GM-2016

Graphene and related Materials: properties and applications

International Conference

Paestum, Salerno (Italy)

May 23-27, 2016

ABSTRACT BOOK

This event is organized by CNR-SPIN and University of Salerno

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INTRODUCTION

The International Conference GM-2016 "*Graphene and related Materials: properties and applications*" brings together experts in the field of fabrication, characterization and application of graphene, graphene oxide and related 2D materials.

The Conference is organized by the Institute for Superconductors, Innovative Materials and Devices (SPIN) of the Italian National Research Council (CNR) and the University of Salerno, under the Patronage of the Italian Ministry of Foreign Affairs and International Cooperation.

The Conference programme is scheduled in oral and poster presentations, with the aim of stimulating discussions and knowledge exchange in the following areas:

- ✓ **Graphene and Graphene oxide**
  - *Synthesis, characterization, properties, and applications*
  - *Growth of large area Graphene*
  - *Physics and chemistry of Graphene*
  - *Graphene for plasmonics and optics*
  - *Field emission from Graphene*
  - *Graphene based nanoelectronic devices*
  - *Graphene and Graphene oxide for energy (battery, capacitor, catalysis, solar)*
- ✓ **Graphene based polymer composites**
  - *Functionalization of Graphene and development of novel sensors*
  - *Graphene for Flexible Electronics, Sensors & Composites*
- ✓ **Graphene-like 2D materials**
  - *Integration of Graphene with other 2D materials*
  - *Electronic, optoelectronic properties and potential applications*
  - *Growth, synthesis techniques and integration methods*
  - *Chemistry and modification of 2D materials*
  - *Structural, electronic, optical and magnetic properties of 2D materials and devices*
  - *Applications of 2D materials in electronics, photonics, energy and biomedicine*

The social events include a visit to the Paestum Archeological site on 25th May and a Gala Dinner on 26th May, and encourage scientific discussions in a relaxed atmosphere.

We wish you a wonderful stay at the GM-2016 International Conference.

Antonio Di Bartolomeo
Filippo Giubileo
Nadia Martucciello
Chairs

COMMITTEES

Conference Chairs:

Antonio Di Bartolomeo
University of Salerno, Italy

Filippo Giubileo
CNR-SPIN Salerno, Italy

Nadia Martucciello
CNR-SPIN Salerno, Italy

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Duesberg, Georg
Trinity College Dublin, Ireland

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Supporting staff:

Vittorio Benvenuto, Marco Caputo, Nicola Funicello, Armando Galluzzi, Laura Iemmo, Giuseppe Luongo, Cristina Ripoli

University of Salerno, Italy

INVITED SPEAKERS

Keynote Lecturers:

Casiraghi, Cinzia
School of Chemistry, University of Manchester, UK

Duesberg, Georg
Trinity College Dublin, Ireland

Invited Speakers:

Barbara, Paola - *Georgetown University, USA*
Boggild, Peter - *Technical University of Denmark*
Bonaccorso, Francesco - *Italian Institute of Technology, Italy*
Bouchiat, Vincent - *Institut Néel, CNRS-Grenoble, France*
Covaci, Lucian - *Universiteit Antwerpen, Belgium*
Eres, Gyula - *Oak Ridge National Laboratory, USA*
Giannazzo, Filippo - *IMM-CNR, Italy*
Goswami, Srijit- *Kavli Institute of NanoScience, TU Delft, the Netherlands*
Ichinokura, Satoru - *University of Tokyo, Japan*
Ki, DongKeun - *Université de Geneve, Switzerland*
Krasheninnikov, Arcady V. – *Aalto University, Finland*
Lambin, Philippe - *Université de Namur, Belgium*
Liscio, Andrea - *CNR-ISOF, Italy*
Lupina, Grzegorz - *IHP Microelectronics, Germany*
Makk, Peter - *University of Basel, Switzerland*
Meir, Yigal - *Ben-Gurion University, Israel*
Merkoçi, Arben - *Catalan Institute of Nanoscience and Nanotechnology, Spain*
Nagashio, Kosuke – *University of Tokyo, Japan*
Navalon, Sergio - *Politécnica de Valencia, Spain*
Nigge, Pascal – *University of British Columbia, Canada*
Nouchi, Ryo - *Osaka Prefecture University, Japan*
Ottaviano, Luca - *University of L'Aquila, Italy*
Pénicaud, Alain - *CNRS, France*
Polini, Marco - *Istituto Italiano di Tecnologia, Graphene Labs, Italy*
Russo, Saverio – *University of Exeter, United Kingdom*
Vignaud, Dominique - *CNRS, France*
Yakimova, Rositsa - *Linkoping University, Sweden*

VENUE

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The **Savoy Beach Hotel** stands in a very spectacular position that **overlooks the Gulf of Salerno**. In fact it is positioned just between the Amalfitan and the Cilento Coast, both in the Unesco World Heritage List. The location offers a perfect mix of culture, sea and nature, being close to the ancient temples of Magna Grecia, the limpid sea reachable through a shadowy pinewood, and the **National Park of Cilento**, one of the largest park in Italy.

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American Bar (extra on payment)	from	11:30	to	23:00
Bar outdoor Pool (extra on payment)	from	11:30	to	23:00
Restaurant "Tre Olivi" (extra on payment)				
Breakfast	from	7:00	to	10:00
Lunch	from	12:30	to	14:30
Dinner	from	19:30	to	22:30
Lunch Buffet	**€.25,00**	**/person**		
Dinner Menu	**€.30,00**	**/person**		
Room Service (€.5,00/person)	from	7:30	to	23:00
Outdoor Swimming pool	from	8:30	to	18:30
Fitness Room	from	8:30	to	18:30
Wi-Fi connection (Free)		**24 h**		
Laundry service (extra on payment)				
Shuttle Service (extra on payment on reservation)				
Beach"Athena"(150m, Free)	from	8:00	to	19:00
Beach Towel	**€.5,00**	**/person/day**		

Room facilities

Bathroom
Telephone
Safe
Minibar (extra on payment)
Wardrobe
Wi-Fi connection (Free 24h)

Amenities

Archaeological site Paestum	from	9:00	to	19:30
Museum of Paestum	from	9:00	to	19:30
Pharmacies available (Paestum, Capaccio, Agropoli)				
Car rental (on reservation, various companies)				
Body massage (on reservation)				
Hair stylist (on reservation, in Paestum)				

SOCIAL EVENTS

The Conference Organizers offer:

- Coffee breaks
- Lunch buffets, May 24th , 25th , 26th
- Excursion trip to the archeological site and museum with English guide
- Conference materials

Excursion on Wednesday, 25th May (Afternoon)

Visit to the Archaeological Site and the National Museum-Guided tour

Paestum has been for a thousand years a romantic ruin in midst of a solemn wilderness. Its Doric temples, hardly surpassed even by those of Athens in noble simplicity and good preservation, produce an incomparable effect of majesty and grandeur. The ancient site is set in a grassy field surrounded by gardens and hills. The site is so charming that you may want to spend time just relaxing here and to the exceptional museum, that holds finds excavated from the site and around, including a set of archaic period Greek metopes. Here you will find the tomb paintings, one of which, the so-called "Tomb of the Diver", is a graceful and expressively naturalistic piece of work, the only existing example of Greek wall painting in Italy.

LIST OF REGISTERED PARTICIPANTS

Surname	*Name*	*Affiliation*	*Country*
Acocella	**Maria Rosaria**	*University of Salerno*	*Italy*
Agovino	**Anna**	*University of Salerno*	*Italy*
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Sansone	**Lucia**	*CNR-IPCB*	*Italy*
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Scudieri	**Carmela**	*University of Salerno*	*Italy*
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Tescione	**Fabiana**	*CNR-IPCB*	*Italy*
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Vacacela Gomez	**Cristian**	*University of Calabria*	*Italy*
van Engers	**Christian**	*University of Oxford*	*United Kingdom*
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Vomacka	**Petr**	*Academy of Science of the Czech Republic*	*Czech Republic*
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Willinger	**Marc Georg**	*Fritz Haber Institute of the Max Planck Society*	*Germany*
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PROGRAMME

MONDAY 23rd, May 2016

10:00 – 14:30	**Registration**

14:30-14:40	***Welcome:***
	Antonio Di Bartolomeo, Filippo Giubileo and Nadia Martucciello, Chairs Gaetano Guerra, Member of local advisory committee and research delegate for the University of Salerno
14:40 – 16:15	***Session: Carrier Transport Properties*** *Chair: Gaetano Guerra*
14:40	**Carrier mobility and density mapping of large-scale graphene,** *Boggild*
15:00	**Electron optics in ballistic graphene,** *Makk*
15:20	**Hydrodynamic electron transport in a graphene field effect transistor,** *Polini*
15:40	**Graphene, related two-dimensional crystals and hybrid structures for energy applications,** *Bonaccorso*
16:00	**Interface Effects on the electronic and electron-phonon coupling of graphene,** *Profeta*
16:15 – 16:45	***Coffee Break***
16:45 – 18:30	***Session: Electric and Magnetic Properties*** *Chair: C.F.J. Flipse*
16:45	**Electronic interactions in N-layer graphene: Fractional Quantum-Hall effect and Even-Odd insulating behavior,** *Ki*
17:05	**Magnetism and entanglement in graphene nanoribbons,** *Hagymasi*
17:20	**Dielectric Screening and Plasmon Resonances in periodic arrays of armchair graphene nanoribbons: a time depend density functional theory approach,** *Vacacela Gomez*
17:35	**Magnetic and Structural anisotropy of Cobalt thin films intercalated under Graphene,** *Carlomagno*
17:50	**Graphene-based Platforms for Biosensing Applications,** *Merkoçi*
18:10	**Fragmentation of 2D materials: New strategies for structural analysis and 2D metrology,** *Liscio*

TUESDAY 24th, May 2016

08:30 – 10:15	***Session: Fabrication Methods*** *Chair: P. Ciambelli*
8:30	**Raman Spectroscopy of Graphene and Related Materials,** *Casiraghi*
8:55	**Kinetics Mechanisms of Large-Area Single-Crystal Graphene Growth,** *Eres*
9:15	**Progress in properties control and application trends of large area graphene on SiC,** *Yakimova*
9:35	**Development of a technology platform for wafer-scale fabrication of graphene devices,** *Lupina*
9:55	**Molecular beam epitaxy of single to few layer graphene on SiC, growth and electronic properties,** *Vignaud*
10:15 – 10:45	***Coffee Break***
10:45 – 12:15	***Session: Fabrication Methods*** *Chair: G. Eres*
10:45	**CVD growth of Graphene on Ge(100): a characterization route of the “as grown” system,** *Scaparro*
11:00	**Transfer of CVD-grown graphene for room temperature gas sensors,** *Rigoni*
11:15	**Direct Observation of CVD Graphene Growth and Related Surface Dynamics of Active Metal Catalysts by In-situ Scanning Electron Microscopy,** *Willinger*
11:30	**The stacking sequence of graphene revealed by in-situ SEM observation of CVD growth and hydrogen etching,** *Wang*
11:45	**Nitrogen doped twisted graphene grown by atmospheric pressure chemical vapor deposition,** *Komissarov*
12:00	**Raman Studies of Strain-Engineered Graphene Grown on Boron Nitride by Molecular Beam Epitaxy,** *Davies*
12:15 – 14:30	***Lunch Buffet***
14:30 – 15:55	***Session: Graphene Applications*** *Chair: C. Casiraghi*
14:30	**Synthesis and Applications of 2-Dimensional Layered Materials,** *Duesberg*
14:55	**Nanostructured graphene for terahertz technology,** *Barbara*
15:15	**Ballistic Josephson junctions in edge-contacted graphene,** *Goswami*
15:35	**Edge reconstruction in Graphene and other two-dimensional systems,** *Meir*
15:55 – 16:25	***Coffee Break***
16:25 – 17:30	***Session: Graphene functionalization*** *Chair: S. Navalon*
16:25	**Fundamental properties and some applications of Graphene Oxide,** *Ottaviano*
16:45	**Formation of Self-Assembled Graphene/Graphene Oxide memristors through the photocatalytic oxidation,** *Kapitanova*
17:00	**Laser induced reduction of GO prepared by a novel modified Hummers' method,** *Longo*
17:15	**Selective edge functionalization of graphene layers with hydroxyl groups for the preparation of flexible conductive carbon paper,** *Barbera*
17:30 – 19:00	***POSTER SESSION***

WEDNESDAY 25th, May 2016

08:30 – 10:20	***Session: Graphene functionalization*** *Chair: G. Duesberg*
8:30	**Additive Free, Single Layer Graphene in Water,** *Penicaud*
8:50	**Tuning fluorine distribution inside graphite oxifluorides,** *Mar*
9:05	**Molecularly defined photodetectors in FeCl3-intercalated graphene,** *De Sanctis*
9:20	**Composite films based on graphene oxide and fluorographene suspensions mixture,** *Nebogatikova*
9:35	**One-step reduction of graphene oxide by a reduced Keggin-type polyoxometalate and nanocomposite formation,** *Debiemme-Chouvy*
9:50	**Thermal and electrochemical exfoliation of fluorinated graphite,** *Batisse*
10:05	**Structural and electrical properties of reduced graphene oxide foams,** *Kondratowicz*
10:20 – 10:50	***Coffee Break***
10:50 – 12:40	***Session: Fabrication Methods*** *Chair: A. Penicaud*
10:50	**Graphenes as metal-free (photo)-Fenton catalysts,** *Navalon*
11:10	**Graphene Oxide as Catalyst and Filler in Thermosets Resins: New Perspectives and Applications,** *Acocella*
11:25	**Laser-induced graphene: a versatile material for the fabrication of flexible electrochemical supercapacitors,** *Lamberti A.*
11:40	**Serinol derivatives for the preparation of few layers graphene,** *Galimberti*
11:55	**Water induced enhancement of epitaxial graphene sensitivity to NO2,** *Flipse*
12:10	**Atomic-Scale Model of Reversible Wettability Transition of Defective Graphene,** *Blonski*
12:25	**Chitosan, a serinol derivative and few layers graphene: from carbon paper to aerogel,** *Guerra S.*
12:40 – 14:30	***Lunch Buffet***
14:30 – 19:00	*EXCURSION to Archeological Site*

THURSDAY 26th, May 2016

08:30 – 10:20	***Session: Graphene and Superconductivity*** *Chair: G. Profeta*
8:30	**Evidence for superconductivity in Li-decorated monolayer graphene,** *Nigge*
8:50	**Superconducting proximity effect in strained/disordered graphene,** *Covaci*
9:10	**Gate-Tunable Proximity 2D macroscale Superconductivity in Hybrid Graphene Devices,** *Bouchiat*
9:30	**Superconductivity in Calcium-Intercalated Bilayer Graphene Detected by in situ Resistivity Measurements in Ultrahigh Vacuum,** *Ichinokura*
9:50	**Hysteretic collapse and revival of the Josephson supercurrent in Al contacted graphene on SiC,** *Jouault*
10:05	**Effect of non-Gaussian noise sources on the Distributions of switching currents in graphene Josephson junctions,** *Guarcello*
10:20 – 10:50	***Coffee Break***
10:50 – 12:20	***Session: Electronic Devices*** *Chair: A. Di Bartolomeo*
10:50	**Graphene heterostructures with wide bandgap semiconductors,** *Giannazzo*
11:10	**Metallic Electrode Contacts to Layered Semiconductors,** *Nouchi*
11:30	**Direct Measurement of the Surface Energy of Graphene and Ultra-flat Transfer Method,** *van Engers*
11:45	**h-AlN and towards van der Waals stacks of few-layer h-AlN with graphene,** *Kakanakova*
12:00	**Dielectric breakdown of hexagonal Boron Nitride,** *Nagashio*
12:20 – 14:30	***Lunch Buffet***
14:30 – 15:50	***Session: EM and Mechanical Properties*** *Chair: P. Boggild*
14:30	**Graphene/polymer multilayers with tailored microwave shielding effectiveness,** *Lambin*
14:50	**Graphene surface treatment, fabrication and characterization of metal/graphene composite materials,** *Silvain*
15:05	**Gas bubbles interaction with graphite based materials and graphene/PDMS composite immersed in water, thermodynamics properties and stability,** *Bartali*
15:20	**Is Graphene the Strongest Material?,** *Hess*
15:35	**Graphene and possible Aeronautical Applications,** *Brelati*
15:50 – 16:20	***Coffee Break***
16:20 – 17:40	***Session: Supercapacitors, Energy and Electrochemical Applications*** *Chair:P. Hess*
16:20	**A 3D flexible micro supercapacitor based on graphene composite,** *Marasso*
16:35	**Silver nanoparticles decorated on graphene for electrochemical applications,** *Casa*
16:50	**Differences between graphene and graphene oxide in gelatin based systems for biodegradable energy storage applications,** *Landi*
17:05	**Native and irradiation-induced defects in two-dimensional inorganic materials,** *Krasheninnikov*
17:25	**Few-layered graphene oxide embedded 1DPhC microcavity for amplified spontaneous emission source,** *Maiti*
20:00	***SOCIAL DINNER***

FRIDAY 27th, May 2016

09:00 – 10:15	*Session: Synthesis, properties and applications of 2D- Materials* *Chair: P. Lambin*
9:00	**Pure and functionalized XBi and XBi_3 (X = B, Al, Ga, In) sheets for applications as topological insulators,** *Gueorguiev*
9:15	**Oxide-interface charge carrier dynamics investigated by optical Second Harmonic Generation,** *Rubano*
9:30	**Adsorption of Small Organic Molecules on Graphene and related 2D materials,** *Lazar*
9:45	**Applications of graphene-based composites,** *Pruneanu*
10:00	**Effect of Post-Exfoliation Treatments on Mechanically Exfoliated MoS_2,** *Budania*
10:15 – 10:45	***Coffee Break***
10:45 – 12:00	*Session: Synthesis, properties and applications of 2D- Materials* *Chair: S. Ichinokura*
10:45	**Comparison of Morphological and Electrical Properties of a Structural Resin Reinforced with two different Exfoliated Graphite Particles,** *Lamberti P.*
11:00	**An enemy of technological substitution: the “sailing ship effect”,** *Filatrella*
11:15	**Selective deformation of MoS_2 monolayer by illuminating laser and magnetotransport of 2D materials probed up to 60 T,** *Jhang*
11:30	**Nanofluidic Ion Transport through Restacked 2D Nanomaterials,** *Raidongia*
11:45	**Closing Remarks**
12:00 –	***Departure***

LIST OF POSTERS

P01	Ardenghi	*Electronic properties of Cantor n-ary set random distribution of impurities in graphene*
P02	Avetissian	*Influence of excitonic effects on high harmonic generation by strong laser field in gated graphene*
P03	Cirillo	*Graphene-based Barriers for Solar Cells synthesized by Cold wall CVD*
P04	Clausi	*Analysis of wrinkles onset and growth in multi-layered graphene-based composite films on flexible Mylar substrates*
P05	Coros	*Supramolecular assemblies of tetrapyridylporphyrin and its metallic complexes with N-doped graphene*
P06	De Santis	*Melt compounding of Poly(Lactic Acid) with graphite-oxide*
P07	Di Bartolomeo	*Leakage and field emission in side-gate graphene field effect transistors*
P08	D'Urso	*Functionalization of Graphene Oxide: a tool to prevent degradation in melt compounded polyesters nanocomposites*
P09	Ecorchard	*Dependency of sorption activity for radionuclides on the concentration of GO on PA66 substrate*
P10	Espinoza-Ramirez	*Reduced graphene oxide films for transparent conductive electrodes*
P11	Gallone	*Graphene – Future applications*
P12	Giubileo	*Low-energy electron-irradiation effect on transport properties of GFETs*
P13	Giuri	*A green in situ reduction of graphene oxide into PEDOT:PSS for photovoltaic application*
P14	Guadagno	*Thermal and Rheological Behavior of TGMDA/Graphene Nanocomposites*
P15	Henych	*Low-temperature water-based synthesis of Graphene oxide/TiO2 composites for destruction of toxic chemicals*
P16	Iemmo	*Two conductance minima in graphene field effect transistors*
P17	Kalenczuk	*Preparation and properties of polyethylene nanocomposites with graphene functionalized with transition metal nanoparticles as flame retardants*
P18	Kim	*Quantum dots attached Graphene oxide for the sensitive detection of ascorbic acid as a biosensor in aqueous solution*
P19	Lam	*Methane gas sensor based on L-ascorbic acid-reduced graphene oxide incorporated with tin oxide*
P20	Lamberti P	*FEM Model and Performance Analysis of a Graphene-Based EM-Shielding Device in Presence of Uncertain Parameters*
P21	Lancellotti	*Performance and Stability improvements of graphene/silicon Schottky barrier solar cells*
P22	Landi	*Light irradiation tuning of surface wettability, optical, and electric properties of GO thin films*
P23	Lee	*Study on TMD/Graphene Based Film Fabrication and Its Applications*
P24	Luongo	*Graphene silicon Schottky diodes*
P25	Ma	*Study on Optical and Electrical Property Changes of Molybdenum Diselenide by Reversible Hydrogenation*
P26	Maggio	*Flexible and Solvent Resistant Graphene Oxide Paper*
P27	Mariconda	*Protection of romp catalyst through polymeric globular shell*
P28	Mijowska	*Nonenzymatic graphene based sensor for glucose detection*
P29	Palomba	*A New Micromechanical Approach for the Preparation of Polymer-Supported Graphene*
P30	Papari	*THz spectroscopy of graphene-like materials and hybrids for the developments of bio-compatible devices*
P31	Pevzner	*Kinetics study of graphene-assisted hydrogen storage and scavenging*

P32	Pogacean	*Electrochemical detection of various organic molecules at electrodes modified with graphene-metallic/bimetallic nanoparticles*
P33	Polichetti	*Graphene-like sensing film inkjet printed on paper for ethanol detection*
P34	Ponticorvo	*Highly Active and Stable Hybrid Catalyst of* MoS_2*-Ni-graphene for HER*
P35	Pospisil	*Photovoltaic Cells with a Hole-Extracting Graphene Oxide Layer Prepared by Material Printing*
P36	Raimondo	*Graphene-based multifunctional epoxy resin for high performance aeronautic structures*
P37	Sadhu	*Highly Efficient Graphene Supports for Fuel Cell Electrocatalysts*
P38	Sansone	*Graphene-Based Thermoelectric Generator*
P39	Santandrea	*Field emission from graphene flakes*
P40	Schiattarella	*Influence of metal type and particle size on the Raman spectrum enhancement of metal decorated graphene*
P41	Scudieri	*Graphene oxide based electrochemical sensor for arsenic detection*
P42	Tescione	*Zein Microparticles Coated by Graphene Oxide Layers: Towards Nanocomposites with Tailored Morphology*
P43	Toto	*Flexible nanostructured composites with graphene/DNA hybrids as multifunctional substrates for biomedical applications*
P44	Trhlikova	*Thermal and electrical properties of graphene, graphite and graphene nanotubes*
P45	Vomáčka	*Magnetic* $MnFe_2O_4$*-rGO composite for removal of model pollutants from water*
P46	Zelechowska	*Templated and template-free methods of 3D porous graphene-based structures manufacturing*
P47	Zilbermann	*One step formation of reduced-graphene-oxide/Co(III)TMPyP system for oxygen reduction reaction*

Abstracts

Monday 23rd

Carrier mobility and density mapping of large-scale graphene

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Type of Contribution: Invited

In this talk, I will overview recent progress in large-area electrical characterization of graphenes electrical properties using non-invasive methods. In terahertz time-domain spectroscopy, the transmission of THz pulses through graphene can be directly translated to the complex conductivity, making spatial mapping of graphene wafers and sheets possible in hours or even minutes. By combination with another non-invasive technique, the micro-four point probe developed at DTU, the often oblivious variations in the electrical continuity and homogeneity can be revealed on several length scales from nanometers to millimeters. We found graphene grown on single crystal copper to be consistently more continuous than graphene grown on commercial copper, which in contrast showed a clear signature of non-Drude preferential backscattering from line defects or grain boundaries. Recently we introduced a thz-transparent back-gate to modulate the carrier density in Thz-TDS measurements and to identify the separate contributions from carrier density and mobility to the conductivity. We also demonstrate graphene mobility mapping entirely without a back gate; here the scattering time is extracted from the frequency dependent conductivity at a constant gate voltage. Recent measurements on commercial graphene samples on large polymer sheets suggests that the method is highly scalable. Finally some perspectives for integration of THz-TDS for fast inline characterization in graphene production and the challenges are outlined.

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Electron optics in ballistic graphene

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Type of Contribution: Invited

Encapsulated or suspended graphene offers a promosing platform for electron optical devices due ballistic nature of electron transport. In graphene gapless p-n interfaces can be formed by electrostatic gating, showing a negative index of refraction and Klein tunneling.

We have developed a method where suspended graphene can be complemented with complex, local electrostatic gating [1] and by taking advantage of this method we realized electron optical elements based on p-n junctions.

We demonstrate that with in suspended graphene a ballistic p-n junction can be formed [2,3] and Fabry-Perot oscillations appear. We investigate the effect of potential smoothness on the oscillation visibility.

In magnetic fields conductance oscillations appear due to the formation of snake states along the p-n interface [4]. We compare our measurements with theoretical simulations, where current distribution calculated show current oscillating back and forth along the p-n interface.

We also show that electrons in ballistic graphene can be guided by gate potentials as photons in optical fibers. However, in our device electrons are not only confined due to critical angle of reflection, but due to the angle dependence of Klein tunneling [5]. Moreover, we demonstrate, that the guiding channel can be filled mode by mode.

Finally, we demonstrate that tunable p-n interfaces can act as beam splitters [6], where the transmission properties can be tuned using local electrostatic gating and that the p-n interface can be substantially moved resulting in peculiar features in magnetic field.

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Hydrodynamic electron transport in a graphene field effect transistor

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Type of Contribution: Invited

Graphene sheets encapsulated between crystals of boron nitride host a unique electron system that due to weak electron-phonon scattering allows micrometer-scale ballistic transport even at room temperature [1,2,3,4]. Above liquid nitrogen temperatures, these electron liquids are expected to display local equilibrium, enabled by strong electron-electron interactions [5,6]. Under these conditions, electrons in doped samples are expected to behave as a viscous liquid and may exhibit hydrodynamic phenomena akin to those observed in classical and quantum liquids. In this talk I will report on results of combined theoretical and experimental work [7,8] showing unambiguous evidence for this long-sought transport regime. In particular, I will discuss how high-quality graphene sheets in the Fermi liquid regime ($k_{\rm B}T \lesssim E_{\rm F}$) exhibit an anomalous (negative) voltage drop near current injection points and whirlpools in the electron current flow. Measurements of these "quasi-local" electrical signals enable to extract the value of the kinematic viscosity of the two-dimensional massless Dirac fermion liquid in graphene, which is found to be an order of magnitude larger than that of honey, in quantitative agreement with many-body theory [8].
Our work represents the first step towards the observation of nearly perfect fluidity [9,10] and quantum turbulence in solid-state devices.

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Graphene, related two-dimensional crystals and hybrid structures for energy applications

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Type of Contribution: Invited

Energy applications are presently driving the development of new materials and processes,[1] able to boost the performance of existing devices or enable new ones.[2,3,4,5] In this context, graphene and other two-dimensional (2D) crystals are emerging as promising materials.[1-5] A key requirement for applications such as flexible electronics and energy storage and conversion is the development of industrial-scale, reliable, inexpensive production processes,[2] while providing a balance between ease of fabrication and final material quality with on-demand properties.
Here, I will show how solution-processing[2] can offer a simple and cost-effective pathway to fabricate various 2D crystal-based flexible and energy devices, presenting huge integration flexibility compared to conventional methods. I will present an overview of graphene and other 2D crystals for flexible and printed (opto)electronic and energy applications, starting from solution processing of the raw bulk materials,[2] the fabrication of large area electrodes[3] and their integration in the final devices.[6,7,8,9]

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Interface effects on the electronic and electronphonon coupling of graphene

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Type of Contribution: Oral

The intercalation of metals, semiconductors, oxygen and hydrogen under epitaxial graphene is an active topic in current graphene research due to the strong influence of the substrate on the electronic properties of graphene. The intercalant often forms a chemical bond with the substrate modifying the electronic properties of the 2D material on top. For example, H intercalation under graphene on SiC causes the formation of a SiH-graphene interface resulting in an unperturbed band structure; the intercalation of oxygen under graphene grown on Ni_3Al alloy causes selective oxidation of Al atoms and formation of Al_2O_3--graphene interface.
For graphene on Ir(111), the oxygen intercalation results in a p-doping of graphene, intercalation of Si under graphene on Ni, Co and Fe results in the formation of corresponding silicides.
These promising results naturally point towards the question how the interface and the electronic structure for graphene and related 2D materials are affected by the type of intercalant.

In this work we studied, by means of experimental and theoretical approach, specific interfaces involving different intercalants and substrates, namely:
Germanium intercalation in graphene grown on Ni(111) substrate and Lithium intercalation in between the carbon buffer layer and the silicon-terminated face of silicon carbide.

