



# Selective Covalent Organic Functionalization Of Patterned Graphene Via 1,3-Dipolar Cycloaddition

*L. Basta, F. Bianco, A. Moscardini, F. Fabbri, L. Bellucci, V. Tozzini,  
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# OUTLINE

➤ Why GRAPHENE?

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- Why GRAPHENE?
- 1,3 Dipolar Cycloaddition of azomethine ylides

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- Organic Functionalization of Graphene via 1,3-DC
- Conclusions & Outlooks

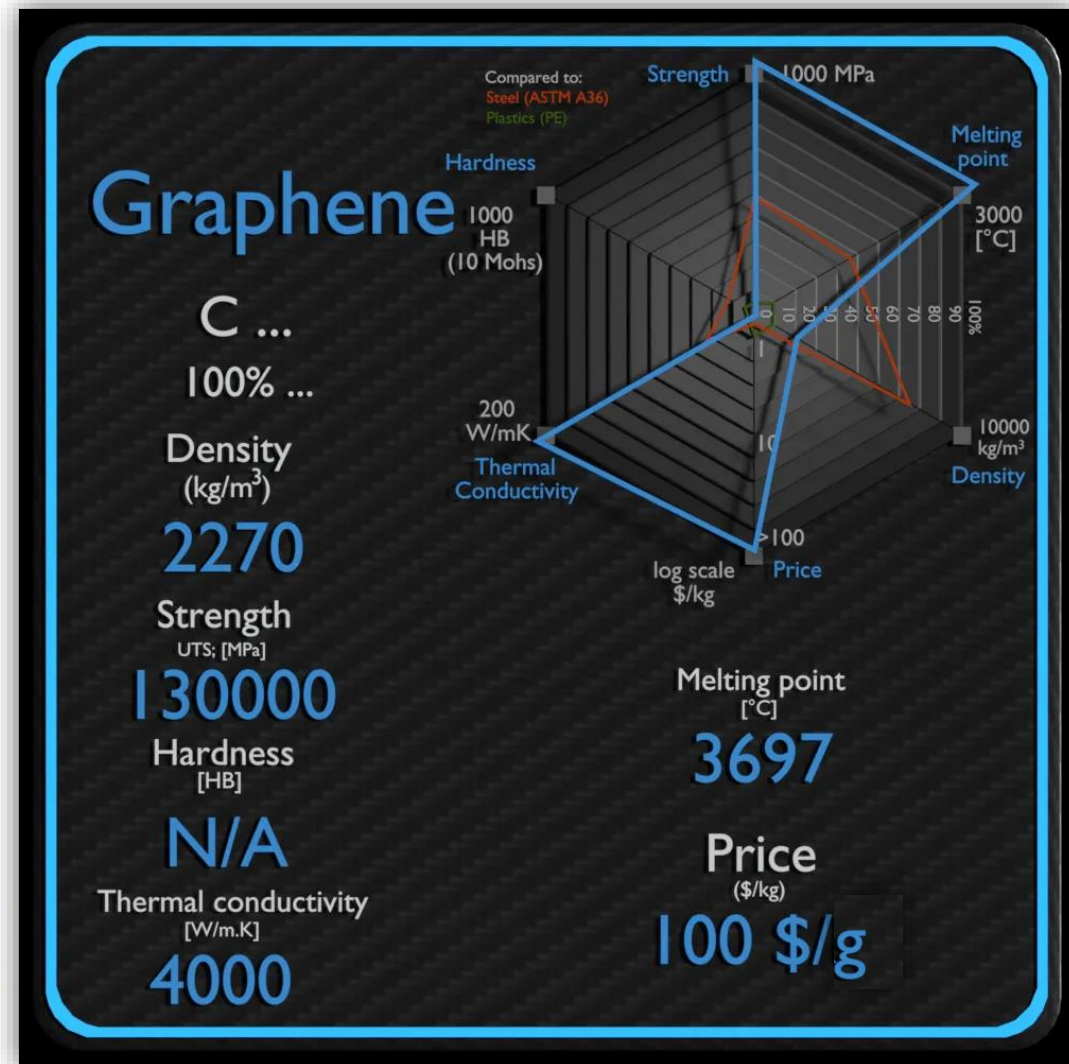
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# GRAPHENE

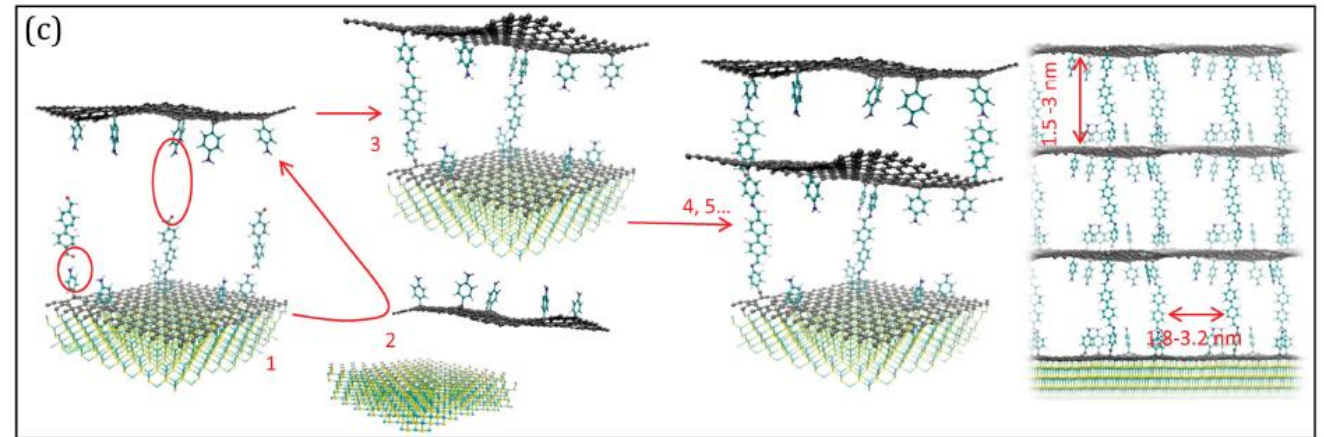
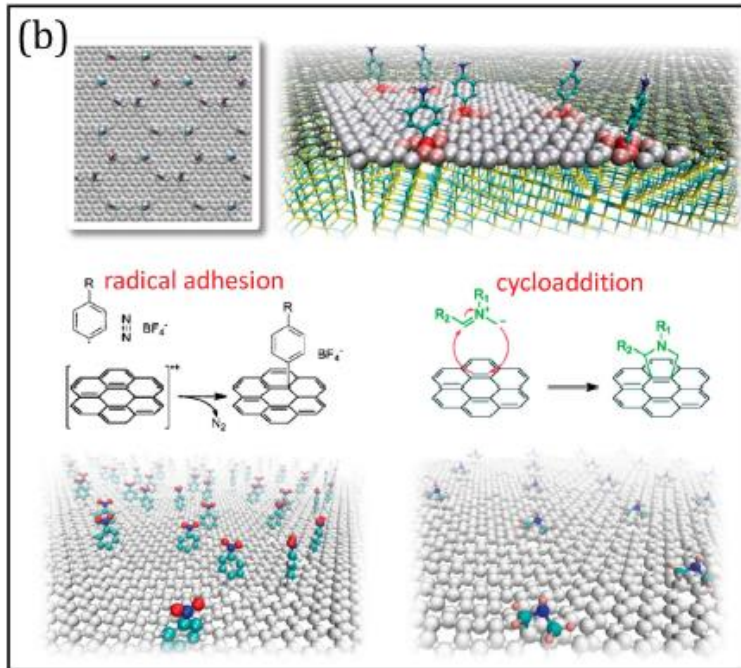
The high specific surface area and the excellent mechanical, electrical, optical and thermal properties of graphene make it an attractive component for high-performance devices.



[Material Properties (web)]

# CHEMICAL FUNCTIONALIZATION

Covalent functionalization of graphene with organic molecules offers the possibility to finely tune the system's physical and chemical properties



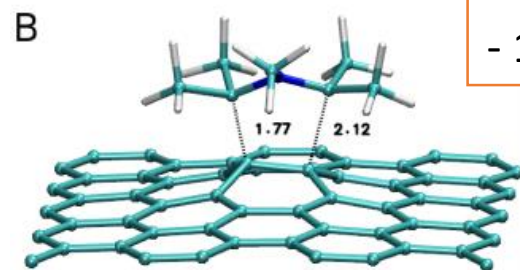
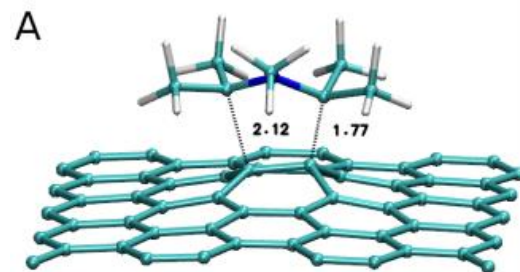
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[*Molecules*, 2020, 25, 339]



# 1,3 DIPOLAR CYCLOADDITION

1,3-DC of azomethine ylide: selectivity, stability (up to 300 °C), reversibility



- 43 kcal/mol  
- 1.87 eV

[L. Bellucci @ NEST]



COMMUNICATION www.rsc.org/chemcomm | ChemComm

### Organic functionalisation of graphenes

Vasilios Georgakilas,<sup>a</sup> Athanasios B. Bourlinos,<sup>a</sup> Radek Zh Panagiotis Dallas,<sup>a</sup> Athanasios K. Stubos<sup>cd</sup> and Christos Trap

Received (in Cambridge, UK) 22nd October 2009, Accepted 14th December 2009  
First published as an Advance Article on the web 13th January 2010  
DOI: 10.1039/b922081j

Graphene sheets derived from dispersion of graphite in pyridine are functionalised by the 1,3 dipolar cycloaddition of azomethine ylide. The organically modified graphene sheets are easily dispersible in water.

### Functionalization of Graphene via 1,3-Dipolar Cycloaddition

Mildred Quintana,<sup>1</sup> Konstantinos Spyrou,<sup>2</sup> Marek Grzelczak,<sup>3</sup> Wesley R. Browne,<sup>3</sup> Petra Rudolf,<sup>4</sup> and Maurizio Prato<sup>1\*</sup>

<sup>1</sup>Center of Excellence for Nanostructured Materials (CEMAT) and INSTM, Unit of Trieste, Dipartimento di Scienze Farmaceutiche, University of Trieste, Piazzale Europa 1, I-34127 Trieste, Italy; <sup>2</sup>Zemke Institute for Advanced Materials, and <sup>3</sup>Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, NL-9747AG Groningen, The Netherlands

**ARTICLE**

Graphene is a single layer of carbon atoms arranged in a hexagonal lattice and one of the few structures that are stable in two dimensions. Its extraordinary properties, such as high carrier mobility, half-integer quantum Hall effect at room temperature, and excellent thermal conductivity, have attracted significant attention. The interaction between gold nanorods and functionalized graphene was followed by HRTEM.

**ABSTRACT** Few-layer graphenes (FLG) produced by dispersion and exfoliation of graphite in N-methylpyrrolidone were successfully functionalized using the 1,3-dipolar cycloaddition of azomethine ylides. The amino functional groups attached to graphene sheets were quantified by the Kaiser test. These amino groups selectively bind to gold nanorods, which were introduced as contrast markers for the identification of the graphene structure. The interaction between gold nanorods and functionalized graphene was followed by HRTEM.

