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Multi-Functional Nano-Carbon Composite Materials Network

COST Action CA15107 meeting

PROGRAMME AND ABSTRACTS

March 8 – 9, 2018
Vilnius, Lithuania

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Programme

Thursday, March 8th

08:30	**Registration**
09:00-09:15	**Welcome**
09:15-10:30	**FLASH Presentations (9 x 6 min talks) – Session Chair Fil Ruddock**
	Jadranka Blazevska Gilev *Thin deposited graphene based nanocomposites films obtained by laser ablation*
	A.Sezai Sarac *Stabilization and carbonization of copolymers of acrylonitrile nanofibers: Carbon nanofiber precursor*
	Radmila Tomovska *Synthesis of graphene/polymer 3D porous composites for CO2 capture*
	Maria Rybarczyk *Curved graphene layers obtained from biopolymer precursor*
	Liutauras Marcinauskas *Deposition of amorphous carbon films at atmospheric pressure*
	Michela Alfe *Graphene-like (GL) layers as building blocks for advanced materials and composites development*
	Maria Kandyla *Surface-enhanced Raman spectroscopy of graphene on non-planar plasmonic nanostructures*
	Branislav Stanković *Application of logistic function to describe kinetics of non-isothermal dehydroxylation of fullerol*
	Vilius Dovydaitis *Deposition of oxygen doped amorphous carbon films by magnetron sputtering*
10:30-11:00	**Coffee Break**
11:00-12:15	**FLASH Presentations (8 x 6 min talks) – Session Chair Radmila Tomovska**
	Alexander Talyzin *Molecular pillar approach to grow vertical covalent organic framework nanosheets on graphene: new hybrid materials for energy storage*
	Marta d'Amora *Toxicity comparison of different carbon-based nanomaterials in zebrafish*
	Silvia Giordani *Carbon nano-onions for diagnostics*
	Valentina Gargiulo *Functional biocompatible interfaces for bioelectronics applications by the integration of eumelanin and graphene-like layers*
	Uwe Popp *3D Printed Carbon Fibre Reinforced PEEK: focus on Medical Applications*
	Hatem Akbulut *Nanocarbon Based Template Synthesis Single Crystalline LiMn2O4 Spinels*
	Mehmet Oguz Guler *Innovative Graphene Based MnO2 / LTO Fullcells for Li-Ion Batteries*

	Malamatenia Koklioti *Photoionduced catalytic properties of metal nanoclusters/graphene ensembles*
12:15- 13:30	**Lunch Break** **Opportunity to Network and start Discussions at the Posters**
13:30- 14:45	**FLASH Presentations (8 x 6 min talks) – Session Chair Silvia Giordani**
	Artyom Plyushch *Highly effective radar absorbing materials based on SiC whiskers*
	Jelena Jovanovic *Kinetics of fulerene polyhydroxylation*
	Anastasios Stergiou *Functionalization and Processing of Graphitic Low-Dimensional Functional Nanocarbons*
	Ivan Radovic *Theoretical modeling of experimental EELS data for monolayer graphene supported by different metal substrates*
	Daphne Davelou *Electronic properties of transition metal dichalcogenide nanoribbons*
	Naum Naveh *Development of nano-structured interphases in carbon-epoxy composites*
	Silvia Marchesan *Green, waste-free functionalization of CNT fibers for supercapacitors and use in water*
	Polina Kuzhir *Graphene based metasurface for THz passive components*
14:45- 15:00	**Breathing break**
15:00- 16:00	**FLASH Presentations (7 x 6 min talks) – Session Chair Maria Candyla**
	Arkady Krasheninnikov *Graphene-Transition Metal Dichalcogenide Heterostructures as Two-Dimensional Nano-Carbon Composite Materials*
	Galina Dovbeshko *Graphene–type composite materials as SEIRA and SERS platforms*
	Serkan Unal *Hybrid Organic-Inorganic Nanomaterials: Preparation of Carbon Nanofiber Supported Pt Nanoparticles*
	Miroslav Huskić *The influence of graphene oxide particle size on the properties of epoxy resin nanocomposites*
	Raul Arenal *Structural and Local Spectroscopic Studies on Hybrid Nanomaterials by Advanced TEM*
	Juan C. Fernandez-Toribio *Mechanical modelling and characterization of CNT fibres the role of alignment*
	Jan Macutkevic *Electromagnetic properties of carbon foams*
16:00- 16:30	**Coffee break**

16:30-17:00	**FLASH Presentation and Short talk – Session Chair Sharali Malik**
	1 x 6 min **Dr Susan Anson** *Opportunities to compliment your research at KMNF*
	1 x 20 min **Mr. Edward Goldwyn** *Potential use of Video for MultiComp*
17:00 – 18:30	**Poster session**
19:00-21:30	**Conference Dinner**

Friday, March 9th

09:30-10:45	MC Meeting	Parallel session:- Other meeting Participants with Mr. Edward Goldwyn.
10:45-11:15	Coffee Break	
11:15-12:30	MC Meeting concluded	
12:30-14:00	Lunch Break	
14:00-15:15	WGs Meetings	
15:15-15:30	Coffee Break	
15:30-16:30	WGs Meetings	
16:30-17:00	Breathing Break	
17:00-18:30	WGs Leaders/Representatives Reporting	

List of poster presentations

1. **Carla Bittencourt**, *Fluorination of Suspended Graphene*
2. **Polona Umek**, *Carbon nano-allotropes based on few layer graphene and fullerene C60: synthesis and characterization*
3. **Aleksandras Iljinas**, *Synthesis of nanostructured amorphous carbon-copper composite films*
4. **Edita Palaimiene**, *Dielectric/electric properties of onion like carbons/epoxy composites*
5. **Matej Micusik**, *Multi-Walled Carbon nanotubes/pollypyrolle composites with different surfactants*
6. **Irina Kuhne**, *Surface attachment of Mn(III) SCO compound on few-layer graphene*
7. **David Tomecek**, *Photoregenerating thin films of phthalocyanines for NO2 and explosive taggants detection*
8. **Jan Vlcek***, Fullerenes in Polymeric Ion Liquid Matrix for Chemical Sensing: Synthesis, Characterization and Sensor Properties*
9. **Darya Meisak**, *Dielectric properties of Fe2O3H2O/epoxy resin composites*
10. **Vytautas Samulionis**, *Efect of WS2 nanotubes on dielectric and ultrasonic properties of polyurethane based composites*
11. **Martin Vrnata**, *Polymeric ionic liquids as sensitive layers for textile gas sensors*
12. **Samaneh Etemadi***, Study and synthesis of in-situ doping of GO with nitrogen (GO-N)*
13. **Dejan Kepic**, *Gold nanoparticles/exfoliated graphene hybrid obtained by gamma irradiation*
14. **Tal Ben Shalom**, *Crystalline Nano Cellulose (CNC) and Carbon Nanotubes(CNT) based composites films and coatings*
15. **Dimitrios Periovoliotis**, *Bimetallic Nanoparticles/Sulfur-doped Graphene Electrocatalysts for Oxygen Reduction Reaction*
16. **Amra Bratovcic**, *Titanium oxide nanospheres coated with carbon xerogel as efficient photocatalysts for the elimination of drugs*
17. **Justina Gaidukevic**, *Formation of Low-Defect Graphene Coating from Graphene oxide-Dye Nanocomposites by Pulsed Laser Treatment*
18. **Sergejs Gaidukovs**, *Dielectric Properties of EVA/Graphene Layered Composites*
19. **Lisaveta Shashkova**, *Effect of graphene grains size on the electromagnetic response at high frequency range*
20. **Diana Malgorzhata Bobrowska**, *Functionalization of carbon nano-onions (CNOs) with triphenylamine and triphenylphosphine derivatives: synthesis and physicochemical properties*
21. **Fatima Boaunis**, *Diameter controlled growth of SWCNTs using Ru as catalyst precursors coupled with atomic hydrogen treatment*

22. **Fatima Boaunis**, *Graphene nanoplatelets coating for corrosion protection of aluminum substrate*
23. **Joanna Breczko**, *The EC-SPR biosensor based on graphene oxide, silica and gold nanoparticles in NADH determination*
24. **Claudio Larosa**, *The role of MWCNTs and SWCNTs on the crystallization of polycarbonate evaluated by XRD, SEM and spectroscopic absorption*
25. **Masooma Ibrahim**, *Chirality-Specific Growth of SWCNTs*
26. **Muslum Kaplan**, *Improvement of Mechanical Properties of Polyethylene Meltblown Webs*
27. **Zoran Eres**, *Copper substrate contamination with compact SiO2 thin film deposits due to reactor tube evaporation in graphene CVD synthesis process*
28. **Georgios Tritsaris**, *Perturbation theory for weakly coupled two-dimensional layers*
29. **Ari Rosling,** *New era of biodegradable composites - ABMcomposite*

Abstracts

Oral presentations

Thin deposited graphene based nanocomposites films obtained by laser ablation

Jadranka Blazevska Gilev

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

Nanocomposites based on poly(methyl methacrylate/butyl acrylate/acrylic acid) with 0.5 and 1 wt% reduced graphene oxide content in relation to polymer were obtained by emulsion mixing technique. The polymer latex composed from poly(methyl methacrylate/butyl acrylate/acrylic acid), in ratio 49,5/49,5/1 wt%, was synthesized by a seeded semi-continuous emulsion polymerization. The rGO was mixed with the polymer latex in presence of crosslinker 1,8-diamino-3,6-dioxaoctane for 5h at 70°C. Under standard ambient conditions by water evaporation, cross-linked nanocomposite films were formed.

Ablation was realized by IR laser of two targets, the nanocomposite and graphene. Composite films were ablated in order to re-arrange the dispersion of rGO in the polymer matrix and to avoid their aggregation. Thin deposited homogenous nanocomposite structure was obtained using IR pulsed transversely excited atmosphere CO_2 laser and incident fluence of 15-20 Jcm^2. The structure was formed by three times repeating the ablation of the composite and graphene using two targets system. Result was, increasing the graphene content without any further agglomeration, which was not possible by convenient method of blending the graphene and the polymer latex.

Deposited films were assayed by means of FTIR, Raman spectroscopy, scaning electron microscopy and contact angle measurements.

Key words: semicontinuous emulsion polymerization, polymer nanocomposites, rGO, laser ablation, SEM, FTIR and Raman spectroscopy.

Stabilization and carbonization of copolymers of acrylonitrile nanofibers: Carbon nanofiber precursor

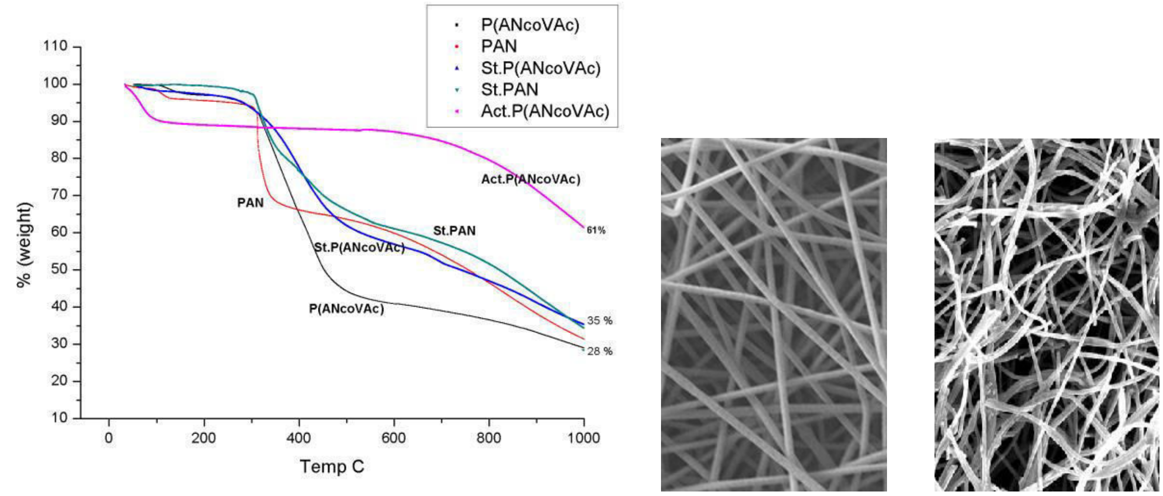
A.Sezai Sarac

Istanbul Technical University,Polymer Science and Tech. & Nanoscience and Nanotech.

Maslak, 34469 Istanbul, Turkey

sarac@itu.edu.tr

Polyacrylonitrile (PAN) is a good choice to produce nanofibers .In the heat-treatment processes that convert PAN fibers to carbon fibers, an essential steps are the stabilization and oxidation which crosslink PAN chains and prepare a structure that can withstand high-temperature processes in the presence and absence of graphene oxide(GO)[1,2,3]. Oxidative stabilization consists of the cyclization of the nitrile groups (C≅N) and the crosslinking of the chain molecules in the form of −C=N−C=N .The stabilization is influenced by the pyrolysis temperature, heating rate, tension of the fiber, stabilization time, the air flow rate, and the precarbonization treatment etc.,. The cyclization process of PAN by a thermal process is strongly related to the presence of ionic groups such as vinylacetate(VAc) and itaconic acid (IA) on the polymeric structure, and the thermal stability of CNFs can be enhanced by the presence of such ionic contents on the copolymer .We have observed that morphology of the nanofibers affected by such ionic groups containing a copolymer structure. In this study the effects of such ionic inclusions in the copolymer on the activation process and GO inclusion of the resulting CNFs and the surface properties were investigated [3],[4].VAc and IA containing terpolymer was also investigated as a carbon nanofiber precursor for the comparison purposes . Electrospun nanofibers were oxidized between 200-325°C. After the oxidation process carbonization was applied at 1000 and 1100°C in the presence of N_2. Viscosity and molecular weigth distribution of samples were measured with Ubbelohde Viscometer and Gel Permeation Chromatography (GPC). Copolymers were analyzed by Thermogravimetric Analysis (TGA)(Fig1) and Differential Scanning Calorimetry (DSC). Spectroscopic characterization of copolymer samples, oxidized and carbonized nanofibers were performed by FTIR-ATR Spectroscopy. Original electrospun nanofibers and oxidized and carbonized nanofibers were investigated by Scanning Electron Microscope (SEM). IA had considerable effect on terpolymer properties and electrospun nanofibers. Moreover, it was proved that oxidation temperature was an important parameter for production of carbon nanofibers. Both morphology and color of the produced nanofiber mats changed when carbonization process was accomplished.



(a) (b) (c)

Fig.1.TGA Thermograms of stabilized AN homopolymer and P(AN-co-Vac) (a) and SEM of P(AN-co-Vac)(b),& Activated form(c)

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Synthesis of graphene/polymer 3D porous composites for CO_2 capture

Radmila Tomovska, Ehsan Mehravar

Institute for Polymer Materials, POLYMAT, University of the Basque Country, Avda Tolosa 72, 20018, San Sebastian, Spain

The suitability of graphene for CO_2 capture comes from its two-dimensional (2D) or platelet like structure that offers a large and easy accessible surface area accompanied by an incredible flexibility and excellent mechanical properties. We aim to extend further the graphene adsorption strength by mixing the graphene platelets with polymer nanoparticles, creating composite porous structures with synergistically improved capability for CO_2 selective capture. Although wide varieties of different materials have been investigated for that aim, polymer-inorganic composites, which have found wide applications in almost all aspects of modern life, have rarely been explored.

In this work, simple, versatile and environmental friendly synthesis of novel 3D porous sponge-like composite materials by self assembly process of graphene oxide (GO) nanosheets during their reduction in the presence of polymer latex (colloidal stable polymer nanoparticles aqueous dispersion) is shown. Upon water evaporation a 3D porous graphene structures with the polymer spontaneously included in it are formed. The challenge is to control the functionalities, morphology and porous structure. For that aim, polymer nanoparticles with two different functionalities were selected (Br and epoxy) and two modifications of the synthesis procedures resulting in a portfolio of different products.

Respective a capacity for CO_2 capture, neat graphene 3D structures have shown to be the most promising material, showing capacity high over the published values in literature for similar structures, likely due to highly porous morphology, low density and high specific surface area. Addition of polymer improves the materials consistency and mechanical properties, but decreases the capturing capacity, due to decrease in the surface area (some of the pores were filled with polymer) and augmentation of the materials density. It was shown that the structure is sensitive to the polymer functionalities and influences importantly the capturing capacity of the materials.

Curved graphene layers obtained from biopolymer precursor

Maria K. Rybarczyk, Marek Lieder

Gdansk University of Technology, Department of Chemical Technology

maria.rybarczyk@pg.edu.pl

The production of carbonaceous solids have been extensively studied, since there is a high demand for (preferably derived from renewable sources) a microporous and/or mesoporous (activated) materials with high specific surface area, as adsorbents and as catalysts support in a variety of environmental and industrial applications.

Curvatures in periodically arrayed hexagonal carbon structures are most often referred to nanotubes (including unzipped nanotubes) or fullerenes. Although, other nano-curved carbonic materials are scarce there are reports on such materials synthesized by employing slow condensation of carbon vapor in high-temperature processes or annealing the diamond particles.

Here, we demonstrate that pyrolysis of chitosan (renewable food waste) in a ZnCl2 melt assisted by the presence of LiCl results not only in a highly porous activated carbon material with a specific surface area of 1317.97 m2/g and the total nitrogen content of 6.5 %, but also induces unexpected curvature in the grown graphitic layers. This is the first work that shows curved graphene layers obtained from a biopolymer precursor by its pyrolytic decomposition in the melted salt media. The well-known carbonization method employing the ZnCl2 melt as the activating agent could result in an unexpected deformation in the grown graphitic layers, if the reacting mixture contains also LiCl.

Deposition of amorphous carbon films at atmospheric pressure

L. Marcinauskas[1,2], **M. Černauskas**[1], **V. Dovydaitis**[1], **M. Milieška**[2], **R. Zabels**[3]

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
3- Institute of Solid State Physics, University of Latvia, Kengaraga Str. 8, LV-1063 Ryga, Latvia

liutauras.marcinauskas@ktu.lt

Amorphous carbon films and carbon nanostructures have attracted considerable interest due to their wide range of excellent properties. Those properties make carbon films and nanostructures suitable for a large variety of application fields such as: biomedicine, tribology, microelectronics, energy, optics, and etc [1-4]. Nowadays a considerable attention is given to the deposition of amorphous carbon films or nanostructures at atmospheric pressure conditions [3-5]. The main advantage of such process is the possibility to replace a high cost vacuum system by new plasma equipment which can be operated simply at air conditions [4].

Amorphous carbon films were deposited on the silicon and silicon-metal substrates at atmospheric pressure using a linear direct current plasma torch. A thin metal layers were deposited on Si substrate by magnetron sputtering technique. Argon or argon-hydrogen mixture was the plasma forming gases. Acetylene (C_2H_2) gas was used as carbon source with various (from 0.026 l/min to 0.143 l/min) flow rates. The substrates were chemically cleaned by acetone and 30-60 s purified in the argon or argon-hydrogen plasma before the deposition. The structural, topographical and compositional characterization of the irradiated carbon films was investigated by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), Raman scattering spectroscopy (RS) and Fourier transform infrared (FTIR) spectrometer. Nanoindentation tests were performed by MTS-Agilent G200 nanoindenter with a Berkovich diamond tip using the continuous stiffness measurement technique. Argon-acetylene and argon-hydrogen–acetylene plasma were studied in the range of 250–800 nm wavelength using an acousto-optic emission spectrometer (OES) IFU AOS4.

OES measurements indicated that the C_2 and CH species are dominated in the argon-hydrogen-acetylene and argon-acetylene plasmas. The introduction of the hydrogen into the plasma increases the fraction of CH radical in the plasma. The SEM measurements indicated that the films deposited without the hydrogen at higher temperatures are rough and consist of columnar structure. The Raman measurements indicated that films deposited without the hydrogen was amorphous carbon with nanocrystalline/glassy carbon phase. The oxygen concentration in the films strongly depends on the formation distance and flow rate of acetylene. The addition of hydrogen flow rate of 0.16 l/min at 5 mm induced the etching of graphitic domains, caused the increase of oxygen concentration about 4 times and initiated the structural transition from the amorphous carbon film to nano-crystalline graphite. The increase of the distance from 5 mm up to 7 mm stipulated the formation of multiphase silicon-carbide/carbon films when the argon-hydrogen-acetylene ratios were 100:2.4:1 and 100:1.2:1. Microhardness and Young's modulus values significantly depended on the plasma composition and formation distance.

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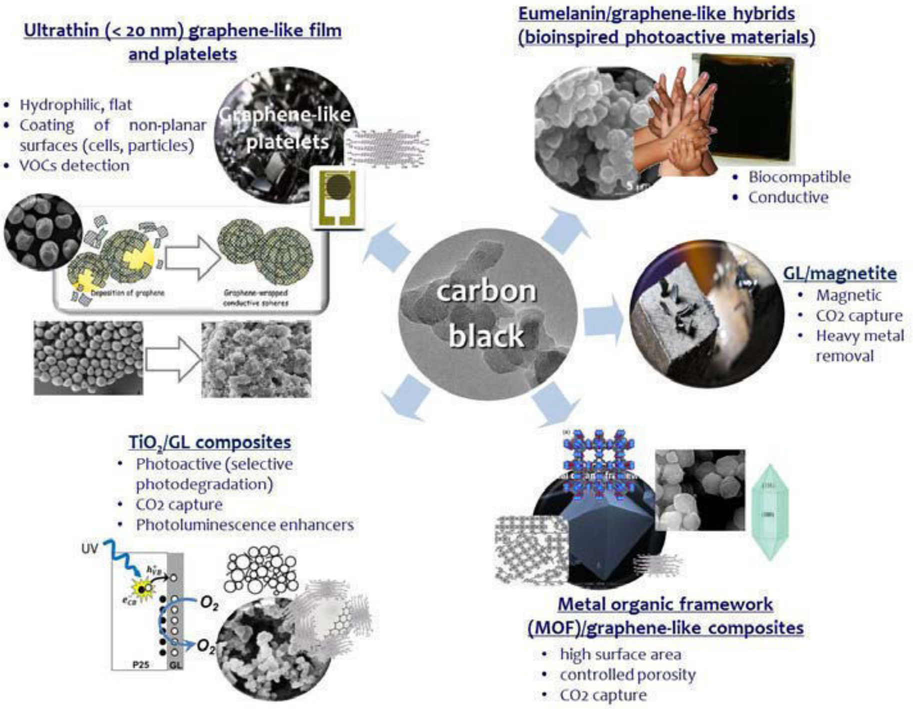
Graphene-like (GL) layers as building blocks for advanced materials and composites development

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

1- Istituto di Ricerche sulla Combustione (IRC) – CNR, P.le Tecchio 80, 80125 Napoli, Italy
2- Dipartimento di Fisica-Università degli studi di Napoli "Federico II", and CNR-SPIN, I-80126 Naples, Italy
alfe@irc.cnr.it

Advanced materials and composites can be developed by exploiting eco-friendly approaches based on the tailoring and destructuring of carbon-based materials from unconventional sources (carbon black, carbonized and pyrolyzed biomasses, char,...). Wet-chemistry approaches are a top-notch choice, thanks to the ability to destructuring carbonaceous matrices leading to graphenic layers with tunable properties. In our approach, the development of cost-effective protocols for advanced materials and composites production is based on the exploitation of the versatility of the carbonaceous moieties, prone to be modified (structuring/de-structuring) at molecular level in mild condition and green solvents (water among all). Starting from carbon black and exploiting a two-step synthetic approach leading to graphene-like layers (GL) [1,2], we designed and produced a wide array of carbon-based materials and composites:



Advanced materials and composites produced exploiting GL.