Although the general aspects of the intercalation represent a fundamental aspect of the research in graphene technology, these two systems have interesting and peculiar physical motivations.
The Ge is promising due to its higher charge carrier mobilities when compared to Si while it is also compatible with CMOS technology. It has been shown that graphene can be grown on Ge by MBE and that graphene on H-terminated Ge and on Ge oxide surface have superb electronic properties that can even exceed the mobilities of free-standing graphene membranes.
Although, the electronic properties of such devices are strongly influenced by the interface structure, to date nothing is known about the interface structure between graphene and Ge.
Previous works on Ge intercalation were done for graphene on SiC for which the intercalated Ge is amorphous and no precise interface structures was reported.

On the other hand, lithium interaction with graphene attracts special attention for fundamental and technological reasons, related to the fabrication of Libased batteries, possible piezoelectric effects, and a predicted superconducting phase.
In the present talk we present a complete structural and electronic characterization of these systems by means of density functional theory. A careful comparison with experimental results allows understanding the microscopic mechanism of the intercalation, the precise atomic configuration of the interfaces and the origin of the measured electronic properties.

Electronic interactions in *N*-layer graphene: Fractional Quantum-Hall effect and Even-Odd insulating behavior

Dong-Keun Ki
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Type of Contribution: Invited

Absence of an energy gap separating conduction and valence bands makes *N*-layer graphene to be highly susceptible to electron-electron interactions. Here, I investigate transport properties of high-quality suspended devices to demonstrate how these interactions change the low-energy properties of Bernal-stacked *N*-layer graphene.

I will first present a clear experimental evidence of even-denominator fractional quantum-Hall (FQH) state in bilayer graphene, occurring at half-filed lowest Landau level on the hole side (i.e., at nu = -1/2). By taking advantage of multiterminal geometry, we show both minimum and concomitant plateau at nu = -1/2 in longitudinal and transverse resistance, respectively, as expected, in addition to other features corresponding to the states at different filling fractions. We note that these findings are well captured by the theory which attributes the -1/2 state to Moore-Read state in terms of the effect of unique N=0 and 1 degeneracy of zero-energy Landau level in bilayer graphene. This study therefore opens a new route to explore the even-denominator FQH states in two-dimensional systems, which has largely been limited to GaAs-based heterostructures.

Secondly, the transport in high-quality *N*-layer graphene of different thickness are investigated very close to charge neutrality, where interactions are known to be strong in graphene. Through the investigations, we have unexpectedly found that up to *N*=8, which is so thick to be considered as a graphite, interactions open a gap at zero magnetic field when *N* is even whereas odd *N* layers remain conducting: that is, the even-odd effect. Surprisingly, the basic aspects of all findings can be understood by the simplest possible tight-binding model that accounts for the effect of a staggered layer potential with a sign changing between layers, $V_i=\square(-1)^i$ ($i=1,..,N$: a layer label), acting on *N*-layer graphene. It provides a systematic picture of how low-energy properties of Bernal-stacked graphene layers evolve as thickness varies, posing a question about the crossover from graphene to graphite.

These studies clearly illustrate that suspended *N*-layer graphene provides rich opportunities to explore new physical phenomena originating from many-body interactions.

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Magnetism and entanglement in graphene nanoribbons

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Type of Contribution: Oral

In the first part of the work we performed electronic structure and magnetic ordering calculations on graphene nanoribbons by applying the mean-field theory for an extended Hubbard Hamiltonian including the effect of temperature and finite doping.

We found that ribbons with zigzag edge orientation possess spin polarized edge states with both antiferromagnetic (AF) and ferromagnetic (FM) coupling between opposite edges. The calculations revealed a strong connection between the electronic and magnetic properties of zigzag graphene nanoribbons, AF ribbons displaying semiconducting, while FM ribbons showing metallic behavior in excellent agreement with our experimental findings [1].

In the second part, we applied the density-matrix renormalization group (DMRG) algorithm to go beyond the single-particle description, and determined the ground state of finite graphene ribbons with various edge configurations keeping block states up to 20 000. Using the elements of quantum information theory, we calculated the entanglement patterns between the carbon atoms, which reveal the intrinsic properties of the true many-body ground state. [2]

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Dielectric Screening and Plasmon Resonances in periodic arrays of armchair graphene nanoribbons: a time depend density functional theory approach

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Type of Contribution: Oral

The plasmon dispersion of low-dimensional materials is a key point in the design and fabrication of a new generation of nanoplasmonic and nanophotonic devices, capable of operating in a wide frequency band from a few GHz up to several THz. The leading building blocks for future nanoarchitectures seem to be monolayer graphene (MG) and its derivatives, which possess a number of electronic, mechanical and thermal properties [1]. Specifically, MG compared to conventional plasmonic materials (e.g., silver and gold) presents a surface plasmon (SP) on the THz scale, which is characterized by strong confinement, large tunability and low losses [2].

A huge surge in interest has been fueled lately by realization of prototype circuit elements embedding graphene based one-dimensional materials, such as graphene nanoribbons (GNRs). These structures are mostly synthetized in periodic planar arrays, offering outstanding semiconducting properties due to their small band Gap [3]. The latter may be suitably tuned by changing the GNR width, chirality and edge functionalization. On the theoretical side, however, a proper ab initio approach [3,4] towards the understanding of the GNR plasmon response to applied electron and photon currents is still lacking.

In the present study, we scrutinize the SP modes of armchair GNR arrays at room and higher temperatures, up to 900 K, considering both the intrinsic and extrinsic (doped/gated) cases. We use time depend (TD) density functional theory (DFT) in linear response (LR) regime, at the level of the random phase approximation (RPA). We observe two high-energy excitations at energies above 3 eV, which are counterparts to the π and σ-π SPs of MG and graphite. More importantly, we predict unprecedented interband and intraband SPs occurring at energies below ~1 eV. The intraband SP is extremely sensitive to changes in the populations of the valence and conduction levels, induced by doping, gating or increase of electronic temperature.

Experimental measurements are strongly suggested to clarify and confirm the validity of our findings. The main message is that DFT based approaches are needed to properly model and design novel nanoscale devices.

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Magnetic and Structural anisotropy of Cobalt thin films intercalated under Graphene

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Type of Contribution: Oral

Ultra-high density magnetic memory devices can be developed from Cobalt (Co) thin films.
Co films below 8MLs have extremely small magnetic domains and particularly high perpendicular magnetic anisotropy: these two features allow one to achieve an easy data storage despite the small size of the magnetic bits.
Such thin films are highly reactive from the chemical point of view and would not resist to ambient pressure without oxidizing. Nevertheless, a safe air exposure is possible if Graphene (Gr) is used as a capping layer on the Co film.

Graphene can be grown on bare Iridium(111) via chemical vapor deposition and Co can be evaporated on it, resulting in a Co/Gr/Ir system. Afterwards, the use of thermal treatments of about 300^0C triggers the *intercalation*, in which Co atoms go through the Gr layer. One then ends up with a Co film sandwiched between Ir and Gr: a Gr/Co/Ir system [1].

Gr/Co/Ir systems are chemically stable and show an enhanced magnetic response whose origin can be linked to the Gr presence [2] or to the Co-Gr coupling [3]. However, in our first investigations we proved that thermal treatments result also into an intermixing process at the Co-Ir interface [4]. This phenomenon gives rise to a Co-Ir alloy and affects the structural anisotropy of the film. Therefore effects on the magnetic anisotropy and, as a consequence, on the overall magnetic response of the whole system are expected.

Using complementary X-Rays techniques based on reflectivity (XRR), diffraction (XRD), and absorption (XANES and EXAFS), we were able to finely characterize the phenomena occurring at the interface. We found that the alloying process is favored by the Gr presence together with the conditions used for the intercalation process and we were able to follow the structural evolution of the system.
Once the thermal effects are fully understood, the intercalation procedure can be optimized in order to tune the magnetic easy axis (and the overall magnetic response) at wish. In other words, one becomes able to tailor the microscopic magnetic properties of the final device through the setting of macroscopic parameters such as film thickness, Gr quality, time and temperatures used for the intercalation.

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Graphene-based Platforms for Biosensing Applications

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Type of Contribution: Invited

There is an increasing demand for biosensing systems based on simple electrical/optical transducing schemes able to achieve cost efficient detection. Among the various biosensing system performance requirements the high sensitivity and selectivity of the response are crucial for applications in diagnostics. Due to the fact that the analytes to be detected in clinical, environmental or food sample are present in very low concentrations the need for biosensing systems that can detect with high sensitivity and selectivity that include very low detection limits along with high reproducibility is an important challenge. To overcome the difficulties in accomplishing all these requirements the main efforts are driven toward signal amplification and noise reduction of biosensing systems by the incorporation of nanomaterials. Since graphene exhibits innovative mechanical, electrical, thermal and optical properties this two-dimensional material is increasingly attracting attention and it is under active research. Graphene-based materials (GBMs) display advantageous characteristics to be used in biosensing platforms due to their interesting properties such as excellent capabilities for direct wiring with biomolecules, heterogeneous chemical and electronic structure, the possibility to be processed in solution and the availability to be tuned as insulator, semiconductor or semi-metal. Moreover, GBMs such as graphene oxide (GO) bears the photoluminescence property with energy transfer donor/acceptor molecules exposed in a planar surface and even can be proposed as a universal highly efficient long-range quencher, which is opening the way to several unprecedented biosensing strategies. The rational behind the use of GO and GBMs in optical and electrochemical biosensing is being studied and explored. We are developing simple, sensitive, selective and rapid biosensing platforms based on the advantageous properties of GBMs while used as electrochemical transducers or revealing agents in a variety of biosensing systems. Examples related to diagnostics applications including bacteria and other analytes (ex. contaminants) detection will be shown. The developed devices and strategies are intended to be of low cost while offering high analytical performance in screening scenarios beside other applications. Special emphasis will be given to (nano)paper/plastic-based platforms that operate in microarray or lateral flow formats with interest for various detections.

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Fragmentation of 2D materials: New strategies for structural analysis and 2D metrology

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Type of Contribution: Invited

The production of large quantities of 2D materials in solution with well-controlled morphological properties of the nanosheets is not only a technological challenge but also a fundamental one, because several scientific aspects still need to be clarified for a detailed understanding of the fragmentation mechanisms and the control of the final products. Furthermore, it is necessary to develop fast and reliable protocols to measure and analyze a large number of 2D objects and as well as to find a set of "robust" parameters to achieve an accurate multi-scale description of the system.

Here we show how these problems can be fruitful solved by using a statistical approach. In particular, the study of the distribution of the morphological parameters represents the key-factor i) to understand the physical mechanisms of the fragmentation in liquid, ii) to test the theoretical models and iii) to explore the mechanical and the structural properties of both the starting material and the final fragments.1 Recently, we developed a fast and automatic procedure based on topographic images to measure, one by one, the exact shape and size of thousands of nanosheets obtained by exfoliation and fragmentation in general.2 Here we monitored the time evolution of the area and the shape distribution of 2D single sheets of graphene oxide (GO) in water during extended sonication treatment. Combining the analysis of images acquired with different microscopies, we monitored the 2D fragments from the millimeter to the nanometer scale. In particular, we showed that the quantitative analysis provides to measure the mechanical properties of the GO sheet such as the fracture strength. Moreover, the analysis of the fragment distributions gives detailed information on the dynamics of the 2D fragmentation providing direct evidence of different regimes given by the interplay of two breaking mechanisms, such as core fragmentation and peripheral erosion. Finally, based on the high-skewed size-distribution of the GO sheets, we propose a new approach to parametrize the polydispersity of the 2D materials. The capability to monitor and to control the morphological and the mechanical properties at nanoscale of large quantities of 2D materials in solution will pave the way towards using these materials as fillers for industrial-scale production of graphene- and 2D-based composites.

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Tuesday 24th

Raman Spectroscopy of Graphene and Related Materials

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Type of Contribution: Keynote

Raman Spectroscopy is the most used technique to probe the properties of graphene. In this talk I will give an overview on how to use this technique to characterize graphene, in particular with focus on liquid-phase exfoliated (LPE) graphene [1]. I will show a simple protocol that allowed us to characterize LPE graphene produced in several ways [2-5]. The same protocol has been used to characterize graphene composite membranes, obtained by mixing graphene with polymers of intrinsic micro-porosity (PIMs) [6].

In the last part of the talk I will show that Raman spectroscopy is also a powerful technique for investigation of ultra-narrow and atomically perfect graphene nanoribbons [7-9].

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Kinetics Mechanisms of Large-Area Single-Crystal Graphene Growth

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Type of Contribution: Invited

In this talk I discuss the effects of the nucleation density on the growth kinetics and quality of graphene. We use a two-step approach that combines some already tested methods with novel methods for suppressing nucleation to show that reducing the nucleation density alters the growth regime from nucleation dominated to islands growth dominated mode. The shift of the growth regime has profound consequences not just for the number of the graphene islands (domains) that form, but also for the size and the crystallinity of graphene. Because it involves multiple sites that each grow as separate single crystal domains, the nucleation dominated regime is accompanied by grain boundary formation when these islands eventually coalescence. In contrast, since the island growth regime starts and propagates from ideally one single isolated nucleation site, it is intrinsically a large area growth mode that produces single-crystal graphene.

In practice, large area graphene growth by suppressing nucleation is subject to conflicting fundamental requirements. Suppressing the nucleation density requires reducing the carbon species concentration, the consequence of which is that the lateral growth rate becomes impractically low. In the first step we reduce the nucleation density by two orders of magnitude using pre-treatment of commercial Cu foils by oxidation at different temperatures and reducing them in H_2 flow immediately prior to growth. An additional order of magnitude of nucleation density reduction is achieved by transient reactant cooling using a brief Ar pulse at the onset of growth. Transient reactor cooling works by collisional deactivation of carbon growth species to control the carbon incorporation process directly. It is different from just changing the growth temperature, which affects both the nucleation and the growth stages equally. Instead, we use a transient process to target only the nucleation stage. Using these growth conditions single crystal graphene islands of 1.5 mm linear dimensions were demonstrated. Finally, we use a kinetic model to show that graphene growth at vanishingly low nucleation density doesn't just mean very few islands. A scientifically more intriguing effect is a different growth mode that appears to occur by a cooperative process that intrinsically produces single-crystal graphene. I discuss several molecular pictures for a cooperative growth process that are consistent with the experimental data and the kinetic model. The kinetic model is described in terms of the impingement rate of CH_4 molecules and the sticking coefficients for two competing steps, random nucleation (s_0) and lateral island growth (s_1). The growth curves have a sigmoidal (S-shape) form characteristic of cooperative processes for the island growth dominated mode that occurs for $s_1 >> s_0$ and change to a simple exponential form for the nucleation dominated mode $s_0 >> s_1$. The significance of the kinetic model is that the quality of the graphene can be predicted simply from the shape of the growth curves.

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Progress in properties control and application trends of large area graphene on SiC

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Type of Contribution: Invited

Graphene can be formed on silicon carbide (SiC) substrates by thermal decomposition during which silicon leaves due to sublimation, while carbon resides on the substrate in an ordered manner. It has been shown that it grows epitaxially on the Si- face of (0001) oriented SiC substrates. One carbon atom thick honeycomb structure of the crystal lattice, similarly to free standing graphene, provides an energy band structure of linear dispersion resulting in peculiar physical properties and shows the finger print of graphene (2D peak) in Raman spectra. Formation mechanism is a top down transformation in which every next carbon monolayer is completed in a reversed growth mode under the previous one. The first step is surface reconstruction of SiC providing a template (buffer layer) for epitaxial growth on the Si-face terminated substrate. C-terminated face has different growth mechanism of which better understanding is needed. Due to the peculiar deposition mechanism and the difference in the faces, the topology of the films is different which implies different physical properties of the films obtained even at similar fabrication conditions. Here we are going to discuss the main consequences of the topological diversity and ways to control the process of uniform material formation, in particular on a large area. The role of the surface reconstructed C-rich layer as a precursor of graphene and its effect on graphene properties will be enlighten. Depending on the buffer layer integrity the subsequently formed graphene may contain defects. The impact of the buffer layer on the graphene thickness evolution of larger area SiC substrates, e.g. diameter of 100 mm is in focus. We will address formation of bilayer inclusions on Si-face grown graphene and their influence on the electronic properties and sensitivity to ambient conditions. Our recent results encompass an improved graphene thickness uniformity with a bilayer occurrence down to 1% over a substrate area of 15x15mm2. This will have a significance concerning different applications, as well as understanding adsorption of functional groups at exposure to atmosphere. The latter effect has been studied in detail and the most interesting results will be communicated. Graphene as a substrate for Van der Waals epitaxy will be discussed and examples of new material systems will be show.
Finally, conclusions reflecting the current progress of the material development and a brief outlook will be given.

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Development of a technology platform for wafer-scale fabrication of graphene devices

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Type of Contribution: Invited

Graphene is considered for a variety of applications in a large number of sectors, among them in microelectronics [1, 2]. In microelectronics, techniques enabling commercial large scale fabrication of devices are not yet in place and further progress towards wafer-scale processing is required. Development of a wafer-scale Si technology-compatible graphene synthesis method and a toolbox of processes dedicated to handling/cleaning/patterning as well as integration of graphene with semiconductors, insulators, and metals is viewed as a prerequisite to practical applications of this material in electronic and photonic devices [3]. In this talk, we will outline how these challenges are addressed to enable fabrication of graphene devices in a 200 mm Si wafer pilot line at IHP.

In particular, we will discuss available options for selective and non-selective graphene growth on 200 mm Si wafers pointing out opportunities and challenges associated with the chemical vapor deposition on Cu and Ge surfaces as well as the Ni-assisted growth. Furthermore, we will describe the efforts devoted to developing methods which enable conformal coverage of graphene with thin layers of semiconductors and insulators without compromising electrical characteristics of the underlying graphene sheet. Finally, the importance of a wafer-scale high-throughput metrology toolbox providing information on graphene characteristics during deposition and their evolution upon further processing will be discussed.

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Molecular beam epitaxy of single to few layer graphene on SiC, growth and electronic properties

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Type of Contribution: Invited

The elaboration by molecular beam epitaxy (MBE) of 2D materials such as graphene does not obey the same rules as 'standard' MBE of 3D materials (e.g. III-V compounds). One main reason stands in the weaker coupling/interaction between the growing 2D material and the substrate, compared to the 3D case. This turns as an advantage, because it releases the constraint of lattice-mismatch with the substrate. On the other hand, the weak coupling can turn into a strong disadvantage, because the substrate no longer imposes its crystallographic orientation to the 2D film. So, nucleation may occur along randomly oriented directions, resulting in the growth of polycrystalline materials with numerous grain boundaries (nanocrystalline material).

SiC, a polar material used as substrate for the MBE growth of graphene, provides a good example of the role of the coupling on the graphene characteristics, since the graphene structure is face-dependent. Indeed, the coupling is much weaker on the (000-1) C-face than on the (0001) Si-face. Twist disorder is found in the former case, while an epitaxial relationship is observed in the latter. The purpose of this talk is to detail the graphene MBE growth conditions and their optimization, and to present the resulting properties, structural as well as electronic, with emphasis on the valence band structure studies close to the Dirac point. Although the face-dependent graphene structure is very similar to what is observed after the more standard process of SiC graphitisation (high temperature anneal), it is noticeable that MBE allows a much easier control of the graphene thickness than graphitisation, at least for the (000-1) SiC case.

CVD growth of Graphene on Ge(100): a characterization route of the "as grown" system

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Type of Contribution: Oral

The direct growth of graphene on CMOS compatible substrates represents a gamechanging breakthrough [1]. Germanium is an ideal candidate: it is a semi-metal, it does not form a stable carbide and large-area single-crystal Ge surfaces on Si wafers are becoming routinely available.

Here we present a systematic study of the CVD growth of graphene on Ge(100) substrates. The samples were grown in a Aixtron Black Magic CVD system using H_2 and CH_4 as precursor gases and Ar as a carrier gas. The growth process was investigated as a function of temperature T, H_2/CH_4 flux ratio R, growth time, background pressure. We found a very narrow window of temperatures suitable for the deposition of good quality graphene ranging between 925°C and the melting temperature of Ge. A proper multi-step ramp in temperature was adopted in order to avoid surface damages such as corrugation and pits. The resulting surface is suitable for a large area deposition of graphene and allows for graphene growth at T=935°C, only a few degree Celsius below the Ge melting point.

Raman spectroscopy and XPS were used to study the graphene quality, domain size and coverage of the grown structures. SEM and AFM microscopy were used for morphological investigations of both graphene films and germanium substrates. Conductive-AFM measurements were carried out in order to investigate the correlation between morphological features and sample local electric conductance.

The joint use of these techniques allowed for a full characterization of the as grown graphene samples without the need of a transfer process on alternative suitable substrates. This characterization route enables the follow: the Ge surface nano-faceting induced by the presence of CH_4 at high temperature and the development of a graphene layer on the Ge nano-faceted surface as a function of the growth parameters.

We were able to deposit a uniform monolayer graphene having size domains larger than 500 nm by using a flux ratio R=100 and T=935°C. For lower values of R we found a multilayer structure with isolated domains of few-layer graphene deposited on a conformal monolayer film.

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Transfer of CVD-grown graphene for room temperature gas sensors

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Type of Contribution: Oral

It is very well known that graphene is a promising material for the fabrication of ultrasensitive and ultrafast electronic sensors due to its large specific surface area, low electrical noise associated with its unique high crystalline single-atom thick two-dimensional structure, and exceptionally high carrier mobility (2×10^5 $cm^2V^{-1}cm^{-1}$) at room temperature (RT). Thanks to all these exciting properties, graphene and graphene-based hybrid systems have attracted great interest for a wide range of applications. Chemoresistive gas sensing is one of them [1,2]. The possibility to operate at RT is one of the main advantages of using graphene as active material for gas sensing, instead of the usual metal oxides based devices which require high operating temperatures.

In this study, a CVD-grown graphene on Cu foil has been transferred on a pre-patterned SiO_2 substrate to fabricate room temperature gas sensor devices. The quality of the graphene layer after the transfer procedure has been verified by Raman spectroscopy.

We have studied the RT sensing behavior of these devices in the presence of oxidizing and reducing target gases (NO_2 and NH_3, respectively) in various relative humidity environments, under both the illumination of 254 nm UV light and in dark conditions. A p-type response is observed, i.e. electron acceptors such as NO_2 and electron donors such as NH_3 can be differentiated by observing their effects on the conductivity. Electron acceptors increase the hole concentration, which leads to a conductivity increase, whereas electron donors increase the electron concentration, leading to a decrease of the conductivity. Response to UV light has been studied both in air and in inert atmosphere, showing that the main effect of UV is to remove the oxygen species adsorbed on top of the graphene layer. During gas exposures, UV light allows to improve the relative response to gases and the recovery of the signal after gas exposure, which is not possible at RT.

A very easy transfer procedure to obtain graphene-based gas sensing devices operating at room temperature is presented. The device responses to ammonia and nitrogen dioxide are shown, at different values of relative humidity, in dark and under UV illumination.

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Direct Observation of CVD Graphene Growth and Related Surface Dynamics of Active Metal Catalysts by In-situ Scanning Electron Microscopy

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Type of Contribution: Oral

During the last three years, we have modified the set-up of a conventional scanning electron microscope in order to enable the observation of catalyst surface dynamics under controlled atmosphere and temperature. Using this instrument, we investigate chemical vapor deposition (CVD) growth of graphene on different metal catalysts. Since the experiments are performed in the chamber of a microscope, it is possible to observe a complete CVD process from substrate annealing through graphene nucleation and growth and, finally, substrate cooling in real time at nanometer-scale resolution without the need of sample transfer. The nucleation and growth of single layer graphene can be investigated at temperatures of up to 1000°C, while at the same time, surface dynamics of the active metal catalyst can be imaged and directly related to the catalytic activity.[1] Due to the high sensitivity of the secondary electron signal to changes in the work function and charge transfer at the surface, we are able to visualize different degrees of graphene-substrate coupling [2] as well as the stacking sequence of few layer graphene.

The observations highlight the dynamic nature of catalysts and reveal the sensitive response of the surface to changes in the chemical potential of the gas phase. Grain orientation dependent growth dynamics and catalytic activity can directly be visualized and investigated. In-situ scanning electron microscopy furthermore covers the spatial resolution of complementary in-situ techniques that provide spectroscopic information, such as ambient pressure X-ray and Raman spectroscopy. It completes the spectroscopic data with visual information and spatially resolved chemical dynamics.

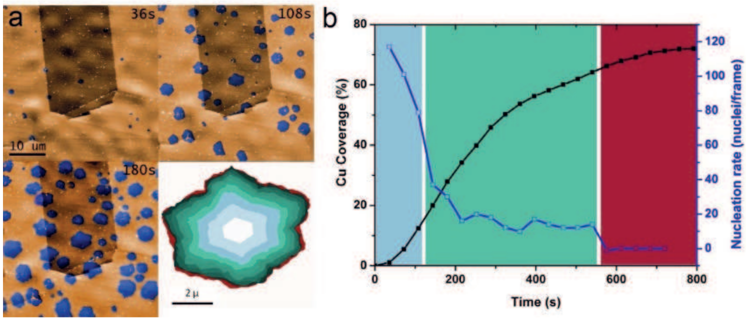

Figure 1: a) shows colorized snapshots taken during low-pressure CVD growth of graphene on copper at 1000°C. The growth and nucleation behaviour can directly be abstracted from the recorded images as shown in b).

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The stacking sequence of graphene revealed by *in-situ* SEM observation of CVD growth and hydrogen etching

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Type of Contribution: Oral

The recognition that the addition of each new layer of graphene modifies the electronic structure and produces a different material with unique properties has generated great interest in the preparation of few layer graphene. However, controlled growth of large-area FLG is a difficult challenge because of incomplete understanding of adlayer graphene growth and the mechanisms of layer stacking. Here we demonstrate that real-time imaging by *in-situ* scanning electron microscopy (SEM) enables the investigation of the growth behavior of adlayer graphene on platinum under controlled atmosphere. Imaging during growth and etching allows to unravel the link between mechanistic details and growth kinetics[1] and to distinguish between graphene layers that are inserted underneath or forming on top of the initial layer. The observation of layer dependent etching rates facilitates the determination of the relative strength of the graphene-graphene and graphene-substrate interaction. Anisotropic etching rates extracted from evolution of the shape of islands and vacancy islands (holes) indicate a strong interaction of graphene edges with the Pt step edges. Using STM imaging and DFT calculations we confirm a strong coupling between the edge atoms of graphene sheets with the Pt substrate.

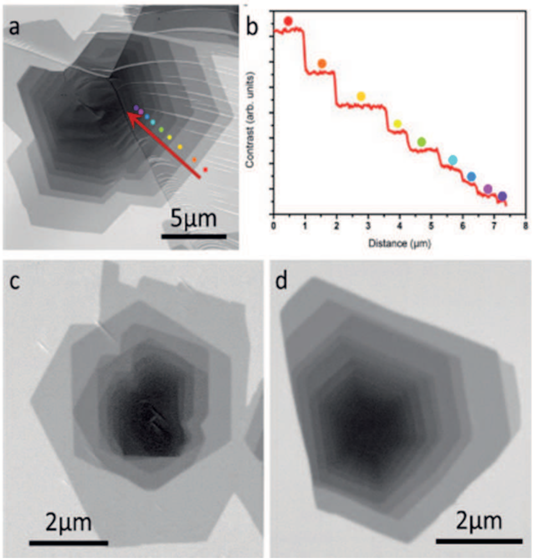

Figure 1 | Real-time images recorded during *in-situ* growth in the SEM. a, b, The SEM image (**a**) and the corresponding plot (**b**) show that up to 9 layers can be distinguished within the contrast range. The different colored dots along the arrow designate the location and corresponding layer number. Note that the lightest shade marked by a red dot corresponds to Pt covered by SLG. **c,** Vertical layer stacking showing a 30° rotation between successive layers. **d,** Hexagonal shape distorted by interaction with the Pt surface in ABA stacked FLG.