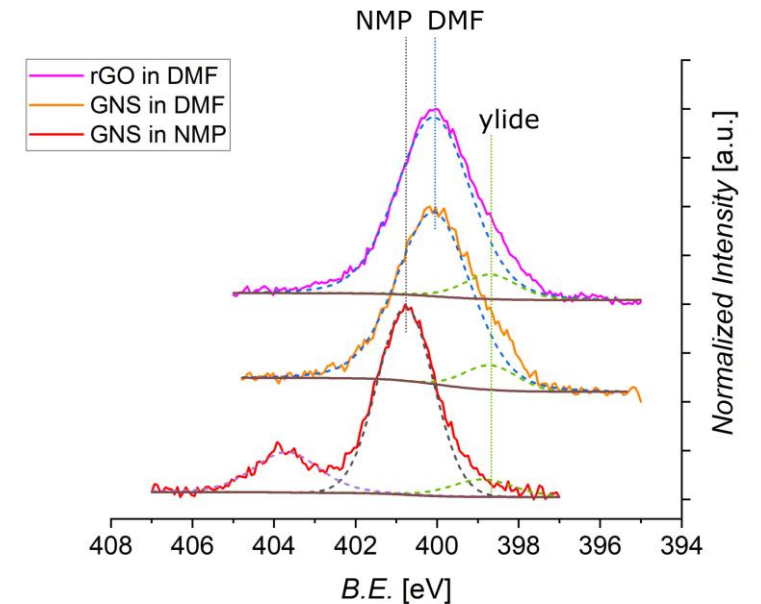
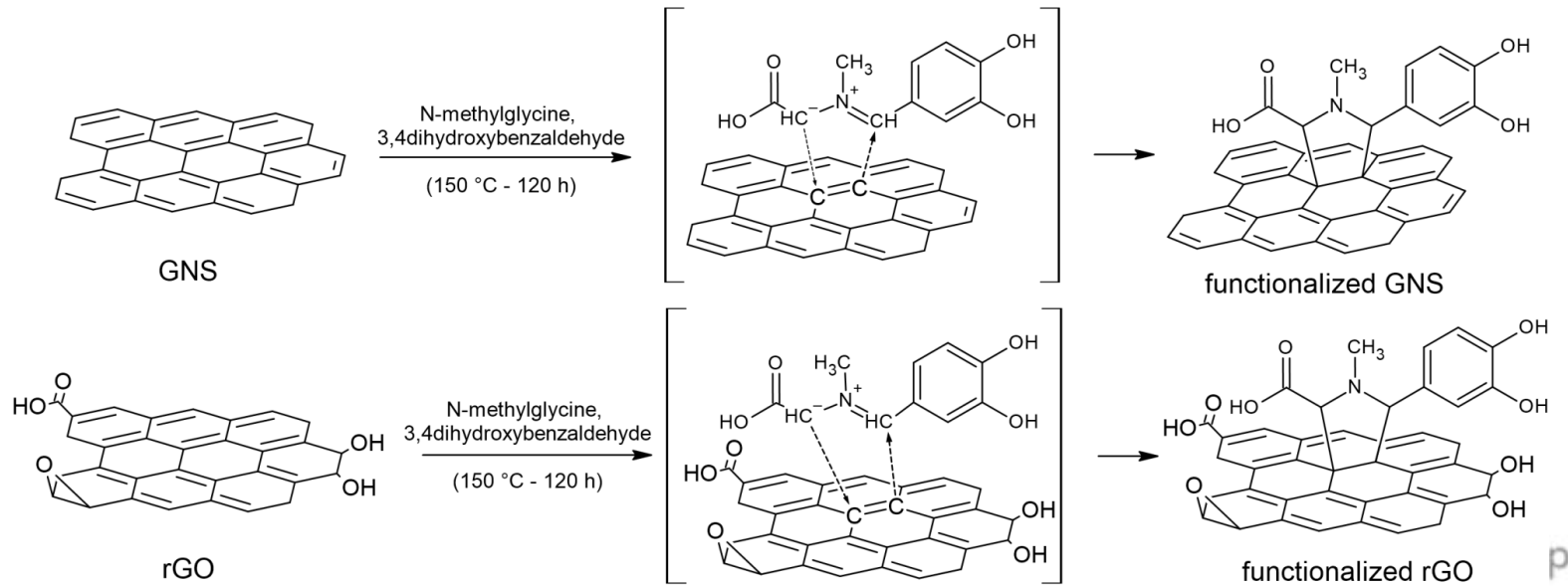
[*Chem. Commun.*, 2010, 46, 1766; *ACSNano*, 2010, 4,6]

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# 1,3-DC OF GNS AND RGO

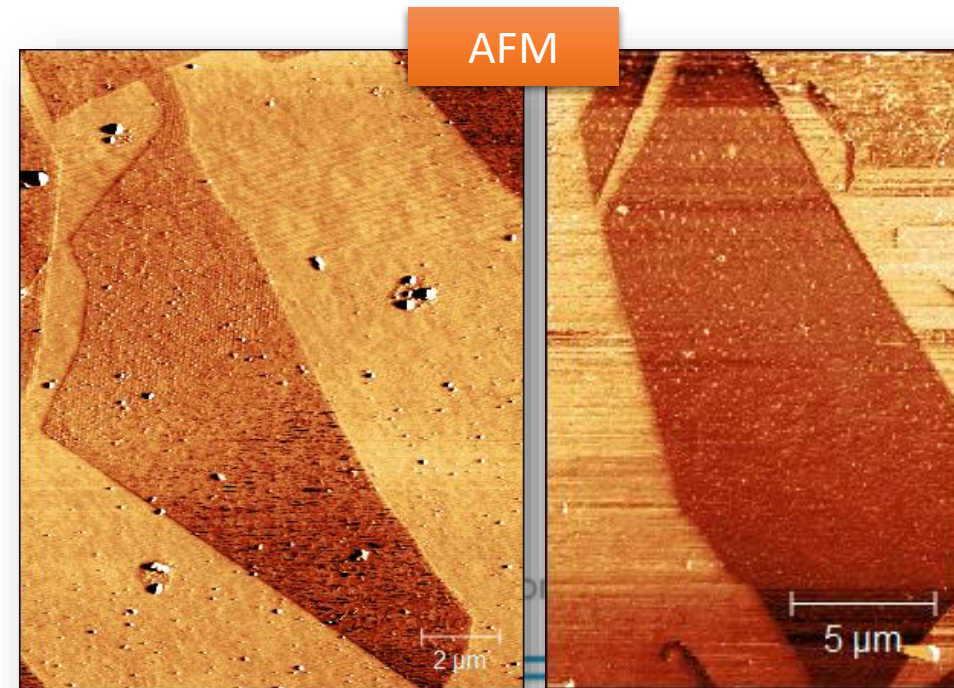
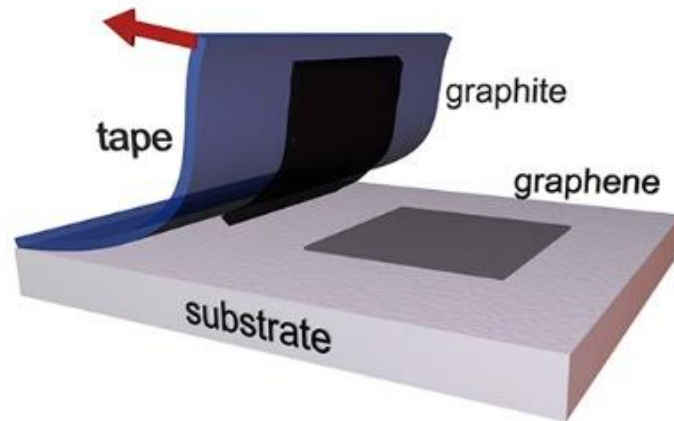
1,3-DC of azomethine ylide was successfully performed on graphene nanosheets and reduced graphene oxide in the liquid phase



[L. Basta, *Nanoscale Advances* (Accepted Manuscript), 2021]

# MECHANICALLY EXFOLIATED GRAPHENE

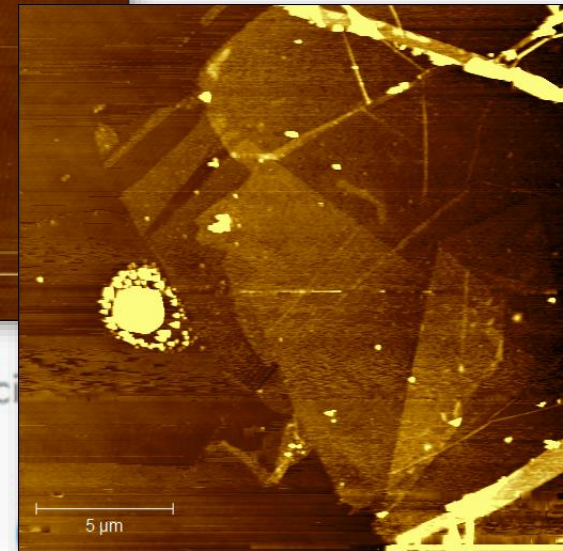
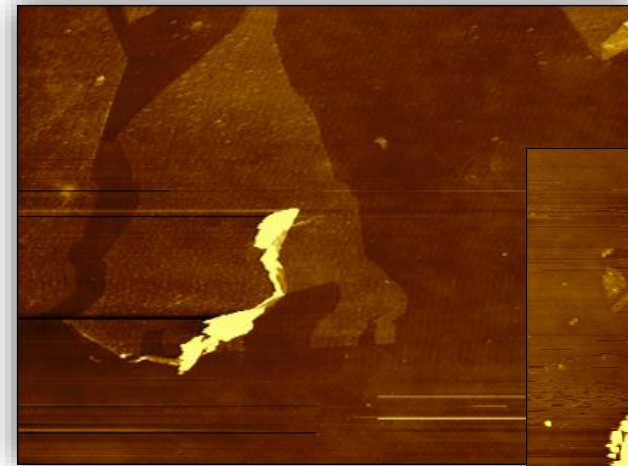
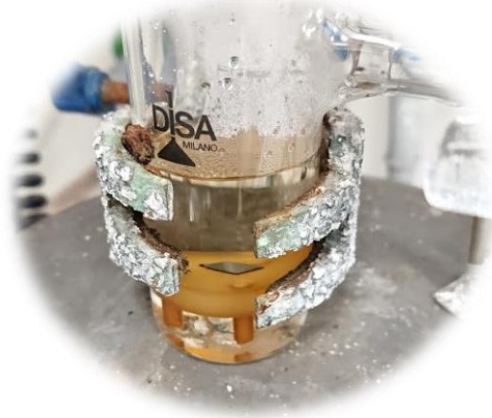
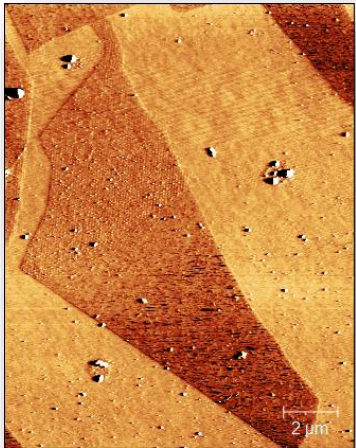
Pristine graphene flakes are widely investigated for optoelectronic applications thanks to their optimal transport properties and low defect structure



Technology

# MECHANICALLY EXFOLIATED GRAPHENE

- Pristine graphene flakes are not (enough) reactive
- NMP weakens the adhesion between graphene and the silica substrate

