

# C'Nano 2018

## THE NANOSCIENCE MEETING

**TULON** December, 11, 12 and 13  
Palais des Congrès Neptune



In partnership with:



### Alain Pénicaud

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### Biography

Alain Pénicaud is a CNRS material scientist specializing in carbon. He started his career crystallizing fullerenes to turn later towards dissolving seemingly insoluble forms of carbons such as graphite and carbon nanotubes. He has published 69 research articles and is the inventor of 8 patents, 3 of them being under a license contract. He is co-founder and shareholder of carbon Waters, a start-up company exploiting research results of his laboratory. A. Pénicaud has also a keen interest into divulgation and has published a few articles and two books on that subject (Editions Ellipses). While the attention has somewhat moved away from graphene to other (non-carbon) 2D materials, A. Pénicaud is exploring the chemistry of other carbon forms such as

### GRAPHENE AND OTHER CARBON NANOFORMS FOR A SUSTAINABLE WORLD

Beyond the rise and fall of scientific fashion, graphene has genuine optimal properties. For a start, it is an all-surface material (there is no inside), it is impermeable if defect free, it is electrically and thermally conducting, mechanically robust relative to its size, light and chemically inert. For these and other reasons, researchers both in the academic and industrial worlds have worked on processing graphene.

Graphene is potentially a sustainable material able to replace metals (heat and electrical transport), indium tin oxide (displays) and if not recycled, simply burned away avoiding hazardous wastes linked to metal disposal. It requires, however, to be formulated in clean ways, i.e. without potentially harmful solvents and/or surfactants. I will describe surfactant-free, aqueous, dispersions of *single layer graphene* Eau de Graphene (EdG), in which hydroxyl ion adsorption stabilizes graphene sheets in water, [1–3] and on the associated newly created start-up company, Carbon Waters.[4] Recent works on adapting the EdG strategy to carbon nanotubes will be described.[5] Finally, starting with a nanocarbon originating from biomethane,[6] conducting nanocarbon inks,[6] conductive rubbers,[7,8] nanocarbon/iron nanoparticle composite electrocatalysts for fuel cell technology,[9,10] and microsupercapacitors can be obtained, all of them might contribute to a cleaner tomorrow.

**References :** [1] G. Bepete et al. Nat. Chem. 9 (2017) 347–352; [2] G. Bepete et al. J.phys. Chem. C. 120 (2016) 28204–28214; [3] G. Bepete et al. Phys. Status Solidi - Rapid Res. Lett. 5 (2016) 1–5; [4] Carbon waters: <https://www.carbon-waters.com>; [5] G. Bepete et al. ACS Nano 2018, DOI: 10.1021/acsnano.8b04341; [6] F. Hof et al. , Carbon 111 (2017) 142-149; [7] K. Kampioti et al., ACS Omega, 2018, 3, 1367–1373 ; [8] ACS, From compost to composites: An eco-friendly way to improve rubber, (2018); <https://youtu.be/i-93J2n76Bs>; [9] F. Hof et al. Chem. Eur. J. (2017), 23, 15283-15288 [10] F. Hof et al. Chem. Eur. J. (2018), 10.1002/chem.201801694

**Keywords:** Nanocarbons – graphene – carbon nanotubes – food waste - supercapacitors - electrocatalyst

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### **Matthieu, Paillet**

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### **CV/ biography** (10 lines max.)

M. Paillet was born in 1978. He received his Ph.D. degree in materials science from the University of Montpellier in 2005. After, he had a post-doctoral position in the group of Pr. R. Martel at the University of Montréal in Canada. Since 2008, he is holding a full-time CNRS researcher position at the Laboratoire Charles Coulomb (University of Montpellier, France). His researches are focused on the physical properties of graphene and carbon nanotubes mainly using Raman and optical spectroscopies.

### **COUNTING GRAPHENE LAYERS: FROM LAB TO STANDARD**

#### **Abstract**

Raman spectroscopy (RS) of graphene-related materials (GRM) is being considered as a fast, versatile, powerful and non-destructive characterization technique. RS is sensitive to the number of layers, their stacking order, the nature and density of defects, the charge carrier density and in-plane strain variations. However, the positions, linewidths, profiles, intensities of the graphene/multilayer graphene (MLG) Raman bands are not only affected by all these perturbations but also depend on the uniformity across the probed area and on the substrate (through optical interference effects, dielectric screening...). An accurate interpretation of Raman spectra becomes then extremely complex and deserves the combined use of complementary diagnosis.