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Nitrogen doped twisted graphene grown by atmospheric pressure chemical vapor deposition

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Type of Contribution: Oral

We demonstrate experimental evidences of the possibility to grow high degree of homogeneity of twisted graphene synthesized by atmospheric pressure chemical vapor deposition from decane precursor and in-situ nitrogen doping of grown films. Temperature of synthesis was 1050 ºC, the carrier gas consisted of mixture of H_2 and N_2 gases. The rate of N_2 gas flow was kept constant, 100 cm^3/min, while the rate of H_2 gas flow was 60 (sample A) and 6 (sample B) cm^3/min. Samples were deposited onto copper foil and then transferred to SiO_2/Si substrate. No polymer was utilized during the transfer procedure. Sample A demonstrates optically high degree of in-homogeneity, whereas sample B remains optically uniform over large scale. Samples were analyzed by micro-Raman and X-ray photoelectron spectroscopies. For Raman spectra we used two excitation wavelengths, 473 and 532 nm. Values of 2D positions, G positions and FWHM 2D evaluated from Raman mapping demonstrate non-monotonic distribution, with two prominent maxima. Detailed analysis of values distribution for sample B allowed associating each maximum to single layer graphene (SLG) or double layer graphene fractions of the film. The blue shift of G and 2D band positions for SLG fraction of the films together with the fact of using of N_2 as a carrier gas gives the possibility to suppose the nitrogen doping of grown graphene. This was proved directly by the XPS study, discovered the graphitic configuration of incorporated nitrogen. Moreover, we observed decreasing of nitrogen concentration from 1% (sample A) to 0.4% (sample B). In its turns, the positions, FWHM and intensity distribution of the 2D band corresponding to the double layer fraction of sample B prove its turobostratic (twisted) structure. Moreover, the elaboration of the Raman spectra revealed for both excitation wavelengths the presence of graphene spots where the intensity of the G band is about 10 times larger (G-resonance) compare to the single layer graphene G band intensity. The observation of the G-resonance directly confirms the twisted nature of graphene grown with the lowest hydrogen feeding rate. Finally, we performed the measurements of transmission coefficient of light in the 400-1000 nm range for sample B to prove its homogeneity. It was obtained that at the wavelength of 550 nm the transmission coefficient is equal to 94%, which corresponds to 2-3 graphene layers.

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Raman Studies of Strain-Engineered Graphene Grown on Boron Nitride by Molecular Beam Epitaxy

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Type of Contribution: Oral

We have grown graphene by molecular beam epitaxy (MBE) on hexagonal boron nitride (h-BN) flakes which are exfoliated from high-temperature high-pressure grown bulk h-BN crystals and mounted on a sapphire substrate. Carbon is evaporated from a heated graphitic filament and the substrate temperature during growth is extremely high for MBE; we estimate ~ 1500 ºC. The graphene forms continuous domains with dimensions of order 15 μm, and exhibits moiré patterns with large periodicities, up to ~30 nm, indicating that the layers are highly strained. Topological defects in the moiré patterns are observed and attributed to the relaxation of graphene islands which nucleate at different sites and subsequently coalesce. In addition, cracks are formed leading to strain relaxation, highly anisotropic strain fields, and abrupt boundaries between regions with different moiré periods. These cracks can also be formed by modification of the layers with a local probe resulting in the contraction and physical displacement of graphene layers. In the Raman spectra of regions with a large moiré period we observe red-shifted G and 2D peaks confirming the presence of strain. This red shifted is shown to correlate with the strain in the graphene sheet. Furthermore, the 2D peak splits into several components; for instance the 2D region of a Raman spectrum recorded in a graphene region with a moiré pattern periodicity of 26.3 nm may be deconvoluted into three peaks. These consist of a high energy peak at 2682 cm^{-1} and two red-shifted peaks at 2583 and 2527 cm^{-1}. The higher energy peak arrises from the presence of graphitic carbon agregates on the surface of the h-BN/graphene heterostructure, whilst the spliting of the two red shifted peaks are speculated to arrise from the complex interactions between the graphene and the h-BN substrate. Our work demonstrates a new approach to the growth of epitaxial graphene and a means of generating and modifying strain in graphene.

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Synthesis and Applications of 2-Dimensional Layered Materials

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Type of Contribution: Keynote

Two-dimensional transition metal dichalcogenides (TMDs) have moved to the foreground of the research community owing to their fascinating properties which make them of great interest for both fundamental studies and emerging applications. Thermally assisted conversion (TAC) of predeposited transition metal films and Chemical vapour deposition (CVD) show great promise for the scalable and industry-compatible synthesis of these materials[1]. Here we outline the production of an assortment of TMDs, including period 6 and 10 metals, by TAC and CVD. [2] We demonstrate their high-quality using an array of characterization techniques including Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy.

The potential of TMDs films for various applications in the realm of electronics and sensing will be discussed. In particular, how chemically to modify and functionalise 2D materials on chip will be presented. It is possible to structure and electrically address the films yielding simple devices such as transistors, diodes and sensors. The fabrication of high-performance gas sensors, with room temperature detection limits in the ppb range for NH_3 will be described in detail[3]. The fabrication of large-scale heterojunction diodes, formed by transferring TMDs onto Si-substrates, will be outlined. [4]

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Nanostructured graphene for terahertz technology

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Type of Contribution: Invited

Atomically thin materials are naturally suited to create quantum confinement in two, one and zero dimensions. This certainly leads to interesting physics, but can it actually be used for practical applications?

Here we show that graphene quantum dots are extremely sensitive, low-noise light detectors in a frequency range that has great promise for applications in many fields, but is technologically still at its infancy, the terahertz range.

Light absorption in graphene causes a large increase in electron temperature due to the small electronic heat capacity and the weak electron-phonon coupling, making it an ideal material for hot-electron bolometers. However, the electrical resistance of graphene does not vary strongly with temperature, thereby limiting the bolometer responsivity.

Nanostructuring greatly increases the temperature dependence of the electrical resistance, due to quantum confinement. We study graphene quantum dots patterned from epitaxial graphene on SiC and we measure their response to terahertz radiation as a function of dot diameter, from 30 nm to 700 nm, and temperature, from 2.4K to 80 K. Our dots show an extraordinarily high variation of resistance with temperature (higher than 430 $\text{M}\Omega\ \text{K}^{-1}$ below 6 K for the smallest dots), leading to responsivities five orders of magnitude higher than other types of graphene hot-electron bolometers.

The surface of SiC shows steps between adjacent crystallographic planes. We study how these steps affect the temperature dependence the graphene quantum dots and their terahertz response.

The graphene quantum dot bolometers show extremely low electrical noise-equivalent power, placing their overall performance well above commercial cooled bolometers. The design scalability also makes them suitable for detector arrays.

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Ballistic Josephson junctions in edge-contacted graphene

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Type of Contribution: Invited

Hybrid graphene–superconductor devices have attracted much attention since the early days of graphene research. Until recently, studies have been limited to the case of diffusive transport through graphene with poorly defined and modest quality graphene/superconductor interfaces, usually combined with small critical magnetic fields of the superconducting electrodes. We discuss a technology to create graphene-based Josephson junctions (JJs) with edge contacts of molybdenum rhenium. The contacts exhibit a well-defined, transparent interface to the graphene, have a critical magnetic field of 8 T at 4 K, and the graphene has a high quality due to its encapsulation in hexagonal boron nitride. This allows us to study and exploit graphene Josephson junctions in a new regime, characterized by ballistic transport. We find that the critical current oscillates with the carrier density due to phase-coherent interference of the electrons and holes that carry the supercurrent caused by the formation of a Fabry–Pérot cavity. Furthermore, relatively large supercurrents are observed over long distances of up to 1.5 μm. We also show that two such graphene JJs can be used to form a superconducting quantum interference device (SQUID). The ability to individually tune the critical currents of the two JJs allows us to create a highly asymmetric SQUID, which reveals information about the current-phase relation in these graphene JJs.

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Edge reconstruction in Graphene and other two-dimensional systems

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Type of Contribution: Invited

The edge structure of two dimensional systems is usually studied with sharp boundary conditions. However, the confining potential in physical systems is expected to be smooth. It is shown that such a smooth confining potential may lead to edge reconstruction and formation of additional edge states. This is demonstrated explicitly for the case of integer and fractional quantum Hall systems, and bi-layer graphene in strong magnetic field. Moreover, the effect is also manifested in two-dimensional topological insulators (TIs), electronic materials that have a bulk band gap like an ordinary insulator but, due to the combination of spin-orbit interactions and time-reversal symmetry (TRS), have protected conducting states on their edges. These edge states are quasi one-dimensional helical edge modes that are expected to come in counter-propagating pairs, due to the time-reversal symmetry. The time-reversal protection of these edge states led to various suggested applications of TIs, ranging from spintronics to quantum computation. Here edge reconstruction leads to spontaneous TRS breaking, a finite Hall resistance at zero magnetic field and possible spin current. Such spontaneous TRS breaking may have important implications on transport properties, as we demonstrate below, and possible applications.

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Fundamental properties and some applications of Graphene Oxide

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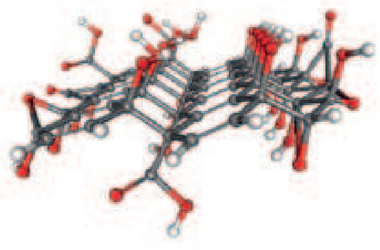
Type of Contribution: Invited



Graphene oxide (GO), the oxidized form of graphene, is a well-known two-dimensional material resulting from the chemical exfoliation of graphite [1]. Initially proposed as a low cost precursor of graphene with potentialities for mass production, GO has gained specific increasing importance among Graphene related two-dimensional materials thanks to its reduction tunable physical/chemical properties. In this paper we review our studies on fundamental properties and potential applications of GO [1-8]. Our GO (prepared via a modified Hummers method with ~ 30 μm average flakes size) has been systematically studied as a function of thermal reduction in ultra high vacuum by X-ray photoemission spectroscopy and Raman spectroscopy. Its reduction degree (sp2 content) has been correlated to its optical contrast on Al2O3 [2] to its wetting properties by means of contact angle measurements [3], and to its surface potential landscape (by means of Kelvin Force Probe Microscopy) [4]. The GO reduction process has been also investigated by exposing GO to extreme-ultraviolet (EUV) light in the 1 – 60 nm wavelength range. Our results demonstrate direct (non thermally assisted) photo reduction of GO [5]. Furthermore, the viability of EUV photolithography has been demonstrated with X-ray Interference Lithography [5]. Once applications come into play we survey a set of studies on: the gas sensing properties of this material [6], its interaction with living matter in view of applications in nano-biology [7], and the fabrication for advanced catalysis of novel organic inorganic nano-composites based on GO and self assembled protein materials [8].

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Formation of Self-Assembled Graphene/Graphene Oxide memristors through the photocatalytic oxidation

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Type of Contribution: Oral

Graphene-based structures have a great potential for high-performance electronics due to its fascinating electrical, thermal and mechanical properties. However, lack of the band gap required for logical operations complicates to use graphene (G) in digital electronics. Graphene oxidation allows to control the band gap from 0 to 4 eV [1]. The two-electrode nonvolatile resistive memory based on Al/graphene oxide (GO)/Al has been previously demonstrated [2].

Here we report the formation of self-assembled G/GO nanoheterojunctions with resistive switching through the simple and ‘green’ photocatalytic oxidation of graphene with ZnO nanoparticles (NPs). ZnO nanocrystals were used to generate charge carriers under UV-irradiation to split the water molecules of a humid environment for local nanoscale graphene oxidation. The formation of G/GO heterojunctions has been confirmed by Raman and electrical measurements. After photocatalytic oxidation the ratio of I_G/I_D in Raman spectra of the samples decreases by 6 times and the D’-peak appears separately that indicates the oxidation of graphene. The I-V curve of the graphene substrate before oxidation demonstrates the linear behavior and high conductivity. The photocatalytic process with ZnO NPs on graphene has lead to a decrease of current through the structure in two orders of magnitude and non-linear behavior that indicates the local formation of GO with a band gap. The fabricated G/GO nanostructures demonstrated the switching of resistance under an electric field with the about 10 on/off ratio at room temperature (Fig. 1). These results indicate that the simple photocatalytic oxidation of graphene with ZnO NPs under UV- irradiation provides a cost effective self-assembled nanoscale memristors based on 2D G/GO heterostructures of high density on large scale substrates.

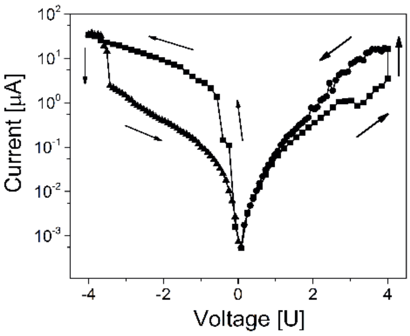

Fig. 1. Resistive switching of G/GO nanostructure.

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Laser-induced reduction of go prepared by a novel modified Hammers' method

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Type of Contribution: Oral

The Hummers' method [1] was developed in 1958 and it is the most common approach for preparing graphite oxide (GO). In order to increase reaction yield and rate, in the last years several modified Hummers' methods based on complex oxidant mixtures have been carried out. More recently, also the use of expanded graphite, characterized by a specific surface area much larger than that of natural graphite, has been proposed [2]. In this way an increase of reaction kinetic and yield can be achieved. However, the surface development can be considerably increased by disaggregating the graphite nanocrystals present in the expanded graphite by a sono-acoustic treatment. To this aim, here the use of graphite nanoplatelets (i.e. small stacks of graphene obtained by exfoliation of expanded graphite, GNP) is proposed as reactant in the Hummers' method. Indeed, the fast GNP oxidation performed by Mn_2O_7 leads to strongly oxidized GO free from unreacted graphite and/or only partially-oxidized graphite. The obtained GO has been reduced in a patterned way by a photo-induced approach based on laser treatment. In particular, a thin film of GO has been deposited on plastic substrate and a Nd:YVO_4 continuous-wave frequency-duplicated laser emitting at 532nm with a power of 20mW, was used to produce the patterned r-GO. An exhaustive characterization of GO and r-GO samples has been performed by SEM, TEM, XRD, FT-IR, and XPS. Data analysis shows that the dehydration is the main chemical reaction involved in this GO photo-reduction process.

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Selective edge functionalization of graphene layers with hydroxyl groups for the preparation of flexible conductive carbon paper

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Type of Contribution: Oral

Few layers graphene edge functionalized with hydroxyl groups (G-OH) were prepared through the reaction of KOH with a nanosized graphite with very high surface area, higher than 300 m^2/g, (HSAG) and with high shape anisotropy [1]. The reaction was performed with the help of either mechanical or thermal energy, in the absence of solvents or catalysts [2]. The insertion of hydroxyl anion is hypothesized to occur on peripheral carbon, via a two-step mechanism: (i) nucleophilic initial addition of a hydroxide ion to the aromatic ring, followed by (ii) loss of a hydride from the negatively charged intermediate.

Wide angle X-ray and Raman analyses revealed that the core of G-OH had the structure of infinite and ideal graphene layers and that the interlayer distance between the few stacked graphene layers was the same as in pristine HSAG. Hydroxyl groups were thus essentially in peripheral positions. Few layers of graphene were observed by high resolution transmission electron microscopy in G-OH aggregates.

Stable water solutions of G-OH were prepared, with concentration up to 4 mg/mL.

Electrically conductive flexible carbon papers, based on G-OH, were prepared by coating a paper support with a G-OH water solution.

This work demonstrates that carbon papers can be prepared without adopting the traditional oxidation-reduction procedure, avoiding harsh reaction conditions, dangerous and toxic reagents, solvents and catalysts and paves the way for selective modification of graphene layers, exploiting the reactivity of aromatic rings.

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Wednesday 25th

Additive Free, Single Layer Graphene in Water

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Type of Contribution: Invited

Full exfoliation of graphite to form thermodynamically stable, negatively charged, graphene (graphenide) flakes in solution can be achieved by dissolution of graphite intercalation compounds (GICs) in low boiling point aprotic organic solvents under inert atmosphere.[1,2] We now report that, under certain conditions, graphenide can be transferred to water as single layer graphene.[3] The organic solvent can then be evaporated to remain with an aqueous graphene suspension of ca 0.15 mg/ml concentration under ambient atmosphere. The Raman spectra (2.33 eV laser) collected in situ on such dispersions show bands at 1343, 1586, 1620 and 2681 cm-1 corresponding to the D, G, D' and 2D bands of graphene respectively. The 2D band at 2681 cm-1 is well fitted with a sharp lorentzian line (~28 cm-1) which is a hallmark of single layer graphene.[4] We have thus succeeded in preparing air stable, bulk suspensions of single layer graphene in water.[3,5] Upscaling towards industrial production of this graphene waters is underway.

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Tuning fluorine distribution inside graphite oxifluorides

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Type of Contribution: Oral

Graphite intercalation compounds (GICs) have been widely studied for their electrochemical applications especially in lithium batteries. Maximum of 2300 Wh/kg energy density has been achieved for primary lithium battery using fluoride-GIC as electrode materials. However, the highest capacities (1200 mAh/g) have been obtained with an oxygen-GIC.

Combined electrochemical mechanisms suggest that oxifluorides are efficient electrode materials. The possible synthesis pathways to get oxifluorides are numerous because of the various oxidation and fluorination ways (Hummers, Staudenmaier, Brodie oxidations, liquid fluorination by HF, solid-gas fluorination by HF or/and F_2…). Moreover, the O-C, F-C, F-O-C bonding can be modulated through the synthesis strategies and defined amount of C-OH, C-O-C, COOH, CF, CF_2, CF_3 can be managed. Those bonding and relative amounts can be quantified by cross-checking the data from several techniques of characterization: IR and Raman spectroscopies, multinuclear (^{19}F, ^{1}H, ^{13}C) solid-state NMR, XRD, TGA analysis.

Here we will present a two-step synthesis process combining Hummers oxidation followed by fluorination, and the inverse one. We will focus on two fluorination ways: direct fluorination by F_2 gas which results in a fluorine gradient into the graphite structure and fluorination by atomic fluorine favoring a homogeneous distribution into graphite.

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Molecularly defined photodetectors in $FeCl_3$-intercalated graphene

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Type of Contribution: Oral

Graphene, a single layer of carbon atoms with honeycomb structure, has emerged as an ideal platform for novel transparent and flexible electronic and opto-electronic devices. To expand its capabilities the electronic and optical properties of graphene can be further tailored by means of chemical bonding of a molecule or a chemical element to its pristine form [1, 2]. The most recent example of the potential of chemical functionalization is the intercalation with $FeCl_3$ of few-layer graphene (FLG). In this case a strong charge transfer occurs between the graphene and the intercalant layers, resulting in heavy p-doping of graphene. This gives rise to a new system which is the best known flexible and transparent conductive material, with a sheet resistance of 8Ω/□ and an optical transmittance as high as 84% [2]. Despite the presence of the highly soluble $FeCl_3$, it has been shown that $FeCl_3$-FLG can withstand to conditions of relative humidity of up to 100% for weeks, as well as temperatures of up to 150 °C in air or as high as 620 °C in vacuum [3]. Furthermore the first study of the work function of large-area (9 mm^2) $FeCl_3$-FLG grown by chemical vapor deposition on Nickel, results in values as large as 5.1eV[4], a key requirement for flexible transparent conductors in modern electronics. These findings position $FeCl_3$-FLG as a viable and attractive replacement to indium tin oxide (ITO), the main transparent conductive material currently used in electronics. In this contribution we report novel opto-electronic properties of $FeCl_3$-FLG. We show for the first time, the ability to control the arrangement of $FeCl_3$ molecules in the lattice of $FeCl_3$-FLG by direct laser writing µm-scale patterns. This gives us control of doping in $FeCl_3$-FLG resulting in controlled p-p' junctions with spatial resolution down to 0.3 µm. We find enhanced photo-response at these planar junctions in the wavelength range from UV-A to visible with at least ten times larger linear dynamical range than previously reported in graphene-based photodetectors. The photo-response of $FeCl_3$-FLG junctions is entirely dominated by the photo-electric effect without any contribution from the photo-thermoelectric effect. These findings are in stark contrast to the dominating photo-thermoelectric effect observed in low-doped graphene junctions. Our experiments pave the way to the molecular design of atomically-thin flexible opto-electronic devices ideally suited for sensing applications where high environmental stability and low footprint is required.

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Composite films based on graphene oxide and fluorographene suspensions mixture

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Type of Contribution: Oral

New perspective, composite, graphene-based dielectric layers were suggested. The layers were obtained from a mixed composite of fluorinated graphene (FG) and graphene oxide (GO) suspensions. The problem of creating insulating and thermally stable inks using graphene suspension is very important for the development of inkjet printing technology. So, the investigated mixture may be used for dielectric ink preparation and most likely become a significant step for the graphene inks technology.

Graphene oxide suspension is a rather known material for the creation of large-area films. Unfortunately, graphene oxide films are thermally unstable and begin to reduce at 100ºC. Fluorographene is more thermally stable then GO, the reducing processes begin at ~ 480°C. The difficulties of traditional fluorination methods limit the FG utilization extremely. We suggested an original method of the fluorination in aqueous solution of hydrofluoric acid [1]. One more attractive feature of the suggested fluorination process is a splitting off for initial graphene flakes and their fragmentation in finer flakes taking place during the fluorination treatment.

The interaction between GO and FG flakes affects the structural and electrical properties of the films produced from the suspension mixture. The FG influence suppresses the reduction processes for GO particles and increases thermal stability of the films. The films demonstrate excellent electrical properties for a wide range of the GO/FG ratio. The films display very low charge densities in the film and at the interface with a silicon substrate in metal-insulator-semiconductor structures (~ $(0.4\text{-}1)\mathrm{x}10^{10}$ cm^{-2}).

The films obtained from the mixture of fluorinated and oxided graphene suspensions are cheap, practically feasible and easy to produce. Low size and high degree of flakes splitting in FG allow us to use a limited volume of the FG suspension in comparison to the GO one for drastical modulation of mixed film properties. Also, the composite suspension suggests its use as a perspective substance for inkjet inks for printing nano- and microelectronic devices.

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One-step reduction of graphene oxide by a reduced Keggin-type polyoxometalate and nanocomposite formation

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Type of Contribution: Oral

Nowadays numerous applications imply the use the graphene sheets which can notably be fabricated by chemical reduction of graphene oxide (GO). This method has the advantage of bulk quantity production but the chemical species used as reducing agent, such as hydrazine, is toxic and does not prevent the aggregation of the reduced GO (rGO) sheets in suspension in the absence of stabilizer. An alternative green method for producing stable rGO has been developed using polyoxometalates (POMs) anions which have redox properties. This method is based on UV-assisted photoreduction of GO in the presence of a sacrificial reagent (isopropanol) that is oxidized while the POMs are photoreduced. Moreover POMs act as anionic stabilizer avoiding the aggregation of rGO and leading to the formation of POM@rGO nanocomposite. However, only small amount of rGO could be obtained in these conditions due to localized laser irradiation.
Therefore, we propose an alternative method based on the use of POMs electrochemically reduced, at room temperature, before their contact with the GO aqueous solution. This method is rapid, non toxic and a high amount of POM@rGO can be prepared. The nanocomposite has been characterized by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). Finally its electrochemical properties have been studied. The Keggin polyoxometalate used in this work is $H_4SiW_{12}O_{40}$ (named SiW_{12}). It is first electrochemically reduced by an electrolysis conducted under a constant potential. During the addition of the reduced POM solution, the brown-colored suspension of GO turns black rapidly indicating the formation of rGO. The black particles were characterized by Raman spectroscopy. The I_D/I_G ratio was 0.83 and 1.08 for GO and rGO, respectively. XPS analyses show a drastic decrease of all the carbon-oxygen contributions detected for the pristine GO. This analysis confirms that most of these groups are removed due to the reduction of GO by the reduced SiW_{12} anions. Moreover, W at the oxidation state +VI is detected. The presence of W was confirmed by the EDS analyses. Finally electrochemistry studies of the black particles deposited on a glassy carbon electrode evidence the redox response of SiW_{12} anions. Therefore we can conclude that they are immobilized on rGO leading to a SiW_{12}@rGO nanocomposite. This finding was confirmed by TEM observations which show the presence of 1-2 nm tungsten oxide clusters on graphene. Actually, a faradaic current, due to the redox properties of SiW_{12}, is superimposed to a high capacitive current due to rGO. Therefore the nanocomposite prepared in the present work could be used as electrode materials of electrochemical capacitors.

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Thermal and electrochemical exfoliation of fluorinated graphite

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Type of Contribution: Oral

Beside graphite oxide, others intermediates and especially graphite fluoride could be of a particular interest for the synthesis of graphene, in order to facilitate exfoliation and to reach a better control of the surface chemistry of resulting graphene. Graphite fluoride could be also a potential candidate for the synthesis of fluorinated graphene.

Here, two different approaches will be presented based on the different strategies of exfoliation, i.e., thermal or electrochemical exfoliation of graphite fluorides synthesised at high temperatures under pure fluorine gas.

In the case of fluorinated HOPG, the thermal treatment leads to the exfoliation of the material with high levels of defluorination. XPS measurements as well as temperature programmed desorption (TGA-MS) and STM measurements were performed to understand the exfoliation mechanism: a thermal treatment between 400 and 1000°C followed by XPS shows a quasi complete defluorination of the sample and a subsequent recovery of the sp^2 hybridization of the C atoms (which has been also observed by high temperature X-ray diffraction). TPD analysis highlights that defluorination occurs by the release of CF_4, C_2F_6 and heavier fluorocarbons gaseous species which could contribute to the exfoliation process. The exfoliation efficiency is also influenced by the rate of heating of the thermal treatment.

The second approach for the synthesis of graphene is based on electrochemical exfoliation and in situ reduction of graphite fluorides in aqueous electrolytes. The use of fluorinated graphite could be an interesting alternative to pure graphite, to both limit the graphene oxidation by previous surface functionalization with fluorine atoms, and weaken graphene sheets interactions in graphite.

Experimentally, we highlight that the controlled fluorination of graphite electrodes under pure F_2 gas at high temperatures and their subsequent pulsed electrochemical exfoliation in various aqueous electrolytes (H_2SO_4, Na_2SO_4 and KOH) allows few-layer graphene to be obtained according to Transmission Electron Microscopy, Atomic Force Microscopy and Raman spectroscopy data. The comparison of various fluorinated graphite precursors with different C-F types and F/C ratios (followed by ^{19}F and ^{13}C NMR) with the resulting exfoliation kinetics and the surface chemistry of the obtained graphene materials, has demonstrated that a F/C ratio of 0.3 combined with repeated exfoliation cycles at -10V/+10V (negative potentials lead to *in situ* reduction of fluorine atoms), is suitable to prepare few layer graphene with a controlled surface chemistry

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Structural and electrical properties of reduced graphene oxide foams

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Type of Contribution: Oral

The growing demand for efficient and safe methods to store and convert energy has inspired scientists to look for new materials for the next-generation electrodes. Reduced graphene oxide, obtained during the hydrothermal reduction of graphene oxide can form a three dimensional, highly porous structure and thus has shown great potential as an electrode material. The sp^2 carbon sites in the RGO materials predominantly control the electronic and transport properties. However, there is still a need to prepare the repeatable methods of RGO foams formation with the well-defined structural and electronic features.

In the following experiments, reduced graphene oxide foams were prepared using ascorbic acid as a reducing agent. The materials in a form of hydrogels with highly developed surface areas and porous microstructures were obtained. In order to adjust the required pore size, SiO_2 particles of different diameters can be used as sacrificial templates that are consequently etched from the material after reduction. Two different methods of hydrogels drying were adapted, namely the supercritical and freeze-drying methods. The drying method influences the final structure of pores and the mechanical properties of samples.

The aim of this work was to determine the structural and electrical properties of reduced graphene oxide foams. Materials (GO and RGO) were characterized using the spectroscopic methods (UV-Vis, FTIR, XPS and Raman spectroscopy). The BET surface area was measured as well as the pore size and pore volume. Both the surface and bulk properties of the materials were determined. Electrical conductivity was measured using a two-point probe method.

Reduced graphene oxide is biocompatible and shows a high electrical conductivity, therefore it can be used as a material for electrodes in enzymatic biofuel cells (EBCs). Due to the higher surface area and accessible pores, the immobilization of enzymes on such structures can be enhanced. EBCs could act as the sources of power for miniaturized implantable devices such as cardiac pacemakers or glucose micropumps.

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Graphenes as metal-free (photo)-Fenton catalysts.

