International Meeting on the Chemistry of Graphene and Carbon Nanotubes

April 22 – 26, 2018
Biarritz, France
Sponsored by:

Centre de Recherche Paul Pascal

Université de Bordeaux

Centre National de la Recherche Scientifique

Société Francophone d'Etude des Carbones

GDR-I / GDR Graphene & Co

LabEx AMADEus

Secrétariat général pour l'investissement

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Nanoscale horizons
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ChemOnTubes 2018 has been organized with the help of Terres & Cie
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Preface

Welcome in Biarritz, back to the Atlantic coast for the 2018 ChemOnTubes conference. Some of you are faithful, regular ChemOnTubers and we are delighted to see you again. Some others are newcomers, and you are more than welcome amid the ChemOnTubes crowd, passionate about chemistry of carbon surfaces and particles. Indeed, since 2010, ChemOnTubes has a subtitle, « international chemistry of graphene and carbon nanotubes » and the conference scope encompasses chemistry of and on graphene and carbon nanotubes and more generally $sp^2$ carbon materials.

We have beneficiated for ChemOnTubes 2018 from the help of Terres & Cie for the practical organization. ChemOnTubes 2018 has been supported by the Centre de Recherche Paul Pascal, CNRS, the University of Bordeaux (Idex, Science & technology Department, the Amadeus Labex network), the research network GDR Graphene & CO, the French-speaking carbon society (SFEC), the R&D center CANOE and the Region Nouvelle Aquitaine. We are glad to welcome the booth of WITec and thank Springer and Nanoscale journals for poster prizes.

We are happy to present you with an exciting program of invited and oral talks, two dedicated evening poster sessions where everything has been thought to promote scientific discussions, the charming setting of Biarritz and most of all, the dedicated ChemOnTubes crowd: The perfect mix to learn things, share ideas, start collaborations, enjoy the talks and the social time with friends and colleagues and come back to your laboratories with renewed energy.

Soyez les bienvenus à Biarritz, en terre basque.

ChemOnTubes 2018 organizing committee
Conference Chair

Alain Pénicaud
CNRS-CRPP
Université de Bordeaux

Organizing team

Marco ALFONSO
Brigitte DELORD
Alain DERRE
Béatrice DUPIN
Ferdinand HOF
Christèle JAILLET BARTHOLOME
Wilfrid NERI
Alain PENICAUD
Emmanuel PICHEAU
Philippe POULIN
Julien ROMAN
Fernando TORRES CANAS
Yun WANG
Jinkai YUAN

Scientific Committee

Eric ANGLARET, Université Montpellier, France
Jeffrey A. FAGAN, NIST, Gaithersburg, USA
Silvia GIORDANI, Istituto Italiano di Tecnologia, Genova, Italy
Esko KAUPPINEN, Aalto University School of Science, Espoo, Finland
Chang LIU, Chinese Academy of Sciences, Shenyang, China
Vincent MEUNIER, Rensselaer Polytechnic Institute, New York, USA
Nikos TAGMATARCHIS, National Hellenic Research Foundation, Athens, Greece
Ester VAZQUEZ FERNANDEZ-PACHECO, Universidad de Castilla-La Mancha, Ciudad Real, Spain
Aldo José Gorgatti ZARBIN, Federal University of Parana (UFPR), Curitiba, PR, Brazil
Program
## Sunday, April 22nd

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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</thead>
<tbody>
<tr>
<td>15h00</td>
<td>Registration</td>
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<tr>
<td>17h00</td>
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<td>Welcome and Opening of the Conference</td>
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### Session S1: Electrochemistry, Energy Storage Conversion and Harvesting

**17h10 Cheng**  
Graphene materials for High-Performance Electrochemical Energy Storage

**17h50 Zarbin**  
Carbon nanotubes/Prussian blue analogues materials for sensors and energy applications

**18h10 Hernandez-f.**  
Photoelectrochemistry as an efficient technique for the assessment of charge transfer in carbon nanostructure/TiO2 composite electrodes

**18h30 Pinault**  
VACNT growth on Aluminium: towards innovative supercapacitor nanocomposite electrodes

**18h50 Jourdain**  
Transport of ions in solution through single-walled carbon nanotubes

*Ending at 19h10*

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<thead>
<tr>
<th>Time</th>
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<tbody>
<tr>
<td>19h15</td>
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<td>Welcome Buffet: Bellevue</td>
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### Monday, April 23th

#### Session M1: Functionalization, Dispersion, Sorting

<table>
<thead>
<tr>
<th>Time</th>
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<tbody>
<tr>
<td>08h30</td>
<td>Herrero</td>
<td>Carbon Nanohorns and Graphene Quantum Dots: Versatile Materials for Wide Applications</td>
</tr>
<tr>
<td>09h10</td>
<td>Prato</td>
<td>Synthesis and Properties of Functionalized Carbon Nanoforms</td>
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<td>Desmecht</td>
<td>Anionic functionalization of nanocarbons: A powerful and versatile tool</td>
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<td>09h50</td>
<td>Setaro</td>
<td>Perylene-based functionalization of carbon nanotubes</td>
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<tr>
<td>10h10</td>
<td>Buckley</td>
<td>Trajectory of Nanotube Dissolution</td>
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#### Session M2: Functional Materials

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>11h00</td>
<td>Cambré</td>
<td>Diameter-dependent optical absorption and energy transfer from encapsulated dye molecules to single wall carbon nanotubes</td>
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<td>11h40</td>
<td>Palma</td>
<td>Controlled Assembly of Carbon Nanotube Nanohybrids for Single-Molecule Investigations</td>
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<td>12h00</td>
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#### Session M3: Composites, Porous Materials, Coatings

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<tbody>
<tr>
<td>14h30</td>
<td>Kalbac</td>
<td>Rational design of graphene - polymer interface</td>
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<td>14h50</td>
<td>Nadiv</td>
<td>Nano-carbon loaded Polymer composites: Dimensionality Matters</td>
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<tr>
<td>15h10</td>
<td>Finner</td>
<td>Percolation in Carbon Nanotube-Composites</td>
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<tr>
<td>15h30</td>
<td>Malik</td>
<td>Characterization of graphene based nanocomposites for potential use in dental/biomedical applications</td>
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<td>15h50</td>
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<td>Self-Assembled Poly (3-hexylthiophene) Nanoparticles / Graphene Oxide Donor-Acceptor Hybrids with Tunable Optoelectronic Properties</td>
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<td>16h10</td>
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#### Session M4: Spectroscopy

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<tr>
<td>16h40</td>
<td>Bartlam</td>
<td>Nanoscale Infrared Identification and Mapping of Chemical Functional Groups on Graphene</td>
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<tr>
<td>17h00</td>
<td>Danné</td>
<td>Photoluminescence of ultrashort carbon nanotubes reveals exciton localization at sp3-defect sites</td>
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<tr>
<td>17h20</td>
<td>Bantignies</td>
<td>Enhancing the Infrared Response of Carbon Nanotubes From Dye interactions</td>
</tr>
<tr>
<td>17h40</td>
<td>WiTec</td>
<td>Advances in Multimodal Confocal Raman Imaging (by J. Englert)</td>
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**Ending at 17h50**

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<tr>
<th>Time</th>
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<tr>
<td>19h30</td>
<td>Poster session (with buffet and drinks)</td>
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### Tuesday, April 24rd

#### Session T1: Functional Materials

<table>
<thead>
<tr>
<th>Time</th>
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<tr>
<td>08h30</td>
<td>Wågberg</td>
<td>Applications of nitrogen functionalized carbon nanotubes</td>
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<tr>
<td>09h10</td>
<td>Mar Bernal</td>
<td>Covalent and Supramolecular Junctions Between Graphene Nanoflakes: Enhancement of Graphene Nanopapers Thermal Conductivity</td>
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<tr>
<td>09h30</td>
<td>Menzel</td>
<td>Carbon Nanostructure Networks as Multifunctional Support Frameworks in Adsorption Applications</td>
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<tr>
<td>09h50</td>
<td>Vejpravova</td>
<td>Graphene - plasmonic metal nanogranular thin film hybrids - role of stacking and topography</td>
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<tr>
<td>10h10</td>
<td>Messner</td>
<td>Carbon Waters: Commercialization of surfactant-free single layer graphene in water</td>
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<tr>
<td>10h30</td>
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<td>Coffee break</td>
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#### Session T2: Functionalization, Dispersion, Sorting

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<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>11h00</td>
<td>Lopes</td>
<td>Chemical synthesis of graphene from benzene at liquid-liquid interface</td>
</tr>
<tr>
<td>11h20</td>
<td>Rio</td>
<td>Nanoring / fullerene complexation</td>
</tr>
<tr>
<td>11h40</td>
<td>Domingues</td>
<td>Can rGO Look Like Pristine Graphene?</td>
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<tr>
<td>12h00</td>
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<td>Lunch time</td>
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#### Session T3: Electrochemistry, Energy Storage Conversion and Harvesting

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<th>Time</th>
<th>Speaker</th>
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</tr>
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<tbody>
<tr>
<td>14h30</td>
<td>Arnold</td>
<td>Tailoring and assembling polymer wrapped carbon nanotubes for electronics and photovoltaics</td>
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<tr>
<td>15h10</td>
<td>Christian</td>
<td>Graphene foam composites for high performance Li ion batteries</td>
</tr>
<tr>
<td>15h30</td>
<td>Huang</td>
<td>Carbon nanotube/Nano-graphene Conductive Additives in Lithium Ion Batteries</td>
</tr>
<tr>
<td>15h50</td>
<td>Hof</td>
<td>Graphitic Intercalation Compounds: a Versatile Nano-Template for the Synthesis of Efficient Multi-Functional Electrocatalysts</td>
</tr>
<tr>
<td>16h10</td>
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<td>Coffee break</td>
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#### Session T4: Health and biology

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>16h40</td>
<td>Vogel</td>
<td>Inhalation toxicity of carbon-based nanomaterials</td>
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<tr>
<td>17h20</td>
<td>Flahaut</td>
<td>Surface area is the best metric for the evaluation of the potential ecotoxicity of nanocarbons</td>
</tr>
<tr>
<td>17h40</td>
<td>Palermo</td>
<td>Eco-sustainable GO-polysulfone composites for water purification</td>
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*Ending at 18h00*
### Wednesday, April 25th

#### Session W1: Health and Biology

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>08h30</td>
<td>Zheng</td>
<td>Controlling Carbon Nanotubes by DNA</td>
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<tr>
<td>09h10</td>
<td>Bianco</td>
<td>When graphene meets small interference RNA</td>
</tr>
<tr>
<td>09h30</td>
<td>Vazquez</td>
<td>Non-Oxidized Graphene for Bioapplications: Preparation, Cytotoxicity and Integration in Hydrogels</td>
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<tr>
<td>09h50</td>
<td>Barrejon</td>
<td>Carbon nanotube membranes as neuronal substrates</td>
</tr>
<tr>
<td>10h10</td>
<td></td>
<td>Coffee break</td>
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#### Session W2: Functionalization, Dispersion, Sorting

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>10h40</td>
<td>Orth</td>
<td>Chemical functionalization and nanocatalysts: a perfect match?</td>
</tr>
<tr>
<td>11h00</td>
<td>Shaffer</td>
<td>Adapting nanotube chemistries to graphenes</td>
</tr>
<tr>
<td>11h20</td>
<td>Hou</td>
<td>Reactivity of Graphenide Dependent on Solvation of Potassium Cation in Solvents</td>
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<tr>
<td>11h40</td>
<td>Regev</td>
<td>Graphite-to-Graphene: Total Conversion</td>
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<tr>
<td>12h00</td>
<td>Valles</td>
<td>Graphene/polyelectrolyte layer-by-layer thin films for multifunctional coatings</td>
</tr>
<tr>
<td>12h20</td>
<td></td>
<td>Poster Awards</td>
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<tr>
<td>12h40</td>
<td></td>
<td>Lunch time</td>
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<tr>
<td>20h00</td>
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<td>Gala dinner: Casino</td>
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### Thursday, April 26th

#### Session Th1: Composites, Porous Materials, Coatings

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>09h00</td>
<td>Zhong</td>
<td>Mechanical Assembling and Structuring Graphene Oxide Based</td>
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<tr>
<td>09h40</td>
<td>Mannering</td>
<td>Controlled 3D Assembly of MWCNT and GO-MWCNT Hybrid Aerogels as Support Frameworks for Catalysis</td>
</tr>
<tr>
<td>10h00</td>
<td>Föllmer</td>
<td>Structuration of lignin-based carbon through liquid crystalline graphene oxide</td>
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<tr>
<td>10h20</td>
<td>MacLucas</td>
<td>Electrophoretic deposition of carbon nanotubes on austenitic steel for surface protection</td>
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<tr>
<td>10h40</td>
<td></td>
<td>Coffee break</td>
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#### Session Th2: Functionalization, Dispersion, Sorting

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>11h10</td>
<td>Alvarez</td>
<td>Carbon nanotubes functionalized with copper hexacyanoferrate nanoparticles for a selective extraction of cesium from nuclear waste</td>
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<tr>
<td>11h30</td>
<td>Bepete</td>
<td>Optical spectroscopy signatures of single walled carbon nanotubes dispersed in degassed water without additives</td>
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<tr>
<td>11h50</td>
<td>González D.</td>
<td>A cleaner production of CNT nanocapsules</td>
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<tr>
<td>12h10</td>
<td>Alfonso</td>
<td>Electrostrictive soft materials for mechanical energy harvesting</td>
</tr>
<tr>
<td>12h30</td>
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<td>Concluding Remarks</td>
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Invited & Oral Contributions
<table>
<thead>
<tr>
<th>Authors</th>
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<th>P.</th>
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<td>Alfonso</td>
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<td>Tailoring and assembling polymer wrapped carbon nanotubes for electronics and photovoltaics</td>
<td>43</td>
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<td>Bantignies</td>
<td>Enhancing the Infrared Response of Carbon Nanotubes From Dye interactions</td>
<td>33</td>
</tr>
<tr>
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<td>Carbon nanotube membranes as neuronal substrates</td>
<td>54</td>
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<tr>
<td>Bartlam</td>
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<td>Bucley</td>
<td>Trajectory of Nanotubide Dissolution</td>
<td>23</td>
</tr>
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<td>Diameter-dependent optical absorption and energy transfer from encapsulated dye molecules to single wall carbon nanotubes</td>
<td>24</td>
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<td><strong>Cheng (Invited)</strong></td>
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<td>Surface area is the best metric for the evaluation of the potential ecotoxicity of nanocarbons</td>
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<tr>
<td>Hernandez-ferrer</td>
<td>Photoelectrochemistry as an efficient technique for the assessment of charge transfer in carbon nanostructure/TiO2 composite electrodes</td>
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<td>Author</td>
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<tr>
<td>Malik</td>
<td>Characterization of graphene based nanocomposites for potential use in dental/biomedical applications</td>
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<td>Carbon Nanostructure Networks as Multifunctional Support Frameworks in Adsorption Applications</td>
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<td>Carbon Waters: Commercialization of surfactant-free single layer graphene in water</td>
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<td>VACNT growth on Aluminium: towards innovative supercapacitor nanocomposite electrodes</td>
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<td>Rio</td>
<td>Nanoring / fullerene complexation</td>
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Graphene materials for High-Performance Electrochemical Energy Storage

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Electrochemical energy storage devices, in particular, supercapacitors, lithium-ion batteries and lithium-sulfur batteries, have been extensively explored. Graphene with different structures and functionalities plays a key role in these energy storage devices for use as electrodes, conductive fillers, coating layers, etc. We have fabricated graphene materials by chemical exfoliation and chemical vapor deposition, and also prepared various graphene-based hybrid electrode materials by mechanical mixing, coating, hydrothermal deposition, and \textit{in-situ} synthesis for supercapacitors, lithium ion and lithium-sulfur batteries. These hybrid electrode materials showed desirable electrochemical properties in terms of long cycling life, good high rate capability, and high reversible capacity. Using graphene in flexible energy storage devices is another emerging field, and we have also explored several kinds of graphene-based flexible electrodes. For example, by coating active materials on a graphene foam-like structure synthesized by CVD, a thin, lightweight and flexible lithium ion battery was assembled to show high rate capability and capacity, and excellent flexibility.
Carbon nanotubes/Prussian blue analogues materials for sensors and energy applications

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Nanocomposite materials formed by the combination of carbon nanotubes (CNTs) and Prussian Blue (PB) have several interesting properties. PB has a general formula Fe$^{III}_4$[Fe$^{II}$(CN)$_6$]$_3$.nH$_2$O and presents important redox, ferromagnetic and multi-electrochromic properties. We recently developed an innovative route to prepare CNT/PB composite materials$^{1-3}$ based on an in situ electrochemical reaction between the iron-based compounds present into the cavities of carbon nanotubes and the ferricianide ions in solution. This approach can be used to prepare different kind of electrodes, including transparent and electrochromic electrodes, and has been extended to other kind of ferricianide compounds, the so-called Prussian blue analogues (PBA) as Ruthenium- and Cobalt-based analogues of PB. In this work, we present the multifunctional character of the CNT/PBA composites for sensors and energy related applications. Thin and transparent films of both iron- or cobalt-filled CNTs were prepared through the liquid-liquid interfacial method developed in the group$^{4,5}$. By cyclic voltammetry, the films were modified with PB, ruthenium purple (RP) or cobalt hexacyanoferrate (CoHCFe), forming three different composites, which were applied as H$_2$O$_2$ electrochemical sensor (limit of detection and quantification of 1.27 e 4.2 nmol L$^{-1}$, respectively, and a sensitivity of 39.6 A M$^{-1}$ cm$^{-2}$ at 0.0 V vs Ag/AgCl); as electrochromic materials and devices (electrochromic efficiencies of 101.2%, response times lower than 5 s and high stability), and as cathodes in ion-batteries, achieving the amazing capacity of 150 mAh$^{-1}$ at 670 mA g$^{-1}$ discharge rates, and 92% retention after 2 thousand cycles with sodium intercalation$^6$. When combined with TiO$_2$, the CNT/TiO$_2$/PB composite showed to be photoresponsive under illumination, and its utilization as photoanode for a dye-sensitized solar cell was demonstrated by the first time$^7$. Under non-optimized conditions, films achieved photocurrents as high as 600 mA cm$^{-2}$ at oxidized states and 100 mA cm$^{-2}$ at open-circuit potential. The exceptional performances of the composites on these applications arise from the intimate interaction between the components due to the synthesis route, proving that high stabilization is necessary to maximize HCMs properties. Besides the innovative preparation routes, a fully characterization will be demonstrated, and the structure/properties relationship will be discussed. Authors acknowledge CNPq, CAPES and INCT-Nanocarbon for the financial support.

References

Photoelectrochemistry as an efficient technique for the assessment of charge transfer in carbon nanostructure/TiO$_2$ composite electrodes

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Electrooxidation and electroreduction of several standard molecules (H$_2$O$_2$, H$_2$O, methanol) on carbon nanomaterial/TiO$_2$ electrodes is studied by cyclic voltammetry, chronoamperometry and chronopotentiometry, under photoelectrochemical conditions in alkaline medium. The photoelectrochemical results, combined with voltammetric studies in dark conditions, and also with ex-situ physical and chemical characterization techniques (UV-Vis, XPS, AFM), allow a proper enlightenment of the morphology and properties of the films. Furthermore, photoelectrochemical characterization reveals a clear behavior of single-walled carbon nanotubes as electron acceptors$^1$, while reduced graphene oxide acts as a hole acceptor (electron donor). Differences between physical mixing and layer-by-layer configuration in the composite preparation are observed in the case of reduced graphene oxide. The value of photoelectrochemical reactions for unraveling the electron-donor or electron-acceptor character of a given carbon nanomaterial forming composites with TiO$_2$ is demonstrated.

Figure: Cyclic voltammograms in the dark, and under illumination for the studied systems.

References
VACNT growth on Aluminium: towards innovative supercapacitor nanocomposite electrodes

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The aim of this work is to develop innovative electrodes materials with high specific capacitance based on vertically aligned carbon nanotubes (VACNT) to be included in supercapacitors. Catalytic chemical vapor deposition (CCVD) is the best method to grow VACNT but considering the aluminium melting temperature (c.a. 660°C), the synthesis of VACNT on such substrates requires a significant reduction in the growth temperature as compared to conventional substrates [1-2]. Our approach is first to identify the most relevant synthesis parameters to achieve VACNT growth at such a low temperature by using precursor mixtures more favourable for a decomposition at low temperature [3]. Our results show that, with a single-step aerosol assisted CCVD process; it is possible to obtain clean, long and dense VACNTs on Al current collectors, with a growth rate at the best level of the state of the art at such low temperature. VACNT are then used to develop new pseudocapacitive electrode materials based on VACNT modified with Electronic Conducting Polymers (ECP) and/or metal oxide electrodeposited in a controlled manner [4]. Nanocomposite electrodes of poly-3-methylthiophene (P3MT) in ionic liquid and manganese oxide in aqueous media both homogeneously deposited on VACNT have been elaborated and evaluation of storage properties will be presented. Finally, we select best nanocomposite configurations for their upscaling in prototype modules demonstrating the industrial feasibility of the approach.

\textbf{Figure:} VACNT grown on Al current collectors for elaboration of PCE or metal oxide nanocomposite and their upscaling

\textbf{References}

Transport of ions in solution through single-walled carbon nanotubes

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The strong interest for nanofluidics stems from the unique transport phenomena that appear as fluids are confined in nanoscale geometries where surface effects become of central importance. Among the different nanochannels studied so far, single-walled carbon nanotubes (SWCNTs) have gained special attention due to their perfect tubular structure, their high aspect-ratio and their smooth walls in addition to other remarkable mechanical, electronic and optical properties. However, creating and studying SWCNT-based nanofluidic systems free of damage, plugs or leaks remain extremely challenging [1].

