Defect-engineered graphene functionalization via cycloaddition reaction: towards a versatile platform for nanoscale devices and 3D heterostructures

~ Luca Basta ~

Internal Supervisor: ***Prof. Luigi Rolandi***

Supervisors: ***Dr. Stefano Veronesi*** *&* ***Dr. Stefan Heun***

SCUOLA NORMALE SUPERIORE

PERFEZIONAMENTO IN NANOSCIENZE

National Enterprise for nanoScience and nanoTechnology

NEST

Outline

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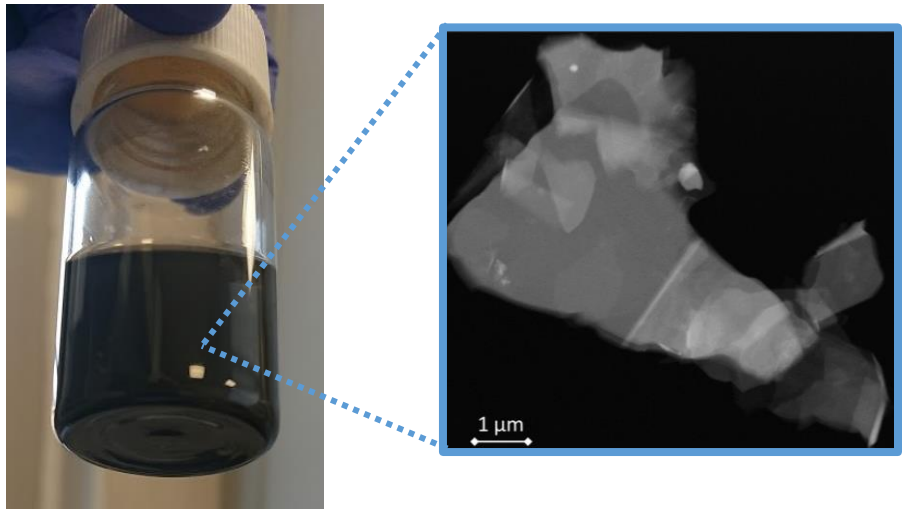
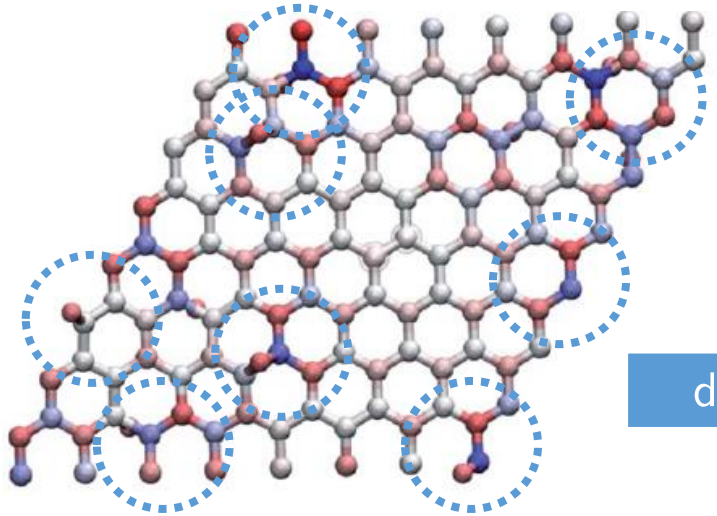
1) Functionalization of dispersed GNS and rGO → ***defects*** for chemical reactivity





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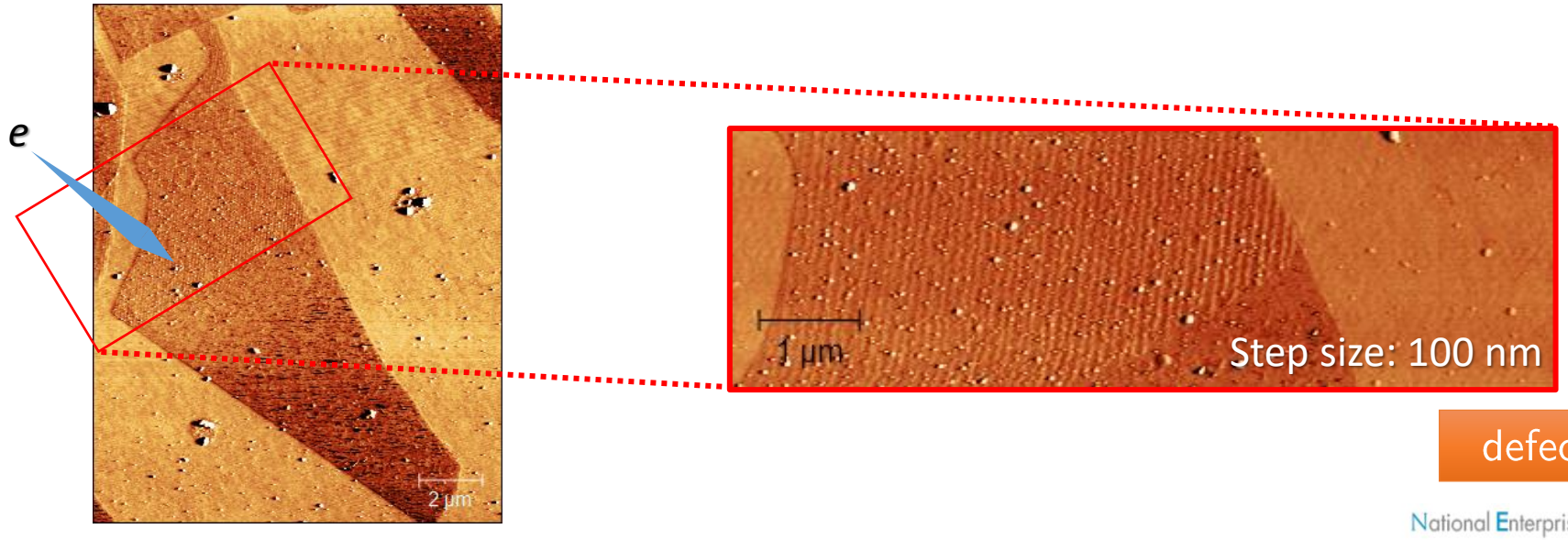

defect pattern

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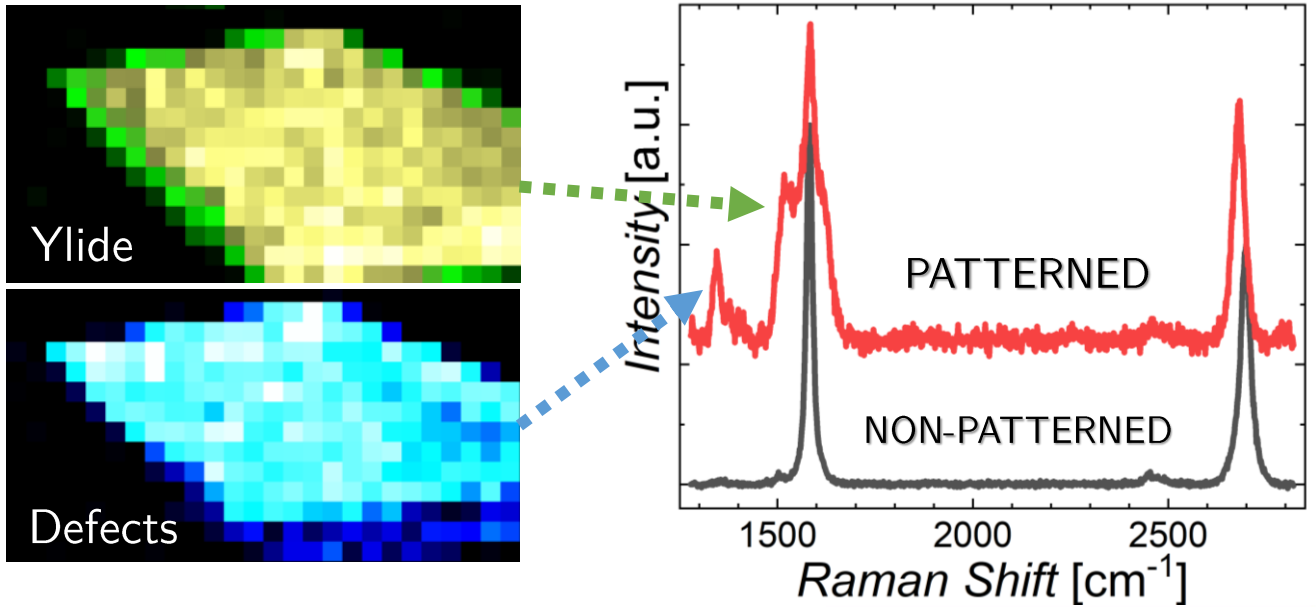

designed selectivity

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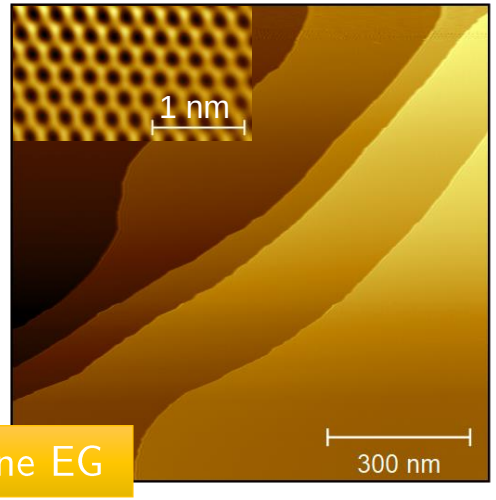
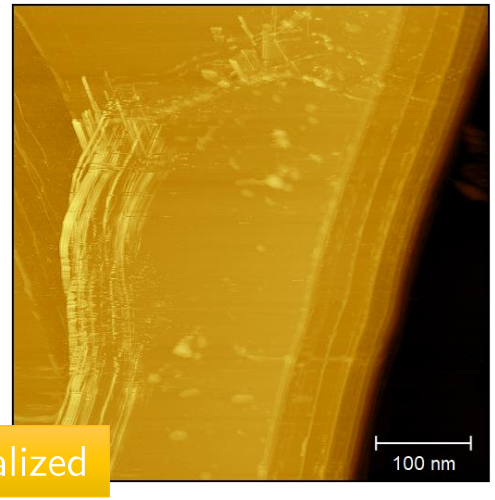


pristine EG



functionalized

Research Focus

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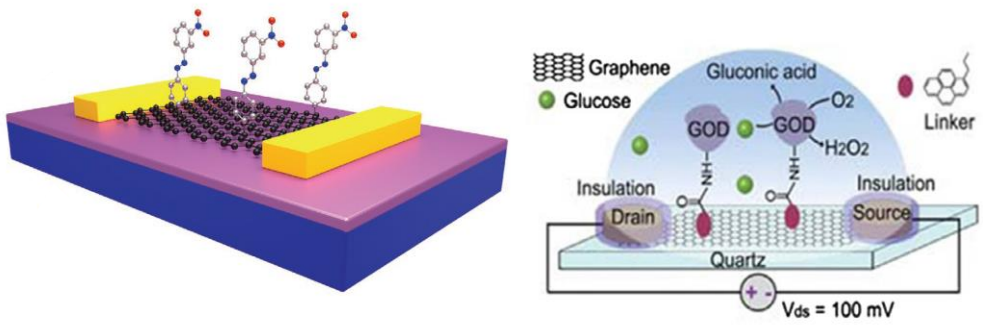

[*Adv. Electron. Mater.*, ***2018***, *4, 1800021*]

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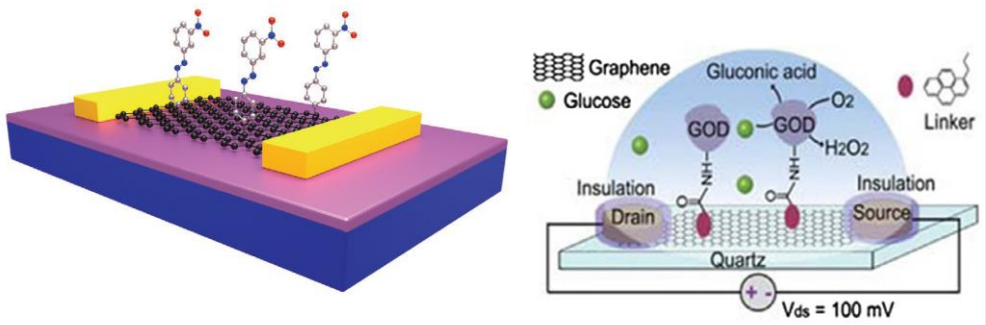