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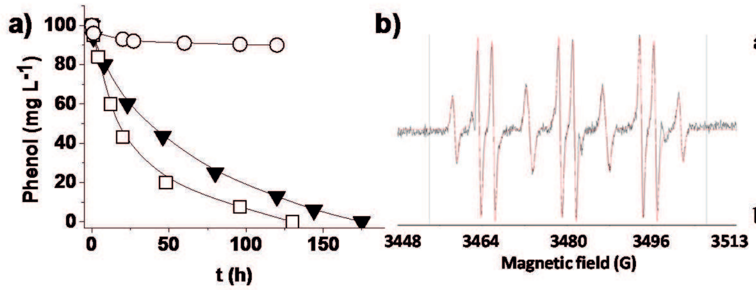
Type of Contribution: Invited

Most of the large scale industrial processes employ homogeneous or heterogeneous catalysts based on transition metals.[1] For the sake of sustainability it would be of interest to develop catalysts based on renewable feedstocks.[1] Carbon materials derived from biomass are clear examples of sustainable materials and, furthermore, they are preferred over expensive inorganic materials. Due to the easy preparation, availability and properties, graphenes (Gs) are attracting increasing interest as metal-free catalysts for oxidation, reduction, acid-base condensation and other reactions typically are carried out using noble or transition metal catalysts.[1]
Herein, we will present that Gs can be used as (photo)Fenton carbocatalysts.[2,3] The Fenton reaction is one of the most useful advanced oxidation processes for remediation of waste waters containing recalcitrant contaminants. The process consists in the generation of highly aggressive $HO^{\cdot}$ radicals by reduction of H_2O_2 with iron (II) salts: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-}$ and $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot}$. Further, UV irradiation promotes the process by photolysis of $Fe(OH)^{2+}$ species to Fe(II) and $HO^{\cdot}$ radical. The wide application of this process is, however, hampered due to: i) the need of acid pH values for an efficient process, ii) the need of iron removal after the chemical treatment with the subsequent sludge formation, iii) the need of artificial UV irradiation to reduce hydrated Fe^{3+} and iv) the occurrence of undesirable side reactions decreasing the selectivity towards HO· formation. In particular, reduced graphene oxide (rGO) is a reusable carbocatalysts that exhibits high efficiency for the selective H_2O_2 decomposition to $HO^{\cdot}$ radicals (> 82 %) achieving turnover numbers of 4,540 and 15,023 for phenol degradation and H_2O_2 decomposition, respectively. These values compare favorably with those achieved with transition metal catalysts. Interestingly, natural Sunlight irradiation assists the rGO activity and expands the pH of operation. Based on experimental data and density functional theory hydroquinone-like groups are proposed as the main active sites for the carbocatalytic process.



a) Temporal profile for phenol degradation using G (square), rGO (triangle) and GO (circle). Catalyst (200 mg L^{-1}), phenol (100 mg L^{-1}, 1.06 mM), H_2O_2 (200 mg L^{-1}; 5.06 mM), pH 3, 20 ºC
b) Experimental and simulated electron paramagnetic resonance of the adduct PBN-OH

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Graphene Oxide as Catalyst and Filler in Thermosets Resins: New Perspectives and Applications

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Type of Contribution: Oral

The synthesis, characterization and functionalization of graphite and graphene oxide allow to achieve not only useful nanomaterials but also highly efficient and eco-friendly catalysts. In particular, exfoliated and functionalized GO can be relevant as fillers of polymers and as catalysts of many different regio, diastereo and enantioselective organic reactions. Especially important is the the dual role of exfoliated GO in thermoset resins, mainly in epoxide and phenolic resins. In fact, the nanofiller not only improves physical properties but also catalyzes the crosslinking reaction, allowing completion of the curing reaction in milder conditions

The first part of the contributes will describe preparation procedures and structural characterizations of graphite oxide,[1] the use of high surface area graphite and graphene oxide both as efficient and metal free catalysts in solvent free conditions for the synthesis of important intermediate[2-4] and how this catalytic activity can be technologically relevant for polymeric matrices. In particular, the dual role of graphite oxide (GO) , as catalyst on the crosslinking reaction assuring higher crosslinking density at lower cure temperature, and as filler for the nanocomposite in epoxy resin[4] and phenolic thermosets, will be described.

The second part of the contribution will be devoted to polyester resins with particular attention to the GO ability to promote the polymerisation reaction of polyester prepolymers and to be a filler for the final thermoset resin. The chemical functionalization of GO during the polymerisation assures a better dispersion reducing the filler aggregation possible observed for graphite-based fillers. A new green GO functionalization to improve dispersion and solubility in polymer matrices will be also described.

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Laser-induced graphene: a versatile material for the fabrication of flexible electrochemical supercapacitors

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Type of Contribution: Oral

Graphene and graphene-like materials have been intensively studied in the field of electrochemical energy storage, and in the last three years the research focus has been broaden on new layered 2D-materials, such as MoS_2 and other transition metal dichalcogenides. Both graphene and MoS_2 have been exploited for fabrication of nanostructured electrodes, since they represent ideal candidates for electrochemical supercapacitors (SCs). Depending on the employed active material, two different charge storage mechanisms can be obtained in SCs. Carbon-based nanomaterials provide the formation of an electrical double-layer distributed on the electrode surface and supply the so-called electrochemical double-layer supercapacitance, while metal-oxides and metal-sulfides contribute to the pseudo-capacitance, which originates from faradaic charge transfer mechanisms.

Recently, laser-induced graphene (LIG) has been proposed as an efficient active material for flexible supercapacitor electrodes. This material consists of a three-dimensional network of multilayer graphene obtained by a laser writing process on polymer surface during which the sp^3-carbon atoms in the polymer are photothermally converted to sp^2-carbon atoms.

Herein we are reporting a rapid one-pot synthesis of MoS_2-decorated laser induced graphene by direct writing of polyimide foils. By covering the polymer surface with a layer of MoS_2 dispersion before processing, it is possible to obtain an in-situ decoration of porous graphene network during laser writing, enabling both electric double layer and pseudo-capacitance behavior. A deep investigation of the material properties has been performed to understand the chemical-physical characteristics of the hybrid MoS_2-graphene-like material. Additionally a simple method to transfer the LIG porous layer obtained onto polyimide sheet to a transparent and elastomeric substrate (PDMS) is proposed. Symmetric supercapacitors have been assembled exploiting polymeric electrolyte and the resulting performances of the here proposed material allow to predict the enormous potentialities of these flexible energy storage devices for industrial-scale production. Moreover the elastomeric nature of the host matrix allows high deformation-tolerance of the fabricated devices that demonstrate great potential for the development of stretchable and wearable energy storage sources highly desired in applications such as artificial skin and other conformal electronic systems.

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Serinol derivatives for the preparation of few layers graphene

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Type of Contribution: Oral

Biobased *Janus* molecule was used to prepare adducts with few layers graphene. Such *Janus* molecule was 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol (serinol pyrrole, SP), a serinol derivative obtained through the reaction of 2,5-hexanedione with 2-amino-1,3-propandiol, known as serinol [1]. The reaction was performed in the absence of solvent or catalyst, with atomic efficiency of about 85%. Green methods were adopted, such as ball milling or the simple heating of the reaction mixture. SP contains the pyrrole ring, suitable for the interaction with carbon allotropes and the hydroxy groups, that can easily interact with polar surroundings and are also suitable functional groups for a variety of reactions, including stepwise polymerizations.

A high surface area nano-sized graphite (HSAG) was used as pristine graphite. X-ray diffraction and Raman analysis revealed that reaction with SP left substantially unaltered the order in the graphitic layers and the interlayer distance. Stable water solutions of HSAG-SP adducts were prepared in concentration range from 0.1 to 10 mg/mL. Few layers graphene was obtained from such solutions, as revealed by high resolution transmission electron microscopy.

Polyurethanes were prepared through the solvent free reaction of SP and 1,6-hexamethylene diisocyanate and polyethers were obtained from SP and 1,6-dibromo-hexane [2]. Oligomers of both polyurethanes and polyethers gave stable interaction with carbon allotropes, such as few layers graphene and carbon nanotubes.

This work demonstrates that is possible to introduce functional groups on graphene layers avoiding the oxidation reaction and, thus, harsh reaction conditions, dangerous and toxic reagents, solvents and catalysts. Moreover, SP allows the preparation of few layers graphene without adopting the two step oxidation-reduction process.

The mechanism for the reaction of SP with graphene layers is discussed.

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Water induced enhancement of epitaxial graphene sensitivity to NO_2

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Type of Contribution: Oral

Epitaxial graphene on silicon carbide has shown a high sensitivity to NO_2 [1]. However, the surrounding environment can strongly influence its sensing capability. Since water is naturally present in the atmosphere, understanding the effect of humidity on the gas sensitivity of epitaxial graphene is important and creates opportunities for gas sensing design. In this contribution, we show experimentally that epitaxial graphene exhibits an enhanced sensitivity for NO_2 under humidity compared to dry condition due to a decrease of the electron concentration of epitaxial graphene. Using Density Functional Theory calculations, we explain this sensitivity enhancement by a water dipole screening that reduces the energy separation between NO_2 lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). This leads to an enhancement of the charge transfer from graphene to NO_2.

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Atomic-Scale Model of Reversible Wettability Transition of Defective Graphene

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Type of Contribution: Oral

The successful isolation of freestanding layers of graphene has triggered an intense interest in the unique structural and electronic properties of this material and its potential applications in various field including nanoelectronics. The comprehension of the interaction of gas molecules including H_2O with graphene is a prerequisite for the design of reliable graphene-based devices operating in the ambient environment. Also, the possibility of water splitting is particularly attractive for hydrogen generation as a sustainable source of energy. Both experimental investigations and theoretical studies indicated that wetting of isolated graphene layers is difficult. Recent optical contact angle measurements performed on an ultraviolet (UV) irradiated graphene sample revealed, however, the reversible wettability transition between hydrophobic and hydrophilic graphene [1]. The presence of undercoordinated carbon atoms enhances the local chemical activity of graphene toward interaction with water and, ultimately, facilitates the dissociation of water molecules. The transition to hydrophilic state was proposed to be a result of dissociative adsorption of H_2O molecules into hydrogen and hydroxyl radicals at vacancy sites in graphene created by UV light. The back transition to the hydrophobic state after removing the UV source and the graphene storage in vacuum would require the H^+ and OH^- products to desorb from graphene. For a single-vacancy defect, the theoretical energy barrier against the desorption reaction was reported to be 3.76 eV.[1] The intrinsic mechanism of the reversible wettability transition phenomena remains thus unclear. Moreover, the theoretical predictions were based on electronic structure calculations in vacuum thus neglecting a possible role of a solvent on a reaction's scenario. Clearly, a systematic study with a consistent theoretical approach has the potential to shed new light on the wettability of graphene.

Here, using density functional theory we show that the H_2O monomer can dissociatively chemisorb if dangling bonds are present in graphene. Once the products are bound near the vacancy site, they serve as a nucleation centers for a water cluster formation. Importantly, the reaction barriers are lowered in the presence of another H_2O molecules. A remarkably simple mechanism of the hydrophobic to hydrophilic transition of defective graphene is proposed in terms of minimalistic two-water model.

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Chitosan, a serinol derivative and few layers graphene. From carbon paper to aerogel

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Type of Contribution: Oral

Due to their three dimensional interconnected structure, carbon based materials have attracted a lot of interest in academic and industrial fields. The network structure gives rise to unique physical properties: low density, high specific surface area and porosity, high electrical conductivity. Ultralight and/or flexible carbon papers and aerogels are among the most investigated carbon-based materials. They can be prepared combining carbon based nanostructures with biosourced materials, that are easy to obtain, nontoxic and environmental friendly.

Typical methods for the preparation of carbon-based paper or aerogel involve the oxidation of graphite or graphitic nanofillers to graphene oxide (GO). Such an approach often involves harsh reaction conditions and toxic reagents, thus counteracting the positive effects of biomass and hindering large scale development.

Aim of this work was the preparation of carbon papers and aerogels starting from stable water solutions of few layers graphene, without any oxidation reaction of the carbon allotrope, leaving thus unaltered the sp2 structure of carbon atoms.

Chitosan (CS) and serinol (2-amino-1,3-propanediol) were used as the biousorced materials. Green reaction, with high atomic efficiency, of serinol with 2,4-hexanedione led to 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol (serinol pyrrole, SP) [1]. The reaction was performed between SP and a high surface area graphite (HSAG), preparing HSAG-SP adducts.

Carbon papers and aerogels made by few layers graphene were easily obtained. HSAG-SP adducts and CS were mixed in a mortar and water solutions were obtained by adding acetic acid. Various HSAG-SP/CS ratios were explored. Simple casting or lyofilization of HSAG solutions led to carbon papers and aerogels, respectively. HRTEM and XRD analysis confirmed that such carbon materials were based on few layers graphene.

This work demonstrates that an innovative biosourced molecule, SP, makes possible to obtain monolithic carbon aerogel and flexible carbon paper directly from graphite, avoiding oxidation to graphite oxide and successive reduction.

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Thursday 26th

Evidence for superconductivity in Li-decorated monolayer graphene

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Type of Contribution: Invited

Monolayer graphene exhibits many spectacular electronic properties [1], with superconductivity being arguably the most notable exception. It was theoretically proposed that superconductivity might be induced by enhancing the electron–phonon coupling through the decoration of graphene with an alkali adatom superlattice [2]. Although experiments have shown an adatom-induced enhancement of the electron–phonon coupling [3], superconductivity has never been observed. Using angle-resolved photoemission spectroscopy (ARPES), we show that lithium deposited on graphene at low temperature strongly modifies the phonon density of states, leading to an enhancement of the electron–phonon coupling of up to $\lambda \simeq 0.58$. On part of the graphene-derived π^*-band Fermi surface, we then observe the opening of a $\Delta \simeq 0.9$-meV temperature-dependent pairing gap [4]. This result suggests for the first time, to our knowledge, that Li-decorated monolayer graphene is indeed superconducting, with $T_c \simeq 5.9$ K.

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Superconducting proximity effect in strained/disordered graphene

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Type of Contribution: Invited

In the first part of the talk a tight-binding approach based on the Chebyshev-Bogoliubovde Gennes method [1] is used to describe disordered single-layer graphene Josephson junctions [2]. Scattering by vacancies, ripples, or charged impurities is included. We present the Josephson current and investigate the nature of multiple Andreev reflections. In the presence of single-atom vacancies, we observe a strong suppression of the supercurrent, which is a consequence of strong inter-valley scattering. Although lattice deformations should not induce inter-valley scattering, we find that the supercurrent is still suppressed, which is due to the presence of pseudomagnetic barriers. For charged impurities, we consider two cases depending on whether the average doping is zero, i.e., existence of electron-hole puddles, or finite. In both cases, short-range impurities strongly affect the supercurrent, similar to the vacancies scenario.

The effect of strong pseudomagnetic fields on the proximity effect [3] is further explored in the second part of the talk. The interplay between quantum Hall states and Cooper pairs is usually hindered by the suppression of the superconducting state due to the strong magnetic fields needed to observe the quantum Hall effect. From this point of view, graphene is special since it allows the creation of strong pseudomagnetic fields due to strain. We show that in a Josephson junction made of strained graphene, Cooper pairs diffuse into the strained region. The pair correlation function is sub-lattice polarized due to the polarization of the local density of states in the zero pseudo-Landau level. We uncover two regimes: (1) one in which the cyclotron radius is larger than the junction length, in which case the supercurrent will be enhanced, and (2) the long junction regime where the supercurrent is strongly suppressed because the junction becomes an insulator. In the latter case quantized Hall states form and Andreev scattering at the normal/superconducting interface will induce skipping edge states.

Our numerical calculations have become possible due to an extension of the ChebyshevBogoliubovde Gennes [1] method to computations on video cards (GPUs).

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Gate-Tunable Proximity 2D macroscale Superconductivity in Hybrid Graphene Devices

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Type of Contribution: Invited.

Graphene turns out to offer a highly suitable platform [1,2] for addressing 2D proximity superconductivity: its surface-exposed and chemically inert 2D electron/hole gas is open for the intimate coupling to superconductors, giving rise to long range superconducting proximity effect. Meanwhile, gate-tunability of the electron mean free path opens the possibility to study the stability of the superconducting phase against quantum fluctuations. I will present a method showing how macroscopic graphene monolayers [3] which can be surface-conjugated to arrays of superconducting islands, whose inter-island distances can be patterned to be either in a diffusive [2] or in the quasi-ballistic limit of the underlying graphene 2D electron gas. Arrays can be made on a large range of geometry and density, up to the highly diluted limit with less than 5% surface coverage and few micrometers in between islands. All devices show superconducting state at low temperature with gate tunability.
In the lower temperature limit (<100 mK) , despite of the relatively long distance in between islands (up to 2µm), a supercurrent was observed among the whole graphene sheet. Interestingly, at the Dirac point, the superconducting state vanishes exponentially in gate voltage and rests in a metallic state [4]. This peculiar behaviour provide evidence for our recently developed theory, and may provide a hint to the understanding of long-standing issue of "zero-temperature" bosonic metallic state observed earlier in a many systems.

The existence of superconductivity coexisting with Quantum Hall Effect at high magnetic fields will be discussed.

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Superconductivity in Calcium-Intercalated Bilayer Graphene Detected by *in situ* Resistivity Measurements in Ultrahigh Vacuum

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Type of Contribution: Invited

Graphene is a single atomic sheet of carbon with various novel properties such as the massless electrons, the high carrier mobility, and the remarkable mechanical strength and flexibility. One property conspicuous by its absence until recently, however, is superconductivity. Many intensive efforts have been made to fabricate superconducting graphene by doping metals like in bulk graphite intercalation compounds (GICs). In a past few years, experimental progress has been made step by step. For example, potassium- and lithium- doped few layer graphene showed Meissner effect observed by *ex situ* magnetization measurements [1, 2]. Furthermore, a recent angle-resolved photoemission spectroscopy (ARPES) reported temperature-dependent energy gap opening, a sign of superconductivity in lithium-decorated monolayer graphene [3]. However, it is difficult to exclude the other origins for the gap-like feature such as a charge-density-wave by spectroscopic measurement without magnetic field. Thus it is important to clarify/confirm the emergence of superconductivity by more direct measurements such as transport measurement.

Here, we show that the zero-resistance state occurs in calcium-intercalated bilayer-graphene which directly proves the superconductivity in macroscopic scale [4]. Calcium-intercalated bilayer graphene has been studied as the most promising candidate for superconducting graphene both experimentary and theoreticaly, while it had not been accomplished because of difficulties in synthesizing high-quality samples and their high reactivity in air. We overcame this difficulty by *in situ* 4-point-probe method under ultrahigh vacuum. While the calcium-intercaleted bilayer graphene exibited the superconducting transition with T_c^{onset} of 4 K, pristine and lithium-intercalated bilayer graphene did not show superconductivity down to 0.8 K. We discuss the origin of superconductivity by comparing these experimental results with previous experiments and theoretical proposals.

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Hysteretic collapse and revival of the Josephson supercurrent in Al contacted graphene on SiC

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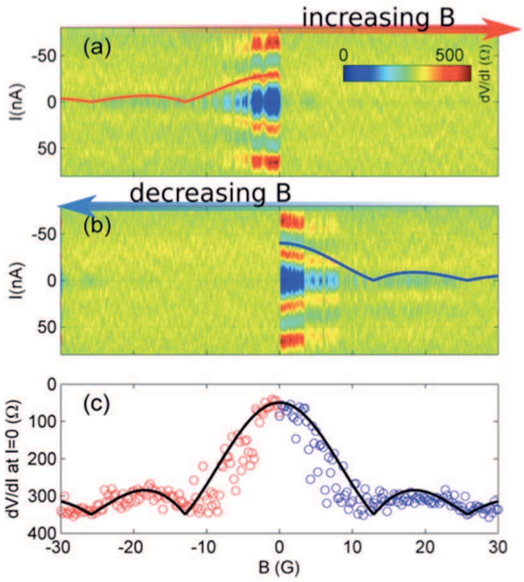
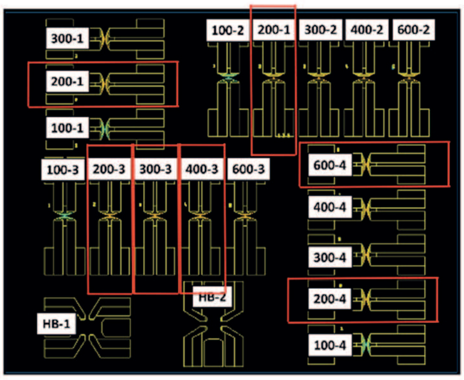
Type of Contribution: Oral

Graphene grown on SiC by Chemical Vapor Deposition (CVD) offer centimeter size monolayer areas on top of which contacts can be deposited with the desired patterning.We report on various submicrometer junctions that have been tested on the same flake with Al/Ti contacts in a planar quasi 2D junction, at low temperature in search for the Josephson effect. In samples with a graphene gap below 400 nm, we have found evidence of Josephson coherence in presence of an incipient Berezinski-Kosterlitz-Thouless transition. A remarkable hysteretic collapse and revival of the Josephson supercurrent is found when the magnetic field is cycled. Similar hystereses are found in granular systems and are usually justified within the Bean Critical State model (CSM). We show that the CSM, with appropriate account for the low dimensional geometry, can partly explain the odd features measured in these junctions.





Red rectangles indicate the measured junctions, the first number (for instance in 200-4) indicates the distance between the Al electrodes

Left: Colormaps of the differential resis- tance dV/dI(B,I) for the junction J300-3, evidencing a large hysteresis. Right: assembly of junctions on the same graphene sheet

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Effect of non-Gaussian noise sources on the distributions of switching currents in graphene Josephson junctions

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Type of Contribution: Oral

The transient dynamics of a noisy *ballistic graphene-based short Josephson junctions* (JJ) is computationally explored in the framework of the resistively and capacitively shunted junction model using the specific non-sinusoidal current-phase relation, characteristic of a JJ made by a graphene layer partially covered by the superconducting electrodes. A superconductor-graphene-superconductor system exhibits metastable states similar to those present in traditional current-biased JJs. We investigate the noise induced escapes from the metastable states, when the external bias current is ramped to retrieve the switching current distribution, i.e. the probability distribution of the passages to finite voltage as a function of the bias current, that is the information more promptly available in the experiments.

We use two different types of statistics for the noise source, i.e. Gaussian to simulate an uncorrelated ordinary thermal bath, and non-Gaussian, correlated *α-stable* (or *Lévy*) *distribution*, generally associated to non-equilibrium processes that induce abrupt jumps, called *Lévy flights*.

We analyze the switching current distribution to show how it is possible to discriminate the noise source through the analysis of the switching current distribution. To do so, we seek for the most efficient estimator to ascertain the nature (Gaussian or non-Gaussian) of the noise source. Our purpose is to pinpoint a method that, given the number of available experimental data, minimizes the false alarm probability, i.e. the probability of detecting a non-Gaussian noise when the actual source is Gaussian (and vice-versa). We finally discuss the practical consequences of the devised detection method.

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Graphene heterostructures with wide bandgap semiconductors

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Type of Contribution: Invited

Graphene (Gr) integration with wide bandgap semiconductors (WBG), such as SiC and III-N (GaN, AlN and AlGaN/GaN heterostructures) can represent the platform for a new class of electronic devices with extremely low power dissipation in the off-state and high operation frequency (up to THz) in the on-state.

Controlled graphitization of hexagonal SiC by high temperature thermal processes provides single or few layers of Gr on large area directly on a WBG. The structural properties of this system (number of Gr layers, stacking sequence, epitaxy with the substrate) crucially depend on the SiC crystal orientation, as well as on the initial surface morphology. Recent investigations on Gr grown on the SiC polar faces (0001) and (000-1), and on the low-index non-polar faces (11-20) and (1-100) will be reviewed [1-3]. A special focus will be given on the vertical current transport at the interface between epitaxial Gr and SiC (0001) and on the possibility of tailoring the contact properties from Ohmic to Schottky by hydrogen intercalation.

An overview of the different approaches recently explored to fabricate Gr heterostructures with III-N will be provided, including the Gr transfer on GaN or AlGaN/GaN [4], the direct CVD growth of Gr on AlN [5], as well as the MOCVD growth of single crystalline GaN on epitaxial Gr on SiC [6]. Among these systems, Gr/AlGaN/GaN deserve particular interest, since they offer the possibility to explore a rich physics and to evaluate new device concepts based on the Gr and AlGaN/GaN 2DEGs in close proximity. Vertical current transport across this heterostructure has been recently investigated by high spatial resolution SPM methods, revealing a high spatial uniformity and a low Schottky barrier between Gr and AlGaN [7], which can be exploited in vertical transistors applications. Finally, the design, implementation and expected performances of novel vertical device concepts based on Gr/WBG heterostructures, such as the *Graphene/SiC Schottky diode with field-effect modulation of the barrier height* and the *Gr-base hot electron transistor on GaN*, will be discussed.

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Metallic Electrode Contacts to Layered Semiconductors

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Type of Contribution: Invited

The operation of semiconductor electronic devices such as field-effect transistors is largely governed by metal/semiconductor interfaces where charge carriers (electrons or holes) are injected from the metallic electrode into the semiconductor channel. A total electric resistance of a semiconductor device is expressed by a summation of the semiconductor channel resistance and the parasitic electrode contact resistances. In a short channel device, the channel resistance is very small, and the contact resistance becomes a dominant contribution instead. The magnitude of the contact resistance is determined by a nature of the charge injection process. Therefore, a proper understanding of the metal contact is crucially important especially for highly integrated circuits consisting of billions of short channel devices. This talk will focus on metallic electrode contacts to emergent ultrathin sheets obtained from exfoliation of layered crystals. This class of materials is now regarded as a promising channel material for post-Si electronics. Specifically, transition metal dichalcogenides as a semiconductor [1] and bilayer graphene with a tunable band gap [2] will be treated in this talk.

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Direct Measurement of the Surface Energy of Graphene and Ultra-flat Transfer Method

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Type of Contribution: Oral

The surface energy of graphene is an important quantity, particularly with respect to the implementation of graphene into devices and modeling of van der Waals interactions[1]. In this contribution we will report a direct measurement of the surface energy of large area CVD graphene using a modified Surface Force Balance (SFB), employing a novel transfer method.

We have measured the surface energy of both single and few layer graphene, finding a value of ~ 0,25 J/m^2. Notably, we find no significant dependence of the surface energy on layer number. We corroborate our findings via contact angle measurements and determination of the adhesion energy between two smooth, large-area graphene sheets immersed in water and sodium cholate solution (an intercalant known for the solvo-mechanical exfoliation of graphene into graphite[2]).

The *graphene*-SFB allows us to perform multiple measurements over large working area (~ 5 mm x 5 mm). Each individual measurement probes a large graphene-graphene contact area (~ 10 µm x 10 µm). Therefore, the graphene surface is required to be extremely smooth. For this we have previously developed a novel transfer method[3]. As an extension of this work we will show how the elastic modulus and thickness of polymer supports influences the transfer efficiency of graphene over large area (cm^2).

In summary, we have developed an apparatus to directly measure the surface energy of graphene in air and different liquid environments, and present the first measurements performed using this instrument. The apparatus can also serve as model graphite electrode of precisely known contact area and we outline future prospects for application of this technique.

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h-AlN and towards van der Waals stacks of few-layer h-AlN with graphene

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Type of Contribution: Oral

Group III nitrides (AlN, GaN, InN) has been established as the dominant semiconductor material system for the development of short wavelengths light emitting diodes (LEDs) and lasers (2014 Nobel Prize in Physics). Group III nitrides naturally crystalize in the wurtzite structure with four-fold coordination of the atoms. Very recently, and for the first time an experimental evidence for "graphite-like" hexagonal AlN (h-AlN) has been reported (Appl. Phys. Lett., 2013), whereby each monolayer is represented as a regular network of AlN hexagons with sp^2-hybridization of the bonds. Graphite-like hexagonal AlN multilayers have been experimentally manifested and theoretically modeled (Phys. Rev. B, 2015). We have previously carried out modelling of a perfect single layer of h-AlN (Eur. Phys. J. B, 2012). Our theoretical study on the structural and electronic properties of single layers of h-AlN further involved the incorporation of selected point defects (e.g., vacancies, as well as substitutional atoms of silicon and carbon) providing the prospect for deliberate tailoring of its electronic properties. Aspects of the structural and electronic properties of functionalized layers of h-AlN have also been calculated, indicating its potential for carbon dioxide capture and storage (J. Phys. Chem. C, 2010), and realization of "ferromagnetic order" towards application in room-temperature spintronics (RCS Adv., 2014). The development of any functional electronics applications of h-AlN would most certainly require its integration with other layered materials, particularly graphene. In the present work, by employing vdW-corrected density functional theory (DFT) calculations, we report on the structure, interaction energy, and electronic properties of van der Waals stacking sequences of few-layer h-AlN with graphene; and find certain number-of-layer-dependent trends (R.B. dos Santos et al., Nanotechnology, 2015, submitted). The various stacking configurations involve of up to three layers of h-AlN, and up to three layers graphene. Particularly, the number of graphene layers (up to three) can be well-controlled for epitaxial graphene which is formed by high-temperature sublimation process on the Si-face of SiC and opens up an experimentally feasible approach for van der Waals epitaxy of h-AlN on graphene. First trials of MOCVD of ultrathin h-AlN on SiC-supported graphene templates will be presented aiming at ultimate control of the deposition kinetics.

