# 2D MATERIAL BASED DEVICES AND PROCESSES FOR INDUSTRIAL APPLICATIONS

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The experimental investigation and computational analysis of nanoscale phenomena is enabling technologies for transforming industrial processes. Nanoscale materials such as graphene or 2-dimensional semiconductors, due to their extreme surface-to-volume ratios and unique optoelectronic properties, are enabling device functionalities that cannot be realized with bulk materials. In this presentation, I will discuss how 2-dimensional materials can be integrated within measurement platforms for characterizing their physical properties and for realizing sensing functionalities within exploratory lab-on-chip devices. Demonstrations include integrated optoelectronic devices and sensors for studying liquid-solid interactions at nanometer scale [1-4]. Potential industrial applications for integrated, 2-dimensional measurement functionalities range from lab-on-chip analysis for natural resources exploration to bottom-up nanomaterial assembly for large-scale device integration.

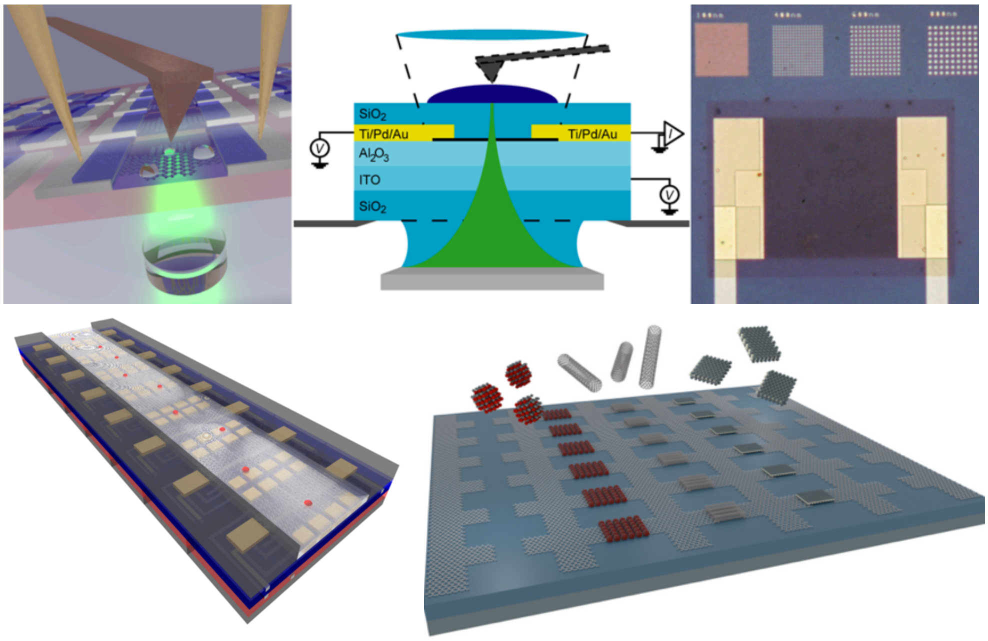

*Figure 1: Examples of exploratory devices and processes using 2-dimensional materials for industrial applications, adopted from references [1-4].*

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# DYNAMIC SPRAY-GUN DEPOSITION: A NEW WAY OF CONCEIVING THE LEGO VIEW FOR 2D AND 1D NANOMATERIALS

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This contribution deals with the fabrication of devices based on graphene based nanomaterials using dynamic spray-gun deposition method implemented through roll-to-roll. We used this technique to fabricate sensors, supercapacitors [1], flexible memories [1] and conformable Electro-Magnetic interference Shielding (EMI) layers. In the first case we exploited the nanostructuration of mixtures of graphene and carbon nanotubes (CNTs) to achieve electrodes for supercapacitors. Indeed the MWCNTs are used as sort of spacers to avoid the restacking of graphene. Thanks to that we can exploit the huge surface of graphene to store charges and at the same time we create channels between the layers allowing the rapid charge and discharge of the device. The use of high quality graphene (<5 layers) and MWCNTs, with a diameter of around 20nm, also improve the conductivity for the electrodes and allowed us obtaining an impressive specific power value of around 100kW/Kg using an industrially suitable technique and not only a lab based one [2-3]. The spray-gun deposition method has been also implemented in the fabrication of GO and CNFs Oxidized based memories. In this case we case spray nanomaterials water based suspensions on a flexible layer previously metallized. The total thickness is around 100nm. After contacting the top with metallic contacts we are able to achieve flexible non volatile memories simply applying a bias (<3V). These memories show bipolar behavior and have been cycled 10000 times. They constitute one of the first examples of information storage devices that can be fabricated using a roll-to-roll implementable method. Finally, we have achieved EMS architectures using nanostructuration of graphene, MWCNTs and carbon nanofibers between polymers layers in order to exploit the Maxwell-Wagner-Sillars effect to absorb X-band frequencies. Thanks to this nanostructuration we are able to trap the charges in sort of micro-capacitors created in the layers. This is a real breakthrough considering that usually heavy metal based layers are used and that in this case mm based conformable layers can be obtained opening the route for new kinds of applications. Also in this case the fabrication will be implemented by roll-to-roll fabrication. During the presentation we will show all the details on the first characterization of devices and we will show also perspectives for other potential field of applications.

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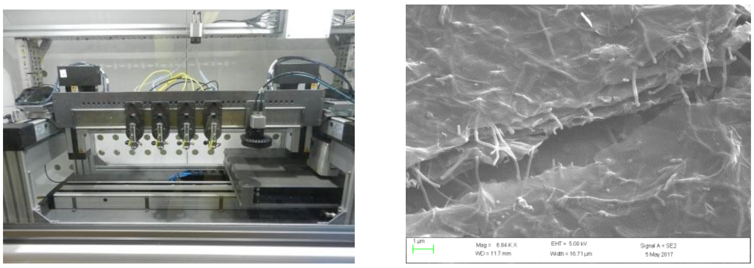

Fig. 1. Large surface deposition facility developed in the frame of the Graphene Flagship on the left; Example of nanostructuration for Supercapacitors using Graphene and Carbon nanofibers.

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# NANOMAT: INNOVATION BY COLLABORATION

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NanoMat, located with its managing office at the Karlsruhe Institute of Technology (KIT), was founded in 1997 as one of the first nano competence centers in Germany. Our members are noted partners from industry and academia that focus their efforts on a variety of application-oriented projects in nanotechnology and materials research.

NanoMat acts as a virtual enterprise, fostering and executing application-oriented R&D projects, as well as organizing dedicated workshops and symposia that encourage information exchange between and within subject areas. Our network also contributes to an active political dialogue on nanotechnology and nanomaterials. In the talk I will discuss recent activities, transfer groups on nano-enabled electronics and biomaterials as well as our work in standardization commitees.

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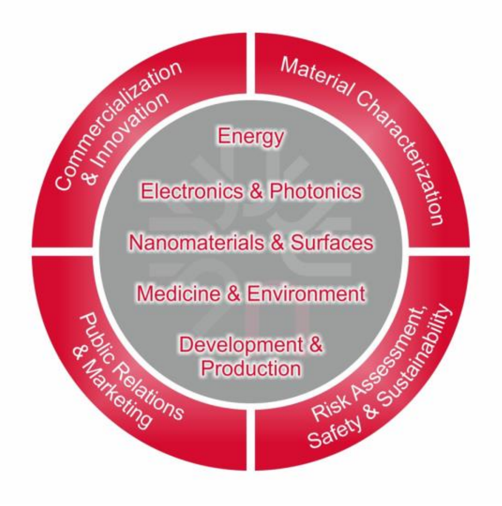

*Figure 1 : Nanomat Topics*

*Figure 2 : Nanomat Logo and Bronze Label*

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# 2D-MATERIALS-BASED NEXT-GENERATION ENERGY DEVICES

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Graphene and related two-dimensional materials (GRMs) are entering several application areas,[1-5] improving the performance of existing devices or enable new ones.[1-5] A key requirement for the implementation of GRMs in the energy field is the development of industrial-scale, reliable, inexpensive production processes,[2] while providing a balance between ease of fabrication and final product quality.

In this context, the production of GRMs by solution processing[2,6] represents a simple and cost-effective pathway towards the development of GRMs-based energy devices, presenting huge integration flexibility compared to other production methods. Here, I will first present our strategy to produce GRMs on large scale by wet-jet milling[7] of their bulk counterpart and then an overview of their applications for energy devices. [3,8,9,10,11,12,13,14]

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# MOLECULAR IMPRINTED FUNCTIONNALIZED GRAPHENE FOR NEW ENVIRONMENTAL ELECTROCHEMICAL SENSORS DEDICATED TO THE DETECTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER

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One of the main challenge of our modern society, is the evaluation and the control of pollution in the environment, especially for the air and water quality. For water, the European Union has edicted the water frameworks directive in 2000. The revision of this directive (2013) defines new thresholds of detection and new settings for the analysis of 45 prioritary micro-pollutants in aqueous media. These micro-pollutants belong to different chemical families including heavy metal ions as Copper, Lead or organic molecules such as Polycyclic Aromatic Hydrocarbons (PAH) for example. This chemical diversity involves the development of specific and sensitive sensors for their detection.

In this way, for performing the detection of anthracene (PAH) in water, we developed CVD graphene electrodes functionalized with a Molecular Imprinted Polymer (MIP). In this sensor the graphene is used as a conductive platform both for performing the electropolymerization of the MIP, and then for detecting the target molecule by electrochemistry method. The selectivity of the sensor is obtained by the MIP layer linked to the graphene surface[1]. The MIP is electropolymerized on the graphene electrode in a solution containing the monomer and the target micropollutant as template molecule. The graphene/MIP electrode is obtained after an electrochemical treatment to extract the template molecules from the polymer layer to create selective cavities with the shape of the template molecule. The graphene/MIP electrode is then ready to detect the target molecule.

We will present, for the first time, the development of a CVD Graphene/MIP sensors for anthracene detection. The different step of the graphene/MIP electrode will be described: (i) exfoliation of the CVD graphene from the Copper to Si/SiO2 substrates for the preparation of the CVD graphene electrode, (ii) electropolymerisation of the MIP and extraction of the template to obtain the CVD Graphene/MIP sensors. Finally the electrochemical behavior of the CVD Graphene/MIP sensors will be studied and its evaluation for the anthracene detection will be determinate in terms of selectivity and sensibility. Concentrations at ppb level have been obtained for the anthracene detection with these sensors[2].

At each steps of the sensors elaboration, we also characterized its properties and structure by different techniques such as, Raman spectroscopy, Atomic Force Microscopy, Scanning Electron Microscopy, and by electrochemistry. With AFM, we were able to evaluate the thickness of the polymer layer on graphene and the morphology of the layer.

We gratefully acknowledge the financial support provided to the PIVOTS project by the Région Centre – Val de Loire (ARD 2020 program and CPER 2015 -2020) and the French Ministry of Higher Education and Research (CPER 2015 -2020 and public service subsidy to CNRS and Université d'Orléans).

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# SMART SYSTEM INTEGRATION OF A CHEMISTOR ARRAY BASED ON POLYMER-FUNCTIONALIZED-CARBON NANOTUBES ENABLES HIGHLY SELECTIVE WATER QUALITY MONITORING

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In the field of water quality monitoring, there is an increasing demand for compact, low cost, multiparameter probes operating in-situ and in real time. For these, selectivity to chemicals remains a critical challenge. To tackle this issue, we adopted the route of non-covalently functionalizing multi-walled carbon nanotubes (MWCNT) with a series of conjugated polymers specially designed to recognize the target analytes [1].

Briefly, we synthetized the various polymers, formulated the MWCNT-polymer inks [2] and optimized the ink-jet printing process of these inks to elaborate the chemistors. We ended up with advanced integration and multiplexing of our MWCNT-based chemistors (Fig. 1): first, we achieved up to 25 sensors made out of 5 different inks integrated on a less than 0.5cm² silicon chip and targeting chlorine, chloride, hardness, nitrate and pH; second, the MWCNT sensors are co-integrated with MEMS sensors on the same “sensor chip”: temperature, pressure, flow rate, conductivity; third the sensor chip itself is integrated at PCB level with a CMOS chip managing the analogic front end and most of the digital functions, forming a “sensor head”; finally, the sensor head is integrated into a wireless, energy-autonomous sensor probe 10 times more compact than commercially available so far. This probe, fabricated in pre-series (35 prototypes) was deployed in a model network (Sense-City, IFSTTAR, France) and in a real network in Almada, Portugal. Events related to chlorination or salt ingress were detected in quasi real-time. [3]

In parallel, characterizations in the lab of over 100 chemistors have shown that, by judiciously choosing the range of initial resistances (between 10kΩ and 120 kΩ) and the polymers, contrasts of sensitivity with respect to pristine MWCNT (ratio between the sensitivity of functionalized and non-functionalized MWCNT, for comparable resistance levels) ranging from 0.05 to 10 may be achieved. For instance, 60 to 80kΩ devices fabricated with the FF-UR polymer (Fig. 1 left) may be up to 20 times less sensitive to pH (pH 5 to 8) than pristine MWCNT and up to 10 times more sensitive to $NaNO_3$ (0 to 100mg/L $NO_3^-$), while being only twice more sensitive to NaOCl (0 to 5 mg/L HOCl) and to $CaCl_2$ (0 to 200 mg/L $Ca^{2+}$) and twice less sensitive to KCl (0 to 250 mg/L $Cl^-$).

These strong results regarding to selectivity in water of functionalized carbon nanotube-based chemistors, obtained on pre-industrial prototypes during the course of the H2020 Proteus project and the CHARMMMAT project Capsule, have triggered various follow up actions: while basic research is ongoing to better understand the outcomes (ANR 4WATER), a startup is being prepared via SATT Paris Saclay funding and several H2020 projects (LOTUS, Fiware4Water) are ongoing to foster field deployment of the solution in actual use cases.

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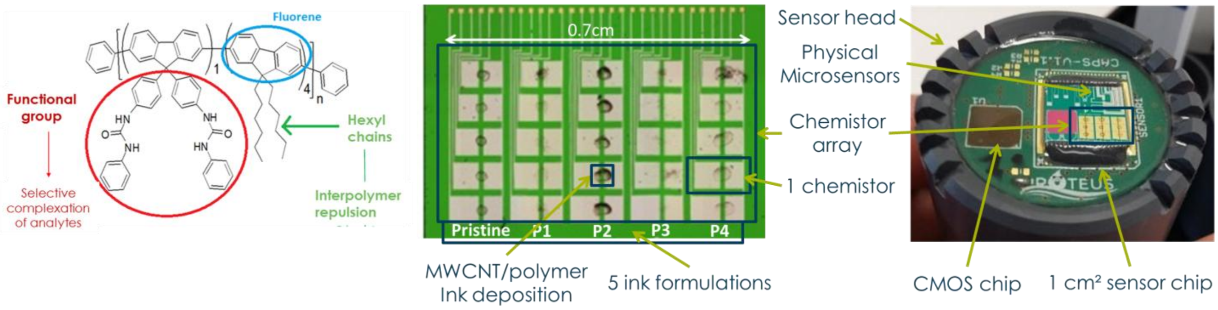

*Figure 1 : Left – FF-UR polymer; middle – chemistor array; right – sensor head in its mechanical package*

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# NEAR INFRARED SENSING AND IMAGING WITH CARBON NANOTUBES

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Carbon nanomaterials such as semiconducting single-walled carbon nanotubes (SWCNTs) are versatile building blocks for optical biosensors. SWCNTs fluoresce in the near infrared (nIR, 900-1700 nm) and their optoelectronic properties are very sensitive to changes in the chemical environment but a) achieving high selectivity and sensitivity and b) targeting or delivering those sensors to specific locations in cells or organisms is still a great challenge. Therefore, we use novel chemical and physical approaches to better understand SWCNT photophysics and enhance the capabilities of SWCNT-based fluorescent sensors for biomedical applications:

1) We tailored the corona phase around SWCNTs to enhance selectivity and photophysics of SWCNT-based sensors for the neurotransmitters dopamine and serotonine[1].
2) SWCNTs were conjugated to nanobodies that can be targeted in vivo to any Green Fluorescent Protein (GFP) moiety. These SWCNTs were used for single-particle tracking and microrheology measurements in living drosophila embryos[2].
3) Peptides were incorporated into the organic corona phase around SWCNTs to target surface receptors on cells (integrins) and label them in the nIR[3].
4) Immune cells were used for programmed sensor transport and release of SWCNTs. They take up SWCNT-based sensors, transport them and release them again.

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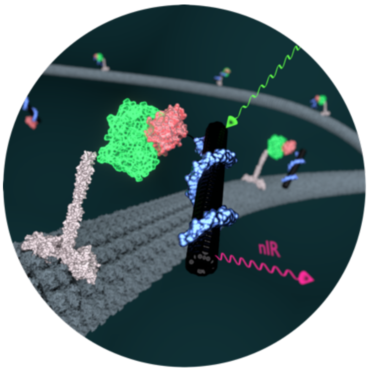

*Figure 1 : nIR fluorescent carbon nanotubes*
for biophotonics

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# BRIGHTENING OF LONG, POLYMER-WRAPPED CARBON NANOTUBES BY LARGE-SCALE SP3 FUNCTIONALIZATION

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Narrowband emission in the near-infrared and electrical generation of excitons make semiconducting single-walled carbon nanotubes (SWNTs) desirable materials for light-emitting devices [1]. Up to now, the efficiency of these devices has been limited by the low photoluminescence quantum yield (PLQY) of SWNTs and strong self-absorption owing to their small Stokes shift. To tackle these shortcomings, the controlled introduction of $sp^3$ defects as exciton trapping sites emerged; leading to red-shifted emission, longer exciton lifetimes and higher PLQYs. However, the synthetic methods to achieve the required low-level functionalization are so far limited to aqueous dispersions of SWNTs with often short tube lengths, residual metallic nanotubes and poor film formation properties. Here, we report a method for the simple and large-scale $sp^3$ functionalization of polymer-wrapped SWNTs in organic, non-halogenated solvents, thereby making it compatible with nanotubes dispersed by shear-force mixing. The low density of exciton quenching sites on shear-mixed SWNTs [2] enables efficient channeling of excitons to emissive defect sites and absolute PLQYs of 4 % for dispersions of long and polymer-wrapped (6,5) SWNTs in toluene. The resulting access to large quantities of high-quality $sp^3$ functionalized SWNTs paves the way toward their application in thin film optoelectronic devices.

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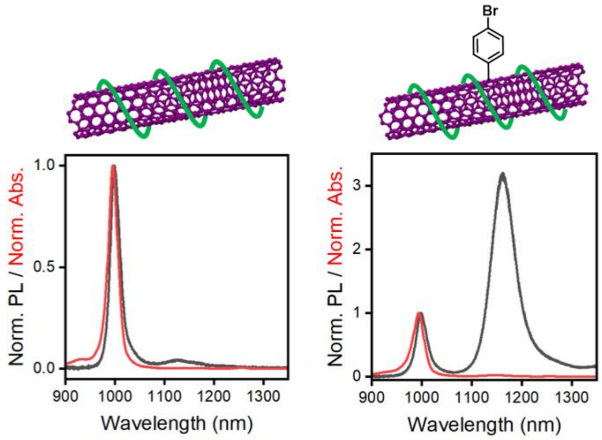

*Figure 1: Comparison of absorption and photoluminescence spectra of pristine (left) and $sp^3$ functionalized (right) polymer-wrapped (6,5) SWNTs in toluene.*

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# ELECTROLUMINESCENCE FROM CARBON NANOTUBES: LOW TEMPERATURE, TAILORED DEFECTS AND SHORT CHANNELS

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The exploration of light matter interaction in carbon nanotube has become an increasingly active research area and boosted by the prospects related to single photon emission in the NIR. Our contribution in the last years has been the development of carbon nanotube based on chip light sources integrated in optical waveguides that are electrically driven [1], and may provide a potential solution to a technological gap existing in silicon photonics. The devices are CMOS compatible, scalable, have a response time below 100 ps [2] and can be spectrally tailored by engineering the photonic environment [3]. Moreover they can be operated as non-classical light sources at the verge of single photon emission [4], and have potential as electrically driven quantum emitters for on chip quantum information processing [5]. Yet, the reproducibility of electrically-generated light emission is often limited by instabilities in current injection. Therefore we are focusing now on understanding and controlling the injection of carriers and the generation and recombination of excitons in pristine nanotubes and in nanotubes with tailored defects. Most importantly we acquired for the first time low-temperature electroluminescence excitation maps which help us to better understand the device physics and to identify regimes of stable excitonic and trionic emission.

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# CRYOGENIC SUPER-LOCALIZATION OF EXCITONS IN CARBON NANOTUBES.

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Rather unexpected for a 1D system, the optical properties of individual carbon nanotube (CNT) - especially at low temperature - exhibit signatures that are usually those of a 0D system. Among them, spectral diffusion, blinking or photon antibunching [1] can be attributed to a (usually unintentional) localization of excitons in local potential well. In the quest for carbon nanotubes based quantum light sources, this unexpected property was exploited to generate promising single photon sources in various photonic designs [2, 3]. Although these 0D signatures are widely observed, the physical origin and the properties of the trapping mechanism are still poorly documented.
Here, by using a spectrally resolved super-localization of the exciton along the nanotube axis, we were able to find the position of each trap along the CNT axis (with 20 nm resolution) (cf figure). In the same time the analysis of the spectral lineshape (in particular the phonon wing profile) allows to determine the trap width. By concatenating results on a large collection of CNTs we found that the typical nearest neighbour distance between traps is 70 nm, that their width is around 20 nm and that the distribution of depth is 50 meV wide. By using quasi-resonant photo-luminescence excitation (PLE) we found that each trap has its own higher order resonances, without any common excited state (that could stand for the free exciton band ). Confirmed by numerical simulation this eliminates the possibility of a flat energetic profile with discrete traps. The potential landscape for the exciton center of mass that allows to simulate the quasi resonant PLE and also the temperature dependant PL, is rather a totally disordered potential.
From the viewpoint of optics, the nanotube behaves like an original emitter where a collection of pseudo two-level systems that can be addressed -within the same diffraction limited spot- either individually through the localized excited states or collectively through higher energy 1D states. This approach could be generalized to create densely packed and individually addressable single-photon sources within the same nanotube using the emerging defect engineering techniques.

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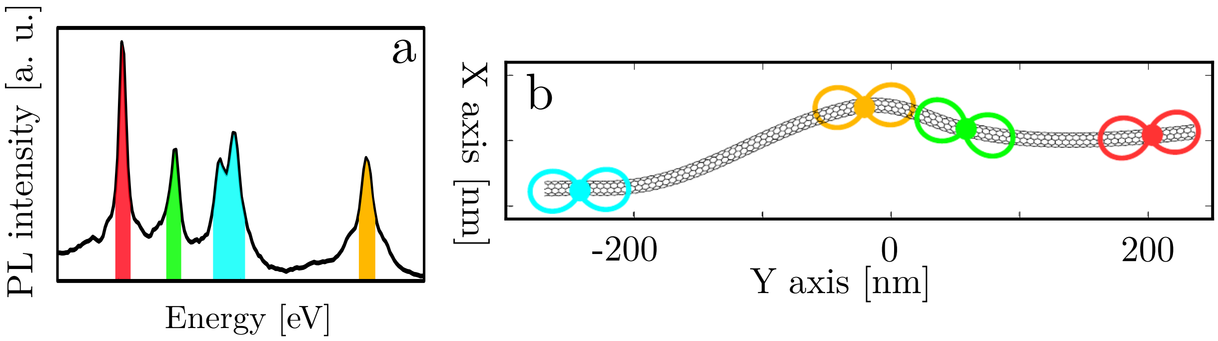

Figure 1: (a) PL spectrum (10 K) . (b) Location of the center of the optical spot in the xy plan, for each lines, together with their corresponding polarization diagram indicating the local orientation of the CNT (a schematic representation of the nanotube is added as a guide to the eye).

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# ACTIVE CONTROL OF SINGLE PHOTON SOURCES USING 2D MATERIALS

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Solid state quantum emitters are a mainstay of quantum nanophotonics as integrated single photon sources (SPS) and optical nanoprobes[1,2]. Integrating such emitters with active nanophotonic elements is desirable in order to attain efficient control of their optical properties but typically degrades the photostability of the emitter itself[2]. In our group, we have developed optomechanical[3] and optoelectrical[4] approaches to either tune energy and decay rate of single photon sources. In this talk, I will present recent experiments[4] that demonstrate a tuneable hybrid device which integrates lifetime-limited single emitters (linewidth: 40 MHz) and 2D materials at sub-wavelength separation without degradation of the emission properties. Our device's nanoscale dimensions enable ultra-broadband tuning (tuning range > 400 GHz) and fast modulation (frequency: 100 MHz) of the emission energy, which renders it an integrated, ultra-compact tuneable SPS. Our latest results show deterministic nano-structuring technique based on electron-beam lithography for shaping polymers with embedded single molecules[5]. Hybrid systems made of 2D material interfaced with single linewidth limited quantum emitter enables manipulation of the emitter properties at the scale of a single molecule, which would have a strong impact for quantum nanophotonics and optomechanics.

