GRAPHENE FLAGSHIP

Workshop Graphene Flagship WP3 Enabling Materials

14-17 February 2022
Online

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GRAPHENE FLAGSHIP

PROGRAMME - WP3 MEETING (ONLINE 14-17 Feb. 2022)

TIME (CET)	MONDAY	TUESDAY	WEDNESDAY	THURSDAY
09:00-09:20	Yanfei Zhao (EPFL)	Antony George (UniJena)	Laure Tailpied (CNRS)	Neeraj P. Mishra (IIT)
09:20-09:40	Cormac Ó Coileáin (UniBwM)	Domenica Convertino (IIT)	Vitaly Babenko (UCAM)	Ji Ma (TUD)
09:40-10:00	Osman Balci (UCAM)	Cian Bartlam (UniBwM)	Ignacio Jimenez (CSIC)	Jincan Zhang (UCAM)
10:00-10:20	Irene Palacio (CSIC)	Arkadiusz Gertych (WUT)	Sébastien Roux (CNRS)	Roberto Muñoz (CSIC)
10:20-10:40	Vladislav Khaustov (IIT)	Yang Li (UCAM)	Adrian Hemmi (UZH)	Gabriela Borin Barin (EMPA)
10:40-11:20	Coffee Break	Coffee Break	Coffee Break	Coffee Break
11:20-11:40	Karolina Czerniak-Losiewicz (WUT)	Leonardo Martini (IIT)	Subash Sharma (UCAM)	Jonathan Coleman (TCD)
11:40-12:00	Alexander Storm (UULM)	Lorenzo Sponza (CNRS)	Camille Maestre (CNRS)	Claudia Backes (UniHeilderberg)
12:00-12:20	José Ignacio Martínez (CSIC)	Rita Tilmann (UniBwM)	Julien Barjon (CNRS)	Xin Chen (FAU)
12:20-12:40	Oliver Hartwig (UniBwM)	Giulia Piccinini (IIT)	hBN Bechmarking (CNRS, RWTH, UCAM, UZH)	Milena Ojrzynska (WUT)
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Speaker	Title	Partner
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Cormac Ó Coileáin	STM characterisation of platinum dichalcogenides	UniBwM
Osman Balci	Synthesis of WS2 and WSe2 single layers from their bulks by CVD	UCAM
Irene Palacio	Functionalization of MoS2 by physical vapor deposition in UHV environments	CSIC
Vladislav Khaustov	High temperature 1H-1T' heterocontact induced irreversible structural phase transition in monolayer CVD grown MoTe2 single crystals	IIT
Karolina Czerniak-Losiewicz	Structural and chemical modification of TMDs monolayers as a route to photoresponse modulation	WUT
Alexander Storm	High-resolution TEM, electron diffraction and electron energy-loss spectroscopy of TMDs and TMPTs	UULM
José Ignacio Martínez	Hydrogen Interaction with Tungsten Disulfide Nanostructures	CSIC
Oliver Hartwig	Understanding the influence of substrate selection in the synthesis of PtSe2	UniBwM

Heterostructures Sessi

Antony Georg	Van der Waals and Lateral Heterostructures of Organic and Inorganic 2D Materials: Synthesis and Device Applications	Uni Jena
Domenica Convertino	Graphene and WS2 as neuronal interfaces: effect on cell viability, neurite outgrowth and electrophysiological properties	IIT
Cian Bartlam	Effects of conformation on subgap states and interlayer transfer in TMDC-organic heterostructures	UniBwM
Arkadiusz Gertych	Gold-assisted exfoliation and transfer of van der Waals heterostructures	WUT
Yang Li	High Temperature Ferromagnetism in few-layer graphene-Fe3GeTe2 Heterostructures	UCAM
Lorenzo Sponza	A simulation toolkit for electronic excitations in realistic 2D systems	CNRS
Leonardo Martini	High-mobility scalable graphene/hBN heterostructure	IIT
Giulia Piccinini	CVD-based twisted bilayer graphene	IIT
Rita Tilmann	Identification of ubiquitously present polymeric contaminations on 2D Transition Metal Dichalcogenides by TOF-SIMS	UniBwM

BN Session

Speaker	Title	Partner
Laure Tailpied	CVD synthesis of sp2-hybridized multilayer boron nitride films	CNRS
Vitaly Babenko	Temperature Stability of Hexagonal Boron Nitride on Pt(111)	UCAM
Ignacio Jimenez	Growth and optical characterization of PVD BN	CSIC
Sébastien Roux		CNRS
Adrian Hemmi	Temperature Stability of Hexagonal Boron Nitride on Pt(111)	UZH
Subash Sharma	Synthesis of hexagonal boron nitride (hBN) on Cu and sapphire	UCAM
Camille Maestre	Advances in selfstanding hBN crystal synthesis via the PDC route	CNRS
Julien Barjon	Growth of hBN crystals at atmospheric pressure	CNRS
	hBN Benchmarking Session (CNRS, RWTH, UCAM, UZH)	

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Neeraj P. Mishra	Catalyst free Direct Growth of Graphene on Insulators	IIT
Ji Ma	Curved Nanographenes and Graphene Nanoribbons: Bottom-up Synthesis and Characterizations	TUD
Jincan Zhang	Graphene transparent conductors by non-covalent doping	UCAM
Roberto Muñoz	Direct Plasma Assisted Growth and Functionalization of Graphene on Insulators of Technological Relevance	CSIC
Gabriela Borin Barin	Bottom-up graphene nanoribbons: towards high performance devices	EMPA

LPE Session

Jonathan Coleman	Liquid pase exfoliation: an update	TCD
Claudia Backes	Defects and oxidation in liquid phase exfoliated nanosheet	Uni Heidelberg
Xin Chen	Non-covalent liquid phase functionalization of 2H-WS2 with PDI: an energy conversion platform with long lived charge-separation	FAU
Milena Ojrzynska	Gram-scale production of graphene flakes based on combined SO3 intercalation-exfoliation method	WUT
Jeremiah Marcellino	Graphene-based printed heating elements for de-icing Liquid pase exfoliation: an update	UCAM

ATTENDEES

Attendees	Partner
Adil Meersha	UCAM
Adrian Hemmi	UZH
Alexander Storm	UULM
Andras Kis	EFPL
Andrea C. Ferrari	UCAM
Antony George	UniJena
Arkadiusz Gertych	WUT
Bérangère Toury	CNRS
Bernd Beschoten	RWTH
Biplob Nandy	UCAM
Boyang Mao	UCAM
Camille Maestre	CNRS
Catherine Journet	CNRS
Cian Bartlam	UniBwM
Coletti Camilla	IIT
Convertino Domenica	IIT
Cormac Ó Coileáin	UniBwM
Crasta Paola	IIT
Chao Wen	UCAM
Christoph Arnold	CNRS
Elaheh Mostaani	UCAM
Elena López Elvira	CSIC
Eugene Alexeev	UCAM
Ewa Dumiszewska	IMIF
Fernando Gomollon Bel	UCAM
Gabriela Borin Barin	EMPA
Georg Duesberg	UniBwM
Goutam Kar	UCAM
Hamideh Ramezani	UCAM
Hao Chen	UCAM
Harneet Kaur	TCD
Hatice Balci	UCAM
Hiltunen Vesa-Matti	IIT
Huanyao Cun	UZH
Ignacio Jiménez Guerrero	CSIC
Ingrid Stenger	CNRS
Irene Palacio Rodríguez	CSIC
Iwona Pasternak	WUT
Jakub Sitek	WUT

Jeremiah Marcellino	UCAM
Ji Ma	TUD
Jincan Zhang	UCAM
Jon Azpeitia Urkia	CSIC
Jonathan Coleman	TCD
José Ángel Martín Gago	CSIC
José Ignacio Martínez Ruiz	CSIC
Jose Munuera	TCD
Juliette Benuat	UCAM
Karolina Czerniak-Łosiewicz	WUT
Kathrin Knirsch	FAU
Khaustov Vladislav	IIT
Klaudia Żerańska-Chudek	WUT
Laia León	CSIC
Laure Tailpied	CNRS
Letizia Diamante	UCAM
Lorenzo Sponza	CNRS
Luigi Occhipinti	UCAM
Małgorzata Giza	WUT
Mar García Hernández	CSIC
Mariusz Zdrojek	WUT
Martini Leonardo	IIT
Matteo Tiberi	UCAM
Michael Mohn	IIT
Michael Mohn	UULM
Michał Świniarski	WUT
Milena Ojrzyńskaį	WUT
Mishra Neeraj	IIT
Mukesh Kumar Tripathi	EFPL
Oliver Hartwig	UniBwM
Osman Balci	UCAM
Ozan Aktas	UCAM
Philippe Steyer	CNRS
Piccinini Giulia	IIT
Rita Tilmann	UniBwM
Roberto Muñoz Gómez	CSIC
Sachin Shinde	UCAM
Sébastien Roux	CNRS
Shona Ni	UCAM
Sohail Abbas	UCAM
Stephan Hofmann	UCAM
Subash Sharma	UCAM

Subodh Gautam	CNRS
Tanweer Ahmed	UCAM
Thomas Greber	UZH
Tossi Camilla	IIT
Ute Kaiser	UULM
Vaishakh Kedambaimoole	UCAM
Vincent Garnier	CNRS
Vitaly Babenko	UCAM
Włodzimierz Strupiński	WUT
Xin Chen	FAU
Yanfei Zhao	EFPL
Yang Li	UCAM
Yarjan Samad	UCAM

ABSTRACTS

High-temperature 1H-1T' heterocontact induced irreversible structural phase transition in monolayer CVD $MoTe_2$ single-crystals

V. Khaustov[1,2], D. Convertino[1], A. Zakharov[3], Z. Gebeyehu[1,4], S. Pace[1,4], S. Forti[1], C. Coletti[1,4]

1. CNI@NEST, Istituto Italiano di Tecnologia, Piazza San Silvestro 12, I-56127 Pisa, Italy.
2. NEST, Scuola Normale Superiore, Piazza San Silvestro 12, I-56127 Pisa, Italy.
3. MAX IV Laboratory, Lund University, P.O. Box 118, Lund, S-22100, Sweden.
4. Graphene Labs, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy.