We recently developed a RS set-up allowing to monitor simultaneously the laser power, transmission, reflection and Raman signal.

In this contribution, we discuss the application of this tool for counting the number of layers of different kind of graphene/MLG samples with the aim to define standard procedures for GRM characterization on different substrates.

**Keywords:** Graphene, Raman spectroscopy, optical contrast, number of layers

11, 12 &amp; 13 décembre

Nanometrology &amp; 2D materials

Characterization, carbon nanotubes, Rayleigh scattering, ultra-clean nanomaterials, quantum electronics

## Ultra-clean single carbon nanotubes for integration in electronic circuits

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Carbon nanotubes have an exceptional crystallinity and hold great promises for quantum technologies. Their integration into electronic circuits is nevertheless challenging due to their sensitivity to contamination and defects. A solution is to mechanically transfer the carbon nanotube at the last step of the nanofabrication process of the device, such that the carbon nanotube stays clean [1,2] as well as the surface of the target device. We have developed a very efficient integration process (integration yield close to 100%) by transferring the nanotube onto the target substrate under vacuum conditions. This process allows the fabrication of devices with a very low electronic noise and the realization of spin-qubits with a decoherence time about two orders of magnitude larger than previous carbon-based qubit [3].

A second challenge for the integration of carbon nanotube is the diversity of their crystalline structure, which induces variations in their electronic properties. In order to characterize and sort the nanotube before its integration, we have built a Rayleigh scattering setup. To have a quantitative characterization of the as-grown tubes, we have calibrated the intensity of the Rayleigh signal by cross-correlating with Raman scattering measurement as well as transmission electron microscopy. Moreover thanks to this cross-correlation with the Rayleigh spectra, we can in fine determine the chirality of single narrow carbon nanotube.

As the process is flexible, it could be in principle used for other applications than quantum electronics and with other nano-objects.

[1] C. C. Wu et al., Nano Letters 10 (2010), pp 1032

[2] J. Weissman et al., Nature Nanotech. 8 (2013), pp 569

[3] F. Pei et al., Nature Nanotech. 10, (2012), pp 630

11, 12 &amp; 13 septembre

Session (Nanometrology &amp; 2D materials)

Keywords: TERS, Graphene oxide, AFM-Raman, 2D TMDC, correlated measurements

## Nanoscale Topographical, Chemical and Electronic Mapping of Carboxyl Graphene Oxide using TERS

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In recent years, Tip Enhanced Raman Scattering (TERS) imaging made a dramatic progress from “once in a lifetime experience” to a routine everyday characterization tool for nanoscale Raman imaging of various materials. This progress was mainly determined by the advent of new generation of TERS instrumentation, development of advanced TERS imaging modes and availability of highly reproducible commercially available TERS probes with high enhancement factors.

Since TERS is intrinsically a hyperspectral imaging tool, it does not rely on a priori knowledge of the spectral properties of the investigated materials and therefore allows discovery of unexpected Raman peaks and mapping the distribution of their intensities. Cross-correlating the TERS with other channels provided by Scanning Probe Microscopy (SPM) such as the topography, surface potential, conductivity, photocurrent, friction etc, is another powerful tool allowing comprehensive characterization of novel materials at nanoscale.

We'll illustrate usefulness of TERS imaging and cross-correlation by probing the distribution of structural defects and chemical groups on a graphene oxide surface. We demonstrate mapping of chemical groups on carboxyl graphene oxide (GO-COOH) surface with an unprecedented spatial resolution of  $\approx 10$  nm using TERS. Furthermore, we extend the capability of TERS by in-situ measurement of local electronic properties in addition to the topography and chemical composition at the sample surface. In-situ topographical, electronic and chemical nanoscopy of the GO-COOH surface reveals that the Fermi level on GO-COOH surface increases with increasing  $I_d/I_g$  ratio, enabling correlation of the local defect density to Fermi level at nanometre length-scales for the first time.

We will also discuss how correlated TERS and SPM measurements can also be applied to other 2D materials (TMDC).