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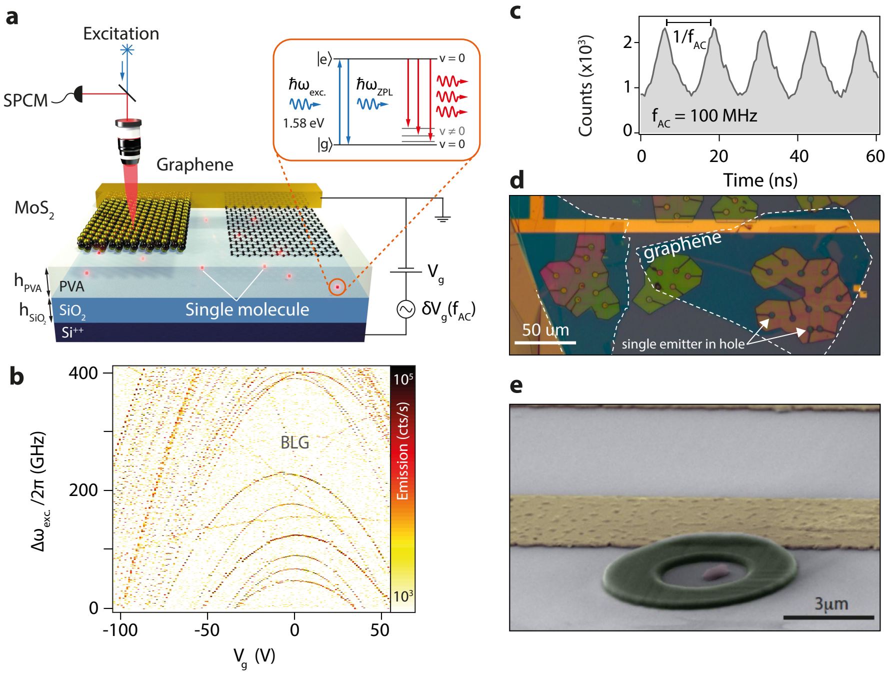

*Figure 1. a: graphene and MoS2 top electrodes for electrostatic tuning of fluorescent molecules. b: Stark shift of an ensemble of single molecules under graphene electrode. c: Histogram of time-resolved single molecule emission intensity modulation (100 MHz). EBL shaped polymer to create support (e) to transfer graphene resonators on top of single crystal containing linewidth limited quantum emitters (d).*

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# OPTICAL PROPERTIES OF 2D MATERIALS AND HETEROSTRUCTURES

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The physical properties of two-dimensional semiconductors, such as transition-metal dichalcogenides (TMDCs), can be modified through the presence of adjacent materials, as in van-der-Waals heterostructures or in covalently functionalized layers. As an example for such an interlayer interaction, we present recent results on the interlayer excitons in $MoSe_2$-$WSe_2$ and $MoS_2$-$WSe_2$ heterostructures [1]. We show that the interlayer excitons are indirect both in real space and in reciprocal space. Furthermore, we predict the structures and properties of two-dimensional antimony oxide [2], which may form if few-layer antimonene is oxidized in ambient conditions. Depending on the stoichiometry, the oxidized antimonene layers are semiconducting with band gaps between 0.8 eV and 4.9 eV. Therefore, oxidation of few-layer antimonene may result in natural heterostructures composed of semiconducting antimonene oxide and semimetallic few-layer antimonene.

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# ELECTRONIC TEMPERATURE DEPENDENT SUPPRESSION OF INTERFERING QUANTUM PATHWAYS IN GRAPHENE RAMAN SCATTERING

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We show that the intensities of the two dominant Raman signals G and 2D of graphene together with their ratio strongly depend on the laser intensity for pulsed excitation because of electron temperature dependent suppression of interfering quantum pathways. High electronic temperatures reached for pulsed laser excitation lead to an asymmetric Fermi-Dirac distribution at the different optically resonant states contributing to Raman scattering. This results in a partial blocking of destructively interfering quantum pathways for G band scattering, which is observed as a super-linear increase of the G band intensity with laser power. The 2D band, on the other hand, exhibits sub-linear intensity scaling due to the blocking of constructively interfering contributions.

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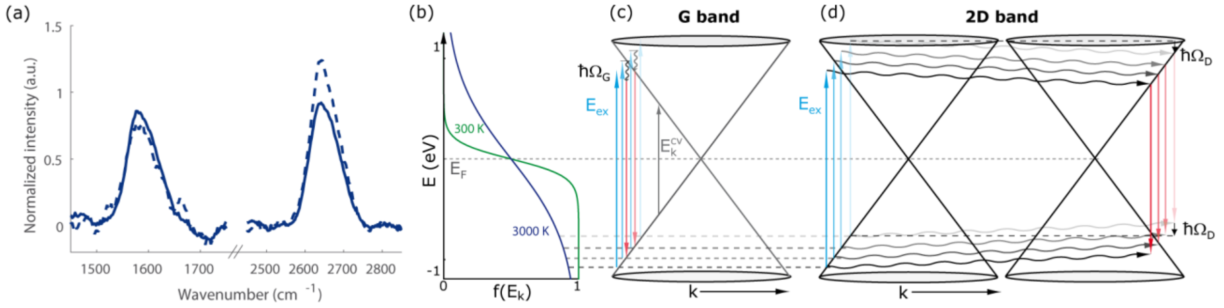

**Figure 1:** (a) Raman G (left) and 2D band (right) normalized by the excitation power (Solid line: 63µW, dashed line: 16µW) for ps pulsed excitation at $E_{ex}$ = 1.96 eV. (b) Fermi-Dirac distribution for low (300K) and high (3000K) electron temperatures. (c,d) Energy level scheme illustrating processes leading to G and 2D band scattering, respectively. Thermal excitation of electrons leads to reduced light absorption for both G and 2D band scattering for initial electron energies below $E_F$. Importantly, for G band scattering this reduction is more pronounced at the electron energy involved in the outgoing resonance ($\boldsymbol{E_{ex} - E_k^{cv} - \hbar\Omega_G}$) as compared to that of the incident resonance ($\boldsymbol{E_{ex} - E_k^{cv}}$). Because interference between these two resonances is predominately destructive[1,2], hot electron distributions result in an increase of the G band intensity.

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# MULTIMODAL KPFM INVESTIGATIONS OF 2D VAN DER WAALS OPTOELECTRONIC INTERFACES

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Atomically thin transition metal dichalcogenides (TMDCs) display exceptionally strong light-matter interactions and a direct bandgap when thinned down to the 2D monolayer, especially suited to highly performant optoelectronic devices. Smart photodetectors with gate-tunable photo-responsivity and temporal response have been realized by incorporating TMDC monolayers into field effect architectures [1]. In addition, several pairs of TMDCs (e.g. $WSe_2/MoS_2$) can form type-II interfaces and have already shown efficient photo-induced electron-hole pairs separation [2], paving the way for atomically thin photovoltaics [3]. Controlling the band alignment at the TMDC/substrate and TMDC/TMDC interfaces, understanding the photo-carrier generation mechanisms, and mastering the charge trapping/release dynamics are three key ingredients to realize efficient optoelectronic devices. In this communication, we will present the works undertaken in our group to implement complementary imaging modes based on the Kelvin Probe Force microscope under ultrahigh vacuum, which when combined should allow addressing all of these issues with a single instrument. First, it will be shown how surface potential imaging and differential surface photo-voltage (SPV) mapping can be used to probe at once the band alignment and the electron-hole quasi Fermi levels splitting under illumination in type II TMDC-based vertical heterojunctions. Then, two time-resolved electrostatic modes will be introduced: KPFM under frequency-modulated illumination [4] and pump-probe KPFM. Both can be used to map 2D images (acquired in data-cube spectroscopy) of the SPV dynamics. It will be argued why the SPV dynamics probed by time-resolved KPFM can be used to predict the photo-response time of TMDC-based photodetectors.

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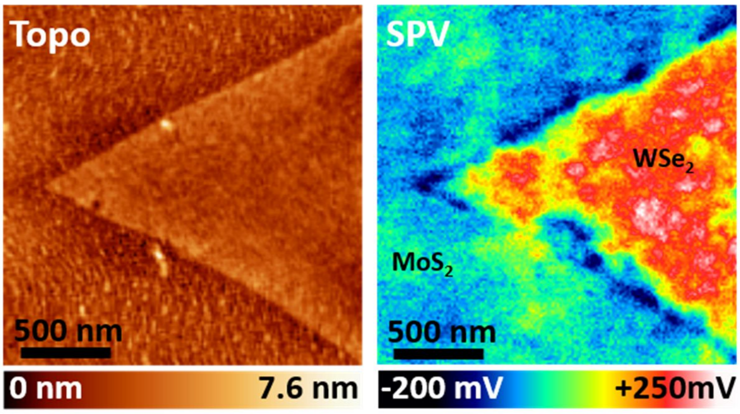

*Figure 1: non-contact Atomic Force Microscopy (nc-AFM) topographic image and differential surface photo-voltage (SPV) image of a vertical $WSe_2/MoS_2$ hetero-junction (substrate: $SiO_2$/doped-Si).*

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# BOTTOM-UP MOLECULAR SYNTHESIS OF ATOMICALLY PRECISE GRAPHENE NANORIBBONS AND QUANTUM DOTS

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Whereas graphene, namely isolated monolayer of graphite, demonstrate exceptional electronic and mechanical properties, its lack of bandgap prohibits its applications as an active semiconductor material.[1] In contrast, graphene nanostructures such as graphene quantum dots (GQDs) and graphene nanoribbons (GNRs) possess open energy gaps, and are promising for nanoelectronic and (opto)electronic applications.[1–3] The properties of such nanoscale graphenes are critically dependent on their size, morphology, and edge configuration, which makes it essential to precisely control their chemical structures. Although, the required precision cannot be achieved by "top-down" fabrication methods such as "cutting" of graphene, bottom-up chemical synthesis can provide atomically precise GQDs and GNRs, either "in solution" by the conventional synthetic chemistry or "on surface" using the method of modern surface science.[1–3] We have thus synthesized GQDs and GNRs with varying structures and properties, for example, achieving fine-tuning of the bandgap and incorporation of heteroatoms.[1–3] We can also covalently functionalize the GNR edges with high accuracy, modulating the electronic properties and supramolecular behavior (Figure 1)[4] or inducing magnetic edge state.[5] Moreover, dibenzo[*hi,st*]ovalene (DBOV) as a highly stable GQD having a combination of armchair and zigzag edges (Figure 2), which showed strong red fluorescence, stimulated emission, and amplified spontaneous emission, making it promising for light emitting and lasing applications.[6] We have more recently achieved regioselective edge bromination of DBOV, allowing for introduction of different functional groups for altering the optoelectronic properties[7] as well as to make DBOV soluble in water for bioimaging applications. These results highlight the high potential of such atomically precise graphene nanostructures for various applications, ranging from nanoelectronics and optoelectronic to spintronics and bioimaging.

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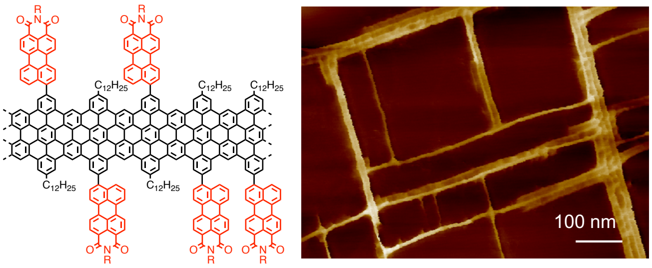

*Figure 1: Chemical structure of a bottom-up-synthesized graphene nanoribbon functionalized with perylene monoimide groups (left) and an atomic force microscope image of its assembly on a graphite surface (right).*[4]

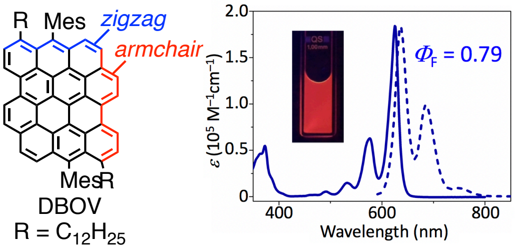

*Figure 2: Chemical structure of DBOV (left) and its absorption and emission spectra. Inset: a photograph of the solution under UV irradiation, showing red fluorescence.*[6]

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# TOWARDS GRAPHENE NANORIBBON TUNNELING FIELD-EFFECT TRANSISTORS VIA A CHEMICAL DOPING ROUTE

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One of the most powerful properties of quasi-1D graphene nanoribbons (GNRs) that are synthesized via the bottom-up approach is the opportunity to form tailored heterojunctions with atomic precision. No other material currently available lets us exercise this level of control over its properties. In this work we synthesized an array of densely packed armchair graphene nanoribbons of N = 7 carbon atoms width (7-AGNRs) having a wide band gap, and perform a controlled conversion into narrow-band-gap 14-AGNRs. The obtained system was investigated *in situ* using ultra-high vacuum (UHV) Raman spectroscopy [1] and characteristic Raman modes of 14-AGNRs were identified for the first time. Using angle-resolved photoemission spectroscopy (ARPES) complimented by simulation of photoemission intensity [2, 3], we unambiguously determine the energy band dispersion of 14-AGNRs. Performing chemical doping of the system *in situ* by Li adatoms, we realized semiconducting-to-metal transition in 14-AGNRs, and by ARPES visualized the lower conduction 1D sub-band of 14-AGNRs. Finally, the array composed of the 14-AGNRs/7-AGNR heterojunctions was transferred onto a $SiO_2/Si$ substrate in the same manner as we did earlier for pristine 7-AGNRs [4], and integrated in a field-effect transistor (FET). We characterized the 14-AGNRs/7-AGNR FET and performed the Li doping of this system in UHV. The interesting feature of our experiment is that the 14-AGNRs become metallic upon the chemical doping, but 7-AGNRs are still semiconducting. We suggest that the tunneling of charge curriers from the metallic to the semiconducting GNRs determine the transport behavior of the FET. Our results suggest that GNRs are a suitable material for the fabrication of tunneling FETs which will be a key component for energy efficient electronics.

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# TOWARDS PHOTO-STABLE GRAPHENE-DYE CROSS-LINKED POLYMERS

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We report on the realization of a novel diketopyrrolopyrrole-graphene covalent cross-linked hybrid with excellent film-forming ability. The material is produced through a Tour type reaction between exfoliated graphene flakes produced in house and a bifunctional diketopyrrolopyrrole derivative bearing two aniline groups. The high solubility in organic solvents (toluene, chloroform, chlorobenzene) allows for efficient spin coating on glass slides, leading to thin films of around 100 nm thickness characterized by a blue color and semitransparency. The presence of graphene flakes is well visible though scanning electron microscopy and confers electrical conductivity to the hybrid. Figure 1 schematize these concepts.

We have investigated the photostability of this composite by probing its behavior under illumination through electron spin resonance spectroscopy (ESR). The ESR measurements state the absence of any charge-transfer process following photo-excitation of the dye component. Complete energy transfer therefore occurs from the photoexcited dye to graphene. In addition, photoluminescence measurements in the NIR confirm the absence of any light emission from graphene. The composite can be therefore considered a photostable species with wide light absorption features, which could pave the way to a new generation of electrically conductive, semitransparent, solution-processed, light-protective coatings.

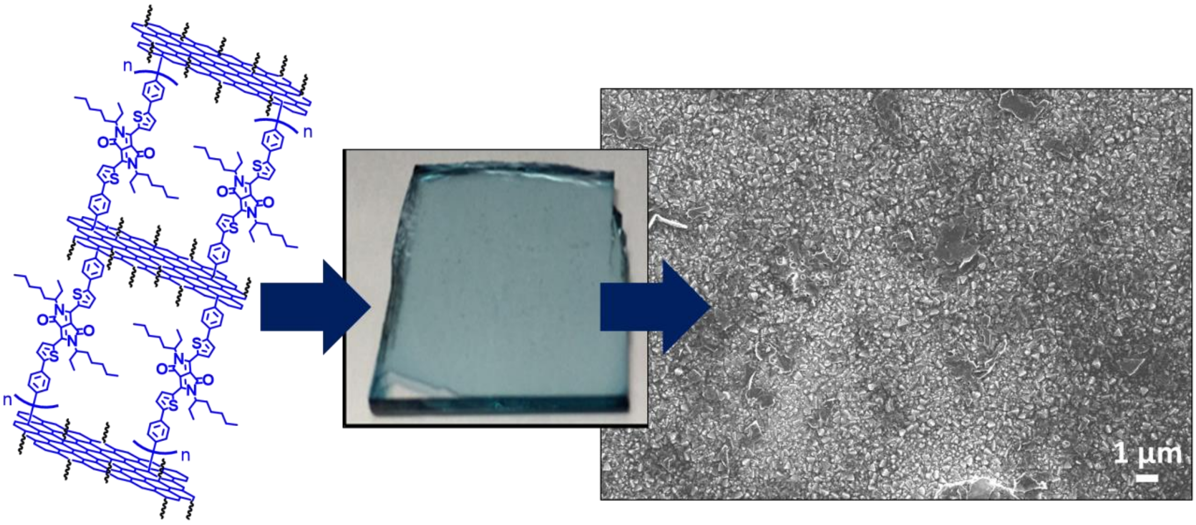

*Figure 1 : A cross-linked diketopyrrolopyrrole-graphene covalent hybrid with excellent film-forming ability, featuring well-dispersed graphene flakes (the roughness of the SEM image background is due to the use of an ITO conductive glass substrate).*

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# GROWTH OF InGaN ON EPITAXIAL GRAPHENE FOR RED LEDS APPLICATION

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The growth of $In_xGa_{1-x}N$ on a lattice-mismatched substrate such as GaN limits the In incorporation to 25% in the alloy before leading to compositional inhomogeneities [1]. This limitation makes impossible the production of efficient red LEDs with InGaN alloy despite its emission over the entire visible range depending on the In content. The growth of an $In_xGa_{1-x}N$ layer on a 2D material could potentially lead to a strain-free growth of the III-N compound allowed by the absence of dangling bonds at the surface of the carbon layer and therefore preventing phase separation in the material regardless of the In concentration. Moreover, it has already been demonstrated that during such a growth process it is possible to obtain an epitaxial relationship with the substrate underneath the graphene [2,3] denoted as 'remote epitaxy'. The resulting $In_xGa_{1-x}N$ layer could then be used as a buffer layer for the subsequent growth of low lattice mismatched $In_yGa_{1-y}N$ quantum wells of a LED structure emitting in the red range. In this manner, we are studying the growth of InGaN on graphene from the nucleation to the formation of a film.

Here is firstly presented the propane/hydrogen chemical vapor deposition (CVD) growth and the characterization of the graphene layer on 1×1cm² n-doped 6H-SiC (0001) substrate. Atomic Force Microscopy (AFM) and Low Energy Electron Diffraction (LEED) experiments along with Raman spectroscopy demonstrate a continuous high quality graphene film rotated by 30° relative to the SiC. Then, the nucleation of the InGaN grown by molecular beam epitaxy (MBE) is presented. Following this, the underlying graphene layer was probed by Raman spectroscopy to evidence a conservation of its quality during the growth process. Finally, it is shown the attempt to deposit InGaN over the entire graphene surface leading to a non-fully coalesced film. Photoluminescence spectroscopy was used to quantify the In concentration and the structural quality of the alloy was examined by X-ray diffraction. The latter technique also indicated an epitaxial relationship between the InGaN and the SiC. Finally, some parasitic growth orientations were also revealed by Reflection High-Energy Electron Diffraction (RHEED) and Electron Backscatter Diffraction (EBSD).

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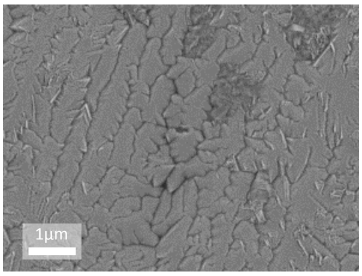

*Figure 1 : SEM image of InGaN grown by MBE on CVD graphene.*

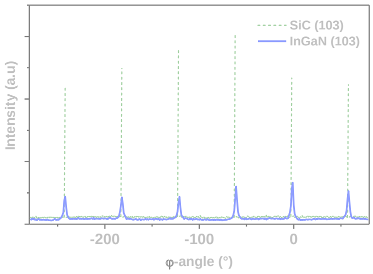

*Figure 2 : X-ray diffraction φ-scan on (103) reflection of InGaN and SiC showing their epitaxial relationship.*

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# Voltage and pressure driven Ion-transport in Angstrom-scale channels

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2D material based, angstrom scale capillaries has been proved to be a potential candidate for molecular transport [1-4]. Ionic motion in such confined channels is affected by direct interactions between channel walls and the hydration shells of ions. Water transport also strongly depends on channel wall material.

Here we demonstrate graphene channels with height down to one atomic plane with atomically smooth walls (graphite and hexagonal boron nitride) for pressure and voltage driven ionic transport to explore water and ion-interactions. Ions transport is markedly enhanced by an applied bias of fractions of volts. This gating effect observed for both wall materials but also rely on material dependent differences. Transport through these channels indicates transistor like electro hydrodynamic behaviour in which small voltages induce strong responses, which can be utilized in building Nano-fluidic circuits responding to external stimuli.

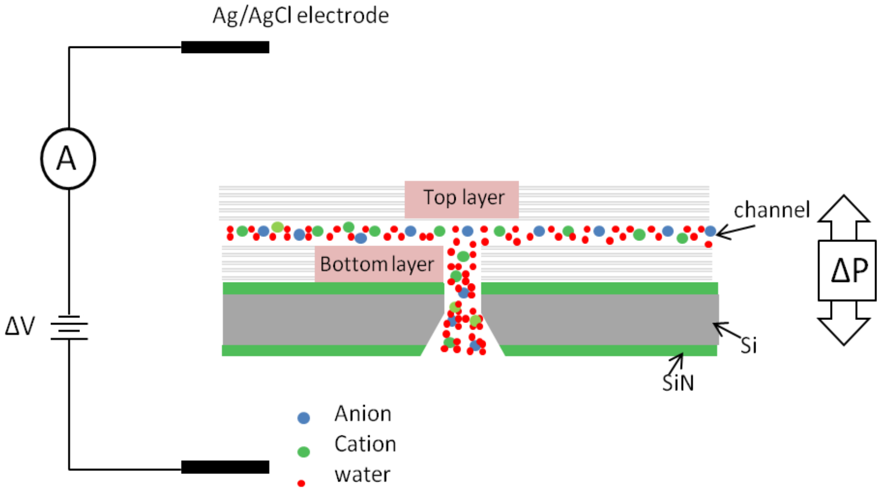

Figure1: Schematic diagram of the pressure and voltage driven ionic transport through angstrom scale channels. Pressure is applied through channels entry and exit.

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# IONIC GLASS GATED 2D MATERIAL BASED FIELD EFFECT TRANSISTOR AND PHOTOTRANSISTOR: $MoSe_2$ OVER $LaF_3$ AS CASE STUDY.

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Modulating the carrier density of two dimensional ('2D') materials is pivotal to tailor their electrical properties, with novel physical phenomena expected to occur at higher doping level. Here, the use of ionic glass as a high capacitance gate is explored to develop 2D material based phototransistor operated for the first time with higher carrier concentration up to $5x10^{13}$ $cm^{-2}$, using $MoSe_2$ over $LaF_3$ as archetypal system. [1] Ion glass gating allows low operating biases, then circumventing the possible electrical breakdown of conventional dielectric gating, while preserving low temperature operation which is not possible using electrolytes gating. It reveals to be a powerful technique combining the high carrier density of electrolyte gating methods while enabling direct optical addressability impeded with usual electrolyte technology. The $LaF_3$/$MoSe_2$ phototransistors demonstrate $I_{ON}/I_{OFF}$ ratio exceeding 5 decades and photoresponse times down to 200 µs, up to two decades faster than $MoSe_2$ phototransistors reported so far. Careful phototransport analysis unveils that ionic glass gating of 2D materials allows tuning the nature of the carrier recombination processes, while annihilating completely the traps contribution in electron injection regime. This remarkable property results in photoresponse that can be modulated electrostatically by more than two orders of magnitude, while at the same time increasing the gain bandwidth product. This study demonstrates the potential of ionic glass gating to explore novel photoconduction processes and alternative architectures of devices._Finally, this approach reveals to be a promising technology to develop 0D based phototransistor for IR detection. [2]

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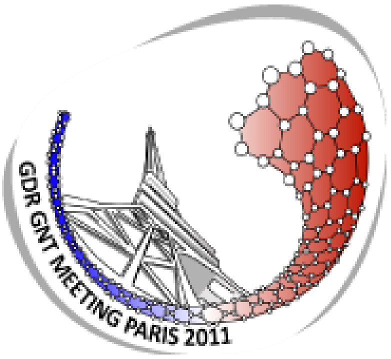
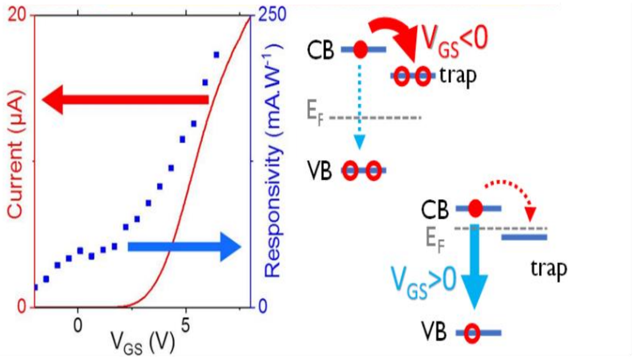


*Figure 1: GNT 2011 conference logo*



(a) (b)

*Figure 2:* (a)Transfer curve in red and responsivity gate dependent in blue; (b) Schemes illustrate relaxation mechanisms for negative biases (top) and for positive biases (bottom)

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# MOVPE GROWTH OF LARGE AREA LAYERED HEXAGONAL BORON NITRIDE

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Hexagonal boron nitride (h-BN) is a wide bandgap semiconductor with a honeycomb lattice structure that matches that of graphene, making it ideally suited for applications in graphene-based nanoelectronics. Realizing high-performance nanoelectronic device structures requires control of materials at the nanoscale. Growing ultrathin layers of h-BN with good uniformity over a large area is challenging. Especially, realizing smooth layers on dangling bond free 2D materials like graphene is a bottleneck, which is under intense investigation. Here we report a scalable, ultra-thin, layered h-BN layers growth by industrially important Metal Organic Vapor Phase Epitaxy (MOVPE) on up to 4” sapphire substrates[1]. This growth process resulted in highly ordered layered h-BN which was vividly evident from high resolution transmission electron microscope images. Structural and optical properties were studied in detail and confirmed realization of highly crystalline layered h-BN. Further this layered h-BN can be lifted off from the sapphire substrates leading to creation of free standing devices[2] or can be bonded to other 2D materials like graphene or dichalcogenides forming van der Waals heterostructures which was confirmed with successful device studies[3]. The interesting results obtained on this technological advancement will be presented with a major focus on bottom-up MOVPE growth of layered h-BN.