Among all known TMDs, $MoTe_2$ is the most attractive candidate for phase change devices [1] and low-resistance contacts [2] due to the low energy difference (i.e., 30 eV/f.u.) between semiconductor-1H and semimetal-1T' phases [3]. However, investigations on experimental phase transition (PT) phenomena in monolayer (ML) $MoTe_2$ are still at an early stage due to the weak air stability of the material. Indeed, we have recently reported an encapsulation approach to stabilize ML $MoTe_2$. [4] To date, there is no consensus about the 1H-1T' transition temperature for ML $MoTe_2$: theoretically, values of 417 ˚C [3] and 927 ˚C [5] are reported, while experimentally it has been measured to be 1075 ˚C [6]. We report irreversible high temperature monocrystalline 1H to mono- or polycrystalline 1T' polymorphism at 730 ˚C in monolayer $MoTe_2$ grown by chemical vapor deposition (CVD) [6]. We unveil a new 1H-1T' heterocontact induced PT mechanism and present experimental AFM/KPFM/Raman/μXPEEM/XPS characterization of the hBN/Graphene encapsulated $MoTe_2$ monolayer samples. DFT calculations are presented to complement the experimental data. Reported routes open new opportunities in the $MoTe_2$ based micro- and nanoelectronics fabrication, phase change devices and can be further studied in other TMDs, their heterocombinations and in Janus materials [7].

We acknowledge that the research activity herein was carried out using the IIT HPC infrastructure.

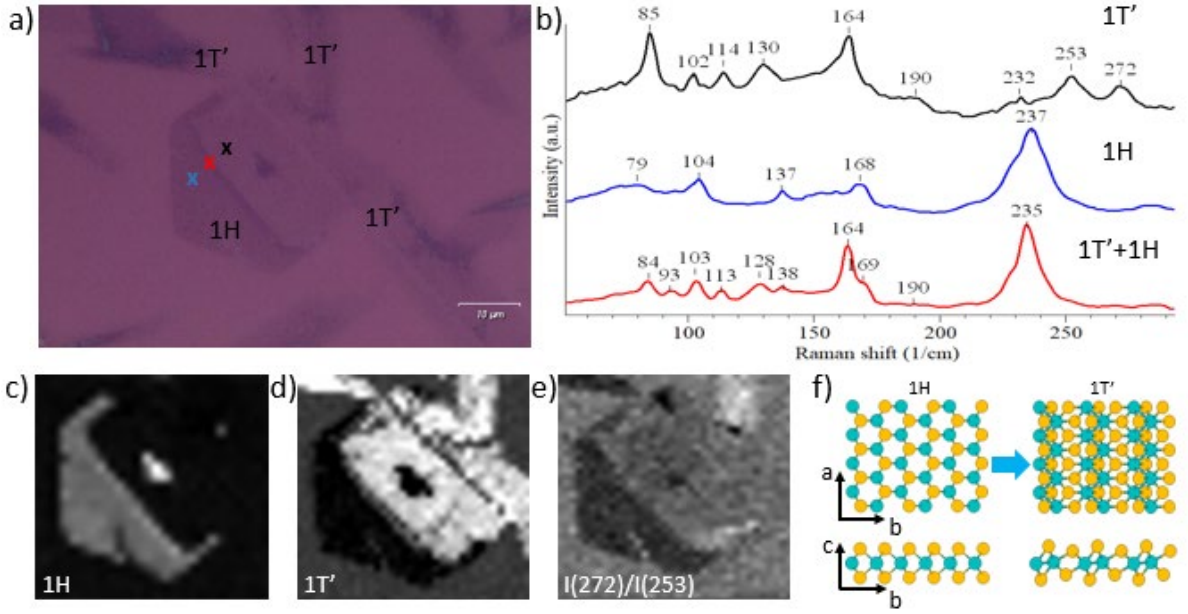

Figure 1|a), Optical image of the heterocontact induced PT propagation. b), Single spot Raman spectra for the blue, red and black spots in a). c, d), 1H/1T' phase Raman mapping. e), Linearly polarized Raman I(272cm-1)/I(253cm-1) value mapping used for 1T' single crystal's direction identification f), Top and side views of 1H and 1T'-$MoTe_2$ ball-and-stick models, blue/orange colors correspond to the Mo/Te atoms respectively.

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2. Ma, Rui, et al. "MoTe2 lateral homojunction field-effect transistors fabricated using flux-controlled phase engineering." ACS nano 13.7 (2019): 8035-8046.
3. Rehn, Daniel A., et al. "Theoretical potential for low energy consumption phase change memory utilizing electrostatically-induced structural phase transitions in 2D materials." npj Computational Materials 4.1 (2018): 1-9.
4. Pace, Simona, et al. "Synthesis of Large-Scale Monolayer 1T′-MoTe2 and Its Stabilization via Scalable hBN Encapsulation." ACS nano 15.3 (2021): 4213-4225.
5. Yuan, Jiaren, et al. "Squeezed metallic droplet with tunable Kubo gap and charge injection in transition metal dichalcogenides." Proceedings of the National Academy of Sciences 117.12 (2020): 6362-6369.
6. Ryu, Huije, et al. "Anomalous Dimensionality-Driven Phase Transition of MoTe2 in Van der Waals Heterostructure." Advanced Functional Materials (2021): 2107376.
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Structural and chemical modification of TMDs monolayers as a route to photoresponse modulation

Karolina Czerniak-Łosiewicz, Arkadiusz P. Gertych, Michał Świniarski, Małgorzata Giza, Zofia Maj, Mariusz Zdrojek

Faculty of Physics, Warsaw University of Technology
Koszykowa 75, 00-662 Warsaw, Poland

Due to their favorable optoelectronic properties, transition metal dichalcogenides (TMDs) monolayers have been widely investigated to be used in optoelectronic applications ranging from photodetectors[1,2] to optical memories[3] and artificial optical synapses[4]. Different TMDs applications require features that can be completely contradictory, such as fast response times and immediate relaxation for the detection or strong persistent photoconductivity for information storage. These contradictory features could be obtained by modifying the layers specifically for a given application, and the structural and chemical modifications should be studied to realize the applicational potential of 2D TMDs.

The modification of TMDs can result from multiple effects, e.g., defects introduction, physisorption of the molecules at the surface, or even transition metal oxide formation. In this communication, we report an on-chip, photocurrent modulation of MoS_2 and WS_2 monolayers by gentle plasma treatment. We obtain a significant enhancement in the photocurrent that shows the dependence on the measurement environment (vacuum or air). This environmental dependence allows us to attribute photocurrent enhancement to different mechanisms of the applied modification. We also note that apart from a large increase of the photocurrent, surface modification via plasma treatment is responsible for a slower response time of the layers.

This study shows how structural and chemical modification can be used to control the performance of the optoelectronic devices based on TMDs and tune the photoresponse to meet the needs of the specific optoelectronic applications.

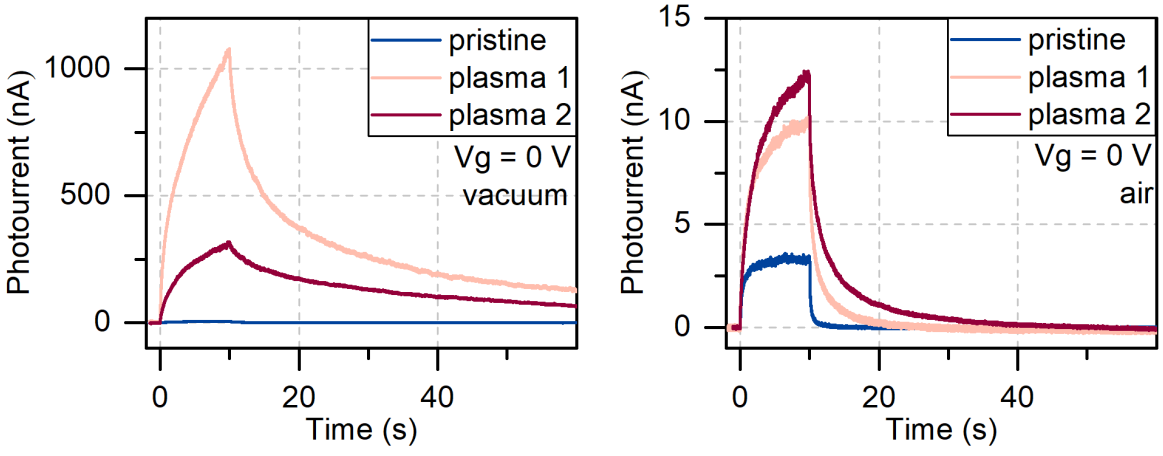

Figure 1 Photocurrent of the untreated (blue lines – pristine) and plasma-treated (once – plasma 1, beige lines, twice – plasma 2, red lines) WS_2 sample in vacuum (left) and in the air (right) showing strongly different photoresponse that depends on the environment of the sample.