We will present ionic current measurements through microfluidic devices containing one or several SWCNTs with diameters between 1.2 to 2 nm showing a linear or, unexpectedly, a voltage-activated I-V dependence [2,3]. Transition from an activated to a linear behavior and stochastic fluctuations between different current levels were notably observed. For linear devices, the high conductance confirmed with different chloride salts indicates that the nanotube/water interface exhibits both a high surface charge density and flow slippage, in agreement with previous reports. In addition, the sublinear dependence of the conductance on the salt concentration points toward a charge-regulation mechanism. Theoretical modelling and computer simulations show that the voltage-activated behavior can be accounted for by local energy barriers along or at the ends of the nanotube. Raman spectroscopy reveals strain fluctuations along the tubes induced by the polymer matrix but displays insufficient doping or variations of doping to account for the apparent surface charge density and energy barriers revealed by ion transport measurements. Finally, experimental evidence points toward chemical moieties at the nanotube mouths as being responsible for the voltage-activated transport of ions through SWCNTs within this diameter range.

References

Carbon Nanohorns and Graphene Quantum Dots: Versatile Materials for Wide Applications

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Nowadays a huge number of different carbon nanomaterials are under studies for obtaining better properties, higher solubility, to attach the desirable molecules to them....in summary to tune them for any possible application. Carbon nanohorns\textsuperscript{1} (CNHs) are horn-shaped tubular structures (similar in structure to single-walled carbon nanotubes) capped with a conical tip. Individual nanohorns tend to cluster and form a globular structure between 80 and 100 nanometres in diameter with the tips of individual nanohorns projecting outward from the centre in all directions. The high purity and the lack of metal particles of produced CNHs is their major advantage compared to carbon nanotubes. On the other hand, graphene quantum dots\textsuperscript{2} (GQDs) are nanometer-sized carbon nanomaterials which present photoluminescent properties due to the quantum confinement and the edge effects.

This communication focuses on the chemical transformations used for modification of carbon nanohorns and the synthesis of graphene quantum dots. It will be also presented some composite hydrogels/GQDs and the effect of the morphology of these carbon nanomaterials on the new materials and how we can take the advantages of the properties of the carbon NANOmaterials in MACROscale systems.

Figure: 1a GQDs, 1b CNHs, 1c Composite Hydrogels/GQDots

The different systems could be modulated in the search of a wide range of applications based on an appropriate surface modification. Any applications require a better understanding of the structure-property correlations. For this reason, a whole set of techniques such as AFM, TEM, SEM, TGA and NMR are often used in our group to characterize the structure of these ensembles. Therefore, in this communication we report our latest development on the functionalization and synthesis of the different materials, with overview at the most important applications, such as materials and medicinal science.

References

Our group has been involved in the organic functionalization of various types of nanocarbons, including carbon nanotubes, fullerenes and, more recently, graphene and carbon nanodots. The chemical functionalization represents an important and versatile tool for tuning the chemical and physical properties of the carbon nanostructures (CNS). For example, chemical functionalization can render CNS dispersible in different solvents.

We are also involved in the interaction of graphene with cells, tissues (as the immune system, nervous system and biological barriers) in order to identify and prevent any possible hazard of graphene and 2D crystals in relation to their physico-chemical properties with a special focus on the most important exposure routes (i.e. lung, skin).

During this talk, we will summarize our most recent results in the chemistry and applications of functionalized CNS.

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Anionic functionalization of nanocarbons: A powerful and versatile tool

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Chemical functionalization of nanocarbons is essential for their applications in various fields such as sensors,[1] biomedical vectors,[2] nanocomposites,[3,4] electronics,[5] energy storage devices[6] and heterogeneous catalysis.[7] Indeed, in their pristine state, carbon nanotubes (CNTs) and graphene sheets tend to stack through π-π stacking which decreases their dispersibility in most organic solvents and water. Therefore, the race for new functionalization protocols featuring high loading, reproducibility, robustness and homogeneity of functions is still on. We recently developed a grafting method using the nucleophilic addition of organolithium compounds followed by electrophilic capture. This method has already been used for the trapping of different electrophiles, either alkanes for dispersion purpose or other dead-end moieties.[8,9] We propose hereby the use of new, easily accessible and atom-economical electrophiles: propargyl bromide,[10] allyl bromide and isopropoxydioxaborolane. These grafted moieties allow the use of a large panel of post-functionalization reactions for introducing a variety of groups of interest. The effectiveness of the first step was confirmed by TGA-MS and Raman analysis. The obtained compounds after post-functionalization were characterized with XPS, which confirmed the presence of desired functions such as immobilized organometallic complex, magnetic nanoparticle precursor, dendrimers or fluorophore. The efficient addition of those derivatives enables the application of our finding in various fields, such as supported homogeneous catalysis or sensor devices.

Figure: Addition of n-Buli on nanocarbons and subsequent electrophilic capture.

References
Functionalization aims at granting compounds with additional features. This is achieved by typically attaching novel groups to the original systems. The aftermath of such process yields complexes whose characteristics often result in more than just the mere sum of the initial products. The specific character of the functionalized structure, moreover, depends upon the way the functionalization strategy has been pursued.

In this contribution, we will focus on the carbon nanotubes functionalization through perylene, an aromatic molecule emitting in the excitation window of most single-walled nanotubes commercially available. We have previously shown that the perylene core of custom surfactants was able to attach though pi-pi stacking interactions onto the sidewall of CNTs while ensuring efficient excitation transfer to the tubes [1,2]. Here we will show how starting from the same elements (perylene and nanotubes) and pursuing different functionalization routines, we achieve systems with different features and functions. In particular, we will compare the characteristics of perylene-comprising polymers wrapped around the tubes with the peculiarities of perylene covalently attached to the nanotubes following a novel conjugation-preserving routine we recently developed [3]. We will highlight the difference among the properties of the final products as well as the applications they would be suitable for.

References
Many methods have been developed to sort SWCNTs based on physical characteristics, typically relying on aggressive and unscalable techniques. Recently, dissolution of nanotubide salts generated by doping with solvated electrons in sodium-ammonia solutions, showed selectivity for the dissolution of specific SWCNTs (diameter or metal/semiconductor)\(^1,2\). In this work we present a careful examination of the purity and selectivity as a function of nanotube charge using a wide range of complementary analytical techniques, including UV-Vis-NIR, photoluminescence and Raman spectroscopy. We find distinct enrichment regimes in the dissolved material as a function of charge added; at low charge the amorphous carbon material is preferentially dissolved, followed by metallic SWCNTs (m-SWCNTs) enrichment as the charge is increased, followed by large diameter semiconducting SWCNTs (sc-SWCNTs) and finally small diameter sc-SWCNTs. When the dissolved fraction yield is maximised, the nanotube distribution matches that of the starting material. Finally in contrast to previous reports, we discover that at the highest levels of charging, there is a reduction in the dissolution of the larger diameter SWCNTs. We explain the rich variety of selective dissolution as a function of charging by a combination of measuring the sodium partitioning between dissolved and undissolved species, considering electronic structure calculation of the SWCNTs and classical Monte Carlo simulations investigating solution energetics. We conclude that the dissolution has a fine balance between the different species’ electron affinities and salting out that occurs at the higher charge densities.

**Figure:** Schematic of the dissolution of a heterogeneous nanotube sample with increasing charge

**References**
Diameter-dependent optical absorption and energy transfer from encapsulated dye molecules to single wall carbon nanotubes

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The hollow core and well-defined diameters of single-walled carbon nanotubes (SWCNTs) allow for creation of unique one-dimensional hybrid structures by encapsulation of various molecules. For instance, we previously demonstrated that in this way dipolar dye molecules can be naturally aligned in an ideal head-to-tail arrangement to create assemblies with a giant total nonlinear optical response.[1] Here, we show that the optical properties of dye molecules encapsulated in SWCNTs can be strongly modulated by the SWCNT diameter, indicating very specific diameter-dependent stacking and interactions of the molecules. The filling is thoroughly characterized by optical absorption, resonant Raman, and two-dimensional infrared photoluminescence excitation (PLE) spectroscopy. Energy transfer probed by PLE spectroscopy shows the absorption spectrum of the dyes to be strongly diameter-dependent, and transient absorption spectroscopy, simultaneously probing the encapsulated dyes and the host SWCNTs, demonstrates sub-picosecond EET from encapsulated molecules to the host SWCNTs. The design of these functional hybrid systems, with tuneable dye absorption, EET depending on the SWCNT diameter and the ability to remove all metallic SWCNTs by subsequent separation, demonstrates potential for implementation in dedicated photo-conversion devices.

Figure: PLE map of dye-filled CNTs. The white ellipse marks the diameter-dependent EET peak positions.

References
Controlled Assembly of Carbon Nanotube Nanohybrids for Single-Molecule Investigations

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We present a universal approach for the generation of multifunctional nanomaterials that employ molecular building blocks assembled on carbon nanotube (CNTs) electrodes. We will demonstrate single-molecule control in the formation of both static and dynamic nanohybrids via the in-solution assembly of classes of molecular materials (organic, inorganic, and biological with promising attributes) to DNA wrapped CNTs.

We will first discuss the in-solution linking of metallic single-walled CNTs (SWCNTs) with different conjugated molecular wires. Conductive atomic force microscopy measurements performed at different locations along the junctions (Figure 1a), allowed us to measure the molecular conductance of a series of oligophenyls, highlighting the potential of an all-carbon based approach for solution-processable molecular electronics.[1]

Furthermore, we produced organic-inorganic heterostructures consisting of single Quantum Dots (QDs) univocally linked at the terminal ends of individual SWCNTs. Monofunctionalized SWCNT-QD heterostructures were obtained and photophysical investigations at the single nanohybrid level showed evidence of electronic coupling (Figure 1b).[2] Moreover, DNA linkers of differing lengths were used as molecular rulers to control the distance, and hence tune the energy/charge transfer between the two nanostructures. A dynamic SWCNT-QD hybrid was assembled using a G-quadruplex DNA linker; the distance between the SWCNT and QD was then be dynamically modulated by the introduction and removal of potassium ions (K⁺).[3] the system was further found to be sensitive to K⁺ concentrations from 1pM to 25mM.

Finally, we will demonstrate the selective electrical addressability of proteins via the use of carbon nanoelectrodes. We investigated different one-to-one CNT-protein configurations and obtained single-molecule evidence of site-specific coupling between SWCNTs and specific proteins of interest (Figure 1c).[4]

By and large, we demonstrate a novel in-solution approach for the assembly of individual molecules on carbon nanotube electrodes with single-molecule control. The assembled heterostructures show promise in the fabrication of solution-processable nanoelectronic devices for applications that range from molecular electronics to sensing.

References

Figure 1 Examples of the different CNT-based nanohybrids assembled
Rational design of graphene - polymer interface

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The interface in between the components of the composite strongly affects its properties Therefore it is of crucial importance to gain a control of the interfaces and modify them in a desired way. In graphene-based composites, the single layer of the graphene itself represents the interface. The graphene can be chemically functionalized, which provides an efficient tool for tuning of such an interface.

For the optimization of the interface one needs to inspect the properties of the interface rigorously. However, in the case of bulk composites it is very difficult to access the interface by available experimental methods. Here we prepared heterostructures composed of graphene grown by chemical vapor deposition and the Poly(3,4-ethylenedioxythiophene) (PEDOT). The graphene was first functionalized by sulfonate and subsequently oxidative polymerization of EDOT has been performed on the functionalized graphene surface. This approach enabled to control each preparation step and to study how the properties of graphene interface are changing during the modification. Using patterned substrates we demonstrate that the proper design of the graphene interface leads to selective growth of the polymer on the functionalized graphene. In addition, the functionalized graphene served for charge compensation and stabilization of the PEDOT. Such a design also leads to superior electronic communication between graphene and the polymer.

\textbf{Figure}: Preparation of the graphene –PEDOT heterostructure.

\textbf{References}


A comparative study was conducted on composite materials having various nanocarbon fillers of different dimensionalities, namely, 1D carbon nanotubes (CNTs), 2D graphite nanoplates (GNPs), and 3D graphite. Comprehensive mechanical, electrical and rheological studies illustrated the complexity of selecting the optimal nanocarbon filler. We found that the mechanical performance of the composite to be optimal near the percolation threshold concentration of the filler for all the nanocarbons. The 1D CNTs strongly affected the electrical conductivity and reinforcement of the composite, yielding a narrow range of optimal performance at the lowest filler concentration (0.15 wt%), albeit at the cost of high viscosity. The 2D GNP s demonstrated a wider range of reinforcement with a milder influence on the viscosity at a moderate GNP concentration (1 wt%). The 3D graphite filler exhibited similar behavior to that of GNPs, although at a much higher concentration (25 wt%). We introduced a robustness factor as a measure of the filler concentration range at which a valuable reinforcing effect is achieved; this factor increases with the filler dimensionality. These contradicting dimensionality effects are condensed into a figure of merit that takes into account the rheological effect, the mechanical enhancement, and the filler concentration and robustness.


The optimal filler road

![Diagram of filler road with 1D, 2D, and 3D fillers, highlighting intrinsic viscosity, percolation threshold, robustness, and optimal concentration areas.](image-url)
Percolation in Carbon Nanotube-Composites

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The design of polymer composites with conducting fillers like carbon nanotubes has a wide range of potential applications in the electronics and photovoltaics industry. Above a critical particle concentration called the percolation threshold, the nanotubes start forming a system-spanning network which strongly affects the macroscopic mechanical and transport properties of the material.[1]

The percolation threshold of a polydisperse system has long been known to scale with the inverse weight-average of the particle length distribution.[2] Invoking connectedness percolation theory, we find that this relation does not generally hold anymore in the presence of external alignment fields, such as electric fields, elongational flow fields and molecular fields provided by nematic liquid-crystalline hosts.[3]

It turns out that polydispersity, which is typically seen as a handicap, can actually aid the formation of nanotube networks within the polymer matrix. As a result, the percolation threshold can be substantially lowered just by tuning the formulation of the composite material.

\textbf{Figure}: The conductivity of a nanocomposite material increases by orders of magnitude as the critical filler concentration, called the percolation threshold, is reached.

\textbf{References}

Characterization of graphene based nanocomposites for potential use in dental/biomedical applications

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Despite some challenges and the fact that carbon nanotubes-polymer composites are sometimes better in some particular performance, graphene-polymer composites may have wide applications in dentistry due to their outstanding properties and the availability of graphene in a large quantity and at low cost. One of the main problems, for patients, associated with dental-polymers is that of location. This stems from the fact they must be situated within the mouth and this proves to be an extremely demanding setting, where exposure to moisture, high temperatures, and abrasion from tooth brushes plus intake of food all have to be dealt with. These conditions can lead to complications such as mechanical failures which negate clinical success and over time mandates remedial work for restoration with associated cost and inconvenience. Graphene has potential applications in dental-polymer materials as it has the required mechanical properties as well as being biocompatible. Here we present new work into the application of graphene for the fabrication of potential dental-polymer materials (figure 1).

\textbf{Figure:} Helium Ion Micrograph of Few-Layer Graphene.
Self-Assembled Poly (3-hexylthiophene) Nanoparticles / Graphene Oxide Donor-Acceptor Hybrids with Tunable Optoelectronic Properties

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Self-assembling strategies have attracted widespread attention in order to create nanostructured charge transfer complexes.\textsuperscript{1} Nanoparticles derived from conjugated polymers play a crucial role in case of self-assembly processes due to their conjugated aromatic structure and encapsulation ability.\textsuperscript{1,2} Poly-3-hexyl thiophene (P3HT), the archetype of conducting polymers, is characterized by the presence of quasi-crystalline domains defining the electro-optical properties. However, reliable control of these nanoscale aggregates plays an essential role to tune charge transport and charge separation properties.\textsuperscript{3}

In this work, we report the self-assembly of novel conjugated polymer nanoparticle/graphene oxide (P3HT\textsubscript{NPs}/GO) composites using a re-precipitation technique. The resulting composites are stable in aqueous dispersions and can be processed directly instead of usual hazardous chlorinated solvents. Photophysical studies reveal that the presence of GO significantly changes the chain organization leading to internal P3HT\textsubscript{NPs} aggregate structure exhibiting very low excitonic coupling interactions. Meanwhile, Raman spectroscopy and cyclic voltammetry reveal that the observed changes in the composites are accompanied by a charge transfer process taking place at the interface between P3HT\textsubscript{NPs} and the GO sheets.

Our synthesis approach leading to novel P3HT\textsubscript{NPs}/GO donor-acceptor hybrid assemblies with tuneable optoelectronic properties and environmental-friendly processing characteristics thus may provide a base for the design of improved functional nanomaterials of interest for thin film photovoltaic or sensing devices.\textsuperscript{4}

References
Nanoscale Infrared Identification and Mapping of Chemical Functional Groups on Graphene

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Typical chemical characterisation of two-dimensional materials (2DMs) often relies on bulk techniques: elemental analysis, FTIR and XPS being common examples. These techniques, combined with nano-scale resolution topological measurements by AFM, allow for elucidation of chemical structure, albeit indirectly. Raman spectroscopy, ubiquitously used when analysing graphene, has a lateral resolution of >500 nm and often can only give detailed information pertaining to polarisable bonding.

Here, we will report results on direct chemical mapping of functionalised monolayer reduced graphene oxide flakes at <30 nm resolutions. This is now possible using AFM coupled infrared spectroscopy, bypassing the diffraction limitations on the spatial resolution of FTIR. This technique has previously been applied to biological materials \cite{1} and self-assembled monolayers \cite{2} amongst many others. Imaging resolutions between 10-100 nm can routinely be achieved, but this technique is yet to be applied to 2DMs.

In analysing a system comprised of pyrene-derived molecules onto reduced graphene oxide flakes, we will show that Raman mapping is not able to distinguish between the different chemical functional groups present on the basal plane. By exciting the flake with a tuneable infrared source, and using an AFM probe to detect thermal expansion, a nanoscale IR spectrum of each surface can be found using AFM-IR. These spectra can be directly correlated to the bulk FTIR spectrum of the pyrene molecules. Further, by mapping the flake at responsive wavelengths, we can report chemical imaging far below the diffraction limit of IR photons, at up to 25 nm resolution.

**Figure:** a Graphical schematic of AFM-IR technique, imaging a pyrene-functionalised graphene surface, b AFM-IR map of flake response at 1036 cm\(^{-1}\) (2 µm scale)

**References**

Nanoscale Imaging of Luminescent Excitons in sp³-doped Single Walled Carbon Nanotubes

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Exciton localization in luminescing carbon nanotubes is subject of intense investigations due to its impact on nanotube emission properties. Using super-resolution microscopy based on single emitter localization, I will present our current efforts to study luminescent defect localization in long and ultra-short carbon nanotube having controlled chemical and morphological properties [1]. We developed an analysis based on super-resolution imaging, which directly reveals that excitons are localized at defect sites in long and ultra-short single walled carbon nanotubes. In particular, we demonstrate that bright photoluminescence can be recovered upon functionalization of otherwise non-luminescent ultrashort carbon nanotubes having dimensions shorter that the exciton diffusion range. The demonstration and control of the emission properties of sp³-doped Single Walled Carbon Nanotubes should find many applications in various domains of research including quantum optics and bioimaging.

References
Enhancing the Infrared Response of Carbon Nanotubes From Dye interactions

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Middle infrared response on a carbon nanotube is very weak because this homonuclear allotrope of carbon does not bear permanent dipoles. Nevertheless, a significant number of infrared phonons are predicted by the group theory. Encapsulating molecules inside nanotubes (called hybrid nanotubes in the following) is a common strategy to add new functionalities. The one-dimensional nature of single-walled carbon nanotubes (SWCNT) internal channels has been exploited here to induce a molecular order and specific interactions which are dependent of the size of the nano container (figure).

Here we report the discovery of a strong dependence on the infrared response of the hybrid nanotube due to confinement effect when dimethylquaterthiophenes are encapsulated inside SWCNTs\textsuperscript{1}. Results are compared to experiments performed on nanotubes where dyes are \(\pi\)-stacked at the outer surface. Surprisingly, the confinement properties lead to an exaltation of the infrared absorption response in the carbon nanotubes from dye molecule interactions. Thanks to the comparison between the experimental investigations and DFT calculations, we elucidate the origin of the large enhancement of this infrared absorption and demonstrate that interactions between conjugated oligomers and nanotubes can be probed.

\textbf{Figure:} Electronic charge density as the function of size of the nano container controlling the molecular order

\textbf{References}
Tuesday, April 24th 2018
Applications of nitrogen functionalized carbon nanotubes

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Nitrogen-functionalized graphene and carbon nanotubes have experienced a tremendous development over the last decade, and applications of such functional centres can be found in a wide field of areas, such as catalysis, energy storage, gas sensors as well as biomedical applications. In my talk, I will summarize the early and latest achievements in this field, including both our own research and others. I will briefly introduce the fundamentals on the chemical stability and reactivity of the various nitrogen functionalities in tubes with different diameters, ranging from narrow diameter single walled tubes over larger diameter multi-walled carbon nanotubes towards the extreme case of graphene sheets. I will then summarize the latest finding on various applications, with an emphasis on catalytic applications for fuel cells, Li-ion batteries and electrolysis.

