

# Booklet of Abstracts



## Graphene & Co GDR-I 2017' Annual Meeting

October, 15th-19th  
Aussois, French Alps

### Topics

Preparation and structural characterizations  
Chemistry and interface with biology  
Spintronics, valleytronics, and photonics  
Atomically-thin membranes  
Emerging properties of 2D materials  
Applications



	Sunday, 15 <sup>th</sup>	Monday, 16 <sup>th</sup>	Tuesday, 17 <sup>th</sup>	Wednesday, 18 <sup>th</sup>	Thursday, 19 <sup>th</sup>	
8:30						8:30
9:00		Nano-mechanics and more	Optical properties			9:00
9:30				Growth and structural properties	Near-field and structure	9:30
10:00		Poster clips	Poster clips			10:00
10:30		Coffee break	Coffee break	Coffee break	Coffee break	10:30
11:00		Electronic structure		Nanofluidics	Growth and structural properties	11:00
11:30			Chemistry and functionalization			11:30
12:00		Lunch		Lunch	Conclusions Lunch	12:00
12:30			Lunch			12:30
13:00						13:00
14:00		Technological, medical, and industrial applications	Graphene	Gapped 2D materials		14:00
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15:00						15:00
15:30		Poster clips				15:30
16:00		Coffee break	Poster session 2	Refreshment		16:00
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## Foreword

The Organizing Committee would like to welcome you to the 2017 annual meeting of the GDR-I « Graphene and Co : From 1D Nanostructures to 2D Materials and their Heterostructures : Basics and Application » in Aussois. In the tradition of the long series of the GDR meetings, we are pleased to gather an increasingly vast community including French, European, Canadian and Brazilian researchers. We tried to arrange a scientific program covering the latest developments in graphene, nanotubes and 2D materials science and technology. As in earlier GDR meetings, we put a special emphasis on the posters sessions, with more than 6 hours hours dedicated to free discussions and a plenary clip for each poster. We encourage invited and contributed speakers to present a poster as well in order to promote further discussions.

We also tried to host this conference in a convivial place and to secure time-slots for informal scientific discussions in view of promoting the development of new or existing collaborations.

We strongly encourage the participation of students and young researchers to the debates. A special session dedicated to open questions to the community is scheduled on Wednesday during the general assembly.

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# Opto-electronics



## **Electrical transport and optoelectronics in TMDCs and their heterostructures**

*Kirill Bolotin (Freie University Berlin)*

Charge carriers in graphene are described by a conceptually simple yet rich model: a two-dimensional gas of weakly interacting Dirac fermions. Monolayer TMDCs, e.g. MoS<sub>2</sub> and WSe<sub>2</sub>, materials closely related to graphene, are significantly more complex. The carriers in TMDCs are affected by the presence of the bandgap, spin-orbit interactions, and strong electron/electron interactions. The lack of inversion symmetry in TMDCs enables optical manipulation of the spin and valley degrees of freedom. Finally, the density of defects and the effects due to them are typically larger. In this talk, I will discuss various manifestations of these properties of TMDCs in electrical transport and optoelectronic measurements. Specifically, the following topics will be covered:

1. Transport at low carrier densities: field effect, scattering mechanisms and mobility limitations, quantum Hall effect
2. The effects of interactions in transport at high carrier densities: superconductivity, phase transitions, and possible quantum spin Hall effects
3. The effects of interactions in optoelectronic measurements: photoconversion, dark and bright excitons, optospintronics, valleytronics

# Nano-mechanics and more

## Optomechanics with Hybrid Carbon Nanotube Resonators

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After two decades of intense development, optomechanics stepped into the quantum regime, notably with demonstrating laser cooling of solid-state mechanical resonators down the quantum groundstate. To further advance and perform truly non-classical quantum tests, optomechanical systems however need to strongly decrease their sensitivity towards decoherence mechanisms, which essentially express as thermal noise.

I will introduce a hybrid optomechanical device, consisting of carbon nanotube resonators at the tip of which an optical scatterer are synthesized. This novel approach enables unprecedentedly low thermal decoherence at room temperature, more than two orders of magnitude below the state of the art. I will describe the optomechanical dynamics of such system within a focused beam of coherent light. The impact of mechanical nonlinearities on the noise dynamics will be analysed, with the perspective of improved mechanical coherence at room temperature. The quantum measurement performance of such optomechanical arrangement will be quantitatively characterized, opening the path towards quantum optomechanics at room temperature and beyond.

## OPTOMECHANICAL MEASUREMENT OF THERMAL PROPERTIES OF $\text{MoSe}_2$

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Thermal properties of 2D solids is a key parameter for both 2D based applications (heat dissipation in Van der Waals heterostructures, 2D optoelectronics) and fundamental studies (role of dimensionality in thermal transport, hybrid devices). While Raman and electrical measurements have established the record thermal conductivity of graphene [1], thermal properties of monolayer transition metal dichalcogenides (TMD) remains challenging to measure. Indeed, large electrical resistivity and strong optical absorption limit transport measurements and generate laser-induced dissipation effects.

We have developed an extremely sensitive optical method to detect vibrations of high Q-factor TMD resonators down to 3K at low laser power (10-100 nW) [2]. That was the starting point for a new type of optomechanical experiments, where we monitor the mechanical properties upon laser power and cryostat temperature changes in order to extract thermal properties.

In this talk, I will show our latest results on thermal conductance ( $K_{\text{th}}$ ) of  $\text{MoSe}_2$  suspended monolayers. We report a variation from  $K_{\text{th}} = 2 \cdot 10^{-5}$  W/K at room temperature, in agreement with previous calculations, given the sample geometry [3]. By reducing the temperature, the thermal conductance first slightly increases before drastically going down at lower temperatures. It separates a regime where thermal conduction is governed by phonon-phonon interactions (high temperatures) from a regime where the phonon mean free path becomes larger than the grain size (diffusive) or the sample dimensions (ballistic) [4]. At low temperatures, such optomechanical measurement remains efficient at low laser power (0.1-1  $\mu\text{W}$ ), thus avoiding lattice heating by more than 1K. We also report the first measurement of specific heat of  $\text{MoSe}_2$  at cryogenic temperatures, analyzing the effect of the photothermal back-action on the mechanical resonator [5].

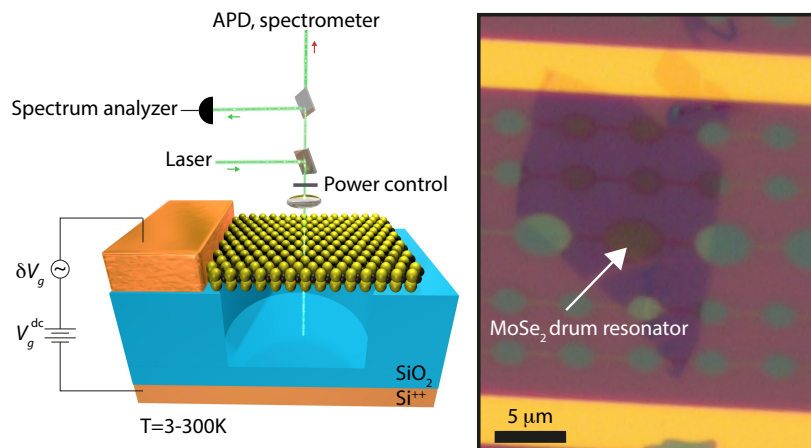


Figure 1. Left : Sketch of the device and experimental setup. This setup allows for optical detection of the motion of monolayer  $\text{MoSe}_2$  resonators from 3 to 300K. Right : optical image of an array of  $\text{MoSe}_2$  drums mechanical resonators.

### References

- [1] Balandin. Thermal Properties of Graphene and Nanostructured Carbon Materials. *Nat. Mater.* 2011, 10, 569.
- [2] Morell, Reserbat-Plantey, Tsioutsios, Schädler, Dubin, Koppens and Bachtold. High Quality Factor Mechanical Resonators Based on  $\text{WSe}_2$  Monolayers. *Nano Lett.* 16, 5102–5108, 2016.
- [3] Kandemir, Yapicioglu, Kinaci, Çağm and Sevik. Thermal Transport Properties of  $\text{MoS}_2$  and  $\text{MoSe}_2$  Monolayers. *Nanotechnology* 2016, 27, 55703.
- [4] Fugallo, Cepellotti, Paulatto, Lazzeri, Marzari and Mauri. Thermal Conductivity of Graphene and Graphite: Collective Excitations and Mean Free Paths. *Nano Lett.*, 14, 6109–6114. 2014
- [5] Barton, et al. Photothermal Self-Oscillation and Laser Cooling of Graphene Optomechanical Systems. *Nano Lett.*, 12, 4681–4686. 2012

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## EFFECT OF UNIAXIAL RELATIVE STRAIN IN TWISTED GRAPHENE LAYERS

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Strain alters the band structure of crystalline materials and can be an additional knob to tune the properties of 2D materials [1]. The prospect of assembling 2D layers into van der Waals heterostructures further widens the possibilities of band engineering since new artificial materials with designed properties are made available. Strain in such van der Waals heterostructures has been largely overlooked since it is generally assumed that those are exempt from strain owing to the weak van der Waals bonds between the layers. In this work, we show that even a small strain difference (relative strain) between the layers can qualitatively alter the band structure of one of the simplest van der Waals heterostructures: twisted graphene layers (TGL).

We have studied twisted graphene layers with a small rotation angle ( $\Theta=1.26^\circ$ ). Scanning Tunneling Spectroscopy (STS) revealed additional peaks in the  $dI/dV(V)$  spectra compared to the two expected van Hove singularities (vHs) in the density of states close to the Dirac energy (Figure 1). We interpret these peaks as resulting from the lifting of the degeneracy of vHs by a small difference in strain in the two layers. A commensurability analysis of the moiré pattern imaged by Scanning Tunneling Microscopy allows to determine that the relative strain in the TGL is mainly uniaxial and small (0.35%). This analysis allows to generate a moiré cell suitable for tight-binding calculations where atomic positions are fixed according to the measured strain. Tight-binding calculations using this cell reproduce accurately all the details of the experimental data. They show that the band structure is completely reconstructed by relative strain. This points out that a small difference in strain between the layers alters the properties of TGL in a much more efficient way than absolute strain usually discussed in the literature.

The influence of relative strain on the local density of states of TGL has strong implications for van der Waals engineering of heterostructures as relative strain between the constituent layers could be exploited as an additional and effective tuning parameter.

### References

[1] Amorim *et al.* Physics reports **617**, 1 (2016).

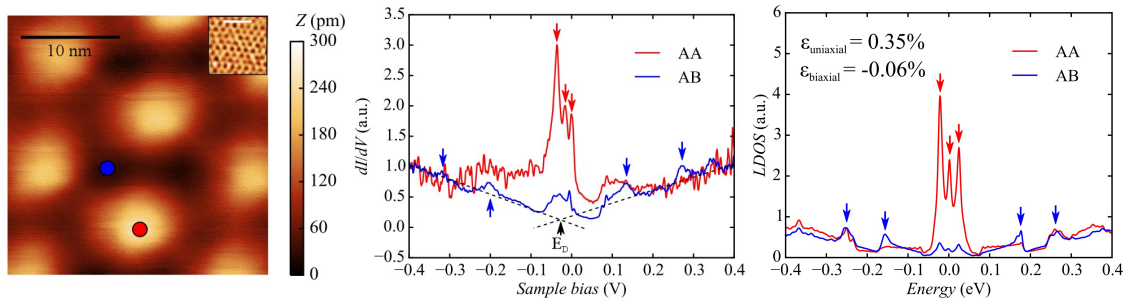


Figure 1 : a)  $(26.37 \times 26.37) \text{ nm}^2$  Scanning Tunneling Microscopy topograph of twisted graphene layers showing the moiré pattern. The sample bias is  $V=-400 \text{ mV}$  and the current setpoint is  $I=50 \text{ pA}$ . Inset : Zoom of the image showing the honeycomb lattice of the carbon atoms in the top layer. The scale bar is  $1 \text{ nm}$ . b) Local density of states recorded by STS at the spots marked with colored dots in Fig. 1a showing multiple van Hove singularities in AA regions (red arrows) and peaks at higher energy in AB regions (blue arrows). The current setpoint is  $I=300 \text{ pA}$  for a bias voltage of  $V=-400 \text{ mV}$ . Local density of states calculated by tight-binding on the atomic positions found by the commensurability analysis which include the relative strain. The three resonances localized in AA regions are in agreement with STS experiments as are the peaks at higher energy in AB regions.

## THEORETICAL INVESTIGATION OF GRAPHENE-PHOSPHORENE NANOCOMPOSITES

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Intralayer deformation in van der Waals (vdW) heterostructures or nanocomposites is generally assumed to be small due to the weak nature of the interactions between the layers. In the present work, we investigate the case of graphene-phosphorene vdW-nanocomposites (see Fig. 1) within the Density Functional Theory framework. We find that the intralayer deformation of phosphorene is surprisingly large in such graphene-phosphorene vdW-nanocomposites. The armchair lattice parameter of phosphorene is indeed predicted to contract by  $\approx 4\%$  when compared to its free-standing form. This leads to important changes in term of phosphorene electronic properties, with its direct optical transition becoming indirect in such vdW-nanocomposites due, mostly, to (induced) strain. Thus, this work points out to strong substrate effects in general in phosphorene -neglected up to now to the best of our knowledge- and paves the way to substrate-controlled stressronic in this bidimensional material.

In addition, we investigate the energy landscape of these graphene-phosphorene nanocomposites as function of the rotation angle between the layers and their stacking sequence. Similarly to what is found for graphene on hexagonal boron nitride [1], germanene on molybdenum disulfide ( $\text{MoS}_2$ ) [2] or silicene on molybdenum disulfide ( $\text{MoS}_2$ ) [3], we find that it is more favorable to align the crystalline directions of the bidimensional materials in play. We discuss the origin of this energy minimum and present several models and tools to investigate this question in general in vdW-heterostructures.

### References

- [1] C. Woods *et al.*, Nat. Phys. **10**, 451 (2014).
- [2] D. Wang *et al.*, Phys. Rev. Lett. **116**, 126101 (2016).
- [3] D. Chiappe *et al.*, Advanced Materials **26**, 2096 (2014).

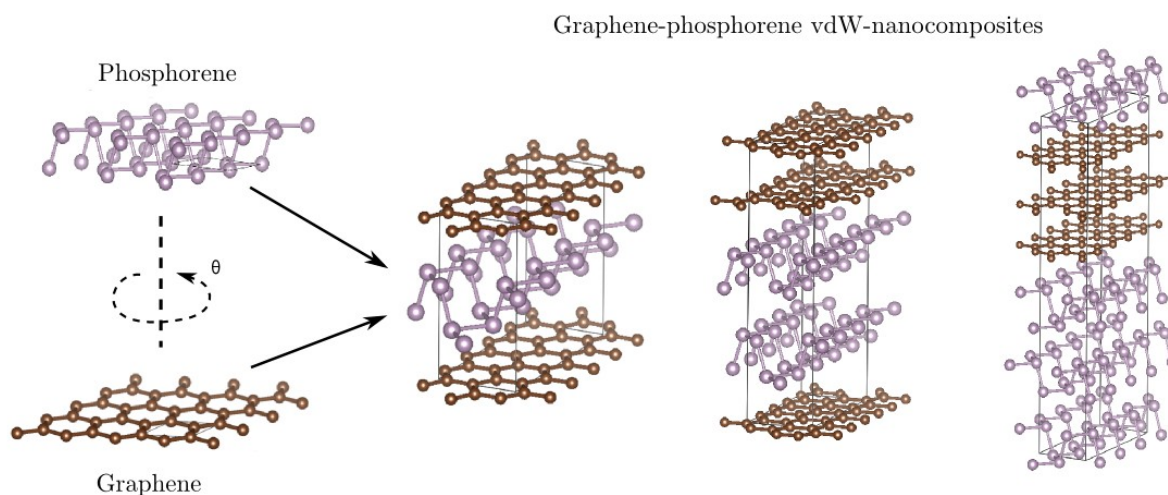


Figure 1 : Schematic representation of graphene-phosphorene vdW-nanocomposites. The properties of these periodically-repeated out-of-plane structures can be tuned by changing the size of graphene or phosphorene domains.

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# Electronic structure

## ELECTRONIC AND OPTICAL PROPERTIES OF BOROPHENE

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Borophene, a two-dimensional monolayer of boron atoms, was recently synthesized experimentally and was shown to exhibit polymorphism [1,2,3]. In its closed-packed triangular form (Fig.1, left panel), borophene is expected to exhibit anisotropic metallic character with relatively high electron velocities. Although being metallic, very low optical conductivities in the infrared-visible light region are predicted. Based on its promising electronic transport properties and its high transparency, borophene could become a genuine lego piece in the 2D materials assembling game known as the van der Waals heterocrystal approach. However, borophene is naturally degraded in ambient conditions and it is therefore important to assess the mechanisms and the effects of oxidation on borophene monolayers (Fig.1, right panels). Optical and electronic properties of pristine and oxidized borophene are here [4] investigated by first-principles approaches. The transparent and conductive properties of borophene are elucidated by analyzing the electronic structure and its interplay with light. Optical response of borophene is found to be strongly affected by oxidation, suggesting that optical measurements can serve as an efficient probe for borophene surface contamination.

### References

- [1] Z. Zhang, E. S. Penev, B. I. Yakobson, *Nat. Chem.*, 8 (2016) 525.
- [2] A. J. Mannix, X.-F. Zhou, B. Kiraly et al., *Science*, 350 (2015) 1513.
- [3] B. Feng, J. Zhang, Q. Zhong et al., *Nat. Chem.*, 8 (2016) 563.
- [4] A. Lherbier, A. R. Botello-Méndez, J.-C. Charlier, *2D Mater.*, 3 (2016) 045006.

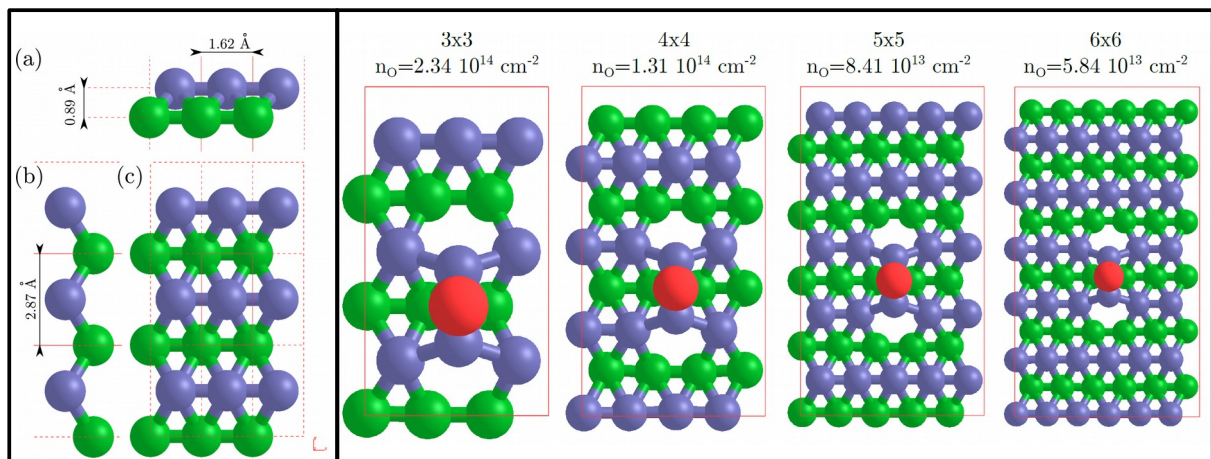


Figure 1 : Left : closed-packed triangular pristine borophene. Right : various densities of oxidized triangular borophene

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## BAND STRUCTURE OF ULTRATHIN SILICA ON RU(0001): A PHOTOEMISSION AND DENSITY FUNCTIONAL THEORY STUDY

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Ultrathin oxides films play an important part in many technological areas such as catalysis, spintronics or nanoelectronics. Over the years, efforts have been made to downsize their thickness to few atomic layers and increase their structural order leading ultimately to 2D oxides crystals. Such optimization of the growth allows to control the nature and number of defects in the films as well as the chemical bonding at the interfaces, parameters which have been shown to play a significant role on transport, dielectric and catalytic properties.

Silica, is a good example of such prolonged development. Nowadays films as thin as half-lamella could be epitaxially grown on metals [1-4]. The structural properties of those metal/oxide interfaces have been characterized and recently unraveled down to the atomic scale in the case of silica/Ru(0001) [4,5]. However, the electronic band structure is yet to be explored. The experimental determination of the electronic properties (energy band gaps, symmetry...) would give insight into the optical, catalytic and electric behaviour of the material.

In this framework, we have investigated the electronic properties of a half-lamella of silica epitaxially grown on Ru(0001) (Fig.(a)) by means of angle-resolved photoemission and density functional theory. The atomic structure and chemical bonding were first characterized by high-resolution XPS, low energy electron diffraction (LEED) and low-temperature scanning tunneling microscopy (LT-STM) leading to good agreement with previous studies [4,5]. Then, the band structure was experimentally determined (Fig.(b)) and discussed in the light of DFT calculations. This study provides insightful understanding on the electronic properties of the atomic oxide layer and metal-oxide electronic coupling.

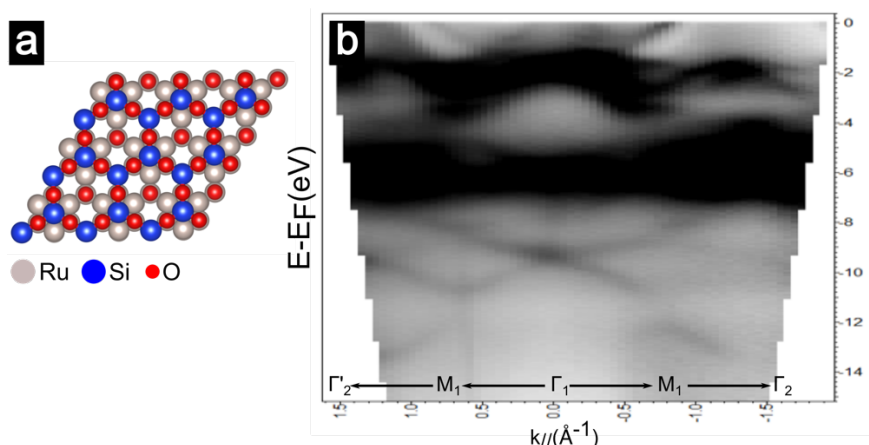


Figure: (a) Structure model of half-lamella of silica on Ru(0001). (b) corresponding ARPES spectra

### References

- [1] C. Büchner *et al.* Chem. Eur. J. 20 (2014) 9176
- [2] X. Yu *et al.* Appl. Phys. Lett. 100 (2012) 151608
- [3] J. Weissenrieder *et al.* Phys. Rev. Lett. 95 (2005) 076103
- [4] S. Mathur *et al.* Phys. Rev. B 92 (2015) 161410 (R)
- [5] B. Yang *et al.* Phys. Chem. Chem. Phys. 14 (2012) 11344

## THERMOELECTRIC PROPERTIES OF GRAPHITE NANOFIBERS

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Graphite nanofibers (GNFs) have been demonstrated in the past as a promising material for hydrogen storage [1] and heat management in electronic devices [2]. Many forms of graphene and other 2D materials have also been proposed as promising thermoelectric materials [3,4].

Here, by means of first-principles (electrons), force constant (phonons) and transport (non-equilibrium Green's function) simulation, we show that GNFs of small diameter [5] can also be an excellent material for thermoelectric applications. It is due to the weak van der Waals interactions that induces low thermal conductance [6,7] and a tooth-like shape of electronic transmission with several gaps, which are necessary ingredients to achieve high thermoelectric performance. This study unveils that the platelet form of GNFs (see Figure 1) in which graphite layers are perpendicular to the fiber axis can exhibit outstanding thermoelectric properties with the figure of merit  $ZT$  reaching 3.55 in a fiber of diameter of 0.5 nm ( $M_A = 4$ ,  $M_Z = 5$ ) and 1.1 for a diameter of 1.1 nm ( $M_A = 6$ ,  $M_Z = 10$ ). Additionally, by introducing  $^{14}\text{C}$  isotope doping, as previously suggested in other graphene nanostructures [8],  $ZT$  can even be enhanced up to more than 5 (see Figure 2), which demonstrates the amazing thermoelectric potential of GNFs.

### References

- [1] A. Chambers, C. Park, R.T.K. Baker, N.M. Rodriguez, J. Phys. Chem. B 102 (1998) 4253-4256.
- [2] R.D. Weinstein, T.C. Kopec, A.S. Fleischer, E. D'Addio, C. Bessel, J. Heat Transfer 130 (2008) 42405.
- [3] P. Dollfus, V. Hung Nguyen, J. Saint-Martin, J. Phys.: Condens. Matter 27 (2015) 133204.
- [4] V. Truong Tran, J. Saint-Martin, P. Dollfus, Nanotechnol. 26 (2015) 495202.
- [5] A. Kimouche, M.M. Ervasti, R. Drost, S. Halonen, A. Harju, P.M. Joensuu, J. Sainio, P. Liljeroth, Nat. Commun. 6 (2015) 10177
- [6] G.A. Slack, Phys. Rev. 127 (1962) 694-701.
- [7] V. Hung Nguyen, M. Chung Nguyen, H. Viet Nguyen, J. Saint-Martin, P. Dollfus, Appl. Phys. Lett. 105 (2014) 133105.
- [8] V. Truong Tran, J. Saint-Martin, P. Dollfus, S. Volz, Sci. Rep. 7 (2017) 2313.

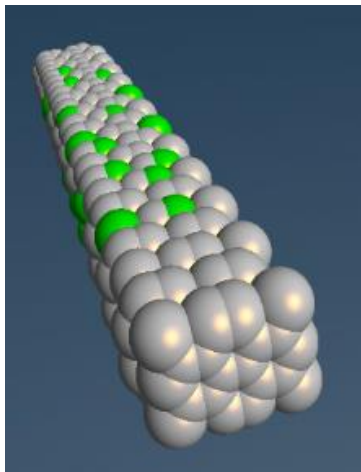


Figure 1: Typical graphite nanofiber including  $^{14}\text{C}$  isotope doping atoms (in green)

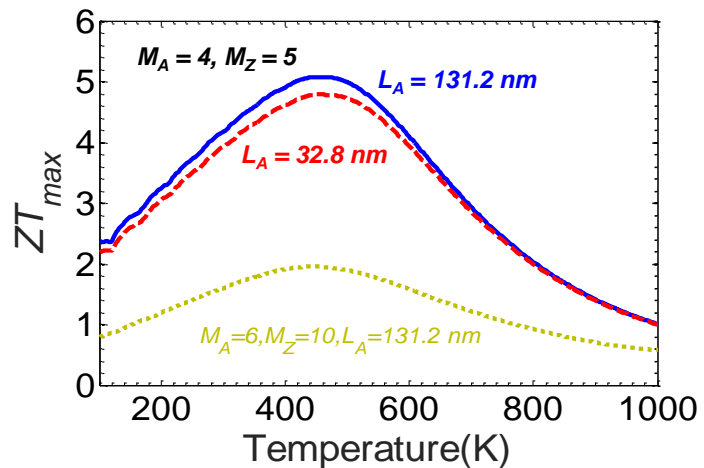


Figure 2: Maximum figure of merit  $ZT_{max}$  in GNFs as a function of temperature in the presence of 50%  $^{14}\text{C}$  isotope doping. Two diameters are considered, characterized by the number of atoms in armchair ( $M_A$ ) and zigzag ( $M_Z$ ) sides of the GNF.