GL layers have been employed for thin films production [1,2], also by ink-jet printing technology. Their ability to act as chemiresistive sensor layer has been proved for alcohols detection [3]. Conductive composites have been also produced growing Metal-Organic Frameworks crystals (Cu-BTC) on GL layers [4]. Biocompatible conductive interfaces have been synthetized by allowing the polymerization of eumelanin precursors in presence of GL-layers [5]. TiO_2/GL photoactive composites have been synthetized by both a solvothermal and copolymerization approaches [6,7]. The bacteriostatic properties of GL layers [8] also opened challenging routes for biocompatible materials fabrication.

These first attempts in the use of graphene-like layers as building blocks for composite materials preparation pave the way for the designing and realization of a large variety of tunable composites for specific applications.

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Surface-enhanced Raman spectroscopy of graphene on non-planar plasmonic nanostructures

M. Kanidi[1,2], A. Dagkli[3], M. Kandyla[1,*], N. Kelaidis[4,5], D. Palles[1], A. Colli[6], A.C. Ferrari[6], E. Lidorikis[3], S. Aminalragia-Giamini[4,7], J. Marquez-Velasco[4,8], A. Dimoulas[4], E.I. Kamitsos[1]

[1]Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vasileos Constantinou Avenue, 11635 Athens, Greece
[2]Department of Material Science, University of Patras, University Campus, 26504 Rio, Greece
[3]Department of Materials Science and Engineering, University of Ioannina, 45110 Ioannina, Greece
[4]Institute of Nanoscience and Nanotechnology, National Center for Scientific Research 'Demokritos', 15310 Athens, Greece
[5]Faculty of Engineering, Environment and Computing, Coventry University, Priory Street, Coventry CV1 5FB, UK
[6]Cambridge Graphene Centre, University of Cambridge, Cambridge CB3 0FA, UK
[7]Department of Physics, University of Athens, Zografou University Campus, 15784 Athens, Greece
[8]Department of Physics, National Technical University of Athens, 9 Iroon Polytechniou st., 15780 Athens, Greece

[*]Email: kandyla@eie.gr

Plasmonic nanostructures in combination with graphene or other 2D materials have already demonstrated a promising potential for the development of high-performance photodetectors, solar cells, optical modulators, fuel cells, chemical and biological sensors. In this work, we take advantage of the remarkable mechanical properties of graphene to combine it for the first time with 3D plasmonic nanostructured silicon substrates for surface-enhanced Raman spectroscopy (SERS).

Large areas of femtosecond laser-structured arrays of silicon nanopillars, decorated with gold nanoparticles, are used as SERS substrates. We probe graphene for its plasmonic-enhanced Raman spectral signal at four excitation wavelengths, which span the visible range of the electromagnetic spectrum. The Raman signal of graphene on the plasmonic 3D substrate is enhanced by 2–3 orders of magnitude, compared with pristine silicon substrates, which allows for probing the fine structure of Raman scattering in graphene. This enhancement is similar to the highest ones measured to date, concerning SERS of graphene on plasmonic substrates, and it is achieved via single-step, cost-effective, rapid laser nanopatterning methods, amenable to large-scale fabrication. Significant enhancement is observed for all excitation wavelengths, across the entire visible electromagnetic spectrum.

Arrays of quasi-ordered Si nanopillars were developed by femtosecond laser processing of silicon (100) in water [1]. The nanostructured Si substrates were coated by thermal evaporation with a nominal 50-nm thick Au layer, resulting in the dispersion of Au nanoparticles on the surface [2]. Monolayer graphene was grown on a catalytic Cu foil substrate by chemical vapor deposition (CVD) and was transferred on the substrates used in this work employing a PMMA scaffolding method. Raman spectra were acquired with a Raman microscope, employing four excitation laser lines (488, 514.5, 633, and 785 nm).

Numerical simulations employing the finite-difference time-domain (FDTD) method [3] confirm the plasmonic nature of the Raman enhancement and elucidate the advantages of the 3D topography of the substrate. Placing graphene on uncoated silicon nanopillars results in enhanced Raman signals (×30–50), compared to flat silicon substrates, similar to those of suspended graphene in air. When the nanopillars are decorated with gold nanoparticles, graphene conforms around them as it bends between nanopillars, sampling the nanoparticles' near field and emitting a strong Raman signal. Due to synergistic effects with the nanopillars, the nanoparticles are no longer indistinguishable, as in the case of a flat substrate. Instead, different nanoparticles become more active for different wavelengths and locations on the pillars. The Raman signal is calculated to increase monotonically with the depth of graphene bending, demonstrating the advantages of exploiting a 3D topography.

Providing a silicon platform for integration with graphene and other 2D materials is essential for future real-world applications in the fields of sensing, photonics, optoelectronics, and medical diagnostics, among others.

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Application of logistic function to describe kinetics of non-isothermal dehydroxylation of fullerol

B. Stanković, J. Jovanović[2], **B. Adnađević**

Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, Belgrade, 11050 R. Serbia

Main author email address: branislav@ffh.bg.ac.rs

Polyhydroxylated fullerenes, also-called fullerenols or fullerols, are derivatives of fullerenes with hydroxyl group formed by chemical modification of covalent C=C bond on their surfaces [1]. Fullerols, $C_{60}(OH)_n$, possess number of extremely important properties, such as: radical scavengers, antioxidant, antimicrobial, anti--cancer and catalytic activity and strong electron affinity. They reduce cardiotoxicity of some drugs and inhibit HIV-protease, hepatitis C virus and abnormal growth of cells. Therefore, fullerols found their applications in: medicine, biology, chemistry, materials science, solar and fuel cells, etc.

In the papers of Goswami et al. [17], thermogravimetric method for calculating number of OH groups (or some other addend) attached at fullerol surface was presented. Thermal activation method is exceptionally simple and economic way for one to obtain fullerol with defined number of OH groups. Since in literature there is no available data on the kinetics of fullerols dehydroxylation, our objective is to thoroughly investigate the non-isothermal dehydroxylation kinetics of fullerol. In other words, our aim is to determine the kinetic complexity, kinetic model, as well as the values of kinetic and thermodynamic parameters.

Non-isothermal kinetics of $C_{60}(OH)_{27}$ dehydroxylation has been investigated. Fullerol dehydroxylation thermogravimetric curves has been recorded at different heating rates ranging from 5 K min^{-1} to 25 K min^{-1}. It was found that fullerol dehydroxylation was an endothermic kinetic complex reaction. Fullerol dehydroxylation conversion curves, at all heating rates, were completely mathematically described by linear combination of two logistic functions. It was proved that complex mechanism of $C_{60}(OH)_{27}$ dehydroxylation consisted from two parallel reactions of dehydroxylation (low-temperature and high-temperature component). The values of kinetic parameters (E_a and ln$A$) and thermodynamic parameters (ΔH^*, ΔS^*, ΔG^*) for activation complex formation have been calculated for both components.

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Deposition of oxygen doped amorphous carbon films by magnetron sputtering

V. Dovydaitis[1], L. Marcinauskas[1], A. Iljinas[1]

1- Department of Physics, Kaunas University of Technology, Studentu str. 50, LT-51368, Kaunas, Lithuania

vilius.dovydaitis@ktu.edu

Amorphous hydrogen free carbon (a-C) and amorphous hydrogenated carbon (a-C:H) films have been a study object for several decades because of their unique mechanical, optical, chemical and electrical properties. Therefore, amorphous carbon films are well suited for a large variety of applications including optics, biomedicine, microelectronics, field of tribological and protective coatings and etc [1-3]. a-C, a-C:H films can be formed by various physical and chemical vapor deposition methods. One of the most widely used methods is magnetron sputtering. The main advantage of magnetron sputtering is the possibility to easily control the deposition process. Because of that, the desired properties and the structure of the amorphous carbon films can be obtained by changing the sputtering power, magnetron configuration, pressure, substrate temperature and other technological parameters [1, 4]. It is also possible to alter properties of the amorphous carbon films by doping them with various elements (Ti, Cr, Si, N, O and etc.) [5-6]. Doping the amorphous carbon films with oxygen is one of the possibilities for improving properties due to the rearrangement of the sp^3/sp^2 ratio. The addition of oxygen changes wettability, optical, mechanical, and tribological properties of carbon films [6].

The oxygen doped amorphous carbon (a-C:O) films were grown using layer-by-layer direct current magnetron deposition method in a 2-3 Pa argon environment using 3 inch graphite target (99.9 at.%). a-C:O films were grown using different sputtering powers (575 W, 885 W and 1360 W) on Si(100) and glass substrates. The elemental composition of films was determined by the energy dispersive X-ray spectroscopy. The thickness of films was measured using profiler. Surface morphology was examined with atomic force microscope. Optical properties of the doped amorphous carbon films were investigated by using UV–VIS–NIR spectrophotometer and null-ellipsometer. The optical band gap (E_g) was calculated using Tauc method. The bonding structure of carbon films was analyzed by microRaman spectroscopy.

It was obtained that the increase of the sputtering power from 575 W to 1360 W resulted in increase of growth rate from ~0.22 nm/s to ~0.45 nm/s. However, the increase of film deposition rate resulted in the increase of surface roughness from ~1.2 nm to 1.7 nm. The highest oxygen content was found in the film deposited at the lowest power. a-C:O films showed high optical transparency of 60-90 % in the visible range. The water contact angle of the doped DLC films was in the range of 85-99^o. The results of Raman spectroscopy revealed that the increase in sputtering power caused I_D/I_G ratio to decrease. Also, because of that the D peak position shifted to lower wavenumbers and the G band became narrower. These results showed that the film deposited at the lowest power had the highest fraction of C=C sp^2 sites. The highest Tauc band gap (1.9 eV) and refractive index (2.20) were obtained for the film deposited at 885 W power due to the lowest oxygen concentration and high fraction of C-C sp^3 sites.

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Molecular pillar approach to grow vertical covalent organic framework nanosheets on graphene: new hybrid materials for energy storage

Jinhua Sun,[1] Alexey Klechikov,[1]Calin Moise,[2] Mariana Prodana,[2] Marius Enachescu,[3] and Alexandr V. Talyzin[4]

[1-] Department of Physics Umeå University S-90187, Umeå (Sweden)
[2] Center for Surface Science and NanoTechnology University Politechnica of Buchartest 060042 Bucharest (Romania)

Main author email address: alexandr.talyzin@umu.se

Hybrid 2D-2D materials composed by perpendicularly oriented covalent organic framework (COFs) and graphene were prepared and tested for energy storage applications. Diboronic acid molecules covalently attached to graphene oxide (GO) were used as nucleation sites for directing vertical growth of COF-1 nanosheets (v-COF-GO). The hybrid material shows forest of COF-1 nanosheets with thickness of ~3 to 15 nm in edge-on orientation relative to GO. The same reaction performed in absence of molecular pillars resulted in uncontrollable growth of thick COF-1 platelets parallel to the surface of GO. The v-COF-GO was converted into conductive carbon material preserving the nanostructure of precursor with ultrathin porous carbon nanosheets grafted to graphene in edge-on orientation. It was demonstrated as high-performance electrode material for supercapacitors. The molecular pillar approach can be used for preparation of many other 2D-2D materials with control of their relative orientation.[1]

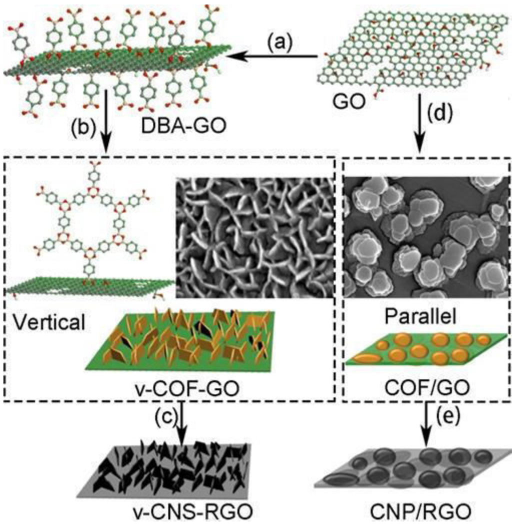

Figure 1 (a) Covalent functionalization of GO with DBA (b) Growth of vertical COF-1 nanosheets using DBA as molecular pillars (d) COF-1 platelets parallel to GO are formed at the same reaction conditions in absence of DBA functionalization. (c,e) carbonization of COF-GO materials.

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Toxicity comparison of different carbon-based nanomaterials in zebrafish

M. d'Amora[1], A. Camisasca[1,2], S. Lettieri[1], S. Giordani[1,3]

1- Nano Carbon Materials, Istituto Italiano di Tecnologia (IIT), via Livorno 60, 10144, Torino, Italy
2- Department of Chemistry and Industrial Chemistry, University of Genoa, via Dodecaneso 31, Genoa, 16145, Italy
3- Department of Chemistry, University of Turin, via Giuria 7, 10125, Turin, Italy

silvia.giordani@iit.it

Carbon nanomaterials (CNMs) are finding increasing applications in nanomedicine. CNMs can be employ as bioimaging probes, carriers for delivery of drugs and therapeutic agents, thanks to their small size and peculiar optic, electronic and physical characteristics [1].
Although different works have tested the in *vitro* toxicity of CNMs and reported their suitability for biomedical applications, a better understanding of their toxicity in a more complex and vertebrate system is still required. To this end, we assess and compare the potential adverse effects of carbon nano-onions (CNOs), carbon nano-horns (CNHs) and graphene oxide (GO), in zebrafish (*Danio Rerio*). Zebrafish is an emerging and ideal model system for high throughput screening of the whole-animal toxicity of nanomaterials, due its external development and optical transparency [2].
In this study, we assess the toxicity of three carbon-based nanomaterials during the development observing six different stages, from the gastrula stage until the completed developed larvae. Our results seek to demonstrate which CNMs is biosafe and consequently adequate for biomedical applications [3].

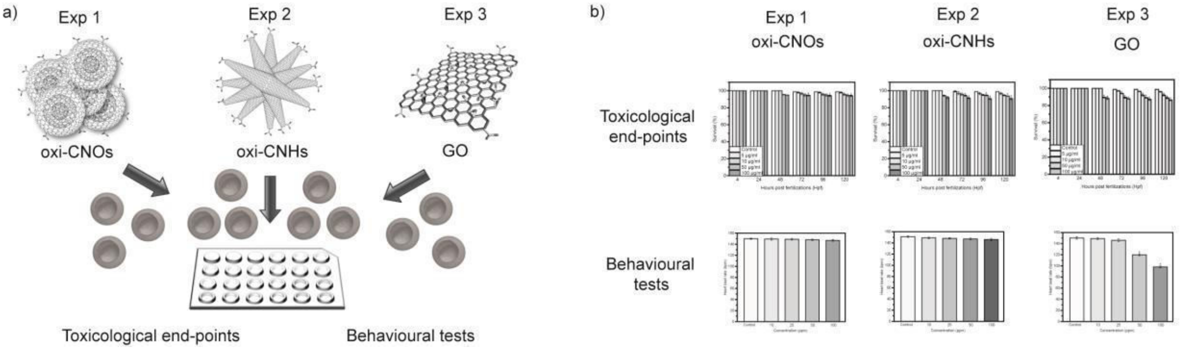

Figure 1. (a). Schematic representation of the experimental protocol. (b) Survival rates and heart beat rates of zebrafish treated with different concentration of oxi-CNOs, oxi-CNHs and GO, as examples of toxicological endpoint and behavioural test, respectively. [3]

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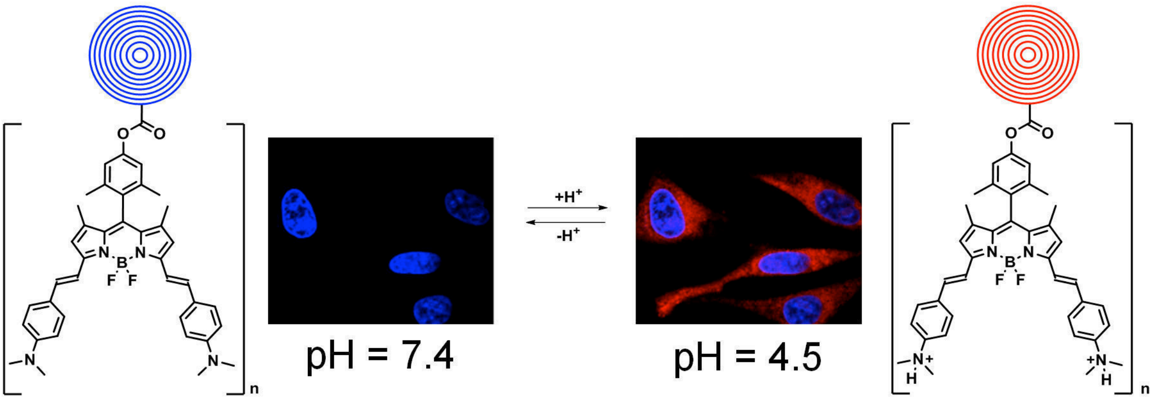
Carbon nano-onions for diagnostics

S. Lettieri[1], M. d'Amora[1], A. Camisasca[1,2], S. Giordani[1,3]

1- Nano Carbon Materials, Istituto Italiano di Tecnologia (IIT), via Livorno 60, 10144, Torino, Italy
2- Department of Chemistry and Industrial Chemistry, University of Genoa, via Dodecaneso 31, Genoa, 16145, Italy
3- Department of Chemistry, University of Turin, via Giuria 7, 10125, Turin, Italy

silvia.giordani@iit.it; s.giordani@unito.it

Multishell fullerenes, known as carbon nano-onions (CNOs), have emerged as a platform for bioimaging because of their cell-penetration properties and minimal systemic toxicity [1]. Here, we describe the covalent functionalization of CNOs with a π-extended distyryl-substituted boron dipyrromethene (BODIPY) dye with on/off modulated fluorescence emission activated by an acidic environment. The switching properties are linked to the photoinduced electron transfer (PET) characteristics of the dimethylamino functionalities attached to the BODIPY core. The on/off emission of the fluorescent CNOs is fast and reversible both in solution and in vitro, making this nanomaterial suitable as pH-dependent probes for diagnostic applications [2, 3].



(a) (b)

Figure 1 Chemical structures and confocal fluorescence images of HeLa cells treated for 1 h with 20 µg mL−1 of fluo-CNOs.
(a) PBS, pH 7.4; (b) acid buffer, pH 4.5.

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Functional biocompatible interfaces for bioelectronics applications by the integration of eumelanin and graphene-like layers

V. Gargiulo[1], M. Alfè[1], R. Di Capua[2], G. M. De Luca[2], T. Skala[3], G. Mali[4], A. Pezzella[5]

1- CNR, Institute for Research on Combustion (IRC), Naples, Italy
2- CNR-SPIN, and Department of Physics "E. Pancini" University of Naples Federico II, Naples, Italy
3- Department of Surface and Plasma Science of Charles University in Prague, Cezth Republic, and Sincrotrone Trieste S.C.p.A., Materials Science Beamline
4- Department of Inorganic Chemistry and Technology of the National Institute of Chemistry, Ljubljana, Slovenia,
5- Department of Chemical Sciences, University of Naples "Federico II", Via Cintia 4, I-80126 Naples, Italy
gargiulo@irc.cnr.it

In the manifold of available materials for functional biocompatible interfaces, the human pigment eumelanin (EU) is currently gaining increasing interest. The large EU non-solubility and the EU low electrical conductivity are the two main obstacles hampered a full fabrication and exploitation of eumelanin-based devices. Among the different strategies under investigation to improve electrical performance of eumelanin thin films, a clear-cut approach lies in hybridization with a suitable conductive counterpart. In this view, π -conjugated systems molecules featuring conducting pathways appear a key choice in the production of new organic materials for electronic (nano)devices. Following this approach, conductive interfaces were designed and fabricated by an efficient integration of EU and graphene like (GL) layers [1,2,3]. The hybrid materials (EUGLs) exhibited quite good adhesion to hydrophilic and hydrophobic surfaces, water stability, biocompatibility and improved electrical conductivity compared to the sole EU pigment due to the presence of embedded GL layers [1]. EUGLs were easily produced allowing eumelanin precursors (5,6-dihydroxyindole (DHI) and/or 5,6-dihydroxyindole-2-carboxylic acid, DHICA [1]) to polymerize in a water suspension of GL layers [1]. Different EU:GL mass ratios were explored with the aim of deepening the comprehension of the interaction between the two conjugate π systems. The chemical-physical, electrical and morphological analyses indicate that the actual composition of the EUGL hybrids could be considered as the outcome of quantitative merging of the starting materials. It can be speculated that both covalent bonds and π-π stacking are expected to be involved in EU:GL interaction. To get more insights on this issue, more sophisticated analytical techniques were employed: X-ray absorption spectroscopy with synchrotron radiation and solid state nuclear magnetic resonance. Comparative AFM inspection of the morphologies of eumelanin, GL and EUGL thin films indicates a consistent modification induced by eumelanin to the GL self-assembling. The hybrid film has locally a more granular surface compared to the EU film (Fig. 1). Electrical dc resistivity was measured in a standard four contacts configuration. All the curves show an ohmic behavior, but with extremely different resistance (Fig. 1).