\textbf{Figure:} Nitrogen functionalities introduced in single-walled carbon nanotubes of various types and doping level.
Covalent and Supramolecular Junctions Between Graphene Nanoflakes: Enhancement of Graphene Nanopapers Thermal Conductivity

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The advances made in nanotechnology have provided a strong impetus for the development of unconventional materials by engineering appropriate building blocks. In this context, graphene and its derivatives, owing to their exceptional intrinsic thermal conductivity, have recently shown great potential as basic building blocks to create macroscopic assembled materials with unique thermal properties. Specifically, large-area freestanding graphene “paper-like” materials have emerged as promising materials to address heat dissipation problems in practical applications. Nevertheless, the thermal conductivity of such networks is strongly limited by the inefficiency of the contact between graphene sheets.

The aim of this work is to design and synthesize both covalent and supramolecular junctions between graphene nanoflakes to create graphene nanopapers with inherently low contact thermal resistance between nanoparticles. The covalent junctions were synthesized by the edge-selective functionalization of graphene nanoflakes to preserve the high conductivity associated to defect-free $sp^2$ structure. The successful functionalization at the edges is confirmed by XPS and Raman spectroscopy. These covalent junctions between graphene nanoflakes lead to a 20% and 150% enhancement of the in-plane and cross-plane thermal conductivity, respectively. The supramolecular junctions between graphene nanoflakes were created using bispyrene derivatives. Here, changes on the thermal conductivity of graphene nanopapers were found to be highly influenced by the organization and assembly of the bispyrene molecules on the surface of the nanoparticles.

Figure: a) Cross-sectional FESEM images of graphene nanopaper (GN) and GN with covalent junctions (CJ-GN). b) In-plane and cross-plane thermal conductivity of GN and CJ-GN.

References
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We investigate the impact of nanocarbon supports (MWNT, GO) on the functional properties of adsorbent nanoparticles (incl. h-BN, MgAl-LDH, NiAl-LDH) for the commercially important desulfurization of hydrocarbon fuels (Fig (a)) and for CO$_2$ adsorption from air. [2],[3] The incorporation of small amounts of 1D and/or 2D nanocarbons into adsorbent nanoparticle powders markedly improves both liquid-phase and gas-phase adsorption in terms of uptake and recyclability while maintaining excellent selectivity. Hybrid MWNT/GO networks are shown to be considerably more effective supports than pure CNT or GO due to a reciprocal spacing effect. Supporting adsorbents onto nanocarbon aerogels, i.e. onto well-structured 3D nanocarbon networks, leads to further significant improvements in adsorption capacity and faster uptake kinetics.

Further, it is explored how the unique properties of 3D nanocarbon networks can be exploited to provide additional functionality beyond the benefits of conventional porous supports. Specifically, it was investigated how the nanocarbons’ unique conductive properties can be utilized for direct electrical heating (Fig (b)). Joule heating studies of reduced graphene oxide (rGO) and MWNT aerogels allowed quantification and comparison of key metrics (heating rates, power density, thermal conductivity), demonstrating very fast and uniform Joule heating of the 3D nanocarbon networks at relatively low energy consumption [1]. These excellent Joule heating properties will provide considerable benefits in context of nanocarbon-supported functional nanoparticles, e.g. by enabling fast, uniform and energy-efficient thermal regeneration of adsorbent nanoparticles.

Figure: (a) LDH/nanocarbon hybrid materials for desulfurization applications (LDH=Layered Double Hydroxide), (b) Schematic of Joule-heated nanocarbon aerogel.

References
We report on plasmonic hybrid thin film structures obtained by sandwiching a single-layer (SLG) or bilayer graphene (BLG) grown by chemical vapor deposition (CVD) between plasmonic (Au, Ag) nanogranular films and various substrates: flat - SiO$_2$(300 nm) on Si and corrugated - SiO$_2$(300 nm) on Si decorated with nanoparticles of various concentrations and sizes. The Raman micro-spectroscopy and atomic force microscopy (AFM) study was carried out after each deposition step. Typical fingerprints of the substrate-driven topography of SLG and BLG were identified as substantial contributions to the principal Raman active modes (G and G’), which show dominant (G$_1$, G’$_1$) and red-shifted (G$_2$, G’$_2$) subbands; the distribution of doping, strain, and level of corrugation in the SLG and BLG were evaluated from the Raman data. The graphene–plasmonic metal interactions resulted in strong enhancement of the Raman signal of the SLG and BLG, and further broadening of the G and the 2D modes. Various scenarios responsible for the observed effects are discussed: graphene–plasmon interaction, charge transfer between the metal and the graphene, and selective enhancement at the lattice and topographic defects. The distribution of hot-spots was found to be dependent on the topography of the graphene. The graphene–plasmonic nanogranular thin film hybrids have demonstrated promising performance as surface-enhanced Raman scattering platforms for in situ detection of various species.

**Figure:** Schematic representation and surface topography obtained by AFM (area 3 x 3 $\mu$m$^2$) of the graphene–gold thin film hybrid on flat (left) and corrugated substrate (right).

**References**
Carbon Waters: Commercialization of surfactant-free single layer graphene in water

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Full exfoliation of graphite to form negatively charged graphene (graphenide) flakes in solution can be achieved by dissolving graphite intercalation compounds in low boiling point aprotic organic solvents such as THF.\cite{1} Unfortunately, graphenide solutions are solely stable under inert conditions and therefore hardly scalable for an industrial application. A new procedure for manufacturing stable single layer graphene dispersed in water (EdG) by simply transferring graphenide solutions into degassed water and evaporating the solvent has been developed.\cite{2-4} With 1 to 3 layers and a low amount of defects \cite{5} EdG exhibits exceptional properties compared to other commercially available graphene dispersions.

The simple procedure in combination with the outstanding properties of EdG led Carlos Drummond and Alain Pénicaud to consider an industrial application and the creation of a start-up company. After 2 years of development and funding from different public organization such as CNRS and the SATT Aquitaine the company Carbon Waters has been founded in November 2017. Its aim is to develop a range of high added value products for R&D and industrial applications.

References

Chemical synthesis of graphene from benzene at liquid-liquid interface

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The development of methodologies that allow the production of graphene with high quality and scalable is still considered a great challenge. The bottom up approach offers a good opportunity to manipulate the size, shape, edge and composition of the final material from appropriate precursors. Thus, chemically synthesized graphene from molecular precursors is a promisor methodology to obtaining graphene on a large scale and with high structural control. However, the insolubility of the species involved in the reactive medium as the graphene sheets become large is one of the main problem associated with chemical synthesis of graphene. Aiming an alternative to solve this problem, a new chemical route to synthesize graphene was developed in our research group, based on reactions at liquid-liquid (L/L) interfaces. The route is based on the polymerization of benzene to poly-paraphenylene using solid FeCl₃, followed by the formation of lateral chains and conversion to graphene through a dehydrogenation reaction. The key-step is the presence of a L/L interface that stabilizes the large molecules and allows the heterogeneous reaction to occur. The present work aims to study variables of chemical synthesis of graphene from benzene at L/L interfaces to control every step of this process, in order to improve the quality of the obtained graphene; to identify the side-products; and to understand the mechanism of formation of the chemically-synthesized graphene. The samples have been prepared in a benzene/water system in which a fixed amount of anhydrous FeCl₃ was continuously added. The film spontaneously obtained at the liquid interface was deposited over different ordinary substrates and characterized by Raman spectroscopy, SEM, X-ray diffraction, XPS and AFM (Figure 1).

Fig. 1: Representative Raman spectrum (A), SEM (B) and AFM (C) images of the synthesized graphene.

These techniques allows the identification of high-quality graphene (mono-, bi- and trilayer) with average area of 2.6 µm², as well as amorphous carbon and iron oxide (hematite and magnetite) as side-products. A fully mechanism, independent of the benzene polymerization, have been proposed. The interfacial route is new, innovative, versatile and very efficient way to chemically-obtained graphene. This work reports the largest graphene sheets ever obtained from molecular precursors. Authors acknowledge CNPq, INCT-Carbon Nanomaterials, F. Araucária, CAPES for financial support.

References

Nanoring / fullerene complexation
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Cycloparaphenylenes ([n]CPPs) represent the shortest possible segment of (n,n) armchair carbon nanotubes (CNTs), and as such may represent a new route to producing chirally selected carbon nanotubes \textsuperscript{1,2}. Current approaches for this envisage controlling synthesis of uniform-diameter single chirality CNTs using CPPs as templates, which has met with limited success\textsuperscript{3}. At the same time complexes of fullerenes with CPPs have been reported, highlighting a high size selectivity of the CPPs to the specific fullerene.

In the current study we explore a new approach, namely using covalent- and non-covalent self-assembly of either functionalized CPPs, or CPP-C\textsubscript{60} hybrid systems, to create new types of “poly-CPP-nanotubes”. These new materials, while also adopting a controlled chirality tubular morphology, show distinctly different chemical, mechanical, electronic and optical behavior to conventional carbon nanotubes.

The first of these families involves chemical cross-linking between neighbouring CPPs using fullerenes as alignment templates. The resultant poly-CPP-nanotubes share some properties with conjugated polymers, notably the ability to add functionality and control electronic properties through functionalisation control. The second family using self-assembly stacking between C\textsubscript{60} and different sizes of [6]-, [8]-, [10]-CPPs to form 1D and 2D networks. While the study is driven by our theoretical modelling, we successfully demonstrate via a joint experimental-theoretical study the first steps towards their production, namely trapping of 2CPP rings around a fullerene dimer (C\textsubscript{59}N)\textsubscript{2}.

References
Can rGO Look Like Pristine Graphene?

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Since its discovery, many studies seeking the application of graphene-based materials have been carried out, mainly focusing in overcome challenges related to the synthesis of good quality materials in a large-scale production.1 Chemical exfoliation is one of the most promising routes to obtain graphene in large amounts, being based in 3 steps:(i) the oxidation of graphite to produce the graphite oxide, followed by (ii) the dispersion of this material in different solvents, in order to produce an aqueous suspension of graphene oxide and, finally, (iii) the suspension reduction that results in the reduced graphene oxide (rGO), which is a graphene derivative that presents many defects and vacancies in its structure, implying in the decrease of some properties, e.g. electrical and thermal conductivity, transmittance, etc. Several works have been reporting the synthesis of rGO approaching different variables during the process, aiming to control the emergence of these defects. However, most of reported products still present a very defective structure, both at the basal plane and at the edges. Based on that, we present a very simple approach to obtain low defective rGO, based on a strict control of the synthesis parameters, such as the reaction temperature and the chemical addition ratio during the oxidation process of graphite. Raman spectra showed the characteristic bands of graphene-based materials. Besides, through the ratio of the intensity of D and G bands (I\textsubscript{D}/I\textsubscript{G}) we were able to confirm the production of a high quality rGO, which presented very low ratios (average of 0.27) mainly in the basal plane, confirming its preservation. Figure 1 presents a comparison between Raman results of a common standard rGO (without parameter control) and the high quality rGO of this work. The distance of defects (L\textsubscript{D}) was also estimated, resulting in values higher than 20 nm, which is comparable to CVD graphene. Thin films of rGO deposited over PET, a flexible substrate, presented high transmittance (75%) at 550 nm and low values of sheet resistance, being below 300 ohm/square. Thus, we were able to produce rGO with characteristics similar to pristine graphene, through a simple route and high yield, promising to be employed in different graphene-based flexible devices. Authors acknowledge FAPESP, MackPesquisa, CNPq and INCT of Carbon Nanomaterials.

Figure 1 – Raman mappings along with the indicated spectra of standard and high quality rGO.

References
Tailoring and assembling polymer wrapped carbon nanotubes for electronics and photovoltaics

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This presentation will detail our recent efforts on manipulating and assembling semiconducting carbon nanotubes wrapped by conjugated polymers to advance the performance of field effect transistors and photovoltaic solar cell and photodetector devices fabricated from nanotubes.

With regards to electronics, recent calculations have indicated that aligned arrays of semiconducting carbon nanotubes will outperform conventional materials in short-channel, aggressively scaled field effect transistors like those used in semiconductor logic and high frequency amplifier technologies. We have developed a self-assembly approach that enables the wafer-scale deposition of arrays of well-aligned nanotubes called floating evaporative self-assembly (FESA). In FESA, a layer of polymer wrapped nanotubes in organic solvent is cast onto an aqueous sub-phase, and the nanotubes spontaneously segregate at the organic/water interface. The aligned nanotubes deposit onto a substrate as it is withdrawn through the interface. We have realized nearly ballistic nanotube array field effect transistors at a density of 50 nanotubes µm\(^{-1}\) that exhibit on-state conductance as high as 0.46 \(G_0\) per nanotube where \(G_0\) is the quantum conductance limit. The saturated on-state current density reaches 900 µA µm\(^{-1}\) and is similar to or exceeds Si FETs when compared at equivalent gate oxide thickness, off-state current density, and channel length.[1]

Nanotube photovoltaics is a promising direction because of nanotubes' tunable bandgaps (0.5 – 1.5 eV), strong optical absorptivity, and ultrafast energy transport. We have discovered how to efficiently harvest excitons from polymer wrapped nanotubes by interfacing them with C\(_{60}\) fullerenes to form a type-II heterojunction with band offsets that exceed the exciton binding energy (internal quantum efficiency for electron transfer is ~90%). The net power conversion efficiency, however, has been limited to a few percent due to poor, short range exciton migration in thicker films. We have recently shown that this short range migration can be attributed, in large-part, to processing-induced defects through experiments in which defects have been intentionally added to nanotubes and experiments in which processing intensity has been reduced. We have developed a diffusion limited defect quenching Monte Carlo model that quantifies that significant gains in exciton harvesting efficiency can be realized if more pristine, longer s-SWCNTs are realized.[2]

If time allows, the bottom-up synthesis and seeded synthesis of narrow, semiconducting, armchair graphene nanoribbons via anisotropic chemical vapor deposition on Ge(001) will also be presented.[3]

References

Graphene foam composites for high performance Li ion batteries

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Ultra-light 3D graphene structures called graphene foams may be produced top-down via chemical exfoliation methods,\cite{1} but they suffer from relatively poor electrical conductivity due to oxidation defects and poor mechanical robustness. Alternatively, high quality graphene foams with very high conductivity may be produced bottom-up via Chemical Vapour Deposition.\cite{2} These unique structures have been investigated for a wide range of applications, such as electrodes in batteries and supercapacitors, biological scaffolds, sensing, and many others.

We describe our research into using these graphene foams in supercapacitors and batteries. Alone, the capacitance of the foams is very low, but it may be significantly improved by the addition of a coating of metal oxide nanoparticles such as Fe\textsubscript{2}O\textsubscript{3}. We developed and optimised an electrochemical procedure for the deposition of Fe\textsubscript{2}O\textsubscript{3} nanowalls uniformly across the whole structure. In this way, we could reach a capacity of over 300 F/g. However, the capacity significantly decreased over extended cycling due to detachment of and damage to the metal oxide layer. To overcome this problem, we added a protective layer of electrochemically-exfoliated graphene oxide (EGO, Figure 1), which successfully stabilised the structure during cycling. Using this technique, it will be possible to produce optimised graphene foam composites with very high capacities and even hybrid structures using other metal oxides. In addition, we were able to further increase the areal capacity of the composites by using EGO as a spacer for adding more layers of oxide nanoparticles.

\begin{figure}[h]
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\caption{Schematic illustration of the preparation process for multilayer EGO-Fe\textsubscript{2}O\textsubscript{3}-GF architectures}
\end{figure}

\textbf{References}

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Carbon nanotube/Nano-graphene Conductive Additives in Lithium Ion Batteries

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Lithium ion batteries (LIBs) have grown to become the main power storage solution for 3C technologies and electrical vehicles since they were first successful commercialized by Sony in 1991. LIBs generally produce an average cell voltage of 3.7-4.2 V and operate on the relatively simple principle of reversible intercalation of Li ions in the cathode and anode. The electric energy is stored or released by repeating these intercalation reactions reversibly. The common used materials for the cathode are lithium metal oxides and some forms of carbon are generally used for the anode. Conductive additives, such as carbon black, graphite, are necessary in the cathode to improve the conductivity of lithium metal oxides. Recently, carbon nanotube (CNT) and graphene have been considered as good opportunities for LIBs additives due to their excellent conductivities.

Graphene New Materials Technology company, based in Shenzhen, China, mainly works on the conductive additives and new nano Si/C anode materials in LIBs. We report here a new conductive additive using CNT/nano-graphene mixture to improve the performance of LIBs using LiFePO₄ (LFP) as cathode. The mixture of CNT/nano-graphene with carbon black constitutes a highly conductive network (Figure 1a) on LFP surface by “point-line-surface” structure which helps lithium ions transfer through the network rapidly to access LFP materials. Charge/discharge curves of LFP/Li metal cell are shown in Figure 1b.

References
Graphitic Intercalation Compounds: a Versatile Nano-Template for the Synthesis of Efficient Multi-Functional Electrocatalysts

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Nano carbon composite materials, especially based on transition metals and metal oxides,\textsuperscript{1} are promising materials for electro catalytic applications related to their high surface areas, electrical conductivity and stability in acidic or basic aqueous solutions.\textsuperscript{2} Graphite can be intercalated by potassium forming a graphite intercalation compound (GIC) of defined stages. GICs can be readily exfoliated to monolayer graphene in organic solvents solely by stirring. These graphenide solutions are composed of charged graphene layers and are thermodynamically stable.\textsuperscript{3,4} In analogy to large flake size graphite, graphitic nano carbons with lateral sizes below 50 nm can also be intercalated successfully and can be dissolved in absolute organic solvents. Graphenide solutions have been used in a variety of different applications e.g. to generate transparent conductive films, quantum dots, and been used to graft functional moieties covalently to the carbon framework.\textsuperscript{6} The advantages of using graphenides as reduction reagent in nanoparticle synthesis are : \textit{i}) graphenide solutions are strong reducing agents and no additional reducing agent is needed, \textit{ii}) the redox reaction takes place in close proximity of the carbon lattice and the decoration of the carbon framework thus proceeds efficiently, \textit{iii}) the amount of reduction agent can be controlled by the concentration of the respective graphenide solution used, \textit{iv}) the by-product of the reaction is only the respective potassium salt, which can be removed easily. The resulting composite materials are interesting and promising earth abundant electrocatalysts, due to their structure, small size, morphology and conductive framework. These nanocarbon / metal nanoparticle composite materials exhibit high bifunctional electro catalytic activity towards ORR and OER as well as long term stability.\textsuperscript{7}

References
Inhalation toxicity of carbon-based nanomaterials

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Most nanoparticles are more hazardous (by mass) by inhalation compared to larger particles with the same chemical composition. Carbon-based nanomaterials such as carbon nanotubes and graphene nanomaterials constitute examples of nanomaterials with the same chemical composition and different shapes. The black pigment carbon black consists of carbon nanoparticles and is a high volume nanomaterial. It is inflammogenic and mutagenic by inhalation and is classified as possibly carcinogenic by IARC. Carbon nanotubes vary in several physicochemical properties including length, diameter, surface area, surface modification, and type and level of impurities, all of which may potentially affect toxicity. Inhalation of carbon nanotubes induces sustained inflammation with low no-effect-levels. One specific long and thick multiwalled carbon nanotube has been classified as possibly carcinogenic by IARC and was recently shown to induce cancer by inhalation [1]. Other long and thick but not short and thin carbon nanotubes have been shown to be carcinogenic. Pulmonary exposure to carbon nanotubes induce long lasting pulmonary acute phase response [2], an established risk factor for cardiovascular disease in humans. Physico-chemical properties of carbon nanotubes have been shown to predict pulmonary toxicity. Carbon nanotube diameter correlated positively with DNA strand breaks (a risk marker for cancer), whereas BET surface area was a predictor of pulmonary inflammation [3]. The inhalation toxicity of graphene nanomaterials is much less investigated and many studies did not include physicochemical characterization of the studied materials. However, studies of pulmonary toxicity of graphene nanomaterials have suggested that graphene oxide and reduced graphene oxide both induce DNA strand breaks and long lasting inflammation following pulmonary exposure in mice [4].

In conclusion, there is evidence that all three carbon-based nanomaterials induce genotoxicity and inflammation following airway exposure.

Reference List


Surface area is the best metric for the evaluation of the potential ecotoxicity of nanocarbons

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Carbon nanotubes (CNTs) are often the emblematic figure of nanoparticles in general, promoted by many for their exceptional physico-chemical properties which have led to applications in almost all fields, and criticized by the others for their potential toxicity toward human health and the environment.

We will focus here on the question of the choice of the most appropriate metric in order to allow the comparison of the results obtained for different kinds of nanocarbons (different carbon nanotubes, few-layer graphene, nanodiamonds) as well as a sample of carbon black, in the case of their environmental impact [1]. Experimental results obtained using an amphibian larvae model (xenopus), very relevant for the aquatic compartment and especially the water column, clearly show that only the specific surface area allows the plot of all the data on the same "master curve" (Fig. 1), even making possible to become predictive and to propose a "Surface effective concentration" SEC50. These results have also been recently extended to the comparison of nanocarbons dispersed in water by either covalent (oxidation) or non-covalent (addition of a surfactant) functionalisation, confirming that the specific surface area is still the relevant parameter. We will also very briefly describe our most recent work related to the "safe by design" approach in the specific case of GO.