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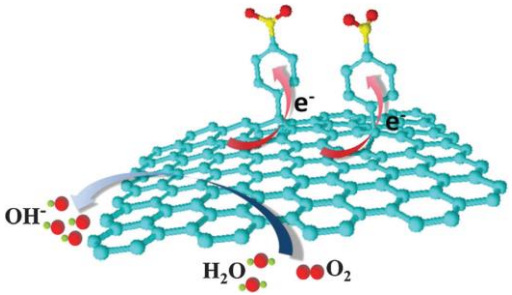

[*Chem. Commun.*, ***2014***, *50, 10672*]

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- realization of *new sensors* exploiting organic molecules as active sites onto graphene surface (selective interaction with *target* molecules)
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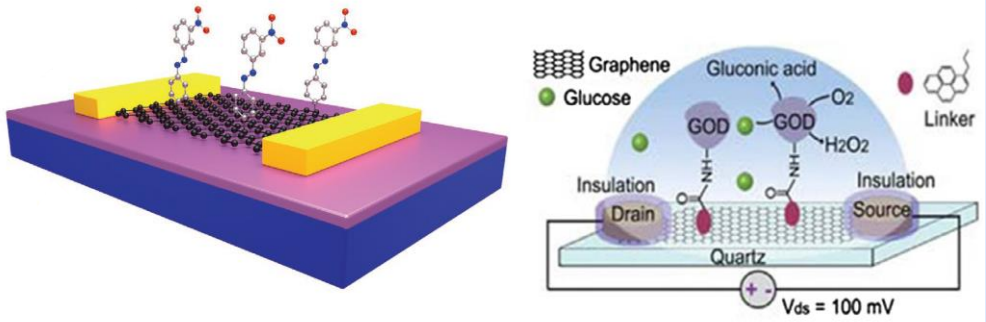
- fabrication of *graphene/molecule/graphene* heterostructures towards multilayer stacking and 3D graphene materials



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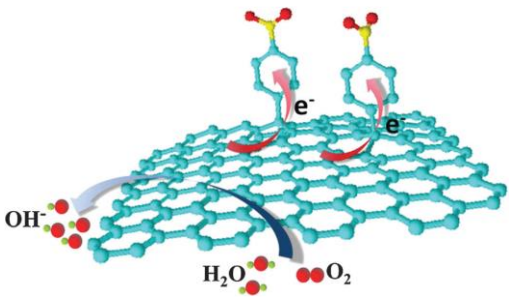

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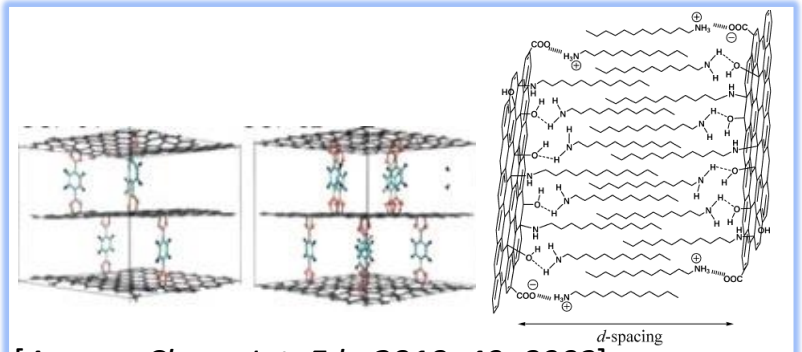
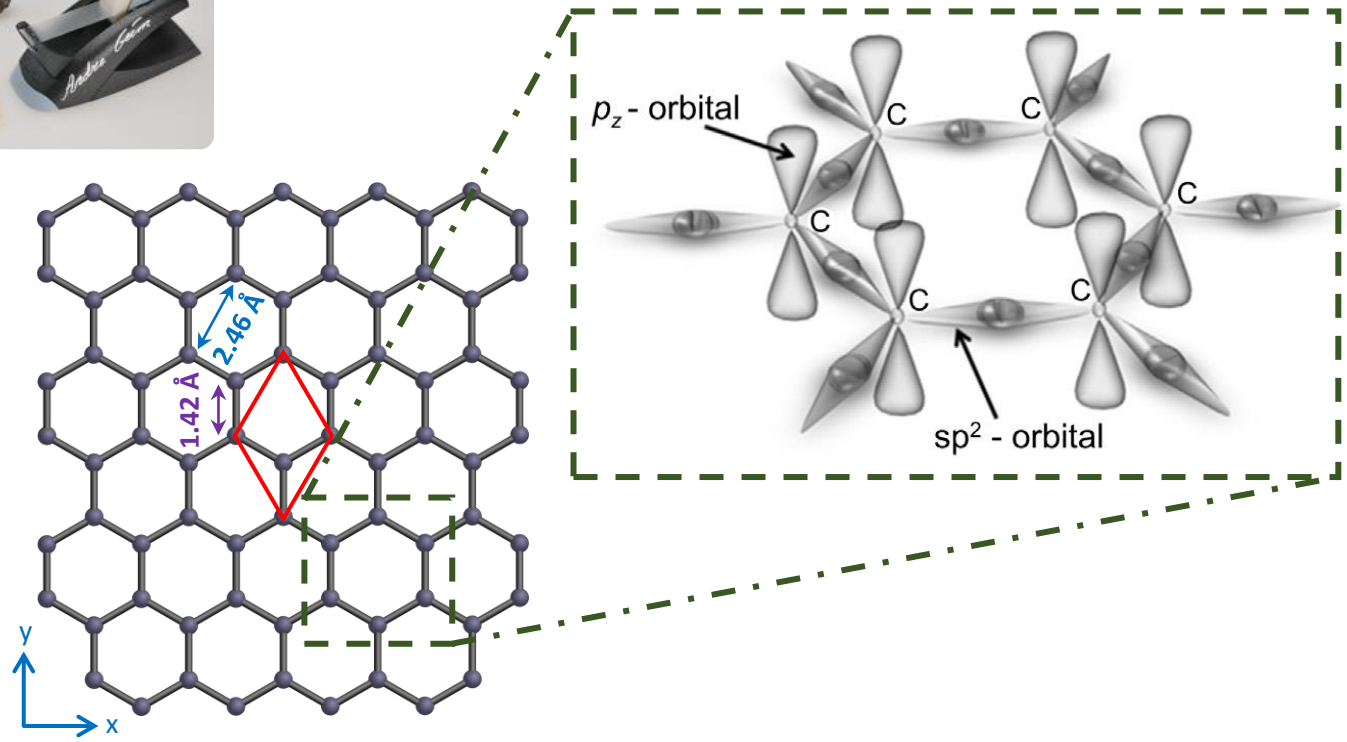


[*Angew. Chem. Int. Ed.*, ***2010***, *49*, *8902*]

Graphene



[*Nanotube Superfiber Mater.*, **2014**, 519]

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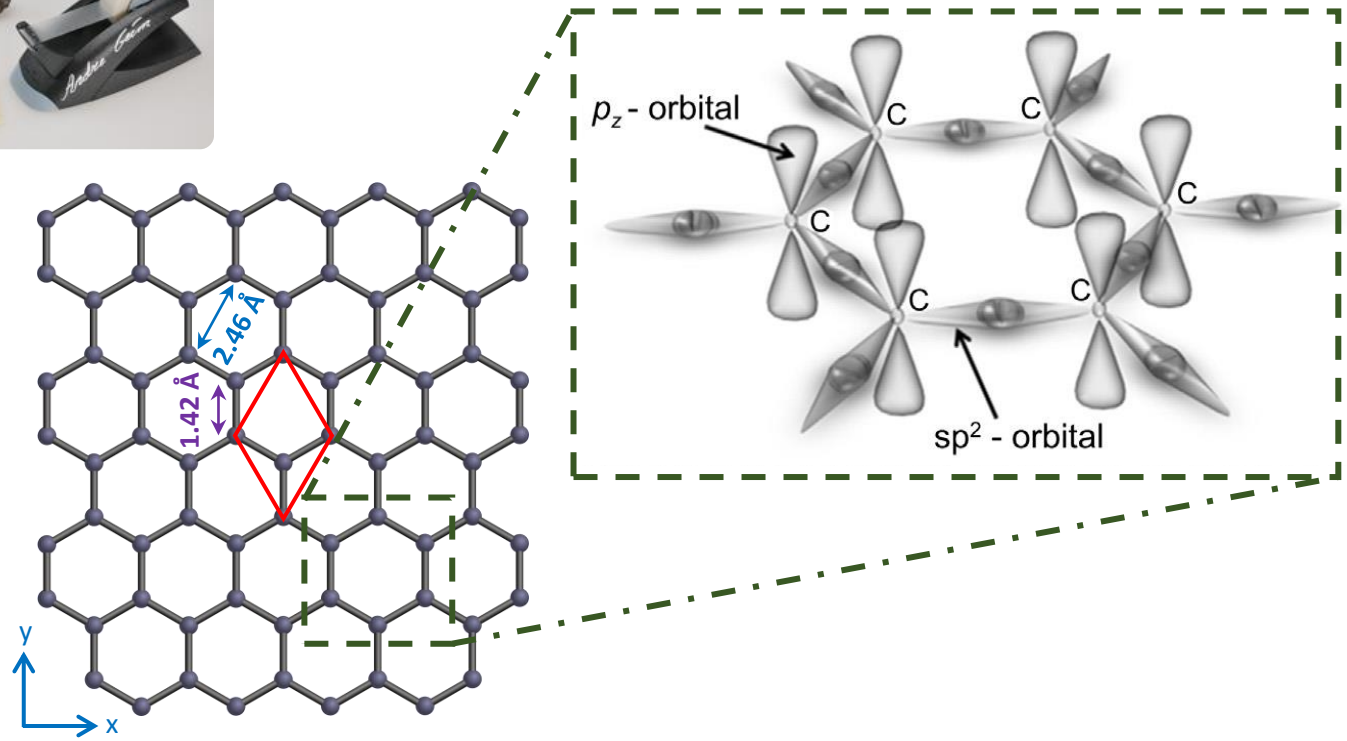

- thermal conductivity
- Seebeck coefficient
- tensile strength
- flexibility
- carrier (ambipolar) mobility
- low noise
- wide-band optical response
- visual transparency

[*Nanotube Superfiber Mater.*, **2014**, 519]