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# IMPROVING THE CRYSTALLINITY AND GROWTH TEMPERATURE OF HBN NANOSHEETS VIA THE $BAF_2$-ASSISTED PDC TECHNIQUE FOR VOC SENSOR APPLICATION

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Hexagonal boron nitrite (*h*BN), or white graphene, is an attractive material for many applications including electronics as a complement to graphene, in anti-oxidation coatings, or light emitters, etc. However, the synthesis of high-quality *h*BN at relatively lower sintering temperature still remains a paramount necessity and occupies the activity of scientists. In this work, high crystalline hBN nanosheets (*h*BNNS) were synthesized via the group II halide-assisted PDCs process [1], [2]. Addition of both the $BaF_2$, as a melting-point reduction agent and $Li_3N$ as a crystallization agent led to production of *h*BN nanosheets with tunable optoelectronic and physicochemical properties at relatively low temperature and atmospheric pressure conditions. For instance, Raman data showed improved crystallinity with the maximum addition of 30 wt.% $BaF_2$ and 5 wt. % $Li_3N$ at 1200 °C and atmospheric pressure, leading to a FWHM value of 12 $cm^{-1}$, which is close to that of the high temperature-high pressure systems [3], [4]. Moreover, TEM and SEM images illustrated typical flakes and multi-layered nano-crystalline *h*BN materials with the crystal sizes of 0.59 – 1.1µm in diameter. Thus, the work provides a new platform for the large-scale synthesis of single crystals of *h*BN at low-temperatures without compromising their optoelectronic and physicochemical properties for application in next generation VOCs sensors.

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# SEPARATION OF SPECIFIC SINGLE CHIRALITY SINGLE-WALL CARBON NANOTUBES IN THE LARGE DIAMETER REGIME

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A two-step aqueous two-phase extraction (ATPE) technique capable of separating large diameter single-wall carbon nanotubes (SWCNTs) to the level of single enantiomers in high concentration and purity is reported. This is achieved through an advanced acid addition methodology that enables fine control of the competitive adsorption of three surfactants on the side-walls of select nanotubes and thereby specifies their partition across the two-phase interface. In total 5 different nanotube species of $\approx 1.41$ nm diameter are isolated including both metallics and semiconductors. The technique is shown to be insensitive to the raw soot and that the unique surfactant shell around each enantiomer allows for their discrimination. The importance of the endohedral environment is also discussed and sorted fractions containing alkanes, water, or absent of filler are prepared. The enantiomers are characterized by absorbance and circular dichroism measurements, resonance Raman and photoluminescence mapping and their potential use in field-effect transistor devices is demonstrated.

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# LPCVD ELABORATION OF HIGH QUALITY GRAPHENE MONOLAYERS FOR GFETS APPLICATIONS

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Given the evolution and the development of research in the nano-technological field, graphene, since its discovery, has always been considered as the most promising candidate and the center of interest of the scientific community. There are several methods of graphene synthesis, but chemical vapor deposition (CVD) method [1] remains the most efficient given the quality and uniformity of the deposited layers.

In this work, graphene has been synthesized with the LPCVD method thus making it possible to obtain graphene on large surfaces with a high quality. The growth process was made on a polycrystalline copper film with various facets. To study the quality and morphology of deposited graphene layers, characterization techniques such as Raman, DRX and MEB spectroscopy were used.

The results show that the annealing favors the cu (111) surface, which increases the probability of obtaining monolayer graphene. The latter confirms that the crystallinity of the growth substrate plays a very important role in the growth mechanism. On the copper surface, the graphene cover is a continuous, high quality monolayer with an $I_{2D}$ / $I_G$ ratio of 2,23. The peak D, responsible for defects, present in the spectra of graphene is in our case absent. With graphene innumerable applications, this work aims to focus on its integration into graphene-based field effect transistors (GFETs).

The GFET is a promising candidate for future high performance applications beyond CMOS. And because of its attractive electronic properties as well as its ability to adapt in radio frequency (RF) or microwave (HF) applications, the applications of electronic [2][3], biological, biomedical, optical detection ...

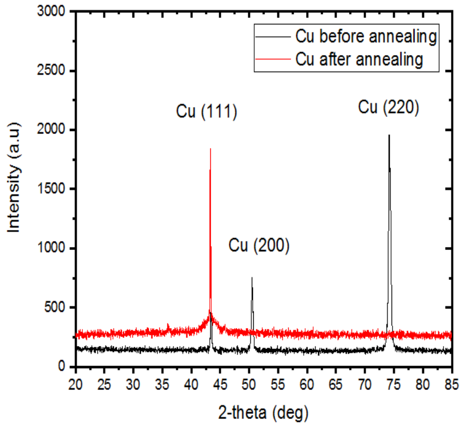

*Figure 1: DRX spectra of copper foil before and after annealing at 1000°C*

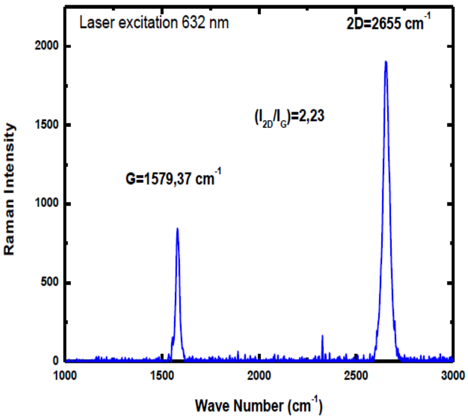

*Figure 2: Raman spectrum of a monolayer graphene*

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# CARBON NANOTUBE-BASED FIELD-EFFECT TRANSISTOR FOR WATER QUALITY MONITORING

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Water is the most essential element for humans since 60 percent of our body is made of water [1]. By this reason, detection of various components or contaminants in drinking water is an important issue for human health. It is thus of primary importance to elaborate sensing devices that are able to probe the quality of water. Many researchers have investigated carbon nanotube (CNT) based gas sensors or biosensors, but CNT-based sensors in water have been relatively scarcely studied. Our team has already studied and developed an ink-jet printed CNT chemistor to selectively detect some analytes in water. The operating principle is based on the variation of the resistivity of a film-like network of CNT when exposed to chemicals dissolved in water. In order to evaluate the interest of sensors based on the field-effect transistors (FETs) as far as sensitivity and selectivity are concerned, we have launched a research program that aims at investigating the use of CNT-based FET to probe the presence of chemical pollutants in water. In particular, it is expected that the signal response of Chem-FET can be amplified due to current modulation by an additional gate electrode [2]. This could lead to the detection of analytes at very low concentrations.

In this paper, we introduce a CNT-FET sensor for water quality monitoring elaborated by printing the sensing CNT material. An unsorted HiPCo single-walled carbon nanotube (HiPCo-SWCNT) ink is deposited between source and drain electrodes to have a semiconducting channel of CNT-FET. The as-fabricated device clearly showed a p-type transistor behavior, and we could reach up to $10^3$ on/off ratio by forming a sparse network of unsorted SWNT with a highly diluted ink (~ 0.001 wt % in *o*-Dichlorobenzene).

After fabrication, the CNT-FET may be directly used as a pH sensor as $H^+$ and $OH^-$ ions transfer the charge to the surface of SWNT and this affects the electrical conductivity of each nanotube [3]. We report on the comparison of the CNT-FET performances as a function of the geometry of the devices, the concentration of the ink and the ink-jet printing parameters. We also compare the performances in air and in water, discuss the aging of the CNT-FET in water, and then analyze the CNT-FET sensitivity to pH.

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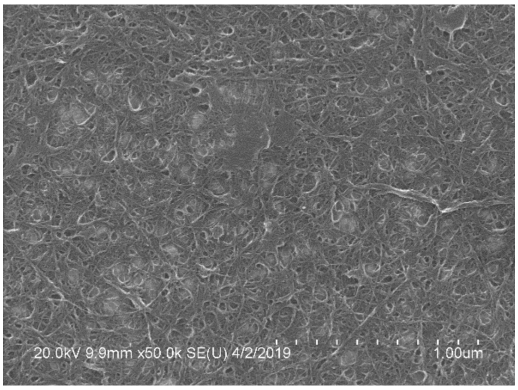

*Figure 1 : Scanning electron microscope (SEM) image of ink-jet printed SWCNT network.*

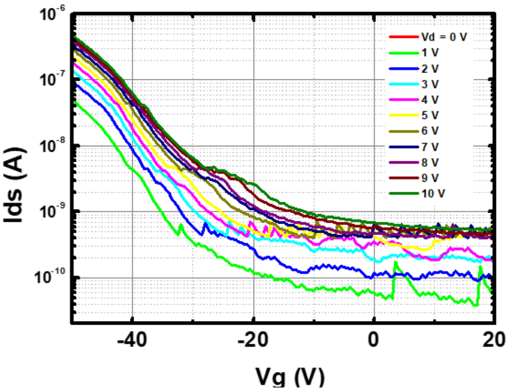

*Figure 2 : Drain current measurement as a function of gate voltage. The gate voltage is swept from – 50 V to 20 V.*

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# CARBON NANOTUBE-BASED SENSOR ARRAY FOR WATER CONTAMINANTS DETECTION

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Fresh water constitutes only 3% of the total water on earth, among which only 0.01% is available for human consumption [1]. Freshwater supply quality is under increased threat of contamination by human activities. In this context, nanomaterial-based chemical sensors for water quality monitoring have attracted strong interests from researchers in the last decades. We focus in this work on multi parameter chemical ohmic sensor arrays based on pristine and functionalized CNT networks.

First, pristine MWCNTs inks were successfully formulated and ink-jet printed on interdigitated electrodes. The obtained CNT layers were characterized using Scanning electron microscopy (SEM) and Raman spectroscopy. The developed chemistors were electrically characterized in water and the response of CNT nanosensors toward changes of pH and concentration of NaOCl was successfully monitored. A linear and reversible response was obtained as a function of pH in the range from 5.4 to 8.2, the appropriate range for water quality control. The sensitivity was 8.6 kΩ by pH unit. A linear relationship between resistance and NaOCl concentration was also observed for concentrations from 0.05 to 5 mg/L (0.1 kΩ.L/mg). However, this raises the concern of selectivity, since the same sensor reacts to several species. To mitigate this, MWCNT were non covalently functionalized with a dedicated conjugated polymers (CP). The printability of the new ink based on CP functionalized MWCNTs is being investigated before sensitivity testing. The effect of CP to MWCNT mass ratio on printability was investigated, which allowed us to obtain uniform and homogenous layers after optimization pocess.

Finally, the ageing of pristine CNT devices in water was studied. Confocal microscope images before and after electrode immersion in water for five days showed loss of MWCNT from electrode surface. It was then confirmed with Raman spectroscopy. It suggests a degradation of the active layer caused by exposure to water, an issue to be mitigated in the future.

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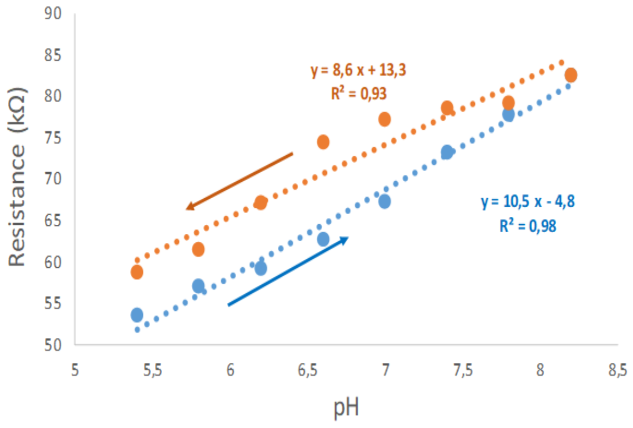

*Figure 1: Electrical response of MWCNT based chemiresistive nanosensor towards the variation of pH*

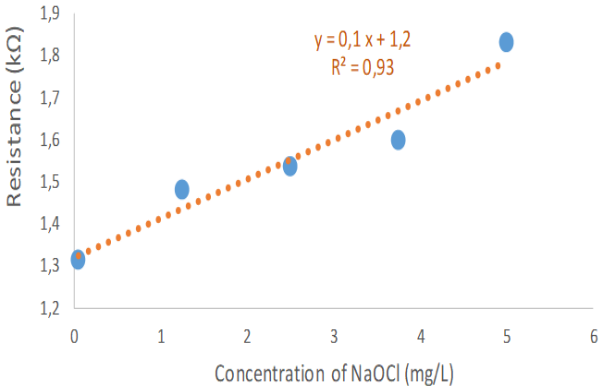

*Figure 2: Electrical response of MWCNT based chemiresistive nanosensor towards increasing concentrations of NaOCl*

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# COLLOIDAL STABILITY STUDIES AND PREPARATION OF TRANSPARENT AND CONDUCTIVE THIN FILMS WITH EAU DE GRAPHENE

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Dispersing carbon nanomaterials in liquid media is a smart way to facilitate processing into more complex materials or devices. Aqueous dispersions of these nanomaterials are usually prepared using passivant agents as polymer or surfactants or by functionalization that introduce functional groups on surface. Both methods are efficient to produce stable aqueous dispersions, but surface modifications contribute to disrupt electrical conjugation and increase electrical resistivity and passivant agents must be removed after deposition to improve electrical contact between particles. In this present study, stable aqueous dispersions of pristine graphene (Eau de graphene) without using passivant agents, or surface functionalization and without sonication treatment[1] have been prepared and some of their colloidal properties were investigated. Aqueous dispersions were prepared by solubilizing $KC_8$ in tetrahydrofuran for 5 days, followed by adding the centrifugated solution to degassed water and solvent evaporation for 5 more days. Tyndall effect revealed the colloidal nature of the sample. Zeta potential values varied between -35 and -40 mV and results from dynamic light scattering revealed a mean hydrodynamic diameter next to 200 nm. UV-vis spectrum showed an absorption band next to 265 nm that is characteristic of graphene electronic transition. Raman spectroscopy was performed *in situ* and the dispersions spectrum revealed a profile typical of mono and few layers graphene, which is in accordance with the previous report from the literature[1]. Graphene aqueous dispersions have also been used to prepare transparent and conductive thin films in liquid-liquid interfaces by mixing them with immiscible solvents under stirring for 24 h, then the material adsorbed at the liquid-liquid interface was deposited on different substrates[2]. Thin films were obtained using biphasic liquid mixtures with high values of interfacial tension as toluene-water or hexane-water, however liquid mixtures with low interfacial tension values induced material aggregation such as ethyl ether-water. UV-vis spectroscopy and 4 probe measurements revealed that thin films prepared in liquid mixtures with high interfacial tensions can be used as transparent electrodes.

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*Figure 1. Water (left) and Eau de graphene (right) inside glass vials and irradiated with red laser.*

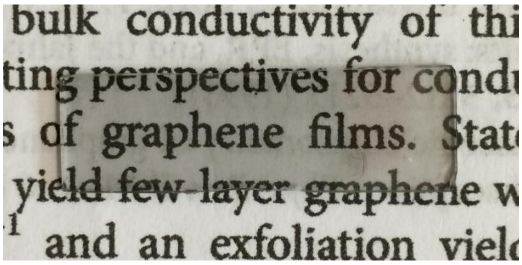

*Figure 2: Thin film of Eau de graphene prepared in water-toluene interface and deposited over glass substrate.*

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# CONFINEMENT OF DYES INTO CARBON AND BORON NITRIDE NANOTUBES: AGGREGATION MECHANISMS AND OPTICAL PROPERTIES

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The inner cavity of nanotubes has been used as a template for the encapsulation of elongated dyes molecules, such as polythiophenes (6T). The 1D confinement of the nanotube wall drives the stacking of the molecules and induces original aggregation effects in their optical properties [1,2]. When confined inside a carbon nanotube, the organics dyes exhibit for instance a surprisingly strong Raman signal clear of its luminescence emission due to an efficiently quenching effect from the nanotube [3]. Here we show that boron nitride nanotubes (Eg~5 eV) having inner diameters between 1 nm to 5 nm provide similar 1D confinement effects with the difference that they preserve the luminescence of the dyes. The resulting 1D nanohybrids (dye@BNNT) shows strong and tunable luminescence emissions depending on the dyes used and the diameter of the BNNT. [4] Experiments on individual dyes@BNNT demonstrate that the BNNT protect the dyes against oxidation and reduce significantly the dyes photobleaching under continuous photo-excitation. Preliminary results on Daphnia Pulex colored with dyes@BNNT suggest that these dye@BNNT nanoprobes have reduced toxicity for multimodal imaging based on Raman and luminescence and that they can be adapted to work in the NIR I window to study biological materials.

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# CVD GROWTH OF GRAPHENE ON SIC FOR METROLOGY

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Propane/hydrogen CVD growth of graphene on SiC, studied since 2010 [1], consists simply to grow graphene from propane in a hydrogen/argon atmosphere. The presence of hydrogen in the gas phase promotes Si excess on the surface, hence making impossible graphene growth without propane flow [2]. This makes propane/hydrogen CVD very different from Si sublimation where graphene grows from a C excess on SiC. To date, the most promising application of graphene grown by propane/hydrogen CVD is the realisation of electrical resistance standard based on QHE in graphene, as shown by Ribeiro-Palau et al. with the demonstration of a $1.10^{-9}$ quantisation in relaxed experimental conditions, e.g. at 5 K, 5 T and 50 µA [3]. In this contribution, we will present the last advances on the propane/hydrogen CVD growth of graphene on SiC for metrological applications.

In a first part, we will discuss on SiC substrate offcut angle and polytype effects on the growth, with a special focus on polytype which has been scarcely discussed. By comparing graphene growth on SiC substrates with different polytype but similar offcut, we will show that 4H-SiC can promote step bunching which is detrimental for metrology. Then, we will present uniform graphene growth on large area. We have for instance grown graphene on 9 1×1 $cm^2$ SiC samples, and on the 4 studied samples, we have observed almost perfect graphene films on 400 $µm^2$ AFM images. We have in addition grown graphene on a 2” SiC substrate on a rotating holder. If we except the presence of nano-aggregates on few part of the wafer, graphene growth appear very uniform. We will finally present few metrological measurements on graphene samples from multi-sample growth and consecutive growth as an additional proof of graphene growth reproducibility.

This work has received funding from the ANR (Graphmet project) and from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme (GIQS project).

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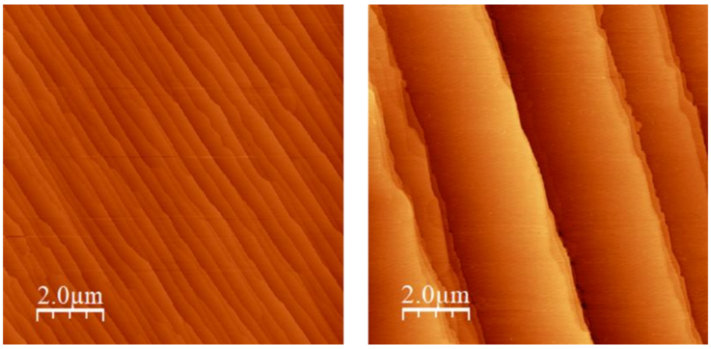

*Figure 1 : AFM images (z-scale = 7 nm) of graphene grown on 6H-SiC and 4H-SiC (with similar offcut) in the same run.*

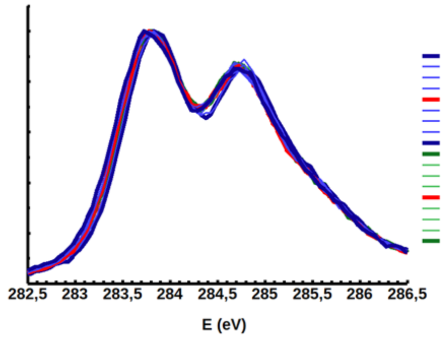

*Figure 2 : 18 XPS spectra on two diameters of a 2” 6H-SiC wafer after graphene growth.*

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# DENSE ELECTROLYTE-GATED SINGLE-WALLED CARBON NANOTUBE NETWORKS AS ARTIFICIAL SYNAPSES

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The conductivity of dense films of purified semiconducting single-walled carbon nanotubes (SWNT) can be varied over several orders of magnitude by electrochemical doping as demonstrated in a variety of lateral and vertical electrolyte-gated SWNT network transistors [1]. The associated doping of the nanotubes also leads to characteristics bleaching of the main absorption features as shown recently in electrochemical cells [2] with very thick (6,5) SWNT layers and large optical densities. Due to the slow movement of electrolyte ions through a dense nanotube network a number of different absorption levels could be achieved by simply applying short voltage pulses. The distinct doping or absorption levels were stable for hours under open circuit conditions. Here, we utilize the combination of fast charge carrier and slow ionic movement in an analogous SWNT/iongel system to achieve synaptic behavior such as computing and learning. By means of gate (presynaptic) voltage pulses the channel (postsynaptic) conductance is varied and can be retained over long periods of time. We investigate the device parameters that enable such operation using aerosol-jet printed and spray-coated carbon nanotube films and iongels.

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# DEVELOPMENT OF A GRAPHENE BASED AMMONIA AND NOX GAS SENSOR.

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Graphene has been demonstrated as a promising material for the development of ultrasensitive gas sensor thanks to its exceptional properties especially its low electronic noise [1]. A graphene based sensor should achieve a molecular sensitivity.

In this context, ONERA, is pushing for the development of an ammonia and NOx sensor. This gas sensor relies on the chemosensitivity of the graphene when exposed to a gas. It is produced by several steps of photo-lithography and graphene transfer.

Firstly, we worked on the reliability of the manufacturing process with a particular attention to the graphene implementation. We compared three graphene transfer methods: electrochemical delamination [2], oxidative delamination [3] and copper etching [4]. For this purpose, we used three comparative techniques: microscopy (morphology, see Fig.1), Hall measurement (electrical properties, see Fig.2) and Raman spectroscopy (crystallinity). This led us to choose copper etching as being a repeatable transfer method.

Currently, we intend to simplify the photo-lithography process, either by reducing the number of steps or by moving from a top contact method to an edge-contact method. These will enhance both graphene quality and electronical response of the sensor through better contact resistivity [5].

As a coming step of this research, we are willing to implant fluorine atoms into the pristine graphene section [6], with the aim of detect both ammonia and nitrogen dioxide molecules. Indeed the electron affinity between the ammonia molecule and the fluorine combined with the high electronegativity of the nitrogen dioxide will induce two distinct responses of the sensor [7].

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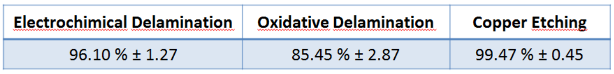

| Electrochimical Delamination | Oxidative Delamination | Copper Etching |
|---|---|---|
| 96.10 % ± 1.27 | 85.45 % ± 2.87 | 99.47 % ± 0.45 |

*Figure 1: Graphene coverage rate depending on the graphene transfer method*

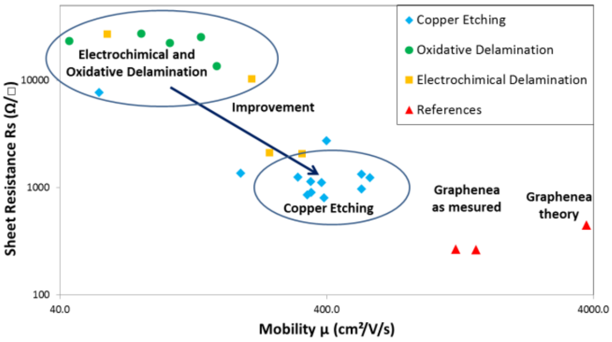

*Figure 2: Progression of the electrical properties through (sheet resistance against electronical mobility) the enhancement of the graphene transfer method*

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# Ethanol sensing with surface-mounted metal-organic-framework functionalized graphene transistors

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Surface-mounted metal-organic frameworks (SURMOFs) are crystalline nanoporous layers constituting of metal cation nodes and organic linker molecules, providing precisely controlled nano-environments for various applications [1,2]. The affinity of the host framework towards specific guest molecules can be tailored by selecting the appropriate SURMOF building blocks. In this work we followed the idea of combining a graphene field effect transistor (GFET) sensitive to environmental changes, with a SURMOF which provides the required selectivity for sensing applications. We have grown Cu(BDC) SURMOF-2 (BDC = Benzene-1,4-dicarboxylate) on top of CVD-graphene on Si/$SiO_2$ (300nm) based on liquid phase epitaxy process. The SGFET devices show shifts in the Dirac voltage under exposure to ethanol molecules but remain insensitive against other gases ($H_2O$, $CO_2$ etc.) and alcohols (IPA, methanol). The response times of the SGFETs are on the order of tens of seconds and resetting occurs at similar timescales by current annealing. Simulations are undergoing to reproduce the experimental observations.

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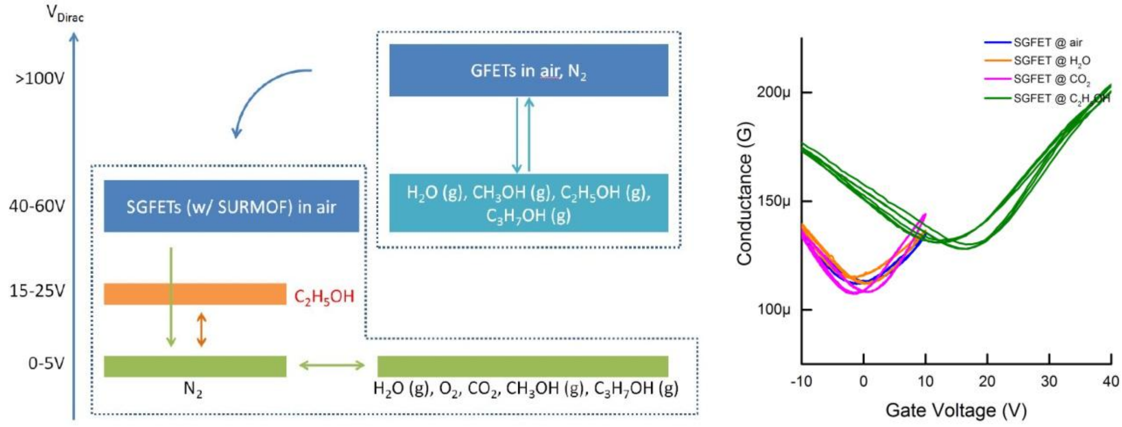

**Left: Schematic showing shifts in the Dirac voltage for graphene-FETs with SURMOF (SGFET) and without (GFET) under exposure to various gases. Selectivity and sensitivity to ethanol is only observed for SGFET. Right: Selected transconductance curves.**

# FERMI LEVEL SHIFT IN CARBON NANOTUBES BY DYE CONFINEMENT

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Dye encapsulation into host single-walled carbon nanotubes is an elegant way to create hybrid nano-systems with tunable opto-electronic properties. To this aim, different kinds of molecules (either electron donor or acceptor, absorbing either in the blue or the red visible range) are encapsulated into metallic or semiconducting nanotubes displaying different diameters [1-4]. Up to now, we have mainly studied encapsulated quaterthiophene derivatives (4T), tetramethyl-paraphenylenediamine (TMPD), tetracyanoquinodimethane (TCNQ) and phthalocyanine (MPc) molecules. In this work, we discuss the optical and the electronic properties of some of our hybrid systems. For instance, using Raman spectroscopy, a significant electron transfer is reported with 4T and TMPD, whose magnitude strongly depends on the nanotube diameter, and on the metallic or semiconducting character. Experiments also suggest a photo-activated electron transfer for small diameter (~9 Å) semiconducting and metallic tubes. Confinement of electron donor (4T) (respectively electron acceptor (TCNQ)) into small diameter tubes leads to a red shift (blue shift) of the optical absorption energy and an increase (decrease) of the photoluminescence intensities, evidenced by the photoluminescence excitation maps [4].