![Figure 1: Surface area allows the comparison of all nanocarbons (0D, 1D, 2D).](image)

\textbf{References}


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Eco-sustainable GO-polysulfone composites for water purification

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The daily use of organic molecules as industrial additives is leading to a high occurrence of organic contaminants in urban wastewater system. These substances, known as Emerging Organic Contaminants (EOCs), are not yet regulated and are not completely removed during conventional wastewater treatments, consequently they are able to enter ground and even drinking water. Due to their potential adverse effect even at low concentrations, new treatments are highly desirable to minimize their impact on ecosystem.

Here, we report the preparation and characterization of a new polysulfone-graphene oxide composite (PS-GO), and its application as adsorbent for the removal of seven selected EOCs, including personal care products and pharmaceuticals, in mixture from tap water. PS-GO membranes were immersed in the EOCs spiked tap water and the removal selectivity and efficiency was monitored by HPLC. Benzophenone-3, ofloxacin, rhodamine b, diclofenac and triton X100 were removed with efficiency higher than 90% in the range of concentration 0.5-5 mg/L after 4 hours of treatment. The mechanism of EOC adsorption on PS-GO was rationalized in terms of an interplay of molecular hydrophobicity and dipole moment. PS-GO shows improved performance with respect to PS and GO separately, in particular for carbamazepine and diclofenac, enhancements in the range 300-600% and 300-800%, depending on pH, were found. In addition, PS-GO favorably competed with commercial activated carbon under the same experimental conditions at low contact time (1-4 hs).

References

Notes
Wednesday, April 25th
DNA and carbon nanotube form a hybrid via noncovalent interactions. The hybrid structure is dependent on both the chirality of nanotube and the sequence of DNA. In this talk, I will provide an overview of our effort in the past fifteen years or so to develop a comprehensive method to sort carbon nanotubes by their electronic structures using the DNA-carbon nanotube hybrids. I will then present two recent progresses we have made: 1. aqueous two-phase extraction method as a faster and more general method for carbon nanotube sorting; 2. new experimental and computational methods for selecting specific DNA sequences that form structurally ordered DNA-carbon nanotube hybrids.
When graphene meets small interference RNA

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Gene therapy is one of the most promising therapeutic modalities to treat diseases like cancer [1]. This therapy is based on the delivery of a variety of exogenous nucleic acids such as plasmid DNA, mRNA, siRNA, microRNA or antisense oligonucleotides. In particular, gene silencing using siRNA is gaining a lot of interest for the specific gene knockdown [2]. Because of its unique chemico physical and structural properties, graphene oxide is currently explored as a potential vector in gene delivery [3]. Generally, the interactions between graphene oxide and single strand DNA or RNA are attributed either to the $\pi-\pi$ stacking or hydrogen bonding [4]. Less studies on the complexation of double stranded DNA or RNA with graphene oxide are instead available. Understanding thoroughly the interactions between double strand RNA and graphene oxide remains uncertain. In this presentation, I will focus on the evaluation of the binding properties between siRNA and graphene oxide [5]. The conformational changes of siRNA induced by graphene oxide of two different lateral sizes and with various amount of oxygenated functional groups have been analysed using different spectroscopic techniques. In addition, the capacity of the complexes to penetrate into the cells will be presented. We believed that our results will improve our understanding of the behaviour of the siRNA/graphene oxide complexes, and thus facilitate the design of appropriate bio/nanointerfaces and new efficient gene silencing systems.

References
Non-Oxidized Graphene for Bioapplications: Preparation, Cytotoxicity and Integration in Hydrogels

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Graphene has emerged as a new material, with outstanding mechanical and electronic properties that will permit a broad range of applications, from microelectronics to composite or even medicine. Although there has been a huge effort directed in the area of nanomedicine, biomedical applications of graphene derivatives have, so far, mainly focused on graphene oxide and reduced graphene oxide. The main reason for this fact is the difficulty to obtain pristine graphene flakes, directly in water or in culture media, due to the intrinsic hydrophobicity of this material.

Our group have recently described an interesting approach for the preparation of stable dispersions of graphene in water, without detergents or any other additives, driven by an easy and eco-friendly ball milling approach.\textsuperscript{1} These aqueous suspensions can be rapidly frozen and, subsequently, lyophilized giving rise to a very soft and low-density black powder.\textsuperscript{2} Powders of graphene can be safely stored or shipped and they can be readily dispersed in culture media within the presence or absence of serum and antibiotics.

During this talk, we will discuss (i) optimized ways to generate graphene dispersions in culture media; (ii) studies of interaction of so-prepared solutions with cells; (ii) the use of graphene in hybrid hydrogels for drug delivery purposes\textsuperscript{3} and for 3D cell culture media.\textsuperscript{4}

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Carbon nanotube membranes as neuronal substrates

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Thanks to their unique structure and their outstanding electrical and mechanical properties,[1] carbon nanotubes (CNTs) are very promising materials for a wide range of applications, including those in the biomedical field.[2,3] In particular, CNTs have attracted tremendous attention as potential substrates for cell culture. Their extra ordinary ability to transport electrons along with their flexible, strong, nano-sized form, makes them the perfect material to interface neurons and stimulate neuronal activity.[4,5] CNTs can be organized in scaffolds made up of small fibers or tubes, which are able to promote growth and differentiation of neurons; besides neuronal adhesion, survival, and growth can be modulated through chemical modification of CNTs.[6,7] These features make CNTs an attractive material for the design of novel neuro-implantable devices able to manipulate neuronal activity and they appear as an ideal material for long-term neural implants.

Here we present how, through the chemical modification of carbon nanotubes, conductive, strong and flexible nanotube films are obtained (Figure 1), which can be used as neuronal substrates to modify neuronal behaviour.

Figure 1. CNTs film obtained under vacuum filtration and SEM image showing the entangled structure of the film.

References:

Chemical functionalization and nanocatalysts: a perfect match?

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Chemical functionalization of carbonaceous materials such as graphene and carbon nanotubes comprises a promising tool for modulating various properties that can be allied with metallic nanoparticles or polymer leading to prominent nanocomposites. Our research group has been engaged in the chemical functionalization of graphene oxide and carbon nanotube seeking several applications mainly involving (i) pesticide degradation; (ii) hydrogen production and (iii) improved electrochemical stability. Regarding pesticide degradation, we obtained nanocatalysts derived from graphene oxide (GO) and carbon nanotube with various groups covalently (imidazole, thiol, hydroxamate) anchored on its carboxylates moieties, obtained as powder and also as thin film by the liquid-liquid interfacial functionalization method. Moreover, nanocomposites with silver metallic nanoparticles were obtained with the thiol-derived GO. The degradation of pesticide is knowingly slow, hence requires efficient catalysts to promote their elimination, which can be used to detoxify stockpiles (pesticides and extended to chemical weapons) and also to monitor their abusive usage with sensors. The designed nanocatalysts evidenced high catalytic activity against various organophosphorus compounds, up to $10^8$-fold enhancements compared to the spontaneous reaction. We were also able to combine different functional groups on the same backbone, i.e., thiol and imidazole groups were functionalized on GO, leading to a bifunctional catalyst that mimics the cysteine protease enzyme. The neighbouring of these groups guarantees a cooperative behaviour in the reaction, that indeed shows higher catalytic response than analogous material with only one functional group present. The thiol–derived nanocomposite with AgNPs was able to not only efficiently degrade pesticides but also to act as a sensor (Surface enhanced raman spectroscopy, SERS) detecting the phenolic product formed upon degradation and also other pesticides such as glyphosate. It should be noted that the knowledge involved in degrading/monitoring pesticides can be extended to chemical weapons since they include many organophosphorus compounds. We have synthesized an analogue of the Tabun chemical weapon in order to evaluate the efficiency of the nanocatalysts.

Another application we seek developing nanocatalysts is hydrogen production. In fact, we synthesized several nanocomposites derived from GO, Ag NPs and Ni NPs, as thin film and have evidenced a pronounced catalytic activity in the production of hydrogen using NaBH₄. We have carried out various kinetic studies following the generation of gas, reaching maximum rates of up to $10^5$ mL min⁻¹ g⁻¹. We highlight the feasibility in handling these thin films and their reuse for hydrogen production, which is novel for this application. Finally, for the third application regarding improving electrochemical stability, we have obtained polymeric nanocomposites of GO and polypyrrole (Ppy) that are covalently linked and evidence a significantly higher electrochemical stability, in contrast to analogous non-covalent composites. In summary, chemical functionalization of carbon-based nanomaterials has shown to be an important tool for obtaining novel materials, highlighting the perfect match for the development of easy handling, recyclable and multifunctional nanocatalysts.

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Adapting nanotube chemistries to graphenes

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Chemical functionalisation is critical to a wide range of nanocarbon technologies, but needs to be versatile and applicable at scale. Existing approaches tend to rely on liquid phase reactions, often requiring damaging sonication or lengthy work up. Over recent years, we have worked on two general strategies that have proved versatile, scalable and effective, without introducing additional damage. Having developed two complementary methods for carbon nanotubes, we have shown that both approaches can be applied to graphene related materials. Specifically, both single layer graphene and graphene nanoplatelets can be functionalised via a gas-phase thermochemical method. Direct TEM imaging confirms covalent modification, without damaging the connectivity of the lattice, as supported by Raman spectrometry and AFM nano-indentation measurements. The grafting methodology can also be applied to commercially-available bulk graphene nanoplatelets, as illustrated by the preparation of anionic, cationic, and non-ionic derivatives. Graphite intercalation compounds (GICs) are well-known precursors that afford isolated graphene layers avoiding framework damage. We have compared grafting from and grafting to techniques for the introduction of polymers. The grafting from approach increases the grafting ratio and solubility of the material in organic solvents, due to the conformation of the polymer. The high reducing potential of charged graphenides can lead to unwanted side reactions, which can be avoided by the use of suitable discharging reagents. The reactivity of the reduced graphenide intermediates can be inconvenient or incompatible with certain reagents. To circumvent such problems, the graphenide can be converted to a stable brominated species, suitable for a wide range of subsequent transformations, including nucleophilic substitutions and direct ATRP polymerisations.

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S. Hodge, D. Buckley, H. Yau, N. Skipper, C. Howard, M. Shaffer, NANOSCALE, 2017, 9, 3150, Chemical routes to discharging graphenides;
Reactivity of Graphenide Dependent on Solvation of Potassium Cation in Solvents

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Functionalization of graphene materials from graphenide, obtained by dissolution of graphite intercalation compounds (GICs) solution (KC\textsubscript{8}), is a facile approach for scalable preparation and improving its processability.\textsuperscript{[1]} Recently, a large variety of high functionally covalent graphene are achieved by reaction of graphenide.\textsuperscript{[1c]}

Since ion solvation of GIC is one of the most important factors on its chemical reactions, here we report a systematic study on the relationship between nature of solvents for solvation of K cation and reactivity of GIC (KC\textsubscript{8}) with two well-known radical reactions. After ultrasonication, KC\textsubscript{8} reacts with 4-iodoaniline or 4-fluorated phenyl diazonium salt to afford GA and GF, respectively (Figure 1a). The results indicate that the reactivity order of KC\textsubscript{8} in common used solvents is the following: DME > THF > NMP > DMF, confirmed by increments of I\textsubscript{D}/I\textsubscript{G} in Raman spectra, Figure 1(b) and of the atomic composition in X-ray photoelectron spectroscopy (XPS). This order is in line with the solvation free energies of K cation, $\Delta G_s(K^+)$. Additionally, the functional degrees are improved by using DME or 18-crown-6 ether as additive in DMF compared to pure DMF, which further confirms the solvation of K\textsuperscript{+} is benefit for the reaction, due to barer negative charge on graphenide. Moreover, control experiment is better reference than pristine graphite for evaluation of graphene functional degree.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{(a) Preparation of GA and GF in different solvents. (b) Increase of ratios I\textsubscript{D}/I\textsubscript{G} in Raman spectra.}
\end{figure}

References

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

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

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

Referencesc
Graphene/polyelectrolyte layer-by-layer thin films for multifunctional coatings

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Due to its exceptional electrical, mechanical, thermal and barrier properties [1], graphene seems very promising to be used in advanced coatings for gas or humidity barriers or electrical shielding, being the aerospace sector one of the key target areas.

The thermal reduction of GO prepared following Hummers’ method [2] has been recently probed to render high yields of processable and highly conductive graphene material through the removal of oxygen-containing functionalities and subsequent restoration of the Csp² network [3]. Thermally reduced graphene oxide (TRGO) represents thus a very good material for the fabrication of multifunctional nanostructured coatings.

Herein, a spray coating layer-by-layer technique was developed to fabricate thin, highly ordered and finely overlapped multilayer graphene coatings, through alternating self-assembly of negatively charged TRGO and a positively charged polyelectrolyte (e.g. polyethyleneimine (PEI)) n times on a substrate. Absorption and Raman spectroscopies combined with atomic force and scanning electron microscopies were used to analyze the rate and mechanism of growth, nanostructure and micromorphology of the self-assembled multilayer (TRGO/PEI)ₙ coatings.

How the lateral dimensions of the graphene flakes, the density of both graphene and polyelectrolyte deposited per cycle and surface unit and the number of deposited bilayers (n) affect the microstructure and properties of the (TRGO/PEI)ₙ multilayer systems was investigated in detail. They were found to be key factors for gaining control and tuning the light transmittance and the electrical conductivity of these structures, which makes them highly promising for EMI shielding applications.

In addition, these (TRGO/PEI)ₙ coatings showed exceptional gas barrier properties, as well as a high flexibility and a good performance as resistive strain sensors, which evidences their multifunctionality and opens the door to a high number of novel applications in the composite industry.

References

Mechanical Assembling and Structuring Graphene Oxide Based Materials

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As a building block, graphene possesses intriguing mechanical, electrical, thermal property and chemical stability. Assembling graphene into macro-structures is very appealing, if those unprecedented properties can be inherited. However, it is the physical interaction between graphene nanosheets mainly control the performance of the assembled materials. On the other hand, it should be noted that graphene is probably the most anisotropic material that has even been discovered, as manifested by the prominent contrast of bending modulus (in the order of ~2kT) and tensile modulus (~1 TP\text{a}), as well as the ballistic electron transport in-plane and tunneling between-planes. Therefore, it is extremely important to improve the alignment of graphene nanosheets in the same direction and reinforce the interaction between them. Keeping this in mind, we propose to employ mechanical strategies, namely dead-end filtration and centrifugal casting, with the advantages of high efficiency, high yield and universal, to super-align and condense-compact graphene nanosheets, both of which result to materials with outstanding performance. Finally, we will also illustrate that the combination of proper rheology properties of graphene oxide based ink and 3D printing technique, materials beyond 2D film with much more complex structures can be obtained.
Controlled 3D Assembly of MWCNT and GO-MWCNT Hybrid Aerogels as Support Frameworks for Catalysis

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Manipulation of nanoscale building blocks into intricate 3D architectures is a challenge underpinning much of the research surrounding nanocarbons. Directed self-assembly of multiwall carbon nanotubes (MWCNTs) and graphene oxide (GO) into porous 3D structures, known as aerogels, provides an opportunity to optimise essential structural parameters, such as micro-, meso- and macroporosity; important for many practical aerogel applications. Here, we report on an emulsion templating technique to assemble nanocarbon aerogels constructed from MWCNTs and hybrid GO-MWCNTs macrospheres (Fig. 1). Investigating the amphilicity and emulsification energy input, the hollow macrospheres of MWCNTs and hybrid GO-MWCNTs are explored with regards to macrosphere size, uniformity and morphology.

Further, this project investigates chemical methodologies to uniformly decorate the aerogel frameworks with catalytically active Cu nanoparticles. Specifically, the following two methods were explored: i.) sublimation of organometallic precursors and ii.) rapid water vapourisation in the presence of inorganic salts. Both fabrication methods lead to Cu decorated macrospheres but with considerable variation in nanoparticle size domains. Probing the kinetics, conversion and selectivity of these nanocarbon supported Cu catalysts through model reactions, such as styrene epoxidation, provides insight on the role of graphitic support structures on active sites. Furthermore, the facile routes established in this project are versatile in that they are easily applicable to many other transition metals used in industry relevant reactions such as Ullmann coupling. We envisage graphitic aerogels in other applications involving flow chemistry and electrothermal conductivity.

References
Structuration of lignin-based carbon through liquid crystalline graphene oxide

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Carbon fibers with their use in aerospace, transportation and energy sectors are in high demand. However, large scale and mass market applications are still hindered because of the high cost of the fiber raw materials. For several decades, the search for alternative and inexpensive precursor materials has included biopolymers. Especially lignin, a widely abundant natural resource containing high quantities of carbon, is considered as an important candidate. So far, lignin-based carbon fibers, which have mostly been prepared by melt-spinning, do not reach the mechanical properties required for high-performance applications.\textsuperscript{[1]}

Compared to conventional carbon fibers, the amorphous nature of a lignin precursor fiber leads to a carbon structure which is lacking a clear orientation along the fiber axis.

We propose lignin-based fibers obtained through a coagulation process, which is of increasing relevance for the production of new precursor materials for carbon fibers. Coagulated lignin fibers however revealed highly porous structures leading to high brittleness. To improve the structuration and overcome the brittleness of pure lignin fibers, we chose liquid crystalline graphene oxide (GO) as reinforcing element. Nanocarbon dispersions forming liquid crystal phases are known to be suitable for wet-spinning applications and the prepared fibers have highly oriented structures.\textsuperscript{[2]}

The incorporation of graphene oxide sheets into lignin fibers thus promises higher carbonization yields and increased orientation of the obtained graphenic planes.

Our carbonized lignin-GO composites show very promising results regarding structure and properties. The results clearly represent an approach towards lignin-based nanocomposite fibers, which could be used as renewable precursor material for carbon fibers with enhanced structuration.

\textbf{Figure}: Structuration of lignin through GO liquid crystals in solution (left: optical micrograph, scale bar 100 µm) and in carbonized films (right: X-ray spectra)

\textbf{References}


\textbf{Notes}
Electrophoretic deposition of carbon nanotubes on austenitic steel for surface protection

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For decades, electrophoretic deposition (EPD) has been used mainly for the processing of ceramic materials. However, it has been recently proven as an effective deposition technique for carbon nanotubes (CNTs). In order to increase the stability of the dispersion as well as promote the deposition of homogeneous films, additives are deployed. Two additives that have been used for EPD in the past are triethylamine and magnesium nitrate hexahydrate. Depending on which additive is used for the deposition, the wetting behaviour of the carbon nanotube films can be adjusted from hydrophilic to near-superhydrophobic making it an interesting approach for the protection of steel surfaces. Furthermore, since CNTs are a proven solid lubricant providing effective friction and wear reduction on steel surfaces, we evaluated the tribological properties of the different coatings with a ball-on-disc tribometer. Adding magnesium nitrate to the colloidal solution leads to the formation of a Mg(OH)$_2$ holding layer, in which the CNTs are mechanically embedded. As a result, the CNTs are held in the contact area providing effective long-time lubrication. Subsequent wear track analysis shows minimal wear on the coated substrate as well as carbon residues as opposed to the uncoated substrate. Chemical analysis reveals the presence of Mg on the film deposited with magnesium nitrate which explains the hydrophilic wetting characteristics. Finally, wear track analysis reveals, only marginal oxidation on the CNT coated substrate, further confirming the protection capability.

References
Carbon nanotubes functionalized with copper hexacyanoferrate nanoparticles for a selective extraction of cesium from nuclear waste

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Single-walled carbon nanotubes (SWCNTs) are functionalized with copper hexacyanoferrate (CuHCF) nanoparticles to prepare solid substrates for the sorption of cesium ions (Cs$^+$) from liquid outflows. The high mechanical resistance and large electrical conductivity of SWCNTs are associated to the ability of CuHCF nanoparticles to selectively complex Cs$^+$ ions in order to achieve membrane-like buckypapers presenting high loading capacity of cesium. The materials are thoroughly characterized using electron microscopy, Raman scattering, X-ray photoelectron spectroscopy and thermogravimetric analyses. Cs sorption isotherms are plotted after having measured the Cs$^+$ concentration by liquid phase ionic chromatography in the solution before and after exposure to the materials. It is found that the total sorption capacity of the material reaches 230 mg.g$^{-1}$, and that about one third of the sorbed Cs (80 mg.g$^{-1}$) is selectively complexed in the CuHCF nanoparticles grafted on SWCNTs.$^1$ These high values open interesting outlooks in the integration of such materials in devices for the controlled sorption and desorption of these ions.

References
Optical spectroscopy signatures of single walled carbon nanotubes dispersed in degassed water without additives

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We study the intrinsic optical spectroscopy (UV-vis-NIR absorption, Raman and photoluminescence) signatures of single wall carbon nanotubes (SWNT) dispersed in degassed water without additives, so called “eau de nanotubes” (EdN). They are found to be very close to those of SWNT dispersed in aqueous suspensions stabilized with surfactants. Absorption peaks appear to be even slightly better resolved for EdN, suggesting sharper excitonic resonances, which is also supported by the Raman data. On the other hand, the photoluminescence signal is significantly weaker. These signatures suggest that SWNT are dispersed as individuals in degassed water, in a similar way single layer graphene was recently shown to be readily dispersable in degassed water [1-3].