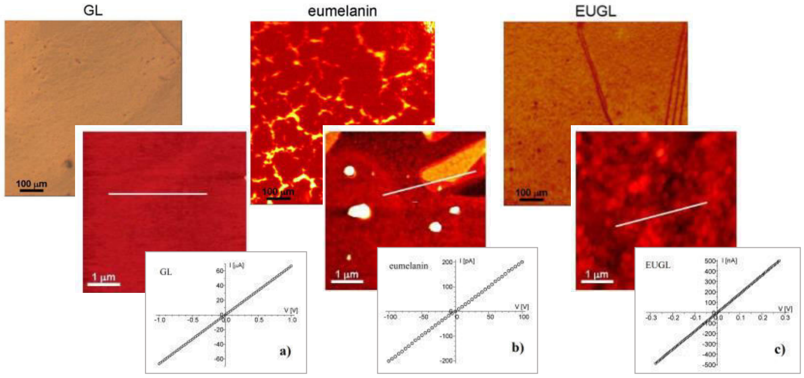

Figure 1 AFM images at different magnifications and IV dc curves of GL, EU and EUGL (1:1 mass ratio)

The study of the collected data is still ongoing however available evidences do suggest that electronic and structural properties are strictly interconnected. The deep understanding of structure-behavior relationship in EUGL hybrids is crucial for expanding the scope of eumelanin in bioelectronics and paving the way to advanced biocompatible organic electrochemical transistor-like interfaces capable to translate cellular activity in electrical signals.

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3D Printed Carbon Fibre Reinforced PEEK: focus on Medical Applications

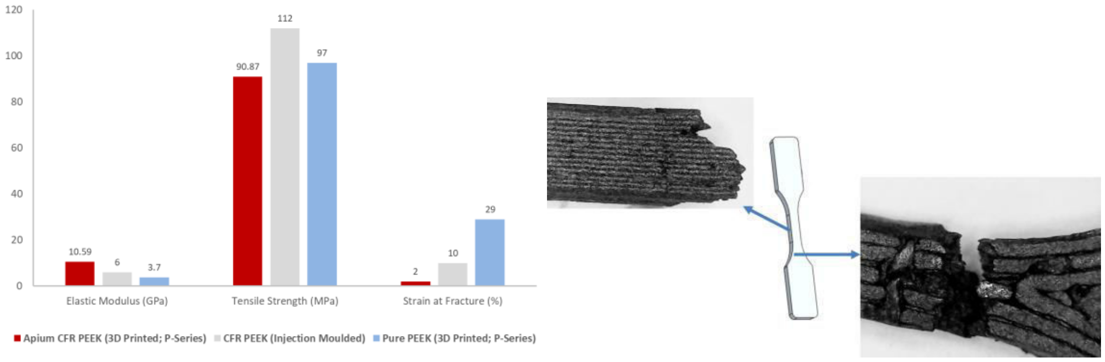
U. Popp[1], **J. Scholz**[1], **B. Okolo**[1]

1- Apium Additive Technologies GmbH, Willy Andreas Allee, 19. D76131 - Karlsruhe, Germany

uwe.popp@apiumtec.com

In the past 25 years there has been a gradual but sustained attempted to use carbon fibre reinforced (CFR) PEEK composite material in medical human implant applications where wear resistance and mechanical stiffness are needed [1, 2]. These CFR PEEK implants are fabricated using either CNC milling or injection moulding methods. With the advent of new manufacturing methods such as Additive Manufacturing (AM; aka 3D Printing), which offers the added advantage of directly using patient-specific data from radiology to develop implants, there is need to explore the applications value of AM CFR PEEK in medical practice. Only recently [3] has it been demonstrated, using 3D printers from Apium Additive Technologies GmbH, that CFR PEEK can be 3D printed at a reasonably good technical quality. A key challenge in this respect has been in the design of the CFR PEEK composite material where the weight fraction of matrix (PEEK) and the reinforcing phase (carbon fibre) as well as the geometry of the fibre phase had proven to be key processing barriers. Presently, the consensual design involves a homogenous distribution of a micro-fibre carbon phase of between 20 to 50 weight percent in a PEEK matrix. In this weight range the mechanical properties (especially stiffness/Young's modulus) of the composite already conform to the minimum bio-mechanical requirements needed for overcoming undesirable stress shielding effects inherent to metallic implants like titanium alloys.

This presentation shows first mechanical (Figure 1a) and fracture surface (Figure 1b) results for 3D printed CFR PEEK which had been loaded in classical tensile mode. The results reveal that there is clearly an appreciation in stiffness values in 3D printed CFR PEEK compared with pure PEEK; considering the relatively low-pressure process involved in the composite formation during the part printing. In comparison with injection moulded (IM) CFR PEEK of the same composition, the 3D printed CFR PEEK also had a higher stiffness while its ductility and tensile strength are relatively lower than that of the IM - CFR-PEEK and the 3D Printed pure PEEK. Optical light microscopy imaging of the 3D Printed CFR PEEK showed that the part is layered, not fully dense and contained interfaces which might prove to be beneficial for inter-body fusion of implants in medical applications.



(a) (b)

Figure 1. (a) Comparison of the mechanical properties if 3D Printed CFR PEEK, Injection Moulded CFR PEEK and 3D Printed pure PEEK. (b) Optical light microscopy image of fracture surface of 3D Printed CFR PEEK revealing process induced interfaces.

The authors acknowledge Mr. Sisidhar Gorantla of Apium for the optical light microscopy images and Dr. Stefan Dietrich of IAM-WK at the KIT for the mechanical testing.

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Nanocarbon Based Template Synthesis Single Crystalline $LiMn_2O_4$ Spinels

H. Akbulut[1], A. Guler[1], S. Ozcan Duman[1], M.O.Guler[1]

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

akbulut@sakarya.edu.tr

Li-ion batteries have some advantages like long cycle life, low cost, thermal stability, high working voltage and no memory effect [1]. Owing to this advantages rechargeable Li-ion batteries are the main components of the secure power sources from small portable electronics to high energy storage systems. However, capacity fading, safety issues, inadequate rate performance and high cost still restrict its application in automobile industry. Among these cathode material, spinel $LiMn_2O_4$ (LMO) cathode which has theoretical capacities of 148 mAh/g is regarded as promising cathode electrode due to their intrinsic properties such as easy production, low cost, less toxic, high potential and environmental safety [2]. Many researchers have reported that enhancing the stability of the spinel structure by substituting metal ions will considerably lower the first discharge capacity [3]. The main reason is that the oxidation potential of the substituent ions in the spinel structure is considerably higher than the unsubstituted $LiMn_2O_4$. Therefore, the amount of substituent ions within the spinel structure should be carefully adjusted in order to obtain higher specific capacities around the 4 V potential window. Several reports have also confirmed that substituting metal ions such as Cr, Co or Ni less than 0.2 % will significantly improve the cyclability [4]. Moreover, surface coatings have been widely employed to prevent micro-strain during cycling and reduce capacity fading in LMO [5]. Recently, graphene, which is two-dimensional structure of carbon, has taken attention owing to its extraordinary conductivity and larger surface area [23]. Moreover, nano layer graphene sheets may also help to prevent to dissolution of Mn2+ ions into the electrolyte and improve the performance of battery efficiency [2,4].

In this study, α-MnO_2 nanorods as a sacrificial template in synthesizing the LMO nanorods and LCMO nanorods are produced by simple microwave hydrothermal synthesis method. As-synthesized templates were then chemically converted into LMO nanorods and LCMO nanorods through a solid state reaction method. LCMO nanorods were then anchored between the layers of graphene sheets by a simple vacuum filtration method and binder free and highly flexible freestanding cathode electrodes are obtained. Electrochemical tests clearly indicated that the G/LCMO samples exhibited better rate capability and cyclic performance than unreinforced and pristine LMO samples. The enhancement in the performance has shown that graphene reinforced freestanding LCMO samples could be a promising candidate for high capacity energy storage applications.

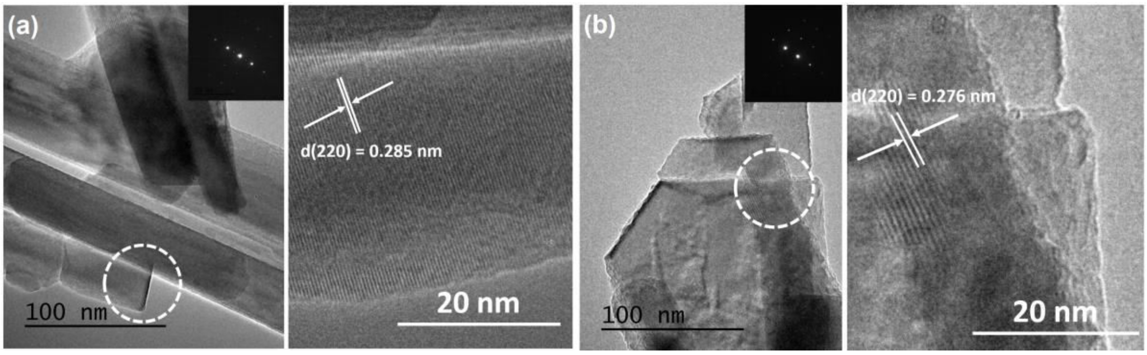

Figure 1. TEM micrographs and SAED patterns of (a) LMO and (b) LCMO samples.

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Innovative Graphene Based MnO_2 / LTO Fullcells for Li-Ion Batteries

S. O. Duman[1], M. O. Güler[1], A. Guler[1], H. Akbulut[1]

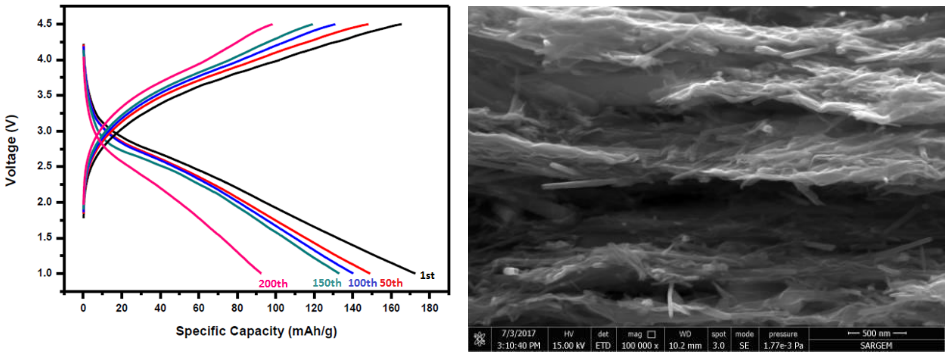
1- Sakarya University, Engineering Faculty, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54187, Sakarya/TURKEY

guler@sakarya.edu.tr

Nowadays there is a considerable effort in progress to develop rechargeable batteries having high capacity and high life cycle to meet the users demand. In this regard, many strategies have been developed such as improving the electronic conductivity of electrodes and ionic conductivity electrolytes, enhancing surface of electrode and increasing lithium diffusion. Recent studies have showed that working with nanostructured composites can offer many benefits, based on their extraordinary compositions and structures to use as functional materials [1]. However, expensive materials and methods to prepare nanostructured materials limit to use these approaches.

Having high theoretical capacity, low cost, low toxicity and natural abundance makes Manganese dioxide (MnO_2) a useful material for application in lithium ion batteries [2]. It is well-known that cathode performance is strongly related with surface area and conductivity. Nanoscale MnO_2 should be reinforced by electrically conductive and flexible material to maximize its electrochemical performance. Due to its unique properties such high specific surface area (2630 m^2/g), flexibilty and high electrical conductivity graphene is one of the most promising materials to use in Li-ion batteries.

In this study, MnO_2 was produced by Microwave Assisted Hydrothermal Method and Graphene Oxide prepared by Hummers' method and following chemically reduced. Graphene/ MnO_2 nanocomposite cathode was produced via ultrasonic homogenizer. Surface and cross-sectional morphology of the Graphene/MnO_2 composite cathode was investigated using field emission scanning electron microscopy (FESEM). Structures of the produced Graphene/MnO_2 composite cathodes were characterized by using X-ray diffraction (XRD) technique and Raman spectroscopy. The electrochemical studies were performed with $Li_4Ti_5O_{12}$ anode.



(a) (b)

Figure 1 :(a) Galvanostatic charge-discharge profiles of Gr-MnO_2/LTO full cell. (b) cross-sectional FESEM image of synthesized Gr-MnO_2 cathode.

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Photoionduced catalytic properties of metal nanoclusters/graphene ensembles

M.A. Koklioti, **A. Stergiou, N. Tagmatarchis***

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens 11635, Greece

mkoklioti@eie.gr

Nowadays, substantial research interest is dedicated to metal nanoclusters (M_{NCs}) due to their unique optical, electronic, physical properties along with good biocompatibility and low toxicity, which are in contrast with their corresponding large nanoparticles [1]. The immobilization of M_{NCs} on graphene sheets allows support effects, which are vital in energy conversion applications [2].

Herein, we investigate the photocatalytic properties of water-soluble nanoensembles based on silver and gold nanoclusters, abbreviated as Ag_{NCs} and Au_{NCs}, and ammonium functionalized graphene (abbreviated as *f*-G) [3]. Briefly, Ag_{NCs} and Au_{NCs} stabilized with α-lipoic acid bearing negative charges at alkaline media and *f*-G possessing positive charges attributed to the presence of ammonium units on their skeleton, were electrostatically coupled. The successful fabrication of the M_{NCs}/*f*-G ensembles (M=Ag, Au) was realized with the aid of absorption and photoluminescence titration assays. Markedly, with the latter the fluorescence quenching of M_{NCs} upon incremental additions *f*-G revealed the development of electronic interactions between the two species at the excited states. Next, the photocatalytic properties of M_{NCs}/*f*-G were assessed by monitoring the efficient reduction of 4-nitrophenol to the corresponding 4-aminophenol. The photocatlytic process is attributed to the development of charge-transfer phenomena between the two components within the M_{NCs}/*f*-G ensembles. In addition, the reduction kinetics decelerated by half when bare M_{NCs} were employed as compared to the M_{NCs}/*f*-G ensembles. Intriguingly, the reaction kinetics for the reduction of nitrophenol was significantly accelerated upon light irradiation of Au_{NCs}/*f*-G ascertaining excellent photocatalytic activity. Three synergistic mechanisms, namely, (a) hydride transfer from Au-H, (b) hydride transfer from photogenerated Au-H species, and (c) hydrogen produced by the photoreduction of water are accountable for the observed high catalytic activity of Au_{NCs}/*f*-G ensembles. Finally, we succeeded on recycling the nanosized catalysts and performing the reduction reaction for successive cycles without loss of activity.

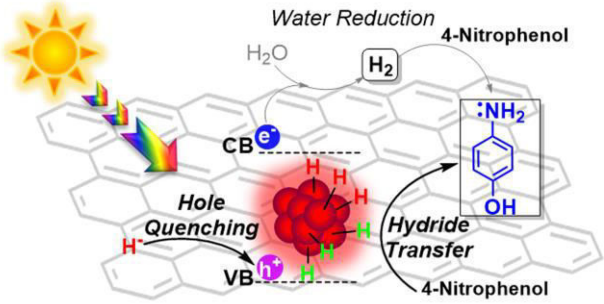

Figure 1. Illustration of the mechanism for the photoinduced catalytic reduction of 4-nitrophenol by M_{NCs}/*f*-G (M= Ag, Au) ensembles.

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Highly effective radar absorbing materials based on SiC whiskers.

A. Plyushch[1], **J. Macutkevic**[1], **J. Banys**[1] , **D. Bychanok**[2],
P. Kuzhir[2], **A. Sokal**[3], **K. Lapko**[3]

1- Faculty of Physics, Vilnius University, Sauletekio 9, Vilnius LT-10222, Lithuania
2- Institute for Nuclear Problems, Belarus State University, Bobruiskaya 11 Minsk, 220030, Belarus
3- Research Institute for Physical-Chemical Problems of Belarusian State University, Leningradskaya Str. 14, Minsk 220030, Belarus

artyom.plyushch@ff.vu.lt

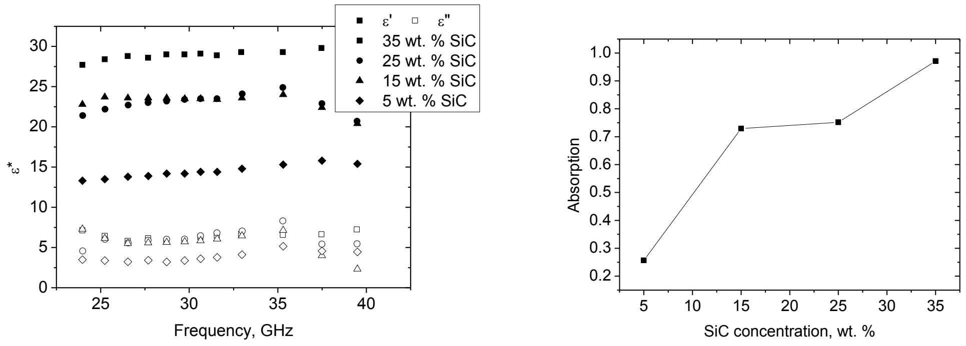
Design and development of effective radar absorbing material (RAM) is the critical point in modern solid state physics. Recently significant progress was achieved in the study of composites with inclusions of carbon nanotubes as RAMs. Silicon carbide is another perspective material for RAMs development.

SiC whiskers were purchased from US Research Nanomaterials, Inc [1]. Alumina phosphate ceramics were prepared according to protocol described in [2] with SiC concentrations of 5, 15, 25, 35 wt. % .

The Frequency dependence of real and imaginary parts of dielectric permittivity in GHz range is presented in figure 1(a). For the calculations of the absorption coefficient of the system with back reflector the following equation may be utilized [3]:

$$S_{11}(\lambda,\tau,\varepsilon) = -\frac{k_z(\exp[2i\tau k_{2z}]-1)+k_{2z}(1+\exp[2i\tau k_{2z}])}{k_z(1-\exp[2i\tau k_{2z}])+k_{2z}(1+\exp[2i\tau k_{2z}])}, \tag{1}$$

where λ is the wavelength, ε and τ are the dielectric permittivity and thickness of the sample, correspondingly. For free space calculations wave vectors $k_z = 2\pi/\lambda$ and $k_{2z} = 2\pi\sqrt{\varepsilon}/\lambda$ should be used. Using (1) an absorption coefficient $A = 1-|S_{11}|^2$ of 0.45 mm thick samples at frequency of 30 GHz was calculated.



(a) (b)

Figure 1 (a) Complex dielectric permittivity of ceramic materials with different content of SiC inclusions in GHz frequency range. (b) Absorption coefficient of 0.45 mm thick samples at frequency of 30 GHz.

As we can see, rise of SiC concentration leads to improving absorbing properties of composite materials from 25 up to 97 %. Since phosphate ceramics itself is highly thermally stable system [4], so we may expect the same thermal stability from the SiC / phosphate composite. We can conclude, that SiC / phosphate ceramic composite is highly perspective material for shielding applications.

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Kinetics of fulerene polyhydroxylation

Jelena Jovanović [1], **Mihajlo Gigov** [2], **Borivoj Adnađević** [1]

1- University of Belgrade - Faculty of Physical Chemistry, Studentski trg 12-16, 11001 Belgrade, Serbia
2- Mining institute Ltd. Belgrade, Batajnički put 2, 11080 Belgrade, Serbia

Main author email address: jelenaj@ffh.bg.ac.rs

The fullerene family (C_{60}, C_{70}, C_{82},…, C_{540}), which are caged spherical molecules, represent the third allotropic carbon modification, and their most stable, most abundant and most explored representative is the C_{60} molecule, which is used in various fields from material science to medicine. However, application of the C_{60} molecule is limited by the fact that it is practically insoluble in water. The hydroxylated derivatives of the fullerene C_{60} obtain completely new physicochemical characteristics and open up the possibility for further derivatization. The polyhydroxylated derivates of fullerene are named fullerols, which can contain different numbers of hydroxyl groups that are formed by chemical modification of the covalent bonds at the surface of C_{60} molecules. Most frequently, fullerols are denoted as $C_{60}(OH)_n$, where "n" should be from 2 to 44. Due to their unique physico-chemical properties: solubility in water, ability of free radical scavenging, antioxidant properties, photo-toxic, photo-catalytic and anti-microbial activity it could be expected that fullerol should found extensive application in various fields of chemistry, biochemistry, pharmacy and medicine. In the literature are presented numerous methods of fullerol synthesis with a defined number of hydroxyl groups [1, 2]. On the contrary, however, the investigations on the kinetics of fullerene polyhydroxylation are sparse. Here, we present systematically investigation of each particular reaction parameter: concentration of all of the reactants: C_{60}, phase-transfer catalyst (CTAB), H_2O_2, as well as temperature and mixing speed on the kinetics of C_{60} polyhydroxylation. The fullerene polyhydroxylation was performed following the modified procedure of Adnađević et al. [3]. The progress of C_{60} polyhydroxylation was followed through the changes in the C_{60} concentration which was determined by measuring the absorbancy at $\lambda = 538$ nm and checking with the Beer's law. The method if the initial rates was applied for the determination the reaction rate against every single reactant, keeping all the other reaction parameters constant. The values of the isothermal rate constants and the kinetics parameters (activation energy and pre-exponential factor) of C_{60} polyhydroxylation were determined.