(1) Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive Photodetectors Based on Monolayer MoS 2. *Nat. Nanotechnol.* **2013**, *8* (7), 497–501. https://doi.org/10.1038/nnano.2013.100.

(2) Kufer, D.; Konstantatos, G. Highly Sensitive, Encapsulated MoS2 Photodetector with Gate Controllable Gain and Speed. *Nano Lett.* **2015**, *15* (11), 7307–7313. https://doi.org/10.1021/acs.nanolett.5b02559.

(3) Zhou, F.; Zhou, Z.; Chen, J.; Choy, T. H.; Wang, J.; Zhang, N.; Lin, Z.; Yu, S.; Kang, J.; Wong, H. S. P.; Chai, Y. Optoelectronic Resistive Random Access Memory for Neuromorphic Vision Sensors. *Nat. Nanotechnol.* **2019**, *14* (8), 776–782. https://doi.org/10.1038/s41565-019-0501-3.

(4) Islam, M. M.; Dev, D.; Krishnaprasad, A.; Tetard, L.; Roy, T. Optoelectronic Synapse Using Monolayer MoS2 Field Effect Transistors. *Sci. Rep.* **2020**, *10* (1), 1–9. https://doi.org/10.1038/s41598-020-78767-4.

High-resolution TEM, electron diffraction and electron energy-loss spectroscopy of TMDs, TMPTs and MOFs

Alexander Storm, Michael Mohn, Janis Köster, Julian Schulz, Haoyuan Qi, Robert Leiter, and Ute Kaiser
Electron Microscopy Group of Materials Science, Ulm University, Germany

In this work, we present our recent advances in the TEM investigation and analysis of few-layer transition metal dichalcogenides (TMDs) and transition metal phosphorus trichalcogenides (TMPTs), as well as our newest in-situ experiments on metal-organic frameworks (MOFs).

Firstly, we show the results of our recent systematic study on exfoliated **TMDs**. We have investigated the signatures of mono- and few-layer MoS_2 and $MoTe_2$ in TEM experiments such as high-resolution transmission electron microscopy (HRTEM), electron energy-loss spectroscopy (EELS), and 3D electron diffraction (ED). Comparing their results, we discuss strengths and limitations of the TEM methods, and benchmark them with respect to their ability to identify the exact number of layers. A reference for the number of layers has been determined by optical contrast and AFM measurements on a substrate. [1]
Secondly, we present the HRTEM study of defects in TMD monolayers, where we employ convolutional neural networks (CNNs) in the image analysis. Our CNNs were trained with simulated HRTEM images and are able to detect the positions of the metal and chalcogen atoms as well as single and double chalcogen vacancies. With the high contrast of $MoTe_2$ monolayers in HRTEM, CNNs can be directly applied on experimental HRTEM images. [2]
Moreover, we report on our recent studies on bilayer WSe_2 at low twist angles and show local relaxation effects at atomic resolution.

The atomically resolved analysis of freestanding few-layer **TMPTs** is difficult, and rarely reported due to their susceptibility to oxidation [3]. Here we present our work on the effect of electron irradiation in freestanding few-layer TMPTs ($MnPS_3$, $FePS_3$, and $NiPS_3$) at TEM acceleration voltages between 30 and 80 kV. Our first-principle calculations predict that the electron beam predominantly removes sulfur from the sample, which is confirmed by combined EELS and EDX experiments. Furthermore, our study reveals that after the defect formation, oxygen is drawn towards the sample and the residual phosphorus and transition metals oxidize, illustrating the sensitivity of TMPTs to oxidation. [4]
In addition, we conducted *in-situ* experiments to study annealing and electron-beam-induced structure transformations of few-layer $MnPS_3$. We observe the formation of new phases with the net formula $\mathrm{MnS}_{1-x}\mathrm{P}_x$ and structure of α- and γ-MnS. We showed that suitable dose rates allow a controlled growth of α-MnS phases embedded in the antiferromagnetic host. Complementary ab-initio calculations prove the stability of the new phases and predict their magnetic and electronic properties. [5]

Hydrogen-free **MOFs** have been designed to enhance the intrinsic sample stability under the electron beam. This endeavor has successfully led to the discovery of MOFs with high electron resilience, enabling aberration-corrected HRTEM imaging down to the atomic scale (0.9 Å resolution) on the organic 2D crystals. Furthermore, our heating experiments have revealed an unexpected phase transition before amorphization, which has been captured in-situ with atomic precision.

[1] J. Köster, A. Storm, T. E. Gorelik, M. J. Mohn, F. Port, M. R. Goncalves, U. Kaiser (2022), (submitted).

[2] J. Schulz (2022), MSc Thesis, Ulm University (in preparation).

[3] J. Köster, B. Liang, A. Storm, U. Kaiser (2021), Nanotechnology 32, 075704.

[4] J. Köster, A. Storm, M. Ghorbani-Asl, S. Kretschmer, T. E. Gorelik, A. V. Krasheninnikov, U. Kaiser (2022), (in preparation).

[5] A. Storm, J. Köster, M. Ghorbani-Asl, S. Kretschmer, T. E. Gorelik, A. V. Krasheninnikov, U. Kaiser (2022), (in preparation).

van der Waals and Lateral Heterostructures of Organic and Inorganic 2D Materials: Synthesis and Device Applications

Andrey Turchanin[1,2]

[1]*Friedrich Schiller University Jena, Germany*
[2]*Abbe Centre of Photonics, Jena, Germany*

van der Waals and lateral heterostructures of 2D materials open broad avenues for the engineering of novel nanomaterials for both basic research and applications. In particular hybrid heterostructures of organic and inorganic materials enable to combine their most attractive and complementary intrinsic properties (*e.g.*, chemical functionalization, charge carrier transport, photo-response, *etc.*) into one material system with novel functionalities. In this presentation I will give an overview of our recent progress on the synthesis, characterization and device applications of such heterostructures composed of various 2D materials such as organic semiconductor nanosheets, transition metal dichalcogenide monolayers, single layer graphene and carbon nanomembranes. It will be demonstrated how these innovative hybrid materials are employed in a variety of devices with advanced properties including phototransistors, rectifiers, photodetectors, ambipolar and anti-ambipolar transistors, electroluminescent light emitters and chemical sensors [1-5].

[1] S. B. Kalkan, E. Najafidehaghani et al., Wafer scale synthesis of organic semiconductor nanosheets for van der Waals heterojunction devices*. npj 2D Mater. Appl.* 5 (2021) 92.
[2] B. Zhao et al., 2D van der Waals heterojunction of organic and inorganic monolayers for high responsivity phototransistors. *Adv. Func. Mater.* 31 (2021) 2105444.
[3] E. Najafidehaghani, Z. Gan et al., 1D p-n junction electronic and optoelectronic devices from transition metal dichalcogenide lateral heterostructures grown by one-pot chemical vapor deposition synthesis. *Adv. Func. Mater*. 31 (2021) 2101086.
[4] D. Kaiser et al., pH Sensors based on amino-terminated carbon nanomembrane and single layer graphene van der Waals heterostructures. *Appl. Phys. Rev.* 8 (2021) 031410.
[5] Z. Tang, A. George et al., Optically triggered control of the charge carrier density in chemically functionalized graphene field effect transistors. *Chem. Eur. J.* 26 (2020) 6473-6478.

Graphene and WS_2 as neuronal interfaces: effect on cell viability, neurite outgrowth and electrophysiological properties

Domenica Convertino[1], Filippo Fabbri[2], Neeraj Mishra[1,9], Mariantonietta Calvello[3], Alessandro Viegi[3], Antonino Cattaneo[3], Lieselot Deleye[4,9], Francesca Franchi[4], Fabio Benfenati[4,9], Lorenzo Albertazzi[5,6], Stefano Luin[2,7], Laura Marchetti[1,8], Camilla Coletti[1,9]

[1]Center for Nanotechnology Innovation @NEST, Istituto Italiano di Tecnologia, Pisa, Italy, [2]NEST Istituto Nanoscienze—CNR and Scuola Normale Superiore, Pisa, Italy, [3]BIO@SNS Laboratory, Scuola Normale Superiore, Pisa, Italy, [4]Center for Synaptic Neuroscience and Technology, Istituto Italiano di Tecnologia, Genova, Italy, [5]Nanoscopy for Nanomedicine Group, Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology (BIST), Carrer Baldiri Reixac 15-21, 08024 Barcelona, Spain, [6]Department of Biomedical Engineering, Institute for Complex Molecular Systems (ICMS), Eindhoven University of Technology, 5612AZ Eindhoven, The Netherlands, [7]NEST, Scuola Normale Superiore, Pisa, Italy, [8]Department of Pharmacy, University of Pisa, Pisa, Italy, [9]Graphene Labs, Istituto italiano di tecnologia, Via Morego 30, I-16163 Genova, Italy

The use of nanotechnology and tissue engineering in biomedicine has been recently exploited for the repair and regeneration of nerve tissue. Among the possible strategies, graphene and 2D materials display a great potential as a peripheral neural interface especially thanks to their peculiar electrical, optical and tribological properties [1-5].