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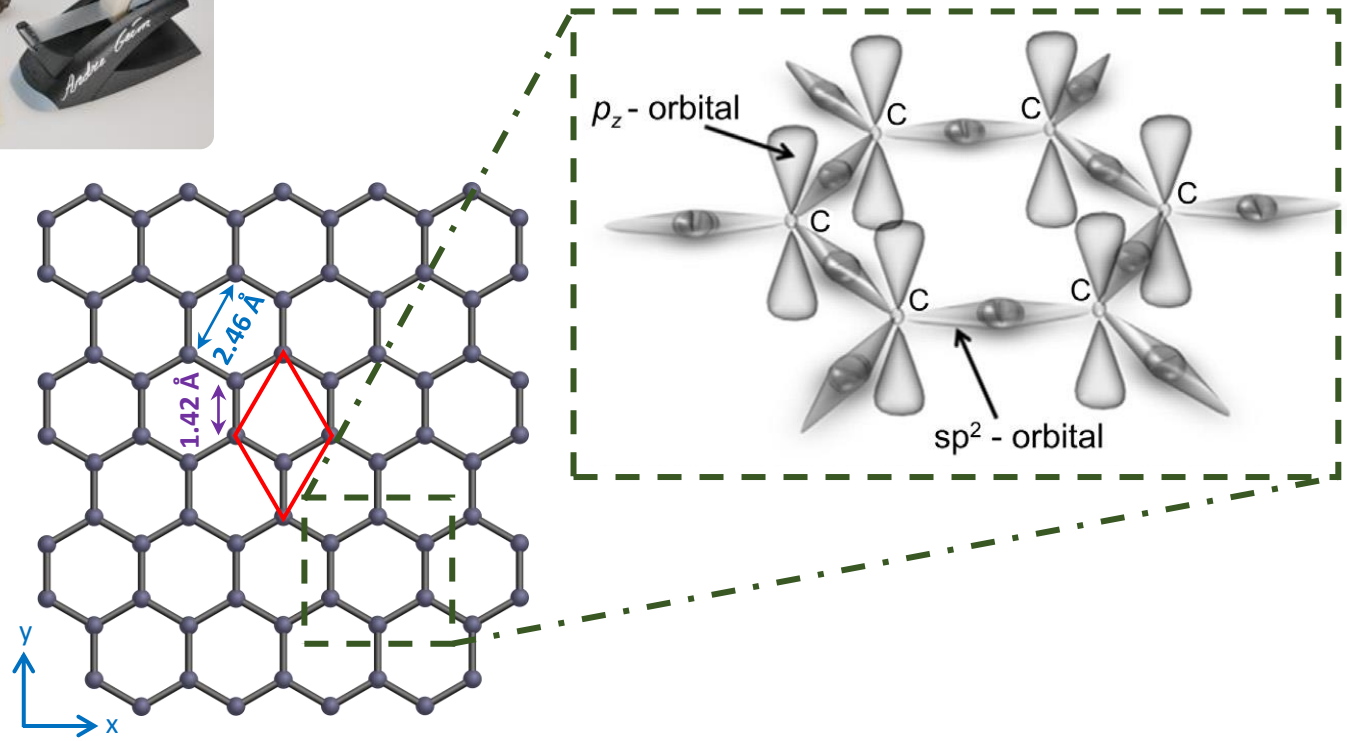

- ❖ thermal conductivity
- ❖ Seebeck coefficient
- ❖ tensile strength
- ❖ flexibility
- ❖ carrier (ambipolar) mobility
- ❖ low noise
- ❖ wide-band optical response
- ❖ visual transparency
- × low chemical reactivity
- × no bandgap

[*Nanotube Superfiber Mater.*, **2014**, 519]

Functionalization

The functionalization of graphene allows to finely ***tune*** or ***enhance*** the system's physical and chemical properties, resulting in a valuable synergistic combination:

- bandgap opening
- transfer doping
- improved dispersibility
- new functionalities

Functionalization

Non-covalent functionalization, via van der Waals, electrostatic, or $\pi - \pi$ interactions:

- ❖ minimal perturbation
- × limited stability and ordering

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[*G. Signore* @ NEST]

1,3 – Dipolar Cycloaddition

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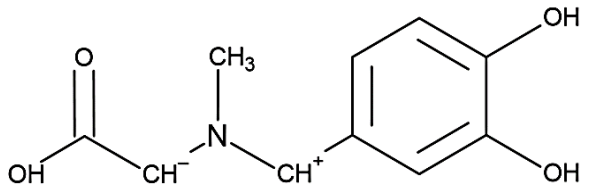
Charge displacement between a dipolar compound (***azomethine ylide***)

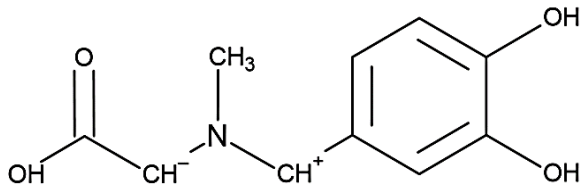
azomethine ylide



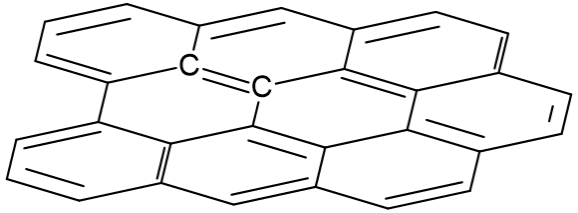
1,3 – Dipolar Cycloaddition

Charge displacement between a dipolar compound (***azomethine ylide***) and a dipolarophile (***C*** = ***C*** of graphene)

azomethine ylide



graphene

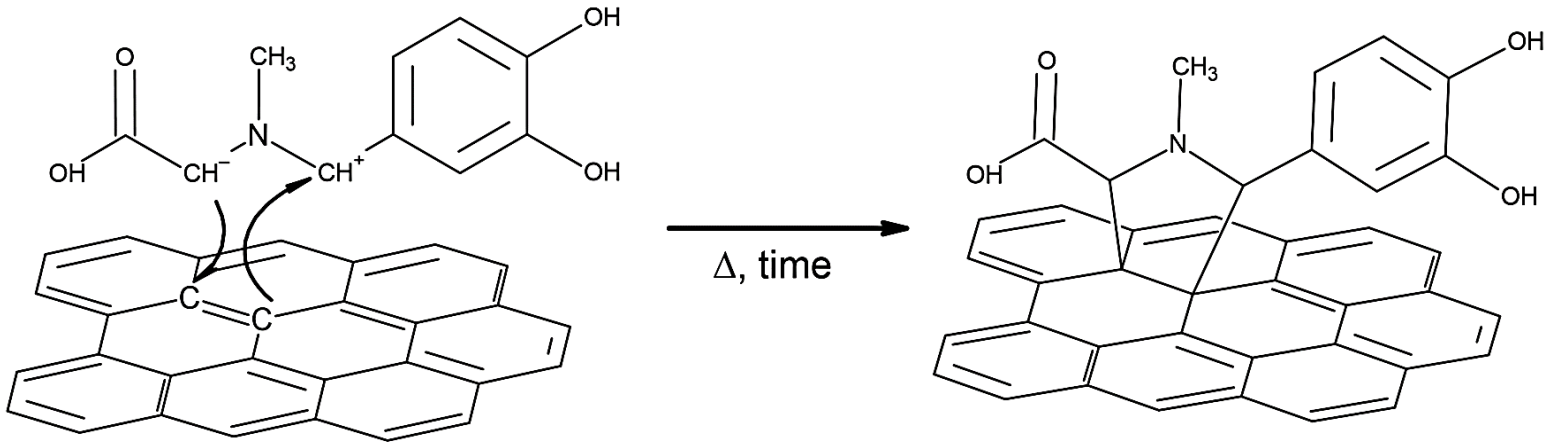


1,3 – Dipolar Cycloaddition

Charge displacement between a dipolar compound (***azomethine ylide***) and a dipolarophile (***C*** = ***C*** of graphene) → closing of a C-atoms ring:

azomethine ylide

graphene



f-graphene

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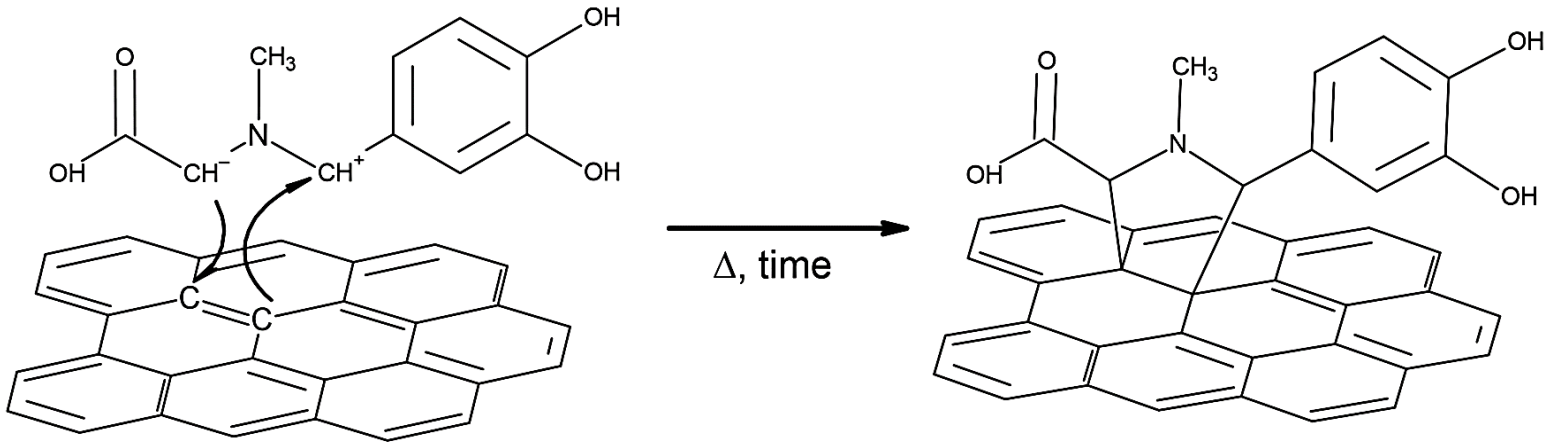

f-graphene

- selectivity
- versatility
- control
- reversibility

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Experimental Results

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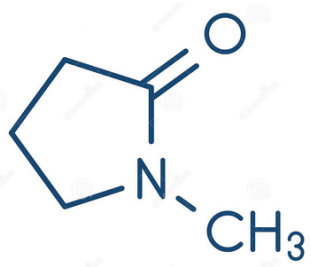
Graphene Nanosheets dispersion - DLS

From Dynamic Light Scattering experiments:

- NMP vs DMF
- sonication vs homogenization



N-methyl-2-pyrrolidone

Dimethylformamide

Graphene Nanosheets dispersion - DLS

From Dynamic Light Scattering experiments:

- ***NMP*** vs DMF BETTER!
- sonication vs ***homogenization*** FASTER!

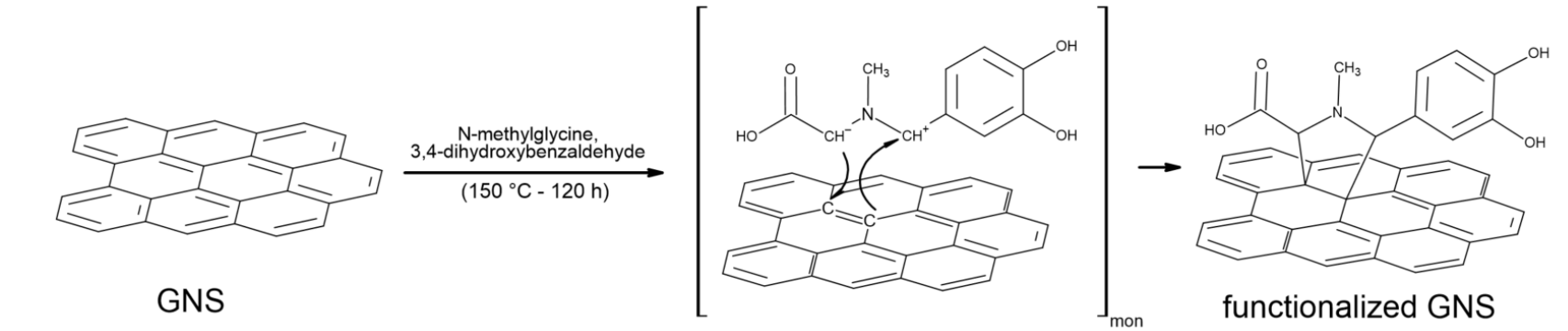
[*A. Moscardini* @ NEST]

