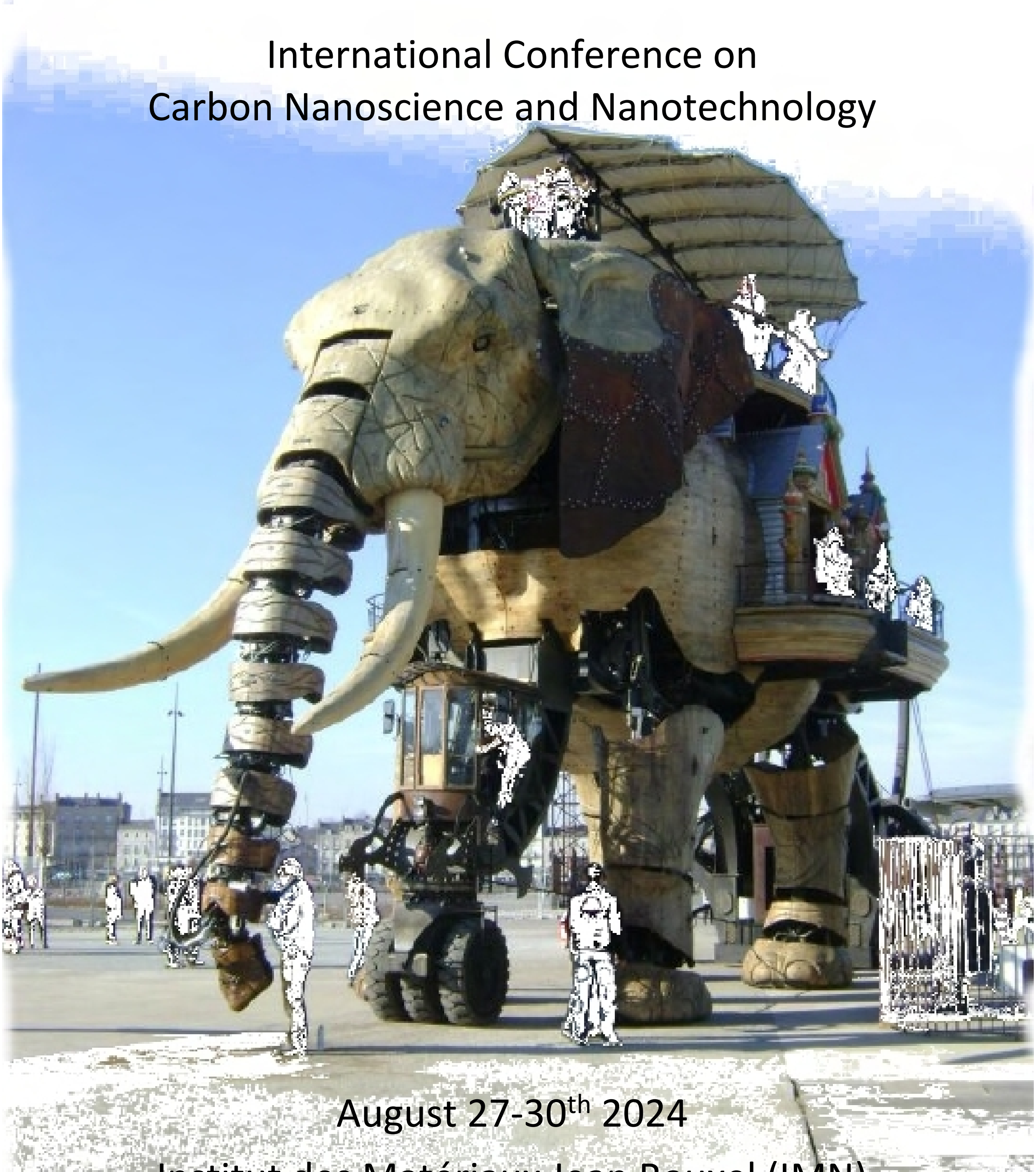
NanoteC24

International Conference on
Carbon Nanoscience and Nanotechnology



August 27-30th 2024

Institut des Matériaux Jean Rouxel (IMN)
University of Nantes, France

NanoteC24

International Conference on Carbon Nanoscience and Nanotechnology

We gratefully acknowledge support from

The British Carbon Group

SFEC Société Francophone d'Etude des Carbones

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IMN INSTITUT DES MATÉRIAUX DE NANTES JEAN ROUXEL

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August 27-30th 2024

Institut des Matériaux Jean Rouxel (IMN)
University of Nantes, France

Welcome to NanoteC24!

This is the 22nd International NanoteC conference organised by the **British Carbon Group**, with the aim of promoting carbon science at the nanoscale as, for example, fullerenes, nanotubes, graphene, nanowires, sp^3 forms, etc. This year is a joint meeting with COST Project Nanospace, Working Group 1.

NanoteC is designed to introduce those with an interest in materials to current research in nanotechnology and to bring together research scientists working in various disciplines in the broad area of nanotubes, graphene, diamond- and fullerene-related nanostructures. Elemental carbon is the simplest exemplar of this nanotechnology based on covalent bonding, however other systems (for example containing boron and nitrogen) are becoming important from a research point of view, and provide alternative components with unique mechanical and electronic properties. Nanotechnology requires an understanding of these materials on an atomic level and this will be the central theme.

The Institute of Materials (IMN): (www.cnrs-imn.fr)
The Institute of Materials was created in 1988 by the renowned French chemist Jean Rouxel. Drawing together chemists, physicists and materials engineers from the CNRS and the University of Nantes, with around 200 researchers and support staff it now represents one of the largest materials research centres in France. Research projects are diverse, including collaborations with industry, and other national and international research organisations.

Organising Committee:

- Chris Ewels
- Samanvitha Kunigal Vijaya Shankar
- Bastien Anezo
- Yann Claveau
- Shunsuke Sasaki

- Colin Bousige (LMI Lyon)
- Jean-Charles Arnault (CEA Paris)

Useful Information

Registration: is at the [Institute of Materials (IMN)]() on Tuesday from midday.

Transport: You can download a phone app to generate and use tickets for the buses and trams (each ticket allows unlimited use of all transport, including changes, for 1 hour) from https://naolib.fr/fr/application-naolib-tram-bus - otherwise tickets can be bought from the bus conductors, and from the Tram stops (not on the trams so make sure you have one before you get on). Tickets must be stamped as you get onto the bus or tram to be valid.

Wednesday Evening: Is a free evening to enjoy the sights, sounds and smells of Nantes! If you don't know where to go, feel free to grab a local organiser and get suggestions. Nantes has a great selection of good restaurants, cafes, bistros and creperies (the local speciality is a crepe or gallette with a cup of cider), as well as some very good bars.

Thursday Evening Banquet: This is to be held at the Lieu Unique at 8pm, a cultural centre close to Nantes Castle. We will provide maps and details on Thursday, we are recommending a walk from the conference (you can leave bags at the conference site if you want), with a built-in Enigma game to solve for those who like a challenge, and some good bars on the way too.

Wi-Fi Access at the Conference : There is EduRoam available. If you do not have Eduroam access, please contact the organisers.

Posters: Feel free to choose any (unoccupied!) board for your poster, bulldog clips are available. There will once again be a **poster prize** for the two best posters at the meeting. Posters can remain up for the whole conference duration, the Tuesday poster session will be accompanied with drinks, crêpes and local Breton games.

Talks: Please upload your talk onto the conference computer in one of the coffee/tea breaks in advance, we will be available to help with this. There are lots of talks – please stick to schedule!

Building Regulations: Please **no food and drink in the lecture theatre**. If you hear the fire alarm for any reason, please leave your stuff and walk out of the nearest available fire door, there are doors in the main entrance lobby of the IMN. The meeting point for everyone present in the building is on the grass area at the back of the Institute.

When you leave: When you leave, **please return your badge and lanyard**, we recycle them for the next conference! We can store luggage at the Institute on Friday, just ask one of the organisers.

Airport Bus: The airport bus runs from the city centre ("Hotel Dieu") every 20 minutes (same ticket also valid for a connecting tram). It takes about 20 minutes, and you should allow around at least 30 minutes on Tram 2 from the Institute to the bus stop at Hotel Dieu to be sure. The timetable is on the Web at www.tan.fr

Jazz Festival: The festival starts in Nantes on Friday and goes on to Sunday.

Easter Eggs: You may find some Easter Eggs at this conference ☺ More will be explained on Thursday before the banquet…

Facebook: Feel free to upload NanoteC photos to our facebook page!

https://www.facebook.com/NanoteC-119653548073210/

Tues Aug 27

12:00-14:00	*Registration*
13.00-14.00	**buffet lunch + install posters**
14.00-14.10	*Welcome and Opening*
14.10-14.50	***Unveiling Phonon Dynamics in Twisted Bilayer Materials*** **Vincent Meunier, Penn State University, USA**
14.50-15.10	*Preparation of phase-pure α-Fe2O3@g-C3N4 direct Z-scheme heterojunction photocatalysts* Alexandro Galan-Gonzalez, Instituto de Carboquímica (ICB-CSIC), Spain
15.10-15.30	*Porosity-controlled conductivity in nanosheet networks facilitates chemiresistive sensing* Hannah Wood, Penn State University, USA
15.30-16.00	**coffee and tea**
16.00-16.40	***Nanodiamonds: CVD synthesis and color centers incorporation for quantum technologies.*** **Mary de Feudis, University of CY Cergy Paris and Chimie ParisTech, France**
16.40-17.00	*Specific colloidal properties of hydrogenated milled nanodiamonds in water* Jean Charles Arnault, Université Paris-Saclay, France
17.00-17.20	*Simulated and experimental azafullerene-based qubits on diamond substrates* Bastien Anezo, Nantes Université, France
17.20-20.00	Drinks, Buffet and Poster Session

Weds Aug 28

09.00-09.40	***Emergent high-conductivity in size-selected nanosheet networks*** **Sean Ogilvie, University of Sussex, United Kingdom**
09.40-10.00	*Synthesis of Graphene and Tungsten Carbides (WC/W2C) Nanosheets via Hot-Wire Chemical Vapour Deposition* Boon Tong Goh, University of Malaya, Malaysia
10.00-10.20	*Feedstock-dependent growth of small diameter B-SWCNTs* Dido Denier van der Gon, University of Vienna, Austria
10.20-10.50	**coffee and tea**
10.50-11.30	***Plasma functionalization of Carbon*** **Carla Bittencourt, University of Mons, Belgium**
11.30-11.50	*Energy from garbage: Recycling Heavy Metal-containing Wastewater Adsorbents for Energy Storage Applications* Marcelo Amaro de Andrade, Nantes University, France
11.50-12.10	*T2 effect in heat capacity of low-dimensional carbon allotropes: effect of size, annealing temperature and sintering pressure* Daria Szewczyk, Institute of Low Temperature and Structure Research PAS, Poland
12.10-12.30	*γ-Graphynes for Efficient Photoinduced Electron Transfer* Olga Stasyuk, University of Girona, Spain
12.30-14.00	**buffet lunch + posters**
14.00-14.40	***Multifunctional Graphene Composites*** **Ian Kinloch, Manchester University, United Kingdom**
14.40-15.00	*Mechanisms and kinetics of prismatic dislocation loop removal during graphitization*

Gabriel Francas, Curtin University, Australia

15.00-15.20 *High-dimensional neural network potential for borophene on metallic surfaces*
Colin Bousige, Université Lyon 1, France

15.20-15.40 *In-plane staging in lithium-ion intercalation of bilayer graphene*
James McHugh, University of Manchester, United Kingdom

15.40-16.10 coffee and tea

16.10-16.30 *Modelling the effects of defects on the properties of graphite*
Kenny Jolley, Loughborough University, United Kingdom

16.30-16.50 *Band structure investigation of nanocrystalline titanium carbide (TiC) particles under gamma radiation*
Elchin Huseynov, Institute of Radiation Problems of Ministry of Science and Education, Azerbaijan

16.50-17.10 *Exploring nanostructured TiO2 photoelectrodes: from preparation to application*
Carlos Martinez-Baron, Instituto de Carboquímica (ICB-CSIC), Spain

17.10-17.30 *The (anti)aromatic properties of cyclo[n]carbons: myth or reality?*
Antony Stasyuk, Universitat de Barcelona, Spain

Thurs Aug 29

09.00-09.20 *All-printed CNT-based electrochromics*
Peter Lynch, University of Sussex, United Kingdom

09.20-09.40 *Emergent Atomic Environments in Twisted Bilayer Graphene and Their Use in the Prediction of the Vibrational Properties*
Dogan Erbahar, Dogus University, Turkey

09.40-10.00 *The effect of 2D nanosheet size on the performance of printed devices*
Anthony Dawson, Trinity College Dublin, Ireland

10.00-10.20 *Direct deposited emulsion-templated composites for monitoring of fabric strain*
Raquel Cano-Cordero, University of Sussex, United Kingdom

10.20-10.50 coffee and tea

10.50-11.30 ***Constructing graphene functional materials using selective oxidation***
Alexandra Carvalho, National University of Singapore, Singapore

11.30-11.50 *XPS measurements confirm sulfophenyl functionalization of graphene as promising transmembrane for direct methanol fuel cell*
Clement Maheu, Nantes Université, France

11.50-12.10 *CNT aerogel electrochemical bio-sensor: A new era in ultra sensitive biomedical technology*
Jyoti Prakash, Bhabha Atomic Research Centre, India

12.10-12.30 *Nanoplastics and Nanocarbons: Contaminants of Emerging Concern*
Sergey Mikhalovsky, ANAMAD Ltd, Sussex Innovation Centre,United Kingdom

12.30-14.00 buffet lunch + posters

14.00-14.40 ***Flattened Carbon Nanotubes: Preparation and Raman signal***
Emmanuel Picheau, National Institute for Materials Science (NIMS), Japan

14.40-15.00 *Functionalized two-dimensional transition metal dichalcogenides for energy applications*
Ioanna Sideri, National Hellenic Research Foundation, Greece

15.00-15.20	*Synthesis, characterization and optical and redox properties of perylene modified MoS2 nanosheets* Eleni Nikoli, National Hellenic Research Foundation, Greece
15.20-15.40	Role of graphene substrate in the formation of MoS2-based nanoparticles with improved NO2 gas sensing Liubov Bulusheva, Nikolaev Institute of Inorganic Chemistry SB RAS, Russia
15.40-16.10	**coffee and tea**
16.10-16.30	*Observation and characterisation of stabilised azafullerene radicals on Au surface* Yuri Tanuma, Jožef Stefan Institute, Slovenia
16.30-16.50	*Multiscale correlative characterisation and patterning of graphene-related nanomaterials* Milo Shaffer, Imperial College London, United Kingdom
16.50-17.30	***Complex carbon astrochemistry around old stars*** **Anibal Garcia Hernandez, Instituto de Astrofísica de Canarias (IAC), Spain**
20.00	**Conference Dinner (Lieu Unique, Nantes)**

Fri Aug 30

09.00-09.40	***Accelerating the prediction of large carbon clusters via structure search: evaluation of machine-learning and classical potentials*** **Carla de Tomas, Imperial College London, United Kingdom**
09.40-10.00	*Optical superabsorbers for energy generation and thermal management* Jose Anguita, University of Surrey, United Kingdom
10.00-10.20	*Sulfurization of Ultrathin Tungsten Carbide Nanoplates: The Impact of the Crystalline Carbide Phase* David Sanchez, Penn State University, USA
10.20-10.40	*Inorganics-in-Organic thermoelectric devices with high power factor* James Neil, University of Surrey, United Kingdom
10.40-11.00	**coffee and tea**
11.00-11.20	*Atomic Scale Modelling of Confined Ionic Liquids* Samanvitha Kunigal, Nantes Université, France
11.20-11.40	*Liquid Interface Assembled Networks of 2D Materials* Joseph Neilson, Trinity College Dublin, Ireland
11.40-12.00	*Highly Functionalised Fullerene Amphiphiles: Molecular Structure and Self-Assembly* Ilija Rašović, University of Birmingham, United Kingdom
12.00-12.20	*Impact of quaternary ammonium ions on the parameters of 2D MoS2 produced by electrochemical exfoliation* Vincent Renard, Trinity College Dublin, Ireland / Université de Nantes

Posters

P1	*Development of a reactive Neural Network Potential for borophene on silver and gold* **Anouar Akacha Delenda**, Pierre Mignon, Colin Bousige Université de Lyon, France
P2	*Bibliometric Analysis and Science Mapping for Nanospace: Descriptive Research* **Musa Akbulut** Igor Sikorsky Kiev Polytechnic Institute, Ukraine

P3 *Carbon foam developed to eliminate oil spills*
Lokmane Abdelkaddous Baidar, Malika Medjahdi, Dominique Baillis, Badra Mahida
University of Djillali Liabes, Sidi Bel Abbes, Algeria

P4 *Green Emissive Carbon Dots: Synthesis, Photoluminescence Mechanism and Use in Photoanodes*
Ana Benito, M. Alvarez, C. Martinez, A. Anson, W. K. Maser
ICB-CSIC, Zaragoza, Spain

P5 *Defect-mediated ionic transport in layered β and β”aluminas*
Suchit Negi, **Alexandra Carvalho**, A. H. Castro Neto
National University of Singapore, Singapore

P6 *Emergent high conductivity in size-selected graphene networks*
Keiran Clifford, Sean P. Ogilvie, Aline Amorim Graf, Hannah J. Wood, Anne C. Sehnal, Jonathan P. Salvage, Peter J. Lynch, Matthew J. Large, Alan B. Dalton
University of Sussex, United Kingdom

P7 *Rheological study of stabiliser blends on rigidity percolation of carbon nanotube dispersions*
Kevin L. Doty, Peter J. Lynch, Aline A. Graf, Matthew Large, Sean Ogilvie, and Alan B. Dalton
University of Sussex, United Kingdom

P8 *Emergent Atomic Environments in Twisted Bilayer Graphene and Their Use in the Prediction of the Vibrational Properties*
Dogan Erbahar, Dilara Ickecan, Yunus Emre Okyayli, Erdi Ata Bleda
Dogus University, Turkey

P9 *Carbon Nanomaterials as Anticancer Drug Nanocarriers*
R. Garriga, T. Herrero-Continente, M. Palos, V. L. Cebolla, J. Osada, E. Muñoz, M. J. Rodríguez-Yoldi
Universidad de Zaragoza, Spain

P10 *Controlling the structure and porosity of carbon-carbon composites to optimize their electrical and mechanical properties*
Lingshu lei, Ian Kinloch, Cristina Valles
The University of Manchester, United Kingdom

P11 *Sustainable C-Nano inks for the preparation of layered photoelectrode films*
W.K. Maser, J. Hernández, J.M. González, A. Galán, J.C. Ciria, A. Ansón, Ana M. Benito
Instituto de Carboquímica (ICB-CSIC), Spain

P12 *Crosslinking of graphene oxide towards explosive percolation in composite materials*
Alexander O. McCann, Peter J. Lynch, Sean P. Ogilvie, Alan B. Dalton
University of Sussex, United Kingdom

P13 *Intercalation of metallic elements within prismatic dislocation cores in graphite*
Paul Mouratidis, Kenny Jolley, Chris Ewels
Loughborough University, United Kingdom

P14 *MoS2/Carbon Nanotube Hybrid Sensors for NO2 Detection*
Edgar Muñoz, Rosa Garriga, Carlos Sánchez-Vicente, José L. Sanjurjo, José P. Santos, Sean P. Ogilvie, Alan B. Dalton, Isabel Sayago
Instituto de Carboquímica (ICB-CSIC), Spain

P15 *Enhancing Traditional Material Modelling Techniques with Machine Learning for Studying Defects in Nuclear Graphite*
Daria Nasartdinova, Kenny Jolley, Paul Mouratidis
Loughborough University, United Kingdom

P16 *Complementation of different techniques for elucidating the metal ion binding mechanisms on the carbonaceous adsorbents*
Raisa Nastas, Irina Ceban (Ginsari), Amelia Bocirnea, Iolanta Balan
Institute of Chemistry of Moldova State University, Republic of Moldova

P17 *Design and preparation of hybrid nanocarbon-MOF materials*
Ioanna K. Sideri, Georgia Basina, Giasemi K. Angeli, Nikos Tagmatarchis
National Hellenic Research Foundation, Greece

P18 *The influence of broken chains defects on the properties of graphene-based and 2H-NbSe2 materials*
Valentyna Sirenko, Ivan Bondar, Kseniia Minakova, Ruslan Mirzoiev
B.Verkin Institute for Low Temperature Physics and Engineering of NAS of Ukraine, Ukraine

P19 *Ligand-Triggered Self-Assembly of Flexible Carbon Dot Nanoribbons for Optoelectronic Memristor Devices and Neuromorphic Computing*
Xue Yong, Lin Ai
University of Liverpool, United Kingdom

P20 *Manual design of point defect arrays in two-dimensional graphenic systems*
Jeanine Salla
Bangalore World University, India

Oral Sessions

Tuesday, 27th August

Unveiling Phonon Dynamics in Twisted Bilayer Materials

Vincent Meunier[1]

[1]*Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, PA, USA*

Vincent,Meunier@psu.edu

The discovery of novel electronic properties in twisted bilayer graphene has sparked intense interest in the field of twistronics. While electronic phenomena in these systems have been extensively studied, the vibrational properties of twisted bilayer materials remain relatively unexplored. This talk presents recent research on the phonon dynamics in twisted bilayer systems, revealing how lattice vibrations are profoundly affected by the moiré superlattice formed by the twist angle between layers.

