applications such as energy storage. Biomass can be an alternative, sustainable, economic and environmental friendly carbon resource that is converted to carbonaceous material biochar by pyrolysis. Biochar could be an ideal candidate for energy storage as a sustainable carbon material. However, it has an amorphous structure which has to be designed to graphite-like structures for a well energy storage [1]. Promoting to graphitization is generally achieved at the higher pyrolysis temperatures (>2000 °C) [2, 3]. Also, the graphitization temperatures can be lowered in the presence of metal and metal salt catalysts [4].

In this work, catalytic structural development of the amorphous biochar derived from industrial tea waste was performed. Fe, Mn and Mg impregnated biochar samples were treated with heat at N_2 atmosphere. The better graphitization could be achieved at 600 °C with Fe impregnation. Fig. 1a shows the development of I_D/I_G ratios determined by Raman. The energy storage capacities of pristine and graphitized biochar is shown Fig. 1b that the energy capacitance was improved many times with graphitization.

.,

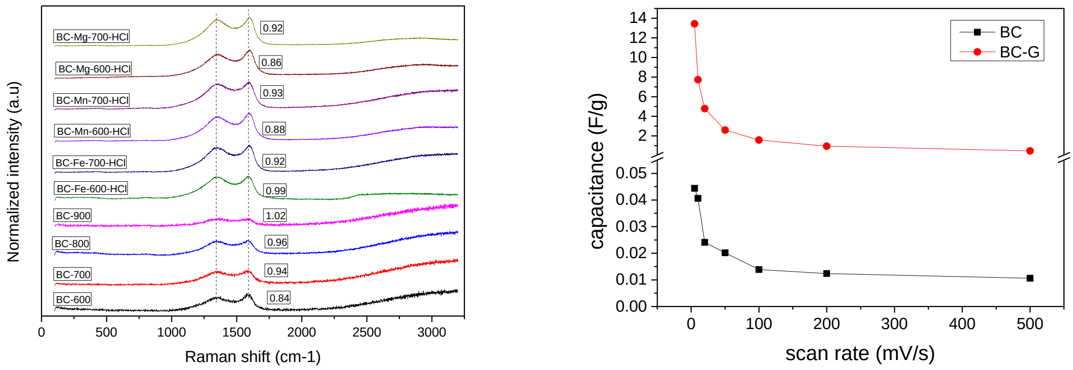


Fig. 1. (a) Raman spectra of the biochar samples, (b) Capacitances of biochar (BC) and graphitized one (BC-G)

Acknowledgement: We would like to thank to COST Action CA15107 (STSM) and Project UAM-Santander “Applications of modified biochars for agro-environmental management” (Spain, Project no: 2017/ASIA/07) for the opportunity to emerge this work.

[1] F.J. Chacón, M.L. Cayuela, A. Roig, M.A. Sánchez-Monedero, Understanding, measuring and tuning the electrochemical properties of biochar for environmental applications, Rev. Environ. Sci. Biotechnol. 16, 695–715, (2017).

[2] A. Woodard, K. Shojaei, G. Nava, L. Mangolini, Graphitization of carbon particles in a non-thermal plasma reactor, Plasma Chem. Plasma Process. 38, 683–694, (2018) .

[3] G.C. Loh, D. Baillargeat, Graphitization of amorphous carbon and its transformation pathways, J. Appl. Phys., 114, 2–9 (2013). doi:10.1063/1.4816313.

[4] T. Kim, J. Lee, K.H. Lee, Full graphitization of amorphous carbon by microwave heating, RSC Adv., 6, 24667–24674, (2016).

Electrodeposition of Sn and Sn/carbon nanotubes composites using choline chloride-based solvent (ethaline) as electrode materials for Li ion batteries

Ana T. S. C. Brandão[1], **Carlos M. Pereira[1,*]**, **A. F. Silva[1]**

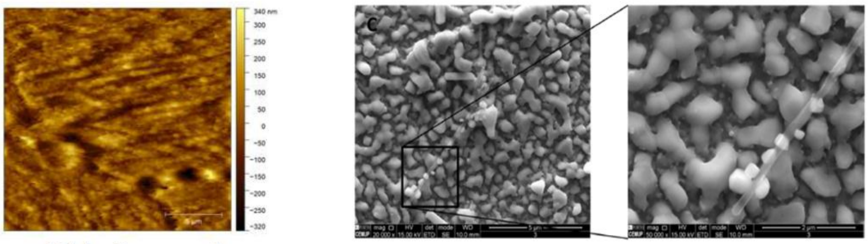
[1] *CIQUP – Physical Analytical Chemistry and Electrochemistry group, Departamento de Química e Bioquímica, Rua do Campo Alegre, s/n 4169 – 007 Porto, Portugal*

* *cmpereir@fc.up.pt*

Abstract: The electrodeposition of metals and alloys from aqueous electrolytes is limited by the narrow electrochemical window and hydrogen evolution. To surpass these disadvantages, in recent years ionic liquids (ILs) and deep eutectic solvents (DES) based on choline chloride have been successfully applied for electrodeposition of different metals [1]. In the past few years, the attention regarding metal composites, namely Sn-carbon materials composites, has increased due to its possible application as anode for lithium-ion batteries due to the great characteristics of carbon [2].

Nano carbons, such as carbon nanotubes show very interesting electrochemical properties. Graphite is been considered as the most commonly used anode material in Li-ion batteries due to the low cost, availability and durability [3]. However, there has been a growing interest in using metals, intermetallic and alloys as alternatives. Sn film anode presents a higher value of theoretical capacity (962 mAh.g^{-1}) compared to graphite (372 mAh.g^{-1}) [4].

The aim of this work was to study the incorporation of carbon materials in tin chloride ($SnCl_2$) electrodeposited matrix in DES based on choline chloride, ethaline. The studied carbon materials for comparison are oxidized multi-walled carbon nanotubes (ox- MWCNT) and pristine multi-walled carbon nanotubes (P-MWCNT). Sn and Sn-carbon nanotubes composites were studied by cyclic voltammetry, chronoamperometry, conductive atomic force microscopy (c-AFM) analysis and scanning electron microscope (SEM) analysis. Surface characterization performed by SEM analysis indicates a good incorporation of MWCNTs in the Sn matrix. Preliminary Li-ion battery studies were performed using Sn and Sn-MWCNTs electrodeposited composites as anodes for capacity and cycle life (charge/discharge) determination.



AFM – Topography
P-MWCNTs

SEM – Surface characterization
P-MWCNTs

Figure 1 AFM and SEM analysis for Sn + P-MWCNTs composite.

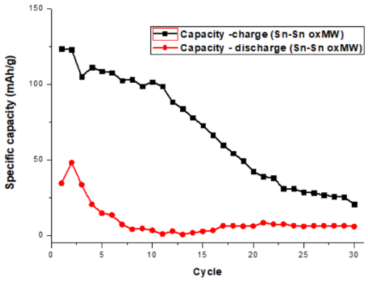


Figure 2 Cycling Performance of Sn-oxMWCNTs (charge/discharge) after 30 cycles.

[1] A. P. Abbott, D. Boothgy, G. Capper, D. L. Davies, R. Rasheed, Journal of the American Chemical Society, 2004, 126, 9142.
[2] S. Zuo, D. Li, Z. Wu, Y. Sun, Electrochimica Acta, 2018, 264, 61.
[3] M. Shafiei, A.T. Alpas, Journal Power Sources, 2011, 196, 7771–7778.
[4] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, Nature, 2001, 414, 359–367.

Nitrogen-Doped Carbon from Renewable Resources

M.K. Rybarczyk, K. Ollik, E. Gontarek, M. Lieder

Gdansk University of Technology, Chemical Faculty, Department of Chemical Technology, 11/12 Narutowicza, 80-233 Gdansk, Poland

Corresponding author email address: maria.rybarczyk@pg.edu.pl

Abstract: The carbon-based catalysts are often synthesised through carbonization of biopolymers containing nitrogen groups. It was shown that chitosan, a natural biomaterial, can be successfully utilized as nanocarbons precursor [1-4]. Chitosan is an N-deacetylated product of chitin which leads to their usage as Nitrogen in-situ dopants into carbon framework. To extend the potential applications, chemical and physical modification is commonly used to tailor, in particular, the electronic properties and catalytic activity of these carbonaceous structures. Different synthesis approaches provide new ways to obtain structures with versatile applications. Here, Carbon-based fluorescent nanomaterials with the size below 10 nm may be exploited for diverse applications such as optoelectronics, chemical sensing and biological labeling. In this work, we report a method to synthesize N-doped Carbon and the fluorescent Carbon Nanodots by hydrothermal carbonization of chitosan.

High-resolution transmission electron microscopy (HRTEM) images revealed that the Carbon Nanodots were monodisperse nanoparticles and had a narrow size distribution of 3-5 nm in diameter. In addition, it was described the different kinds of currently used or tested carbon structures.

The yield of the received Carbon Nanodots was about 7.0% and the sample is readily soluble in water to form a stable aqueous solution. The further functionalized solid phase was investigated for the oxygen reduction reaction. The observation indicate that besides the type of nitrogen site (pyridinic or graphitic), also other properties like the total N content, the surface area and the degree of graphitization might influence the ORR activity. It seems the best ORR activity could be achieved if an optimal balance of surface area, active site density, and electron conductivity were found [5-6].

Acknowledgement

COST Association and COST Action CA15107 Multi-Functional Nano-Carbon Composite Materials Network (MultiComp) is acknowledged for the financial support.

[1] A. Kucinska and A. Cyganiuk and J. P. Lukaszewicz, Carbon, 2012, 50, 3098-3101.
[2] M.K. Rybarczyk, M. Lieder and M. Jablonska, RSC Adv., 2015, 5, 44969-44977.
[3] L. Zhao, N. Baccile, S. Gross, Y. Zhang, W. Wei, Y. Sun, M. Antonietti and M.-M. Titirici, Carbon, 2010, 48, 3778-3787.
[4] B. Aghabarari, M. V. Mart´ınez-Huerta, M. Ghiaci, J. L. G. Fierro and M. A. Pe˜na, RSC Adv., 2013, 3, 5378–5381.
[5] M. Vikkisk, I. Kruusenberg, S. Ratso, U. Joost, E. Shulga, I. Kink, P. Rauwel and K. Tammeveski, RSC Adv., 2015,5, 59495.
[6] M. Nunes, IM. Rocha, DM. Fernandes, AS. Mestre CN. Moura, AP. Carvalho et al., Rsc Adv. 2015, 5, 102919.

Titanium oxide meso-porous materials modified with carbon for photo-catalytic degradation of organic dyes

Silva M.R.F.,[1] **Lourenço M.A.O.**,[1] **Tobaldi D.M.**,[1] **Seabra M.P.**,[1] **Ferreira P.**,[1]

[1]*CICECO – Aveiro Institute of Material, University of Aveiro, 3810-193 Aveiro, Portugal*

E-mail: mrfs@ua.pt

Photocatalysis can resolve contamination issues in low level organic polluted air and wastewaters. Several inorganic oxides have been used as photocatalysts. Titanium oxide (TiO_2) is the most chosen oxide, due to its strong oxidation ability, high efficiency, as well as good thermal, photo and chemical stabilities together with its cost effectiveness compared with other oxides. TiO_2 has three main crystallographic polymorphs: anatase, brookite and rutile. Anatase is the most used phase as photocatalyst because of its high activity. Nonetheless, the mixture of different phases such as anatase with brookite [1] or rutile [2] proved itself to possess elevated photocatalytic degradation ability, surpassing the photocatalytic rates of the single phases. Additionally, materials such as graphene oxide (GO) [3] and carbon nanotubes (CNT) [4] can increase TiO_2 photocatalytic activity. The desirable TiO_2-based material also should have high specific surface areas to allow for the organic pollutants to contact with the photocatalyst's surface.

In this work, we proposed an alternative yet environmental friendly way to produce TiO_2-based photocatalysts.[5] Macro- and meso-porous TiO_2 materials, with different crystalline phases, were produced in absence of surfactant templates, and using distinct kinds of thermal treatments. The photocatalytic materials were characterized regarding their structural and morphological features via X-ray diffraction; Raman and Fourier-transform infrared spectroscopy; scanning electron microscopy; and -196 °C N_2 adsorption-desorption isotherms. The photocatalytic ability was studied via the photocatalytic degradation of Rhodamine B (RhB) in the liquid-solid phase. All TiO_2 samples showed a highly noticeable blue shift in the UV-Vis spectra of the degradation of RhB, showing photosensitization phenomena. On the contrary, the TiO_2/carbon-based composites, prepared with GO and CNT, were efficient in the photodegradation of rhodamine B, without displaying said photosensitization effect.

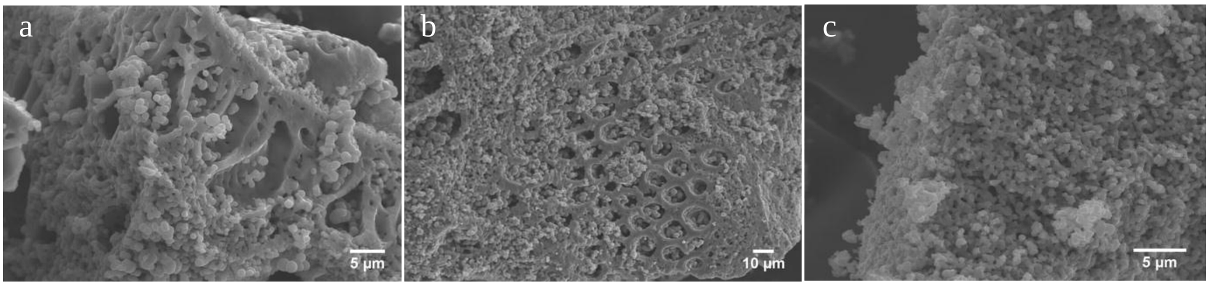


Figure 1. Titanium oxide particles: a) porous; b) with graphene oxide; and c) with carbon nanotubes.

Acknowledgements:

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), and, in part, in the scope of the Smart Green Homes Project POCI-01-0247-FEDER-007678, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement.PF is thankful to FCT for the Investigator FCT.

[1] A. Di Paola, M. Bellardita, and L. Palmisano, "Brookite, the Least Known TiO2 Photocatalyst," *Catalysts*, vol. 3, pp. 36–73,(2013).

[2] D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. A. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood, A. Walsh, and A. A. Sokol, "Band alignment of rutile and anatase TiO 2," vol. 12, pp. 10–13, (2013).

[3] E. Kusiak-Nejman, A. Wanag, Ł. Kowalczyk, J. Kapica-Kozar, C. Colbeau-Justin, M. G. Mendez Medrano, and A. W. Morawski, "Graphene oxide-TiO 2 and reduced graphene oxide-TiO 2 nanocomposites: Insight in charge-carrier lifetime measurements," *Catal. Today*, vol. 287, pp. 189–195, (2017).

[4] K. Woan, G. Pyrgiotakis, and W. Sigmund, "Photocatalytic Carbon-Nanotube-TiO_2 Composites," *Adv. Mater.*, vol.21, pp. 2233–2239, (2009).

[5] J. G. Yu, Y. R. Su, and B. Cheng, "Template-Free Fabrication and Enhanced Photocatalytic Activity of Hierarchical Macro-/Mesoporous Titania," *Adv. Funct. Mater.*, vol. 17, pp. 1984–1990, (2007).

Carbon Nano-Onions interfacing with neurons

Silvia Giordani[1], Michele Baldrighi[1], Massimo Trusel[2] and Raffaella Tonini[2]

1- Nano Carbon Materials, Istituto Italiano di Tecnologia, Via Livorno 60, 10144, Turin

2- Neuroscience and Brain Technology, Istituto Italiano di Tecnologia, via Morego 30, Genova, Italy

Corresponding author email address: silvia.giordani@iit.it

Abstract: Multi-shell fullerenes, also known as carbon nano-onions (CNOs) are structured by concentric shells of carbon atoms and display several unique properties, such as a large surface area to volume ratio, low density and a graphitic multilayer morphology [1]. They are emerging as platforms for biomedical applications because of their ability to be internalized by cells and low toxicity *in vitro* and *in vivo* [2]. The development of drug delivery devices based on carbon onions for biomedical studies requires the understanding of their biological response as well as the efficient and safety exposition of the nanomaterial to the cell compartment where it is designed to operate. In my research group we have developed a versatile and robust approach for the functionalisation of CNOs, involving the facile introduction of a number of simple functionalities onto their surface. To probe their possible applications as a platform for therapeutic interventions on CNS diseases, we injected fluorescently labeled CNOs *in vivo* in mice hippocampus. Their diffusion within brain tissues and their cellular localization were analyzed *ex vivo* by confocal microscopy, electron microscopy and correlative light-electron microscopy techniques. The subsequent fluorescent staining of neuronal cells populations indicates they efficiently internalize the nanomaterial. Furthermore, the inflammatory potential of the CNOs injection was found comparable to sterile vehicle infusion, and it did not result in manifest neurophysiological and behavioral alterations of hippocampal-mediated functions [3]. These results encourage further their development as brain diseases-targeted diagnostics or therapeutics nanocarriers.

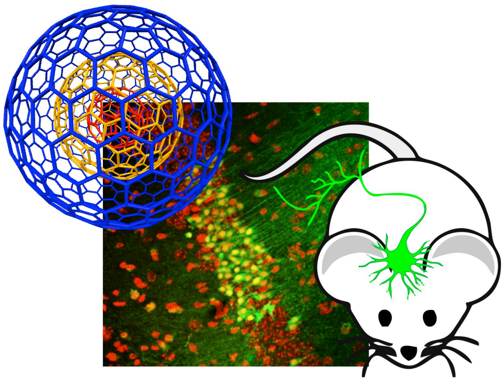


Figure 1 Fluorescein-tagged CNOs infused in vivo render hippocampal cells fluorescent.

[1] J. Bartelmess and S. Giordani, Carbon Nano-onions (multi-layer fullerenes): chemistry and applications, Beilstein J. Nanotechnol. 5, 1980 (2014).
[2] M. d'Amora, M. Rodio, J. Bartelmess, G. Sancataldo, F. Cella Zanacchi, A. Diaspro and S. Giordani, Biocompatibility and biodistribution of functionalized carbon nano-onions (f-CNOs) in a vertebrate model, Scientific Reports, 6, (2016)
[3] M. Baldrighi, M. Trusel, R. Tonini and S. Giordani, Carbon Nanomaterials interfacing with neurons: an in vivo perspective, Frontiers in Neuroscience, 10, 1–27 (2016)
[4] M. Trusel, M. Baldrighi R. Marotta, F. Gatto, M. Pesce, M. Frasconi, T. Catelani, F. Papaleo, P. Pompa, R. Tonini and S. Giordani, Internalization of Carbon Nano-onions by hippocampal cells preserves neuronal circuit function and recognition memory ACS Appl. Mat. & Inter. 10 (20), 16952 (2018).

Assessment of the toxic potential of carbon nanomaterials

M. d’Amora[1], **S. Giordani**[1, 2]

1- Nano Carbon Materials, Istituto Italiano di Tecnologia, Via Livorno 60, 10144, Turin, Italy
2- Chemistry Department, Università di Torino, via Giuria 7, 10125, Turin, Italy

silvia.giordani@iit.it

Carbon nanomaterials (CNMs) are widely employed in biomedical applications being suitable for targeted drug delivery, imaging and in theragnostic, because of their excellent mechanical, optical, and thermal properties [1]. Although different studies have preliminary assessed the *in vitro* toxicity of CNMs, it is essential to evaluate their interaction with a more complex and *in vivo* bio system. To this end, we report a careful evaluation and *in vivo* screening of the potential toxic effects of oxidized carbon nano-onions (oxi-CNOs), oxidized carbon nano-horns (oxi-CNHs), graphene oxide (GO) and oxidized nano diamonds (oxi-NDs) on the development of zebrafish (*Danio Rerio*) [2, 3]. This is an excellent and predictive vertebrate model organism for assessing toxicity of numerous nanomaterials at the whole animal level, due to its external development and optical transparency [4]. Briefly, zebrafish eggs were exposed to different concentration of carbon nanomaterials and the different toxicological and behavioural end-points were monitored during the development by a visible test. Our findings clearly show the good biocompatibility of oxi-CNOs, oxi-CNHs and oxi-NDs at the tested concentrations. On the other hand, GO presents a toxicity dose dependent, causing a perturbation on the behavioural end-points and developmental delay with different malformations. Moreover, we demonstrate that CNOs are more biocompatible than the other three carbon nanomaterials and consequently more suitable and promising for biomedical applications.

[1] J. Bartelmess, S. Quinn, S. Giordani, Carbon nanomaterials: multi-functional agents for biomedical fluorescence and Raman imaging, Chemical Society Reviews, 44(14), 4672-4698, (2015).

[2] N. Nunn, M. d'Amora, N. Prabhakar, A. Panich, N. Froumin, M. Torelli, I. Vlasov, P. Reineck, B. Gibson, J. Rosenholm, S. Giordani, O. Shenderova, Fluorescent Single-Digit Detonation Nanodiamond for Biomedical Applications, Methods and Applications in Fluorescence, 6, (2018).

[3] M. d’Amora, A. Camisasca, S. Lettieri, S. Giordani, Toxicity assessments of different carbon nanomaterials in zebrafish during development, Nanomaterials, 7(12), (2017).

[4] M. d'Amora, M. Rodio, G. Sancataldo, R. Brescia, F. Cella Zanacchi, A. Diaspro, S Giordani, Biocompatibility and biodistribution of functionalized carbon nano-onions (f-CNOs) in a vertebrate model, Scientific Reports, 6, (2016).

Compatibilization of thermoplastic alloys with modified GO

A. Kol, S. Kenig and N. Naveh

Polymers and Plastics Engineering Dept., Shenkar College, Israel

Corresponding author: N. Naveh, naumn@shenkar.ac.il

Abstract: Graphene Oxide (GO) can function as a potential compatibilizer and reinforcement for immiscible polymer blends, especially if functional groups are introduced by reactive mixing. In this work Polypropylene (PP) / Polyamide (PA) alloys were studied. By controlling the thermodynamics and blending dynamics it is possible to localize GO at the interface, resulting in optimal compatibility and electrical conductivity with the lowest GO content possible. Expandable graphite was oxidized to several oxidation levels (10 - 40%) and modified by amino silane (AS) and octyl silane (OTES) to yield GO-AS and GO-OTES [1]. This way, GO was driven to the interface during time controlled blending.

Significant enhancement of mechanical properties is demonstrated by using less than 3 wt.% GO. GO is unstable at the processing temperature and is reduced to rGO, yet the surface treatment by AS moderates the reduction process.

Figure 1 demonstrates the influence of different oxygen levels on storage and loss modulus of PP-GOAS/PA blend [2]. The three peaks of PP/20%GOAS/PA in Figure 1B represent different phases, the one at ~30ºC is identifiable with the interface where GOAS is localized. HRSEM images (Figure 2) support this evidence.