In the first part of this talk, we will report our results on the effect of chemical vapor deposition (CVD) graphene on neonatal dorsal root ganglion (DRG) neurons [6]. We find that axons on graphene are significantly longer (up to >70%) with respect to controls during the early developmental phase (Fig. 1), confirming the trend previously reported for embryonic DRG neurons on epitaxial graphene [7]. We focus on the axonal transport of nerve growth factor (NGF), the neurotrophin involved in the development of peripheral neurons, as a key player in the axonal elongation of DRG neurons on graphene. We observe a reduction in the retrogradely moving vesicles in favor of a locally stalled population only in the first two days of culture, with the same time-dependent fashion observed for the axonal elongation (Fig. 1).

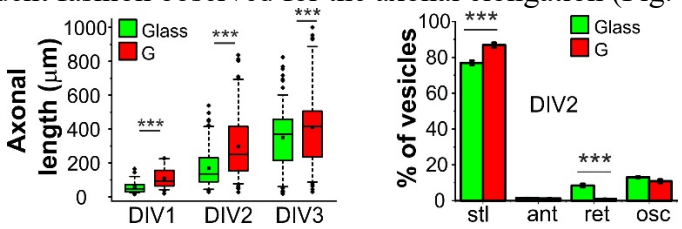

Fig.1: Increased axonal length and altered axonal transport in DRG neurons grown on graphene.

A cause/effect link between the altered NGF axonal transport and the axon elongation on graphene is proposed thanks to electrophysiological and structural studies [6].

The second part of the talk will focus on transition metal dichalcogenides (TMDs), that have gained interest for their possible adoption in biological and/or biomedical environments [5]. We use uniformly CVD-grown WS_2, known for its photoelectric properties, as a platform to culture neuronal-like cells (SH-SY5Y neuroblastoma cell line) and compare its performance with graphene and standard controls. Optical microscopy and viability assays indicate that SH-SY5Y cells grow well on WS_2, showing a neurite length and viability comparable to the controls.

Our results, in part obtained in a collaborative framework with WP4, are aimed at understanding the 2D materials/neurons interface, with special attention to the molecular mechanisms that govern axon outgrowth, a critical point for regenerative medicine.

[1] Shin, Advanced Drug Delivery Reviews, 105, 255-274 (2016).
[2] Liu, ACS Appl. Mater. Interfaces, 9, 14677−14690 (2017).
[3] Qian, NPJ Regen. Med., 6, 31 (2021).
[4] Bramini, Front. Syst. Neurosci. 12:12 (2018).
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[6] Convertino, Nano Lett. 20, 3633–3641 (2020).
[7] Convertino, Front. Neurosci., 12:1 (2018).

Gold assisted exfoliation and transfer for van der Waals heterostructures

Arkadiusz P. Gertych, Małgorzata Giza, Karolina Czerniak-Łosiewicz,
Michał Świniarski, Jakub Sitek and Mariusz Zdrojek

Faculty of Physics, Warsaw University of Technology
Koszykowa 75, 00-662 Warsaw, Poland

Prototyping new van der Waals heterostructures using mechanical exfoliation is essential in studying any properties of various 2D stacks. Especially, it is an important step for choosing layer assembly with high commercial potential for future CVD growth due to the time-consuming optimization of the growth process. In recent years several variations of scotch tape exfoliation have been shown, which replaced the traditional tape with polymer (e.g., PDMS)[1] or metal (e.g., Au)[2] film. The last one is intriguing as it can produce large area (~mm^2) 2D flakes and is highly reproducible, eliminating the main disadvantages of the mechanical exfoliation process.

In this report, in the light of recent developments, we review different methods of mechanical exfoliation and stacking techniques in order to find an optimal route for the assembly of 2D layers into van der Waals heterostructures. We focus on air-stable TMDs (MoS_2, WS_2, $MoSe_2$, WSe_2) and hBN. To assess the quality of produced 2D layers and van der Waals heterostructures, standard characterization techniques were used, such as optical imaging, Raman spectroscopy, PL measurements, and AFM. Finally, we discuss the unique advantages of different techniques and showcase the use of the most fruitful method for us - gold assisted exfoliation and transfer of 2D layers.

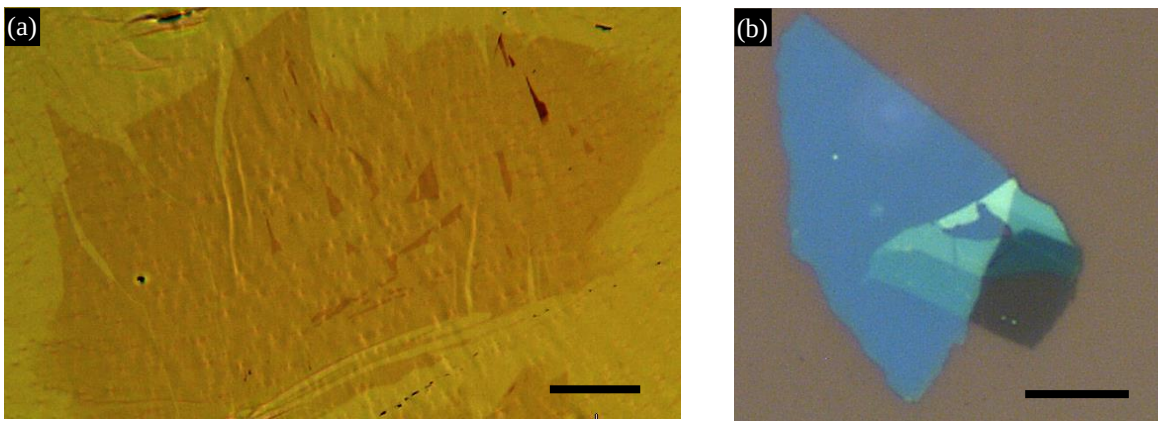

Figure 1 Optical images of produced samples. (a) Large area MoS_2 flake exfoliated on gold.. Scale bar is equal to 200µm. (b) Small area hBN/WS_2 heterostructure on SiO_2/Si substrate made using polymer asisted tranfer. Scale bar is equal to 10µm.

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A simulation toolkit for electronic excitations in realistic 2D systems

Elisa Serrano-Richaud[1], Etienne Carré[1,2], Hakim Amara[1], Sylvain Latil[3], Lorenzo Sponza[1] and François Ducastelle[1]

[1] *Université Paris-Saclay - ONERA - CNRS, LEM, Châtillon, France*
[2] *Université Paris-Saclay - UVSQ - CNRS, GEMaC, Versailles, France*
[3] *CEA, IRAMIS, SPEC, GMT, Gif-sur-Yvette, France*

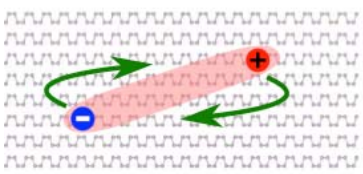
The experimental study of 2D materials and their heterostructures is one of the most rapidly growing fields in material science. In few years, the focus moved from investigating the properties of pure materials to controlling exotic phenomena in complicated heterostructures. Theoretical developments can simply not grow at the same pace.

The limitation is more fundamental than technical. Owing to their being bulkless surfaces, 2D materials are extremely sensitive to their surroundings and atomic arrangement. As a consequence, a quantitative theory to be comparable with experiments must treat long-range and short-rage interactions on the same footing while handling complicated morphologies (e.g. large moiré patterns, defects, long stacking sequences). At the time, such a complete theory does not exist.

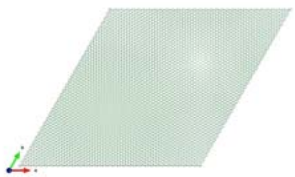
On one hand, ab-initio simulations can treat interactions of different nature, but they are limited in the structural complexity accessible. On the other hand, semi-empirical approaches and model Hamiltonians can describe very large and complicated systems – made of tens of thousands of atoms – but rely on assumptions about the relevant interactions.

In this talk, I will present three on-going works on the modelling of optical properties in 2D materials. All have in common the development of tools and procedures precisely conceived to be applied to experimentally realistic structures. I will speak about the modelling of:

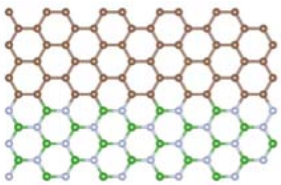
1. free excitons in black phosphorus (BP) thick films,
2. the electronic structure of twisted boron nitride (BN) bilayers,
3. the electronic structure of graphene (Gr) and BN nanoribbons and lateral heterostructures.