Using first-principles calculations, we investigate the phonon spectra of twisted bilayer graphene [1,2] and transition metal dichalcogenides [3] across a range of twist angles. Our results demonstrate the emergence of new vibrational modes localized within the moiré supercell, as well as significant modifications to the phonon dispersion relations compared to untwisted bilayers. Furthermore, we present a universal theoretical framework for predicting the vibrational properties of twisted bilayer systems, providing insights into the interplay between interlayer coupling, symmetry breaking, and phonon hybridization. The findings not only advance our fundamental understanding of lattice dynamics in low-dimensional materials but also opens up new avenues for engineering thermal and thermoelectric properties in van der Waals heterostructures.

Time permitting, I'll introduce a visual technique to illustrate polarized Raman spectroscopy's effects. This method helps students grasp how normal mode symmetry interacts with experimental conditions to produce distinct patterns in polarization plots.

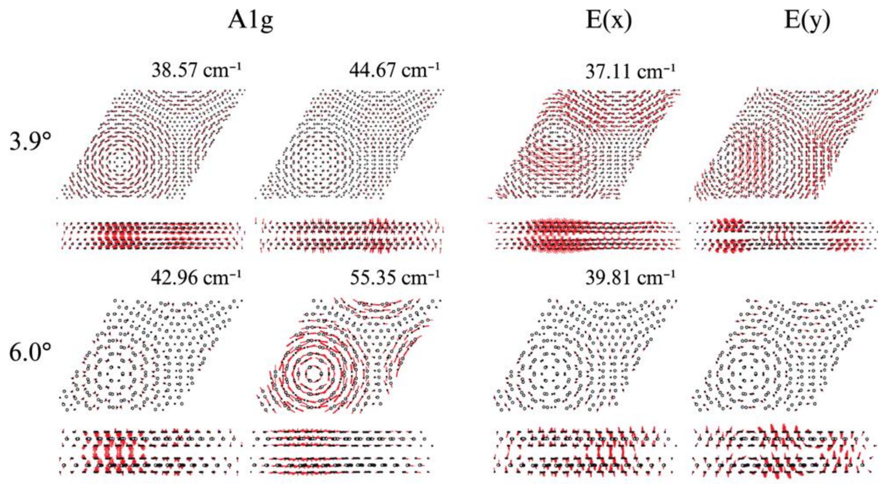

Figure 1: *Illustration of Raman active modes in twisted bilayer MoS2 for two small angles. The soliton network created by the moiré pattern leads to the emergence of localized phonons, depending on the angle and the symmetry of the normal mode. Adapted from Ref. [3].*

References

1. M. Lamparski, B. Van Troeye, V. Meunier, *2D Materials* 7 (2), 025050 (2020)
2. N Sheremetyeva, M Lamparski, C Daniels, B Van Troeye, V Meunier, *Carbon* 169, 455-464 (2020)
3. B. Klein, L. Liang, and V. Meunier, *J. Phys.: Condens. Matter* **36** 365301(2024)

Preparation of phase-pure α-Fe_2O_3@g-C_3N_4 direct Z-scheme heterojunction photocatalysts

Alejandro Galán-González[1], *Juan G. Galindo-Callén*[1], *Isaías Fernández*[1], *Nestor J. Zaluzec*[2], *Raúl Arenal*[4,5,6], *Sofie Cambré*[7], *Ana M. Benito*[1], *Wolfgang K. Maser*[1]

1 Instituto de Carboquímica (ICB-CSIC), C/ Miguel Luesma Castán 4, 50018 Zaragoza, Spain.

2 CICA-Centro Interdisciplinar de Química e Bioloxía, Universidade da Coruña, Rúa As Carballeiras, 15071 A Coruña, Spain

3 University of Chicago, Pritzer School of Molecular Engineering and Argonne National Laboratory / Photon Science Directorate, Lemont, Illinois, USA.

4 Nanostructured and Organic Optical and Electronic Materials, Physics Department, University of Antwerp, 2610 Antwerp, Belgium

5 Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain

6 Laboratorio de Microscopias Avanzadas (LMA), Universidad de Zaragoza, C/ Mariano Esquillor s/n, 50018 Zaragoza, Spain

7 ARAID Foundation, 50018 Zaragoza, Spain

agalan@icb.csic.es

The use of graphitic carbon nitride (g-C_3N_4) as photocatalyst in the last fifteen years has garnered significant attention owing to its semiconducting properties (2.7 eV bandgap) and its robustness, showing high thermal and chemical stability.[1] Therefore, it has been deemed an ideal platform to form heterojunctions along with other semiconductors (metal oxides mainly) to boots the overall photocatalytic activity.[2] In this regard, hematite (α-Fe_2O_3) is an ideal candidate owing to its excellent band alignment with g-C_3N_4, which leads to the formation of direct Z-scheme heterojunctions.

This work presents a novel approach towards this integration in which phase-pure hematite nanoparticles are directly grown on g-C_3N_4 sheets, see Figure 1. For this, a two-step preparation process was developed. First, g-C_3N_4 is impregnated with $FeCl_3$ in an ultrasound probe, followed by a phase-conversion step in a microwave reactor. Careful control of the $FeCl_3$ concentration during impregnation affords control over the phase-purity of the as-grown hematite nanoparticles. The Z-scheme mechanism of the hybrid photocatalysts was proven by electron spin resonance (ESR) and its efficacy as photocatalyst is demonstrated in the degradation of a common dye, methylene blue, yielding two-fold enhancement of the photocatalytic activity compared to the base g-C_3N_4 and α-Fe_2O_3.

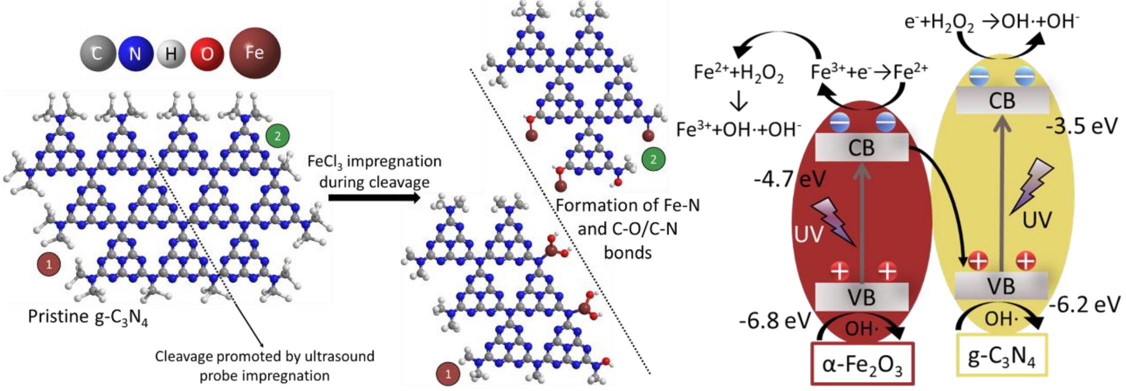

Figure 1. Schematic of the g-C_3N_4 cleavage and impregnation process (left panel) and band structure of the Z-scheme hybrid photocatalysts (right panel)

References

1 S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang and P. M. Ajayan, *Advanced Materials*, 2013, **25**, 2452–2456.

2 A. Mishra, A. Mehta, S. Basu, N. P. Shetti, K. R. Reddy and T. M. Aminabhavi, *Carbon N Y*, 2019, 149, 693–721.

Funding: MCIN/AEI/10.13039/501100011033 under PID2022-139671OB-100; DGA under T03_23R.

Porosity-controlled conductivity in nanosheet networks facilitates chemiresistive sensing

Hannah J. Wood[1,2]**,** Sean P. Ogilvie[1], Aline Amorim Graf[1], Jonathan P. Salvage[3], Peter J. Lynch[1], Jeremy M. Thorpe[1], Matthew J. Large[1], Gabriel Garcia[4], Yameng Cao[4], Nick Martin[4], Izabela Jurewicz[5,6], Mauricio Terrones[2] and Alan B. Dalton[1]

[1]University of Sussex, Brighton, East Sussex, BN1 9RH, UK
[2]Pennsylvania State University, State College, Pennsylvania, 16801, USA
[3]University of Brighton, Brighton, East Sussex, BN2 4GJ, UK
[4]National Physics Laboratory, Teddington, London, TW11 0LW, UK
[5]University of Surrey, Guildford, Surrey, GU2 7XH, UK
[6]Advanced Materials Development, Guildford, Surrey, GU2 7YD, UK
hjw5453@psu.edu

Transition metal dichalcogenides such as molybdenum disulfide (MoS_2) are layered materials of great interest due to their interesting thickness-dependent properties and potential for a range of printed electronic devices. Networks of MoS_2 nanosheets are exfoliated in the surfactant-assisted liquid phase; often water-based systems ideal for cost effective production of inks on the larger scale. The non-covalent relationship between surfactant and nanosheet allows for effective isolation of polydisperse nanomaterial [1]. This work looks at the subsequent size selection and deposition of these MoS_2 sheets yields chemiresistive devices capable of sensing ammonia (NH_3) and nitrogen dioxide (NO_2) down to levels of 10 ppb and 50 ppb. An enhancement of nanosheet network conductivity of two orders of magnitude from 10^{-5} S m^{-1} to 10^{-3} S m^{-1} can be interpreted in terms of nanosheet size and network [2,3]. The optimisation of the porosity and size of nanosheets comprising these networks elucidates the sensitive response to chemical analytes. The devices shown to be sensitive to 10 ppb NH_3 have a current response shown over multiple cycles highlighting the potential for MoS_2 devices to be a promising sensing material for these analytes.

References

1. S.P. Ogilvie, M.J. Large, M.A. O'Mara, P.J. Lynch, C.L. Lee, A.A.K. King, C. Backes and A.B. Dalton, *2D Materials* **6** (3), 031002 (2019). 10.1088/2053-1583/ab0dc3
2. S. Barwich, J. Medeiros de Araújo, A. Raffert, C. Gomes da Rocha, M.S. Ferreira, J.N. Coleman, *Carbon* **171**, 306-319 (2021). 10.1016/j.carbon.2020.09.015
3. A.G. Kelly, D. O'Suilleabhain, C. Gabbett and J.N. Coleman, *Nature Reviews Materials* **7**, 217–234 (2022). 10.1038/s41578-021-00386-w

Nanodiamonds:

CVD synthesis and color centers incorporation for quantum technologies. Mary De Feudis

University of CY Cergy Paris and Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, France.
mary.de-feudis@cyu.fr

Diamond, a solid composed of carbon atoms, is an extremely interesting material for its technological and scientific applications such as those in nuclear physics and power electronics. Recent progress achieved in controlling diamond synthesis has made it possible to produce very pure crystals and incorporate and control atomic impurities and carbon vacancies in the crystal lattice. The appropriate impurity-vacancy combinations can give rise to special defects known as color centers, such as the nitrogen-vacancy (NV), which exhibits exceptional quantum properties with optically addressable spins. The use of diamond containing color centers has paved the way for the development of innovative quantum technologies, such as very high-resolution magnetometry, quantum information processing, and extreme-conditions sensing [1-3]. Nevertheless, the development of quantum sensors at the nanometric scale remains one of the most interesting challenges. In this respect, the development of reliable nanoparticle synthesis techniques that allow the desired defects to be incorporated and their quantum optical properties to be modulated is crucial. Two major methods have been used to synthesize nanodiamonds (NDs) at an industrial scale: the detonation and the milling techniques [4]. The first one is a bottom-up method based on the detonation of carbon-containing explosives in a closed chamber. The second one is a top-down technique based on the milling of diamond microcrystals synthesized at high-pressure high-temperature (HPHT). Although these methods have enabled large-scale production, their use for quantum technologies presents some limitations related to the complex post-treatments required to purify the NDs and enhance their optical properties. In the ongoing exploration of the ND synthesis world, recent new results have been achieved with the development of a very promising technique: the plasma-assisted chemical vapor deposition (CVD) [5, 6]. With this technique, it is possible to synthesize high-quality NDs by a simple manufacturing procedure, getting good control of both nanoparticle growth process and color center formation. In this work, the CVD-ND growth process optimization is presented, showing the impact of different plasma parameters and gas phase composition on the nanoparticle crystallinity, size, and shape. Morphological characterizations evidence the production of small (around 100 nm) and well-faceted ND particles. The incorporation of strategic impurities such as nitrogen, silicon and germanium for the production of quantum ND containing NV, SiV and GeV color centers respectively, will be thoroughly explored. The high flexibility of the CVD growth technique will be discussed as the SiV and GeV color center incorporation can be tuned within NDs by varying the gas phase composition despite the impurities originating from a solid wafer. Eventually, the quantum properties of the incorporated color centers have been successfully investigated under extreme pressure conditions (up to ~180 GPa), showing a monotonous blue shift of their optical zero-phonon line. Since their luminescence remains stable, SiV and GeV centers emerge as high-pressure nanosensors for superconductivity experiments [7].

References

[1] G. Villaret, et al., Applied Physics Letters 122 (19) 2023, p. 194001.
[2] A. Hilberer, et al., Physical Review B 107 (22) 2023, p. L220102.
[3] M. Pompili, et al., Science 372 (6539) 2021, p. 259.
[4] N. Nunn, et al., Curr. Opin. Solid State Mater. Sci. 21 (1) 2017, p. 1.
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Specific colloidal properties of hydrogenated milled nanodiamonds in water

Jean-Charles ARNAULT[1]**,** Lorris SAOUDI[1], Hugues GIRARD[1], Emmanuel DARTOIS[2]

[1] *Université Paris-Saclay, CEA, CNRS, NIMBE, CEDEX, 91 191, Gif-Sur-Yvette, France*

[2] *Institut des Sciences Moléculaires d'Orsay, UMR8614, CNRS, Université Paris-Saclay, France*

jean-charles.arnault@cea.fr

Fluorescent MND are currently under active investigations for nanomedecine or quantum nanosensors [1]. Indeed, milled nanodiamonds (MND) of excellent core crystallinity can host various color centers (NV, SiV,…). MND also demonstrate comparable electronic properties to bulk material, including similar band gap and equivalent position of conductive and valence bands, according to their surface chemistry [2]. This aspect renders MND appealing for energy-oriented applications including photo(electro)catalysis. The former applications imply a fine control of their colloidal properties. Although the stability of oxidized MND colloids is well understood, further comprehension is still needed to explain the behavior of their hydrogenated counterparts (H-MND).

In this study, we will correlate the surface chemistry and the colloidal behavior of MND hydrogenated under different conditions (atmospheric pressure, 600°C-750°C). Through an original semi-quantitative IR spectroscopy approach, we will show that the maximum amount of C-H bonds that can be imparted to MND by annealing is reached as early as 650°C. The latter temperature is not sufficient to get rid of all oxidized terminations, which is completed only above 700°C, as evidenced by additional FTIR and XPS measurements. Consequently, H-MND annealed below and above 700°C evidence different colloidal behaviors in terms of sonication time needed to suspend them and resulting concentration, which sheds light on the mechanisms that underline their stability. Moreover, at annealing temperatures of 650°C and above, we evidenced the systematic presence of a dip at 1330 cm^{-1} in the IR absorption spectrum, so far attributed to a Fano-type interference, which would betray the presence of a surface conductive layer for stable nanoparticles. It is absent for the sedimented H-MND particles. Lastly, cryo-EM observations revealed a particular spatial organization of hydrogenated MND in water with chain-like structures extending over micron range.

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Simulated and experimental azafullerene-based qubits on diamond substrates

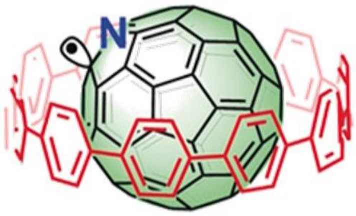
Bastien Anézo [1,2*], Yuri Tanuma [2],Denis Arčon [2,3], Chris Ewels [1]

[1]Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France.

[2] Institute Jožef Stefan, Jamova 39, 1000 Ljubljana, Slovenia. 3Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia

*bastien.anezo@cnrs-imn.fr

Discrete energy levels of electronic spins at the molecular level are a promising platform for creating qubits. A major challenge remains how to build complex circuits from molecular spin entities with sufficiently long coherence times. The azafullerene C59N stands out from other spin active molecules, especially when encapsulated in cycloparaphenylene (CPP) [1]. This creates the supramolecular complex [10]CPP@C59N, which demonstrates desired coherence times at room temperature [2], as well as having significantly higher yields than comparable fullerene like molecules (desired for scalability). The targeted quantum systems need readout control of the quantum molecular spin states, and for this we have chosen the negatively charged nitrogen vacancy (NV-) embedded in diamond substrates, already used in similar system [3].
We simulate both [10]CPP@C59N and NV- using density functional theory (DFT). Addressing the coupling between the vacancy, the separated molecules and the supramolecular complex allows us to identify relevant parameters of the system, including surface interactions, dipolar magnetic coupling, and zero field splitting (ZFS) modulation. We will pursue the study by developing an experimental setup of the qubit and the readout control, through optically detected magnetic resonance (ODMR) using the NV- centres. The goal of this work is to make a proof of concept of the system and study its scalability with related molecules [4].



$C_{59}N^{\bullet} \subset$ [10]CPP

Figure 1: [10]CPP@$C_{59}N$ supramolecular complex consisting of a $C_{59}N$ azafullerene radical encapsulated by a [10]cycloparaphenylene ring. The radical on a carbon neighbour of the nitrogen is marked [1].

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Wednesday, 28th August

Emergent high-conductivity in size-selected nanosheet networks

Sean P. Ogilvie[1], Keiran Clifford[1], Hannah J. Wood[1], Aline Amorim Graf[1], Peter J. Lynch[1], Matthew J. Large[1], Alan B. Dalton[1]
[1] *University of Sussex, Brighton, UK*
s.ogilvie@sussex.ac.uk

Liquid-phase exfoliation has become a widespread and versatile approach for production of dispersions of layered nanosheets for a range of printed electronic applications. However, these dispersions typically comprise broad size distributions from bulk-like to few-layer nanosheets and the influence of nanosheet size on electrical transport properties remains relatively unexplored. Here, we demonstrate an approach combining high-throughput surfactant exfoliation [1] with liquid cascade centrifugation to yield large quantities of size-selected nanosheets to elucidate the size-dependent properties of nanosheet networks of graphene [2] and MoS_2 [3]. Importantly, for both materials, electrical conductivity is found to increase to record-high values for few-layer small-nanosheet networks. This observation is understood in terms of the structure and composition of these networks, identifying improved connectivity and reduced junction resistance in the few-layer systems. These enhanced conductivities enable application of graphene and MoS_2 nanosheet networks as printed thermoelectrics and chemiresistive gas sensors, respectively, highlighting the potential of size selection approaches to realise new functionalities in nanosheet networks.

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Synthesis of Graphene and Tungsten Carbides (WC/W_2C) Nanosheets via Hot-Wire Chemical Vapour Deposition

Boon Tong Goh[1]**,** Nur Afira binti Anuar[1], Kae Lin Wong[1], Keat Hoe Yeoh[2]

[1]Low Dimensional Materials Research Center, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

[2]Jeffrey Sachs Center on Sustainable Development, Sunway University, Bandar Sunway, 47500 Petaling Jaya, Selangor Darul Ehsan, Malaysia

** gohbt@um.edu.my*

Abstract

Lately, 2D materials has attracting a great intention among the material researchers owing to its fascinating physical, electrical, mechanical, and electrochemical properties, including high-surface area to volume ratio, high-surface mobility, high-flexibility, and high-transparency, making them an essential element in nanotechnology. These 2D materials include graphene, transition metal dichalcogenides (TMDCs), transition metal nitrides and carbides (MXenes), transition-metal diborides (MBenes), metal oxides, etc. In this work, we synthesis large-area graphene and tungsten carbide (WC/W_2C) nanosheets directly grown on c-Si and quartz substrates using a novel technique of hot-wire chemical vapour deposition at low substrate temperatures (<500 °C). Prior to the deposition, an argon plasma process was employed to induce the formation of W NPs, which act as a metal catalyst to facilitate the growth of large-area monolayer or multi-layer nanosheets. The average grain size of WPs was in between 24.3 nm to 7.4 nm. These 2D materials demonstrated excellent optical transparency (> 80 %), low sheet resistance (718 – 966 Ω/sq.), and high photocurrent density under the visible light irradiation (~ 2 mA/cm^2 at 1.5 $V_{Ag/AgCl}$) for hydrogen production via water-splitting process. We are expecting that these 2D materials could give desirable properties for efficient supercapacitor and hydrogen fuels in the coming future.