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# GRAPHENE: FROM MATERIAL TO APPLICATIONS

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The discovery of the graphene by Geim and Novoselov has generated a great interest due to its promising applications. In spite of a strong craze of the scientific community, it seems that graphene has not yet raised all the expected challenges. However some unexpected applications like gaz sensing [1], which still focus scientific efforts [2], are stimulating. Indeed these applications adress many societal needs from air-pollution measurement (caused by fine particles which are known as the first cause of excess mortality in Europe [3]), up to GreenHouse Gaz (GHG) emissions in agriculture ($N_20$, $CH_4$ and $CO_2$), admitted as a major source of anthropic GHG. In this last area, which motivated this work, the advent of virtuous agricultural practices, known as agroecology, will take advantage of efficient gas sensors allowing to better understanding of the soils GHG emissions to reach carbon neutrality [4].

In this aim, we designed a versatile electronic system, aiming to push graphene from laboratories to applications. The system includes most of the laboratory electronic devices functions: current source, low noise amplification, configurable switching matrix, synchronous detection and driveable magnetic source. It is controlled by an Analog Digilent board programmable in java script which drives an analog electronic board and a magnetic field source (cf. Figure 1). We performed tests using a square sample of graphene grown on SiC under low pressure Argon [5]. The system can be used in 3 modes: magnetotransport, magnetometer and doping-meter. The first mode allows to use classical **magnetotransport** characterizations, such as: V(I), resistivity & Hall voltage coefficient under weak or strong magnetic field (pulsed mode) allowing, *in fine*, to get mobility (µ) and doping (n). The **magnetometer mode** takes advantage of a spinning current method [6] which reduces the residual voltage offset and allowed us to demonstrate the use of graphene for magnetometry. We notice that significant low frequency noise remains, in agreement with previous work [7], which needs to be overcomed in further work. The **doping-meter mode**, which is relevant for gaz sensing, is based on a Hall voltage measurement under a modulated magnetic field exposure [8]. The design of the system will be freely available in a near future.

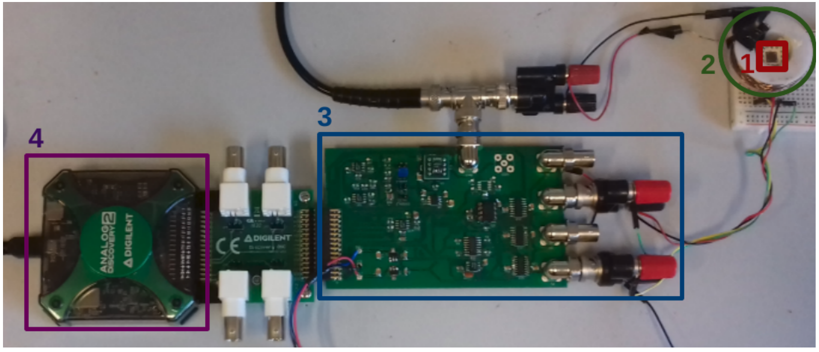

*Figure 1 : Graphene electronic board (1: graphene on SiC, 2: magnetic coil, 3: analog board, 4: digital board).*

**Acknowledgments:**
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# HIGHLY SENSITIVE CARBON NANOTUBE AND GRAPHENE-BASED PHOTODETECTORS FABRICATED VIA FEMTOSECOND LASER PATTERNING

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The photodetectors based on carbon nanomaterials, such as graphene and carbon nanotubes (CNT), attract a huge interest in the last few years. Maskless femtosecond laser processing potentially can drastically reduce the cost of detectors and make the whole production process resist-free [1, 2]. This work aims for fabrication of highly responsive and wavelength selective graphene and CNT based photodetectors via femtosecond laser patterning at near the ablation threshold limit.

Single-walled CNT (SWCNT) were deposited onto Si/SiO$_2$ substrate using gas-phase process formation based on thermal decomposition of ferrocene in the presence of carbon monoxide. The duration of deposition process limits the number of nanotube on the surface (~1 SWCNT per 10 µm$^{-2}$). Single-layer graphene was CVD-grown on 25 µm thick copper foil for 30 minutes at 1050-1070°C and methane gas was used as a carbon source. Further, it was transferred onto Si/SiO$_2$ substrate via standard technique using PMMA layer. Source and drain 100/15 nm Au/Ti electrodes were fabricated by photolithography, the gate electrode was p$^{++}$ Si substrate. The distance between source and drain electrodes varied from 1.5 to 20 µm. We used 515 nm 280 femtosecond pulsed laser to process the structures.

We study the optoelectronic response of pristine and functionalized devices under femtosecond and continuous wave laser irradiation. We demonstrate that the photocurrent generation in p-p$^+$ junctions formed in single-layer graphene and CNT is related to the photo-thermoelectric effect. The photoresponsivity of our laser patterned single-layer graphene junctions is shown to be as high as 100 mA/W (Fig. 1) with noise equivalent power less than 6 kW/cm$^2$ [3]. For SWCNT the broadband photosensitivity has been demonstrated with the responsivity up to 300 mA/W (Fig. 2). This work shows that the fully integrated photodetector with high responsibility and low noise is feasible by maskless patterning on graphene and SWCNT surfaces through ultrafast laser processing.

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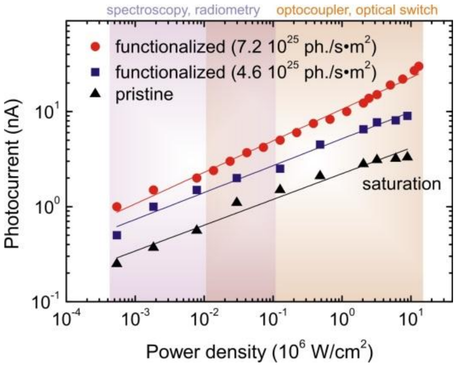

*Figure 1 : Photocurrent as a function of incident power density measured at pristine and functionalized graphene.*

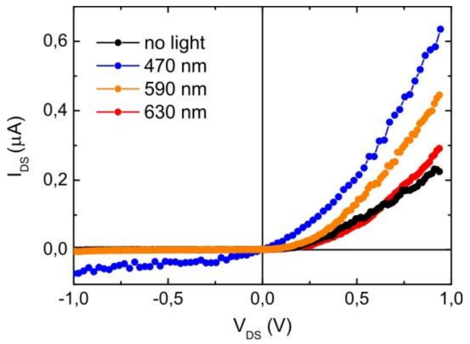

*Figure 2 : Output CVC of SWCNT photodetector upon 470, 590 and 630 nm irradiation.*

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# LARGE SCALE TRANSFER OF 2D MATERIALS FOR MICROELECTRONICS

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Last years, the growth of 2D materials made lot of progresses concerning the quality of materials and the size of substrates. Almost of 2D materials can be now prepared on large wafers and then they are becoming promising materials for microelectronics applications [1]. Unfortunately, growth substrates are not suitable for these applications where the quality of the substrate is a key factor for devices quality. Sometimes, the use of a metal as catalyst is required (ex: Cu or Pt for graphene growth) and also the substrate is contaminated during the growth and then degraded. Then a transfer on a substrate compatible with microelectronics is necessary.

In this work, the transfer is studied in order to transfer 2D material for microelectronics applications. It means that the transfer method has to be compatible with clean rooms and the final substrate has to be a large wafer (200-300 mm). Several types of transfers have been considered to choose the most convenient for large wafer scale transfer [2]: wet transfer, the “historical” method, more recent method as layer-resolved transfer [3] and standard methods from microelectronic as direct bonding and smart-cut™ technologies [4].

Preliminary results on smart-cut™ drive us to study the damage due to implantation beam of different 2D materials. The wet transfer seems to be better adapted for small pieces. But direct bonding (Figure 1) and layer-resolved transfer seems to be more promising methods for large wafer scale transfer, depending of 2D materials. For instance, direct bonding required a very low roughness and then only materials growing directly on Si or SiO2 can ben tested. This method has been applied to MoS2, GaSe… However, layer-resolved transfer has been tested on all types of materials, including graphene growing on substrates with a layer of Pt and Cu.

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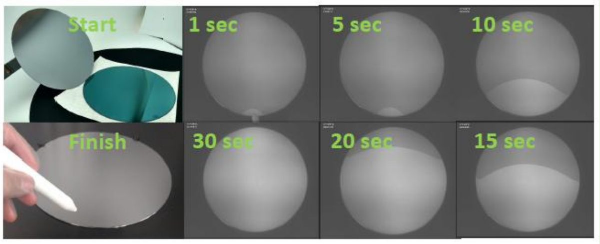

*Figure 1 : Direct bonding.*

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# LOCAL PHOTOCURRENT CHARACTERIZATION OF GRAPHENE/SILICON HETEROJUNCTION BY AFM-BASED METHODS

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Many 2D materials like graphene and TMDCs exhibit compelling optoelectronic properties, which make them interesting for future use in photovoltaics. Heterostructures build-up of these materials and 3D crystals benefit from exceptional features of thin layered materials and already established production know-how of 3D materials. Even though there are reliable macroscopic methods for heterojunction characterization, deeper understanding of fundamental photo-induced effects at the heterojunctions is needed to investigate the effects of number of layers of 2D material, defects, ionic doping or aging.

Our study is targeted on the characterisation of photovoltaic properties of exfoliated graphene (2D)/n-silicon (3D) heterostructures by advanced Atomic Force Microscopy (AFM) based techniques: current measurement by conductive AFM mapping (C-AFM) [1] complemented by local I-V characterization [2]; and surface potential measurement by Kelvin Probe Force Microscopy (KPFM). Obtained results were supplied by additional information provided by Raman spectroscopy and photoluminescence characterisation and compared to results given by macroscopic surface potential measurement by Scanning Kelvin Probe Microscopy (SKP).

We further show the importance of systematic characterisation of the bare p and n doped silicon substrate to distinguish the influence of carrier diffusion through silicon and photoeffects generated at the heterojunction.

The work was supported by the Czech Science Foundation (GACR 17-18702S) and Charles University Grant Agency (GAUK 1484218).

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# MULTILAYER SP$^2$-HYBRIDIZED BORON NITRIDE CVD GROWTH, HANDLING AND CHARACTERIZATION

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Boron nitride (BN) is identified as a strategic material for many purposes related to the integration of graphene and 2D materials in devices and the fabrication of van der Waals heterostructures. On the basis of exfoliated flakes from single crystals, utility of BN has been demonstrated for its ability to provide clean encapsulation environment as capping layers, its capability to preserve electronic properties of graphene as supporting insulating material and its dielectric properties in heterostructures as layers [1,2,3]. Thus, it becomes mandatory to have scalable synthesis and characterization procedures for providing suitable and reliable boron nitride material according to these three identified needs.

In this work, we are interested in the BN growth on metallic substrate (copper, platinum, nickel) by chemical vapor deposition, with borazine as BN precursor. We perform parametric studies with the aim of better understanding of the growth mechanism. We present the results of our advances on the handling technique to transfer the CVD BN film from their initial substrate to the suitable host substrate for characterization or device fabrication. We focus particular emphasis to the sample characterization by cross-checking various and complementary spectroscopic and imaging techniques (SEM, Raman spectroscopy, HRTEM imaging, STEM-HAADF, electron diffraction, EDX). By this way, we have endeavored to fully characterize the quality - level and the nature of the impurities, stacking fault amount or crystallinity at the macro and nanoscale - and the structure - roughness, thickness, domain size and stacking sequence - of the BN film.

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# OPTICAL MICROSCOPY OF TRANSIENT STATES IN 2D MATERIALS

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We investigate the optical response of graphene, TMDCs and heterostructures thereof to fs pulses. Confocal pump-probe microscopy using high numerical aperture (NA) objective provides detailed insight into the dynamics and energies of transient states with high detection sensitivity and ~200 fs temporal resolution (Figures 1, 2). We discuss the signal formation process and contrast observed in confocal pump-probe microscopy of 2D materials using high NA objectives and present our findings on the different materials. In the presence of external perturbations, we observe drastic variations in the signal transients within few hundred nanometers (Figure 2) that can be correlated with the local PL emission properties and lifetimes.

Acknowledgment: We thank J. Förste and A. Högele (LMU Munich) for providing samples.

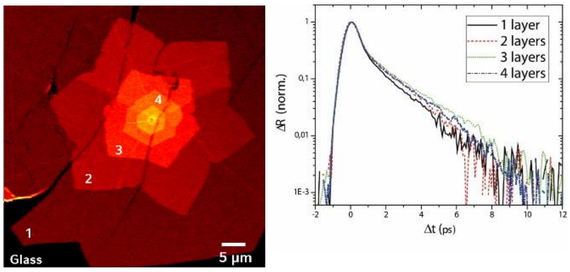

*Figure 1: Pump-probe image of graphene (1-5 layers) detected at $\Delta t$ = 0 and signal transients recorded for different layer numbers.*

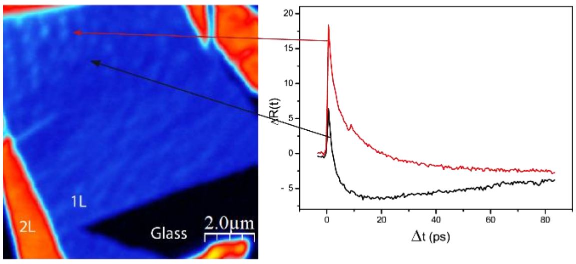

*Figure 2: Pump-probe image of mono- and bi-layer MoSe$_2$ detected at $\Delta t$ = 0 and signal transients recorded at the marked positions.*

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# PROBING DYNAMICAL STRAIN IN GRAPHENE ELECTROMECHANICAL RESONATORS

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Suspended graphene is a model atomically-thin nanomechanical system. In particular its low-mass, high Young's modulus, negligible bending rigidity combined with ultrastrong adhesion and impermeability position graphene as a material of choice for fundamental opto-electromechanical studies and for applications in sensing [1]. Now, a timely challenge consists in probing and exploiting the intrinsic electronic, vibrational and optical properties of graphene within nanomechanical devices.

Here, we make use of micro-Raman spectroscopy to perform comprehensive studies of single-layer graphene membranes suspended over a Si/SiO$_2$ substrate and subjected to a pressure load [2]. In such microcavities, the intensity of the Raman modes depends very sensitively on the displacement of the membrane relative to the Si substrate, which acts as the bottom mirror of the cavity. In addition, the frequencies of the Raman modes provide quantitative information about local strain and doping.

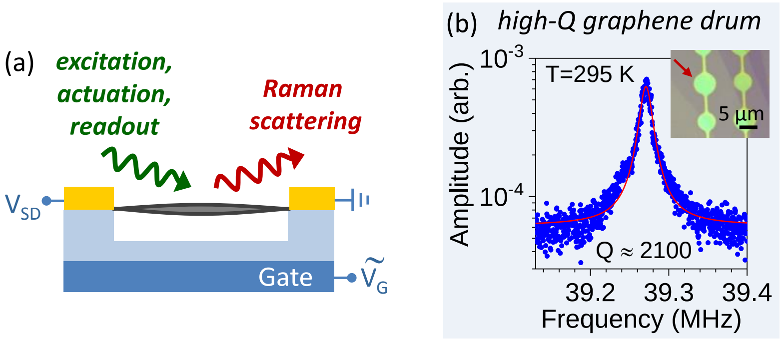

*Figure 1: (a) Schematic of combined optomechanical readout and Raman spectroscopy on a graphene electro-mechanical resonator (b) Mechanical response of a monolayer graphene drum (see inset) measured on our opto-electromechanical setup at IPCMS.*

We will first briefly review the case of suspended graphene subjected to an electrostatic pressure [3]. Second, we will present our very recent experimental results on the interplay between the macroscopic vibrational modes and the optical phonons in high-quality electro-mechanical resonators made from suspended graphene monolayers (Fig. 1). For the first time, we observe *dynamical* optical phonon softening when the graphene monolayer is strongly driven near mechanical resonance. These results pave the way towards studies of other strain-coupling phenomena and more broadly electromechanical control of light-matter interactions in two-dimensional materials and related heterostructures.

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# Sensing neuron ion channels with graphene transistors

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2D materials such as graphene offer an ideal platform for recording and culturing neural networks, regarding its exceptional neuronal affinity [1] and the presence of readily accessible surface charges which give the unprecedented possibility to realize a direct electrical coupling with cells. Among their successful bio-integrations, we show that graphene field effect transistors (G-FETs) enable the detection of individual spikes within neurons networks [2] and ultimate sensing of sub-cellular events such ion channel activity [3]. We will underline the significant contribution of grain boundaries - within the polycrystalline graphene FET channel - which provide highly sensitive sensing sites (figure). This ultra-sensitive and biocompatible neuroelectronics open new ways for achieving high spatio-temporal resolution and wide-field mapping of neuronal activity.

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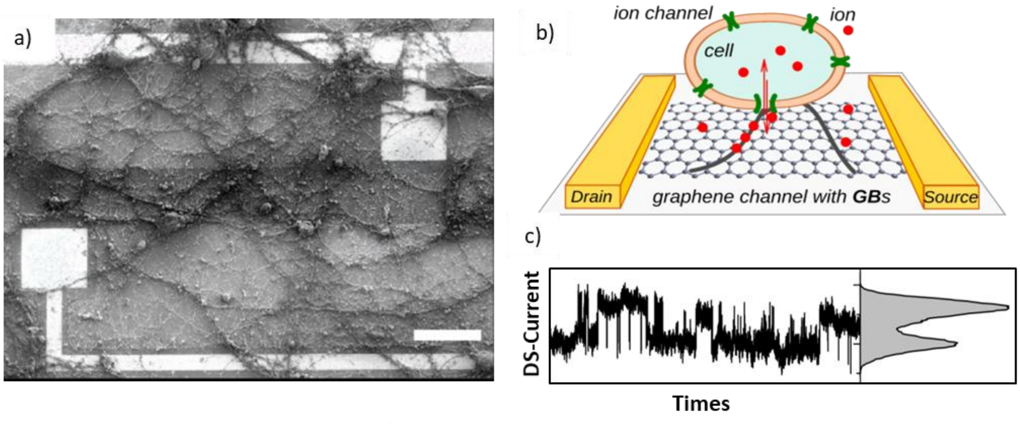

*Figure. (a) SEM micrograph of primary hippocampal neurons cultured on graphene field effect transistors (DIV21). Sacle bar 50µm (b) Illustration of randomly opening and closing ion channel above a graphene grain boundary crossing the transistor channel. (c) Typical time-trace and histogram of the drain-source of G-FETS, showing the modulation between two conductance states.*

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# SYNTHESIS AND OPTICAL PROPERTIES OF GRAPHENE QUANTUM DOTS

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The outstanding electronic, optical and mechanical properties of graphene strongly inspire the scientific community at both the fundamental and applicative levels. However, the key scientific issue that needs to be addressed is the control and the modification of the electronic properties of graphene, and notably the opening of a sizable bandgap. For the last decade, a great attention has been paid to the size reduction of graphene using conventional top-down approaches (lithography and etching, thermal treatments and oxidation of bulk materials) to fabricate graphene quantum dots (GQDs)[1] or graphene nanoribbons (GNRs).[2] However, top-down approaches do not permit to manipulate the structure of the material at the atomic scale. In particular, they do not allow a sufficient control of the morphology and oxidation state of the edges, which drastically impact the properties. In order to truly control, with the required level of precision, the morphology and the composition of the materials and of its edges, the bottom-up approach is the relevant way to proceed[3][4].

Recently, we reported on the synthesis and single photon emission properties of triangular-shaped GQDs.[5] While, this initial report focused on functionalized nanoparticles, we now turn to non-functionalized graphene quantum dots that are in terms of structure are closer to real graphene. Here, we described the synthesis, the dispersion and optical properties of a series of rod-shaped particles and we studied the structure-properties relationship in these graphene quantum dots. To this end, we designed a series of GQDs with a given edge type and by changing only one parameter (one dimension, namely the length or the width – Figure 1), we expect to follow simply the evolution of the optical properties.

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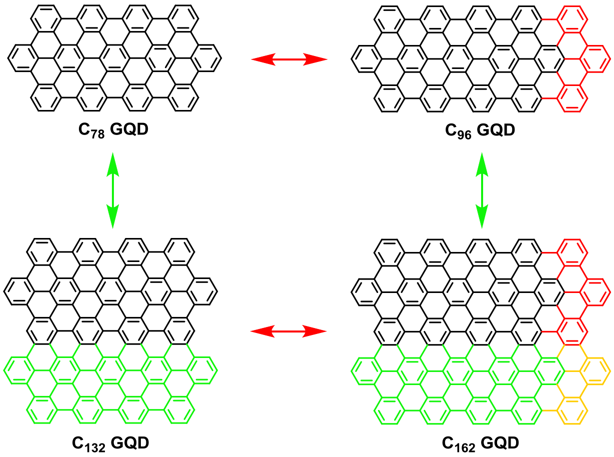

*Figure 1: Structure of rod-shaped GQD designed for the study of the structure-properties relationship.*

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# TAILORING CARBON-NANOTUBE THIN FILM ARCHITECTURES: FROM NEMATIC ORDERED FILMS TO AEROGELS

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In order to make use of the outstanding thermal, electronic and optical properties of carbon-nanotubes many applications require the development of strategies to control their orientation and arrangement in large area films. In this regard, we target films with two distinctly different arrangements of carbon nanotubes, namely those with long range, aligned, nematic order and those in which the nanotubes resemble an aerogel. Aligned films may find application as reflective coatings, facilitate high thermal conductance and have already been used as the active layer in polarizers and field effect transistors. On the other hand, aerogels absorb light effectively and offer a lowered thermal conductance, due to air filled voids between the nanotubes, which makes them a potential candidate in thermoelectric devices and the light harvesting layer in solar cells. However, the one-dimensional nature of a carbon nanotube has posed a challenge to the field in reproducibly realizing these architectures to date. In this work we show that simple filtration can be used to realize both. A custom dead-end filtration setup capable of measuring the transmembrane pressure whilst simultaneously recording absorption spectra is used to determine the different filtration regimes required for carbon nanotube alignment and those for aerogel formation. Cake resistance coefficients are also calculated during film formation allowing for aerogel thickness and porosity to be controlled.

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# THE EFFECT OF ENDOHEDRAL FILLING ON FULLERENE:NANOTUBE SOLAR CELLS

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Recently, the optical properties of single walled carbon nanotubes were shown to be drastically improved upon their filling with long-chain linear alkanes. This is to be expected as the optical properties of a carbon nanotube are strongly coupled to the dielectric constant (ε) of their surrounding environment, however, the effect remains to be quantified. Furthermore, endohedrally filled nanotubes have yet to be used in assembled devices such as nanotube:$C_{60}$ solar cells and it is unclear what role the filler will play on the trapping and quenching of excitons. In this work aqueous two-phase extraction is used to prepare single chirality nanotube populations with water ($\varepsilon \approx 80$) and alkane ($\varepsilon \approx 2$) fillers and these are compared to unfilled or empty ($\varepsilon \approx 1$) nanotubes. Transient absorption spectroscopy is used to measure the exciton lifetime and photoluminescence spectroscopy the quantum yield of each sample. A thin film of each is then used as the donor layer in organic solar cells and characterized by external quantum efficiency and IV measurements.

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# TRANSFER OF 2D MATERIALS USING THE SPALLING PROCESS

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Nowadays two-dimensional (2D) materials are one of the main development direction to improve the performances of a lot of applications, and especially in microelectronics. However, a reliable, contamination-free and wafer-scale process to transfer 2D materials from their growth substrates to a wanted target is still lacking. Indeed, the vastly studied wet transfer, as well as other processes (roll-to-roll, tape exfoliation, etc...), present clear limitations for industrial production (like surface contamination, re-use of growth substrates, area's size transferred…) [1-3]. Lately, a new way to manipulate 2D materials was reported, usually called "spalling", which is based on the strain induced by a metallic layer [4-6] (Fig.1). This process potentially scalable, avoid organic contamination as well as provide a better control on the number of layers of the 2D materials. This new method was studied by comparing the properties of few-layers-thick TMDs (MoS$_2$ and WS$_2$) after wet transfer and after spalling transfer. The elements of comparison chosen were the roughness (by AFM), the contamination (by Raman spectroscopy), defects by optical microscopy and the electrical mobility (by four probes measurements). Moreover, the capability of capping to control the number of layers transferred was demonstrated (Fig.2), which is a highly useful property for 2D materials multi-stacking and devices fabrication.