The kinetically complex reaction of C_{60} polyhydroxylation in the presence of CTAB as phase transfer catalyst have clearly defined kinetics limiting stage with Ea=34.9 kJ mol^{-1} and ln$A$=11.8 min^{-1}. It was found that the reaction of fullerol formation in regard to the reactants, can be described with the equation: $v = k\,[C60]^{1}\,[CTAB]^{0.9}\,[H2O2]^{1}\,[NaOH]^{0.6}$

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Functionalization and Processing of Graphitic Low-Dimensional Functional Nanocarbons

Anastasios Stergiou

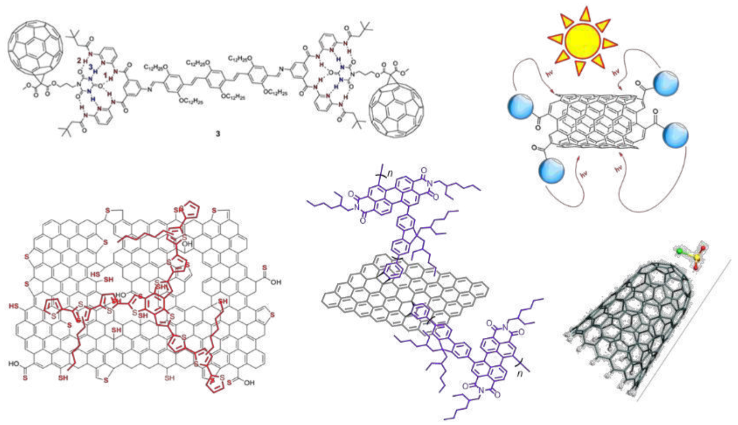
Theoretical and Physical Chemistry Institute (TPCI), National Hellenic Research Foundation (NHRF)

48 Vassileos Constantinou Avenue, Athens 11635, Greece

Up to date low-dimensional nanocarbons (LDNCs) like fullerenes (0D), carbon nanotubes (1D), graphene (2D) and carbon nanohorns (pseudo 1D) are considered the most promising candidates for the development of metal-free functional materials for energy and electrical applications. These graphitic nanostructures have exceptional electronic and mechanical properties and nowadays a roadmap for their feasible chemical and supramolecular functionalization is available and capable to overcome their poor dispersion ability and the consequent difficulties in processing.

This presentation will focus into our recent progress in functionalization and processing of these unique nanocarbons: the development of i) C_{60}-based electron donor-acceptor supramolecular architectures through hydrogen bonding motifs[1], ii) carbon nanotube/fluorescent carbon dots composites[2], iii) graphene/photoactive polymer composites[3], iv) sulfur-doped graphene/oligothiophene composites[4] and v) a novel procedure for the non-oxidative and non-destructive individualization of single wall carbon nanohorns[5].

We intend to display, in brief, the challenges we face during processing of these all-carbon nanostructured materials and the strategies we follow to overcome the drawbacks and access functional LDNC-base materials. Selected data from this work, conclusions and outlooks will be also discussed.



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Theoretical modeling of experimental EELS data for monolayer graphene supported by different metal substrates

A. Politano[1], I. Radović[2], D. Borka[2], Z.L. Mišković[3], G. Chiarello[1]

1- Dipartimento di Fisica, Università della Calabria, 87036 Cosenza, Rende, Italy
2- Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia
3- Department of Applied Mathematics, and Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

iradovic@vin.bg.ac.rs

We present a theoretical modeling of the electron energy loss spectroscopy data for monolayer graphene supported by Pt(111), Ru(0001), and Ni(111) substrates. In order to reproduce the experimental loss function, we have used a two-dimensional, two-fluid hydrodynamic model for inter-band transitions of graphene's π and σ electrons and an empirical Drude-Lorentz model in the local approximation for metal substrates. The agreement between the theoretical curves and the experimental data is very good in the cases of graphene supported by Pt and Ru substrates. Conversely, the agreement is less satisfactory for the case of graphene/Ni, presumably due to the strong hybridization between the π states of graphene and the *d* bands of Ni, which is not accounted for in the model.

Electronic properties of transition metal dichalcogenide nanoribbons

G. Kopidakis[1,2], I. N.Remediakis[1,2], E. Kaxiras[3] , D. Davelou[1,2]

[1]Department of Materials Science and Technology, University of Crete, GR-71003 Heraklion, Crete, Greece
[2]Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology Hellas (FORTH), GR-71110 Heraklion, Crete, Greece
[3]Department of Physics and Harvard's Paulson School of Engineering and Applied Sciences,
Harvard University, Cambridge MA 02138, USA.

**d.davelou@materials.uoc.gr*

The isolation of graphene and other materials of atomic thickness has generated enormous interest in two-dimensional (2D) crystals. Single layers cleaved from layered materials such as graphite, boron nitride, and molybdenum disulfide (MoS_2) have been studied extensively, both experimentally and theoretically. 2D MoS_2 and other semiconducting Transition Metal Dichalgogenides (TMDCs) exhibit novel optoelectronic properties, different from their bulk counterparts, and metallic states at their edges [1]. We present first-principles calculations on four representative TMDCs, MoS_2, $MoSe_2$, WS_2, WSe_2, in various 1D nanoribbon configurations. We compare the thermodynamic stability and the electronic structure of the 2D bulk and 35 different quasi-1D nanoribbons for each of the four materials. We use Density-Functional-Theory (DFT) as implemented by the open-source package GPAW [2]. In each case, we perform calculations for the total energy and the band structure and we consider the reconstructions of the zigzag metal-terminated edge by adding different amounts of chalcogen adatoms. The 1D structures we investigated have positive edge energies when the chalcogen chemical potential is close to the energy of the bulk chalcogen phase, and negative edge energies for higher chemical potential values. We find that the reconstruction with two chalcogen adatoms per edge metal atom is the most stable under usual experimental conditions and that all 1D nanoribbon structures consist of a semiconducting bulk bounded by edges with metallic character [3].

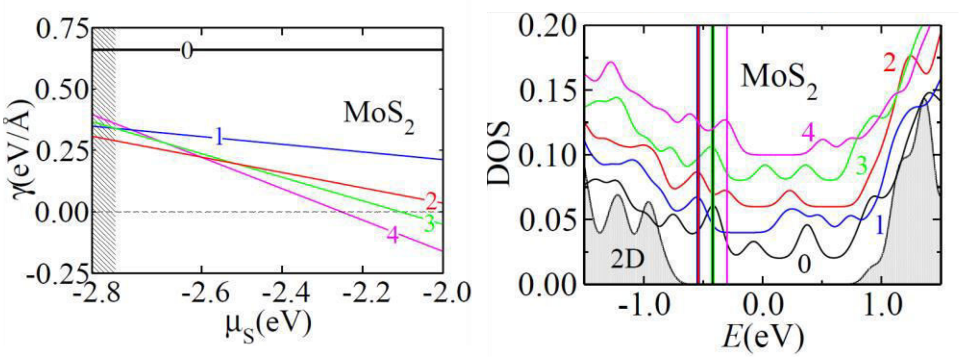

Figure 1: (left) Calculation of the edge energy of MoS_2 nanoribbons as a function of the chemical potential of Sulfur. (right) Comparison of the Density of States of 1D TMDCs and 2D nanosheet. Vertical lines represent the Fermi level of 1D TMDCs. For 2D TMDCs the Fermi level is set at zero.

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Center for Surface Science and NanoTechnology
University POLITEHNICA of Bucharest

Development of nano-structured interphases in carbon-epoxy composites

A. Caron[1], N. Naveh[1], C. Moise[2] and M. Enachescu[2]

[1] Polymers and Plastics Engineering Dept., Shenkar College of Engineering and Design, Israel
[2] Center for Surface Science and Nanotechnology, Univ. Politehnica of Bucharest, Romania

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

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

In this work carbon fibers were either oxidized or coated with carbon nanotubes. CNTs were applied onto the fibers or fabric from a CNT/acetone dispersion at various concentrations, or deposited by pulsed laser deposition (PLD) on a cold finger stage. HRSEM Micrographs from PLD show even, well dispersed coating of segregated CNTs.

Oxidation is clearly shown by an increase of up to 50% in the polar component, either by wet chemistry or via plasma treatment. The oxygen surface content (atomic) as measured by EDS is in the range 2-4%. Oxidized fibers show a higher degree of surface roughness, suggesting that the nitric acid has etched the fiber surface, increasing the specific area.

Contact angles and surfaces energies are unaffected by CNT deposition, in spite of the nanostructured pattern achieved on the fiber surface. This is an indication of wetting comparable to the untreated fiber.

Short beam testing (ASTM D2344) revealed that 60 sec plasma treatment increases the ILSS by 13% while the 0.1 wt% CNT coating increases the ILSS by 17%. The flexural strength (ASTM D7264) increased by 10% with wet oxidation and by 20% after plasma treatment.

Microdroplet pull-out tests were performed with a custom made micro-vise jig. The droplet was cured on a single carbon filament in a three-step curing cycle from 80 to 160°C. Preliminary results will be shown and compared to other studies.

Green, waste-free functionalization of CNT fibers for supercapacitors and use in water

D. Iglesias,[1] E. Senokos,[2-4] B. Alemán,[2] L. Cabana,[2] C. Navío,[5] R. Marcilla,[4] M. Prato,[1,6,7]
J. J. Vilatela,[2] and S. Marchesan[1]
1. Dip. Sc. Chim. Farm., Università di Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy 2. IMDEA Materials Institute, c/Eric Kandel 2, Getafe, 28906 Madrid, Spain 3. E. T. S. de Ingenieros de Caminos, Universidad Politécnica de Madrid, 28040 Madrid, Spain
4. IMDEA Energy Institute, Parque Tecnológico de Móstoles, Avda. De la Sagra 3, Móstoles, 28935 Madrid, Spain
5. IMDEA Nanoscience Institute, Faraday 9, Cantoblanco, 28049 Madrid, Spain 6. Carbon Nanobiotechnology Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20009 Donostia−San Sebastian, Spain 7. Basque Fdn Sci, Ikerbasque, Bilbao 48013, Spain

Dip. Sc. Chim. Farm., Università di Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy

The assembly of carbon nanotubes (CNTs) aligned into fibers (CNTFs) is a useful route to exploit and apply the remarkable physico–chemical properties of CNTs in numerous research areas. CNT functionalization has been widely studied for its implementation into composites and devices.[1,2] However, CNTF functionalization is still in its early stages due to the challenges inherent to the preservation of CNTF macroscopic morphology. Here, we describe a detailed investigation of the gas-phase derivatization of CNTFs by means of ozone that was generated *in situ* from a UV lamp and atmospheric oxygen. In contrast with liquid-based methods to oxidise CNTs, this gas-phase protocol maintains CNTF macrosocpic morphology, while singificantly increasing its hydrophilicity (Fig. 1, *left*). The reaction product is thoroughly characterized by Raman spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, and scanning electron microscopy. Its acquired hydrophilicity allows CNTF electrochemical characterization in aqueous systems, while this was not possible for the pristine material. As a proof of principle, the oxidized CNTF is employed as an active material in all-solid supercapacitor flexible devices (Fig. 1, *right*).[3]

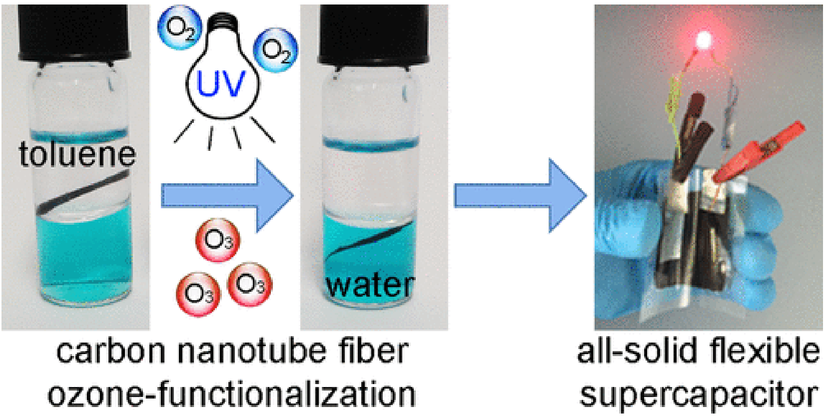

Fig. 1. UV-ozone functionalization of CNT fibers renders them hydrophilic (*left*). The material can be used in all-solid flexible supercapacitors (*right*).[3]

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Graphene based metasurface for THz passive components

Alesia Paddubskaya[1], Polina Kuzhir[1], Tommi Kaplas[2], Yuri Svirko[2]

[1] *Institute for Nuclear problems of Belarusian State University, Minsk, Belarus*

[2] *Institute of Photonics, University of Eastern Finland, Joensuu, Finland*

Growing interest in THz science is due to its many important applications, including THz imaging, microscopy, non-destructive testing, tomography, medical diagnosis, health monitoring, environmental control, chemical and biological identification, and in future communication networks. These applications require efficient, durable and robust components capable of generating, manipulating and detecting of THz radiation[1]. According to just published "The 2017 terahertz science and technology roadmap"[2] among the most important challenges are passive quasi-optical components, i.e. shields, filters, polarizers and collimators.

The main drawback of existing THz components is their restricted tunability, which is the must for future THz devices. We propose to resolve the problem by combining unique properties of graphene[3], including its ability to tune the Fermi level with external doping or biasing, with the outstanding opportunities that gives the metasurface paradigm[4], i.e. 'designer' materials technology (see,[5] for negative refractive index metamaterials and electromagnetic (EM) cloaking.

The concept of EM components relying on plane graphene structures has been proposed in our recent works[6],[7]. As a next step, in this paper we propose graphene-based metasurface composed of array of hemispheres in order to design tunable passive components THz applications.

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Graphene-Transition Metal Dichalcogenide Heterostructures as Two-Dimensional Nano-Carbon Composite Materials

A. V. Krasheninnikov^{1,2}

1- Helmholtz Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Germany
2- Department of Applied Physics, Aalto University School of Science, Finland

e-mail: a.krasheninnikov@hzdr.de

Fabrication of heterostructures composed from two-dimensional (2D) materials held together by van der Waals forces by various techniques made it possible to develop materials with unusual properties [1]. Encapsulating 2D materials between chemically inert graphene sheets also gave unique opportunity to protect reactive 2D materials from the interaction with the environment, e.g. from oxidation. Moreover, the encapsulation made it possible to minimize the electron beam-induced damage [2] and study the atomic structure of many marginally-stable 2D materials using transmission electron microscopy (TEM).

In my presentation I will give a brief summary of the theoretical results relevant to the behavior of graphene-transition metal dichalcogenides (TMD) heterostructures obtained in collaborations with several experimental groups [3-4]. Specifically, it will be shown that encapsulation made it possible to monitor the behavior of native defects in TMDs in the real time [3] and observe Peierls-type distortions [4].

Finally, I will touch upon carbon nanotubes encapsulated with iodine chains as another example of carbon nano-composite materials. Unusual structural distortions and charge density waves were observed in these systems and the results were rationalized using first-principles calculations [5].

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Graphene–type composite materials as SEIRA and SERS platforms

G. Dovbeshko[1], **A. Dementjev**[2], **O. Posudievsky**[3]

1-Institute of Physics , National Academy of Sciences of Ukraine, 46 Prospect Nauki, Kiev 03680, Ukraine
2- Center for Physical Sciences and Technology Savanorių ave. 231, Vilnius, Lithuania
3- I.V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, 28, Prospect Nauki, Kiev 03028, Ukraine

gd@iop.kiev.ua

In this report we discuss a problem of application of graphene, oxide graphene, carbon nanotubes and composite materials on their basis for SEIRA and SERS spectroscopy. Experimentally we showed that graphene, graphene oxide or other 2D materials as MoS_2, $MoSe_2$, WS_2 etc. does not show giant enhancement coefficients. In SEIRA, we got the enhancement coefficients of about 10 for biological molecules adsorbed on graphene oxide surface and those for SERS of about 100. The largest enhancement in SERS (about 10^5) was registered by us for poly-A biopolymer adsorbed on single-walled carbon nanotubes placed on the nanostructured metallic periodic structure. No large enhancement was registered for biopolymers on the graphene-type structures.

We calculated the charge transfer rate in the systems of biological monomer on graphene-type structure and found it equal to 0.1e or drastically less. Thus, the mechanism of enhancement connected with chemical nature should be supported by other reasons as local electromagnetic fields enhancement or optical effects (e.g interference). The luminescence suppression by metallic-like support should be taken into account.

We present the results on SERS and SEIRA spectra of biological monomers, polymers, components in living cells with application of graphene oxide and BN nanoparticles. Here we rise and answer the next questions. Should we always strive to achieve a large enhancement or not? Is there an alternative view on surface enhanced spectroscopy? What are the advantages and disadvantages of SERS spectroscopy? What type of substrate could be most efficient as SERS platform for biopolymers?

This work was supported by the STCU 6175, NATO SPS 985291 and joint Ukrainian-Lithuanian Project (2018-2019).

Hybrid Organic-Inorganic Nanomaterials: Preparation of Carbon Nanofiber Supported Pt Nanoparticles

Mahdieh Shakoori Oakoole, Serap H. Soytas, Serkan Unal

Sabancı University, Istanbul, Turkey

serkanunal@sabanciuniv.edu

Hybrid organic-inorganic structures, such as a conductive carbon nanofiber network decorated with inorganic nanoparticles, are promising materials for energy storage and conversion applications. In this study, a one-pot microwave-assisted synthesis was carried to prepare a hybrid structure consisting of carbon nanofiber (CNF) supported platinum nanoparticle catalysts for potential fuel cell applications. CNF-supported Pt samples were prepared through the electrospinning of a solution of in-house synthesized poly(acrylonitrile-*co*-N-vinylpyrrolidone) (P(AN-*co*-nVP)) copolymer containing $PtCl_2$ salt, consequent microwave reduction in hydrazine hydrate solution and carbonization. The random copolymer structure and the rapid microwave reduction allowed a good control of the size and distribution of Pt nanoparticles, which were characterized by high resolution TEM. The effect of the carbonization temperature on the growth and distribution of Pt particles was also investigated in detail to achieve a homogenous particle size distribution and the highest electroactive surface area (ECSA). Lastly, the incorporation of carbon nanotubes (CNTs) into CNFs during the electrospinning process was studied on selected samples. Pt nanoparticles with an average size of 1.751 nm in diameter was obtained in the case of CNT-free samples, while 0.862 nm Pt nanoparticles were observed with a narrower size distribution in the CNT-containing CNF/Pt hybrid structures. In addition to the Pt particle size, the accessibility of Pt particle surface was found to play a critical role in determining the ECSA properties of these hybrid structures.

The influence of graphene oxide particle size on the properties of epoxy resin nanocomposites

M. Huskić[1,2], **S. Bolka**[2], **A. Vesel**[3], **M. Mozetič**[3], **V. Veselinović**[4], **A. Anžlovar**[1], **E. Žagar**[1]

1- National Institute of Chemistry, Department of Polymer Chemistry and Technology, Hajdrihova 19, 1000 Ljubljana, Slovenia
2- Faculty for Polymer Technology, Ozare 19, 2380 Slovenj Gradec, Slovenia
3- Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia
4- University of Banja Luka, Faculty of Medicine, Bulevar vojvode Petra Bojovića 1 A, 78 000 Banja Luka, Bosnia and Herzegovina

miro.huskic@ki.si

Graphene oxide (GO) has attracted great attention during the last ten years. On one side it serves as a precursor for graphene and on the other side its physical and mechanical properties make GO interesting material for the production of high strength polymer nanocomposites [1]. However, the impact of any filler on the physical, chemical and mechanical properties of the polymer (nano)composites depends not only on the fillers properties but also on the filler's particle size, the particle distribution within the polymer matrix and the filler/polymer surface interactions.

There are two main problems in the preparation of GO/polymer nanocomposites. First, GO exists only as a dispersion in water or some polar solvents. Once dried, it forms a graphite oxide with layered structure that can not be easily exfoliated back to the GO. Second, GO is hydrophilic and therefore hard to be dispersed into the mostly hydrophobic polymers. Therefore, surface modification of GO is needed to increase a compatibility between GO and polymer matrix [2].

In our work GO/epoxy nanocomposites were prepared without drying the GO after its synthesis. By mixing a suspension of GO with an amine curing agent we enabled a good distribution of GO particles with simultaneous GO surface modification.

Graphene oxide (GO) was synthesized from the expanded graphite with particle size of 130 µm (GO130) and 1200 µm (GO1200). XPS analysis showed that the GO130 was oxidized to a higher degree than the GO1200. The oxygen/carbon ratios were 0.54 and 0.51 for the GO130 and GO1200, respectively. Particle size of GO was determined by DLS and SEM. Since GO particles are not spherical the DLS results can be used as semi-qualitative approximation for the GO particle sizing only. For both samples the bi-modal particle size distribution was observed with the average particle size of 1.43 µm and 2.07 µm for the GO130 and GO1200, respectively.

After the synthesis, the GO was kept in a form of viscous slurry in methanol to prevent the formation of graphite oxide. The slurry was mixed with a hardener and methanol was evaporated. The nanocomposites with GO content from 0.25 to 1.0 wt.% were prepared by mixing the epoxy resin, hardener and hardener/GO mixture and cured. The particles were homogeneously distributed within the polymer matrix as indicated by SEM on the plasma etched samples. The glass transition temperature increased with the addition of GO from 81 °C for the pure epoxy to up to 90 °C for the nanocomposites with 1.0 wt.% GO. The Young's modulus increased by 35 and 30 % with the addition of GO130 and GO1200, respectively, while the tensile strength increased for 10 % only when GO1200 had been added. The optimum concentration of GO in the nanocomposite was found to be from 0.25 to 0.50 wt.%.

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Structural and Local Spectroscopic Studies on Hybrid Nanomaterials by Advanced TEM

Raul Arenal[a,b]

[a] *Laboratorio Microscopias Avanzadas, INA, U. Zaragoza, 50018 Zaragoza - Spain*
[b] *Fundacion ARAID, 50018 Zaragoza - Spain*

In the last two decades, transmission electron microscopes (TEM) have undergone a large number of improvements allowing ~ 100 meV (even few tens of meV) energy resolutions for a sub-nanometer electron beam. These performances offer new possibilities for probing the optical, dielectric and electronic properties of nanomaterials with unprecedented spatial information, as well as for studying the atomic configuration of nanostructures. I will present a selection of recent works taking advantage of these new capabilities [1-12]. These works will concern the study of the atomic structure & configuration of nanostructures (including doped carbon nanotubes and bio-nanomaterials), as well as opto-electronic properties studies carried out via electron energy loss spectroscopy (EELS) measurements of different kind of nano-objects (inorganic nanotubes and metallic nanoparticles). These works will illustrate the study of properties with extreme spatial resolution enabled by a Cs probe corrected STEM combined with the use of a monochromator.