Keywords: Graphene; WC/W_2C nanosheet; Tungsten nanoparticles; Hot-wire chemical vapor deposition; Water-splitting

Feedstock-dependent growth of small diameter B-SWCNTs

D.M. Denier van der Gon[1]**,** R. Pinna Brito[1], M.E.H. Maia da Costa[2], C.A. Senna[2], R. Prioli[2]
C. Reinoso[3], O.H. Heckl[1], P.Ayala[1]

[1]*University of Vienna, Faculty of Physics, Boltzmanngasse 5, 1090 Vienna, Austria*

[2]*Departamento de Fïsica, PUC-Rio, Rua Marquês de São Vicente, 225 - 22451-900 Gávea, Rio de Janeiro, Brazil*

[3] *Yachay Tech University, Hda. San Josés/n y, Urcuqui 100115, Ecuador*

dido.denier.van.der.gon@univie.ac.at

The electronic properties of single-walled carbon nanotubes (SWCNTs) are intrinsically dependent on their structure. For some applications, a synthesis method capable of producing tubes with a narrow diameter distribution is extremely attractive. Additionally, the electronic properties of SWCNTs can be tuned through the incorporation of substitutional heteroatoms into the tube walls. Nitrogen and, to a lesser extent, Boron have been reported as the natural substitutional dopants. In this context, we have shown in the past that using Tri-isopropyl Borate (TIB) as C and B feedstock, and an iron based catalyst in a high-vacuum CVD system [1], we are able to synthesise SWCNTs with a peculiarly narrow diameter distribution (0.9 to 1.5nm). Using TIB gives rise to SWCNTs with thinner, and more stable tubes using basically the same catalysts but using a different C source.

We have further investigated the versatility of our liquid feedstock and strikingly, we have found that the synthesis results are consistently small diameter SWCNTs with a narrow distribution, almost regardless the type of metal catalyst, and catalyst supports, over a temperature range of 300°C. Using an optimally low base pressure in the high vacuum system and taking advantage of the low vapor pressure of TIB are also key ingredients for this method. All this hints that the properties of the final product are mainly determined by the feedstock, with only minor modifications resulting from variations in catalysts, supports, and temperatures employed during the HV-CVD synthesis. The catalysts can be easily removed using either chemical or mechanical purification. The material has been studied using Raman spectroscopy and optical absorbance to understand their diameter distribution. Furthermore, overall microscopy inspections were done by SEM. The doping levels, and bonding configuration of heteroatoms have been studied from an XPS approach.

Since these structures exhibit a highly narrow diameter distribution, they are ideal for use as templates in the synthesis of linear carbon chains, which are one-dimensional arrangements, that strictly require small diameter tubes for their materialization. Our first steps towards this objective will be shown.

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Plasma functionalization of Carbon

Carla Bittencourt[1]

[1]*Chimie des Interactions Plasma-Surface, Research Institute for Materials Science and Engineering, University of Mons,*
23 Place du Parc, 7000 Mons, Belgium
carla.bittencourt@umons.ac.be

This talk will explore the diverse landscape of carbon materials, characterized by the varying hybridization states of carbon atoms – specifically sp^1, sp^2, and sp^3. These hybridization states lead to the formation of distinct allotropic structures, each with unique properties and applications. The ability of carbon to form strong covalent bonds with itself and a wide array of elements results in a vast spectrum of compounds, from small molecules to complex solids. This versatility highlights the foundational role of carbon chemistry in organic chemistry and biochemistry, which is essential for the emergence of life on Earth. The focus will be on surface chemistry, which significantly influences the physical and chemical properties of nanostructured carbon materials. By introducing heteroatoms, such as oxygen, nitrogen, fluorine, or sulfur, into carbon structures, a variety of functionalities are achieved, enhancing reactivity and performance beyond that of pristine carbon nanostructured materials. The discussion will particularly emphasize innovative surface modification techniques, including plasma treatments and low-energy ion irradiation. These methods allow for near-precise control over the surface characteristics of carbon nanostructures, facilitating tailored applications across various fields such as catalysis, energy conversion, sensing technologies, and biomedicine.

Pyrolized Films for Spin-on Nanocrystalline Graphene

Natalie E. Galfe[1], Maximilian Wagner[1], Florian Herdl[1,2], Sebastian Klenk[1], Marc Paulik[2], Cormac Ó Coileáin[1], Kangho Lee[1], Georg S. Duesberg[1]

[1]Institute of Physics, EIT4 & SENS Research Center, University of the Bundeswehr München, Werner-Heisenberg-Weg 39,

85577 Neubiberg, Germany

[2] KETEK GmbH, Hofer Str. 3, 81737 München, Germany

natalie.galfe@unibw.de

20 Years after its discovery the reliable and controllable large-scale synthesis of graphene remains one of the key challenges for it to be used in the many proposed applications. CVD synthesis on copper, which allows growth of high-quality layers, still necessitates a transfer process [1].

Here, we present a novel method for direct fabrication of graphenic carbon layers via a simple spin-on and subsequent pyrolization process. The method does not require a catalyst and thus is applicable on multiple substrates. We fabricate these pyrolized photoresist films (PPF) as structured and large-area films with decreasing – down to nanometrically thin – thicknesses, as determined by atomic force microscopy (AFM) prior and post pyrolization. X-ray photoelectron spectroscopy (XPS) confirms the predominant sp^2-nature of our films [2, 3] and Raman spectroscopy shines light on how the nanocrystallinity of the films increases with decreasing film thickness [3, 4]. Transmission electron microscopy (TEM) imaging allows to observe domains with hexagonal nanocrystalline atomic structure.

These films open a cost-efficient, reliable and scalable integration route for directly grown two-dimensional graphenic carbon materials as an alternative to catalytically grown CVD-graphene demanding a transfer process. We demonstrate the use of PPF films as resistive gas sensing devices which yields exciting results for NO_2 sensing. This versatile graphenic carbon film holds promise for a plethora of future applications, ranging from gas sensing to customizable 2D-compatible electrodes and a variety of other scalable devices [5].

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T^2 effect in heat capacity of low-dimensional carbon allotropes: effect of size, annealing temperature and sintering pressure

Daria Szewczyk[1], Olesia Romantsova[1,2], Andrzej Jeżowski[1], Alexander I. Krivchikov[1,2]

[1]*Institute of Low Temperature and Structure Research PAS, Wrocław, Poland*

[2] *Institute for Low Temperature Physics and Engineering, NASU, Kharkiv, Ukraine*

d.szewczyk@intibs.pl

We present a comprehensive investigation of the low-temperature heat capacity in the range of 1.9 - 50 K for a diverse set of diamond samples. Our study includes detonated nanodiamonds annealed at 1000°C, 1600°C, and 2000°C; nanodiamonds synthesized under pressures of 1 GPa to 5 GPa; and larger microdiamonds fabricated via spark plasma sintering with annealing temperatures from 1400°C to 1900°C, alongside a room temperature reference sample. Our findings reveal a significant influence of graphitization on the specific heat of the diamonds. A strong size effect is observed, along with a novel phenomenon characterized by an additional T^2 term in the low-temperature heat capacity, which correlates with the degree of graphitization across the samples. We provide an in-depth analysis of this phenomenon in relation to sample dimensions (micro versus nano), annealing temperatures, and sintering pressures. Finally, we compare our results with those obtained from a pure graphene sample, serving as a benchmark for our findings.

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γ-Graphynes for Efficient Photoinduced Electron Transfer

Olga A. Stasyuk[1], Anton J. Stasyuk[2], Alexander A. Voityuk[1], Miquel Solà[1]

[1]*Institute of Computational Chemistry and Catalysis, Department of Chemistry, University of Girona,*
C/ M. Aurèlia Capmany, 69, 17003, Girona, Spain
[2] *Faculty of Pharmacy and Food Sciences, University of Barcelona, Av. Joan XXIII 27-31, 08028, Barcelona, Spain*
olga.stasyuk@udg.edu

The unique combination of sp^2–sp carbon atoms, an extended π-conjugated structure and evenly distributed dehydrobenzo[*n*]annulene pores provide excellent performance of γ-graphynes in gas separation, water purification, sensors, and catalysis. The number of acetylene units connecting two adjacent six-membered rings can gradually change (Fig. 1) to form γ-graphynes with extended polyyne chains [1]. We demonstrate that γ-graphyne is an efficient electron acceptor due to its low LUMO and its ability to delocalize an excess charge [2]. Moreover, its electron-withdrawing character is enhanced when moving from γ-graphyne to γ-graphtriyne. In contrast to other 2D sheets, electronic properties of γ-graphyne are not sensitive to vacancy defects.

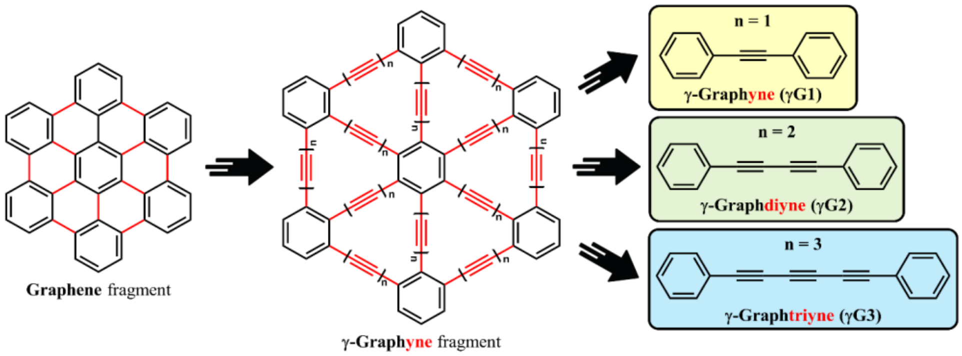

Figure 1. Representation of γ-graphynes with different number of acetylene units.

Investigation of photoinduced electron transfer in non-covalent complexes of γ-graphynes with typical electron-acceptors and electron-donors by TDDFT method shows that the lowest excited states with donors are charge-separated states formed by the electron transfer from the donor to γ-graphyne. In the case of $Sc_3N@C_{80}$ partner, the extended acetylene linkages between phenyl rings reduce the movement of fullerene over γ-graphyne surface and facilitate electron transfer, which occurs on sub-nanosecond time scale [3].

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Accelerating the prediction of large carbon clusters via structure search: evaluation of machine-learning and classical potentials

Carla de Tomas[1], Jean-Marc Leyssale[2]
Patrick Rowe[3] Bora Karasulu[4]
[1]Imperial, SW7 2BX, London, UK

[2] University of Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, F-33400 Talence, France

[3] AbCellera, Vancouver, Canada

[4] Warwick University, Coventry, UK

c.detomas@imperial.ac.uk

From as small as single carbon dimers up to giant fullerenes or amorphous nanometer-sized particles, the large family of carbon nanoclusters holds a complex structural variability that increases with cluster size. Capturing this variability and predicting stable allotropes remains a challenging modelling task, crucial to advance technological applications of these materials. While small cluster sizes are traditionally investigated with first-principles methods, a comprehensive study spanning larger sizes calls for a computationally efficient alternative.

Here, we combine the stochastic *ab initio* random structure search algorithm (AIRSS) with geometry optimisations based on interatomic potentials to systematically predict the structure of carbon clusters spanning a wide range of sizes. We first test the transferability and predictive capability of seven widely used carbon potentials, including classical (EDIP, ReaxFF, Tersoff, REBO-II, LCBOP-I, AIREBO) and machine-learning (GAP-20) potentials. Results are compared against an analogous cluster dataset generated via AIRSS combined with density functional theory optimizations. The best performing potential, GAP-20, is then employed to predict larger clusters in the nanometre scale, overcoming the computational limits of first-principles approaches. Our complete cluster dataset describes the evolution of topological properties with cluster size, capturing the complex variability of the carbon cluster family. As such, the dataset includes ordered and disordered structures, reproducing well-known clusters, like fullerenes, and predicting novel isomers.

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Mechanisms and kinetics of prismatic dislocation loop removal during graphitization

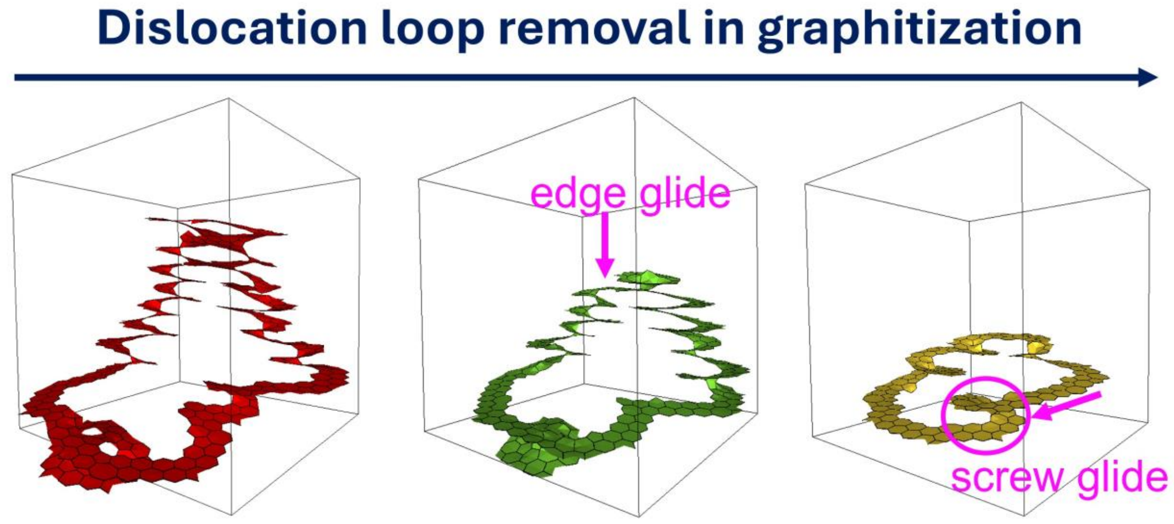
G. R. Francas[1]**,** J.W. Martin[1], K.J. Putman[1], I. Suarez-Martinez[1], N.A. Marks[1]

[1]*Dept. of Physics and Astronomy, Curtin University, Perth, Australia*

gabriel.francas@postgrad.curtin.edu.au

Graphite is an integral material for the green revolution, playing key roles in energy storage, lightweight vehicle construction and steel recycling. Manufacturing synthetic graphite typically requires heating carbon precursors to extremely high temperatures (up to 3000˚ C) [1] which facilitates the progressive growth of ordered crystallites and removal of defects. The concentration and ease of removal of these defects is a determining factor in how well a precursor can graphitize [2]. Our recent work has shown that prismatic screw dislocations are an important defect which is removed during graphitization [3].

Molecular dynamics simulations have been performed to study prismatic dislocation loops during graphitization. Newly developed analysis tools reveal the complex structure of these loops, being dispersed in three dimensions with alternating screw and edge components in multiple slip planes. These tools also enable the time-evolution of the loops to be tracked, clarifying the mechanisms of their removal and the kinetics of this process. Loop removal involves edge glide through kink formation and propagation, followed by a slower screw glide mechanism. The activation energy computed for loop removal of 2.9±0.3 eV is consistent with recent experimental work by ourselves and in agreement with the lower range of activation energies found for graphitization.



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High-dimensional neural network potential for borophene on metallic surfaces

Colin BOUSIGE[1]**,** Pierre MIGNON[2], Abdul-Rahman ALLOUCHE[2], Neil INNIS[1]

[1] Laboratoire des Multimatériaux et Interfaces, CNRS, Université Lyon 1, Villeurbanne, France
[2] Institut Lumière Matière, Université Lyon 1, Villeurbanne, France
colin.bousige@cnrs.fr

Single layer materials have drawn a lot of attention due to their peculiar physical properties (opto-electronic properties, high conductivity, flexibility…). In particular, it has been predicted that boron could exist as a single atomic layer in distinctive crystallographic configurations (allotropes), called *borophene* – in reference to the carbon equivalent, graphene. Borophene is one of the only 2D material with metallic behaviour, among other interesting properties [1]. Recent studies have focused on the synthesis of such material under various allotropic forms, the obtained allotrope depending on the substrate used and experimental parameters such as synthesis temperature [2–5]. However, the link between the various synthesis parameters and the obtained allotrope is still unclear. To be able to control the synthesis of allotropes selected for their wanted properties, one needs a good understanding of the growth mechanisms and phase transitions at stake in this system. Therefore, a strong theoretical support is needed, with accurate reactive simulations of large systems. However, while ab initio simulations are accurate, they are slow and do not allow studying large systems – and classical Molecular Dynamics require a force field that is not available for this system.

In this work [6], we have developed a new atomic potential using a machine learning approach [7–9], which allows us to explore multiple structural arrangements of borophene allotropes on metal substrates. The developed potential presents the advantage of performing fast simulations with a level of accuracy comparable to ab initio calculations [10]. Here, we will present the methodology to develop this machine learning potential as well as the various borophene allotropes that have been simulated on Ag surfaces, and present our first results on the growth and phase transitions in this system using our machine learned potential.

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In-plane staging in lithium-ion intercalation of bilayer graphene

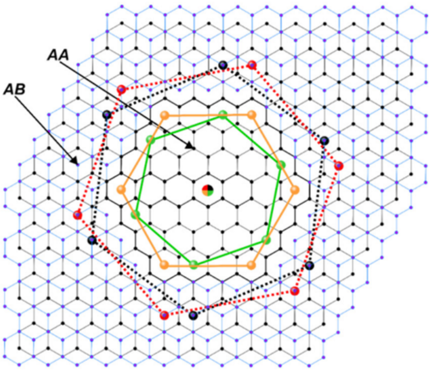
James G. McHugh[1,2], Thomas Astles[1], Rui Zhang[1], Madeleine Howe[1], Zachary A.H. Goodwin[1,2], Sergey Slizovskiy[1,2], Daniil Domaretskiy[1], Andre K. Geim[1,2], Vladimir Falko[1,2], Irina V. Grigorieva[1,2]

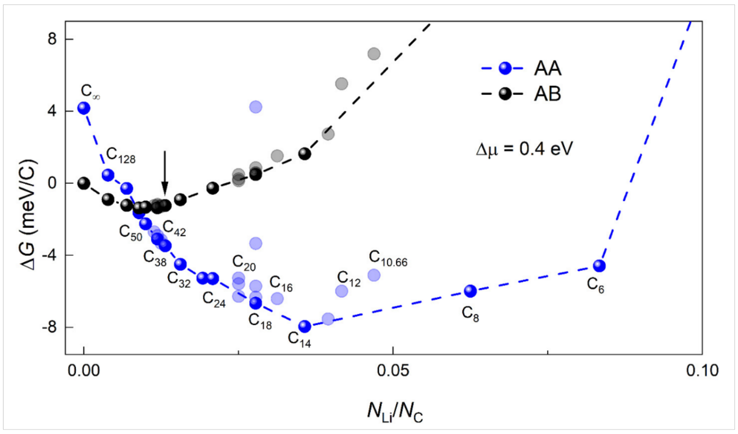
[1] *Department of Physics and Astronomy, University of Manchester*

[2] *National Graphene Institute, University of Manchester*

james.mchugh@manchester.ac.uk

The ongoing efforts to optimize rechargeable Li-ion batteries has led to significant interest in the intercalation of nanoscale derivatives of bulk layered compounds such as, e.g., bilayer graphene (BLG)[1-3]. Lithium intercalation of BLG has been demonstrated previously, but the factors underpinning ion storage capacity, charge-discharge rates, and the associated limiting mechanisms remain poorly understood. Here, magnetotransport measurements were used to understand the in-operando intercalation dynamics of BLG devices, which is found to exhibit four, distinct *in-plane* intercalation stages (I to IV), corresponding to well-defined Li-ion densities, with transition between the stages occurring rapidly (within 1 sec) over the entire device area. Stage IV provides a stoichiometric compound $C_{14}LiC_{14}$ with maximum $n_{Li} \approx 2.7 \cdot 10^{14} cm^{-2}$, notably lower than n_{Li} for fully intercalated graphite.





Density functional theory (DFT) calculations are used to understand this behaviour, confirming that $C_{14}LiC_{14}$ corresponds to the thermodynamic equilibrium for intercalated AA-stacked bilayers, while another observed stage ($C_{18}LiC_{18}$) is close to this equilibrium configuration. Earlier stages (I and II) occur at much lower n_{Li} and are attributed to metastable states within the original AB stacking. A stacking transition occurs at a threshold Li density of $\sim 0.9 \cdot 10^{14} cm^{-2}$, resulting in a rapid increase by >250% in Li ion density through the formation of AA domains bounded by basal dislocation loops. Irreversible deformation of the pristine BLG lattice by these dislocations in turn facilitates faster charging in later cycles. Together, our findings both reveal the mechanism and limits of electrochemical intercalation of BLG, while hinting at possible avenues for increasing the Li storage capacity.

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Modelling the effects of defects on the properties of graphite

Kenny Jolley[1]**,** Paul Mouratidis[1], Daria Nasartdinova[1]

[1]*Dept. of Chemistry, Loughborough University Epinal Way, Loughborough, LE11 3TU, UK*

k.jolley@lboro.ac.uk

Graphitic materials exhibit a variety of defects, including crystal defects like dislocations and point defects such as vacancies or interstitial clusters. This study employs density functional theory (DFT) and molecular dynamics (MD) calculations to investigate the properties of defected graphite, focusing on basal and prismatic dislocations, point defects, and the intercalation of metallic atomic dopants.