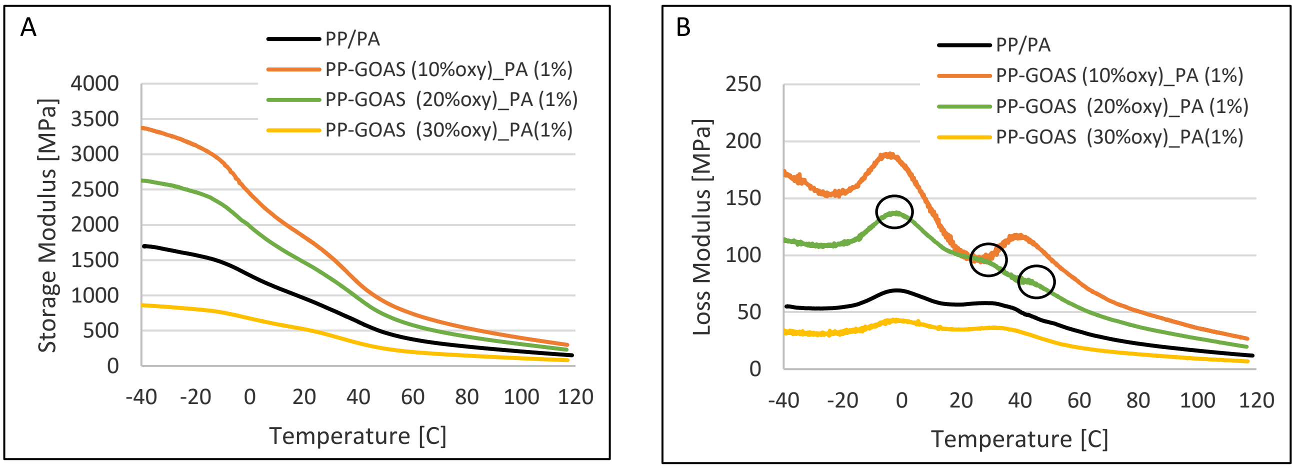


Figure 1: DMA analysis. Influence of different oxygen levels on storage (A) and loss (B) moduli of PP-GOAS/PA blend.

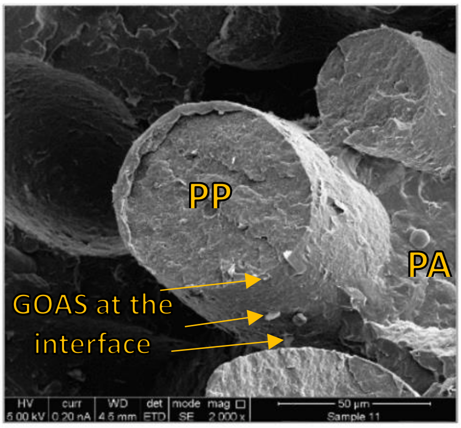


Figure 2: HRSEM of PP/20%GOAS/PA. GOAS at the interface.

[1] A. Kol, N. Naveh and S. Kenig, PPS-34, Cancun, Mexico, December 2017.
[2] A. Kol, N. Naveh and S. Kenig, SAMPE Europe, Southampton, England, September 2018.

Deposition of CNT-based composite coatings from the gas phase and their implementation for optics and energy storage

Naoufal. Bahlawane

Luxembourg Institute of Science and Technology (LIST), Material Research and Technology (MRT) Department, 41, rue du Brill - L-4422 Belvaux – Luxembourg

Carbon nanotubes are versatile building blocks for nanocomposite coatings destined to large number applications including, the elimination of toxic transition metal ions,[1] bio-sensing[2] and heterogeneous catalysis[3, 4] owing to their high specific surface area. Whereas, their electrical property is an asset to design active electrodes for the electrochemical energy storage,[5] and piezo-resistive strain-sensors.[6] Finally, their optical property is prized for the reduction of stray-light in highly demanding optical instruments.[7, 8]

Involving CNT as a building block in nanocomposite coatings is always associated with integration challenges, which drives the continuous development of innovative approaches and chemistries for their synthesis. Pulsed electrodeposition aided injection CVD was, for instance, developed for the uniform insertion of CNT into hydroxyapatite.[9] As a second example from the literature, we might also state the CNT growth at low temperature, 480°C, via the plasma enhancement of the catalytic effect.[10]

Here, we report on a single pot synthesis process that relies on the implementation of a catalyst-promoter single step approach for the growth of CNTs. This purely thermal process allows a sustainable growth of CNTs on various substrates starting a temperature of 320°C, and uses economically and environmentally sound reactants. The source of carbon in this investigation is ethanol and the process tolerates the presence of water impurity, which opens the possibility of implementing biomass-derived ethanol with no need of extensive purification.

In this presentation, we will show the ability of this approach to growth randomly oriented, as well as vertically aligned CNT forest at temperatures compatible with substrates such as aluminium foil. CNT-based composite coatings, produced in a two-steps single pot process, offer a high degree of freedom including the architecture and composition of the matrix. Application examples from our study will include active electrodes for the electrochemical energy storage and super-black coatings for stray-light mitigation for space applications.

1. Hosseinzadeh, H., et al., *Preparation of novel multi-walled carbon nanotubes nanocomposite adsorbent via RAFT technique for the adsorption of toxic copper ions.* Science of the Total Environment, 2018. **640**: p. 303-314.
2. Song, C.K., et al., *Fluorescence-based immunosensor using three-dimensional CNT network structure for sensitive and reproducible detection of oral squamous cell carcinoma biomarker.* Analytica Chimica Acta, 2018. **1027**: p. 101-108.
3. Gopannagari, M., et al., *Influence of surface-functionalized multi-walled carbon nanotubes on CdS nanohybrids for effective photocatalytic hydrogen production.* Applied Catalysis B-Environmental, 2018. **236**: p. 294-303.
4. Kumi, D.O., et al., *Effect of a titania covering on CNTS as support for the Ru catalysed selective CO methanation.* Applied Catalysis B-Environmental, 2018. **232**: p. 492-500.
5. Ma, S.B., et al., *A novel concept of hybrid capacitor based on manganese oxide materials.* Electrochemistry Communications, 2007. **9**(12): p. 2807-2811.
6. Li, M., et al., *Piezoresistivity of resin-impregnated carbon nanotube film at high temperatures.* Nanotechnology, 2018. **29**(36): p. 365702.
7. Basheer, H.J., et al., *Low-Temperature Thermal CVD of Superblack Carbon Nanotube Coatings.* Advanced Materials Interfaces, 2017. **4**(18): p. 1700238.
8. Bahlawane, N., C. Pachot, and U. Lafont, *Innovative CNT-based composite coatings for the stray light reduction*, in *International Conference on Space Optics — ICSO 2016*. 2017, SPIE. p. 1056212.
9. Liu, S.J., et al., *Preparation and characterization of implanted Fe catalyst in hydroxyapatite layer for uniformly dispersion carbon nanotube growth.* Applied Surface Science, 2018. **455**: p. 75-83.
10. Labbaye, T., et al., *Enhancement of catalytic effect for CNT growth at low temperature by PECVD.* Applied Surface Science, 2018. **453**: p. 436-441.

The comparison of SWCNT/polyethylene nanocomposites prepared in micro- and laboratory extruder

M. Huskić[1,2], **V. Žepič-Bogataj**[3], **E. Žagar**[1]

1- National Institute of Chemistry, Department of Polamer Chemistry and Technology, Hajdrihova 19, 1000 Ljubljana, Slovenia
2- Faculty for Polymer Technology, Ozare 19, 2380 Slovenj Gradec, Slovenia
3- TECOS, Slovenian Tool and Die Development Centre, Kidriceva 25, SI-300 Celje, Slovenia

Corresponding author email address: miro.huskic@ki.si

Polymer nanocomposites with carbon nanotubes (CNT) have been a topic of extended research for about 20 years [1]. However, the changes observed in mechanical, electrical and other properties with the addition of CNT to the polymer matrix are very diverse, for which several interpretations exist. The most probable explanation is the use of different CNT types, which are usually synthesized in various laboratories and are diffenerentiated by the purity, length, diameter… Diverse properties of nanocomposites can also be a consequence of different processing methods and processing parameters.

In our work we used industrial grade SWCNT to prepare SWCNT / polyethylene nanocomposites. Masterbatch Tuball 801 (OCSiAl, Luxembourg) with 10 wt.% of SWCNT in polyethylene wax, was mixed with the low density (LDPE, DOW LDPE 780 E NATURAL, Dow Chemicals Company, USA) and high density (HDPE, HDI2061 NATURAL, Braskem IDESA, Mexico) polyethylene using Minilab microcompounder equipped with MiniJet injection moulding machine. The temperature of compounding was 220 °C, time of mixing was 10 minutes, screw speed was 200 rpm, and the SWCNT concentration was spaned in between 0.05 % and 0.5 %. The nanocomposite with 0.4 % SWCNT was also prepared in a laboratory twin-screw extruder Labtech-LTE (screw diameter = 20 mm, L/D = 44), operating at 220 °C and screw speed of 100 rpm. Samples for mechanical testing were prepared by a KraussMaffei KM 80/380 CX injection moulding machine.

Thermal properties were determined by a Mettler Toledo DSC1 differential scanning calorimeter, and mechanical parameters (i.e. Mouldus of elasticity, tensile strength and elongation at break) were determined by tensile testing using a Shimadzu AG-X plus.

SWCNT acted as a weak nucleating agent for crystallization, thus increasing the temperature of crystallization (start) but reducing the rate of crystallization. Therefore, the crystallization of PE proceeded in a broader temperature range and the enthalpy of crystallization was reduced. The influence was higher for the HDPE than for the LDPE.

The tensile modulus and strength increased with increasing the SWCNT concentration. At a concentration of 0.5 % SWCNT, the modulus and strength of LDPE increased for 70 % and 28 %, respectively. Lower increase in modulus (25 % and 20 %) was observed for the HDPE. However, elongation at break reduced for 26 % in the case of LDPE, while for the HDPE the increase for 16 % was observed.

The influence of processing parameters (injection speed, melt temperature, holding pressure and holding time) during injection moulding on the mechanical properties were determined for the nanocomposite with 0.4 % SWCNT via Taguchi DOE Analysis. The optimum parameter of the melt temperature identified was 200 °C, while by changing the values of other processing variables it is possible to significantly maximize the elastic modulus, or tensile strength or to minimize the elongation at break.

ACKNOWLEDGEMENT:

The authors acknowledge the Ministry of Higher Education, Science and Technology of the Republic of Slovenia for co-financing the Programme MARTINA - MAteRials and TechnologIes for New Applications, under which a part of this work was carried out.

[1] G. Pandey and ET Thostenson, Carbon Nanotube-Based Multifunctional Polymer Nanocomposites, Polymer reviews, 52, 355-416, (2012).

ELECTRONIC PROPERTIES OF SWCNTs ON DETECTING NO_2 and H_2 MOLECULES

Mircea Bercu[1], Calin Moise[2], Marius Enachescu[2]

[1]Faculty of Physics, University of Bucharest, PO Box MG11, Romania

[2] Center for Surface Science and Nanotechnology University Politehnica Bucharest, Romania

Single walled carbon nanotubes (SWCNTs) properties reveal that it is one of the most adequate material to nano-structured gas sensor. This contribution investigates molecules interaction to surface of the carbon nanotube by means of Density Function Theory (DFT), Hartree - Fock theory at Abinitio and semi empirical level of approximation. The bonding energy of NO_2 and H_2 molecules were studied in relation to their equilibrium sites on an armchair (5,5) SWCNTs model. These molecules were chosen for the difference in their bonding energy as about 900meV and 80meV respectively. The results at different level of approximation were compared and discussed, also considering those already reported. In spite of the disagreements regarding the H_2 position on the surface of the nanotubes where the minimum energy is reached the important fact is that H_2 has a very week interaction energy relative to NO_2 as all approximations indicated. Beyond the bonding energy used as a direct sign of molecules detection capability, we consider the changes in density of states (DOS) of SWCNTs due to the adsorbed species. The integral intensity variation of DOS spectra corresponding to the carbon nanotube in interaction with the molecules was estimated relative to that of a pure one. These results were also related to the number of the captured molecules in an attempt to have an insight to the sensitivity of the nano-sensor. An external electric field has been preliminary considered to look for the increasing of the bonding energy of adsorbated species onto the nano- tube surface. The results on extra-polarisation effect on molecular detection looks not satisfactory relative to HF-PM3 approach being necessary a higher level of approximation.

Terrylene filled Single Walled Carbon Nanotubes as precursor to n=5 Nanoribbons

C. Berkmann[1], L. Shi[1], H. Kuzmany[1], T. Saito[2], T. Pichler[1], P. Ayala[1]

1- University of Vienna, Faculty of Physics, 1090 Wien, Austria
2- National Institute of Advanced Industrial Science and Technology (AIST),JAPAN

claudia.berkmann@univie.ac.at

The semiconducting property of some graphene nanoribbons can play an important role in addressing the issue of finding novel materials for the semiconducting industry. In this context, the metallicity and possible bandgap of the nanoribbon is defined by the structure of the edges (zigzag or armchair) and the width of the nanoribbon. However, synthesizing such structures with a controlled morphology is one of the greatest challenges in this field. In this study we investigated the use of the precursor molecule Terrylene encapsulating it inside single walled carbon nanotubes (SWCNTs) for the synthesis of nanoribbons via a controlled reaction. The benefit of this approach is that the spatial confinement of the molecule imposed by the SWCNT ensures that it is aligned with respect to the SWCNT axis. After filling the SWCNTs with Terrylene, the end of the molecules connect among each other during a heat treatment forming nanoribbons with the same width as the Terrylene molecule. The filling was performed by first opening the SWCNTs by heating them in air and then heating the Terrylene powder and a bucky paper of SWCNTs sealed in a quartz tube at high vacuum for several days. To determine whether the filling with Terrylene was achieved, the samples were investigated via Raman spectroscopy, photoluminescence (PL) spectroscopy and transmission electron microscopy (TEM). After filling and repeatedly washing the sample to remove excess material, Raman measurements reveal the presence of the molecules. Furthermore, the PL signal of the Terrylene shows changes after encapsulation and solubilization compared to merely Terrylene suspended in solvent. These results strongly suggest that using Terrylene as a precursor molecule encapsulated in SWCNTs represents a truly viable pathway to produce width controlled nanoribbons.

ESR SPECTROSCOPY AS A NEW METHOD TO ANALYZE THE SYNERGY BETWEEN TWO DIFFERENT NANOFILLERS DISPERSED IN AN ELASTOMER MATRIX

Aleksandra Ivanoska-Dacikj[1*], Gordana Bogoeva-Gaceva[1, 2], Srećko Valić[3, 4, 5]

[1] Research Center for Environment and Materials, Macedonian Academy of Sciences and Arts, Krste Misirkov 2, 1000 Skopje, R. Macedonia

[2] Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University,
Rugjer Bošković 16, 1000 Skopje, R. Macedonia

[3] Rudjer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

[4] School of Medicine, University of Rijeka, Braće Branchetta 20, 51000 Rijeka, Croatia

[5] Centre for Micro- and Nanosciences and Technologies, Radmile Matejčić 2, 51000 Rijeka, Croatia

Email of corresponding author: aivanoska@manu.edu.mk

ABSTRACT

In this study electron spin resonance (ESR) investigations on hybrid natural rubber based nanocomposites loaded with 2 phr of multi-walled carbon nanotubes (MWCNT) and various concentrations of expanded organically modified montmorillonite (EOMt) (0; 8 and 16 phr) were reported. The temperature dependence of the resonance line parameters in the range 160–353 K was analyzed. From the obtained results it was evident that the presence of the EOMt influences the appearance of the ESR spectra. This influence makes it possible to assess the state of dispersion of the hybrid nanofiller in the rubber matrix only by analyzing the line shape of the resonance ESR spectra. The Lorenzian line shape indicates good dispersion of the nanofillers while Dysonin line shape suggests re-agglomeration. The increase of the *g*-factor, or resonance line position values, when EOMt is present in the matrix suggests that the EOMt and MWCNT interact in such a way that the content of the defects in the multi-walled carbon nanotubes decreases.

Cytotoxicity evaluation of graphene nanomaterials

C. Menezes[1], A. Mendes[1], C. Roxo[1], F. Campos[1], R. Afonso[1], L. Farcal[2], F. Gonçalves[1], C. Ziemann[3], S. Burla[2], O. Creutzenberg[3], H. Oliveira[1,4]

[1]Department of Biology & CESAM, University of Aveiro, Aveiro, Portugal;

[2] BIOTOX Srl, Cluj-Napoca, Romania;

[3] Fraunhofer Institute for Toxicology and Experimental Medicine ITEM, Hannover, Germany

[4] CICECO − Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal

E-mail: holiveira@ua.pt

Graphene-family nanomaterials (GFNs) hold excellent physicochemical properties that confer them numerous applications. Nevertheless, GFNs potentially widespread use is raising considerable concerns about their toxic potential towards the environment and human health. Safety of GFNs is being matter of research worldwide, but the results are so far yet controversial and therefore proper toxicological risk assessment of GFNs is needed.

Within the scope of the PLATOX project, funded by the FP7-SIINN ERA-NET on Nanosafety, commercially available GFNs were selected and their *in vitro* toxicity was assessed in murine RAW 264.7 macrophages and MRC-5 lung fibroblasts (0-50 µg/cm^2), using spherical carbon black as reference. The effects on cell viability were investigated after 24 and 48h of exposure using lactate dehydrogenase release and AlamarBlue® assays. Based on the cell viability results the benchmark dose 30 (BMD30) for the GFNs was calculated. Cellular uptake, effects on cell-cycle dynamics, production of reactive oxygen species (ROS) and inflammatory responses were analyzed by flow cytometry.

Results show that both carboxyl graphene and single layer graphene markedly impaired metabolic activity of macrophages. For the doses tested, the cell viability of MRC-5 fibroblasts was not affected. Carboxyl graphene, graphene nanoplatelets and single layer graphene oxide were strongly internalized by RAW 264.7 cells. Additionally, GFNs differently affected cell cycle dynamics of macrophages. Upregulation of pro-inflammatory factors TNF-α and MCP-1 was observed for single layer graphene oxide and graphene oxide. Increase in the levels of ROS was observed mostly at 0.5BMD30 doses. Altogether, the obtained results will enable the establishment of a toxicity ranking for the studied GFNs.

Graphene oxide polymer composite fibers as torsional shape memory actuators

J. Yuan[1], P. Poulin[1]

1- Centre de Recherche Paul Pascal – CNRS, University of Bordeaux, 115 Avenue Schweitzer, 33600 Pessac, France

poulin@crpp-bordeaux.cnrs.fr

Abstract: The processing of nanocarbons in polymer fibers is a route towards a variety of electro-active materials potentially useful in energy production and conversion. In particular, we show recent progresses related to the development of new shape memory torsional actuators. Graphene reinforced polymer fibers exhibit significant improvements of their shear modulus. As a result, such fibers can absorb a high amount mechanical energy when twisted at high temperature. This energy can be stored by quenching the materials to low temperature. It can be further restored by heating the material above its glass transition temperature. The fiber untwists and acts as a torsional actuator capable of generating an exceptionally high torque associated to a giant energy density. In addition, the temperature at which the maximum of energy is released can be tuned by changing the programming conditions.

We will also briefly summarize other activities of the Centre de Recherche Paul Pascal on CNT based fibers, including development of conductive textiles, new microelectrodes for biofuel cells, and scale-up of an original fiber wet spinning process.

MnO_2 polymorphs/rGO Nanocomposites: Positive Electrode Performance in the Li-ion Batteries

M. O. Guler, Ş. O. Duman, H. Akbulut

Sakarya University, Engineering Faculty, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54187, Sakarya/TURKEY

akbulut@sakarya.edu.tr

Abstract: In this study, α, β, γ polymorphs of MnO_2 structures were synthesized via rapid and facile microwave assisted hydrothermal method and Graphene Oxide (GO) structure was produced via oxidation of graphite by Hummers' method. Two different methods used to reduce the produced Graphene Oxide. Firstly, Graphene/MnO_2 flexible free-standing cathodes were prepared by chemical reduction process. GO/MnO_2 composites obtained by ultrasonic homogenizer and then they filtered through a vacuum filtration technique. Hydrazine hydrate (HH) was used as reductive agent and 2mmol HH solution was poured on GO/MnO_2 and rGO/MnO_2 was obtained (Figure 1). The charge-discharge characteristics of the cathodes were performed in the voltage range from 1.5 V to 4.5 V at a constant current density of 0.1 mA cm^{-2} using CR2016 coin cells. The initial capacity of rGO/ α, β, and γ MnO_2 free-standing cathodes shown 321 $mAhg^{-1}$, 198 $mAhg^{-1}$, and 251 $mAhg^{-1}$, respectively. rGO/α-MnO_2 cathode displayed a better electrochemical reaction and cycling performance, which exhibited 229 $mAhg^{-1}$ specific capacity after 200 cycles with 72% capacity retention. Secondly, rGO/MnO_2 flexible free-standing cathodes were prepared by thermal reduction process with thermal reduction in Argon atmosphere at 700°C. The obtained thermal reduced graphene (TrGO) and MnO_2 polymorphs were combined by ultrasonic homogenizer as mentioned above. The initial capacity of α- MnO_2 /TrGO, γ-MnO_2 / TrGO free-standing cathodes were indicated 200 $mAhg^{-1}$, and 128 $mAhg^{-1}$, respectively. β-MnO_2 /rGO cathodes did not respond to electrochemical cycling. This result was attributed to clogging of 1x1 tunnel type structure of β-MnO_2 and therefore doping technique was used to widen the tunnels. Co and Ni doping has been used because of their suitable ionic radius. The initial capacity of Co-β-MnO_2/TrGO and Ni-β-MnO_2/TrGO, free-standing cathodes were yielded 136 $mAhg^{-1}$, and 120 $mAhg^{-1}$ discharge capacities, respectively

.

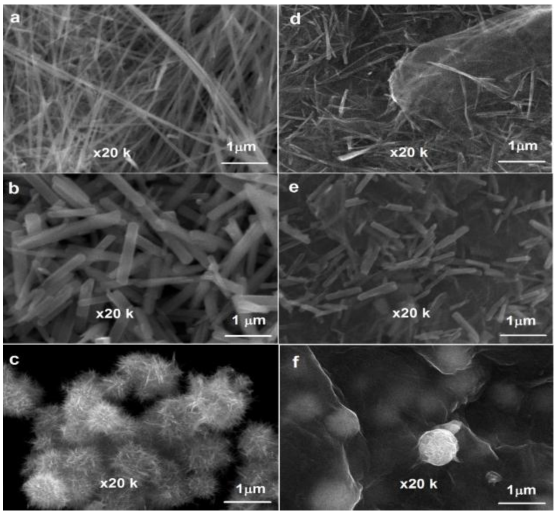


Figure.1. Surface morphologies of (a) α- MnO2, (b) β- MnO2, (c) γ-MnO2, (d) Graphene/α-MnO2, (e) Graphene/β-MnO2, and (f) Graphene/γ-MnO2 free standing cathodes

Graphite-to-Graphene: Total Conversion

M. Buzaglo, I. Pri Bar, M. Varenik, L. Shunak, S. Pevzner and O. Regev
Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

Corresponding author email address: oregev@bgu.ac.il

Abstract: Graphene production has been intensively studied since its emergence in 2004, to accelerate its entrance to the application field in a reasonable price and quality. The most suitable methods for graphene mass production are top-down mechanochemical approaches, such as sonication and high-shear mixing. However, these techniques are limited to liquid medium, which requires graphene stabilization, solvent removal, and results in very low yields (<3%). Another top-down mechanochemical approach, ball milling, nowadays an established technique for producing nanomaterials, is a good candidate for generating the shear and impact forces needed to produce graphene from graphite. This method has been used to produce graphene from graphite in both wet (liquid media) and dry (solid media) milling. In these previous studies, the dry milling resulted in high content of amorphous carbon, while the wet milling resulted in more crystalline products, but required extremely long milling procedures (>20 hr.). Furthermore, in some cases, subsequent sonication was used to improve the relatively low yields.

In this study, graphite flakes were pre-mixed with solid organic diluents to prevent re-aggregation of the obtained graphene sheets, and to minimize the formation of amorphous carbon during the dry milling process. In the non-protected milling, there is a continuous fragmentation leading to amorphous carbon formation while in a diluent-protected milling, the diluent adsorbs part of the impact forces (low milling energies), and therefore enables the exfoliation into graphene sheets (due to shear forces), followed by their fragmentation at higher milling energies. Next, all the diluent is completely removed via filtration with suitable solvents, to obtain the graphene product (see figure).