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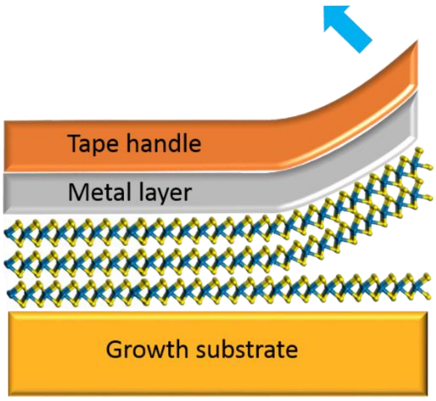

*Figure 1 : Schematic illustration of spalling process*

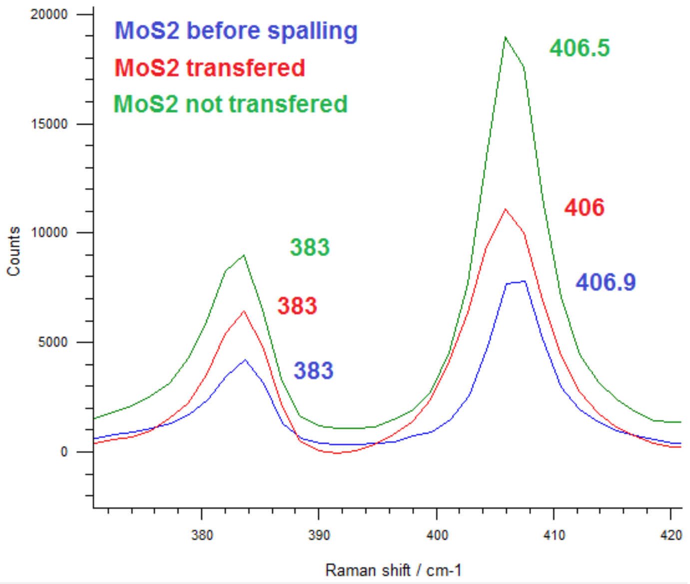

*Figure 2 : Raman spectroscopy of a few layers thick MoS$_2$ before and after transfer by spalling process. The decrease of the peak-to-peak width indicates a decrease of the layers' number after spalling.*

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# EXCITONS IN SINGLE AND FEW LAYERS HEXAGONAL BORON NITRIDE

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The dependence of their optical spectra on the number of layers is crucial for the characterization of 2D materials. However, while Raman spectra can be intuitively understood from the splitting of phonon modes in few-layer systems, much less is known about the splitting of excitonic peaks in absorption spectra.

We study the prototype 2D system hexagonal Boron Nitride (hBN), a wide band-gap insulator which is known for its strong excitonic effects and its UV luminescence, and investigate theoretically its optical properties in single and few layers.

To this end, we employ both *ab-initio* techniques and an excitonic tight-binding model, which maps the Bethe-Salpeter equation onto an effective tight-binding Hamiltonian with few parameters [1]. In this way, we obtain a simple description of excitons in hBN and a precise characterization of their symmetries and optical selection rules.

We discuss the mechanisms involved in the splitting of excitonic states in multilayer hBN systems, with focus on the splitting of the lowest bound exciton, which dominates the absorption spectra. We construct a simple one-dimensional model that provides a qualitative understanding of the absorption spectrum as a function of the number of layers [2]. In particular, we show that one can distinguish between surface excitons, localized on the outer layers, and excitons localized on the inner layers. The surface excitons are found to be the lowest in energy, and can be optically active.

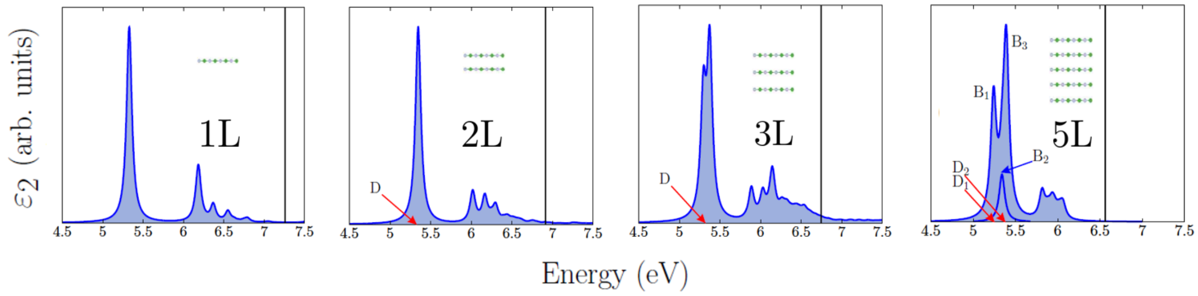

*Figure 1 :* Ab initio *absorption spectrum of hBN from single layer (left) to pentalayer (right). The spectrum is dominated by the Davydov splitting of the lowest bound state into bright (B) and dark (D) states.*

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# ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF GRAPHENE NANOANTENNAS

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We investigate the electronic structure and the optical response of graphene nanoantennas (GNAs) of various shapes by using technical means adapted to different lengthscales. In a first approach, the classical local Drude model is applied to unveil the plasmonic resonances of sufficiently large GNAs under variable doping concentrations, e.g. via external electrostatic gating. In this way, the GNAs' resonance frequencies can be dynamically tuned[1] over a broad spectral range even after the fabrication of the structures. This renders them quite unique and various applications exploiting this feature can be envisioned. For GNAs, however, with a size below a critical dimension of around 10 nm, the classical model starts to fail in describing the optical response accurately since it does not account for finite size effects when expressing the intrinsic optical properties of graphene. Particularly for triangular GNAs, not only the size of the nanoantenna, but also its edge termination type is crucial for its electronic structure and, therefore, its optical properties [2]. In Fig. 1, we show results obtained from tight-binding (TB) model simulations, which show that the zigzag (zz) terminated GNA exhibits many degenerate states at zero energy, while for an armchair (ac) edged GNA a large energy gap opens up around the Fermi energy and even one additional doping electron changes the Fermi energy of the system dramatically. Figure 2 reveals the different behaviour of the edge types in a static electric field. In the zz case, the charge accumulates at the edges of the antenna, whereas in the ac case it distributes among all the atoms in the antenna and shows dipolar character. Finally, we investigate the time-dependent behaviour of the GNA in response to optical excitation pulses and show efficient nonlinear frequency conversion processes, such as second and third harmonic generation [3], using both TB based methods and time dependent density functional theory.

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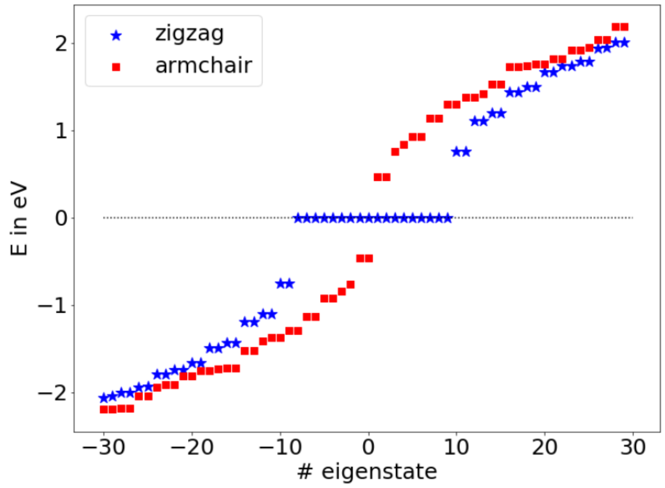

Figure 1: Energy of the electronic eigenstates of triangular graphene nanoantennas with side length 4.5 nm near the Fermi energy. The red squares refer to armchair edged nanoantennas (396 atoms), blue stars to zigzag edged ones (438 atoms). State #0 denotes the highest occupied state.

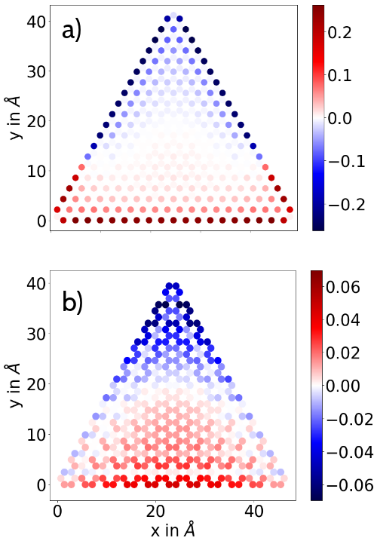

Figure 2: Induced charge density in a constant electric field for zigzag (a) and armchair (b) edged GNAs.

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# DFT+TB METHODS FOR ELECTRONIC TRANSPORT PROPERTIES OF MULTIWALL CARBON NANOTUBES AND GRAPHENE KIRIGAMI

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Combining Density Functional Theory (DFT) and Tight-Binding (TB) methods is a suitable multiscale approach to tackle atomistically the electronic structure and charge/spin transport properties of complex systems such as carbon-based nanostructures [1,2]. In this presentation, I will illustrate such an approach with two cases: a 1D large-diameter multi-wall carbon nanotube (MWCNT) and a 2D graphene kirigami plane. In both cases, the large size of the nanostructure makes it difficult (impossible) to study it solely by DFT methods and one must rely on TB methods whose parameters are adjusted on specific and affordable DFT calculations. In the first part dedicated to MWCNT, the impact of the inherent 1D moiré on the electronic and transport properties, including the generation of new Dirac points will be discussed and compared to experimental measurements [3]. In the second part, mechanical, electronic, and thermal transport properties of highly stretchable graphene kirigami will be presented [4].

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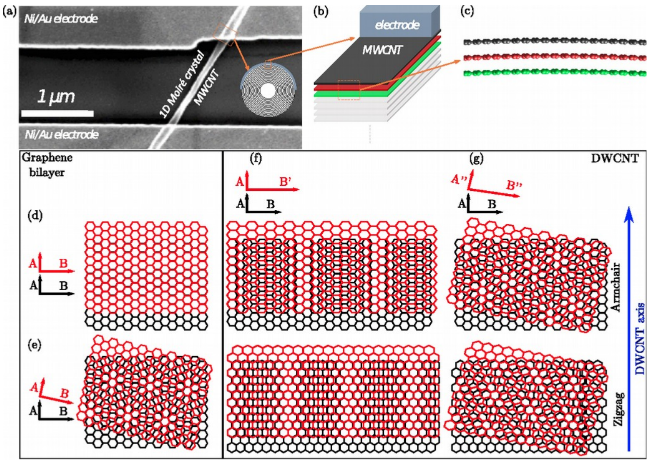

*Figure 1 : Impact of 1D moiré pattern in MWCNT*

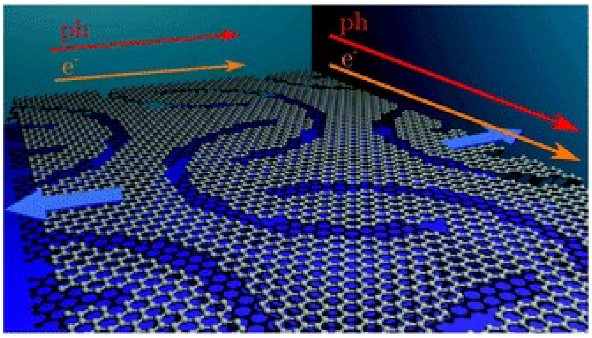

*Figure 2 : Mechanical, Thermal, and Electronic properties of graphene Kirigami*

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# LOW-FREQUENCY PHONON DYNAMICS AND RELATED THERMAL PROPERTIES OF AXIALLY STRESSED SINGLE-WALLED CARBON NANOTUBES

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Synthesis temperatures of composite materials are usually far less than the ones of their use, thus carbon nanotubes (CNTs) embedded into a polymer matrix undergo significant axial stress. We develop a continuous theory, which describes low-frequency phonon dynamics and related low-temperature physical properties of axially stressed SWCNTs [1]. The proposed theory is a simple, convenient and effective tool since its application requires knowledge of only three material constants characterizing a nanotube and the magnitude of its axial stress.

The low-frequency phonon spectrum of the stressed SWCNT is calculated and discussed. It is shown that, like in the case of a stretched string, tensile stress increases the SWCNT eigen frequencies, while the axial compression decreases them, and the most significant frequency changes can be observed for the modes with radial polarization. It is found that when a SWCNT is stretched, the quadratic dispersion law of the lowest-frequency branch in its phonon spectrum changes to the linear one. The results obtained are used to analyze low-temperature ($T$<70 K) heat capacity and thermal conductance of individual nanotubes. We demonstrate that the stretching leads to a decrease in SWCNT heat capacity, while the compression causes its increase. A significant change in the behavior of SWCNTs heat capacity at ultra-low temperatures ($T$<4 K) also has been found. As is known, without axial stress at the low-temperature limit, the phonon heat capacity of a SWCNT is proportional to $T^{1/2}$ [2]. However, as shown in this work, in the presence of stretching, the low-temperature dependence of the specific heat of an individual SWCNT becomes linear in $T$. As for thermal conductance in a stressed SWCNT, according to our results, axial stress hardly affects phonon thermal transport since stretching or compression only slightly change the frequencies of the modes mainly contributing to the thermal conductance of an individual SWCNT. Influence of investigated effects on the corresponding macroscopic properties of CNT-based composite materials are discussed as well.

D. V., M. A. and S. B. acknowledge financial support from the Russian Foundation for Basic Research (grant № 18-29-19043 mk).

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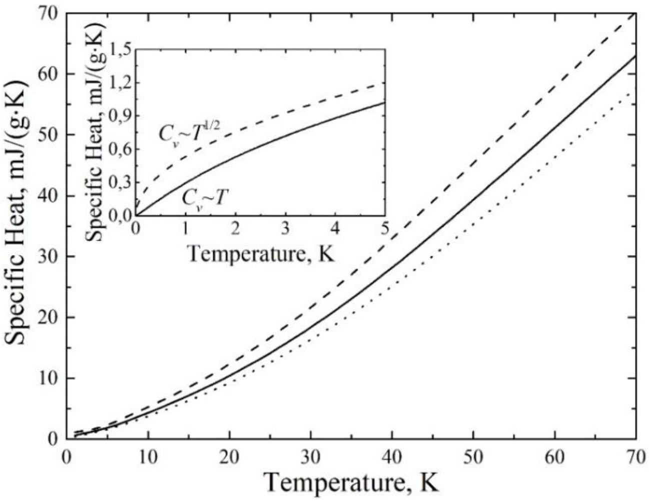

*Figure 1:* Specific heat of a non-stressed (solid curve), an axially compressed (dashed curve) and a stretched (dotted curve) SWCNTs (10,10). The inset shows the behavior of the specific heat dependence of a non-stressed (dashed curve) and an axially stretched (solid curve) SWCNTs on a large scale.

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# GRAIN BOUNDARIES IN TRANSITION METAL DICHALCOGENIDES: ELECTRON TRANSPORT PROPERTIES

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The interest in polycrystalline 2D transition metal dichalcogenides has recently increased significantly. Indeed, it has been shown that some grain boundary geometries give rise to metallic quasi-1D states, which can even result in a Tomonaga-Luttinger liquid [1]. As a dominant defect, on the other hand, the presence of grain boundaries is expected to significantly affect the electron transport properties. In this contribution, we focus on the rather common mirror twin boundary (MTB) with a 60° angle between adjacent grains in $MoS_2$, see fig. 1. Our simulations are based on an atomistic tight binding model [2] recalibrated with DFT calculations, and on the Landauer-Büttiker Green's function approach. The spin-orbit coupling, which is an important factor for transition metal dichalcogenides, is taken into account. The band structure of a zigzag $MoS_2$ ribbon (z-$MoS_2$) with a periodic MTB along its axis, see fig. 1, shows the appearance of dispersive grain boundary states within the bulk gap, as also reported by density functional theory calculation [1] and scanning tunneling spectroscopy [3]. We investigate the conductivity robustness of these states against short-range (Anderson) and long-range (Gaussian) potential disorders. In order to completely suppress the additional edge contribution to transmission, we introduce roughness at the ribbon edges [4]. Long-range disorder is effective only close to edges of the transmission plateaus, see fig. 2(a), where conductive channels are activated or deactivated. Conversely, short-range disorder is found to affect the transmission coefficient over the whole energy range, see fig. 2(a). A quantitative scaling analysis of the different quasi-ballistic, diffusive and localized transport regimes will be presented. When the MTB is orthogonal to the transport direction, the conductance of 2D $MoS_2$ decreases for both electrons and holes, see fig. 2(b). This is due to the lower density of states around the MTB region, which acts as a barrier.

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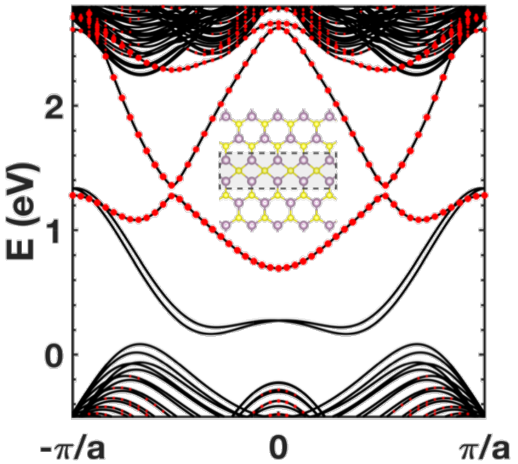

*Figure 1: Band structure of a 10 nm-wide z-$MoS_2$ with a MTB along its axis. The red dots indicate the states located at the grain boundary. The other bands within the bulk gap correspond to edge states. Inset: Sketch of a MTB highlighted in a grey box, in $MoS_2$*

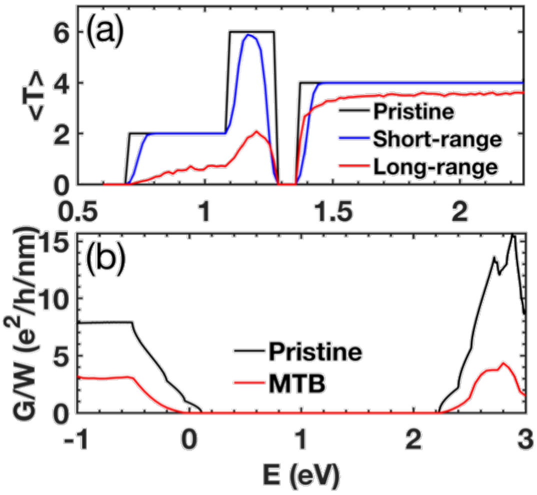

*Figure 2: (a) Average transmission coefficient vs. energy along the MTB (black) with short-range (blue) and long-range (red) disorders over a ribbon section with 100 nm length. The averaging is over 100 disorder realizations. (b) Conductance per unit of width vs. energy for pristine 2D $MoS_2$ (black line) and in the presence of a transverse MTB (red line).*

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# GDR GRAPHENE AND CO 2019 MEETING: ELECTRONIC AND GAS SENSING PROPERTIES OF LATERAL HETEROSTRUCTURES: COMBINING MATERIALS OR PHASES

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Results on the electronic and transport properties of 2D heterostructures will be presented here. Focus is given on two types of heterostructures, namely a lateral arrangement of a metallic (1T) molybdenum disulfide ribbon embedded between two semiconducting structures (2H) of the same material (1T/2H $MoS_2$) and a graphene ribbon embedded within hexagonal boron nitride (G/hBN). Using quantum-mechanical calculations based on density functional theory and the non-equilibrium Greens functions approach, we unravel the structural, electronic, and transport properties of these hybrid materials. For the first class of heterostructures, 1T/2H $MoS_2$, a single point-defect analysis could assess the stability of the hybrid system, while the electronic transport properties extracted from the electronic transmission spectra could be linked to the local current across the monolayer. A clear asymmetry of the current flowing across the hybrid monolayer was found and was attributed to the atomistic characteristics of the materials interfaces (Fig.1). The response of the material on a biaxial strain enhances this asymmetry and can be further used to tune the material. The results suggest a careful experimental design and tuning of the gate voltage in order to obtain a desired electronic conductance pattern. For the second class of heterostructures, G/hBN, we expose the hybrid material to certain gases, such as NO, $NO_2$, $NH_3$, and $CO_2$ (Fig.2) and study the response of the material based on its interactions with these molecules. The electronic transport properties reveal that for a distinct applied two-port voltage, the nitrogenous gases can be detected through the dictinct and significant variations in the conductance of the heterostructure, while this is not the case for the other gas molecules. In the end, we discuss the relevance of these materials for biological and gas sensing.

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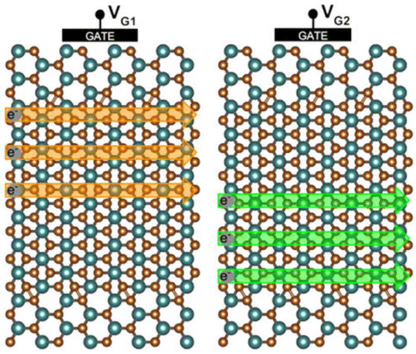

Figure 1: Different parts of the 2D heterostructure accommodate the electronic current based on gate tuning [1].

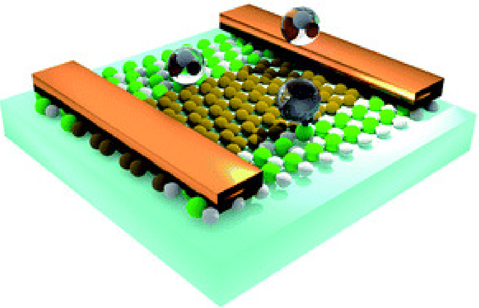

Figure 2: A setup for gas sensing [**?**]

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# STRUCTURAL AND ELECTRONIC PROPERTIES OF GRAPHENE/MOS$_2$ BILAYERS AND TWISTED MOS$_2$ BILAYERS

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We report the structural and electronic properties of graphene/MoS$_2$ bilayer heterostructures and twisted MoS$_2$ bilayers. These theoretical studies are done using Density Functional Theory [ABINIT software] with Van der Waals corrections. We focus in particular on the analysis of the interlayer spacing between layers, the relaxed positions of atoms and the electronic band dispersions.
For graphene/MoS$_2$ bilayer heterostructures (figures 1 and 2), we consider bilayer heterostructures with different supercell geometries, with and without optimized bilayer heterostructures. These heterostructures are created with supercells having different magnitudes of lattice mismatch: graphene(4x4)/MoS$_2$(3x3) [4:3], graphene(5x5)/MoS$_2$(4x4) [5:4] and graphene(9x9)/MoS$_2$(7x7) [9:7]. Furthermore, we perform a detailed analysis of the atomic and electronic structure of the twisted bilayer MoS$_2$ with different rotation angles.

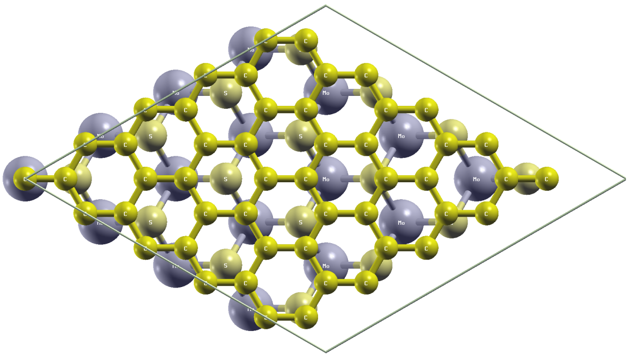

Figure 1: Structure of graphene/MoS$_2$(5:4).

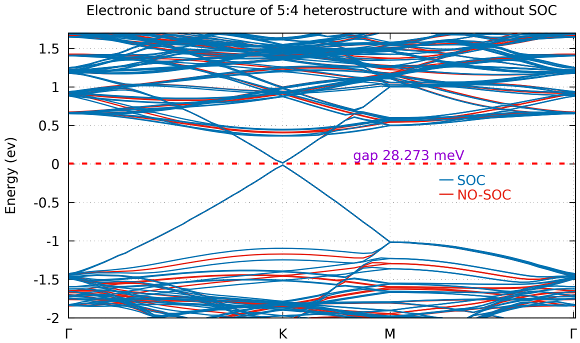

Figure 2: Electronic band structure of graphene/MoS$_2$(5:4) with and without spin-orbit coupling (SOC).

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# CHIRALITY MANIFESTATION IN ELASTIC COUPLING BETWEEN THE LAYERS OF DOUBLE-WALLED CARBON NANOTUBES

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A search for new relatively easy physicochemical methods for structural identification of carbon nanotubes represents a key challenge. Here[1], analyzing the experimental data on double-walled carbon nanotubes (DWCNTs) obtained by us and taken from literature, we have expressed the magnitude of elastic coupling between two tubular walls forming a DWCNT as a simple function dependent not only on DWNCT diameters but also on the difference between the chirality angles of the constituent nanotubes. To get this result, which allows us to relate more precisely the structural parameters of a DWCNT with frequencies of its radial breathing-like modes (RBLM), we have developed a new model for the RBLM dynamics that takes into account a possible deposition of water molecules from ambient air onto the DWCNT surface[2].

The proposed model develops the continual approach to DWCNT dynamics[3] and the theory of coupling oscilators[4], where the interlayer coupling $G'$ is taken as a quadratic function of nanotube's diameters $d_{out}$ and $d_{in}$. However, at some finite range any function without extreme points can be approximated by a linear one. In addition, since a dependence of elastic coupling of two flat graphene sheets on their twist angle $\Delta\theta$ can be presented as a series with basic functions $f_n = \cos(6n\Delta\theta)$, where $n$=0,1,2… (see similar consideration in Ref. 5), we come to the following simple form for the interlayer coupling $G'$:

$$G' = G_0 + G_1(d_{out} - d_{in}) + G_2(d_{out} + d_{in}) + G_3(d_{out} + d_{in})\cos(6\Delta\theta),$$

where $G_0 \div G_3$ are the constants independent on structural parameters of DWCNTs. The developed framewok allowed us to get close values of coefficients $G_0 \div G_3$ both from our own data and the data[4]. In spite of the fact that the dependence of $G'$ on $\Delta\theta$ is small, the higher prevalence of DWCNTs comprising two walls with identical handedness can be predicted. Application of the results obtained for identification of DWCNTs is also considered.

S.R., D.L. and M.A acknowledge financial support from the Russian Foundation for Basic Research (grant № 18-29-19043 mk).

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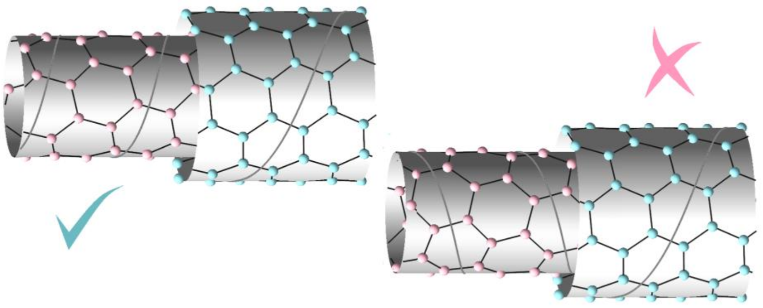

*Figure 1:* Most likely, both layers in double-walled carbon nanotubes have the same handedness.