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# ELECTRONIC AND VIBRATIONAL PROPERTIES OF V<sub>2</sub>C-BASED MXENES: FROM EXPERIMENTS TO FIRST-PRINCIPLES MODELING

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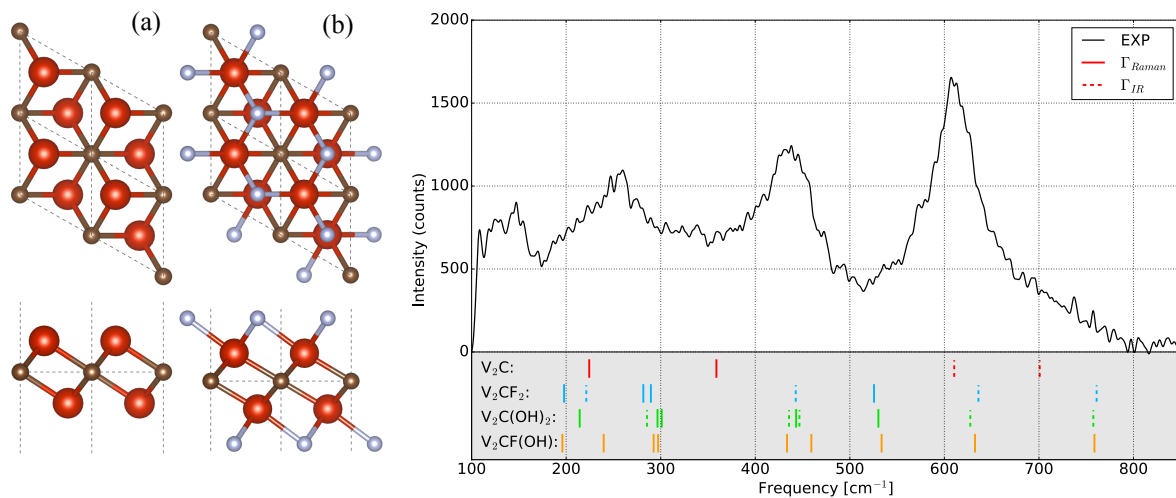
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In the present work, I focus on the characterization of V<sub>2</sub>C-based MXene systems and deal with structural, electronic and vibrational properties. Firstly, I describe the pristine bare V<sub>2</sub>C monolayer (see Fig. 1(a)). Using first-principles calculations, I obtain the optimized crystal structure and the relative electronic band structure. Secondly, I calculate the vibrational normal modes thanks to density functional perturbation theory (DFPT) within the harmonic approximation. I discuss the Raman and infrared activity of the modes and compare the former with an experimental Raman spectrum (see Fig.2).

On top of the calculations for the pristine V<sub>2</sub>C, I perform a systematic analysis of 2D V<sub>2</sub>CT<sub>2</sub> mono-sheets (with T=F,O,OH) (see Fig.1(b)) with the aim to establish the role of surface terminal groups in the electronic and vibrational properties. More specifically, I show the improvement in approximating the experimental Raman peaks positions when considering 2D fully-terminated V<sub>2</sub>CT<sub>2</sub> systems (see Fig.2).

Finally, I present some recent results obtained for systems with mixed terminal groups (see Fig.2). The actual agreement between our experimental and theoretical results is relatively good and some perspectives for reducing the remaining discrepancies are proposed.



**Figure 1:** Atomic structure of (a) **Figure 2:** Raman spectrum of the exfoliated V<sub>2</sub>C collected at room temperature and (b) terminated V<sub>2</sub>C. The calculated phonon frequencies of the V<sub>2</sub>C, V<sub>2</sub>CF<sub>2</sub>, V<sub>2</sub>CT<sub>2</sub> (T=F,O,OH) with V and C V<sub>2</sub>C(OH)<sub>2</sub> and V<sub>2</sub>CF(OH) mono-sheets are included under the atoms in red and brown, experimental spectrum for comparison. Raman and infrared active respectively and the terminal frequencies are represented by solid and dashed lines, respectively. groups in blue.

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# Technological, medical and industrial applications

## MACROSCOPIC GRAPHENE ON INSULATOR FILMS FOR ELECTRONIC AND BIOMEDICAL APPLICATIONS

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We have developed a chemical vapor deposition (CVD) technique<sup>1</sup> of graphene on copper foils, which allows to produce a continuous hole-free graphene film up to macroscopic sizes (20x30 cm). The graphene film can then be transferred to a host substrate of any type, silicon wafers, glass, polymer etc. The transferred layer consists of a graphene poly-crystal strictly monolayer without holes, presenting electronic mobility of 5000 cm<sup>2</sup>/v/s and low square resistance (less than 1000 Ohm/square for an undoped monolayer).

I will present the applications of this process that we seek to develop in the fields of nanomechanics<sup>2</sup>, electronics and in the biomedical fields. For this latter application, we show that the combined aspects of cyto-compatibility<sup>3</sup>, flexibility and electrical conduction<sup>3</sup> open up new horizons for the realization of useful devices for the care of wounds. This involves the realization of new generation intelligent dressings based on the integration of graphene integration into intimate contact with the wound. the electrical dressing allows a reduction in the total healing time and is promising for chronic wounds.

### References

- [1] Z. Han et al, Advanced Functional Materials, **24**, Issue 7, Pages: 964–970, 2014
- [2] H. Tash et al. 2D Materials **4**, 025023 (2017).
- [3] F. Veliev et al, Biomaterials, Elsevier, **86**, pp.33–41 (2016).
- [4] F. Veliev et al. Frontiers in Neurosci. doi: 10.3389/fnins.2017.00466 (2017).

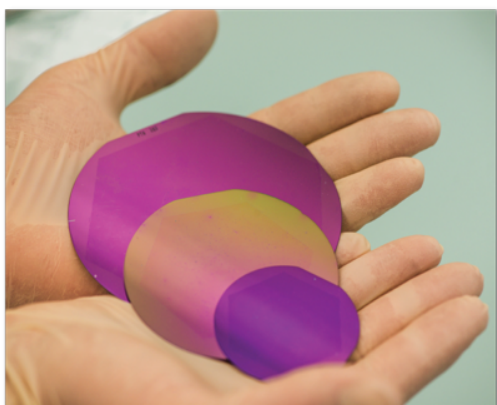


Figure 1 : Oxidized Si Wafers (2, 3 et 4 inches) Covered with monolayer graphene.



Figure 2 : Graphene on polymer wound dressing with electrical function.

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## NEW SCALABLE PROCESS FOR STABLE AND EFFICIENT GRAPHENE DOPING USING A PLATINUM SALT

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Graphene is an ideal material for future transparent conductive films (TCF) due to its extraordinary electrical and mechanical properties combined with high optical transparency. Today the needs of the TCFs have been increasing for flexible devices such as touch screens and organic light-emitting diodes (OLED). However, despite high carrier mobility, the sheet resistance of high quality graphene grown by chemical vapor deposition (CVD) remains far from that required for high performance electrodes due to its low carrier density. Graphene doping is thus essential to increase the carrier density for such practical applications. Ex-situ chemical doping by charge transfer mechanism is known to be particularly efficient to decrease the graphene sheet resistance. Metal chloride salts and more particularly gold chloride such as AuCl<sub>3</sub> or HAuCl<sub>4</sub> are reported to be among the most efficient wet chemical doping agents [1, 2]. Nevertheless such doping based on adsorbed species on the graphene surface without any chemical bonding presents a critical issue of stability [2].

Here, we demonstrate a new p-doping process using a platinum salt, which leads to high doping efficiencies as well as good temporal and thermal stabilities. A comparative study using PtCl<sub>4</sub> and HAuCl<sub>4</sub> dopant solutions was performed on monolayer graphene grown by CVD. For gold salt, the dopant effect is progressively lost when storing the sample in air atmosphere. Very interestingly, for PtCl<sub>4</sub>, a good stabilized doping efficiency can be maintained on long term (Figure 1). Higher the dopant amount deposited on the graphene surface is, lower the stabilized sheet resistance is, but lower the transmittance is. A low cost and large area compatible automotive spray process was innovatively used in order to accurately tune this dopant amount and also promote homogeneous deposit and reproducible performances. Optimized doping process with PtCl<sub>4</sub> led to a decrease of the sheet resistance down to 80% with respect to that of pristine un-doped graphene, corresponding to a stabilized sheet resistance of 135Ω/□ for a transmittance of 95 %. Moreover, it was shown that good improved electrical performances can be maintained for freshly doped samples annealed up to 200°C. Dopant features were studied using advanced characterization techniques. Atomic resolution TEM analysis revealed a formation of peculiar 2D amorphous network of Pt-Cl on graphene surface (Figure 2) which prevents metal diffusion on the surface. Chemical and morphological stability of gold and platinum salt during the thermal annealing were compared using in-situ XPS and in-situ TEM observations. Finally, the mechanisms of the efficient stable doping will be discussed.

### References

- [1] S. Bae et al., *Nature Nanotechnology*, 5 (2010) 574-8 and supplementary information  
 [2] K. C. Kwon et al., *J. Mater. Chem. C*, 1 (2013) 253-9

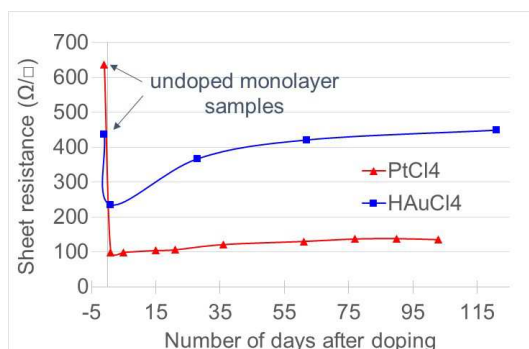


Figure 1: Evolution of sheet resistances with respect to time for some PtCl<sub>4</sub> and HAuCl<sub>4</sub> doped samples.

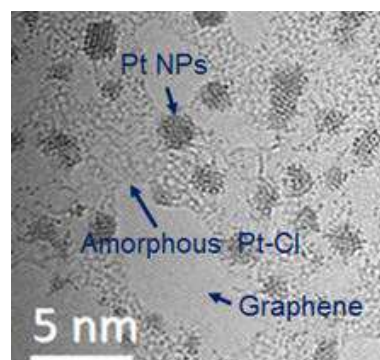


Figure 2: Atomic resolution TEM image of Pt-Cl amorphous 2D network formed on graphene surface.

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## In-situ TEM observation of doped MWNTs for electromigration study in CNT interconnect devices

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Miniaturization of transistor technology have led to decrease the dimensions of Copper (Cu) Back-end-of-line (BEOL) interconnects. As the width approach its electron mean free path (MFP) length, resistivity of Cu increases exponentially. Carbon nanotube (CNT) with its high conductivity, ballistic transport and high MFP has emerged as alternative candidate.

The CNT-interconnect devices has inherent problem of variable resistance due to 1:2 ratio growth of metallic to semiconductor growth, Gaussian distribution of diameter and variable contact resistance. Understandably not easy, structure control during growth of CNT holds the key [1]. Another method is by doping MWNTs to decrease variability with the added advantage of improved conductance [2].

Electromigration, movement of atoms during biasing, leads to breakage of interconnects. In this work, in-situ observation was carried out to study the structural properties of doped MWNTs using low-voltage transmission electron microscopy (LV-TEM). The Pt-salt dopants are inserted inside CNTs, expected to be a stable unit structure taking into account their integration into devices. However, in-situ heating experiments showed a crystallization of Pt around 350°C with an appearance of facets. We were also able to modify the phase and structure of dopants using electron beam irradiation as shown in figure 1. A simultaneous EELS analysis revealed a decomposition of Pt and Cl. From these results, the doping mechanism and the possible system degradation will be discussed.

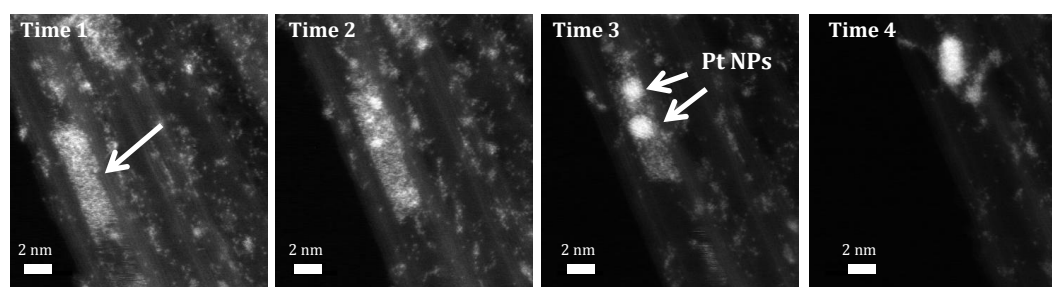


Figure 1: STEM images of a structure change of amorphous Pt-Cl to crystalline Pt inside the CNT under the electron beam irradiation.

[1] S. Zhang, L. Kang, X. Wang, L. Tong, L. Yang, Z. Wang, K. Qi, S. Deng, Q. Li, X. Bai, F. Ding and J. Zhang Nature, **543** (2017), 234

[2] D. Loc Duong, H. lee, K. Kang Kim, J. Kong, S. Mi Lee and Y. Hee Lee, Acs Nano, **4** (2010), 5430

## NEW HOT FILAMENT CVD PROCESS TO IMPROVE THE ELECTRICAL CONDUCTIVITY OF CARBON NANOTUBE FORESTS

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Vertically-aligned carbon nanotubes (CNT forest) have great potential in various electrical applications such as energy storage (lithium battery electrode [1]), microelectronic interconnects [2] or electrical cable [3]. These high end applications however require control and tuning of the CNT structure and electrical performances. To this end, we introduce here an original implementation of hot-filament-assisted catalytic chemical vapor deposition (CVD) in which filaments are made out of graphite. Besides complete elimination of metallic contamination, the array of graphite filaments in close proximity with the substrate creates a unique CNT growth mode combining an activated gas phase and fast switching infrared heating.

In this communication, we investigate the role of graphite hot filaments on the low pressure CVD growth of CNT forest using acetylene feedstock gas and alumina-supported iron catalyst. In particular, the growth kinetics, the morphology and the electrical resistivity of CNT forest obtained in standard CVD and graphite hot filament CVD (HF-CVD) have been compared. An original strategy based on pulsed growth was developed to measure the kinetics (fig.1). Each pulse corresponds to a specific set of process parameters (e.g. substrate or filament temperature). We obtained similar kinetics with two distinct activation energies for both thermal and HF-CVD processes. However, the catalyst lifetime, hence CNT forest height, is drastically enhanced with the new graphite HF-CVD process.

About electrical performances, since the quantification of the conductivity of CNT forest is a complex task, a dedicated protocol was developed. Localized growth of vertical CNT bundles, followed by mechanical alignment on the substrate is performed to obtain horizontal CNT bundles with controlled dimensions. Electrodes are finally patterned on the CNT bundle to carry out two and four point probe electrical measurements (fig2). Preliminary results indicate a > 30 % improvement in CNT resistivity with HF-CVD compared to thermal CVD. Furthermore, contrary to thermal CVD, the resistivity is uniform along of the CNT bundle with HF-CVD. This is linked to the enhanced catalyst lifetime which ensures uniform CNT density from the top to the base of the CNT forest. These results are confirmed by micro-Raman spectroscopy and electron microscopy analysis of the CNT structure, which also improves with HF-CVD.

The mechanisms driving the enhanced catalyst lifetime, CNT structural quality and electrical conductivity with graphite HF-CVD will be discussed.

### References

- [1] S. Liatard, K. Benhamouda, A. Fournier, R. Ramos, C. Barchasz, J. Dijon, Chem. Commun. **51**, 7749 (2015)
- [2] Dijon J, Chiodarelli N, Fournier A, Ramos R (2013). MRS Proceeding 1559
- [3] N. Bahabtu, M.J. Green, Pasquali (2008). Nano Today, 24-34.

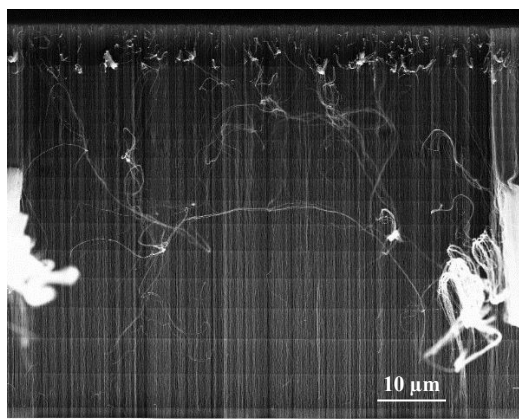


Figure 1 : SEM picture of a CNT forest grown with a pulsed HF-CVD process.

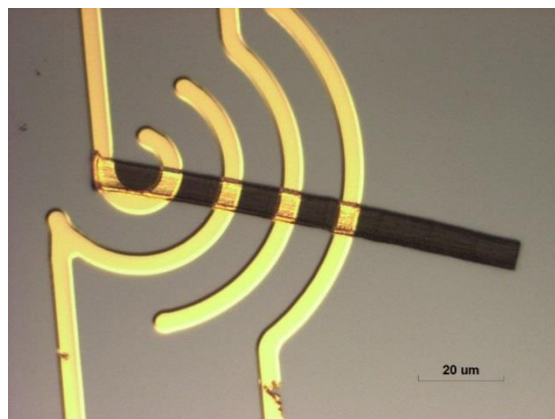


Figure 2 : Optical picture of an electrical device with horizontal CNT bundle connected with 4 circular electrodes.



# Electronic and transport properties

## A GRAPHENE ZENER-KLEIN TRANSISTOR COOLED BY A HYPERBOLIC SUBSTRATE

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Engineering of cooling mechanisms is a bottleneck in nanoelectronics. Whereas thermal exchanges in diffusive graphene are driven by defect-assisted supercollisions [1], the case of high-mobility graphene on hBN is radically different with a prominent contribution of remote phonons from the substrate. Here, we show that a bilayer graphene on hBN transistor can be driven in the Zener-Klein tunneling regime where current is fully saturated (Figure 1). Using sensitive GHz noise thermometry [2], we show that ZK-tunneling triggers a new cooling pathway due to the emission of hyperbolic phonons polaritons (HPPs) in hBN by out-of-equilibrium electron-hole pairs (Figure 2). The most obvious consequence is a reversal of the This mechanism is by far the most efficient in graphene and promotes graphene Zener-Klein transistors as a valuable route for power RF amplification.

### References

[1] A. Betz et al., Nat. Phys., 9 (2013) 109

[2] W. Yang et al., accepted in Nature Nanotech. (2017)

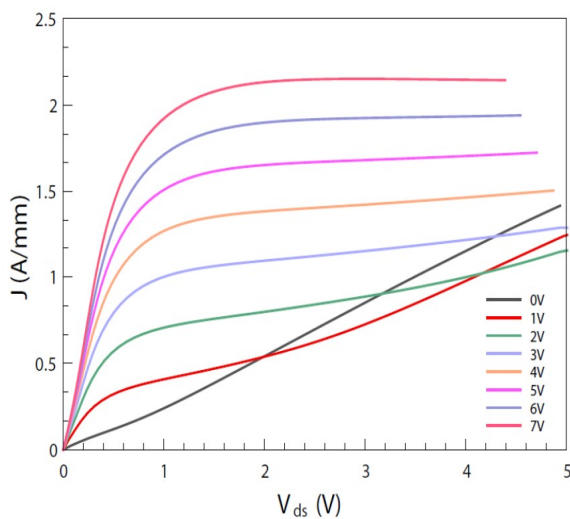


Figure 1 : Current saturation in *n*-doped high-mobility bilayer graphene on hBN transistor with a channel length of 4  $\mu\text{m}$ . At charge neutrality transport is dominated by Zener-Klein tunnelling.

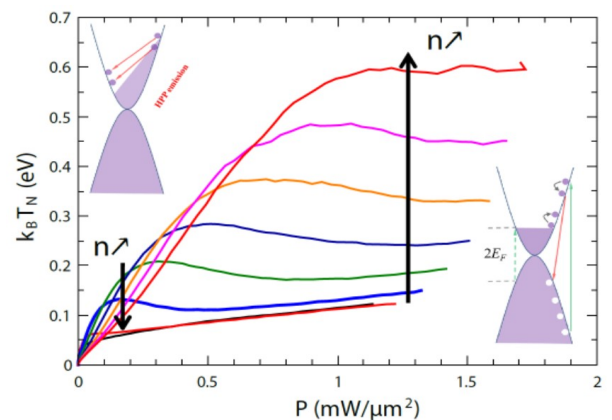


Figure 2 : Current saturation in *n*-doped high-mobility bilayer graphene on hBN transistor with a channel length of 4  $\mu\text{m}$ . At charge neutrality transport is dominated by Zener-Klein tunnelling.

# MAGNETIC-FIELD DRIVEN AMBIPOLAR QUANTUM HALL EFFECT IN EPITAXIAL GRAPHENE CLOSE TO THE CHARGE NEUTRALITY POINT

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Homogeneous Graphene Monolayer of large size can be produced on Silicon Carbide (SiC) and demonstrated its potential for fundamental physics (renormalization of the Fermi velocity) and applications (electrical metrology). The SiC substrate influences dramatically the structural and electrical properties of graphene. In particular, charge transfer takes place between graphene and the SiC/Graphene interface. Here, we evaluate the influence of disorder on graphene on SiC close to the charge neutrality point (CNP) by various methods based on transport measurements: i) at room temperature, by analyzing the dependence of the resistivity on the Hall coefficient; ii) by fitting the temperature dependence of the Hall coefficient down to liquid helium temperature; iii) by fitting the magnetoresistances at low temperature. All methods converge to give disorder of amplitude 20 meV. This is an intermediate values between what is reported for graphene on hBN (5 meV) and graphene on SiO<sub>2</sub> (50 meV). Because of this relatively low disorder, close to the CNP, at liquid helium temperature, unusual features can be observed. First, the sample resistivity does not exhibit the standard value  $\sim h/4e^2$  but increases when  $T$  is lowered and has an insulating behavior. This can be interpreted as the onset of Anderson localization. Besides, the Hall magnetoresistance changes its sign as a function of magnetic field, as shown in Fig. 1. The Hall resistance first becomes negative (hole type), but at higher magnetic field cancels and eventually stabilizes on a positive quantum Hall plateau (electron type). When the Hall resistance cancels, the longitudinal resistance shows a clear maximum. The usual Drude model based on two fluids (electrons and holes) fails to explain the data. By contrast, data are better explained by assuming asymmetry of the disordered density of states (DOS) at the CNP. In two-dimensional electron gases, an asymmetric DOS (*e.g.* created by Coulomb impurities) shifts the position of the quantum Hall plateaus [1]. The effect appears similar but more dramatic in graphene because of the ambipolar nature of this material. The microscopic origin of the asymmetric disorder cannot be unambiguously determined. However, we propose a model [2] based on the SiC substrate steps which distort the DOS. This model reproduces qualitatively the main observed features in magnetic field and temperature.

## References

- [1] R. Haug, R. Gerhardt, K. v. Klitzing and K. Ploog, [Phys. Rev. Lett. 59, 1349 \(1987\)](#)  
 [2] A. Nachawaty, M. Yang, W. Desrat, S. Nanot *et al.*, [Phys. Rev. B 96, 075442 \(2017\)](#)

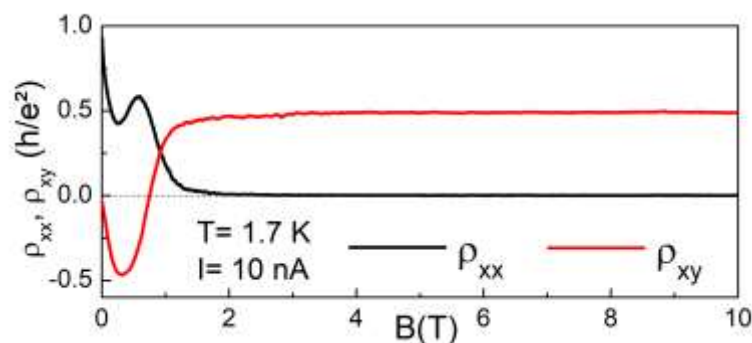


Figure 1: Longitudinal (black line) and transverse (red line) magnetoresistances observed at low temperature in a Hall bar made of graphene on SiC. Due to a specific disorder, the Fermi energy increases with magnetic field. At zero magnetic field, the Fermi energy lies below the CNP. At  $B = 1$  T, the Fermi energy has increased and is aligned with the CNP: the Hall resistance cancels, whereas a bump appears in the longitudinal resistance.

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## **STRONG COUPLING BETWEEN A CARBON NANOTUBE BASED QUANTUM DOT CIRCUIT AND A MICROWAVE CAVITY**

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Circuit quantum electrodynamics allows one to probe, manipulate and couple superconducting quantum bits using cavity photons at an exquisite level. One of its cornerstones is the possibility to achieve the strong coupling which allows one to hybridize coherently light and matter. Mesoscopic-QED inherits the c-QED toolbox and applies it to nano-circuits, which can range from closed systems (“atomic limit”) to open systems [1]. I will present cavity transmission and simultaneous transport measurements on a quantum dot circuit –a Cooper pair splitter- embedded in a microwave cavity. The Cooper pair splitter has a double quantum dot (DQD) architecture with an extra superconducting contact at the center. This hybrid circuit is implemented in a carbon nanotube. In contrast with standard asymmetric cavity-DQD coupling between the two quantum dots [2, 3], we demonstrate here symmetric coupling to internal transition of the double quantum dot. The central superconducting electrode allows modulation of the interdot tunneling, yielding to the coupling to internal degrees of freedom. By using this new coupling scheme, the strong coupling of a photonic system to a hybrid circuit has been reached [4]. Our findings open the path to ultra-long distance entanglement of quantum dot based qubits. They could be adapted to many other circuit designs, shedding new light on the roadmap for scalability of quantum dot setups.

I will also present current development on a nanofabrication technique allowing integration of pristin carbon nanotube in mesoscopic-QED devices. From this perspective we can envision carbon nanotube based circuit with high tunability and very low decoherence.

### **References**

- [1] L.E. Bruhat et al., PRX 6, 021014 (2016)
- [2] Mi et al., Science 10, 2469 (2016)
- [3] A. Stockklauser et al., PRX 7, 011030 (2017)
- [4] L. E. Bruhat, T. Cubaynes, et al. arXiv:1612.05214 (2016)

## 2D-0D HETEROSTRUCTURES FOR SPINTRONICS

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We report on the fabrication of 2D-0D heterostructures embedded in both planar and vertical nano-indented tunnel junctions for nanospintronics. Our devices based on Graphene-aluminum clusters peculiar structure show robust and reproducible features of single-electron transport[1] combined with magnetic functionalities[2]. We demonstrate that a single ferromagnetic electrode allows tuning the environmental charge hold by the nanoclusters, which provides spin-valve like magnetoresistance signatures with unique features, without need of spin coherent tunnelling transport. Beyond the capacity of graphene to act both as an electrode and as a platform for 2D-0D Van der Waals heterostructures, we extend its capabilities to reproducible magnetic functionalities on scalable device, opening up new prospects for multifunctional devices.

### References

[1] F. Godel et al., *Advanced Materials* 2017, 29 (3), 1604837 .

[2] L.D. Mouafo et al., *to be submitted*.

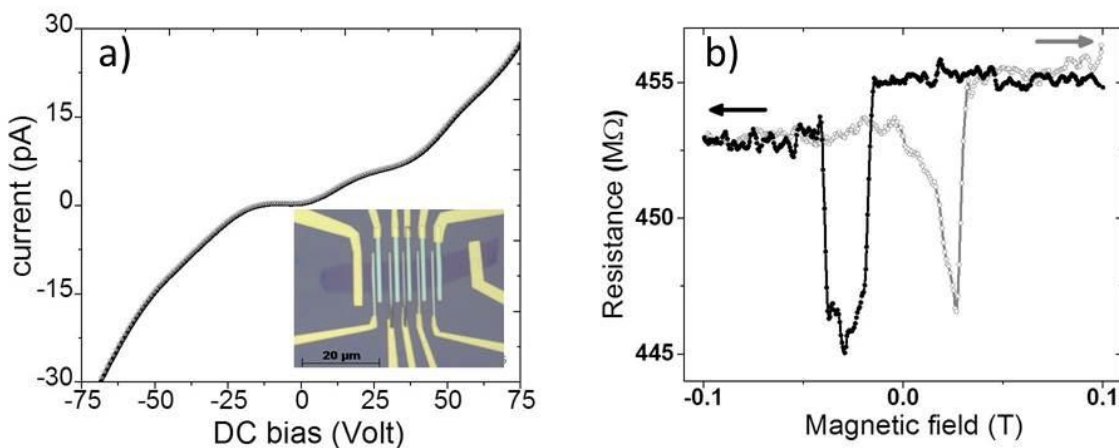


Figure : (a) Current-Voltage characteristics of a 2D-0D heterostructure measured at 1.5K (Inset : optical image of the device) showing well-defined Coulomb staircases. (b) Magnetoresistance characteristics of the same device showing spin-valve like signature.

# MAGNETOPLASMONIC ENHANCEMENT OF FARADAY ROTATION IN PATTERNED GRAPHENE METASURFACES

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When the time reversal symmetry is broken by a magnetic field, graphene displays strong non-reciprocal magneto-optical effects in the terahertz range such as Faraday rotation (FR) [1]. Unfortunately, these phenomena are linked solely to the cyclotron resonance (CR) and as such appear at very low frequencies ( $< 1$  THz) for practically achievable magnetic fields, therefore limiting their potential for applications. However, in this work we show that in periodic graphene-based structures (metasurfaces), and at room temperature, FR can be enhanced at frequencies well above the CR via the excitation of magneto-plasmons [2]. We have studied experimentally and theoretically the possibilities that various types of metasurfaces (square dots, circular antidots and metal-ring resonators on top of continuous graphene) offer to this end and compare their advantages and drawbacks (see Figure 1). Specifically, we find that graphene squares allow reaching the highest Faraday rotation among these structures. Graphene antidots show lower values of FR but permit to tune, via electrostatic gating, the amplitude and (simultaneously) the resonant frequency of the Faraday rotation [3]. Finally, metal-ring resonators offer the possibility to control the amplitude of the magneto-plasmonic resonance independently from its frequency. In all cases our simulations agree very well with the experimental data.