References


_Notes_
A cleaner production of CNT nanocapsules

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Filled single-walled carbon nanotubes (SWCNTs) are of interest for a wide variety of applications ranging from sensors to magnetoelectronic devices and going through the development of smart contrast and therapeutic agents in the biomedical field. In general, regardless of the method employed, bulk filling of carbon nanotubes results in the presence of a large amount of external non-encapsulated material. Therefore, further processing is needed to achieve a sample in which the selected payload is present only in the inner cavities of the nanotubes. Here, we have developed a sustainable system to process samples of filled SWCNTs with poor water-soluble materials, and report on a straightforward approach that allows the removal of non-encapsulated compounds in a time efficient and environmentally friendly manner, using water as a “green” solvent, while minimizing the residual waste. The results presented herein pave the way toward the production of large amounts of high-quality closed-ended filled nanotubes, also referred to as carbon nanocapsules (Fig. 1). The green protocol allows a 95% reduction in water waste, which gets contaminated with hazardous heavy elements. The developed methodology benefits from a synergistic combination of both Soxhlet and dialysis (Fig. 1).1 It allows the efficient removal of the large excess of non-encapsulated material present after filling carbon nanotubes. The methodology holds special interest for the manipulation of radioactive systems where reduction of the residual waste is a must, but can be employed for the external removal of other payloads. A quick on-site assessment the proper removal of external salts has been carried out by visual inspection of the filtrate, avoiding the consumption of the sample in the process, while preserving the encapsulated payload and structural integrity of the SWCNTs. We foresee the use of such optimized purification protocol as a path toward high-quality SWCNT nanocapsules, exclusively endohedral, to be employed not only in the biomedical field but also in other applications where the presence of non-encapsulated material can be detrimental.

References

Electrostrictive soft materials for mechanical energy harvesting

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The needs of innovative technologies for the energy harvesting are significantly increasing to satisfy the requests of electronic devices, IC and microfluidic systems, autonomous sensors, MEMs, etc. Harvesting energy from the ambient energy losses, as mechanical vibrations, liquid flows and pressure changes raises challenges for the efficient conversion of mechanical energy into electrical energy. Graphene-based liquid crystals (GOLC) are expected to display large dielectric permittivity and changes of permittivity in response to flow. Thus, they could be used in variable capacitors for the generation of electrical energy. In this new approach the major challenges consist in achieving a giant dielectric constant and a large variation of capacitance. Prepared GOLC were analysed by dielectric spectroscopy in static condition and under flow. The observed large contribution of the electric double layer capacitance limits the exploitation of the flow-tunable dielectric properties. Analysis to discriminate the bulk properties are still in progress. Further studies will be performed to verify the validity of these systems as electrostrictive soft materials.

![Diagram of GOCL dispersion](image)

Fig.1 – Flow induced dielectric properties of a GOCL dispersion
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The critical role of carbon-based nanofillers in cementitious composites

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Cement is by far the most important and widespread building material in the industrialized world, used for a wide range of applications in the construction industry (4.2 billion tons of cement were produced in 2016). However, the production of cement results in approximately the same weight of CO\textsubscript{2} emission, which should be minimized. Nano-Fillers (NF)-reinforced cement composites could reduce its required amounts in various structural applications while keeping similar mechanical properties.

We explore the effect of few carbonaceous NF, namely, graphene nano-platelets (GNP), graphene oxide (GO) and carbon nanotubes (CNT) on the mechanical and rheological properties of the cement matrix. The major hurdles are (1) dispersing the NF in the cement matrix (2) controlling the elevated cement viscosity associated with the NF loading. We found that addition a superplasticizer (SP) and a defoamer to a GO\textit{-loaded} system produces the best results among the above mentioned NFs at lowest additive concentration. The superiority of GO could be related to its hydrophilic nature, which increases its compatibility with the aqueous-based cement matrix. We demonstrate that the GO-loaded system enhances the \textit{compressive and flexural strengths} by 30\% and 60\%, respectively, at GO concentration as low as 0.025 wt\%. The SP increases the \textit{fluidity} of plane cement by 50\%, while its addition to NF-loaded systems results in fluidity enhancement of 43\%, 37\% and 29\% for GNP, CNT and GO, respectively.
Towards multiplexed imaging with dyes encapsulated inside single-walled carbon nanotubes

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A specific approach in optical imaging consists of using contrast agents to enable the marking of structures of interest with known optical signatures. However, commonly used contrast agents such as fluorescent dyes suffer from stability issues. It has been shown in our group [1] that dyes encapsulated inside carbon nanotubes (CNTs) are protected from degradation and present a giant Raman signature with narrow emission peaks, free of background fluorescence. In this work, we studied the encapsulation process of α-sexithiophene in long (>2 µm) single-walled carbon nanotubes (SWNTs) by Raman hyperspectral imaging. We directly showed that the encapsulation process begins at the opened ends of the SWNTs, and that the molecule organizes into two segments following the axis of the SWNTs. By varying encapsulation parameters, namely concentration and temperature, we showed that the encapsulation of α-sexithiophene in SWNTs is a thermally activated and sequential process.

Furthermore, the large quantity of available organic dyes allows the development of a library of Raman nanoprobes from dyes encapsulated in single-walled carbon nanotubes (dyes@SWNTs), making encapsulated dyes particularly interesting for multiplexing applications in biomedical and related fields. In this optic, SWNTs were cut to obtain a shorter and more homogeneous length distribution. Several organic dyes were encapsulated in these shortened SWNTs, each showing a specific Raman signature. We also show that these nanoprobes can be covalently functionalized with antibodies for active targeting of biomarkers.

References

The viscosity of diluted carbon nanotube and graphene oxide aqueous inks

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The fabrication of thin films and fibers with carbon nanotubes (CNTs) and graphene is often the preferred way for their application. Some of the most convenient methods for the preparation of the films and fibers typically require well-dispersed liquid suspensions or inks of the nanoparticles. One of the key issues in the performance of those fabrication processes is the control of ink viscosity.

In the present work, we study the viscosity of different CNT and graphene oxide (GO) diluted inks at different concentrations, 5 temperatures between 25 and 45\degree C, and various aqueous media. Previously to viscosity measurements, an assessment of the suspension stability and the determination of the density at ambient temperature are effected. As we work with diluted suspensions, all the liquids behave as Newtonian, and thus viscosity measurements are performed with capillary viscometers. Multi-walled carbon nanotubes (MWCNTs), various covalently functionalized MWCNTs, two types of single-walled carbon nanotubes, and GOs with different oxidation degrees are tested. Viscosity dependence on the ink concentration and the temperature is evaluated and modeled.

Viscosities of CNT inks show a linear dependence of concentration up to at least 3 mg·mL\textsuperscript{-1}. GO dispersions also show a linear dependence up to concentrations of approximately 2 mg·mL\textsuperscript{-1}. The viscosity up to concentrations of at least 4 mg·mL\textsuperscript{-1} can be well fitted to a Maron-Pierce model. Viscosity dependence with temperature can be fitted to an Arrhenius type model in the studied range. Our results are relevant for technological and industrial applications utilizing diluted carbon nanomaterials inks.
On the Rational Design of Aqueous Graphene Dispersants

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The production of graphene dispersions has been shown to be a promising route to scale-up of 2d materials, particularly for conductive inks and incorporation into composites. The ability to exfoliate graphene into water requires either direct functionalisation of the graphene flake or noncovalent dispersants. By π-stacking onto the graphene basal plane, ionic polyaromatic hydrocarbons such as pyrene butyric and pyrene sulphonic acid (PySA) have been shown to stabilise exfoliated graphite\textsuperscript{1,2} and reduced graphene oxide\textsuperscript{3} in water with the ionic head enabling charge stabilisation and an ionic interaction with the aqueous medium. Previously it has been shown that the ionic group type attached to a pyrene core as well the spacing between that and the core can influence the degree of stabilisation, but only commercial pyrene molecules have been investigated so far.

In this work, the impact of a butyl spacer between the anionic sulphonic acid ‘head’ and the pyrene ‘core’ of a graphene dispersant has been modelled using molecular dynamics and peak mean force computations, showing the butyl pyrene sulphonic acid-graphene system reaching a lower energy conformation upon adsorption of the stabiliser. After the successful synthesis of the target molecule, PyBuSA, we employed it in the production of aqueous graphene dispersions. This was achieved through both the in-situ reduction and stabilisation of graphene oxide and sonication-induced exfoliation of graphite. We found that the concentration of graphene material in both systems increase by 2.5 times. Further characterisation of the graphene materials showed that this was not to the detriment of flake quality but solely owed to the inclusion of an alkyl spacer in the stabiliser molecule.

Figure: a Graph showing measured increase in concentration using PyBuSA compared to PySA, b AFM micrograph and profile of PyBuSA stabilised rGO flake.

References
Chemical functionalization of carbon nanotubes for composite functional materials

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Carbon nanotubes (CNTs) have demonstrated exceptional mechanical, thermal and electrical properties, and are regarded as one of the most promising reinforcement materials for the next generation of high performance structural and multifunctional composites with tremendous application potentials. However, to date, most application attempts have been hindered by several technical roadblocks, such as poor dispersion and weak interfacial bonding. Functionalization of nanotubes was suggested to be an effective way to overcome these technical issues and then to realize the full potential of nanotubes as reinforcement materials.

Within this contribution, we will review our most recent achievements in the field of functionalized carbon nanotubes and their applications in composite functional materials. Moreover the experimental study, the structural and electronic properties of the hydroxyl, amine and carboxylic acid groups, used as sidewall functionalizations by interacting with various single-wall carbon nanotubes, were investigated by using ab initio calculations. Thereafter, we have analyzed the established chemical bonding by subsequent esterification, anhydridation or amidization between covalently functionalized carbon nanotubes in order to get better understanding of the interactions between these nanostructures.
Improved photocatalytic activity of different ZnO\textsubscript{NPs} and their ZNO\textsubscript{NPs}-GO composites

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Graphene with its unique physical and chemical properties has attracted increasing interest in recent years\textsuperscript{1}. Its transparency and electrical conductivity, as well as its easy processing when prepared from graphene oxide, position graphene as a good candidate for optoelectronic applications\textsuperscript{2}. It has been observed that ZnO nanocrystalline semiconductor with different morphologies is a promising material for solar cells and photocatalytic applications due to its high electronic mobility, wide range of energy, high photoactivity and transparency at visible light\textsuperscript{3}. The combination of graphene properties and nanostructured ZnO would provide a unique platform for the development of nanostructured materials with improved photoactivity.

Therefore, a novel method has been developed to prepare ZnO by microwave that has allowed synthesizing ZnO-GO hybrid materials by ultrasound bath in order to improve the efficiency of the photocatalytic reaction of methylene blue degradation. The method facilitated the establishment of interactions between ZnO and GO, which resulted in improved catalytic materials. Three types of GO with different degrees of oxidation (2, 4 and 16 hours) were analyzed, resulting the 4 hours-oxidized (GO2) in hybrids with greater activity. Also, hybrid materials with different ZnO:GO ratios were prepared using the optimum GO2 material. The ZnO-GO2 hybrid materials exhibited high conversions compared to ZnO alone (and even to TiO2 P25), whereby the hybrid synthesized at 10:1 (ZnO:GO) ratio exhibits the highest final conversion. Moreover, ZnO treated at 200ºC improves the photocatalytic activity of ZnO without heat treatment. The photoelectrochemistry, XRD, Raman and TEM of the prepared hybrid materials reveal important structural differences both in crystalline order and in the ZnO-GO interaction that could be the cause of the different catalytic efficiencies observed.

![Figure: TEM images of a) ZnO at 200ºC in air, b) ZnO as-synthesized and c) ZnO-GO2 (3:1 w/w) composite.](image)

References

Aqueous dispersions of single-layer poly-hydrogenated graphene, properties and applications

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The chemisorption of hydrogen transforms graphene into an insulator, leading to the prediction that important electronic or magnetic properties will emerge.\cite{1} The chemical stability and the difficulty to produce only single-layers of graphene makes hydrogenation difficult to control, and this has hampered efforts to tune its electronic or magnetic properties. If these challenges can be met while preserving the intrinsic quality of single-layer graphene for electron and spin transport, then graphene may indeed become a leading candidate material in the roadmap for next-generation information technologies.\cite{2} Graphite intercalation compounds can be readily exfoliated down to single-layers in aprotic solvents due to the favorable entropic contribution of dissociating counter-ions, yielding graphenide solutions.\cite{3} The resulting graphenide solutions are a source of high quality single-layer graphene\cite{4-6} and have also been utilized as a starting material for the bulk synthesis of covalently functionalized graphene including hydrogenation of graphene\cite{7}. Here, we prepared aqueous dispersions of single-layer poly-hydrogenated graphene by reacting a negatively charged graphene solution in THF with methanol,\cite{8} followed by transfer and stabilization in water. Characterization of the reaction product poly-hydrogenated graphene was carried out by thermogravimetric analysis coupled with mass spectrometry (TGMS), Raman spectroscopy, UV-vis-NIR absorption spectroscopy, photoluminescence spectroscopy and XRD. The optical spectroscopy signatures of the poly-hydrogenated graphene measured in water give evidence that the dispersions contain single layers of covalently functionalized graphene. This solution-based method of producing poly-hydrogenated graphene allows uniform and controllable deposition of poly-hydrogenated graphene thin films with thicknesses ranging from a single monolayer to several layers over large areas. Electrical characterization of the transparent conducting films of restacked poly-hydrogenated graphene sheets showed that optoelectronic properties can thus be tuned over several orders of magnitude, making them potentially useful for flexible and transparent semiconductors and carbon based ferromagnetic materials.

References

Combined Therapy Using Carbon Nanotubes

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The ability of carbon nanotubes to penetrate the cell membrane, together with the flexibility of their functionalization chemistry, has promoted them as one of the most interesting platform for the design of a new class of nanomaterial-based Drug Delivery System.\textsuperscript{1–3} The vast majority of CNT based DDS has been produced for studies in oncology and have demonstrated to play an important role in this field. CNTs have been used as carriers for many cytotoxic drugs, gene therapy agents, photodynamic and photothermal therapy.\textsuperscript{4} Furthermore CNT possess structural characteristics, such as the high surface area and the chemical reactivity, that make simple the design of new DDS able to carry two, or more, bioactive compounds.\textsuperscript{5–7} Such devices are actually being studied and revealed efficient in combined therapy studies. For example, CNTs have been used in combined therapy studies as carriers for pairs of cytotoxic drugs, pairs of gene transfection agents and in many of the possible combination of bioactive agents that are actually used in classic clinical approaches. Here we report the synthesis and the study of a multimodal drug delivery system based on short oxidized multiwalled CNTs. The drugs selected were doxorubicin, frequently reported as gold standard for the drug delivery ability study on CNTs, and metformin, an approved drug in type B diabetes therapy, which was recently reported as antimitabolic drug for the treatment of chemo-resistant tumor. The biodistribution of the system was investigated in 4T1 tumor bearing mice using different radioactive tracers and different time point. To fully understand the \textit{in vivo} behaviour of our new material we also studied how different type of administration can affect its pharmacokinetic. Finally, a small study of \textit{in vivo} toxicity was made to evaluate the effect on tumor development and the biological tolerance of the system.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Structure of the Drug Delivery System}
\end{figure}

References

Reinforcement and workability aspects of graphene-oxide loaded-cement nanocomposites

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Nanocarbons such as nanotubes or graphene have been employed to enhance the performance of cementitious composites due to their extraordinary mechanical and transport properties\textsuperscript{1-6}. Specifically, the use of hydrophilic graphene oxide (GO) is of great potential due to its compatibility with the water-based cement matrix\textsuperscript{5,7,8}. However, the addition of GO (or other nanocarbon fillers) to the cement matrix results also in increased viscosity\textsuperscript{2,5,6,9}, which reduces its workability and jeopardizes its casting process. In this study, we explore and optimize the GO-cement system focusing on the mechanical and the rheological properties. The high viscosity induced by the GO addition is lowered by adding a superplasticizer (SP)\textsuperscript{1,5,6,9}, the concentration of which tunes the flow properties of the cement nanocomposites for a desired application. It was demonstrated that GO enhances the compressive and flexural strength of the cement (35\% and 66\%, respectively) at extremely low GO concentrations of 0.025 – 0.05 wt \%, better than carbon nanotubes, and at lower concentrations. In all systems an optimal nanofiller concentration (ONC) defines the concentration at which the best enhancement is obtained. We compare the reinforcement efficiency (enhancement/ONC) of the GO, GO-SP and CNT-SP systems, where the GO-SP system demonstrate superiority. The GO is also more involved in the hydration reaction as evidenced by calorimetry study. Air bubbles are caged in the cement at high filler concentrations (see scanning electron microscopy figure) while a smooth surface is imaged for filler concentration below ONC (not shown). The introduction of the reinforcing efficiency robustness and figure of merit terms for various nanofillers provides an important comparison tool between filled systems in the field of cement nanocomposites.

\textbf{Figure:} Scanning electron microscopy micrograph of cement loaded by 0.05 wt \% GO (arrows) as a filler. The cement matrix particles surround and reacts with the GO.

\textbf{References}

Orientations and texture instabilities in graphene oxide liquid crystals

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Graphene oxide dispersions are easily obtained in water. Due to the high aspect ratio of the flakes, liquid crystals then forms a nematic phase at moderate concentrations \cite{1,2}, which allows to design various composites with nanoparticles. Preparing organized materials and thin films from these dispersions however requires a good control of the liquid crystal ordering during the deposition and the drying of the films.

Here we have focused on mechanical instabilities that are frequently observed in thin graphene liquid crystal layers, when they are submitted to weak constraints. We have shown how to create and stabilize large-sized periodic textures (millimeter scale, see fig.1). The patterns have been characterized under optical and electronic microscopies. They result from the peculiar elastic and rheological properties of the graphene oxide liquid crystals. Our results also clarify why long-standing hypotheses on the presence of exotic phases \cite{1} at large concentrations are present in the literature.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{example_textures.png}
\caption{Example of large-sized textures (700\textmu m x 1mm) of nematic graphene oxide liquid crystals observed under polarizing optical microscope.}
\end{figure}

References
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Solution processable carbon nanotube biosensing devices: A Nanoscale Multi-Sensing Platform

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Electrical detection methodologies are among the most promising candidates for the fabrication of miniaturized, ultra-sensitive and portable biomarker detection protocols. Advances in nanofabrication techniques and novel nanoscale tools have opened up new avenues for developing electrical analytical methods that can be effectively merged with miniaturized hardware. Moreover, electrical (bio)sensing based on nanomaterials offers unique advantages, such as simplicity, low-cost processability, and label-free real-time electrical detection in a non-destructive manner. In this context, there has been great interest in the use of one-dimensional nanostructured materials for the development of new nanoscale biosensors, and single walled carbon nanotubes (SWCNTs) emerged as strong candidates.\textsuperscript{1} Here we present a strategy for the fabrication of reconfigurable and solution processable nanoscale biosensors with multi-sensing capability, based on individual SWCNTs. DNA-wrapped (hence water-soluble) CNTs were immobilised from solution between two pre-patterned electrodes via dielectrophoresis (DEP). The CNTs were functionalized with specific nucleotide sequences to be employed as selective recognition elements for analytes of interest.\textsuperscript{2} In particular, we will demonstrate the electrical detection of hybridization and de-hybridization events on few CNTs in device configurations. Additionally, as a proof-of-concept, we functionalized our CNTs with three different steroid selective aptamers, and employed our devices for the simultaneous detection of these hormones on the same biochip. This allowed us to detect on the nanoscale devices and in real-time physiological relevant concentrations of specific hormones correlated to several stress and neuro-trauma conditions.\textsuperscript{3,4} The herein presented strategy is of general applicability for the electrical sensing of multiple biomarkers in real time and with high sensitivity. Furthermore, the environmentally friendly and low-cost fabrication method (aqueous solution-processable via DEP) can be scaled up in array configurations for the development of nanoscale point of care and portable biosensing platforms.

References

Single-step chemical strategy for the formation of
SWCNT molecular junctions in aqueous solution

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Single-walled carbon nanotubes (SWNTs) exhibit a wide range of electromechanical properties and their unique 1-D nanostructures make them ideal as building blocks for nanoelectronics devices. They can be either metallic or semiconducting, which gives rise to significant electrical versatility. Notably, it is of importance to control the formation of junctions between distinct nanotubes, as well as between SWCNTs and functional molecules or nanostructures for the development of SWCNT-based electronics. Metallic SWCNTs can be used as nanoelectrodes where a single molecule can be immobilized between two or more SWCNT segments, forming a molecular junction. In this regard, we recently presented an approach for the assembly of SWCNT-based molecular transport junctions,1 and single-molecule heterostructures, directly in solution.2,3 For these studies, we employed DNA to wrap the SWCNTs making them water soluble and addressing only their carboxylic terminal functionalities to tether individual molecules to nanotubes via simple amidation reactions. Despite the successful formation of SWCNTs based junctions in water, the numerous steps involved in the experimental procedure prove to be time consuming and dramatically affected the final yield of molecular interconnections. Therefore, a new chemical route is needed for the controlled fabrication of one-dimensional and multi-terminal SWCNT junctions to overcome the aforementioned problems.

In this work, we demonstrate a novel single-step chemical strategy to form SWCNT molecular junctions in aqueous solution and with high-yield. Bi-diazonium salts4,5 were used to covalently link end-to-end SWCNTs in aqueous solution; we compared this chemical approach to the direct amidation reaction scheme previously employed, demonstrating a higher yield and single step junction formation. Additionally, we propose an improvement over the amidation linking strategy, via the use of a copper-free ring strain promoted 1,3-dipolar cycloaddition as a second linking step. By and large, different chemical approaches for the tethering of individual molecules to carbon nanoelectrodes are desirable for specific single-molecule electronics applications from sensing to thermoelectricity, as it can allow to modulate the conductance across the molecular junction.6

References
Joule-heatable hybrid nanocarbon network supports for CO₂ capture

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Supporting Layered Double Hydroxides (LDH) on multi-walled carbon nanotubes (MWCNT) or graphene oxide (GO) improves the CO₂ adsorption capacity of the LDH¹,². Combining GO and MWCNT to create a hybrid nanocarbon support enhances the adsorption capacity even further, in particular by enhancing the multi-cycle stability of the LDH over repeated temperature swing adsorption (TSA) measurements³. Thermally reduced graphene oxide (rGO) aerogels show promising electrical and thermal conductivities, making them suitable as low voltage/power input local heaters. Interesting applications may be found in catalysis, gas heating and solid state adsorbents regeneration⁴.