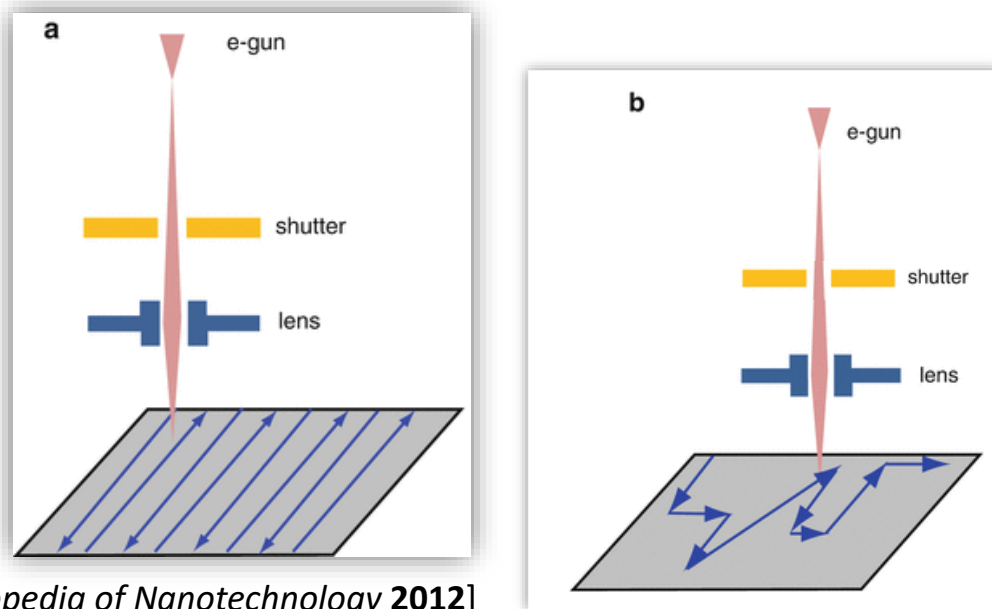


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# E-BEAM DEFECTS PATTERN

Precise control in defects patterning allows a fine tailoring of the surface chemistry of graphene → electron irradiation (exposure of graphene sheet to focused beams of energetic electrons)



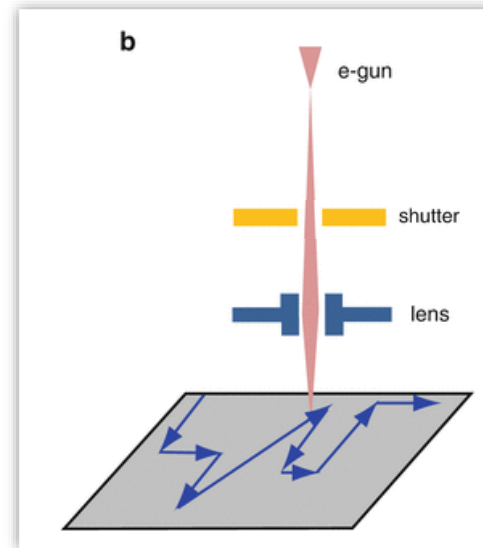
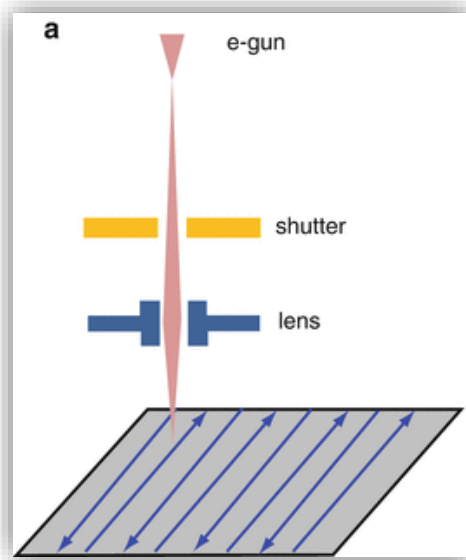
[EBL, *Encyclopedia of Nanotechnology* 2012]

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SPATIAL RESOLUTION

CONTROLLED DESIGN

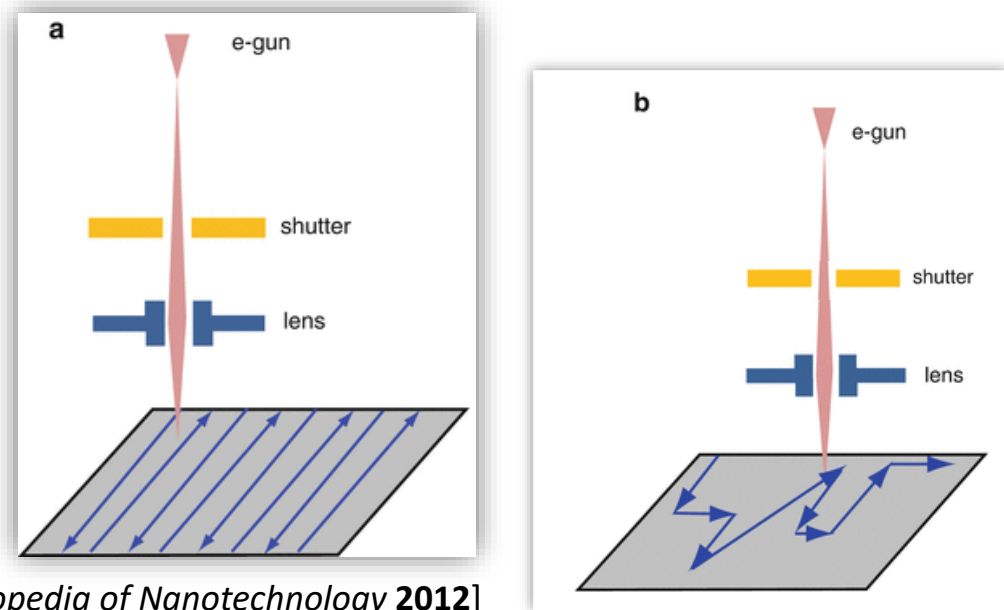
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ENHANCED SURFACE CHEMICAL REACTIVITY

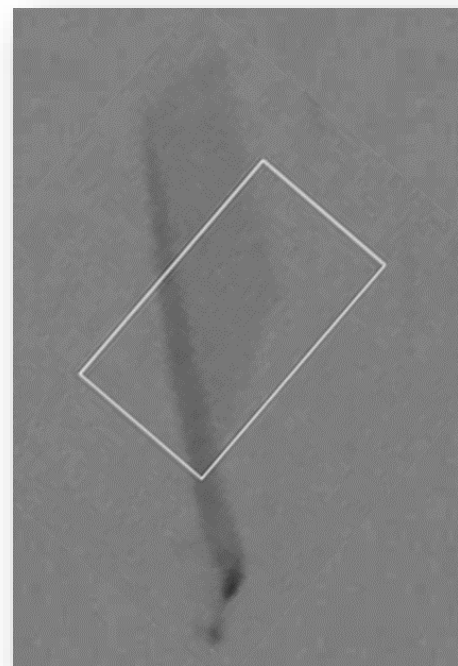
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# PATTERNED GRAPHENE FLAKES

30 kV, 40.000  $\mu\text{C}/\text{cm}^2$

Step size: 100 nm



Substrate surface effects on electron-irradiated graphene

Luca Basta<sup>a</sup>, Aldo Moscardini<sup>b</sup>, Stefano Veronesi<sup>a</sup>, Federica Bianco<sup>a,\*</sup>

<sup>a</sup>NEST Laboratory, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza San Silvestro 12, 56127, Pisa, Italy

<sup>b</sup>NEST Laboratory, Scuola Normale Superiore, Piazza San Silvestro 12, 56127, Pisa, Italy

## Abstract

Chemical, mechanical, thermal and/or electronic properties of bulk or low-dimensional materials can be engineered by introducing structural defects and novel functionalities. When using particles irradiation



[L. Basta, F. Bianco, arXiv:2103.15725 (2021)]