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# EXCITON MANIPULATION IN HETEROSTRUCTURES OF 2D MATERIALS

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The discovery of graphene marked the start of research in 2D electronic materials which was expanded in new directions with $MoS_2$ and other layered semiconducting materials. They have a wide range of interesting fundamental properties and potential applications. New opportunities are enabled by the band structure of transition metal dichalcogenides (TMDCs) in which we could harness the valley degree of freedom for valleytronics and next-generation photonics. Long-lived interlayer excitons in van der Waals heterostructures based on TMDCs have recently emerged as a promising platform for this, allowing control over exciton diffusion length, energy and polarisation. I will show here how by using $MoS_2$/$WSe_2$ van der Waals heterostructures, we can realize excitonic transistors with switching action, confinement and control over diffusion length at room temperature in a reconfigurable potential landscape. Heterostructures with a long-range moiré potential such as in $MoSe_2$/$WSe_2$, on the other hand, offer the way to control polarization, emission and wavelength emitted by different optically active regions in the moiré.

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# CONTROL OF EXCITON RADIATIVE LIFETIME IN VAN DER WAALS HETEROSTRUCTURES

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Optical properties of atomically thin transition metal dichalcogenides are controlled by robust excitons characterized by a very large oscillator strength [1,2,3].

Encapsulation of monolayers such as $MoSe_2$ in hexagonal boron nitride (hBN) yields narrow optical transitions approaching the homogeneous exciton linewidth [4,5]. In this work, we go a step further by showing that the exciton linewidth is mainly dominated by its radiative component and demonstrate that the exciton radiative rate in these van der Waals heterostructures can be tailored by a simple change of the hBN encapsulation layer thickness as a consequence of the Purcell effect [6].

The time-resolved photoluminescence measurements together with cw reflectivity and photoluminescence experiments show that the neutral exciton spontaneous emission time can be tuned by one order of magnitude depending on the thickness of the surrounding hBN layers. The inhibition of the radiative recombination can yield spontaneous emission time up to 10 ps. These results are in very good agreement with the calculated recombination rate in the weak exciton-photon coupling regime. The analysis shows that we are also able to observe a sizeable enhancement of the exciton radiative decay rate.

Understanding the role of these electrodynamical effects allow us to elucidate the complex dynamics of relaxation and recombination for both neutral and charged excitons.

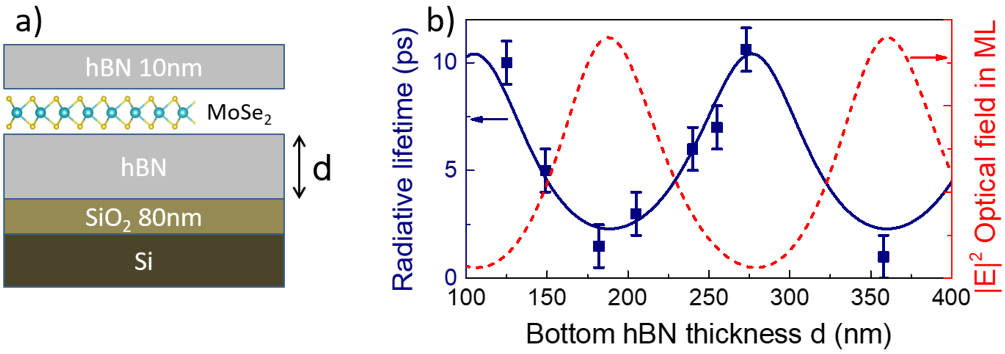

*Figure: a) Sketch of a $MoSe_2$ monolayer encapsulated into hBN layers and deposited on a $SiO_2$/Si substrate. b) Measured radiative lifetime of the neutral exciton (square points) as a function of the bottom hBN thickness. Short (long) lifetimes are reported when the monolayer is located at antinode (node) of the optical field.*

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# FILTERING THE PHOTOLUMINESCENCE SPECTRA OF ATOMICALLY-THIN SEMICONDUCTORS WITH GRAPHENE

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Monolayer semiconductor transition metal dichalcogenides (TMDs) are appealing systems for the investigations of strong light-matter interactions and are ideal building blocks for an increasing number of applications in nanophotonics, opto-electronics and valleytronics [1]. However, atomically-thin TMDs exhibit quite complex excitonic manifolds and their emission spectra are typically composed of a large number of features, arising from neutral excitons but also charged excitonic compounds, biexcitons, spin-dark excitons, localized defect-induced emission and possibly exciton-phonon replicas [2-5]. On a practical level, implementations in photonic devices would profit from the existence of a prominent single emission line. Here, we use differential reflectance and micro-photoluminescence spectroscopies at low temperatures to demonstrate that an atomically thin-semiconductor stacked onto a graphene monolayer is virtually neutral, resulting in photoluminescence spectra composed of one single, narrow -down to 1.7 meV- emission line. Neutrality is confirmed by the absence of any absorption feature from charged excitons (trions). In addition, the low temperature lifetime of bright neutral excitons in TMD/graphene is short (~2 ps), yet very similar to the value measured in bare monolayers [2] indicating that non-radiative transfer to graphene has a minimal impact on bright excitons. Interestingly, these observations are valid both for "dark" ($WSe_2$, $WS_2$) and "bright" ($MoSe_2$, $MoS_2$) TMDs. Together with the recent observation of large valley polarization and coherence in TMD/graphene heterostructures [5], our results pave the way for novel atomically-thin light emitting opto-valleytronics devices.

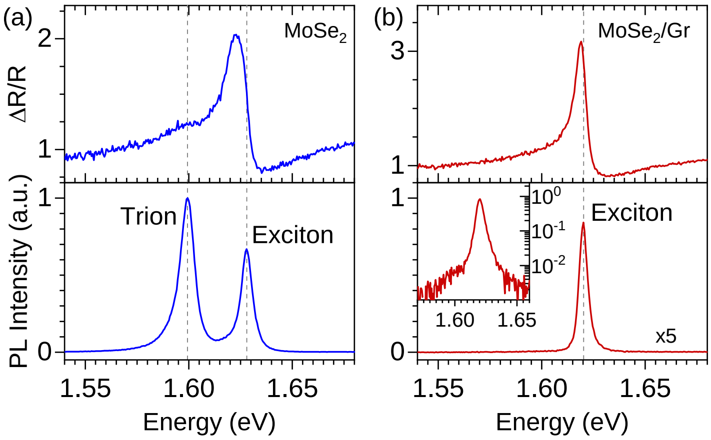

Figure 1 - *Differential reflectance spectra ΔR/R and photoluminescence (PL) spectra of (a) a $MoSe_2$ monolayer and (b) a monolayer $MoSe_2$/monolayer graphene heterostructure, both encapsulated in boron nitride. The inset in (b) shows the PL spectrum on a semi-logarithmic scale. The data are recorded at a temperature of 4 K. PL spectra are recorded in the linear regime with a 532 nm continuous wave laser.*

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# ALIGNING OPTICAL RESONANCES OF ARMCHAIR CARBON NANOTUBES AND ZIGZAG GRAPHENE NANORIBBONS

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The advances in metal surface assisted bottom-up self-assembling of zigzag graphene nanoribbons (ZGNRs) [1] and armchair single-wall carbon nanotubes (SWCNTs) [2] have urged us to revise the optical properties of such structures in a systematic way to verify some theoretically predicted regularities in their absorption spectra [4, 5, 6]. Combining the density functional theory (DFT) with non-orthogonal tight-binding model (TBM) (see Fig. 1), we investigate 693 optical absorption resonances of 57 armchair carbon nanotubes and 1041 absorption resonances of 59 zigzag graphane nanoribbons continuously spanning the tube (ribbon) lateral sizes from 0.5(0.4) nm to 8.1(12.8) nm. The lateral size dependence for both types of structures is analyzed with the Kataura plots and the common patterns within the optical spectra are revealed with the digital image processing of linear correlation and maximum likelihood maps. The found patterns and high degree of alignment between the SWCNT$(n,n)$ and ZGNR$(w)$, when $n = w + 1$, shown in Fig. 2, provide guidelines on avoiding an optical crosstalks between the mentioned structures in complex optical nanocircuits and pave the way towards reliable nanodevice spectroscopy. This also implies that the interpolating formulae available for armchair SWCNTs [7] can serve as a good estimate of ZGNR optical transition energies.
**Acknowledgement**. This work was supported by EU H2020 RISE Project CoExAN (H2020-644076), the RCN (grant No. 274853), and the RCN CoE funding scheme (project No. 262633 “QuSpin”).

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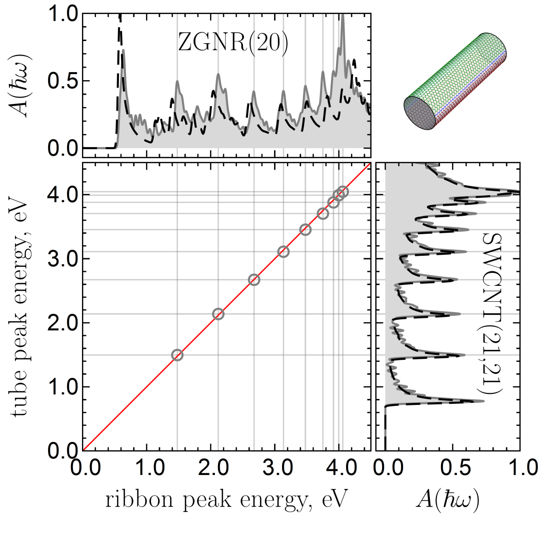

Figure 1: Comparison between DFT (solid gray) and fitted TBM (dashed black) optical absorption spectra of SWCNT$(21,21)$ and ZGNR$(20)$. Red line stands for the reference dependence $E_{\mathrm{tube}} = E_{\mathrm{ribbon}}$. Top right corner inset shows decomposition of the SWCNT$(w+1,w+1)$ into two ZGNR$(w)$ (red and green) if two zigzag chains of C atoms (blue) are removed.

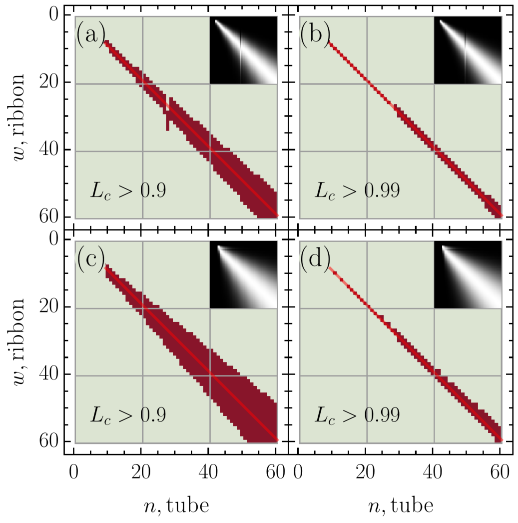

Figure 2: The maximum likelihood maps characherizing degeree of alignment between optical resonances of SWCNTs and ZGNRs: (a-b) the nearest-neighbor TBM; (c-d) multi parameter TBM fitted to DFT. Red lines $n = w + 1$ are used as reference. Insets present full likelihood maps as raster images. In plots the maps are descriminated below the specified threshold for $L_c$.

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# Indirect to Direct Gap Crossover in Two-Dimensional InSe Revealed by Angle Resolved Photoemission Spectroscopy

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Atomically thin films of III-VI post-transition metal chalcogenides (e.g. InSe) form an interesting class of two-dimensional semiconductor that feature a strong variation of their band gap as a function of the number of atomic layers. Specifically for InSe, there is an expected crossover from a direct gap in the bulk to a weakly indirect band gap in monolayers and bilayers [1].

Here, we apply angle resolved photoemission spectroscopy with sub-micrometer spatial resolution (μ-ARPES) to visualise the layer-dependent valence band structure of mechanically exfoliated crystals of InSe (see Fig. 1). Due to the high-quality glovebox encapsulated samples [2], we show that for 1 layer and 2 layer InSe the valence band maxima is away from the **Γ**-point, forming an indirect gap with the conduction band edge. In contrast, for four or more layers the bandgap becomes direct, in good agreement with theoretical predictions and photoluminescence observations [3]. These results are important as an increased understanding of InSe's band structure could lead to advances in InSe based optoelectronic applications.

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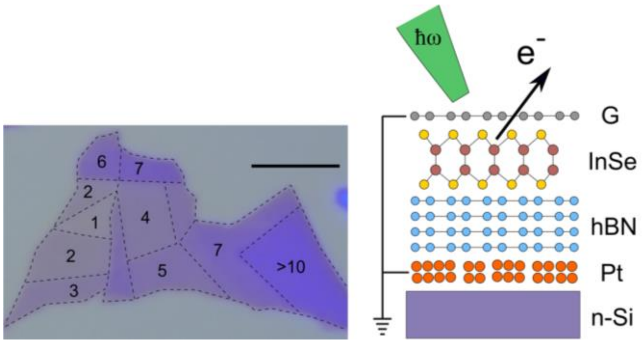

*Figure 1: Left: Optical microscope image of a mechanically exfoliated InSe crystal. Scale bar 10μm. Right: Schematic of the 2D heterostructure.*

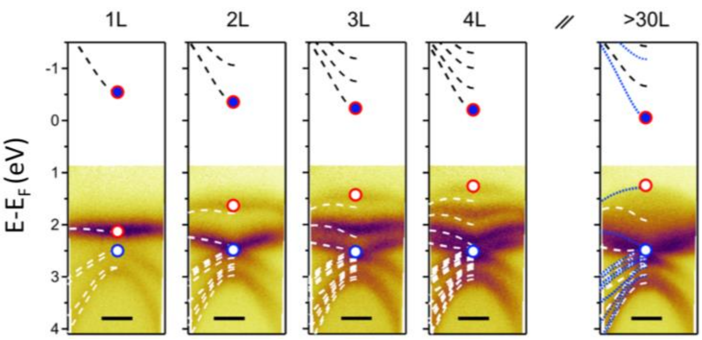

*Figure 2: Layer-dependent dispersion of InSe around **Γ** showing how the valence band of InSe changes. Scale bar $0.2\dot{A}^{-1}$ Images published in [3].*

# CHARGE MODULATION SPECTROSCOPY OF SEMICONDUCTING SWCNT NETWORKS

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Solution-processed networks of semiconducting single-walled carbon nanotubes (SWCNTs) are promising candidates for electronic circuits, as they combine high charge carrier mobilities with mechanical flexibility. However, fundamental aspects such as the influence of the composition of the SWCNT network on charge transport in field-effect transistors remain unclear. Here, we investigate charge accumulation and transport in two model systems: networks of only (6,5) SWCNTs and networks with five different semiconducting nanotubes (selected from HipCO SWCNTs) using charge-modulated absorption and photoluminescence spectroscopy. Charge modulation spectroscopy is ideally suited to study the nature and distribution of mobile (not trapped) carriers in working transistors. We find that mobile charges are predominantly located on and move through those SWCNTs with the smallest bandgaps, even if they represent only a small proportion of the network. In agreement with previous experimental and theoretical studies the mobile carrier distribution changes with applied gate voltage [1,2]. Our findings highlight the importance of the network composition for charge transport in SWCNT thin films and thus device performance.

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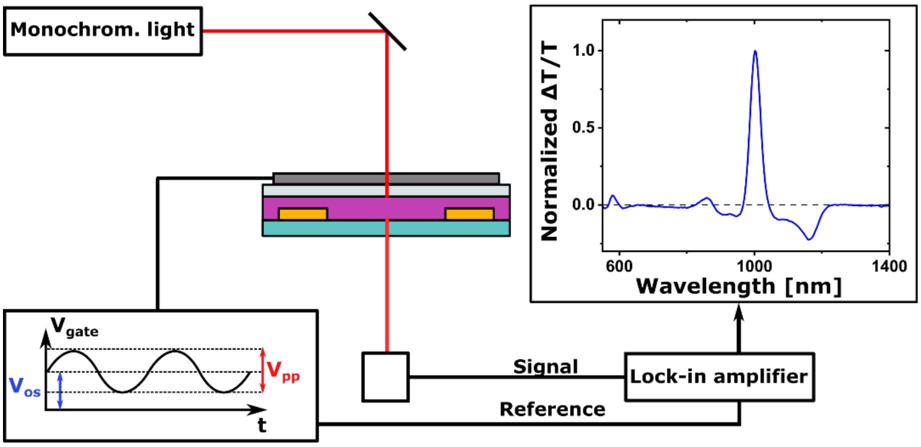

*Figure 1: Schematic of the experimental principle of charge modulation spectroscopy.*

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# CLASSIFICATION OF HRTEM IMAGES OF CARBON NANOTUBES USING A DEEP LEARNING APPROACH

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Carbon nanotubes are valuable for nanotechnology, electronics, optics, and other fields of materials science and technology. Many of their potential applications depend critically on the chirality of the nanotubes. It is, therefore, a long-standing challenge to produce or to select carbon nanotubes of a specific chirality [1]. Atomic resolution electron microscopy is a powerful and accurate tool to assign the chirality of single-walled carbon nanotubes. It is however a tedious and time-consuming task for the human eye. To allow for a faster and easier chirality identification, we have designed an automated image recognition procedure based on a convolutional neural network (CNN). Our training data set contains all 261 chiralities of nanotubes within a diameter range of 4.8-23.0 Å. The dataset is populated with synthetic images from atomic configurations obtained in molecular dynamics simulations using the LAMMPS software package [2]. To obtain a diverse and realistic data set, we run a total 1000 annealing trajectories at high temperature to introduce defects into the nanotubes. Based on these geometries, using the multislice technique as implemented in the Dr. Probe software, we simulate HRTEM images with different aberration coefficients and orientations (5 per geometry, 1.3M total) [3]. The neural network architecture includes four convolutional layers (3x3 kernels), two max-pooling layers, two dense layers, and a dropout layer [4]. For performance improvements, we use an analytical procedure for determining the diameter of the nanotubes. Based on this, the nanotubes are assigned one of nine overlapping size classes. For each of them we have trained 40 instances of the CNN. When analyzing an image, 40 sub-images of random orientations (vertical and horizontal flips) are extracted and then processed by each of the CNN instances, which aggregates into the chirality estimation of our system. Based on other simulated images of known chirality, an accuracy of over 96% is achieved this way. Applied to real HRTEM images, statistical analysis becomes possible which is the key to analyzing samples.

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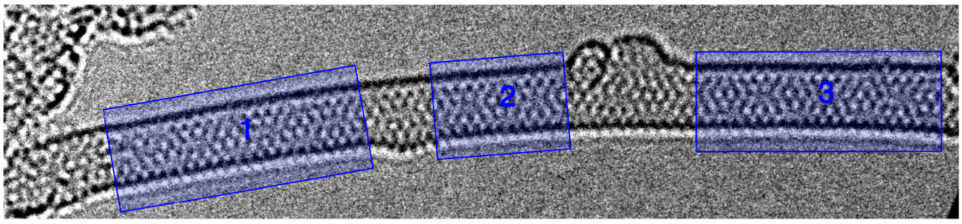

| region | chirality 1 |
|---|---|
| 1 | 11-6 |
| 2 | 11-6 |
| 3 | 11-6 |

Figure 1: HRTEM image and chirality estimations based on our automated system

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# CONDUCTANCE QUANTIZATION IN BILAYER GRAPHENE QUANTUM WIRES

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While quantized conductance in itself is one of the most striking effects in mesoscopic physics, the additional iso-spin degree of freedom makes bilayer graphene a particularly interesting candidate. We theoretically investigate conductance quantization in bilayer graphene quantum wires and quantum point contacts in presence of a magnetic field. For a perpendicular magnetic field, we find a peculiar interweaving pattern describing the crossover from size quantization to Landau quantization. For large gaps and wide channels we find an accidental degeneracy. In the case of an in-plane magnetic field, spin splitting leads to additional interesting effects.

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# DOPING-DEPENDENT ENERGY TRANSFER FROM CONJUGATED POLYELECTROLYTES TO (6,5) SINGLE-WALLED CARBON NANOTUBES

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Efficient sorting of semiconducting or even monochiral single-walled carbon nanotubes (SWCNTs) can be achieved by polymer-wrapping on a large scale [1]. Having removed the excess free polymer, the energy transfer and hence the emission properties of the polymer/nanotube hybrids can be investigated, e.g., via photoluminescence excitation-emission (PLE) maps. Furthermore, the exchange of the sorting polymer with other conjugated polymers for a given type of SWCNT is possible and thus the formation of a range of new hybrids. Here, we employ polymers with ionic pendant side chains, so called conjugated polyelectrolytes (CPE) to re-disperse (6,5) SWCNTs in methanol. Nanotube dispersion with either anionic or cationic polyfluorene-based CPEs show good photoluminescence when the nanotubes are excited directly via E22. However, as demonstrated in Figure 1, the energy transfer from the polymer to the (6,5) nanotube is blocked for the anionic CPE, although it is clearly observed for the cationic CPE. As CPEs are known for their self-doping properties, we investigate the origin of the energy transfer and emission differences by tailored chemical doping of the dispersions and electrochemical doping of networks.

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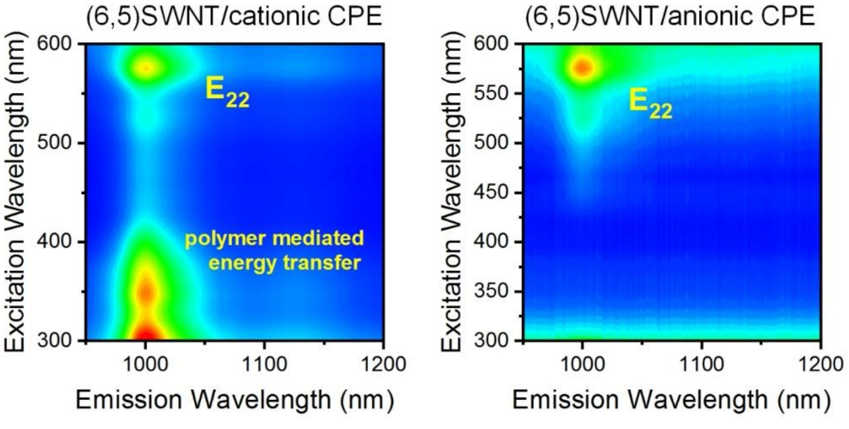

*Figure 1 : Photoluminescence excitation-emission (PLE) maps for cationic and anionic CPE wrapped (6,5) SWNTs.*

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# EFFICIENT N-DOPING OF SWCNT NETWORK TRANSISTORS

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For the practical application of semiconducting single-walled carbon nanotubes (SWCNTs) networks in field-effect transistors (FETs) and integrated circuits efficient p- and n-doping is necessary. Achieving unipolar n-type transistors with SWCNTs using air-stable electrodes (e.g. gold) is still challenging. Recently, guanidino-functionalized aromatic compounds (e.g. ttmgb) have been shown to be efficient n-dopants for FETs with (6,5) SWCNT networks.[1] These devices show unipolar electron transport with high carrier mobilities, complete suppression of hole currents, excellent on/off current ratios and steep subthreshold swings, and almost no hysteresis. Here, we investigate the effects of electrode materials with different work functions on charge injection, contact resistance and the overall performance of SWCNT FETs with or without ttmgb-doping by gated and temperature-dependent four-point probe measurements. Furthermore, we apply ttmgb-doping not only to large bandgap (6,5) SWCNTs but also mixed networks based on polymer-sorted HipCo nanotubes and large diameter, small bandgap plasma torch SWCNTs.

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# ELECTRICAL CHARACTERIZATION OF H-BN FOR ITS USE IN ELECTRONIC TRANSPORT DEVICES

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Hexagonal boron nitride (h-BN), after being used for many years simply as lubricant, is now of extreme importance for many state-of-the-art experiments in other 2D materials physics, from electronic transport [1] to optics [2]. In electronic transport devices with graphene, it is used as dielectric materials to protect the graphene from its environment, to provide a monoatomic flat substrate, and to be a very effective heat-sink for power dissipation [3]. To this aim, h-BN needs to have a well-known dielectric constant and a large breakdown voltage.

In this contribution, we present our measurements of the dielectric constant by fabricating metal-hBN-metal capacitor devices. By measuring the admittance as a function of the frequency in the GHz range, we could deduce the capacitance of different devices made with various h-BN thicknesses. Consequently we were able to deduce the dielectric constant of h-BN. Additionally we increased the voltage applied to the capacitors to measure the breakdown electric field and the associated maximum charge density. The measured values are consistent with independent measurement using quantum hall effect [3]. Finally we compared h-BN electric characteristics from different growth sources (HPHT [4] and Polymer Derived Ceramics [5]) and show only small differences. In comparison with optical methods, the advantage of ours is to mimic the actual environment and geometry of graphene transistor.

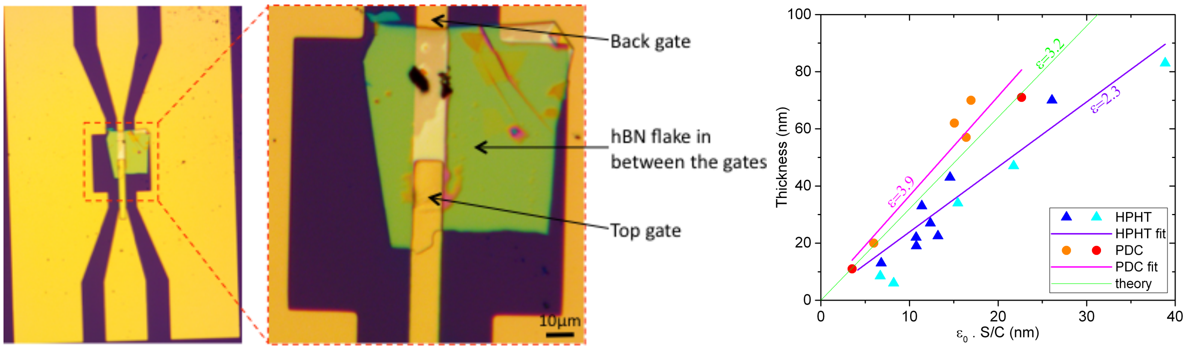

Figure 1: (left) Metal-hBN-metal capacitor with zoom-in on the active zone. (right) Deduction of the dielectric constant from the capacity measurement on different h-BN flakes

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# ELECTRON COHERENCE TRANSFER AND EDGE STATES IN MAGNETIC GRAPHENE NANORIBBONS

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Graphene, a well-defined two-dimensional honeycomb network of carbon atoms, shows impressive electrical and mechanical properties [1]. Quasi-onedimensional nanoribbons of graphene have emerged particular interest. By introducing magnetic edges in graphene nanoribbons, for instance, ferromagnetic couplings and superior spin filtering are predicted [2,3], making them promising materials for future spintronic devices. Conventional techniques such as unzipping of carbon nanotubes, however, do not deliver the necessary degree of purity to design such systems.