Dislocations are a crucial concept in materials science, governing the plastic deformation and damage evolution of materials. In layered materials such as graphite, there are two general types of interlayer dislocations: basal and prismatic. Basal dislocations can induce buckling within the layers. This effect is examined by calculating the formation energy of buckled structures compared to those held flat. The results indicate that buckling is primarily initiated by the edge component of basal dislocations, which influences hydrostatic strain perpendicular to the dislocation line. The study also considers the buckling of dislocated multilayer supercells, providing insights into structural deformation in bulk graphite.

The structure, energetics, and mobility of prismatic dislocations are also investigated. These prismatic cores consist of a graphene edge (either zigzag or armchair) that can be bonded or free-standing. Calculations show that prismatic dislocation cores remain stable at high temperatures, approximately 1500 K, in bulk graphite. Beyond this threshold, bond breaking within the dislocation core facilitates climb, grain-boundary motion, and the annealing of damage through prismatic dislocation glide. These findings offer valuable insights into the behaviour of graphite at elevated temperatures, enhancing our understanding of its mechanical properties and potential applications in high-temperature environments.

The diffusion and intercalation of metallic atomic dopants in graphite are significant for various engineering and nanotechnology applications. This study examines the intercalation and diffusion of Li and Na within defected graphite. Prismatic dislocation cores contain voids larger than the graphene interlayer spacing, potentially providing a channel for ion diffusion within bulk graphite. This has important implications for fission product diffusion and energy storage applications involving Li/Na diffusion. The research contributes to a deeper understanding of the complex interplay between dislocations and intercalation in graphite, with broad implications for energy storage and other applications.

Band structure investigation of nanocrystalline titanium carbide (TiC) particles under gamma radiation

Elchin M. Huseynov, Raisa R. Hakhiyeva
Institute of Radiation Problems of Ministry of Science and Education, 9 B.Vahabzade, Baku AZ 1143, Azerbaijan

This study is focused on the band structure of nanocrystalline titanium carbide (TiC) particles under gamma radiation exposure. Utilizing advanced spectroscopic techniques and computational modeling, we analyze the electronic properties and alterations caused by gamma irradiation. These findings enhance our understanding of the radiation tolerance and potential applications of TiC in environments subjected to high levels of radiation, such as in nuclear reactors and space exploration. The study also provides insights into the broader implications for the stability and functionality of nanocrystalline materials under extreme conditions [1-3]. The infrared (IR) spectra of nanocrystalline TiC samples were compared before and after exposure to gamma radiation at doses of 5 Mrad, 15 Mrad, 50 Mrad, and 150 Mrad in the wavenumber range of 400–4000 cm^{-1}. The spectral analysis revealed four distinct peaks in the sample before exposure to gamma radiation. The wavenumbers corresponding to the Ti-C bond in TiC nanoparticles were measured both before and after gamma radiation exposure. The alterations in TiC nanoparticles induced by gamma radiation were elucidated using appropriate analytical methodologies. Furthermore, the impacts of gamma radiation were discussed in relation to the wavenumbers associated with potential surface bonds on the nano TiC particles. The study also explores the optimized bond structure of TiC nanoparticles and potential bond alterations induced by gamma radiation.

The studies indicate that high doses of gamma radiation induce substantial changes in the FTIR spectra of nano TiC particles. Specifically, at a gamma radiation dose of 150 Mrad, the major peaks corresponding to Ti-O or C-O bonds observed prior to irradiation vanish entirely. Simultaneously, new peaks emerge at wavenumbers of 920 cm^{-1} and 1005 cm^{-1}, which are attributed to defects or bonds involving Ti-OH, Ti-O, and CO with varying spatial oscillations. Additionally, the peak at 650 cm^{-1}, indicative of the Ti-C bond, disappers under high-dose radiation due to the prevalence of peaks associated with hydroxyl groups formed by Ti and C radicals during irradiation.

Moreover, amorphous transmutation is observed at relatively high doses of gamma radiation. Nano TiC particles, characterized by their large specific surface area (SSA), exhibit heightened sensitivity to environmental changes, which is markedly enhanced under high-dose gamma radiation. Consequently, the adsorption capacity of nano TiC particles results in -OH groups becoming prominent at around 3500 cm^{-1}, a feature exacerbated by gamma radiation.

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Exploring nanostructured TiO_2 photoelectrodes: from preparation to application

Carlos Martínez-Barón[1]**,** Víctor Calvo[1], Miguel Ángel Álvarez-Sánchez[1], José Miguel González-Domínguez[1], Alejandro Ansón-Casaos[1], Wolfgang K. Maser[1], Ana M. Benito[1]
[1]*Instituto de Carboquímica (ICB-CSIC), 50018 Zaragoza, Spain*
cmartinez@icb.csic.es

Photoelectrochemical (PEC) water splitting for the production of green hydrogen critically relies on the development of suitable photoelectrodes. Nanostructuring and sensitizing approaches are considered important pathways to achieve further advances.

In the present work, we report several ways for preparing TiO_2 photoanodes that notably differ from those applied in typical screen-printing techniques. First, we present a novel aqueous processing of TiO_2 nanoparticles by means of cellulose nanocrystals. This allows the fabrication of highly porous and efficient TiO_2 films, showing a 3-fold enhancement of the PEC performance as compared to those achieved with commercial TiO_2 pastes [1]. Second, we show that hydrothermally produced TiO_2 nanorods result in photoelectrodes with impressive photocurrent response and charge transfer properties towards efficient PEC water splitting. In order to push light absorption towards the visible range, we further report the successful sensitization of TiO_2 photoanodes using a D-π-A dye molecule, even offering photocurrents with long-term stability [2]. Finally, we demonstrate that the combination of xanthene dyes and graphene oxide leads to a unique hybrid serving as TiO_2 sensitizer, which not only increases light absorption, but also enhances charge transfer within the PEC system [3]. These findings represent an important contribution towards the fabrication of photoelectrodes meeting criteria of efficiency and sustainability.

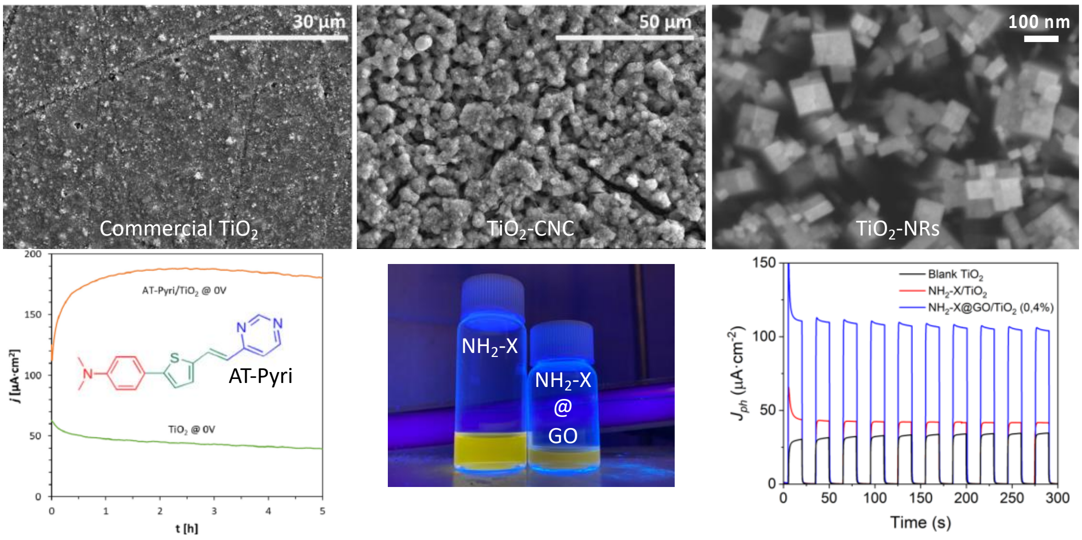

Figure 1. Summary of the present work, including nanostructures and PEC measurements.

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The (anti)aromatic properties of cyclo[n]carbons: myth or reality?

A.J. Stasyuk[1,2], G. George[3], O.A. Stasyuk[3], M. Solà[3], F. Plasser[4]

1. *Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona (UB), Barcelona, Spain*
2. *Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*
3. *Institute of Computational Chemistry and Catalysis, Universitat de Girona, Girona, Spain*
4. *Department of Chemistry, Loughborough University, Loughborough LE11 3TU, U.K.*

antony.stasuk@gmail.com

Cyclo[n]carbons are a new allotropic form of carbon that are arranged in a circular fashion. First detected in 1989 by Diederich et al.[1] the structure of these molecules, especially cyclo[18]carbon (C18), was debated for over 30 years, with chemists considering two possible structures: a D9h polyynic structure with alternating single and triple bonds, and a D18h cumulenic structure with only double bonds. The synthesis and structural characterization of C18 by Kaiser et al.[2] in 2019 confirmed its polyynic structure through atomic force microscopy (AFM) and scanning tunneling microscopy (STM). Today, the cyclocarbon family includes more than 5 representatives whose structure has been reliably confirmed. However, the high reactivity of such molecules largely limits the experimental study of their properties, leaving a huge room for theoretical research. Molecular orbital analysis and analysis of ring currents allowed to assume that cyclo[n]carbons with $n \vdots 4$ are antiaromatic, while other molecules with an even number of carbon atoms are aromatic

Our computational study of ground and excited state properties of cyclo[n]carbons revealed their strong electron acceptor nature, comparable to that of C_{60} fullerene.[3,4] The excited state simulations show that both aromatic (C_{18}) and antiaromatic (C_{16}) cyclocarbons can only be favorably engaged in electron transfer with strong electron donors, such as zinc-phthalocyanine and pentacene. The similarity of the electronic properties of C16 and C18 cyclocarbons raises the question of the appropriateness of their division into aromatic and antiaromatic categories. Detailed analysis using magnetic and electronic descriptors of aromaticity for C_{16} to C_{30}, in conjunction with analysis of aromatic stabilization energy, led us to very controversial conclusions.

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Thursday, 29th August

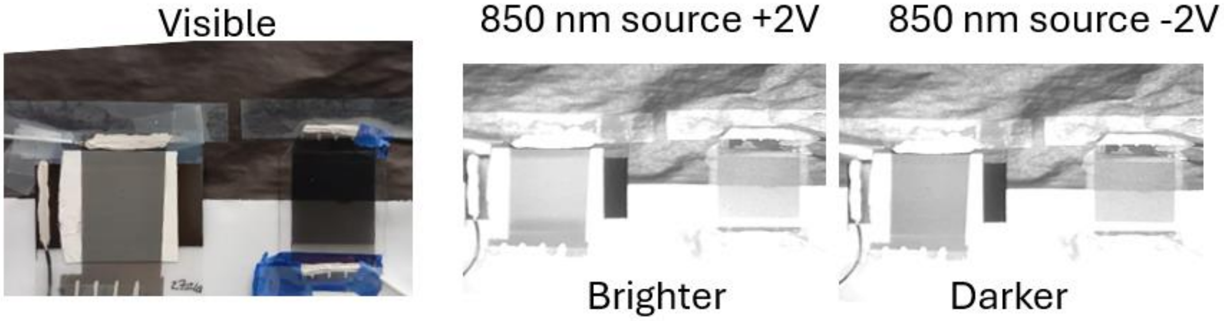
All-printed CNT-based electrochromics

Peter Lynch, Manoj Tripathi, Raquel Cano CorderoSean Ogilvie, Alan Dalton

University of Sussex, Brighton, East Sussex, UK

p.j.lynch@sussex.ac.uk

Infrared electrochromics help address heating due to invisible solar (near infrared) and black body radiation (mid-infrared). The optical properties of carbon nanotubes in the infrared are easily accessible in the potential range accessible by supercapacitors[1,2]. However, due to the position of the Fermi level not being centred between the valence and conduction bands the optical effects of biasing are asymmetric. A transparent electrolyte device has the reflective effects of modulation of both electrodes. In this study, we use hexagonal-boron nitride (hBN) as an optical scattering material in the electrolyte due to hBN having a high refractive index and well-established liquid processing parameters. This all-liquid processed device enables the reflective response to be wholly due to the top electrode. In addition to devices that control thermal properties, this enables the study of optical properties of single electrodes in reflectance and facilitates spectroscopic studies in regions that generally require special substrates in transmission.



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Carbon-based Electrochromic Thermal Management for Coatings

Zongtao Zhang*, Jose V. Anguita, S. Ravi P. Silva

University of Surrey, Guildford, Surrey, GU2 7XH, UK

zongtao.zhang@surrey.ac.uk

We propose the use of carbon-based electrochromic (EC) materials as a structurally integrated robust thermal management solution for future sustainable building design, thermal imaging, and spacecraft thermal control. At present, carbon-based electrochromic devices encounter notable challenges, such as a low on-off ratio, restricted cycling endurance, and a lack of scalable manufacturing techniques. In this report, we highlight recent innovations in carbon nanotube (CNT) and graphene-integrated electrochromic materials for thermal management, together with prototype designs focused on real-world applications. Our recent research progress on flexible and scalable carbon-based electrochromic devices will be presented, highlighting their broadband appeal for optical modulation capabilities across a wide thermal radiation range (wavelength of 4.5 ~ 25 μm) and for solar radiation (wavelength of 0.25 ~ 2.5 μm). The exploration of carbon-based electrochromic materials offers new prospects in advanced and highly efficient thermal management systems in emerging energy-related applications.

The effect of 2D nanosheet size on the performance of printed devices

Anthony Dawson[1], Prof. Jonathan Coleman[2]

Trinity College Dublin

andawson@tcd.ie

Printed networks of materials such as few layer MoS2 nanosheets enable the production of low-cost but poorer performance devices. Printed networks are arrays of nanoparticles deposited across a large area, with nanoparticles contacting one another at junctions. The poor performance of nanosheet networks is due to low nanosheet network mobility of about 0.1 cm2/Vs, this is in part due to inter-nanosheet junctions.

To improve network mobility of printed networks, we must better understand these junctions. To achieve this, size-controlled networks have been developed by tuning nanosheet dimensions and characterising their electrical performance. Tuning of nanosheet aspect ratio from 500 to 100 has been achieved for the first-time using Sonication Induced Scission.

Using this size selection technique, devices of a range of nanosheet sizes are developed, and their electrical properties characterised, revealing new insights into charge transport in these nanosheet networks.

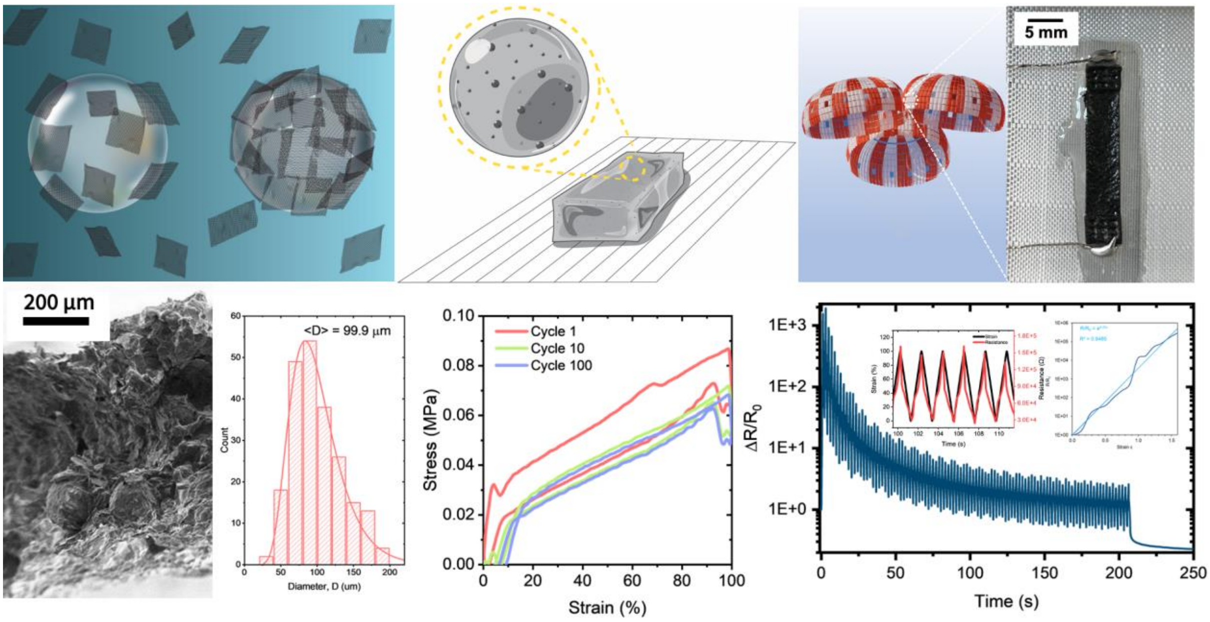
Direct deposited emulsion-templated composites for monitoring of fabric strain.

Raquel Cano, S. Ogilvie, P. Lynch, A. Dalton

University of Sussex, Brighton, East Sussex, UK

r.cano-cordero@sussex.ac.uk

The need for developing stretchable, wearable, soft-strain sensors has risen in recent decades due to their relevance in various fields such as smart textiles, real-time monitoring, soft robotics, medical applications, and human motion detection. As is widely known, the creation of strain sensors encounters the difficulty of balancing different properties such as high sensitivity, adequate flexibility, good hysteresis and durability, and easy adaptability for incorporation into different surfaces. In this study, we are utilising liquid- exfoliated graphene nanosheets and commercially available silicones to develop the next generation of nanocomposite strain sensors. The graphene network is structured via emulsification to produce graphene-coated silicone droplets enabling high conductivity at relatively low graphene loadings[1]. When combined with a highly elastic, flexible silicone matrix, this yields excellent electromechanical properties with a robust exponential response to applied strain. These emulsion-templated composites are robust to more than 500 cycles up to 100% strain and at a strain rate of 100%/s. The sensor exhibits good ohmic conduction, with an average conductivity of 0.8 ± 0.08 S/m. For the single, high strain rate (100%/s) strain to break measurement a well-defined ($R_2 = 0.95$) exponential response is observed up to 200% strain, featuring an extremely high relative resistance change of $2\text{x}10^5$ and a Gauge Factor of ~70. Moreover, these composites exhibit minimal hysteresis when deposited on a fabric substrate during cyclic strain, providing a system for monitoring high-performance fabrics.



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Constructing graphene functional materials using selective oxidation

Alexandra Carvalho[1]**,** Gavin K. W. Koon[2], Katarzyna Z. Donato[2], Maxim Trushin,[1,2,3] Ricardo K. Donato[2], A. H. Castro Neto,[1,2,3]

[1]*Institute for Functional Intelligent Materials, National University of Singapore, 117544, Singapore.*

[2]*Centre for Advanced 2D Materials, National University of Singapore, 117546, Singapore.*

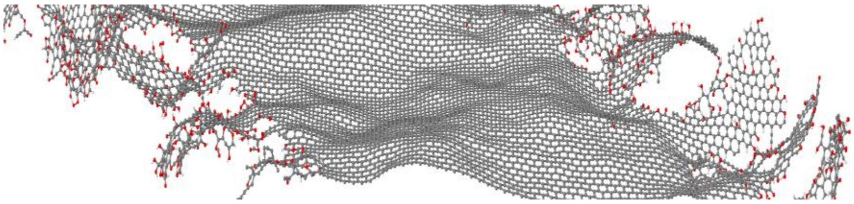
[3]*Department of Materials Science and Engineering, National University of Singapore, 117575, Singapore.*

carvalho@nus.edu.sg

Graphene, the first isolated two-dimensional material, has exceptional physical properties that make it a prime candidate for electronics applications. However, its crystalline form is difficult to process, especially in an aqueous medium, limiting its practical usage. Graphene oxide materials, on the other hand, are easier to process and to functionalise, but they are highly disordered.

The oxidation of graphene oxide creates a variety of epoxy, carboxyl, and hydroxyl groups both in the basal layers and at the edges. Understanding and controlling the formation of such functional groups is an essential step to control how graphene and graphene oxide interact with water. An example is the dependance of the surface charge on the pH of the water and how it influences scrolling and unscrolling.

We then examine the energetics and signatures of the different functional groups present in graphene and graphene oxide to provide insight into selective functionalisation and material design. We show how a highly processable graphene-based material, forming suspensions in many solvents, was created by hydrolytic oxidation of the graphene at the edges while preserving the properties of the basal plane. This illustrates how the control of edge and surface reactions can be the key to creating graphene-based functional materials with a place in the realm of industrial applications.