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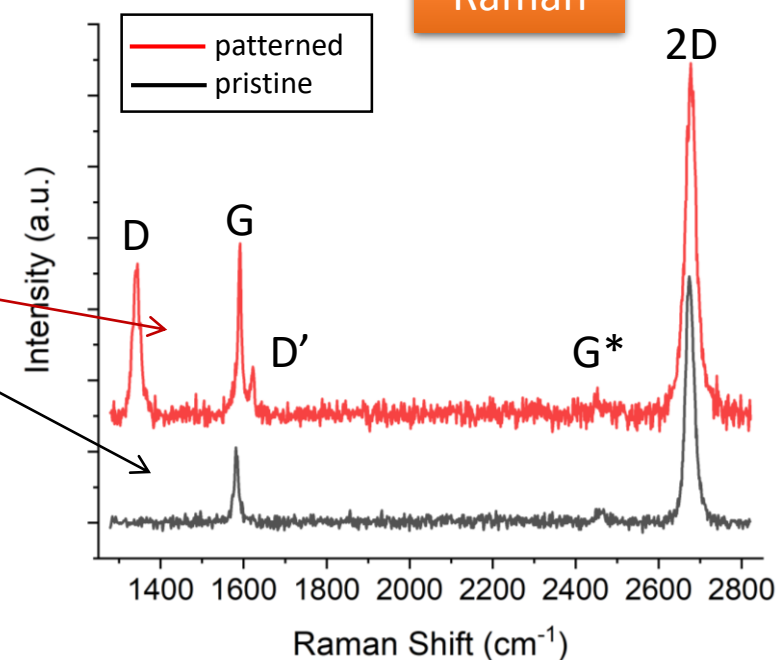
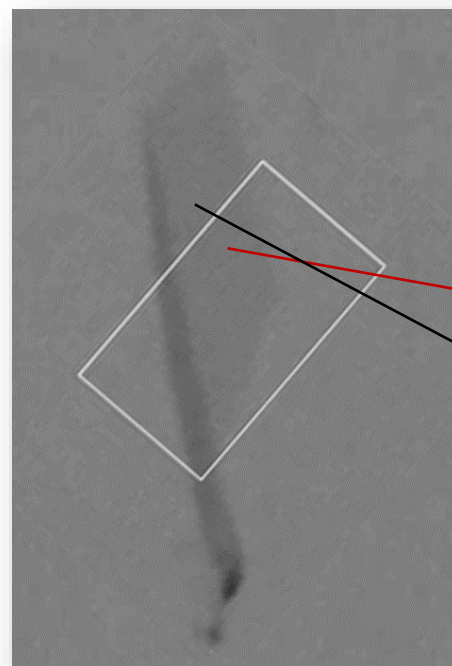
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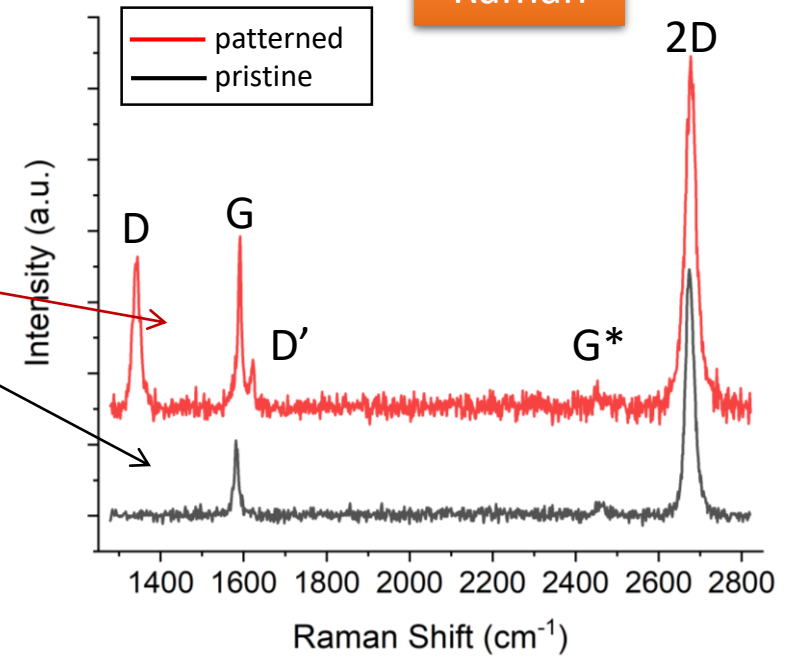
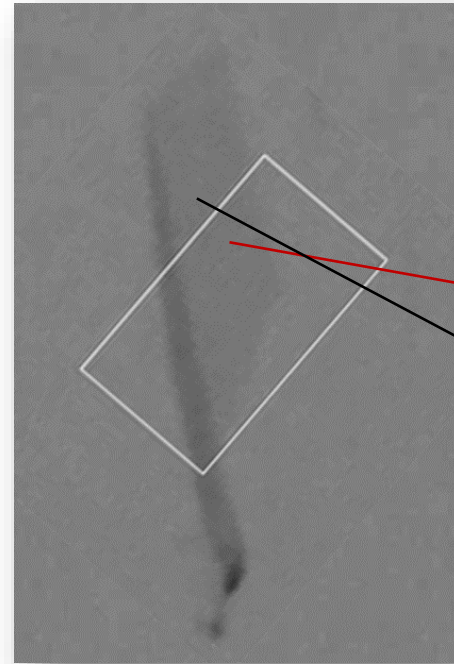
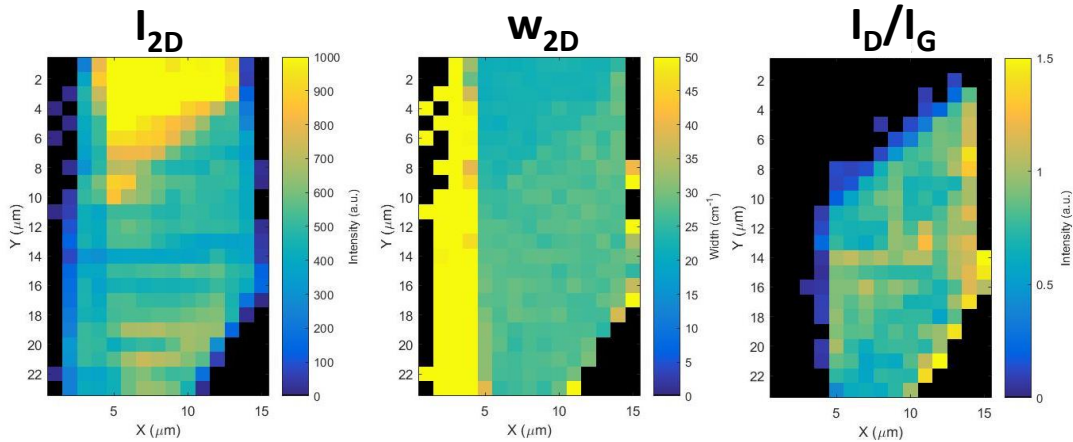
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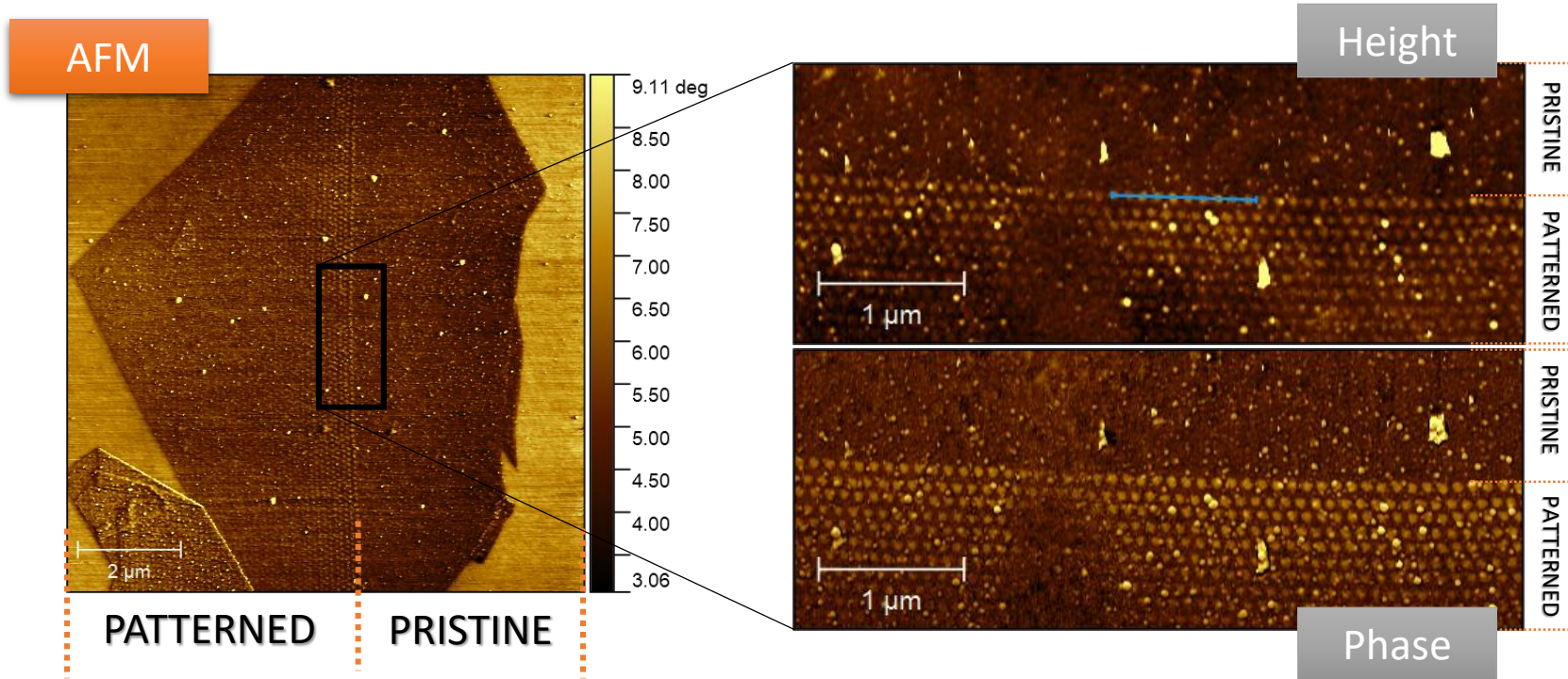


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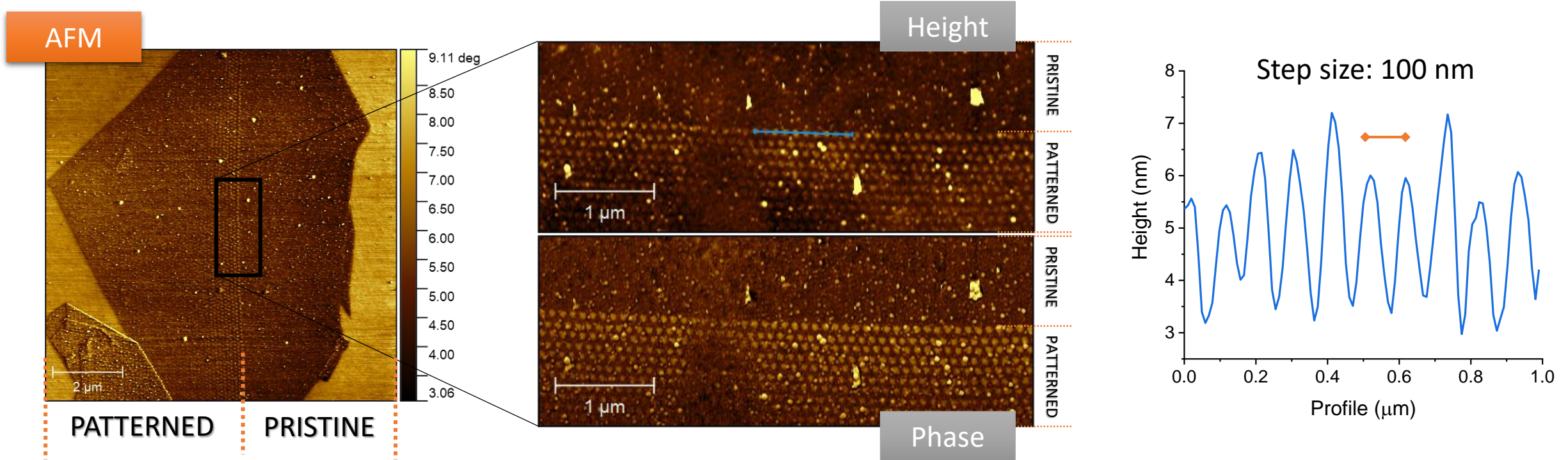
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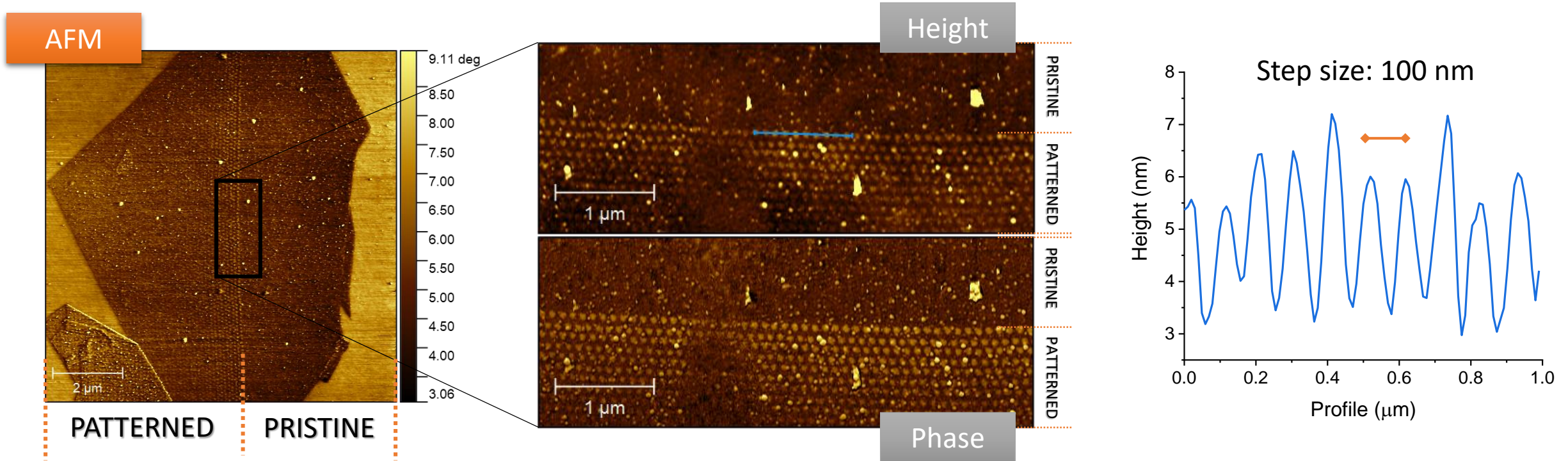


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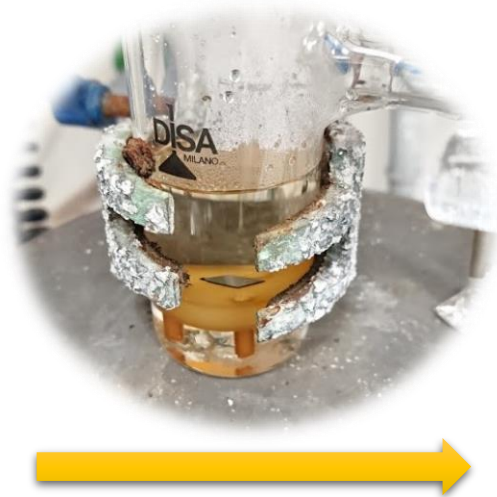
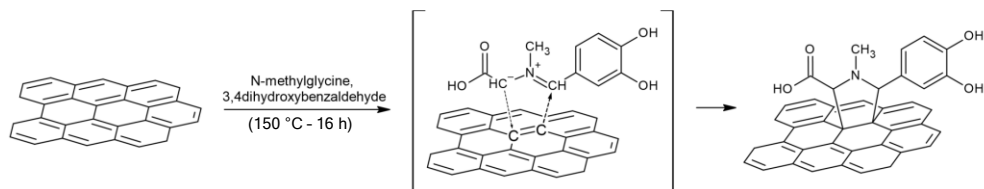