By utilising an ultra-clean synthetic bottom-up approach, we were able to create graphene nanoribbons with great purity [4]. We were furthermore able to functionalize the ribbon edges with nitronyl-nitroxide radicals, which serve as magnetic sites. Via electron paramagnetic resonance spectroscopy, we gain a comprehensive picture of the interactions between the magnetic radicals and the nuclei. The coherence time reaches microseconds at W-band frequencies at liquid nitrogen temperature, and sub-microseconds at room temperature. Using a combination of continuous-wave and DEER spectroscopy, we obtained evidence of the existence of a magnetic edge state in the nanoribbon [5], and unravel its interaction with nuclei using hyperfine spectroscopic techniques. We show HYSCORE spectroscopy results, which reveal interesting interaction patterns. Spectra will be compared to simulations to gain a full picture on electron-nuclei interactions.

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# ELECTROSTATICALLY CONFINED NANOSTRUCTURES IN GAPPED BILAYER GRAPHENE

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Quantum nanostructures are ubiquitous in our modern technologies. We focus on the theoretical modelling of electrostatically induced nanostructures in two-dimensional (2D) materials, such as quantum point contacts (QPCs) or quantum dots (QDs) [1, 2, 3]. A crucial step towards the functionalisation of 2D atomic lattices consists of understanding how the properties of different materials can be exploited. The recent realisation of electrostatic confinement in 2D materials (if a sizeable bandgap can be induced and controlled with an external electric field) represented a major step forward, allowing confinement without complications from atomic edges [4, 5]. Here, we are concerned with electrostatically confined QPCs and QDs in gapped bilayer graphene (BLG). We investigate how the band-inversion and the mini-valleys of the BLG dispersion, and the non-trivial Berry curvature and corresponding magnetic moment of the states, manifest in the one- or zero dimensional states inside the confined structure. These manifestations can be seen in quantum transport experiments. For example, they determine the degeneracies of the low-energy minibands / - levels and their valley splitting. In a QPC, the number of available channels, and hence the height of the first conductance step upon doping depends on the width of the channel and the size of the induced gap. For QDs, we observe either singlet or triplet ground states depending on the gap and the dot size. We establish the robustness of these states upon population of the dot with multiple Coulomb-interacting electrons. Full understanding of the electronic properties of these nanostructures in gapped BLG allows their design and control in future applications.

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# EXCITON-POLARITON RELAXATION IN SINGLE-WALLED CARBON NANOTUBE NETWORKS

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Exciton-polaritons are hybrid light-matter quasiparticles that form upon strong coupling of an excitonic transition and a photon mode, e.g. in a Fabry-Pérot cavity. They show intriguing properties such as small effective mass and strong non-linearities that can lead to inversionless polariton lasing. Owing to their unique optical and electronic properties semiconducting single-walled carbon nanotubes (SWCNTs) have emerged as an excellent material to create optically and electrically pumped exciton-polaritons at room temperature.[1,2] For their practical application and to possibly achieve polariton lasing, efficient relaxation is important. Here we investigate the impact of various parameters, such as nanotube density, detuning of the cavity and excitation wavelength, on the relaxation of polaritons in metal-clad microcavities with purified and polymer-wrapped (6,5) SWCNTs by angle-resolved reflectivity and photoluminescence spectroscopy. We find that intrinsic phonons, e.g. the D-mode (165 meV), seem to play an important role in the relaxation dynamics of SWCNT exciton-polaritons. We also find that high packing-densities of nanotubes enhance polariton relaxation compared to cavities with equal coupling but with well-separated SWCNTs in a matrix.

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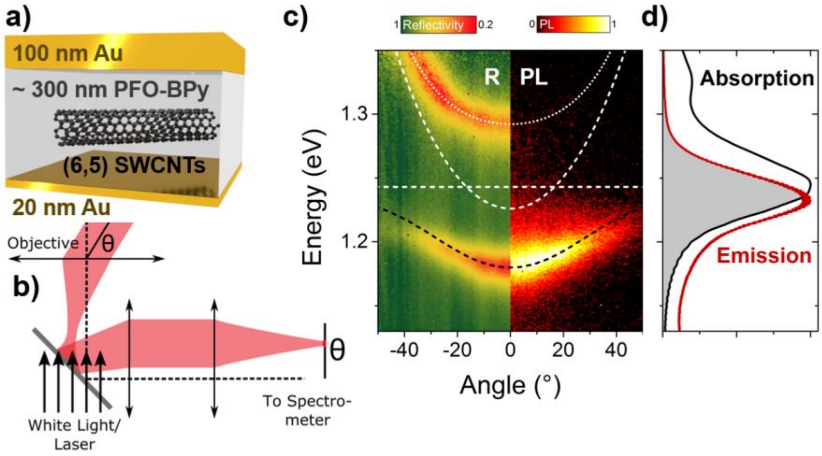

*Figure 1 :* a) Schematic of a gold-clad microcavity with (6,5) SWCNTs embedded in polymer matrix. b) Schematic of angle-dependent optical measurement: By switching the illumination between laser and white light, reflectivity and photoluminescence measurements can be acquired from the same sample position. c) Characteristic polariton modes (reflectivity and photoluminescence) measured in a SWCNT-filled microcavity as depicted in a). d) Absorption and emission of SWCNT reference for comparison.

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# EXFOLIATED NEAR-INFRARED FLUORESCENT CALCIUM COPPER SILICATE NANOSHEETS FOR BIOIMAGING

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The near-infrared (nIR) region of the electromagnetic spectrum displays specific features (*e.g.* absence of background fluorescence and deep light penetration into tissue) which make it extremely appealing for bioimaging purposes. There is therefore a high interest to expand the available literature of fluorophores able to emit in these wavelengths: examples of established materials include single-walled carbon nanotubes, quantum dots and organic dyes.

Within such a frame, a very interesting material which embraces promising photophysical properties is represented by Egyptian Blue ($CaCuSi_4O_{10}$, EB). This silicate pigment presents a lamellar crystal structure which can be easily exfoliated into 2D nanomaterials (*i.e.* nanosheets, NS): our focus is thus to comprehend how the nanoscale of these structures affects the nIR fluorescence, and if they can be employed as bioimaging agents. The strong and highly-stable nIR fluorescence of EB NS, which is centered at around 930 nm, is surprisingly retained even for the smallest obtained sizes (below *Abbe´*s resolution limit of optical microscopy, ≈ 500 nm for nIR wavelengths). As proof-of-principle concepts, imaging experiments in *Drosophila* embryos as well as in leaves of *Arabidopsis thaliana* were successfully carried out, highlighting the high potential held by such novel nIR fluorophore.

In conclusion, we managed to design a top-down approach to exfoliate EB bulk powder into NS of reduced sizes; consequently, we assessed this material´s phophysical properties in comparison to state-of-the-art nIR fluorophores, and underlined *via in vivo* imaging how it can be used to study biological systems.

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# Infrared luminescence and absorption of bulk Black Phosphorus at low temperature

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Atomic layers of Black Phosphorus (BP) have been recently isolated, ten years after graphene. BP stands out in the 2D-materials panorama by its unique semiconducting properties: direct bandgap which can be tuned by the layer number in a wide range of wavelengths from visible (monolayer) to mid-infrared (bulk) [1]. Despite many investigations on thin layers, the optical properties of the bulk crystals remain poorly known.

In this work, we investigate photoluminescence (PL) and absorption properties of bulk BP at 2K [FTIR]. The PL intensity appears comparable to high quality InAs crystals (Fig. 1) confirming the suitability of BP for infrared applications. Two peaks are evidenced at 0.275 eV and 0.26 eV. The highest energy peak is particularly narrow (FWHM = 3.8meV) and is tentatively attributed to exciton recombination, thanks to the temperature dependence of PL spectra from 2K to 300K. The discrepancy of the bulk BP luminescence properties toward the one of 40 nanometer thick BP layers [2] will be discussed. The temperature dependence of the linewidth, peak energy and intensity is analysed with the conventional semiconductor models.

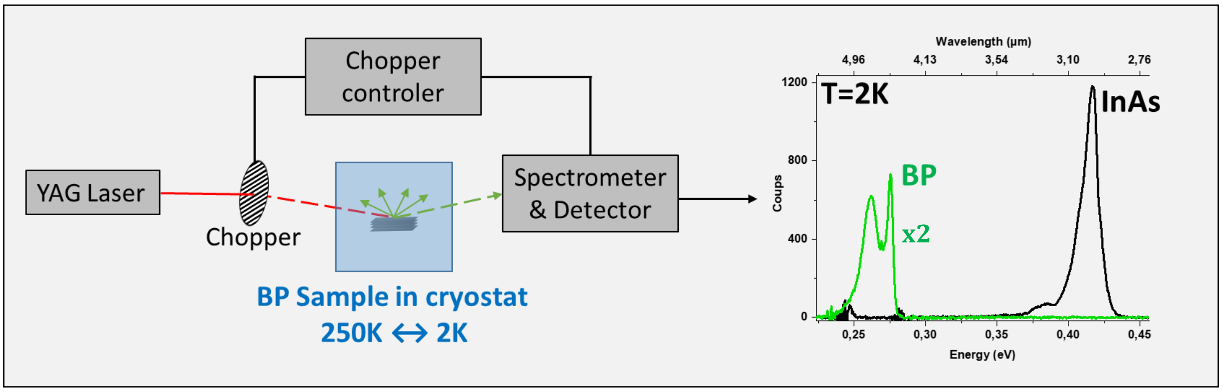

Fig. 1. Summary outline

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# LATTICE MODELS TO STUDY THE GROWTH OF SINGLE WALLED CARBON NANOTUBES

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Recent progress towards an efficient and selective synthesis of carbon nanotubes should be complemented with an improved understanding of their growth mechanisms. We recently proposed a thermodynamic modeling of the interface [1] showing that, at low temperature, only zigzag or armchair tubes are stable. Chiral tubes become stable at higher temperature because of the configurational entropy of the tube edge in contact with the catalyst, that is a key element of the model. This enables us to link the catalyst interfacial properties and the temperature with the resulting equilibrium chiral distribution.

Here, we study the growth of SWNTs using Monte Carlo simulations performed on a simple lattice-gas model for each tube chirality. This enables us to directly study the tube/catalyst interfaces, assess the validity range of our analytic approach [1], and to improve the link between interfacial energies and the resulting SWNT chiral distribution.

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# MICROSTURUCTURE ANALYSIS OF NON-GRAPHITIC CARBON

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Carbon occurs in many forms, of which diamond (made up of sp3 hybridized carbon) and graphite (made up of sp2 hybridized carbon) are the most common ones. Among the sp2 hybridized carbons the so called "non-graphitic carbons" (NGCs), a million-ton-scale material, are of significant relevance for applications and comprise a plurality of carbons such as activated carbon, glassy carbon, etc. NGCs consist of graphene stacks typically possessing nanometre dimensions and substantial structural disorder. In particular, as major structural feature the graphene stacks possess rotational and translational disorder[1], i.e. a "turbostratic" arrangement. This absence of long-range crystallographic order causes broad and overlapping scattering maxima in wide-angle scattering, also contributing to the definition of NGCs by IUPAC. A quantitative description of the sp2-polyaromatic microstructure, showing substantial disorder compared to graphite, is desirable for linking material properties to the microstructure. Ruland and Smarsly introduced a novel evaluation approach of wide-angle scattering data of non-graphitic carbons (NGCs), providing meaningful structural parameters quantifying size and disorder of the graphene stacks[1]. The general structure of NGCs is depicted in Fig. 1. The main structural dimensions of these stacks are generally described by the parameters La and Lc, which are the average lateral extension and the stack height, respectively. Further important and relevant parameters are the C-C bond length, the average distance a3 between the layers, and also parameters quantifying the substantial degree of disorder in the stacking and the layers themselves.

NGCs have a broad scope application (molecular sieves, filters and electrode material in batteries) and thus represent an important class of materials both in research and industrial applications. Hence, a quantitative determination of the aforementioned Ångstrom-scale microstructure based on experimentally accessible structural parameters is crucial for the fundamental understanding of the linkage between material properties and the microstructure. The latter comprises macroscopic properties like hardness, chemical stability or thermal and electrical conductivity and hence defines the final application.

To calculate the microstructure data from the measured data "CarbX" is used as software developed by members of the Smarsly's group in Giessen[3]. In this way, the theoretical measurement curve can be adapted to the measured data according to the model of Ruland and Smarsly, so that the desired microstructure parameters can be obtained therefrom. This program has now been extended so that instead of the fee-based program Mathematica by Wolfram Research now the free program GNU Octave can be used for the calculation in the background. The use of Octave has the great advantages over Mathematica that it is both free and the calculation is much faster at the same time with constant accuracy. The result of an example is shown in Fig. 2.

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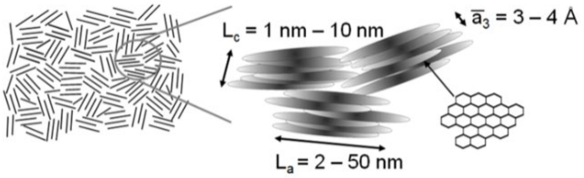

*Figure 1: Basic structure of NGCs. NGCs consist of a turbostratic arrangement of parallel sp2 layers (Adapted from [4]).*

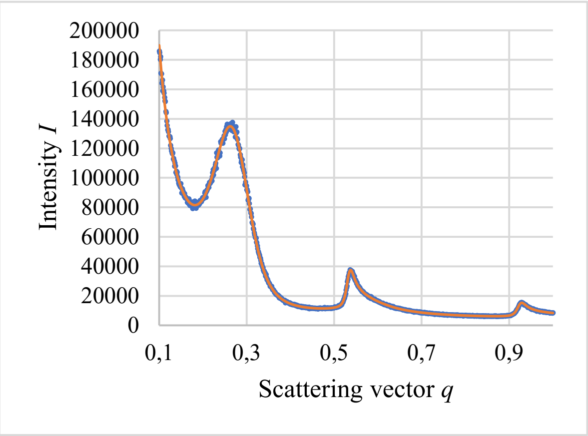

*Figure 2: Sample for adjustment with Octave. Blue: Theoretical simulated scattering data. Orange: Determined adjusted scattering data.*

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# MULTI-SCALE MODELLING OF NANO-SENSORS BASED ON CARBON NANOTUBES (CNTS) AND CONJUGATED POLYMERS FOR WATER QUALITY MONITORING

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We study resistive chemical sensors based on percolating networks of CNTs functionalized non-covalently by conjugated polymers. A change of resistance is expected in water upon complexation of a target ion by a specifically designed polymer probe. Multi-scale modelling aims at understanding and predicting the response of the sensor.

First, we derive the functional dependence of the effective resistance of random percolating networks of stick nanowires on elementary physical parameters (nanowire linear resistance per unit length, nanowire/nanowire contact resistance, metallic electrode/nanowire contact resistance) [1]. This understanding of the three main contributions, of different physical origins, to the whole, experimentally measured sensor resistances, is useful for the design of optimal sensor dimensions and sensible element densities.

Then, we study by means of variable-charge molecular dynamics, based on ReaxFF force field (within LAMMPS), the geometrical features of non-covalent functionalization of CNTs by conjugated polymers [2]. We benchmark the performance of ReaxFF force field for pi-pi stacking interacting compounds against other high-level electronic (DFT) methods, with a focus on the level of theory needed to model accurately London dispersion interactions (wave-function based theory vs. density functional theory) and to capture charge transfer from the organic molecule (or conjugated polymer) to the CNT -- this charge transfer is suspected to act as a doping and to modulate the sensor response.

Finally, we study the complexation of target ions (e.g. chlorine, copper, calcium) by the polymer probes -- designed specifically for their affinity towards given ions -- by means of molecular dynamics simulations in solvent (water) with GROMOS classical force field, within GROMACS code. We test numerically the expected selectivity of the polymer probes to different ions, finding the possible binding sites and their corresponding binding energies. We confirm the binding energies obtained with this classical force field by ab-initio (DFT) calculations -- with CP2K code -- and derive association constants for the different ions and binding sites, with free energy calculation techniques using GROMACS.

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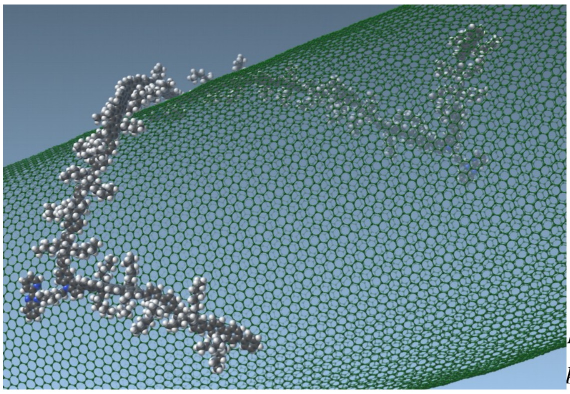

*Figure 1 : CNT / conjugated polymer interaction.*

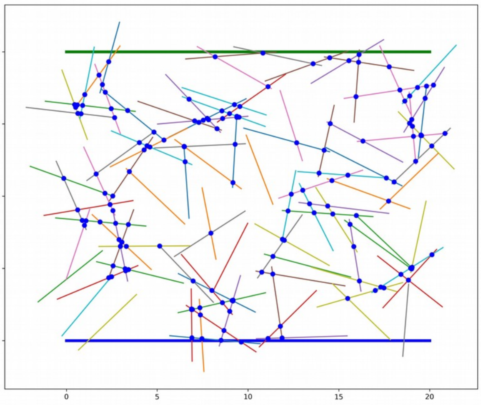

*Figure 2: Random 2D percolating network of stick nanowires (e.g. CNTs) whose effective resistance is decomposed into three different contributions.*

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# Multi-terminal SNS junctions in bilayer graphene weak links

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We are presenting an experimental study of proximity induced superconductivity in bilayer graphene in a multi-terminal configuration. The major goal of this work is to establish long channel junctions, where the superconducting reservoirs can reinforce the supercurrent. The devices are fabricated by assembling bilayer graphene/hexagonal boron nitride van der Waals heterostructures [1]. Edge contacts are made with superconducting titanium/aluminum electrodes. The device is connected via edge. We have observed clear signature of ballistic transport in our devices as well as long range induced superconductivity with the help of superconducting reservoirs.

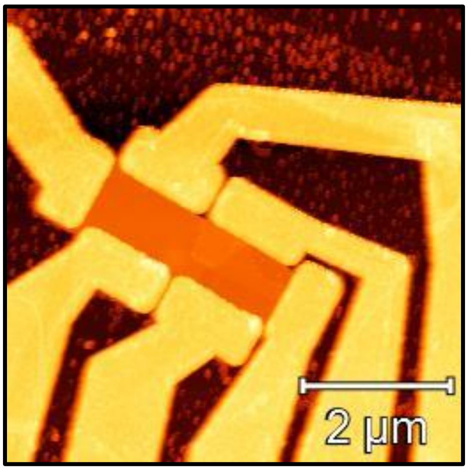

**Figure 1: AFM image of 6-terminal device**

Long weak link channels pave the way to investigate more complex devices by adding more gates (e.g. superconducting quantum interferometer, quantum dots etc) [2]. By using multi-terminal device structure, we are able to induce superconductivity in long and narrow channel (3 µm and 4 µm) by using side electrodes. Moreover, in order to understand the behavior of supercurrent, we have also performed magnetic interferometry experiments by probing its interference patterns [3, 4]. Thus, our work gives insights of long channel supercurrent and a way to realize superconducting long channel by using superconducting reservoirs.

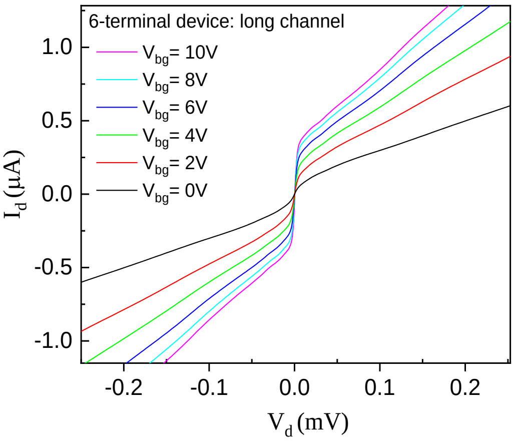

**Figure 2: Current-Voltage (IV) characteristics of long channel (3 µm)**

*Keywords:* superconductivity; bilayer graphene.

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# N-TYPE SINGLE-WALLED CARBON NANOTUBE FIELD-EFFECT TRANSISTORS – A COMPARISON OF DOPANT SYSTEMS

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Efficient, stable and solution-processable n-dopants are still rare but in high demand for organic electronic and thermoelectric applications. Common dopant/semiconductors systems suffer from several drawbacks – most importantly poor stability of dopant and doped semiconductor as well as unstable device performance under operating conditions. We have recently introduced 1,2,4,5-tetrakis(tetramethylguanidino)benzene (ttmgb), a guanidino-functionalized aromatic (GFA) compound, as a strong two-electron donor for networks of single-walled carbon nanotubes (SWCNTs) to create n-type field-effect transistors (FET) with high electron mobilities and high on/off current ratios [1]. Here, using sparse networks of (6,5) SWCNTs as the semiconductor, we compare ttmgb to well-established dopant systems [2-4]: DMBI derivatives and various metallocene dimers (see Figure 1). We carefully adapt the dip-coating technique used for ttmgb these dopants with higher redox potentials in order to optimize the FET performance for each dopant. Drastic differences in key device parameters such as hysteresis, subthreshold swing, threshold voltage shifts, increase in electron mobility compared to the undoped reference sample are correlated with dopant strength and mechanism. Temperature-dependent FET measurements create a more comprehensive picture of electron-only transport in the originally ambipolar SWCNT networks.

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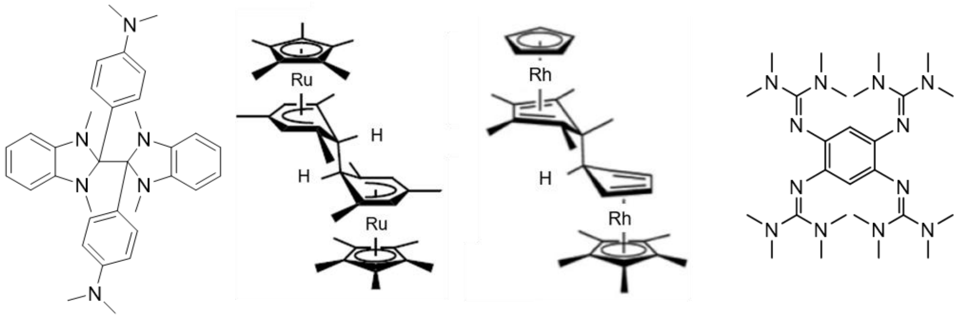

**N-DMBI** **[Ru(mes)(cp*)]$_2$** **[Rh(cp)(cp*)]$_2$** **ttmgb**

*Figure 1: Investigated dopants for n-type SWNT transistors.*

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# OPTICAL PROPERTIES OF GRAPHENE QUNATUM DOTS

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Graphene is a key material for nanoelectronics. Nevertheless, its zero gap makes it unsuitable for applications needing semiconductors with sizeable energy gaps. One way to open a gap in graphene is to use size reduction effects. The reduction of one dimension leads to carbon nanotubes and graphene nanoribbons that are 1D carbon nanostructures. Reducing one more dimension leads to 0D graphene quantum dots. The optical properties of carbon nanotubes have been investigated for approximately 20 years, while the study of graphene quantum dots and nanoribbons is at its infancy.

Among potential application of these $sp^2$ carbon nanostructures, the use of carbon nanotubes and graphene quantum dots as quantum emitters attracts a lot of attention. In this poster, I will present our recent results on the optical properties of graphene quantum dots synthesized by bottom-up chemistry [1].

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# Power dependent photocurrent response of carbon nanotube pn-junctions

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The development of carbon nanotube based light sources and detectors as on-chip optoelectronic transducers for future near-distance data communication with light is an active field of research [1,3]. Recently we have explored the potential of p-Si / SWCNT pn-junctions for photodetection in the near-infrared [4], unfortunately with limited success due to unsuitable band alignment. On the other hand metal / SWCNT junctions based on (9, 8) nanotubes can generate sizable photocurrents in the near-infrared, however the responsivity depends sensitively on the device architecture and the substrate (Fig.1-2). To find optimum conditions for photocurrent generation in the telecom band we have compared the photoresponse of (9, 8) nanotubes on Si substrates and on sapphire, used embedded local gates to form pn-junctions and measured scanning-gate photo-current intensity maps. Interestingly we encounter a reduced responsivity with increasing light power which we discuss in the context of exciton-exciton annihilation when using a picosecond supercontinuum light source for characterization.