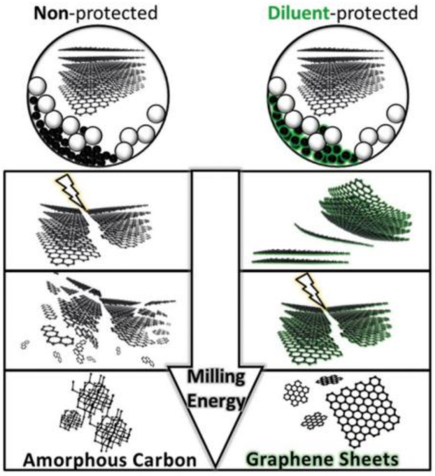


Figure: Schematic view of a non-protected (left panel) and a diluent-protected (right panel) milling of graphite flakes. During the non-protected milling, there is a continuous fragmentation leading to amorphous carbon formation. However, in a diluent-protected milling, the diluent adsorbs part of the impact forces, and therefore enables the exfoliation into graphene sheets. Further milling results in decreasing their lateral dimension as a result of fragmentation. The graphene product is then washed with a suitable solvent to remove the diluent. Black - graphite flakes, White - milling balls.

M. Buzaglo, I. Pri Bar, M.Varenik, L. Shunak, S. Pevzner and O. Regev, Graphite-to-Graphene: Total Conversion, Advanced Materials, 29, 1603528, (2017).

Eco-friendly methodology to produce reduced graphene oxide sheets

C. Nunes[1,2], A. Barra[1], O. Tutunaru[3], A. Pantazi[3], R. Mesterca[3], N. M. Ferreira[1,4], M. Enăchescu[3,5], P. Ferreira[1]

[1]CICECO, [2]QOPNA, [4]I3N - University of Aveiro, Portugal,
[3]Center for Surface Science and NanoTechnology, University Polytechnic of Bucharest, Romania,
[5]Academy of Romanian Scientists, Romania

claudianunes@ua.pt

The graphene-based hybrid materials have been successfully employed in a wide range of biological applications, as biosensors or drug delivery systems. However, for this type of applications, biocompatible and non-toxic materials are required [1]. The chemical synthesis of reduced graphene oxide (rGO) from graphene oxide (GO) allows its further functionalization and it is a facile and cost-effective method. Moreover, the use of a green reducing agent as caffeic acid (CA), do not compromise its use in biological applications [2].
The main aim of this work was the development of a green one-step strategy to synthesize rGO sheets decorated with CA nanoparticles (rGO-CA). Therefore, the effect of the CA content (9, 33, 50, and 100 wt%) in the production of rGO sheets by hydrothermal treatment was studied. The structure, morphology and electrical conductivity properties of the rGO-CA materials were assessed.
The XRD diffraction patterns of rGO revealed a decrease of GO d-spacing in the materials treated with CA due to oxygen containing groups removal. The characteristic peaks of rGO at 2θ equal to 5 and 43° are present in all samples. Furthermore, the Raman spectra of all reduced samples showed the presence of the characteristic bands of graphitic materials (D, G, 2D, D+G and 2D'), corroborating the presence of rGO. The morphological analysis (SEM and STEM) revealed the presence of a multilayer wrinkled structure of rGO sheets and CA nanoparticles in all samples, with the material synthetized with CA 9% showing the highest content in nanoparticles (Figure 1). In addition, this material (CA 9%) revealed the uppermost electrical conductivity.
The hydrothermal treatment of GO in the presence of CA is an effective reduction method to produce rGO sheets. The use of just 9% of caffeic acid seems to be enough to maximize the electric conductivity properties, being the resulting sample promising for further functionalization. Moreover, this eco-friendly methodology allows its use for biological applications.

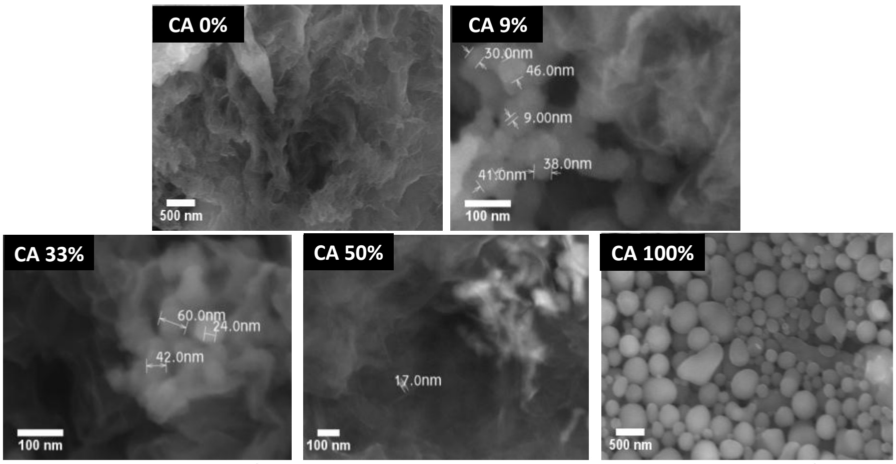


Figure 1 - SEM images of rGO-CA materials synthetized with 0, 9, 33, 50, and 100 wt% of CA.

Acknowledgements: CICECO-Aveiro Institute of Materials POCI-01-0145-FEDER-007679 (Ref. FCT UID/CTM/50011/2013) and i3N (Ref. FCT UID/CTM/50025/2013) are financed by national funds through the FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement. CN, NMF and PF thank FCT for the grants (SFRH/BPD/100627/2014; SFRH/BPD/111460/2015; and IF/00300/2015, respectively). This work was supported by a STSM grant from COST ACTION CA15107 – MULTICOMP. The project M-ERA-NET2/0021/2016 – BIOFOODPACK - Biocomposite Packaging for Active Preservation of Food is acknowledged for funding.

[1] Nguyen, K., Zhao, Y. Nanoscale, 6, pp. 6245-6266 (2014)
[2] Bo, Z., Shuai, X., Mao, S., Yang, H., Qian, J., Chen, J., Yan, J., Cen, K. Sci. Rep., 4, 1-8 (2014)

Designing peptide / graphene derivatives hybrid hydrogels through fine tuning of molecular interactions

Jacek K. Wychowaniec[1,2,♦,*], **Maria Iliut**[1,3], **Mi Zhou**[4], **Jonathan Moffat**[5], **Mohamed A. Elsawy**[1,2], **Wagner A. Pinheiro**[1,6], **Judith A. Hoyland**[4,7], **Aline F. Miller**[2,8], **Aravind Vijayaraghavan**[1,3] and **Alberto Saiani**[1,2]

1- School of Materials, The University of Manchester, Oxford Road, M13 9PL, Manchester, UK
2- Manchester Institute of Biotechnology, The University of Manchester, Oxford Road, M13 9PL, Manchester, UK
3- National Graphene Institute, The University of Manchester, Booth Street East, M13 9PL, Manchester, UK
4- Division of Cell Matrix Biology and Regenerative Medicine, Faculty of Biology, Medicine and Health, The University of Manchester, M13 9PL, UK
5- UK Asylum Research an Oxford Instruments company, Halifax Road, HP12 3SE, High Wycombe, UK
6- Military Institute of Engineering, Praça Gen Tibúrcio 80, Urca, Rio de Janeiro, RJ 22290-270, Brazil
7- NIHR Manchester Musculoskeletal Biomedical Research Centre, Manchester Academic Health Science Centre, Central Manchester NHS Foundation Trust, Manchester, United Kingdom
8- School of Chemical Engineering and Analytical Sciences, The University of Manchester, M13 9PL, UK
♦- Current address: NanoBioMedical Centre, Adam Mickiewicz University, ul. Umultowska 85, 61-614 Poznań, Poland

**jacek.wychowaniec@amu.edu.pl*

Abstract: Hydrogels which are highly hydrated materials have come to the fore front for the design of biocompatible and mechanically tuneable 3-dimensional (3D) scaffolds which offer opportunity for bio-functionalization [1]. Recently strategy of incorporating graphene based nano-fillers in hydrogels has been used to tailor mechanical strength and conductivity and add binding sites for bio-functionalization to regulate cell behaviour, including proliferation, differentiation and protein synthesis to promote specific tissue regeneration [2]. As underlined by a number of authors the key challenge when designing hybrid materials is the understanding of the molecular interactions between the nano-filler and the matrix and how these affect the final properties of the bulk material. For the purpose of this work three rationally designed β-sheet self-assembling peptides: VEVKVEVK (V8), FEFKFEFK (F8) and FEFEFKFE (FE) with varying physiochemical properties and five GDs with varying surface chemistries have been used to formulate selection of hybrid hydrogels [3] (Fig. 1).

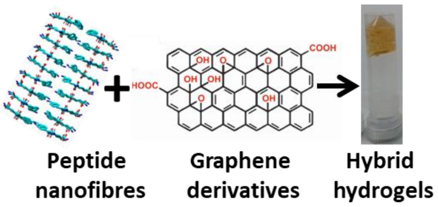


Figure 1 Graphical abstract outlining the purpose of this work.

The interplay of various molecular interactions between nano-fibres and graphene based materials was investigated using variety techniques including atomic force microscopy and oscillatory rheology. In particular hydrophobic and electrostatic interactions were found key to the design of bulk hydrogels with tuneable mechanical properties. Human mesenchymal stem cells (hMSCs) were then 3D encapsulated in the FE, FE+ graphene oxide (GO) and FE+ reduced graphene oxide (rGO) hydrogels and cultures were maintained for 14 days. Using Live-Dead staining, it was clear that cell viability was maintained at >95 % over 14-day culture period for all samples. This indicated non-cytotoxicity of the 3D culture systems for hMSC cells. This work clearly shows how interactions between peptides and GDs can be used to tailor the mechanical properties of the resulting hydrogels, allowing the incorporations of these nano-fillers in a controlled way, and opening the possibility to exploit their intrinsic properties to design novel hybrid peptide hydrogels for biomedical applications.

Acknowledgments: The authors acknowledge financial support of the Engineering and Physical Sciences Research Council (EPSRC): NOWNANO DTC (EP/G03737X/1) and DTA from the University of Manchester.

1. Kumar, D.; Workman, V. L.; O'Brien, M.; McLaren, J.; White, L.; Ragunath, K.; Rose, F.; Saiani, A.; Gough, J. E., Peptide Hydrogels-A Tissue Engineering Strategy for the Prevention of Oesophageal Strictures. *Advanced Functional Materials* **2017,** *27* (38).
2. Krishna, K. V.; Menard-Moyon, C.; Verma, S.; Bianco, A., Graphene-based nanomaterials for nanobiotechnology and biomedical applications. *Nanomedicine* **2013,** *8* (10), 1669-1688.
3. Wychowaniec, J. K.; Iliut, M.; Zhou, M.; Moffat, J.; Elsawy, M. A.; Pinheiro, W. A.; Hoyland, J. A.; Miller, A. F.; Vijayaraghavan, A.; Saiani, A., Designing Peptide/Graphene Hybrid Hydrogels through Fine-Tuning of Molecular Interactions. *Biomacromolecules* **2018**.

Localization of the graphene oxide in living cells using confocal Raman microscopy

M. Bodik[1], **M. Eliasova Sohova**[1,2], **P. Siffalovic**[1,3], **N. Bugarova**[4], **M. Labudova**[5], **M. Zatovicova**[5], **T. Hianik**[2], **M. Omastova**[4], **E. Majkova**[1,3], **M. Jergel**[1] **and S. Pastorekova**[5]

1- Institute of Physics, Slovak Academy of Sciences, Dubravska cesta 9, 845 11 Bratislava, Slovakia
2- Faculty of Mathematics Physics and Informatics, Comenius University, Mlynska dolina F1, 842 48 Bratislava, Slovakia
3- Centre of Excellence for Advanced Materials Application, Dubravska cesta 9, 845 11 Bratislava, Slovakia
4- Polymer Institute, Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava, Slovakia
5- Institute of Virology, Biomedical center of SAS, Dubravska cesta 9, 845 05 Bratislava, Slovakia

Corresponding author email address: michal.bodik@savba.sk

Abstract: Thanks to its oxygen-containing functional groups the graphene oxide (GO) is easily functionalized, what makes it a good candidate for the use as a drug delivery nanoplatform. The GO detection in the interior of the cells is challenging due to the lack of the GO fluorescence. The Raman spectroscopy can easily identify the GO-associated G and D Raman bands. Using the confocal Raman mapping (CRM), we were able to detect the GO cellular uptake without further labeling of the GO. The CRM allows to track the label-free GO at cellular level what is important for the investigation of the nanomaterial-cell interaction without modification of the nanomaterial.

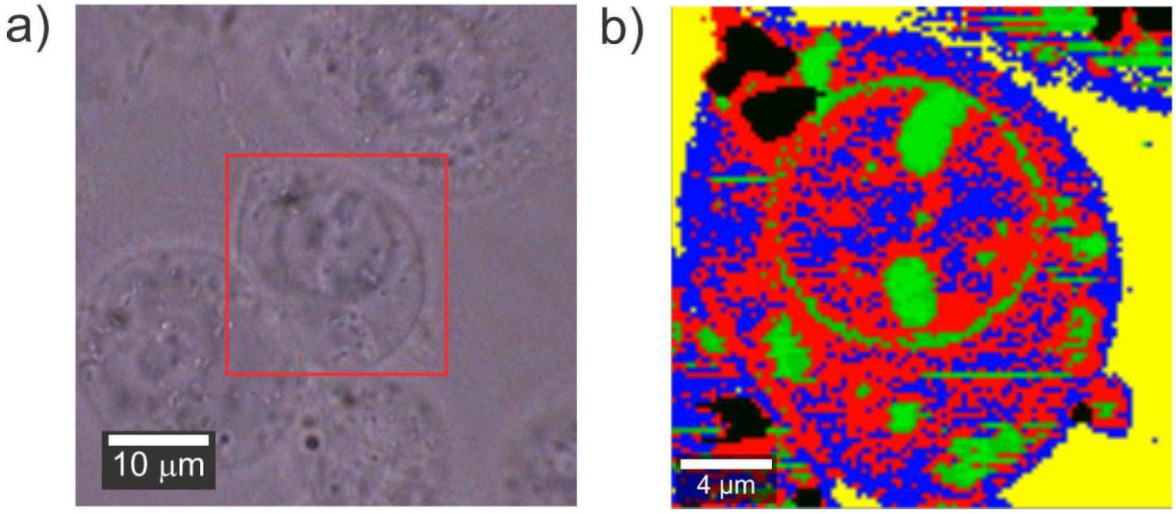


Figure 1 Internalization of GO in C33 cell: a) bright field image, b) false colour image based on Raman mapping.

Engineering Spin Switchable Molecules by Assembly on Few Layer Graphene

Grace G. Morgan

School of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

Email: grace.morgan@ucd.ie

Much effort has therefore been expended in recent years to develop the materials assembly of spin crossover (SCO) complexes and impressive results have been achieved in stabilizing and isolating monodisperse nanoparticles,[1] nanocrystals,[2] thin films,[3] micro- and nanopatterned media,[4] Langmuir-Blodgett surface mono- and multilayers[5] and hysteretic soft media assemblies.[6] The dimensional reduction of SCO complexes has been observed to have an effect on the magnetic behaviour of the materials.[7] This is a result of the electronic bistability being related to the collective behaviour of the SCO centres in the crystalline lattice. We have shown that the SCO properties were retained for Fe(III) SCO complexes.[8] Here, we now probe the efficacy of attaching Mn3+ complexes in different spin states on few layer graphene (FLG). Characterization of the bulk materials and resulting composites will be discussed and a number of techniques such as Raman spectroscopy, AFM and SQUID magnetometry will be included.

1. a) J. –F. Létard, O. Nguyen and N. Daro, Patent FR2894581, **2007**; b) E. Coronado, J. R. Galán-Mascarós, M. Monrabal-Capilla, J. García-Martínez, P. Pardo-Ibañez**,** *Adv. Mat*. **2007**, *19*, 1359-1361; c) A. Tokarev, L. Salmon, Y. Guari, W. Nicolazzi, G. Molnár, A. Bousseksou, *Chem. Commun*. **2010**, *46*, 8011-8013;
2. a) V. Martínez, I. Boldog, A. B. Gaspar, V. Ksenofontov, A. Bhattacharjee, P. Gütlich, J. A. Real, *Chem. Mater*. **2010**, *22*, 4271-4281; b) I. Boldog, A. B. Gaspar, V. Martínez, P. Pardo-Ibañez, V. Ksenofontov, A. Bhattacharjee, P. Gütlich, J. A. Real, *Angew. Chem., Int. Ed*. **2008**, *47*, 6433-6437; c) F. Volatron, L. Catala, E. Rivière, A. Gloter, O. Stéphan, T. Mallah, *Inorg. Chem*. **2008**, *47*, 6854-6586.
3. a) S. Cobo, G. Molnár, J. A. Real, A. Bousseksou, *Angew. Chem. Int. Ed.* **2006**, *45*, 5786-5789; b) G. Molnár, S. Cobo, J. A. Real, F. Carcenac, E. Daran, C. Vieu, A. Bousseksou, *Adv. Mater.* **2007**, *19*, 2163-2167; c) G. Agustí, S. Cobo, A. B. Gaspar, G. Molnár, N. O. Moussa, P. Á. Szilágyi, V. Pálfi, C. Vieu, M. Carmen Muñoz, J. A. Real, A. Bousseksou, *Chem. Mater*. **2008**, *20*, 6721-6732.
4. a) M. Cavallini, I. Bergenti, S. Milita, G. Ruani, I. Salitros, Z. –R. Qu, R. Chandrasekar, M. Ruben, *Angew. Chem. Int. Ed.* **2008,** *47*, 8596-8600; b) M. S. Alam, M. Stocker, K. Gieb, P. Müller, M. Haryono, K. Student, A. Grohmann, *Angew. Chem. Int. Ed.* **2010**, *49*, 1159-1163.
5. a) P. Coronel, A. Barraud, R. Claude, O. Kahn, A Ruaudel-Texier, J. Zarembowitch, *J. Chem. Soc., Chem. Commun*. **1989**, 193-194; b) D. R. Talham, *Chem. Rev*. **2004**, *104*, 5479-5501.
6. a) P. N. Martinho, Y. Ortin, B. Gildea, C. Gandolfi, G. McKerr, B. O'Hagan, M. Albrecht, G. G. Morgan, *Dalton Trans*. **2012**, *41*, 7461-7463; b) C. Gandolfi, G. G. Morgan, M. Albrecht, *Dalton Trans*. **2012**, *41*, 3726-3730.
7. T. Forestier, A. Kaiba, S. Pechev, D. Denux, P. Guionneau, C. Etrillard, N. Daro, E. Freysz, J. –F. Létard, *Chem. Eur. J*. 2009, **15**, 6122-6130.
8. P. N. Martinho, T. Lemma, B. Gildea, G. Picardi, H. Müller-Bunz, R. Forster, T. E. Keyes, G. Redmond, G. G. Morgan, *Angew. Chem. Int. Ed*. 2012, **51**, 11995-11999.

Electrical conductive chitosan - reduced graphene oxide flexible bionanocomposites

A. Barra[1], N. M. Ferreira[1,2], M. A. Martins[1], O. Lazar[3], A. Pantazi[3], A. A. Jderu[3], S. M. Neumayer[4,5], B. J. Rodriguez[4], M. Enăchescu[3,6], P. Ferreira[1], C. Nunes[1]

1- CICECO - Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal
2- I3N, Department of Physics, University of Aveiro, 3810-193 Aveiro, Portugal
3- Center for Surface Science and NanoTechnology, University Polytechnic of Bucharest, Romania
4- School of Physics & Conway Institute of Biomolecular and Biomedical Research, University College Dublin, Belfield, Dublin 4, Ireland
5- Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, 1 Bethel Valley Rd. Oak Ridge, TN 37831, USA
6- Academy of Romanian Scientists, Bucharest, Romania

abarra@ua.pt

Electrical conductive materials have tremendous interest for distinct biological applications, as biomedical sensors or electrically conductive food packaging [1,2]. However, the biodegradability and toxicity of conventional materials are limited. Therefore, the development of biocomposites, using nontoxic electrical conductive fillers and natural biopolymers can gather all the required conditions [3].

Herein, electrical conductive bionanocomposites of chitosan with several loads (0, 25, 40, 45, 48 and 50% w/w) of reduced graphene oxide were developed by an eco-friendly methodology. The reduced graphene oxide was hydrothermally reduced in the presence of caffeic acid, dispersed into chitosan and the films prepared by solvent casting. The homogeneity of the reduced graphene oxide dispersion into chitosan matrix was evaluated through the analysis of topography and electrical conductivity from the micro to the nanoscale. Figure 1 presents the surface morphology and electrical conductivity of the composite with the highest reduced graphene oxide load (50% w/w) and the greatest in-plane electrical conductivity (8.4 mS·cm^{-1}). The incorporation of reduced graphene oxide into chitosan lead to an improvement of films mechanical resistance and stability in acidified solutions. Moreover, the antioxidant activity of films was 80 times higher than observed for the pristine chitosan. This work reports the production of chitosan-based films with the highest electrical conductivity and the upmost tensile strength, achieved using a green methodology. The eco-friendly strategy behind the design of these flexible biomaterials confers them an enormous potential for food packaging and biological applications.

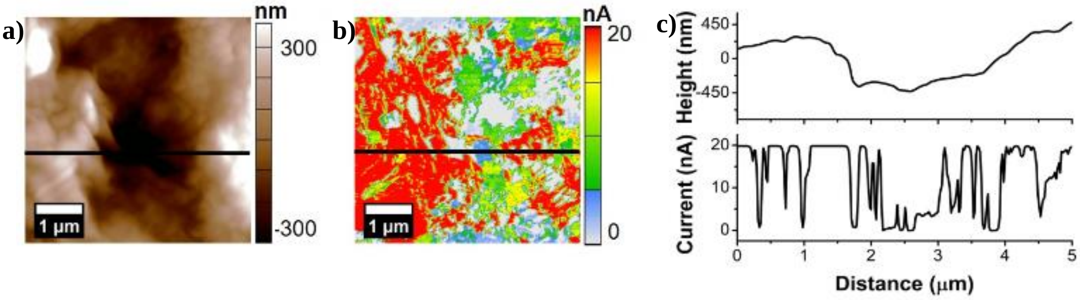


Figure 1. Surface morphology and electrical conductivity of the bionanocomposite with 50% of rGO: **a)** AFM topographic images (5 µm x 5 µm), **b)** CAFM current map (5 µm x 5 µm), and **c)** Height and current value profiles of the marked areas in the AFM and CAFM images.

Acknowledgements: This work was developed within the scope of the projects: CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013); and I3N (FCT REF. UID/CTM/50025/2013) financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. The project M-ERA-NET2/0021/2016 – BIOFOODPACK - Biocomposite Packaging for Active Preservation of Food is acknowledged for funding together with ECSEL-H2020 project 1/1.1.3/31.01.2018, POC-SMIS code 115833 - R3PowerUP. CN, NMF and PF thank FCT for the grants (SFRH/BPD/100627/2014, SFRH/BPD/111460/2015 and IF/00300/2015, respectively). This research was partially supported by COST action 15107, Grants No. 101016-080937 and 38973. This publication has emanated from research supported in part by a research grant from Science Foundation (SFI) under the US-Ireland R&D Partnership Programme Grant Number SFI/14/US/I3113. Some of the measurements were performed on equipment funded by SFI (SFI/07/IN1/B931).

[1] Y. Wang, Y. Wang, and Y. Yang, Graphene–Polymer Nanocomposite-Based Redox-Induced Electricity for Flexible Self-Powered Strain Sensors, Adv. Energy. Mater., 1800961, pp. 1–9, (2018).
[2] B. Roodenburg, S.W.H. De Haan, J.A. Ferreira, P. Coronel, P.C. Wouters, V. Hatt, Toward 6 log10 pulsed electric field inactivation with conductive plastic packaging material, J. Food Process Eng., 36, pp. 77–86, (2013).
[3] G. Kaur, R. Adhikari, P. Cass, M. Bown, P. Gunatillake, Electrically conductive polymers and composites for biomedical applications, RSC Adv., 5, pp. 37553–37567, (2015).