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Dielectric breakdown of hexagonal Boron Nitride

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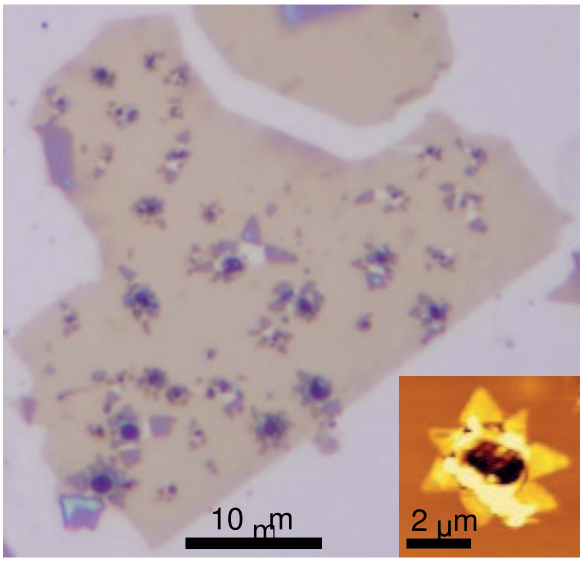
Type of Contribution: Invited

Hexagonal boron nitride (*h*-BN), an insulating layered material with a wide band gap, is widely utilized as the substrate and gate insulator to achieve high carrier mobility in layered channel materials, especially graphene. However little study has been conducted on the statistical analysis of the breakdown voltages and the breakdown mechanism. Generally the dielectric breakdown of SiO_2, conventional three-dimensional (3D) amorphous oxides is simply explained by a percolation model. It has not been determined whether the dielectric breakdowns of 2D layered materials follow the general breakdown phenomena for 3D amorphous oxides. In this study, the dielectric breakdown process of BN is investigated electrically and mechanically using conductive atomic force microscopy (C-AFM) and proposed a breakdown model for insulating layered material.



The obtained dielectric field strength is ~12 MV/cm, which is comparable to the conventional SiO_2. After the hard dielectric breakdown, BN fractured like a flower with equilateral triangle fragments. However, when applied voltage is stopped just in the middle of the dielectric breakdown, the formation of hole was clearly observed, which does not penetrate to the bottom metal electrode. Subsequent IV measurement at the hole indicates that the remaining BN layer in the hole is still electrically inactive. Based on these observation, the layer-by-layer breakdown is suggested for BN from the viewpoint of physical fracture and electrical breakdown. Moreover, the statistical analysis on breakdown voltages by Weibull plot suggests the anisotropic formation of defects. These results are unique to the layered materials, unlike the conventional 3D amorphous oxides.

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Graphene/polymer multilayers with tailored microwave shielding effectiveness

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Type of Contribution: Invited

Artificial multilayers composed of a few graphene planes separated by dielectric layers are interesting metamaterials with unique electromagnetic properties from the GHz to the infrared domains [1]. In particular, the ability these multilayers have to shield microwaves mostly by electromagnetic absorption has attracted a growing interest in the last two years [2].

After a short description of how graphene/polymer multilayers can be fabricated, the basic principles that govern their electromagnetic properties will be reviewed. A simple formulation of the reflectance and transmittance of the multilayers will be derived. Experimental measurements will be presented and analyzed on the ground of this formalism. It will be shown that the absorbance of a graphene/polymer multilayer can be optimized from 50% in free air up to 100% if the multilayer lies on a substrate with specially designed characteristics.

Tuning the conductivity of the graphene planes, *e.g.* by electrostatic doping, modifies the transmittance of the structure. This ability will be discussed and illustrated. It makes it possible to tune the electromagnetic shielding effectiveness of graphene/polymer multilayers almost at will.

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Graphene surface treatment, fabrication and characterization of metal/graphene composite materials

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Type of Contribution: Oral

Since their discovery in 2004 by Andre Geim, graphene is intensively studied. Theory predicts huge mechanical, thermal and electrical properties to graphene that makes them interesting as reinforcements in material composites. Several publications already exist on the addition of graphene into a polymer matrix showing an enhancement of physical properties. The resulting composite material possesses better mechanical, thermal and electrical properties than the pure matrix. However just a few limited studies exist in the literature concerning the use of metal-matrix due to the extreme conditions of processing for the composite. Furthermore, some difficulties are still a critical issue like the dispersion of the graphene inside the matrix and the interface resistance, *i.e.* thermal, mechanical, between the graphene and the metal-matrix. Despite that, the perspective of obtaining better properties than pure metallic matrix encourages scientists to persevere in this way.

In this present work, two different surface treatments have been performed and the evolution of the chemistry of the surface has been studied by X-Ray Photoelectron Spectroscopy and Raman Spectroscopy. Electroless deposition of metal nanodots onto the graphene surface has been performed and the surface evolution of the graphene sheets have been characterized par scanning electron spectroscopy. The dispersion of the metallic powders with the treated graphene sheets has been optimised and then the graphene + metal powder mixtures have been densified using uniaxial hot pressing. Density and physical properties of the composite materials have been measured. Finally, reproducible increases of the metal properties have been measured showing a real composite effect.

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Gas bubbles interaction with graphite based materials and graphene/PDMS composite immersed in water, thermodynamics properties and stability

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Type of Contribution: Oral

The study of the interaction of gas bubbles with surfaces immersed in liquid media is important in fundamental science as well in many applications like gas storage, self-cleaning surfaces and microfluidics. Moreover recently some authors as Lu et al [1] have provided a new insight on the importance of gasses confined in liquid media, such as the stability of air nanobubbles on graphite immersed in water. Nevertheless many aspects in this topic remain unexplored and for that reason in this work we investigated the interaction of carbon-based materials and PDMS (polydimethylsiloxane) with gas bubbles when these materials are immersed in water media. We studied the adhesion and stability of the gas (Air, Ar, He and N2) bubbles on the surface of Graphene, Graphite and PDMS. Bare PDMS membranes have been prepared by mold casting and thermal cross-linking of commercial siloxane elastomer (KiT184 Dow Corning). The graphite has been prepared by mechanical exfoliation of HOPG graphite, while monolayer graphene film has been grown by catalytic chemical vapour deposition on copper and transferred onto PDMS surface by gluing the graphene/copper foil on partially crosslinked PDMS, with thermal ending of the reticulation process and subsequent etching of copper in acidic bath. The materials surface was analyzed from the physical and chemical poin of view by X-ray photon electron spectroscopy (XPS), atomic force miscroscopy (AFM) and Raman spectroscopy . Surface wettability was studied by contact angle measurements. The adhesion and stability of the gas bubbles were determined by captive contact angle measurements. The results showed that the adhesion of the gas bubble on materials, is-related the gas polarizability that can promote in some cases also a “gasphillic” behaviour of the surface (for instance for He on HOPG). However one of the most surprising phenomenum was the instability of the PDMS surface in contact with gas bubbles. The continuous re- arrangement of the PDMS surface made the polymer acting as a “pumping system” which can double the volume of a bubble in 48 hours. This “surface-pumping” effect was absent for HOPG . This was exploited to enhance the surface stability of PDMS through applying a flake of graphene onto it. The graphene layer on PDMS- allowed to avoid the “surface-pump” effect, making the surface stable for days. This kind of composite surface, being also transparent and conductive, is of great interest for many applications.

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Is Graphene the Strongest Material?

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Type of Contribution: Oral

From experimental nanoindentation data, density functional theory (DFT) calculations, molecular dynamics (MD) simulations, a two-dimensional (2D) model of local bond-breaking, and a 2D version of the Griffith relationship of global energy balance a consistent set of 2D mechanical properties of intrinsic and defective graphene, consisting of the Young's modulus, fracture strength, fracture toughness, line (edge) energy, and critical strain energy release rate were derived. It is argued that owing to the basic 2D nature of directed covalent bonding the 2D form of the elastic and nonlinear fracture properties should be preferred to characterize intrinsic and defective 2D solids. Since monolayers are not 2D objects in the strict mathematical sense it is possible to formally estimate bulk properties, which, however, depend on the assumed layer thickness. This particular problem can be avoided if only 2D mechanical properties are considered. Despite their widespread use, bulk properties should only be employed for a formal comparison of the mechanical properties with those of better known conventional materials to get new insight into the quality of bonding of the new class of 2D solids. Since the strong chemical bonds are restricted to the plane no conventional bulk material with graphene's outstanding properties exists, as a simple comparison of graphene and graphite shows. According to this fact, graphene should be called the strongest monolayer material to avoid any misinterpretation. A formal comparison of mechanical properties is presented for graphene and diamond. It turns out that within the relatively large experimental errors involved in both cases the stiffness and strength of graphene are comparable with the outstanding properties of diamond, while its toughness is not a remarkable property due to the brittle nature at normal temperatures. This becomes clear in a comparison with steel, a material used in the literature to demonstrate the extraordinary strength of graphene. It is important to keep in mind that the knowledge of several relevant mechanical properties may be needed to meet the specific requirements of a technical application and therefore an extraordinary strength alone may not be sufficient.

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Graphene and possible aeronautical applications

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Type of Contribution: Oral

Type of Contribution: Oral

Composite materials, based on fibers such as carbon or glass, are replacing metal-based components in many applications, particularly in the aeronautics production where raw materials are obtained by means of a multilayer composite.

Graphene has extraordinary electrical and mechanical features and the properties of Reduced Graphene Oxide (rGO) can be modulated by just varying the degree of reduction of the material.

These capabilities open new perspectives in many common applications such as medicine, industry and scientific disciplines to obtain innovative technical solutions to allow to overcome the limits or drawback of actual technologies and realize new devices / systems with major performance.

Our team, that works to Finmeccanica Aeronautics, has developed some innovative solutions based on the Graphene, for De-Icing application and Non Destructive Inspection test.

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A 3D flexible micro supercapacitor based on graphene composite

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Type of Contribution: Oral

Micropower sources and small-scale energy storage units are eligible candidates to increase the performances and battery life of today's mobile devices and moreover to enable a new generation of energy autonomous systems which gain electrical power from micro harvesting or integrated solar cells. One of the components of these harvesting systems are micro-supercapacitors (MSCs), miniaturized devices, fabricated through Micro Electro Mechanical Systems (MEMS) technology, in which the active material of the electrodes provides very high specific capacitance ranging from 1 to 100 mF/cm^2.

Different kinds of carbon based nanostructured materials have been employed as electrodes in supercapacitors, such as nanotubes, reduced Graphene Oxide (rGO), onion-like carbon, among others. Besides the absence of a gold standard for the nanostructures, the carbon-based materials are the most promising electrodes for MSCs since having an extremely high active surface area, optimal control in pore dimension and distribution and low chemical reactivity, guaranteeing a huge interface for the ion to interact with the surface with fast and reversible reactions. Moreover, carbon-based materials can act as skeletons for the loading of active materials able to guarantee faradaic reaction that can further improve the energy storage capability of the electrode. Another important issue to be counted is that next MEMS generation is evolving towards polymer substrates to cut off costs and to be embedded in flexible devices.

In this work a hybrid graphene-based flexible micro-supercapacitor (MSC) exploiting a novel nano-composite material was fabricated and extensively characterized. The MSC electrodes have been obtained from a synthesized composite aerogel of Reduced Graphene Oxide (RGO) and polycrystalline nanoparticles of molybdenum (IV) oxide (MoO_2) and then dispersed in a solution containing poly(3,4-ethylenedioxythiophene) (PEDOT). Three-dimensional (3D) MCSs were fabricated through a LIGA (Lithographie, Galvanoformung, Abformung)-like process to obtain high Aspect Ratio (AR) microstructures in Polydimethylsiloxane (PDMS) replicas. A specific capacitance value of 94 F/g was obtained and 14 mF/cm2 were achieved on the device. Finally, bending test demonstrates good performance preservation in a U shape conformation of the device.

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Silver nanoparticles decorated on graphene for electrochemical applications

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Type of Contribution: Oral

Supercapacitors [1] are energy storage devices, which have attracted considerable interest over the past decade due to their applications in electric vehicles, electronic devices and electrochemical catalysis [2]. High power, quick return, long cycle life and high specific area are the mainly properties that a material has to show to be used in these fields. Metal oxide and metal nanoparticles (NPs) exhibit large surface area to volume ratios at the nanoscale and hence are excellent materials where large surface areas are required. Carbon materials (activated carbons, carbon aerogels, and nanostructures) have been widely studied as electrical double layer capacitors (EDLCs). Among them graphene is a very attractive carbon-based material thanks to its open 2D structure and amazing electronic conductivity. In particular, few papers have been published reporting metal based electrodes combined with carbon materials, despite a synergy that arise from the high redox activity or Faradaic process of the NPs, combined with the high conductivity and non-Faradaic process of graphene [3]. However, it is usually difficult to achieve uniform and homogeneous fine nanoscale coating of the graphene surface through conventional deposition techniques [4]. In this paper, we report a green and facile synthesis of very fine silver nanoparticles uniformly decorated graphene for supercapacitor application. Starting from graphite flakes, graphene has been prepared through Vitamin C reduction of graphene oxide, obtained by modified Hummers' method, further decorated with silver nanoparticles obtained by a dopamine ”in situ” mediated silver nitrate reduction process. For the characterization of both materials: Infrared spectroscopy, Raman spectroscopy, X-Ray Diffraction analysis, Transmission Electron Microscopy and TG-DTG analysis have been performed. For the electrochemical characterization, cyclic voltammetry tests have been obtained by using an Amel Potentiostat. The high value of measured specific capacitance makes silver decorated graphene really suitable to be used as supercapacitor electrode.

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Differences between graphene and graphene oxide in gelatin based systems for biodegradable energy storage applications

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Type of Contribution: Oral

Bio-based materials have recently attracted great interests for their potential use in a wide range of technical applications such as zero-waste environmental sensors, transient electronics and biomedical implants[1,2]. In this contest, Gelatin based materials are particularly interesting for the following reasons: Gelatin is an animal protein obtained by a controlled hydrolysis of the fibrous insoluble collagen present in bones and skin, which nowadays are abundant waste products of meat processing[3]. The amphiphilic nature of the gelatin can be intentionally used in order to obtain self-assembled artificial structures and bio-based meta-materials. Recently, a new biodegradable transient device based on a mixture of gelatin, water-glycerol and graphene flakes (GF) has been proposed as energy storage system[4,5]. In that case, the gelatin served as both solid electrolyte and binder for holding together the hydrophobic graphene flakes[6] with the water/glycerol molecules[7]. Also at very low concentrations of GF (0.2 wt%), the resulting dielectric properties show values of the surface capacitance of about 3 orders higher than those measured in traditional device based on activated carbon. Starting from these results, it can be expected that the hydrophilic nature of the graphite oxide (GO) in combination with its layered structure further increase the performances of these type of devices. In the present study, a biodegradable/transient device has been obtained by replacing the GF with the GO. It has been characterized by cyclic voltammetry measurements and impedance spectroscopy analysis. Results show that, despite the good dispersion achieved, the devices based on GO have a value of the surface capacitance that is about one order of magnitude smaller than the value obtained by using GF.

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Native and irradiation-induced defects in two-dimensional inorganic materials

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Type of Contribution: Invited

Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN sheets and transition metal dichalcogenides (TMD) were manufactured. Among them, TMD sheets have received particular attention, as these materials exhibit intriguing electronic and optical properties. Moreover, the properties can further be tuned by introduction of defects and impurities. In my talk, I will present the results [1] of our first-principles theoretical studies of defects (native and irradiation-induced) in inorganic 2D systems obtained in collaboration with several experimental groups. I will further discuss defect- and impurity-mediated engineering of the electronic structure of 2D materials.

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Few-layered graphene oxide embedded 1DPhC microcavity for amplified spontaneous emission source

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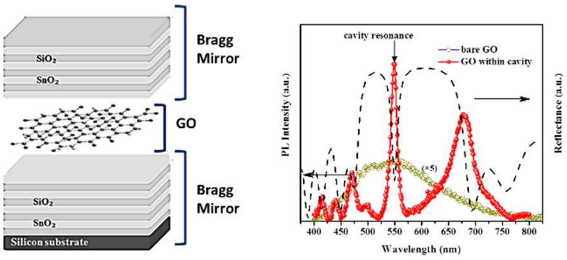
Type of Contribution: Oral

Extensive rich physical properties of graphene and its intermediate product graphene oxide (GO), make them promising candidates for photonic applications [1,2]. Optical micro-cavities can be designed by engineering structural defects in photonic crystals (PhCs) and used to control spontaneous emission from active materials [3, 4]. In this study, a novel amplified spontaneous emission (ASE) system based on GO embedded sol-gel fabricated all-dielectric one-dimensional photonic crystal (1DPhC) micro-resonator is presented**.** The schematic of the structure is shown in figure 1(a). Figure 1(b) compares the PL spectra obtained from a bare GO film on a Silicon substrate and that from GO layer inserted between two Bragg reflectors comprising of alternating layers of SiO2 and SnO2. It can be observed that the GO emissions at the micro-cavity resonance and at the band edges are extremely enhanced compared to the PL emission from the no-cavity structure and within the photonic stop-band it is completely suppressed. Continuous tuning of the a novel amplified spontaneous emission (ASE) peak by modulating the photonic stop band with the detection angle was also reported, making the GO incorporated 1DPhC a novel and attractive system for integrated optic applications.



Figures 1. (a) Schematic of the GO embedded Bragg Mirror. (b) Comparison of PL spectra of bare GO layer on a substrate and GO layer within the micro-cavity obtained under 325 nm excitation.

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Friday 27th

Pure and functionalized XBi and XBi3 (X = B, Al, Ga, In) sheets for applications as topological insulators

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Type of Contribution: Oral

By employing first-principles calculations, we predict the band structure and the stability of XBi and XBi_3 (X = B, Al, Ga, and In) buckled honeycomb sheets [1]. We obtain that the band gap values for this new class of two-dimensional materials depend on both the spinorbit coupling (SOC) and the group-III element involved. A clear effect of the including the SOC in the calculations is the lifting of the spin degeneracy of the bands at the Γ point of the Brillouin zone. The nature of the band gaps, direct or indirect, is also governed by taking into account SOC besides being dependent on the group-III element involved. In the case of XBi sheets, band inversions naturally occur for GaBi and InBi. These 2D sheets are recognized as *potential candidates for topological insulators (TI).* On the contrary, a similar type of band inversion, as obtained for the XBi, is not observed for the band structure od sheets with the alternative stoichiometry XBi_3. We conclude that only ab-initio calculations taking into account SOC, may successfully predict which of these buckled sheets exhibit sizable band gaps, thus identifying those XBi and XBi_3 sheets suitable for applications in room-temperature spintronic devices and as TIs. Furthermore, we also consider the functionalization of XBi sheets. We demonstrate that hydrogenation of XBi sheets stabilizes them and, importantly, preserves their TI properties [2]. Moreover, the hydrogenation leads to opening significant band gaps in XBi (for X = B, Al, band gaps of H-XBi exceed 1 eV) sheets making them eligible candidates for room-temperature electronic applications. We found that the nature of the band gap, direct or indirect, and the band-inversion strength (BIS) which is a measure for the topological insulating properties depend on the group III element involved as well as on the spatial configuration of the sheet and the applied strain. We identify sizable band inversions, indicating TI properties for the hydrogenated GaBi and InBi in their chair-like conformations and for hydrogenated BBi and AlBi under strain. Finally, we demonstrate that also some halogenated XBi sheets Y-XBi (X = B, Al; Y = F, Cl, Br, I) are prospective candidates for applications as TI [3]. An essential factor favoring the research exploration into Bi-containing 2D materials is the availability of Bi-precursors for various deposition techniques, including CVD, as employed for depositing BiSe, and atomic layer deposition, as employed for depositing bismuth titanate thin films.

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Oxide-interface charge carrier dynamics investigated by optical Second Harmonic Generation

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Type of Contribution: Oral

The technology for growing ultrathin oxide films or hetero-structures is nowadays approaching the same level of atomic control as in the case of semiconductors. Yet, in contrast to semiconductors, strong electron correlations lead to novel and sometimes exotic states at the interface. One of the most relevant examples of this, is the formation of a twodimensional electron gas (2DEG) at the interface between two textbook band insulators, LaAlO3 (LAO) and SrTiO3 (STO). In spite of an intense research effort, the physical origin of the 2DEG is still controversially discussed. One particular aspect was quite under-investigated so far: the interfacial charge carrier dynamics. The challenge is to merge ultrafast time-resolution and interface-only sensitivity together. Optical Second Harmonic Generation (SHG) possesses both qualities and it is thus the ideal tool for achieving this goal. The technique is based on the induction of light waves of frequency 2ω by incident waves of frequency ω. The process couples to the symmetry breaking at the interface, being the generation from the centrosymmetric bulk material suppressed: it is therefore completely background-free. SHG is a multifunctional tool. It displays: (i) spectral resolution (Spectroscopy), (ii) in-plane lateral resolution (Imaging), (iii) phase resolution (Phase-reference) and (iv) time resolution (Pump-Probe). Here we present our recent results on Pump-Probe to study the dynamical evolution of the 2DEG system when it is driven out of equilibrium by an intense optical pulse. The time resolution can be as short as an optical pulse duration (100 fs). Our results clearly show that the SHG signal is strongly affected by excitation of the sample with an UV-pulse (350 nm) at time t=0, and that the charge carrier dynamics depends qualitatively, and not only quantitatively, on the number n of LAO over-layers. We identify three basic microscopic processes, whose interplay sets up a complex dynamics of the transient interfacial polarity. First, an initial ultrafast diffusion of electrons sets up both a screening and a photo-Dember-induced electric field, that compete in opposition for modifying the interfacial polarity. Second, on a time-scale of hundreds of picoseconds, a transient polarity emerges because of the trapping of holes at the interface.

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Adsorption of Small Organic Molecules on Graphene and related 2D materials

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Type of Contribution: Oral

We present a combined experimental and theoretical study aimed at understanding of the behavior of small organic molecules (acetone, acetonitrile, dichloromethane, ethanol, ethyl acetate, hexane, and toluene) on the surface of graphene, graphite and their halogenated derivatives. We measured the isosteric enthalpies of adsorption and entropies by inverse gas chromatography for a large interval of coverages. The interaction between the surface and the organic molecules was calculated by various *ab initio* methods using both finite and periodic graphene models [1]. Accurate experimental enthalpies enabled to assess the shortcomings of theoretical approaches, in particular with respect to the treatment of van der Waals interaction, which governs the molecule-graphene interaction. We observed several phenomena as a function of coverage: the adsorption enthalpies at low coverage (less than 2%) were influenced by the presence of high-energy sites in graphene and graphite [2], and the clustering of ethanol molecules on graphene and graphite altered the measured adsorption enthalpies at high coverage [3]. Consequently, we used the theoretical calculation and the inverse gas chromatography to estimate the surface energy of graphite fluoride [4]. Finally, we present preliminary results of adsoprtion of molecules on fluorographene and phosphorene.

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Applications of graphene-based composites

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Type of Contribution: Oral

In this work, various methods for graphene synthesis (cCVD-IH, chemically and electrochemically) are presented. The morphological and structural characterizations of the composites are performed by Transmission Electron Microscopy, Atomic Force Microscopy and X-ray Powder Diffraction.

The cCVD-IH synthesized graphene are generally decorated with metallic/ bimetallic nanoparticles and prove to have excellent electro-catalytic properties towards the oxidation of various organic molecules (carbamazepine, s-captopril, bisphenol-A, adenine, guanine).

Several biological effects (cytotoxicity, oxidative stress induction, cellular and mithocondrial membrane alterations) induced by graphene oxide, thermally reduced graphene oxide and nitrogen-doped graphene on human dental follicle stem cells are also presented. Graphene oxide shows the lowest cytotoxic effect, followed by the nitrogen-doped graphene. Thermally reduced graphene oxide exhibits high cytotoxic effects. Both graphene oxide and nitrogen-doped graphene seem to be valuable candidates for usage in dental nanocomposites.

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Effect of Post-Exfoliation Treatments on Mechanically Exfoliated MoS_2

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Type of Contribution: Oral

A study is presented on post-exfoliation thermal annealing in air and ultrasonic treatments performed on mechanically exfoliated MoS_2 flakes on oxidised silicon substrates. Postexfoliation treatments on mechanically exfoliated graphene have been previously reported to enable formation of large area single-layer nanosheets of graphene [1].

Ultra-sonication of MoS_2 flakes on SiO_2 without prior annealing resulted in almost complete removal of flakes, indicating weak bonding at the MoS_2/SiO_2 interface. Thermal annealing at 270 ℃ prior to ultrasonic treatment was found to significantly increase the interface adhesion and prevent removal of MoS_2 flakes. We consider that the improved adhesion is due to effusion of water vapour and other impurities from the interface resulting in greater contact area. Samples were also annealed in the range of 75 ℃ to 175 ℃ followed by ultrasonic treatment. This resulted in small residual MoS_2 fragments due to breakage and/or partial removal of overlying MoS_2 flakes. Increase in annealing temperature to 460 ℃, resulted in decomposition of MoS_2 [2].

Contrary to post-exfoliation experiments on graphene, we observed that whilst the adhesion of MoS_2 is considerably enhanced upon annealing, no single-layer MoS_2 flakes resulted. Although the two materials have very similar interlayer van der Waals interaction, the corrugation upon annealing on oxide substrates is dissimilar due to structural difference in the materials. Interaction between out of plane Mo and S atoms gives MoS_2 a higher bending rigidity [3] in comparison to graphene which is a single layer of carbon atoms. The adhesion of a thick MoS_2 flake to the substrate is reduced due to low contact area. Therefore, ultrasonic treatment without prior annealing results in removal of all top layers of the flake but sometimes a few bottom layers remain adhered to the substrate only at places where it was in contact. This results in non-uniform and discontinuous fragments on the substrate.

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Comparison of Morphological and Electrical Properties of a Structural Resin Reinforced with two different Exfoliated Graphite Particles

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Type of Contribution: Oral

The improvement of polymer composites properties in the aircraft industry is a topic of increasing interest in both basic and technological research driven by the need of weight reduction which in turn entails for lower fuel consumption, maintenance costs, etc. Along this stream polymer nanocomposites based on carbon nanotubes (CNTs), nanofibers (CNFs) and more recently graphite nanoparticles have been manufactured by dispersing such nanofillers within polymer matrices (typically thermosetting epoxy). The intrinsic remarkable properties of such nanofillers and the large interfacial areas between them and the polymer matrix leads to electrically conducting reinforced nanocomposites that show also superior mechanical, thermal, gas barrier and flame retardant properties compared to those of the neat resin. In this paper the results of an experimental study concerning the preparation and characterization of epoxy/amine-based composites (TGMDA), suitable for the fabrication of structural aeronautic parts, filled with two types of exfoliated graphite particles, i.e. partially exfoliated graphite (pEG) and carboxylated partially exfoliated graphite (CpEG) are presented. The two systems differ in the exfoliation degree (56% and 60%, respectively) and for the content of carboxylate groups. The relationship between the physical properties of the filler and electrical behavior of the resulting nanocomposites is considered. The structural difference between the two types of exfoliated graphite (EG) and their dispersion within the resins is investigated by means of Raman spectra and SEM images. The incorporation of CpEG results in a sharp insulator-to-conductor transition with an electrical percolation threshold (EPT) as low as [0.025-0.1] %wt typically achieved with 1D fillers like CNTs, whereas for the pEG-based composites EPT ranges in the wider interval [2-3] %wt. The low EPT and relatively high electrical conductivity (~0.1 S/m at 1.8%wt for CpEG reinforced composite) may be attributed to the observed higher concentration of carboxylated groups at the edge of graphene sheets that affects the filler/resin compatibility and to attractive intermulecolar bonding between the EG particles. The dielectric characterization shows that 6.5wt% pEG loaded composite has a relatively high permittivity value (~1000). The good conductivity and tunable permittivity values allow to tailor suitable electromagnetic (EM) properties required for EM compatibility issues and hence indicate that these graphene-based nanocomposites are promising candidates for the fabrication of aeronautic materials with multifunctional characteristics.

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An enemy of technological substitution: the “sailing ship effect”

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Type of Contribution: Oral

Technological competition between a limited number of technologies in providing similar services is a fairly common feature of our economies. Often this competition is limited to two technologies, and entails the advent of a new technology as well as the response of the incumbent technology. The response of an old technology to a new one is a phenomenon which has been observed in quite a few cases, and is referred to as the “sailing-ship effect” – named after the battle between the old canvas and the new steam-engines to provide propulsion for ships. Such effect describes the dynamical interactions between different technologies, and is thus a further (and not-so-often considered) mechanism that prevents technological superiority from implying economic viability in the short term. We will illustrate some economic aspects and technological factors that determine such competition in the context of digital superconducting electronics. Since superconductivity was discovered many expectations on its use have emerged. Many applications have been attempted, from magnetic levitation trains to cryogenic cables, and many revolutions have been announced. A revolution which got very close to become a reality was that of superconducting computers. IBM spent huge human and financial resources between 1965 and 1983 trying to build a “Josephson computer”. However, despite the many progresses, the project was dropped: the incumbent semiconductor technology, despite being inferior from the point of view of performance, was being incessantly developed, thus partly displacing the new technology. In this paper we present the idea of the sailing-ship effect in mathematical form (De Liso and Filatrella 2008, 2011) and provide a simplified version of the model, linking the model to the actual case of superconducting technology. mathematical formulation of the model contains both technical characteristics (e.g., the maximum performances compatible with the physics law) and economic factors (e.g. interest rates). The analysis of the model suggests that a sailing-ship effect has displaced the superconducting technology in the case of computers. We finally discuss some technical factors that should be considered to foresee the success of applications.