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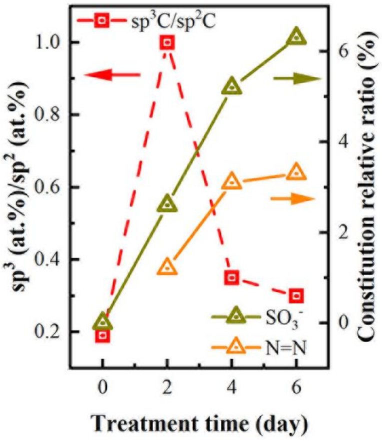
XPS measurements confirm sulfophenyl functionalization of graphene as promising transmembrane for direct methanol fuel cell

Clément Maheu[1,2], Weizhe Zhang[3], Max Makurat[3], Xue Liu[3], Xiaofang Kang[3], Xiaoting Liu[4,5], Yanglizhi Li[4], Thomas J.F. Kock[3], Christopher Leist[6], Andy Jiao[3], Haoyuan Qi[6], Ute Kaiser[6], Luzhao Sun[4], Zhongfan Liu[4], Jan P. Hofmann[2], Grégory F. Schneider[1]*

[1]*Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France*
[2]*Surface Science Laboratory, Technical University of Darmstadt, 64287 Darmstadt, Germany.*
[3]*Leiden Institute of Chemistry, Faculty of Science, Leiden University, Einsteinweg 55, 2333CC Leiden, The Netherlands.*
[4]*Center for Nanochemistry, Beijing Science and Engineering Center for Nanocarbons, Peking University, Beijing, China.*
[5] *Beijing Graphene Institute (BGI), Beijing, China.*
[6] *Electron Microscopy Group of Materials Science, Ulm University, Ulm, Germany.*
clement.maheu@cnrs-imn.fr & g.f.schneider@chem.leidenuniv.nl

An ideal proton exchange membrane should only let protons through and be leak-tight for fuels. Graphene is impermeable to water and poorly conducts protons. To address this, we chemically functionalized monolayer graphene with 4-sulfobenzenediazonium (4-SBD) [1]. This treatment converts sp^2 carbons from graphene into functional sp^3 dislocations paired with sulfophenyl groups. Such functionalization has been confirmed by combining Raman spectroscopy and XPS measurements. The latter provide numerous pieces of information, including the sp^3/sp^2 ratio and the SO_3^- content as a function of the 4-SBD treatment duration (*i.e.* graphene treated during 2, 4, 6 days have been compared). Detrimental effects have also been observed such as oligomerization under too long 4-SBD treatment. The resulting transmembrane becomes selective to protons. This is a consequence of the combination of sp^3 dislocations and polar groups, which result in hydrophilic ion paths through graphene. Conductances up to ~50 S cm^{-2} are obtained, which is ~5000 fold higher than in pristine graphene. Finally, a direct methanol fuel cell has been assembled, and evidence power densities up to 1.6 W mg^{-1} or 123 mW cm^{-2} under standard cell operation (60 ^{o}C), a value ~two-fold larger than that of micron-thick films of Nafion 117.



XPS semi-quantitative analysis of the functionalized graphene membranes.

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CNT aerogel electrochemical bio-sensor: A new era in ultra sensitive biomedical technology

Jyoti Prakash[1,2]

[1]*Advanced Carbon Materials Section, Materials Group, Bhabha Atomic Research Centre, Mumbai 400085 India*

[2] *Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094 India*

jprakash@barc.gov.in

Carbon nanotube (CNT)-based electrochemical biosensors constitute a rapidly expanding domain in biomedical research, owing to their distinctive properties facilitating highly sensitive and selective detection of biomolecules. Nevertheless, conventional CNT-based electrochemical biosensors face challenges, including intricate fabrication processes, limited selectivity and sensitivity, high costs, and a restricted lifespan.

In our laboratory, we have pioneered the development of a novel generation of CNT aerogel-based electrochemical biosensors that surmount these limitations. These sensors are crafted through a floating catalyst chemical vapor deposition process, yielding freestanding CNT aerogel films endowed with notable features such as high porosity, electrical conductivity, tensile strength, and mechanical integrity. These attributes render them exceptionally suitable for deployment as ultra-sensitive biomolecule detectors, capable of discerning even minute quantities of biomolecules with heightened sensitivity and selectivity. Notably, the CNT aerogel films maintain their bio-sensing prowess under various deformations, including bending, twisting, stretching, and knotting. This versatility makes them well-suited for integration into wearable sensing devices. Furthermore, this presentation will delve into a comparative performance analysis of CNT aerogel sensors vis-à-vis traditional glassy carbon electrodes, printed three-electrode paper, and gold-printed electrodes. This comparative analysis aims to underscore the distinct advantages offered by CNT aerogel-based sensors. The utilization of CNT aerogel-based electrochemical biosensors holds the potential to revolutionize the field of biomedical sensing and diagnostics. By delivering a sustainable, reliable, and cost-effective solution for detecting biomolecules in complex matrices, these sensors are poised to make a significant impact on advancing biomedical research and applications.

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Nanoplastics and Nanocarbons: Contaminants of Emerging Concern

Sergey Mikhalovsky[1,2]**,** Matt Illsley[1], Rosa Busquets[2], Yury Zabulonov[4]

[1] ANAMAD Ltd, Sussex Innovation Centre, Falmer, Brighton, BN1 9SB, UK
[2] Chuiko Institute of Surface Chemistry, 17, General Naumov str., Kyiv, 03164, Ukraine
[3] Kingston University, Penrhyn road, Kingston upon Thames, KT1 2EE, UK
[4] Institute of Environmental Geochemistry, 34A, Academician Palladin Ave., Kyiv, 03142, Ukraine

sergey.mikhalovsky@anamad.co.uk

The global threat of environmental pollution with plastics has now been recognised. Although the pollution with large pieces of plastic is quite visible, it is the microplastics (MP) which pose a growing concern regarding their impact on aquatic life and human health. Current water treatment technologies remove most of larger MPs in terms of weight% but their efficiency is dependent on the particle size, moreover, the degradation of larger particles results in the production of nanoplastics (NP) which are then discharged in extremely large numbers but very small weight%. In addition to their own ecotoxicity, the NPs carry substantial quantities of other adsorbed substances, which include priority pollutants and other contaminants of emerging concern (CECs). Current methods are inefficient in removing NPs from water, the main entry point to the biota, food chain and human consumption.

Carbon nanomaterials (CNM) should also be considered as CECs. It has been shown that 6% of CNTs escape from wastewater treatment plants [1]. CNTs are among the most recalcitrant materials with estimated half-life of 1400 years in the environment [2]. At present, per- and polyfluorinated alkyl substances, or PFAS, which have a half-life of dozens of years are dubbed “forever chemicals” and considered a serious threat to the environment and health even at extremely low concentrations. It should be noted that the chemical inertness of some types of CNM does not guarantee their safety; PFAS are extremely inert, nevertheless, they have been proved to cause a negative impact on health at the cellular level. Due to their large specific surface area, nanoparticles could also adsorb and transport significant quantities of soluble toxic pollutants further exacerbating their harmful effect on the environment. It has been shown that graphenes could aggregate in water and eventually transfer from the aqueous phase to the sediment. Whether they remain in the sediment or could be leached back into water following chemical and biotransformations is unclear. It is known that some pesticides such as DDT or hexachlorobenzene were banned from use dozens of years ago, but they still migrate from the soil into water causing health concerns and this transportation route for CNM cannot be ignored. At present, advanced oxidation processes (AOP) are considered capable of destroying NP pollutants, however the initial results show slow kinetics of NP removal. We discuss an innovative atmospheric nonthermal 3-D plasma technology, which combines several AOPs and could improve the efficiency of carbon and polymer nanoparticles removal.

Acknowledgments

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Flattened Carbon Nanotubes: Preparation and Raman signal

Picheau Emmanuel[1]

[1]*International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan*

picheau.emmanuelvincentdavid@nims.go.jp

Carbon nanotubes (CNTs) are generally considered cylindrical objects. However, under certain circumstances a flattened geometry is more stable than the cylindrical counterpart. It is for instance possible to collapse a cylindrical CNT into its flattened shape by applying pressure, or to obtain spontaneously flattened CNT if its diameter is large enough (~ 5 nm for a single wall CNT [1]). Being identical to bilayer graphene nanoribbons but closed on their edges by atomically smooth cavities, flattened carbon nanotubes possess interesting properties of great potential.[2]

After a review of the last 25 years of literature about flattened CNTs, the presentation will focus on the obtaining of spontaneously flattened CNTs from multi-walled sample and their Raman signal.[3] Being involved in the process, carbon combustion will be discussed as well, notably as an efficient carbon materials treatment/purification method.

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Functionalized two-dimensional transition metal dichalcogenides for energy applications

Ioanna K. Sideri[1], Nikos Tagmatarchis[1]

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

isideri@eie.gr

Functionalized two-dimensional transition metal dichalcogenides (2D TMDs) have emerged as a promising frontier for advancing energy applications. This talk will delve into the methodologies employed for the covalent functionalization of MoS_2, highlighting strategies for precisely tuning the surface chemistry of TMDs.[1] By leveraging covalent modifications with chromophores, we harness synergistic effects to engineer tailored properties in these 2D TMDs.[2] The hybrid TMDs exhibit enhanced capabilities in facilitating electron and energy transfer, paving the way for improved light harvesting and potential advancements in optoelectronic device performance (Figure 1). Electrochemical studies showcase their prowess in electrocatalysis, emphasizing their potential in sustainable energy conversion technologies. Additionally, the fabrication of cells for photocurrent measurements demonstrates their efficiency in harnessing solar energy. We also explore the realm of biosensing, focusing on host-guest interactions facilitated by hydrogen-bonding formations. Through this comprehensive examination, we aim to elucidate the transformative potential of functionalized 2D TMDs in various energy applications, advancing the field of materials science toward sustainable and efficient energy solutions.

The research project was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “2nd Call for H.F.R.I. Research Projects to support Faculty Members & Researchers” (Project Number 2482).

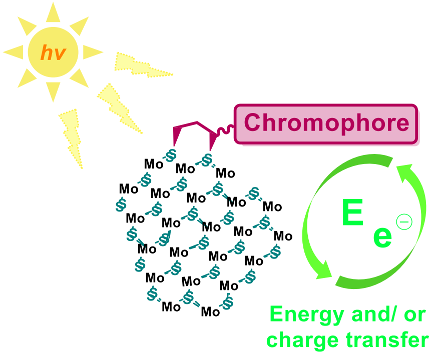

Figure 1: Electron and/ or energy transfer in functionalized TMDs with chromophores.

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Synthesis, characterization and optical and redox properties of perylene modified MoS_2 nanosheets

Eleni Nikoli[1]**,** Ruben Canton-Vitoria[1], Nathalie Zink-Lorre[2], Ana Maria Gutierrez-Vilchez[2], Fernando Fernandez-Lazaro[2], Nikos Tagmatarchis[1]

[1]TPCI, NHRF, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece

[2] Area de Quimica Organica, Instituto de Bioingenieria, Universidad Miguel Hernandez, 03202, Elche Brighton, Spain

enikoli@eie.gr

Chemical modification of 2D-TMDs with photoactive molecules has emerged as of great interest due to the development of photoinduced electron transfer phenomena, that could be exploited in various optoelectronic applications. Previous studies on molybdenum disulfide (MoS_2), the most representative TMD, have shown mainly the electron acceptor character of MoS_2, contrary to recent literature that unveiled the electron donor capability of MoS_2 nanosheets upon functionalization with a perylene diimide (PDI) derivative [1,2]. In this study, we further investigate the synthesis and characterization of MoS_2 nanosheets functionalized with PDI derivatives. The covalent attachment of PDI derivatives on exfoliated MoS_2 is accomplished by initially filling sulfur vacancies via lipoic acid conjugation, resulting in a carboxylic acid-functionalized MoS_2. Subsequent condensation with PDI derivatives produces the desired MoS_2-PDI hybrids. The successful formation of MoS_2-PDIs was verified through complementary analytical techniques such as Raman and IR spectroscopy and thermogravimetric analysis. Additionally, the photophysical properties of MoS_2-PDIs were also assessed. UV-Vis and photoluminescence spectroscopy revealed distinct absorption and emission profiles for PDI derivatives, with strong emission quenching observed in the corresponding MoS_2-PDI hybrids. Time-resolved fluorescence decay analysis indicated new deactivation pathways of photoexcited PDIs. Furthermore, the redox properties were explored by square wave pulse voltammetry, which demonstrated shifts in the redox potentials of PDIs within the hybrids. These findings provide a comprehensive understanding of the synthesis, structure, and properties of MoS_2-PDI hybrid materials, highlighting their potential for advanced optoelectronic applications.

The research project was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “2nd Call for H.F.R.I. Research Projects to support Faculty Members & Researchers” (Project Number 2482).

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Role of graphene substrate in the formation of MoS_2-based nanoparticles with improved NO_2 gas sensing

L.G. Bulusheva[1], S.A. Lavrukhina,[1] and A.V. Okotrub[1]

[1]*Nikolaev Institute of Inorganic Chemistry SB RAS, 3 Acad. Lavrentiev ave., 630090 Novosibirsk, Russia*

bul@niic.nsc.ru

In this work, we investigated the influence of the nature of the substrate on the formation of a MoS_2 coating from the deposited precursor $(NH_4)_2MoS_4$, the transformation of this coating during annealing under ultra-high vacuum (UHV) conditions, and the sensor performance of the resulting samples. The substrates used were surface-oxidized silicon wafer, few-layer graphene synthesized by CVD, and exfoliated graphene film obtained by laser reduction of fluorinated graphene (rFG). MoS_2 coatings were prepared by applying an equal amount of an aqueous precursor solution to the substrates, followed by the addition of hydrochloric acid and heating in a vacuum at 400 °C. The electronic state of the samples was determined by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the BESSY II synchrotron station before and after annealing in the spectrometer chamber at 1000 °C. XPS experiments detected a new high-energy component in the Mo 3d spectra of the annealed samples corresponding to under-coordinated Mo atoms. This component was especially high in the spectrum of MoS_2 located on CVD graphene. According to Raman spectroscopy, MoS_2 layers are well aligned along the SiO_2 surface and are randomly oriented, including vertically on carbon surfaces. The vertical orientation provides a firm bonding between the components of the hybrid sample, accompanied by electron density transfer from MoS_2 to graphene, as evidenced by NEXAFS spectroscopy data. This causes p-type doping of MoS_2, which is further enhanced when under-coordinated Mo atoms bind oxygen from air molecules. Tests of annealed samples as gas sensors showed that MoS_2 located on SiO_2/Si or rFG is capable detecting NO_2 only at elevated temperatures and cannot be restored. The sensor MoS_2 on CVD graphene was operated at room temperature and showed fast response and low limit of NO_2 detection. Moreover, the response to NO_2 was ~20000 times higher than to NH_3; this is a record value among those published. Such good characteristics of the sensor are associated with the accessible surface of vertically oriented small MoS_2 nanoparticles, strong bonding with graphene, which ensures a fast response of the sensor, and oxidation of edged molybdenum atoms, which modifies the interaction of MoS_2 with NO_2 and NH_3.

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Observation and characterisation of stabilised azafullerene radicals on Au surface

Yuri Tanuma[1], Gregor Kladnik[2,3], Marion van Midden Mavrič[1], Bastien Anézo[1,4], Nikos Tagmatartchis[5], Chris Ewels[4], Dean Cvetko[1,2,3], Denis Arčon[1,2]

[1] *Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*

[2] *Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia*

[3] *CNR-IOM, Istituto Officina dei Materiali, Basovizza Area Science Park, 34149 Trieste, Italy*

[4] *IMN, CNRS UMR6502, 2 Rue de la Houssiniere, BP 32229, 44322 Nantes, France*

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

yuri.tanuma@ijs.si

Azafullerene $C_{59}N$ is a fullerene radical that is proposed to be a platform of molecular qubits [1]. This molecule has one nitrogen atom replacing a carbon atom of parent C_{60} fullerene giving $C_{59}N^{\bullet}$ radical. However, the unpaired electron distributed on the cage surface makes the radical highly reactive and it immediately forms a dimer $(C_{59}N)_2$ with a neighbouring $C_{59}N^{\bullet}$ radical [2].

Aiming to create stable extended $C_{59}N^{\bullet}$ radical lattices, we deposit $C_{59}N$ on Au(111) surface with and without [10]cycloparaphenylene ([10]CPP) co-deposited layer. The later entraps the $C_{59}N^{\bullet}$ in its ring and protect the radicals from re-dimerisation [3,4]. Each film with controlled thickness is characterised by using X-ray photoemission (XPS) and X-ray absorption fine structure (NEXAFS) spectroscopy, scanning tunnelling microscopy (STM) and density functional calculations (DFT).

Polarised NEXAFS measurements reveal that the $C_{59}N$ molecules in the 1st layer are stabilised with the radical orbital pointing toward the Au substrate [5]. On this sacrificial layer, we observe stable radicals $C_{59}N^{\bullet}$ almost until the 2nd layer is completed. At this point they start to form non-radical dimers. In contrast, deposition of 1 monolayer of $C_{59}N$ on pre-deposited [10]CPP layer followed by thermal annealing generates $C_{59}N^{\bullet}\subset$[10]CPP supramolecular radicals with a high positional order on a hexagonal lattice. This guest-host complex structure is clearly observed by STM. Detailed molecular structures and interactions among $C_{59}N^{\bullet}$, [10]CPP and Au surface will be discussed.

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Multiscale correlative characterisation and patterning of graphene-related nanomaterials

Milo S.P. Shaffer[1,2], Yuhan Li[1]

[1] Department of Materials, Imperial College London, South Kensington Campus, London, SW7 2AZ, UK

[2] Department of Chemistry, Molecular Sciences Research Hub (MSRH), Imperial College London, 82 Wood Lane, London, W12 0BZ, UK

m.shaffer@imperial.ac.uk

Macroscale assemblies and composite structures, built upon graphene and graphene-related nanomaterials, are promising for a range of applications and devices. Consequently, there is growing demand for more comprehensive characterisation of graphene-based structures. The primary challenges revolve around understanding the morphology, dispersion, and spatial arrangement of the individual graphene flakes, as well as their interactions with other material phases. This presentation presents multiscale and multidimensional characterisation methodologies for investigating various graphene-based structures, employing a combination of optical and electron microscopy techniques, image processing and analytical methods.

Confocal laser scanning microscopy (CLSM) is developed as a valuable tool for microstructural investigation of graphene nanomaterials and nanocomposites, exploiting the technique's distinctive features, including high-contrast and non-invasive imaging, as well as depth discrimination. Using confocal reflection and total interference contrast imaging, the flake thickness distribution in graphene oxide (GO) films can be mapped rapidly and quantitatively. In addition to passive characterisation, CLSM can be used for simultaneous imaging and processing studies [1]: GO films can be selectively reduced in-situ to produce electrically conductive functional patterns at a range of lengthscales from millimetre to sub-micron. The versatility is demonstrated by direct writing "RC" circuits using the simple low power laser within the CLSM. Multi-modal tracking allows the conversion mechanism to be explored during the process, including 3D architectures by controlled ablation.

Full characterisation of graphene dispersion, particularly in nanocomposites, requires methods for volumetric characterisation; a variety of complementary 3D imaging methodologies are therefore developed. Non-destructive CLSM stack imaging, using reflection and fluorescence modalities, is applied for large-scale examination of graphene nanocomposites. General guidelines are established through discussions of applicability, sample requirements and imaging conditions. 3D characterisation methods based on destructive, serial array tomography are developed, enabling correlative optical and electron microscopic imaging. Multiscale correlative characterisation is demonstrated to be highly significant in extracting rich structural details, unveiling the local organisation, flake orientation, and morphology of various graphene nanocomposites. The availability of 3D datasets provides exciting opportunities to quantify structural features, as demonstrated through statistical dispersion and distribution analysis of functionalised graphene nanocomposites. This study provides valuable insights into the real structure of graphene films and nanocomposites; the methodologies developed will be widely applicable in the nanomaterials field.

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Complex carbon astrochemistry around old stars

D. A. García-Hernández[1,2]

[1]*Instituto de Astrofísica de Canarias (IAC), C/ Vía Láctea s/n, E-38205 La Laguna, Spain*

[2] *Departamento de Astrofísica, Universidad de la Laguna (ULL), E-38206 La Laguna, Spain*

agarcia@iac.es

Old and dying stars as common as our Sun, are wonderful astrochemistry laboratories and a dominant source of complex carbon molecular nanostructures (i.e., nanocarbons) in space. I will talk about complex nanocarbons around old stars with a special emphasis on the detection and formation of fullerenes, the most complex molecules detected to date in space. I will talk about the multidisciplinary research needed to understand the presence and evolution of these complex nanocarbon species around old stars and identify their chemical formation routes along with the possibility of discovering the existence of new fullerene-related species in space. Finally, I will briefly show the power of networking via the COST Action NanoSpace as a tool to understand nanocarbons in space as well as to encourage the collaborations between the carbon astrochemistry community and the multiple interdisciplinary research fields represented in NanoSpace.