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MECHANICAL MODELLING AND CHARACTERIZATION OF CNT FIBRES: THE ROLE OF ALIGNMENT

Juan C. Fernandez-Toribio[1], **A. Ridruejo**[2], **M. Shaffer**[3], **J.J. Vilatela**[1]

1- IMDEA Materials Institute, Eric Kandel, 2, Tecnogetafe, 28906, Getafe, Madrid (Spain)
2- Department of Materials Science Polytechnic Unviersity of Madrid, 28040, Madrid (Spain)
3- Imperial College London, London SW7 2AZ, UK

juancarlos.fernandez@imdea.org

One of the most exciting challenges regarding carbon nanotubes consists on their assembly into macroscopic structures in order to fully utilize their outstanding mechanical properties. However, this transference from the nano- to the macro-scale has been showed highly inefficient and different approaches have been followed to this effect. Thus, the most promising one consists on assemblying nanotubes in the shape of a macroscopic fibre. This way, CNT fibres take advantage of the high anysotropy of their nanobuilding blocks by means of aligning them along an axis, maximizing the contact area and, therefore, the transference of properties. This is why the alignment plays an important role in the final mechanical behaviour showed by the fibre. However, this relationship has been established in a qualitative way and it has not been included in the mechanical models available in the literature. To this aim, this study is focused on both measuring orientation and developing a model which takes it into account.

For this purpose, a comparative study about the most widely used techniques to measure orientation has been carried out. Firstly, x-ray synchrotron source has been used to develop SAXS analysis. This way, the diffraction pattern is closely related to the orientation distribution of nanotubes (Figure1 b). On the other hand, Raman analysis consists on monitoring the evolution of the G peak with the rotation angle of the fibre (Figure1 a). Therefore, by means of the Raman polarized theory the orientation distribution can be calculated and compared to SAXS results (Figure 1 c).

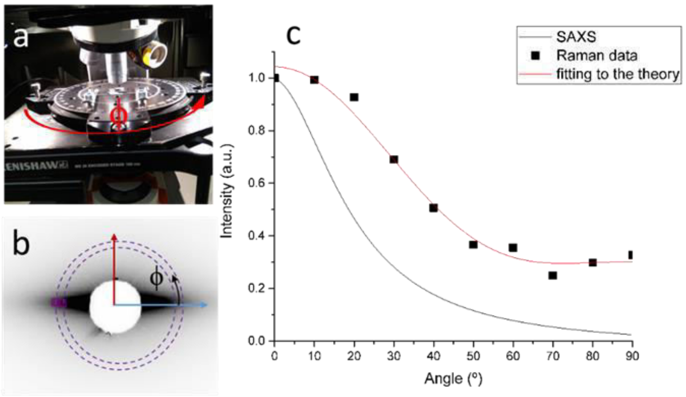

Figure 1 : a) Set-up mounted for measuring orientation by Raman ; b) SAXS pattern of a CNT fibre ; c) Intensity of both Raman and SAXS for a sample where Raman data has been fitted to the theory

Finally, using a mechanical model clasically used for polymer fibres, it has been possible to establish a quantitative relationship between macroscopic Young's modulus and orientation. According to this model the fibre can be thought as a network of rigid fibrillar elements which tend to align themselves towards the fibre's axis when the fibre is stretched. As a result, it has been demonstrated that the role of alignment in the mechanical properties is dominant.

Electromagnetic properties of carbon foams

J. Macutkevic[1], M. Letellier[2], P. Kuzhir[3], J. Banys[1], V. Fierro[2], A. Celzard[2]
[1]*Faculty of Physics, Vilnius University, Sauletekio 9/3, 10022, Vilnius, Lithuania*
[2]*Institut Jean Lamour, UMR CNRS e Universit_e de Lorraine n_7198, ENSTIB, 27 rue Philippe Seguin, BP 21042, 88051, Epinal cedex 9, France*
[3]*Institute for Nuclear Problems, Belarusian State University, 220030, Minsk, Belarus*

jan.macutkevic@gmail.com

This presentation addresses the relationship between structural and electromagnetic (EM) properties of model vitreous carbon foams, i.e., presenting different porous structures in terms of bulk density, cell size and connectivity, while having the same composition and the same carbon texture. EM properties were investigated over a wide frequency range, from 20 Hz up to 250 THz. The bulk density is the main parameter controlling the EM behaviour up to ~50 GHz, as no change was found by varying other structural parameters such as cell size or interconnectivity in such frequency range. At low frequency, foams behave similarly to metals and, when the density increases, the reflection increases and the absorption decreases. The behaviour changes above ~50 GHz, absorption becoming the main mechanism. For cellular foams, transmission and reflection tend to be negligible in the infrared region, and behave like black bodies. However, reticulated foams present non-negligible transmission that increases with cell size. Resonance phenomena were observed for reticulated foams between about 0.2 and 3 THz. A simple model considering the fundamental mode TE10 of a rectangular waveguide whose largest dimension was the average cell diameter was proposed to predict minima and maxima of these resonances.

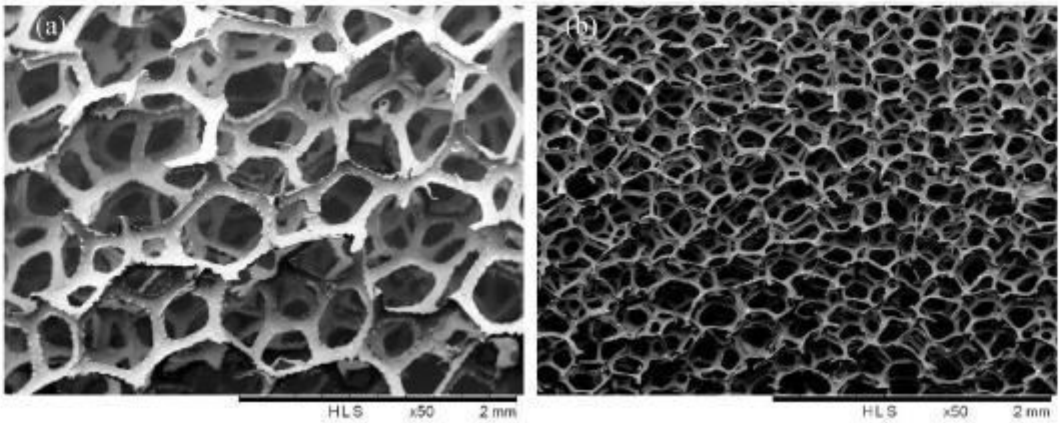

Fig. 1 Reticulated carbon foams having a) 30 pores per inch, b) 80 pores per inch.

Opportunities to complement your research at KNMF

S.M. Anson

Karlsruhe Institute of Technology (KIT), Helmholtz Programme Science and Technology of Nanosystems (STN), Karlsruhe Nano Micro Facility (KNMF), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Susan Anson susan.anson@kit.edu

Pushing the frontiers of research is challenging, and often requires the use of complex, high end state of the art nano and micro structuring and characterisation equipment. The Karlsruhe Nano Micro Facility (KNMF) offers a broad portfolio of nano and micro structuring and characterisation equipment to external users from across the globe. Funding by the Helmholtz Association means that more than 150 users a year, from across the globe, benefit from no fee access to this equipment and the expertise of the staff. The technologies are organised in two laboratories.

The laboratory for microscopy and spectroscopy offers a range of methods for the investigation of the microstructure and elemental and chemical composition of materials. Technologies such as 3D Atom Probe Tomography, Transmission Electron Microscopy and X-Ray Photoelectron Spectroscopy, Single Crystal X-ray Diffraction and Time-of-Flight Mass Spectrometry and other advanced microscopic and analytical methods can be selected either individually or in combination with other characterisation of structuring methods as required.

The laboratory for micro and nano structuring specialises in the multimaterial structuring and replication of nano and micro-scale features. The opportunities range from using lithographic methods such as e-beam lithography with a resolution of down to <1nm and dip pen nano lithography, through thin layer methods such as atomic layer deposition to laser structuring, direct laser writing, injection moulding and 3D printing.

The close proximity of the in-house research at KIT ensures that the latest advances scientific knowledge and state-of-the-art the technology development are available to our users. We are a collaboration-oriented facility, where our technology experts work together with our users to achieve the desired results. KNMF technologies can often be adapted to suit individual user needs.

Proposals can be submitted via the web page, at any time and the two submission deadlines are 15 January and 30th June each year. No fee access is awarded on the basis of scientific merit assessed by an independent peer review panel. Details on our 25 technology clusters, contact details of their experts, and how to register as user and apply to KNMF can be found on www.knmf.kit.edu

Multi-functional role of graphene in liquid crystal display devices

V. Marinova[1] and D. Dimitrov[1,2]*

1- Institute of Optical Materials and Technologies, BAS, Sofia, Bulgaria
2 Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria

vmarinova@iomt.bas.bg

Recently, graphene displays enormous potential to extend the landscape of photonic and optoelectronics technology owing to its exceptional optical, electrical and mechanical properties [1,2]. Moreover, it is regarded as an excellent candidate to replace conventional Indium Tin Oxide (ITO) conductive electrodes due to its outstanding properties as very high conductivity, excellent transparency in a broad spectral range, flexibility, etc. Numerous applications of graphene as a channel in field-effect transistors (FETs), transparent conductive electrode in varieties of optoelectronic devices, in sensors, and integrated electronic circuits have been reported [1-3].

Our work is focused on the controllable growth of single- and multilayer graphene by CVD technique, its detailed characterization using AFM, SEM, Raman, electrical and optical analysis and graphene application as transparent conductive electrode in liquid crystal display devices. Modulation characteristics as driving voltage, phase modulation, response time will be discussed and compared with the reference devices using conventional ITO electrodes. Moreover, the multifunctional role of graphene as conductive as well as alignment layer in liquid crystal device will be discussed.

Furthermore, graphene nanoparticles addition in polymer dispersed liquid crystal structures will be presented as an effective way to reduce the driving voltage for the application of proposed devices as smart windows.

In addition, novel flexible devices, based on graphene for displays and image processing will be demonstrated

The proposed devices could found applications in display holography, as phase retarders, optically addressed spatial light modulators, etc.

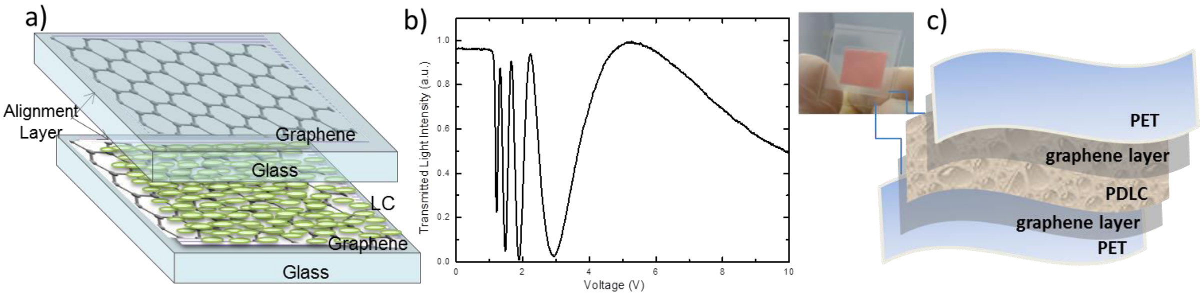

Fig.1.(a) Schematic structure of LC device with graphene conductive electrodes, (b) Voltage-Transmittance characteristic of graphene – based LC device and (c) flexible polymer dispersed liquid crystal device using graphene electrodes.

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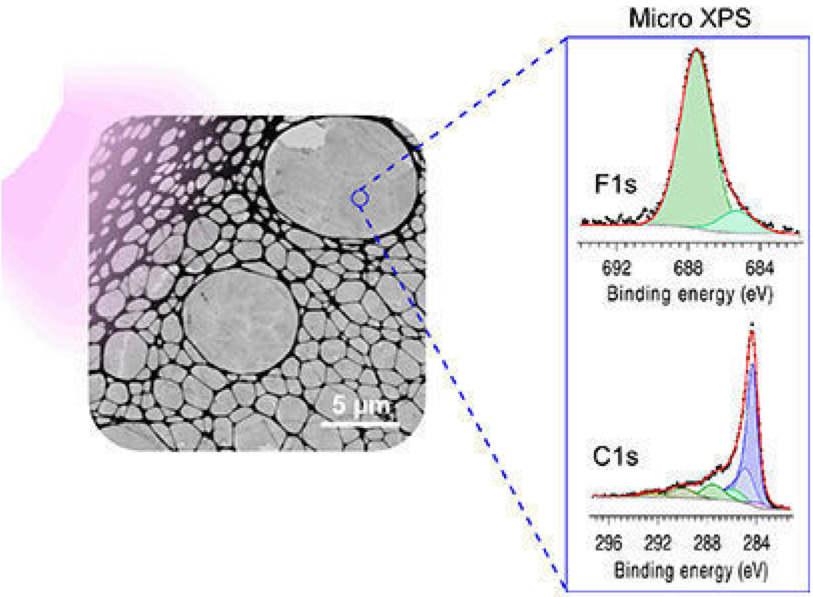
Poster presentations

Fluorination of Suspended Graphene

Claudia Struzzi, Mattia Scardamaglia and Carla Bittencourt

Chimie des Interactions Plasma-Surface, CIRMAP, University of Mons, Mons, Belgium

Suspended graphene is exposed to different fluorine-containing species produced by a plasma source. We investigate the fluorination process by selecting two different kinetic energies for the ions striking the graphene surface. The chemical-bonding environment is discussed, and the control of the graphene-fluorination homogeneity is investigated at the individual graphene sheets. The modifications of the electronic and structural properties are examined by scanning photoelectron microscopy, micro-Raman analysis, and scanning electron microscopy. The results are compared with those obtained for supported graphene on copper. Suspended graphene provides a quasi-ideal model for investigating the intrinsic properties of irradiated carbon nano-systems while avoiding damage due to backscattered atoms and recoil due to a supporting substrate.



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Carbon nano-allotropes based on few layer graphene and fullerene C_{60}: synthesis and characterization

P. Umek[1], T. Knaflič[1], J. I. Tapia[2], C. Bittencourt[3], D. Arčon[1,4] and M. Quintana[2]

1- Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia
2- A Instituto de Física, Universidad Autonoma de San Luis Potosí, Manuel Nava 6, Zona Universitaria 78290, San Luis Potosí, SLP, Mexico
3- Chemie des Interactions Plasma-Surface, University of Mons, Avenue Nicolas Copernic, 1, B-7000 Mons, Belgium
4- Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia

polona.umek@ijs.si

Fullerites, nano-onions, and nanodiamonds were synthesized by ultrasonication of few-layer graphene (FLG) and fullerene C_{60} in *N,N*-Dimethylformamide (DMF). In some cases alkali chlorides (KCl, RbCl or CsCl) or ferrocene were added to a reaction mixture. The ultrasonication of C_{60} molecules in DMF produces large quantities of face-centred cubic fullerites (fcc) with a cell parameter of 1.42 nm and very narrow diameter distribution (22 ± 3 nm). The addition of FLG during the ultrasonication process additionally to fullerites, yields to the formation of defective nano-onion structures mainly at edges of the graphene sheets. Increasing the ultrasonication time under the addition of C_{60}, prompted the formation of carbon nanodiamonds deposited on the surface of fullerites (Figure 1a and b). From experimental analysis, it is concluded that the extreme conditions generated by acoustic cavitation provoke the formation of defective nano-onions through the auto-assembly of small graphene pieces directed by pep stacking interactions onto C_{60}. These particles are then converted into more stable nano-diamonds during ultrasonication.

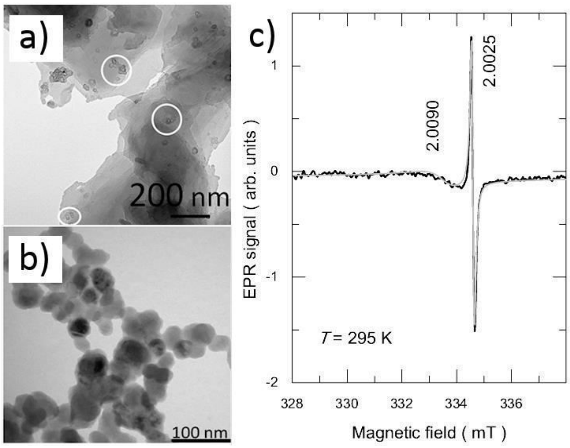

Figure 1 TEM images (a and b) and EPR signal (c) of a sample synthesized by ultrasonication of graphene and C_{60} in *N,N*-dymethylformamide. A solid light gray line in figure c) is a fit to a model comprising a narrow Lorentzian and a broader Dyson-like component.

Further, electron paramagnetic resonance (EPR) technique was employed to characterize the samples (Figure 1c). In all cases EPR signals are composed of two components, a broader asymmetric one at lower fields and narrower symmetric at higher fields. Fitting the spectrum two a sum of Lorentzian and a Dyson line shape leads to an excellent fit yielding g-factor values of g_1= 2.0025 and g_2 = 2.0090, respectively. Whereas the former is very close to the electron free value expected for the more sp2-rich regions, the latter is more in the range expected for a polymer like or diamond-like environments with a mixture of sp2- and sp3-hybridized states. The spectrum thus clearly shows nanostructural inhomogeneities. The intensity of both components varies among different samples. In addition, samples were characterized with XRD and FTIR as well.

Synthesis of nanostructured amorphous carbon-copper composite films

A. Iljinas[1], L. Marcinauskas[1], M. Černauskas[1], Ž. Rutkūnienė[1], R. Ramanauskas[1], R. Zabels[2]

1- Department of Physics, Kaunas University of Technology, Studentu str. 50, LT-51368, Kaunas, Lithuania
2- Institute of Solid State Physics, University of Latvia, Kengaraga Str. 8, LV-1063 Ryga, Latvia

aleksandras.iljinas@ktu.lt

Recently, a considerable attention is given to the research of carbon films with metal impurities and various carbon nanostructures, obtained using metal catalyst [1-4]. A number of metals that form carbides (Ti, V, Cr, Fe, Ni), as well as those that do not form carbides (Cu, Au, Pd, Pt) are used as doping elements for amorphous carbon composites and films or as catalyst for carbon nanostructures [1-2]. The copper is one of the most popular metals used in the formation of carbon composites or nanostructures (graphene, carbon nanotubes) due to low solubility of carbon in copper, low cost, and availability [2-4].

The thin copper film of 20 ± 5 nm thickness was deposited on silicon substrates by direct current magnetron sputtering at room temperature. The amorphous carbon films were deposited by plasma-enhanced chemical vapour deposition. The synthesis was performed on the silicon substrates covered by the copper layer. The deposition was performed on the 25 °C and heated substrates at 300 °C, 520 °C and 700 °C temperatures using an acetylene gas at 40–70 Pa pressure. The surface morphology, microstructure and elemental composition of nanostructured carbon-copper composite films were investigated. It was demonstrated that the substrate temperature has influence on the size of copper nanospheres. The oxygen concentration was reduced from 19.9 at.% to 3.2 at.% with the increase of temperature from 25 °C to 700 °C. The scanning electron microscopy images indicated the growth of amorphous carbon films with the randomly distributed nanostructures. The index of refraction was reduced from 2.15 to 1.68 with the increase of the temperature from 25 °C to 700 °C. The surface roughness measurements demonstrated that the surface roughness values increased with the increase of the temperature. The FTIR spectra indicated that the fraction of the sp^2 C-O, sp^3 and sp^2 $CH_{2\text{–}3}$ sites were reduced and the olefin sp^2 C=C stretching bands were replaced by the sp^2 C=C stretching vibration of the aromatic rings with increase of the substrate temperature. The increase of the substrate temperature lead to the graphitization, enhanced the amount of sp^2 C=C sites and caused to the formation of the nanocrystaline graphite clusters. The nanohardness values of the nanostructured amorphous carbon-copper films varied in the range of 0.2–3 GPa. The highest nanohardness (~3 GPa) and elastic modulus (~110 GPa) values of the deposited film were obtained at 520 °C.

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Dielectric/electric properties of onion-like carbons / epoxy composites

E. Palaimiene[1], J. Macutkevic[1], S. Schaefer[2], A. Celzard[2], J. Banys[1]

1- Institute of Applied Electrodynamics and Telecommunications, Vilnius University, Sauletekio 3, LT- 10257 Vilnius, Lithuania
2- Univ Lorraine, CNRS, Insitut Jean Lamour, UMR 7198, 27 Rue Philippe Seguin,BP 21042, F-88051 Epinal 9, France

Main author email address: edita.palaimiene@ff.vu.lt

Onion-like carbons (OLC) are quasi-spherical nanoparticles consisting of fullerene-like carbon layers enclosed by concentric graphitic shells and it is predicted to have different properties from other carbon nanostructures, such as graphite, nano-diamond, or carbon nanotubes, due to their highly symmetric structure and may be used in different applications [1]. However, investigations of OLC based composites are quite rare in comparison with composites with other carbon allotrope modifications. Therefore, the aim of present work is to investigate the dielectric properties of OLC and epoxy resin composites dielectric properties with different OLC aggregate size and at different OLC concentrations in the frequency range 20 Hz – 24 GHz and at room temperature.

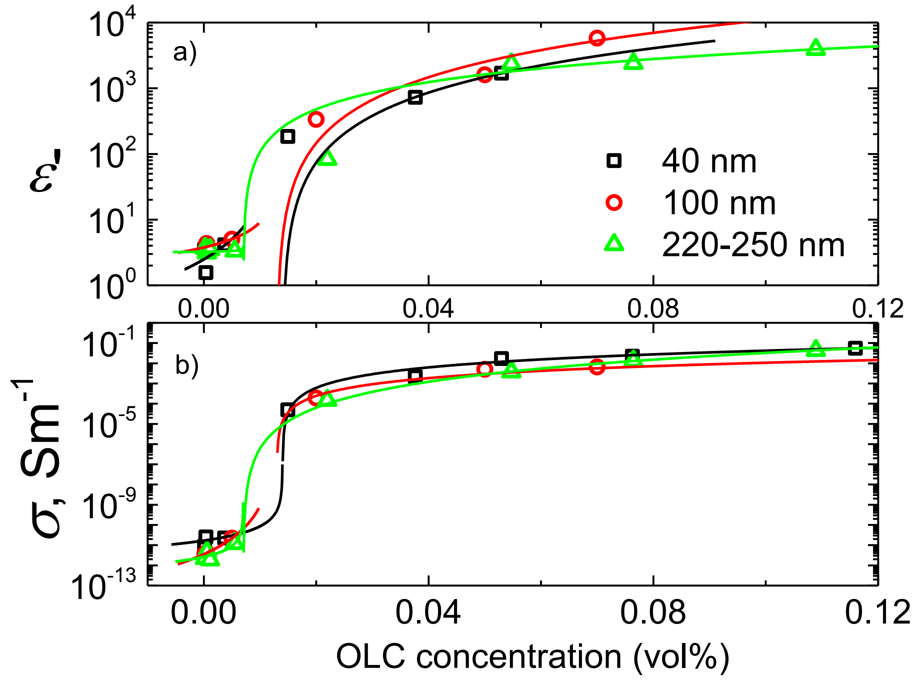

Figure 1. The effective permittivity (a) and the electrical conductivity (b) of OLC/epoxy composites vs OLC concentration and aggregate size at frequency 1.21 kHz and room temperature.