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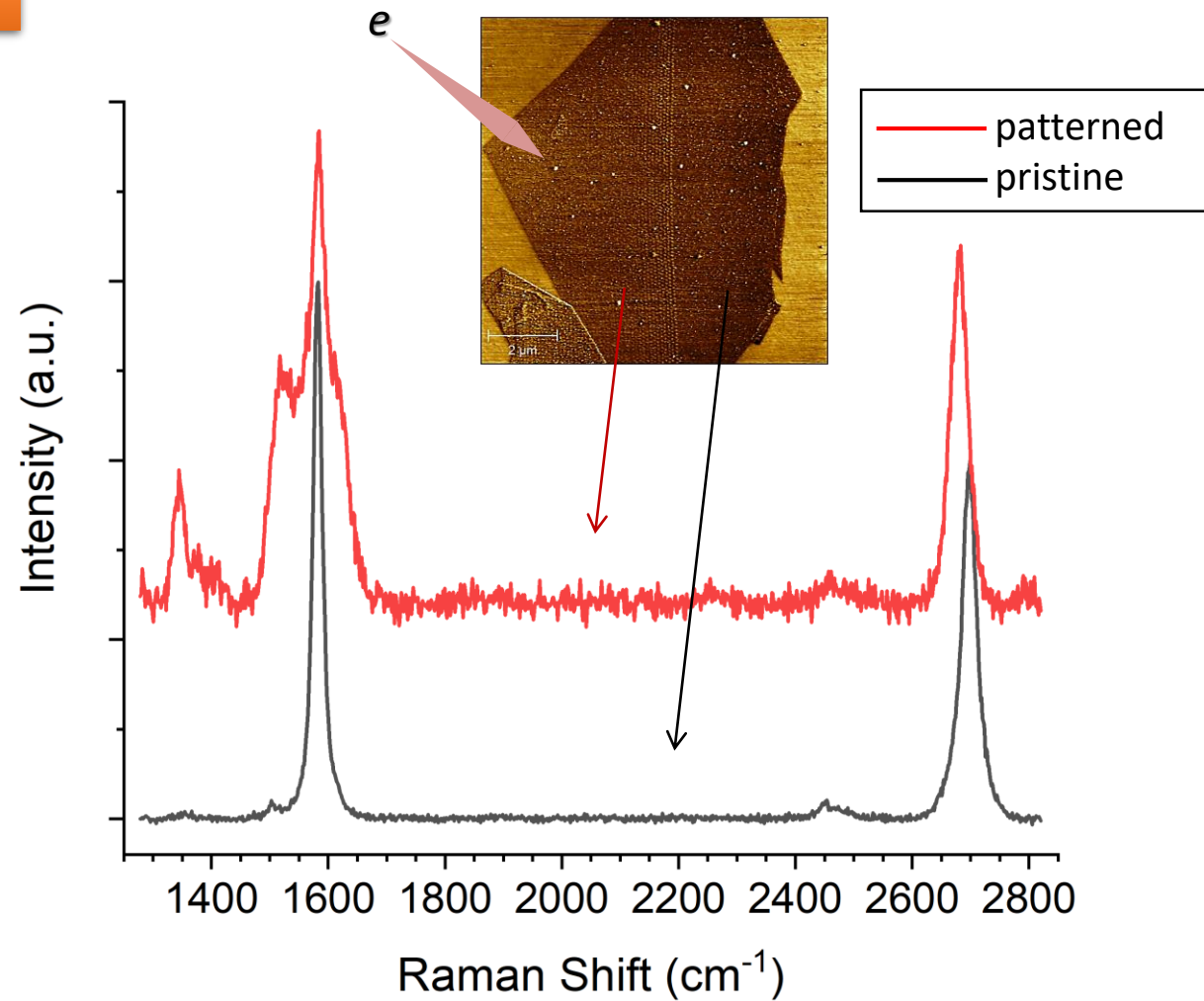
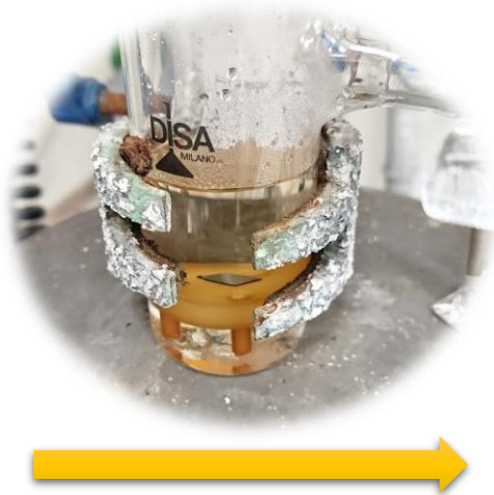
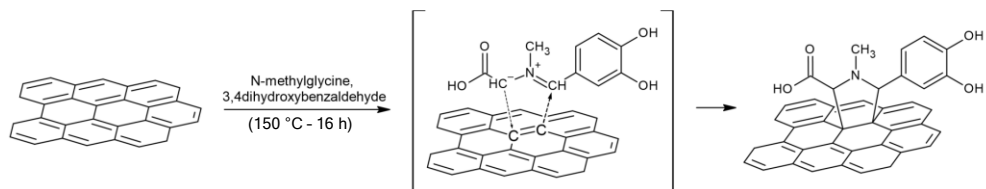


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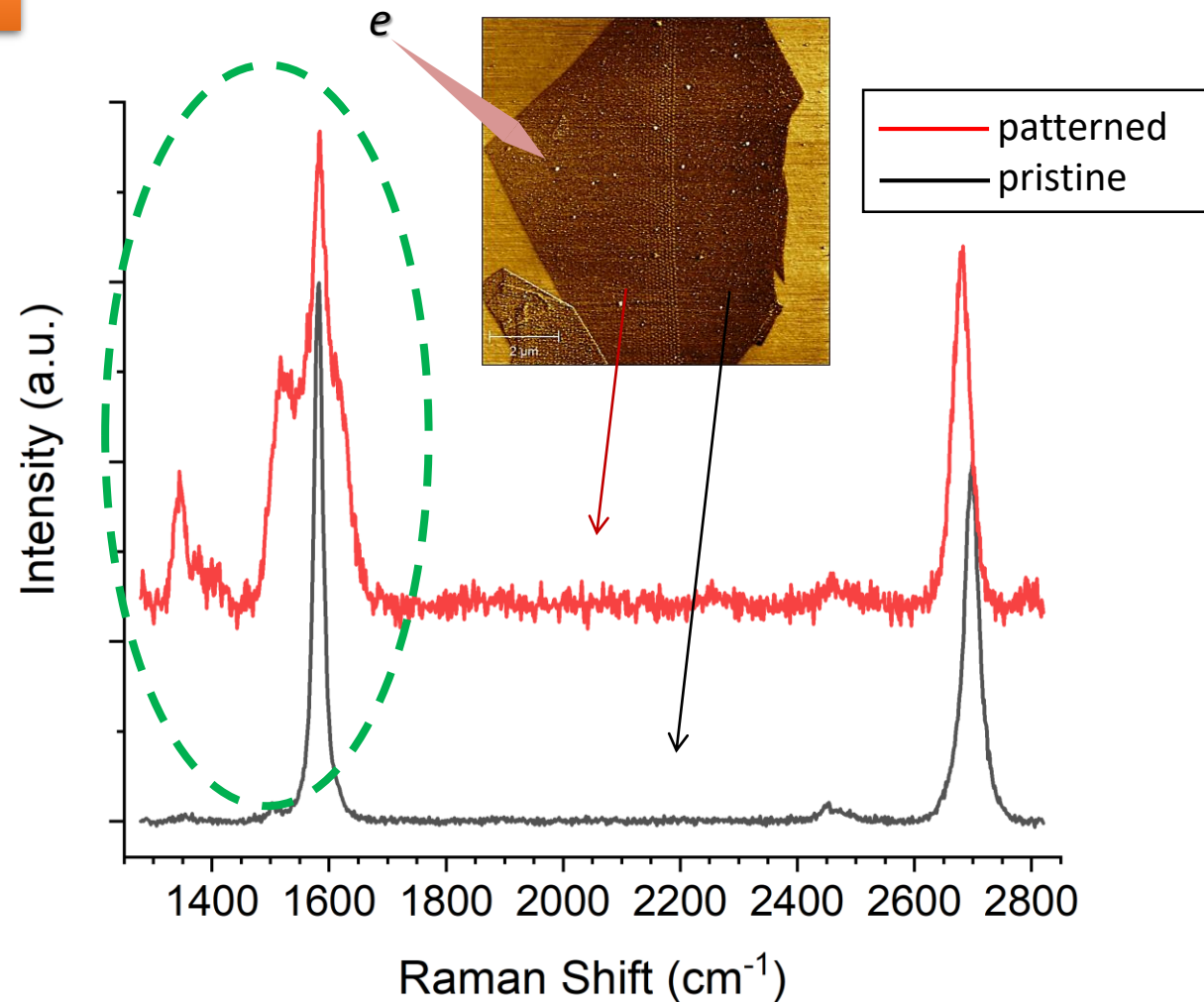
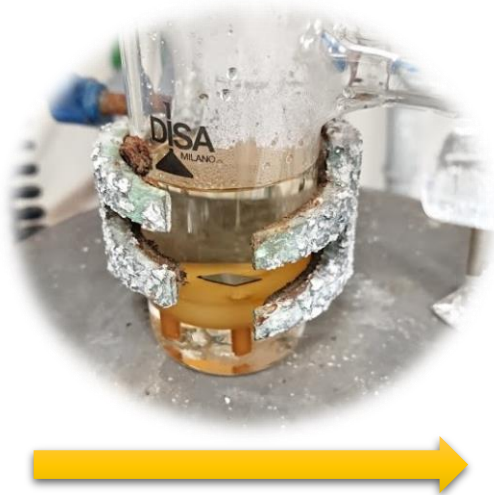
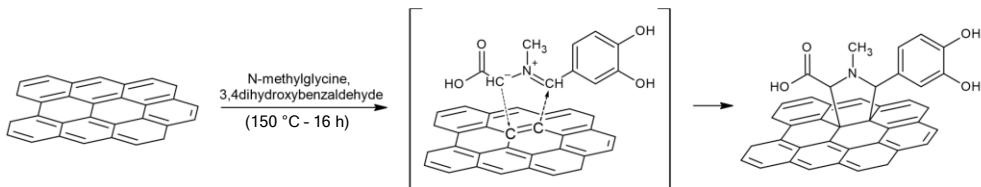
# 1,3-DC OF PATTERNED GRAPHENE

Raman



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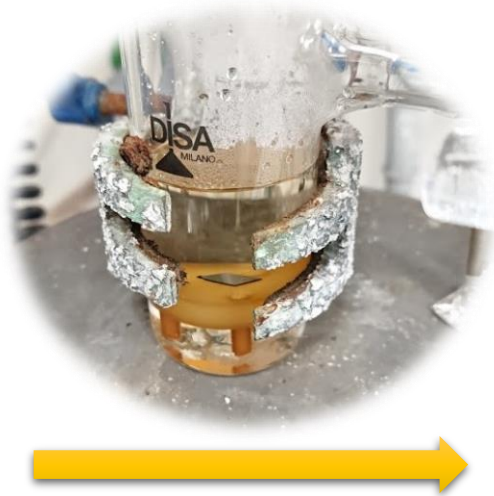
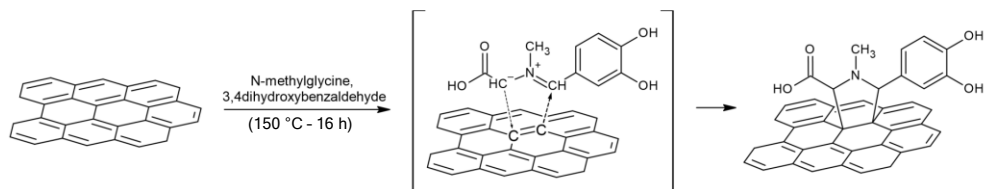
Raman