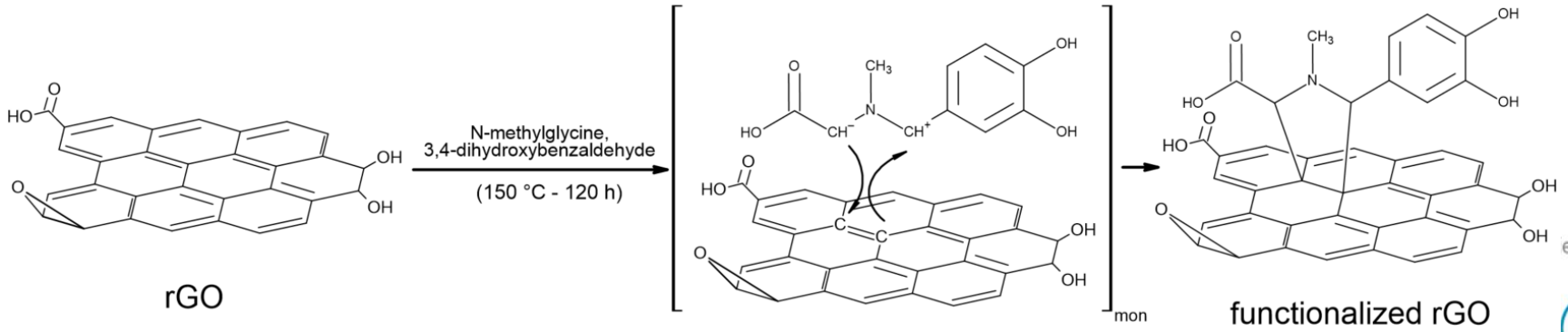
1,3-DC of GNS and rGO

GNS in NMP/DMF, rGO in DFM: 0.2 mg/mL

150 °C – 120 h

(stirring and N_2 flux)

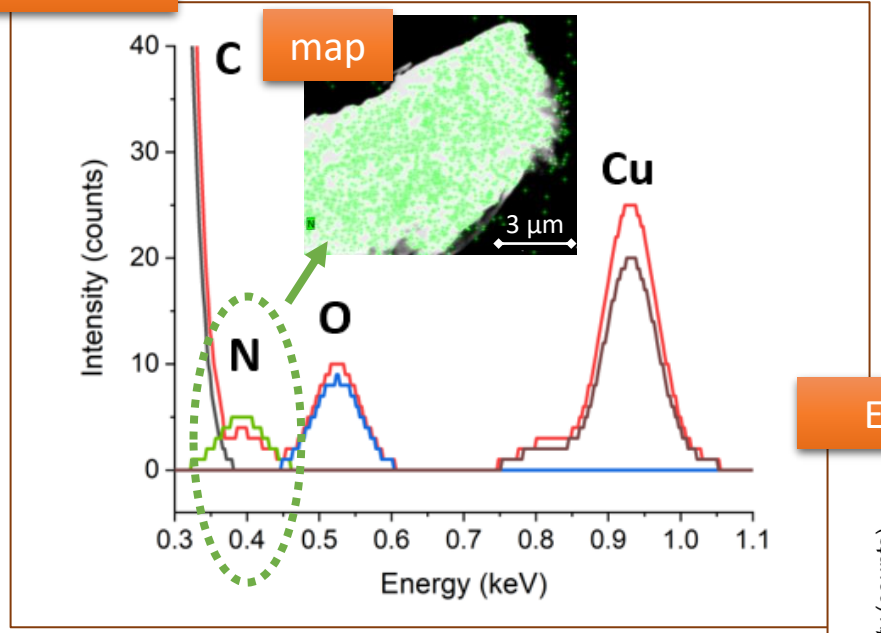




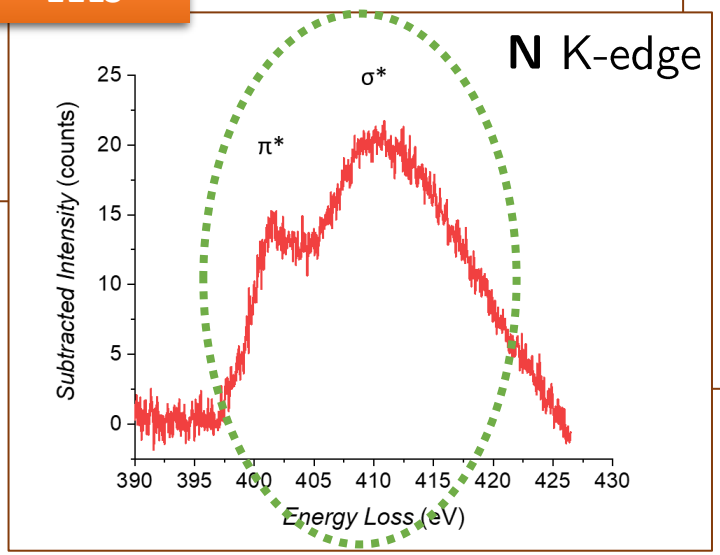
[*S. Rubini* @ IOM-CNR, Trieste]

EDX - EELS - XPS

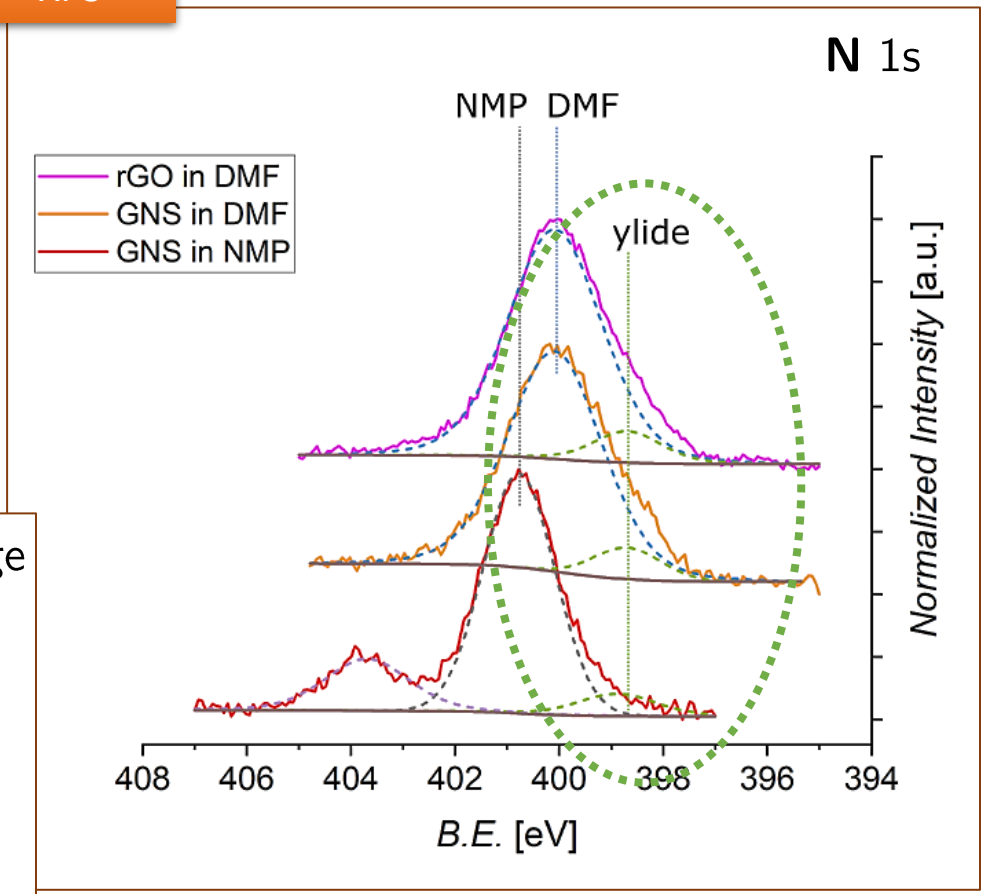
EDX



EELS



XPS

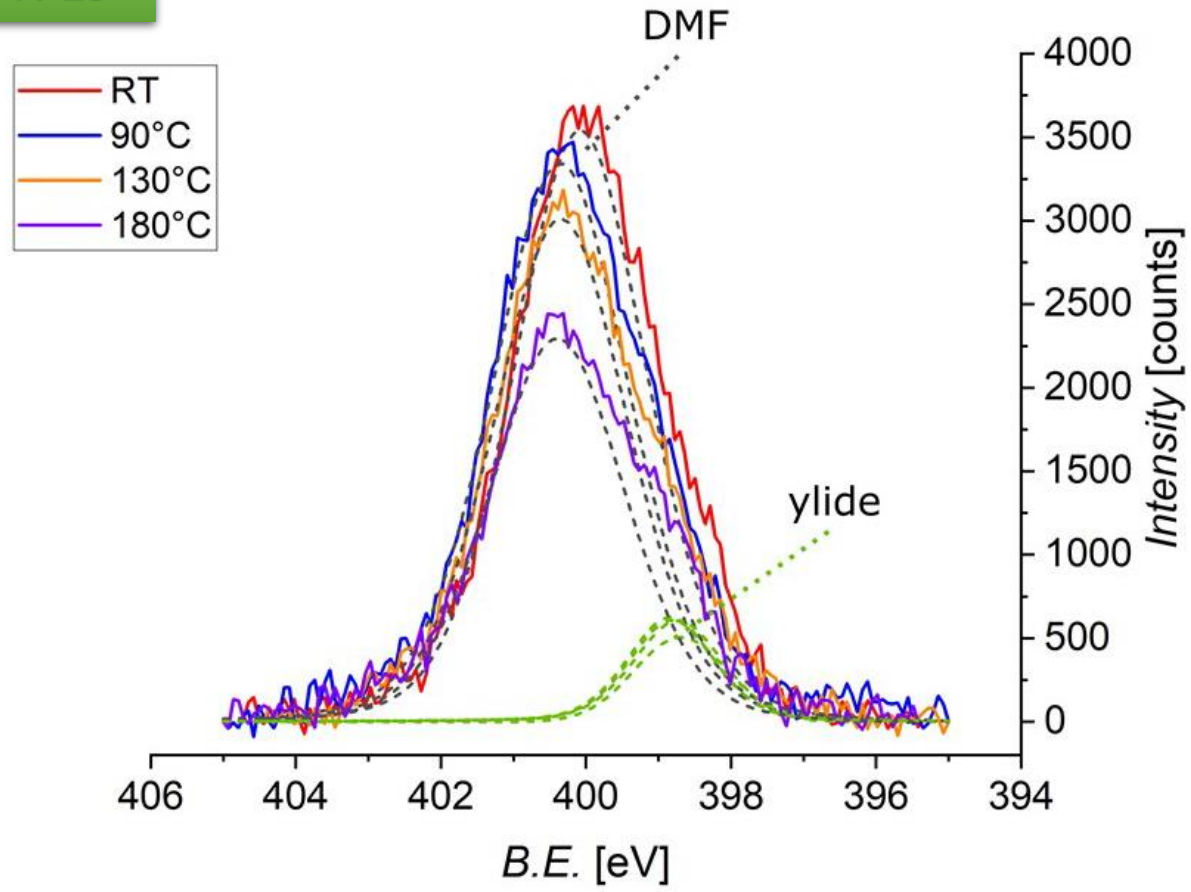


[*A. Griesi* @ NEST]

1,3-DC of azomethine ylide!

XPS

N 1s



STABILITY

XPS

The estimated efficiency of the functionalization is 1 azomethine ylide every 225 carbons in case of GNS in NMP, 1 ylide every 170 carbons for GNS in DMF, and 1 ylide every 110 carbons for rGO in DMF.