The chemical functionalisation used in this work allows the preparation of more complex hierarchical structures, combining the properties of carbon based structures operating on different lengthscales to tailor the electrical, thermal, and mechanical properties as well as morphology to specific applications.

Figure: LDH supported on nanocarbon supports.

References
³ De Marco,M. et al., Carbon, Volume 123, October 2017, Pages 616-627
Efficient MALDI-MS Platform based on Functionalized CVD Graphene for Carbohydrate Detection

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Mass spectrometry (MS) is a valuable tool for functional genomic, proteomic, and glycomic studies. Particularly, the combination of MS with microarrays is one of the most powerful technique for the structural analysis of oligosaccharides.\textsuperscript{1} On the other hand, graphene has emerged in the last decade as a promising next generation material due to the combination of its electronic, mechanical and thermal properties. In particular, graphene exhibits high desorption/ionization efficiency and good conductivity, thus being a promising candidate as component for Matrix-assisted laser desorption/ionization (MALDI) matrices.\textsuperscript{2} In addition, the chemical functionalization of graphene allows the modification of its chemical and physical properties, as for example an enhancement of the adsorption capability of functional biomolecules, resulting in very stable interfaces.\textsuperscript{3} Taking advantage of the graphene properties, herein, covalently modified chemical vapor deposited (CVD) graphene is used as platform for an efficient detection of different oligosaccharides by MALDI analysis and, in some cases, optical microscopy.

\textbf{Figure:} Schematic representation for the functionalized graphene-based MALDI-MS platform with carbohydrates.

\begin{center}
\includegraphics[width=\textwidth]{schematic_representation.png}
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\textbf{References}
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Graphene-Induced Enhancement of Water Vapor Barrier in Polymer Nanocomposites

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Reduction in water vapor permeability is both fundamentally important and a practical necessity in the polymer industry for packaging and protective applications. The barrier of polymers is significantly improved by inclusion of impermeable lamellar fillers, increasing the diffusion path of gas or water vapor molecules. The most common “barrier-modifier” for polymers is clay, which is less effective for reducing water vapor permeability since it absorbs water, swells and also degrades other properties (e.g., mechanical strength). In this study we focus on graphene as the barrier filler in polyurethane, examining the influence of its lateral size and concentration on both water vapor permeability and the mechanical properties. We demonstrated optimal barrier and mechanical enhancements at low graphene loading of 2 and 1wt%, respectively. We tested few lateral dimension of graphene and found that the larger size (25µm) exhibited an optimal barrier enhancement (50% reduction). In addition we found correlation between the onset of the barrier and an increase in the polymer viscosity.

\textbf{Figure:} Water vapor permission through polyurethane film.

\textbf{References}
Direct Covalent Coupling of Porphyrins to Graphene

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Graphene–porphyrin nanohybrid materials with a direct covalent linkage between the graphene carbon network and the functional porphyrin unit have been successfully synthesized \textit{via} a one-pot reductive diazotation approach. A graphite–potassium intercalation compound (KC\textsubscript{8}) was dispersed in THF\textsuperscript{[1]}, and different isolated porphyrin–diazonium salts were added. The direct covalent binding and the detailed characterization of the functional hybrid material were carried out by Raman spectroscopy, TG-MS, UV/vis, and fluorescence spectroscopy. LDI-ToF mass spectrometry was introduced as a new versatile and sensitive tool to investigate covalently functionalized graphene derivatives and to establish the composition of the respective nanohybrid materials.\textsuperscript{[2]}

**Figure:** Directly covalent linked graphene-porphyrin nanohybrids.

**References**


A novel CVD (chemical vapor deposition) method is presented to grow vertically aligned carbon nanotube (CNT forest) for electrical applications such as energy storage (lithium battery electrode [1]) or electrical cable [2]. Carbon hot filaments were added to a thermal-CVD process in order to activate the gaseous precursors while preventing metallic contamination often observed with traditional metal filaments [3]. The parallel array of carbon filaments is not brittle under carbon atmosphere and improves process reproducibility.

A kinetic and electrical investigation was performed to understand the effect of carbon HF-CVD on the CNT growth and performances. Kinetic analysis showed the growth lifetime (CNT height) was 5 to 10 times higher in carbon HFCVD compared to thermal-CVD while the growth rate was unchanged. This demonstrates a slower catalyst deactivation via HF-CVD. This was confirmed by monitoring the electrical resistance of CNT bundles along their length (figure). For thermal CVD-grown bundles, the resistance increases as the number of tube in the bundle rapidly decreases because of fast catalyst deactivation. This effect was used to quantify the catalyst lifetime during CNT growth. Comparing the catalyst lifetime and effective CNT growth duration can give insight into the mechanisms and physical parameters governing the maximum CNT forest height.

Figure: SEM picture of four circular electrodes Au/Pd deposited on a densified CNT bundle.

References
Innovatives Methodologies to Develop Porous 3D Scaffolds Based on PEDOT and CNT for Tissue Engineering

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Carbon Nanotubes (CNT) are one of the most promising nanomaterials to be used in tissue engineering, especially, as previously reported by our group, to interface with electrically active tissue, such as neuronal and cardiac tissues. Their inherent electrical properties and cylindrical shape are the key features to improve and boost the neuronal growth and functionality. [1]

Tissue engineering requires the manufacture of tridimensional scaffolds to be implanted, mimicking the tissue of interest to develop the functionality of the region replaced. Nevertheless, CNTs are not suitable to create three-dimensional structures by themselves, therefore polymers can be used as matrix to hold the CNTs in a 3D structure. As first proof of concept, our group developed CNTs-based 3D scaffolds using PDMS as the matrix, which was useful to evaluate the effect of the CNTs in the third dimension in neurological tissue [2]

Poly (3,4-ethylene dioxythiophene), or commonly known PEDOT, is one of the most used conductive polymers due to his high conductivity, stability and biocompatibility. The design of implants based on this kind of conductive materials offers the opportunity to reduce gliosis, improve the adaptability and increase the charge-transfer energy. However, very little is reported about the combination of conductive polymers and CNTs, and to the best of our knowledge, only 2D films have been synthesized and tested in vitro. [3]

In this work, we have adapted two known methodologies to polymerize conductive polymers to our 3D systems: chemical oxidation, which includes the Vapor Phase Polymerization (VPP) [4] and polymer dispersion in solution, and electrochemical deposition. We present the use of derivatives of these methodologies in order to create 3D structures taking into account considerable characteristics as the controlled composition and porosity, conductivity, mechanical toughness and biocompatibility to be applied in electroactive cells as neurons or cardiomyocytes.

References
Surface properties of highly aligned multi-walled carbon nanotubes depending on N doping

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Specific multi-walled carbon nanotubes (MWCNT) provide a high potential for scientific and industrial application due to their unique physical and chemical properties, which depend on their morphology. Therefore, highly aligned N-doped MWCNT with different morphologies (tubular, bamboo-like) were synthesized using a sublimation-based chemical vapor deposition (CVD) method. For their synthesis, different N containing precursors and ferrocene as iron catalyst precursor were used. As is known, N-doping leads to more defects in the carbon lattice but the as-synthesized N-MWCNT show surprisingly a significant higher alignment compared to the undoped MWCNT [1]. The reason for this high alignment is the formation of a solid iron carbide catalyst particle, stabilized by the presence of N in the gas phase, even before the CNT synthesis starts. Not only the formation of iron carbide, also its morphology are important for a high CNT alignment, mainly influenced by the ferrocene and N concentration in the gas phase. However, aside from the morphology, we also focus on the surface properties of these different N-doped MWCNT. Usually, N-doping leads to hydrophilic surfaces [2], but here we show that N-doped MWCNT can also exhibit superhydrophobic surfaces.

Figure: Images of the water droplets deposited on the N-doped MWCNT carpets (dynamic contact angle measurements) - a) toluene/pyrazine, b) toluene/benzylamine, c) acetonitrile.

References
Novel Insights in the Reductive Exfoliation/Functionalization of Synthetic Carbon Allotropes

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The tuning and optimization of the material properties of synthetic carbon allotropes (SCAs) - like fullerenes, carbon nanotubes, and graphene - for their implementation into applications is an important aspect of current research. For this purpose, the covalent derivatization of SCAs with functional entities has become a frequently used technique. The wet-chemical approach of functionalization relies on alkali metal intercalation as initial activation step in order to generate the negatively charged SCA-ide intermediates. A problem arising from the activation via alkali metal intercalation is that after the addition of the electrophilic trapping reagent, remaining charges on the respective SCA framework lead to undesired side-functionalization reactions. Therefore, we developed a new method to oxidize and to spectroscopically characterize these remaining charges in an inert way.\[1\]

Figure: Sketch of PhCN color change after electron uptake.

References

We are interested in exploring the wealth of “non-standard” and often low-symmetry carbon nanoforms that exist, many of which involve mechanical deformation of sp² sheets of graphitic carbon under the influence of external stimuli, such as surface absorbed pi-stacked molecular species, or internal stacking forces. In this poster we discuss two such species, the spontaneous formation of carbon nanoscrolls when graphene and fullerenes are mixed¹, and the structure of screw dislocations in graphite. Such large scale problems can be addressed using realistic interatomic potentials such as AIREBO², in this case within the LAMMPS molecular dynamics package³, and compared directly with experimental HRTEM images.

Figure: (left) Fullerene encapsulated in carbon nanoscroll (now obtained experimentally in the group of Mildred Quintana), and screw dislocation in graphite (centre) before relaxation, (right) after geometrical optimisation.

References
Black phosphorus-polyaniline based thin film: a stability study

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Black phosphorus (BP) has begun to enjoy the rise of fame in 2014¹, when its stripping has led to 2D layers of phosphorene. The intriguing potential properties of this material have, however, mostly been limited to theoretical predictions, once its high instability under environmental conditions leads to its degradation. Targeting its manipulation and future applications, we present the synthesis of a BP-polymer nanocomposite aiming to overcome BP deterioration. Here, the liquid/liquid (L/L) interfacial method² was employed to obtain a freestanding thin film of BP covered by the conducting polymer polyaniline (PANI). For this purpose, aniline was polymerized in a deaerated dispersion of BP (0.025 mg mL⁻¹, acetonitrile) and, after the solvent exchange to a biphasic system (aqueous HCl solution/toluene), a self-standing green film of BP/PANI was observed at the L/L interface (Figure 1).³ Raman spectroscopy showed the coexistence of the two components modes in the BP/PANI spectra, confirming the successful synthesis of the thin film, with the polymer in its conducting form (emeraldine salt). Infrared spectra attested the unstable nature of BP, exhibiting bands related to modes resulting from the phosphorus oxidation, and suggested the protective role of PANI with the absence of these bands for BP/PANI. Thus, the stability of both bare and capped material was evaluated through their exposure to the same ambient conditions. Raman and infrared spectroscopies alarmed the beginning of the decomposition process with only 3 days of exposure for the uncapped material and of about 50 days for the BP covered by PANI. Besides, the complete decomposition of bare BP happens with about 10 days and, as the monitoring of BP incorporated in the nanocomposite is still in progress, we have not yet been able to observe its complete deterioration, which has already indicated an increase of about 1500% in the stability. Scanning electron microscopy corroborated with Raman and infrared observations, showing the characteristic bubbles on BP surface for the degraded bare material (Figure 1). Overall, this work not only provides the synthesis of a novel nanocomposite, but also prints to an innovative route towards the development of transferable thin films, suitable to build new BP-based devices. Authors acknowledge CNPq, CAPES, Fundação Araucária, NENNAM, INCT-Nanocarbon, L’Oréal-UNESCO-ABC.

References
Large, fast and reversible visible-light switching of the conductivity in SWCNT-FET device decorated by photoactive complexes

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Their unique electrical properties make carbon nanotubes excellent candidates to be integrated in multifunctional optoelectronic devices. Functionalization of SWCNTs by inorganic complexes or organic molecules is highly desired for tuning the electrical response of nanohybrid devices by light stimuli and therefore building useful sensors.

Here we present large, fast and reversible photoinduced switching of the conductivity of Single wall carbon nanotube field effect transistor (SWCNT-FET) devices decorated by Ru(II)(trisbipyridine)-pyrene dyads upon visible light irradiation. This dyad molecule was designed to take advantage of the sensitizing properties of the ruthenium chromophore and the ability of the pyrene motif to form π−π interactions with the nanotube.

The induced photoactive switching is fast (less than 1 second), completely reversible, and promotes an increase in current of more than three orders of magnitude under visible light illumination. The switching shows wavelength selectivity, where only excitation in the metal to ligand charge transfer band of the Ru(II)(trisbipyridine) can activate it.

The proposed mechanism for the observed current switching involves successive triplet-triplet excitation transfer processes from the Ru chromophore to the nanotube via the pyrene.

This result underlines the importance of molecule design for the functionalization of SWCNTs in order to tune their properties with benign energy inputs such as visible light.

References

Controlled Assembly of Multifunctional Nanohybrids for Single-Molecule Investigations

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Abstract:
There has been a great interest in developing strategies to assemble functional materials with nanoscale accuracy towards the fabrication of platforms for single-molecule investigations. Single-molecule investigations can elucidate processes that would not otherwise be seen in ensemble measurements. Here we present the assembly of multifunctional nanohybrids with carbon nanotube (CNT) electrodes. We demonstrate single-molecule control in the positioning and placement of molecules on DNA wrapped CNTs. We report the in-solution attachment of single green fluorescence proteins (GFP) specifically to the ends of individual CNTs (see figure 1a). This was carried out with two GFP mutants, each engineered to exhibit genetically encoded azide groups in distinct locations: one with the azide close to GFP’s chromophore, and one with the azide further away from the chromophore. Atomic force microscopy (AFM) and photoluminescence (PL) techniques were used to characterise the CNT-GFP nanohybrids, which underlined the importance of bioengineering the proteins’ attachment sites for optimising the electronic coupling.

In addition to the CNT-GFP hybrids, single quantum dots (QDs) were attached to the ends of individual CNTs (see figure 1b), where the distance between each was defined by a DNA linker of a specific length. AFM and PL techniques demonstrated the clear distance dependency of the CNT-QD communication, where shorter distances displayed a higher degree of energy transfer from QD to CNT. Furthermore, dynamic hybrids were designed using a G-quadruplex linker between the CNT and QD, which allowed the distance between each to be contracted or extended by environmental stimulation.

These systems demonstrate a novel approach for the controlled assembly of one-to-one nanohybrids, where the position and orientation of single molecules is carefully considered. The heterostructures show promise in the bottom-up fabrication of nano electronic devices for applications in chemical or biological sensing, as well as for light harvesting and optoelectronic devices.

Figure 1: Schematic of (a) CNT-GFP nanohybrid and (b) CNT-QD nanohybrid.

References
Chemically exfoliated graphene in aqueous solution of 1-cyclohexyl-2-pyrrolidone

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Chemical exfoliation of graphite in liquids is one of the most promising methods for obtaining graphene where a scalable and low-cost process is needed. This work focuses on the evaluation of 1-cyclohexyl-2-pyrrolidone (CHP)/water mixtures as a medium for the chemical exfoliation of natural crystalline graphite into graphene. The surfactant behaviour of CHP was evidenced, and stable dispersions of few-layer (≤ 6) graphene with lateral dimensions of ~ 200 nm and low defect density were obtained in aqueous solution of CHP. The graphite/graphene conversion yield was about 1.6%, giving dispersions with concentration of 6 μg mL⁻¹ (estimated). The decrease in the interfacial energy was shown to be fundamental for the chemical exfoliation process. Besides, the "molecular wedge" type structure, as well as the formation of an intercalated solvent layer, seems to play also an important role in the exfoliation of the edges and sheets of graphene. A mechanism of graphite exfoliation in the CHP/H₂O system was proposed.
Mechanochemical synthesis of “Sweet Green Graphene”. Part II

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One of the main challenges in nanomaterial science is their use in the biology area. In this area, the transformation of biologically active compounds into viable products is often extremely time consuming and expensive. In the past, the use of cocrystals have solved most of these problems,[1] including poor hydration stability,[2] compressibility,[3] poor thermal properties,[4] low solubility and insufficient solubility.[5] Cocrystals are supramolecular structures of, at least, two neutral organic molecules interacting via intermolecular interactions such as π–π stacking, van der Waals forces and/or hydrogen bonds. In the last few years, different groups have demonstrated that cocrystals can be formed mechanochemically.[6] Mechanochemistry has also gained increasing importance in diverse fields of chemistry,[7] principally in the exfoliation and functionalization of nanomaterials like graphene.[8] It has also many advantages such as shorter reaction times, higher product yields and the elimination of (harmful) organic solvents.

Here we report the development of an environmentally friendly, cheap and simple approach for the synthesis of aqueous soluble few-layer graphene, useful for biological purposes, in the form of cocrystal with glucose.[9] The prepared graphene have been characterized by TEM, X-ray diffraction, TGA, Raman spectroscopy. This study aims to use carbohydrates (D-glucose) as exfoliating agents and open up new possibilities for preparing graphene materials, in large-scale, for biological applications.

References
Multifunctional thin film nanocatalysts derived from graphene: from pesticide degradation to hydrogen production

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A new class of catalysts derived from functionalized graphene has been attracting increasing interest due the multifunctionalities that can be incorporated and/or modulated. Herein, we report thin film nanocatalysts derived from functionalized graphene oxide (GO) that were synthesized by the interfacial liquid-liquid method, seeking overall multifunctionality hence two applications were pursued: pesticide degradation and hydrogen production. For pesticide degradation, two nanocatalysts were obtained containing imidazole (GOIMZ) and hydroxamate (GOHM) groups, that were directly anchored on the carboxylate moieties of GO (Figure 1-A). The samples were fully characterized and by the FTIR it’s possible to confirm the functionalization through the amide bonds bands. The catalytic response with the GOIMZ and GOHM were confirmed by the kinetic profile obtained from pseudo-first order reaction with organophosphates (model diethyl 2,4-dinitrophenyl phosphate DEDNPP and the pesticide Paraoxon, (Figure 1-C) presenting an impressive rate enhancements of 10^6-fold, among the highest reported for these heterogeneous reactions. The post-reaction characterization were carried out and showed no lixiviation. For the second application, i.e. hydrogen production, nanocomposites derived from reduced graphene oxide (rGO), silver nanoparticle (Ag) and metallic nickel (Ni) were obtained through the previous described routes leading to rGO/Ag and rGO/Ni (Figure 1-B). Both materials were processed in a thin film form and they were applied in the catalytic hydrolysis of NaBH₄, by following the kinetics of the generated gas. The reactions with rGO/Ag and rGO/Ni presented high volumes of H₂ produced and with maximum rates (mL min⁻¹ g⁻¹) of 44894 and 92830, respectively. The results indicate an excellent option for hydrogen production with an easily handling.

Figure 1: Synthesis and catalytic study with the nanocatalysts.

In summary, we show a strategic design of nanocatalysts for organophosphorus and hydrogen production. Their prominent catalytic activity and recycling feature allied with the facile use as thin films are promising for several applications. The authors are grateful to CNPq, CAPES, L’Oréal-UNESCO-ABC, INCT-Carbon Nanomaterials, Fundação Araucária, PIBIC/CNPq/UFPR and UFPR for financial support.

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Density Functional Modelling of Fully Collapsed Carbon Nanotubes

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The spontaneous collapse of large-diameter single nanotubes (SWNT) generates a new class of low dimensional structures, also known as closed-edged bilayer graphene nanoribbons (CLBGN) [1]. Such innovative systems represents a rising star on the horizon of materials science, since they exhibit peculiar mechanical and interesting electronic properties, and may hold promise for overcoming some limitations of graphene based high-performance nanoscale devices [2]. Experiment shows that the final configurations of CLBGNs are composed of two flat nanoribbons, whose connected edges resemble single-walled carbon nanotubes, showing non-trivial dependency on their initial guess geometry [3]. One of the unique properties of these new nanoribbons is the presence of edge cavities, which can be filled with molecules, or metals [4].

In this initial study we explore the collapse behaviour of different chirality carbon nanotubes as a function of their diameter, using density functional theory (DFT) based methods. We explore the effect of using different exchange-correlation functionals and the importance of dispersion corrections. We find that end cavity size is a direct function of the initial nanotube diameter, and confirm that metastable collapsed structures can form at intermediate nanotube sizes.

Figure: Left panel: Interlayer distance comparison with graphite and collapsed carbon nanotube with AB-stacking. Right panel: Total energy per atom of circular and collapsed nanotubes: either zigzag (a) and armchair (b).