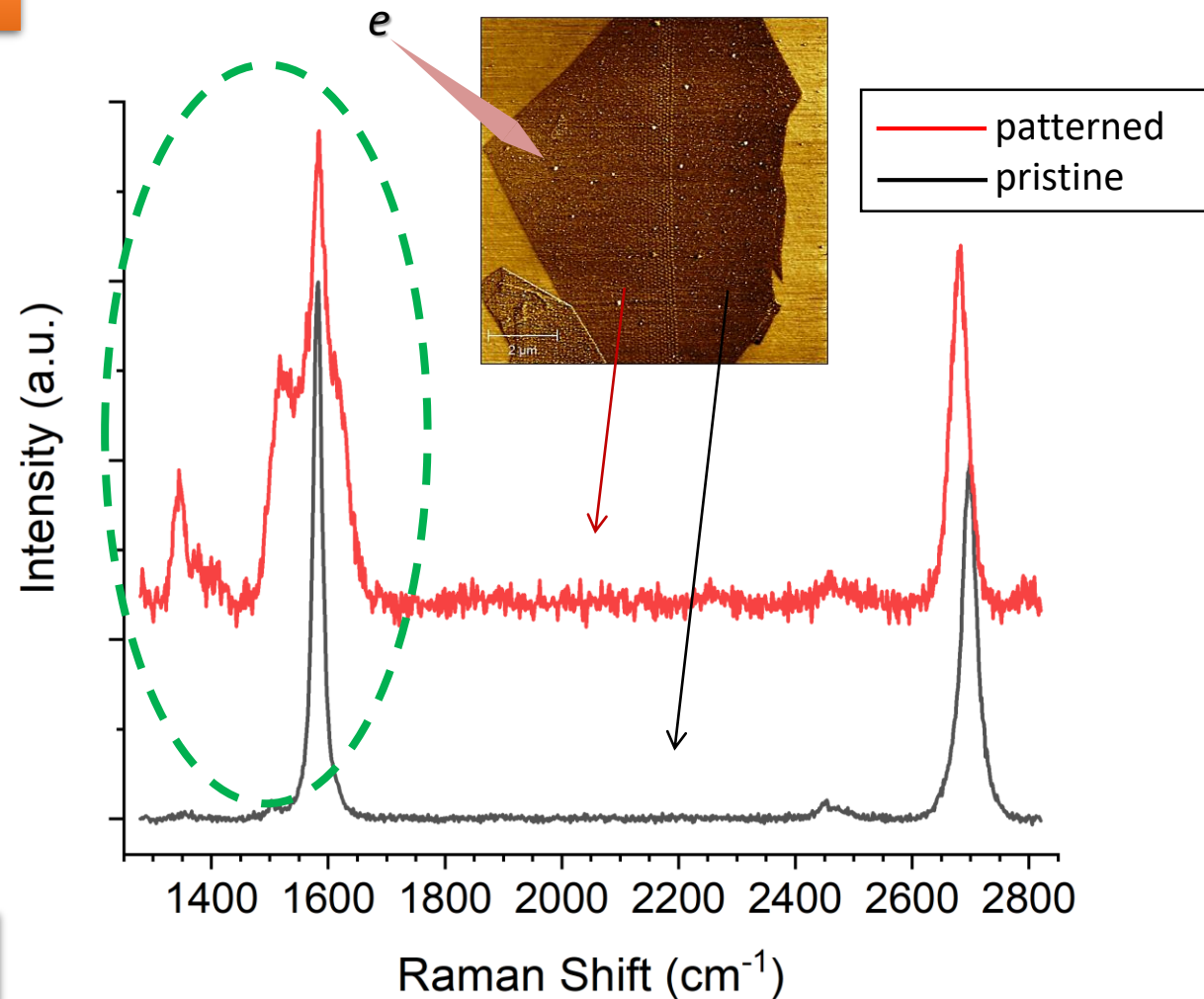


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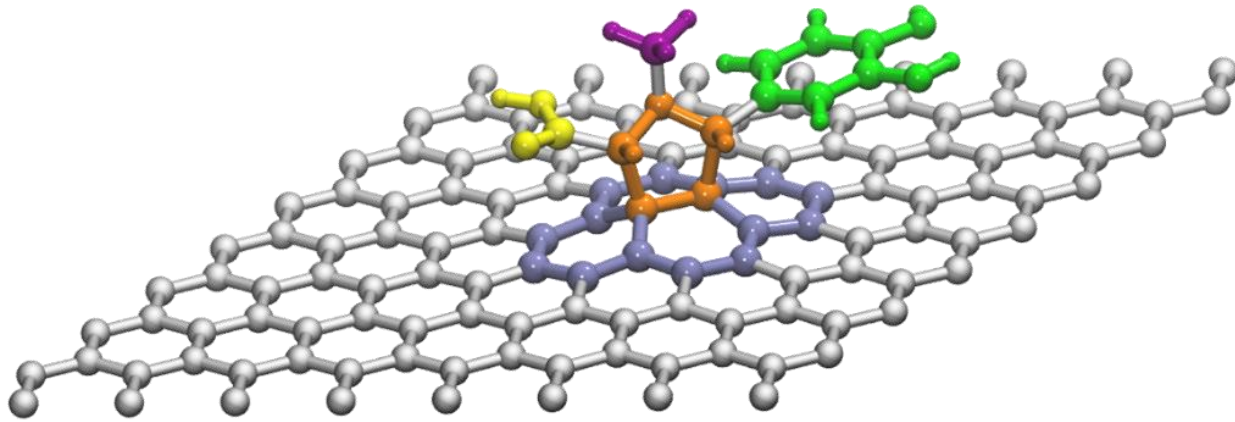
Raman



SELECTIVITY



# DFT – POWER SPECTRUM



[L. Bellucci @ NEST]

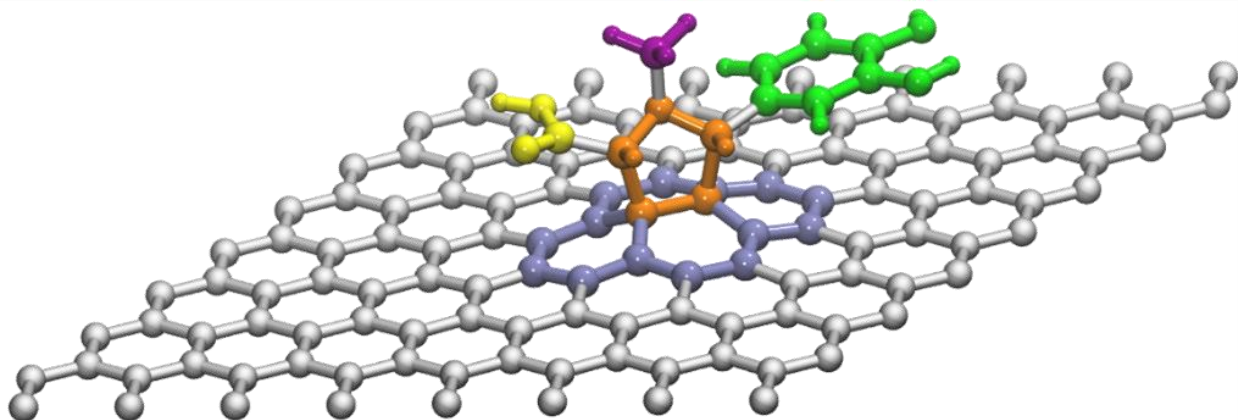


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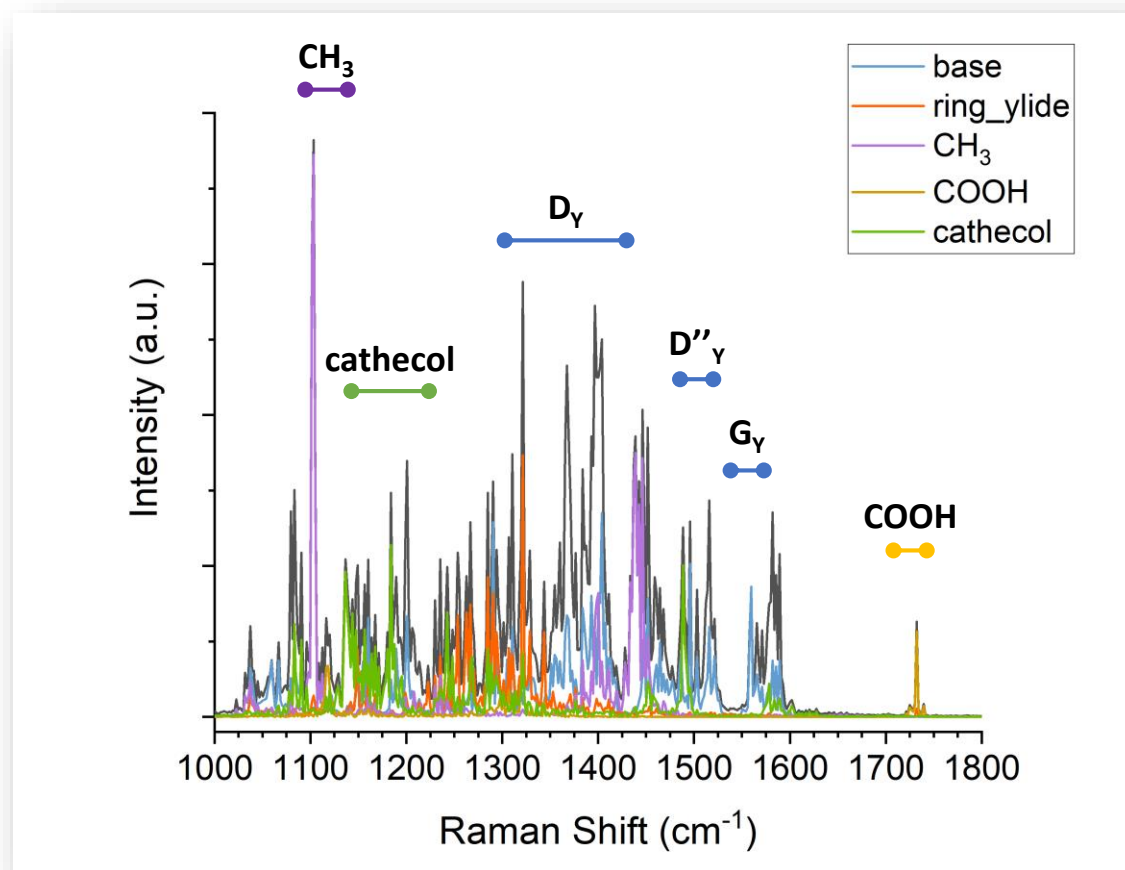
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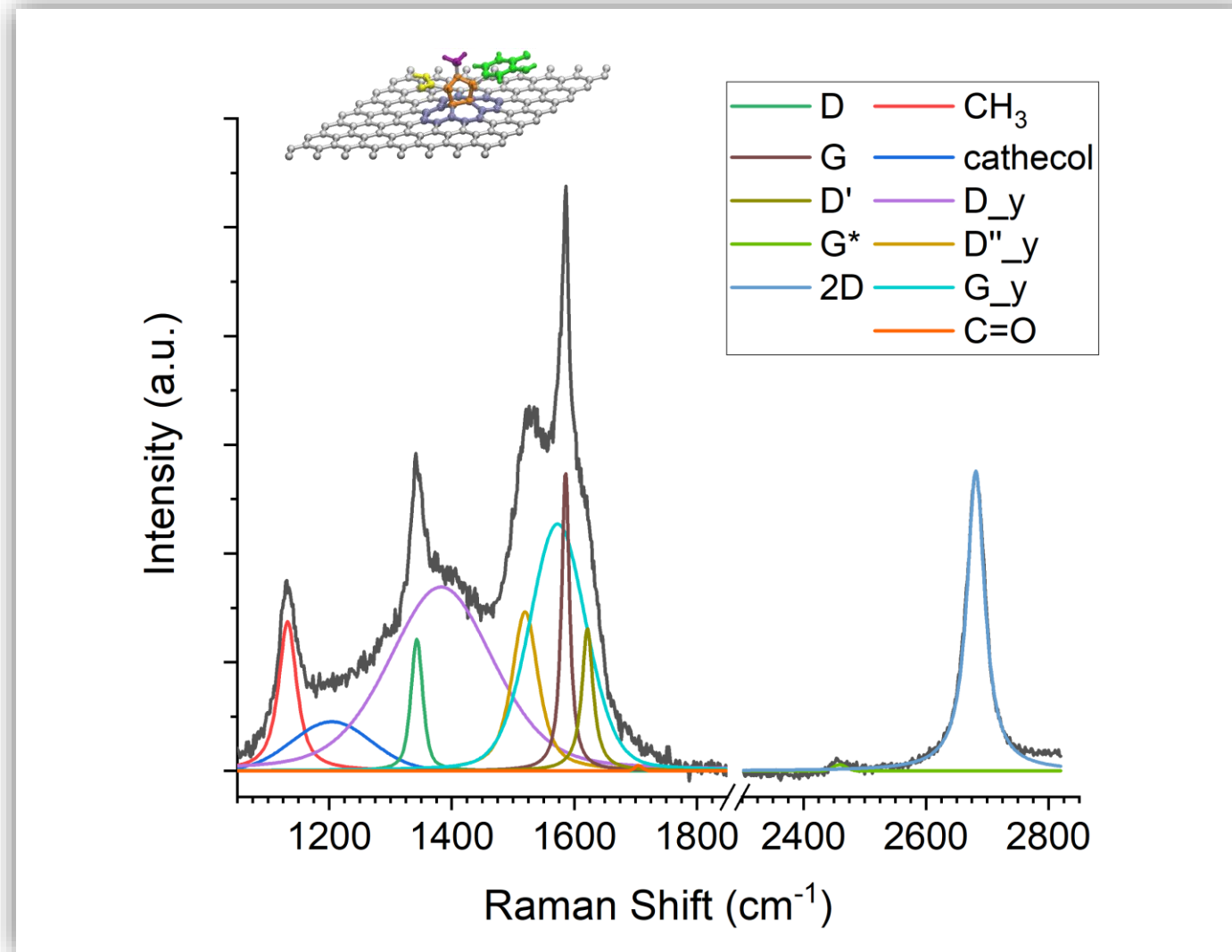
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[L. Bellucci @ NEST]