Graphene-like layers based inkjet printed chemiresistors

V. Gargiulo[1], M. Alfè[1], F. Villani[2], F. Loffredo[2], B. Alfano[2], M. L. Miglietta[2], L. Verdoliva[2], R. Di Capua[3,4], T. Polichetti[2]

1- Institute for Research on Combustion (IRC)-CNR, Naples, Italy
2- ENEA C.R. Portici, Portici, Naples, Italy
3- Dipartimento di Fisica "E. Pancini", Università di Napoli "Federico II", Napoli, Italy
4- CNR-SPIN UOS Napoli, Napoli, Italy
gargiulo@irc.cnr.it

Abstract: The detection and quantification of VOCs are crucial issues for the air quality monitoring and an increasing request of low-cost, eco-compatible VOCs sensors able to work at room temperature is emerging. Such objective can be pursued by merging new material sensing properties with eco-sustainable fabrication processes and substrates. Amongst the nanostructured gas sensing systems, carbonaceous nanomaterials have proved to be promising in the production of high performance chemical sensing devices due to their electrical and structural properties (high surface area, high chemical and thermal stability and functionalization capability). In the last years, graphene and related materials (GRMs) have been extensively employed in many sensing experiments and they have been exploited for the detection of a widespread range of chemicals, including VOCs [1,2].

Starting from the findings of our previous work on sensing capabilities of graphene-like (GL) layers to ethanol [3], in this work we investigated the possibility to process GL layers aqueous suspension by means of inkjet printing (IJP) to test its processability by an eco-sustainable sensor fabrication process. Indeed, the IJP technology, namely a deposition method from liquid phase, permits an efficient use of different functional inks reducing the amount of waste products, and nonflexible and flexible substrates (as paper substrates). We explored the possibility to fabricate ethanol chemiresistors by printing onto different substrates an aqueous suspension of GL layers obtained through a two-step oxidation/reduction method starting from a nanostructured carbon black [4,5]. The GL layers-based ink was inkjet printed onto three different substrates with interdigitated Cr/Au electrodes (glossy paper, alumina and silicon dioxide), accordingly to the same printing parameters. The sensor devices were exposed to 50 ppm of ethanol at RT in dry N_2, setting the voltage at 1 V. The electrical responses of the sensor devices, analyzed in terms of conductance variation when exposed to this analyte (Figure 1), indicated process repeatability both at fixed substrate (intra-substrate reproducibility) and by varying the substrates (inter-substrate reproducibility) [6].

Overall, in this study we demonstrated the feasibility of manufacturing printed VOC sensors onto flexible substrates by merging a low-cost and sustainable process with a new nanomaterial having suitable sensing properties.

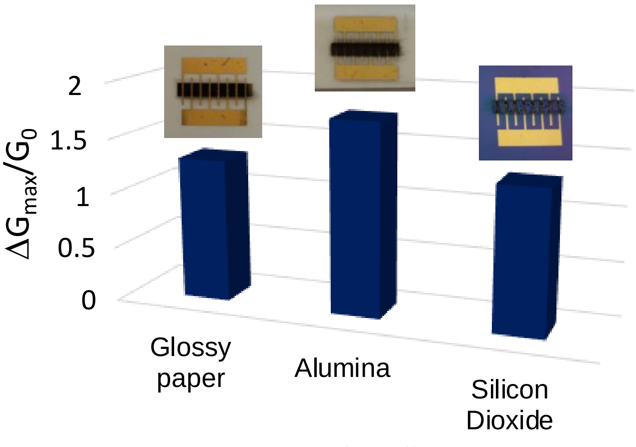


Figure 1 Electrical responses of the different sensor devices

[1] S.S. Vaerghese, S. Lonkar, et al. Recent advances in graphene based gas sensors, Sensors and Actuators B, 218, 160-183, (2015).

[2] A. Lipatov, A. Varezhnikov, et al. A. Highly selective gas sensor arrays based on thermally reduced graphene oxide, Nanoscale, 5(12), 5426–5434, (2013).

[3] V. Gargiulo, B. Alfano, et al. Graphene-like layers as promising chemiresistive sensing material for detection of alcohols at low concentration, Journal of Applied Physics, 123, 024503, (2018).

[4] M. Alfe', V. Gargiulo, et al. Wet Chemical Method for Making Graphene-like Films from Carbon Black, ACS Appl. Mater. Interfaces, 4, 4491−4498 (2012).

[5] M. Alfe, V. Gargiulo, et al. Tuning the surface morphology of self-assembled graphene-like thin films through pH variation, Applied Surface Science, 353, 628−635, (2015).

[6] F. Villani, F. Loffredo, et al. Graphene-like based-chemiresistors inkjet-printed onto paper substrate, Proceeding CNS18.

Embedding graphene-like layers in metal organic frameworks: the effect on gas sorption at high pressure

M. Alfè[1], **A. Policicchio**[2], **V. Gargiulo**[1]

1- Istituto di Ricerche sulla Combustione (IRC-CNR), P.le V. Tecchio 80, 80125 Napoli, Italy
2- Physics Department - Università della Calabria, Via Ponte P.Bucci - Cubo 31C, 87036 Arcavacata di Rende (CS), Italy

Corresponding author email address: alfe@irc.cnr.it

Abstract: Metal-organic frameworks (MOFs), are an attractive and versatile new class of coordination polymers with fascinating 3D topologies, large compositional and structural variety featuring numerous applications such as gas storage, separation of fluids, catalysis, sensing, biomedicine, fuel purification, etc. [1].

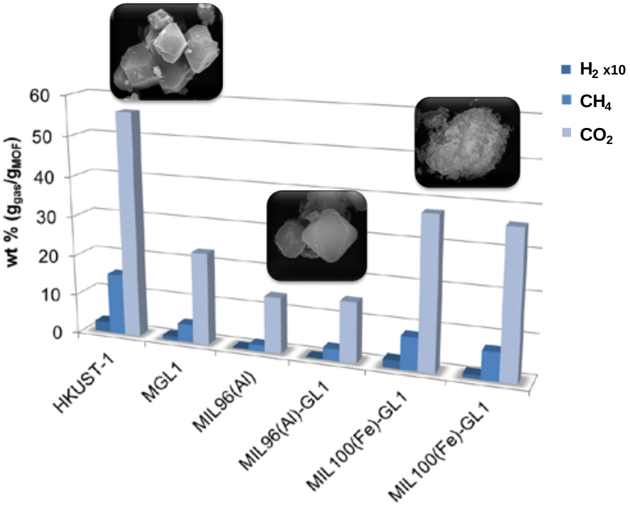


Figure 1 Hybrid GL/MOF gas adsorption capacities.

In this study hybrid MOF have been produced by intercalating the crystalline structure of three 1,3,5-benzenetricarboxylic acid (BTC) based MOFs (HKUST-1, MIL-96 (Al) and MIL-100(Fe)) with graphene-like layers (GL, 5 wt. %) obtained from a nanostructured carbon black through a wet chemical approach [2,3]. The materials were tested for the evaluation of H_2, CH_4 and CO_2 adsorption capacities. The adsorption/desorption tests have been carried out at room temperature and in 0 ÷ 80 bar pressure range for H_2, 0 ÷ 50 bar for CH_4 and 0 ÷ 15 bar for CO_2. All measurements have been acquired using an optimized Sievert-type (volumetric) apparatus f-PcT for accurate and reliable gas adsorption measurements [4]. The adsorption isotherms were collected and compared to highlight differences or similarities inter- and infra-classes since different adsorption properties can be adducted to the different interaction between the sorbent and the adsorbent species, and that can be related to the structural, morphological and chemical properties of the samples. It was found that in all cases the neat samples did not reach saturation indicating the possibility of uptake improvement increasing pressure and/or changing working temperature conditions. As a general trend the hybrid MOF exhibit a quicker saturation for all the analyzed gases (negligible in the case of hydrogen). The gap in terms of maximum wt. % between the analyzed samples results negligible or difficult to be appreciated in the case of hydrogen uptake, while it became significant in the case of CH_4 and CO_2 uptakes. Looking at the microtextural features, the samples with the higher surface areas and enhanced microporous character exhibit the highest CO_2 and CH_4 uptakes. Studies devoted to correlate the adsorption capacities with porosity and specific surface area are ongoing in order to understand if the higher storage capacity of the samples can be simple ascribed to a higher specific surface area of the sample or to specific surface characteristics (hydrophilicity/hydrophobicity) induced by the presence of graphene-like layers.

[1] N. Stock, S. Biswas, Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites, Chem. Rev. 112:933-969, (2012).
[2] M. Alfe, V. Gargiulo, L. Lisi, R. Di Capua, Synthesis and characterization of conductive copper-based metal-organic framework/graphene-like composites, Mater. Chem. Phys. 147:744-750, (2014).
[3] M. Alfe, V. Gargiulo, R. Di Capua, Tuning the surface morphology of self-assembled graphene-like thin films through pH variation, Applied Surface Science, 353, 628−635, (2015).
[4] A. Policicchio, E. Maccallini, G.N. Kalantzopoulos, U. Cataldi, S. Abate, G. Desiderio, R.G. Agostino, Volumetric apparatus for hydrogen adsorption and diffusion measurements: Sources of systematic error and impact of their experimental resolutions, Review of scientific Instruments 84, 103907, (2013).

Electrical dc characterizations and impedance spectroscopy on eumelanin and graphene-like/eumelanin hybrids

R. Di Capua[1], **M. Alfè**[2], **V. Gargiulo**[2], **A. Pezzella**[3]

1-Department of Physics "E. Pancini" University of Naples Federico II and CNR-SPIN, Via Cintia snc, I-80126 Naples, Italy
2- Institute for Research on Combustion (IRC)-CNR, Naples, Italy
3- Department of Chemical Sciences, University of Naples "Federico II", Via Cintia snc, I-80126 Naples, Italy

roberto.dicapua@fisica.unina.it

Abstract: We report about the preparation and characterization of hybrid compounds obtained combining graphene-like layers and eumelanin pigment. Among the different kinds of natural melanin pigments, eumelanin is the one showing the highest electrical conductivity. Its electrical properties are known to be tunable by acting on the water amount and on the specific functionalization of the pigment [1,2], as well as by realizing eumelanin-based hybrid compounds [3,4]. Together with its biocompatibility, the sensitivity of electrical conductance of eumelanin to the chemical interactions with surrounding molecules makes such pigment and the related hybrids of enormous potential interest for biosensing applications.

In view of exploiting the large potentialities of such materials, we recently performed detailed studies on conductivity properties of pure eumelanin, neat graphene-like layers, and hybrid materials obtained by interfacing them, together with some biocompatibility and sensing tests [3-9].

In this work, the main results of electrical characterizations will be illustrated. I-V characteristics showed a general ohmic behavior; dc-electrical conductivity values on various samples can be compared to infer information on the conducting mechanisms, revealing an increase of conductivity from eumelanin to hybrids with graphene layers of several orders of magnitudes (depending on the specific composition of the hybrid compound). In addition, the current decay vs. time under constant supplied voltage observed on some samples is probably related to the double conducting channel, electrons and ions, characterizing the electrical transport of melanin pigments. Impedance spectroscopy (IS) measurements provides further insights of the transport mechanisms of our samples; the analysis of IS curves with the most trustworthy equivalent models shed light on the role of grains and microscopic effects on the dynamics of electrical carriers.

The results obtained so far with hybrid compounds are encouraging, in view of general understanding of fundamental physics of eumelanin and eumelanin-based hybrids, in order to optimize their properties for biocompatible applications.

[1] M.M. Jastrzebska, H. Isotalo, J. Paloheimo, H. Stubb, Electrical conductivity of synthetic DOPA-melanin polymer for different hydration states and temperatures, J. Biomater. Sci., Polym. Ed., 7, pp. 577-586, (1995).

[2] T. Eom, K. Woo, B.S. Shim, Melanin: A Naturally Existing Multifunctional Material, Appl. Chem. Eng., 27, pp. 115-122, (2016).

[3] V. Gargiulo, M. Alfè, R. Di Capua, A.R. Togna, V. Cammisotto, S. Fiorito, A. Musto, A. Navarra, S. Parisi, A. Pezzella, Supplementing π-systems: eumelanin and graphene-like integration towards highly conductive materials for the mammalian cell culture bio-interface, J. Mater. Chem. B, 3, pp. 5070-5079, (2015).

[4] G.P. Papari, V. Gargiulo, M. Alfè, R. Di Capua, A. Pezzella, A. Andreone, THz spectroscopy on graphene-like materials for bio-compatible devices, J. Appl. Phys., 121, pp. 145107, (2017).

[5] M. Alfè, V. Gargiulo, R. Di Capua, F. Chiarella, J.-N. Rouzaud, A. Ciajolo, Wet chemical method for making graphene-like films from carbon black, ACS Appl. Mater. Inter., 4, pp. 4491-4498, (2012).

[6] M. Alfè, V. Gargiulo, L. Lisi, R. Di Capua, Synthesis and characterization of conductive copper-based metal-organic framework/ graphene-like composites, Mater. Chem. Phys., 147, pp. 744-750, (2014).

[7] M. Alfè, V. Gargiulo, R. Di Capua, Tuning the surface morphology of self-assembled graphene-like thin films through pH variation, Appl. Surf. Sci., 353, pp. 628-635, (2015).

[8] R. Di Capua, V. Gargiulo, M Alfè, Graphene-like layers from unconventional carbon sources: New perspectives on hybrid materials and π-system synergisms, Eurasian Chem.-Technol. J., 18, pp. 263-274, (2016).

[9] V. Gargiulo, B. Alfano, R. Di Capua, M. Alfè, , M. Vorokhta, T. Polichetti, E. Massera, M.L. Miglietta, C. Schiattarella, G. Di Francia, Graphene-like layers as promising chemiresistive sensing material for detection of alcohols at low concentration, J. Appl. Phys., 123, 024503_1-8, (2018).

Graphene in sintered 3D Printed polymer-metal composites?

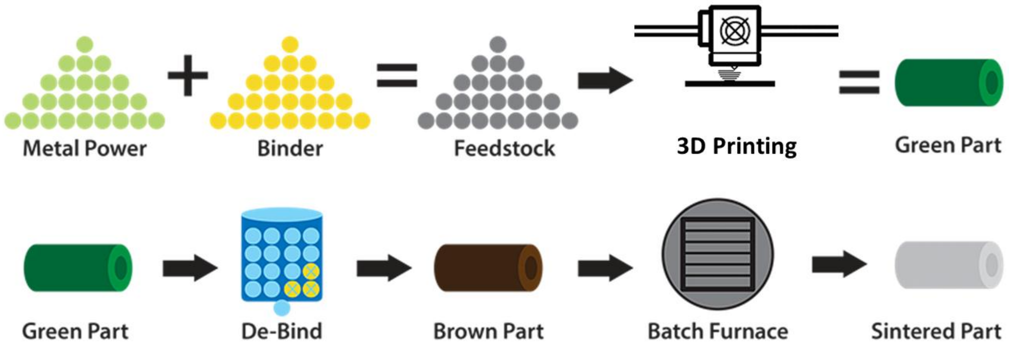
U. Popp[1], B. Okolo[1]

1- Apium Additive Technologies GmbH, Willy-Andreas-Allee 19, 76131 Karlsruhe

Corresponding author email address: uwe.popp@apiumtec.com

Abstract: In recent times, there has been a sudden interest at using 3D printing technologies to process metallic materials in a cost efficient way. Laser based 3D printing technologies are still beyond the cost consideration of most small and medium enterprises (SME) in Europe thus making it still operationally prohibitive for SME's to run such facilities in-house free of supplier constraints. In order to reach the SME market space using metal 3D printing, a printing approach quite similar to industry-established metal injection moulding (MIM) process has been developed. This approach requires that the material which is to be processed is ideally a relatively low melting temperature polymer matrix filled with a metallic powder phase having a weight composition in the range of 60 to 80% metal and rest binder polymer. The powder size distribution of the filler metallic material is as narrow as possible in order to realize a composite of as much as possible homogenous microstructure. This polymer based metal composite, typically in filament form, is 3D printed using the material extrusion technology. The printed part, called the green-body, is then post-treated first by tactfully separating the metal from the polymeric phase using either a temperature assisted processes or a fluid based media (liquid or gas) which dissolves out the normally soluble polymeric phase. This "debinding" process results in the formation of a brown-body which is technically polymer-free but only sufficiently structurally stable to preserve the geometric form of the printed part with or without a back-bone phase. The brown-body is then sintered at temperatures close to the melting point of the metallic material initiating several physical processes which assist the bonding and densification of the metal material till a metallurgically convenient material composition is formed (illustration in Figure A). It is typical that the formed material is not pore-free often when fully processed containing porosities in the range of 2 to 7 % depending on starting material composition as well as 3D printing, debinding and sintering conditions. Each pore structure in the sintered part serves as a notch essentially providing the site from where, due to over-bearing stress concentration, structural failure could initiate in the sintered part when mechanically loaded. Therefore if the microstructure of the sintered part could be influenced in such a manner that there is a reduction of pore size and thus porosity then the structural integrity of the sintered part may be improved. It is here being rationalized that a likely way such a structural interference could occur is by introducing graphene to the stock material then following on with the printing, debinding and sintering processes. Candidate materials for this would be the martensitic precipitation hardening steel 17-4PH and 316 L stainless steel. Graphene is known to show preferential bonding to Fe, Cu and Ni; these elements already exist in rationed quantities in 17-4PH and 316 L steel.

The purpose of my presentation is to motivate this topic by sharing the 3D printing work we have done on 316 L and to discuss the structural outcome of the process on the sintered parts. We are interested in exploring this uniquely new aspect of processing and materials design, to study the resulting metallurgy then seek applications thereof for such a material.



Adapted from: https://www.worldclasstech.com/mim

Figure 1: Metal 3D Printing process adapted from Metal Injection Moulding process

PRODUCTION OF CONDUCTIVE POLYMER BASED COMPOSITE FILMS WITH IR CO_2 LASER

Jadranka Blazhevska Gilev

Faculty of Technology and Metallurgy, University St.Cyril and Methodius, Ruger Boskovic 16, 1000 Skopje, FYR of Macedonia

jadranka@tmf.ukim.edu.mk

Abstract: Production of electrically conductive thin poly(methyl methacrylate/buthyl acrylate/ hydroxyethyl methacrylate)/1wt.% multi-walled carbon nanotubes and graphene films, were achieved by deposition with pulsed IR CO_2 laser [1]. Ablation was realized by IR irradiation of two targets, the nanocomposite and graphene. Laser ablation was performed by varying the energy of the laser, deposition inert atmosphere and number of pulses [2]. Towards optimizing the parameters for the laser ablation we obtained conductive polymer composite films and carbon nanostructures [3]. The properties of the deposited composite films were evaluated by FTIR, Raman spectroscopy, SEM microscopy and contact angle measurements. The goal was to optimize the laser system parameters in favor of obtaining stoichiometry transfer between targets and depositing films with no significant defects in the structure, and successful production of electrically conductive composite films evaluated by four probe resistivity meter.

Keywords: pulsed IR CO_2 laser ablation, polymer/MWCNT/graphene nanocomposites, and electrically conductive deposited films

[1] Krebs, H.; Weisheit, M.; Faupel, J.; Suske, E.; Scharf, T.; Fuhse, C.; Störmer, M.;Sturm, K.; Seibt, M.; Kijewski, H.; Panchenko, E.; Buback, M. Pulsed Laser Deposition (PLD) - A Versatile Thin Film Technique. Adv. Solid State Phys., 43, 101-107, 2003.

[2] Scharf,T.; Krebs, H. Influence of inert gas pressure on deposition rate during pulsed laser deposition. Appl. Phys. A., 75 (5), 551-554, 2002.

[3] Kalsoom U., Shahid Rafique M., Shaheen R., Fatima K., Metal based Synthesis of Graphene by Pulsed Laser Deposition Technique, International Journal of Scientific & Engineering Research, 5, 3, 2014.

Nano-catalysts based on N-doped carbon nanomaterials

D. Iglesias[1], A. Giuliani[1], M. Melchionna*[1], S. Marchesan[1], A. Criado[2], L. Nasi[3], C. Tavagnacco[1], F. Vizza[4], M. Prato[1,2,5], P. Fornasiero[1,6], *et al.*

1 - Chem. Pharm. Sc. Dept., University of Trieste, Trieste, Italy. 2 - CIC biomaGUNE, San Sebastiàn, Spain. 3 - CNR-IMEM Institute, Parma, Italy. 4 - ICCOM-CNR, Florence, Italy. 5 - Ikerbasque, Basque Fndn. for Science, Bilbao, Spain. 6 - 5ICCOM-CNR, Trieste, Italy.

**email: melchionnam@units.it*

Abstract: Composites of carbon nanomaterials are attracting great interest for a wide variety of applications [1, 2], including catalysis [3] for sustainable processes [4]. In this work we describe the use of the convenient bioadhesive polydopamine to attain N-doping of a variety of carbon nanostructures, which were tested for electrocatalytic hydrogen peroxide production. Hydrogen peroxide is a versatile product that is used worldwide, especially as bleaching agent and cheap disinfectant. At industrial level, it is produced through the anthraquinone process, which is energy-intensive and relies on the use of a precious metal (palladium). There is thus a huge interest in developing low-cost and low-energy alternative production methods. Here [5] we describe the preparation and characterization of N-doped carbon nanostructures as metal-free electrocatalysts for the sustainable production of hydrogen peroxide from the reduction of molecular oxygen. The nanomaterials have been analyzed by a variety of techniques including TEM, EDX, Raman, TGA, electrochemistry methods, etc. Amongst the nanocarbons tested, carbon nanohorns revealed to possess the ideal porosity and N-type doping that allowed to achieve excellent performance as electrocatalysts, over a wide range of pH values, and with long term stability.

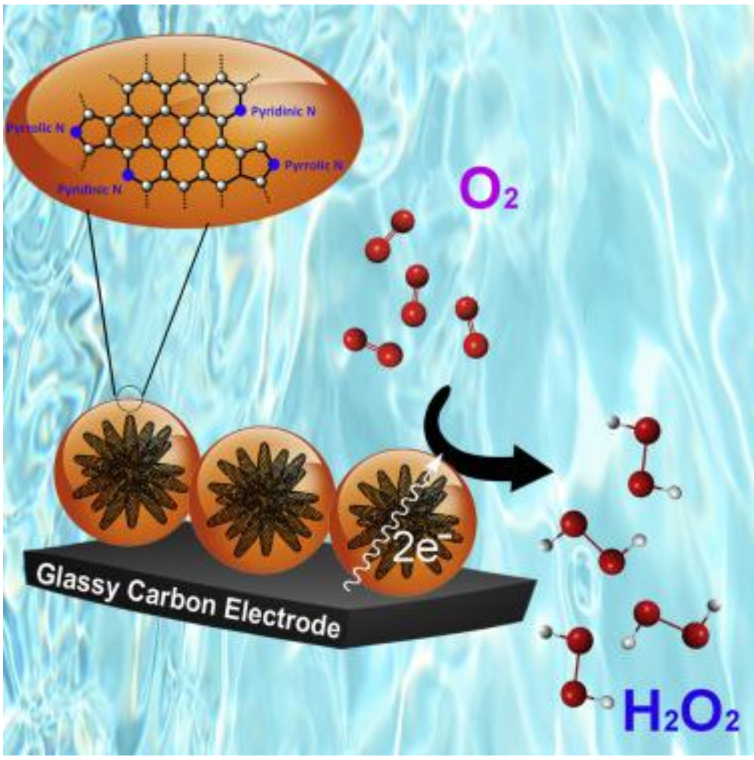


Figure 1. N-doped carbon nanohorns are excellent nanocatalysts for hydrogen peroxide production [5].