## References

- [1] I. Crassee, et. al., *Nature Physics* 7, 2011, 48–51  
 [2] J-M Poumirol et. al., *Nature Communications* 8, 2017, 14626  
 [3] P. Q. Liu et. al., *Optica*, 2 2009, pp. 135-140.

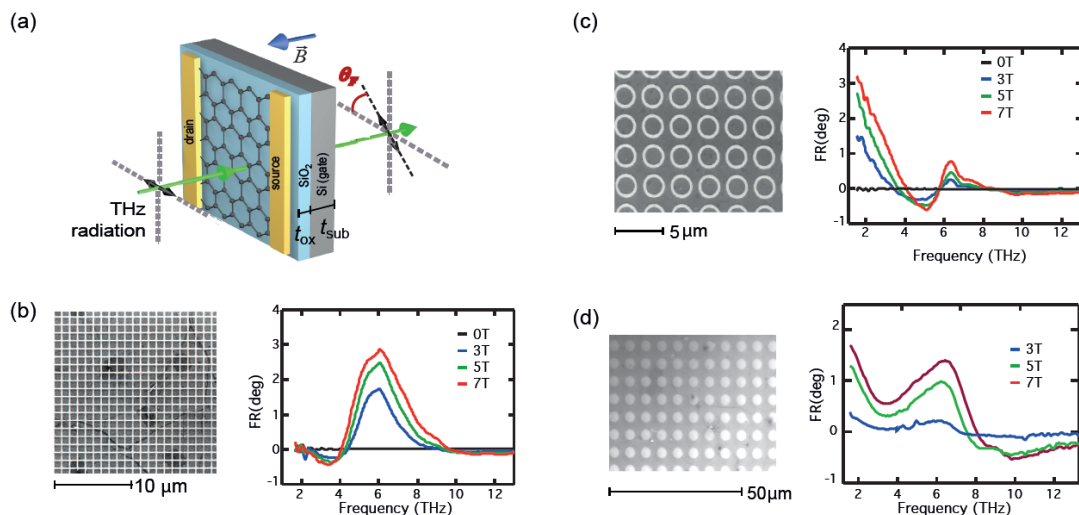


Figure 1 : (a) Diagram of the measurement configuration.  $t_{ox} = 280\text{nm}$ ,  $t_{sub} = 525\text{nm}$  (b) left : SEM pictures of the nano-patterned graphene square dot lattice sample. Right : Faraday rotation measured on this sample for different magnetic fields. (c) and (d) same as (b) but for hybrid metal-graphene sample and anti-dot square array.

# Opticals properties

## NANOCAVITY-COUPLED CARBON NANOTUBES FOR NEAR-INFRARED PHOTONICS

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The tunability of light-matter coupling allows for the observation of various physical phenomena ranging from spontaneous emission enhancement via the Purcell effect (in the weak coupling regime) to Bose-Einstein condensation of exciton-polaritons (strong coupling regime). For the practical exploitation of these interactions near-infrared emitting single-walled carbon nanotubes (SWCNTs) are an excellent building block as they combine highly bound excitons with large oscillator strength and narrow transitions with high charge carrier mobility. Here, we show that in order to tune light-matter interactions in SWCNTs, surface lattice resonances (SLRs) supported by periodically arranged gold nanodisks can be readily implemented (Figure 1). The formed plasmonic crystals combine the high quality factors of photonic cavities with much smaller mode volumes due to the sub-diffraction mode confinement of surface plasmons.

For thin (100 nm) layers of sorted (6,5) SWCNTs on such nanodisk arrays we take advantage of the weak coupling regime to increase emission efficiency and improve directionality. By varying the interdisk distance the random network of (6,5) SWCNTs (emitting nonpolarized light at  $\sim 1000$  nm) is turned into a broadband tunable ( $\sim 1000$ -1500 nm), directional and polarization-selective light source [1]. For samples with thick (200-300 nm) layers of (6,5) SWCNTs, we achieve strong coupling and the formation of new quasiparticles, plasmon-exciton polaritons (Figure 1). We use the coupled-oscillator model to quantify this regime and to fit experimental reflectivity and photoluminescence results. The extracted coupling strength values of around 125 meV place these plasmon-exciton polaritons at the lower limit of the ultrastrong coupling regime (i.e.,  $>10\%$  of the excitonic transitions energy) [2]. Electrically driven operation of the discussed plasmonic crystals [3,4] together with adjustments of additional parameters (e.g., SWCNT density, SLR dispersion and excitation conditions) may further advance insights into plasmonic crystals in the near-infrared and the growing field of plasmon-exciton polaritons, quantum condensation and polariton lasing.

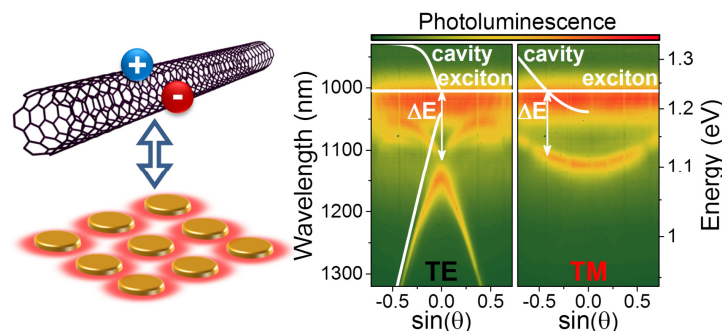


Figure 1: Illustration of (6,5) SWCNTs coupled to plasmonic crystals (left), and (right) angle- and polarization-resolved photoluminescence in the strong coupling regime (uncoupled exciton, upper and lower SLRs states are indicated with the white lines).

### References

- [1] Y. Zakharko, et al., Nano Lett. 16, 3278 (2016).
- [2] Y. Zakharko, et al., Nano Lett. 16, 6504 (2016).
- [3] Y. Zakharko, et al., ACS Photonics 3, 2225 (2016).
- [4] Y. Zakharko, et al., Optics Express 25, 18092 (2017).



## Fine structure of excitonic states in hBN/TMD monolayer/hBN van der Waals heterostructures

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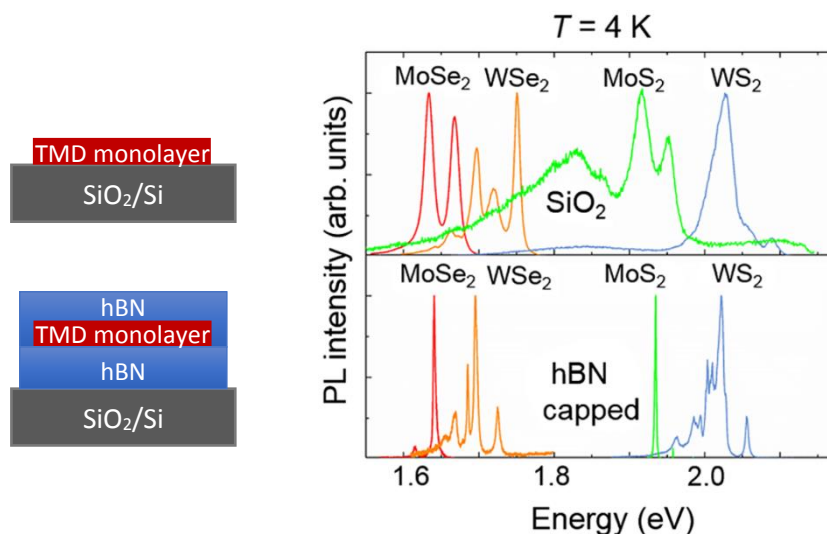
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Transition Metal Dichalcogenides (TMDs) have emerged as a very enthralling class of 2D materials presenting strong light-matter interaction governed by robust excitons and interesting valley selective optical selection rules. Nevertheless, in-depth studies of these properties have been prevented by large optical transition linewidths (a few tens of meV) resulting from inhomogeneous broadening. To tackle this problem, we fabricated van der Waals heterostructures by encapsulating TMD monolayers into hBN (see Fig). This new dielectric environment composed of atomically flat and charge free surface of hBN induces a strong reduction of TMD excitonic transitions linewidths which approach the homogeneous limit (<2 meV) (see Fig) [1]. As a consequence, we are able to identify several excitonic species in the optical spectra.

First, we performed non-standard polarization-resolved photoluminescence experiments by exciting and collecting signal from the edge of the heterostructures [2]. When the electric field is oriented perpendicular to WSe<sub>2</sub> or WS<sub>2</sub> monolayers, we observe the dark exciton state which is forbidden in standard normal incidence experiments. Further investigation with magneto-photoluminescence experiment revealed the fine structure of this dark exciton [3]. Secondly, by embedding the van der Waals heterostructure in a charge tunable device, we access both positive X<sup>+</sup> and negative X<sup>-</sup> trions. Thanks to the narrow linewidths, we clearly measure a splitting of 6 meV between the intravalley and the intervalley X<sup>-</sup> trion of WSe<sub>2</sub> [4]. Finally, we highlighted an “upconversion” phenomenon resulting in the emission of the B exciton and of the excited states of the A exciton (2s, 3s) when we excite resonantly the A exciton ground state (1s) [5].

### References

- [1]: F. Cadiz et al., *Excitonic linewidth approaching the homogeneous limit in MoS<sub>2</sub> based van der Waals heterostructures: accessing spin-valley dynamics*, PRX 7,021026 (2017)  
 [2]: G. Wang et al., *In-plane Propagation of Light in Transition Metal Dichalcogenide Monolayers: Optical Selection Rules*, PRL 119, 047401 (2017)  
 [3]: C. Robert et al., *Fine Structure and Lifetime of Dark Excitons in Transition Metal Dichalcogenide Monolayers*, arXiv:1708.05398, PRX submitted (2017)  
 [4]: E. Courtade et al., *Charged excitons in monolayer WSe<sub>2</sub>: experiment and theory*, PRB 96, 085302 (2017)  
 [5]: M. Manca et al., *Enabling valley selective exciton scattering in monolayer WSe<sub>2</sub> through upconversion*, Nature Communications 8, 14927 (2017)



## STUDYING THE GROWTH OF SINGLE-WALLED CARBON NANOTUBES BY OPTICAL MEANS

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<sup>2</sup>Laboratoire d'étude des microstructures, CNRS-ONERA, Châtillon, France.

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Controlling the structure and arrangement of single-walled carbon nanotubes (SWCNTs) directly during their growth constitutes a central bottleneck for the applications of SWCNTs in numerous fields including microelectronics. Catalytic chemical vapor deposition (CCVD) is currently the most popular method for synthesizing SWCNTs because it offers more defined and versatile growth conditions, thus allowing to grow SWCNTs with a better control of their structure, orientation, surface density and purity. Although many groups reported catalyst systems and growth conditions yielding high selectivity for specific diameters or chiral structures, a profound understanding of the processes impacting the structural distribution of SWCNTs is still missing. Two main reasons can explain the difficulty to experimentally correlate growth and structural features: 1) monitoring the growth of single-walled carbon nanotube still remain challenging 2) determining SWCNT structure usually requires a combination of methods. These two problems are even more acute when dealing with individual nanotubes.

In this contribution, we will show optical methods of spectroscopy and microscopy that help addressing this issue. First, we will present *in situ* and *ex situ* Raman measurements used to study the dynamics of the different populations of SWCNTs during their growth by CCVD [1]. Importantly, this study reveals that the nanotube diameter distribution strongly evolves during SWCNT growth but in dissimilar ways depending on the growth conditions. The origins of these evolutions will be discussed. Second, we will show how polarization-based optical methods can be used to monitor the growth of individual SWCNTs on substrates and determine their structure. We will notably show that individual SWCNTs on substrate can be imaged during their growth at close to millisecond time resolution. We will also propose a model for interpreting the optical spectra of individual SWCNTs as a function of the cross-polarization angle and of the substrate of interest [2].

### References

[1] Navas et al, ACS Nano 2017, 11, 3081–3088

[2] Monniello, Tran, Jourdain et al., in preparation.

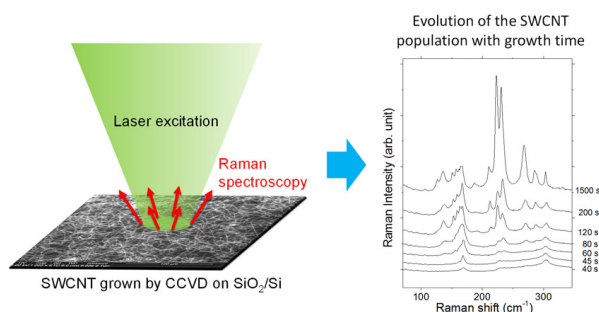


Figure 1: *In situ* Raman studies showing the evolution of the SWCNT diameter distribution during growth.

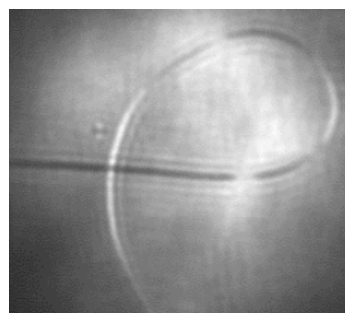


Figure 2: Individual SWCNT on a Si/SiO<sub>2</sub> substrate imaged by polarization-based optical microscopy.

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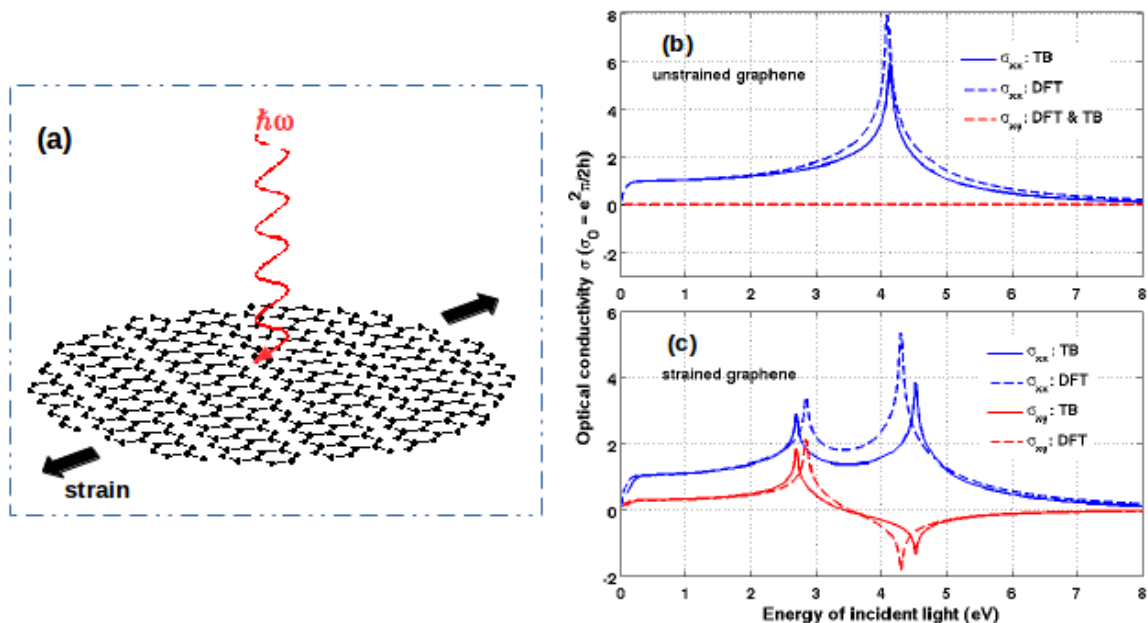
## OPTICAL HALL EFFECT IN STRAINED GRAPHENE

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The Hall effect is a fascinating phenomenon describing electrical conduction transverse to an applied electric field in systems subjected to a magnetic field. Although most of the studies have concentrated on static cases, the optical Hall effect is another exceptional feature [1]. When passing an optical medium in a magnetic field, the polarization of light can be rotated either when reflected at its surface (Kerr effect) or when transmitted through the system (Faraday rotation). This phenomenon is a direct consequence of the optical Hall effect arising from the light-charge carrier interaction in solid state systems under the influence of magnetic field, in analogy with the static effect. The optical Hall effect has been explored in many thin films [2] and also more recently in 2D layered materials [3]. In this talk [4], we present an alternative approach based on strain engineering to achieve an optical Hall conductivity in graphene without magnetic field. Essentially, strain breaks the lattice symmetry and hence can result in a finite optical Hall conductivity (see Fig.1). First-principles calculations also predict this anomalous Hall effect in other 2D materials. Combining with the possibility of tuning the light energy and polarization, the strain amplitude and direction, and the nature of the optical medium, large ranges of positive and negative Hall conductivities are predicted, thus opening the way to use these atomistic thin materials in novel specific opto-electro-mechanical devices.

### References

- [1] M. Schubert et al., J. Opt. Soc. Am. A **33**, 1553-1568 (2016).  
 [2] V. A. Volkov et al., JETP Lett. **43**, 326-329 (1986); F. Kuchar et al., Phys. Rev. B **33**, 2965 (1986); Y. Ikebe et al., Phys. Rev. Lett. **104**, 256802 (2010); M. Kargarian et al., Sci. Rep. **5**, 12683 (2015).  
 [3] T. Morimoto et al., Phys. Rev. Lett. **103**, 116803 (2009); I. Crassee et al., Nat. Phys. **7**, 48-51 (2011); R. Shimano et al., Nat. Commun. **4**, 1841 (2013).  
 [4] V. Hung Nguyen, A. Lherbier, and J.-C. Charlier, 2D Mater. **4**, 025041 (2017).



**Figure 1:** Schematic of the opto-electro-mechanical graphene-based system (a). Optical conductivities predicted by DFT and TB approaches in graphene without (b) and with strain (c).

# Chemistry and functionalization

# MILD COVALENT FUNCTIONALIZATION OF SINGLE-WALLED CARBON NANOTUBES BY ELECTRO-ACTIVE GROUPS FOR BIOELECTROCHEMICAL SENSORS

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In this talk, a mild covalent functionalization process of single-walled carbon nanotubes (SWCNTs) will be presented. The process uses microwave irradiation in mild acidic conditions to convert pre-existing defects to COOH functional groups on SWCNT side-walls, without damaging their structure integrity and electronic properties. These anchorage groups are used to graft electroactive ferrocene derivatives (see Figure 1). Experimental results from Raman scattering spectroscopy, thermogravimetric analysis coupled to mass spectrometry, X-ray photoelectron spectroscopy and scanning transmission electron microscopy (STEM) coupled to electron energy loss spectroscopy (EELS) at the atomic resolution will be shown. These complementary techniques allow asserting the covalent nature of the functionalization process and the localization, at a molecular level, of the grafted ferrocene groups. Indeed, since the functionalization process is very soft, we have carefully checked that impurities have no contribution for the resulting biosensor. The resulting functionalized SWCNTs are incorporated at a glassy carbon electrode (GCE) with some specific enzymes and the obtained bioelectrochemical sensor is characterized towards the successful detection of D-sorbitol in aqueous solutions. Several other applications of this kind of bioelectrochemical device will also be presented as interesting future perspectives of this work.

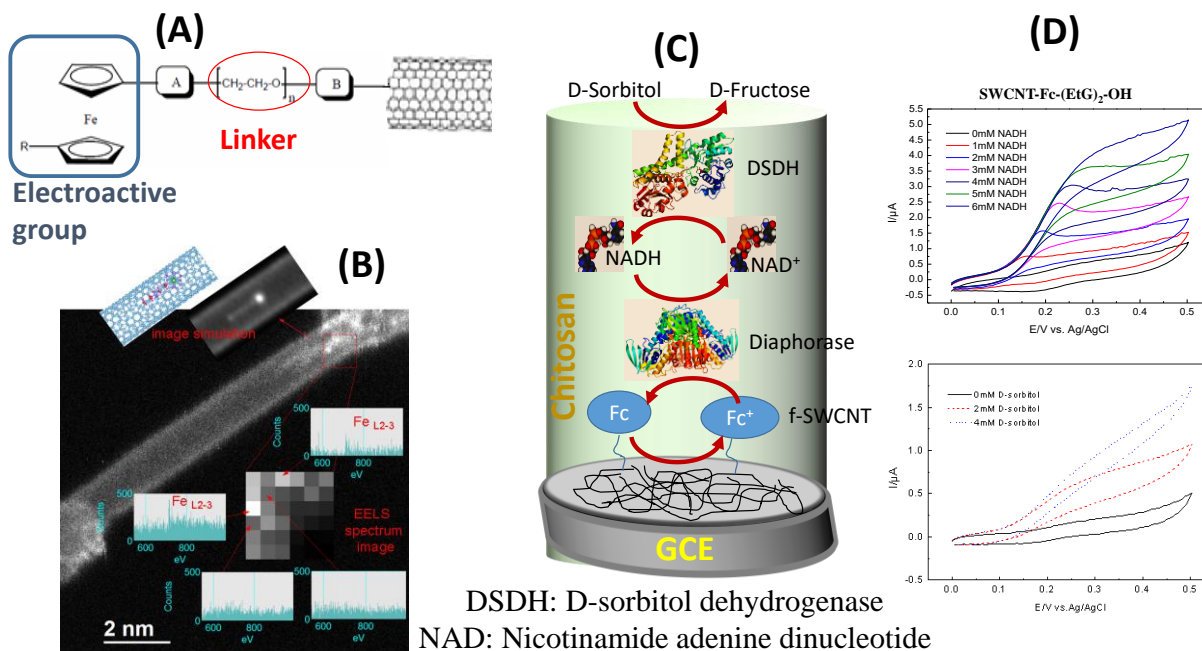


Figure 1 : (A) Covalent functionalization of single-walled carbon nanotubes (f-SWCNT) with ferrocene derivatives; (B) The covalent grafting will be checked by several advanced techniques such as STEM coupled to EELS; (C) The complete biosensor made with f-SWCNT, and NADH cofactor and enzymes for the electrochemical detection of D-sorbitol in aqueous solution; (D) The cyclic voltamperograms obtained with the biosensor, for several NADH concentrations in solution (top) and for the complete biosensor with several D-sorbitol concentrations in solution (bottom).

## BACKSIDE ABSORBING LAYER MICROSCOPY: WATCHING GRAPHENE CHEMISTRY

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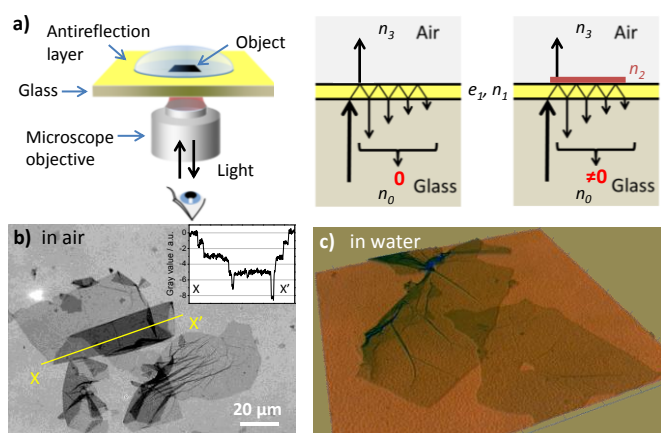
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The rapid rise of 2-dimensional nanomaterials implies the development of new versatile, high-resolution visualization and placement techniques. For example a single graphene layer becomes observable on Si/SiO<sub>2</sub> substrates by reflected light under optical microscopy because of interference effects when the thickness of silicon oxide is optimized.<sup>1,2</sup> However, differentiating monolayers from bilayers remains challenging and advanced techniques like Raman mapping, atomic force microscopy (AFM) or scanning electron microscopy (SEM) are more suitable to observe graphene monolayers. The two first are slow and the third one is operated in vacuum so that in all cases real-time experiments including notably chemical modifications are not accessible.

Here, we introduce a new wide-field optical microscopy technique: Backside Absorbing Layer Microscopy (BALM), which uses Anti-Reflection and Absorbing (ARA) layers to achieve extreme contrast at an interface.<sup>3</sup> It combines the vertical *sub*-nm sensitivity of an AFM with the versatility and real-time imaging capabilities of an optical microscope. We demonstrate that this technique allows imaging very easily 2D materials like graphene oxide and MoS<sub>2</sub>, both in air and in water, with extremely high resolution (see Figure). In addition, it also provides chemical contrast: we are notably able to clearly differentiate GO flakes from reduced graphene oxide flakes (r-GO) even though they only differ by the density of oxygen functions. BALM also permits to monitor surface reactions *in situ*. As examples, we followed the deposition of nanoparticles on GO and we took advantage of the high-resolution and real-time imaging of BALM to study the dynamics of the adsorption of small molecules on GO. Finally we show that, thanks to its favorable geometry, the BALM technique can be naturally combined with other techniques, notably electrochemistry and that its use is not limited to 2D materials.

### References

- [1] P. Blake, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth and A. K. Geim, *Appl. Phys. Lett.* 91 (2007), 063124.  
 [2] S. Roddaro, P. Pingue, V. Piazza, V. Pellegrini and F. Beltram, *Nano Lett.* 7 (2007), pp. 2707-2710.  
 [3] S. Campidelli, R. Abou Khachfe, K. Jaouen, J. Monteiller, C. Amra, M. Zerrad, R. Cornut, V. Derycke and D. Ausserré, *Sci. Adv.* 3 (2017), e1601724.



**Figure:** a) Representation of the BALM geometry: the image is obtained in reflected light microscopy; the contrast is enhanced for the part of the sample which is very close to the surface and the half-space on the top remains accessible. b) BALM image of GO imaged in air; inset: light intensity as a function of the number of layers. c) BALM image of GO obtained in water (RGB, with topographical representation of the total reflected intensity).

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# Graphene for interfacing neurons

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Graphene offers an ideal platform for recording and culturing neural networks, regarding its exceptional neuronal affinity and the presence of readily accessible surface charges which give the unprecedented possibility to realize a direct coupling with cells. Here, we report the cytocompatibility study of pristine monolayer graphene, and its significant advantage for neuromedicine and fundamental research compared with the current electrodes materials of neuronal interfaces. We have shown that CVD-grown graphene monolayers [1] actively promotes neurites outgrowth without any surface functionalization with cell-adhesive coating (for instance poly-L-lysine). Our investigation with Raman spectroscopy show the impact of graphene crystallinity on the neurons adhesion and further growth, the monolayer becoming cell-repulsive with increasing amount of defect [2]. The ability to control the neuronal affinity of the graphene-coated substrate opens the way to a variety of applications for patterning long-lasting (in-vitro) neural networks (Fig.1) and for in-vivo implants with reduced inflammatory response and glial scars [3].

Moreover, the nano-structuration of those large ( $\text{mm}^2$ ) graphene monolayers allows the fabrication of dense arrays of highly sensitive field effect transistors [4]. The graphene liquid-gated transistors (G-FETs, fig.1b) show reproducible electrical properties (mobility and sensitivity being around  $6000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  and  $3\text{-}4 \text{ mS/V}$ ) and allow a rapid detection of very small ( $75 \text{ } \mu\text{V}$ ) potential spikes comparable with neuronal signaling. As graphene could be transferred on a wide range of substrate, we realize graphene FETs arrays on Si/SiO<sub>2</sub>, glass and polyimide substrates and interfaced them with primary neurons (during about 21 days) to record their spontaneous electrical activity (Fig.1c). We are also investigating how structural 1D defect can interact with neurons and improve the GFET sensitivity [5].

## References

- [1] Z. Han, A. Kimoche, D. Kalita, A. Allain, H. Arjmandi-Tash, A. Reserbat-Plantey, L. Marty, S. Pairis, N. Bendiab, J. Coraux, V. Bouchiat, *Adv. Func. Mat.*, 24 (2014) 964-970.
- [2] Veliev, F., Briancon-Marjollet, A., Bouchiat, V., Delacour, C. *Biomaterials*, 86 (2016). 33-41.
- [3] V.S. Polikov, P.A. Tresco, W.M. Reichert, *Journal of Neuroscience Methods* 148 (2005) 1–18
- [4] Veliev, F., Han, Z., Briancon-Marjollet, A., Bouchiat, V., Delacour, C. (2017). *Frontiers in Neuroscience*, 11, 466.
- [5] Veliev, F., Kalita, D., Bourrier, A., Belloir, T., Bouchiat, V., Delacour, C. (2017) arXiv preprint arXiv:1705.00295.