The concentration dependence of the effective permittivity and the electrical conductivity at the frequency 1.21 kHz is presented in Fig. 1. The rapid increase of both effective permittivity and electrical conductivity indicate the percolation threshold below 1 vol% for all OLC aggregate sizes. The percolation threshold value is quite low in comparison with OLC / polyurethane composites [2]. Above percolation threshold the effective permittivity and electrical conductivity are quite high (effective permittivity higher as 10^3 and electrical conductivity higher as 0.01 S/m) and almost independent from OLC aggregate size.

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MULTI-WALLED CARBON NANOTUBES / POLYPYRROLE COMPOSITES WITH DIFFERENT SURFACTANTS

M. Mičušík[1], J. Kuliček[1], P. Gemeiner[2], M. Mikula[2,] M. Omastová[1]
1-Polymer Institute, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
2-Department of Graphic Arts, Faculty of Chemical Technology SUT in Bratislava, Radlinského 9, 812 37, Bratislava, Slovakia

matej.micusik@savba.sk

In our work multi-walled carbon nanotubes (MWCNT)/PPy counter electrodes (CE) were prepared in the presence of different surfactants. Two methods for the preparation of MWCNT/PPy composites were used. First method was the chemical oxidative polymerization of pyrrole on MWCNT surface in the presence of different types of surfactants. Second method was the electrochemical deposition of PPy layer onto the MWCNT decorated FTO glasses. For the improvement of MWCNT dispersion and for improving the PPy morphology we have used different surfactants. Surfactants play important role during MWCN suspension preparation and also during pyrrole polymerization.

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

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

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Surface attachment of Mn(III) SCO compound on few-layer graphene

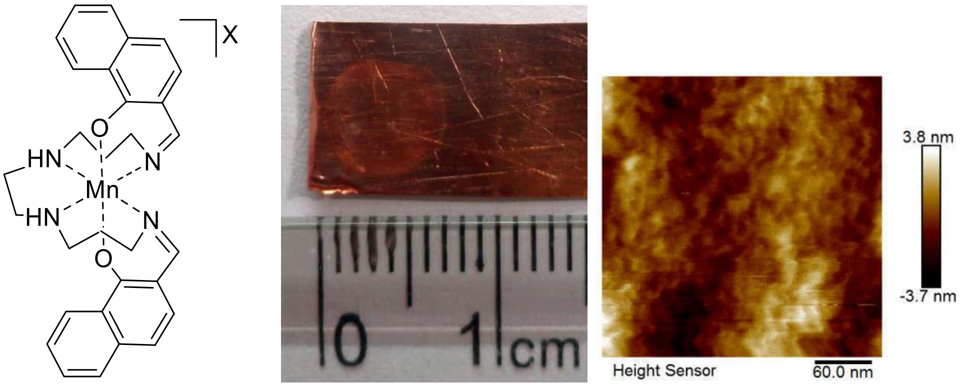
Irina A. Kühne[1], **Sharali Malik**[2], **Brian Rodriguez**[3] **Grace G. Morgan**[1]

1- School of Chemistry, University College Dublin (UCD), Belfield, Dublin 4, Ireland
2- INT, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
3- School of Physics, Conway Institute, Belfield, Dublin 4, Ireland.

irina.kuhne@ucd.ie

The phenomenon of spin crossover in metal complexes is known since the early 1930s,[1] and has attracted since then a lot of interest. Through their possible hysteretic effects, potential applications of these molecules include their use as molecular switches in data storage and in displays.[2–4] At low temperatures, it is energetically favorable for spin crossover compounds to be in a low spin state, and by application of an external stimulus, like heat, light, pressure or applied magnetic field,[5,6] it is possible for the spins to occupy the energetically higher orbitals, resulting in a high-spin state of the molecule.

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



(a) (b) (c)

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

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Photoregenerating thin films of phthalocyanines for NO_2 and explosive taggants detection

D. Tomeček[1], P. Fitl[1], M. Hruška[1], E. Marešová[1], J. Vlček[1], Š. Havlová[1], M. Vrňata[1]

1- Department of Physics and Measurements, University of Chemistry and Technology, Prague, Technická 5

David.Tomecek@vscht.cz

Detection of explosives is an important activity undertaken for military, counter-terrorism and homeland security applications. Direct vapor detection of many explosive compounds is a difficult task, as their vapor pressure is extremely low. [1] Therefore the so-called "detection taggants" such as 2-nitrotoluene (2-NT) or 2,3-dimethyl-2,3-dinitrobutane (DMDNB) are used to facilitate the explosive detection by security forces (i.e. the preventive detection of an explosive before detonation is taken into account, not the consequent analysis of explosion products). [2] Our work deals with detection of 2-NT and DMDNB on chemiresistors based on phthalocyanines (disc shaped molecules containing carbon and nitrogen atoms). At first, we tested those materials for direct detection of the taggants but we obtained negligible responses. Despite the fact that phthalocyanines are very sensitive to NO_2 gas [3-6], they do not respond to NO_2 groups bonded to organic skeleton in taggants. However, if it was possible to release the NO_2 groups from the molecules, we could easily detect taggants. Indirect method of taggant detection would be formed.

For the taggant decomposition step we tested several approaches (physical or chemical) and finally used the treatment by pulsed ultraviolet radiation ($\lambda = 266$ nm) generated in a Nd-YAG laser. With that kind of analyte activation, we observed strong responses for 2-NT on the phthalocyanine chemiresistors (Fig. 1). [7] To support the detection mechanism theory, we analyzed photoproducts of taggants' decomposition. MS spectra showed strong depreciation of signals related to 2-NT (65, 91, 92, 120 and 137 amu) and slight increase of the NO_2 characteristic molecular peak (46 amu). No responses were recorded for a blind experiment with pure synthetic air, so the NO_2 should not come from the interaction of laser light with the air molecules. No or negligible responses were also obtained when 2-NT was exchanged to toluene (TOL), so it is probable that the NO_2 comes from the taggant. Based on these experiments, we believe that the 266 nm laser induces the release of NO_2 from 2-nitrotoluene molecules which can be then detected by phthalocyanine chemiresistors.

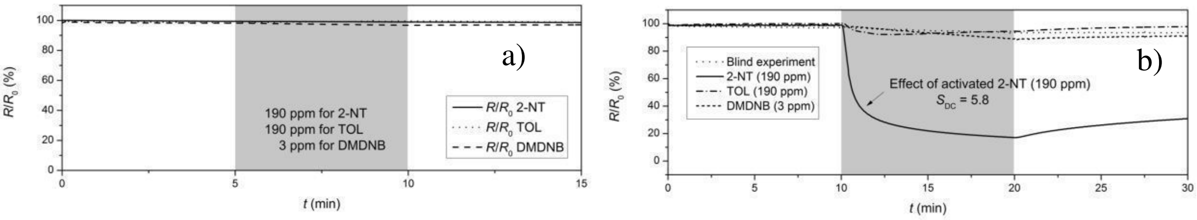

Fig. 1: Direct vs indirect approach of taggant detection on a silver phthalocyanine chemiresistor: a) Direct approach – negligible response, b) indirect approach – response of 5.8 when expressed as the ratio of electrical resistances.

This contribution also presents photoregeneration procedure for phthalocyanines from NO_2 exposure. NO_2 desorption from phthalocyanine sensitive layers is generally a slower process when compared with the sorption one which results in the disproportion of an optimal operating temperature (↓ temperature ↑ dc-response ↑ regeneration time). Here we evaluate the efficiency of the photoregeneration recovery process ($\lambda = 375 - 850$ nm) in comparison with a thermal pulses-based recovery process (temporal increases of a sensor operating temperature from 40 °C to 120 °C or 150 °C). In the next step, this study is heading to employ phthalocyanine-fullerene composite films to improve the efficiency of light absorption.

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Fullerenes in Polymeric Ion Liquid Matrix for Chemical Sensing: Synthesis, Characterization and Sensor Properties

R. Šípka[1], E. Marešová[1], Š. Havlová[1], D. Tomeček[1], P. Fitl[1], M. Vrňata[1], J. Vlček[1]

1- Department of Physics and Measurements, University of Chemistry and Technology Prague, Technická 5, CZ16628, Prague 6, Czech Republic

Main author email address: vlcekj@vscht.cz

Polymeric ionic liquids (PILs) are the new class of materials with unique features for sensor devices [1, 2]. PILs exhibit ion carrier conductivity, therefore can be effectively used as chemiresistor. Resistance of such chemiresistor depends on mobility of ions in PILs and any molecule of gas permeating into PILs material can affect this ion mobility. Adding of a small portion of nanocarbon material (fullerene, CNTs, graphene flakes etc.) into the PILs matrix can modulate this behaviour towards selectivity and sensitivity enhancement. Analogically similar observation is known from chemiresitors based on semiconducting oxide containing CNTs [3].

In this contribution we present the new class of nanocomposite material for chemiresistive and optical gas sensing consists of PILs matrix (Tetrabutylphosphonium sulfopropylacrylate (P_{4444}SPA) as a copolymer) in form of hydrogel containing nanocarbons - fullerene C_{60} and C_{70}. We study the efect of phosphonium ion size, specifically for Tetrabutylphosphonium (P_{4444}), Tributylmethylphosphonium (P_{4441}) and Tributyloctylphosphonium (P_{4448}). These phosphonium size variations are beneficial in terms of ion mobility. We describe synthesis process of nanocomposite from sonication of nanocarbons in PILs precursors to photopolymeration into the form of hydrogel. Nanocomposites in form of thin films are polymerized on sensor substrate consisting of alumina substrate plate with platinum interdigitating electrodes system. Nanocomposite films are prepared on silicon (100) and fused silica substrates as well for characterization purposes. We present morphological characterization of prepared nanocomposite by SEM and their characterization by Raman. Sensor behavior of such materials was tested as responses to basic gas analytes (alcohol vapours, NO_x) in concentration of 10 ppm in synthetic air.

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Dielectric properties of $Fe_2O_3H_2O$/epoxy resin composites

D. Meisak[1], J. Macutkevic[1], Dz. Bychanok[2], G. Gorokhov[2], P. Kuzhir[2]

1-Vilnius University, Physics faculty, Saulėtekio st. 9, LT-10222 Vilnius
2-Research Institute for Nuclear Ploblems BSU, Bobruiskaya st. 11, 220030 Minsk

dariameysak@gmail.com

In present work dielectric properties of composite materials, based on Yellow Iron Oxide Nanorods ($Fe_2O_3H_2O$) are studied in wide temperature (200 K-450 K) and frequency (20 Hz-1 MHz) ranges.

To prepare the composites commercially available epoxy resin Epikote-828 and Yellow Iron Oxide Nanorods ($Fe_2O_3H_2O$ alpha, 98 %, 50 nm×10 nm) were used as the matrix and as nanoinclusions, respectively. A standard procedure for dispersing inclusions in a polymer matrix was used [1]. Fabricated samples had 0, 5, 10, 20, 30, 40 vol. % filler concentrations. The complex permittivity was measured in the frequency range from 20 Hz to 1 MHz with LCR HP4284A. Each measurement was accompanied by heating from 200 K to 450 K [2].

The experimental dependence of the composites permittivity on the concentration at room temperature and frequency 129 Hz allows to determine the percolation threshold, which is 30 vol. %. The dielectric properties of composites below the percolation threshold are determined mainly by relaxation in a pure polymer matrix [2].

According to the Vogel-Fulcher law the relaxation time on cooling increases as follows [2]:

$$\tau = \tau_0 e^{\frac{E_B}{k_B(T-T_0)}} \qquad (1),$$

where τ_0 is the relaxation time at very high temperature, E_B is the activation energy, T_0 is the glass transition temperature. The average relaxation time was obtained as $\tau = 1/\nu_{\max}$, where $\nu_{\max}$ is the frequency corresponding to the maximum of the permittivity imaginary part at given *T*. The temperature dependence of the relaxation time is shown in Figure 1(a).

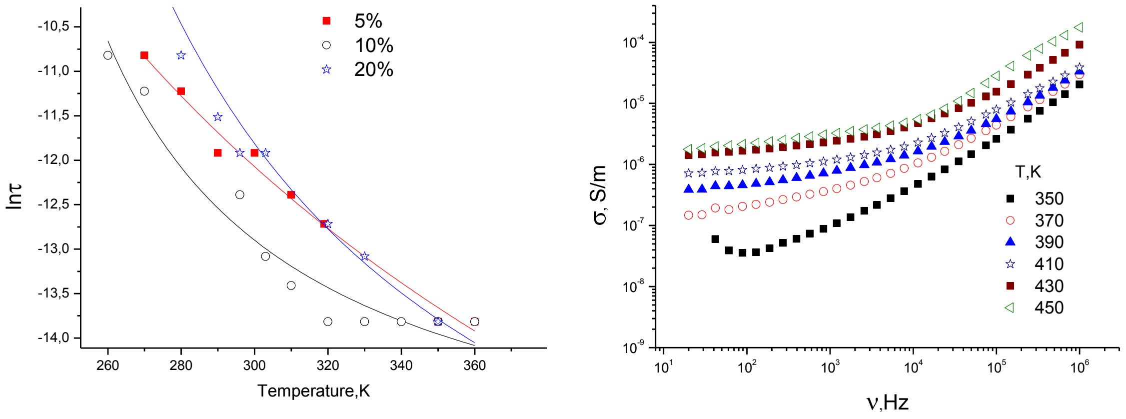
(a) (b)

Figure 1 (a) Temperature dependence of the average relaxation time for $Fe_2O_3H_2O$/epoxy resin composites below percolation threshold. The solid lines correspond to the approximations by formula (1). (b) Frequency dependence of electrical conductivity for $Fe_2O_3H_2O$/epoxy resin composites with nanoinclusions concentration equals to 20 vol. %.

The frequency dependence of the electric conductivity calculated as $\sigma = 2\pi\nu\varepsilon_0\varepsilon''$, for the composite with nanoinclusions concentration of 20 vol. % is shown in Figure 1(b). The DC conductivity observed at low frequencies is caused by the hopping conductivity [3]. A similar behavior of conductivity was observed for all other investigated composites as well as pure epoxy resin. It should also be noted that the DC conductivity increases significantly when nanoinclusions concentration increases. Thus, because of the finite conductivity of the epoxy resin at high temperatures the electric conductivity occurs in composites both above and below the percolation threshold.

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Efect of WS_2 nanotubes on dielectric and ultrasonic properties of polyurethane based composites

J. Macutkevic[1], A. Zak[2], V. Samulionis[1], J. Banys[1]

1- University of Vilnius, Sauletekio al. 9, LT-00122 Vilnius, Lithuania

2 - HIT - Holon institute of Technology, 52 Golomb st., Holon 58102 Israel

vytauutas.samulionis@ff.vu.lt

Broadband dielectric properties of tungsten disulfide (WS_2) nanotubes/polyurethane (PU) composites over a wide temperature range (300 K - 450 K) are presented for concentrations up to 2 wt%. Although no electrical percolation was observed in composites, at room temperature the dielectric permittivity of thermosetting composites with 2 wt% inclusions is 2 time higher than the dielectric permittivity of the pure polymer, that indicate that the composites are suitable for antistatic applications. Broadband dielectric properties of the composites are mainly governed by the α relaxation, the dynamics of the ”soft” molecular segment of the PU chain. The Vogel-Fulcher temperature decreases with increase in the concentration of the WS_2 nanotubes. At higher temperatures (above 380 K) the electrical conductivity dominates in properties of pure PU and composites with the WS_2 inclusions as well. The DC conductivity increases with the WS_2 concentration in thermosetting composites, while its activation energy is almost independent from the WS_2 concentration far from melting point [1]. The DC conductivity has some change in slope close to 420 K temperature.

Above room temperature the large longitudinal ultrasonic wave attenuation maxima and the velocity dispersion was observed in PU/WS_2 composites. It was found that the attenuation peak in composites shifted to lower temperatures after addition of WS_2 nanoparticles. The ultrasonic attenuation data of thermosetting composites were fitted to the relaxation equation with the single temperature dependent relaxation time. The thermal activation energy of the relaxation process, which was calculated from the ultrasonic data, was found to increase in PU with the concentration of WS_2 nanotubes. Such change of the activation energy was observed earlier in PDMS polymer composites with ZnO nanoinclusions [2]. At low temperature the longitudinal ultrasonic velocity increases in polymer with WS_2 nanotubes what is determined by an increase of elastic modulus of composite. Such reinforcement could be due to larger elasic modulus of WS_2 , as well as polymer and nanotube interaction at the surface layer adhering the nanoparticles.

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Polymeric ionic liquids as sensitive layers for textile gas sensors

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

Department of Physics and Measurements, University of Chemistry and Technology Prague, Czech Republic

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

We focus on the preparation of a fabric-based chemiresistors with a sensitive layer based on Polymeric Ionic Liquids (PILs), namely Tetrabutyl phosphonium sulfopropylacrylate (P_{4444}SPA). The PILs represent a new class of polymeric materials, which possess the unique properties such as high conductivity, non-volatility, low toxicity and ability to form coatings which can actively respond to external stimuli [1]. Therefore, they are promising materials for e.g. gas sensing [2].

The basis of the proposed sensor is a nonwoven fabric (70% polyester, 30% polyamide) on whose surface carbon interdigital electrodes (the space between the electrodes 0.5 mm) were realized by screen printing technology (DEK 248 printer). To obtain a continuous polymeric film, we applied a monomer mixture on the surface of the sensor and subsequently polymerized it directly on the fabric using the LMI-6000 Fiber-Lite white light source (200 kLux) for 20 min.

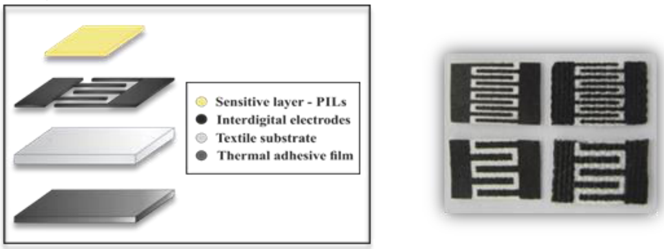

Figure 1 Vertical architecture of textile chemiresistor (left); its real appearance indicating variable distances between the electrodes (right).

The prepared fabric sensors were tested to gaseous analytes (NO_2, CH_3OH, diethylmalonate and 4-bromacetophenone) at the uniform concentration of 10 ppm. All measurements were carried out at room temperature. The response of the sensors were measured by both DC- and AC- signals. The DC-sensitivity of active layer was evaluated as the ratio $S_{DC} = R_{air}/R_{gas}$. The highest DC-sensitivity of the sensor was observed in the atmosphere containing NO_2 ($S_{DC} = 2,1$), then in 4-bromacetophenone ($S_{DC} = 1,3$) and CH_3OH ($S_{DC} = 1,2$).

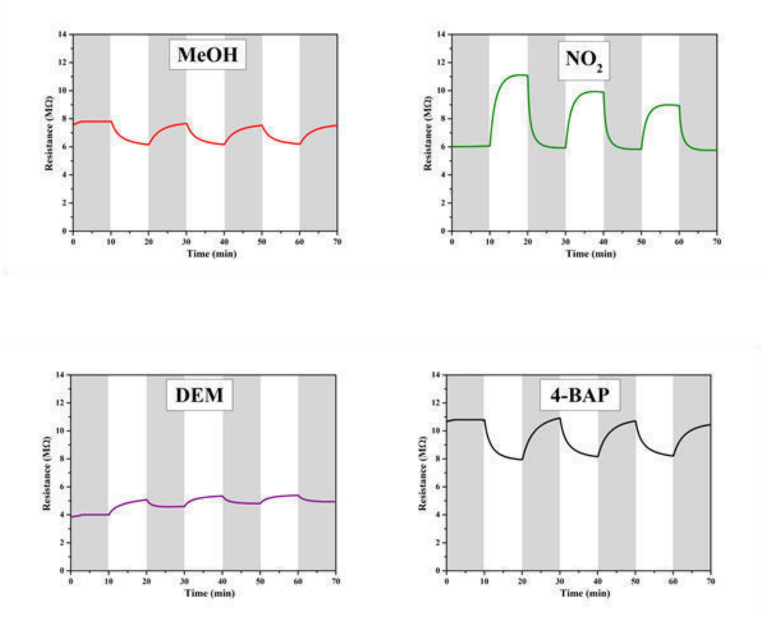

Figure 2 DC-responses of chemiresistor to 10 ppm of methanol, nitrogen dioxide, diethylmalonate and 4-bromoacetophenone.

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Study and synthesis of *in-situ* doping of GO with nitrogen (GO-N)

Siamak Eqtesadi, Azadeh Motealleh, Samaneh Etemadi* and Rune Wendelbo

Abalonyx AS, Forskningsveien 1, 0373 Oslo, Norway

Abalonyx has worked extensively with synthesis and characterization of graphene oxide (GO) and reduced graphene oxide (rGO) in lab-scale and larger scales up to 1.1 Kg/day. In this work, we focused on modification of GO, both functionalization (N doping) and neutralization of acidity of GO with ammonia and nitrogen plasma, and characterization of NGO which obtained by these two different methods. Most of the experimental work has been done at Abalonyx (Norway) and University of Extremadura (Spain).

A simple, rapid and scalable wet-chemical method was selected for the synthesis of NGO only by ultrasonic treatment of GO in aqueous solution of ammonia. The content and configuration of N atoms can be readily tuned by controlling the ultrasonication time and bath temperature. A certain amount of powder was added to the ammonia solution and then subjected to ultrasonic bath at 35 °C for 1 h. The suspension was washed and then dried at room temperature staying over the night.

In the second approach, outsourced to Haydale Ltd, GO was placed in a chamber and exposed to NH_3 gas in a "cold" plasma generator at room temperature.

Different characterization methods confirmed that N content in ultrasonic and plasma NGO is around 3.44 and 5.41 (at.%), respectively. The N content in ultrasonic NGO (3.44 at.%) is close to other similar works reported maximum 4 at.% for Nitrogen. Close to 50% of this amount belongs to pyridinic and graphitic N that facilitate oxygen reduction reaction (ORR).