[1] S. Malik, A. V. Krasheninnikov, S. Marchesan, Beilstein J. Nanotechnol. 9, 20-21 (2018).
[2] D. Iglesias, S. Bosi, M. Melchionna, Marchesan, et al. Curr. Top. Med. Chem. 16, 1976-1989 (2016).
[3] M. Melchionna, M. Prato, P. Fornasiero. Catal. Today 277, 202-213 (2016).
[4] M. Melchionna, P. Fornasiero, ChemCatChem 9, 3274-3284 (2016).
[5] D. Iglesias, A. Giuliani, M. Melchionna, S. Marchesan, et al. Chem 4, 106-123 (2018).

Characterization of Reinforced Poly(lactide) Composite Nanofibers

Ivan Ristic[1], **Aleksandra Miletic**[1], **Milena Marinović-Cincovic**[2], **Krisjanis Smits**[3], **Danica Piper**[1], **Suzana Cakic**[4], **Branka Pilic**[1]

[1]*University of Novi Sad, Faculty of Technology, Blvd. cara Lazara 1, 21000 Novi Sad, Serbia*

[2] *University of Belgrade, Institute for Nuclear Sciences ˝Vinča˝, p. fah 522, 11001 Belgrade, Serbia*

[3]*University of Latvia, Institute of Solid State Physics, 8 Kengaraga Street, Riga, LV-1063, Latvia*

[4]*University of Niš, Faculty of Technology, Blvd. Oslobodjenja 124, 16000 Leskovac, Serbia*

Corresponding author email address:ivan.ristic@uns.ac.rs

Abstract: In this paper, reinforcing of electrospun poly(lactide) (PLA) nanofibres was achieved with the addition of multiwalled carbon nanotubes (MWCNT). Different amounts of MWCNT (0,2; 0,5; 2 and 3 wt%) were loaded to study its influence on the thermo-mechanical properties of PLA fibers. Scanning electron microscopy and transmission electron microscopy analysis revealed that the average diameters of composite nanofibers decreased when the MWCNT content increased. According to TEM results it was confirmed that within nanofibers with lower amount of filler, carbon nanotubes existed as single tubes, randomly dispersed through fiber volume, figure 1, because the concentration was too low and no strong forces between them were present. With increasing of the amount of MWCNT, inhomogeneity in fiber increases, part of them form aggregates and in that form MWCNT were present in the matrix. By DSC results it is evident that the presence of carbon nanotubes in PLA matrix had significant influence on crystallization behaviour of PLA nanofibers, because the decrease of crystallization temperature (Tc) was detected. Also, the addition of MWCNTs to PLA fibers affects melting temperatures, enabling generation of α' form, while had no influence on ordered PLA α crystal. Decrease of enthalpy of degradation was observed because MWCNTs are well known for good heat conductivity, and with that, second step of degradation slowed down, as confirmed by TGA measurement. Addition of MWCNTs caused the increase of both elasticity and tensile strength of nanofibers. Conductivity measurement results showed that by applied technique it is possible to obtain conductive fibers, whereby it is confirmed that an increase in the MWCNT content does not affect the increase in the conductivity of the fiber, since for all composite fibers the conductivity was 170 Omh sq^{-1}.

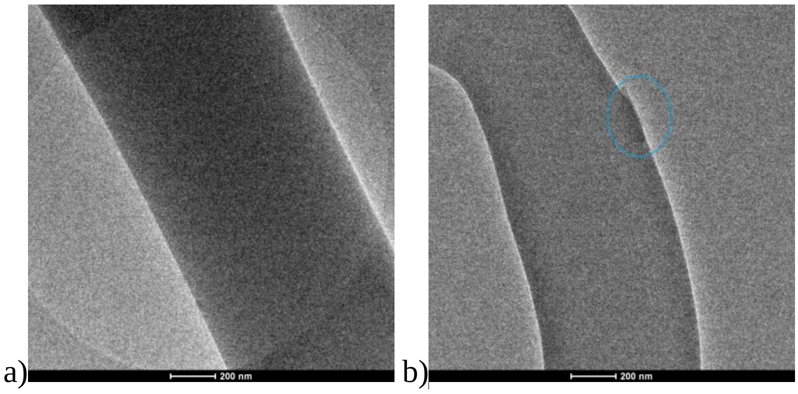


Figure 1. TEM micrographs of pure PLA nanofibers (a), PLA-0.5%MWCNTs (b) composite nanofibers.

Acknowledgements
Authors would like to thank Ministry of Education, Science and Technological Development Republic of Serbia (Project No. III 45022) and COST action CA15107 for support.

Microwave Plasma CVD Deposited Nanocrystalline Diamond Films for Protection of Zirconium Nuclear Fuel Rod Cladding

F. Fendrych[1], **I. Kratochvilova**[1], **P. Ashcheulov**[1], **A. Taylor**[1], **P. Hozak**[1],
J. Vlcek[1], **R. Skoda**[2], **J. Skarohlid**[2], **M. Simonik**[3], **S. Johnson**[4]

1 - Institute of Physics, Academy of Sciences of the Czech Republic, Department of Functional Materials,
Na Slovance 2, CZ-18221 Prague 8,
2 - Faculty of Mechanical Engineering, Czech Technical University, Zikova 4. CZ-16607 Prague 6,
3 - Westinghouse Electric Czech Republic s.r.o., U Zemepisneho ustavu 1, CZ-16000 Prague 6,
1,2,3 - Czech Republic,
4 - Westinghouse Electric Company, LLC, 5801 Bluff Road, Columbia, SC 29250, U.S.A.

Corresponding author email address: fendrych@fzu.cz

Abstract: We provide the proof of concept that nanocrystaline diamond (NCD) film can be utilized as a protective coating for zirconium alloy nuclear fuel cladding (NFC). Zirconium alloy (Zircaloy2) is a material used in all modern hot steam water cooled commercial 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). Recently, many materials have been applied to protect zirconium alloys surfaces to overcome the abovementioned issues, but without any significant success. We have successfully demonstrated the possibility to homogeneously cover a cylindrical rod-shaped Zircaloy2 nuclear fuel cladding by a 300 nm thick protective NCD layer using the Linear Antennas MicroWave Plasma Enhanced Chemical Vapour Deposition (LAMWPECVD) apparatus[1]. NCD coated Zircaloy2 rods underwent a set of corrosion tests, namely a reactor irradiation test and hot steam oxidation. A number of characterization methods (scanning electron microscopy-SEM, Raman spectroscopy, X-ray diffraction-XRD and X-ray photoelectron spectroscopy-XPS) were employed [2], [3] both before and after these two well-established corrosion testing methods confirming that a thin NCD layer can serve as a protective coating on zirconium-based NFCs in the harsh environment of a nuclear reactor, even at substantially elevated temperatures (Figure 1). Zircaloy2 nuclear fuel cladding was covered by a 300 nm thick protective polycrystalline diamond layer using LAMWPECVD deposition technique. The polycrystalline diamond layer protects zirconium alloy surface against undesirable oxidation and consolidates its chemical stability while preserving its functionality. NCD anticorrosion protection of Zircaloy nuclear fuel rods can significantly prolong lifetime of Zirconium alloy in nuclear reactors even above Zirconium phase transition temperatures [4].

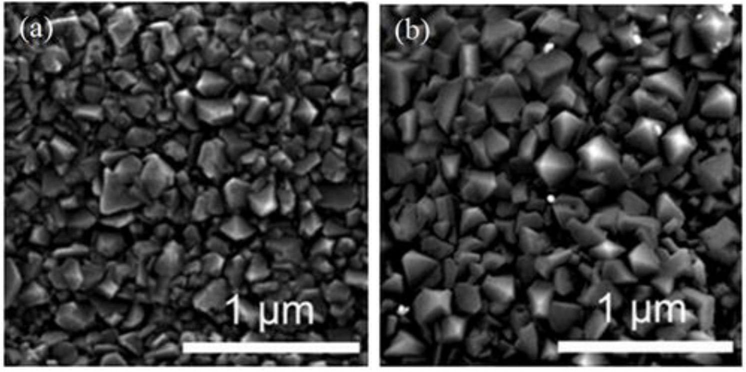


Figure 1 SEM of the initial surface of a Zr alloy sample covered with 300 nm thick NCD (a) and the surface after 30 days of exposure to 360 °C hot water (b). No microstructural changes were observed in the hot-water-processed NCD film.

Financial support of the MSMT CR grant no. LTC17083 (Nano-Carbon Composite Materials for Energy Conversions, Storage and Nuclear Energetics) in frame of the EU Action COST CA15107 MultiComp is gratefully acknowledged.

[1] F.Fendrych, A.Taylor, L.Peksa et al., Journal of Physics D: Applied Physics 43 (2010) 374018.
[2] I.Kratochvilova, R.Skoda, J.Skarohlid, P.Ashcheulov et al., J Mater Process Technol 2014; 214: 2600–2605.
[3] J.Skarohlid, P.Ashcheulov, F.Fendrych et al.: Nature / Scientific Reports 7, Article number: 6469 (2017), DOI:10.1038/s41598-017-06923-4.
[4] European patent PCT/CZ2014/000101 - WO2015/039, Title of invention: LAYER PROTECTION THE SURFACE OF ZIRCONIUM ALLOYS USED IN NUCLEAR REACTORS
Patent Number: WO2015039636-A1; CZ201300727-A3; CZ305059-B6, Inventor(s): SKODA R; SKAROHLID J; KRATOCHVILOVA I; FENDRYCH F; TAYLOR A.

Nitrogen-doped transition metal dichalcogenides decorated with silver nanoparticles for surface-enhanced Raman scattering

M. Koklioti[1], C. Bittencourt[2], I. Saucedo[3], M. Quintana[3,4] and N. Tagmatarchis[1*]

1- Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens 11635, Greece
2- Chimie des Interactions Plasma-Surface, University of Mons, 20 Place du Parc, 7000 Mons, Belgium
3- Instituto de Física, Universidad Autónoma de San Luis Potosí, Manuel Nava 6, Zona Universitaria, San Luis Potosí, SLP 78290, Mexico
4- Microscopia de Alta Resolución, Centro de Investigación en Ciencias de la Salud y Biomedicina, Universidad Autónoma de San Luis Potosí, Av. Sierra Leona 550, San Luis Potosí, SLP 78210, Mexico
tagmatar@eie.gr

Transition metal dichalcogenides (TMDs) are at the forefront of the current research investigations of 2D layered materials beyond graphene, especially for energy applications. However, to fully harness their potential, chemical functionalization is an absolute necessity for their establishment in rational applications, from which chemical sensing through Raman enhancement signal is considered among the most exciting ones.

Herein, we report – for the first time – a simple one-pot modification of few-layered MoS_2 and WS_2 sheets, employing nitrogen plasma treatment and simultaneous decoration with silver nanoparticles (Ag_{NPs}), for two different plasma exposure and metal deposition times, toward the preparation of N-doped and with Ag_{NPs} decorated TMDs. The employed method offers numerous virtues, including straightforwardness, controllability, fast functionalization time, and absence of wet processes that may require additional work up procedures. The successful surface modification of TMDs was evaluated through Raman and X-ray photoelectron spectroscopy (XPS), while transmission electron microscopy (TEM) imaging verified the decoration with Ag_{NPs}. Furthermore, the newly developed N-MoS_2/Ag_{NPs} and N-WS_2/Ag_{NPs} hybrids were employed as surface-enhanced Raman scattering (SERS) substrates, to detect Rhodamine B (RhB) at very low concentration. Markedly, it was found that the SERS efficiency, by observing clearly all RhB Raman active bands, depends on both doping and deposition time as well as the type of TMD employed as substrate. Charge-transfer phenomena witnessed between RhB and the modified TMDs, along with the polarized character of the hybrid system, causing dipole-dipole coupling interactions, were ascribed for the enhancement of the Raman signal acquired. Finally, considering the coordination of aromatic moieties via π-S interactions with TMDs, we accomplished the sensitive detection of polycyclic aromatic hydrocarbons such as pyrene, anthracene and 2,3-dihydroxy naphthalene, at very low levels, by employing N-MoS_2/Ag_{NPs} as SERS substrate.

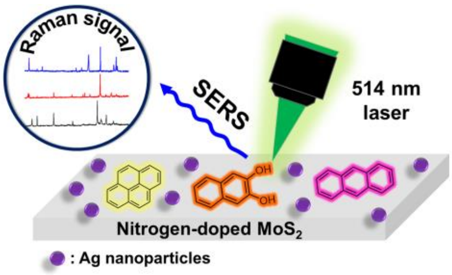


Figure 1 Schematic representation of N-doped and decorated with Ag_{NPs} TMDs as SERS substrates

References

M. A. Koklioti, C. Bittencourt, X. Noirfalise, I. Saucedo, M. Quintana, N. Tagmatarchis, ACS Appl. Nano Mater. (2018), DOI: 10.1021/acsanm.8b00747.

Acknowledgments

This work was supported by a STSM Grant from the COST Action CA15107. Financial support through a PhD scholarship by the General Secretariat for Research and Technology (GSRT) – Hellenic Research Foundation for Research and Innovation (HFRI) to Malamatenia Koklioti is acknowledged.

Optical constants obtained from reflection electron energy-loss spectroscopy spectra

L.H. Yang[a], H. Xu[a], A. Sulyok[b], M. Menyhárd[b], Z.J. Ding[a], and **K. Tőkési**[c]

[a]*Key Laboratory of Strong-Coupled Quantum Matter Physics, Chinese Academy of Sciences; Hefei National Laboratory for Physics Sciences at Microscale and Department of Physics, University of Science and Technology of China, Hefei 230026, Anhui, P.R. China*

[b]*Institute for Technical Physics and Materials Science Centre for Energy Research, Hungarian Academy of Sciences (MTA), P.O. Box 49, H-1525 Budapest, Hungary*

[c]*Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI), P.O. Box 51, Debrecen, Hungary*; *ELI-ALPS, ELI-HU Non-profit Ltd., Dugonics tér 13, H-6720 Szeged, Hungary, EU*

The optical properties, as one of the most important physical properties of materials, arouse a continuous interest of researchers. Optical methods based on reflectance spectroscopy, absorption spectroscopy and spectroscopic ellipsometry are the most widely employed approaches to obtain optical properties of materials. Accurate measurement of optical data by optical methods in a photon energy range up to 10^2 eV is still insufficient; delicate experimental conditions are required when measuring data in vacuum ultraviolet region (20-50 eV). Fortunately, such information is essentially contained in electron energy loss spectroscopy (EELS) spectrum.

In recent years Da et al. [1] have developed a reverse Monte Carlo (RMC) method based on the reflection electron energy loss spectroscopy (REELS) to obtain optical constants in a rather wide range of energy loss of electrons. 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, $\mathrm{Im}[-1/\varepsilon(\omega)]$, where $\varepsilon(\omega)$ is the complex dielectric function of the material. The advantage of this method is that it provides the ELF and thereby the dielectric function and optical constants in a much wider photon energy range (i.e. energy loss range ~100 eV) than that of usual optical measurements.

In the present work, reflection electron energy loss spectra of Ir and Sm were measured at several primary energies ranging from 0.5 keV up to 2 keV and in a wide energy-loss range. A reverse Monte Carlo simulation was performed to extract ELFs of those metals from experimental REELS spectra [2,3]. The reliability of the obtained optical data has been confirmed by applying the Thomas-Ritchie-Kuhn (f-sum rule) and the perfect-screening sum rules (p-sum rule).

[1] B. Da, Y. Sun, S. F. Mao, Z. M. Zhang, H. Jin, H. Yoshikawa, S. Tanuma, and Z. J. Ding, J. Appl. Phys. **113** (2013) 214303.

[2] L.H. Yang, M. Menyhárd, A. Sulyok, K. Tőkési, and Z.J. Ding, Applied Surface Science **456** (2018) 999.

[3] L.H. Yang, H. Xu, A. Sulyok, M. Menyhárd, K. Tőkési, and Z.J. Ding, to be published.

Synergy effects of triglycine sulphate and graphite nanoplatelets in properties of epoxy resin composites

J. Macutkevic[1], A. Plyushch[1], V. Samulionis[1], J. Banys[1], Dz. Bychanok[2], P. Kuzhir[2], S. Mathieu[3], V. Fierro[3], A. Celzard[3]

1- Vilnius university,Sauletekio 9,Vilnius LT-10222, Lithuania
2- Belarusian State university, Bobruskaya str. 11, Minsk 2200300 Belarus
3- Universite de Lorraine, 27 Rue Philippe de Seguin, Epinal Cedex 9, France

Corresponding author email address: jan.macutkevic@gmail.com

Ferroelectric polymeric materials are very attractive in various applications due to the possibility make large area, flexible and cheap devices [1]. Ferroelectric polymeric materials can be obtained by two different ways: by producing a ferroelectric polymer or by introducing ferroelectric particles into non ferroelectric polymer matrix [2]. The amount of wel known ferroelectric polymers is very restricted (mostly is known Polyvinylidene Fluoride (PVDF) [3]). Therefore, the second way seems to be more attractive. In this presentation the sinergy effects were investigated in both systems. First, of all epoxy resin composites with 30 wt. % of triglycine sulfate (TGS) and up to 1 wt. % of graphite nanoplatelets (GNP) were fabricated and studied by means of broadband dielectric spectroscopy (20 Hz – 3 GHz). It was demonstrated that the dielectric properties are mainly governed by the Maxwell-Wagner relaxation at lower frequencies (below 1 MHz) and by diffuse ferroelectric soft mode at higher frequencies (above 1 MHz). The ferroelectric origin of the phase transitions was also confirmed by piezoelectric investigations. Although the phase transition temperature is independent of GNP concentration, the piezoelectric and dielectric (above 1 MHz) properties of composites are strongly improved by GNP in a broad temperature range. This gives evidence for the strong synergy between GNP and ferroelectric particles. The synergy effect appears due to the better distribution of TGS particles in ternary composites and the creation of electric fields by GNP inside the composite.

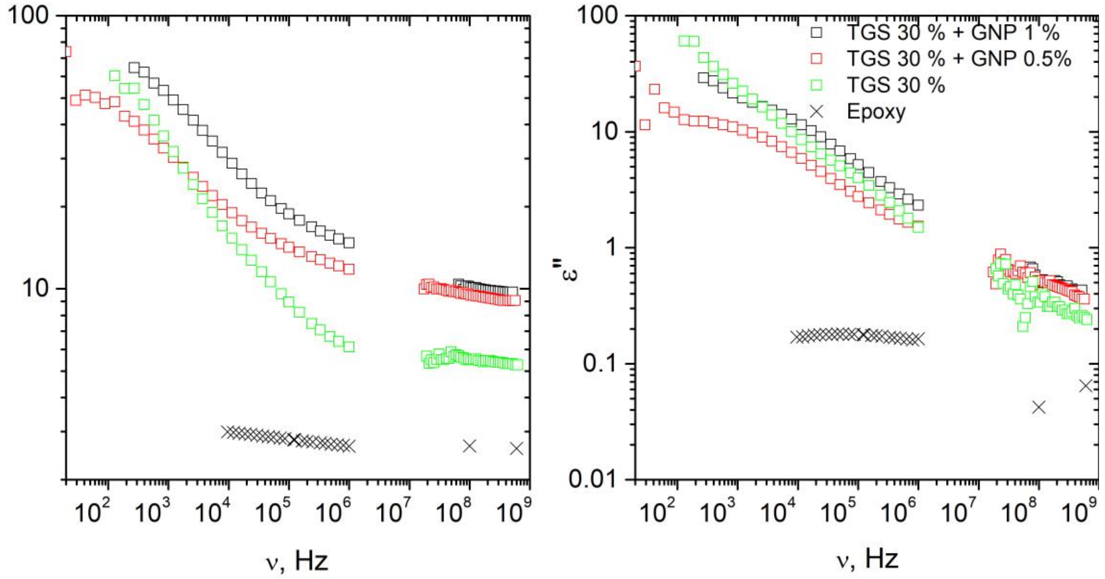


Figure 1 Dielectric spectra of hybrid TGS/GNP epoxy resin composites at room temperature.

[1] M. A. Marcus, Ferroelectric polymers and their applications, Ferroelectrics 40, 29-41 (1982).

[2] Y. Bai, Z. Y. Cheng, V. Bharti, H. S. Xu, Q. M. Zhang, High-dielectric-constant ceramic-powder polymer composites, Applied Physics Letters 76, 3804-3806 (2000).

[3] P. Martins, A. C. Lopes, S. Lanceros-Mendes, Electroactive phases of polyvinylidene fluoride : determination, processing and applications, Progress in Polymer Science 39, 683-706 (2014).

Effect of additive powders on the tribological properties of alumina coatings

L. Marcinauskas[1,2], **J. S. Mathew**[1], **M. Milieška**[2], **R. Česnavičius**[3], **R. Kėželis**[2], **M. Kalin**[4]

[1]Department of Physics, Kaunas University of Technology, Studentų str. 50, LT-51368 Kaunas, Lithuania
[2]Lithuanian Energy Institute, Breslaujos str. 3, LT-44403 Kaunas, Lithuania
[3] Department of Mechanical Engineering, Kaunas University of Technology, Studentų str. 56, LT-51424 Kaunas, Lithuania
[4]Laboratory for Tribology and Interface Nanotechnology, University of Ljubljana, Bogišićeva 8, 1000 Ljubljana, Slovenia

liutauras.marcinauskas@ktu.lt

Alumina (Al_2O_3) coatings are the most commonly used industrial-material for the protection of metallic parts due to high hardness, good strength, toughness, excellent chemical resistance, tribological and electrical insulation properties [1-2]. The tribological properties of alumina coatings could be enhanced due to the addition of carbon materials (graphite, carbon nanotubes, etc) or metal oxides (ZrO_2, TiO_2, etc) [3-6]. The tribological properties of alumina composite coatings deposited by plasma spraying depend on many factors such as: the type of additive material, its content, feedstock powder size, torch power, spraying distance, plasma torch design, etc [1, 4-6]. So, it is very important to determine the optimal deposition parameters in order to spray the alumina composites with improved tribological properties.

The aim was to investigate the tribological properties of Al_2O_3, Al_2O_3-graphite and Al_2O_3-ZrO_2 coatings. The coatings were deposited on stainless steel substrates (AISI 304L) at atmospheric pressure. For the formation, Al_2O_3, Al_2O_3-10 wt.% graphite and Al_2O_3-10 wt.% ZrO_2 powders were used. The deposition was performed using an air-hydrogen plasma at various distances. The surface morphology was investigated using a scanning electron microscopy (SEM). The elemental composition of the coatings was measured by energy dispersive X-ray spectroscopy (EDS). The surface roughness was determined using a Mitutoyo Surftest profilometer. Phase composition of the coatings was investigated by X-ray diffractometry. The tribological properties of the sprayed coatings were measured using a CETR-UMT-2 ball-on-disc tribometer.

It was obtained that the addition of graphite and ZrO_2 powders decreased the surface roughness of the sprayed coatings. SEM and EDS measurements demonstrated that graphite and ZrO_2 were homogenously distributed on the surface. The addition of graphite increased the oxygen concentration in the composites. The XRD measurements demonstrated that the dominant phases in the Al_2O_3 and Al_2O_3-graphite coatings were α-Al_2O_3 and β-Al_2O_3, and with Al_2O_3-ZrO_2 it was tetragonal-ZrO_2. The friction coefficient of Al_2O_3 coatings varied in the range of 0.74-0.75, whereas with the addition of graphite, the friction coefficient was reduced twice. The wear rate for the Al_2O_3 and Al_2O_3-graphite coatings were similar being in the range of $\sim 10^{-5}$ mm^3/Nm. Meanwhile, the alumina-zirconia coatings showed the lowest wear rate due to a plastic deformation.