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Selective deformation of MoS_2 monolayer by illuminating laser and magnetotransport of 2D materials probed up to 60 T

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Type of Contribution: Oral

2-dimensional transition metal dichalcogenide (TMDC) materials such as MoS_2 have attracted much research interest for future electronics and optoelectronics due to their unique electrical properties. The optical and electronic properties of TMDC can vary depending on the number of layers. In this presentation, we report one can thin down the thicker layers of TMDC by illuminating laser. For MoS_2 monolayer, we selectively deformed the part of monolayer with laser and generated a periodic modulation of the structure. We argue the difference in the thermal expansion between substrate and the MoS_2 monolayer can give rise to the mechanical deformation when shining laser. The strain engineering might provide a useful tool with enhancing the performance of electronic and optoelectronic devices based on TMDC materials. In addition, we report the magneto-transport of 2D TMDC materials probed up 60 T.

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Nanofluidic Ion Transport through Restacked 2D Nanomaterials

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Type of Contribution: Oral

Electrolytes confined in nanochannels with characteristic dimensions comparable to the Debye length show transport behaviors deviating from their bulk counterparts. Fabrication of nanofluidic devices typically relies on expensive lithography techniques or the use of sacrificial templates with sophisticated growth and processing steps. We recently reported an alternative approach where unprecedentedly massive arrays of nanochannels are readily formed by restacking 2D nanomaterials, such as graphene oxide (GO)[1] and exfoliated clay sheets[2]. Nanochannels between 2D sheets are successfully constructed as manifested by nanofluidic phenomena such as surface charge governed ion transport[1] and ionic current rectification[3] for electrolyte concentrations up to 50 mM. Nanofluidic devices based on restacked 2D nanomaterials have distinct advantages such as low cost, facile fabrication, ease of scaling up to support high ionic currents, and flexibility. Given the rich chemical, physical and mechanical properties of layered materials, they offer many exciting new opportunities for studying and even manufacturing nanofluidic devices.

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Posters

Tuesday, 24th, 17:30

Electronic properties of Cantor n-ary set random distribution of impurities in graphene

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Type of Contribution: Poster

The aim of this work is to study the electronic properties of graphene under random impurities which are distributed in the energy line following the Cantor n-ary set box distribution. This implies that for each iteration k, the possible energy values of the random impurities lie in the line segment of the Cantor n-ary set in the interval (-a/2,a/2). By applying the full T-matrix approximation, the electronic density of states is obtained for each iteration k and the limit k -> ∞ limit is taken. A metal-insulator transition is obtained for critical values of a, where a resonance peak in the DOS at the Fermi level is split in two bands that shift towards the band edges when the width a increases. In turn, the electronic density of states for k = 2 only enhance the van Hove singularities, resonant and antiresonant states for k > 2. In the other side, the Cantor set signatures are shown through a spectrum rearrangement for different values of a, where resonant states split in two narrow peaks for k -> ∞. These results are important to study the transport properties in graphene with doped-based fractal superlattices, magnetic or electric barriers or multilayers with triadic patterns and for systems with a hierarchical distribution of energy barriers, where the phenomenon of ultradiffusion appears as a manifestation of the underlying ultrametric topology and where the whole structure of the spectrum is analogous to that of quasiperiodic crystals.

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Influence of excitonic effects on high harmonic generation by strong laser field in gated graphene

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Type of Contribution: Poster

Graphene has attracted enormous interest since its experimental discovery. Due to its unique properties graphene can serve as an active medium for nanolasers and frequency multipliers. In the works [1] we have considered multiphoton interaction of a graphene and graphene bilayers with strong radiation fields of arbitrary polarization. It has been shown that there is an intense radiation of harmonics at the particle-hole annihilation from the superposition states induced by a pump wave. However these results are applicable when the electron-electron interaction effects are negligible.

On the other hand, it is well established that electron-electron interactions, and specifically excitonic effects, are essential for the optical properties of ordinary semiconductors. In an intrinsic graphene the formation of bound excitons is prevented because of gapless dispersion law and absence of bound states in the Coulomb problem. Nevertheless, excitonic resonances can exist and a signature of their presence has been seen in graphene linear optical response [2]. Thus, it is expected that many-body effects will also be essential at the nonlinear interaction of the radiation field with graphene. In this context, it is worthy to note that in graphene it is possible to tune the electron-electron Coulomb interaction by choosing the dielectric constant of the substrate on which graphene is deposited.

In the present paper the microscopic theory of gated graphene interaction with strong laser fields is developed taking into account electron-electron interactions. We consider laser fields of frequencies from THz to optical ones. To take into account the Coulomb interaction we use the self-consistent Hartree-Fock approximation that leads to closed set of integro-differential equations for the single-particle density matrix. The latter is solved numerically. Numerical calculations show that one can reach the efficient generation of high harmonics with laser fields of moderate intensities. At that for the specific frequencies and Fermi level one can achieve considerable enhancement of the harmonic generation rate due to the Coulomb-mediated scattering between the electron-hole pairs.

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Graphene-based Barriers for Solar Cells synthesized by Cold wall CVD

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Type of Contribution: Poster

Graphene films may be considered an effective alternative as window electrode, in replacement Indium or Fluorine Tin Oxide, because of their excellent transmittance [1]. Indeed, graphene is recently attracting great attention not only for its outstanding electrical and optical properties [2], but also for the gas barrier properties [3]. This last characteristic is particularly suitable for photovoltaic (PV) application, since it is well known that the protection of flexible solar cells from the atmospheric degradation agents still represents a challenge for ensuring an acceptable lifetime.

For the graphene synthesis Chemical Vapor Deposition (CVD) of monolayer graphene on copper has emerged as one of the most competitive growth methods for securing the industrial exploitation of graphene [4]. However, the long processing time and the very high production cost for high-quality CVD graphene are still central challenges for the industrial exploitation of this material. Cold wall CVD system allows for faster, more efficient heating and cooling, shorter growth time, and less gas consumption [5]. This method provides a more uniform substrate heating, it reduces the chemical reactions which can take place in the gas phase at high temperature known to contaminate graphene and it allows for very fast cooling rates, leading to high quality monolayer graphene.

In this study, the growth of graphene on a copper foil though a cold wall CVD has been optimized to prepare a transparent barrier film of PET-graphene, thought to be applicable with a double functionality of window electrode and of barrier film for flexible solar cells.

In particular, after graphene synthesis an improved method has been developed to transfer graphene on the PET substrate. A comprehensive characterization was performed of the obtained barrier films, including an investigation of the optical and electrical properties of the PET-graphene system analyzing the relationship between the transmittance and the surface resistance. Furthermore, the evaluation of the oxygen and water vapor barrier properties was performed, since they represent the main degradation factors for thin film solar cells. Moreover, the morphology of surface was analyzed by Atomic Force Microscopy to assess the smoothness of the film surface which is crucial in optoelectronic devices [6]. Finally, X-Ray Diffraction analysis and thermal characterization were carried out on both pristine and graphene coated PET substrates.

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Analysis of wrinkles onset and growth in multi-layered graphene-based composite films on flexible Mylar substrates

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Type of Contribution: Poster

Flexible membranes are widely used in aerospace components when it is required to combine lightweight with specific optical properties and thermal resistance, in particular in thermal blankets for satellites and propulsion systems for solar sails. Their general performance can be theoretically improved by embedding graphene nanoplatelets (GnPs) in the polymer film, but their use is still severely limited by aspects related to the manufacturing. The structural and physical properties of flexible composite multi-layered films (MLFs) strongly depend on film thickness and homogeneity, which makes the interaction of the carbon nanoparticles and polymer matrices with the substrate a crucial aspect of the manufacturing process. Instability patterns, such as wrinkles, can arise on multiple scales as a consequence of thermal gradients or stresses during manufacturing, and affect the overall mechanical properties of the films.

In this work, large scale flexible composite MLFs were fabricated by spray coating polymer/GnPs dispersions over Mylar substrate in multiple layers. The onset and growth of surface wrinkles due to thermal gradients during the manufacturing process was investigated by optical and electron microscopy as a function of the number of layers and GnP concentration. Experimental results were used to define a finite element model for the nonlinear static analysis of the flexible GnP-based composite layers to predict the out-of-plane deformations. In particular, wrinkles formation and how the presence of GnPs affects the overall mechanical properties of the MLFs are studied through ad hoc models.

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Supramolecular assemblies of tetrapyridylporphyrin and its metallic complexes with N-doped graphene

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Type of Contribution: Poster

The preparation of supramolecular assemblies of (metallo)tetrapyridylporphyrins (MTPyP; M= Fe, Co, Mn) with N-doped graphene is presented. N-doped graphene is synthesized in two steps: first, graphene oxide, well dispersed in water, react with urea by solvothermal method. Then, the obtained dried solid was thermally treated in a stream of argon. As such, using either the intermediate or the final N-doped graphene, we were able to obtain the desired nanocomposites by two methods. The iron(III), cobalt(III) and manganese(III) complexes of the porphyrin were employed for these assemblies. The non-covalent attachment was assessed by UV-Vis absorption and Raman spectroscopy, followed by X-ray diffraction for a full characterization of the porphyrin-N-doped graphene composites.

Their peroxidase-like activity was further measured, together with the influence of metallic center on the catalytic behavior of the composites. The ability of iron-containing nanomaterial to be used for hydrogen peroxide detection is also presented.

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Melt compounding of Poly(Lactic Acid) with graphite-oxide

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Type of Contribution: Poster

Biodegradable polymers are raising an increasing interest as a promising alternative to petroleum-based materials since they can be produced from renewable resources at reasonable costs. Among all the possible biodegradable polymers, the most commonly studied is poly(lactic acid) (PLA). However, the PLA has some limitations such as poor thermal and mechanical resistance and limited barrier properties which prevent its complete access to industrial sectors such as packaging. Recently, graphene has gained significant attention as a filler to enhance polymer properties: graphene-incorporated polymers usually show not only much enhanced gas-barrier properties and reinforced mechanical strength but also improved thermal properties when properly dispersed in the polymer matrix.

The aim of this work is to overcome the limitations of PLA by incorporating Graphite Oxide in the PLA matrix. In particular, the influence of two GO types (Graphite Oxide and Graphite Oxide Intercalation Compounds) and amount (3 and 6 wt.%) on PLA thermal and barrier properties was investigated. These GOs were melt mixed in a twin screw extruder with different mixing times and characterized by differential scanning calorimetry (DSC), rotational rheometry and water sorption tests. Preliminary results show that the compounds exhibit a lower crystallization time and a lower water diffusion.

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Leakage and field emission in side-gate graphene field effect transistors

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Type of Contribution: Poster

We fabricate planar graphene field-effect transistors with self-aligned side-gate, using a single lithographic step. We demonstrate side-gating below 1V with conductance modulation of 35% and transconductance up to 0.5 mS/mm at 10 mV drain bias. We measure the planar leakage along the SiO_2/vacuum gate dielectric over a wide voltage range, reporting rapidly growing current above 15 V. We unveil the microscopic mechanisms driving the leakage, as Frenkel-Poole transport through SiO_2 up to the activation of Fowler-Nordheim tunneling in vacuum, which becomes dominant at higher voltages. We report a field-emission current density as high as 1μA/μm between graphene flakes. These findings are important for the miniaturization of atomically thin devices.

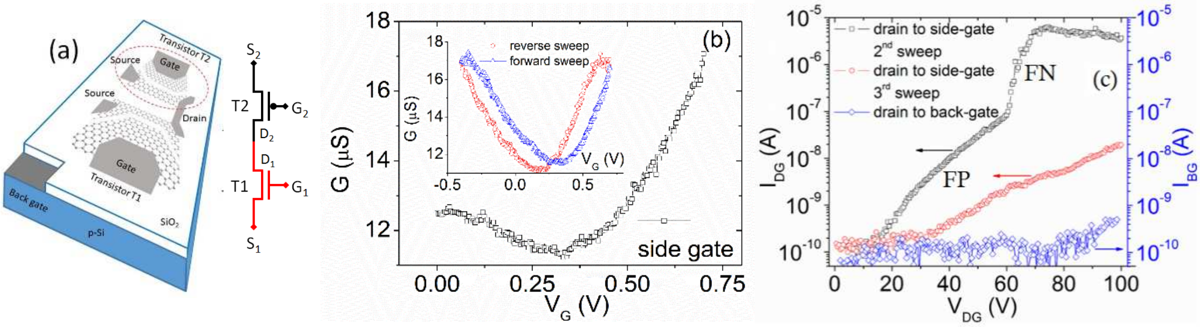

Fig. 1: (a) Layout of the device. (b) Conductance modulation by side-gate. (c) Side-gate to channel current leakage

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Functionalization of Graphene Oxide: a tool to prevent degradation in melt compounded polyesters nanocomposites

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Type of Contribution: Poster

Graphene oxide (GO), obtained by thermal or mechanical exfoliation of graphite oxide, is a 2D carbon nanostructure containing many hydrophilic groups, such as hydroxyl, epoxy and carboxyl acids [1], making it promising in many potential applications.
In particular, GO has recently been used both as catalyst [2,3] for important organic reactions and as filler of polymers[4].
In fact, it is well known that the addition of graphene oxide (GO) in polymer matrices can improve thermal and mechanical resistance, as well as gas barrier properties.[5]
In this study we assess that the incorporation of GO in several commercial biodegradable polyesters induces polymer degradation during melt processing.
Herein, we show that covalent functionalization of GO minimizes polymer degradation in melt processing, thus allowing the production of polyesters/GO nanocomposites.(Fig.1)

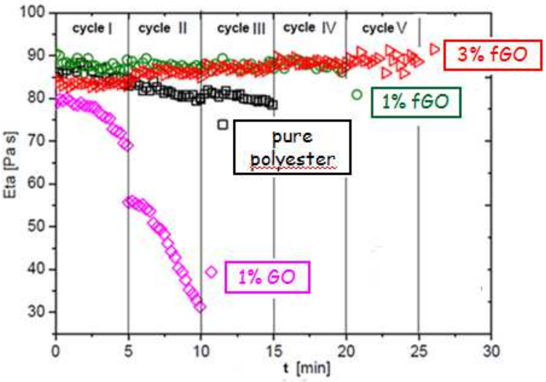

Figure 1. Influence of carbon fillers on commercial polyester melt processing.

We carried out functionalization of GO (fGO) both by introduction of alkyl groups and by introducing acetyl groups. For the latter case, a new and facile green method is proposed.

Both functionalizations reduce the acidic groups present on GO's surface, which are probably the major responsible for promoting thermal degradation during melt compounding.

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Dependency of sorption activity for radionuclides on the concentration of GO on PA66 substrate

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Type of Contribution: Poster

The graphene chemistry has a wide application. We have focused our interest on the preparation and study of its composites for sorption of radionuclides. Concretely, the graphene oxide (GO) on PA66 as a substrate in different ratios. There we supposed the interaction between the PA66 and GO by hydrogen bridge bonds through the functional groups as carboxy and alkoxy. The radionuclides could be coordinated by the rest of free functional group of GO in a water solution.
The preparation of GO was already described by Štengl V.[1] where the oxidation of exfoliated graphite obtains graphene oxide. The commercial PA66 was modified in an autoclave before its reaction with GO. There were used two types of an autoclave for the preparation with/without stirring. In the case, where the stirring has been used, the GO was mixed with after pre-preparation of PA66 in the autoclave and father were stirred at room temperature and pressure. In the second case, GO was added to the Teflon lined together with pre-preparated PA66 and the reaction continues in the autoclave at 160°C. The resulting products were characterised by X-ray powder diffraction, Raman, FTIR, ^{13}C CP/MAS NMR spectroscopy. The morphologic determination was done by scanning electron microscopy (SEM). The quality of starting material (GO sheets) was verified also by high resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM). The sorption activity was tested with radionuclides ^{137}Cs and ^{85}Sr for all concentration set of PA66-GO samples. There was found a concentration at which there was saturation of active sites and thus the maximum of sorption of radionuclides was reached.

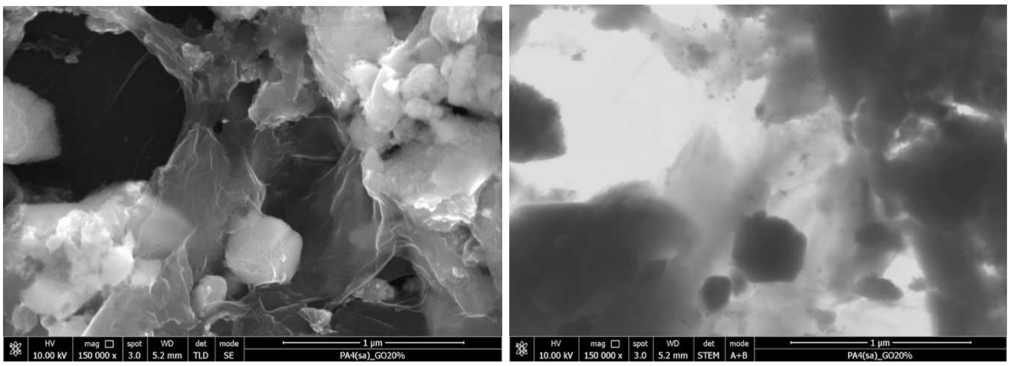

Fig. 1 SEM (right) and STEM (left) image of PA66-GO composite

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Reduced graphene oxide films for transparent conductive electrodes

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Type of Contribution: Poster

Graphene is a material which nowadays is being widely investigated due to its properties and potential applications, especially as transparent conductive electrodes (TCEs). For this particular application, it is needed to establish methods to produce it as a thin film adhering to different substrates and to optimize its physical properties, such as its conductivity, transparence, uniformity, roughness, and thickness.

In the present work chemically synthesized graphene oxide films were deposited by immersion onto glass substrates functionalized with molecular anchors, producing a thin film with a high optical transmittance, which can be reduced by chemical agents such as hydrazine, glucose, or citric acid to increase its electrical conductivity, so that it can function as a TCE.

The following methodology was used in the preparation of the films: synthesis of graphene oxide (GO) by the modified Hummers method, deposition of GO by immersion on glass substrates previoulsy derivatized with (3-aminopropyl)-triethoxysilane (APTES), which acts as a coupling agent between the glass substrate and the GO, and subsequent reduction by single or combined chemical agents such as hydrazine, sodium borohydride, citric acid, glucose, zinc/HCl, or by thermal reduction.

The films deposited in this manner were characterized by ultraviolet-visible spectroscopy to obtain the maximum transmittance at 550 nm and Van der Paw to measure the sheet resistance.

With the transmittance data and electrical measurement, we observed the variation the results of films deposited related to the method used, with this we obtained five fabrication methods that presented transmittance values between 80 and 95%, and resistance sheet Rs between 7 and 60k ohms / sq.

Films were further analyzed by using Raman spectroscopy to assess the microstructural evolution of the films upon reduction and conductive AFM to get topographical and conductive images of the films.

From the topographic images we can conclude that the film is mainly flat, because the Rms varies between 3 and 5 nm. The broadening of the distribution graph for the image leads to the conclusion that the conductivity is not entirely uniform in the film. One can also observe, by comparison between the topographic and conductance graphs, that in the areas containing more deposited material the electric conductance is greater.

With the methods proposed in this paper can be obtained films to RGO that are conductive and transparent. The decision of which method to employ will reside in the form of reduction to use, as some reducing agents are toxic and contaminants such as hydrazine, and others are more environmentally friendly, such as citric acid or thermal reducting.

Acknowledgments

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Graphene – Future applications

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Type of Contribution: Poster

The Graphene and reduced graphene oxide (rGO), as a consequence of their physical/chemical properties, are promising candidates for the realization and production of new and efficient devices and/or end-users solutions. The aims of present study is the exploration of the possible applications of the Graphene and reduced Graphene Oxide, for new or existing commercial and military products. The following areas will be considered:

1. The acoustic wave generation of grahene-like materials: the grapheme allows the exploring the possibility to generate acoustic waves, both in air and in liquid, taking advantage from both the electrostatic approach and the thermo acoustic effect, without any mechanically moving parts.
2. Technological solutions based on the physic-chemical properties of grapheme: this allows the realization of high performance devices (absorption filters and sensors for detection of pollutants and water area, with particular attention to environmental issues and applications in the field of clean energy), taking into account the advantages of reliability, compactness and low cost compared to conventional solutions.
3. The transparency property allows the transmission to RF: the use of this material, lightweight, electrically conductive and transparent to RF can significantly reduce the size and cost of such coatings for RF structures. This is significant for many marine and airborne applications and we propose to analyze and highlight the best performances obtained with respect to the use of conventional materials.
4. The electronic high mobility property allows the realization of high frequency RF devices, superseding the Terahertz boundaries (eg. transistors up to 500GHz and beyond).
5. Other application in the devices and component areas (eg. Supercapacitors) will be taken into account.

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Low-energy electron-irradiation effect on transport properties of graphene field effect transistors

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Type of Contribution: Poster

The use of scanning electron microscopy (SEM), transmission electron microscopy (TEM) as well as electron beam lithography (EBL) and focus ion beam (FIB) processing in ultra-high vacuum represents a necessary step for the fabrication and characterization of graphene based devices. Consequently, graphene devices during fabrication or under test are necessarily exposed to high vacuum and electron irradiation that may considerably affect their electronic properties.

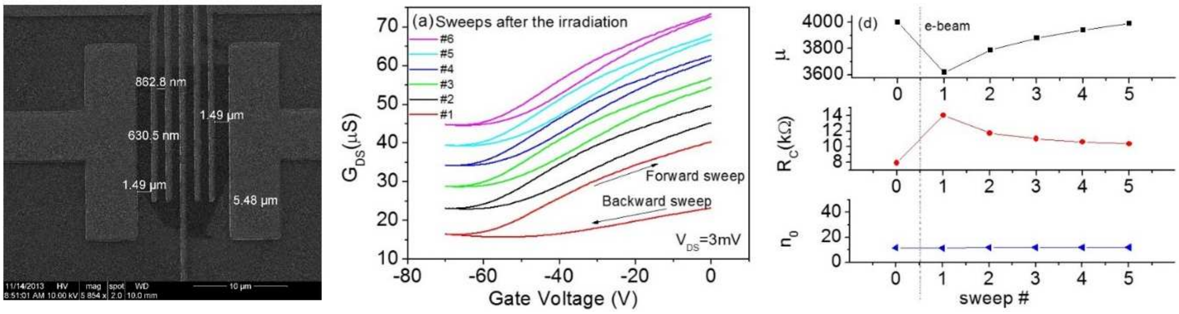

Figure 1. SEM image of the device. Transfer characteristics measured after electron-beam irradiation of the device. Effect of the irradiation.

We study the effects of low-energy electron beam irradiation up to 10 keV on graphene based field effect transistors. We fabricate metallic bilayer electrodes to contact mono- and bi-layer graphene flakes on SiO_2, obtaining specific contact resistivity $\rho_c \approx 19\, k\Omega\ \mu m^2$ and carrier mobility as high as 4000 $cm^2V^{-1}s^{-1}$. By using a highly doped p-Si/SiO_2 substrate as back gate, we analyze the transport properties of the device and the dependence on the pressure and on the electron bombardment. We demonstrate that low energy irradiation is detrimental on the transistor current capability, resulting in an increase of the contact resistance and a reduction of the carrier mobility even at electron doses as low as 30 e^-/nm^2. We also show that the irradiated devices recover by returning to their pristine state after few repeated electrical measurements.

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A green in situ reduction of graphene oxide into PEDOT:PSS for photovoltaic application

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A green and simple method was used to develop Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/graphene nanocomposites in order to enhance the electrical conductivity of the polymeric matrix for photovoltaic (PV) applications. Graphene is a 2D single layer of sp2-bonded carbon atoms characterized by high specific surface area, Young's modulus, thermal stability, mobility of charge carriers and outstanding transport phenomena such as quantum Hall effect observable even at room temperature. Moreover, a further attractive property of graphene is that it can be readily chemically functionalized paving the way to the wide class of graphene-based materials. This is one of the key-aspect to understand the versatility of graphene on a wide range of applications as electrical and optical devices. For this reason, we managed graphene oxide (GO) with different oxidation degrees. Due to the presence of hydroxyl and epoxide groups at the surface of the basal planes and carbonyl groups at the edges, GO is one of the most promising for the large-scale production and solution processability of graphene material. However, these functional groups could decrease the electrical properties of graphene thus hindering the mobility of charge carriers; consequently the reduction of GO is deemed necessary aiming at PV applications. In this work, glucose was used as green reducing agent to in situ reduce graphene oxide (GO) into PEDOT:PSS. Firstly, the efficacy of reducing method was evaluated on the neat GO. GO was, then, dispersed into PEDOT:PSS by solvent swelling method and the same reduction treatment was used. Nanocomposite films were realized by spin coating on different substrates and characterized by several techniques. Finally the film with the better properties was implemented in a hybrid solar cell, based on perovskite as active layer, in order to evaluate the impact on the device performance. The improve of the wettability and adhesion of Perovskite precursor onto nanocomposite hole transporting layer by the cooperative effect of graphene oxide (GO) and glucose doping was evaluated.

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Thermal and Rheological Behavior of TGMDA/Graphene Nanocomposites

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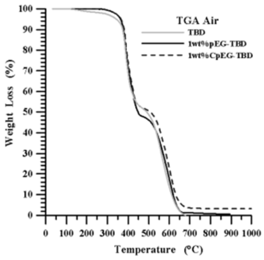
Type of Contribution: Poster

This work presents the thermal and rheological behavior of a tetrafunctional epoxy resin (TGMDA) filled with two types of graphene nanoparticles, namely partially exfoliated graphite (pEG) and carboxylated partially exfoliated graphite (CpEG), differing essentially for the content of carboxylated groups and for the exfoliation degree: 56% for pEG and 60% for CpEG. Exfoliated graphite is prepared using traditional acid intercalation followed by a sudden treatment at high temperature (900°C). The epoxy matrix is prepared by mixing TGMDA with a reactive diluent 1,4-butanediol diglycidyl ether (BDE) which decreases the viscosity of the epoxy precursor facilitating the nanofiller dispersion in the matrix. The curing agent 4,4'-diaminodiphenyl sulfone (DDS) is added at a stoichiometric concentration with respect to all the epoxy rings. The inclusion of the pEG and CpEG samples in the epoxy mixture significantly modifies the rheological behaviour of the mixture itself. The epoxy mixture, indeed, shows a Newtonian behavior; on the contrary the complex viscosity of the nanocomposites clearly shows a shear thinning behavior at 3 wt % of pEG content and at 0.75 wt% of CpEG content. The increase in complex viscosity with the increasing of pEG and CpEG content is mostly caused by a dramatic increase in the storage modulus of the nanocomposites. All the graphene-based epoxy mixtures are cured by a two-stage curing cycle: a first isothermal at the lower temperature of 125°C for 1 h and a second isothermal stage at the higher temperature of 200°C for 3 h. TGA curves of the two nanofillers indicate an amount of carboxylated groups of about 10 wt% for the sample CpEG. The different thermal behavior shown by the pEG and CpEG is consistent with the difference in the percentage of exfoliation degree and well correlates with the rheological behavior of investigated graphene-epoxy nanocomposites. TGA curves of the pEG and CpEG based nanocomposites highlight a stabilizing effect of the graphene-based nanoparticles in the first stage of the degradation. Self-assembly mechanisms determined by attractive interactions between edge-carboxylated graphene particles promote good electrical and mechanical performance.

pEG and CpEG samples, characterized by the same weight, show a difference in volume.



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Low-temperature water-based synthesis of Graphene oxide/TiO_2 composites for destruction of toxic chemicals

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Type of Contribution: Poster

Combining TiO_2 photocatalyst with graphene and graphene oxide (GO) was suggested as an attractive way how to enhance its activity by decreasing the electron-hole recombination, improved adsorption capacity and extension of light absorption into the visible region[1,2]. However, only economically reasonable production of GO/TiO_2 composites in sufficient quality and quantity may lead to real applications.

Here, we demonstrate two syntheses of GO/TiO_2 which may meet these requirements. GO was prepared from natural graphite by our original procedure[3], using intensive cavitation in a pressurised reactor and modified Hummers method. GO/TiO_2 composites were prepared by homogeneous hydrolysis with urea[4] and thermal hydrolysis of peroxo-complexes[5]. Both methods utilise $TiOSO_4$ as a common industrial source of Ti, use water as a cheapest solvent and proceed at ambient air and low temperature (<100°C). These methods avoid any organic precursors or solvents, autoclaving and high temperature calcination. The prepared composites were characterised by XRD, XPS, Raman and FTIR spectroscopies, nitrogen physisorption and microscopic techniques (SEM, TEM, AFM). Their decontamination activity was tested on degradation of warfare agent simulant DMMP using in-situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), gas model compound butane using GC-MS and real warfare agents Soman, Agent VX and Yperite using HPLC. Materials characterization confirmed successful preparation of GO/TiO_2 composites with enhanced photocatalytic activity. The production of the selected samples will be scaled to a pilot production in 10, 25, and 50 L reactors and their decontamination activity will be verified.