1. Free excitons in BP



2. Twisted BN bilayer



3. Gr/BN lateral HS

High-mobility scalable graphene/hBN heterostructures

Leonardo Martini[1], Vaidotas Miseikis[1,2], David Esteban[3], Jon Azpeitia[3], Sergio Pezzini[4], Paolo Paletti[1,2], Domenica Convertino[1,2], Mar Garcia Hernandez[3], Ignacio Jimenez[3], Camilla Coletti[1e,2]

1. *Center for Nanotechnology Innovation @ NEST, Istituto Italiano di Tecnologia, Piazza San Silvestro 12, 56127, Pisa, Italy*
2. *Graphene Labs, Istituto italiano di tecnologia, Via Morego 30, I-16163 Genova, Italy*
3. *Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, E-28049 Madrid, Spain*
4. *NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza San Silvestro 12, 56127, Pisa, Italy*

Obtaining graphene over wafer-scale, while preserving its electrical and optical qualities is a challenging goal whose achievement would allow the integration of this appealing 2D materials in high-tech applications. To date, h-BN is the most suitable encapsulant to build graphene-based heterostructures with superior performance [1], although most results have been obtained with exfoliated h-BN[2].
Here we present the realization of graphene/h-BN heterostructures with scalable techniques. h-BN continuous films were grown by Ion Bean Assisted Deposition (IBAD)[3] directly on Si/SiO_2 substrate, with no further transfer step required. The material was first characterized by Raman spectroscopy and atomic force microscopy (AFM) revealing the atomic flatness required for the implementation of graphene/based electronics. High-quality graphene single-crystal arrays were grown by CVD[4] on copper. Graphene was transferred on the target substrates (h-BN and commercially available SiO_2/Si) using a semi-dry approach[5,6]. Raman spectroscopy was adopted to investigate the properties of the graphene crystals transferred on h-BN and SiO_2/Si, indicating a reduction in the graphene strain on h-BN with respect to Si/SiO_2. Moreover, we fabricated and tested Hall bar devices to investigate the mobility and carrier density, at room temperature and in ambient condition. The residual carrier density in the tested devices is between $8x10^{10}$ cm^{-2} and $20x10^{10}$ cm^{-2}, with carrier mobilities around 10 000 cm^2/Vs on h-BN substrate, which doubles the average mobility value we measure on SiO_2/Si [6,7].
This work represents a first step toward the realization of high-mobility graphene/based scalable devices. The quality of the presented scalable heterostack paves the way to the implementation of high-performing devices in electronics and opto-electronics applications.

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 881603-Graphene Core3.

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Figures

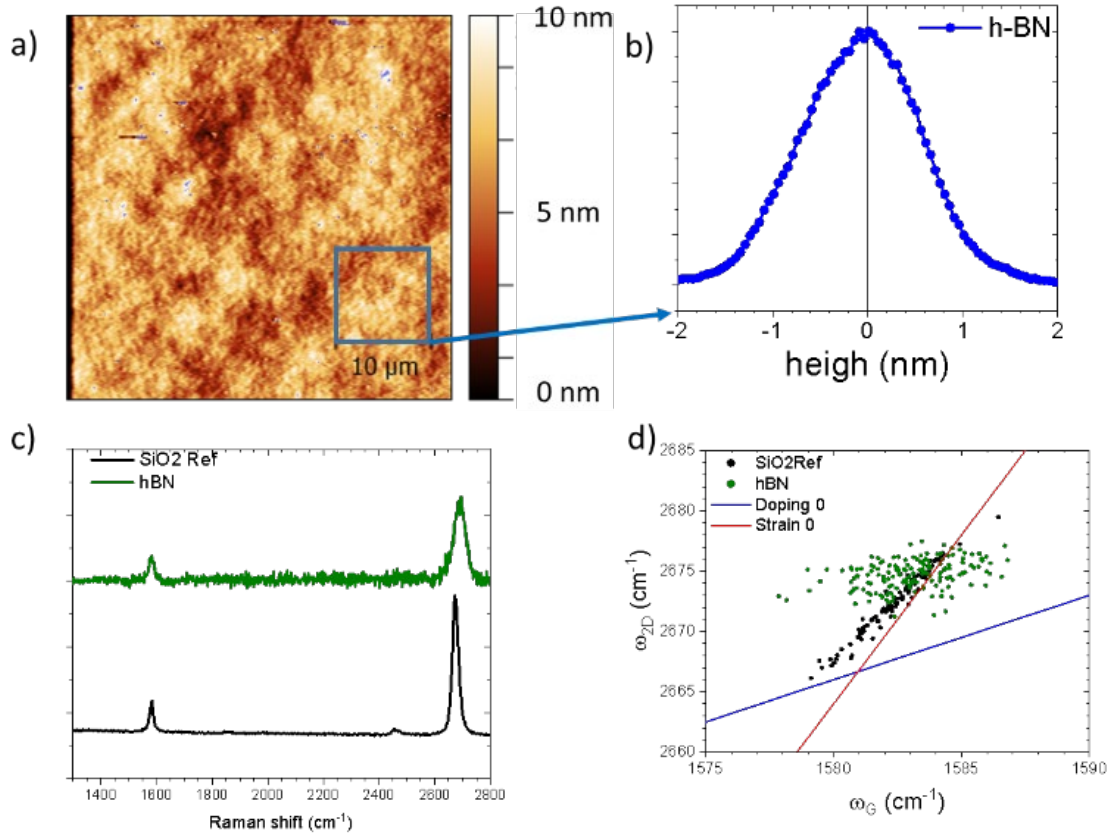

Figure 1 a) AFM characterization of a pristine hBN film. b) Height distribution over a 10x10 µm area indicates an average roughness comparable with that of commercially available SiO_2/Si. Comparison of the Raman spectra of single crystal CVD graphene on hBN and on commercially available SiO_2/Si. d) 2D-G Raman-peak correlation plot of single crystal graphene transferred on SiO_2 /Si and PVD-hBN.

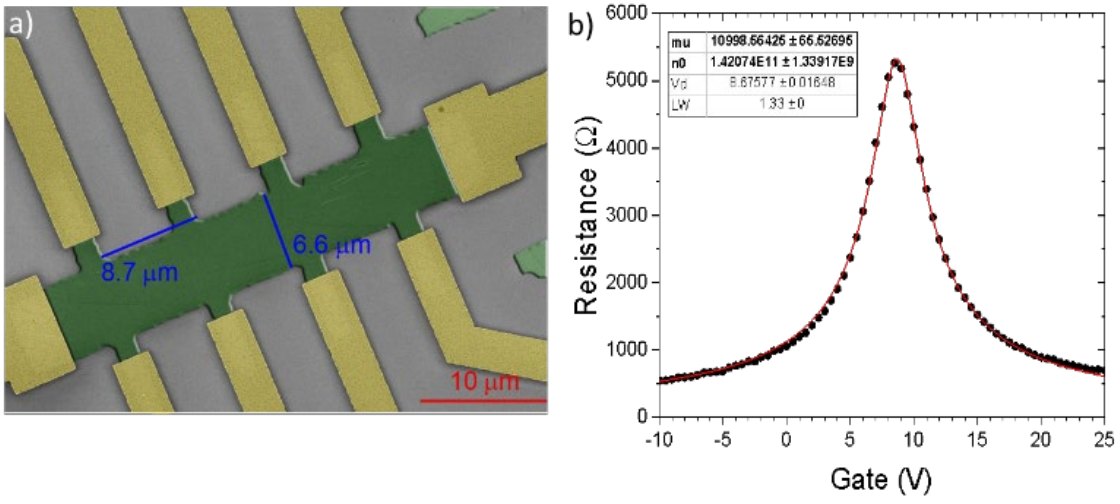

Figure 2 a) False-color SEM image of a graphene Hall bar on PVD-hBN. b) Electrical characterization of graphene on h-BN performed in ambient condition. The reported mobility of 10000 cm^2/Vs is higher than the average value obtained on SiO_2/Si.. The Dirac point is at $n_0 = 1.5x10^{11}$ cm^{-2}.

CVD-based twisted bilayer graphene

G. Piccinini,[1,2] V. Mišeikis,[2,3] K. Watanabe,[4] T. Taniguchi,[5] C. Coletti[2,3], S. Pezzini[6]

[1]*NEST, Scuola Normale Superiore, Piazza San Silvestro 12, 56127 Pisa, Italy*
[2]*Center for Nanotechnology Innovation @NEST, Istituto Italiano di Tecnologia, Piazza San Silvestro 12, 56127 Pisa, Italy*
[3]*Graphene Labs, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*
[4]*Research Center for Functional Materials, National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Japan*
[5]*International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Japan*
[6]*NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza San Silvestro 12, Pisa 56127, Italy*

Twisted bilayer graphene (TBG) is certainly the major driving force of the novel paradigm of *twistronics*, which aspires at understanding and engineering the emergent electronic properties of twisted (i.e., rotationally faulted) two-dimensional materials.

On one hand, large twist-angles ensure electronic decoupling between graphene layers, giving the possibility to control the carrier distribution in each layer with double-gates, while on the other hand, small twist-angles lead to strong interlayer coupling, causing flat bands and correlated phases near the so-called magic angle.

In this work, we investigate both the large and small twist-angle regime, by using arrays of graphene crystals which are synthesized via chemical vapor deposition (CVD) on copper and which share the same orientation [1]. The CVD-based TBG enable a deterministically-selectable angle twisting, a device-scale uniform twist angle, and an atomically-clean interlayer interface.

First, we employ dual-gated 30°-TBG [2] (Fig. 1(a)) to demonstrate simultaneous ultra-high mobility and conductivity, unattainable in a single-layer of graphene [3]. We find quantitative agreement with a simple phenomenology of parallel conduction between two pristine graphene sheets, with a gate-controlled carrier distribution. Based on the parallel transport mechanism, we then introduce a method for *in situ* measurements of the chemical potential (μ) of the two layers. In particular, by keeping one of the layers charge-neutral, it is possible to probe μ in the other one with a resolution in the meV range (comparable to hBN-spaced structures [4]) (Figure 1(b)). This twist-enabled approach, neither requiring a dielectric spacer, nor separate contacting, has the potential to greatly simplify the measurement of thermodynamic quantities in graphene-based systems of high current interest.