[1] S. Goel, S. Björklund, N. Curry, U. Wiklund and S. V Joshi, Axial suspension plasma spraying of Al_2O_3 coatings for superior tribological properties, Surf. Coatings Technol., vol. 315, pp. 80–87, (2017).

[2] B.J. McEntire, B.S. Bal, M.N. Rahaman, J. Chevalier and G. Pezzotti, Ceramics and ceramic coatings in orthopaedics, J. Eur. Ceram. Soc., vol. 35, pp. 4327–4369, (2015).

[3] K. Hentour, A. Marsal, V. Turq, A. Weibel, F. Ansart, J.M. Sobrino, Y. M. Chen, J. Garcia, P.F. Cardey and C. Laurent, Carbon nanotube/alumina and graphite/alumina composite coatings on stainless steel for tribological applications, Mater. Today Commun. vol. 8, pp. 118-126, (2016).

[4] J.W. Murraya, G. A. Ranceb, F. Xua and T. Hussain, Alumina-graphene nanocomposite coatings fabricated by suspension high velocity oxy-fuel thermal spraying for ultra-low-wear, J. Eur. Ceram. Soc., vol. 34, pp. 1819-1828, (2018).

[5] S. Yugeswaran, V. Selvarajan, M. Vijay, P.V. Ananthapadmanabhan and K.P. Sreekumar, Influence of critical plasma spraying parameter (CPSP) on plasma sprayed Alumina–Titania composite coatings, Ceram. Int., vol. 36, pp. 141–149, (2010).

[6] B. Liang, G. Zhang, H. Liao, C. Coddet and C. Ding, Friction and wear behavior of ZrO_2–Al_2O_3 composite coatings deposited by air plasma spraying: Correlation with physical and mechanical properties, Surf. Coatings Technol., vol. 203, pp. 3235–3242, (2009).

Additive manufacture for microwave and THz components realization

P. Kuzhir[1]

1- Institute for Nuclear problems of Belarusian State University, Minsk Belarus

polina.kuzhir@gmail.com

Abstract: The first realization of three-dimensional (3D) “optical black hole” in microwave frequencies was presented recently on the basis of carbon hollow spheres [1,2]. Carbon-based cellular periodic structures of 100-300 microns cells might, from our point of view, offer interesting alternative for perfect absorption’ applications, as they will demonstrate resonant behavior in THz-infrared frequencies and therefore possibly might block electromagnetic energy in particular space spot [3,4].

Alternatively, lossy photonic crystals comprising nanocarbon based polymer composite skeleton of particular sophisticated cellular or layered geometry could be realized by additive technologies. Having a precise control of the structure and geometry of the 3D template, we will come to regular conductive cellular structure with pre-defined electromagnetic response.

The possibility to achieve perfect absorption of microwave-THz radiation by 3D-printed cellular or layered structures will be discussed in this communication along with different ways to tune the electromagnetic response.

[1] D. Bychanok,S. Li, A. Sanchez-Sanchez, G. Gorokhov, P. Kuzhir, F.Y. Ogrin, A. Pasc, T. Ballweg, K.Mandel, A. Szczurek, V. Fierro, and A. Celzard, Hollow carbon spheres in microwaves: bio inspired absorbing coating // Appl.Phys.Lett. 108, 013701 (2016)

[2] D. Bychanok, S. Li, G. Gorokhov, 1 K. Piasotski, 1 D. Meisak, P. Kuzhir, E.A. Burgess, C.P. Gallagher, F.Y. Ogrin, A.P. Hibbins, A. Pasc, A. Sanchez-Sanchez, V. Fierro, and A. Celzard, Fully carbon metasurface: absorbing coating in microwaves // J. Appl. Phys. 121(16):165103 (2017)

[3] Andrzej Szczurek; Alberto Ortona; Luca Ferrari; Ehsan Rezaei; Ghouti Medjahdi; Vanessa Fierro; Dzmitry Bychanok; Polina Kuzhir; Alain Celzard, Carbon periodic cellular architectures // Carbon, 88, 70–85 (2015)

[4] M. Letellier, J. Macutkevic, P. Kuzhir, J. Banys, V. Fierro, A. Celzard, Electromagnetic properties of model vitreous carbon foams // Carbon, 122, 217-227 (2017)

RUBBING AS A POWERFUL TOOL FOR MASS PRODUCTION OF TWO-DIMENSIONAL ATOMIC MATERIALS

G. Shmavonyan

National Polytechnic University of Armenia, 105 Teryan street, Yerevan, 0009, Armenia

gshmavon@yahoo.com

Recently 2D atomic materials, nanostructures and hybrid heterostructures have attracted much attention. Because of their unique properties and 2D nature, 2D materials are ideal candidates for developing 2D flexible and hybrid electronics. As the latter is lightweight, rugged, bendable, rollable, portable, and potentially foldable, it promises low-cost and large-area 2D material nanodevices and nanoproducts.

Nowadays there exist numerous techniques for obtaining 2D atomic materials. Their scaling up is still not straightforward due to the difficulty of the setup, the relatively low yield to fulfill the potential market demand and usage of different chemicals, solutions and devices. Here we report the substrates [1, 2] and rod [3-5] rubbing methods for mass production of high quality, large size and low cost 2D atomic materials, hybrid structures and devices directly on any substrate.

The substrates rubbing method [1, 2] for obtaining 2D materials (graphene, h-BN, etc.), their hybrid structures, dispersion and powder consists in putting pristine bulk (graphite, h-BN, MoS_2, etc.) layered material (i.e. crystalline powder), hydrogenated fullerenes, carbon nanotubes, etc. between two solid state substrates with atomically flat or terraced surfaces and rubbing the substrates against each other manually or mechanically in any direction, so that the crystalline powder uniformly spreads between them and covers the surfaces of the two substrates with it. As a result, mono- and few layers consisting of nanostripes are formed, which are mono- and few- atomic layers of exfoliated flakes organized in self-assembled narrow bands of nanosized quantum dots. The formed nanostripes are new nanstructures and are first reported in [1, 2], which can find wide application in different areas. Thus, the substrates rubbing method is an extremely simple (one step process), fast (lasts only seconds), cost-effective, chemical- and transfer-free, reliable, highly productive, ecologically clean, universal (allows obtaining any 2D material on any substrate) and industrially scalable method for obtaining high quality and extremely large size 2D materials (including their dispersion and powder), hybrid structures and devices on flexible and rigid substrates. The substrates rubbing method will foster the development of flexible electronics.

The rod rubbing method [3-5] allows obtaining 2D atomic layers by repeatedly rubbing (manually and mechanically) a pristine layered bulk material rod (i.e. graphite) or drawing lines by the rod (i.e. pencil) along the same path on insulating (paper, glass, mica, ceramics, plastic, etc.), semiconducting (Si, SiC, ZnO, etc.) or metallic (cobalt, etc.) substrates. The obtained top-most layer of the multilayer structure is a 2D atomic layer, i.e. mono- and few layer graphene. The formed 2D layer consists of multiple nanostripes (as in the case of the substrates rubbing method). The rod rubbing method is an extremely simple, fast (lasts only seconds), cost-effective, chemical- and transfer-free, reliable, highly productive, ecologically clean, universal (allows obtaining 2D material on any substrate) and industrially scalable method for obtaining both 2D atomic layers and 2D layer/multilayer structures on any substrate with ultraflat or rough surface and fabricating flexible, portable and disposable pencil-on-paper 2D devices. The substrates rubbing method will enable the development of 2D material-based and paper-based devices and flexible electronics.

So, rubbing (rod or substrates) is a powerful tool for mass production of any 2D atomic material, structure and device with an extremely large size on any substrate, as well as 2D material enhanced nanoproducts and consumer products [6].

[1] Shmavonyan G.Sh., Vázquez Vázquez C., López-Quintela M.A. Transl. Mater. Res., IOP Publishing, 4 (2), 025001, 2017.

[2] López-Quintela M.A., Shmavonyan G.Sh., Vázquez Vázquez C., Patent No: ES 2575711 A1, Publication date: November 3, 2016, WO 2016/107942 A1.

[3] Shmavonyan G.Sh., Mailian A.R., Mailyan M.R., López-Quintela M.A. European Conference on the Synthesis, Characterization and Applications of Graphene.(GRAPHEsp), Abstract book, p. 41, February 18-21, 2014, Lanzarote, Spain.

[4] Shmavonyan G.Sh., Mailian A.R., Mailian M.R., Vázquez Vázquez C., López-Quintela M.A. 4th International Colloids Conference: Surface Design and Engineering, Paper P3.07, June 15-18, 2014, Madrid, Spain.

[5] Shmavonyan G.Sh., Vázquez Vázquez C., López-Quintela M.A. 5th International Colloids Conference: Surface Design and Engineering, Paper P067, June 21-24, 2015, Amsterdam, Netherlands.

[6] Shmavonyan G.Sh. Monograph Chapter "Graphene, two-dimensional atomic materials and their hybrid structures" in the 3-volume Coherent Textbook "Optical Nanospectroscopy", Vol. 3: Applications, McMillan N. (Eds.), Publisher De Gruyter, 2018.

Planar Perovskite Solar Cells Using Coordination Fullerene Polymers as Acceptor Layer

C. Moise[1], A. Pumnea[1], K. Winkler[2], E. Gradzka[2], M. Wysocka-Zolopa[2], M. Enachescu[1]

1 Center for Surface Science and Nanotehnology University POLITEHNICA of Bucharest ROMANIA

2 Institute of Chemistry, University of Bialystok POLAND

Perovskite solar cells can be composed of thin film of perovskite donor and fullerene derivative acceptor sandwiched between a PEDOT:PSS coated ITO positive electrode and a low work function metal negative electrode. So far, [6,6]-phenyl-C_{61}-butrilic acid methyl ester ($PC_{60}BM$) and its corresponding C_{70} derivative ($PC_{70}BM$) have been dominantly used as the acceptors in these solar cells.[1]

We will present our recent and preliminary work regarding a solar cell using C60-Pd_3 coordination fullerene as acceptors layer. The cell structure is GLASS/ITO/PEDOT-PSS/PEROVSKITE/C60-Pd3/LiF/GOLD. Very thin LiF layer was introduce to optimize Fermi levels.

The C60-Pd_3 was synthesized by group of Prof. Winkler, and all the other materials have been purchased from Sigma Aldrich.

The best cell was generating 500mV in 1 Sun light but reproducibility is rather poor demanding much efforts for optimization. The cell degradation in air is also a key point requiring some encapsulation to avoid contact with air and humidity.

1. Meng, L.; You, J.; Guo, T.F.; Yang, Y. *Acc. Chem. Res.* **2016**, *49*, 155-165.

Poster Presentations

Casted Bio-based Polyurethanes Nanocomposites Processed by Ultrasonic Dispersion of Ultra-Small Content of Multiwall Carbon Nanotubes Stabilized by Metallic Oxide Nanoparticles

S. Gaidukovs[1], E. Skadins, K.Smirnova, G.Gaidukova[2]

1- Institute of Polymer Materials, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena 3/7, LV-1048 Riga, Latvia

1- Institute of Applied Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena 3/7, LV-1048 Riga, Latvia

Corresponding author email address: sergejs.gaidukovs@rtu.lv

Abstract:

In the present investigation, we prepared solution casted polyurethane nanocomposites filled with the ultra-small content (below 0.5 wt.%) of the complex nanoparticles of CNT, ZnO, OMMT, SiO_2. Bio-based polyol was used as a matrix to disperse the several nanoparticles by the use of the ultrasonic treatment for 15 min. The preparation scheme is shown in Figure 1. Pristine unmodified CNT does not show the good stable dispersion in the polar polyol. Experimentally it was concluded that small content of the metallic oxide nanoparticles can stabilize the dispersion of CNT in the polyol matrix. Finally, the processed dispersions of polyol and nanoparticles were blended with the isocyanate and casted on the Teflon surface to produce free films for further investigations. The free films of the bio-based polyurethanes is the same as reported previously [1].

It was concluded that the mechanical and thermal properties of the bio-based polyurethane – carbon nanotubes nanocomposites are significantly enhanced. The modulus of elasticity of the nanocomposites showed increase for 2-folds in comparison to unfilled system. Thermal stability in the air of the nanocomposites increased also. Electron microscopy showed some extent of the agglomeration of nanoparticles in the polymer matrix.

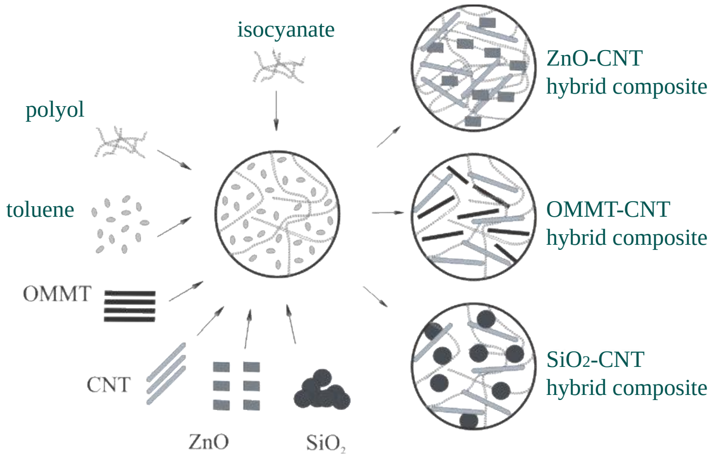


Figure 1 Schematic preparation of nanocomposites.

[1] Gaidukov, S., Cabulis, U., Gromilova, K., Tupureina, V., Grigalovica, A. Preparation and structural properties of free films from rapeseed oil-based rigid polyurethane-montmorillonite nanocomposites. International Journal of Polymer Science, 834595, 1-8, (2013).

Deposition of amorphous carbon films and nanostructures at atmospheric pressure

A.Iljinas[1]*, L. Marcinauskas[1,2], M. Černauskas[1], V. Dovydaitis[1], P. Valatkevičius[2]

1- Department of Physics, Kaunas University of Technology, Studentu str. 50, LT-51368, Kaunas, Lithuania
2- Lithuanian Energy Institute, Breslaujos 3, LT-44403 Kaunas, Lithuania

aleksandras.iljinas@ktu.lt

Amorphous carbon films and carbon nanostructures (nanotubes, graphene, glassy carbon, carbon black, nanocrystallites and etc.)) have attracted considerable interest due to their unique mechanical, tribological, optical or electrical properties. These fascinating properties make the carbon materials very promising candidates for the application in a electronics, optics, engineering or biomedical fields [1-4].

The formation of carbon films or nanostructures were performed at atmospheric pressure using a direct current plasma torch [5]. The deposition was done on the silicon-gold substrates. A thin gold (~20 nm) layer was sputtered on silicon substrate using magnetron sputtering. Argon or argon-hydrogen mixture were used as plasma forming gases. Meanwhile an acetylene gas was used as precursor (flow rate varied from 0.026 l/min to 0.066 l/min). The substrates were chemically cleaned and also kept for 30-60 s in the argon or argon-hydrogen plasma before starting the formation. Surface morphology was investigated by scanning electron microscopy (SEM). The elemental composition was analyzed by energy dispersive X-ray (EDX) spectroscopy. The bonding structure was investigated by Raman scattering (RS) spectroscopy and Fourier transform infrared (FTIR) spectrometer. The SEM measurements demonstrated that the amorphous carbon films prepared without the hydrogen consists of columnar structure. It was obtained that the columns size decreased with the decrease of acetylene flow rate. The content of the oxygen in the films was up to 10 at. %. The RS results indicated that the carbon films are graphite-like with glassy carbon phase and graphite micro/nano-crystallites. The nanocrystalline graphite films or micro and nanosize carbon were formed with the addition of the hydrogen gas.

[1] S. Neuville, New application perspective for tetrahedral amorphous carbon coatings, QScience Connect, 8, 1–27, (2014).
[2] J. Robertson, Diamond-like amorphous carbon, Materials Science and Engineering, 37, 129-281, (2002).
[3] K.A. Shah and B.A. Tali, Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A review on carbon sources, catalysts and substrates, Materials Science in Semiconductor Processing, 41, 67–82, (2016).
[4] W.W. Liu, S.P. Chai, A.R. Mohamed and U. Hashim, Synthesis and characterization of graphene and carbon nanotubes: a review on the past and recent developments J. Ind. Eng. Chem., 20, 1171–1185, (2014).
[5] Marcinauskas L., Černauskas M., Milieška M., Reso D. The effect of hydrogen addition in argon-acetylene plasma on the structure of amorphous carbon films, Journal of non-crystalline solids, Vol. 466–467, 1–7, (2017).

Carbon/Molybdenum Carbide Based New Hybrid Inorganic Nanomaterials

P. Umek[1], D. Vengust[1], M. Vilfan[1], A. Mrzel[1]

1- Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

Polona.Umek@ijs.si

Abstract: We report herein the synthesis of hybrid inorganic materials composed of densely grown carbon nanowires on the surface of molybdenum carbide fibers. A direct carburization approach of $Mo_6S_{9-x}I_x$ ($4.5 < x < 6$) nanowire bundles [1] of different morphologies was used for the synthesis of molybdenum carbide nanofibers [2]. The typical nanowire length is up to several micrometers with a diameter between 10 and 20 nm. As carbon source was used ethane (C_2H_4). Gram quantities of molybdenum carbide nanowires composed of mainly MoC and Mo_2C phases were obtained. Further reduction in hydrogen (H_2) atmosphere gave a single phase Mo_2C nanowires. Characterization with electron microscopy revealed that at the surface of Mo_2C nanofibers grown amorphous carbon nanowires reach in length up to 100 nm and have diameters between 10 and 20 nm (Figure 1). In the next step, the surface of this hybrid material served as substrate for the formation of platinum nanoparticles. The nanoparticles with diameters of several nanometers readily formed from the water solution of platinum metal complex at room temperature at surfaces of the carbon nanowires. Straight forward and efficient decoration of synthesized hybrid material by platinum nanoparticles in combination with transformation pathways of molybdenum carbide nanowires, gives rise to novel hybrid materials comprising platinum/nanocarbon fibers/molybdenum carbide based nanowires which are promising in a wide range of different applications including composite, sensors and catalyst.

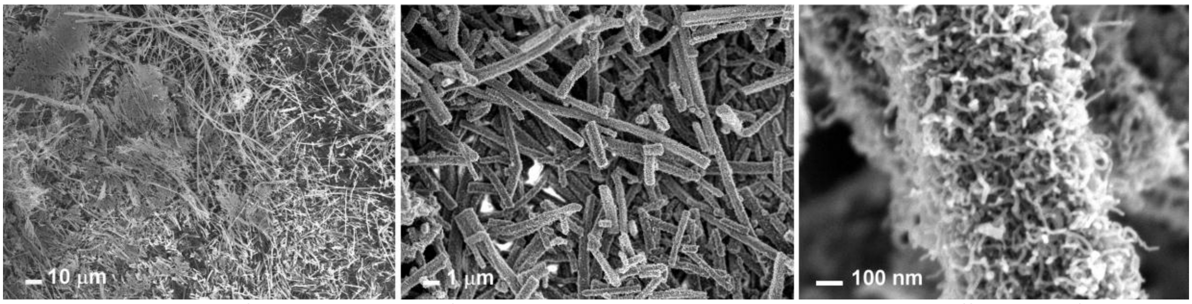


Figure 1 SEM images of molybdenum carbide fibres covered with carbon nanowires (C/MoC_2) taken at different magnifications.

[1] M. Remškar, A. Mrzel, M. Viršek and A. Jesih, Inorganic nanotubes as nanoreactors: the first MoS_2MoS_2 nanopods, Adv. Mat. Vol. 19, 4276–4278 (2007).

[2] D. Vengust, J. Ravnik, A. Mrzel and M. Vilfan, Molybdenum carbide nanowires: facile synthesis, a new hybrid phase and their use as transparent electrodes, RSC. Adv. Vol. 6, 90806–90812 (2016).

The influence of multi-walled carbon nanotubes on crystallization behavior of poly(lactide)

Nevena Vukić[1], Jelena Tanasić[1], Suzana Cakić[2], Milena Marinović-Cincović[3],
Jaroslava Budinski-Simendić[1], Ivan S Ristić[1]

[1]University of Novi Sad, Faculty of Technology, Novi Sad, Serbia
[2]University of Nis, Faculty of Technology, Leskovac, Serbia
[3]University of Belgrade, Vinča Institute of Nuclear Science, Belgrade, Serbia

Poly(lactide) (PLA) is a biobased, biodegradable and biocompatible thermoplastic aliphatic polyester with a broad range of applications. One of the most important PLA properties is a degree of crystallinity, because it influences the proccessability and the application of this polymer, especially in medicine and pharmacy. The degree of crystallinity for poly(lactide) can be controlled in various ways, for example, by adding of nanoparticles which can influence the crystallization of poly(lactide) by a heterogeneous nucleus effect. Due to the high surface area, carbon nanotubes can be a highly efficient nucleating agent for poly(lactide). The crystallization rate of PLA composites with carbon nanotubes depends on the applied CNT modification method, CNT dispersion and the concentration of the nanotubes in the composite material. In this research the influence of the chemically functionalized multi-walled carbon nanotubes (MWCNTs) on the crystallization behavior of poly(L-lactide) was investigated. Functionalization of MWCNTs was carried out through the oxidation reaction with nitric and sulfuric acid. Series of PLLA-MWCNT nanocomposites, with different contents of functionalized MWCNTs (0.7, 1.6 and 2.1wt%), were synthesized via ring-opening solution polymerization of L-lactide. Crystallization kinetics was investigated by differential scanning calorimetry (DSC) and application of Ozawa isoconversional method. It is shown that the addition of carbon nanotubes can influence the kinetic parameters of the poly(L-lactide) crystallization, primarily the activation energy, as well as the order of the crystallization reaction. The effects of functionalized MWCNTs on the crystallization behavior of PLA were investigated also by X-ray diffraction analysis (XRD) and it was confirmed that the MWCNTs increased the crystallinity of PLA nanocomposite materials.

Keywords: *Poly(lactide), multi-walled carbon nanotubes, crystallization kinetics, differential scanning calorimetry.*

Acknowledgements

Authors would like to thank Ministry of Education, Science and Technological Development Republic of Serbia (Project No. III 45022) and COST action CA15107 for support.

Synthesis of titanium dioxide – carbon xerogel composites

Amra Bratovcic[1]

1 University of Tuzla, Faculty of Technology, Univerzitetska 8, 75000 Tuzla, Bosnia and Herzegovinat

amra.bratovcic@untz.ba

Abstract:

TiO_2-carbon xerogel composites were prepared by sol-gel polymerization using resorcinol (R) and formaldehyde (F) as carbon and titanium (IV) butoxide as precursor, respectively, in the presence of a cationic surfactant (HDA, hexadecyamine). In this synthesis procedure, HDA (S) was dissolved in n-heptane and heated at 65°C under reflux and stirring (450 rpm). A mixture containing resorcinol (R), formaldehyde (F) and water (W) was added dropwise into the above solution. After this addition, the proper amount of titanium butoxide was added drop by drop to the mixture. The molar ratio of the mixture was R/F = 1/2, R/W = 1/14 and R/S = 4.5. The formed gel was aged at 65 °C for 24 h under stirring, and after that the suspension was filtered and the obtained solid, which has an intense orange color. Pyrolysis of organic xerogel-titanium oxide composites to obtain the corresponding carbon xerogel-titanium oxide composites was carried out at 900°C in a tubular furnace using a N_2 flow.