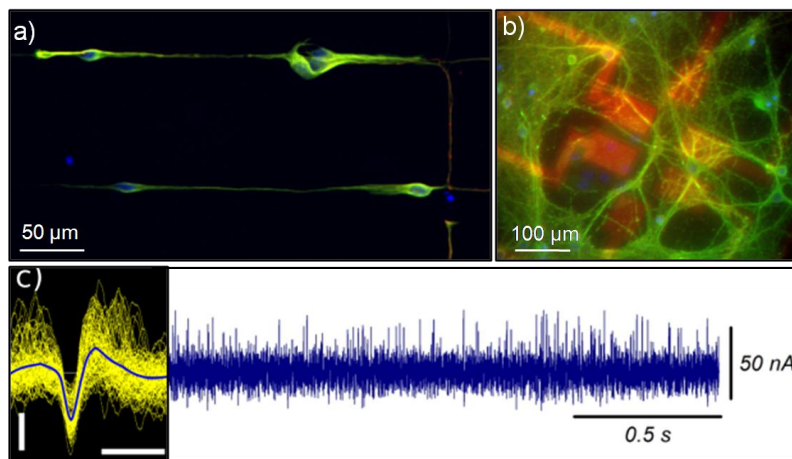


Figure 1: (a) Enhanced growth and confinement of primary hippocampal neurons (DIV2) on graphene micro-patterns. IF staining: the nuclei (bleu), the neurites (green) and the axons (red). (b) Neurons cultured 21 days on graphene FETs array. (c) Surimposed extracellular spikes (scale bar 2ms and  $200 \mu\text{V}$ ) detected with the G-FETs(left), obtained from the drain-source current  $I_{SD}$  time-traces (right).

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# SUPRAMOLECULAR SELF-ASSEMBLY OF PORPHYRINS MOLECULES ONTO SINGLE WALLED CARBON NANOTUBES PROBED BY OPTICAL SPECTROSCOPY

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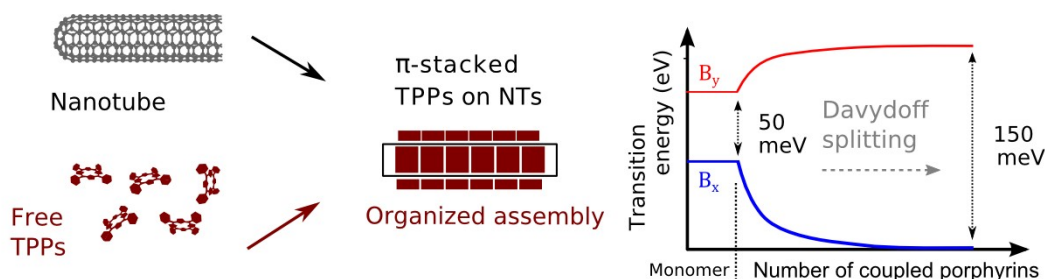
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The unique  $sp^2$  structure of a carbon nanotube makes it an ideal template for the adsorption of organic molecules. Our groups have developed donor/acceptor nanosystems based on tetraphenylporphyrin (TPP) molecules adsorbed on the outer surface of nanotubes (fig. 1). A very efficient energy transfer occurs from the TPP layer to the nanotube [1], leading to a resonant enhancement of the NT photoluminescence (PL). The outstanding chemical stability of the compounds together with preliminary evidences of a cooperative reaction [2] raises the question of the organization at the TPP/NT interface.

In this study, different porphyrin derivatives have been experimented to test the ability of the porphyrins to couple around the nanotube. Then, polarized PL spectroscopy has been used to probe the optical transitions of the  $\pi$ -stacked TPPs [3]. The main result is an amplification of the energy splitting between the TPP transitions, interpreted as a Davydoff splitting. Using a linear chain dipole coupling model, this effect is linked to the organization of the TPP layer on its nanotube template [3].

## References

- 1) Roquelet, C et al. (2010). Quantum efficiency of energy transfer in noncovalent carbon nanotube/porphyrin compounds. *Applied Physics Letters*, 97(14), 141918.
- 2) Vialla, F., **Delport, G.**, Chassagneux, Y., Roussignol, P., Lauret, J. S., & Voisin, C. (2016). Diameter-selective non-covalent functionalization of carbon nanotubes with porphyrin monomers. *Nanoscale*, 8(4), 2326-2332.
- 3) **Delport G.**, Vialla, F., Roquelet C., Campidelli S., Voisin C. & Lauret, J. S Optical evidences of the self-assembly of porphyrins around single walled carbon nanotubes. *Under revision*



**Fig. 1.** Process of self-assembly of porphyrins on carbon nanotubes, leading to a dipole coupling effect.

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# Graphene

## TUTORIAL ON GRAPHENE SPINTRONICS & VALLEYTRONICS

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Graphene has been heralded as the ideal material to achieve long spin propagation and further control the spin degree of freedom, in the quest of advancing non-charge-based information processing and computing, and for creating a new generation of active (CMOS compatible) spintronic devices together with non-volatile low energy MRAM memories. However, despite ultralow intrinsic and Rashba spin-orbit couplings (SOC) in clean graphene ( $\mu\text{eV}$  range), measured spin lifetimes remain in the range of several nanoseconds. This is orders of magnitude shorter than initially predicted, but already enough to envision disruptive non-charge-based room-temperature applications [1]. Simultaneously, the emergence of extra quantum degrees of freedom (sublattice pseudospin, valley isospin) in the electronic description of low energy excitations, points towards new approaches for information processing [2], extending the playground to valleytronics or multifunctional electronic devices harnessing all these degrees of freedom in combination with light or other external fields [1].

Besides, the physics of graphene “can be enriched and manipulated” by harvesting the large amount of possibilities of proximity effects with magnetic insulators, strong SOC materials (like metal-transition dichalcogenides-TMDC), topological insulators, etc. One challenge is to endow a sizable spin-to-current conversion efficiency by enhancing spin-orbit interaction (say up to meV), or to understand if similar valley Hall currents can be generated. Claims have been made that very large spin Hall effect, as well as topological valley Hall currents could be generated by using chemical functionalization with hydrogen or Au/Cu ad-atoms, or interfacing graphene with TMDC or hBN substrates [3]. Those results are however fiercely questioned [4] and the understanding of spin/valley dynamics for Dirac fermions in all those heterostructures remains elusive.

In this talk, after reminding some basic concepts of the electronic properties of graphene and other 2D materials, I will discuss the fundamentals of spin transport for Dirac fermions propagating in graphene, scrutinizing the effect of substrate and interfaces, as well as impurities and ad-atoms. The role of “pseudospin” in driving spin dephasing and relaxation will be explained in the ultraclean limit and the impact of proximity effects on spin lifetime anisotropy will be discussed [5]. Second, I will show how chemical functionalization (fluorine, gold and thallium ad-atoms) and proximity effects with other 2D materials can generate spin-dependent phenomena such as spin filtering, quantum spin Hall and tunable spin Hall effects [6]. Finally I will overview the open issues concerning valley Hall effect and valleytronics in the context of TMDCs and graphene/TMDC or hBN heterostructures.

### References

- [1] S. Roche et al, 2D Materials 2, 030202 (2015). J. Schaibley et al. Nature Reviews Materials 1, 16055 (2016)
- [2] L. E. F. Foa Torres, S. Roche, and J. C. Charlier, *Introduction to Graphene-Based Nanomaterials: From Electronic Structure to Quantum Transport* (Cambridge University Press, Cambridge, 2014). A. Rycerz, J. Tworzydł and C. W. J. Beenakker, Nature Physics 3, 172 - 175 (2007)
- [3] J. Balakrishnan et al., Nature Physics 9, 284 (2013). J. Balakrishnan et al., Nat. Comm. 5, 4748 (2014). A. Avsar et al., Nat. Comm. 5, 4875 (2014), R.V. Gorbachev et al. Science 346, 448 (2014).
- [4] Y. Wang, X. Cai, J. Reutt-Robey, and M. S. Fuhrer, Phys. Rev. B 92, 161411 (2015). A. A. Kaverzin and B. J. van Wees, Phys. Rev. B 91, 165412 (2015). Z. Wang et al, Nat. Comm. 6, 8339 (2015)
- [5] D. Van Tuan et al, Nature Physics, 10, 857–863 (2014); D. Van Tuan et al., Sci. Rep. 6, 21046 (2016); A.W. Cummings and S. Roche, Phys. Rev. Lett 116, 086602 (2016).
- [6] A. Cresti et al, Phys. Rev. Lett 113, 246603 (2014). D. Van Tuan and S. Roche, Phys. Rev. Lett. 116, 106601 (2016); D. Van Tuan et al. Phys. Rev. Lett 117, 176602 (2016); A. Cresti, B. Nikolic, J.H. Garcia, S. Roche, Rivista Nuovo Cimento 39,587-667 (2016). J.H. Garcia, A.W. Cummings, S. Roche, Nano Lett. 17 (8), 5078–5083 (2017). A.W. Cummings, J.H. García, J. Fabian, S. Roche, arXiv:1705.10972. J.M. Marmolejo-Tejada et al. arXiv:1706.09361.

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# Growth and structural properties

## ON DEMAND ANGLE CONTROL IN VAN DER WAALS HETEROSTRUCTURES

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Fabricating layered heterostructures from the assembly of layered 2D crystals (so called, van der Waals (vdW) materials) has emerged as a new paradigm in nano-structured materials. One intriguing feature of these hybrid systems is that device characteristics often depend critically on the crystallographic orientation between adjacent layers. A well-known example is graphene on boron nitride, where at zero relative angle between the two materials, a long-range Moiré potential strongly modifies the graphene band structure. Experimental studies of these effects however have remained significantly constrained, owing to the inability to precisely control the rotation order. Here we use a new device architecture where the crystallographic alignment between layers can be manipulated in situ, while characterizing the electronic response. Variation in the rotational orientation to better than 0.5 degree enables fine tuning of the Moiré wavelength (Fig. 1b-c) in graphene/BN heterostructures providing a new avenue to dynamically tune the graphene bandstructure. In twisted layer devices consisting of graphene in direct contact to HOPG graphite, the interlayer coupling can be varied by more two orders of magnitude. This transmission is characterized by a 60° periodicity corresponding to crystal symmetry with additional sharp decreases around 22° and 39°, which are among the commensurate angles of twisted bilayer graphene.

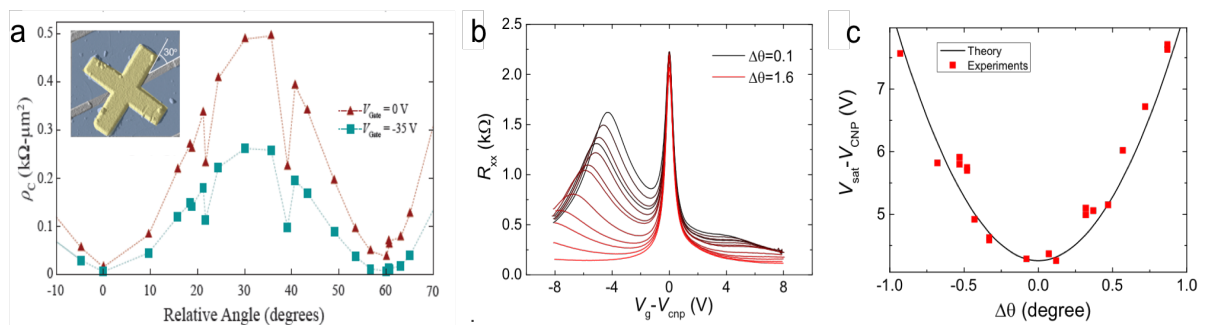


Figure 1: a Angular dependence of the resistivity from a graphene layer to graphite. b Variation of the resistance as a function of the back-gate for different layer alignment. c Variation of the position of the satellite peak observed in a as a function of the angle.

This new technique allows, for the first time, a systematic experimental exploration in twisted layered structures van der Waals heterostructures and it represents the first demonstration of in-situ modification of a 2D crystal band structure by controlled rotation of its angular orientation.

### References

- [1] T. Chari et al., Nano Letters 16, 4477–4482 (2016).

## CHEMICAL SYNTHESIS OF 2D HEXAGONAL BORON NITRIDE NANOSHEETS

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Boron nitrides (BN) are materials that contain an equal number of boron (B) and nitrogen (N) atoms. They exist under three crystalline forms that are isoelectronic to similarly structured carbon lattices: graphite-like hexagonal BN (h-BN) -the most stable phase under standard conditions-, diamond-like cubic BN (c-BN) - well known for its strong hardness- [1], and wurtzite BN (w-BN). Due to a structural analogy with graphite, h-BN shares common properties with it, such as an anisotropy along and perpendicular to a basal plane, high mechanical strength and thermal conductivity, and good lubrication. On the other hand, the unique structural characteristics of h-BN give it many other important electrical, optical and chemical characteristics.

With the continuous development of microelectronics, research on 2D materials, including h-BN, has attracted prime interest. A combination of different 2D structures with h-BN in stacked or integrated planar heterostructures can inherit the advantages / properties of h-BN and hetero-components and generate new functionalities that are of great interest to the scientific and industrial communities.

As a consequence, the development of a novel source for highly crystallized h-BN crystals, suitable for a further exfoliation, is a prime scientific issue. This presentation proposes a promising approach to synthesize pure and well-crystallized h-BN flakes, which can be easily exfoliated into Boron Nitride NanoSheets (BNNSs) [2]. This new accessible production process represents a relevant alternative source of supply in response to the increasing need of high quality BNNSs. The synthesis strategy to prepare pure h-BN is based on a unique combination of the Polymer Derived Ceramics (PDCs) route with the Spark Plasma Sintering (SPS) process [3]. Through a multi-scale chemical and structural investigation, it is clearly shown that obtained flakes are large (fig.1), defect-free and well-crystallized, which are key-characteristics for a subsequent exfoliation into relevant BNNSs.

### References

[1] Y. J. Tian, et al., *Nature*, 493 (2013), pp. 385-388.

[2] S. Yuan, B. Toury, C. Journet, A. Brioude, *Nanoscale*, 6 (2014), pp. 7838-7841.

[3] S. Yuan, S. Linas, C. Journet, P. Steyer, V. Garnier, G. Bonnefont, A. Brioude, B. Toury, *Scientific Reports*, 6 (2016), 20388.

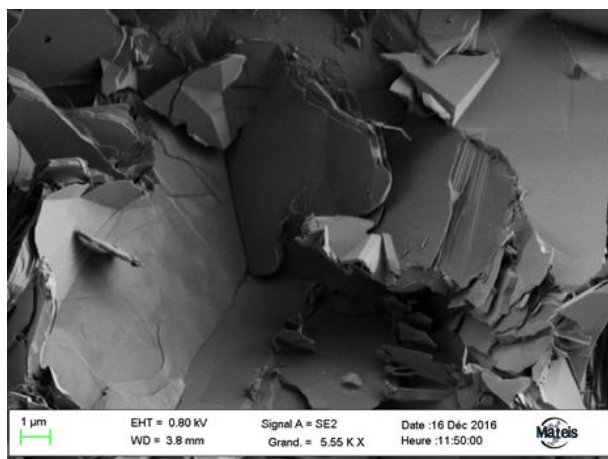


Figure 1: SEM image showing stacked h-BN layers with micrometric sizes.

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## EPITAXIAL GROWTH OF LOW DOPED MONOLAYER GRAPHENE ON 4H-SiC (0001) AT LOW ARGON PRESSURE

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Thermal decomposition of silicon carbide (SiC) provides transfer free and wafer-scale homogeneous graphene forming on a semi-insulating substrate. Large-area monolayer graphene growth was initially developed at the atmospheric pressure (around 900 mbar) in an argon ambient and at high temperature ( $>1650^{\circ}\text{C}$ )[1], [2]. However, it remains challenging to obtain films with different and controlled characteristics such as the number of graphene layers or the doping by tuning the growth parameters. In this work, we optimized the epitaxial growth of monolayer graphene (1LG) on 4H-SiC (0001) under a low argon pressure[3] of 10 mbar. This intermediate pressure allows growing a continued 1LG in a short process time of  $\sim 1\text{h}30$ .

Here, we discuss the initial growth stages from buffer layer to 1LG as a function of annealing temperature (same heating rate). The combined Raman spectroscopy and atomic force microscopy (AFM) analyses show that a buffer layer, fully covering the Si-face of SiC, forms as the first step of growth ( $1600^{\circ}\text{C}$ ). Subsequently, 1LG starts to grow at step edges ( $1700^{\circ}\text{C}$ ) and continue to cover the buffer layer with a step-flow growth mechanism, as shown in the literature[4], [5]. Eventually, continued large-scale graphene films were achieved at  $1750^{\circ}\text{C}$  with a reproducible process (Fig.1). These graphene films were characterised by Raman, STM and electrical measurement. The integrated intensity of G-band in Raman spectra normalized with respect to a HOPG reference,  $A_{\text{G}}/A_{\text{G-HOPG}}$ , of each spectrum in Raman map is very close to the experimental value reported for a 1LG[6]. Atomically resolved scanning tunnelling microscopy evidences a (6x6) superstructure, indicative of 1LG covering a reconstructed interface layer (Fig.2)[7]. Moreover, quantum Hall plateau values observed in our graphene layers confirmed both continuity and thickness of the 1LG film[8]. The carrier density of  $p_{\text{Hall}} \sim 10^{10} - 10^{11} \text{ cm}^{-2}$  in 1LG films can be achieved at 1.7K in helium atmosphere. Thus, our as-grown 1LG graphene films with low p-type carrier density provide perspectives for further studies and applications on graphene.

### References

- [1] C. Virojanadara *et al.*, *Phys. Rev. B*, 78 (2008), pp. 245403.
- [2] K. V. Emtsev *et al.*, *Nat. Mater.*, 8, 3 (2009), pp. 203–207.
- [3] P. Landois *et al.*, *Phys. Chem. Chem. Phys.*, 19, 24 (2017), pp. 15833–15841.
- [4] W. Norimatsu and M. Kusunoki, *Phys. Chem. Chem. Phys.*, 16, 8 (2014), pp. 3501.
- [5] G. Yazdi, T. Iakimov, and R. Yakimova, *Crystals*, 6, 5 (2016), pp. 53.
- [6] N. Camara *et al.*, *Phys. Rev. B*, 80 (2009), pp. 125410.
- [7] P. Lauffer *et al.*, *Phys. Rev. B*, 77 (2008), pp. 155426.
- [8] B. Jouault *et al.*, *Appl. Phys. Lett.*, 100 (2012), pp. 052102.

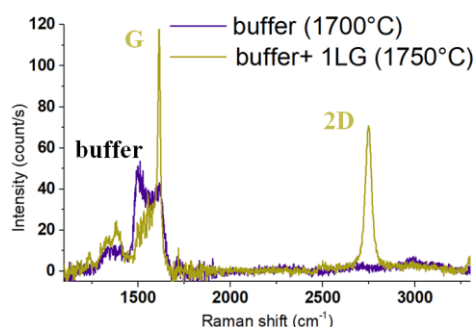


Figure 1: representative Raman spectra of buffer layer without graphene covered (violet) and monolayer graphene covering buffer layer (yellow).

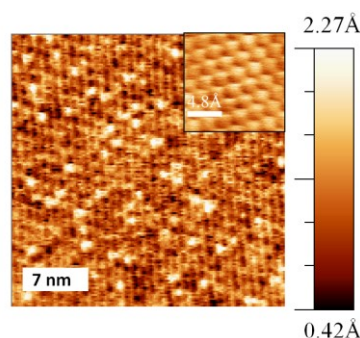


Figure 2: scanning tunneling microscopy image; inset demonstrates an atomic resolution.

## ***Growth modes and chiral selectivity of SWNTs***

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Since 25 years, significant progress has been achieved in the controlled synthesis of Single Walled Carbon Nanotubes (SWNTs), but we are still facing difficult issues concerning the yield and selectivity of their synthesis by Chemical Vapor Deposition. In such a complex problem, real understanding only results from coupling different experimental techniques, from chemical engineering approaches to atomic scale investigations by e.g. Transmission Electron Microscopy, with modelling and computer simulations<sup>[1]</sup>.

We have investigated the tube nucleation<sup>[2]</sup> and the state of a simple catalyst such as Ni, in presence of carbon<sup>[3]</sup>. Sustainable tube synthesis requires a dewetting of the catalyst nanoparticle, along with the growth of the carbon walls, to avoid its encapsulation and deactivation. We show that the properties of the Ni/sp<sup>2</sup> carbon interfaces are driven by the carbon fraction dissolved in the NP<sup>[4]</sup> that depends on the CVD process parameters, in particular on the choice of the carbon bearing precursor. These different carbon feeding regimes give rise to different growth modes<sup>[5]</sup>, corresponding to different structures of the NP/nanotube contact areas.

For carbon saturated nanoparticles<sup>[7]</sup>, the interface is reduced to a line contact, in which case a near armchair selectivity is sometimes reported, while lower dissolved carbon fractions lead to a lateral surface contact between the tube and the catalyst NP<sup>[8]</sup>. In the former case, we can develop a statistical thermodynamics model to relate the chirality distribution with the interfacial energy of armchair or zigzag bonds with the catalyst. Including the configurational entropy of the tube edge proves essential to obtain chiral distributions in fair agreement with the experimental ones. This model will thus support a systematic computer search for new selective catalysts.

### **References:**

- [1] Amara, H. *et al.* Phys. Rev. B **79**, 014109 (2009).
- [2] Amara, H. *et al.* Phys. Lett. **100**, 056105 (2008).
- [3] Magnin, Y. *et al.* Phys. Rev. Lett., **115**, 205502, (2015).
- [4] Diarra, M. *et al.* Phys. Rev. Lett., **109**, 185501 (2012).
- [5] Fiawoo, M.-F. C. *et al.* Phys. Rev. Lett., **108**, 195503 (2012).
- [6] Weatherup, R. S. *et al.* J. Am. Chem. Soc., **136**, 13698–13708 (2014).
- [7] He, M. *et al.* Carbon, **113**, 231-6 (2017) ; Nanoscale **4**, 7394 (2012).
- [8] J.-M. Aguiar-Hualde *et al.* Carbon N. Y. **120**, 226–232 (2017).



# Nanofluidics

## Nanofluidics: fluid transport at the molecular scale

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Nanofluidics is the frontier at which the continuum picture of fluid mechanics meets the atomic nature of matter. New models of fluid transport are expected to emerge from the confinement of liquids at the nanoscale, with potential applications in ultrafiltration, desalination and energy conversion [1-3]. Nevertheless, advancing our fundamental understanding of fluid transport on the smallest scales requires mass and ion dynamics to be ultimately characterized across an individual channel to avoid averaging over many pores. A major challenge for nanofluidics thus lies in building distinct and well-controlled nanochannels, amenable to the systematic exploration of their properties.

In this context a system of particular interest is represented by individual Nanotubes : measurements and simulations have found that water moves through carbon nanotubes at exceptionally high rates owing to nearly frictionless interfaces [4,5]. These observations have stimulated interest in nanotube-based membranes, yet the exact mechanisms of water transport inside the nanotubes and at the water-carbon interface continue to be debated, because existing theories do not provide a satisfactory explanation for the limited number of experimental results available so far. This lack of experimental results arises because, even though controlled and systematic studies have explored transport through individual nanotubes, none has met the considerable technical challenge of unambiguously measuring the permeability of a single nanotube.

In this seminar we will revisit the current state of the art of nanofluidics and we will discuss how nanoassembling and manipulation offer new tool to investigate the fluid transport at a scale where the limit of the classic description is met [2]. We will finally present our recent studies on fluid transport in individual nanotubes and we will put them in the perspective of the new field of carbon nanofluidics [6].

### References

- [1] L. Bocquet, E. Charlaix, **Chemical Society Reviews** **39**, 1073 - 1095 (2010)
- [2] D. Cohen-Tanudgi, J. Grossman, **Nanoletters** **12**, 3602-3608 (2012)
- [3] A. Siria *et al.*, **Nature** **494**, 455-458 (2013)
- [4] J.K. Holt *et al.*, **Science** **312**, 1034-1037 (2006)
- [5] K. Falk, F. Sedlmeier, L. Joly, R. R. Netz, L. Bocquet, **NanoLetters** **10**, 4067 (2010)
- [6] E. Secchi, S. Marbach, A. Niguès, D. Stein, A. Siria, L. Bocquet, **Nature** **537** 210 (2016)

## In-situ measurement of the length distribution of polymer-wrapped (7,5) single-walled carbon nanotubes in solution by analytical ultracentrifugation

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Single walled carbon nanotubes (SWCNTs) have a unique structure property correlation which allows the nanotube's chiral index and hence its diameter to be determined by spectroscopic methods such as absorption, fluorescence or Raman spectroscopy. In contrast, the length of a carbon nanotube has little influence on its optical properties and the AFM method has evolved as a standard approach to measure nanotube length distributions, even though the characterization method requires specific substrates and additional preparation steps and is associated with uncertainties due to nanotube bundling on surfaces or selective adsorption. Over the years, a range of in-situ methods have been explored such as dynamic light scattering, electrospray differential mobility analysis, diffusional trajectory, shear-aligned photoluminescence anisotropy, length analysis by nanotube diffusion method, and more recently analytical ultracentrifugation (AUC) and the electric-field induced differential absorption spectroscopy method (EFIDAS). Most of these methods have been explored for aqueous CNT dispersions whereas highly enriched semiconducting SWCNTs (>99% purity) can nowadays be obtained through wrapping of CNTs with polymers in toluene. These non-aqueous dispersions are of great interest for device applications [1, 2] and methods to measure in-situ the length distribution of CNTs in toluene, such as EFIDAS [3], are required. Here we show that AUC can be used to determine the in-situ length distribution of polymer-wrapped (7, 5) tubes in toluene. In AUC, the temporal and spatial dependent optical absorption is measured under centrifugation. By established data processing procedures (SEDFIT) the sedimentation coefficient distribution is obtained. Converting the coefficient distribution into length distribution is however challenging. It requires an appropriate model that correlates the sedimentation velocity to the length. Also, AUC is based on optical absorption and therefore yielding a volume distribution and not a number distribution as out of the analysis of AFM data. We will show how these challenges can be met and present a procedure that very nicely maps the AUC derived in-situ length distribution onto the corresponding ex-situ AFM data. Our data suggests that the friction coefficient of polymer-wrapped (7, 5) CNTs in toluene and its length dependence is very different to ionic surfactant-wrapped CNTs in water, as studied in the pioneering work of Fagan et al. [4].

### References

- [1] G.J. Brady, Y. Joo, M-Y. Wu, M.J. Shea, P. Gopalan, and M.S. Arnold, *ACS Nano* (8) 2014, pp. 11614-11621
- [2] F. Hennrich, W. Li, R. Fischer, S. Lebedkin, R. Krupke and M. Kappes, *ACS Nano*(10) 2016, pp. 1888-1895.
- [3] W. Li, F. Hennrich, B.S. Flavel, M.M. Kappes and R. Krupke, *Nanotechnology* (27) 2016, 375706
- [4] C.A.S. Batista, M. Zheng, C.Y. Khripin, X.Tu and J. Fagan, *Langmuir* (30) 2014, pp. 4895 - 4904.

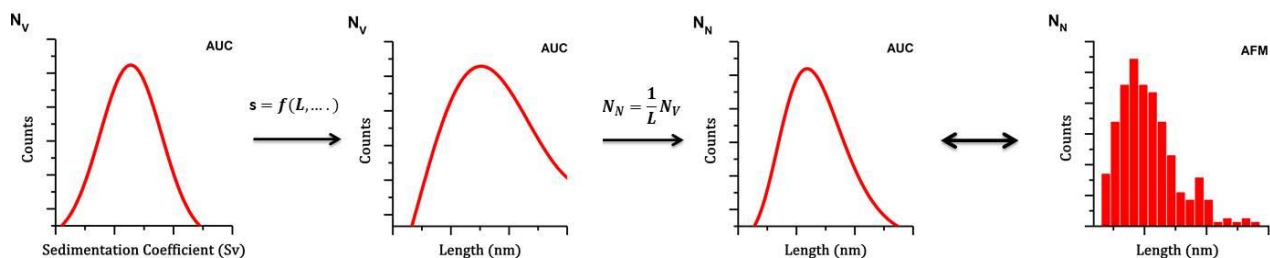


Figure 1: Converting AUC sedimentation coefficient distribution to length distribution. Comparison with AFM length distribution.