11, 12 &amp; 13 septembre

Nanometrology &amp; 2D Materials

Keywords: graphene, doping, STM, molecule

## Electronic interaction between organic molecules and nitrogen doped graphene

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Tailoring the properties of graphene is of fundamental interest to uncover new functionalities and open new opportunities for graphene based applications. In this context, substitutional doping and molecular functionalization have focused tremendous efforts. Nitrogen doping obtained by replacing some carbon atoms by nitrogen atoms appears to be particularly interesting as it allows to perform n-doping with minor structural perturbations. This chemical doping can also modify the interaction of graphene with organic molecules that can be exploited for sensing or catalysis. To probe this effect at the molecular level, scanning tunneling microscopy and spectroscopy experiments have been performed on model systems with electron donor (porphyrin) [1,2] and electron acceptor molecules [3] adsorbed on multilayer pristine and doped graphene on SiC(000-1). Local spectroscopy allows to measure resonances arising from the molecular states and to reveal the electronic coupling and charge transfer between the molecules and the graphene. On doped graphene, a local modification of the charge transfer between molecules and graphene occurs at the doping sites. Recent measurements on electron acceptor molecules show such local modification of the charge transfer together with an effect of the electric field between the tip and graphene that can modify the charge transfer. This effect provides a route to tune the electronic interaction between molecules and graphene.

[1] V. D. Pham et al., ACS Nano 8, 9403 (2014)

[2] V. D. Pham et al., Sci. Rep. 6, 24796 (2016)

[3] V. D. Pham et al., submitted

11, 12 &amp; 13 December

Session - Nanometrology and 2D materials

 Keywords: 2D materials, application, MoS<sub>2</sub>, black phosphorus, electronic, discrete components

### Title: Stabilizing 2D platforms toward discrete components

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Recently a new generation of 2D materials extending graphene's properties has arisen with new features at hand: semiconductors, insulators, superconductors, topological insulator, etc. Probably one of the key families is 2D semiconductors that widen the perspectives introduced by graphene by overcoming its lack of bandgap. Among these materials, TMDCs and Black Phosphorus are probably the most prototypical examples. After only a few years of investigation, these materials have shown properties already comparable to those of more usual semiconductors. However, it has been shown that their transport properties critically depend on their structural and chemical properties (number of layers, strain, doping, quality, etc.) challenging their potential use for applications. It is thus essential to develop specific integration protocols targeted for large scale devices development in order to fully exploit these materials in potential microelectronics applications.

Aiming at RF applications, we seek 2D semiconductors materials with potential for a high carrier density and high bias. In this work, we focused on the study of molybdenum disulfide (MoS<sub>2</sub>) and few-layer black phosphorus. We target a transistor design as a test vehicle for our 2D materials, and studied the influence of the metal contact as well as the passivation layers by combining electrical measurements with Raman micro-spectroscopy and photoluminescence. Additionally, we showed that growing passivation layers<sup>[1,2]</sup> is a key requirement to stabilize our 2D materials platforms as illustrated in Figure 1 for MoS<sub>2</sub>. Our results highlight that passivation protocols are an entree point for further development of 2D semiconducting platforms for RF microelectronics.

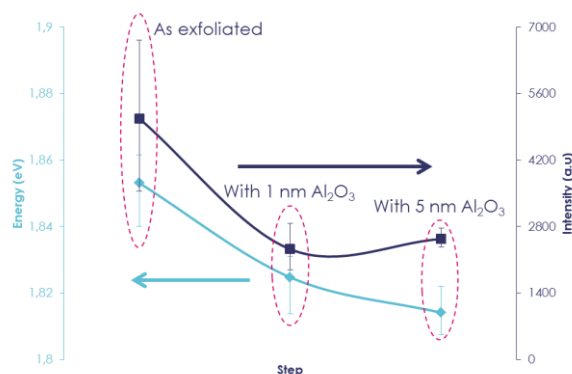


Figure 1 : Variation of the photoluminescence metrics of the MoS<sub>2</sub> over the passivation process

### References

- [1] Mzali et al. « Stabilizing a graphene platform toward discrete components » APL **109**, 253110 (2016)  
 [2] Galceran et al. « Stabilizing ultra-thin black phosphorus with in-situ-grown 1 nm-Al<sub>2</sub>O<sub>3</sub> barrier » APL **111**, 243101 (2017)