Elemental composition of f-GNS and f-rGO

	C (%)	N(ylide) (%)	N(solv) (%)	O (%)
GNS in NMP	80.2	0.34	3.7	15.7
GNS in DMF	82.1	0.45	4.6	12.8
rGO in DMF	72.6	0.60	5.4	21.4

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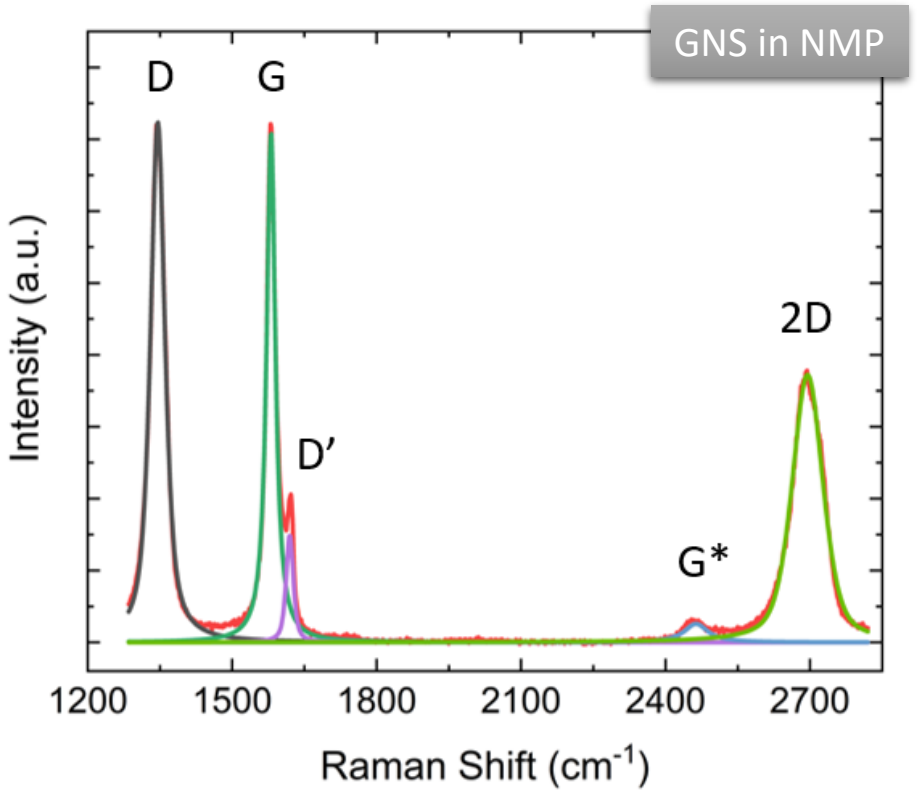
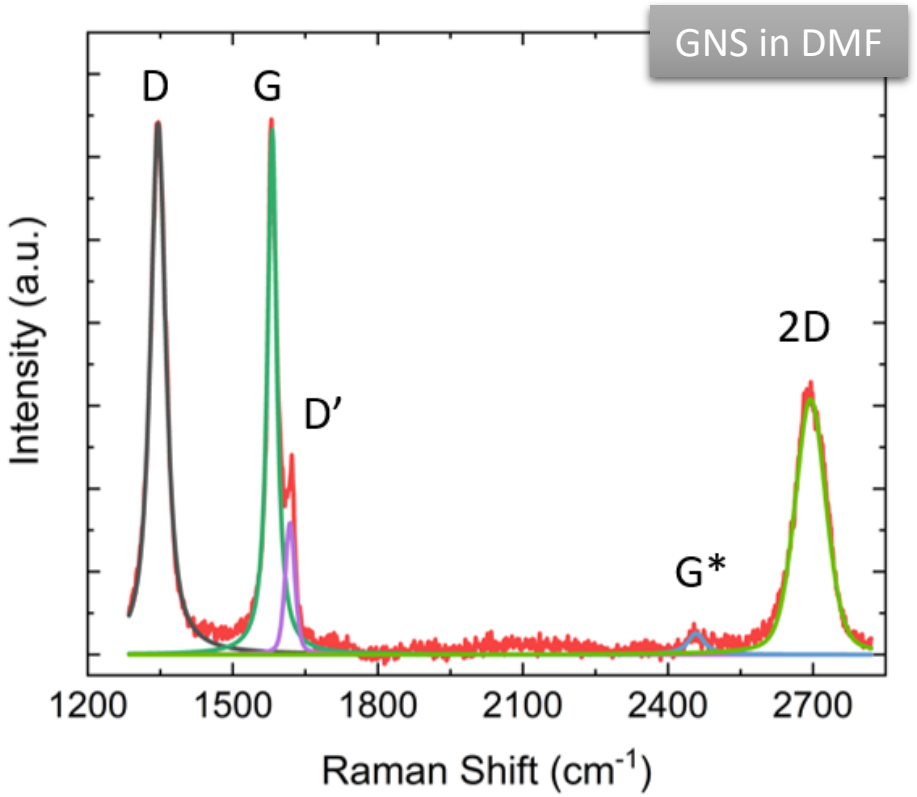
Raman analysis





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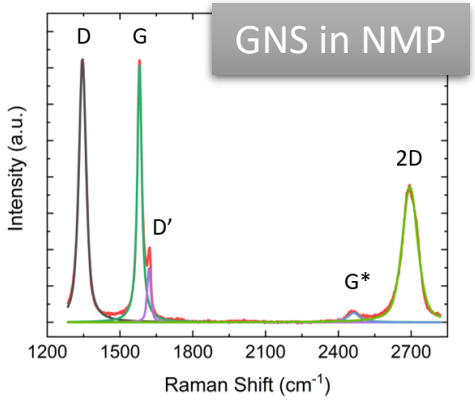
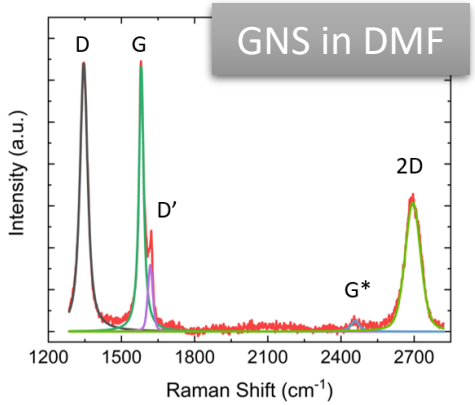
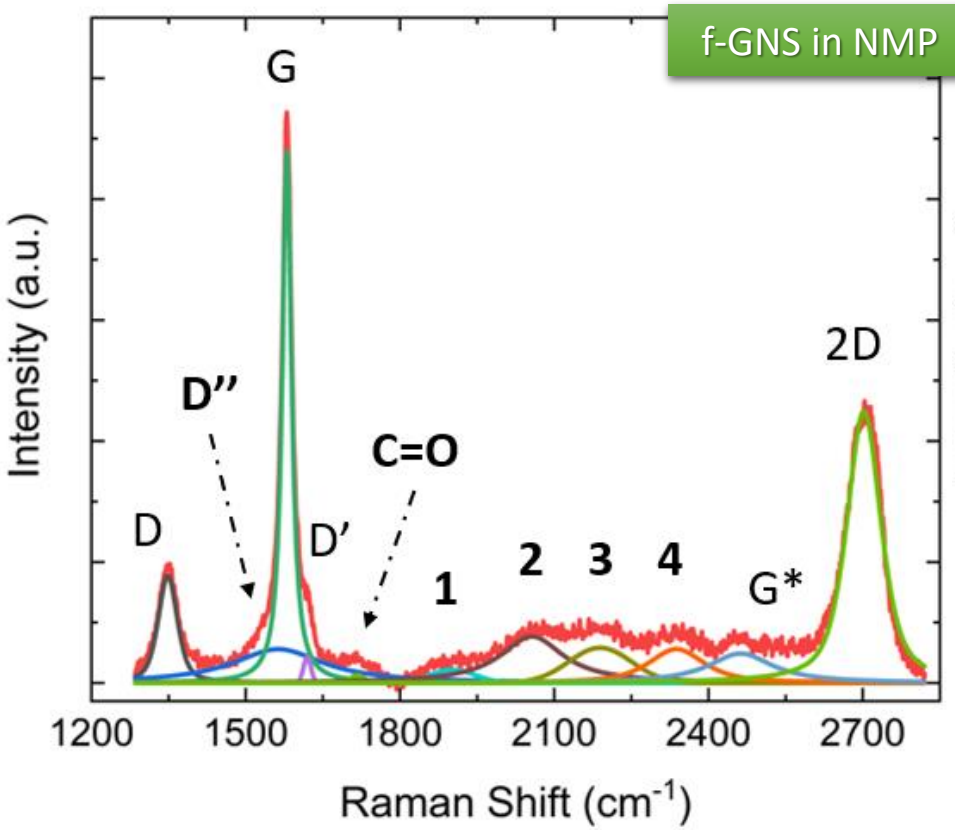


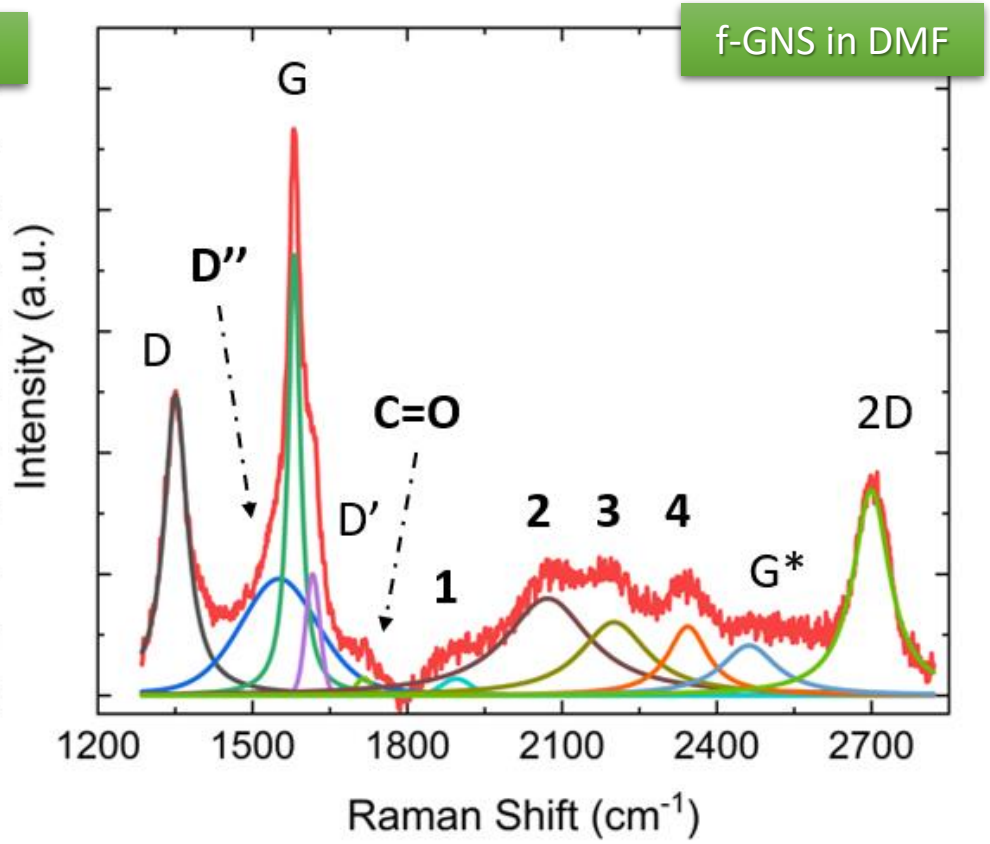
GNS in DMF



f-GNS in NMP



f-GNS in DMF



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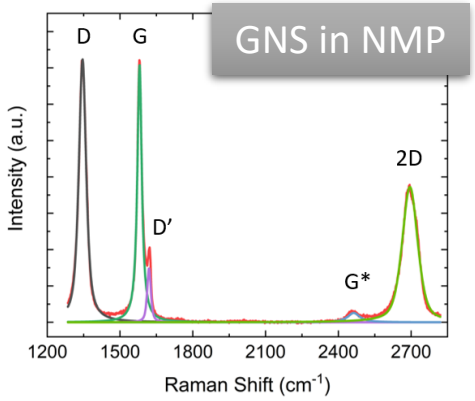