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# Gapped 2D materials

## QUANTUM DOTS IN 2D-SEMICONDUCTORS: LARGE-SCALE, DETERMINISTIC SINGLE-PHOTON SOURCES AND QUANTUM DEVICES

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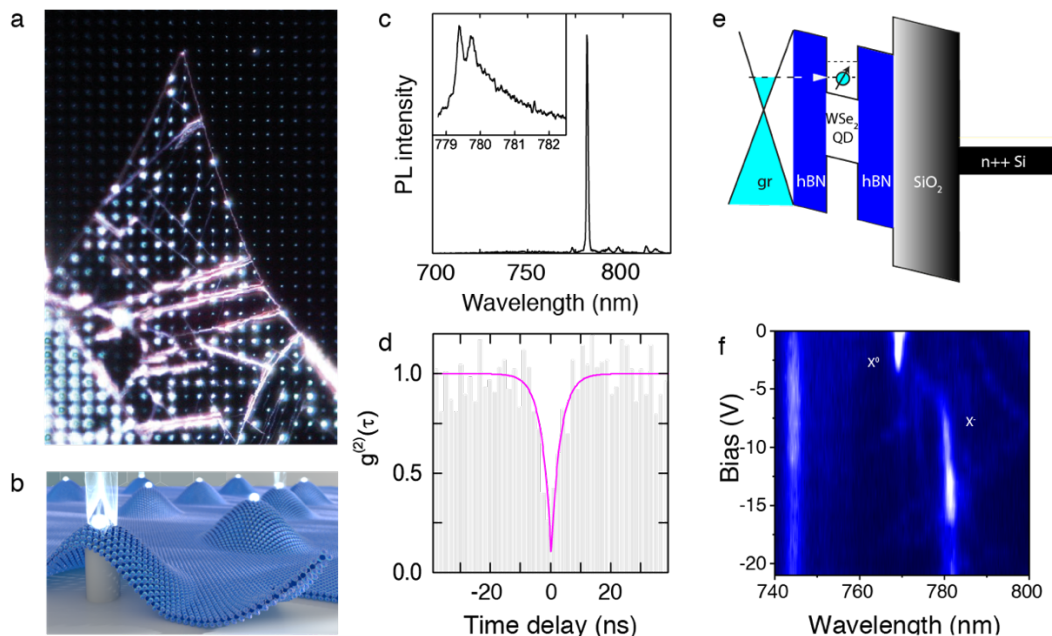
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The atomically-thin semiconductor family of transition metal dichalcogenides (2d-TMDs) offer technological advantages as platforms for quantum devices. Lack of dangling bonds, atomically-precise interfaces, absence of nuclear spins and ease of integration to form 2d heterostructures are just a few. I will present how we can deterministically create quantum dots (QDs) in 2d-TMDs, in large-scale arrays<sup>1</sup>. The QDs are single-photon sources, and exhibit better stability than their randomly-occurring counterparts. They are formed by stamping the monolayer flakes onto silica substrates that are patterned with nanopillars, over which the flake tents. I will report on the method and on the optical and magneto-optical characterization of the emitters. The QDs can be embedded within 2d-heterostructures to form functional quantum devices: we have used WSe<sub>2</sub> and WS<sub>2</sub> monolayers, along with graphene and hexagonal boron nitride, to create quantum light-emitting diodes that produce electrically driven single-photons<sup>2</sup>. Finally, I will introduce our current work: achieving charge-tunability of the WSe<sub>2</sub>-QDs using field-effect type 2d-heterostructures. We are able to controllably charge the QDs with single-electrons and single-holes within the same device – the first step towards the use of spin and valley pseudospin of confined carriers as optically addressable matter qubits in 2d materials.

### References

- [1] Palacios-Berraquero, C. *et al.* Large-scale quantum-emitter arrays in atomically thin semiconductors. *Nat. Commun.* **8**, (2017).  
 [2] Palacios-Berraquero, C. *et al.* Atomically thin quantum light-emitting diodes. *Nat. Commun.* **7**, 12978 (2016).



**Figure 1.** Monolayer of WSe<sub>2</sub> on nanopillar substrate: dark-field optical microscopy image (a) and schematic (b). c. Low temperature photoluminescence spectrum from a deterministic WSe<sub>2</sub> QD, d. photon-correlation measurement from WSe<sub>2</sub> QD confirming single-photon emission. e. Band diagram of charge-tunable 2d-heterostructure. f. Emission wavelength with respect to applied bias across heterostructure in (e), showing sharp change from X<sub>0</sub> to X-line.

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## GRAPHENE BASED ASYMMETRIC NANOSTRUCTURES FOR DETECTING TERAHERTZ RADIATION.

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Efficient detection of THz radiation is still a challengeable task. Increase in the sensitivity of the THz radiation detectors range can be achieved by reducing the size of the sensor element. Graphene is an almost ideal material for creating nanoscale structures that are suitable for this purpose. One of the major advantages of graphene is its high carrier mobility and the associated large coherence length, so that the band structure is determined by the size quantization and can be controlled via the geometry of the structure.

In this work we study graphene, graphene nanoribbons (GNRs) and carbon nanotubes (CNTs) embedded into a THz range antenna with asymmetric metallization so that the sensitive element is p-doped at the contact with gold and n-doped at the contact with vanadium (see Figure 1). We prove that such a structure operates as a Schottky diode [1]. Detection of the radiation takes place through the so-called rectification: due to asymmetry of the IV curve mean current under harmonically changing voltage is not zero. In case of a CNT rectification takes place due to transport through a Schottky barrier at V contact directly related to the nanotube's bandgap. In case of graphene the situation is more complicated. Transport of carriers through the p-n junction depends on the angle between the normal to the junction and the carrier momentum. For normally incident electrons there is no energy barrier and they shunt the nonlinear transport. At the same time current of the non-normally incident electrons is non-linear function of the applied voltage [2,3]. This scenario is evidenced by the temperature dependence of the response of our structures to the radiation.

Frequency dependence of the response is determined by excitation of the plasma waves in the channel between the antenna sleeves. To our knowledge it is the first time plasmonic effects are proved to affect the operation of graphene base THz radiation detection [4].

### References

- [1] I. Gayduchenko, A. Kardakova, G. Fedorov, et al., J. Appl. Phys. 118, 194303 (2015)
- [2] M. I. Katsnelson, K. S. Novoselov and A. K. Geim, Nature Physics 2, 620 - 625 (2006)
- [3] S. Sutar, E. S. Comfort, J. Liu, T. Taniguchi, K. Watanabe, and J. U. Lee, Nano Lett., 12, 4460–4464 (2012)
- [4] V. Ryzhii, T. Otsuji, M. Ryzhii, V.G. Leiman, G. Fedorov, et al., J. Appl. Phys. 120, 044501 (2016)

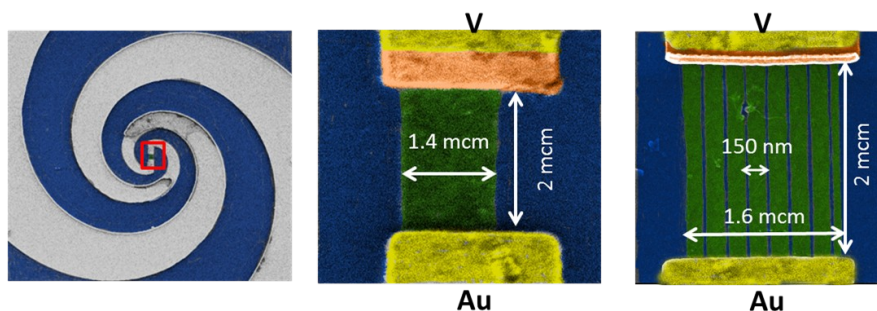


Figure 1 : False color SEM images of (left to right): the antenna, graphene sample, GNR sample

## Exciton dispersion and layer stacking in hexagonal boron nitride

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Among 2D materials, hexagonal boron nitride (hBN) stands out owing to its wide band gap (~6 eV in the bulk) and the possibility to tune it by nanostructuring. In this context, several investigations have been carried out on hBN thin films, most of them focusing on the mono-layer. However fundamental aspects of exciton formation and relaxation in hBN are still unclear at the bulk level. For instance, the usual theory of light emission in indirect-gap semiconductors, recently invoked [1,2], contrasts with its very high intensity [3,4,5].

In this work we address the question from the theoretical side. Established theoretical simulations of the band structure predict the single-particle gap to be direct in the monolayer and indirect in the bulk [6,7], pointing to a relation between the nature of the gap and the presence (and stacking) of additional layers. How and to which extent this affects the exciton formation and dispersion is still not understood. We calculated the dispersion of the lowest energy excitons in monolayer and two bulk polymorphs of hBN (AA' and ABC stacking) as a function of the exchanged momentum and performed a detailed analysis. To do that we adopted two approaches: on one hand quantitative results rely on the solution of the ab-initio Bethe-Salpeter equation. On the other hand, deep understanding of the fundamental mechanisms is gained through a tight-binding modelling of the excitonic problem.

### References

- [1] G. Cassabois, P. Valvin and B. Gil, *Nature Photonics*, 10 (2016), pp. 262-266.
- [2] R. Schuster *et al.*, *arXiv:1706.04806v1* (2017), pp. 1-11.
- [3] K. Watanabe, T. Taniguchi and H. Kanda, *Nature Materials*, 3 (2004), pp. 404-409.
- [4] K. Watanabe and T. Taniguchi, *Int. J. Appl. Ceram. Technol.*, 8 (2011), pp. 977-989.
- [5] L. Schué *et al.*, *Nanoscale*, 8 (2016), pp. 6986-6993.
- [6] T. Galvani *et al.*, *Phys. Rev. B*, 94 (2016), pp. 125303-125317.
- [7] B. Arnaud, S. Lebègue, P. Rabiller and M. Alouani, *Phys. Rev. Lett.*, 96 (2006), pp. 026402-026405.

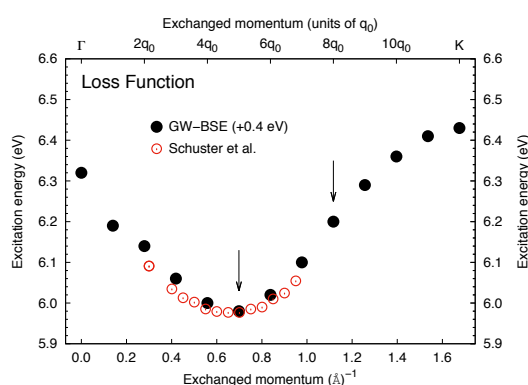


Figure 1: Dispersion of energy loss peak: black theory, red experiment

## IMPACT OF PHONON SYMMETRIES ON THE OPTICAL RESPONSE OF HEXAGONAL BORON NITRIDE

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Hexagonal Boron Nitride (hBN) and graphite share the same honeycomb structure,  $sp^2$  hybridization and many properties such as high thermal and chemical stabilities. The difference between them is the electronic band structure. While graphite is gapless with the maximum (minimum) of valence (conduction) lie at K points in the Brillouin zone, the band gap of hBN is predicted indirect. Recently, two-photon spectroscopy demonstrated experimentally the indirect nature of the bandgap with an emission line at 5.955 eV (called iX) corresponding to the indirect exciton. Five phonon-replicas (LO, TO, LA, TA, ZA) were identified showing that the optical properties of hBN come from phonon-assisted transitions [1]. In our work, we made polarization-resolved photoluminescence detected along two directions (parallel and perpendicular to the  $c$ -axis of hBN). We observed a strong dependence of the emission intensity on polarization (wave-vector  $k \perp c$ -axis case) as shown in Fig.1. This strong dependence reflects the phonon symmetries in hBN. Moreover, we obtained the missing optical out-of-plane phonon mode (ZO) as shown in Fig.2 in agreement with the phonon band structure [3-4]. This gives a full understanding of the six phonon replicas in hBN and strongly confirms the indirect nature of the bandgap.

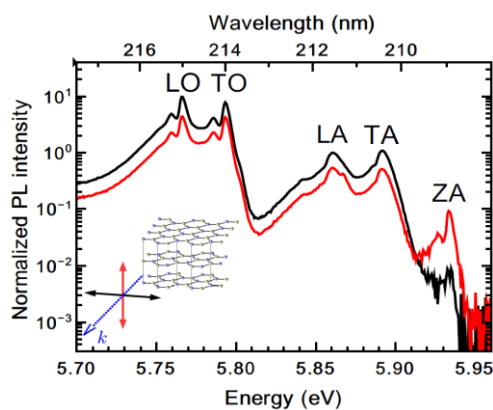


Figure 1: Polarization-resolved PL spectroscopy in bulk hBN at 8K with emission wave vector  $k$  perpendicular with  $c$ -axis.

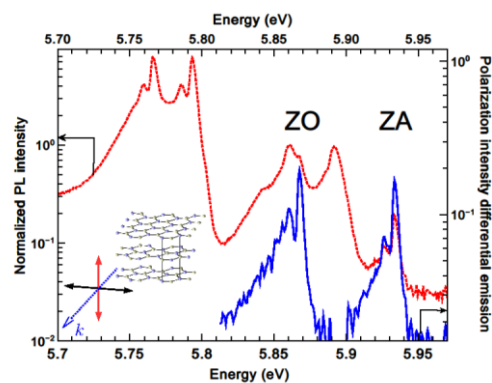


Figure 2: Polarization intensity differential emission spectrum corresponds to the difference of the polarization-resolved PL.

### References:

- [1] G. Cassabois et al, Nature Photonics, **10**, 262-266 (2016).
- [2] Vuong et al, 2D Materials, **4**, 011004 (2017).
- [3] Serrano et al, PRL, **98**, 095503 (2007).
- [4] Cusco et al, PRB, **94**, 155435 (2016)

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van der Waals heterostructures

# CHARGE VERSUS ENERGY TRANSFER IN ATOMICALLY-THIN GRAPHENE-TRANSITION METAL DICALCOGENIDE VAN DER WAALS HETEROSTRUCTURES

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Van der Waals heterostructures, made from stacks of two-dimensional materials, offer promising routes towards novel optoelectronic devices. The performance of such devices is governed by near-field coupling through, e.g., interlayer charge and/or energy transfer. New concepts and experimental methodologies are required to properly describe atomically-thin heterointerfaces. In this talk, I will present an original study, performed at IPCMS, of interlayer charge and energy transfer in single-layer graphene (Gr)/single-layer molybdenum diselenide (MoSe<sub>2</sub>) heterostructures using a combination of micro-photoluminescence and Raman scattering spectroscopies (see figure below). The photoluminescence intensity in Gr/MoSe<sub>2</sub> heterostructures is massively quenched and increases linearly with the incident photon flux, demonstrating a drastically shortened room temperature exciton lifetime in MoSe<sub>2</sub>. Key complementary insights are provided from a comprehensive analysis of the graphene and MoSe<sub>2</sub> Raman modes, which reveals a net photoinduced electron transfer from MoSe<sub>2</sub> to graphene. Remarkably, as the incident photon flux increases, the steady state Fermi energy of graphene saturates at  $290 \pm 15$  meV above the Dirac point. This reproducible behavior is observed both in ambient air and in vacuum and will be discussed in terms of intrinsic factors (i.e., band offsets) and environmental effects. The absence of a correlation between exciton dynamics and the presence of a net charge transfer strongly suggests that additional non-radiative coupling mechanisms, such as interlayer energy transfer, are the dominant mechanisms between atomically-thin transition metal dichalcogenides and graphene. Finally, these mechanisms can be inhibited by using a hexagonal boron nitride (hBN) barrier in between graphene and MoSe<sub>2</sub>. Based on this finding, Gr/hBN/single-layer molybdenum disulfide (MoS<sub>2</sub>)/hBN heterostructures, demonstrating linewidths close to the ideal homogeneous limit, have been fabricated at the University of Basel. First results on these heterostructures will be also presented.

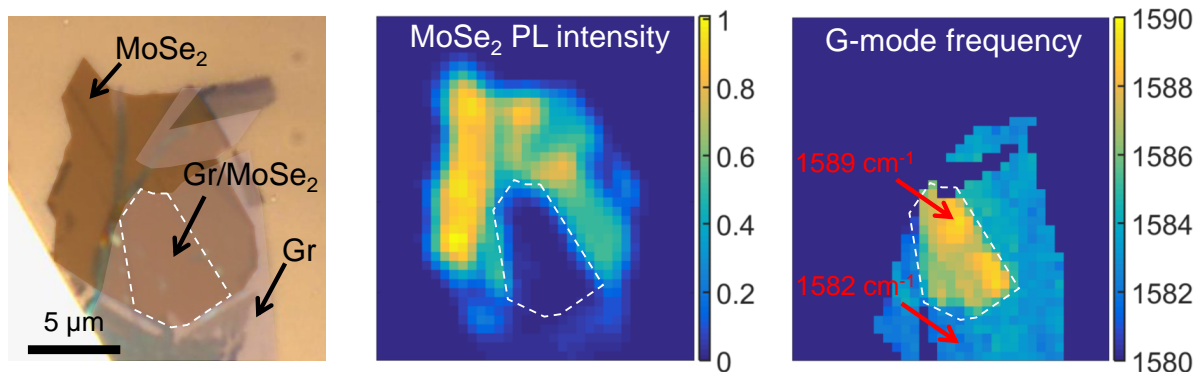


Figure 1: Left: Optical image of a single-layer graphene/single-layer MoSe<sub>2</sub> van der Waals heterostructure deposited onto a Si/SiO<sub>2</sub> substrate. The coupled part of the heterostructure is represented by the white dashed contour. Middle: MoSe<sub>2</sub> photoluminescence intensity map recorded in ambient air with an incident photon flux  $\Phi_{\text{ph}} = 2 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$ . A massive quenching (by a factor of  $\sim 300$ ) of the photoluminescence intensity is observed for the coupled part of the heterostructure. Right: Raman map of the G-mode frequency  $\omega_{\text{G}}$  recorded in ambient air with an incident photon flux  $\Phi_{\text{ph}} = 2 \times 10^{22} \text{ cm}^{-2} \text{ s}^{-1}$ . The G-mode frequency is higher on the coupled part than on the rest of the sample, suggesting a higher doping level in graphene when coupled to MoSe<sub>2</sub>.

# ELECTROSTATIC TUNING OF THE LUMINESCENCE FROM INTERLAYER EXCITON IN MOSE<sub>2</sub>/WSE<sub>2</sub>

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In analogy with III-V heterostructures, the stacking of different 2d semiconducting materials allows for the engineering of their electronic properties. In particular the model case of heterobilayers of transition metal dichalcogenides has shown promising luminescence features that originate from interlayer excitons, where electrons and holes lie in different layers. Experimental studies have reported near-infrared emission with long lifetime [1] and valley coherence time [2], larger than nanoseconds but with significant discrepancies.

Here we demonstrate precise electrostatic control over the luminescence features from MoSe<sub>2</sub>/WSe<sub>2</sub> heterobilayer embedded in a vertical double-gated heterostructure (Figure 1) [3]. By disentangling the effects of carrier concentration and out-of-plane field, we achieve comprehensive tuning of the photoluminescence intensity, linewidth, energy (over a range larger than 100 meV) and lifetime (from 10 ns to larger than microseconds). We finally discuss the nature of the emitting quasiparticles. This work offers important guidelines for the fundamental and technological optoelectronic applications that rely on exciton manipulation.

## References

- [1] P. Rivera et al., *Nature Communications*, 6:6242.
- [2] P. Rivera et al., *Science*, 351, 6274, pp. 688-691.
- [3] F. Vialla et al., *in preparation*.

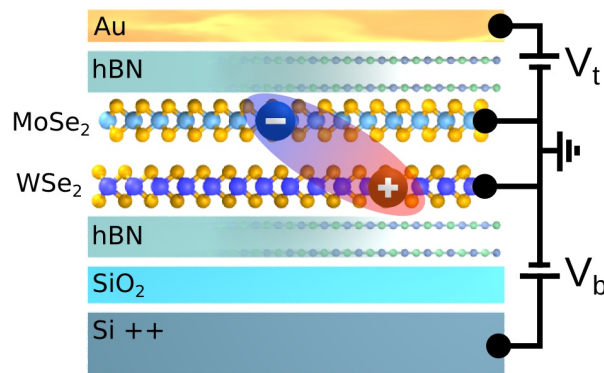


Figure 1: Schematics of the double-gated van der Waals heterostructure based on a MoSe<sub>2</sub>/WSe<sub>2</sub> heterobilayer.

## Near field and structure

## ELECTRON CONFINEMENT IN NANOSTRUCTURED 2D MATERIALS

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The edges of nanostructures (edges, islands, nanoribbons) can have a strong impact on their electronic properties. The presence of localized electronic states and electron scattering processes at edges can strongly modify the electron transport. Although electron scattering at defects has been studied at the atomic scale for many years [1-3], understanding the electron scattering at edges is crucial if we are to optimize nanostructure shapes and properties. Significant periodic modulation of the density of states has been observed in scanning tunneling microscopy images of silicene nanoribbons on the Au(110) [4] and Ag(110) surfaces [5]. This is strongly reminiscent of recent atomic-scale studies of monolayer graphene edges [6] where the electron scattering behaved in a unique way. At graphene edges, quantum interference channeling results from the localization of the electron scattering on to the density of states of the graphene C-C bond lattice. The exact shape of each quantum interference pattern depends on the edge structure and not on the electron energy. We proposed a completely new model for understanding quantum interferences in monolayer graphene, since previous models were found to fail when it came to explaining quantum interferences at edges. We will consider how this can be applied to other nanostructures such as nanoribbons.

### References

- [1] M.F. Crommie, C.P. Lutz, D.M. Eigler, *Nature* 363 (1993) pp. 524-527.
- [2] B.G. Briner, Ph. Hofmann, M. Doering, H.-P. Rust, E.W. Plummer, A.M. Bradshaw, *Phys. Rev. B* 58 (1998) 13931.
- [3] L. Simon, C. Bena, F. Vonau, D. Auble, H. Nasrallah, M. Habar, J.C. Perruchetti, *Eur. Phys. J. B* 69 (2009) pp. 351-355.
- [4] M.R. Tchalala, H. Enriquez, A.J. Mayne, A. Kara, S. Roth, M.G. Silly, A. Bendounan, F. Sirroti, Th. Greber, B. Aufray, G. Dujardin, M. Ait Ali, H. Oughaddou, *Appl. Phys. Lett.* 102 (2013) pp. 083107.
- [5] M.R. Tchalala, H. Enriquez, A. J. Mayne, A. Kara, G. Dujardin, M. Ait Ali, H. Oughaddou, *J. Phys. Conf. Ser.* 491 (2014) pp. 012002.
- [6] H. Yang, A.J. Mayne, M. Boucherit, G. Comtet, G. Dujardin, Y. Kuk, *Nano Letters* 10 (2010) pp. 943-947.

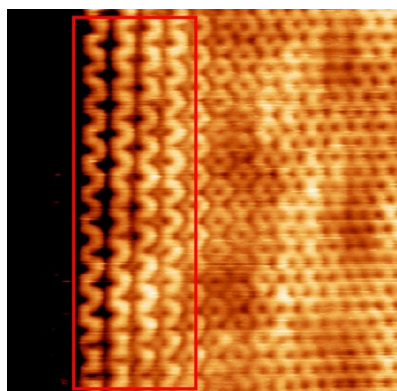


Figure 1 : Quantum interferences on graphene.

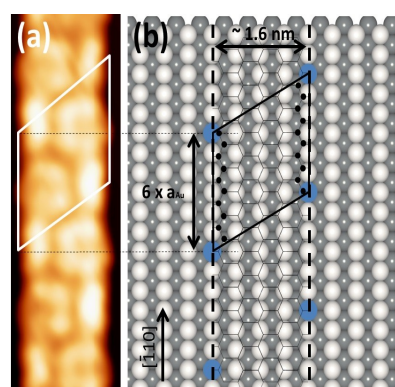


Figure 2 : Silicene Nanoribbons on Au(110)

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## LOCAL INVESTIGATION OF BAND OFFSETS IN GRAPHENE-TRANSITION METAL DICHALCOGENIDE HETEROSTRUCTURES.

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We study the electronic properties of van der Waals (vdW) based heterostructures, combining graphene and atomically thin semiconducting Transition Metal Dichalcogenides (TMDs) films, by using low temperature scanning tunneling microscopy/spectroscopy (STM/S) in ultra-high vacuum. The vdW structures are made either by exfoliating and transferring WSe<sub>2</sub> flakes onto epitaxial graphene on SiC(0001), or by growing by molecular beam epitaxy (MBE) monolayer (1L) of either MoSe<sub>2</sub> or WSe<sub>2</sub> flakes on similar substrates (Fig. 1a). We then locally probe the local density of states of the TMD flakes using scanning tunneling spectroscopy (STS). STS provides a direct and local access to the band onsets and then to the electronic band-gap of the TMD (Fig. 1b) [1].

A noteworthy result is presented in Fig. 1b : The dI/dV spectra measured on 1L-MoSe<sub>2</sub> are strongly impacted by the number of graphene layers below the TMD flake. As shown on the figure, the spectra are rigidly shifted towards negative biases by 130 mV when going from bilayer (BLG) to single-layer graphene (SLG). This shift is observed for both 1L-MoSe<sub>2</sub> and 1L-WSe<sub>2</sub> flakes, and is still present for 3L-WSe<sub>2</sub>. Additionally, this effect does not depend on the TMD preparation method. As detailed in the article [2], our experimental data indicate the absence of Fermi level pinning, which was recently predicted for stacked junctions made of two-dimensional materials coupled by vdW interactions [3].

Additionally, we have observed band bending close to charged defects of the TMD layers, either edges or point defects. They induce an upwards energy shift (by 0.2 to 0.5 eV) of the TMD band onsets over a distance of several nanometers. These values will be discussed in relation with the specific form of dielectric screening in thin dielectric films [4], which is thought to be relevant for some electronic properties of the TMD materials.

### References

- [1] M. Ugeda et al., *Nat. Mater.*, 13 (2014), pp. 1091-1095.
- [2] T. Le Quang et al., *2D Mater.*, 4 (2017), 035019
- [3] Y. Liu et al., *Sci. Adv.*, 2 (2016) e1600069.
- [4] L. V. Keldysh, *JETP Lett.*, 29 (1979), pp. 658-661.

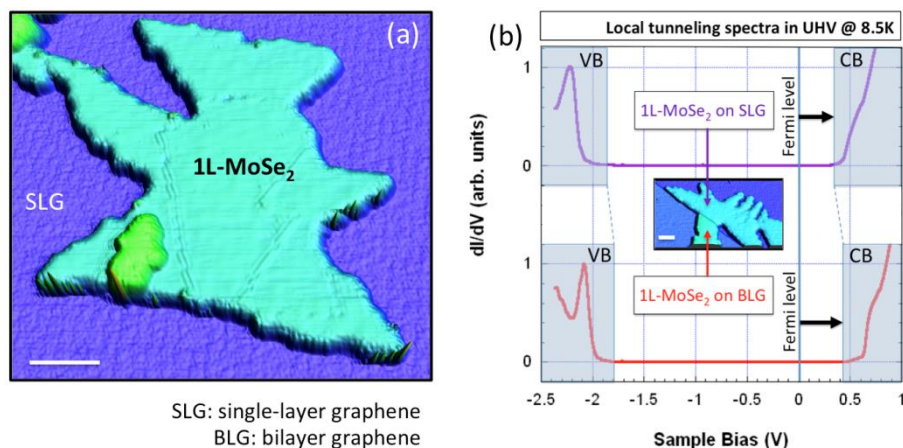


Figure 1 : (a) STM image of a monolayer MoSe<sub>2</sub> island on a graphitized SiC(0001) substrate. (b) dI/dV (V) spectra obtained on a similar island residing partly on a SLG terrace (top curve) and partly on a BLG terrace (bottom curve). Scale bars : 10 nm.

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## STUDY OF 2D MATERIALS AT VAN DER WAALS INTERFACE

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Two dimensional (2D) materials are the fundamental building blocks to construct novel van der Waals (vdW) heterostructures. As the 2D materials are only a few atoms thick, the atomic structure, presence of defects, and interface between the 2D materials will strongly dictate the resulting materials properties [1]. For example, it has been shown that stacking angle between MoS<sub>2</sub> and graphene changes the band gap of the MoS<sub>2</sub> layer [2]. Thus, studying the interaction at the interface between different 2D materials is needed to understand the resulting properties from the vdW heterostructures. Here, we present a study of the interaction at the interface between MoSe<sub>2</sub> and graphene, and the influence it has on growth and defects using low voltage aberration corrected transmission electron microscopy (LVAC-TEM).

The vdW heterostructures are fabricated by direct growth of 1 monolayer (ML) of MoSe<sub>2</sub> on 1 ML graphene, thereby preserving an ideal vdW interface between the two layers. The MoSe<sub>2</sub> and graphene are grown by molecular beam epitaxy (MBE) and by chemical vapor deposition (CVD), respectively. In the as grown film, we identified a preferential orientation in the vdW stacking of 2° and 27°, and high density of inversion domain boundaries (IDB).