References
[4] This work is performed within the framework of the ANR Project ANR-16-CE24-0008-01 « EdgeFiller », in collaboration with CRPP Bordeaux and CEMES Toulouse.
Gold Nanoparticles decorated Reduced Graphene Oxide (RGO) as highly sensitive electrochemical genosensing platform

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Graphene has attracted scientific community for its unique structural properties, as light transparency from visible to infrared, excellent thermal and electrical conductivity, high specific surface area, good biocompatibility, high strength and environmental stability [1]. Such functionalities are typically fully exploited in devices and systems, as field-effect transistors (FETs), sensors, supercapacitors, field emitters and solar cells [2]. Colloidal nanocrystals (NCs) or nanoparticles (NPs), prepared by means of solution-based colloidal chemistry routes, are optimal candidates for functionalizing graphene, as their unique size- and shape-dependent optoelectronic properties can be effectively conveyed to graphene, resulting in hybrid materials with outstanding functionalities, promising for advanced technological applications [3]. In this work, a novel colloidal hybrid material, based on Reduced Graphene Oxide (RGO), uniformly coated by Au NPs, is proposed as a novel genosensing platform for the sensitive detection of micro-RNA221. Such short sequences of RNAs, families of small, non-coding RNA fragments, have been found as important clinical biomarker candidates for many diseases, including cancer.

The new colloidal hybrid material is based on pyrene-carboxylic acid (PCA) surface modified RGO flakes, uniformly coated, by a dense and interconnected layer of thiol-capped Au NPs, 2-3 nm in size, synthesized by an \textit{in-situ} colloidal method. The synthesis has been optimized by tuning different experimental parameters, in order to achieve a hybrid material highly concentrated in RGO flakes and highly covered by Au NPs, having a uniform morphology and a narrow size distribution. The Au NP decorated RGO flakes have been integrated on carbon screen-printed electrodes (SPCE) and such a platform demonstrates an improved electrocatalytic activity towards electrochemical reactions of common reagents for enzyme-amplified bioassays, thus envisaging a great potential for enhancing the transducer sensitivity. Such a potential has been assessed by performing a hybridization assay based on alkaline-phosphatase catalytic signal amplification, using the novel hybrid flakes for the electrochemical determination of the micro-RNA221 sequence in Human serum spiked samples. The proposed platform resulted effective for the detection of microRNA sequences in real biological samples in an assay range of 1 – 5000 pM with a limit of detection of 0.7 pM (7 amol in 10 \textmu L) (RSD % = 13).

References.

Notes
Self-assembled core-shell CdTe/poly(3-hexylthiophene) nanoensembles as novel donor-acceptor light harvesting systems

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Fabrication of core-shell nanostructures has gained much attention over recent decades to obtain a single materials are composed of two or more different components. Hence, the properties of such nanostructures are even have new properties as compared to single component systems. The re-precipitation technique is one typical procedure to synthesis a self-assembled nanostructures.\textsuperscript{1,2}

In this work, we create a novel self-assembled core-shell nanostructures consisting of regioregular poly(3-hexylthiophene) nanoparticles (P3HT\textsubscript{NPs}) and CdTe quantum dots (CdTe\textsubscript{QDs}) was accomplished by employing a re-precipitation approach. The structure, morphology and composition of CdTe\textsubscript{QDs}/P3HT\textsubscript{NPs} nanoensembles were confirmed by high-resolution scanning transmission microscopy (TEM) and dynamic light scattering studies (DLS). Photophysical studies reveals that effective quenching of the characteristic photoluminescence of CdTe\textsubscript{QDs} at 555 nm, accompanied by simultaneous increase of emission of P3HT\textsubscript{NPs} at 660 and 720 nm, reveals photoinduced charge-transfer processes. Lastly, photoelectrochemical assays on CdTe\textsubscript{QDs}/P3HT\textsubscript{NPs} films show the improved charge separation and increased photocurrent compared to CdTe\textsubscript{QDs} which is directly related to the unique core-shell configuration of CdTe\textsubscript{QDs}/P3HT\textsubscript{NPs} nanoensembles. The fabrication of novel core-shell hybrid materials via self-assembly is transferable to other types of conjugated polymers and semiconducting nanoparticles and opens new pathways for the design of improved optoelectronic devices.\textsuperscript{2}

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Graphene/AuNps SERS thin films

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We explore the preparation and use of graphene dispersions and graphene-nanoparticles composites via wet routes in order to create organized thin films (for passivation, adhesion and design of SERS substrates, see Fig.) At large concentrations, the liquid crystal ordering is an opportunity to spontaneously organize the materials. At lower concentrations, a special care has to be taken during the deposition of the thinnest films.

In this work, we have focused on the design and the characterization of thin layers made of graphene oxide and gold nanoparticles (GO/AuNps) for their Surface Enhanced Raman Spectroscopy (SERS) properties. The objective here is to establish the main rules that control (during the deposition) the structure of the films and their resulting SERS properties. We have used various techniques such as dip-coating, spin coating with varying parameters, as well as surface functionalization before deposition. The thin films have been characterized by AFM and their performance have been tested with Raman spectroscopy.

Figure: Design of thin films of graphene and graphene/NPs composites via wet routes
Surfactant-free synthesis of nanoperforated graphene/nitrogen-doped carbon nanotube composite for supercapacitors

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A nanoperforated graphene/carbon nanotube (PG/CNT) composite is fabricated by electrostatic interaction of graphene oxide (GO) and nitrogen-doped CNTs, and subsequent catalytic carbon gasification. The nitrogen-doped sites (pyridinic N sites) of the CNTs are protonated under the acidic conditions owing to the lone pair electrons, rendering the CNTs positively charged. The nitrogen-doped CNTs are uniformly incorporated into PG to form the PG/CNT composite through electrostatic attraction between the positively charged CNTs and the negatively charged GO. The resulting PG/nitrogen-doped CNT (N-CNT) composite exhibits outstanding electrochemical properties, showing high specific capacitance (288 F/g at 0.5 A/g) and high rate capability (267 F/g at 20 A/g) as well as excellent cycling stability (99% capacitance retention after 30,000 charge/discharge cycles). This is attributable to not only the formation of high concentration of edge sites in PG and improvements of cross-plane ion diffusion owing to the nanoperforations, but also the enhancements in the ion-accessible area and in-plane ion diffusion due to incorporation of N-CNT nanospacers into PG.

Figure: Schematics of nanoperforated graphene.

References
Integration of covalent and non-covalent functionalized SWCNTs in FETs

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Metal nanoparticles attached to carbon-based nanostructured materials enable new nanoelectronic solutions for energy storage (e.g. fuel cells, supercapacitors) \cite{1} and for chemical, biochemical \cite{1,2,4} and optical sensors \cite{2,3,4}. A requirement for electronic sensors is the design of a versatile nanoelectronic transducer. In the ideal case, such a component can be functionalized with nanoscopic building blocks in a modular way that allows selective response and tuning of the sensitivity of the device. Nanoelectronic field-effect transistors (FETs) using individualized single-walled carbon nanotubes (SWCNTs) have been proposed as FET channel material \cite{5,6}.

Recently, we presented a scalable on-chip functionalization approach for SWCNTs between palladium electrodes in the geometry of a field-effect transistor with preformed gold nanoparticles based on the Hirsch-functionalization of SWCNTs (Fig. 1) \cite{5}. This method is wafer-level compatible and comprises two stages of flow chemistry (Fig. 2). In a new chemical approach, we propose the deposition of dispersed SWCNTs by using alkylthioate functionalized pyrene which allows selective attachment of noble metal nanoparticles (Fig. 3). The concept for this type of FET channel is shown in the schematic representation (Fig. 4).

\textbf{Fig. 1}: Chemical concept of a SWCNT functionalized with a gold nanoparticle by the Hirsch-approach, \textbf{Fig. 2}: Atomic-force microscope image of a CNT-FET transistor channel showing SWCNTs decorated with gold nanoparticles, \textbf{Fig. 3}: Chemical concept of non-covalent attached gold nanoparticle to SWCNTs, \textbf{Fig. 4}: Schematic representation of a SWCNT-based field-effect transistor system used as an optical sensor.

\textbf{References}

SYNTHESIS AND APPLICATIONS OF GRAPHENE-TRIAZINE HYBRID HYDROGELS

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The introduction of aminotriazines in polymeric hydrogels has been successfully used to strengthen the mechanical properties of gels, bind DNA for reverse gene transfection, or remove metal ions through adsorption. Based on our experience in the preparation of triazine derivatives, we presently carry out the syntheses of 2,4-diaminotriazine-based hydrogels.

Graphene-based polymer nanocomposites have been widely listed for many applications due to their outstanding electrical properties. Our group has recently focused on non-covalent interactions between graphene and aminotriazines; thus, the preparation of hydrogels combining both graphene and 1,3,5-triazines could further introduce new functionalities, leading to preparations of more effective graphene-based hydrogels. Herein, we carry out the syntheses of graphene triazine-based hybrid hydrogels, both chemically and physically crosslinked, and evaluate their mechanical and swelling properties, as well as their possible applications.

![Graphene-Acrylic Monomers Reaction](image)

**Figure**: Overview syntheses of physically (up) and chemically (down) graphene-triazine based hydrogels

References

Synthesis of alkylated graphene by the combination of oxidative and reductive functionalization

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The controlled covalent functionalization of graphene remains a challenging task, in particular using graphene oxide as starting material. Reported functionalization approaches either lack in determining the quantification or they do not discriminate between covalent and non-covalent functionalization. The application of a two-step procedure consisting of the formation of oxo-functionalized graphene followed by chemical reduction leads to the access to the complete surface of graphene for functionalization. While Raman spectroscopy is powerful to determine the degree of in-plane lattice defects and the degree of functionalization, the method fails detecting changes in the presence of defects close to 1\%.\textsuperscript{[1]} We find that sensitive thermogravimetric analysis coupled with gas chromatography and mass spectrometry can prove alkylation. Moreover, the results demonstrate that the chemically exfoliated reduced graphene oxide is a suitable precursor for reductive chemistry and furthermore, its efficiency of being functionalized is comparable to reductive functionalization of pristine graphene and graphite, respectively.

Figure: Reaction scheme of the reductive functionalization of oxo-graphene

References

Functionalisation approaches to generate biodegradable graphene oxide-based conjugates

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Although significant research is conducted on the use of graphene and other two-dimensional (2D) materials in the area of biomedicine, very little is still known about their biodegradation possibilities. In consequence, tailoring the design of surface-functionalized sheets rapidly degrading or to accelerate the activity of specific oxidative enzymes, is fundamental.

Kurapati et al. demonstrated that human myeloperoxidase (hMPO) catalyses the degradation of graphene oxide (GO) in the presence of $\text{H}_2\text{O}_2$.\textsuperscript{1} The authors propose that the hydrophilic nature of GO and its colloidal stability in aqueous media are crucial factors for its biodegradation by peroxidases. More recently, they have also studied the surface-functionalization of GO with two well-known substrates of horseradish peroxidase (HRP), namely coumarin and catechol.\textsuperscript{2} These GO conjugates have the ability to degrade more effectively compared to unmodified GO using HRP.

In this contribution, I will present the effect of the functionalisation of GO with a chemotactic peptide in the degradation capacity of the new hybrid. These kind of peptides are known to interact better with the cells, which would improve the potential of the final material in biomedical applications. Different techniques such as Raman and transmission electron microscopy are used to assess the biodegradation. The results prove and evidence the biodegradability of this novel hybrid nanomaterial using hMPO in the presence of $\text{H}_2\text{O}_2$, eventually being a promising candidate in the biomedicine field.

![Figure: General scheme showing functionalisation and biodegradation steps.](image)

References

From Nano to Macroscale: Graphene Quantum Dot-aerogels for sensing polyaromatic compounds

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Graphene Quantum Dots (GQDs) have received a great deal of attention due to their photolumincent properties, high water solubility and biocompatibility. Furthermore, these nanoparticles present high surface area-to-volume ratio, laminar graphitic structure and planar surfaces that are able to bind other molecules by π−π interactions. These excellent properties make that GQDs can be used as materials for solar cells, in analytical science [1] or in biomedical applications.[2] However, the tendency for aggregation of these fluorescent nanoparticles in dry states is a limiting factor that can affect the photoluminescence behavior.[3] In an effort to prevent this agglomeration, nanoparticles can be incorporated into appropriate matrices.

In particular, the incorporation of nanoparticles within three-dimensional polymer matrices such as hydrogels to form nanocomposites is a useful strategy not only to preserve the photoluminiscent properties, but also to enhance the mechanical properties or the response to certain stimuli. Taking advantage of this synergistic effect, hydrogel nanocomposites have found applications in diverse fields, for example biomedical applications.[4]

In this work, a hydrogel based on GQDs is prepared. This nanocomposite is completely characterized and their sensing properties are also studied at different pH media and in the presence of several molecules. Our GQDs-based nanocomposite has also been proven to be a sensor for polyaromatic compounds in water.

Figure: a) Transmission Electron Microscopy (TEM) of GQDs; b) Digital photo and c) Cryo-Scanning Electron Microscopy (Cryo-SEM) of the nanocomposite.

References

Notes
Graphene oxide (GO) is a highly defective chemically modified form of graphene containing many different types of oxygen functional groups on its basal plane and edges.\textsuperscript{1,2} Their presence imparts hydrophilicity and allows for easy processing from water dispersions into multilayered macroscopic assemblies.

In this work we focus on the macroscopic assembly of GO into free-standing membranes,\textsuperscript{4} aerogels\textsuperscript{5} and thin film layers\textsuperscript{6}. We discuss the critical effect of chemisorbed water for the fabrication of conductive electrode materials,\textsuperscript{4} the influence of pH on the self-assembly process and the chemical and morphological properties in aerogels,\textsuperscript{5} as well the interface transport properties of thin film layers on semiconducting metal oxides. The value of GO as highly functional and tunable platform for the development of macroscopic multi-layer assemblies and their impact for improved functional device structures will be emphasized.\textsuperscript{4,6}

\textbf{Figure:} Macroscopic multilayer assemblies of GO dispersions into (top) GO papers, (middle) GO aerogels, (bottom) GO films

\textbf{References}
Novel interfaces for sensing implants based on modified CVD Graphene.

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Graphene has shown to be a promising next generation material due to its electronic, mechanical and thermal properties. It exhibits a wide variety of potential applications in the field of biomedicine such as sensing, bioelectronics, implants and drug deliver.[1] In addition, chemical functionalization of graphene allows the modification of the physical and chemical properties,[2] which is a mandatory step for the attachment of functional biomolecules. This work is focused on the development of novel modifications on Chemical Vapor Deposited Graphene (CVDG) surfaces based on the combination of covalent and non-covalent modifications in order to produce stable organic interfaces for biomedical devices. The generated interfaces allowing the development of sensing and biocompatible implants.

**Figure 1:** Scheme of functionalization in different architectures.

\textbf{References}

Covalent Functionalization of SWCNTs with Pyridines

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The covalent functionalization of carbon allotropes is a main topic for researchers in the field of nanomaterials.\textsuperscript{[1]} Despite the low reactivity of these allotropes, the reduction of single walled carbon nanotubes (SWCNTs) yields a highly reactive carbon species, which is capable of reacting with numerous molecules.\textsuperscript{[2]} To enable further reactions we introduced a heteroatom bearing group such as pyridine. Additionally, we tested the corresponding diazonium compound of pyridine without prior charging of the allotrope.

\textbf{Figure:} Schematic functionalization pathways.

\textbf{References}

Polymeric nanocomposites of graphene and carbon nanotubes covalently linked with polypyrrole

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Functionalization by a covalent bond is a strategic tool for modulating the properties of carbon-based nanomaterials. The possibility of combination between graphene or carbon nanotubes and conductive polymers by a covalent bond causes synergism and has potentiated the applications in supercapacitors, sensors or artificial muscles. Herein, we carried out the functionalization of (i) CNTs and (ii) graphene oxide (GO) with pyrrole monomers. Two approaches were adopted for the functionalization (i) directly on the carbon structure of CNTs through a covalent bond with the pyrrole derivative (Py) and (ii) on the carboxylic groups of GO with the formation of an amide bond with Py. Subsequently, the functionalized materials were chemically polymerized in aqueous solution containing pyrrole, leading to novel polymeric nanocomposites: Poly-SWCNT-BPI and Poly-GOPy (Figure 1), which were subsequently reduced with NaBH₄ in order to improve the conductivity of the material (Poly-rGOPy). For comparison purposes, analogous non-covalently bonded nanocomposites were obtained. The materials were obtained as a solid and a thin film. The later was obtained by the interfacial liquid-liquid functionalization method.

Figure 1: Schematic representation of synthesis and characterization of nanocomposites.

All the samples were fully characterized by infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Raman spectroscopy, cyclic voltammetry (CV) and X-ray photoelectron microscopy (XPS). The analyses confirmed the functionalization by a covalent bond on the CNTs and GO, in addition to the polymerization with the polymer in its oxidized form, i.e. most conductive. Moreover, by SEM analysis the homogeneity of the covalently linked nanocomposites is evidenced. Finally, the electrochemical studies show that the covalently linked nanocomposite remains stable for 300 cycles, presenting higher stability than the precursors and the non-covalently linked nanocomposites which are stable only for 20 cycles. The anchored monomers on surface of CNTs and GO takes part on the polymerization process with the Py monomers on the medium, providing the chemical linkage between polymer and carbon structure (GO or CNT). Overall, the obtained results indicates that the covalently bond nanocomposite is promising for supercapacitors, evidencing the excellent interaction provided by the covalent bonding.

Highly Conducting, Sustainable, Nanographitic Rubber Composites

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Food waste can be transformed into high value nanocarbon and renewable hydrogen through energy efficient transformation of methane resulting from decomposition of food waste.\textsuperscript{1,2} After purification, well defined, high concentration dispersions of nanocarbon, calibrated in size were obtained and characterized.\textsuperscript{2} Several are the uses of the nanocarbon dispersions: in batteries, as carbon dots or as fillers in polymer composites. Multifunctional nanocomposites with natural rubber latex (NR) were prepared by an environmentally friendly route that some of us have developed with carbon nanotubes and graphene species.\textsuperscript{3,4} NR is a natural polymer composed mainly of poly (cis-1,4-isoprene). The preparation of NR nanocomposites with nanocarbon (NC) aims to combine synergistically the properties of the two materials, thereby extending these application possibilities. In this study superior thermal and electrical properties of the composites are reported. In particular, highly conducting rubbers were obtained with only 10 wt\% of fraction filler, 11 orders of magnitude higher than the pure polymer.\textsuperscript{5} Nowadays, in order to reach conductivity values as high as that obtained with 10 wt\% graphitic nanoparticles, composites with commercial fillers must include as much as 25 wt\% filler content. Furthermore, piezoresistive experiments have been performed and have shown that the rubber composites may be used as deformation monitors.

These green composites could be used in a variety of applications such as sealing of electronic devices and sensors. These graphitic nanoparticles represent a viable alternative to commercially available fillers.

Figure: TEM images of 10 wt\% natural rubber/nanocarbon composite

References

1. European community funded FP7 project PLASCARB. \url{http://www.plascarb.eu/}
Microsupercapacitors Produced from Nanocarbons Originating from Food Waste

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Electrochemical double layer capacitors (EDLCs), as one kind of energy storage devices, have been the subject of numerous studies in recent years due to their high power density property.\(^1\) Compared with batteries, charge/discharge process is very fast, without chemical reactions involved, in the double layer of electrolyte ions which forms at the interface between electrolyte and electrode of active materials. Due to their high surface-to-volume ratio, carbon materials such as carbide-derived carbons, onion-like carbons, carbon nanotubes, reduced graphene oxides and graphene are favourable to supercapacitor studies.\(^2\)

Herein, we report a new class of nanocarbons (NC\(_{\text{bio}}\)) derived from biogas by using a cold microwave plasma process.\(^3\) NC\(_{\text{bio}}\) nanocarbons have turbostratic packing structure and their surface can be fully accessible by ions. EDLCs (Figure 1) using NC\(_{\text{bio}}\) nanocarbons (NC\(_{\text{bio}}\)-NCs) were fabricated by ink-jet printing on flexible substrates, PET and PI. EDLCs show very good power density and their capacitances can be easily controlled. They thus represent sustainable, low cost, EDLCs with power densities up to 50 W/cm\(^3\).

Figure 1: (a) Scheme of micro supercapacitor produced from nanocarbons from biogas. (b) Picture of a printed micro supercapacitor on PI substrate. (c) Ragone plot of micro supercapacitors of different printing passes.

References

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Understanding the burning of MWCNT/ carbon shells mixture – A kinetic study

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The EdgeFiller project proposes to use flattened "dogbones" carbon nanotubes (Figure 1) for electronic applications\textsuperscript{2}. Flattened tubes can be obtained from a MWCNT, by extracting concentric tubes from each other, allowing the larger ones to collapse\textsuperscript{3}. A first step to carry out the extraction consists in opening the ends of the tubes\textsuperscript{4}.

The present study focusses on the way to finely control the opening step by thermal oxidation, and to determine kinetic parameters thanks to thermogravimetric analysis (TGA). The aims of this study are:

(i) To be able to open the tubes without oxidizing the walls.
(ii) To oxidize a maximum of concentric carbon shells (onion structure) present in commercial samples.

Thanks to the quasi-isotherm method (dynamic TGA method with feedback), we have been able to preferentially burn the ends as well as the carbon shells rather than the walls of the tubes (Figure 2). Several kinetic models have been tested to understand the mechanisms involved in this oxidation.

\textbf{Figure 2:} Quasi-isothermal measurement with TEM images of MWCNT sample at the beginning and after 70\% of weight loss.

References
2. This work is performed within the framework of the ANR Project « EdgeFiller », in collaboration with IMN Nantes and CEMES Toulouse.
Graphene and CNT composite fibers: from shape memory torsional actuators to biofuel cell electrodes.