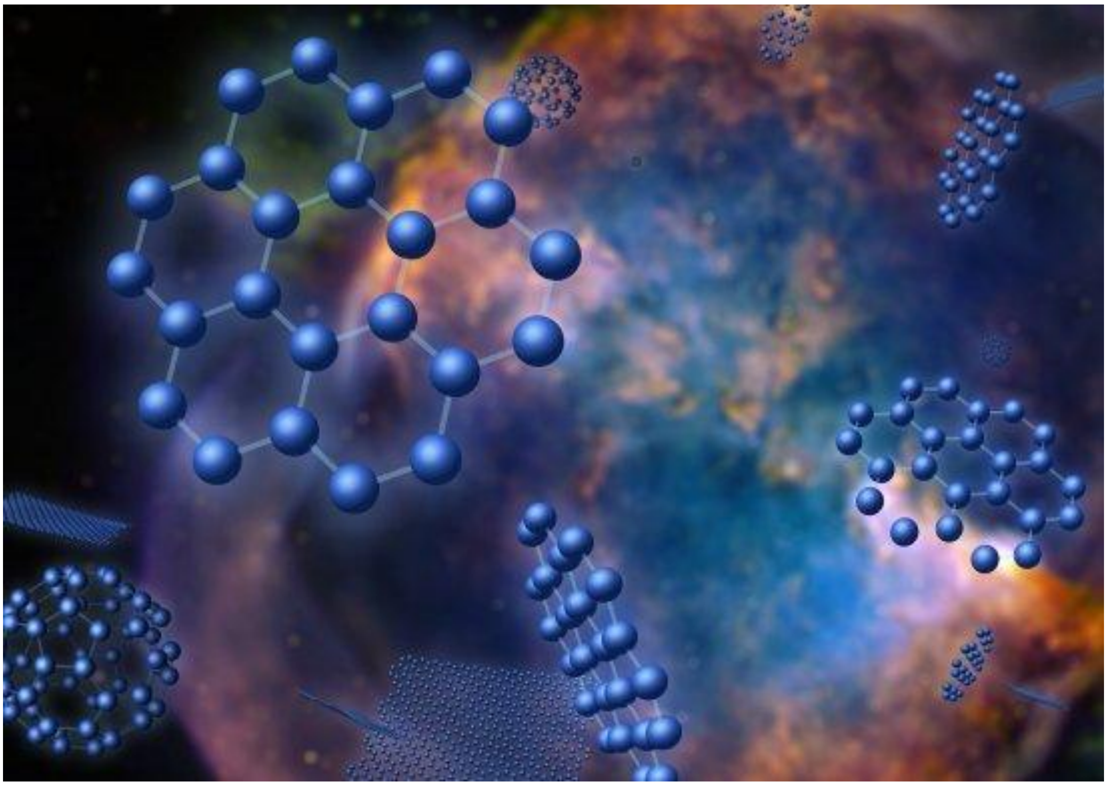

Image Caption: Artist’s impression of the fullerenes and other nanocarbons like planar C_{24} found around an old star; a Planetary Nebula. The detection of such complex nanocarbons around old stars as common as our Sun suggests that these molecules and other allotropic forms of carbon such as carbon nanotubes, among others, should be widespread in space. Source: Servicio MultiMedia (IAC).

Friday, 30th August

Multifunctional Graphene Composites

Ian Kinloch

T.B.A

Optical superabsorbers for energy generation and thermal management

José V. Anguita, Zongtao Zhang, James George Neil and S. Ravi R. Silva

[1] *University of Surrey, Guildford, Surrey, GU2 7XH, UK*

j.anguita@surrey.ac.uk

Our ability to build an energy-sustainable future depends the development of smart materials that are able to adapt their optical properties according to energy demand and the optical energy available in their surroundings. Such materials are thus suitable for autonomous thermal management, and suitable for applications in energy-sustainable buildings, energy harvesting from surrounding heat, smart solar thermal collectors and thermal management for spacecraft. Here we use nanostructures of carbon nanotubes and graphene to produce nanostructured optical super-absorbers. These surfaces are able to behave as near-perfect blackbody sources, and thus suitable to harness the energy absorbed from their local surroundings. They are suitable also to produce electricity directly via a suitable thermoelectric generator. We present recent innovations in such optical absorbers and also present a new method for low-cost and large-scale production of these, using nano-offset printing (NanoOPS). We use this method to produce the nano-scale absorbers on low-cost flexible substrates, and propose this technique for the realisation of thermal management systems. We furthermore show its implementation and operation in a space-qualified composite for the Sentinel-V spacecraft mission.

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Highly Functionalised Fullerene Amphiphiles: Molecular Structure and Self-Assembly

Ilija Rašović[1]

[1]*School of Metallurgy and Materials, University of Birmingham, United Kingdom*

i.rasovic@bham.ac.uk

The controlled bottom-up design of macroscopic materials from self-assembled molecular precursors is a hot topic bridging the worlds of supramolecular chemistry and materials science and engineering. Since the early development of a theory of hydrocarbon self-assembly in water[1], more complex structures have been synthesised from an ever more diverse field of amphiphiles[2], with particular inspiration sought from the realm of biology in the form of peptide amphiphiles[3].

The simple design principle of choosing between areas of a molecule to be solvophobic and solvophilic can lead to both exquisite control and non-trivial complexity of the subsequent self-assembled structure. The fullerenes offer a promising starting point for the synthesis of such next-generation materials assembled from amphiphilic precursors; their inherent hydrophobicity can be chemically modified by functionalisation at multiple sites with suitable hydrophilic groups, leading to a large range of amphiphilic molecular structures.

Recently, to this end, we developed a simple one-pot method for covalent functionalisation of fullerene cages, leading to highly water-soluble amphiphilic derivatives that self-assembled into macroscopic materials with hierarchical structure[4]. Most interestingly, there was a correlation between the starting fullerene size and shape (C_{60}, C_{70}, C_{84} and C_{90-92}) and the structure and mechanical properties of the subsequent self-assembled materials.

In this talk, I will outline these results before ruminating on some of the exciting questions they have opened up, which I am looking to explore. These include thinking about possible applications of these materials—and necessary experiments to assess them—as well as how computational methods might help us to accelerate the design and synthesis not only of future iterations of these materials but also of similarly highly functionalised fullerene derivatives.

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Inorganics-in-Organic thermoelectric devices with high power factor

James George Neil[1]**,** José V. Anguita, S. Ravi P. Silva,

[1] *University of Surrey, Guildford, Surrey, UK*

j.g.neil@surrey.ac.uk

There is much low-grade energy generation in our current infrastructure in the form of waste heat. Within the UK, industrial processes produce low-grade heat waste of around 70% of the energy use [1]. As such, harvesting wasted heat using thermoelectric devices could improve the efficiency of current energy systems. By integrating suitable technology driven by the Seebeck effect with next-generation solar cells will enhance the viability of energy supply [2]. At the moment, thermoelectric energy-harvesting systems are expensive and use toxic components. In order for the wider adoption of thermoelectric technologies, the development of new materials with higher performance and lower cost is required.

Organic thermoelectric materials provide a promising alternative to enhance thermoelectric performance due to their low cost and non-toxicity. However, these materials tend to exhibit lower thermoelectric performance. Recent investigations show multilayered nanostructures offer a route to significantly improve their performance [3]. We present a facile metal/PEDOT:PSS multilayer structure that features high thermoelectric performance, and controllable properties based on the stack structure used. Further analysis of the band structure suggests an energy-filtering effect as being critical for these observations. This results in an enhancement to the Seebeck coefficient alongside electrical conductivity, allowing for significant enhancement to the thermoelectric performance in these devices. We further discuss the use of carbon nanostructures to further enhance the performance.

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Atomic Scale Modelling of Confined Ionic Liquids

Samanvitha K V Shankar, Yann Claveau, Tojo Rasoanarivo, Chris Ewels, Jean Le Bideau

Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, F-44000 Nantes, France
Samanvitha.Kunigal@cnrs-imn.fr

Ionic liquids (IL) have emerged as one of the most promising alternatives for traditional organic electrolytes in electrochemistry. Their low flammability and wide electrochemical window has gained significant attention for their application in energy storage devices such as batteries, super capacitors and fuel cells[1]. Although they possess high viscosity and lower ionic conductivities in comparison to organic solvents, their high energy density, higher operating voltages and non-flammability makes them attractive and safe electrolyte candidate in super capacitors. Study of dynamics of ions in the mixture of metal salts and ILs is necessary to understand their application in hybrid capacitors.

EMIM-TFSI (ethyl,methylimidazolium and bis(trifluoromethylsulfonyl)imide) is one of the most studied IL for its application in super capacitors. We employ molecular dynamics to investigate the influence of Li, Na and Zn within EMIM-TFSI in terms of metal ion concentration, size and charge.[2] Molecular dynamics offers an advantage of gaining a molecular level picture of systems in the experimentally relevant timescales. We provide a complete analysis of structure, lifetime of ion pairs and diffusion coefficients of ions in the system. Through this, we observe that the influence of metal cation on the conductivity is rather indirect and that EMIM-TFSI ion pair lifetimes drives the conductivity. Furthermore, the metal - TFSI ion pair lifetimes are significantly longer than EMIM-TFSI ion pairs and increases with increase in concentration of metal cation. This in turn leads to reduced ion exchange and thus decreased diffusion in such systems. This negative impact of increased concentration of metal cation should be taken into account while developing IL based hybrid capacitors. This paves the way for further studies on the customized design of ionic liquid confinement systems for specific all-solid devices. Our current goal is to confine the above-mentioned IL system in a solid matrix such as Silica and study the changes in dynamics of such systems in comparison to previously studied non-confined IL system.

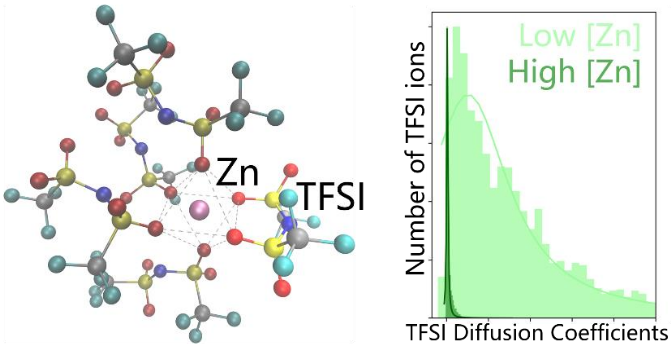

Fig: (left) co-ordination sphere of TFSI around Zn; (right) Histogram of individual diffusion coefficients of TFSI as a function of concentration of Zn.

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Liquid Interface Assembled Networks of 2D Materials

Joseph Neilson[1]**,** Jonathan Colaman[1]

[1] *CRANN and School of Physics, Trinity College Dublin, Dublin D02, Ireland*

neilsonj@tcd.ie

Printed electronics is a field which is rapidly expanding across academia and industry, and uses solution processing to enable the fabrication of electronic components. While printed electronics tend to display lower performance than traditional silicon-based electronics, they have significant advantages like low-cost, mechanical flexibility, and large area deposition compatibility. Potential applications include wearables, point-of-care healthcare devices, e-skins and many more. The 2D materials family, containing conductors such as graphene and semiconductors such as molybdenum disulphide (MoS_2), have desirable electronic characteristics, mechanical flexibility, and compatibility with solution-based processing, making them the ideal functional materials for future printed electronics inks.

However, to exploit 2D materials in these applications, it is essential to develop methods to produce large-area and high-quality networks wherein the inter-nanosheet junctions do not hinder carrier transport. Thus, enabling networks with electronic properties equivalent to the individual nanosheets. In theory, this can be achieved by reducing junction resistance to a value much smaller than the nanosheet resistance (i.e. $R_J \ll R_{NS}$). So far, there have been several approaches to reduce R_J including chemical crosslinking, or using mechanical pressure.[1] We believe that a promising strategy is gain more control over the deposition process to improve network morphology and further reduce junction resistance.[2]

Here, we report the deposition of large-area, densely tiled monolayers of graphene and MoS_2 nanosheets via assembly at the immiscible liquid-liquid interface (Figure 1A). We demonstrate the capability to sequentially layer these monolayers into multilayer networks, and systematically measure their thickness-dependant electrical properties. Using mechanically conformable electrochemically exfoliated nanosheets, along with our advanced deposition process, we present conductive graphene networks with $R_J < R_{NS}$, (figure 1B) and MoS_2 thin film transistors with field-effect mobility approaching that of individual nanosheets (40 cm^2 V^1 s^1) (Figure 1C). The capability to achieve such network properties paves the way to next-generation printed heterostructures based on 2D materials.

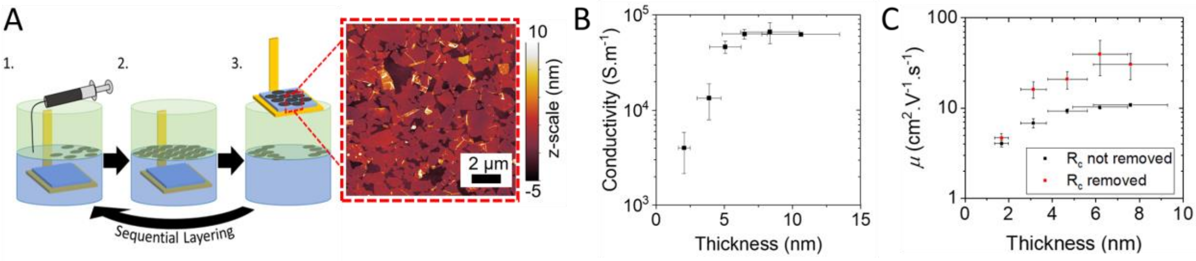

Fig. 1. A. Schematic representation of the liquid interface deposition process used in this work B. Plot of graphene network conductivity versus thickness C. plot of MoS_2 network mobility versus thickness

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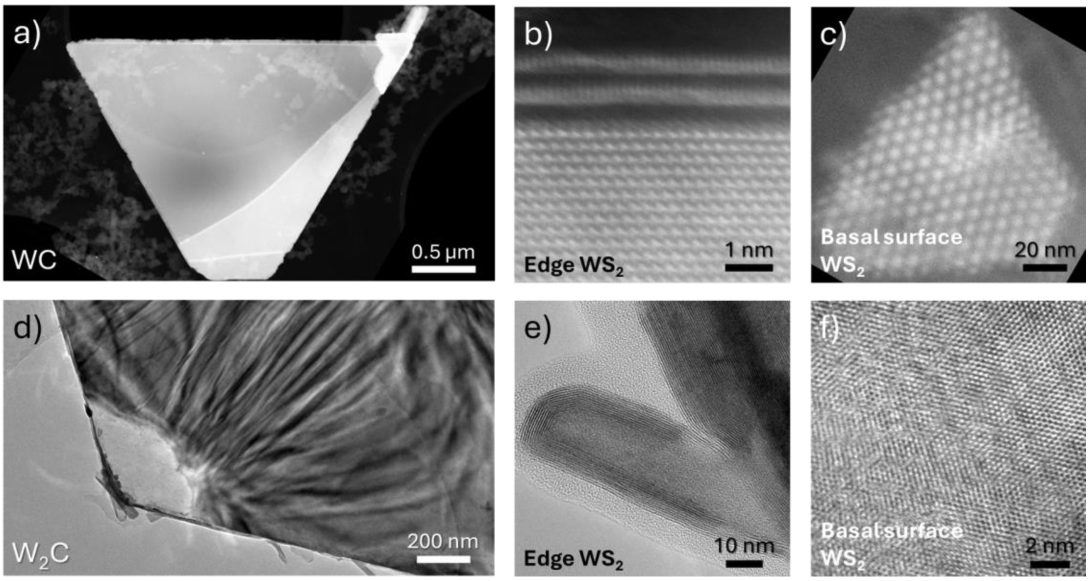
Sulfurization of Ultrathin Tungsten Carbide Nanoplates: The Impact of the Crystalline Carbide Phase

David E. Sanchez[1], Jiayang Wang[1], Alex J. Sredenschek[1], Susan B. Sinnott[1], Mauricio Terrones[1]

[1]*Pennsylvania State University, University Park, Pennsylvania, USA*

des5765@psu.edu

Recent efforts have been made to integrate layered (MXenes) or non-layered (ultrathin) transition metal carbides (TMCs) with layered transition metal dichalcogenides (TMDs) [1, 2]. Pioneering work by Rothschild *et al.* implemented a hydrogen sulfide (H_2S) heat treatment process to synthesize core-shell non-layered tungsten mono-carbide (WC), layered tungsten disulfide (WS_2) nanoparticles [3]. In this talk I will present a combined experimental-computational work that highlights the synthesis and structural characteristics of crystalline, non-layered tungsten carbide [4, 5] and layered WS_2 heterostructures synthesized via a two-step high temperature sulfurization in H_2S. Finally, I will provide experimental-computational evidence that the crystalline phase (WC or W_2C) of the non-layered ultrathin tungsten carbide is critical for converting to layered TMDs.



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Impact of Quaternary Ammonium Ions on the Properties of 2D MoS_2 Synthesized via Electrochemical Exfoliation

Vincent Renard[1, 2]**,** Antony Dawson[2], Tian Cafrey[2], Cian Gabbett[2], Eoin Cafrey[2] and Jonathan Coleman[2]

[1]*IMN, CNRS UMR6502, 2 Rue de la Houssiniere, BP 32229, 44322 Nantes, France*

[2] *Trinity College Dublin, College Green, Dublin 02, Ireland*

vincent.renard@etu.univ-nantes.fr

Molybdenum disulfide (MoS_2) is a prominent member of the transition metal dichalcogenides (TMDs) family, garnering significant attention for its potential in next-generation semiconducting devices. This study explores the electrochemical exfoliation of MoS_2 nanosheets, with a focus on understanding how different quaternary ammonium ions impact the exfoliation efficiency and the resultant electrical properties of the nanosheet networks. Electrochemical exfoliation is a favored cheap and scalable method for producing high-quality MoS_2 nanosheets with promising electrical results. [1] However, inconsistency in the process (stemming from the use of various ions, solvents, sonication times, and washing techniques) complicates the reproducibility and optimization of the material's electronic properties.

In this work, we systematically investigate the role of quaternary ammonium ions, specifically analyzing their influence on the exfoliation process and the subsequent electrical performance of MoS_2 nanosheets. We utilized Liquid-Liquid Interfacial Deposition (LLID) to accurately transfer the exfoliated nanosheets onto substrates, enabling precise electrical characterization.

Our findings indicate that while the exfoliated MoS_2 nanosheets exhibit mobility and on-off ratios within expected ranges, they fall short of the highest values reported in the literature. [1-4] Notably, tetraoctylammonium (TOA^+) ions emerged as the most effective exfoliation agent, producing nanosheets with superior size metrics, conductivity, mobility, on-off ratio and overall network performance. Furthermore, we observed a trend with the alkyl chain length of the quaternary ammonium ions and the threshold voltage of the resulting transistors. Longer alkyl chains appeared to reduce p-doping or enhance n-doping effects, bringing the threshold voltage closer to zero and, in some cases, slightly above it.

In conclusion, this research contributes to the broader understanding of ion-mediated exfoliation processes and presents a pathway for producing 2D MoS_2 materials with tailored electrical properties. These insights pave the way for the scalable production of high-performance MoS_2-based devices, offering a valuable addition to the field of 2D materials and their applications in advanced electronics.

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Posters

Development of a reactive Neural Network Potential for borophene on silver and gold

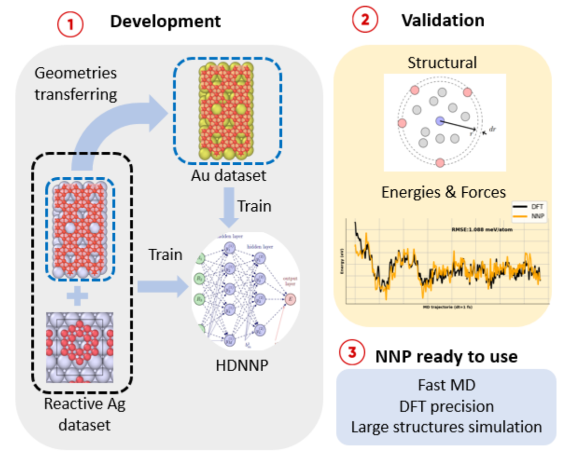
Anouar Akacha DELENDA[1]**,** Pierre Mignon[1], Colin BOUSIGE[2]

[1]Institut Lumière Matière (iLM), UMR5306 Université Lyon 1-CNRS, Université de Lyon 69622 Villeurbanne, France

[2] Laboratoire des Multimatériaux et Interfaces (LMI), UMR5615 Université Lyon1-CNRS, Université de Lyon 69622 Villeurbanne, France

anouar-akacha.delenda@etu.univ-lyon1.fr

Single-layer borophene is the only metallic 2D material, with a high degree of polymorphism that has attracted attention due to its exceptional properties, such as high thermal and mechanical resistance and transparency in the UV/VIS spectrum, which can lead to promising optoelectronic applications. However, there is no clear recipe for the synthesis of the desired allotrope. Furthermore, in order to establish a guideline for the synthesis protocol, we need to know (i) the stability of various boron sheets, (ii) the dependence between experimental parameters and the obtained allotropes, (iii) the impact of metal substrates, and (iv) the hidden mechanism of the growth process. These arguments point towards the necessity of large-scale simulation support. The latter point is motivated by the need to differentiate between the edges and the center of borophene islands. In addition, it is more practical to allow the observation of moiré patterns and surface corrugations. Unfortunately, the available methods are either inefficient (slow), like ab initio molecular dynamics, or lack precise potential, like classical molecular dynamics. In this work, we have developed two machine-learning-based interatomic potentials for borophene deposited on Ag and Au substrates, using a high-dimensional neural network potential (HDNNP) [1]. We have successfully extended an existing Ag-based HDNNP [2], to enable reactive molecular simulations, and present a robust and efficient method called data transfer, to extend a machine learning-based potential [2] already developed for borophene Ag-based substrate, to other metals (Au). Both potentials are able to reproduce the structures, energies and forces provided by density functional theory (DFT) calculations, with the same accuracy, and faster by several orders of magnitude. We have deployed the reactive potential to stimulate the growth of boron deposited on Ag(111) at 0k, and we revealed that boron nanoribbons (BNRs) are a potential form of borophene. In the future, these machine-learning-based tools will be used to perform large-scale simulations, while incorporating synthesis parameters (pressure, temperature, etc.) to predict experimental conditions for borophene growth pathways.