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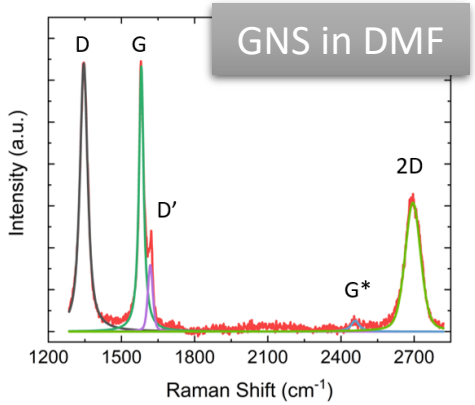
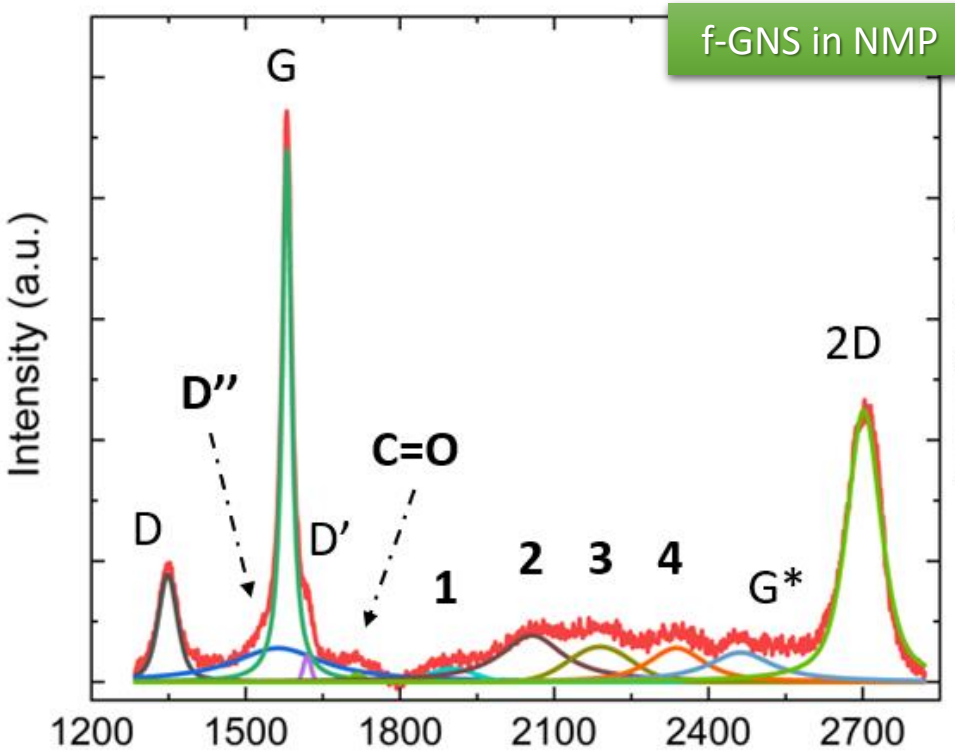
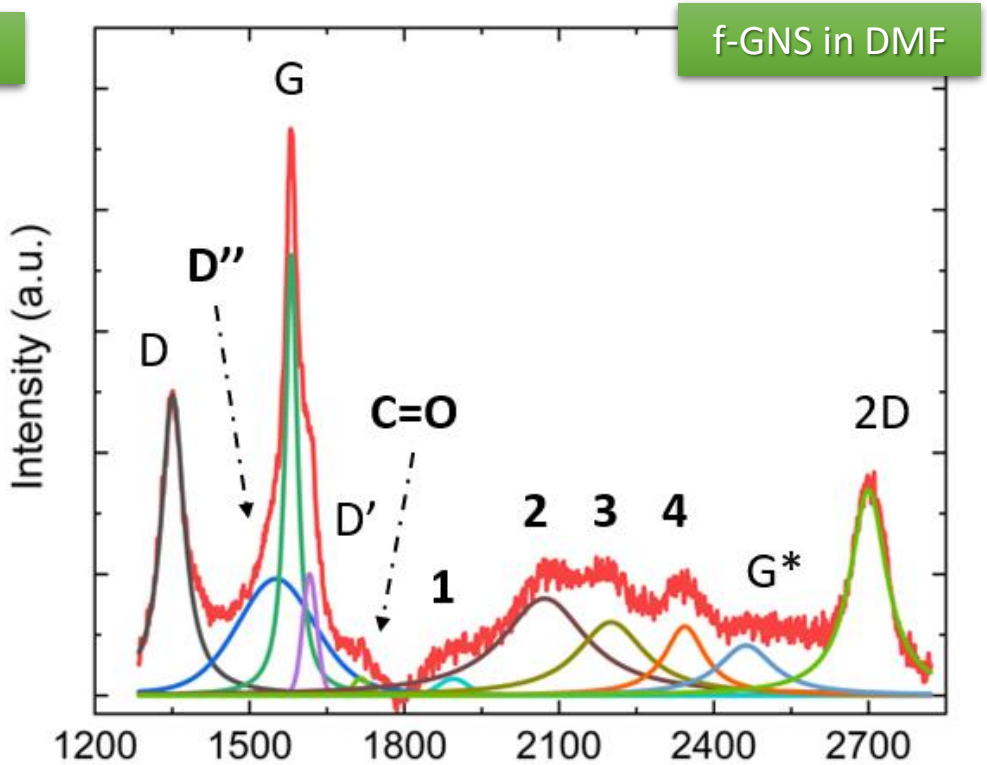


f-GNS in NMP



- I_D/I_G : 1.02 → 0.20

f-GNS in DMF



- I_D/I_G : 1.01 → 0.68

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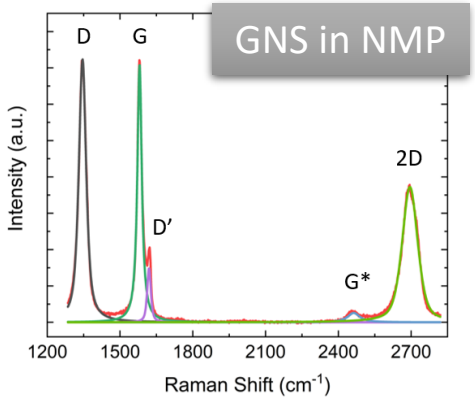
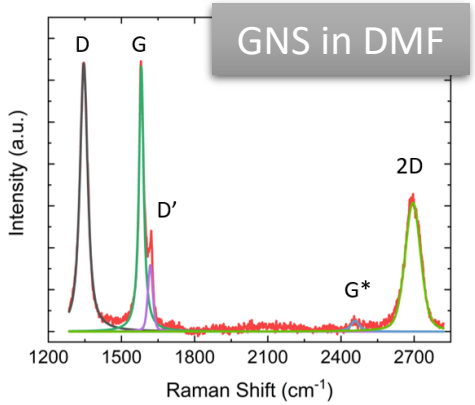
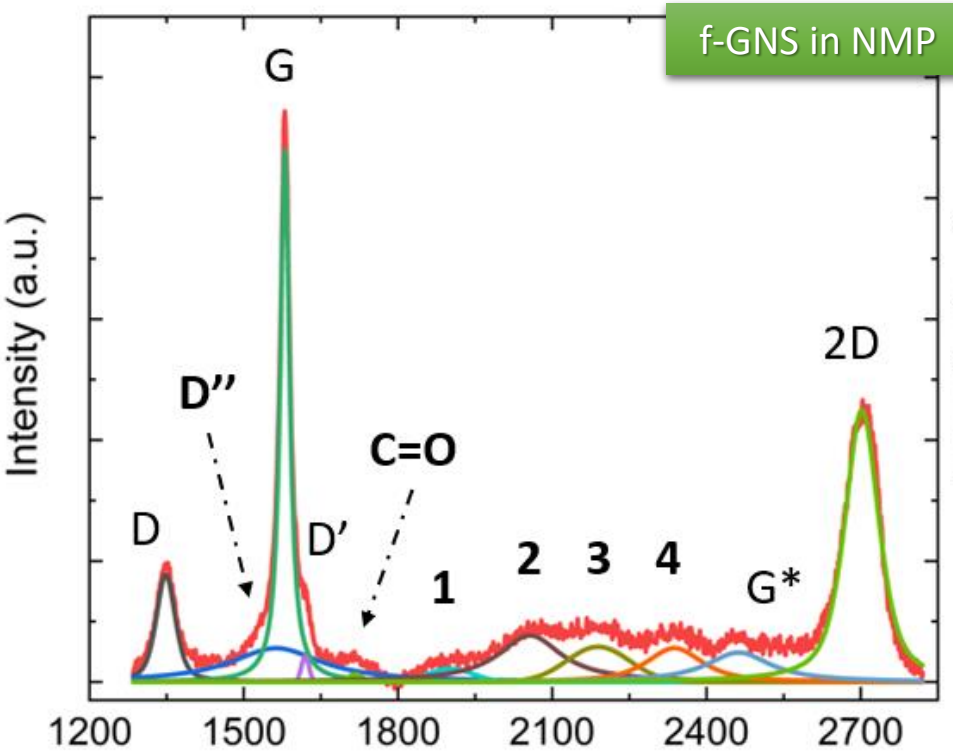


GNS in DMF

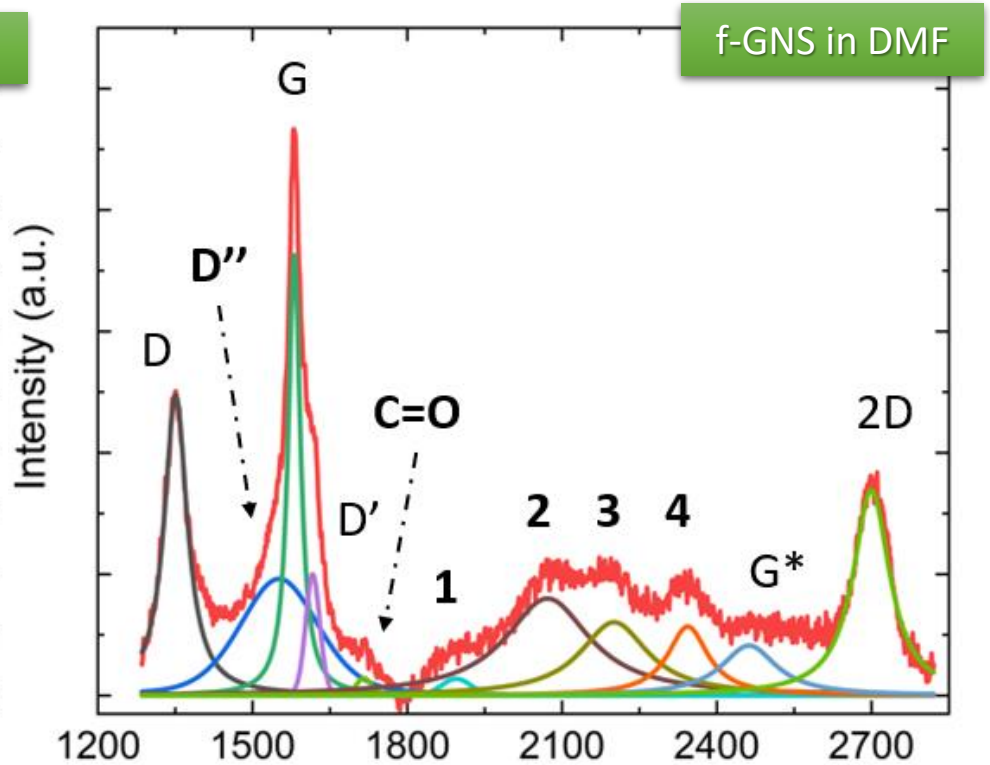


f-GNS in NMP



- I_D/I_G : 1.02 → 0.20
- I_{2D}/I_G : 0.53 → 0.51

f-GNS in DMF



- I_D/I_G : 1.01 → 0.68
- I_{2D}/I_G : 0.49 → 0.49

Raman analysis

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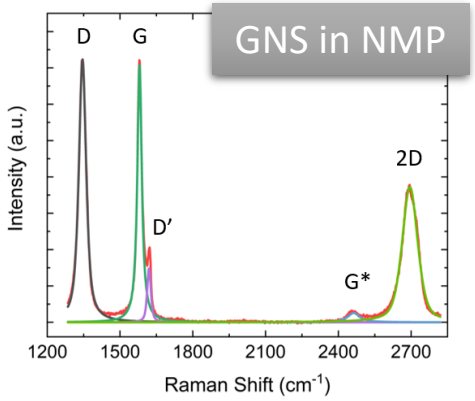