In the case of plasma NGO, the N content of 5.41 at.% is in the middle range of the amounts reported in literature for ORR applications. According to our findings plasma treatment results in a range of N content from 3 to 8 at.%.

NH3 has also been used to neutralize the acidity of graphene oxide so that we can now supply dispersible neutral and basic GO for applications where acidity is not desirable.

Keywords: Graphene oxide (GO), Nitrogen doping, ultrasonic, nitrogen plasma, basic GO

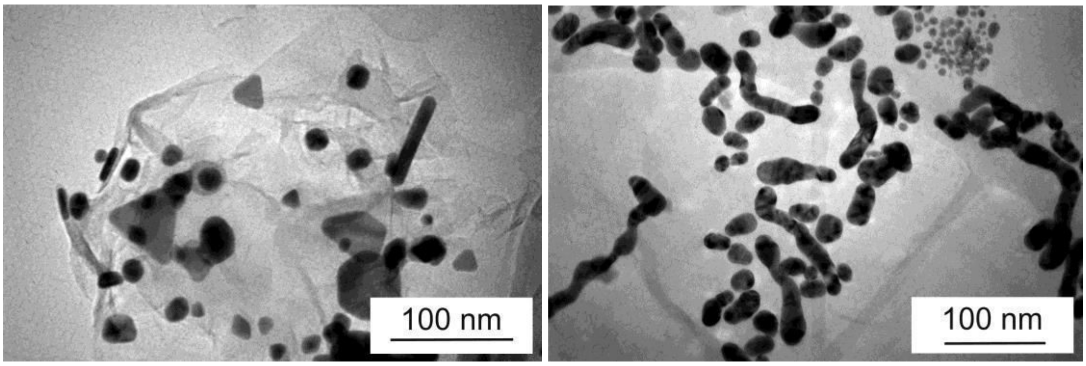
Gold nanoparticles/exfoliated graphene hybrid obtained by gamma irradiation

D. Kepić[1], **Z. Marković**[2], **D. Jovanović**[1], **M. Budimir**[1], **D. Kleut**[1], **D. Bajuk-Bogdanović**[3], **V. Pavlović**[4], **B. Todorović Marković**[1]

1- Vinča Institute of Nuclear Sciences, University of Belgrade, P.O.B. 522, 11001 Belgrade, Serbia
2- Polymer Institute, Slovak Academy of Sciences, Dubravska cesta 9, 84541 Bratislava, Slovakia
3- Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia
4- Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Zemun, Serbia

Main author email address: d.kepic@vin.bg.ac.rs

Gold nanoparticles decorated graphene sheets present a good surface-enhanced Raman spectroscopy (SERS) platform for the development of ultrasensitive analytical applications [1]. Here, we prepared gold nanoparticles/exfoliated graphene hybrid by gamma irradiation of chloroauric acid as a precursor in the presence of electrochemically exfoliated highly oriented pyrolytic graphite (HOPG). The effects of various irradiation doses (1, 5, 10 and 20 kGy) on the size and shape of synthesized nanoparticles were studied. It was found that the presence of HOPG leads to the formation of gold nanoparticles of triangular, spherical, hexagonal, trapezoidal and rod-shape morphology. On the other hand, irradiation of chloroauric acid solution without HOPG results mainly in irregular shaped nanoparticles, however, certain amount of square shaped nanoparticles is observed. According to statistical analysis of gold nanoparticles/graphene hybrid, nearly half of the nanoparticles have sizes in the 11-20 nm range for all of the applied doses. The increase of irradiation dose results in the increase of the amount of smaller nanoparticles (up to 10 nm in size). Nevertheless, for the highest applied dose agglomeration of nanoparticles takes place leading to the formation of particles that exceed 100 nm in size. Presented synthetic route is fast, simple and low-cost since it does not require the use of a gold nanoparticle stabilizer.



(a) (b)

Figure 1. TEM images of gold nanoparticles synthesized by gamma irradiation of 1 kGy (a) in the presence of HOPG and (b) in the absence of HOPG.

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

T. Ben Shalom[1], Yuval Nevo[2], S. Lapidot[2] and O. Shoseyov[1]

[1] *The Robert H. Smith Faculty of Agriculture, Food and Environment, the Hebrew University of Jerusalem, Rehovot 76100, Israel*
[2] *Melodea Ltd. The Robert H. Smith Faculty of Agriculture, Food and Environment, the Hebrew Universit y of Jerusalem, Rehovot 76100, Israel*
Talbs87@gmail.com

ABSTRACT

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

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

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

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

Bimetallic Nanoparticles/Sulfur-doped Graphene Electrocatalysts for Oxygen Reduction Reaction

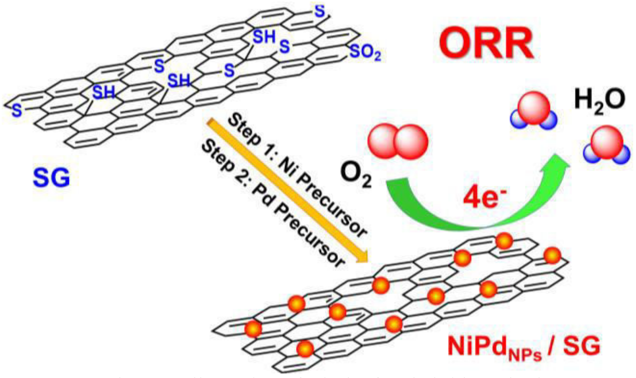
D. K. Perivoliotis[1], **N. Tagmatarchis**[1]

1- Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece

dimperiv@eie.gr

Exploring new electrocatalysts with enhanced catalytic activity towards oxygen reduction reaction (ORR) and stability for replacing Pt is a prerequisite for the sustainable commercialization of fuel cell devices. In this context, Pd has been proposed as a viable alternative to Pt as it possesses comparable catalytic activities with Pt, albeit with lower cost. Importantly, when Pd is combined with less active but cheaper metals (i.e. Ni, Co, Cu) highly efficient and cost effective metal nanoparticle (MNP) electrocatalysts can be produced. Their superior catalytic behavior is attributed to the properly tuned “strain” and “alloying” effects, arising from their specific structure (alloyed, core-shell, etc.). [1-2] The introduction of dopants (i.e. nitrogen, sulfur and phosphorus) into graphene lattice can efficiently tune its electronic states rendering it an ideal platform for catalytic MNPs, offering improved catalytic activity and extreme stability. In more detail, sulfur doping serves multiple benefits, including (i) controllable growth of MNPs, (ii) increased electrical conductivity and (iii) improved interactions between the MNPs and substrate, which results in modified electronic structure of MNP and thus lower oxygen adsorption and dissolution energies [3-4].

Herein, bimetallic Ni and Pd nanoparticles ($NiPd_{NPs}$) with different composition supported on SG were examined towards the ORR.[5] A two-step modified polyol method was applied to prepare surfactant-free $NiPd_{NPs}$ uniformly distributed on SG substrate (Scheme 1). The newly prepared $NiPd_{NPs}$/SG hybrid materials were morphologically imaged by FE-SEM and characterized with complementary techniques comprising Raman spectroscopy, X-ray diffraction and thermogravimetric analysis. Their electrocatalytic performance toward ORR was evaluated through rotating disk electrode voltammetry, followed by the Koutecky – Levich analysis to identify the exact reaction kinetics. Finally, accelerated durability tests and chronoamperometric tests were performed to assess their long-term stability. To conclude, the results suggested that the proposed nanostructured hybrid electrocatalysts exhibit enhanced electrochemical performance as compared to reference materials rendering $NiPd_{NPs}$/SG hybrids viable for energy conversion applications.



Scheme 1 Illustration of $NiPd_{NPs}$/SG hybrid synthesis

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Titanium oxide nanospheres coated with carbon xerogel as efficient photocatalysts for the elimination of drugs

Amra Bratovcic,[1] **Esther Bailón-García,[2] Agustín F. Pérez-Cadenas,[2] Francisco Carrasco-Marín,[2] Francisco J. Maldonado-Hódar[2]**

[1]Department of Physical Chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, Univerzitetska 8, 75000 Tuzla, Bosnia and Herzegovina
[2]Grupo de Investigación en Materiales de Carbón. Dpto. de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, España.

amra.bratovcic@gmail.com

In recent years, special attention is being paid to the treatment of a series of organic compounds known as emerging pollutants (ECs), present in water, such as personal care products, detergents and pharmaceuticals, among others. Many of these compounds are widely used as anti-inflammatories, analgesics, lipid regulators, antibiotics and disinfectants. To avoid a high accumulation of ECs in the aquatic environment, strategies are being developed based on the use of advanced oxidation processes (AOP) to achieve the destruction of these contaminants in water. The objective of this work has been the development of TiO_2-xerogel carbon composite materials and analysis of the influence of morphology, crystallinity and the presence of mixture of phases on the corresponding photocatalytic activity.

Formation of Low-Defect Graphene Coating from Graphene oxide-Dye Nanocomposites by Pulsed Laser Treatment

J. Gaidukevič[1], R. Trusovas[2], G. Niaura[3], I. Mališauskaitė[1], J. Barkauskas[1]

1- Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko str. 24, LT-03225 Vilnius, Lithuania
2- Department of Laser Technologies, Center for Physical Sciences and Technology, Savanoriu Ave. 231, Vilnius LT-02300, Lithuania
3- Department of Organic Chemistry, Center for Physical Sciences and Technology, Sauletekio av. 3, LT-10257 Vilnius, Lithuania

Main author email address: Justina.gaidukevic@chf.vu.lt

Graphene has drawn attention as a perspective allotrope of carbon due to its extraordinary physical and chemical properties such as large surface area, high conductivity and chemical stability. According to the literature, graphene can be widely used as an electrode material in energy, electronic and sensor devices [1]. Usually graphene is produced by using pulsed laser deposition, chemical vapor deposition, epitaxial growth on silicon carbide or metal substrates. There is still a need for new production methods which are distinguished by repeatability and can be implemented in mass production. One branch of graphene producing methods is based on the reduction of GO to graphene. Thermal and chemical reduction are the most frequently used processes for the removal of oxygen-containing groups. However, during the thermal reduction a large number of defects that deteriorate the electrical properties of graphene are created, while the chemical reduction includes the use of hazardous aggressive materials such as hydrazine [2]. Recently, several groups have demonstrated that GO can be reduced using photo-irradiation, such as UV-induced photocatalytic, photo-thermal treatment using a pulsed Xenon flash, and laser reduction [3−5]. The advantage of these methods is that photo-irradiating processes do not rely on the use of chemicals or high temperatures and shorten the reaction time from several hours to a few minutes.

The aim of this work was to prepare graphene-dye nanocomposite coatings and to perform their reduction applying laser irradiation.

Graphene oxide (GO) was prepared from the natural graphite by the synthesis protocol reported by Yan et al. [6]. In a typical experiment, graphite powder was treated with conc. H_2SO_4, $K_2S_2O_8$ and P_2O_5. Later, this pre-oxidized graphite was subjected to oxidation by Hummer's method using $NaNO_3$, H_2SO_4 and $KMnO_4$ [7]. Obtained brown powder was dried and used for the fabrication of GO and GO-Dye coatings. Six dyes (Acridine yellow, Neutral red, Malachite green, Auramine O, Congo red and Evans blue) from three different classes (Acridine, Arylmethane and Diazo) were used for the preparation of nanocomposite coatings. Two series of coatings with dye concentration of 5.0 mas.% and 20.0 mas.% have been made. Fabrication protocol included the filtering into a distilled water through a polycarbonate (PC) membrane filter. The thickness of all coatings was maintained equal to 400 nm. The obtained coatings were dried at room temperature, cut-off from cylinder and treated using the picosecond laser (Atlantic, 10 ps, 100 kHz, Ekspla) working at the 1064 nm. Prepared samples were tested by different methods (Raman spectroscopy, contact angle measurements).

The results show that the level of GO reduction to graphene phase dependent on the structure of a dye (as well as the concentration of a dye) used for the preparation of a nanocomposite.

Acknowledgments

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Dielectric Properties of EVA/Graphene Layered Composites

A.Barkane, R.Vaivodiss, S.Gaidukovs[1]

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

The present paper report demonstration of multiwalled carbon nanotubes (MWCNTs), graphene nanosheets (GR) composites with ethylene vinylacetate (EVA) polymer for high-performance EMI shielding application. EVA composites contain dispersed varying concentration of GR and MWCNT and GR/MWCNT mixtures. These compositions were melt processed in the shape of layered films i.e. sandwiches (Fig.), which were cut in the round plate shape and tested at different temperatures by dielectric spectroscope further. Carbon nanoparticles were also incorporated as internal layer in sandwich structures. Dielectric constants and polymer relaxation behavior was obtained. The volume conductivity of these layered composities is in the range 10^6 – 10^{10} S/cm. The applications of the prepared composites is proposed for electrostatic dissipators and antistatic films, coating and adhesives.

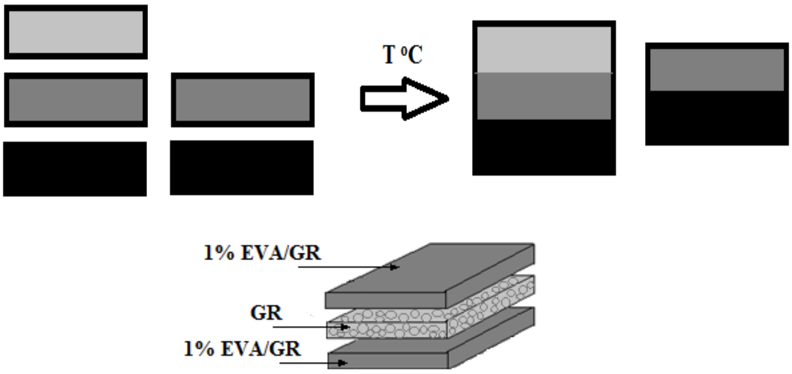

Figure 1 Specimen schematic preparation

Effect of graphene grains size on the electromagnetic response at high frequency range

E. Shashkova[1], **A. Paddubskaya**[1], **K. Batrakov**[1], **P. Kuzhir**[1], **T. Kaplas**[2], **Y. Svirko**[2], **N. Reckinger**[3], **M. Lobet**[3], **P. Lambin**[3]

1- Research Institute for Nuclear Problems, Belarusian State University, Bobruiskaya str. 11, Minsk, Belarus, 220030
2- Institute of Photonics, University of Eastern Finland, P. O. Box 111, Joensuu, Finland, FI-80101
3- Physics Department, University de Namur, 61 Rue de Bruxelles, Namur, Belgium, B -5000

shashkova.eliz@gmail.com

Among a variety of graphene fabrication techniques, such as mechanical exfoliation of graphite [1], sublimation of epitaxial SiC [2] and catalyst-assisted chemical vapor deposition (CVD) [3], the CVD is the most promising one for scalable graphene fabrication. However, the polycrystalline character of CVD graphene, the presence of defects, multiple impurities and irregularities in the graphene sheets effect on its transport, thermal and electrical properties and as result reduce the performance of graphene-based electronic devices [4]. On the other hand, due to the electromagnetic coupling of graphene grains, one may expect that at high frequency range the electromagnetic response of such a polycrystalline structure is less sensitive to the grain size.

In this communication, the influence of CVD graphene grain size on the electromagnetic shielding performance of graphene\polymer multilayers in the microwave (26 – 36 GHz) and terahertz (0.1 – 1.5 THz) frequency ranges has been investigated both experimentally and theoretically. The graphene of two typical grain size, i.e. ~20 µm and ~ 400 µm, were synthesized by CVD deposition at atmospheric pressure on a copper substrate. Sandwich-like graphene\PMMA structures with 3 and 6 graphene layers were produced. The electromagnetic response in microwave frequency range was measured using the scalar network analyzer R2-408 R. The electron relaxation time and value of chemical potential for both sample types were monitored through time-domain THz spectroscopy (TDTS). The Rigorous Coupled-Wave analysis (RCWA) method has been applied to analyse theoretically the role of graphene grain size in the total high-frequency electromagnetic shielding performance of graphene-based multilayers. It has been demonstrated that increasing the average graphene grain size from 20 to 400 µm does not significantly change the EM properties of polycrystalline CVD graphene in microwaves, whereas influence the THz response.

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Functionalization of carbon nano-onions (CNOs) with triphenylamine and triphenylphosphine derivatives: synthesis and physicochemical properties

D. M. Bobrowska[1], **L. Echegoyen**[2], **M. E. Plonska-Brzezinska**[1*]

1-Institute of Chemistry, University of Bialystok, Ciolkowskiego 1K, 15-245 Bialystok, Poland.
2- Department of Chemistry, University of Texas at El Paso, 500 W. University Ave., El Paso, TX 79968, USA.

**mplonska@uwb.edu.pl*

In the recent years, the carbon nanomaterials have received a lot of attention due to their large surface areas, high thermal stabilities, unusual electronic properties and broad absorption spectra. One of them is carbon nano-onions (CNOs) which are spherical and typically 6-8 nm zero-dimensional particles, consisting of concentric shells of graphitic carbon [1]. In this study, we used "small" CNOs received by annealing of ultradispersed nanodiamond (ND) particles (about 5 nm in diameter) at 1650ºC under a 1.1 MPa He atmosphere [2]. It seems that the CNO structures in some areas can even compete with commonly used carbon nanotubes or fullerene structures [3]. CNOs have large surface areas and can be easily integrated into macromolecular systems due to their high chemical reactivity compared with other carbon nanostructures.

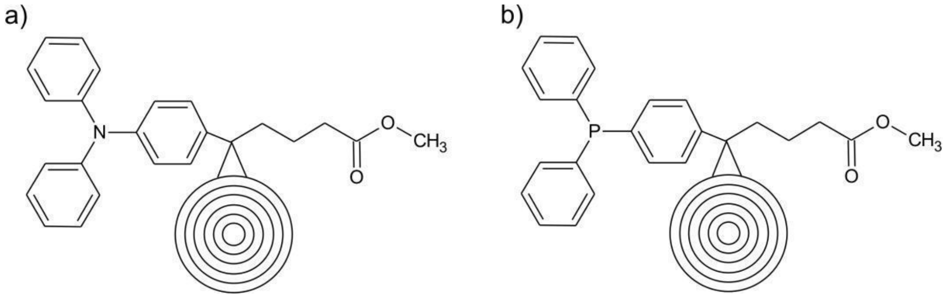

Figure 1. Scheme of structures of the triphenylamine (a) and triphenylphosphine (b) CNO derivatives.

The covalent functionalization of CNOs by triphenylamine or triphenylphospine was investigated. The route of syntheses was developed and the novel carbon nanomaterials were characterized by FT-IR, Raman, UV-Vis and fluorescence spectroscopy, ^{1}H NMR, scanning electron microscopy and electrochemical measurements. The studies showed that the CNO derivatives possess the interesting electrochemical, photophysical and electrocatalytic properties and they could be used in energy and sustainability applications such as organic solar cells.

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Diameter controlled growth of SWCNTs using Ru as catalyst precursors coupled with atomic hydrogen treatment

F.Z. Bouanis[1,2*], I. Florea[2], M. Bouanis[3], D. Muller[4], A. Nyassi[3], F. Le Normand[4], D. Pribat[2,5]
[1]University Paris Est, IFSTTAR, Boulevard Newton, 77420 Champs-sur-Marne, France

[2]Laboratory of Physics of Interfaces and Thin Films, UMR 7647 CNRS/ Ecole Polytechnique Palaiseau-France

[3]Laboratory of Catalysis and of Corrosion Materials (LCCM), Faculty of Sciences, University Chouaib Doukkali, B.P. 20, M-24000 El Jadida, Morocco

[4]ICube-Laboratory of Engineering, Computer Science and Imagery,University of Strasbourg-CNRS, 23, rue du Loess, Strasbourg Cedex 67037, France
[5] Department of Energy Science, Sungkyunkwan University, Suwon, Korea

Abstract

Single walled carbon nanotubes (SWCNTs) have shown outstanding potential in nanoelectronics due to their exceptional properties such as high mobility, high current density, as well as good chemical and mechanical stabilities [1-3]. However, SWCNTs can be either metallic (m-SWCNTs) or semi- conducting (s-SWCNTs), depending on the tube diameter and chirality [4]. It is also well established that SWCNT-based electronic devices require the absence of metallic specimens (m-SWCNTs) because they significantly degrade device performance [2]. Therefore, the synthesis of SWCNTs with well-controlled diameter and chirality is currently the biggest challenge for the SWCNTs community.

In this work, we present a practical approach for controlling Single Walled Carbon Nanotubes (SWCNTs) diameter distribution through thin film Ru catalyst coupled with hydrogen pre-treatment. Uniform and stable Ru nanoclusters were obtained after dewetting the Ru thin films under atomic hydrogen pre-treatment. SWCNTs were synthetized by double hot filament chemical vapor deposition (d-HFCVD) on SiO_2/Si substrates at different temperatures. We found that the temperature is an important synthesis parameter that influences the diameter distribution of the final SWCNTs. Statistical analysis of the Raman radial breathing modes evidences the growth of highly enriched semi-conducting SWCNTs (about 90%) with narrow diameter distribution that correlates directly with the catalyst particle size distribution. Electrical measurement results on as-grown SWCNTs show good thin-film transistor characteristics.

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[*] **Corresponding author at:** *University Paris Est, IFSTTAR, Boulevard Newton, 77420 Champs-sur-Marne, France*

Tel: +33 (0) 1 69 33 43 85, E-mail address: fatima.bouanis@ifsttar.fr (Fatima Zahra Bouanis)

Graphene nanoplatelets coating for corrosion protection of aluminum substrate

F.Z. Bouanis[1,2*], P. Moutoussay[1], N. Dominique[1], I. Florea[2], D. Pribat[2,3], T. Chaussadent[1], P. Chatellier[1]
[1]*University Paris Est, IFSTTAR, Boulevard Newton, 77420 Champs-sur-Marne, France*

[2]*Laboratory of Physics of Interfaces and Thin Films, UMR 7647 CNRS/ Ecole Polytechnique Palaiseau-France*

[3]*Department of Energy Science, Sungkyunkwan University, Suwon, Korea*

Abstract

The corrosion of metal structures is recognized as one of the most serious problems in the modern societies as it results in the loss of more than one hundred billions of dollars in damage each year [1]. Intense efforts have been made to find protective coatings that inhibit the process of metal corrosion. Recently, graphene is considered as a highly promising new coating material for corrosion inhibiting coatings [2], because of its impermeability and hydrophobic properties [3,4], which allow it to create a barrier against gases and liquids when it is in a corrosive environment. The graphene is considered chemically and thermally stable [5,6], inert under different atmosphere [7], low cost coating and environmental friendly.