Then, we investigate small-angle TBG, assembled from separated CVD graphene single-crystals. Via low-temperature dual-gated magnetotransport we demonstrate the hallmarks of a 2.4°-twisted superlattice, including tunable regimes of interlayer coupling, reduced Fermi velocity, large interlayer capacitance, and density independent Brown-Zak oscillations.

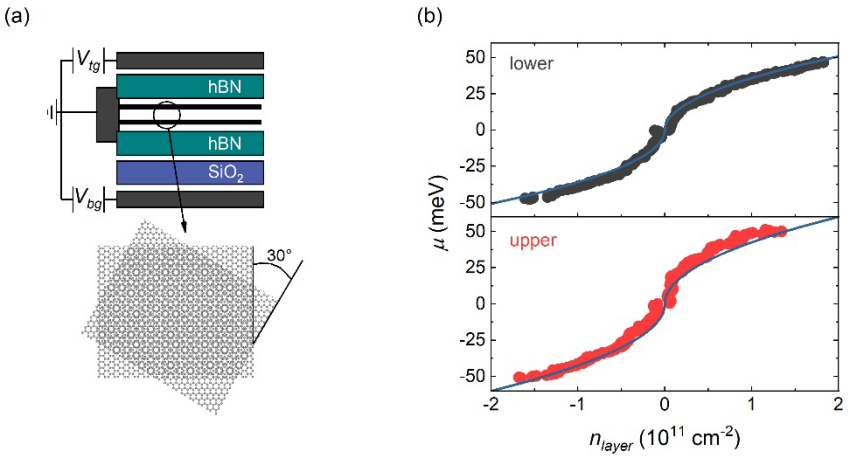

Figure 1: (a) Schematics of the lateral section of the investigated device. CVD-grown 30°-twisted bilayer graphene is encapsulated between hBN flakes. (b) Experimentally measured chemical potential as a function of the carrier density for the two graphene layers (black and red circles). The blue lines are fits to the Dirac dispersion.

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CVD synthesis of sp2-hybridized multilayer boron nitride films

Laure Tailpied[1], Amandine Andrieux-Ledier[2], Frédéric Fossard[1], Jean-Sébastien Mérot[1], Jean-Manuel Decams[3], Annick Loiseau[1]

1: LEM ONERA-CNRS, 2: DPHY/CMT, 3: Annealsys

Since graphene isolation in 2004, the 2D materials is a blooming research field. Due to its unique properties, sp^2 hybridized boron nitride (BN) has been acknowledge as a key towards integration of other 2D materials in devices. Indeed, it is structurally very close to graphene – their lattice mismatch is only 1.7%- a semiconductor, atomically flat and thermally and chemically inert. It is therefore a choice material to be used in the van der Waals heterostructures with other 2D materials either as a top layer to protect another 2D material from its environment [1], or as a dielectric interlayer [2] and mostly, as a flat substrate [3]. However, these applications have been demonstrated using mechanically exfoliated BN from low defective and highly crystalline single crystals. Yet, this process limits the size of the devices that can be created to sub millimeter scale. In order to develop devices at a wafer scale, it is therefore critical to master the synthesis sp^2 hybridized BN layers at low cost, large scale and high quality.

In that respect, the goal of the researches we have undertaken is to develop the synthesis of sp^2-hybridized multilayer BN films with structural specifications fitting these requirements. We have already successfully obtained heteroepitaxial growth of a few nanometer-thick sp2 hybridized BN film of well-stacked and flat layers on Ni (111) surface of polycrystalline substrate [4]. Here, we will present our work on Rapid Thermal CVD from Annealsys (www.annealsys.com). We will show how we successfully adapt our growth process to this new reactor on centimeter monocrystalline nickel substrates. We will detail the crucial step of nickel surface preparation before the synthesis for these Ni(111)/YSZ/Si(111) pseudosubstrate, and how it can impact the quality of the synthetized BN. We will present the results of the structural and quality characterization of the BN films from the macroscale to the nanoscale (OM, SEM, TEM, AFM, LEED, Raman and luminescence spectroscopies) on the growth substrate and after transfer onto dedicated substrate.

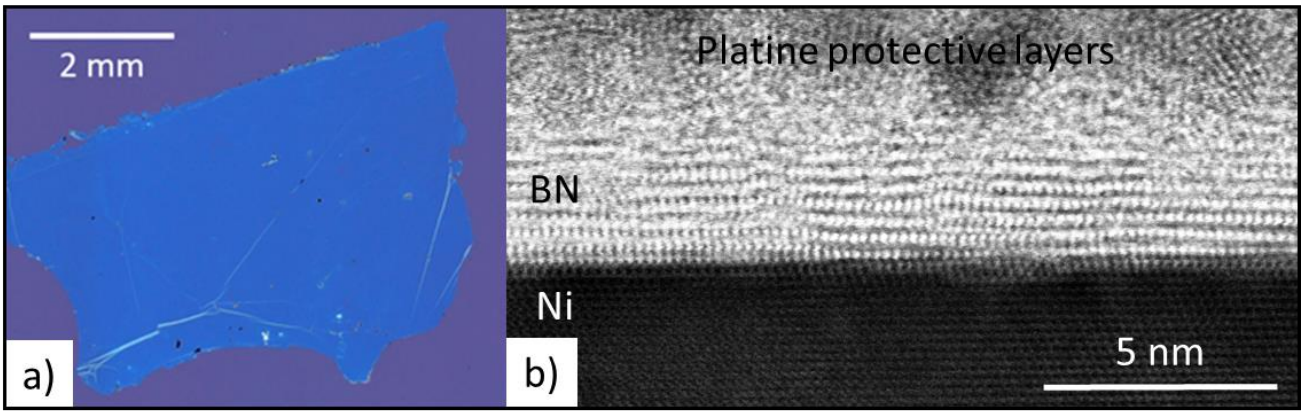

Figure 1: All the results present here are obtained on the Annealsys RTCVD (a) Optical microscopy image of a BN film grown on Ni(111)/YSZ/Si(111) pseudosubstrate and transferred on SiO2/Si, showing the large scale transfer.(b) HRTEM image of multilayers BN film grown on nickel (111) showing the thickness and the regular stacking of the BN layer (MATMECA, Titan G2 Centrale Supelec, 300 kV).

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Growth and optical characterization of PVD BN

I. Jiménez, J. Azpeitia, D. Esteban, R. Gago
ICMM-CSIC

The growth of BN by ion beam assisted deposition can be controlled by several parameters like the substrate temperature, ion energy and momentum transfer in the ion-boron collision. Such conditions yield amorphous or nanocrystalline BN which exhibits distinct spectroscopic features in FTIR, XANES or UV-vis. However, characterization using these techniques is not possible as a routine quality test for BN films grown on the substrates required by device scientist. Ellipsometry seems a promising routine measurement which can be performed on any substrate. It provides the optical constants of the BN film, but does not provide direct information on the type of bonding, microstructure and nanostructure of BN.
We are trying to correlate our large dataset of BN growth conditions, with the FTIR and UV spectroscopic results and the ellipsometry optical constants. Some results will be presented of this ongoing research.

Temperature Stability of Hexagonal Boron Nitride on Pt(111)

Adrian Hemmi, Huanyao Cun and Thomas Greber

Universität Zürich, Physik-Institut, Winterthurerstrasse 190, 8057 Zürich, Switzerland

To synthesize high-quality hexagonal boron nitride (h-BN) or to improve its crystalline order, high temperatures for treatment are required. Recent synthesis strategies employ boron and nitrogen segregation processes in metals that lower the preparation temperature towards 1000 °C, while the crystalline order of the target material appears to be preserved. However, different solubility of boron and nitrogen in metals lead to segregated structures that range from a single boron layer (borophene) to boron nitride structures that have limited thickness or to millimeter-sized h-BN flakes. Here, we investigate single layer boron nitride on twinned Pt(111) thin films with in-situ methods at high temperatures. Our experiments indicate that Pt(111) is a substrate with limited performance for both scenarios, the high temperature recrystallization/deposition of h-BN as well as for segregation of well-defined structures.

Advances in selfstanding hBN crystals synthesis via the PDC route

Camille MAESTRE

Bérangère TOURY, Philippe STEYER, Vincent GARNIER, Catherine JOURNET

camille.maestre@univ-lyon1.fr

Laboratoire des Multimatériaux et Interfaces, CNRS, UMR 5615,
University of Lyon, F-69622, Villeurbanne, France.
Laboratoire Matériaux Ingénierie et Science, UMR CNRS 5510, INSA de Lyon, France

Whether used as a substrate or as an active layer, high quality 2D hexagonal boron nitride holds great promise for future research and applications in optoelectronics in particular. Vapor-phase processes such as Chemical Vapor Deposition can achieve large scale coverage, but selfstanding hexagonal boron nitride crystals provide exfoliated nanosheets (BNNS) of unrivalled purity and crystal quality which are still preferred for demanding applications. In order to obtain high quality and large BNNSs, we propose a synthesis route by the Polymer Derived Ceramics (PDCs) process combined with a sintering step. [1,2] The hBN obtained by this method has already demonstrated a very high crystalline quality attested by a Raman FWHM value of 7.6 cm^{-1}, one of the best reported in literature so far. [2] Our study aims at understanding the growth mechanisms of hBN crystals and the generation of crystalline defects in order to better control the synthesis and provide hBN with the desired quality.