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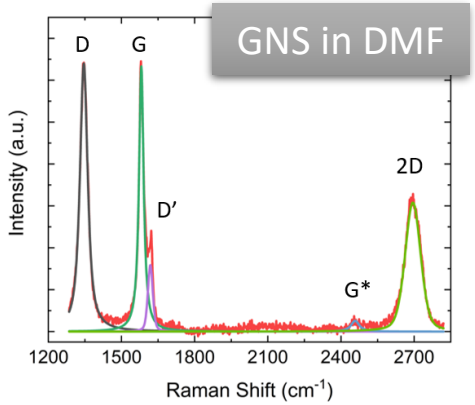
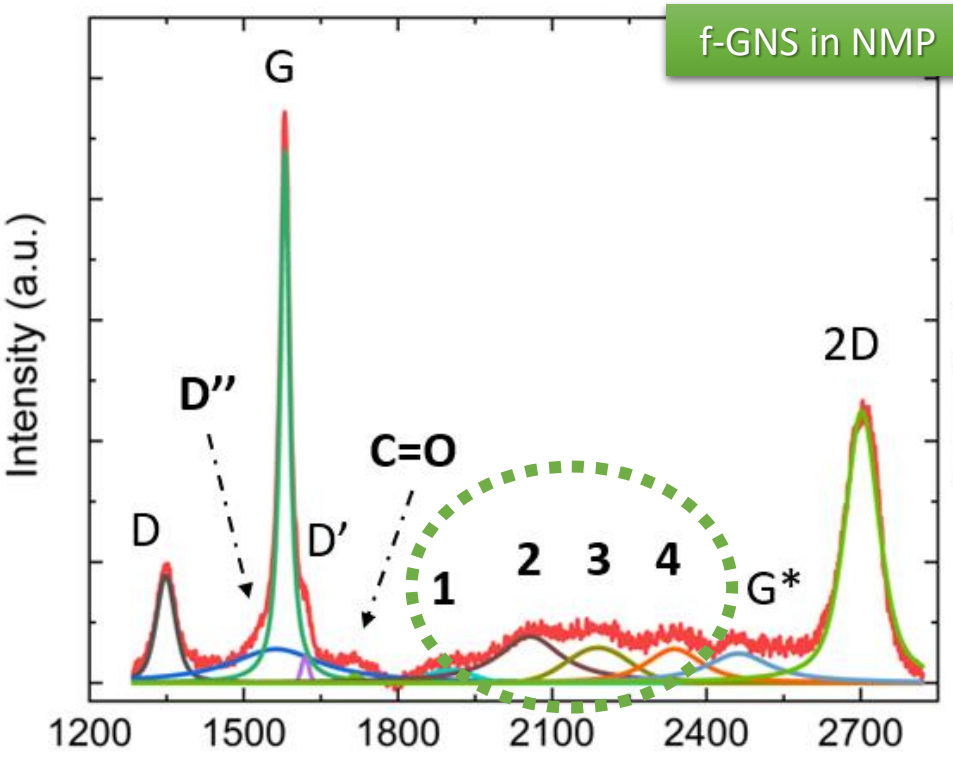
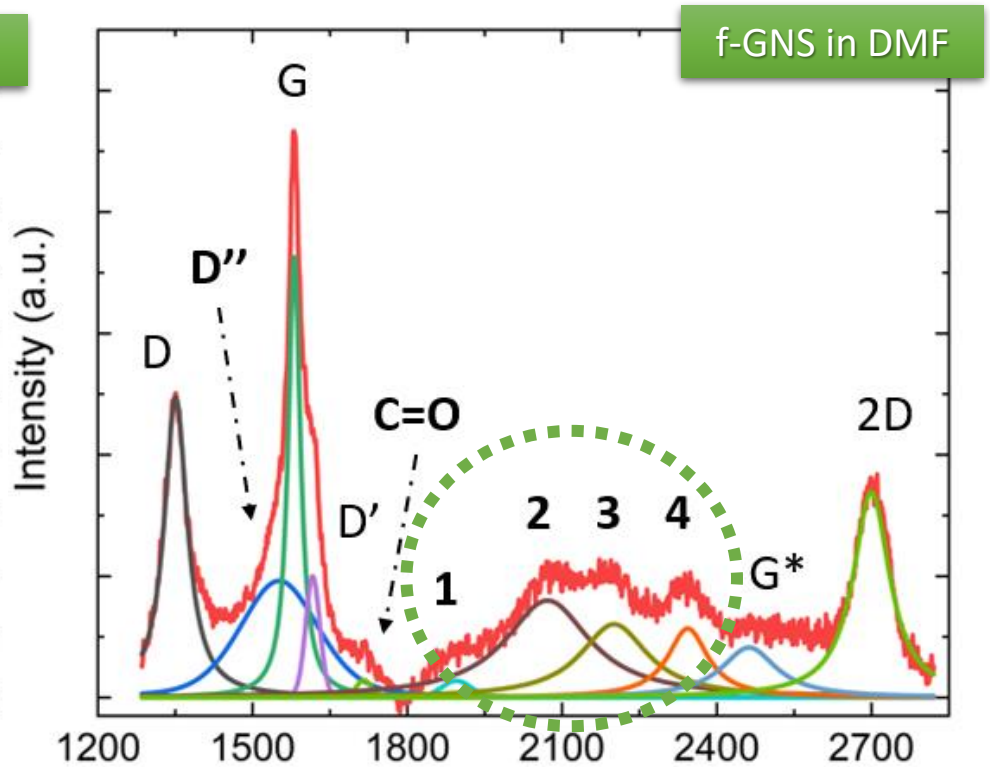


f-GNS in NMP



- I_D/I_G : 1.02 → 0.20
- I_{2D}/I_G : 0.53 → 0.51
- New peaks!

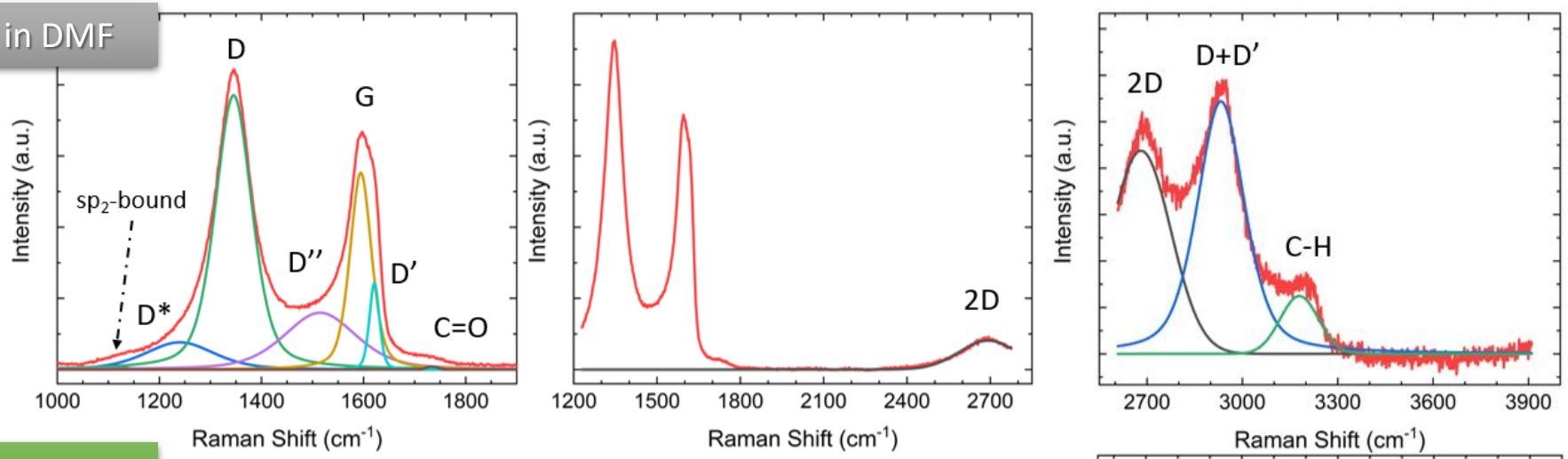
f-GNS in DMF



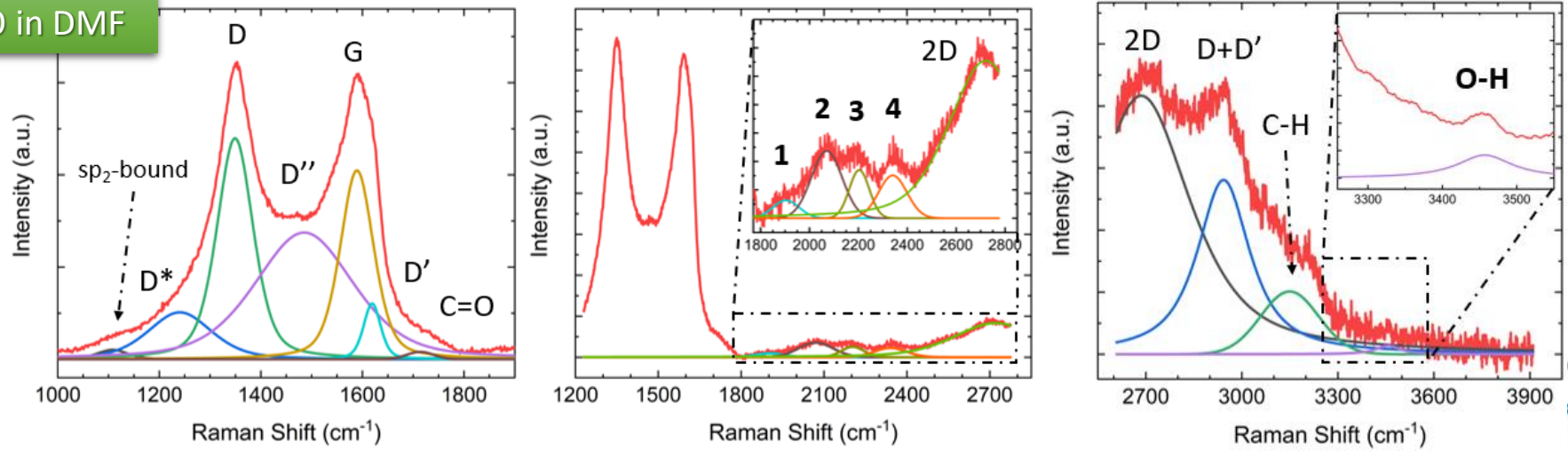
- I_D/I_G : 1.01 → 0.68
- I_{2D}/I_G : 0.49 → 0.49
- New peaks!