Acknowledgements

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Two conductance minima in graphene field effect transistors

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Type of Contribution: Poster

We produced graphene-based field-effect transistors by contacting mono- and bi-layer graphene by sputtering Cr, Ni, Ti or Nb as metal electrodes with a Si/SiO$_2$ substrate used as the back-gate. We performed electrical characterization of the devices by measuring their transfer and output characteristics. We clearly observed the presence of a double-dip feature in the conductance curves that we explain as the effect charge transfer from the contacts, causing different doping of graphene under the contacts and in the channel. We show that the double dip enhances the hysteresis in the transfer characteristics. Elucidation of the origin of the double dip is of technological importance since the observed distortion indicates a deterioration of the gate voltage response of the device. Although a possible drawback in circuitry applications, we also suggest that such a feature can be conveniently exploited to develop graphene based memory devices.

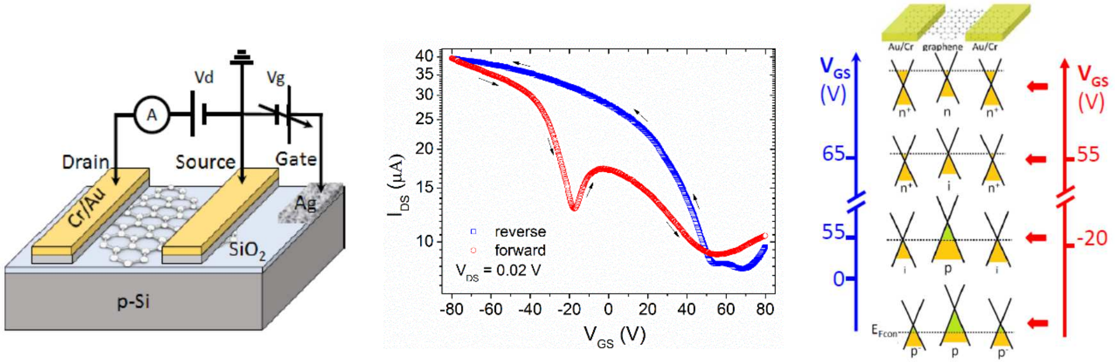

Fig. 1: Layout of the device. Output characteristic of the transistor showing gate-hysteresis and a double-dip feature. Model to explain the double dip in the forward and reverse loop.

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Preparation and properties of polyethylene nanocomposites with graphene functionalized with transition metal nanoparticles as flame retardants

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Type of Contribution: Poster

Flame retardants, mainly based on halogens, phosphorus, inorganic and melamine compounds, are playing a major role in improving the flame retardancy of polymer materials. Recently, new retardant approaches for polymers have been developed using nanoadditives. Carbon nanomaterials such as graphite, carbon nanotubes, graphene oxide and graphene have been extensively used into various polymer systems for improving their flame retardant properties. It was found that significant enhancements on the thermal, mechanical, electrical and gas barrier properties were achieved by introducing very low loadings of graphene into polymer matrix [1,2].

The aim of our study was to reveal the flame retardancy of polyethylene (PE) and transition metal/graphene (Me-RGO) based nanocomposites. Graphene functionalized with transition metals (Fe, Co, Ni) was prepared using two step synthesis: (1) homogenous precipitation and (2) reduction of graphene oxide (synthesized via modified Hummers methods) with sucrose. Finally, the nanocomposites of PE/Me-RGO were synthesized by extrusion. The samples were characterized by high resolution transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectroscopy and X-ray diffraction (XRD). The thermal stability and flame retardancy of investigated samples were studied by means of thermal gravimetric analyzer (TGA) and microcalorimeter, respectively. The addition of functionalized graphene into polymer matrix demonstrated remarkable improvement the thermal stability and flame retardancy of the polymer matrix.

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Quantum dots attached Graphene oxide for the sensitive detection of ascorbic acid as a biosensor in aqueous solution

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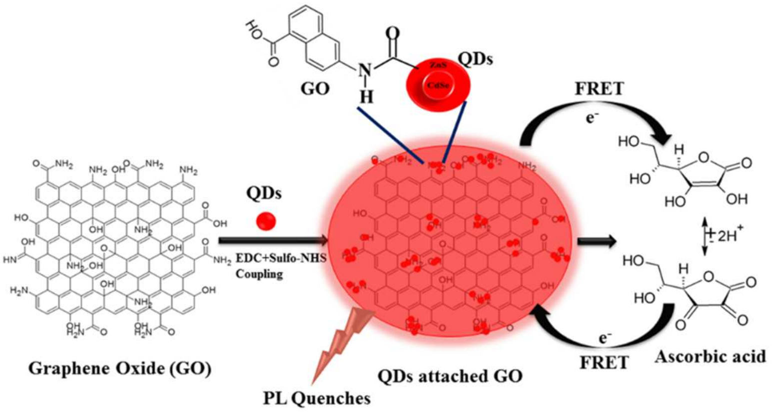
Type of Contribution: Poster

Graphene oxide is an oxidized form of graphene with polar functional groups and has gained much attention in the nanotechnology due to its amazing oxidation reduction properties [1]. Ascorbic acid is an essential water soluble vitamin that can perform several biochemical reactions in human beings at molecular level [2]. In this work, we prepared quantum dots (QDs) attached graphene oxide (GO) for the sensitive detection of ascorbic acid in aqueous solution. QDs were immobilized on the surface of GO by using EDC/NHS-sulfo coupling reaction. The QDs attached graphene oxide was characterized by using several analytical tools such as SEM, FTIR, Raman Spectrophotometer and PL. The fluorescence of GO-QDs was quenched by the interaction between ascorbic acid and GO-QDs. The fluorescence of GO-QDs was quenched by various concentrations of ascorbic acid in aqueous solution at ambient temperature.



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Methane gas sensor based on L-ascorbic acid-reduced graphene oxide incorporated with tin oxide

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Type of Contribution: Poster

Among metal oxide semiconductor gas sensors, tin oxide has been intensively studied due to the advantages of high gas sensitivity, stability and fast response. However, metal oxide gas sensor has numerous drawbacks such as high operating temperature and power consumption. The high operating temperature also results in short life and shift in response. In order to improve the conductivity of metal oxide, additive material such as reduced graphene oxide has been searched recently for their advantages of high sensitivity, fast response and good conductivity. In our work, graphene oxide obtained from Hummer's method is reduced by L-ascorbic acid which has shown to have high reduction level with good conductivity compared with other reducing agents we used such as D-glucose, hydrazine and sodium borohydride. It is found that the reducing power of D-glucose and sodium borohydride are much weaker than that of hydrazine and ascorbic acid. Ascorbic acid has shown to have comparable reducing power to hydrazine while maintaining a good gas sensitivity. Gas sensor based on the L-ascorbic acid-reduced graphene oxide has shown to have high sensitivity towards methane gas which is due to the incomplete removal of the oxygen functional groups on graphene oxide during the reduction process. While the hydrazine-reduced graphen oxide has shown to have the lowest sensitivity which is due to the strongest reducing power of hydrazine which completely removes the oxygen functional groups on graphene oxide. The improvement of sensitivity of the hybridization is due to the synergistic p-n junction effect between the reduced graphene oxide and tin oxide. In this work, gas sensor based on L-ascorbic acid-reduced graphene oxide incorporated with tin oxide has shown to have the highest sensitivity with good conductivity among the reducing agents we used. The approach of this work could be applied to fabricate room temperature gas sensor.

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FEM Model and Performance Analysis of a Graphene-Based EM-Shielding Device in Presence of Uncertain Parameters

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Type of Contribution: Poster

Based on recent experimental results showing the electromagnetic behavior of a novel device for RF-shielding application of graphene, in this work a numerical analysis is presented in order to realize a model useful as a support in the design phase.

The RF-shielding device obtained with a succession of Graphene(Gph)/ Polymethylmethacrylate (PMMA) layers as in sandwiches in the presence of uncertain parameters within a more complex context of Robust Design of Electromagnetic (EM) shields is considered. It covers the description of modelling and performance analysis of the device physically fabricated within the context of the EU 7th Framework Program under grant NO 604391 Graphene flagship. The necessity of such a kind of study is a direct consequence of the unsatisfying usual approach in referring to the main parameters *nominal values* in the systems under examination, thus possibly leading to (especially for new generation materials) malfunctioning devices. Performances could, indeed, be very different from what was really aimed at and it can also end up with physically unrealizable final design products. Moreover this kind of study can be used to understand the effect of the assumed model, the effect of the production process parameter or the effect of the measured data on the performance function by exploiting the implicit sensitivity analysis on which the design is based. The Ka-band ([20-40]GHz) is taken into account for a FEM model of the EM behavior of the devices. The Comsol Multiphysics® RF Module has been chosen as modelling environment. As far as the simulated structure is concerned it is approximated as infinitely extended along the vertical direction, while a planar EM incident wave is considered, traveling along the horizontal direction, orthogonally to the planes of Gph and PMMA, stacked in pile.

The determination of the Scattering Parameters has allowed to determine the chosen *Objective Function* (the Shielding Effectiveness - SE- of the simulated device), through which the model validation has been carried out, comparing the simulated SE with the measured data. In particular, since the final goal is the determination of the most important parameters and the way and extent they influence the whole system performance this has, indeed, been accomplished exploiting a Design of Experiments approach, aiming to *virtually prototype* an efficient Graphene Based-EM Shield. The chosen variable parameters are: the number of replicated "cells" in the structure (a cell is made of a Gph and a PMMA layer); the electrical conductivity of the Gph Layer (since it is a newgeneration material its fabrication intrinsically suffers from heavy uncertainties); the thickness of the PMMA layer. Dex scatter plot and main effect plot will be used in order to extract information regarding the most influencing parameter, the type of dependence with respect to the assumed space parameter and the order of dependence. A Vertex analysis on the SE will be furtherly conducted leading to the bounding of the performance function due to the assumed uncertainties.

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Performance and Stability improvements of graphene/silicon Schottky barrier solar cells

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Type of Contribution: Poster

Few-layer graphene films, grown by chemical vapor deposition, are used to fabricate graphene/silicon Schottky barrier solar cell. A full understanding of the electronic behavior of graphene/silicon heterojunction is of great interest, since its structure is the simplest among the graphene based solar cells. The crucial steps in the device fabrication are: i) the transfer method of graphene, as this determines the quality of the film and the interface between graphene and the silicon absorber substrate, possibly compromising the device performances; ii)the doping of graphene ; iii)the realization of antireflection treatments, aimed to reduce the optical losses due to the sunlight reflection on the top of the solar cell; iv)the introduction of an appropriate intermediate layer between graphene and silicon to reduce the dark current, to block the majority carriers injected into the frontal electrode at forward bias, to reduce surface recombination velocity and to passivate silicon surface.

In this work, we fabricate and characterize graphene/n-silicon solar cells. After the realization of graphene films by Chemical Vapour Deposition we employ a graphene transfer method specifically designed for wet processing which is, at the same time, simple, effective, and capable of maintaining intact the intrinsic features of few-layer graphene films on the pre-patterned silicon substrate. Then we dope the graphene films by nitric acid vapor to increase the graphene work function and conductivity and successively deposit, on the top of the device, a double layer antireflection coating. The beneficial effects of the implementation of the different process steps are evidenced in terms of solar cells electrical performance and stability. The preliminary, encouraging results, obtained introducing an innovative graphene/silicon interfacial layer -realized with a lower thermal budget respect to the classical thermal oxidation for silicon surface passivation-are also analyzed and discussed and set the basis for the development of a new type of graphene/interlayer/silicon solar cell.

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Light irradiation tuning of surface wettability, optical, and electric properties of GO thin films

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In the last years, the possibility to produce electronic devices based on flexible polymeric substrate has attracted wide interest. In this field, graphene oxide (GO) presents many advantages related to its relatively low-cost and up-scalable process[1,2]. However, oxygen-containing functional groups make GO hydrophilic and almost insulating. Therefore, an effective reducing process is necessary to make the GO films conductive and hydrophobic. Laser-scribing technology is an inexpensive reducing process, that does not need harmful reducing agents and expensive equipment[2]. In this study, a GO water dispersion has been drop casted and air dried onto polyethylene terephthalate (PET) flexible substrate. The resulting films have been activated through UV pre-treatment and then patterned with a laser sources at different intensities. The laser scribing method decreases the optical transmittance leading to a colour migration from brown to black for the exposed films. Analysis of the films with optical and electronic microscopy show that the initially stacked GO sheets have been converted into well-exfoliated rGO sheets. The reduction of the GO layers to rGO layers has also been confirmed by infrared spectroscopy and by the electrical measurements. In particular, the resulting rGO films treated with a CO_2 laser at 5 W/cm^2 shows a charge carrier mobility of about 2000 $cm^2V^{-1}s^{-1}$. The wettability of the resulting films has been also investigated by contact angle measurements. In particular, the dependence of the wettability on the laser treatment has been correlated to the change in conductivity and thus to the morphology and the level of chemical reduction of rGO. It allows to control the adhesion between metal contacts and graphene surface by controlling the morphology and the surface property of the films. In conclusion, reduction via focused laser beam allows to directly pattern conducting rGO in an insulating GO matrix, without the need for pre-patterned mask or substrates. At the same time, is possible to tune both its wettability and optical properties quickly and on a micrometric scale. This strategy could provide a good opportunity to develop substrates to satisfy the requirements of portable, flexible, and transparent micro-electronic devices.

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Study on TMD/Graphene Based Film Fabrication and Its Applications

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Type of Contribution: Poster

The production of hydrogen by photocatalytic water splitting has attracted much, recently. Photocatalytic material requires two characteristics, capability of exciton generation and catalytic surface for hydrogen evolution reaction (HER). Since transition metal dichalcogenides (TMDs) satisfy these requirements, it has been investigated for their application as photocatalyst over the past few decades. The most popular TMD material, MoS_2, has a two different crystal phase, 1T- and 2H-MoS_2, and they have metallic- and semiconducting-properties, respectively. 1T-MoS_2 shows outstanding catalytic effect for HER, and exfoliated 2H-MoS_2 has a direct band-gap for light absorption. However, the photocatalytic efficiency of such TMDs nanosheets for hydrogen evolution reaction (HER) is still not enough for the practical use as catalyst, which is supposed to be caused by the inevitable restacking TMDs nanosheets during electrode preparation process. Moreover, the low conductivity of TMDs impedes the electrons transport upon HER. MoS_2 based heterostructure with high conducting material has been regarded as a candidate to overcome these limitations. Therefore, the development of for scalable fabrication methods for MoS_2 based heterostructure remains as an important challenge in TMD-based research field. Here, we present a facile synthetic method to fabricate TMD electrode on transparent electrode indium tin oxide (ITO) for PEC and characterization of TMD-based hybrid thin film. Monolayer of graphene oxide (GO) and MoS_2 sheets were prepared by modified hummers method and n-butyllithium intercalation method, respectively. Then, TMD-based films were deposited on ITO substrate by several methods; including Langmuir Blodgett, spin coating, spray coating and simple filtration method on Anodisc After annealing as-prepared GO film or using hydrazine reduction method to reduce as reduced graphene oxide (rGO), Thin TMDs film was placed on rGO film by using spin coating or spray coating. In addition, membrane method we developed enables to fabricate thin film by simple filtration. The filtration is implemented with a target material to make a film on Anodisc. Then, the produced films were floated on the surface of KOH to remove Anodisc. Finally, it was able to be transferred to any substrate needed. The films were characterized by SEM, AFM, Raman and UV-Vis, which reveals that the TMD film was uniformly distributed on any substrate which is including another film fabricated by the same membrane method. We also demonstrated that the coverage of TMD on the substrate or film can be controlled by mass of the material in filtration step. We believe that further work with optimization of the photoelectrode structure will significantly enhance photocurrent efficiencies. Therefore, the future possibility to have hydrogen energy at a low cost, with clean material to the environment, seems to be closer, since most of the demands for an appropriate hydrogen evolution material are achieved by TMDs.

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Graphene-Silicon Schottky diodes

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We etched a n-Si wafer to form arrays of Si-nanotips emerging from a SiO_2 layer on which we transferred CVD grown monolayer graphene. We measured the electrical characteristics of the junction and found a rectifying behavior with On/Off ratio increasing with decreasing temperature and at room temperature higher than $1.5\cdot 10^2$ at ±0.5V. The ideality factor of the diode is near-ideal with a value of 1.5 at room temperature. The Schottky barrier height monotonically increases from reverse to forward bias, with a value of 0.36±0.02 eV at zero bias. This behavior can be explained as a combination of graphene features and image force barrier lowering. The diode shows photoresponse and fotovoltaic effect when exposed to visible light. The photoresponse is pronounced at near infrared (IR) radiation.

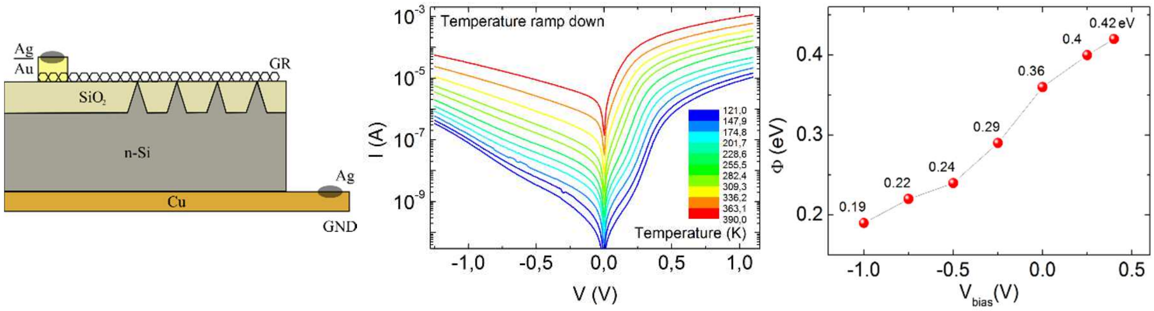

Fig. 1: Layout of the device showing the graphene/Si-tip. I-V characteristics at different temperatures. Barrier height as a function of the bias.

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Study on Optical and Electrical Property Changes of Molybdenum Diselenide by Reversible Hydrogenation

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Type of Contribution: Poster

Hydrogenation is one of the chemical functionalization methods, which has been investigated as an approach for modulate electronic structure in nanomaterials, since it was theoretically suggested that electronic structure can be modified by degree of hydrogenation of graphene like two-dimensional (2D) materials such as transition metal dichalcogenides (TMDs). In the case of graphene, its electronic structure with zero band-gap has been expected to be opened by surface hydrogenation. Compared to wide researches for hydrogenation reactions on graphene surface, the other 2D materials, ones on TMD was not sufficiently studied. In this study, we have studied the surface hydrogenation reaction on TMDs.

Similar to the concept of graphene functionalization, chemical functionalization is known for leading to modification of their electronic and optical properties. Theoretical calculations predicted that the electronic structure of single-layer TMDs also can be tuned by hydrogenation. However, its experimental demonstration has not been realized so far. In addition, TMDs can be used as outstanding catalyst for hydrogen evolution reaction (HER). Therefore, the systematic investigation of hydrogenation on TMDs cannot only unveil the modified electronic structures in TMDs, but also can provide the critical information to understand the interaction between hydrogen atom (or molecule) and TMDs, which is fundamentally important for improving HER efficiency. Here we show modification of electronic properties in $MoSe_{2,}$ one of TMD materials, which is synthesized by chemical vapor deposition (CVD) process. The photoluminescence (PL) intensity and peak position indicates a direct band gap of 1.54 eV for the single-layer $MoSe_2$. After the hydrogenation by H_2 plasma treatment, semiconducting properties of single-layer $MoSe_2$ turn into insulator. In a step-by-step PL results, hydrogenation reaction started from edge to center. Also, we confirmed the hydrogen atoms only react with selenium atoms (Se) in X-ray photoelectron spectroscopy (XPS) analysis. This study demonstrates the great potential of controlling electronic property of single-layer $MoSe_2$ and fundamentally understanding about hydrogenation as a surface functionalization study.

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Flexible and Solvent Resistant Graphene Oxide Paper

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Type of Contribution: Poster

The ability of graphene oxide (GO) aqueous suspensions to form robust GO paper is largely improved by basification of the suspension before processing. In particular, casting procedures, which are generally unsuitable for production of robust GO paper [**1**], become suitable for the case of basified GO (b-GO) suspensions, leading to flexible, dense and free-standing papers. Thermal treatments of b-GO paper easily produce complete loss in stacking order of graphene layers while thermal treatments of GO paper lead to their crushing and to only partial loss of stacking order. Moreover, X-ray diffraction analyses indicate that the degree of parallelism of graphene oxide with respect to the paper surface remain high ($0.6 < f < 0.7$) even after loss of graphene stacking order. Differently from usual GO papers, b-GO papers maintain their dimensional integrity when dispersed in organic solvents [**2**] as well as in acidic, neutral or basic aqueous solutions. These relevant b-GO features (improved filmability by casting, maintenance of film integrity by thermal and microwave treatments and improved solvent resistance) can be rationalized by formation of covalent bridges between GO layers. Spectroscopic characterizations [**3**] and simple chemical arguments suggest that these covalent bridges between GO layers could be constituted by ether bonds.

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Protection of romp catalyst through polymeric globular shell

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Type of Contribution: Poster

Self-healing materials are currently being considered for real engineering applications in the field of structural materials. The first self-healing system for thermosetting resins was proposed by White et al. It consists of incorporating a microencapsulated healing agent and a ruthenium catalyst (5% by wt) within an epoxy matrix. An approaching crack ruptures embedded microcapsules releasing the polymerizer agent into the crack plane through capillary action. Polymerization of the healing agent is triggered by contact with the embedded catalyst, bonding the crack faces. The high amount of ruthenium catalyst used in the composite material and its high cost are major problems.

In the attempt to significantly reduce the amount of metathesis catalyst and increase at the same time the properties of the epoxy matrix, the Hoveyda Grubbs II generation catalyst (HG2) was covalently bonded to graphene oxide [1]. Unfortunately, this system which allows a significant reduction of the amount of ruthenium complex to be used (0.5% by wt) and therefore substantial cost savings, is deactivated at temperatures above 90°C and is not suitable to obtain self-healing materials able to support high aerodynamic loads. In fact, for many mechanical targets fixed for structural applications, a glass transition temperature (Tg) of 180°C minimum is required. To achieve this goal, a proper chemical formulation and curing cycles at high temperatures are necessary. These drastic processing conditions deactivate the embedded self-healing components.

This study explores a new strategy to protect catalytic sites based on Ru catalyst covalently bonded to graphene sheets. Units of monomers around the ruthenium atoms were polymerized forming a globular shell around the catalytic sites. Protected Ru-functionalized graphene sheets were found able to allow high curing temperatures. This strategy allows to overcome important drawbacks related to the deactivation of self-healing mechanism in structural materials for aeronautic primary structures.

The protection of catalytic sites can allow more drastic conditions during the curing cycle. Furthermore, the possibility to integrate the very interesting properties of graphene based-particles inside thermosetting self-healing materials represents one of the most pursued target for many industrial application. The proposed strategy could represent a revolutionary approach to open new applications in the field of self-healing structural materials.

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Nonenzymatic graphene based sensor for glucose detection

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Type of Contribution: Poster

Development of fast and reliable methods for glucose sensing is of significant importance in many areas, such as clinical diagnostics, biotechnology, and the food industry. Recently, direct electrocatalytic oxidation of glucose at nonenzymatic biosensor seems to be an attractive method compared to enzymatic electrodes due to chemical and thermal stability of materials, reproducibility of results, simplicity of operation, oxygen limitation-free and high sensitivity. Palladium nanostructures are of great interest due to their extensive applications in gas sensor and diverse catalytic fields. Recently palladium has been also found as an efficient electrocatalyst for nonenzymatic oxidation of glucose. Meanwhile, graphene posses a large surface area, high stability and excellent conductivity, which makes it a promising carrier for the electrocatalyst nanoparticles.

In this study, a nonenzymatic electrochemical biosensor was developed for the detection of glucose based on platinum electrode modified with reduced graphene oxide – palladium nanocomposite (Pd-rGO). The Pd-rGO nanohybrid was synthesized in a solvothermal process. The proposed biosensor can be applied for the quantification of glucose with a wide linear range covering from 1 to 14 mM (R = 0.998). The experiment results also showed that the sensor exhibits good reproducibility and long-term stability, as well as very high sensitivity (98.7 μA mM^{-1} cm^{-2}).

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A New Micromechanical Approach for the Preparation of Polymer-Supported Graphene

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Type of Contribution: Poster

Owing to the unique physicochemical properties, graphene has potential to change electrical engineering, physics and medicine fields in the coming years. Graphene was isolated from graphite by Geim and Novoselov using a micromechanical exfoliation method (known as 'Scotch-tape' method). This technique was based on the peeling out of the graphite crystals. Recently, the use of graphene nanoflakes has been proposed by the same authors to fabricate graphene laminate [1], consisting of the overlapping layers of graphene and few layer graphene nanoflakes with arbitrary shapes and random in-plane orientation. This material is very attractive for flexible electronics, indeed used as coating it strongly improves the electrical and thermal conductivity of plastic substrates. Gaphene laminate has been prepared by drying an ink containing graphene nanoflakes deposited on paper or PET substrates, followed by a compression-rolling process. In our contribution an alternative micromechanical approach without any post deposition treatment to deposit graphene-based coatings on plastic substrate surfaces by using graphite nanoplatelets (GNP) is presented. This method involves a combination of shear stress and friction force applied to GNP in order to exfoliate it and transfer the as generated single-layers and/or few layers of graphene to the substrate. Thermoplastic polymeric films are very suitable substrates for this coating process, because of their ability to interact with graphene layers by C-H/π physical bonds. Such an approach has the great advantage of large-area sample preparation and wide tunability of the coating layer thickness that allows to obtain even transparent conductive films in the visible spectral region. Graphene based layers have been prepared on low-density-polyethylene or poly(methyl methacrylate) substrates and morphologically/structurally characterized by scanning electron microscopy, transmission electron microscopy and X-ray diffraction. The electrical properties have been studied in dark condition and under white light illumination. A negative photoconductivity has been observed in the investigated samples.

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THz spectroscopy of graphene-like materials and hybrids for the developments of bio-compatible devices

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Type of Contribution: Poster

Organic electronics is a promising field for investigating a series of materials offering relevant advantages with respect to traditional electronics as the possibility to create bendable circuits compatible with human biology.

Graphene for its electrical properties (and abundance) represents the desirable compound to trigger a strong development of bioelectronics although its properties are strongly affected by topology, defects and external contamination [1]. This problem can affect the reproducibility and yield of the production of bioelectronics devices. The issue can be circumvented by the use of graphene-like (GL) layers, a graphene related materials (GRM) which are composed of stacks of few graphene layers [2] having micrometer size on average. The loss of the pure two dimensional conduction is compensated by a lower reactivity with a higher versatility due to the initial stable liquid phase of the GL suspensions[2,3].

In the THz region, graphene and GL compounds have attracted much interest as promising candidates for photosensitive and optoelectronic devices. At very high frequencies, however, transport and quantum efficiency in multi-layer graphene structures can be strongly influenced by particle size and stacking configuration. In this contribution we present THz time-domain spectroscopy of GL and GL hybrids obtained by drop casting on silicon dioxide substrates. We provide the electrodynamic characterization of both pure and eumelanin-GL hybrids [4], which are valuable materials for the next generation of bio-devices.

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Kinetics study of graphene-assisted hydrogen storage and scavenging

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Type of Contribution: Poster

Solid-state hydrogen storage is a major challenge in energy-related applications. It requires an acceptor of high-gravimetric hydrogen capacity operated at relatively low temperatures and fast absorption-desorption kinetics. Magnesium is a potent candidate for hydrogen storage, however, its slow hydrogen absorption/desorption kinetics, taking place only at high temperatures, limits its practical application in hydrogen storage.

Improved kinetics have been achieved in composites consisting of transition-metal catalysts, nanocarbons and Mg. Gas-solid catalytic hydrogenation is a multistage reaction involving hydrogen atom spillover, from the catalyst to the carbon and then to the acceptor, followed by nucleation and growth of metal hydride. We recently found that in composites of unsaturated organic material with metallic catalyst, the addition of carbon nanotubes (CNT) or graphene nanoplateles (GNP) spillover agents resulted in an enhancement of two orders of magnitude in the hydrogen adsorption kinetics. In the case of organic material, the adsorption is irreversible and may be applied to hydrogen scavenging in enclosures where the presence of hydrogen should be avoided. We previously showed that Pd-decorated CNTs, as hydrogen spillover agents loaded into Mg, accelerate hydrogen absorption/desorption kinetics by more than one order of magnitude. Graphene additives (e.g., GNPs) possess a well-defined planar (2-D) geometry of low curvature compared to (1-D) CNT's high curvature. CNT curvature determines the barriers to hydrogen surface diffusion and also enhances the adsorption strength, thus reducing hydrogen mobility. Therefore, GNPs may accelerate the absorption/desorption kinetics of reversible hydrogen storage systems. In this study the influence of graphene additive will be discussed in the terms of the hydrogen absorption/desorption kinetics

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Electrochemical detection of various organic molecules at electrodes modified with graphene-metallic/bimetallic nanoparticles

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Type of Contribution: Poster

Graphene sheets decorated with metallic/bimetallic nanoparticles were synthesized by Radio Frequency catalytic Chemical Vapor Deposition (RF-CVD).