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Bibliometric Analysis and Science Mapping for Nanospace: Descriptive Research

Musa Akbulut[1]

[1] Igor Sikorsky Kiev Polytechnic Institute, Beresteiskyi Ave, 37, Kyiv,
Ukraine, 03056, Ukraine, musaakbulut55@gmail.com

Introduction: The innovative and advanced technologies provided by nanospace have the potential to create a more sustainable and advanced world in the future. Therefore, nanotechnology and nanoscale research are constantly increasing their importance in science and industry.

Objective: This study was carried out to present the studies that emerged as a result of bibliometric analyzes related to nanospace to the attention of researchers from a holistic perspective.
Material and Methods: The data were obtained from the "Web of Science Core Collection" database on 13 June 2024. Analyses were made with the R- studio program. In the analyses, co-citation and occurrence network analysis of authors, cited authors, countries, institutions, cited journals and references and keywords were performed. Ethics committee approval was not obtained since human and animal were not included in the study and published studies on pressure injury in the field of nursing were used for data collection. The study was conducted in accordance with the principles of the Declaration of Helsinki.

Result: As a result of the research, 2346 studies on nanospace were reached. 1726 studies were determined to be research articles in the nanospace and research articles. It was determined that the Journal of the American Chemical Society (n = 4924) has the highest number of studies on nanospace, and the most cited study was the study titled "Nanocarbons for the Development of Advanced Catalysts" with 1138 citations in 2013.

Conclusion: As a result of our research, it was seen that the research trends and popular points of this field are nanospace, graphene, nanotubes, performance, carbon nanotubes keywords. In addition, it is thought that the results of the bibliometric analysis of nanospace can help researchers, engineering and institutions to find researchers, countries or institutions with which they can cooperate.

Keywords: nanospace, graphene, nanotubes, bibliometric analysis.

Carbon foam developed to eliminate oil spills

Lokmane Abdelkaddous BAIDAR[1]**,** Malika MEDJAHDI [2], Dominique BAILLIS [3], Badra MAHIDA [4]

[1]LGCE, 2 Rue Kadi Ben Kadi, BP 89, 22000 Sidi Bel Abbes, Algérie

[2] University of Djillali Liabes, Sidi Bel Abbes, Algeria

lokmanbaidar17@gmail.com

The modified sponge has proved to be an effective sorbent to remedy oil pollution [1-2], given its exceptional characteristics, such as a highly porous three-dimensional structure, low density, low cost, thermal stability and excellent mechanical strength [3-4]. In this work, flexible polyurethane sponges were modified with active coals based on marine waste to obtain a good absorbent used for the elimination of oil spills. The composites obtained were characterized by numerous analyses such as optical microscopy, FT-IR spectroscopy, density measurements, mechanical compression and water absorption tests. High hydrophobic/oleophilic character and absorption capacity were observed for the manufactured sponges (43.28 g/g in the water/oil mixture). Reusability tests showed that the modified sponges still maintained high absorption capacity (85%) after six regeneration and reuse cycles.

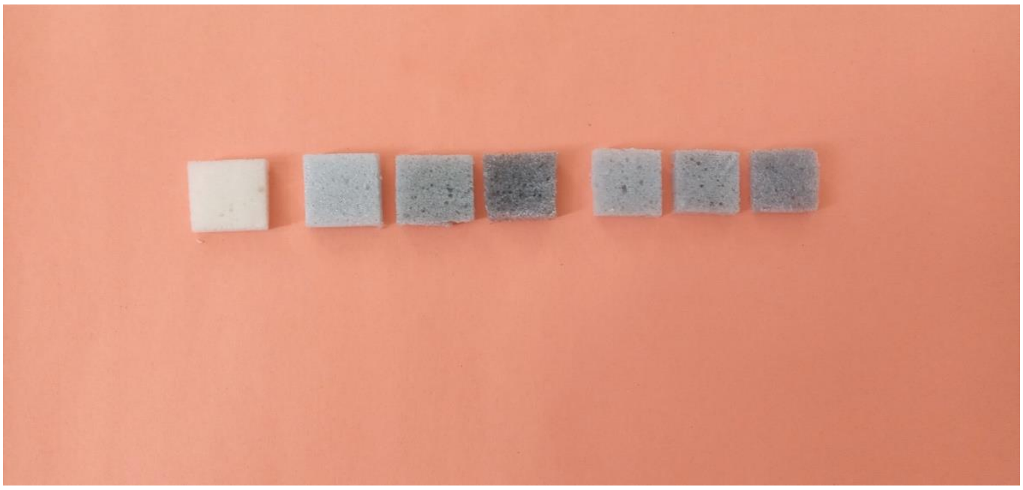

Figure 1. Polyurethane/activated charcoal composite with different particle sizes and ratios

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Green Emissive Carbon Dots: Synthesis, Photoluminescence Mechanism and Use in Photoanodes

Ana M. Benito[1], M.A. Álvarez,[1], C. Martínez[1], A. Ansón[1], W.K. Maser[1]

[1]*Instituto de Carboquímica (ICB-CSIC), C/Miguel Luesma Castán 4, E-50018 Zaragoza (Spain)*
abenito@icb.csic.es

Carbon dots (CDs) have emerged as exciting nanostructure due to their unique combination of properties. Highly water-soluble and exhibiting tunable, bright photoluminescence emission, CDs offer a promising alternative to conventional quantum dots, which are often plagued by toxicity concerns [1]. Size, structure and optical properties are critically controlled by the nature of the precursor materials, incorporation of heteroatoms and the reaction conditions [2]. The wide variety of CDs species with different structure and PL emissions reveal versatility for application in many research fields, such as biomedicine, photocatalysis, photoelectrochemistry, and photovoltaics [3].

This study focuses on green-emitting CDs synthesized using a bottom-up approach at various temperatures via a hydrothermal process. We analyze the structural and optical characteristics of these CDs and propose a mechanism that explains their green light emission. Furthermore, we demonstrate the crucial role of structure and photostability of CDs integrated into titanium dioxide (TiO2) photoanodes for achieving improved performance in photoelectrochemical water splitting, a process that generates hydrogen fuel [4].

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Defect-mediated ionic transport in layered β and β”aluminas

Suchit Negi[1], **Alexandra Carvalho**[1], A. H. Castro Neto,[1,2,3]

[1]Institute for Functional Intelligent Materials, National University of Singapore, 117544, Singapore.

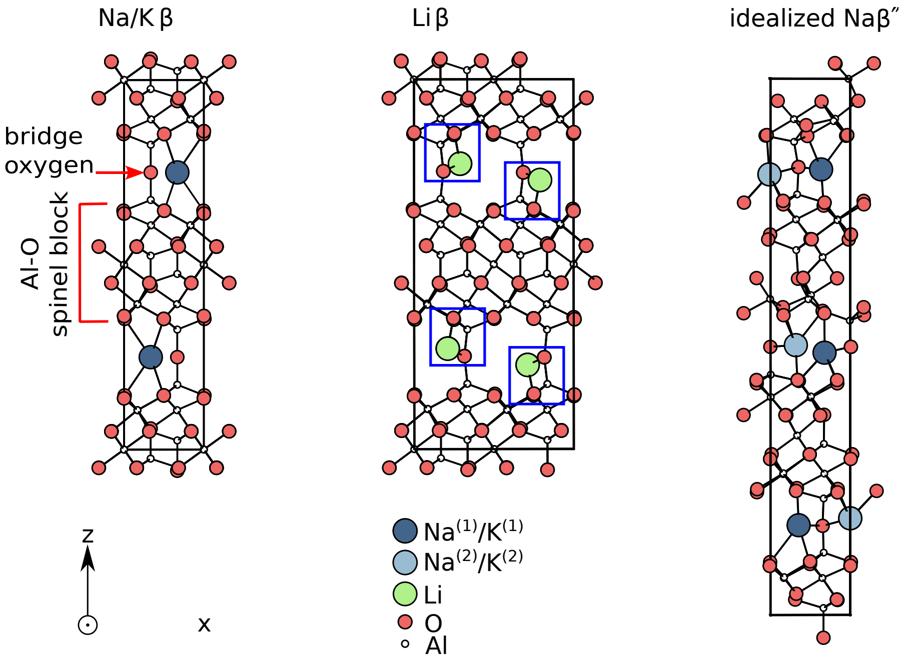
[2]Centre for Advanced 2D Materials, National University of Singapore, 117546, Singapore.

[3]Department of Materials Science and Engineering, National University of Singapore, 117575, Singapore.

carvalho@nus.edu.sg

Alkali metal β/β″ aluminas are among the fastest ionic conductors, yet little is understood about the role of defects in the ion transport mechanism. We used density functional theory (DFT) to investigate the crystal structures of β and β″ phases, and vacancy and interstitial defects in these materials. We find that charge transport is likely to be dominated by alkali metal interstitials in β-aluminas and by vacancies in β″ aluminas.

Lower bounds for the activation energy for diffusion are found by determining the minimum energy paths for defect migration. The resulting migration barriers are lower than the experimental activation energies for conduction in Na β and β″ aluminas, suggesting a latent potential for optimization. The lowest activation energy of about 20 meV is predicted for correlated vacancy migration in K [1]



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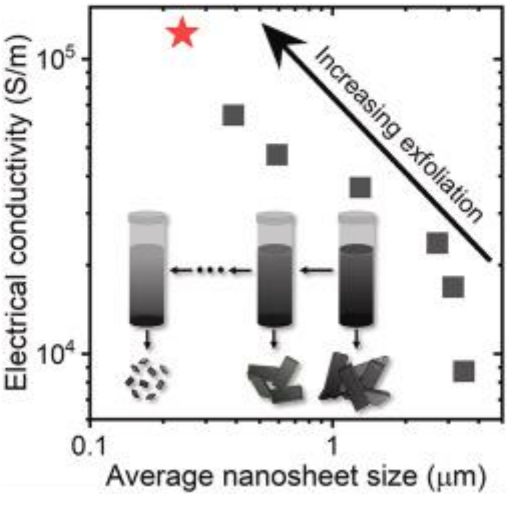
Emergent high conductivity in size-selected graphene networks

Keiran Clifford[1], Sean P. Ogilvie[1], Aline Amorim Graf[1], Hannah J. Wood[1], Anne C. Sehnal[1], Jonathan P. Salvage[1], Peter J. Lynch[1], Matthew J. Large[1], Alan B. Dalton[1]

[1] *University of Sussex, Brighton, East Sussex, UK*

keiran.clifford@sussex.ac.uk

Nanomaterial networks are attractive for a diverse range of printed device applications including electronics, sensing, energy capture and storage. At present, the influence of morphology on the network properties, such as electrical transport, is poorly understood. Here, we develop an understanding of structure-property relationships in these systems by performing size selection from bulk to few-layer graphene. We observe size-dependent electrical conductivity spontaneously during film formation, with the smallest nanosheets realizing electrical conductivity exceeding 10^5 S/m, a record value for liquid-exfoliated graphene and competitive with electrochemically exfoliated graphene. Given the high electrical conductivity exhibited by these networks, and the applicability of graphene as a model layered nanosheet system, we explore the use of this size-selected graphene for thermoelectric applications. We interpret our understanding of the high conductivities obtained in terms of nanosheet packing and its influence on the number density and nature of inter-sheet junctions. This work represents an approach to overcome junction-limited electronic transport and enable nanoparticulate networks for printed device applications.



Rheological study of stabiliser blends on rigidity percolation of carbon nanotube dispersions

Kevin L. Doty[1], Peter J. Lynch, Aline A. Graf, Matthew Large, Sean Ogilvie, and Alan B. Dalton

[1]*University of Sussex, Brighton, East Sussex, UK*

Kd378@sussex.ac.uk

Abstract:

Electronic products, such as printed electronics, have become an essential part of our daily lives. The properties of printed electronic devices depend upon several factors, such as material properties, film thickness, and homogeneity. Carbon nanotubes (CNTs) have incredible mechanical, electrical, and thermal properties that can be utilized as a conductive ink for the printed device. Nanotubes are highly conductive, but inks containing them tend to have a low weight fraction when the nanotubes are well-dispersed. This limits the printing throughput achievable for applications requiring high conductance. Rheology can used to measure dispersion morphology[1], and thereby different dimensions of CNT bundles or aggregates found in an appropriate stabiliser. Stabilisers, such as carboxymethyl cellulose (CMC) and polyvinyl pyrrolidone (PVP), play a role in nanotube dispersion via wrapping[2], making them imperative to film production as well. Here, we show differing concentrations of different single-walled and multi-walled CNTs with differing stabiliser blends to develop rheological understanding of nanotube dispersion on total ink weight fraction.

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Emergent Atomic Environments in TWisted Bilayer Graphene and Their Use in the Prediction of the Vibrational Properties

Dogan Erbahar[1,*], Dilara Ickecan[2], Yunus Emre Okyayli[3], Erdi Ata Bleda[2]

[1]*Dogus University, Faculty of Engineering, Dept. of Mechanical Engineering, Umraniye, 34775, Istanbul, Turkey*

2 Marmara University, Dept. of Physics, 34722, Ziverbey, Istanbul, Turkey

[3] *Gebze Technical University, Dept. of Physics, 41400, Gebze, Kocaeli, Turkey*

**** derbahar@dogus.edu.tr***

While Bernal stacked bilayer graphene bears two distinct atom types in its lattice, there exists no analytical framework addressing the number of atomic environments that emerge in twisted bilayer graphene superlattices. In this work, we have computationally analysed 140 different twisted bilayer superlattices using descriptor functions to study the emergent local environments. Our study reveals that the number of atoms with unique local environments depend on the superlattice size linearly. Moreover, this linear dependence manifests itself on two distinct lines in accordance with their respective space groups. Unique local features of structures of lattices appearing on these lines automatically suggests a new classification scheme based on the local environment. The use of local environments in the investigation of vibrational properties is introduced as a possible application and is discussed with respect to the existing literature. Molecular dynamics simulations are performed to calculate the phonon density of states of the 140 structures as well as the local phonon density of states of their individual atoms. The similarity of the contributions of local density of states coming from atoms with the same local environment is demonstrated. Local phonon density of states of the atoms with unique local environments is then used to train a machine learning model. This model is used to predict the phonon spectra of twisted bilayer structures. Performance of the trained model is cross validated and discussed thoroughly via different selection of training and test sets, and it is shown that the model proves effective in predicting the vibrational properties of any given twisted bilayer structure. The possible applications of the generic method presented which reaches far beyond twisted bilayer graphene is also discussed.

Acknowledgements

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Carbon Nanomaterials as Anticancer Drug Nanocarriers

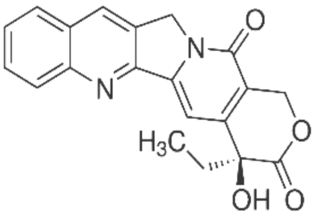
R. Garriga[1], T. Herrero-Continente[2], M. Palos[3], V. L. Cebolla[4], J. Osada[2], E. Muñoz[4], M. J. Rodríguez-Yoldi[3]

[1] *Departamento de Química Física, Universidad de Zaragoza, Spain,*
[2] *Departamento de Bioquímica y Biología Molecular, Universidad de Zaragoza, Spain,*
[3] *Departamento de Farmacología y Fisiología, Universidad de Zaragoza, Spain,*
[4] *Instituto de Carboquímica (ICB), CSIC, Spain*
rosa@unizar.es

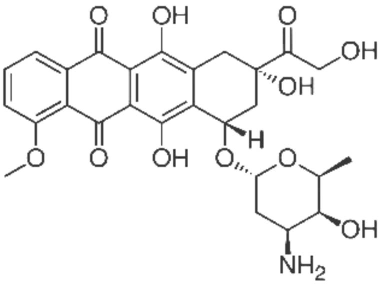
Carbon nanomaterials are promising as drug nanocarriers suitable for medical treatments, due to their large surface area and chemical stability that allows efficient loading of drugs via both covalent and non-covalent interactions. The enhanced permeability and retention (EPR) effect enables these nanomaterials to transport chemotherapeutic agents preferentially to tumor sites as compared to healthy tissues, thereby reducing toxic side effects. Much research activity has been devoted to performing experiments either by systemic administration and localized drug delivery strategies.

Camptothecin (CPT) is a more potent anticancer agent than other well-known anticancer drugs such as doxorubicin (DOX). However, CPT practical use in viable cancer therapeutic systems is greatly hampered due to its low solubility in biological media, so developing new drug delivery nanocarriers for CPT would be of high interest.

In this work, the potential of carbon nanotubes (CNT), graphene oxide (GO), reduced graphene oxide (RGO) and carbon nanodiamonds (ND) as nanocarriers for CPT and DOX drug delivery were compared. *In vitro* studies were performed on human epithelial colorectal adenocarcinoma (Caco-2) cells. The highest improvement in CPT anticancer activity was observed for RGO nanocarriers. On the contrary, when it comes to DOX, ND showed the highest efficiency [1].



CPT



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Controlling the structure and porosity of carbon-carbon composites to optimize their electrical and mechanical properties

Lingshu lei[1], Ian Kinloch[1] and Cristina Valles[1]

[1]*The University of Manchester, Manchester, M13 9PL, U.K.*
lingshu.lei@postgrad.manchester.ac.uk

Abstract

Carbon-carbon composites comprised of fillers dispersed in a carbonized binder matrix are widely used as high-power electrical contacts in rail transport and power generation. The formulation of the composite contains main components and is often empirical, rooted in a century of industrial know-how. A key morphological parameter is the open porosity of the composites, which controls the physical and electrical properties and facilitates the infiltration of molten metal for higher performance carbon-carbon-metal composites. Herein, the role of the different components of the formulation was studied to understand their relationship to the porosity.

Initially, a formulation for the fabrication of carbon-carbon composites using coal tar pitch as a binder and sulphur as a catalyst was designed. Needle coke, carbon black, and graphite were employed as carbon fillers. In the manufacturing process, different loadings of sulphur as well as varying content and types of carbon black were used to investigate the density, shrinkage, carbon yield, and open porosity of the composites. The experimental results revealed that increasing the loadings of sulphur and carbon black resulted in higher bulk density and reduced the open porosity of the carbon-carbon composites, which led to better mechanical properties. Additionally, the increase in carbon black content resulted in an enhancement in the electrical conductivity of the samples.

Keywords

Carbon composites; Sulphur; Open porosity; Electrical properties; Mechanical properties

Sustainable C-Nano inks for the preparation of layered photoelectrode films

W.K. Maser[1], J. Hernández[1], J.M. González[1], A. Galán[1], J.C. Ciria[2], A. Ansón[1], Ana M. Benito[1]

[1]Instituto de Carboquímica (ICB-CSIC), C/Miguel Luesma Castán 4, E-50018 Zaragoza (Spain)

[2]Universidad de Zaragoza, Departamento de Informática e Ingeniería de Sistemas, E-50009 Zaragoza, Spain

wmaser@icb.csic.es

This study presents our findings on the preparation of sustainable water-based inks of various types of carbon nanostructures including graphene oxide, carbon nanotubes, carbon dots and related hybrid materials. It focuses on the use of these dispersions for liquid-phase processing into layered photoelectrodes [1-8]. Key issues of nanostructurization for the creation of functional hybrids and achieving environmentally-friendly processing solutions are underlined. The importance of establishing favorable interface interactions for attaining effective charge-transfer properties and enhanced performance of layered photoelectrodes employed in photoelectrochemical water-splitting reactions towards the production of green hydrogen is discussed.

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Crosslinking of graphene oxide towards explosive percolation in composite materials

Alexander O. McCann, Peter J. Lynch, Sean P. Ogilvie, Alan B. Dalton

University of Sussex, Brighton, East Sussex, UK

am2053@sussex.ac.uk

Explosive percolation describes an experimentally novel phenomenon where network connectivity in a composite material coincides with an additional modification of the host system. Materials produced with highly localised filler particles and emergent conductive paths can show sharp percolative transitions and high conductivities beyond those of the bulk filler as part of the explosively grown network.