The MoSe<sub>2</sub>/graphene vdW heterostructure is investigated by *in situ* electron irradiation experiments to understand the formation of defects in MoSe<sub>2</sub> and their effect on the heterostructure. Different line defects are observed during the electron irradiation for the first time. Three different Se vacancy line (VL) defects are identified as single, double and triple VL defects from comparison with structure simulation by density functional theory. We observe the movement of the MoSe<sub>2</sub> layer independently on graphene, which remains stationary, during the formation of these VL defects. To separate the signals of graphene and MoSe<sub>2</sub>, fast Fourier transform based image filtering is used to follow their dynamics independently during the formation of VL defects in MoSe<sub>2</sub>.

### References

[1] Novoselov, K. S, et al. *Science*, 353 (2016), aac9439.

[2] Jin, W., et al. *Phys. Rev. B*, 92 (2015), 201409.

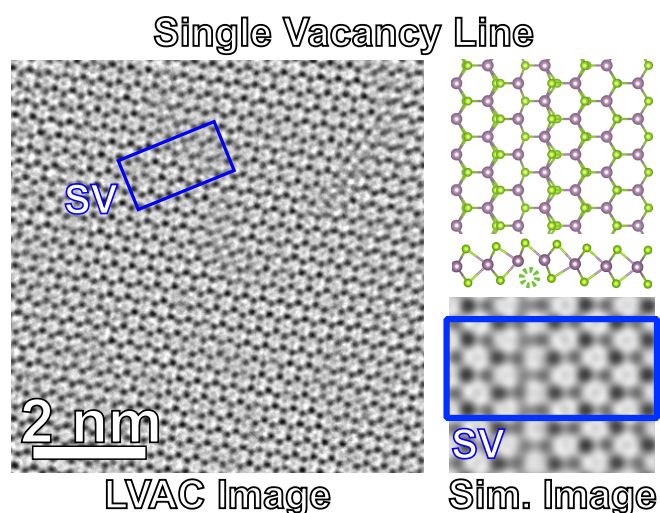


Figure 1: Single vacancy line defect in MoSe<sub>2</sub> shown in low voltage aberration corrected TEM image, with corresponding DFT calculated atomic model and simulated TEM image. Blue box inset in LVAC TEM image is a simulated image of single vacancy line defect overlaid onto the matching defect.

## Growth and structure II



## DENSITY DRIVEN SODIUM 2D PHASE TRANSFORMATION ON EPITAXIAL GRAPHENE.

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Graphene is an easily accessible platform whose unique properties can accordingly be tailored along various strategies [1, 2]. Decorating Gr with adsorbates has been proven to be an efficient such strategy and, among the others, alkali metals (e.g. Li, Na, Cs, K) have been extensively explored due to their well known capability to transfer charges to graphene [3, 4]. Resolving and controlling the structure of alkali atom phases decorating graphene from atop (adsorbed) and below (intercalated) is of uttermost importance, as: i) it permits to rationalise and control the charge transfer, hence to control electronic doping and work-function; ii) it opens the way to breaking the equivalence of the two carbon sub-lattice in graphene, hence to generate the often elusive band-gap at the Dirac point.

We will present the so-far unknown [3] structural evolution, as a function of density, of a Na layer deposited on epitaxial graphene grown on an Ir(111) single crystal. By means of in-operando reflection-high energy electron diffraction (RHEED) we discovered multiple periodicities in two-dimensional Na lattices[5]. We interpret our observations as the evidence of a phase transition, whereby the repulsive Na-Na interactions lead the system to lock first on the Ir lattice and second on the graphene lattice, as the Na density increases. The evolution from the Ir-locked phase to the graphene-locked one has been carefully analyzed and rationalized in the framework of “rotation epitaxy”[6].

### References

- [1] R. Balog. et al., Nat. Mater., 9 (2010), pp. 315-319.
- [2] D. Usachov et al., Nano Lett., 11 (2011), pp. 5401-5407.
- [3] M. Papagno et al., ACS Nano, 6 (2012), pp. 199-204.
- [4] C. Struzzi et al., Phys. Rev. B, 94 (2016), pp. 085427 (1-10).
- [5] S. Lisi et al., to be submitted.
- [6] A. D. Novaco et al., Phys. Rev. Lett., 38 (1977), pp. 1286-1289.

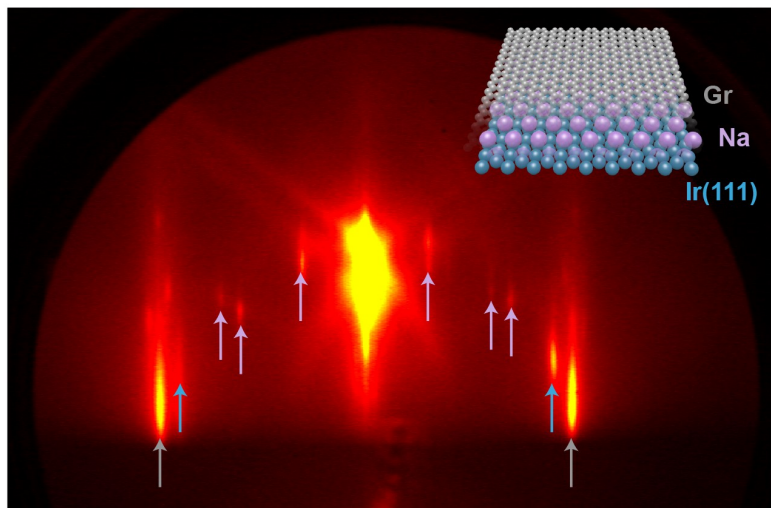


Figure 1. Representative RHEED pattern of graphene/iridium(111) during sodium deposition (17.0keV primary electron beam energy, incidence angle  $<3^\circ$ , beam aligned along the (1,-2,1) direction with respect to the iridium(111) surface). Colored arrows highlight the contributions coming from graphene (grey), sodium (purple) and iridium(111) (Blue). All the additional diffraction streaks are due to moiré interference effects.

## LOW PRESSURE CVD GROWTH OF BORON NITRIDE ON METALLIC SUBSTRATES

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Heterostructures made from graphene and hexagonal boron nitride (hBN) are studied for the most part for the enhancement of graphene properties [1], but also for the combination of both materials properties in optoelectronics (wide bandgap of hBN with the conductivity of graphene for instance) [2]. However, if the synthesis is now well controlled for graphene, there is a big challenge remaining for BN in order to get large-area high-quality films. Therefore the technique of Chemical Vapour Deposition (CVD) is attractive due to its low cost, scalability and reproducibility, in comparison to mechanical exfoliation for instance.

In this work, we first present the CVD growth of BN on polycrystalline copper and nickel foils at low pressure in a hot wall vertical reactor, using borazine as the precursor, and H<sub>2</sub> as the carrier gas. We investigate the role of the underlying grain orientation on the growth mode and the quality of the BN film in terms of morphology, crystallinity, thickness, domain size.

To that aim, we have developed a specific wet transfer protocol for BN from the nickel substrate to characterization support, such as TEM grids and silica wafer. This polymer-free technique does not contaminate the film and provides square centimeters of intact BN film.

We propose a multi-scale characterization with complementary spectroscopic and imaging techniques: Raman, MEB, EBSD, HRTEM and EELS, to have an in-depth knowledge of the structure and properties of the BN film, essential for their integration in devices.

### References

[1] Wang L. et al. Science 342, 614-617 (2013)

[2] Levendof, M. P. et al. Nature 488, 627-632 (2012)

# Posters

## ENHANCING THE INFRARED RESPONSE OF CARBON OF CARBON NANOTUBES FROM DYE INTERACTIONS

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Infrared response on a carbon nanotube is weak because this homonuclear allotrope of carbon does not bear permanent dipoles. Here, we report the discovery of an exaltation of the infrared absorption response in single-walled carbon nanotubes from dye molecule interactions. A study performed on dimethylquaterthiophene confined into the hollow core of single-walled carbon nanotubes or  $\pi$ -stacked at the outer surface of the latter leads to a symmetry breaking, allowing us to probe interactions between both subsystems. The nature of these interactions is discussed taking into account the tube diameter (figure 1). This new phenomenon opens a new route to detect weak vibrations thanks to a confinement effect.

### Reference

[1] A. Belhboub et al. J. Phys. Chem. C 2016, 120, 28802–28807

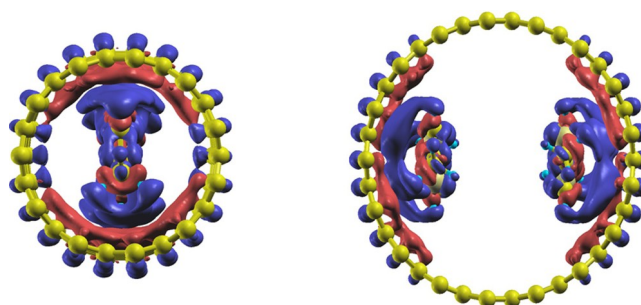


Figure 1 : Electronic charge density difference with isovalues of +0.0003 (red) and  $-0.0003$  (blue) electrons per angstrom<sup>3</sup> for 4T@(11,0) (left) and 4T@(17,0) (right).

# ATOMISTIC SIMULATION OF ELECTRONIC TRANSPORT IN PLANAR GRAPHENE-MOS<sub>2</sub> HETEROSTRUCTURE DEVICES

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The outstanding electronic properties of graphene [1] are well-known, and make it one of the most fascinating materials currently investigated in the field of nanoelectronics. However, to harness its full power - such as the extremely high electronic conductivity - and make it a suitable candidate for the creation of electronic devices such as transistors or diodes, it is necessary to overcome its shortcomings such as the absence of a band gap. Coupling it with other 2D materials is a promising option [2,3] to solve this issue. In its monolayer form, MoS<sub>2</sub> behaves as a semiconductor with a ~2.2 eV direct band gap, and several vertical devices combining graphene and MoS<sub>2</sub> have already been studied and demonstrated [4,5]. Here, we investigate a planar graphene-MoS<sub>2</sub> structure [6] in order to assess its potential for electronic devices.

In this work, we investigate a 2D material transistor with graphene source/drain regions, MoS<sub>2</sub> channel, and silicon oxide gate/backgate. We use a full-band atomistic tight-binding (TB) approach to describe the structure (see Fig. 1), and the Non-Equilibrium Green's Function (NEGF) method to model electronic transport. We adopted the MoS<sub>2</sub> TB model presented in [6], due to its good accuracy with a relatively low number of fitting parameters used. Refinements to the G-Mo and G-S coupling are still underway, guided by DFT simulation of the graphene/MoS<sub>2</sub> junction. After selecting an adequate transport direction and supercell size, we investigated the transfer characteristics for different conduction band offsets between the two materials. Preliminary results are shown in Fig. 2. The high Ion/Ioff ratio observed here is a strong enhancement compared to pure-graphene transistors.

## References

- [1] K.S. Novoselov, V.I. Fal'ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, Nature, 490 (2012) 192-200.
- [2] V.H. Nguyen, F. Mazzamuto, A. Bournel, P. Dollfus, J. Physics D: Appl. Phys. 45 (2012) 325104.
- [3] Y. Wang, Z. Ni, Q. Liu, R. Quhe, J. Zheng, M. Ye, D. Yu, J. Shi, J. Yang, J. Li, J. Lu, Adv. Funct. Mater. 25 (2015) 68-77.
- [4] D. Stradi, N. R. Papior, O. Hansen, M. Brandbyge, Nano Lett. 17 (2017) 2660-2666.
- [5] L. Britnell et al., Science 335 (2012) 947-950.
- [6] X. Liu, J. Gao, G. Zhang and Y.-W. Zhang, Nano Res. 10 (2017) 2944-2953.
- [7] E. Ridolfi, D. Le, T. S. Rahman, E. R. Mucciolo, C. H. Lewenkopf, J. Phys. Cond. Matter 27 (2015) 365501.

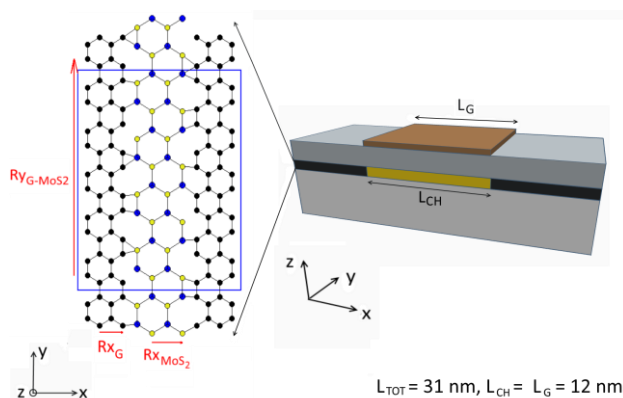


Figure 1 : Atomic structure at the junction (left)  
Representation of the device (right) in which  
brown = gate, black = graphene, yellow = MoS<sub>2</sub>,  
and grey = SiO<sub>2</sub>

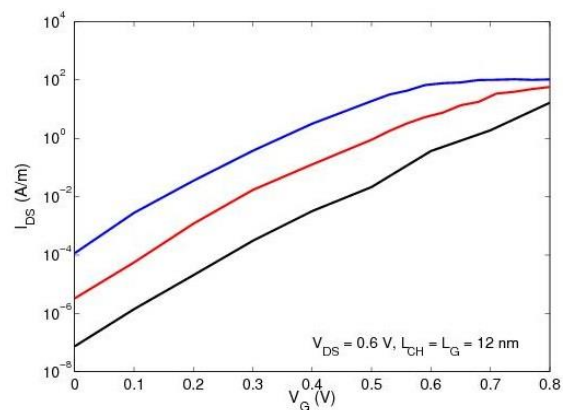


Figure 2 : Current as a function of gate voltage, for  
an offset of lowest CB between Graphene and MoS<sub>2</sub>  
of 0 eV (blue), 0.1 eV (red), and 0.2 eV (black)

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## EXPLOITING ONE DIMENSIONAL CONFINEMENT FOR TUNABLE SINGLE-PHOTON GENERATION WITH CARBON NANOTUBES

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Carbon nanotubes have recently proven to be promising nano-emitters for future single-photon sources spanning the near infra-red and the telecom wavelengths [1,2,3]. Coupling the nanotube to a micro-cavity brings an invaluable handle to control single-photon emission, regarding the rate, the yield, the directionality and the extraction. All those features are related to the so-called Purcell effect that results from the interaction of a quasi-two-level system with a high Q and low mode-volume optical cavity. In carbon nanotubes though, the situation is slightly more complex due to the intimate coupling of the excitonic levels with the acoustic phonon bath, resulting in the well-known phonon wings [4]. This additional degree of freedom brings a very rich physics that can be exploited to enlarge the bandwidth of the source in view of multiplexing. A consequence of the non-Markovian decoherence induced by the phonon bath is the asymmetry between the phonon-assisted absorption and emission processes. Using those transitions in the Purcell regime can lead to an enhanced single-photon efficiency above the standard limit imposed by the emitter and cavity intrinsic losses [5,6]. We developed a widely tunable cavity technique, based on laser-engineered optical fibers to investigate this effect. We measured the single-photon emission properties both in the cw and time-resolved modes and explain the strong asymmetry of the efficiency with respect to the detuning.

### References

- [1] A. Jeantet et al., Phys. Rev. Lett. **116**, 247402 (2016)
- [2] S. Khasminkaya et al., Nat. Phot. **10**, 727 (2016)
- [3] X. Ma, et al., Nat. Mat. **10**, 671 (2015)
- [4] F. Violla et al., Phys. Rev. Lett. **113**, 057402 (2013)
- [5] A. Jeantet et al., Nano Letters **17**, 4184 (2017)
- [6] Y. Chassagneux et al., *arXiv:1706.05204*

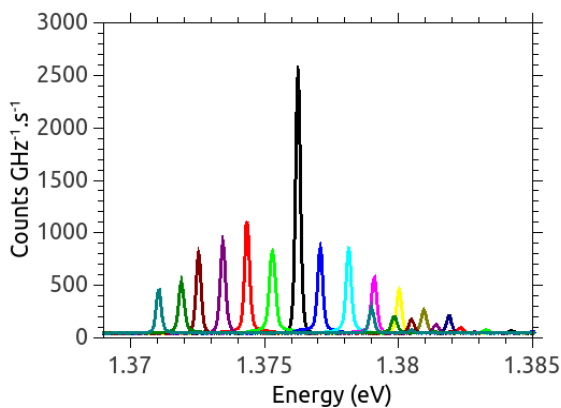


Figure 1 : Spectra of the output of a CNT coupled to a cavity for several detunings.

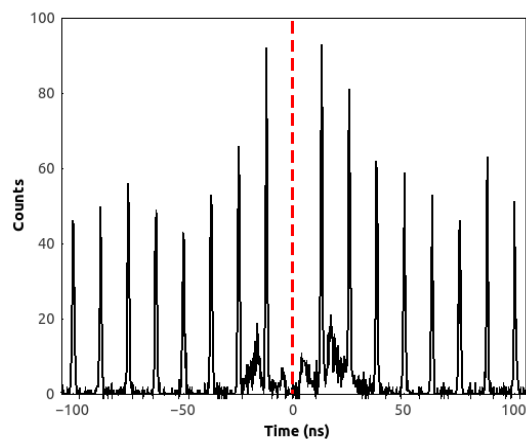


Figure 2 : Pulsed intensity correlation of the output of the cavity coupled to a single CNT at 10 K showing a single photon purity greater than 99%.

# STAMPING CARBON NANOTUBES FOR CIRCUIT QUANTUM ELECTRODYNAMICS

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Dry transfer technique of CVD-grown carbon nanotubes is an important step to embed them in high quality devices. This is for example instrumental towards the fabrication of quantum electrodynamics circuits such as double quantum dots (DQD) in order to achieve the strong spin-photon coupling [1]. We need to combine high finesse microwave cavities with high quality carbon nanotube. The fabrication of such structures is a priori an experimental challenge since the superconducting microwave cavities made of metals such as Al or Nb are not compatible with the growth conditions of carbon nanotubes.

Here we present improvements in our current stamping technique [2, 3], for which the carbon nanotubes have to be exposed to an electron lithography step. This is detrimental for the nanotube quality as found from Raman spectroscopy, where defect associated signal (the D band) was observed. We have developed a stamping technique based on cantilevers where the tubes are directly deposited on the contacts [4]. This allows us to obtain higher tube quality, an increased tube transfer yield with better tube selection, suspended nanotubes, and the possibility to reuse our lithographed devices.

This method can be easily extended to transfer tube in other devices where selection of a single tube is important.

## References

- [1] J. J. Viennot, M. C. Dartiailh, A. Cottet, T. Kontos, *Science* **349**, 408 (2015).
- [2] J. J. Viennot, J. Palomo, T. Kontos, *Appl. Phys. Lett.* **104**, 113108 (2014).
- [3] M. M. Desjardins, J. J. Viennot, M. C. Dartiailh, L. E. Bruhat, M. R. Delbecq, M. Lee, M.-S. Choi, A. Cottet, T. Kontos, *Nature* **545**, 71 (2017).
- [4] J. Weissman et al. *Nature Nanotech.* **8**, 569 (2013).

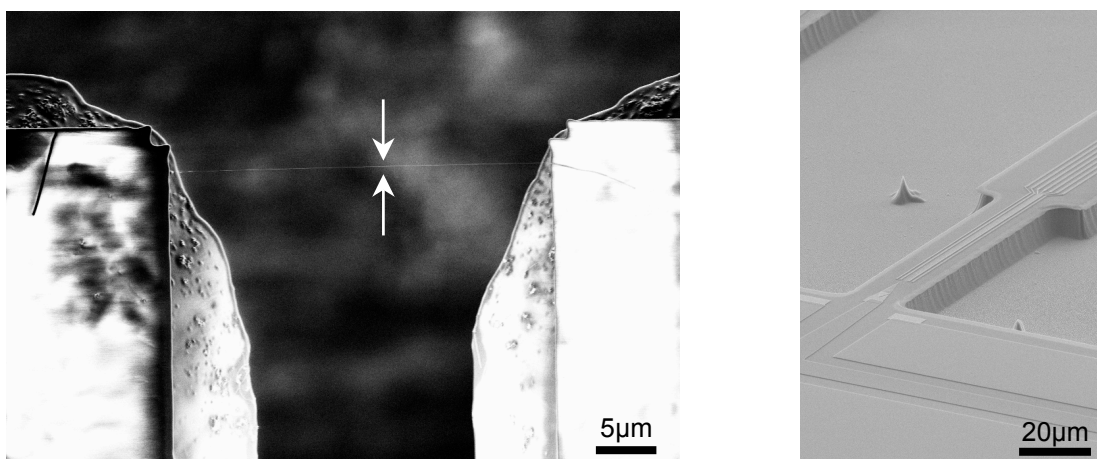


Figure: (left) As-grown carbon nanotube suspended over 2 cantilevers.  
(right) Microwave cavity where the tube is transferred.

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## UNDERSTANDING ELECTRICAL TRANSPORT IN CARBON NANOTUBE YARNS

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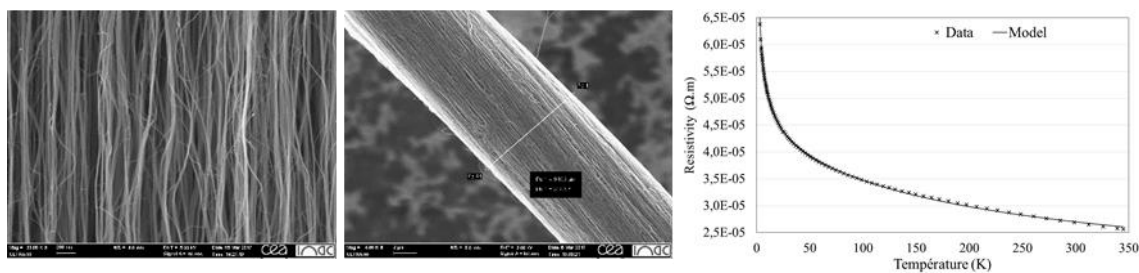
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Metal substitution in electrical wiring by high conductivity materials like carbon nanotubes (CNT) is interesting for rather short term applications in space or avionic [1]. Several techniques exist to make CNT cables; the most suitable eco-friendly process for large scale production are dry spinning directly from Chemical Vapor Deposition (CVD) growth process either fluidized bed or Vertically Aligned CNT (VACNT). We have developed a new process of cable production based on hot filaments CVD system that allows us to produce state of the art cable assembly starting from VACNT. Unfortunately, we face the current resistivity limitation around 1 m $\Omega$ .cm [2], as encountered by other groups for the last 10 years. The basic reasons for this limitation are unclear. Is it related to the intrinsic CVD tube quality or to the CNT organization inside the cable induced by the VACNT that limits the electrical contact and the coupling between the tubes in the macroscopic structure?

To put some light on this point, we performed electrical transport measurements between 3 K and 350 K. Several carbon nanotube yarns have been prepared with various conditions. First, yarns with different carbon nanotube lengths have been made in order to differentiate the individual carbon nanotube conductivity from the lobar yarn conductivity. Second, the yarn density have been investigated to highlight their impacts on the electrical contacts between carbon nanotubes and third, acid treatments have been done to see the effect of dopants on the conductivity.

Our first results show a semi-conducting behavior of our cables. Such result is very surprising due to the metallic behavior expected in the case of our multiwall CNT with diameter around 6 nm. All the experiments allowed us to model the electrical conductivity as a function of temperature. This relatively simple model is based on well known electrical transport theories like Variable Range Hopping [3] and Fluctuation Induced Tunneling model [4]. Our model distinguishes the temperature dependence between the carbon nanotube conductivity and the inter nanotube contact conductivity. Experimental data are very well fitted with the model and fit parameters give us valuable information on our material.



*Figure 1. From left to right: VACNT Scanning electron microscope (SEM) picture, CNT Yarn SEM picture, CNT Yarn Resistivity (data and model) vs Temperature*

### References

- [1] P. Jarosz, C. Schauerma, J. Alvarenga, B. Moses, T. Mastrangelo, R. Raffaele, R. Ridgley et B. Landi, 2011, *Nanoscale*, **3**, 4542.
- [2] K. Liu, Y. Sun, R. Zhou, H. Zhu, J. Wang, L. Liu, S. Fan et K. Jiang, 2010, *Nanotechnology*, **21**, 045708.
- [3] S. N. F. Mott et E. A. Davis, 1971, *Electronic processes in non-crystalline materials*, Clarendon Press.
- [4] A. B. Kaiser, G. Düsberg et S. Roth, 1998, *Phys. Rev. B*, **57**, 1418.

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# INVESTIGATION OF THE ATOMIC AND ELECTRONIC STRUCTURE OF THE VAN DER WAALS HETEROSTRUCTURE $\text{MoSe}_2$ -GRAPHENE

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In the route to novel functionalities of two-dimensional (2D) materials, three-dimensional entities conceptualized from 2D-lego pieces have drawn particular attention because of the dimensionality effect and exotic properties [1,2]. As 2D layers are held together by a van der Waals (vdW) force, vertical heterostructures based on these layers are a genuine approach which offers a fertile platform to study fascinating van der Waals-driven properties: commensurate lattice coincidence, electronic structure and band structure line-up, spin-orbit coupling induced by proximity effect and by inversion symmetry breaking.

In this poster, we report on the synthesis and characterization of the van der Waals heterostructure:  $\text{MoSe}_2$ /free-standing-graphene by molecular beam epitaxy. This fabrication approach consists of depositing  $\text{MoSe}_2$  on graphitized graphene-SiC substrate, leading to a pure vdW interface. This enables to study properly the intrinsic properties as well as vdW-type interactions in this 2D system. We employed surface-sensitive techniques in order to probe structural and electronic properties of the heterostructure ranging from atomic resolution (STM-STS) to microscopic scale (X-ray diffraction using synchrotron radiation, photoemission electron microscopy). At the atomic standpoint, the STM shows point defects and twin boundaries in the  $\text{MoSe}_2$  layer. This kind of defects is in general observed in MBE-2D layers due to Se vacancies and domain merging. STS measurement at selected point on  $\text{MoSe}_2$  layer indicates a band gap of 2.1 eV separating the valence band maximum and conduction band minimum. Regarding the microscopic scale measurements, we found that the crystallographic directions of the  $\text{MoSe}_2$  lattice align perfectly along the ones of graphene, resulting in only one commensurate configuration. This structural analysis by X-ray diffraction is well consistent with the constant energy map in  $k$ -space of the electronic band structures of  $\text{MoSe}_2$ -graphene probed by photoemission. We observe a clear evolution of the band structure of the graphene-heterostructure compared to the one of bare graphene, which is a direct consequence of the interlayer coupling between the  $\text{MoSe}_2$  layer and graphene. Finally, substrate-induced interactions will be also discussed by comparing the resulting data with the MBE- $\text{MoSe}_2$ /graphene grown by chemical vapour deposition on Pt/SiO<sub>2</sub>/Si substrate.

## References

[1] G. R. Bhimanapati, et al. ACS Nano, 9, 11509 (2015)

[2] Y. Lui, et al., Nat. Rev. Mater. 1, 16042 (2016)

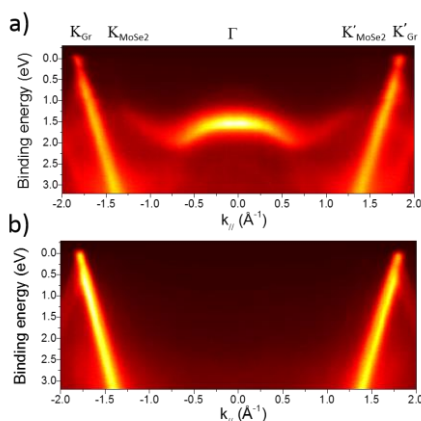


Figure 1 :  $k$ -PEEM of the heterostructure  $\text{MoSe}_2$ /graphene (a) and pristine graphene/SiC (b)

## INFLUENCE OF DEFECTS, STRAIN, AND CHARGED IMPURITIES ON EXCITONS IN NATURAL AND SYNTHETIC MoS<sub>2</sub> SOURCES

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Few- and single-layer MoS<sub>2</sub> host substantial densities of defects. A chemical treatment eliminating defects has allowed to demonstrate a photoluminescence quantum yield close to unity and long lifetimes [1]. Nevertheless, the nature of defects in non-treated samples and their role in radiative and non-radiative recombination remain as open questions. They are thought to influence the doping level, the crystal structure, and the binding of electron-hole pairs. We disentangle the concomitant spectroscopic expression of all three effects, and identify to which extent they are intrinsic to the material or extrinsic to it, i.e. related to its local environment. We do so by using different sources of MoS<sub>2</sub> – a natural one and a novel one prepared at high pressure and high temperature – and different substrates bringing varying amounts of charged impurities, and by separating the contributions of internal strain and doping in Raman spectra (Fig.1). Photoluminescence unveils various optically-active excitonic complexes. We discover a defect-bound state having a low binding energy of 20 meV, that does not appear sensitive to strain and doping, unlike charged excitons. Conversely, the defect does not significantly dope or strain MoS<sub>2</sub>. Scanning tunneling microscopy and density functional theory simulations point to substitutional atoms, presumably individual nitrogen atoms at the sulfur site.