# RAMAN ANALYSIS

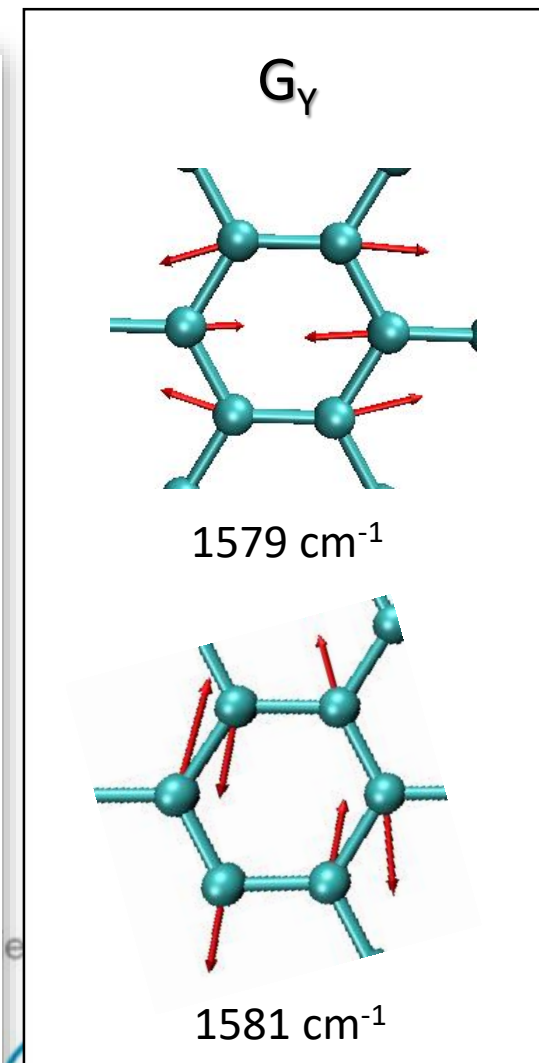
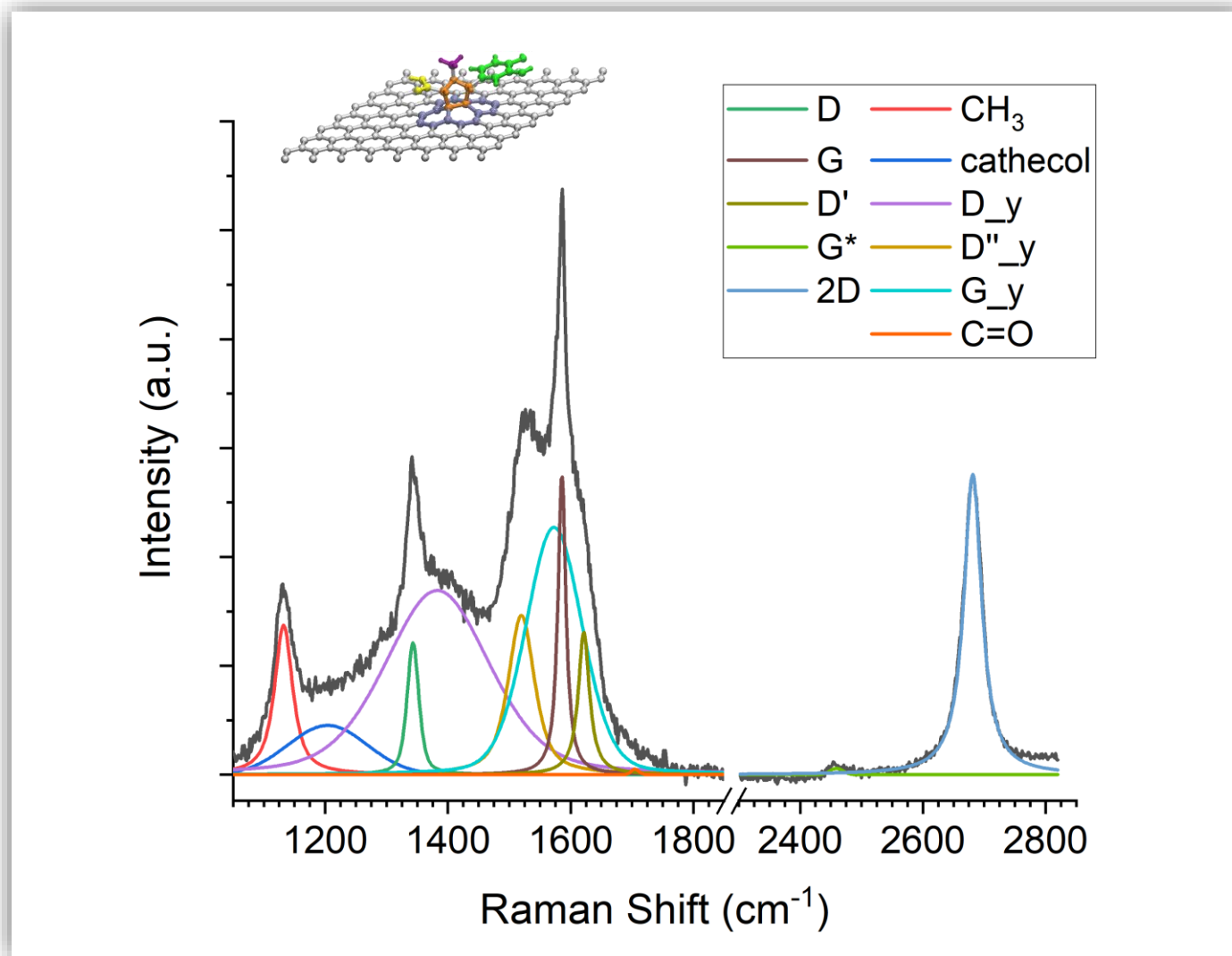


[L. Basta, in preparation]

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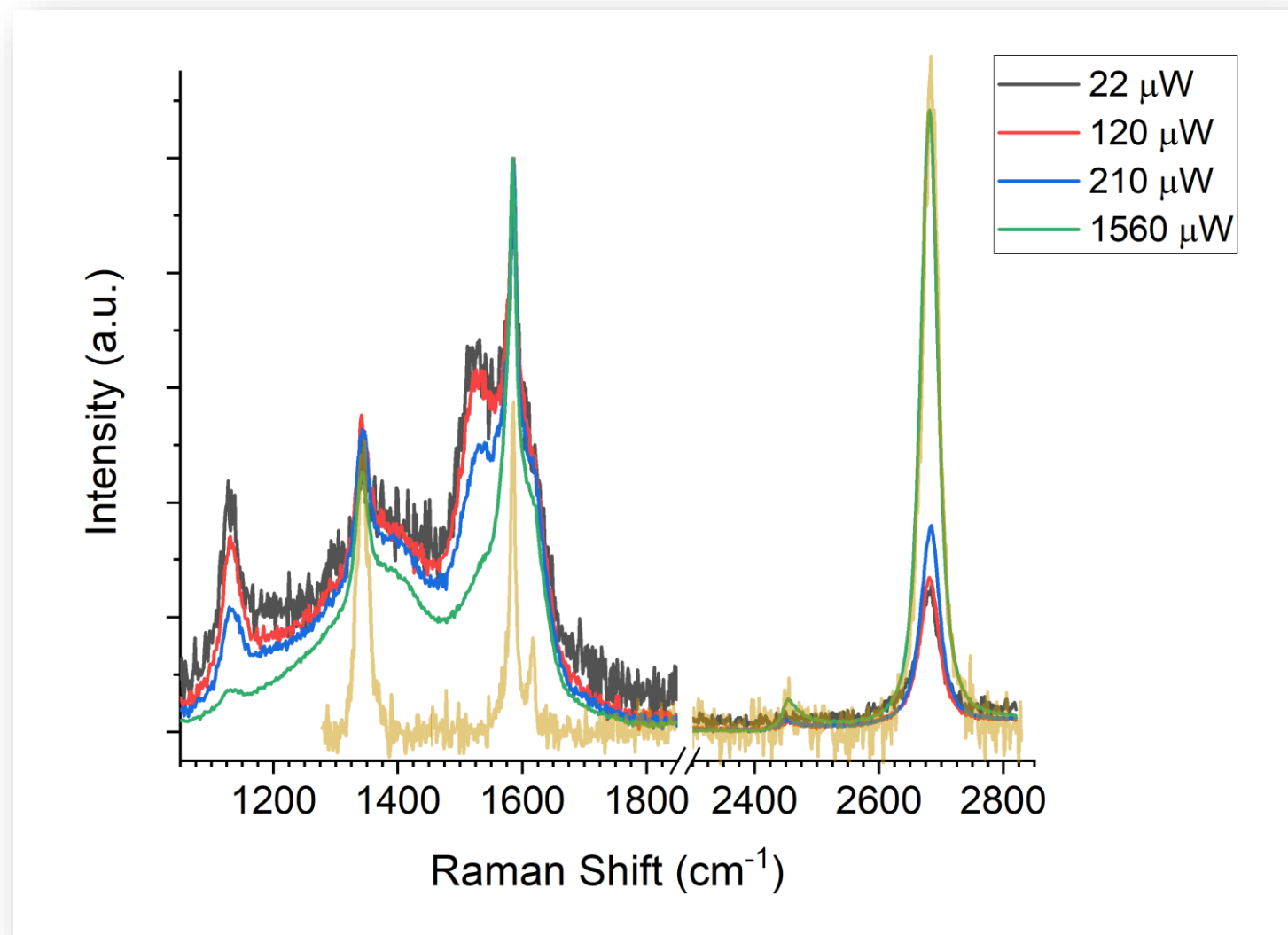