TiO_2-carbon xerogel composite was refereed as CHTi20 (20 corresponding to the theorical percentage of titanium oxide present in the carbonized composite, e.g. CHTi20 should contain 20% wt. of TiO_2). A pure carbon xerogel (CH) was prepared following the same sol-gel method used for CHTi20 synthesis (but without TiO_2). The synthetized CHTi20 was studied in photocatalytic degradation of paracetamol under Vis and UV light. The results showed much better photocatalytic activity under UV light.

Polymerized Ionic Liquids as Sensitive Layers of Chemiresistors

M. Vrňata, E. Marešová, J. Vlček, P. Fitl, D. Tomeček, R. Šípka

Department of Physics and Measurement, University of Chemistry and Technology in Prague, Technická 5, Prague 6, CZ-166 28, Czech Republic

Corresponding author email address: martin.vrnata@vscht.cz

Abstract: Polymerized ionic liquids (PILs) have been reported for the first time in 1998, and a brief overview of their properties can be found in [1]. Their electrotransport properties are unique (when compared with other organic substances), as they are purely ionic conductors. Surprisingly still, their applications in chemiresistors are at a pioneering stage. A few reports are dedicated to sensitive layers based on composites containing PILs, e.g. [2].

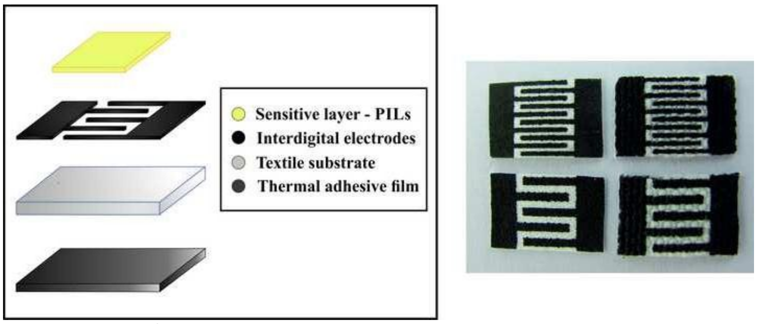


Figure 1 Vertical architecture of the chemiresistor (left) and its real appearance indicating variable distances between the electrodes (right).

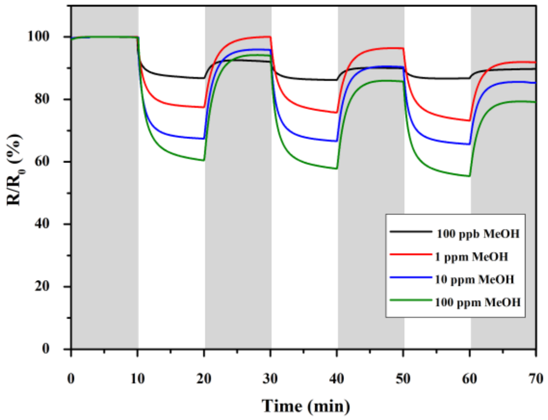


Figure 2 Response of sensor based on poly(tributylhexylphosphonium 3-sulfopropylacrylate) to methanol vapors (concentrations 100 ppm, 10 ppm, 1 ppm and 100 ppb).

This contribution presents pioneering research of chemiresistors on textile substrates equipped with graphite electrodes and in-situ polymerized poly(tetrabutylphosphonium 3-sulfopropylacrylate) or poly(tributylhexylphosphonium 3-sulfopropylacrylate) sensitive layers. Both DC- and AC- responses to 10 ppm of methanol, nitrogen dioxide, 4-bromoacetophenone and diethylmalonate were then investigated at laboratory temperature – the reference was "pure" synthetic air. The evaluation of these responses is detailed in [3]. The DC- responses varied from 0.48 to 1.36 and AC- responses from 8 to 26 deg. It was shown that sensor dynamics depends mainly on molecular weight of the analytes. Moreover, the magnitude of AC-responses correlated both qualitatively and quantitatively with the dipole moment of the analyzed molecule.

[1] N. Nishimura and H. Ohno, 15th anniversary of polymerised ionic liquids, Polymer, vol. 55, pp. 3289–3297, (2014).
[2] C. Willa, J. Yuan, M. Niederberger, D. Koziej, When Nanoparticles Meet Poly(Ionic Liquid)s: Chemoresistive CO$_2$ sensing at room temperature, Advanced. Functional Materials, vol. 25, pp. 2537–2542, (2015).
[3] M. Vrňata, D. Kopecký, F. Vysloužil, V. Myslík, P. Fitl, O. Ekrt, J. Hofmann, L. Kučera, Impedance properties of polypyrrolic sensors prepared by MAPLE technology, Sensors Actuators B Chemical, vol. 137, pp. 88–93, (2009).

Preparation and characterization of bio-based polybutylene succinate / graphene biodegradable composites

O.Platnieks[1], **V.K.Thakur**[2], **S. Gaidukovs**[1],

1- Institute of Polymer Materials, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena 3/7, LV-1048 Riga, Latvia
2-Cranfield University, College Road, MK43 0AL Bedfordshire, United Kingdom

Corresponding author email address: oplatnieks@gmail.com

Abstract:
Bio-based and biodegradable materials are of great interest to reduce growing pollution problems. We prepared and characterized the composite based on the bio-based polybutylene succinate (PBS) and the bio-source graphene. PBS is a biodegradable aliphatic polyester derived from renewable and fossil resources, with potential being 100% bio-based. PBS/graphene composite films were prepared varying the filler content from 0.5 till 6 wt.%. These films were characterized by thermal differential calorimetry (DSC) dynamic mechanical analysis (DSC), thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA), thermomechanical analysis (TMA) and dielectric spectroscopy (DS) properties.

Poly-Ionic Liquids With Fullerenes Nanocomposite Materials for Gas Chemiresistors: Synthesis and Characterization

R. Šípka, J. Vlček, E. Marešová, J. Otta, Š. Havlová, P. Fitl, D. Tomeček, M. Vrňata

Department of Physics and Measurement, University of Chemistry and Technology in Prague, Technická 5, Prague 6, CZ-166 28, Czech Republic

Corresponding author email address: vlcekj@vscht.cz

Abstract: Polymeric ionic liquids (PILs) are the new class of materials with unique features for sensor devices [1-3]. 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 can affect this ion mobility by filling of their free space and also direct chemical interaction with ionic species. We found that addition of nanocarbons into the PILs can also improve selectivity and sensitivity.

In this contribution we present gas sensing by nanocomposites consists 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 (P4444) and Tributyloctylphosphonium (P4448). We describe synthesis 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 impedance changes (in range of 1 mHz - 1 MHz) to selected gas analytes (alcohol vapors, NO_x, CO_2). Material behaviour was fitted by Randles-circuit and sensitivity is then determined from the Warburg impedance as an ion mobility change. Values of Warburg impedance of 191.9×10^{-9} S $s^{1/2}$ and of 418.9×10^{-9} S $s^{1/2}$ for pure PILs P4444 and P4448 respectively were evaluated from electrochemical impedance measurement. Warburg impedance evaluated for samples with addition of C_{60} was even higher in comparison with pure PILs - 112% and 105% for P4444 and P4448, respectively. We present characterization of prepared nanocomposites by Raman, UV-VIS and impedance spectroscopy.

[1] E. Marešová, D. Tomeček, P. Fitl, J. Vlček, M. Novotný, L. Fišer, Š. Havlová, P. Hozák, A. Tudor, T. Glennon, L. Florea, S. Coyle, D. Diamond, Z. Skaličan, M. Hoskovcová, M. Vrňata, Textile chemiresistors with sensitive layers based on polymer ionic liquids: Applicability for detection of toxic gases and chemical warfare agents, Sensors and Actuators B: Chemical, 266, pp. 830-840, (2018).

[2] A. Tudor, L. Florea, S. Gallagher, J. Burns, D. Diamond, Poly(Ionic Liquid) Semi-Interpenetrating Network Multi-Responsive Hydrogels , Sensors, 16, 1-16, (2016).

[3] B. Ziołkowski, D. Diamond, Thermoresponsive poly(ionic liquid) hydrogels, Chemical Communications, 49, 10308-10310, (2013).

Laser Patterning of Fullerene Thin Films

P. Fitl, J. Otta, J. Vlček, D. Tomeček, Š. Havlová, E. Marešová, M. Vrňata

1- Department of Physics and Measurement, University of Chemistry and Technology in Prague, Technická 5, Prague 6, CZ-166 28, Czech Republic

fitlp@vscht.cz

Abstract: 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 fullerenes and other organic semiconductors. The source substrates were prepared as follows: Thin glass slides with sputtered metal layer (gold - thickness ~ 100 nm) were cleaned and dried. Side with sputtered metal was then covered with a thin layer of purified organic substances – C60, Phthalocyanines, Porphyrines, deposited by organic molecular evaporation in high vacuum chamber (10-5 Pa, dep. Rate ~ 0.1-10nm/min, substrate temp. 20 – 300 °C). The temperature of deposition source and substrate was selected for each substance so as to achieve optimal growth rate and to avoid thermal decomposition of materials. In the next step CW laser depositions were carried out from these substrates. The deposition apparatus include micro CNC machine (minimal step adjustable to 300 nm) equipped with the semiconductor laser (405 nm, 50 mW, spot 4 microns) in continual mode and focusing optics. The distance between source substrate and target (i.e. glass, silicon or alumina substrates) was varied between 1-100 micrometers. Deposition process was held in an inert gas (Argon, Nitrogen) at atmospheric pressure. Morphology and microstructure were studied by optical, electron microscopy and AFM. Chemical composition of deposited structures was studied by FTIR. It was proved that chemical structure of all chosen substances is not affected by this deposition technique. The best lateral resolution of prepared structures was obtained for source layer thickness of 100-150 nm. Employing our technique we are able to achieve precise and reproducible laser transfer of fullerenes to the substrate with lateral structural resolution of 6 microns.

Wake effect in the interaction of an external charged particle with a graphene-sapphire-graphene structure due to excitation of plasmon-phonon hybrid modes

I. Radović[1], V. Despoja[2], L. Karbunar[3], Z. L. Mišković[4]

1- Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia
2- Institute of Physics, Bijenička 46, HR-10000 Zagreb, Croatia
3- School of Electrical Engineering, University of Belgrade, Bulevar Kralja Aleksandra 73, 11120 Belgrade, Serbia
4- Department of Applied Mathematics, and Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

iradovic@vin.bg.ac.rs

Abstract: We study the wake effect due to excitation of a plasmon-phonon hybrid mode in a sandwich-like structure consisting of two doped graphene sheets, separated by a layer of Al_2O_3 (sapphire), which is induced by an external charged particle moving parallel to the structure. The response function of each graphene is obtained using two approaches within the random phase approximation: an *ab initio* method that includes all electronic bands in graphene and a computationally less demanding method based on the massless Dirac fermion (MDF) approximation for the low-energy excitations of electrons in the π bands. The response of the sapphire layer is described by a dielectric function consisting of several Lorentzian terms. We evaluate the total electrostatic potential in the plane of the upper graphene sheet for a particle moving at the sub-threshold speed for the wake effect in a single, free graphene. We show that, when the space between graphene sheets is air, there is only a sharp, somewhat asymmetric peak in the potential at the position of the particle. On the other hand, when the space is filled with sapphire, there is a prominent wake pattern in the potential behind the particle resulting from a low-frequency plasmon-phonon mode. It can be noted that the analytical MDF model reproduces the overall shape and the period of quasi-oscillations in the wake potential obtained from the *ab initio* calculations.

EVALUATION OF THE OPTICAL PROPERTIES OF ACRYLIC RESIN DENTURE BASE MATERIAL (PMMA) MODIFIED WITH GOLD NANOPARTICLES

Veselinović V[1], Trtić N[1], Adamović T[1] ,Rudolf R[2]

1. *University of Banja Luka, Faculty of Medicine, Department of Dentistry, Bulevar vojvode Petra Bojovića 1A, 78 000 Banja Luka valentina.veselinovic1@gmail.com natasa.trtic@gmail.com dr.tijanalatincic@live.com*
2. *University of Maribor, Faculty of Mechanical Engineering, Smetanova ulica 17, 2000 Maribor, Slovenia Zlatarna Celje d.o.o., Kersnikova 19, 3000 Celje, Slovenia, rebeka.rudolf.rudolf@um.si*

Corresponding author email address: valentina.veselinovic1@gmail.com

BACKGROUND: Polymethylmethacrylate (PMMA) is the most widely used mobile denture base material [1]. Addition of different kind of nanoparticles to PMMA is the most attractive directions in the improvement of mechanical and biological materials properties [2,3]. The patient interprets the success of a mobile denture therapy from two aspects: function and aesthetics in which the ability to restore the gingival color is very important. To date, there are no studies that dealt with the aesthetic parameters of the color change of PMMA for denture base after its modification with gold nanoparticles.

AIM: This study aimed to evaluate optical properties of novel composite - heat-cured PMMA incorporated with different amounts of gold nanoparticles, produced by Ultrasonic Spray Pyrolysis (USP) from the precursor solution Au (III).

MATERIAL AND METHOD:. The synthesis of polymethylmethacrylate PMMA (ProBase Hot Monomer, IvoclaVivadent, Liethenstein) modified with highly dispersed gold nano-particle (AuNPs) are performed in special manner. The colour difference between the control PMMA and the remaining samples PMMA/AuNP1-3 with embedded gold nanoparticles containing 0.12, 0.43, 0.74 and 0 (wt.%) gold nanoparticles were evaluated. Specimens without gold nanoparticles served as control. A spectrophotometer Datacolor SF600 plus was used to measure the color in L* (brightness), a* (red-green), b* (yellow-blue) in CIELAB system.

RESULTS: Color changes of denture base acrylic resins were significantly affected by addition of gold nanoparticles ($p<0.05$). The optical properties of the PMMA incorporated with gold nanoparticles changed depending on the amount gold nanoparticles. The color difference, expressed in terms of value ΔE, are in the range from 2,6 – 4,9.

CONCLUSION: The results indicated that optical properties of novel PMMA resin material modified with gold nanoparticles strongly correlating with concentration of AuNPs and have a strong influence on esthetic aspect of prosthetic therapy, which could lead to more patient satisfaction.

Keywords: polymethilmethacrylat, denture base, gold nanoparticles, color properties

[1] Hisada, K.; Takeshita, T. "Poly(methyl methacrylate) (PMMA)-based denture base materials with good biocompatibility" Jpn. Kokai Tokkyo Koho, JP 2007332044 A 20071227 (2007)

[2] Pal KS, Ranganath LM, Gaikwad AV, Sarapur S, Jain SK Nanoparticles in prosthodontics – boon or bane, IJOCR., 3:8 (2015)

[3] Goiato MC, Zuccolotti BC, dos Santos DM, Sinhoreti MA, Moreno A. Effect of intrinsic nanoparticle pigmentation on the color stability of denture base acrylic resins. J Prosthet Dent. 110(2):101-6. (2013)

Crystal growth of conjugated oligomers on graphene

J. Kiilsholm[1], O. Albrektsen[2], M. Huss-Hansen[3] M. Knaapila[3], J. Kjelstrup-Hansen[1]

1- Mads Clausen Institute, University of Southern Denmark, 6400 Sønderborg, Denmark
2- Mæersk Mc Kinney Moller Institute, University of Southern Denmark, 5230 Odense, Denmark
3- Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

matti.knaapila@fysik.dtu.dk, jkh@mci.sdu.dk

Abstract: We present studies of crystal growth of optically active conjugated polymers and oligomers on a graphene surface in a phototransistor setup. The main emphasis is on thiophene and pyrrolopyrrole type rigid molecules vacuum deposited on CVD or solution grown graphene. The study shows that the crystal size and the molecular alignment can be controlled depending on the deposition conditions. These influence photoabsorption and thus the device performance.

Reinforcement of Glassy and Rubbery Epoxy Polymers with 1-D, 2-D and 3-D Carbon Nanostructures

D. J. Giliopoulos[1], P. I. Xidas[1], D. Gournis[2], D. N. Bikiaris[1], K. S. Triantafyllidis[1,*]

1- Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
2- Department of Materials Science and Engineering, University of Ioannina, Ioannina, Greece

Corresponding author email address: ktrianta@chem.auth.gr

Abstract:

Improvement of polymers' properties by incorporation of small fractions (e.g. ≤ 5 wt%) of inorganic nano-additives is related with two parameters: a) homogeneous dispersion of the nano-objects within the polymer and b) good interfacial properties between the polymer matrix and the surface of the nano-filler. Both these parameters are strongly dependent on the morphology, structure and surface properties of the nano-additives and their chemical affinity with the polymer.

In the present study, three different types of carbon nanostructures (1-D carbon nanotubes, 2-D graphene oxide and 3-D mesoporous carbon nano-particles) were used as nano-additives to epoxy resin polymers. In order to improve interaction with the resin, their surface was organically modified with different types of modifiers. The carbon nanostructures were characterized for their structural, morphological and surface properties which were correlated with the thermal, mechanical and conductivity properties of the respective epoxy - carbon nanocomposites.

The good dispersion of carbon nanotubes within the epoxy polymer after functionalization with hexamethylene diamine can be seen in the TEM images of Figure 1.

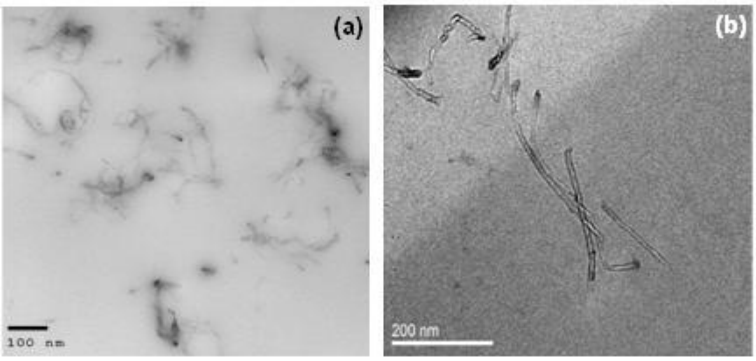


Figure 1. TEM images of a) rubbery and b) glassy epoxy-CNTs nanocomposites prepared with hexamethylene diamine modified MWCNTs (CNTs loading was 0.1 wt%)

The tensile strength measurements of the rubbery epoxy nanocomposites prepared with the pristine and functionalized MWCNTs revealed a substantial improvement of the mechanical properties offered by the amine-functionalized CNTs. More specifically, a simultaneous increase of Young's modulus, tensile stress, tensile strain and toughness up to 34%, 154%, 118% and 453% respectively, was recorded for CNTs loading of 0.1 wt%, compared to the pristine epoxy. In the case of the nanocomposite with pristine MWCNTs, an increase of tensile stress, tensile strain and toughness was recorded (28%, 142% and 331% respectively) accompanied though by decrease of Young's modulus, indicating that unmodified carbon nanotubes can substantially improve the toughness but not the stiffness of the rubbery epoxy polymer. With regard to the graphene oxide (GO) nano-fillers, the dynamic mechanical analysis of the glassy epoxy nanocomposites containing 0.01 to 1 wt% GO showed that the increase of GO concentration induces a parallel increase of polymer's stiffness as indicated by the decrease of storage modulus. More results on the thermal, mechanical and conductivity properties of the epoxy polymer nanocomposites prepared with CNTs, GOs and mesoporous carbon fillers will be presented and discussed.

Low-Kinetic Energy Nitrogen Ion Irradiation of Vertically-aligned Carbon Nanotubes

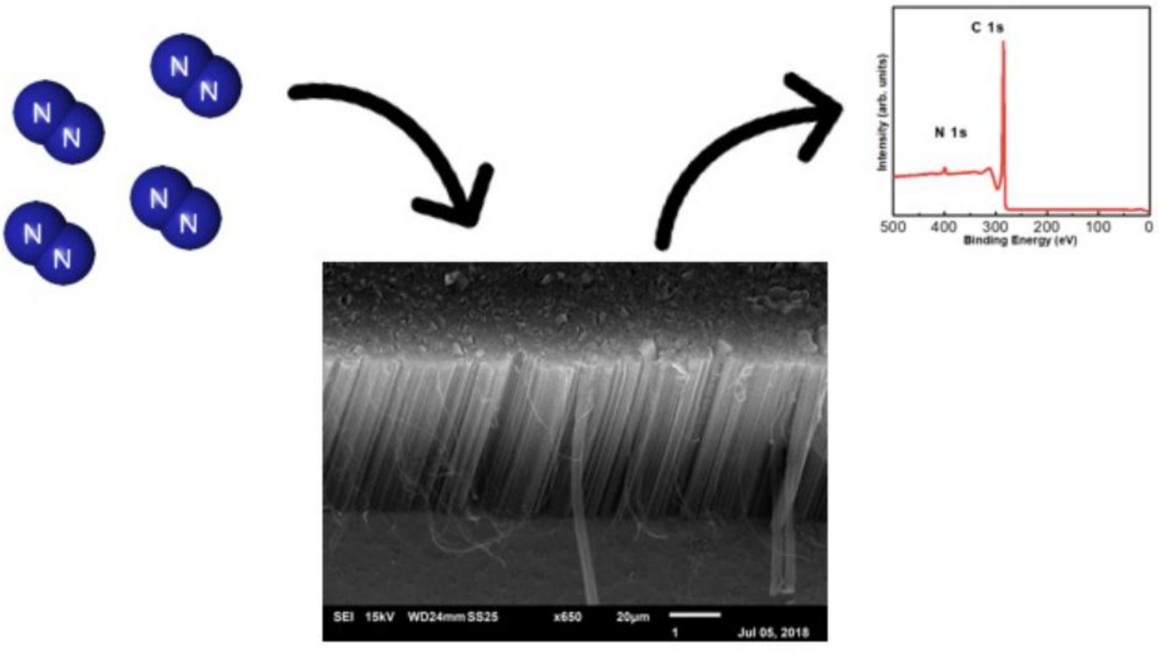
Sebastián I. Cortez[1], Ayrton Sierra[2], Jean-François Colomer[2], Carla Bittencourt[3]

1- Yachay Tech University, School of Physical Sciences and Nanotechnology, Urcuquí 100119, Ecuador
2- Research group on carbon nanostructures (CARBONNAGe), University of Namur, Belgium
3- Chemistry of Interaction Plasma Surface (ChIPS), University of Mons, Belgium

sebastian.cortez@yachaytech.edu.ec

In this work we analyze the grafting of Nitrogen atoms at the tips of vertically-aligned Carbon Nanotubes (v-CNTs) synthesized by catalytic chemical vapor deposition (CCVD) at atmospheric pressure [1]. For the v-CNT synthesis the iron catalyst was prepared by magnetron sputtering on an Al_2O_3 buffer layer deposited on Si wafers with native SiO_2, the precursor used for the growth was C_2H_4 at 750 ℃ ［2］. For the nitrogen grafting we used an ion gun operated at different acceleration voltages in the range of 0.5 to 4.0 kV. SEM images indicated that the alignment of the carbon nanotubes is not affected by the ion irradiation. By XPS, we observed that the content and the Nitrogen configuration in the hexagonal lattice (pyridinic, pyrrolic, or graphitic) vary with kinetic energy of the nitrogen ions. Defect formation will be discussed comparing XPS and Raman results recorded on the nitrogen grafted samples using different ion kinetic energy.

[1] Scardamaglia, M., Amati, M., Llorente, B., Mudimela, P., Colomer, J., Ghijsen, J., Ewels, C., Snyders, R., Gregoratti, L. and Bittencourt, C. (2014). Nitrogen ion casting on vertically aligned carbon nanotubes: Tip and sidewall chemical modification. Carbon, 77, pp.319-328.
[2] Tran, K., Heinrichs, B., Colomer, J., Pirard, J. and Lambert, S. (2007). Carbon nanotubes synthesis by the ethylene chemical catalytic vapour deposition (CCVD) process on Fe, Co, and Fe–Co/Al2O3 sol–gel catalysts. Applied Catalysis A: General, 318, pp.63-69.