It has previously been demonstrated that composites of graphene oxide (GO) and polymer latex that form segregated networks, lead to low percolation threshold and localisation of conductive pathways. Mild in-situ reduction of the GO drives chemical modification of the MAA-containing copolymer matrix to produce species with phenolic groups, which are known crosslinking agents. This advantageous chemical modification is made possible by the exothermic energy release of GO around 200 ˚C, promoting extremely high local temperatures. This leads to conductivities exceeding those of densely packed networks of reduced graphene oxide, illustrating the potential of explosive percolation to realise low-loading composites with dramatically enhanced electrical transport properties.[1]

To further explore how this phenomenon is enabled, films of both pristine and crosslinked GO have been produced. Graphene oxide has been blade-coated into macroscopic freestanding films and characterised. Characterisation of these GO papers and their subsequent reductions at various temperatures displays a many-fold increase in conductivity with temperature as various oxygenated groups are removed from the surface.

Introduction of MAA as a crosslinking agent to GO films and subsequent low-temperature reduction reveals order-of-magnitude increases in conductivity compared to non-crosslinked films, in both blade-coated freestanding macroscopic papers and thin films deposited via the Langmuir-Schaefer method. Studies of the thermal reduction kinetics of these crosslinked films elucidate upon the mechanism enabling this phenomenon, including the notable exothermic reaction of GO circa 200 ˚C.

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Intercalation of metallic elements within prismatic dislocation cores in graphite

Paul Mouratidis[1], Kenny Jolley[1], Chris Ewels[2]

[1]*Dept. of Chemistry, Loughborough University Epinal Way, Loughborough, LE11 3TU, UK*
[2]*IMN, CNRS UMR6502, 2 Rue de la Houssiniere, BP 32229, 44322 Nantes, France*
p.mouratidis@lboro.ac.uk

Graphitic materials often display line defects, including crystal dislocations. This study employs density functional theory (DFT) calculations to investigate defected graphite, focusing on prismatic dislocations and the intercalation of metallic atomic dopants. Understanding how these dopants diffuse and intercalate in graphite is essential for various engineering and nanotechnology applications. This research examines the behaviour of lithium (Li), sodium (Na), and potassium (K) atoms within defected graphite. Prismatic dislocation cores create voids larger than the usual graphene interlayer spacing, potentially facilitating ion diffusion through bulk graphite. These findings have important implications in energy storage technologies involving Li, Na, and K.

Graphite is conventionally used as the negative electrode in Li-ion batteries due to its ability to reversibly intercalate lithium exothermically between graphitic layers. The highest density intercalated phase, LiC_6, is one of the most studied alkali-graphite compounds.[1] This is a Stage-1 graphite intercalation compound (GIC), where graphene layers are superposed, each separated by a layer of Li positioned above the centres of graphene hexagons. There is significant interest in developing sodium-ion battery technology, but this effort is complicated by the difficulty of intercalating sodium into graphite. The most stable sodium-intercalated phase, NaC_8, is endothermic with a positive enthalpy of formation of +19.9 kJ mol^{-1}.

We confirm previous findings that lithium and potassium intercalation in pristine graphite are exothermic, forming LiC_6 at maximum density and KC_8, while sodium intercalation forming NaC_8 is endothermic. However, with prismatic edge dislocations[2], sodium intercalation along the dislocation cores becomes exothermic due to the lower graphite density at the cores and local curvature facilitating charge trapping.[3] This may explain the small concentrations of sodium intercalation observed experimentally in graphite. This discovery could pave the way for using heavily defective, dislocation-dense graphite for sodium storage in battery anodes.[4]

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MoS_2/Carbon Nanotube Hybrid Sensors for NO_2 Detection

Edgar Muñoz[1]**,** Rosa Garriga[2], Carlos Sánchez-Vicente[3], José L. Sanjurjo[3], José P. Santos[3], Sean P. Ogilvie[4], Alan B. Dalton[4], Isabel Sayago[3]

[1] *Instituto de Carboquímica (ICB), CSIC, Miguel Luesma Castán 4, 50018 Zaragoza, Spain*
[2] *Departamento de Química Física, Universidad de Zaragoza, 50009 Zaragoza, Spain*
[3] *Instituto de Tecnologías Físicas y de la Información (ITEFI), CSIC, 28006 Madrid, Spain*
[4] *Department of Physics, University of Sussex, Brighton BN1 9RH, UK*
edgar@icb.csic.es

NO_2 is an air pollutant arising mainly from combustion processes. Exposure to even low levels of NO_2 has been associated to an increase in susceptibility to respiratory infections and possible effects on human immune system. In addition, interaction of NO_2 and other NO_x with water, oxygen and other chemicals in the atmosphere can form acid rain, which harms ecosystems [1]. Therefore, it is crucial to develop sensors capable of detecting extremely low concentrations of NO_2 at the ppb level (0-150 ppb).

MoS_2 nanosheets offer promise as sensitive materials for NO_2 detection, due to their high surface-to-volume ratio, high adsorption coefficient and thickness-dependent electrical/chemical properties [2]. We here report on the response to low NO_2 concentrations of a resistive gas sensor based on films of MoS_2 nanosheets and MoS_2/multiwall carbon nanotubes (MWCNT). The sensors showed very good sensitivity and selectivity to NO_2 with negligible responses to interfering gases such as methane and ethanol. An improved sensor response was achieved for MoS_2/MWCNT (4:1) hybrids (Fig. 1). The sensing mechanism will be also discussed.

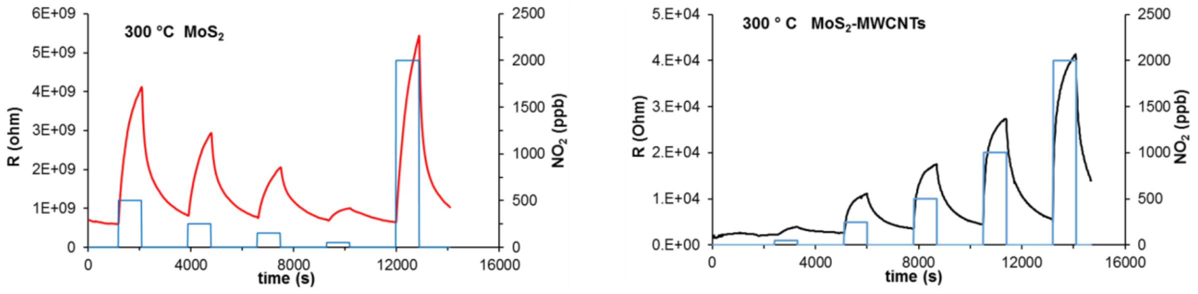

Fig. 1. Performance of MoS_2 and MoS_2/MWCNT (4:1) hybrid sensor layers for NO_2 detection in dry air at 300ºC.

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Enhancing Traditional Material Modelling Techniques with Machine Learning for Studying Defects in Nuclear Graphite

Daria Nasartdinova[1], Kenny Jolley[1], Paul Mouratidis[1]

[1]*Dept. of Chemistry, Loughborough University Epinal Way, Loughborough, LE11 3TU, UK*

d.nasartdinova@lboro.ac.uk

Graphitic materials play a crucial role in various applications, including acting as a moderating material in nuclear reactors. Despite their long-standing use in this field, further research is needed to understand the formation and evolution of radiation-induced defects over time. Traditional computational techniques such as density functional theory (DFT) and molecular dynamics (MD) are commonly used to investigate the behaviour of these materials.

DFT is well known for its high accuracy in predicting material properties, but it is computationally intensive. Conversely, MD is more computationally efficient, but lacks the precision of DFT. This has spurred interest in taking advantage of machine learning (ML) to bridge this gap. By training ML models on DFT datasets, the aim is to develop interatomic potentials that approximate the potential energy of atoms based on their coordinates. This approach could potentially be integrated into MD simulations, offering a balance between computational efficiency and accuracy that is comparable to that of DFT.

Although the integration of ML presents a promising avenue for enhancing our understanding of nuclear graphite material properties, several challenges remain. These include the need for extensive training databases and ensuring the flexibility of the resulting potentials to accurately model a variety of defects. Addressing these challenges is essential for advancing the application of ML in this field. The poster presented at Nanotech 2024 will aim to present some early work on fitting a machine leaning model and any early challenges that have been encountered.

In conclusion, the combination of machine learning with traditional computational techniques such as DFT and MD holds significant potential for advancing the study of graphitic materials in nuclear reactors. This will not only deepen our understanding of radiation-induced defects in graphite but also contribute to the broader application of ML in material science, paving the way for innovative solutions in nuclear technology and beyond.

Complementation of different techniques for elucidating the metal ion binding mechanisms on the carbonaceous adsorbents

Raisa Nastas[1]**,** Irina Ceban (Ginsari)[1], Amelia Bocirnea[2], Iolanta Balan[1]

[1]*Institute of Chemistry of Moldova State University, 3, Academiei str. 2028 Chisinau, Republic of Moldova*

[2]*National Institute of Materials Physics, 405A, Atomistilor, 077125 Magurele, Romania*

nastasraisa@yahoo.com; raisa.nastas@sti.usm.md

The presence of functional groups on the carbonaceous adsorbents plays an important role on their specific properties: acid-base character, catalytic properties, selective adsorption of metal ions etc. The present work aimed at the characterization of carbonaceous adsorbents surface chemistry (by using XPS spectroscopy and potentiometric titration) and elucidation of metal ions binding mechanisms on the adsorbents by computational modelling (DFT B3LYP method using 3-21G(d) basis set; calculations were carried out taking into account the solvent (water) based on the IEFPCM option of the Gaussian09 program package).

In the study, carbonaceous adsorbents obtained from nut shells (CA-N) and from apple wood (CA-M) modified with nitric acid (CA-Mox) and with nitric acid and urea mixture (CA-Nox-u/CA-Mox-u), and samples modified with metals ions (Cu (II), Co (II) and Sr (II)). By potentiometric titration, on the oxidized carbonaceous adsorbents (CA-Mox, CA-Nox-u, CA-Mox-u) were identified four types of acidic functional groups with distinct pK. The XPS spectra, in addition to the bonds associated with the matrix of carbonaceous materials, bonds indicating the presence of oxygenated functional groups (C-C bond at 284.5 eV, C=C at 285 eV, C-OH and C-O-C structures at 286.6 eV, C=O and COOH at ~288.5 eV, O-C=O at ~290.5 eV) are identified, also due to the bonding between functional groups and metal ions. O 1s spectra show two main contributions associated to C=O bonds, at ~531.5 eV, and C-OH and C-O-C groups at ~533.2 eV. Computational modelling was applied to calculate the geometrical and electronic structures of all the studied systems.

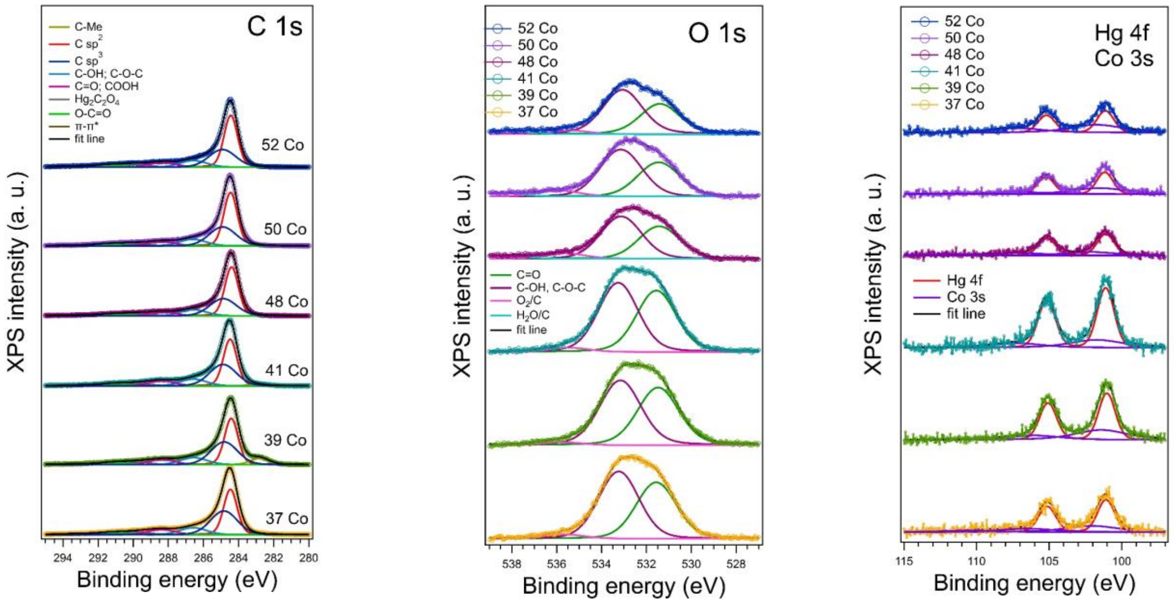

Figure. XPS spectra of carbonaceous adsorbents.

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Design and preparation of hybrid nanocarbon-MOF materials

Ioanna K. Sideri[1]**,** Georgia Basina,[1] Giasemi K. Angeli,[1] Nikos Tagmatarchis[1]

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

isideri@eie.gr

Currently, MOFs, due to their tunable structural and functional characteristics, are emerging as a sustainable alternative for solar-driven H_2 production. Aiming in advancing their performance, hybridization of MOFs with nanocarbons e.g. fullerenes, holds great promise.[1] In this context, a series of nanocarbon-MOF hybrids were prepared and characterized. Specifically, following the synthesis and characterization of engineered advanced nanocarbons, the *in-situ* or post-synthetic preparation of hybrid MOFs was realized. Emphasizing the tunable nature of MOFs, modified C_{60} bearing -COOH groups and azafullerene $(C_{59}N)_2$ were prepared to explore their post-synthetic installation and/or impregnation, aiming to create hybrid materials with enhanced performance. In this work, full optimization protocols are presented for the *in-situ* modification of selected MOFs relying on the use of carboxylate modified C_{60}, to prepare hybrid networks, as well as for the post-synthetic nanocarbon modification with the use of C_{60} and $(C_{59}N)_2$. All hybrid materials were characterized in detail using state-of-the-art spectroscopic, thermal and imaging techniques. The presented results advance the field of synthesis and preparation of such materials based on the synergy of MOFs and nanocarbons, aiming in the rational design of efficient materials towards photocatalytic H_2 production.

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The influence of broken chains defects on the properties of graphene-based and 2H-NbSe$_2$ materials

Valentyna Sirenko[1]**,** Ivan Bondar[1], Kseniia Minakova[2], Ruslan Mirzoiev[1]

[1]*B.Verkin Institute for Low Temperature Physics and Engineering of NAS of Ukraine, 47 Nauky Ave., Kharkiv, 61103, Ukraine*

[2] *National Technical University "Kharkiv Polytechnic Institute", 2 Kyrpychova str., 61002, Kharkiv, Ukraine*

sirenko@ilt.kharkov.ua

The synthesis of new materials with unique low-temperature properties, characterized by pronounced anisotropy, led to the observation, generally made by neutron-diffraction methods, of completely new features of the electronic and vibrational characteristics of such systems.

Recently, "graphene rush" has stimulated numerous experimental and theoretical studies of low-dimensional inorganic conductors. Despite this, the influence of inhomogeneities of crystal structure puts even more questions than answers both in graphene and dichalcogenides of transition metals – their role on the formation of nanofilms and nanotubes as well as on the unique properties of considered nanostructures still remains unclear [1]. Therefore, a detailed analysis of the features of the vibrational and electronic properties of such nanostructures as well as an influence of various types of defects on considered materials is an actual problem.

The present work is based on the study and comparative analysis of the behavior of graphene-based and containing defects layered 2H-NbSe$_2$ materials by changing temperature, revealing their general laws and the possibilities of controlling their electronic properties.

The main research methods are measurements of elastic and inelastic scattering of X-rays and neutrons in comparison with the results of the original numerical experiment.

During the experiment, the intervals of temperature stability were established in layered crystals formed both by monoatomic layers (graphene nanofilms) and multilayered "sandwiches" (dichalcogenides of transition metals) with defects of various types. The influence of defects with broken bonds on the local densities of electronic states (LDOS) of graphene materials was also detected and analyzed.

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Ligand-Triggered Self-Assembly of Flexible Carbon Dot Nanoribbons for Optoelectronic Memristor Devices and Neuromorphic Computing

Xue Yong, Lin Ai[1,2]

[1]*University of Liverpool, Liverpool, UK*

[2] *Zhengzhou University, Zhengzhou, China*

xue.yong@liverpool.ac.uk

Carbon dots (CDs) are widely utilized in sensing, energy storage, and catalysis due to their excellent optical, electrical and semiconducting properties.1 However, attempts to optimize their optoelectronic performance through high-order manipulation have met with little success to date. In this study, through efficient packing of individual CDs in two-dimensions, the synthesis of flexible CDs ribbons is demonstrated technically. Electron microscopies and molecular dynamics simulations, show the assembly of CDs into ribbons results from the tripartite balance of π–π attractions, hydrogen bonding, and halogen bonding forces provided by the superficial ligands. The obtained ribbons are flexible and show excellent stability against UV irradiation and heating. CDs ribbons offer outstanding performance as active layer material in transparent flexible memristors, with the developed devices providing excellent data storage, retention capabilities, and fast optoelectronic responses. A memristor device with a thickness of 8 µm shows good data retention capability even after 10^4 cycles of bending. Furthermore, the device functions effectively as a neuromorphic computing system with integrated storage and computation capabilities, with the response speed of the device being less than 5.5 ns. These properties create an optoelectronic memristor with rapid Chinese character learning capability. This work lays the foundation for wearable artificial intelligence.2

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Manual design of point defect arrays in two-dimensional graphenic systems

Jeanine Salla[1]

[1]*Department of A. I. Studies, Bangalore World University, India*

jsalla@bangaloreworldu-in.co.nz

Complete the angled grid, with each graphene point defect appearing only once in each 3x3 square, each row, and each column. The defect structures shown above the grid are, from left to right, a monovacancy, C_3N, oxygenated divacancy, Stone-Thrower-Wales / Deanes / Bond-rotation defect, divacancy, oxygenated monovacancy, pristine graphene, substitutional nitrogen defect, and hydroxylated graphene patch [1].

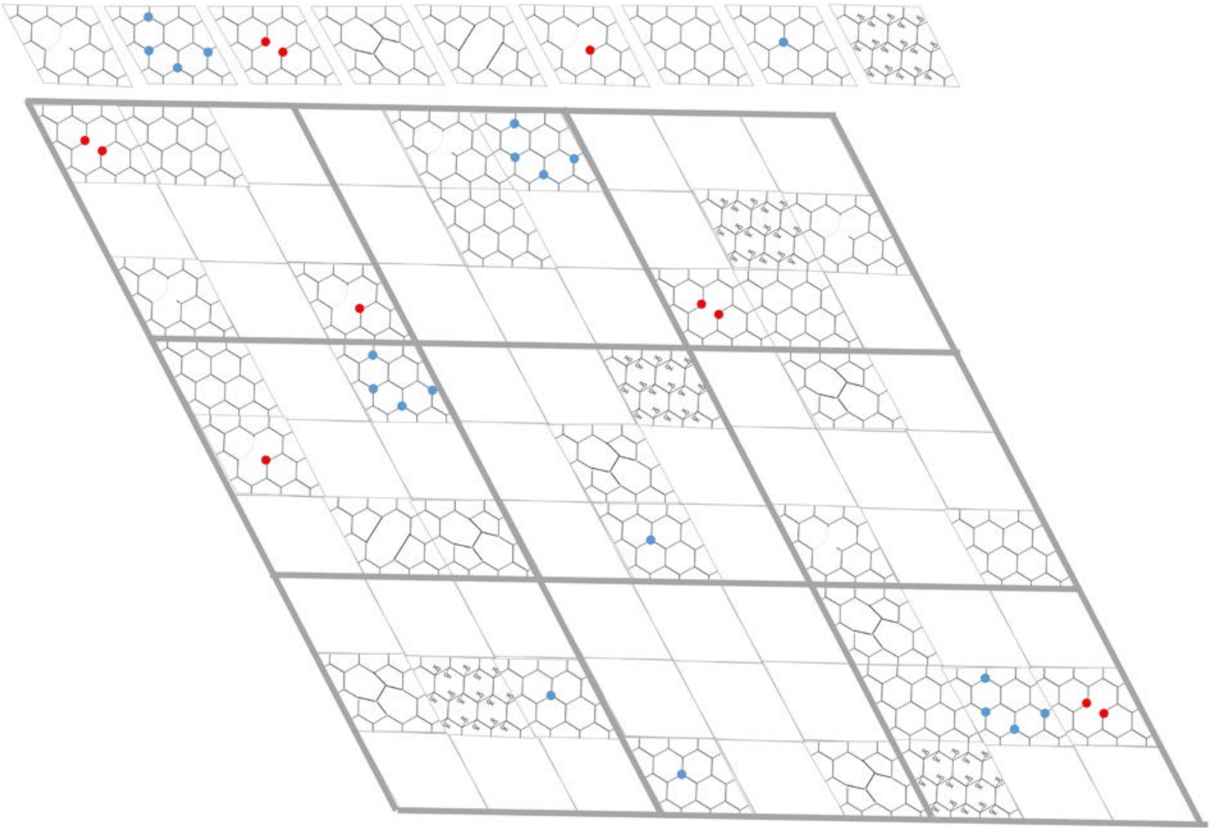

Figure 1: 9x9 supercell (compoared of 3x3 sub-grids)
of manually organised point defects in a coherent 2D-graphene grid.

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