[L. Basta, in preparation]



# LASER-INDUCED DESORPTION

The recovering towards the spectrum of clean defected graphene indicates the desorption of the ylide and the reversibility of the functionalization



# CONCLUSIONS

- Controlled and spatial resolved defects engineering via EBL (~ 100 nm)

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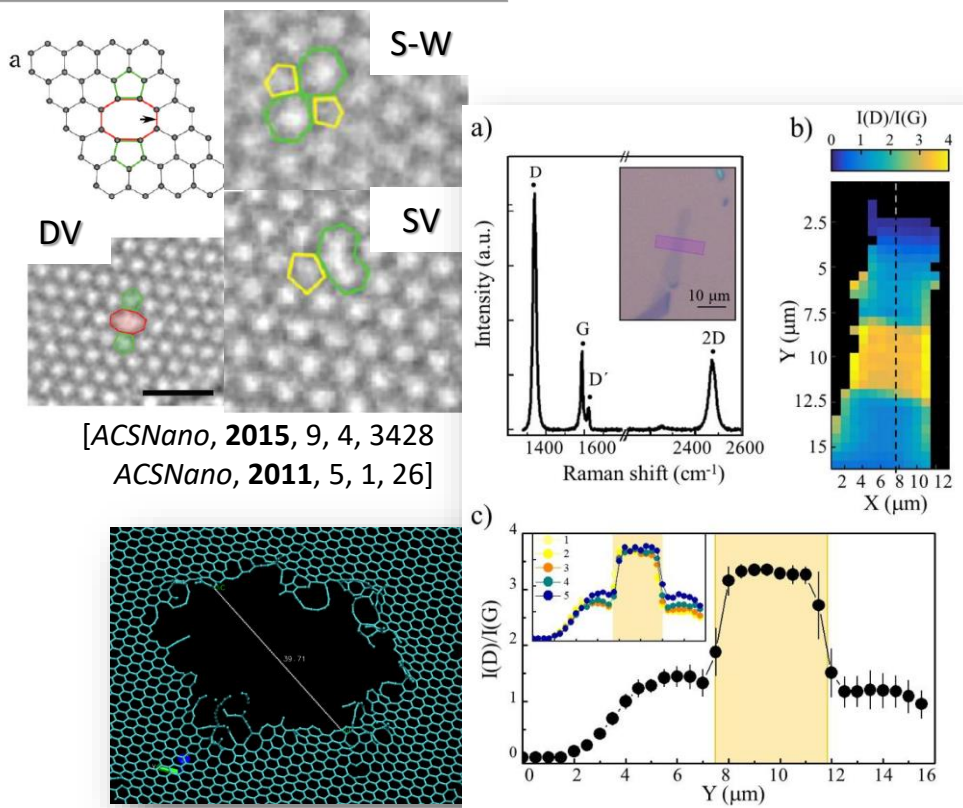
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- DFT simulation of the PS in agreement with the Raman spectra
- Recovery of the Raman spectra of clean defected graphene indicates reversibility of the functionalization

# OUTLOOKS

## Investigation on defects

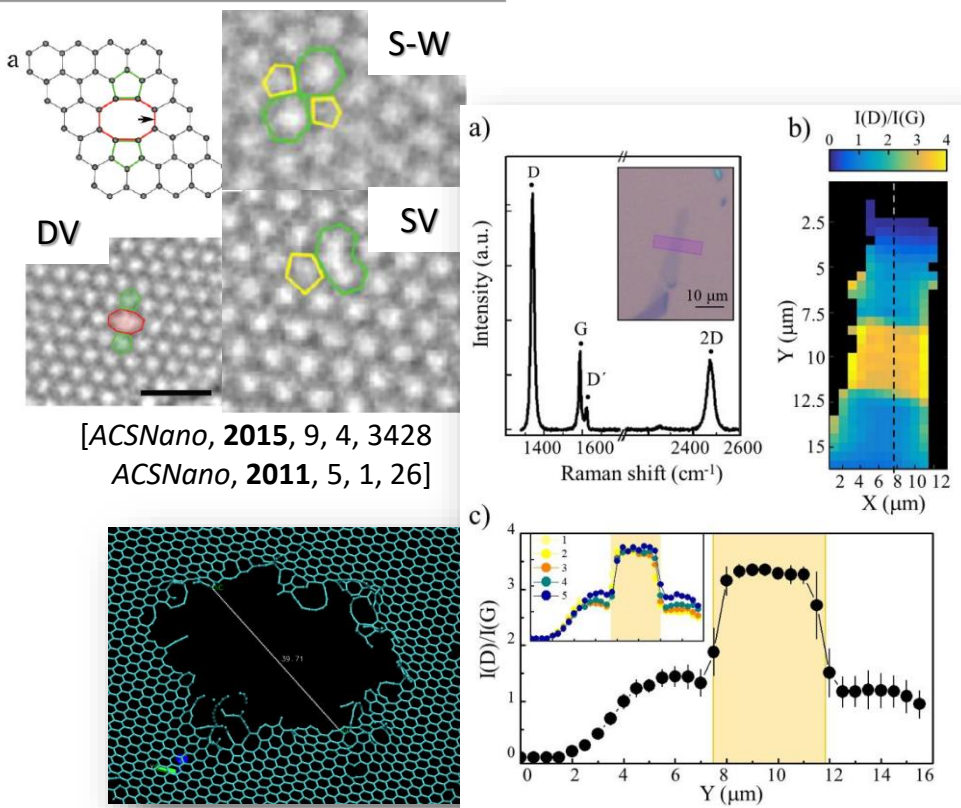


[*L. Basta, arXiv, 2021*;  
*L. Bellucci, F. Bianco @ NEST*]

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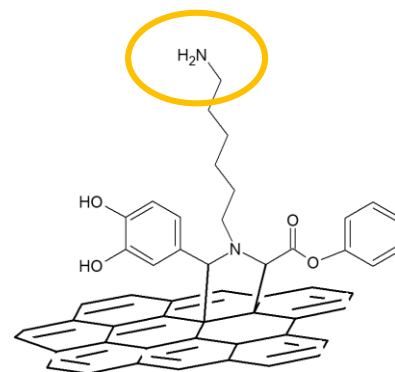
## Investigation on defects



[*ACS Nano*, **2015**, 9, 4, 3428  
*ACS Nano*, **2011**, 5, 1, 26]

[*L. Basta, arXiv, 2021*;  
*L. Bellucci, F. Bianco @ NEST*]

## Synthesis of a new ylide



[*A. Moscardini @ NEST*]

Patterned functionalization  
with:

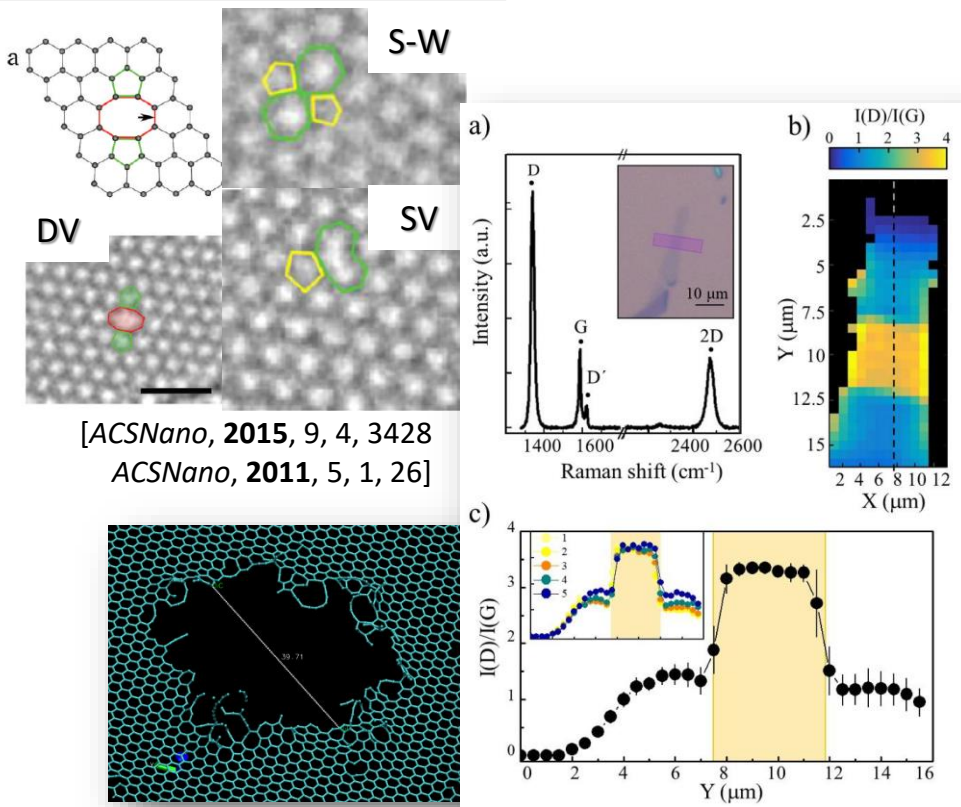
- Fluorophores
- Gold NP (with linker)

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# OUTLOOKS

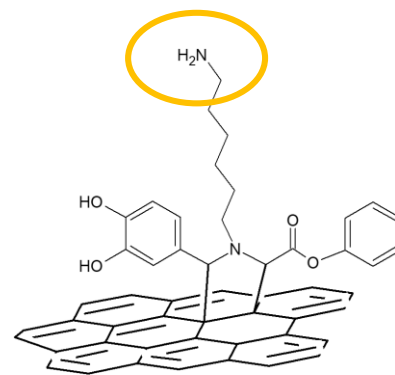
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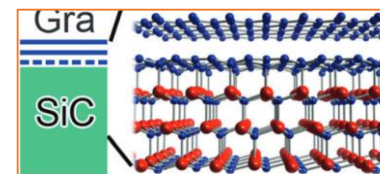


[*A. Moscardini @ NEST*]

Patterned functionalization  
with:

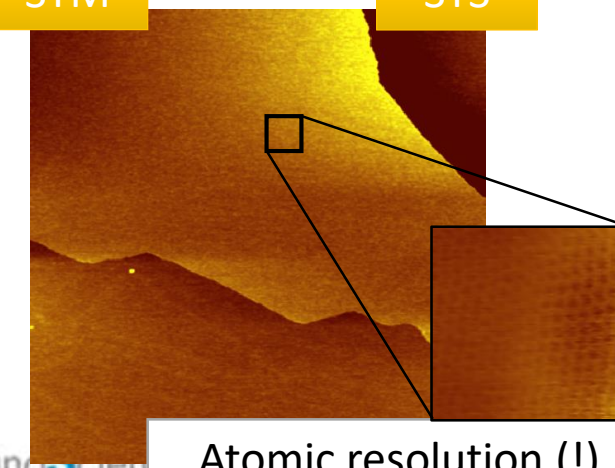
- Fluorophores
- Gold NP (with linker)

## Epitaxial ML Graphene



STM

STS



Atomic resolution (!)



# PEOPLE



Aldo Moscardini



Filippo Fabbri



Stefano Veronesi

Stefan Heun



Federica Bianco



Luca Bellucci



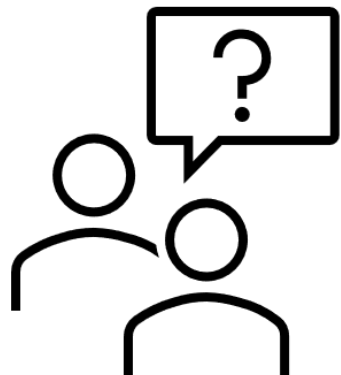
Valentina Tozzini

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*THANK YOU*

*FOR YOUR ATTENTION*



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