SEM and X-ray tomography observations (Figure 1) give insights into nucleation and growth orientation. To search for defects in the crystal, its optical (see Figure 1) and electrical properties are explored. BNNSs exfoliated from these crystals have been used to make metal-hBN-metal capacitor devices to measure the dielectric constant and breakdown electric field of hBN, found to be 3.136 and 0.64 $V.nm^{-1}$ respectively, *i.e* very close to the theoretical values. Such routine functional measurements allow to evaluate the global quality of the crystal and constitute a powerful tool for the optimization of the process parameters.

These BNNSs have also been used to encapsulate transition metal dichalcogenides (TMDs). Such van der Waals heterostructures have been tested by optical spectroscopy. The photoluminescence width of WSe_2 and $MoSe_2$ neutral exciton lines at 4K were measured within the 2-3 meV range, while non-encapsulated TMD monolayers exhibit photoluminescence linewidths of a few tens of meV. These results demonstrate that these BNNSs are relevant for future electronic and opto-electronic applications.

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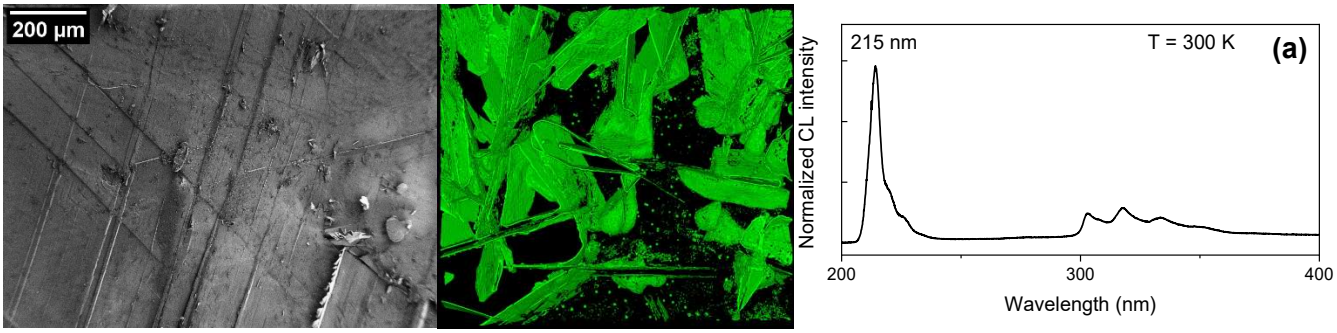

Figure 1: (left) low magnification SEM view of the crystal surface; (middle) 3D extracted view of entangled crystals inside the as-obtained ingot from X-ray tomography; (right) Cathodoluminescence measurement of a PDC hBN crystal [3].

Growth of hBN crystals at atmospheric pressure

Julien Barjon

Univ Paris Saclay, UVSQ, CNRS, GEMaC, F-78000 Versailles, France

In this work we implemented the atmospheric pressure high temperature (APHT) method for hBN fabrication. We fabricated centimeter-scale hBN crystals whose quality is assessed from Raman, electron diffraction and time-resolved cathodoluminescence and compared to reference HPHT crystals.

Catalyst-free Direct Growth of Graphene on Sapphire

N. Mishra[1,2], S. Forti[1], L. Martini[1], and C. Coletti[1,2,]

[1]*Center for Nanotechnology Innovation @ NEST, Istituto Italiano di Tecnologia , Piazza San Silvestro 12,56127 Pisa, Italy*

[2]*Graphene Labs, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*

Polycrystalline monolayer graphene was grown on C-plane sapphire (Al_2O_3) substrates by chemical vapor deposition (CVD) as reported in [1]. Grown graphene was characterized by different analysis tools such as Raman, SEM, STM, LEED, and AFM. Subsequently, graphene was easily transferred to other insulating substrates like SiO_2/Si for device fabrication. In this work, as grown and transferred graphene data are compared. Also, we report a thourough study on the aging of graphene on sapphire.

Acknowledgment: The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 881603-Graphene Core3.

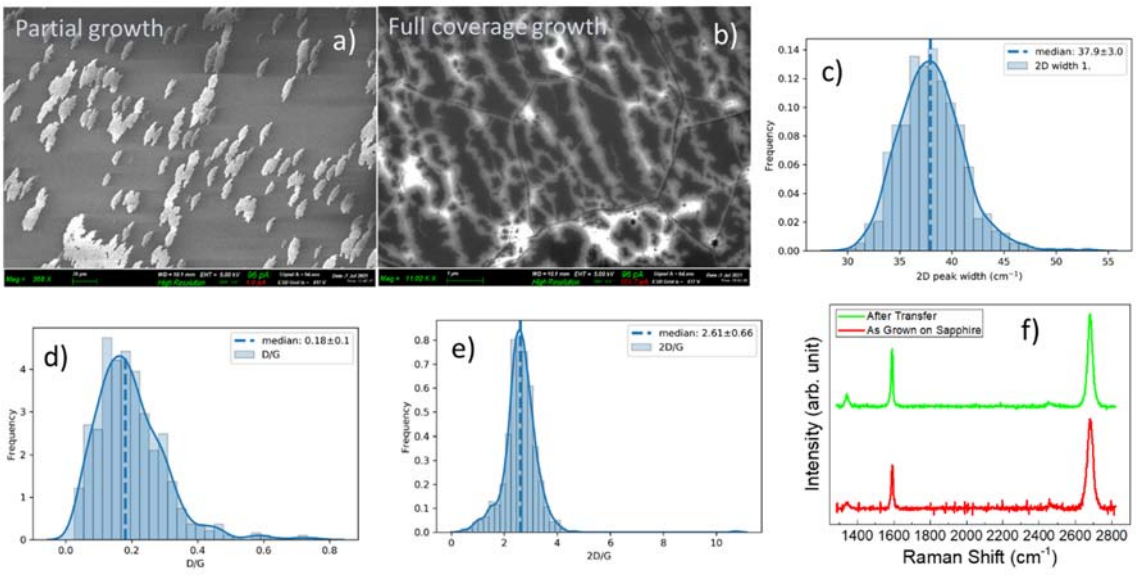

Figure 1: a) SEM image of partially grown graphene on sapphire, b) SEM image of full coverage graphene on sapphire, c-e) Raman 2D peak width, D/G and 2D/G intensity ratio of graphene on sapphire, f) comparison of Raman spectra of graphene before and after transfer.

Reference:

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Curved Nanographenes and Graphene Nanoribbons: Bottom-up Synthesis and Characterizations

Ji Ma, Xinliang Feng

Center for Advancing Electronics Dresden (cfaed) and Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany

Curved π-conjugated polycyclic hydrocarbons (or nanographenes) has become an important research targets owing to their fascinating intermolecular packing and extraordinary chiraloptical properties resulting from their contorted conformation. In general, two distinct approaches have been established for the synthesis of curved nanographenes: one is the incorporation of steric strain in their periphery, the other is to introduce the non-hexagonal rings (i.e. pentagon, heptagon, octagon) in their skeleton which induce the nonplanar nature. The resultant curvature in a π-conjugated system often yields an unusual electronic structure and unprecedented physical properties. Here, I will talk the reasonable synthesis of several curved nanographenes and graphene nanoribbons with different topologies, such as saddle-shaped and wavy-shaped open-shell radicaloids,[1] azulene-embedded helical nanographenes,[2] and curved graphene nanoribbons with multiple edge structures[3] as well as the periodic cove-zigzag edged graphene nanoribbons[4]. Apart from the synthetic strategies, the structure-property relations of these π-systems as well as their optical, electronic and magnetic properties will be also presented. Our work provides a new insight into the synthesis of functional curved aromatics as well as their potential applications in nanoelectronics and spintronic devices.

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[3] J. Am. Chem. Soc., 142 (2020), 18293.

[4] J. Am. Chem. Soc., 143 (2022), 228.

Direct Plasma Assisted Growth and Functionalization of Graphene on Insulators of Technological Relevance

Roberto Muñoz[1], Elena López-Elvira[1], Carmen Munuera[1], Mar García-Hernández[1]

[1]*Materials Science Factory, Instituto de Ciencia de Materiales de Madrid (ICMM), C/ Sor Juana Inés de la Cruz nº 3, E-28049 Madrid. SPAIN*

In this talk, I present our research during the last year working in two different topics. The first topic is the direct growth of graphene films on sapphire, a substrate of maximum relevance for graphene implementation. Direct growth of graphene on insulating substrates or semiconducting layers continue being an ambition, as large scale transfer degrades the material properties or contaminate the interface in between. To face this challenge, we devised new protocols to growth graphene on semiconducting oxides (SiO_2, TiO_2) at low temperature by using plasma-CVD [1]. Now, we are extending our approach to synthesize graphene on sapphire (Al_2O_3-c plane) at moderate temperature. Low temperature synthesis avoids generation of wrinkles in graphene, being this the main drawback of direct growth on sapphire substrates [2].
The second topic is the graphene functionalization in "low vacuum" plasma environment. Previous works in graphene functionalization in ultra-high-vacuum (UHV) demonstrate the feasibility of this method and the advantages therein [3]. On the other hand, the protocol has some limitations. UHV is not fast, not cost effective and for the same reason it is not easy to implement in an industrial environment. The "low vacuum" functionalization represents a step forward in this "vacuum" functionalization strategy implementation. I will explain the advantages of this method and the preliminary results.