In this work, we study the properties of graphene nanoplatelets as an effective anticorrosion coating for aluminum substrate in 0.5 M NaCl at room temperature (25°C). Scanning and transmission electron microscopy and Raman spectroscopy reveal the high quality multilayer graphene nanoplatelets. The modification of the corrosion resistance characteristic were investigated by open circuit potential (OCP), followed by electrochemical tests such as potentiodynamic polarization (Tafel curves) and electrochemical impedance spectroscopy (EIS). The electrochemical results show that the graphene nanoplatelets provides effective resistance against corrosive medium. Scanning electron microscopy (SEM), Raman spectroscopy and Energy Dispersive X-ray (EDX) studies carried after immersion in corrosive medium confirm that graphene coated aluminum surface is well protected compared to the uncoated substrate.

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[*] **Corresponding author at:** *University Paris Est, IFSTTAR, Boulevard Newton, 77420 Champs-sur-Marne, France*

Tel: +33 (0) 1 69 33 43 85, E-mail address: fatima.bouanis@ifsttar.fr (Fatima Zahra Bouanis)

The EC-SPR biosensor based on graphene oxide, silica and gold nanoparticles in NADH determination

J. Breczko[1], **E. Regulska**[1], **M.E. Plonska-Brzezinska**[1]

1- Institute of Chemistry, University of Bialystok, Ciołkowskiego 1K, 15-245, Bialystok, Poland

j.luszczyn@uwb.edu.pl

Oxidized and reduced forms of nicotinamide adenine dinucleotide (NAD^+ and NADH) are one of the most often determined organic compounds due to their biological activity [1]. The problems with the redox behaviour of the $NADH/NAD^+$ couple on the bare solid electrodes are mainly associated with its irreversibility and large activation energy. Decrease of the overpotential and enhancement of the electron transfer rate in $NADH/NAD^+$ redox system are the most important requirements, that must be met to achieve an effective electrochemical determination [2]. Conjunction of different type of nanoparticles with promising chemical, electrochemical and catalytic properties allows to predict a noticeable improvement of a detection ability of an electrochemical sensor.

The main goal of presented work was to develop a biosensor containing three types of structures: graphene oxide (GO), silica nanoparticles (SNPs) and gold nanoparticles (GNPs) for effective electrochemical and optical determination of NADH [3]. The significant increase of the specific surface area and stability of the nanoparticles can be expected due to the presence of SNPs. The graphene is responsible for the good conductivity of the sensor. It also should increase the surface area of the sensor available for the analyte. Finally, the catalytic properties of GNPs toward NADH can be expected. The usage of such nanostructures catalyzing NADH oxidation in the sensor construction allow to expect the enhancement of its electrochemical sensitivity. Additionally, oxidized NAD^+ exhibits the electrostatic affinity to the GNPs functionalized with carboxylic groups from the top of constructed biosensor surface, what gives a possibility for optical detection. This aim was achieved by the application of the electrochemical surface plasmon resonance (EC-SPR) method, which is a combination of optical SPR technique with electrochemical response. Simultaneous recording of two signals during the measurements is an additional way to improve the quality of detection.

The subsequent steps in biosensor formation, the manner of structure organization and the layer thickness were verified by different methods. Electrochemical oxidation of NADH was performed with the usage of differential pulse voltammetry method (DPV). Performed studies showed, that a gold electrode modified with GO, SNPs and GNPs exhibits an enhanced sensitivity toward NADH electrochemical oxidation process. Enhancement of the electrochemical sensitivity toward NADH, as a result of electrode modification, was proved by lower values of LOD (0.0236 mM) and LOQ (0.0707 mM) in comparison with corresponding parameters calculated for non-modified gold electrode. DPV and SPR signals registered for different amount of NADH were correlated with its concentration into linear relationship: $y = 8.6388x - 0.0109$; $R^2 = 0.9997$ and $y = 1305.8x -74.098$; $R^2 = 0.9913$ respectively.

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The role of MWCNTs and SWCNTs on the crystallization of polycarbonate evaluated by XRD, SEM and spectroscopic absorption

Claudio Larosa[1]* , Attilio Converti[1], Nicola Bragazzi[2], Marius Enãchescu[3], Malik Sharali[4]
[1]Department of Civil, Chemical and Environmental Engineering, University of Genoa, via all' Opera Pia 15, 16145 Genoa, Italy
[2]School of Public Health, Department of Health Sciences (DISSAL), University of Genoa, Genoa, Italy;
[3]Politehnica University of Bucharest, Center of Surface Science and Nanotechnology, 313 Splaiul Independentei, 060042, Bucharest, Romania
[4]Forschungszentrum Karlsruhe, Institut für Nanotechnologie, D-76021 Karlsruhe, Germany
Correspondent author: Claudio.Larosa@unige.it Tel: 01035338200

In the last decades, Multiwall Carbon Nanotubes (MWCNTs) have received remarkable attention because of their mechanical and electrical properties [1-3]. In order to expand further their versatility, in the current study MWCNTs were functionalized using organic solvents [4] to load transparent polymers of interest, such as polycarbonate and nylon 6,6. These were utilized to obtain sunscreen composites and optical devices of broad interest. For this purpose, the dispersed phase and stability of MWCNTs in a medium solvent play a major role in the final properties of the composites. The organosylane derivative was employed to coat externally MWCNTs. Sylane compounds can effectively improve the stability of carbonaceous structure with respect to chlorinated solvents [5] and open a vast array of applications exploiting the optical features of transparent polymer composites. However, because of their chemical shape, MWCNTs and Single wall Carbon Nanotubes (SWCNTs) remain structures highly capable to aggregate in dimensional clusters, which cannot be suspended in a medium solvent for a long time [6]. Therefore, chlorinate solvents with an assisted sonochemical action can reduce attraction forces and favour the reduction of aggregates formation. Thus, solutions were mixed by blending and utilized to load polycarbonate. On the other hand, although chlorinate solvents favour dispersion they reduce stability in solution, unstable after a few days.

3-propylamino-chlorosilane improves dispersion at the beginning by initial swelling of MWCNTs and SWCNTs and later by dissolution. The solvent plays also a key role to increase the compatibility with polycarbonate.

The effects on carbonaceous structures are reported as comparison. MWCNTs dispersed in *3-propylamino-chlorosilane* can load polycarbonate to obtain a set of composite film with different ratio MWCNTs/polycarbonate in a Petri dish. Composites conserve film transparency with several grades of gray, as shown in Figure 1. In order to investigate the amorphous nature of polycarbonate loaded on new composites, X-ray diffraction (XRD) and thermal analysis were employed. Raman spectroscopy of composites was also used. MWCNT$_S$ were dispersed in *3-propylamino-chlorosilane* and, then, in a chlorinated solution of polycarbonate. Thickness layer with progressive ratio MWCNTS/polycarbonate was maintained constant. Our goal was to utilize low quantities of MWCNTs and SWCNTs able to change the mechanical properties without compromising the transparency of composites. MWCNTs well dispersed were able to change the color of polycarbonate from colourless to grey with advantage for the composite in terms of optical stability. Others investigations were focused to evaluate crystallization process in the polycarbonate: the effect was different with very small amount of MWCNTs in polycarbonate. The analysis showed a partial crystallinity change on polycarbonate. Preliminary results of indentation and optical absorption tests will be reported.

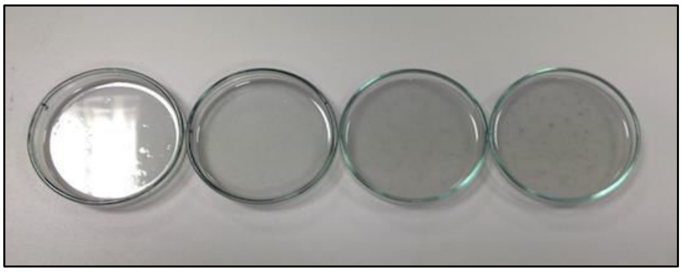

Figure 1: MWCNTs /polycarbonate composites on Petri dish.

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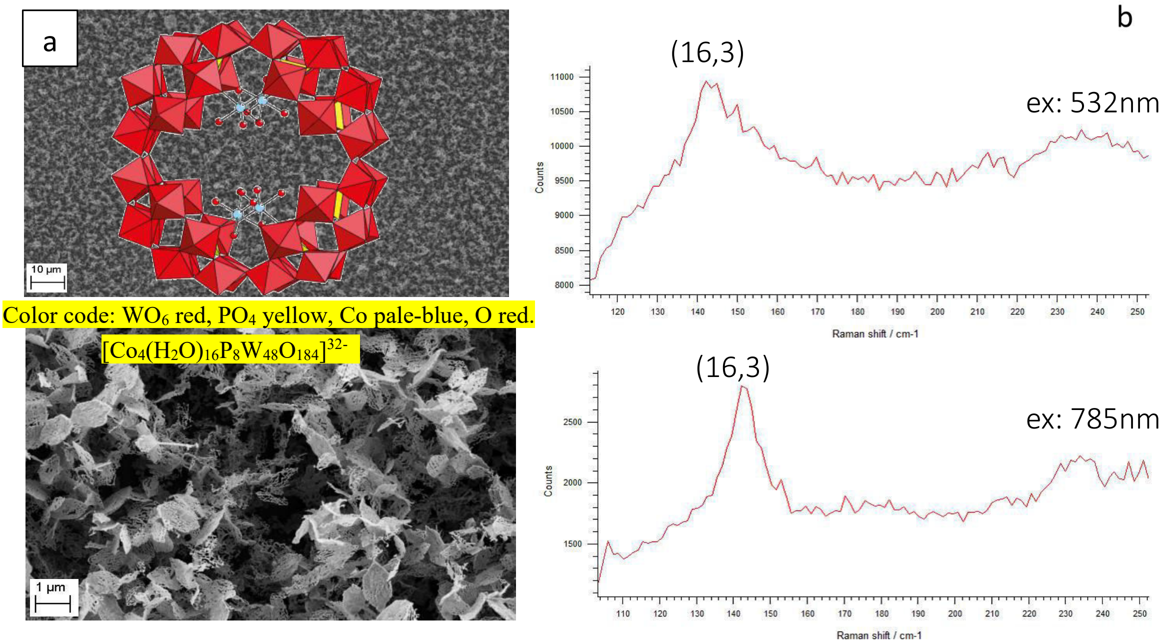
Chirality-Specific Growth of SWCNTs

M. Ibrahim[1], S. Malik[2], A. K. Powell[3]

[1] *Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Germany.*
[2] *Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Germany.*
[3] *Institute for Applied Materials (IAM-AWP), Karlsruhe Institute of Technology (KIT), Germany.*

masooma.ibrahim@kit.edu

Carbon nanotubes are considered to be the material of the future. They are of two types of nanotubes, single-walled and multi-walled (**SWCNT** and **MWCNT**). The former can be considered as a hollow cylinder formed by rolling a piece of graphene sheet and could be either metallic or semiconducting depending on the manner of rolling denoted as (n,m) (chirality) and diameter. **SWCNTs** with identical chiral indices are among very promising candidates in various potential applications ranging from electronics and energy to biomedicine [1]. The growth of **SWCNTs** is usually carried out from a hydrocarbon as carbon source in the presence of a metal catalyst such as Fe, Co, Mn, Cu, and Ni [2]. The use of mixed metal catalysts has also been probed in order discover the ideal catalyst [3]. These synthetic ways provide mixture of different chiralities. Since most of the future applications for SWNTs will need pure chirality tubes, there has been growing interest to separate the chirality pure tubes from the mixture. Although the post-purification procedure result in comparably high yield of specific chiralities; still such ways are costly and time consuming, and could change the properties of the tube. Very recently a breakthrough came in this field from an attempt which allowed production of single-chirality **SWCNTs** at an abundance of >92% by using a polyoxometalates (**POM)** based catalyst [4]. It is expected that this strategy of growing **SWNTs** with desired structure and chirality using robust POMs catalysts can become a standard approach.



Color code: WO_6 red, PO_4 yellow, Co pale-blue, O red.

$[Co_4(H_2O)_{16}P_8W_{48}O_{184}]^{32-}$

Figure 1. (a) SEM overview of SWCNTs grown from **$Co_4P_8W_{48}$** nanocrystal catalysts (b) Raman spectra of the RBM region of the SWCNTs

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Improvement of Mechanical Properties of Polyethylene Meltblown Webs

M. Kaplan,

Bartin University, Faculty of Engineering, Department of Textile Engineering, Bartin Kutlubey Kampüsü / Bartin, Turkey

muslumkaplan24@gmail.com

Abstract

Nonwovens have been used widely worldwide, and their usage has been increasing recently. Majority of the nonwovens, which are widely seen, are dry, wet and polymer laid. Polymer-laid nonwovens are produced directly from extrusion of polymers and include both spunbond and meltblown. Melt blowing process is a single step process that converts polymeric raw materials into a fibre network and a useful web [1].

Thin fiber drawing at diameters 1-5 µm [2]. Major markets for meltblown fabrics include medical, hygiene, industrial and filtration. Many meltblown webs are often layered between two spunbond fabrics and bonded [3]. This structure is called a spunbond, meltblown, spunbond composite (SMS) because meltblown provides good barrier properties and the spunbond add support and abrasion resistance [4].

In this study, to increase the tensile strength of meltblown PE webs, the hot press was applied after the winding. The effect of different temperature and periods on the mechanical properties of PE meltblown web was investigated.

Figure 1 shows the tensile strength of one and twolayer PE meltblown webs at different temperatures. It has been determined that the breaking strength of the single and double layer PE webbing is decreased rapidly at 120 ° C for 1 minute and the material structure is deteriorated when 2 minutes hot pressing is applied.

One and twolayer PE webs were found to have the highest value of tensile strength when hot pressed at 110 ° C. It is also seen that increasing the process time to 2 min increases the tensile strength.

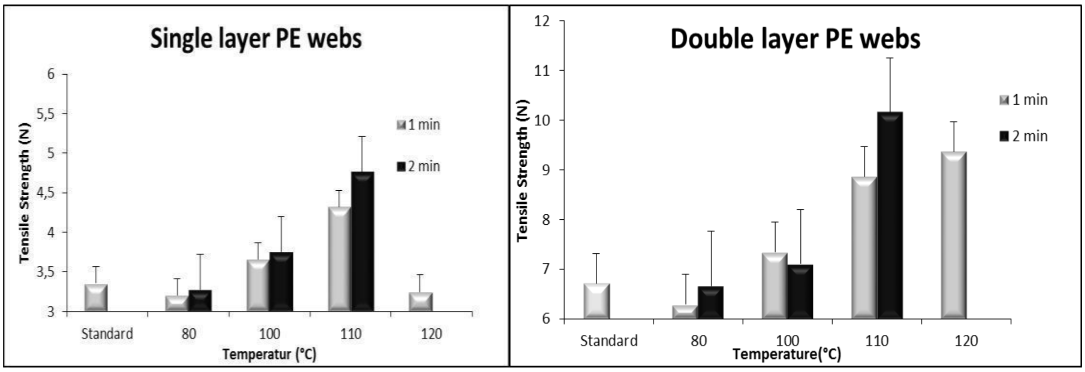

Figure 1: The thensile strength of samples

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Copper substrate contamination with compact SiO_2 thin film deposits due to reactor tube evaporation in graphene CVD synthesis process

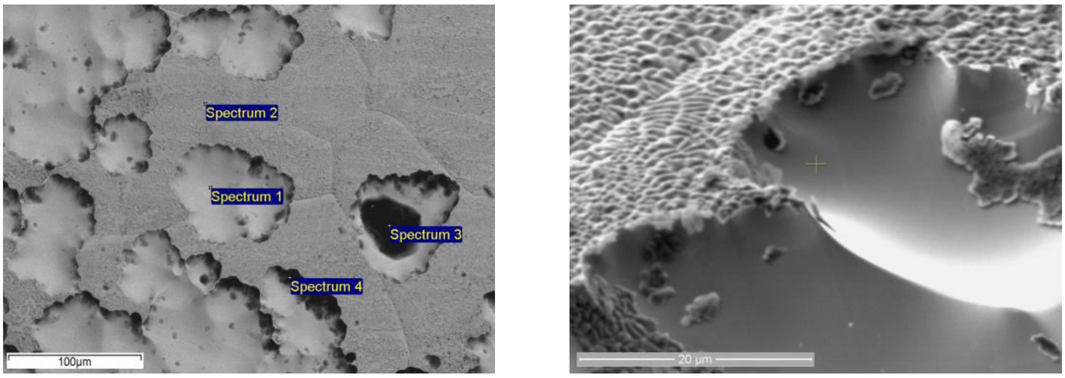
Z.Eres[1], J.Sancho Parramonn[1], F.Zupanič[2]

1- Rugjer Boskovic Institute, Bijenicka cesta 54, 10000 Zagreb, Croatia
2- Faculty of Mechanical Engineering, Smetanova ulica 17, 2000 Maribor, Slovenia

zeres@irb.hr

Copper is material of first choice as substrate for single-layer graphene (SLG) synthesis in CVD process. Substrate annealing on high temperature is done prior to synthesis step to enlarge domain size from few microns to few hundred microns range. It is common practice to use flow of low-pressure hydrogen gas in annealing process to simultaneously remove surface oxides.

However, if pressure during annealing is too low it can enable sublimation of reactor tube material, usualy made of silicon-dioxide, and deposition of this material onto substrate surface. Here we report on such case where CVD reactor tube is made of fused silica, annealing temperature was 1000 °C, pressure was 3 mTorr, no hydrogen gas was used, duration of annealing was 24h. After rapid cooling samples were conducted to room-temperature electropolishing in H3PO3 based electrolyte [2] to obtain ultra-smooth surface. Contrary to our expectations, SEM images revealed moon-like surface morphology with two distinguishing parts: meshy straight plateau and smooth craters as shown in Figure 1.



(a) (b)

Figure 1. (a) SEM image of copper substrate after electropolishing. Four typical regions are selected for EDS analysis: Spectrum 1-4. Results of analysis presented in table 1 shows that thin film is most probably composed of SiO_2. (b) SEM image of copper substrate with higher magnification shows meshy structure of thin silica film.

Table 1 - EDS analysis results (atomic percentage)

Position	C	N	O	Na	Si	P	Cl	K	Ca	Cu
Spectrum 1										100
Spectrum 2	13.15		26.03		8.16					52.66
Spectrum 3	56.56	17.66	24.13	0.49	0.35		0.64	0.17		
Spectrum 4	87.99		8.71			0.01			0.43	5.04

Carbon residue (Spectrum 3-4) were not fully identified but it also contained elements naturally found in tap water although DI-water was used throughout this experiments. Smooth craters (Spectrum 1) were identified as pure copper substrate that is etched and partly polished in electrolyte. Meshy straight plateau (Spectrum 2) were identified as thin SiO_2 film. According to electropolishing time in excess of 2h and current of less than 5 mAcm^{-1} it seems that this thin film is compact and non-conductive to electric current with strong adhesion to substrate surface. Therefore it forms excellent passivisation layer that could be used in future graphene device production line.

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Perturbation theory for weakly coupled two-dimensional layers

Georgios A. Tritsaris[1,*], Sharmila N. Shirodkar[1], Efthimios Kaxiras[1], Paul Cazeaux[2],
Mitchell Luskin[2], Petr Plecháč[3] and Eric Cancès[4]

[1] John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA
[2] School of Mathematics, University of Minnesota, Minneapolis, Minnesota 55455, USA
[3] Department of Mathematical Sciences, University of Delaware, Newark, Delaware 19716, USA
[4] Université Paris Est, Ecole des Ponts and INRIA, 77455 Marne-la-Vallée, France

**current address: Deregallera Ltd, Caerphilly, CF83 3HU, UK*

The physics of two-dimensional systems, composed of one or several layers that have thickness of a single atom or a few atoms, is becoming ever more interesting as the realization of such nanostructures with essentially any desirable combination of materials are within grasp of experiment [1]. Atomistic materials modelling and *ab initio* simulation can accelerate the discovery of novel two-dimensional materials with tailored optoelectronic properties but a big challenge in this direction is the modelling of twisted assemblies or assemblies comprising layers with different in-plane lattice constants, for which naive structural models would involve exceedingly large supercells.

Here, a simple framework is presented for the study of the electronic properties of weakly coupled, atom-thick structures [2]. Within this framework, we calculate the electronic structure of prototypical commensurate and twisted bilayers of graphene (Gr) and hexagonal boron nitride (h-BN), and of a Gr/h-BN heterostructure, which we compare with reference full-scale density functional theory calculations. We find that for relatively large twist in the twisted assemblies, the perturbation of electronic states near the Fermi level is negligible. The capabilities of our method open the path for fast computational screening of layered assemblies of any composition or relative orientation for targeted design of advanced composite materials.

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New Era of Biodegradable Composites – ABMcomposite

Ari Rosling

ABMcomposite (technical), Hepolamminkatu 11, 33720 Tampere, Finland

In the recent years, bio-based and biodegradable products have raised great interest because sustainable development policies tend to expand with the growing concern for the environment and the use of non-renewable resources.

Arctic Biomaterials Oy (ABM) is a company producing bio-based and/or biodegradable compound and composite solutions for demanding technical and medical applications. ABM has a combined experience of over 200 years of biopolymer knowhow. This in depth knowledge we offer to our customers and partners to develop biomaterials to meet their needs. ABM commits to join our customer's journey in finding sustainable technical solutions to their products starting from product and mold design to optimized material formulation. The biodegradable glass fiber reinforced materials produced with ABM's own technology enables us to fulfill customer needs in technical and medical applications in an environmentally friendly way and offer an alternative to several oil-based technical plastics.

The composite materials are produced on our long-fiber-reinforced thermoplastic (LFT) line. This proprietary biodegradable long glass fiber compounding technology increases the ABM composite materials temperature resistance and mechanical properties to new levels and opens a variety of possible application areas in the field where technical plastics are being used.

Along with the sustainable aspects and physico-mechanical properties ABM also produces aforementioned materials with additional specific high-value functionalities, e.g. antistatic, flame resistant, antimicrobial and colored products.

COST Action CA15107 meeting

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