The composite materials based on graphene and metallic/bimetallic nanoparticles were next used for the modification of various substrates (gold, platinum) and then employed in the electrochemical study of various organic molecules: *s*-captopril, adenine, guanine.

The detection and electrochemical degradation of *s*-captopril was investigated with a gold electrodes modified with graphene-AuAg composite.

The study of adenine and guanine electrochemical oxidation was investigated with electrodes modified with graphene-Pt nanoparticles composite.

The electrodes modified with the composite materials generally showed a strong electro-catalytic effect towards the detections of organic molecules.

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Graphene-like sensing film inkjet printed on paper for ethanol detection

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Type of Contribution: Poster

The detection of volatile organic compounds (VOCs) is an always current topic that widely attracts the scientific community for being crucial in several applications mainly related to environment, health and industrial processes monitoring. Among the VOCs, ethanol is a common organic vapour frequently employed as reference parameter for food quality control, fermentation process or human breath thus resulting in an increasing request of low-cost, eco-compatible ethanol sensors able to work at room temperature. Such objective can be pursued by merging new material sensing properties with eco-sustainable fabrication processes and substrates. In this framework, the inkjet printing (IJP) technology, a deposition method from liquid phase, well addresses this demand for its patterning capability, which permits an efficient use of different functional inks so reducing the amount of waste products, and the employable (nonflexible and flexible) substrates. The latter issue promotes the use of paper as low cost and eco-sustainable substrates.

In this perspective, we fabricated an ethanol chemiresistor by IJP an aqueous suspension of graphene-like (GL) layers. The sensing ink was prepared through a two steps oxidation/reduction method starting from a nanostructured carbon black [1,2]. GL layers as other graphene related materials present interesting properties for sensing applications at room temperature: high conductivity and stability, large specific surface areas and tunable performances. The GL layers-based ink was deposited by IJP onto glossy paper where interdigitated Cr/Au electrodes were previously e-beam evaporated. The printing parameters were optimized in order to obtain uniform, conductive and reproducible sensing films. The final sensor device was exposed to 50 ppm of ethanol at RT in dry N_2, setting the voltage at 1 V. Differently from pristine graphene that is completely insensitive to ethanol, GL material shows a conductance variation when exposed to this analyte. This sensitivity may be attributable to adsorption or desorption of molecules on the surface of the GL layers film assisted by the presence of residual oxygen functional groups, mainly carboxylic groups, as confirmed by X-ray Photoemission Spectroscopy.

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Highly Active and Stable Hybrid Catalyst of MoS_2-Ni-graphene for HER

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Type of Contribution: Poster

Hydrogen is the cleanest energy carrier, exhibiting the highest specific energy density, as a matter of fact, it is increasingly considered as the future fuel, as well as the best alternative to fossil fuel. Water electrolysis for hydrogen production has many advantages, such high purity, simple process, no pollution and source multiplicity. Industrial water electrolysis, usually carried out using a liquid alkaline electrolyte and Ni as active catalyst, is characterized by low production rates and efficiency, high energy consumption, voluminous systems, and safety issues. The acidic process could represent an alternative, but, due to corrosion issues, requires the utilization of costly noble metals (Pt, Ir, Ru). Therefore, there is a major need to develop new active and cheap electrocatalysts for water splitting, which would offer low overpotentials for the hydrogen evolution in acidic media. Ni-based metals or alloys have been widely used for their reduced cost and catalytic properties in alkaline media. By adding Cu, Cr, P, Nb and W [1] a good stabilization towards corrosion has been recently obtained. Moreover, MoS_2 nanostructures have been successfully tested as catalysts for hydrogen evolution reaction (HER) in aqueous solution. Even if bulk MoS_2 is not active for the HER, it has been forecasted an excellent electrocatalytic activity, linearly dependent by the number of edge sites [2]. Carbon materials are widely utilized for dispersing catalytic metal nanoparticles, due to their high surface area, effective porous structure and good electrical conductivity. In this framework, graphene sheets [3] have been used as template to deposit metal catalysts for electrocatalysis.

Here, we report a one-step synthetic strategy for the preparation of MoS_2-Ni-graphene nanohybrid obtained by thermolysis of suitable precursors in organic solvent. The nanohybrid consists of nanosheets of MoS_2 mainly covering nanoparticles of NiS, on few layer graphene (FLG) obtained by physical exfoliation of graphite. A comprehensive physico-chemical characterization was performed, aimed to evidence the contribution of the different components and optimize surface area, morphology and particle size, that are factors promoting/enhancing catalytic performances. Based on the results obtained with several electrochemical characterizations we considered that the MoS_2-Ni-graphene nanohybrid is a promising electrocatalyst for hydrogen generation.

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Photovoltaic Cells with a Hole-Extracting Graphene Oxide Layer Prepared by Material Printing

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The paper deals with the study of light conversion efficiency of photovoltaic cells with inkjet-printed graphene oxide (GO) layer. Graphene, GO and also reduced form of GO are very promising materials with excellent optical and electrical properties and due to this fact, they can be used e.g. for the preparation of various types of electronic devices.

In our work we focused on the use of GO as a hole-extracting (hole-transport) layer in bulk heterojunction organic solar cells (OSC) based on DPP(TBFu)$_2$:PC$_{60}$BM blend. It was also studied the influence of the layer thickness and the reduction of GO (chemically, by UV radiation, by annealing etc.) on the efficiency of the photovoltaic conversion.

Electrical properties were evaluated by measuring of current-voltage (I-V) characteristics and by using of impedance spectroscopy. Capacitance-voltage measurements were also investigated. Some of obtained data for I-V characteristics (measured under illumination 950 W/m^2) are shown in Fig. 1.

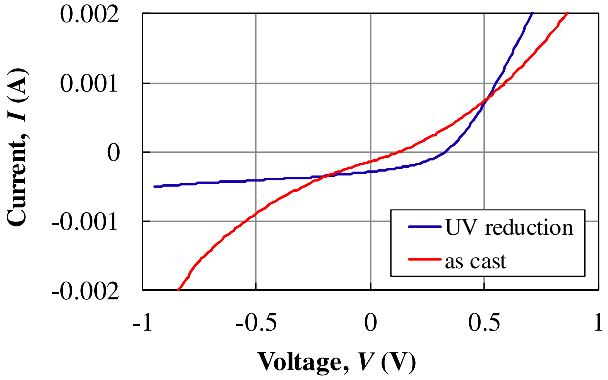

Fig. 1. Light I-V characteristics of as cast and UV-reduced GO layer in bulk heterojunction organic solar cells based on DPP(TBFu)$_2$:PC$_{60}$BM blend

It was found that reducing of GO layer by UV radiation has the biggest influence on the final conversion efficiency of such OSC – the efficiency was increased about 8 times. Further optimization of photovoltaic cells with GO layer can lead to higher conversion efficiency.

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Graphene-based multifunctional epoxy resin for high performance aeronautic structures

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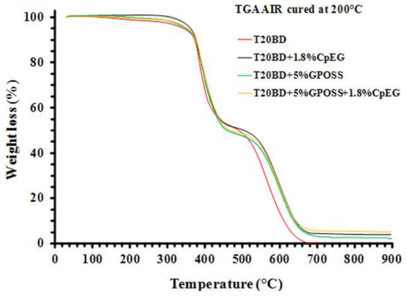
Type of Contribution: Poster

Multifunctional materials are necessarily composite materials, and the strong growth in the use of composites has been greatly influenced by multifunctional design requirements. Aeronautic structures differ from other structures due to their high demands for performance and lightweight. In this contest, graphene-based composites will have a game-changing impact on the performance and efficiency of future airframes. This is due to the electrical and other unique properties of graphene that allow efficient integration of lightning strike protection, flame retardancy, impact resistance and other functions combined in new multifunctional products for use in the aviation industry. This work presents the formulation of the carboxylated partially exfoliated graphite (CpEG) based multifunctional epoxy resin T20BD+5%GPOSS+1.8%CpEG characterized by improved thermal, fire resistance and electrical conductivity. This sample is prepared by mixing an epoxy precursor, tetraglycidyl methylene dianiline (TGMDA) with a reactive diluent 1,4-butanediol diglycidyl ether (BDE) at a concentration of 80%:20% (by wt), respectively, then adding GPOSS flame retardant at 5% by wt, CpEG nanofiller at 1.8% by wt and finally the 4,4'-diaminodiphenyl sulfone (DDS) curing agent is added at a stoichiometric concentration with respect to all the epoxy rings (TGMDA, BDE and GPOSS). All the samples reported in the table below are cured by a two stage curing cycle: a first isothermal at the lower temperature of 125°C for 1 h and a second isothermal stage at the higher temperatures up to 200°C for 3 h. Fire resistance of the solidified epoxy samples is characterized by limiting oxygen index (LOI) measurement (ASTM 2863) and mass loss calorimetry in order to obtain peak of heat release rate (PHRR) data (ISO 13927). The increase of LOI value and the decrease of the PHRR value, observed when GPOSS is used, together with the high electrical and mechanical properties and good thermostability imparted by CpEG nanofiller, confirm the successful obtainment of a multifunctional system for high performance aeronautic structures.

SAMPLE	LOI (%O_2)	PHRR (Kw/m^2)	T_{ig} (s)
T20BD	27	540	40
T20BD+5%GPOSS	33	327	42
T20BD+1.8%CpEG	25	882	64
T20BD+5%GPOSS+1.8%CpEG	30	560	80



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Highly Efficient Graphene Supports for Fuel Cell Electrocatalysts

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Graphene nanomaterials are increasingly important with their distinct properties such as high electrical conductivity, high contact surface area and enormous stability. Therefore, graphene has been used as promising catalyst support in energy conversion and storage systems. In order to achieve high catalytic activity a specifically guided growth of catalyst on graphene support surface with delicate controllability is highly preferred. Therefore, we modify graphene surface in two different ways such as graphene functionalization with various active functional groups and fabrication of nanocomposites with intrinsically conducting polymers e.g. polypyrrole (PPy). We have successfully modified graphene oxide by the functionalization with free amine groups (GO-NH_2), RGD peptide (GO-RGD) and Nitrogen doping (N-GO). Platinum (Pt) catalyst nanoparticles have been deposited on these functionalized GO (f-GO) using ethylene glycol modified method. The dispersion of Pt deposited F-GO has been enhanced and stable optimized dispersions in organic solvents were obtained. The cyclic voltametry (CV) results showed a high electrochemical surface area (ECSA) of 147 m^2/g for GO-RGD compared to Pt/carbon black (Pt/C, 80 m^2/g_{Pt}) and Pt/GO (99 m^2/g_{Pt}). On the other hand, we also fabricated GO/PPy/CB (carbon black) hybrid nanocomposites as catalyst support and deposited Pt catalyst nanoparticles. The

CV results showed a high ECSA of 153 m^2/g_{Pt}. These modified graphene nanomaterials including Pt/fGO and hybrid composites have been successfully used in proton exchange membrane fuel cell (PEMFC) electrodes. The Pt nanoparticles distribution on various modified graphene surfaces, which may significantly influence their properties such as electrical conductivity, electrocatalytic activity when they used as catalyst support and fuel cell performance will be discussed more in details.

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Graphene-Based Thermoelectric Generator

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Type of Contribution: Poster

Thermoelectric (TE) materials are expected to play an increasingly important role in power generation, solid-state cooling and heating systems, so these devices can convert thermal energy from a temperature gradient into electrical energy.

Polymers are very attractive to exploit next-generation thermoelectric materials due to their low-cost, light weight, facile processability and environmentally-benign characteristics. Their relatively low thermal conductivity provides an effective strategy to improve thermoelectric performance. However, their electrical conductivity is too low.

Electroactive polymers such as polyaniline, polythiophene, and polypyrrole have likewise been studied for their electrical capabilities. Polyaniline (PANI) has found widespread use as a conductive polymer due to its solution processability for varied applications including sensors, actuators, memory devices, and energy storage devices.

Recently, it has been demonstrated that the introduction of low dimensional nanostructures in composites materials has significantly improved TE characteristics due to intercomponent junctions, thereby leading to phonon scattering and hoping of charge carriers. In addition, the use of graphene, solution-processable graphene oxide (GO) and its reduced form (rGO) in polymer-based TE composites have attracted much attention due their exceptional electrical, thermal and mechanical characteristics allowing a better tuning of the TE properties in PANI/rGO composites.

Here we report a prototype of a graphene based/PANI thermoelectric generator (TEG) fabricated on a polymer substrate using a facile and cost effective fabrication process.

The composite exhibits a more ordered molecular structure than that of pure PANI, which is due to the π–π, electrostatic and hydrogen bond interactions between PANI and rGO nanosheets. The ordered structure and the formation of a charge transfer complex due to aniline acting as an electron donor and rGO as an electron acceptor increases the carrier mobility. As a result, the electrical conductivity and thermoelectric power of the composite are improved compared with pure PANI.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used for analyses of morphology and structure of the products while Raman spectroscopy is employed to investigate the characteristic mode structure of each component and its evolution into the composites. Thermal and electrical conductivities are determined by photothermal IR radiometry and four probes method, respectively.

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Field emission from graphene flakes

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Type of Contribution: Poster

We report the observation and characterization of field emission current from individual single- and few-layer graphene flakes laid on a flat SiO_2 / Si substrate. Measurements were performed in a scanning electron microscope chamber equipped with nanoprobes which allowed local measurement of the field emission current. We achieved field emission currents up to 1μA from the flat part of graphene flakes at applied fields of few hundred volt per micrometer. We found that the emission process is stable over a period of several hours and that it is well described by a Fowler–Nordheim model for currents over five orders of magnitude.

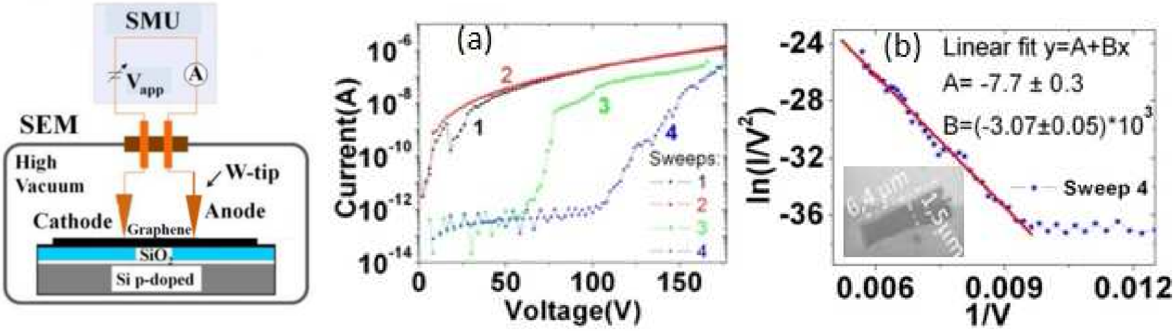

Fig. 1: Field emission measurement setup. I-V characteristics in a sequence of voltage sweeps with increasing graphene-anode distance. Fowler-Nordheim model fitting to experimental data.

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Influence of metal type and particle size on the Raman spectrum enhancement of metal decorated graphene.

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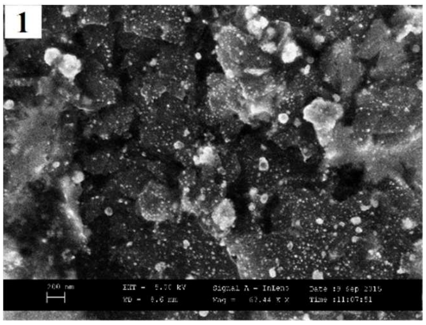
Type of Contribution: Poster

Raman spectroscopy represents a powerful tool for structurally characterize materials, and it is widely employed on graphene (GR) to provide information about the number and orientation of layers, the quality and types of edge, doping, and defects
References
[1].
Metal nanoparticles (NPs) are well-known for inducing Surface Enhanced Raman Scattering (SERS) effect in the material which they are deposed on; the nature of this effect can vary depending on the metal, the geometry and roughness of these structures [2].
Aiming at investigating the influence of the metal type and the related morphology on the Raman spectrum, herein we present a Raman analysis on four GR/metal hybrids (Pd, Ag, Pt, Au) supported by a morphological characterization.
Metal decoration was made on pristine GR, produced by the exfoliation of natural graphite into an ultrapure H_2O-isopropanol mixture [3]. A microwave treatment supplied the energy required for the metal precursors reduction so that the metal structure directly stuck onto the pristine GR surface [4].
Under AFM and SEM observation, the metal particles appear tightly anchored to the GR, with a size distribution that ranges from tens of nanometers to microns (Fig.1).

1



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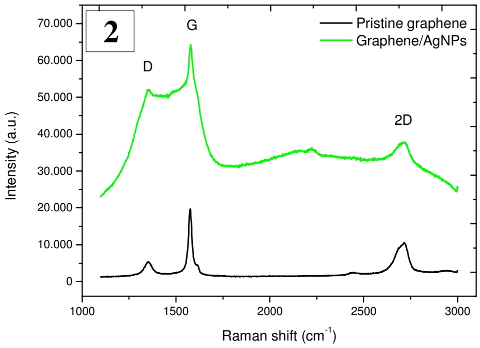

As expected, Raman analysis evidences a variety of phenomena ascribed to the presence of metals onto GR. As an example, Fig.2 reports the Raman spectrum of GR/Ag hybrid compared to that of GR. For all the synthetized materials, SERS effect due to the presence of nanometric metal clusters of variable dimensions and amplification factors within a range 2-130 (depending on the peak) have been recorded, attesting the establishment of chemical bonds between GR and metal NPs [5]. For some metal the rise of forbidden Raman bands has also been observed. The heterogeneity in the detected amplifications of the Raman signal, even in different areas of the same sample, was finally correlated to the different morphology of metallic nanostructures, randomly distributed on the surface.

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Graphene oxide based electrochemical sensor for arsenic detection

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Type of Contribution: Poster

Arsenic compounds are known for their ecotoxicological consequences, geochemistry and their effects on human health and environmental. In natural waters arsenic (As) is mostly found as inorganic oxyanions such as trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). There are several techniques for detection of arsenic compounds. Among them, voltammetric methods are preferred to analytical ones because the first present relatively lower cost, lower power consumption and higher sensitivity in the analysis of As amount. Noble metal nanoparticles (Au, Ag, Pt) electrodes have been studied as electrochemical sensor for detection of As in aqueous solution [1]. These electrodes need to work in strongly acidic media and their production is expensive. On the contrary, non-precious metals, such as iron oxide-based materials, are cheaper and environmentally friendly [2]. In particular, magnetite (Fe_3O_4), founded very effective in the removal of heavy metals [3] and used in combination with nanocarbons to improve stability and ability to work in continuous flow systems, have never been studied for detection purpose. Graphene Oxide (GO) is considered an excellent nanoplatform to develop electrochemical sensors, due to the nature of the atoms on its surface, and its controllable defects density that modulates the sensor sensitivity. Moreover, it has been proved that ultra-thin GO nanosheet is high sensitive and selective to arsenic by using an electrode based on GO coupled with leucine molecules [4].
In this work, we present a novel and stable electrochemical sensor made of Fe_3O_4/GO deposited on a glassy carbon (GC) electrode for electroanalytical detection of As, via cyclic voltammetry in aqueous and phosphate buffer solutions. The electrode shows a very good relation between current response and amount of arsenic in a concentration of pollutants ranging from micromolar to nanomolar. Our sensor is easy to use, inexpensive and has allowed fast, sensitive and selective detection of As in non-acid media (pH7), showing excellent reproducibility and stability response.

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Zein Microparticles Coated by Graphene Oxide Layers: Towards Nanocomposites with Tailored Morphology

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Zein is a protein extract from corn which shows high film-forming ability, biodegradability and biocompatibility. Due to its inherent properties, zein finds many potential applications in food and pharmaceutical industries including, but not limited to, coating and free-standing films for packaging materials. However, at present the functional properties of protein bioplastic materials are not as good as those of synthetic polymers: generally they have worse water barrier properties and lower tensile strength and elongation [Gennadios, A. (Ed.). (2002). Protein-based films and coatings. CRC Press]. Great efforts have thus being devoted toward the improvement of the macroscopic performances of such class of materials. As an example, according to Taylor et al., the functional properties of films made from kafirin protein microparticles are generally superior to those of films cast directly from a solution [J. Taylor et al., J Agric Food Chem, 57, 6729-6735 (2009)]. Moreover, it is worth noting that protein microspheres can be ingeniously exploited as templates to guide the self-assembly of nanoparticles, thus allowing the straightforward production of multifunctional composite materials having a 3D segregated morphology.

The present work fits in this frame, as it reports the preparation procedure of nanocomposite films of zein and graphene oxide (GO) having a tailored morphology. Specifically, a simple water/alcohol-based procedure has been exploited to prepare films from zein microspheres on whose surface GO sheets are selectively segregated. First, a colloidal dispersion of zein microparticles has been obtained [Y. Wang and G.W. Padua, Langmuir, 26, 12897-12901 (2010)]. Then, an aqueous dispersion of GO has been added: the different surface charge among the GO sheets (negative charge) and zein microparticles (positive charge) allows GO layers to self-assemble on the surface of the microspheres through electrostatic interactions. Once prepared the starting dispersion of GO-coated zein microparticles, different conditions have been explored to verify the feasibility of producing films by casting the colloidal GO/zein dispersion. The effect of different parameters on the production of free-standing films from the GO-armoured microspheres has been examined. Specifically, different zein and GO concentrations, solvent evaporation conditions, amount of crosslinker and type and amount of plasticizer have been investigated. Morphological, thermal and mechanical analyses have been carried out to preliminary assess the possibility of realizing free-standing and homogenous films from GO-coated zein microparticles rather than from simple GO/zein solutions.

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Flexible nanostructured composites with graphene/DNA hybrids as multifunctional substrates for biomedical applications

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Type of Contribution: Poster

Multifunctional materials designed by integrating a hybrid component with bioactive and thermal/electrical properties in a polymeric support matrix have many attractive features for applications in the biomedical and biotechnology fields. For example, it is well known that cells sense the stiffness of their microenvironment, and they can regulate their shape and proliferation according to the rigidity of the underlying substrate. Moreover, flexible substrates with specific electric properties can be an ideal tool in applications involving electro-responsive cells, such as neuronal cells.

This work illustrates the engineering and fabrication of nanostructured composite materials that are made of a polymeric matrix based on elastomer (polydimethylsiloxane, PDMS) reinforced with graphene nanoplatelets (GNP), with the aim to exploit the biocompatible character and the high flexibility of the matrix, together with the exceptional mechanical strength, light weight, good thermal and electrical conductivity of the nanofillers. In combination with the GNP reinforcement, DNA was used to improve the dispersion of the nanoparticles within the matrix. The properties of the final composites after cure were characterized using several techniques, including electric impedance spectroscopy, which allowed to have an overview of their multifunctional features. Thermal analysis by calorimetry was conducted to study the curing process of the nanocomposites. Mechanical properties of composites with PDMS matrix of different elasticity were characterized using the nanoindentation technique.

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Thermal and electrical properties of graphene, graphite and graphene nanotubes

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Type of Contribution: Poster

The paper is focused on the measurement of temperature dependence thermal and dielectric properties of graphite, graphene nanotubes (GNT) and graphene, which are used like in additive into the cement or slag or like in additive into the kaolin. These composites have better electrical conductivity and thermal properties. Graphene, GNT and graphite are good dispersibility in water and excellent mechanical properties [1].

Temperature dependence of thermal parameters (thermal diffusivity, thermal conductivity, and specific heat capacity) were determined using a step-wise method. Fractal model of heat transport was used for the determination of thermal parameters [2]. This model is independent on the geometry and on the type of the sample heating, and includes heat losses too. Electrical properties were evaluated by measuring of current-voltage (I-V) characteristics and by using of impedance spectroscopy.

Studied materials are good for using into the building materials, isolating materials and filler for composites. Thus achieve strength, temperature toughness, increase chemical resistance.

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Magnetic $MnFe_2O_4$-rGO composite for removal of model pollutants from water

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Type of Contribution: Poster

Manganese ferrite nanoparticles - reduced graphene oxide composite ($MnFe_2O_4$-rGO) was prepared by a very simple one-pot hydrothermal synthesis route under reflux in an air atmosphere. Graphene oxide used in the synthesis was prepared by our ultrasound-assisted method from natural graphite[1]. Different amounts of graphene oxide were added during the synthesis of $MnFe_2O_4$ nanoparticles.
Numerous methods were used for characterization of the prepared composite samples such as high resolution scanning and transmission electron microscopy (HRSEM, HRTEM), X-ray Diffraction (XRD), Atomic force microscopy (AFM), High angle annular dark field scanning transmission electron microscopy HAADF-STEM and energy dispersive X-ray spectrometry (EDS) elemental mapping, UV/Vis and IR spectroscopy and surface area measurement (BET).
Sorption tests showed benefits of presence even small amount of reduced graphene oxide in the sample. Adsorption capabilities of the magnetic substrate were dramatically improved and removal of model pollutant from water enhanced. The great advantage is also a possibility of magnetic separation of the composite material from water for further manipulation or recycling. $MnFe_2O_4$-rGO composite could be considered as excellent material for efficient adsorption of different types of pollutants from contaminated water.

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Templated and template-free methods of 3D porous graphene-based structures manufacturing

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Porous graphene-based materials are of the great industrial and academic interest due to their low density and high surface area, good electrical conductivity, chemical stability and low cost of fabrication. Self-assembled graphene structures can found their place in different fields as for example in water remediation, tissue engineering and regenerative medicine, sensors, biosensors and thermal energy storage. Significant scientific and industrial interest has grown for their use as free-standing electrodes for electrochemical devices such as batteries, fuel and biofuel cells or supercapacitors. [1,2] Such three-dimensional structures were obtained by controlled reduction of graphene oxide (GO) suspended in a polar solvent. Generally, chemical or physical methods can be used to reduce oxygen functional groups in GO and create three-dimensional network of interconnected graphene flakes [1,2]. Such, so called self-assembled free standing graphene hydrogels were then directed to the suitable drying process e.g. vacuum freeze-drying or supercritical drying. The obtained porous graphene-based structures were characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy and electrochemically. The results revealed they microporous structure and good electrical properties, making them useful for electrochemical energy production and storage.

Similarly, hard templating method was used to produce porous 3D graphene-based structures, but with more uniform pore sizes and distribution. Silica particles of different diameters were used to template the 3D carbonaceous material. The silica particles were synthesized using the traditional sol-gel method. In the next step graphene oxide suspension was mixed with silica particles water dispersions. For the creation of porous graphene-based structures, the hydrothermal method was used for all samples. After etching of silica followed by drying at room temperature, the pores remained their size and shape without significant collapse [2]. This method of templating graphene-based porous structures using silica particles as hard templates seems to be promising and need further investigations.

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One step formation of reduced-graphene-oxide/Co(III)TMPyP system for oxygen reduction reaction

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Effective Oxygen Reduction Reaction (ORR) is essential for the development of clean energy fuel cells. The existing Pt-based catalysts are highly efficient but too expensive and rare for mass production. Therefore, low cost non-precious metals catalysts are necessary.The ORR catalysis using carbon-supported transition metal porphyrins is well known for decades, yet their relative low activity and stability towards ORR are not sufficient for usage in fuel cells. Recently, graphene and its derivatives, and especially heteroatom doped graphene, have shown promising catalytic ORR activity. The incorporation of Cobalt-porphyrin into a graphene functionalized electrode could supposedly combine the advantages of both catalysts.

This work presents a simple one step strategy to prepare graphene/Co-porphyrin catalyst on electrode surface instead of the tedious layer-by-layer methods reported so far. Our method is based on the direct electrochemical reduction on glassy carbon of graphene-oxide (GO) in the presence of CoTMPyP (Cobalt-5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin) in the solution. While electrostatic interaction and π-π stacking adsorb the CoTMPyP to the GO in the solution, the electrodeposition of the GO encage the CoTMPyP on the electrode surface.The ORR activity of glassy carbon electrode that was functionalized using this method was characterized by an onset potential of -0.05V and +0.37V vs. Ag/AgCl in 0.1M NaOH and in 0.1M H_2SO_4 respectively, while reduced-GO functionalized electrode, without CoTMpyP, was characterized by an onset potential of -0.16V and -0.20V vs. Ag/AgCl in the same solutions. Surprisingly, the usage of N-doped-GO have not yielded better results with onset potentials of only -0.13V and +0.15V vs. Ag/AgCl in the alkaline and acidic solutions respectively. Detailed results will be presented.

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