Our work shows the way to a systematic understanding of the effect of external and internal fields on the optical properties of two-dimensional materials [2].

### References

- [1] M. Amani *et al.* *Science*, 350 (2015), pp. 1065–1068.  
 [2] S. Dubey *et al.*, *submitted to ACS Nano*

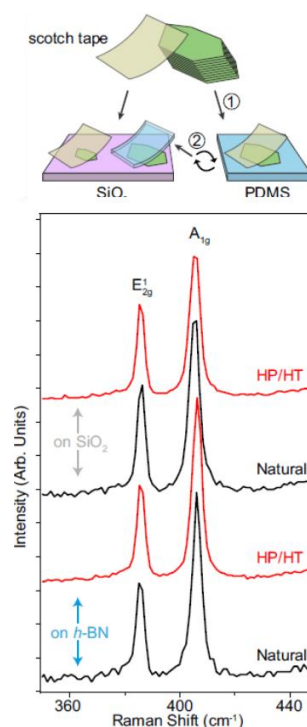


Figure 1 : Top: we compare two sources of MoS<sub>2</sub> deposited on two different substrates (SiO<sub>2</sub> and h-BN) by using two techniques (direct exfoliation and PDMS transfer). Bottom: Raman spectra from the two sources onto the two substrates.

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## IN SITU RAMAN SPECTROSCOPY OF ISOTOPICALLY LABELED BILAYER $^{12}\text{C}/^{13}\text{C}$ GRAPHENE UNDER HIGH PRESSURE

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Graphene can be considered as one of the simplest nano-materials, and also constitutes a reference for all two-dimensional systems. Such low-dimensional crystals present an intrinsic mechanical strength approaching the theoretical strength predicted by Griffith in 1921 for a defect-free crystal [1]. This brings the possibility for a gigantic tuning of physical properties using mechanical stress. Most of the time, such 2D materials are deposited on a substrate, i.e., they are integrated in larger 3D system which need to be taken into account. Thus, understanding the mechanical interaction of graphene with its environment is of crucial importance in order to design new electro-mechanical coupling based devices.

High pressure techniques allow obtaining large mechanical strains in graphene sheets deposited on substrates. In our experiments, supported graphene is loaded in a pressure transmitting medium (PTM) within a diamond anvil cell (DAC) pressure apparatus. The strain in the graphene sheet is thus transferred by the bulk substrate volume reduction governed by its equation of state [2]. Recently, it has been shown that this transfer takes place with a certain efficiency depending on the substrate, before reaching a quasi-unbinding configuration between the layer and its substrate at a critical strain rate [3,4]. However, the effect of the pressure transmitting medium on the mechanical response of graphene layers under pressure can be large, and difficult to dissociate from the substrate mechanical contribution.

We present preliminary results of our high-pressure experiments on an isotopically enriched bilayer graphene which allows measuring simultaneously the effect of the Si/SiO<sub>2</sub> substrate and the PTM state on the mechanical behavior of graphene. The strain in graphene sheets is measured by in situ Raman spectroscopy. The very sensitive in-plane E<sub>2g</sub> phonon energy is used to monitor the lattice distortion. In our system, one graphene sheet presents carbon natural isotopic abundance, while the other is enriched in <sup>13</sup>C allowing to differentiate the signal of the graphene sheet in contact with the PTM with respect to the one in contact with the substrate.

We studied two different PTM: (i) a 4:1 methanol-ethanol mixture which is known to remain liquid up to 10.5 GPa and thus constitutes a reference, (ii) nitrogen which undergoes crystallization at 2.4 GPa and a structural reconstruction at 4.8 GPa. Our results show that the solid polycrystalline PTM state causes strain inhomogeneity in the top graphene layer. Nitrogen structural phase transition provokes a relaxation of stress in the two graphene sheets. A difference in mechanical behavior between the two layers is observed as a function of the PTM, which cannot be explained by the respective compressibility of the PTM studied. Our results point out that the mechanical behavior of the atomic sheets seems to be independent on the equations of states of the PTM, but severely dependent on its thermodynamic state.

### References

- [1] C. Lee, X. Wei, J. W. Kysar *et al.*, 2008, *Science*, **321**, 385-388.
- [2] J. E. Proctor, E. Gregoryanz, K. S. Novoselov *et al.*, 2009, *Physical Review B*, **80**, n°7.
- [3] C. Bousige, F. Balima, D. Machon *et al.*, 2017, *Nano Letters*, **17**, 21-27.
- [4] R. S. Alencar, K. D. A. Saboia, D. Machon *et al.*, 2017, *Physical Review Materials*, **1**, n°2.

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## LOW VOLTAGE MICROSCOPY AND SPECTROSCOPY WITH ATOMIC RESOLUTION PROJECT

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Nanotubes are widely studied for more than twenty five years but there are still a lot of open questions concerning their structure at the atomic scale such as the coupling between inner and outer tubes [1], arrangement of molecules onto or into the tube [2]. Moreover with the emergence of 2D materials heterostructures, it appears also mandatory to obtain information on their topology and defects. Observing these structures at conventional TEM voltage (80 to 200 kV) is getting more and more difficult due to the sensitivity of the structures with respect to the energy of electrons, the current and the overall dose. Indeed, these parameters can induce structural modifications such as reorganization of molecules, chemical reactions up to the destruction of chemical bounds [3]. It appears mandatory to study these structures with a reduced impact of the electron beam and such a challenge can be accomplished by reducing the voltage down to 40 kV and more.

Moreover, reducing the tension is also a must when dealing with Electron energy loss spectroscopy (EELS). This technique is a powerful tool to study the composition of a nano-object, the chemical bounds at the atomic scale [4]. EELS can also provide singular information on the dielectric response of a material, by studying the momentum dependence of the losses [5]. This capability is of particular interest for anisotropic materials. The emergence of monochromated sources gives access to small bandgap determinations, exciton structure of 2D materials [6].

However reducing the tension below 80 kV also implies reducing the spatial resolution in imaging mode, which is mainly driven by chromatic aberrations of the optical design and is no more corrected by spherical aberration correctors. A brand new generation of corrected microscopes is emerging due to the high demand of non-invasive observation of fragile structures at low tension. We present here the project of microscopy, which is dedicated to the structural observation of nanometric hybrid structures and physics related to the van der Waals interaction between their components.

### References

- [1] A. Ghedjatti, Y. Magnin, F. Fossard, G. Wang, H. Amara, E. Flahaut, J.-S. Lauret and A. Loiseau, *ACS Nano* 2017, 11, 4840–4847
- [2] Y. Almadori et al., *J. Phys. Chem. C* 2014, 118, 19462–19468
- [3] S. Skowron, T. Chamberlain, J. Biskupek, U. Kaiser, E. Besley and A. Khlobystov; *Acc. Chem. Res.*, 2017, 50 (8), pp 1797–1807
- [4] R. Senga and K. Suenaga, *Nat. Commun.* 6 : 7943 (2015)
- [5] F. Fossard, L. Sponza, L. Schué, C. Attacalite, F. Ducastelle, J. Barjon and A. Loiseau, *Phys. Rev. B* 96, 115304 (2017)
- [6] L. Tizei, Y. Lin, M. Mukai, H. Sawada, A. Lu, L. Li, K. Kimoto and K. Suenaga, *Phys. Rev. Lett.* 114, 107601 (2015)

## Probing the dielectric response of exfoliated black phosphorus in free standing conditions

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Ultra-thin Black Phosphorus (BP) is a 2D semiconductor characterized by a direct and tunable band gap associated to high carriers mobility (1-3). Studying suspended thin layers of pristine BP is however challenging due to its strong degradation through a thickness dependent and photo-assisted oxidation reaction by adsorbed moisture oxygen (3). Using a protective transfer procedure from glovebox to our TEM-EELS operating at 40kV, we probe the dielectric response of suspended BP down to the monolayer in the range 0.5-40 eV, that include band gaps threshold and surface/volume plasmons energies for BP. The dispersion of the plasmons as a function of the momentum is also measured and simulated for both in-plane and orthogonal crystallographic directions.

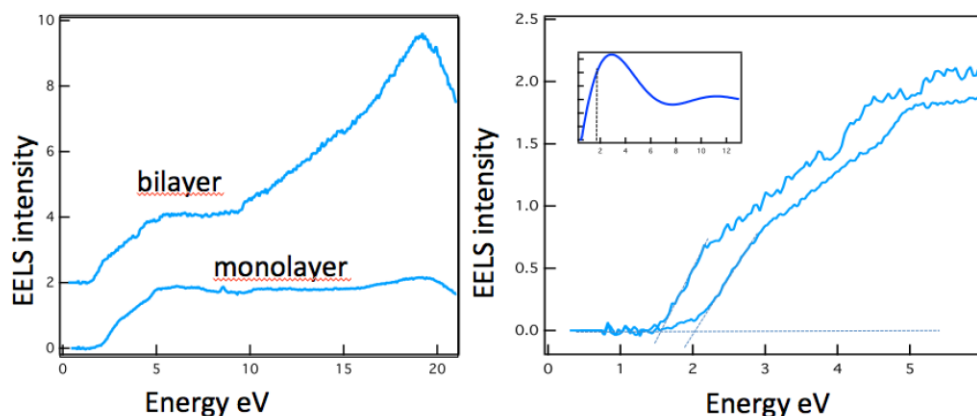


Fig 1 : (left) : Electron Energy Loss spectra of a black phosphorus bilayer and monolayer in the optical limit. (right) Close-up of the band-gap region.

(1)Liu *et al*, ACS Nano (2014)(2)Qiao *et al*, Nature Comm (2014)(3) Long *et al*, Nano Letter (2016)(4)Favron *et al*, Nature. Mater. (2015)

## PFO SORTED S-SWNT NETWORKS FOR OPTOELECTRONICS

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The rise of efficient extraction techniques triggered a renewal of interest in semiconducting carbon nanotubes (s-SWNT) research. It represents a great interest for optoelectronics, with outstanding properties in field-effect transistor, and s-SWNT ability to efficiently emit light in the near-IR range. In particular, polyfluorene (PFO) wrapped s-SWNT (s-SWNT@PFO) display strong photoluminescence, and could be coupled with photonic devices such as microring resonators [1,2] to control photoluminescence linewidth and enhance photoluminescence intensity.

The main challenge for using s-SWNT@PFO in optoelectronics lies in the difficulty to establish good electrical contact with a PFO embedded carbon nanotube. We propose to investigate these issues by tuning the amount of PFO wrapping around s-SWNT. A low pressure annealing process is used to selectively remove PFO around s-SWNT without burning nanotubes themselves (Figure). The resulting s-SWNT@PFO networks are then probed by AFM, Raman spectroscopy, absorption, photoluminescence and electrical experiments.

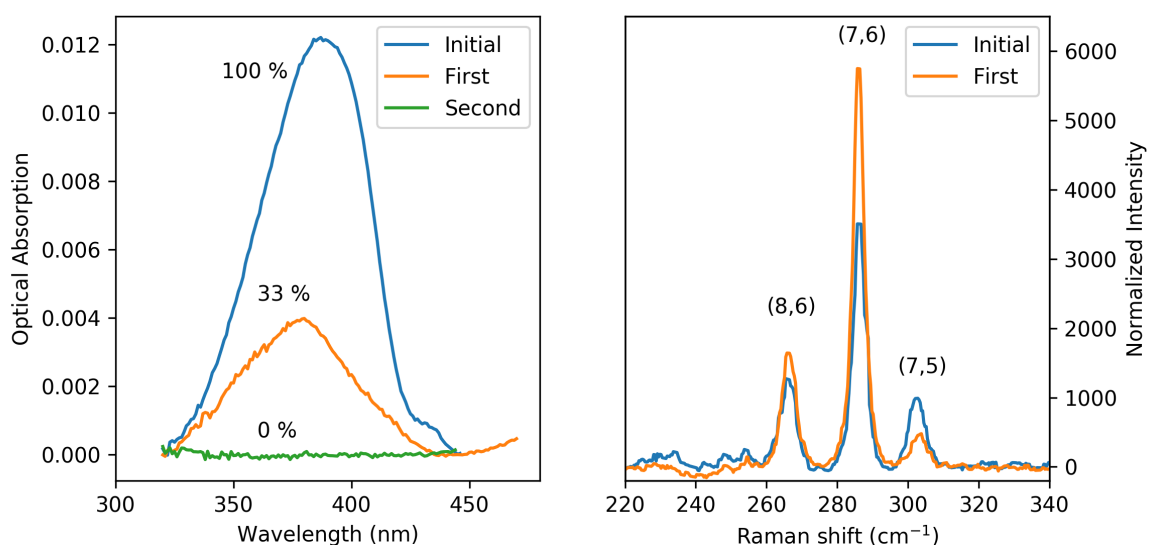


Figure : Left: Typical evolution of PFO absorption peak during successive selective annealing (Initial=before annealing, First=after first annealing, and Second=after second annealing). Right: Typical Raman spectra in the RBM region of s-SWNT before and after first annealing.

### References

[1] A. Noury, X. Le Roux, L. Vivien and N. IZARD, *Controlling carbon nanotube photoluminescence using silicon microring resonators*, *Nanotechnology* **25**, 215201 (2014)

[2] A. Noury, X. Le Roux, L. Vivien and N. IZARD, *Enhanced light emission from carbon nanotubes integrated in silicon micro-resonator*, *Nanotechnology* **26**, 345201 (2015)

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## FABRICATION OF VAN DER WAALS HETEROSTRUCTURE FOR OPTO-ELECTRONICS

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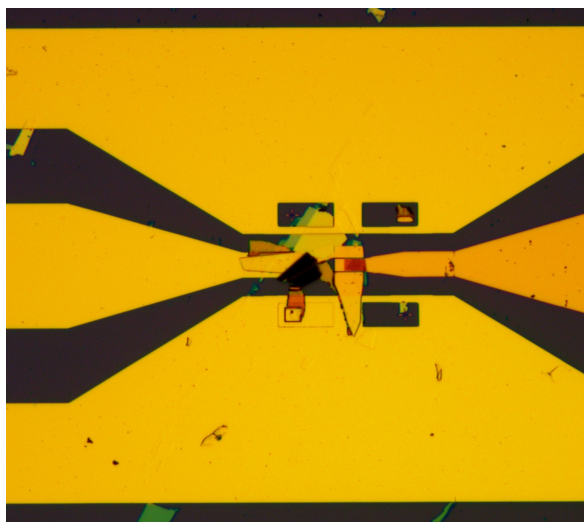
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Intrinsic characteristics of 2D materials (bandgap, doping, mobility) can be largely modified by the control of their thickness and of their environment (electric field, dielectric environment, etc.). This flexibility is unique compared to bulk semiconductors and open a window of opportunity for the development of optoelectronic devices.

State of the art optical telecommunications use near infrared signal carriers modulated up to 20 GHz (before multiplexing) which can propagate through zero-dispersion fiber on large distances with typically 0,2db/km of losses, consequently the current bottleneck on bitrate is the dynamics of photodetectors. The extreme thinness of 2D materials allows for both the exploration of new photodetection geometries and the maximization of detection speed thanks to the minimization of photocarriers drift.

We have developed a fabrication platform for 2D materials heterostructures embedded in coplanar waveguides on top of low luminescent quartz. This unique geometry will allow for the study of the photodetection mechanisms at stake in original heterostructures using a low temperature 40 GHz vectorial network analyzer with optical access.



*Figure 1 : A characteristic coplanar rf-waveguide with a 2D heterostructure in a field effect transistor geometry.*



*Figure 2 : Detail of a bilayer graphene on hexagonal Boron Nitride transistor on top of a low luminescent quartz substrate. The graphene has a ribbon shape and is sandwiched between the source (S) and the drain (D) electrodes.*

## Gold-intercalated graphene on Re(0001)

Graphene, a one-atom thick material made of carbon atoms, presents a weak intrinsic spin-orbit coupling. Inducing large spin-orbit coupling in graphene would allow to use graphene in active elements of spintronics, such as the Das-Datta spin field effect transistor.

We have investigated the local density of states of gold-intercalated graphene on Re(0001) by means of low-temperature scanning tunneling spectroscopy measurements. The intercalation of a sub-monolayer of gold atoms was monitored by reflection high energy electron diffraction. The lattice mismatch and the strong electronic coupling between graphene and rhenium result in a periodic undulation of graphene on top of rhenium. This long wavelength beating is called a moiré superlattice. As opposed to the moiré of graphene on rhenium, gold-intercalated regions show a shallow moiré of graphene on gold ascribed to the local decoupling of graphene from rhenium. The decoupling is confirmed by Raman spectroscopy measurements.

Spectroscopy measurements show broad resonances at large energies, attributed to a giant spin-orbit splitting ( $\sim 100$  meV) induced in intercalated graphene by gold atoms. The spin-orbit splitting is found to be moiré-sensitive: we find correlations between the energies at which we observe the resonances and the topography. At smaller energies, we find no spatial variation of the density of states: the superconducting character of rhenium extends to graphene via the proximity effect both in intercalated and in non-intercalated regions.



## DEVELOPMENT AND CHARACTERIZATION OF METAL NANOPARTICLES ; ANALYSIS OF « ALLOY EFFECTS » IN CATALYSED CARBON NANOTUBES GROWTH

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Nowadays, Chemical Vapor Deposition is the most studied and promising method in carbon nanotube synthesis. This method involves converting gaseous state carbonaceous precursor into a solid material via a nanoparticle or catalytic film.

Nevertheless, this process suffers from a lack of structural control because the mechanisms of growth of nanotubes are still poorly known. One of the research path focuses on the influence of the solubility of carbon atoms within catalytic nanoparticles. It is accepted, nickel is an efficient catalyst in the carbon nanotubes growth by its ability to solubilize carbon, unlike platinum<sup>[1]</sup>.

Furthermore, the members of the ANR "Synapse" in which this project belongs have a good understanding of this system in particular with the description of the nickel-carbon phase diagram<sup>[2]</sup>. Thus, in order to observe the effect of the solubility, Ni<sub>x</sub>Pt<sub>1-x</sub> nanoparticles alloyed in the metallurgical sense, of well-defined size and composition have been synthesized by colloidal pathway.

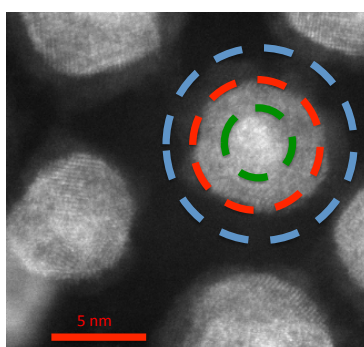
This synthesis route has been favored by its simplicity of implementation, its monodispersed character of the particles and its reproducibility. For this, Platinum (II) acetylacetonate and Nickel (II) acetylacetonate in presence of reducing agent (hexadecandiol) in organic medium were used. OAc and OAm (surfactants) were utilized to block the growth of the particles, producing small sizes and protecting the NPs from oxidation. However, the distant redox potentials of Pt<sup>2+</sup>/Pt<sup>0</sup> and Ni<sup>2+</sup>/Ni<sup>0</sup> generate different kinetics of reductions, producing particles of core-shell structures. This problem could be solved by playing on the temperature.

Finally, in order to study the influence of carbon solubility on the nanotubes growth, a complete structural study of the catalysts NPs was carried out by transmission electron microscopy.

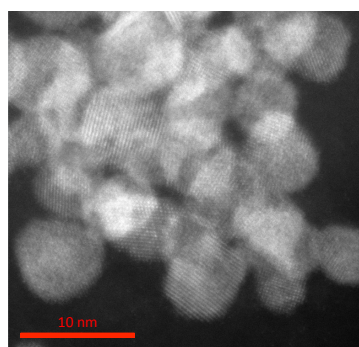
### References

[1] J. M. Aguiar-Hualde, Y. Magnin, H. Amara, C. Bichara, Carbon, 2017, 18, 3850-3856.

[2] C. E. Dahmani, M. C. Cadeville, J. M. Sanchez, J. L. Morán-López, The American Physical Society, 1985, 55, 1208-1211.



*Figure 1: Ni<sub>3</sub>Pt core-shell with platinum in core (green), nickel in shell (red) and organic layer (blue) in HAADF analysis*



*Figure 2: Alloyed Ni<sub>3</sub>Pt in HAADF analysis*

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## OPTIMIZING THE MECHANICAL STRENGTH OF SILK BY TUNING THE CONTENT OF CARBON NANOTUBE INTAKE IN BOMBYX MORI WORMS

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Single-Walled Carbon Nanotubes manufactured using HIPCO process yields very small diameter (0.9nm) and long length tubes. These have been utilized to prepare a composite fiber called Carbon Nanotube Silk using a systemic approach. This is realized by coating the SWCNTs on the mulberry leaves which upon metabolism by silkworm leads to Carbon-Nanotube-enriched silk.

Presence of SWCNTs is assessed in the worms and in their byproducts (silk strands and droppings). We have studied mechanical strength of these naturally enriched fibers by tuning the concentration of SWCNTs on the food. The results suggest that the breaking strength of the silk increases upon the presence the Carbon Nanotube but that, beyond a certain concentration, the breaking strength saturates and then decreases as shown in the figure 1. This saturation could be either due the nanotoxicity of SWCNTs on the worms affecting the silk quality or that there exists an optimum SWCNT concentration which could be reinforced into the silk fibers by employing this natural method. In future, we would like to wove these SWCNT enriched silk fibers into fabric and test the mechanical properties for possible technological applications.

### References

[1] Wang, Jun-Ting, et al. "Directly obtaining high strength silk fiber from silkworm by feeding carbon nanotubes." *Materials Science and Engineering: C* 34 (2014): 417-421..

[2] Wang, Qi, et al. "Feeding single-walled carbon nanotubes or graphene to silkworms for reinforced silk fibers." *Nano Lett* 16.10 (2016): 6695-6700.

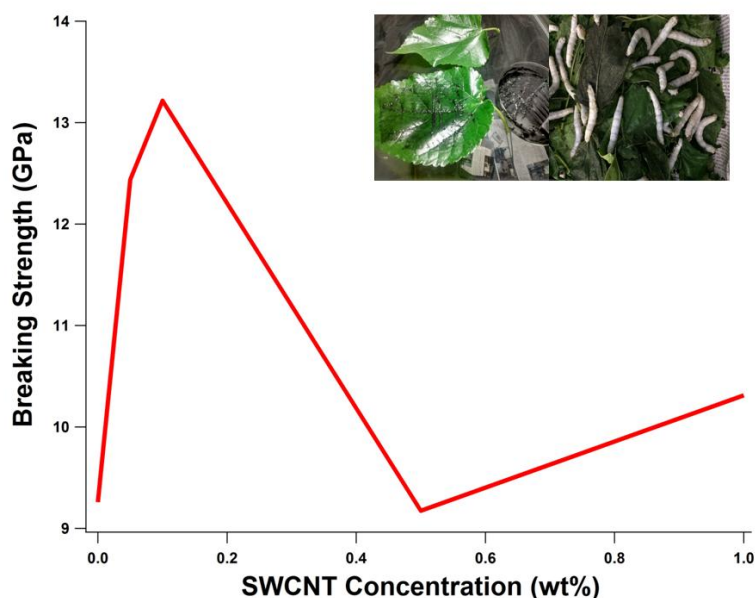


Figure 1 : Breaking strength in GPa of a silk strand vs. concentration of SWCNT in wt% (1% = 1g SWCNTs dissolved in 100ml Isopropyl Alcohol) fed to the silkworms. (Inset: SWCNTs coated on a mulberry leaves, silkworms feeding on these leaves)

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## Electronic properties of the MoS<sub>2</sub>-WSe<sub>2</sub> heterojunction

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### ABSTRACT

Since 2004, the 2D materials family has been ever growing and now encompasses different kinds of materials with different electronic properties (metal, semiconductors, insulators, superconductors...). One exciting aspect of these materials is their ability to be isolated, transferred and stacked on top of each other to create new structures. Within this family, semiconducting transition-metal dichalcogenides (TMDCs) have triggered a large number of studies, especially for applications in next-generation optoelectronics nanodevices. In this work, we present a comprehensive study of point defects in MoS<sub>2</sub> monolayer system and in-plane junction made of two monolayers of MoSe<sub>2</sub> and WSe<sub>2</sub>. For point defects studies, the electronic density of states for a sulfur vacancy, and Fe, B, C, N substitutional atoms are calculated. For characterize the in-plane junctions, the sample was prepared by depositing MoSe<sub>2</sub> and then WSe<sub>2</sub> materials with the same coverage of 0.6 monolayer via molecular beam epitaxy method on graphitized SiC(0001) substrates. DFT simulation and scanning tunneling microscopic/spectroscopic results performed at 8.5 K in ultra-high vacuum both showed a type-II alignment between MoSe<sub>2</sub> and WSe<sub>2</sub>. A valence band offset of 0.3 eV and a conduction band offset of 0.1 eV are found in STS experiments.

## References

- [1] K. S. Novoselov *et. al.*, *Electric Field Effect in Atomically Thin Carbon Films*, Science 306, 666 (2004).
- [1] M.-H. Chiu *et. al.*, *Determination of band alignment in the single-layer MoS<sub>2</sub>/WSe<sub>2</sub> heterojunction*, Nat. Commun. 6, 7666 (2015).

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## OPTICAL PROPERTIES OF CORE-SHELL SYSTEMS BASED ON CARBON NANOTUBES

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The single-wall carbon nanotubes are currently studied and developed because of their unique physical properties. In particular, single-photon emission at room temperature has been recently reported ([1], [2]). This has been achieved by surface chemistry that creates point-like defects that localize the nanotube's exciton. The design of these defects allows to create potential well with deepness far above  $kT$  leading to the antibunching at room T. The last achievement reports  $g^2(0) < 0.01$  at room T and in the telecom wavelength bands ([2]).

Concomitantly, first Cavity Quantum Electrodynamics experiments have been carried out using nanotubes as the quantum emitter. In particular, Purcell effect and cavity feeding has been recently reported ([3],[4]).

In order to integrate nanotubes in devices, efforts have to be made on the material side. Nanotubes being essentially made of surface atoms their electronic and optical properties are influenced by their local environment. For instance, blinking and spectral diffusion processes are observed in low temperature experiments. Moreover, nanotubes are fragile objects that are degraded by standard lithography processes needed to build real photonics devices.

Our strategy is to synthesize core/shell nanostructures: the nanotube is the active core, while a polymer acts as protective shell. Here, we will discuss our preliminary results about the influence of the shell on the emission properties of single nanotubes investigated by microphotoluminescence experiments at low temperature.

### References

- [1] Ma, X., et al., *Nature Nanotechnology*, 10(8), 671–675, (2015).
- [2] X. He, et al., *Nature Photonics*, 11, 577–582, pp. 200-205, (2017).
- [3] Jeantet, A., et al., *Physical Review Letters*, 116(24), 247402, (2016).
- [4] Jeantet, A., *Nano Lett.*, 17 (7), pp 4184–4188 (2017).

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# MOIRE ENGINEERING IN 2D MATERIALS BEYOND GRAPHENE VIA DISLOCATION THEORY

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Lateral and vertical heterostructures of 2D materials are emerging as platforms both for novel physics and for engineering of devices with exceptional properties. Here we consider layered 2D materials beyond graphene, and the electronic structure origins of moire patterns and their defects in these systems [1]. We show that moire patterns are equivalent to dislocation arrays, and vice versa. The dislocations are of a unique type that we describe as van der Waals dislocations, for which we present a complete geometrical description, explaining both stretch and twist moire patterns. With this framework we explain not only bilayer graphene moire patterns, but also moire patterns formed by more complex 2D materials on crystalline substrates with different symmetry. We present a simple computational scheme, which reduces the complexity of the electronic interaction between layers in order to make the problem computationally tractable. With this computational scheme we simulate these van der Waals dislocation arrays, allowing us to predict and explain all observed moire patterns in the 2D materials literature. We extend this analysis as well to defects in moire patterns, which have been reported recently, and which are the result of defects of the same symmetry in the constituent 2D material layers. As examples, we show (i) that interface misfit dislocations in lateral heterostructures of 2D materials lead to similar interface misfit dislocations in moire patterns of layered structures, and (ii) that linear defects in constituent layers, such as anti-phase boundaries, lead to linear moire defects in layered structures. These defects are topological states with potentially extraordinary electronic properties, and can be engineered using our dislocation framework.