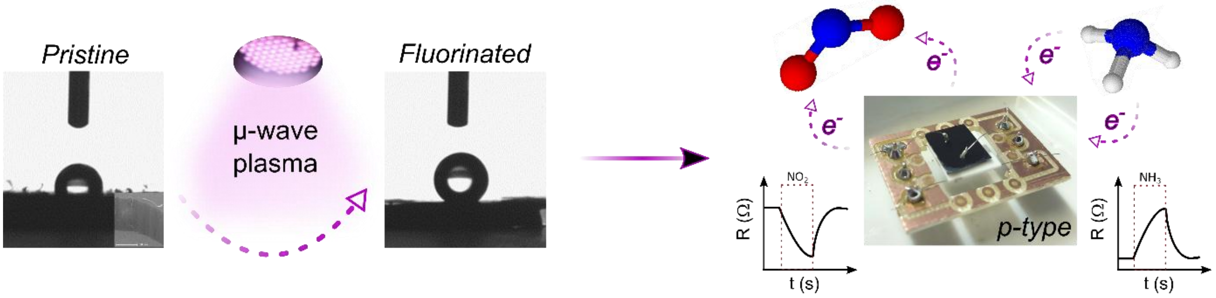
Gas Sensing Properties of Fluorinated Carbon Nanotubes

C. Struzzi[1], M. Scardamaglia[1], J. Casanova Chafer[2], N. Brutin[1], R. Snyders[1], E. Llobet[2], C. Bittencourt[2]

1- Chemistry of Interaction Plasma Surface (ChIPS), University of Mons, Belgium
2- MINOS-EMaS, Department d'Enginyerie Electronica, Universitat Rovira I Virgili, Tarragona, Spain

carla.bittencourt@umons.ac.be

Vertically aligned Carbon Nanotubes (v-CNTs) are exposed to different fluorine-containing species produced by a plasma source; Ar:SF_6, Ar:F_2 and CF_4 were used. The chemical-bonding environment of the fluorine species grafted at the CNT surface and hydrophobic character are discussed. The modifications of the electronic and structural properties are examined by synchrotron-based. We investigate the fluorination process of the v-CNTs and their gas sensing response towards NO_2 and NH_3. The effect of the humidity is assessed. It is demonstrated that fluorination, causing the increasing of the surface hydrophobicity, reduces the moisture interference and enhances the sensor response towards NH_3.



Novel approach to increase the electrical conductivity of polymer composite fibers

Frank Clemens* and Tutu Sebastian

Empa, Laboratory for High Performance Ceramics
Überlandstrasse 129, Dübendorf, Switzerland

Research & development of conducting polymer fibers is vital especially in the anti-static workwear applications to avoid the electrostatic charge build up. The most common practice to develop such fibers is to incorporate carbon fillers in the polymer matrix. However; at high concentrations of fillers the flexibility of the polymer is compromised. Hence it is essential to achieve this high conductivity with minimum amount of carbon fillers. Earlier studies show that the conductivity of the composite is influenced by the filler properties such as morphology, particle size, aspect ratio etc. So, a particular interest is taken in studying high aspect ratio fillers, such as carbon nanotubes and graphene where a percolation threshold can be achieved at low filler content and therefore higher electrical conductive can be achived.

One of the main disadvantages of high aspect ratio fillers is their price. According to this, new research activities have started to investigate composite materials of low cost carbon black and high cost carbon nanotubes to adjust the electrical conductivity. A new approach has been validated for achieving a high conductivity polymer composite by mixing two immiscible polymers and concentrating the carbon fillers in just one polymer matrix. Studies to improve the properties of conducting ceramic-polymer nanocomposites are undergoing.

Empa holds a state-of –the –art microcompounder for nanocomposite fabrication where *in-situ* rheological measurement along with extrusion of fibers in to different diameters is feasible at low feed content (5-6 gram of material). This provides the possibility for investigating expensive raw materials at minimum cost. Not only that, a scale up study is also viable here with the high volume compounder and extruder.

*MC member

Functionalization of carbon based materials for applications in filtering membranes

G. Moise – Vătui[1], C. Fratilă, A. Slobozeanu, S. Vâlsan, C. F. Ciobotă

1- National R&D Institute for Non-ferrous and Rare Metals, 102 Biruintei Blvd, Ilfov, Romaniac

Corresponding author email address: ***g.moise@imnr.ro***

Abstract:
The aim of the paper is to present some technological alternatives in obtaining and functionalization of three types of membranes based on carbonic materials.
In the field of filtering membranes the phenomenon of biological annihilation prevents their normal activity in micro and nanofiltration processes. Removal and eradication of biofilms is generally accomplished by mechanical processes, acid or alkali detergents or disinfectants. However, the effectiveness of these chemicals is strongly affected by factors such as pH, temperature, solubility, concentration and exposure time [1].

In this context, the dynamics of developing new strategies for controlling the formation of biofilms on micro and nanofiltration membranes or on food and medical products is emphasized.
Nanostructured materials, such as carbon nanotubes and graphene, have been developed as modeling systems in nanoscience and nanotechnology. These carbon-based materials are a special class and have attracted attention because of their superior surface area and outstanding electronic, mechanical and thermal properties.
We tackled three main directions in obtaining carbon based membranes. First, we obtained 3D polymeric structures impregnated with carbon materials. In the second direction we obtained noble metals functionalization of carbon based structures using thermal evaporation method. The third direction implies obtaining the composites membranes based on carbonic materials and metallic nanomaterials.

[1] R. Houdt, C.W. Michiels, Biofilm formation and food industry, an emphasis on the bacterial outer surface, J. Appl. Microbiol. 109 1117-1131 (2010)

Acknowledgement: Program Nucleu: 1807/2018: Tehnologii emergente pentru dezvoltarea materialelor neferoase avansate cu valoare adaugată ridicată - EMERNEF

Graphene oxide-modified electrodeposited ZnO / Cu_2O heterojunction solar cells

N. Ma. Rosas-Laverde[1,2], J. Cembrero[1], J. Orozco-Messana[1], A. Pruna[3*]

Department of Materials and Mechanical Engineering, Universitat Politecnica de Valencia, Valencia, Spain
[2]Department of Materials, Escuela Politécnica Nacional, Quito, Ecuador
[3]Center for Surface Science and Nanotechnology, Polytechnic University of Bucharest, Bucharest, Romania,
ai.pruna@gmail.com

New approaches are required for developing novel solar energy converters with improved performance and lower cost. While ZnO/Cu_2O based heterojunction solar cells have attracted interest lately, electrochemical deposition gained increased recognition as a versatile synthesis technique. In this work, ZnO/Cu_2O heterojunction solar cells were fabricated by electrodeposition methods. The solar cell performance was studied with the incorporation of graphene oxide (GO) nanosheets at the ZnO/Cu_2O junction given that it can be improved through either interface traps [1] or by hindering the charge recombination in electron-transfer processes [2]. The effect of optimization of junction interfaces in terms GO oxidation or reduction state on the cell performance (short-circuit current density J_{sc} and open-circuit voltage V_{oc}) has been investigated.
Structural characteristics were measured by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer. Field Emission Scanning Electron Microscopy (FESEM) Bruker working at a 2kV was employed for the morphology investigation. The photoelectrical properties were performed by using potensiostat (PGSTAT 302N AUTOLAB) equipped with AM 1.5G illumination from a calibrated solar simulator with irradiation intensity of 100 mW/cm^2.
The obtained results indicate a marked effect of GO on the ZnO-Cu_2O -based solar cell due to improved charge separation, and increased conductivity, respectively.

Acknowledgements

Financial support from Escuela Politécnica Nacional (Project number PIMI 15-09) and Secretaria de Educación Superior, Ciencia, Tecnología e Innovación (SENESCYT) and Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI (project number PN-III-P1-1.1-TE-2016-1544) is gratefully acknowledged.

References

[1] Y.S. Lee et al., Energy Environ. Sci. 6 (2013) 2112.
[2] J.L. Song et al., Physica E 81 (2016) 14.

Morphological and structural investigations of electrodeposited Ni-Sn alloy/reduced graphene oxide composites from deep eutectic solvents

Sabrina Patricia Rosoiu[a], Aida Ghiulnare Pantazi[a], Aurora Petica[a], Anca Cojocaru[a,b], Stefania Costovici[a], Teodor Visan[a,b], Marius Enachescu[a], Liana Anicai[a*]

[a]*Center of Surface Science and Nanotechnology, University Politehnica of Bucharest, Splaiul Independentei 313, Bucharest, 060042, Romania*
[b]*Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 132 Calea Grivitei, Bucharest, Romania, 010737, Bucharest, Romania*

**Corresponding author's email: liana.anicai@cssnt-upb.ro*

In recent years, graphene related materials attracted considerable attention and they have great potential in the electronics field owing to their superior mechanical properties and electrical and thermal conductivities. The addition of graphene to the binary Sn alloys may contribute to the accomodation of the large volume change of Sn during cycling process when they are used as anodes of Li ion batteries or may contribute to the mitigation of whiskers growth when applied in electronic interconnections. The use of ionic liquids in general and of choline chloride based ones in particular was found to be suitable media to form stable graphene based dispersions overcoming the agglomeration problems [1-3].

The present paper presents several experimental results regarding the morphological and structural characterization of Ni-Sn alloy/reduced graphene oxide composite coatings from choline chloride based ionic liquids on Cu substrates. Electrolytes containing Sn (II) and Ni (II) salts in choline chloride-ethylene glycol eutectic mixtures (Sn:Ni molar ratio in electrolyte between 1:1 - 3:1) with additions of 0.1-0.5 g/L ammonia functionalized graphene oxide have been used, showing a very good dispersability and stability for more than 96 h. The obtained composite deposits are adherent and uniform onto metallic substrates, with thicknesses of about 10-12 µm at 30-40 mA/cm^2 for 30 min. under ultrasound stirring.

SEM, Raman, XPS and XRD analysis evidenced the successful insertion of reduced graphene oxide into the metallic Ni-Sn alloy matrix (see Fig.1).

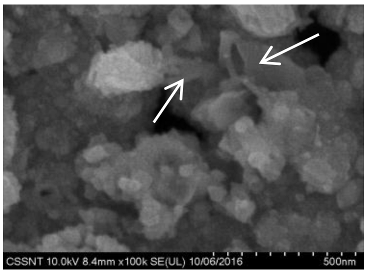


Fig.1 SEM image of Ni-Sn alloy / reduced graphene oxide composite coating
(50 mA/cm^2 30 min., 50^{o}C)

Atomic Force Microscopy (AFM) investigations to get more details on the local morphology features are also discussed.

Acknowledgements: The work was supported by Romanian Ministry of Education and by Executive Agency for Higher Education, Research, Development and Innovation Funding, under NOVTINALBEST project 38/2016, M Era Net Program.

[1] Y.Tong, S. Bohmb, M. Song, Graphene based materials and their composites as coatings, *Austin J. Nanomed. Nanotechnol.* 1(1), 1003, 2014.
[2] N. Liu, F. Luo, H. Wu, Y. Liu, C. Zhang, J. Chen, One-Step Ionic-Liquid-Assisted Electrochemical Synthesis of Ionic-Liquid-Functionalized Graphene Sheets Directly from Graphite, *Adv. Funct. Mater.* 18, 1518–1525, 2008.
[3] M.H. Chakrabarti et al., One-pot electrochemical gram-scale synthesis of graphene using deep eutectic solvents and acetonitrile, *Chem.Eng.J.* 274, 213–223, 2015.

Multiwalled carbon nanotubes-silver nanocomposite coatings from ionic liquids analogues – morphological and structural analysis

<u>Aida Ghiulnare Pantazi[a]*</u>, Sabrina Patricia Rosoiu[a], Aurora Petica[a], Oana Tutunaru[a], Teodor Visan[a,b], Marius Enachescu[a], Liana Anicai[a]

[a]Center of Surface Science and Nanotechnology, University Politehnica of Bucharest, Splaiul Independentei 313, Bucharest, 060042, Romania
[b]Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 132 Calea Grivitei, Bucharest, Romania, 010737, Bucharest, Romania

**Corresponding author's email: liana.anicai@cssnt-upb.ro*

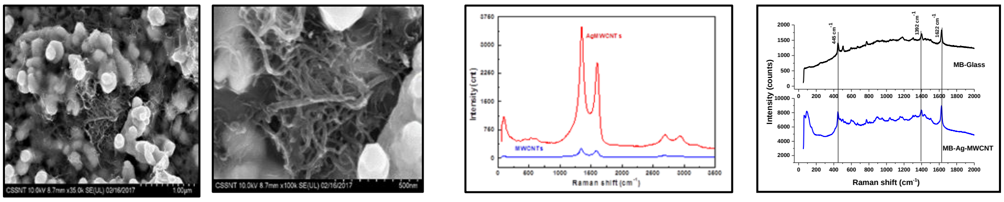
The paper presents some experimental results related to the morphological and structural characterization of electrodeposited Ag composites with carbon nanotubes (denoted Ag-MWCNT) involving ionic liquids analogues based on novel eutectic mixtures of choline chloride-triethanolamine (IL-TEA) (1:1 molar ratio) containing 0.1 M nicotinic acid (NA). Dispersion stability of multi-walled carbon nanotubes (MWCNTs) was found to be excellent in the used eutectic solvent. According to SEM, Raman, XPS and XRD analysis, the carbon nanotubes were successfully inserted into the metallic matrix (see Fig.1a).

Atomic Force Microscopy (AFM) investigations to get more details on the local morphology features, including the roughness parameters, Ra (arithmetic average of measured microscopic peaks and valleys) and RMS (root mean square of measured microscopic peaks and valleys) are also discussed.

Metallic light grey coatings, with a good adherence and uniformity onto the Cu substrate have been obtained at a working temperature of 70-80°C for 1 hour, at current density values between 2 -5 mA/cm^2. XRD pattern suggested a good crystallinity of the Ag-MWCNT composite layer, with crystallites average sizes of about 28 nm.

The Raman scattering intensities for the D and G bands of MWCNTs were found to be significantly enhanced as compared to those of pure MWCNTs (see Fig.1b), suggesting a potential use as a surface enhanced Raman scattering (SERS) substrate.

The preliminary tests using methylene blue (MB) as probe molecule showed that the obtained Ag-MWCNT composite coatings may be promising for SERS applications (see Fig.1c).



(a) (b) (c)

Fig.1 (a) SEM micrographs at different magnifications for Ag-MWCNT composite coatings; (b) Raman spectra of Ag-MWCNT composite coating and commercial MWCNTs; (c) Raman spectra of 2.86 ppm MB on glass and on Ag-MWCNT composite coating

Acknowledgements: Part of this work was supported by the NOVTINALBEST project 38/2016, M Era Net Program.

Manufacturing and dispersion of SWCNTs as a prerequisite for nanodevice building using Electron Beam Lithography

Geanina Mihai, Călin Moise, Aida Pantazi, Oana Lazăr, Ştefania Marin, Marius Enăchescu

Center for Surface Science and Nanotechnology – University Politehnica of Bucharest

Splaiul Independentei 313, Bucharest, Romania

E-mail: marius.enachescu@cssnt-upb.ro

Single Walled Carbon Nanotubes (SWCNTs) were obtained using a new laser chamber design for carbon ablation by Kr-F excimer laser. The SWCNTs were obtained by ablating the Ni-Co and Pt-Co doped target.

These SWCNTs were dispersed in dimethylformamide (DMF) using a combination of ultrasound sorces and spin coated onto a SiO_2/highly doped Si substrate with deposited gold electrodes. After the identification of the deposited SWCNTs, they were contacted to the prior designed electrodes using Electron Beam Lithography.

All these efforts were prerequisites for building future micro- and nanodevices using EBL as a technique for device contacting. The results of the entire process were evaluated using Scanning Electron Microscopy, Energy Dispersive Spectroscopy and Atomic Force Microscopy.

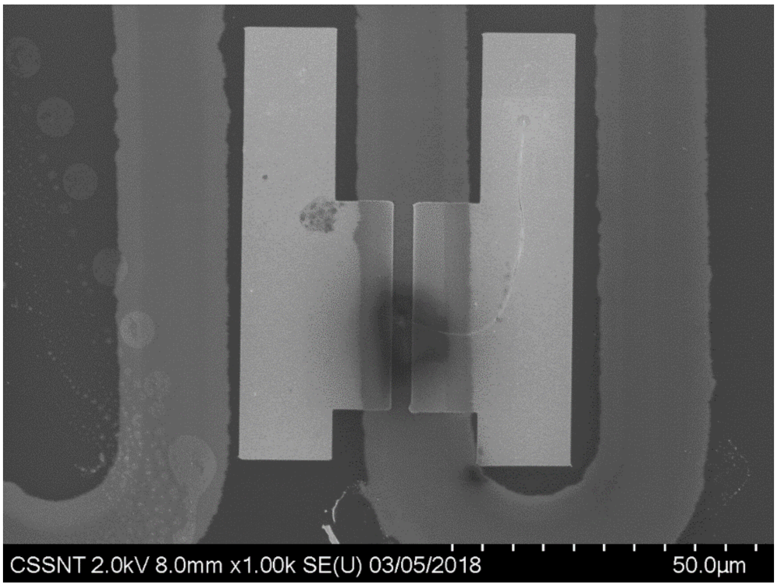


Figure 1. Nano-FET using SWCNT

[1]. S. Gorelick, V.A. Guzenko, J. Vila-Comamala, C. David, Nanotechnology 21 (2010) 29.

[2]. C. Vieu, F. Carcenac, A. Pepin, Y. Chen, M. Mejias, A. Lebib, L. Manin-Ferlazzo, L. Couraud, H. Launois, Applied Surface Science 164 (2000) 111-117.

[3]. P.A. Williams, S.J. Papadakis, A.M. Patel, M.R. Falvo, S. Washburn, R. Superfine, Applied Physics Letters 85 (2003) 5.

[4] E. Stern, G. Cheng, J. F. Klemic, E. Broomfield, D. Turner-Evans, C. Li, C. Zhou, and M. A. Reed, Methods for fabricating Ohmic contacts to nanowires and nanotubes, J. Vac. Sci. Technol. B 24 (2006) 231-236

[5] C. Vieu, F.Carcenac, A. Pe´pin, Y. Chen, M. Mejias, A. Lebib, L. Manin-Ferlazzo, L. Couraud, H. Launois, Electron beam lithography: resolution limits and applications, Applied Surface Science 164 (2000) 111–117

Antimicrobial activity of collagen matrices loaded with SWCNTs and essential oil

Stefania Marin[1], Mădălina Georgiana Albu Kaya[1], Geanina Mihai[2], Marius Enachescu[2], Maria Katsikogianni[3]

[1] *Collagen Department, Division Leather and Footwear Research Institute, National Institute for Textile and Leather Research and Development, Bucharest, Romania*
[2] *Center of Surface Science and Nanotechnology, University Politehnica of Bucharest, Splaiul Independentei 313, Romania*
[3] *Department of Chemistry and Biosciences, University of Bradford, Bradford, United Kingdom*

The aim of this study was to design, develop and evaluate new composites based on a natural polymer – collagen (COLL) used for tissue regeneration, single wall carbon nanotubes (SWCNTs) and essential oil in order to prevent infections in wound healing process. To obtain the collagen matrices, collagen gel, with the initial concentration of 1,92%, was adjusted to the final concentration of 1% and the pH was modified to 7.4 using 1M sodium hydroxide. SWCNTs were ultrasonicated for 2 hours, in essential oil solution, before usage. The homogenized solutions of essential oils with SWCNTs have been added over collagen gel in different proportions and all the samples were cross-linked using glutaraldehyde solution. By freeze-drying of gels during 48 hours, the spongious forms (matrices) were obtained. The antimicrobial activity of all the matrices obtained was testes against *S. aureus* and *E. coli* bacteria, investigating zones of inhibitions, inhibition of growth in wet conditions and biofilm analysis through spectrophotometry. All the samples were characterized by scanning electron microscopy (SEM) before and after the antimicrobial activity assay. The results showed that only the samples containing thyme essential oil presented zones of inhibition against *S. aureus* and *E. coli* strains. The samples incubated in solution without bacteria presented no biofilm formation, the values obtained from spectral analysis being very high, ranging around 0.6 cm^{-1}, values comparable to the control sample values. For samples with essential oil the results showed that the samples are more effective against *S. aureus*, the absorbance values being lower in this case than in tha case of *E. coli* interaction. So, it was proven, the efficiency of thyme essential oil firstly against *E. aureus* strain and then against *E. coli* strain. The results obtained of the designed matrices recommend these formulations as wound dressings with potential antimicrobial activity in skin wounds treatment.

Platinum decorated reduced graphene oxide for PEM fuel cells applications

Adriana Marinoiu[1], **Oana-Andreea Lazar**[2], **Aida Pantazi**[2], **Geanina Mihai**[2], **Marius Enachescu**[2]

[1]RD Institute for Cryogenics and Isotopic Technologies - ICSI, 4 Uzinei St., Rm Valcea, 240050, Romania, adriana.marinoiu@icsi.ro
[2]Center for Surface Science and Nanotechnology, Politehnica University of Bucharest, 060042, Romania

As a promising nanomaterial with excellent electronic, thermal, optical and mechanical properties, graphene is used increasingly more often in energy storage and energy conversion applications such as lithium ion batteries, solar cells, supercapacitors, fuel cells, etc. In this work, the synthesis and characterization of platinum decorated graphene (Pt-Gr) electrocatalysts for PEM fuel cells are reported.

The structural, optical and morphological properties of the prepared samples were studied using different characterization techniques, such as X-ray diffractometry, Scanning Transmission Electron Microscopy, Element Dispersive X-ray Spectroscopy and Raman Spectroscopy. According to the obtained results the investigated materials possess adequate properties, which are enabling their use in new improved electrodes for PEMFC.

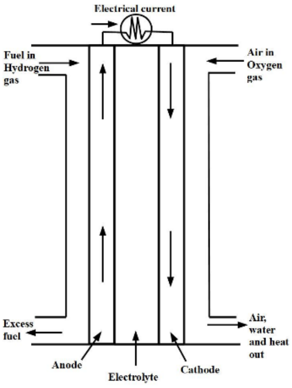


Figure 1. Schematic design of a PEM fuel cell

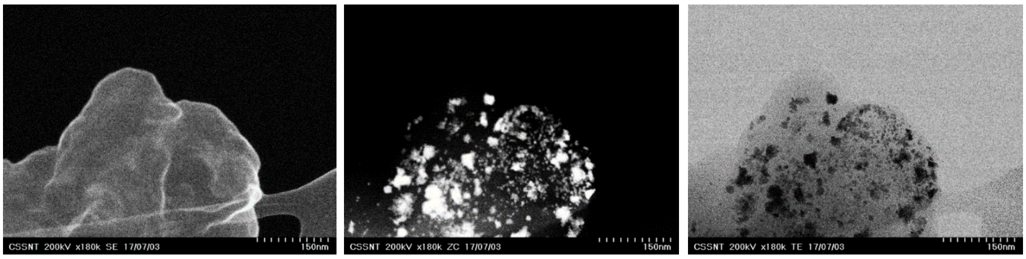


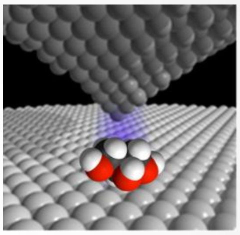
Figure 2. Co-localized SE - secondary electrons (left), ZC - phase contrast (middle) and TE - transmission electrons (right) images of the Pt/rGO_x sample

References

[1]. A. Marinoiu, M. Raceanu, E. Carcadea, A. Pantazi, R. Mesterca, O. Tutunaru, S. Ion, D. Bala, M. Varlam, M. Enachescu,"Noble metal dispersed reduced graphene oxide and its application in PEM Fuel Cells", ISBN 978-953-51-6257-5 (2018)

MultiComp

cost



UNIVERSITATEA POLITEHNICA DIN BUCUREŞTI

UPB

1818