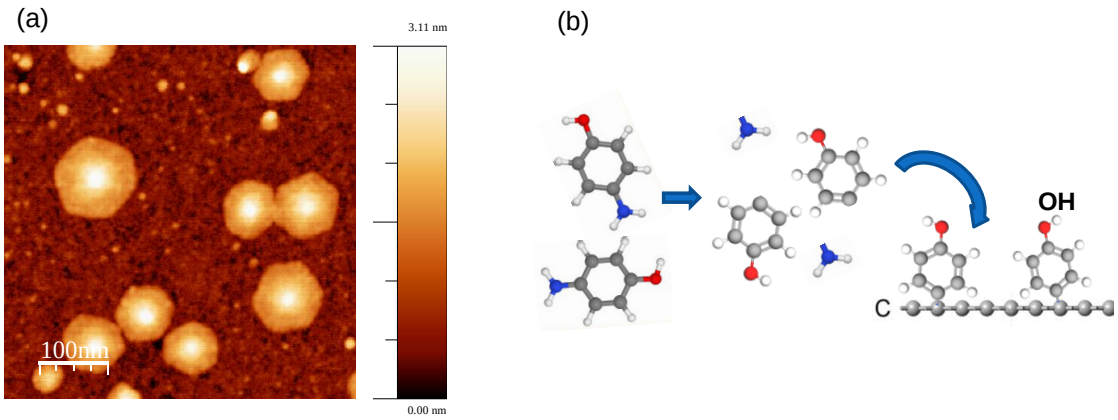

Figure 1. (a) AFM topographic images of the graphene hexagonal crystal grown on sapphire substrate. (b) Graphene functionalization with linker molecule aminophenol

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Bottom-up graphene nanoribbons: towards high performance devices

Gabriela Borin Barin, Pascal Ruffieux, Roman Fasel

Nanotech@surfaces Laboratory, Empa, Dübendorf, Switzerland

Graphene nanoribbons (GNRs) show exciting properties deriving from electron confinement and related band gap tunability[1]. The ability to tune GNRs' electronic and magnetic properties at the single atom level makes them an ideal platform for a wide range of device applications, from classical transistors to spintronics. In this contribution, we show the necessary steps to bring GNRs from ultra-high vacuum (UHV) to device integration focusing on our progress on the synthesis of magnetic nanographenes and on the characterization and transport measurements of armchair graphene nanoribbons. After the UHV bottom-up growth, GNRs were transferred using a polymer-free[2] and/or an electrochemical delamination method[3]. GNRs transferred onto a graphene/SiC substrate allowed us to image transferred GNRs for the first time with STM resolution as well as observe 9-AGNRs' frontier orbitals on G/SiC. In addition, we successfully intercalated GNRs using carbene-based molecules in UHV, which decrease the GNRs-Au interaction facilitating their dry-transfer onto SiO_2/Si substrates. This was a crucial step towards our in-situ (meaning *in vacuum*) dry-transfer protocol development.

Together with our device partners, we made important progress by integrating 5-, 9-, and 17-AGNRs into field-effect transistors with different gate and contact configurations.

As a brief overview, we developed narrow finger-gate devices that allowed to gate 9-AGNRs separately from graphene source and drain and we integrated 17-AGNRs in a FET configuration using graphene contacts. In addition, we developed a device configuration with a double-gate (DG) structure which achieved high I_{on}/I_{off} up to 10^5, and excellent, highest to date, I_{on} = 12 μA with 9-AGNRs as active material[4].

With respect to magnetic nanographenes, we have realized an extensive list of open-shell diradical molecules for which very high singlet-triplet excitation energies[5] (up to 100 meV) could be achieved. Very recently, we developed on-surface synthesis protocols allowing to achieve one-dimensional triangulene-based chains and showed that this spin-1 chain indeed behaves like the so-called Haldane chain with a gapped magnetic excitation spectrum in the bulk and fractional moments at the chain termini.[6]

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Non-covalent liquid phase functionalization of 2H-WS_2 with PDI: an energy conversion platform with long lived charge-separation

Gerhard Binder[1†], Tobias Scharl[1†], Alejandro Cadranel[1], Xin Chen[1], Claudia Backes[2], Kathrin C. Knirsch[1], Dirk M. Guldi[1]*, and Andreas Hirsch[1]*

[1]*Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg*
[2]*Faculty 10, Mathematics and Natural Sciences, University of Kassel*

Transition metal dichalcogenides are attractive 2D materials in the context of solar energy conversion.[1-2] Previous investigations have focused predominantly on the properties of these systems.[3-5] The realization of non-covalent hybrids with, for example, complementary electroactive materials remains underexplored to this date for exfoliated WS_2. In this contribution, we explore WS_2 by means of exfoliation and integration together with visible-light absorbing and electron accepting perylene diimides into versatile electron-donor acceptor hybrids. Important is the distinct electron donating feature of WS_2. Detailed spectroscopic investigations of **WS_2-PDI** confirm the electron donor/acceptor nature of the hybrid and indicate that green light photoexcitation leads to the formation of long lived **$WS_2^{\bullet+}$-$PDI^{\bullet-}$** charge-separated states.

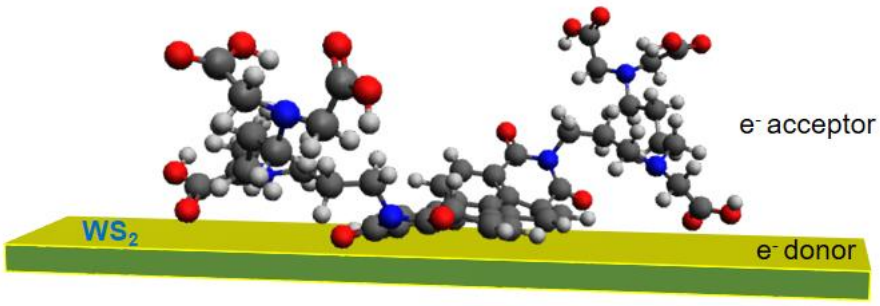

Figure 1. Graphic illustration of the possible structure of WS_2-PDI hybrids.

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Gram-scale production of graphene flakes based on combined SO_3 intercalation-exfoliation method.

Milena Ojrzyńska[1], Andrzej Daniewski, Anna Dużyńska[1], Mariusz Zdrojek[1]
[1]*Warsaw University of Technology, Faculty of Physics, Poland*

High quality and high yield production of graphene flakes is the holy grail of today's graphene technology that would allow commercialization and industrialization. Recently developed innovative methods still suffering from low quantities, controllable qualities, processability, and costs. Here, we developed a simple, yet compelling chemical route for industry-scale production of few-layer graphene that relay on simultaneous non-oxidative intercalation and exfoliation of raw graphite in oleum with nearly 100% efficiency, one of the highest ever reported. High yield is enabled because un-bounded SO3 molecules dissolved in sulfuric acid can effectively intercalate the graphite boosting spontaneous exfoliation and providing undefected, thin graphene flakes. The X-ray and vibrational spectroscopy confirm the absence of defects and oxides in the graphene layers and the electron microscopy and diffraction method show the structure. The graphene produced by this method is readily used for water-based suspension that intrinsically avoids aggregation, and it performs excellently in applications such as conductive films, capacitors, and composites.

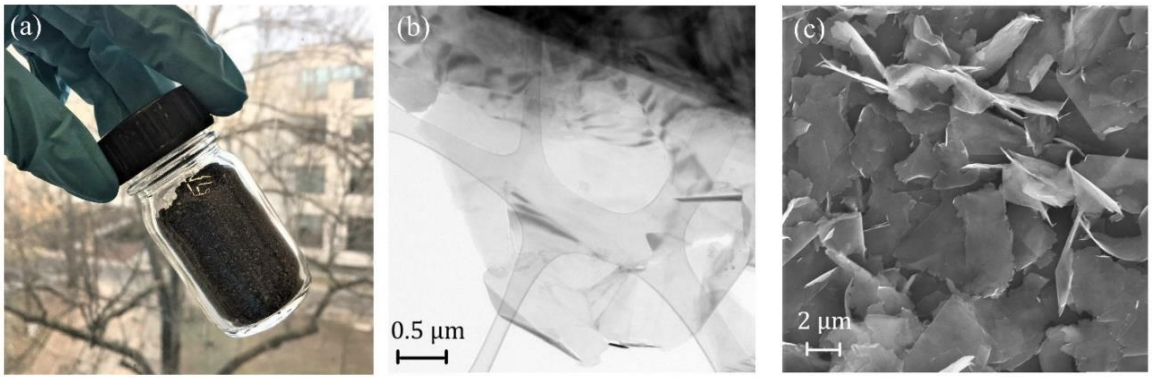

Fig 1. Gram-scale production of graphene flakes intercalated and exfoliated in oleum: (a) due to non-oxidative intercalation environment – 100% of graphite flakes are exfoliated down to FLG and MLG confirmed by (b) TEM and (c) SEM images.