## References

[1] P. Pochet, B. C. McGuigan, J. Coraux and H. T. Johnson; Applied Materials Today **9** 240-250 (2017).

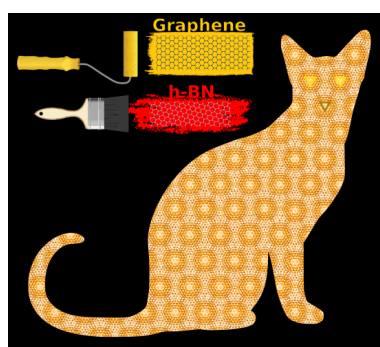


Figure 1 : Artistic view of Moiré engineering.

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# TOWARD $\pi$ -EXTENDED PORPHYRIN, ALTERNATIVE ROUTE TO FUSED UNACTIVATED AROMATIC RINGS BY THERMAL CYCLODEHYDROGENATION

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**Abstract:**  $\pi$ -extended molecular systems are of great interest according to their optical properties and more specifically due to their strong absorption and emission in NIR region. These systems may find applications in organic electronic (solar cells, photodetectors, light-emitting-diodes, thin film transistors, etc.). To reach a bathochromic shift, it is required to fuse precursors' aromatic rings which is usually performed by standard Scholl reaction using oxidative agents such as  $\text{FeCl}_3$ ,  $\text{AuCl}_3$  etc. However, this method presents some limitations such as partial fusion, chlorination or in some cases do not proceed as in the case for pyridyl-disubstituted dibenzo[5]helicene<sup>1</sup>. Fused-porphyrins are good candidates for NIR optical application as the porphyrin core intrinsically presents a strong absorption in visible region. Although, the fusion of porphyrin with Polycyclic Aromatic Hydrocarbons (PAHs) undergoes direct red-shift to NIR region. However, the Scholl reaction on such porphyrins succeed only under very specific conditions. Indeed, as demonstrated by Yamane et al. in 2004, the fusion occurred only when porphyrin is metallated with nickel and PAHs activated with donor groups<sup>2</sup>. Unfortunately, the metalation of porphyrin with nickel causes fast deactivation of the porphyrin excited stated while the substitution with donor groups drastically limits to tune the periphery of the molecule. In 2012, Thompson et al. proposed an alternative method to fuse porphyrin with PAHs in a single step by thermal cyclodehydrogenation<sup>3</sup> without nickel metalation or donor substituents on the aromatic moieties. The solubility and processability of fused compounds were conserved but a mixture of syn/anti isomers was reported due to asymmetric PAH studied.

The interesting optical properties of tetraanthracenylporphyrin (TAP) has been described by Anderson et al. with the fusion of [5,10,15,20-[4,5-bis-(2,4,6-trimethylphenoxy)anthracene]porphyrinato]nickel(II)<sup>4</sup>. Nevertheless, the fusion was achieved by Scholl reaction and proceeded only under the very specific conditions mentioned above. I present the results obtained for the fusion of nickel free and unactivated TAP using the alternative thermal cyclodehydrogenation method (figure 1). The use of symmetric anthracene moieties fused with porphyrin allows to encompass the problem of syn/anti isomers which leads to a single fused product. Finally, thermal cyclodehydrogenation could be used as alternative method to prepare graphene quantum dots from polyphenylene molecules, which do not react under standard Scholl condition.

## References

1. O. Yamane, K. Sugiura, H. Miyasaka, et al. *Chem. Lett.*, **2004**, 33 (1), 40–41.
2. A.L. Pinardi, J.I. Martinez, A. Jancarik et al. *Chem. Commun.*, **2014**, 50 (13), 1555.
3. V.V. Diev, C.W. Schlenker, K. Hanson et al. *J. Org. Chem.*, **2012**, 77 (1), 143–159.
4. N.K.S. Davis, A.L. Thompson, and H.L. Anderson, *J. Am. Chem. Soc.*, **2011**, 133 (1), 30–31.

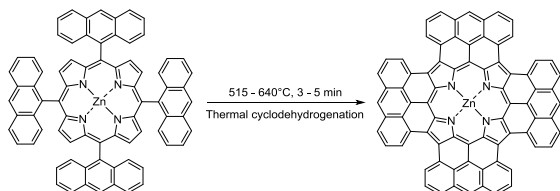


Figure 1: Thermal cyclodehydrogenation of tetraanthracenylporphyrin (TAP)

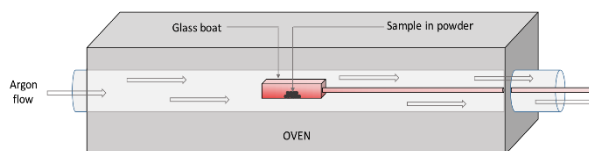


Figure 2: Oven set-up for thermal cyclodehydrogenation

## LUMINESCENCE PROPERTIES OF h-BN

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Hexagonal boron nitride (hBN) is a wide bandgap semiconductor of about 6.4 eV. Its structure is similar to graphene with an almost matching honeycomb lattice (~1.7% matching). It is considered as the most suitable substrate for preserving carrier mobility in graphene [1]. It is also used as a capping protective layer, which enhances luminescence properties of transition metal dichalcogenides [2], or decreases exciton-exciton annihilation in WS<sub>2</sub> [3]. hBN is also used in many 2D devices [4]. As a key material for 2D heterostructures, it is crucial to better understand hBN intrinsic properties.

Luminescence spectra exhibiting the deep UV emissions of hBN can be found in the literature already in 1992 [5]. In 2004, the NIMS group in Japan studied in more details hBN, stressing its high luminescence efficiency and demonstrating its stimulated emission [6]. Since then, NIMS has been providing most of the groups all around the world with good quality crystals, which allows for more investigation. Luminescence in the deep UV originates from excitonic recombinations even at room temperature [7, 8, 9]. Still, exciton properties in hBN are much less understood than in other 2D semiconductors.

In this work, I will present the latest cathodoluminescence results on bulk hBN, following our previous studies on the impact of defects [8,9] and layer confinement on the luminescence properties [8,10]. Thanks to the spectral calibration of the set-up, we could assess the internal quantum efficiency (IQE) of luminescence as a function of the temperature (from 5 K to 300 K), the depth of the excitation by varying the electron beam energy, and the excitation power. In particular, we show that the IQE remains stable from 4 to 300 K indicating a large exciton binding energy. Moreover, strong non radiative surface effects are observed with a strong IQE drop at low excitation depths. These results are discussed and compared to other reference semiconductors such as diamond and ZnO.

### References :

- [1] C.R. Dean et al. Nature nanotechnology (2010)
- [2] O. Ajayi et al. 2D Materials (2017)
- [3] Y. Hoshi et al. Physical Review B (2017)
- [4] T. Das et al. FlatChem (2017)
- [5] A. Lukomskii et al. Journal of applied spectroscopy (1992)
- [6] K. Watanabe et al. Nature materials (2004)
- [7] K. Watanabe et al. International Journal of Applied Ceramic Technology (2011)
- [8] A. Pierret et al. Physical Review B (2014)
- [9] L. Schué et al. 2D Materials (2016)
- [10] L. Schué et al. Nanoscale (2016)

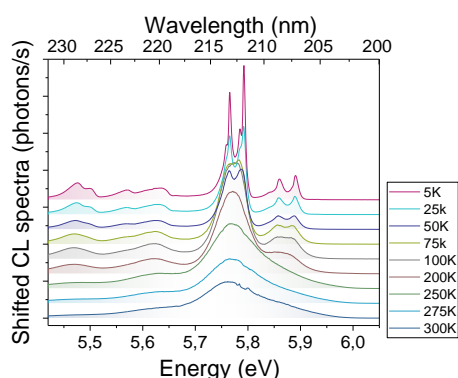


Figure 1: Temperature dependence on the luminescence

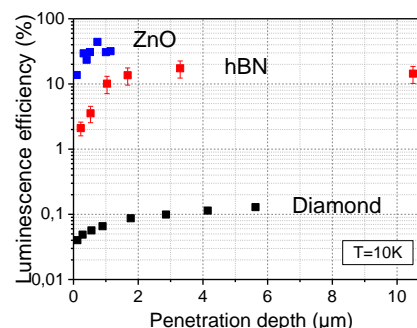


Figure 2: Luminescence efficiency as a function of the depth of excitation

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## MICROSUPERCAPACITORS PRODUCED FROM NANOCARBONS ORIGINATING FROM FOOD WASTE

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Electrochemical double layer capacitors (EDLCs), as one kind of energy storage devices, have been the subject of numerous studies in recent years due to their high power density property.<sup>1</sup> Compared with batteries, charge/discharge process is very fast, without chemical reactions involved, in the double layer of electrolyte ions which form at the interface between electrolyte and electrode of active materials.

Carbon materials, due to their inexpensive and high surface-to-volume ratio properties, are favorable to supercapacitor studies. They are active carbons, carbide-derived carbons, onion-like carbons, carbon nanotubes, reduced graphene oxides and graphenes.<sup>2</sup> Carbon materials have also been applied on pseudocapacitors by using carbon/metal oxide, for examples, MnO<sub>2</sub>, SnO<sub>2</sub> and RuO<sub>2</sub>, improving the energy density close to battery.<sup>3</sup> Capacitance of pseudocapacitors arises from both faradic redox reactions and the electrochemical adsorption/desorption of ions at the electrode/electrolyte interface. Therefore, metal oxides generally have much higher special capacitance compared with that of carbon materials for EDLCs.

To know the possibility of capacitor application for new nanocarbon materials, it is better to remain in the study of EDLCs to understand the pure physical charge/discharge process that happens at the material surfaces. Some researches on EDLCs were reported recently. EDLCs produced by onion-like carbons<sup>4</sup> have small relaxation time constant of only 26 ms due to their fully accessible surface and the power density is in the range of 10<sup>2</sup> W/cm<sup>3</sup>. EDLCs based on reduced graphene oxide<sup>5</sup> using methane-plasma treatment exhibit a high power density of 495 W/cm<sup>3</sup>.

Herein, we report a new class of nanocarbons (NC<sub>bio</sub>) derived from biogas by using a cold microwave plasma process.<sup>6</sup> NC<sub>bio</sub> nanocarbons have turbostratic packing structure and their surface can be fully accessible by ions. EDLCs (Figure 1) using NC<sub>bio</sub> nanocarbons (NC<sub>bio</sub>-NCs) were fabricated by ink-jet printing on flexible substrates, PET and PI. EDLCs show extremely very good power density and their capacitances can be easily controlled. They thus represent sustainable, low cost, EDLCs with power densities up to 50 W/cm<sup>3</sup>.

### References

- [1] J. R. Miller and P. Simon, *Science*, **2008**, *321*, 651.
- [2] P. Simon and Y. Gogotsi, *Acc. Chem. Res.*, **2013**, *46*, 1094.
- [3] Y. Wang, Y. Song and Y. Xia, *Chem. Soc. Rev.*, **2016**, *45*, 5925.
- [4] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna and P. Simon, *Nature Nanotech.*, **2010**, DOI:10.1038/nnano.2010.162.
- [5] Z. Wu, K. Parvez, X. Feng and K. Mullen, *Nature Commun.*, **2013**, DOI: 10.1038/ncomms3487.
- [6] F. Hof, K. Kampioti, K. Huang, C. Jailliet, A. Derre, C. Paukner, P. Poulin and A. Penicaud, *Carbon*, **2017**, *111*, 142.

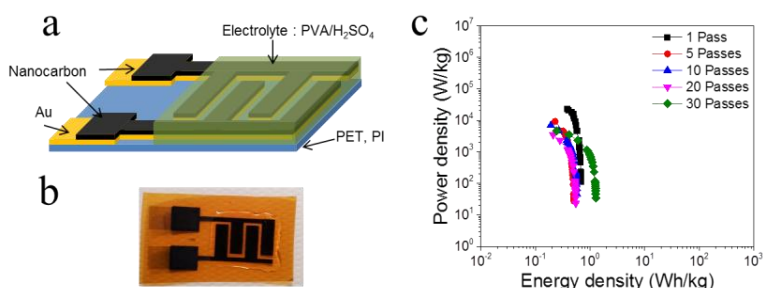


Figure 1 : (a) Scheme of micro supercapacitor produced from nanocarbons from biogas. (b) Picture of a printed micro supercapacitor on PI substrate. (c) Ragone plot of micro supercapacitors of different printing passes.

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# EXPLORING THE ELECTRON TRANSPORT IN QUANTUM HALL DEVICES BASED ON GRAPHENE GROWN BY CVD ON SiC TO IMPROVE THE ELECTRICAL RESISTANCE STANDARD

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In order to develop a reliable and practical electrical resistance standard, metrologists aim at exploiting the robustness of the quantum Hall effect (QHE) in graphene, coming from the very large energy gap between the two first Landau levels. Recent progress have been made by using graphene grown by hydrogen/propane CVD on SiC and prominent results have been obtained: the Hall resistance quantization has been observed with an excellent accuracy (below 1 ppb) in convenient experimental conditions (magnetic field of 3.5 T, temperature of 10 K or current of 0.5 mA) much simpler than those required by GaAs/AlGaAs heterostructures [1].

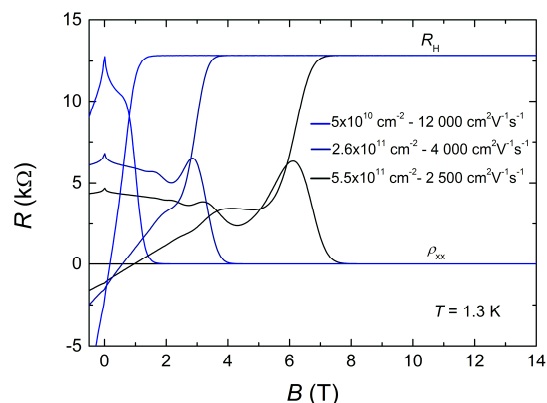
With the objective to understand the underpinning physics of these devices and its relation to the structural properties, extensive magnetotransport measurements have been performed in several samples with various characteristics: growth conditions, Hall bar size, electron concentrations ( $0.5\text{-}20 \times 10^{11} \text{cm}^{-2}$ ) adjusted by Corona discharge.

Main efforts were concentrated on quantum Hall plateaus at Landau level filling factor  $\sim 2$  and  $\sim 6$ , where measurements of the accuracy as well the temperature and current dependences of both the Hall resistance  $R_H$  and the longitudinal resistivity  $\rho_{xx}$  were performed. The objectives were to identify: the dissipation mechanism, the quantum Hall state breakdown current, the coupling between  $R_H$  and  $\rho_{xx}$ ... The expected Efros and Shklovskii model of variable range hopping between counter propagating quantum Hall edge states give an apparently correct description of the dissipation in certain cases [2] but fails in other ones. Attempts have been made to correlate the observations to the available structural properties of the samples (bilayer inclusions, orientation of the Hall bar with respect to the SiC steps...) with the hope to identify the structural key properties of the system graphene/SiC determining the ideal Hall quantization and the low dissipation. The quality of the interface layer between graphene and SiC ( $(6\sqrt{3} \times 6\sqrt{3}) - R30^\circ$  reconstructed layer) is likely to play a crucial role. Quantitative characterizations are required to confirm this assumption. Finally, even if graphene on SiC has already demonstrated impressive performance as a quantum Hall resistance standard, the question remains to know whether it is the material of choice to go beyond, with operating magnetic field down to 1 T for instance.

## References

[1] R. Ribeiro-Palau *et al.*, *Nature Nanotech.*, 10, 965 (2015)

[2] F. Lafont *et al.*, *Nature Commun.*, 6, 6806 (2015)



*Figure 1: Hall resistance ( $R_H$ ) and longitudinal resistivity ( $\rho_{xx}$ ) as a function of the magnetic flux density in a  $100 \mu\text{m}$ -wide Hall bar made of CVD graphene on SiC at various electron doping adjusted by Corona discharge.*

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## NEMATIC VS LAMELLAR ORDER IN COLLOIDAL AQUEOUS SUSPENSIONS OF NANOSHEETS

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Ordering 2D colloidal particles at the nanometer length-scale is currently a challenging and active research area in materials science.<sup>1</sup> Such ordering can spontaneously appear when anisotropic objects form liquid-crystalline phases. Well known for organic species, this tendency also exists for disk-like mineral particles<sup>2,3</sup>, thus leading to nematic, lamellar and columnar mesophases<sup>4,5</sup>. In the case of nanosheets (defined as two-dimensional crystallites of sub-micronic diameter and of well-defined, small, thickness comparable to the unit-cell size)<sup>6</sup>, nematic and lamellar phases were reported for clay particles<sup>7,8</sup>, graphene and graphene oxide<sup>9,10</sup>, titanates<sup>11</sup> or niobates<sup>12,13</sup> but so far, no columnar phase was ever described for such objects. Among nanosheets, phosphoantimonate single layers ( $\text{H}_3\text{Sb}_3\text{P}_2\text{O}_{14}$ ) were shown to display a liquid-crystalline lamellar phase<sup>14</sup> comprised of planar solid-like sheets (i.e. in which all atoms involved in a layer are covalently bonded) dispersed in water. Upon dilution, the lamellar spacing could be increased 100 fold, leading to 1D periodicities tunable from 1.5 to 225 nm. For such systems, significant differences were observed for two compounds of the same family,  $\text{H}_3\text{Sb}_3\text{P}_2\text{O}_{14}$  and  $\text{HSbP}_2\text{O}_8$ , as the former leads to a lamellar phase whereas the latter only shows a nematic phase. Likewise, clay and graphene nanosheets self-assemble into nematic phases whereas niobates and phosphates sometimes display lamellar phases. The physical origin of such a difference in behavior remains largely unknown so far but might be ascribed to differences in sheet size, rigidity, polydispersity, and/or interaction potentials.

In this context, we will present the results of our recent detailed structural investigation by polarized-light optical microscopy and x-ray scattering of both lamellar and nematic phases in the system of phosphoantimonates.

- [1] Coleman J.N. et al. (2011). Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science* **331**, 568-571.
- [2] Gabriel J.-C. P., Davidson P. (2000). New Trends in Colloidal Liquid Crystals Based on Mineral Moieties. *Adv. Mater.* **12**, 9-20.
- [3] Davidson P., Gabriel J.-C. P. (2005). Mineral Liquid Crystals. *Current Opinion Coll. Inter. Sci.* **9**, 377-383.
- [4] Brown A. B. D., Ferrero C., Narayanan T. & Rennie A. R. (1999). Phase separation and structure in a Concentrated Colloidal Dispersion of Uniform Plates. *Eur. Phys. J. B* **11**, 481-489.
- [5] Van der Kooij F. M., Kassapidou K. & Lekkerkerker H. N. W. (2000). Liquid Crystal phase transitions in suspensions of polydisperse plate-like particles. *Nature* **406**, 868-871.
- [6] Paineau E., Philippe A.-M., Antonova K., Bihannic I., Davidson P., Dozov I., Gabriel J.-C.P, Imperor-Clerc M., Levitz P, Meneau F., Michot L.J. (2013). Liquid-crystalline properties of aqueous suspensions of natural clay nanosheets *Liq. Cryst. Rev.* **1**, 110-126.
- [7] Michot L.J., Bihannic I., Maddi S., Funari S.S., Baravian C., Levitz P., Davidson P. (2006). Liquid crystalline Aqueous Clay Suspensions. *PNAS* **103**, 16101-16104.
- [8] Paineau E., Antonova K., Dozov I., Bihannic I., Baravian C., Davidson P., Imperor-Clerc M., Meneau F., Madsen A., Levitz P., Michot L.J. (2009). Liquid-crystalline nematic phase in aqueous suspensions of a disk-shaped natural beidellite clay. *J. Phys. Chem B.* **113**, 15858-15869.
- [9] Kim J.E., Han T.H., Lee S.H., Kim J.Y., Ahn C.W., Yun J.M., Kim, S.O. (2011). Graphene oxide liquid crystals. *Angew Chem Int Edit.* **50**, 3043-3047.
- [10] Xu Z., Gao, C. (2011). Aqueous liquid crystals of graphene oxide. *ACS Nano* **5**, 2908-2915.
- [11] Sasaki T. and Watanabe. M. (1998). Osmotic Swelling to Exfoliation. Exceptionally High Degrees of Hydration of a Layered Titanate. *J. Am. Chem. Soc.* **120**, 4682-4689.
- [12] Yamaguchi D., Miyamoto N., Fujita T., Nakato T., Koizumi, S., Ohta N., Yagi N., Hashimoto T. (2012). Aspect-ratio-dependent phase transitions and concentration fluctuations in aqueous colloidal dispersions of charged plate-like particles. *Phys Rev E.* **85**, 011403.
- [13] Miyamoto N., Fujita T., Nakato T. (2002). Liquid crystalline nature of  $\text{K}_4\text{Nb}_6\text{O}_{17}$  nanosheet sols and their macroscopic alignment. *Advanced Materials* **14**, 1267-1270.
- [14] Gabriel J.-C. P., Camerel F., Lemaire B.J., Desvaux H., Davidson P., Batail P. (2001). Swollen Liquid-Crystalline Lamellar Phase Based on Extended Solid-Like Sheets. *Nature* **413**, 504-508.

### References

- [1] S. Ample, *Proc. MEMS 2008*, pp. 100-103.
- [2] A. B. Stract and S. Ample, *Tech. Digest IEDM 2009*, pp. 200-205.
- [3] S. Mart and S. O. Lution, *J. Journal* ., 23 (2006), pp. 300-315.

# INNOVATIVE 3D AND 2D GRAPHENE NANOSTRUCTURE PLATFORMS FOR HIGH PERFORMANCE SUPERCAPACITOR DEVICES

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Supercapacitors (SCs), known commonly as electrochemical double layer capacitors (EDLCs), have recently emerged as promising high performance energy storage devices in a wide range of technological applications (e.g. from aerospace industry to biomedicine) due to their peculiar properties in terms of high power density and capacitance, excellent reversibility as well as long cycling stability. In spite of the intensive investigations conducted over the past decade in this domain, important drawbacks need to be overcome in order to design ultra-high electrochemical performances in the near future. For that purpose, several research activities are being studied by employing nanostructured carbonaceous architectures (e.g. different forms of graphene), advanced electrolytes (ionic liquid derivatives) or device configuration analysis (e.g. integration and compatibility of SC components with microelectronics industry) among others. In this direction, from the material perspective, architectures based on graphene nanostructures such as vertically-oriented graphene nanosheets (VOGNs) (Figure 1) and highly reduced graphene hydrogels (GHs) (Figure 2) have exhibited interesting capacitive properties by modifying their chemical surface through doping treatments, functionalization based on pseudo-capacitive materials (e.g. electroactive conducting polymers and transition metal oxides) or by controlling the spacing graphene sheets (e.g. porosity) including molecular pillars of various lengths (HD: hydrazine, ED: ethylene diamine and DB: 1,4-diaminobutane respectively), which might open up a new dimension in the field of SCs to be explored in-depth.

In this study, we present our recently reported works dealing with VOGNs and GHs nanostructures to be employed as high performance EDL materials for symmetric supercapacitors. The results demonstrated, for example in the case of VOGNs, an areal capacitance of  $2 \text{ mF cm}^{-2}$ , a power density of  $4 \text{ mW cm}^{-2}$  and an energy density value of  $4 \mu\text{Wh cm}^{-2}$  using a high and stable cell voltage of 4 V in presence of  $\text{N}_{1114}$  TFSI ionic liquid electrolyte. Additionally, 80% of the initial capacitance was retained after 300,000 galvanostatic charge-discharge cycles at a high current density of  $2 \text{ mA cm}^{-2}$  at different working temperature ranges. Such performances demonstrated the potential of this architecture to be integrated as a reliable on-chip micro-power source in miniaturized electronic devices. In this regard, GHs opens also a new and interesting alternative to develop SCs based on high specific capacitive properties (by mass), where the mass of the electrode makes an important difference compared to micro-supercapacitors based on VOGNs ( $\sim 20 \mu\text{g}$ ). Accordingly, specific capacitances of 190 F/g at a current density of 0.5 A/g and cycling stability over 2000 cycles at 10 A/g were evaluated. Furthermore, a high capacitance of 123 F/g could be retained at a very high current density of 100 A/g. Therefore, regarding the state-of-the-art, these results have been proven as one of the best electrochemical performances reported in literature by comparison with other graphene nanostructures.

## References

- [1] D. Aradilla, M. Delaunay et al. *J. Mater. Chem. A*, 3 (2015), pp. 19254-19262.
- [2] D. Aradilla, M. Delaunay et al. *Current Smart Mater.*, (2017), Just accepted.
- [3] H. Banda, D. Aradilla et al. *J. Power Sources*, 360 (2017), pp. 538-547.

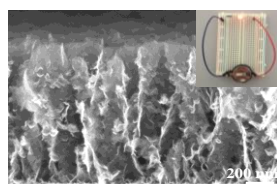


Figure 1: SEM image of VOGNs on silicon substrates. Inset shows a technological application of a VOGN-Based micro-supercapacitor.

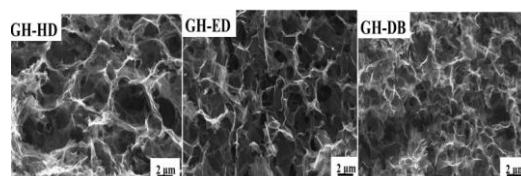


Figure 2: SEM image of the GHs frameworks

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# Scientific and social program

	Sunday, 15 <sup>th</sup>	Monday, 16 <sup>th</sup>	Tuesday, 17 <sup>th</sup>	Wednesday, 18 <sup>th</sup>	Thursday, 19 <sup>th</sup>	
8:30		<i>Chair: A. Siria</i> Invited: Pierre Verlot	<i>Chair: C. Voisin</i> Invited: Yuriy Zakharko			8:30
9:00		Oral: Antoine Reserbat-Plantey	Oral: Emmanuel Courtade	<i>Chair: A. Loiseau</i> Invited: Rebecca Ribeiro		9:00
9:30		Oral: Loïc Huder	Oral: Vincent Jourdain	Oral: Catherine Journet	<i>Chair: J. Coraux</i> Invited: Andrew Mayne	9:30
10:00		Oral: Benoit van Troeye	Oral: Viet Hung Nguyen	Oral: Tianlin Wang	Oral: Jean-Yves Veuillen	10:00
10:30		Poster clips #1-4	Poster clips #16-24	Oral: Christophe Bichara	Oral: Carlos Alvarez	10:30
11:00		Coffee break	Coffee break	Coffee break	Coffee break	11:00
11:30		<i>Chair: S. Roche</i> Invited: Aurélien Lherbier	<i>Chair: S. Campidelli</i> Invited: Manuel Dossot	<i>Chair: A. Noury</i> Invited: Alessandro Siria	<i>Chair: J. Dijon</i> Oral: Simone Lisi	11:30
12:00		Oral: Muriel Sicot	Oral: Stéphane Campidelli	Oral: Pranauv Balaji Selvasundaram	Oral: Henri Prévost	12:00
12:30		Oral: Philippe Dollfus	Oral: Cécile Delacour	Lunch	Conclusions	12:30
13:00		Oral: Aurélie Champagne	Invited: Gérauld Delport	Lunch	Lunch	13:00
13:30		Lunch	Lunch		Shuttle → train station (13:15)	13:30
14:00		<i>Chair: A. Pénicaud</i> Invited: Vincent Bouchiat	<i>Chair: J.-C. Charlier</i> Tutorial: Stephan Roche	<i>Chair: N. Izard</i> Invited: Carmen Palacios-Berraquero		14:00
14:30		Oral: Hélène Le Poche		Oral: Georgy Fedorov		14:30
15:00		Oral: Dipankar Kalita	Poster session 2 #15-24	Oral: Lorenzo Sponza		15:00
15:30		Oral: Lorie David		Oral: Phuong Vuong		15:30
16:00		Poster clips #5-9		Refreshment		16:00
16:30		Coffee break		<i>Chair: V. Bouchiat</i> Invited: Guillaume Froehlicher		16:30
17:00	Arrival, registration, check-in and dinner	<i>Chair: F. Vialla</i> Invited: Emmanuel Baudin		Oral: Fabien Vialla		17:00
17:30		Oral: Benoit Jouault				17:30
18:00		Oral: Tino Cubaynes		<i>Chair: C. Voisin, A. Loiseau</i> GDR/GDR-I general assembly		18:00
18:30		Oral: Jean-François Dayen	Apéritif			18:30
19:00		Oral: Jean-Marie Poumirol	Dinner	Conference dinner and party		19:00
20:00		Poster clips #10-15				20:00
20:30		Dinner				20:30
21:00	Poster session 1 #1-14	Poster session 1 #1-14				21:00
21:30	Welcome address <i>Chair: C. Voisin</i> Tutorial: Kiril Bolotin					21:30