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The processing of nanocarbons into fiber form provides a route towards a variety of electro-active materials potentially useful in energy production and conversion. In particular, we show recent progresses related to the development of new shape memory torsional actuators and highly efficient microelectrodes for biofuel cells. Graphene reinforced polymer fibers exhibit significant improvements of their shear modulus. As a result, such fibers can absorb a high amount mechanical energy when twisted at high temperature. This energy can be stored by quenching the materials at low temperature. It can be further restored by heating the material above its glass transition temperature. The fiber untwists and acts as a torsional actuator capable of generating an exceptionally high torque associated to a giant energy density. In addition, the temperature at which the maximum of energy is released can be tuned by changing the programming conditions. Graphene or CNT fibers also exhibit electrical conductivity and can serve as efficient microelectrodes in bio-electrochemical applications. In particular, we present a new fiber spinning methodology that allows the one-step production of fibers made of CNTs and imbricated enzymes which act as catalysts for the reduction of O₂. The enzymes are distributed from the core to the surface of the fibers. As a result the present fibers exhibit enhanced activity compared to conventional microfibers which are surface coated. Lastly, scale-up efforts of the present technologies will be discussed.
In this work we explore how the realised morphology of SWCNT networks is affected by a variety of factors: dispersing solvent(s), stabilising/de-stabilising agents, and substrate transfer/sample preparation techniques were explored. Atomic Force Microscopy (AFM) was extensively used to study the resulting morphologies. A marked difference in alignment, degree of individualisation of the SWCNTs, porosity and network surface coverage was observed.

**Figure:** AFM micrograph of a SWCNT network obtained via flocculation-induced interfacial assembly

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Ab initio study on the exfoliation process of “Sweet Green Graphene”. Part I

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First isolated in 2004,[1] graphene has sparked a great scientific interest thanks to its peculiar mechanical and electronic properties, which promise to upgrade many technologies, from microelectronics to biosensing and nano-medicine.[2] These potential applications require stable graphene dispersions with a good balance between yield and ease of manipulation, where graphene electronic properties are retained. Exfoliation of graphite via non-covalent intercalation of small organic molecules[3] represents a promising strategy to obtain high quality graphene avoiding chemical modifications that can compromise its electronic features. Mechnochemistry is a good methodology for generating shear force, which can thus provide a simple, eco-friendly and low-cost mass production of high-quality exfoliated graphene and its further functionalization.[4] Among the many molecules that have been proposed as exfoliating agents, only a few ones successfully exfoliate and stabilize graphene in aqueous media.[5]

Here we present the comparison between 2,4,6-triamino-1,3,5-triazine, also known as melamine and different carbohydrates, sucrose, fructose and glucose. We explained the role of melamine on stable graphene aqueous dispersions through the nature of water-melamine-graphene interactions with state-of-the-art density functional theory (DFT) calculations within a super-cell slab periodic approach. From our theoretical insight and comparison with experimental result, we propose the role of melamine in a microsolvation model where the subtle interplay between non-covalent interactions, namely dispersion and hydrogen-bonding, provides the necessary thermodynamic driving force to stabilize the graphene-water dispersions.[5]

These results directed us to study different supramolecular coverages of the carbohydrates with different symmetries on graphene. The results, discussed in this contribution, provided useful insights on the decision making of which carbohydrate to use, as melamine replacement and new non-toxic molecule that can conveniently co-adsorb with water on graphene, thus enabling its effective use in aqueous media. This approach provides insight into new supramolecular networks with capacity to prepare graphene materials in large-scale for biological applications.

References

Notes
Elaboration of carbon nanofibers from a natural precursor by electrospinning

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Available carbon fibers are made from petroleum derivatives (PAN) and have a high costs. Thus, the development of low-cost carbon fibers through the use of precursors from biomass seems to be an interesting alternative. Lignin is one of the most promising precursors. In addition to its high abundance and its low cost, lignin has other advantages as a high carbon percentage ($\geq 60\%$) which after heat treatment gives a high carbon yield, essential for the application in the field of composite materials. In recent years, electrospinning has emerged as a promising way for the preparation of new lignin-based fibrous materials. Despite the advantages of using electrospinning and a possible use of a cheap natural precursor such as lignin, nowadays there are to date relatively few studies dealing with the elaboration of carbon fibers by electrospinning.

In these studies, precursor fibers are obtained from a wet-spinning process: electrospinning. Most of the time, these fibers are composed of a mixture of lignin and a polymer used as a plasticizer to ensure lignin spinning\textsuperscript{1}. Electrospinning allows with the application of high voltages to obtain polymer nanofibers with a diameter that typically varies from several hundred nanometers up to one millimeter in the case of yarn nanofibers\textsuperscript{2}. With such small diameter, fibers will have greater properties than those of large diameter. Generally, a first part consists in carrying out formulation of the lignin/polymer mixture in order to obtain uniform precursor nanofibers after electrospinning. The results show that the total weight percentage of the mixture and the variation of the lignin/polymer ratio affect directly the morphology of the nanofibers. A second part of these studies is dedicated to the transformation of the precursor fiber into carbon fiber. The heat treatment is separated in two stages: the oxidative thermostabilization allowing the lignin to become infusible with its crosslinking, then followed by the carbonization of the fibers ($T \approx 1000 \, ^\circ \, C$) under inert atmosphere. Works of formulation, elaboration and characterization on the synthesis of carbon fibers by electrospinning will be detailed.

\textbf{Figure} : (a) Picture of carbon nanofiber mat ex-lignin, (b) SEM picture of a carbon nanofiber ex-lignin (scale = 200 nm)

\textbf{References}


Fast Exfoliation and Functionalisation of 2D Crystalline Carbon Nitride

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Graphitic carbon nitrides (g-CN) have gained interest recently due to their two-dimensional structures, analogous to graphene, and their complementary properties including inherent semiconductivity with tunable band gap and optical characteristics.\textsuperscript{1} Many applications have been investigated, but success has been limited by the poor solubility of g-CNs. Several methods have been adopted to synthesise few-layer carbon nitride nanosheets (FL-CNs). Unfortunately, many of these processes damage the structure, altering the properties of interest.\textsuperscript{2}

Polytriazine imide (PTI) is more crystalline than its heptazine-based counterpart, and its exfoliation into high quality 2D FL-CN crystals is, therefore, attractive. Reductive charging has been used previously to dissolve a variety of 2D nanomaterials.\textsuperscript{3} In this work we have used reductive methods to successfully exfoliate PTI into non-damaged FL-PTI with high yield. High resolution TEM, together with AFM, provides direct evidence of the structure and crystallinity of the FL-PTI. This framework charging method avoids the damage associated with sonication methods, and provides an order of magnitude increase in concentration. This framework charging was used to functionalise FL-PTI by reaction of the charged salt with different alkyl bromides. The approach may be generalised in future, to a wide range of reagents and functional groups. These functionalised FL-PTI may afford interesting materials for their use in electrochemical devices, water splitting photocatalysis, metal-free chemical catalysis, and nanomedicine.

\textbf{Figure:} Schematic illustration of the framework charging and functionalisation of PTI.

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\end{enumerate}
Modeling polymer nanocomposites of bio-sourced thermoset resins and carbon nanotubes

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Epoxy-based thermoset resins are widely used in the transportation sector, in which they play a central role for the protection of metal substrates. However, the properties of those polymers have proven insufficient for applications in aircrafts. Developing novel resin formulations with improved properties is therefore of major importance. On one hand, the properties of thermoset resins can be improved by incorporating nanocharges in the polymer matrix. On the other hand, designing high-performance materials with a reduced carbon footprint also constitutes a strong technological driver. In this work we perform molecular dynamics (MD) simulations to study structural and thermomechanical properties of a novel family of benzoxazine thermoset resins based on paraphenylene diamine, in which carbon nanotubes can be dispersed. As a first step, we model the structure and properties of the polymer matrix with an increasing degree of crosslinking. An iterative crosslinking-relaxation methodology is developed to construct the simulation cells. This crosslinking-relaxation methodology allows the construction of highly cross-linked polymer networks from a given set of monomers. After optimization of the forcefield, several properties of the resin are computed such as volume swelling, network topology, gelation point, glass transition temperature and Young's modulus. The dependence of these properties on the crosslink density and temperature is also investigated. The results of the simulations are compared with existing theoretical or experimental data; and a very good agreement is observed, which allows to understand the influence of the chemical structure of the monomer and the incorporation of the nanotubes on the resin performances [1].

\textbf{Figure:} Snapshot of a CNT inserted in a polybenzoxazine box (left) and polybenzoxazine sandwiched between two graphene sheets (right).

\textbf{References}

Structural and colloidal properties of oxidized single-walled carbon nanotubes

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Due to their unique properties single-walled carbon nanotubes (SWCNTs) have found numerous applications in diverse fields including memory devices, energy storage, electronic systems, composite materials, catalysis and biomedical applications. However, the special properties are observable mainly for SWCNTs that are debundled, individualized and stabilized in solution. One way to debundle, individualize and have the SWCNTs stable is the functionalization via oxidation. Common oxidation methods include gas phase oxidation and liquid phase oxidation. Both are used as purification methods and also for improving the chemical reactivity of the graphitic SWCNT network. In this way, the as-synthesized SWCNT are purified from metallic impurities while oxygen groups are attached to the carbon surface. The presence of oxygen-containing groups facilitates the exfoliation of SWCNT bundles, and increases the solubility in polar media. Besides, oxidation is one of the shortening strategies that can be used in order to improve the SWCNT biocompatibility for biomedical applications.

In this work, air oxidation at different temperatures and HNO₃ treatments under different conditions were performed on HipCO SWCNTs. Afterwards, the oxidized SWCNT samples were dispersed in sodium dodecyl sulfate (SDS) in order to have a stable aqueous dispersion of SWCNTs and avoid their aggregation. Next, centrifugation was effected to remove residual catalyst particles, amorphous carbon, and tube bundles. All the samples were characterized by optical absorption spectroscopy, Raman spectroscopy, dynamic light scattering and zeta potential techniques.

Particle size decreases after oxidation. Besides, after centrifugation the particle radiuses are the lowest. The optical spectra of oxidized SWCNT samples present an attenuation of the electronic transition bands. However, they are mostly recovered once the centrifugation purification treatment is applied. An indirect assessment of structural changes in SWCNTs was performed using Raman spectroscopy.
Experimental and DFT studies of functionalisation in MoS$_2$ and Graphene Oxide

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Besides graphene, MoS$_2$ is the most studied 2D material because of its potential applications in nanoelectronics, optoelectronics, spintronics, catalysis, energy storage and biomedicine [1]. In order to tailor the properties of TMDs, add novel functionalities and control their processability in different environments, chemical functionalization of the 2D sheets is crucial [2]. Combining experimental and DFT studies, we have investigated the functionalization of MoS$_2$ with photoactive species through covalent and non-covalent approaches. We find preferential covalent functionalisation at the sheet edges [3], with pyrene- moieties strongly pi-stacking on the MoS$_2$ surface in both covalent- and non-covalent cases. Interestingly pyrene appears to protect the surface from oxidation during laser irradiation, through a catalyzed polymerization process we are exploring at present. We also show how Pyrene derivatives can attach to graphene surfaces with charge transfer that leads to useful supercapacitive behavior.

In parallel we have been investigating the behavior of water and associated functional groups with graphene oxide (GO) surfaces. In a “top-down” approach we use near-IR measurements at different humidity to reveal the different functional group behavior and degree of hydrogen-bonding interaction with absorbed water, while our “bottom-up” approach is to use controlled functionalisation coupled to density functional calculations to design specific crystalline functionalized graphene phases.

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Biomimetic iron(II) α-keto acid complex grafted on carbon nanotubes via poly(amidoamine) dendrimer for catalytic aerobic oxidation of organic compounds

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α-ketoglutarate (α-KG)-dependent non-heme oxygenases are well known enzymes for catalysing a myriad of biological oxidation/oxygenation reactions through formation of high-valent iron-oxygen species from dioxygen as active oxidant. So-far developed functional models are far from practical use as they fail to deliver at catalytic rates due to decomposition.[1] Anchoring homogenous complexes over robust solid supports with high surface area have shown enhanced activity.[2-3] Among solid support, carbon nanotubes (CNTs) known for its intrinsic properties are noteworthy and were used as the solid platform to tether a biomimetic iron(II)-benzoylformate complex supported by a nitrogen-rich ligand functionalized at the extremities of modified polyamidoamine (PAMAM) dendrimers. The amine terminated dendrimers could be easily modified and subsequently anchored to the surface of CNTs bearing alkenyl functionalities[4] and linked to nitrogen ligands employing one-pot CuAAC click reactions.

The developed one-pot synthesis is highly efficient discarding the necessity of isolation of any intermediate unstable azide derivatives and results in loading of higher density of covalently linked ligands on CNTs support. The immobilized iron(II) complex on reaction with O2 undergoes oxidative decarboxylation of the metal-coordinated benzoylformate to benzoate along with the generation of an iron-oxygen intermediate capable of oxidizing organic substrates. The CNTs tethered complex showed selective catalytic oxidation of sulfides and alcohols to the corresponding sulfoxides and aldehydes, respectively, under ambient conditions using dioxygen as the oxidant.

Figure: Protocol for the synthesis of Carbon nanotubes functionalized with dendrimer linked iron(II) catalyst.

References
Cross-linked single walled carbon nanotubes and polytriazine-imide for energy storage applications

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Single walled carbon nanotubes (SWCNTs) are widely used as energy storage electrodes owing to their good electron transport, high conductivity, and their outstanding electrochemical and thermal properties.[1, 2] Nevertheless, SWCNT based electrodes normally suffer from low intrinsic resistances and poor interconnectivity.[3] To address these problems, SWCNTs have been cross-linked to reduce the intertube and interbundle separation, increase surface area and enhance ion accessibility.[4] Herein, cross-linked SWCNTs were produced via sodium naphthalide in dimethylacetamide (DMAc) with p-diiodobenzene (p-DIB) as a cross-linking agent.[5] The as-synthesized SWCNT-p-DIB buckypaper had a good sheet conductance of 2.6 sq/Ω. As a route to produce higher energy and high power density electrodes, SWCNTs were cross-linked, in the same method, but hybridised with polytriazine-imide (PTI). The addition of PTI, which contains nitrogen, should enhance redox reactions and increase ionic conductivity and subsequently mass transportation.[6, 7] Electrochemical characterisation of these hybridised materials will also be presented.

\textbf{Figure}: Scheme of cross linking SWCNTs and PTI via reductive agent.

\textbf{References}

Crumpled graphene/binary metal oxides composites for supercapacitors

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The interest in supercapacitors has growing over the years mainly due to their high-power density, long-life cyclability and fast charge-discharge reactions when compared to batteries.\cite{1} Among the broad range of materials exploited for this purpose, graphene and transition metal oxides are promising materials, largely by the high conductivity and surface area of the former one and due to the pseudocapacitance of the last ones.\cite{2} Even having such characteristics, these materials present some drawbacks like the restacking of the 2D materials during the construction of supercapacitor and the low conductivity of the metal oxides, which strongly compromise the capacitive behaviour of the material. These drawbacks are easily overcome changing the sheet-like structures of graphene into 3D crumpled graphene balls and decorating this carbon-based material with the metal oxide. A different approach can be also exploited synthesizing binary transition metal oxides, which improve the electrochemical performance of such oxides. With this motivation, the present work shows the first attempt to synthesize in one single step nanocomposites of crumpled graphene balls and binary metal oxides of manganese and iron. The materials were synthesized using a graphene oxide dispersion mixed or not with the metal oxides precursor (anhydrous FeCl\textsubscript{3} and MnCl\textsubscript{2}.2H\textsubscript{2}O) with ratio of 1:0.25:0.25 w/w. This mixture was nebulized into a quartz tube at 400 °C and pure crumpled graphene (pure CG) or iron/manganese oxide/crumpled graphene composites were obtained. The electrochemical behaviour of both materials was evaluated from the electrodes (fluorine-doped tin oxide) covered with the dispersion of CG or CG-Fe/Mn. In Figure 1 (a) the 3D structure of the pure crumpled graphene is clearly observed, which is a result of a capillary compression process of the droplets of water filled with graphene oxide. In Figure 1 (b), the rectangular shape of the cyclic voltammetric (CV) curve for CG-Fe/Mn resemble the behaviour of ideal electrochemical capacitor. The charge-discharge (CD) curves for CG and CG-Fe/Mn in Figure 1 (c) show a huge difference, demonstrating better capacitive behaviour for the composite. The specific capacitance of the composite is far from acceptable values, being equal to 29.7 F/g. Different ratios of graphene oxide and metal precursors will be evaluated to achieve better results.

\textbf{Figure 1}: (a) SEM image of the pure CG; (b) CV curves and (c) CD curves for pure CG and CG-Fe/Mn.

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Porous, Conductive Thin Films from Functionalised SWCNT Aerogels

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Single-walled carbon nanotubes (SWCNTs) have a multitude of remarkable properties including high strength and stiffness, surface area and thermal and electrical conductivity. Unlocking these superlative properties requires exfoliation of the SWCNT bundles and dispersion in a suitable solvent. Reductive dissolution is an effective route to individualised nanotubes that preserves the high aspect ratio and retains the sp\textsuperscript{2} carbon framework whilst providing a handle for subsequent functionalisation.\textsuperscript{1} Such solutions can be covalently crosslinked using dielectrophiles to give low-density, interconnected SWCNT networks with high electrical conductivity and specific surface area.\textsuperscript{2}

Through substrate surface modification it is possible to cast such networks as thin films, giving highly conductive devices with accessible porosity. The networks’ properties are dependent on the crosslinking moiety thus different compounds can be utilised to tune the various material properties. Devices of this kind show promise in various applications from photovoltaics, sensors and catalysts to conductive inks and coatings.

\textbf{Figure:} Reaction sequence for the individualisation and crosslinking of SWCNTs and scanning electron micrographs of an aerogel film.

\textbf{References}

Micro-scale energy storage devices prepared by inkjet printing

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There is an exciting opportunity to develop printed energy storage devices for the rapidly emerging flexible electronics, especially as the increasing energy demand for next-generation portable and electronic miniaturized devices has flashed an intensive interest to explore energy storage devices at the micro-scale [1]. Notwithstanding, preparing capacitors at this scale has to face challenges derived from conventional sandwich like geometry, especially with the settlement with the industry of high scalability for reproducing these devices. However, inkjet printing can be a perfect technique for designing these micro-devices because of its low cost, good resolution and in particular the non-contact nature.

In this work, we have printed a micro-scale dielectric capacitor on the PEN substrate (left figure), where both electrodes were printed using a water dispersion of multi-walled carbon nanotubes (CNT) and the polymer layer were printed based on a low cost PVDF@Arkema water solution. The flexible CNT electrodes and high-permittivity PVDF layer in between actually form a sandwich-like capacitor geometry. Dielectric characterizations of our devices gave the relative permittivity of PVDF of 10 and the losses of ~0.001 at 100 Hz, indicating that the printed micro-scale device is indeed an effective capacitor configuration. Further high field characterizations shown an excellent energy storage performance, namely an energy density of ~3.81J/cc under an electric field of 350 MV/m (right figure) which approaches the values obtained in the macro-scale PVDF film capacitors.

Figure. A typical micro-capacitor printed on PEN substrate (left) and Energy storage density as a function of electric field of a PVDF film (right).

Bibliography:
Non-conjugated polymer dots: shining light on structure and fluorescence

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Polymer Dots (PDs) are a novel class of carbon nanomaterials, which received considerable attention in the last decade thanks to their interesting optical properties, particularly to the characteristic strong photoluminescence (PL). Cheap, green and biologically safe, PDs are a promising new tool in the fields of optoelectronic devices, sensors and biological labelling. Synthesis methods of PDs include self-assembly, crosslinking of linear polymers, polymerization and hydrothermal treatment of polymers or small molecules. At the state of the art, it is ascertained that a non-conjugated polymeric structure, independently of the presence of other emissive sources, can cause a bright PL based on the crosslink-enhanced emission (CEE) effect. Here crosslinking contributes to immobilize the polymer, i.e. to decrease its vibrational and rotational freedom, and thus facilitates the radiative relaxation processes. Nevertheless, to the best of our knowledge, a complete elucidation of the chemical structure of PDs and its relationship to their PL properties is still missing. The present study is aimed to reveal the chemical features that originate the high fluorescence of the polymer dots (PDs). Therefore a type of PDs is synthesized by a microwave irradiation and the structure is elucidated. Once the structure is known, a novel room temperature synthesis route is employed to obtain a comparable structure, which interestingly also reflects the photoluminescence behavior of the previous PDs. In light of this, the sole origin for the PDs photoluminescence was identified in the interaction of functional groups jointly located on the PDs polymeric structure. Finally, to better understand the relationship structure-photoluminescence, little chemical variations on the structure of the PDs were introduced in the synthesis route and their influence on the optical properties was investigated.

Figure: two pathways for the obtaining of fluorescent non-conjugated PDs.

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<td>Sayed-Ahmad Baraza</td>
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<td>Stringer</td>
<td>David</td>
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<td>VERDAN</td>
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<td>Vogel</td>
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<td>Wang</td>
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**Chamomile Tubes 2018**

**Functionalization, Dispersion, Sorting**

**Electrochemistry, Energy Storage Conversion and Harvesting**

**Composites, Porous Materials, Coatings**

**Health and biology**

**Functional Materials**

**Spectroscopy**

**Corporate talk**

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**Welcome**

**Cheng**

**Break**

**Poster session**