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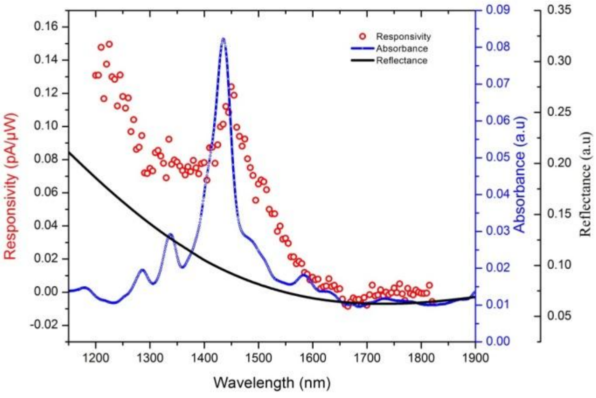

*Figure 1: Photocurrent spectrum of (9, 8) SWCNT on 800nm-SiO$_2$ / Si substrate*

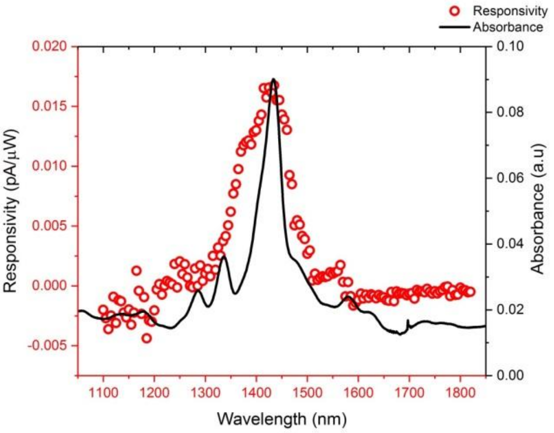

*Figure 2: Photocurrent spectrum of (9, 8) SWCNT on sapphire substrate*

# PROBING ENHANCED LIGHT-MATTER INTERACTION IN GRAPHENE ON PLASMONIC-PHOTONIC CRYSTALS BY RAMAN SPECTROSCOPY

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Graphene and carbon nanotubes have unique optical and electrical properties and are of great interest for applications in nanoscale light emitting and light detection devices. Unfortunately, the intrinsic light-matter interaction of these graphene based nanomaterials is rather weak due to their low-dimensionality and measures to enhance it such as, e.g., the integration into optical microcavities and photonic crystals have been considered [1,2]. In our present work, emphasis is laid on enhancements via so-called stacked complementary plasmonic-photonic crystal (SC PlasPhCs), which combine strongly localized plasmonic and high-Q photonic guided resonances to give rise to hybrid plasmonic-photonic resonances at visible and near infrared frequencies. SC PlasPhCs were previously employed as platforms to enhance fluorescence from molecules [3]. Here, we study the enhancement of the light-matter interaction in graphene transferred onto SC PlasPhC substrates by Raman spectroscopy, complementary reflection measurements, and simulations. By tuning the SC PlasPhC structural parameters (lattice distance and air-hole diameter), enhancement contributions of Raman excitation and emission can be tailored.

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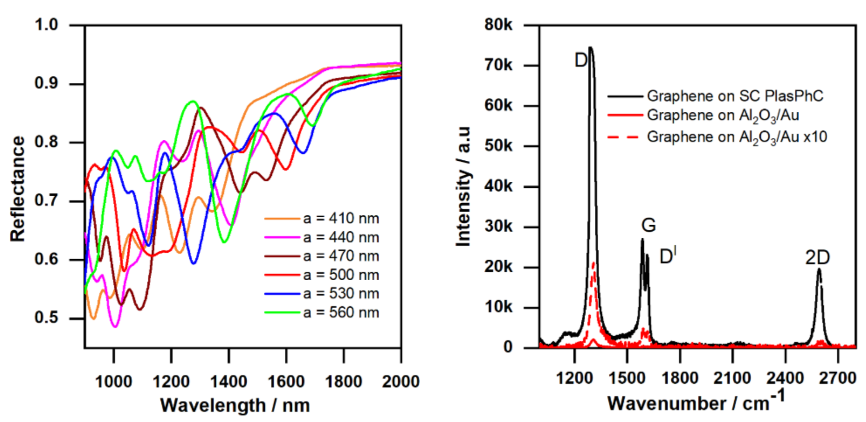

*Left: Reflectance spectra of plasmonic-photonic crystals (SC PlasPhCs) for different air-hole lattice distances. Right: Raman scattering enhancement of graphene on SC PlasPhC is about two orders of magnitude as compared to graphene on 5nm-$Al_2O_3$/Au.*

# QUANTUM TRANSPORT IN TRANSITION METAL DICHALCOGENIDES LATERAL HETEROJUNCTIONS

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Novel prospects for the quasi-perfect assembly of lateral and vertical heterostructures have been recently proposed by combining layers of two-dimensional materials (2DMs) [1]. Those 2DMs-based heterostructures are characterized by dangling-bond free surfaces and atomically abrupt interfaces [2]. Such features combined with the large number of existing 2DMs offer opportunities for inventive device engineering at the atomistic scale.

From a quantum mechanical perspective, the fundamental properties of lateral heterojunctions (LHs) are determined by the nature of the adjacent 2DMs, the long-range coupling between the layers and the interface local electronic characteristics.

In this research, we present an investigation of multiple LHs composed of transition metal dichalcogenides (TMDs) such as MoS2, WS2, MoSe2 and WSe2.

First, density functional theory (DFT) [3] is used to explore the electronic structures (band alignment, charge exchange, ...) of supercells formed by two TMDs. Afterwards, DFT and tight-binding techniques [4] based on Green's function methods are applied to investigate electronic transport through the junction (see Fig.1). The resulting conductances are found to depend on the TMDs electronic structures matching and on scattering ensuing from the junction.

The results presented in this research intend to answer to the lack of characterization of TMDs-based LHs which represent an enabling device engineering technology for next-generation electronics .

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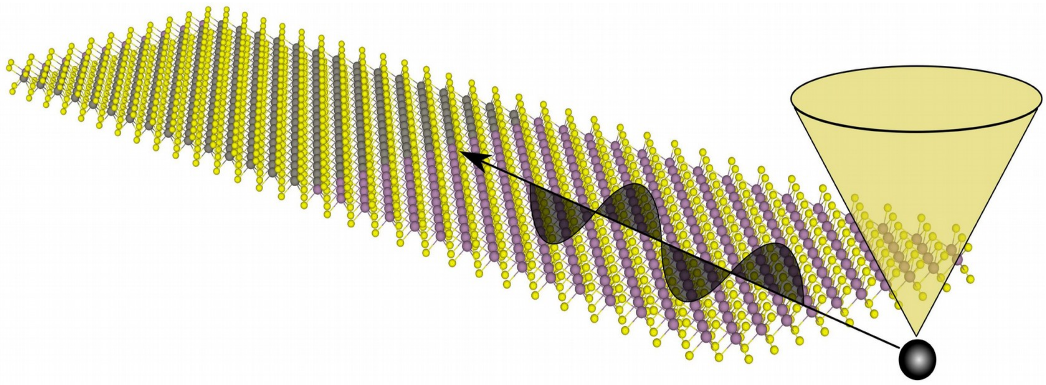

*Figure 1 : Modelling quantum transport through lateral heterojunction.*
*Charge carriers are injected in TMD1 and collected in TMD2.*

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# TELECOM BAND SINGLE PHOTON SOURCES FROM CARBON NANOTUBE IN FIBERED MICRO-CAVITY

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Single photon sources are the corner stones of quantum cryptography and quantum telecommunication. Among the requirements a high photon anti-bunching, a high brightness as well as an easy device integrability are needed. Room temperature operation and electrical injection are other important assets sought for large scale integration.

Carbon nanotubes are thus promising candidates as their wavelength emission can be tuned in the telecom bands by selecting their diameter appropriately. Their high excitonic binding energy (300meV), their integrability, and the observation of electro-luminescence by several teams [1] are additional arguments in their favor especially since their luminescence and photon anti-bunching are strong both at room and at cryogenic temperatures [2]. However the luminescence is limited by a low quantum yield (<10%) and the practical implementation relies on the ability to enhance it through the Purcell effect, using a high finesse cavity. We manufactured such high finesse cavity at the apex of an optical fiber, with the ability to move on several millimeters, allowing us to characterize the same nano-emitter deposited on the back mirror in free space and in cavity [3]. Not only we observed a Purcell effect, but using the micro-cavity tunable length we studied the influence of the mode volume on the efficiency spectrum [4]. In addition, we were able to show that carbon nanotubes can be single photon source on several THz thanks to the cavity feeding effect (i.e. the ability to force the emission of photons with a cavity non-resonant with the emitter zero phonon line) [3].

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# TRANSPORT PROPERTIES OF MULTITERMINAL GRAPHENE BASED JOSEPHSON JUNCTIONS

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We report an experimental study on the electronic transport in graphene based Josephson junctions in multiterminal device geometry. In our devices, h-BN encapsulated graphene acts as a Josephson weak link connected to two superconducting electrodes on its two parallel edges. The other two transverse edges of the graphene are connected to two normal metal electrodes. This device geometry results in two graphene based junctions orthogonal to each other, namely the superconductor/graphene/superconductor (SGS) junction and the normal metal/graphene/normal metal (NGN) junction. Applying a control current/voltage in the transverse direction to the Josephson weak link significantly modifies the electronic transport through the Josephson junction [1]. A recent theoretical investigation has shown the possibility of observing nonlocal transport processes in multiterminal Josephson junctions [2]. In the light of this, we have experimentally studied low temperature electronic transport across SGS junction as a function of an applied control current/voltage across the NGN junction and vice versa. As charge carrier density as well as charge carrier type in graphene can be easily tuned by an applied gate voltage, it provides us an additional experimental parameter which can be tuned. We observe tuning of supercurrent with an applied control current/voltage as well as signatures of crossed Andreev reflections in our devices. The transport features attributed to crossed Andreev reflections are found to be most prominent in the vicinity of the charge neutrality point of the graphene weak link. These features become less pronounced at higher charge carrier densities due to the presence of supercurrent. We have explained the origin of the observed crossed Andreev reflections in our devices by employing the beam splitter analogy considering that the central graphene region acts as a beam splitter.

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# GATE-DEFINED QUANTUM POINT CONTACTS AND QUANTUM DOTS IN BILAYER GRAPHENE

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Graphene and bilayer graphene (BLG) are attractive platforms for spin qubits, thanks to their weak spin-orbit and hyperfine interaction, promising long spin-coherence times. This has motivated substantial efforts in studying quantum dot (QD) devices based on graphene and BLG. The problem of edge disorder in etched graphene can be completely circumvented in BLG, thanks to a tunable band-gap in the presence of a perpendicularly applied electric field, a feature that allows introducing electrostatic confinement in BLG.

However, until very recently, essentially all gated BLG devices were limited by leakage currents due to shortcomings in opening a clean and homogeneous band gap. A very recent breakthrough in this field has been the introduction of graphite back-gates. Together with the technology of encapsulating BLG in hexagonal boron nitride (hBN) crystals, giving rise to high quality hBN-BLG-hBN heterostructures, the use of a graphite back gate allows for a homogeneous and gate tunable band gap in BLG. We will show that this technological improvement allows for an unprecedented quality of quantized conductance measurements and most importantly, allows realizing complete electrostatic current pinch-off. The latter finally offers the possibility of electrostatically confining carriers in BLG and allows implementing quantum dots with a high level of control and low disorder [1]. We will report on the formation of gate-controlled single, double and triple QDs [1] as well as on the shell filling of BLG QDs in the very few carrier regime [2].

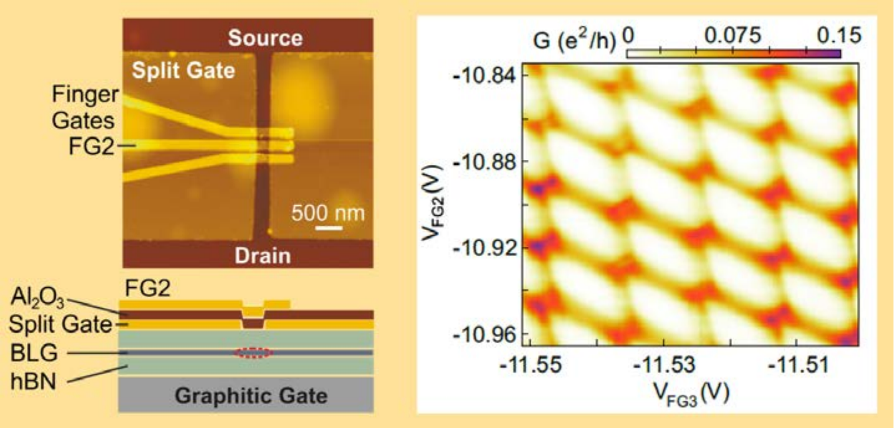

*Figure 1: Top-gated bilayer graphene quantum device with multiple finger gates (top-left: atomic force microscope image; bottom-left: illustration of the cross-section of the device), which allows realizing single and double quantum dots. On the right, we show conductance measurements in the multi-electron range highlighting double quantum dot operation. Taken from Ref. [1].*

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# ELECTROSTATIC SUPERLATTICES ON SCALED GRAPHENE LATTICES

graph-and-co19 - Vortragssaal - Wednesday, October 30, 2019 - 9:30/9:50 (20min)

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The scalable tight-binding model [1] is applied to simulate quantum transport in clean graphene subject to electrostatic superlattice potentials, including both types of graphene superlattices: moiré patterns due to the stacking of graphene and hexagonal boron nitride (hBN) lattices (Fig. 1), and gate-controllable superlattices using spatially modulated gate capacitance (Fig. 2). In the case of graphene/hBN moiré superlattices, consistency between simulation and our own experiment is to be limited to low or zero magnetic field regimes, due to the adopted simple model Hamiltonian [2] with higher-order terms like vector potential and Dirac mass terms dropped. In the case of gate-controllable superlattices, no higher-order terms are dropped, and the simulations are expected to be exact. Revisiting a recent experiment reporting on graphene subject to a gated square superlattice with periodicity of 35 nm [3], our simulations show an excellent agreement, revealing the emergence of multiple extra Dirac cones at stronger superlattice modulation (Fig. 2).

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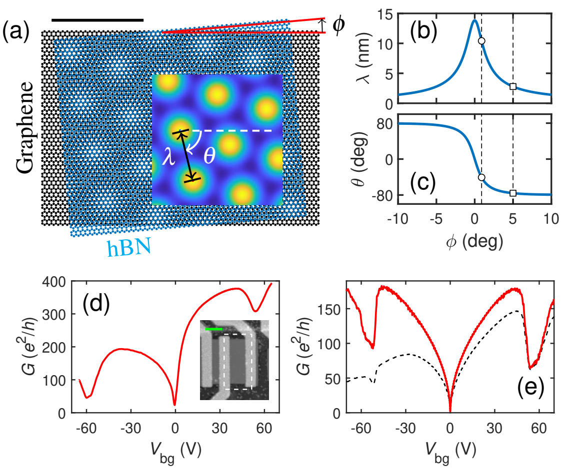

Figure 1: (a) An example of stacked graphene and hBN lattices with twist angle $\phi = 5°$ showing the resulting moiré pattern with wave length $\lambda$ and the orientation angle $\theta$. The overlay of the color map is given by the moiré model potential proposed in [2]. The $\phi$ dependence of $\lambda$ and $\theta$ are shown in (b) and (c), respectively. (d) Experimentally measured two-terminal conductance as a function of back gate voltage $V_{bg}$ at low temperature. Inset: the AFM image of a typical junction similar to the measured device. Scale bar: $1\mu$m. (e) Simulated conductance as a function of $V_{bg}$ at zero temperature with Fermi energy in the leads fixed (black dashed) and floating (red).

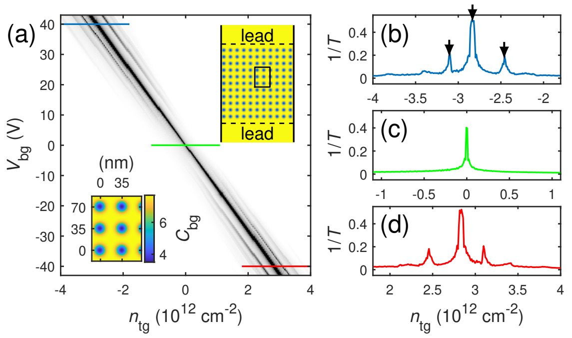

Figure 2: (a) Inverse transmission $1/T$ as a function of top-gate-contributed carrier density $n_{tg}$ and back gate voltage $V_{bg}$ for the simulated virtual device similar to one of those reported in [3]. Upper inset: Device geometry with the modulated back gate capacitance profile showing a spatial modulation of periodicity $\lambda = 35$nm. The boxed region is magnified in the lower inset with the color bar calibrating the value of back gate capacitance $C_{bg}$ in units of $10^{10}$cm$^{-2}$V$^{-1}$. The three horizontal color lines marked on the main panel of (a) correspond to the line cuts shown in (b)–(d).

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# ELECTRONIC INTERFEROMETER IN A GRAPHENE MOIRÉ SUPERLATTICE

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Sequential stacking of layers of different two-dimensional materials, forming so-called van der Waals (vdW) solids, allows the engineering of arbitrary new materials with designed properties [1]. One of the most prominent examples is a graphene sheet placed on top of a hexagonal boron nitride (hBN) substrate [2]. The lattice mismatch between the two lattices generates a moiré superlattice [3], which modulates the electronic band structure and features interesting new physics.

Here, we present measurements on a device based on a graphene/hBN vdW heterostructure with such moiré superlattice. With the combination of overall back gate and local top gate forming a pnp-junction we are able to study the effect of the superlattice by probing the superlattice charge carriers confined to the electronic interferometer [4]. The decoding of the resulting interference patterns in magnetic field gives insight into the transport properties of the charge carriers in the newly formed superlattice minibands.

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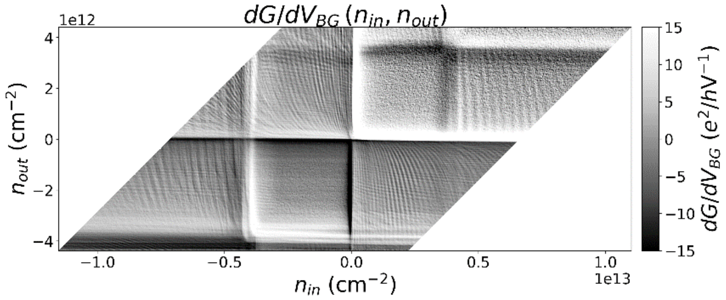

*Figure 1 : Graphene moiré superlattice pnp junction.*

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# Signatures of van Hove Singularities Probed by the Supercurrent in a Graphene-hBN Superlattice

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The band structure of graphene can be strongly modified if its lattice is aligned with the one of a boron nitride substrate. A moiré superlattice forms, which manifests itself by the appearance of new Dirac points, accompanied by van Hove singularities. In this work, we present supercurrent measurements in a Josephson junction made from such a graphene superlattice in the long and diffusive transport regime, where the critical current depends on the Thouless energy. We can then estimate the specific density of states of the graphene superlattice from the combined measurement of the critical current and the normal state resistance. The result matches with theoretical predictions and highlights the strong increase of the density of states at the van Hove singularities. By measuring the magnetic field dependence of the critical current, we find the presence of edge currents at these singularities. We explain it by the reduction of the Fermi velocity associated with the van Hove singularity, which suppresses the supercurrent in the bulk while the electrons at the edges remain less localized, resulting in an edge supercurrent. We attribute these different behaviors of the edges to defects or chemical doping.

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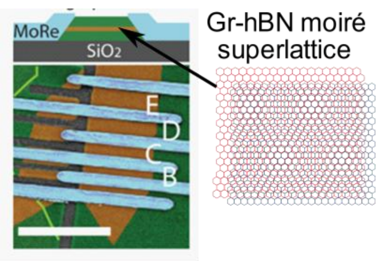

*Figure 1 : Schematics of the sample measured. A graphene layer is encapsulated in hBN, forming a moiré superlattice with the bottom layer. A supercurrent is induced in the superlattice using the superconducting proximity effect.*

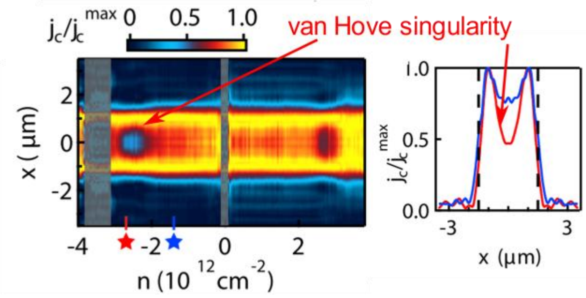

*Figure 2 : Supercurrent distribution in the sample. At the van Hove singularity, the current flows mainly on the edges.*

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# STRAIN SUPERLATTICES IN DRAPED GRAPHENE

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The potential of tailoring electronic properties by merging different two-dimensional (2D) materials seems limitless [1-3]. In this work [4], we demonstrate a novel technique of engineering electronic properties in 2D materials by periodically strain modulating their lattice. Akin to a plastic wrap pulled taut at its edges, graphene under extreme (>10%) strain forms nanoscale ripples when the sheet is draped over Copper step substrates (see Fig.1). Within these ripples, carbon-carbon bond lengths vary, creating alternatively dense and rare regions that represent different electronic couplings between atoms, similar to systems of two different materials. Thus, a single graphene sheet effectively becomes an electronic superlattice in which novel electronic states arise at the interfaces. Combining scanning tunneling microscopy and atomistic calculations, we find that these electronic states are driven by intense interfacial pseudo-gauge (i.e. pseudo-magnetic and electric) fields on the order of 100 T and $10^7$ V/m. Such a technique of manipulating electronic states can be helpful to realize longstanding theoretical proposals, such as valley filters, snake states and electron optics in graphene and other two-dimensional materials..

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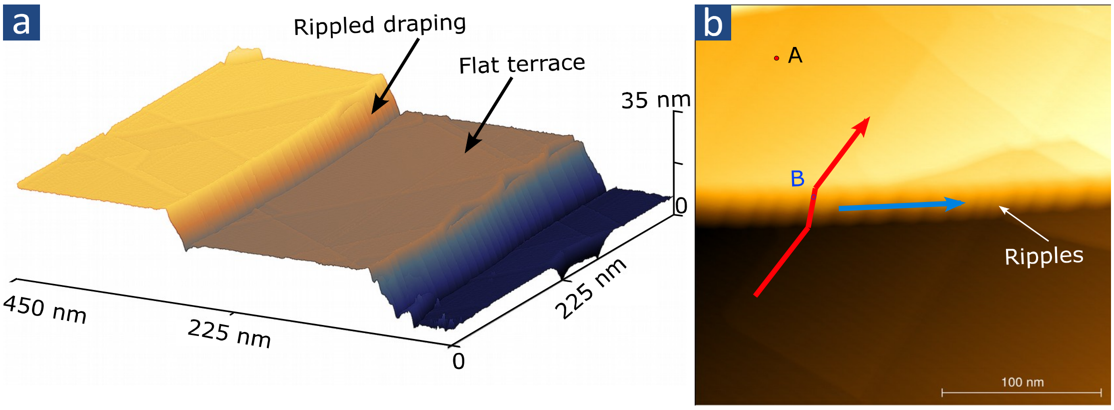

*Figure 1: Strain Superlattices by draping Graphene over Copper step edges.*

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# CONDUCTIVITY TUNING OF POLYCRYSTALLINE GRAPHENE BY MECHANICAL STRAIN

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Nanocrystalline graphene (NCG) is a highly interesting material for photonic and piezotronic applications as shown by a study from 2015 [1]. Strain gauge factors on the order of 20 are reported for NCG [1]. This is substantially higher compared to single- or microcrystalline graphene where values are between 1.5 – 7 [2]. The origin of this enhanced piezoresistivity is not fully clear so far, but it is believed that grain boundaries play an important role in this effect.

Here, we study how the detailed atomic structure and chemical composition at graphene grain boundaries influence their electronic transport behaviour. Density functional theory and the tight binding approximation are used together with the non-equilibrium Green function method to calculate the transport properties. Moreover, we investigate the relation between grain boundary structure, mechanical strain, and conductance modulation. From these results we calculate strain gauge factors and compare them to experimental values.

Our results show that mechanical strain modulates the transport gap nearly linearly in a strain range from -10% to +10% (Fig. 1). Interestingly, the detailed grain boundary structure does not change the modulation behaviour substantially. This is in analogy to results we recently obtained in another study [3]. We show that the strain-induced conductance modulation in graphene bicrystals can be understood in terms of the strain modulation of the electronic structure of pristine graphene. With this information the transport gap for a given misorientation and strain state can be calculated solely from the bulk band structure without explicit knowledge of the grain boundary. Lastly, we give an outlook of these implications on graphene grain boundaries beyond bicrystals.

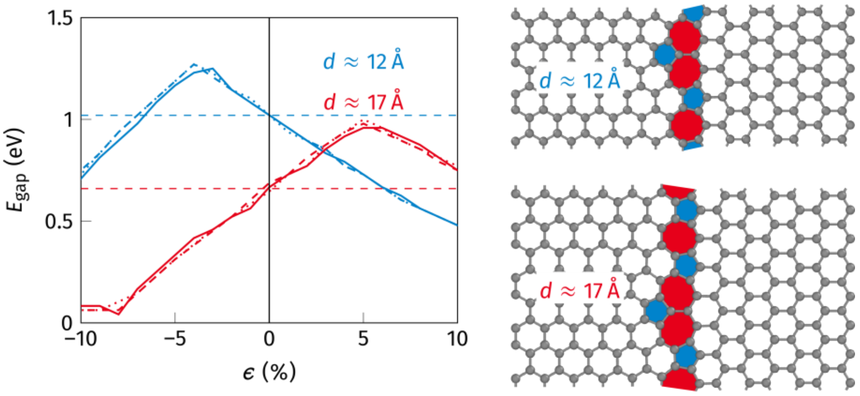

*Figure 1 : Strain-induced conductance modulation for different graphene bicrystals.*

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# Imaging Dirac charge carrier dynamics in graphene nanodevices

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Quantum transport in nanodevices is usually probed thanks to measurements of the electrical resistance or conductance, which lack the spatial resolution necessary to probe local-scale electron behavior. Here, we will discuss how to get real-space local information on peculiar quantum transport phenomena inside two types of graphene mesoscopic devices: graphene quantum rings and graphene constrictions. The results were obtained using low temperature scanning gate microscopy (SGM), which consists in mapping the electrical conductance of a device as an electrically-biased sharp metallic tip scans in its vicinity [1].

If the tip-induced perturbation is relatively small, SGM is an imaging technique giving access to the local density of states inside mesoscopic devices [2]. The regime of large tip-induced perturbation can also be interesting in the case of graphene: depending on tip voltage and tip-sample distance, one can tune the shape, size, and smoothness of the moving scattering region associated with the tip, and eventually create a moving circular pn-junction within the device. We will illustrate how the different SGM modes helped to unveil peculiar aspects of relativistic charge carrier dynamics within graphene devices, including Klein tunneling, Fabry-Perot interferometry and relativistic quantum scars [3-4].

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