Raman analysis

rGO in DMF

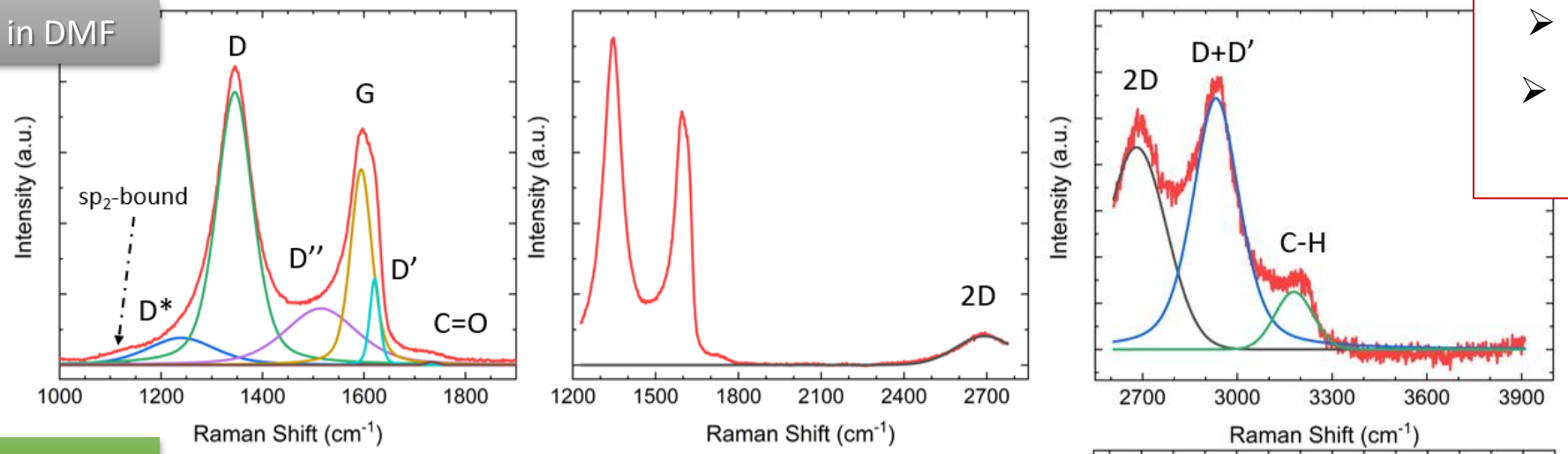


f-rGO in DMF



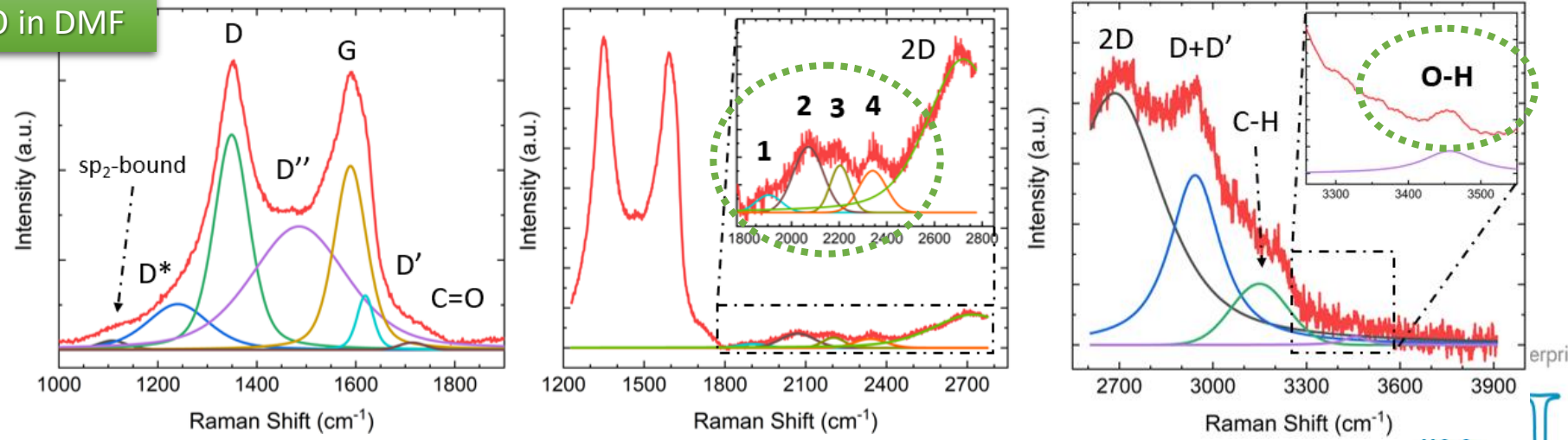
Raman analysis

rGO in DMF



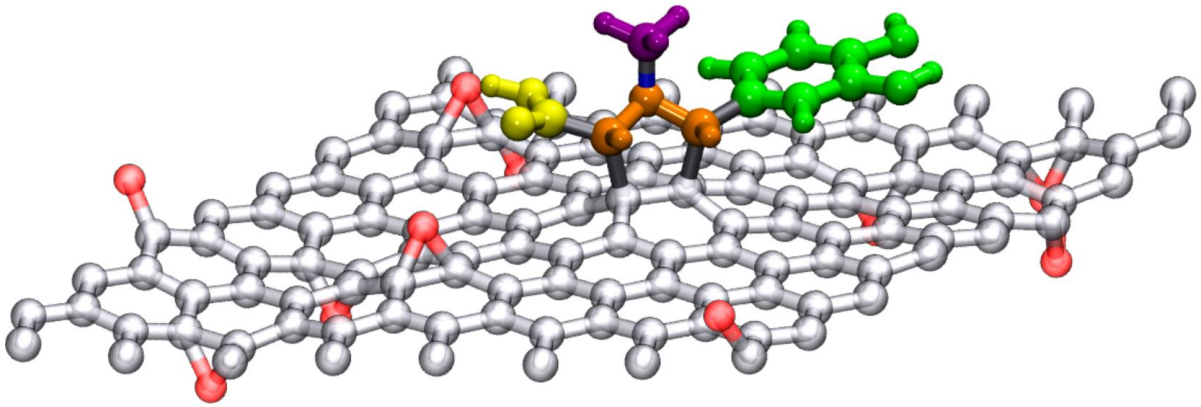
- I_D/I_G : 1.39 → 1.17
- $I_{D''}/I_G$: 0.29 → 0.67
- New peaks!

f-rGO in DMF



[*L. Bellucci* @ NEST]

DFT – Power Spectrum



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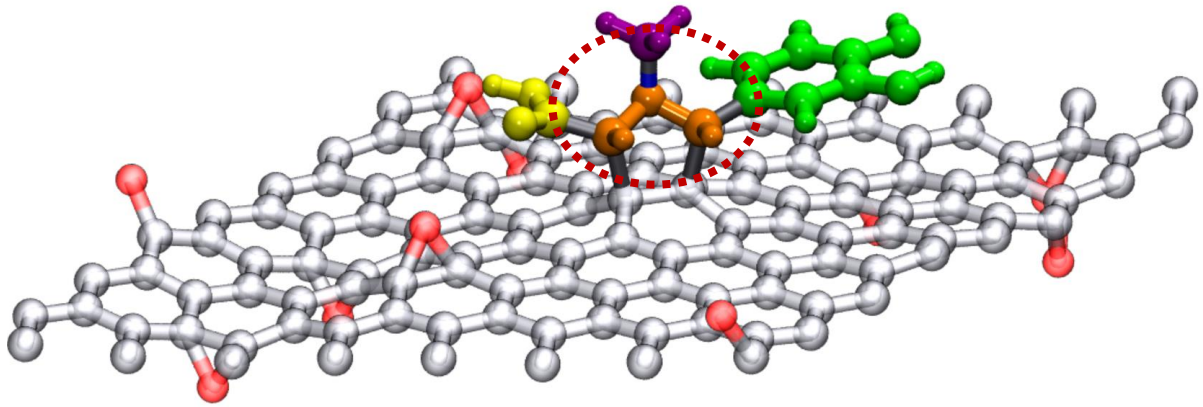
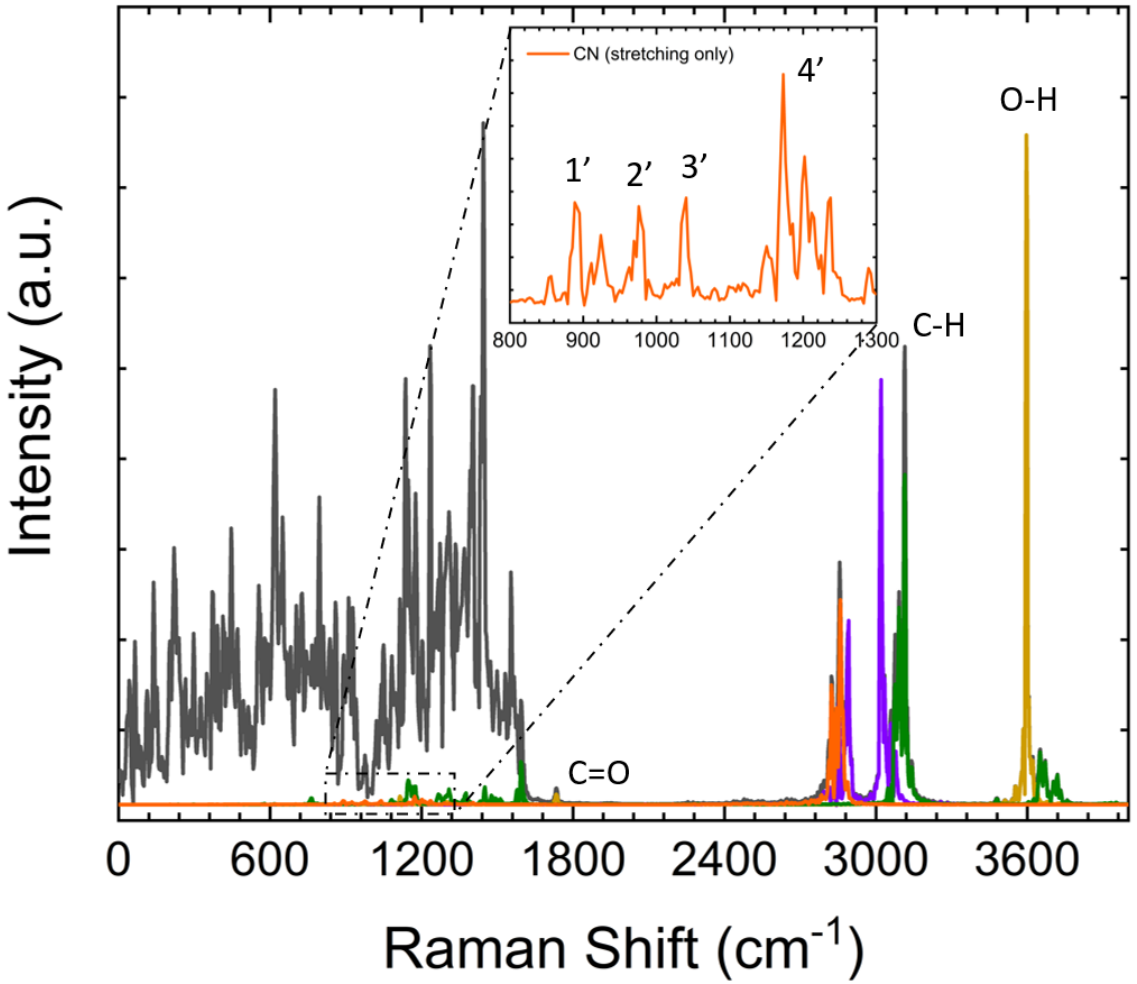
DFT – Power Spectrum

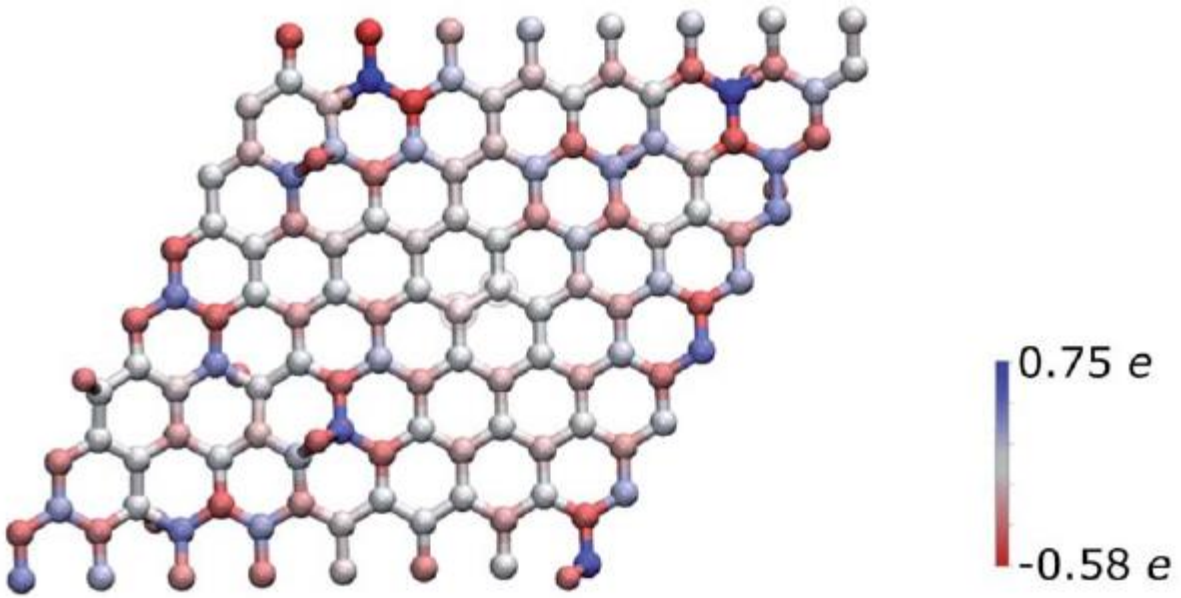


C–N (stretching)



DFT – Charge localization

pristine rGO

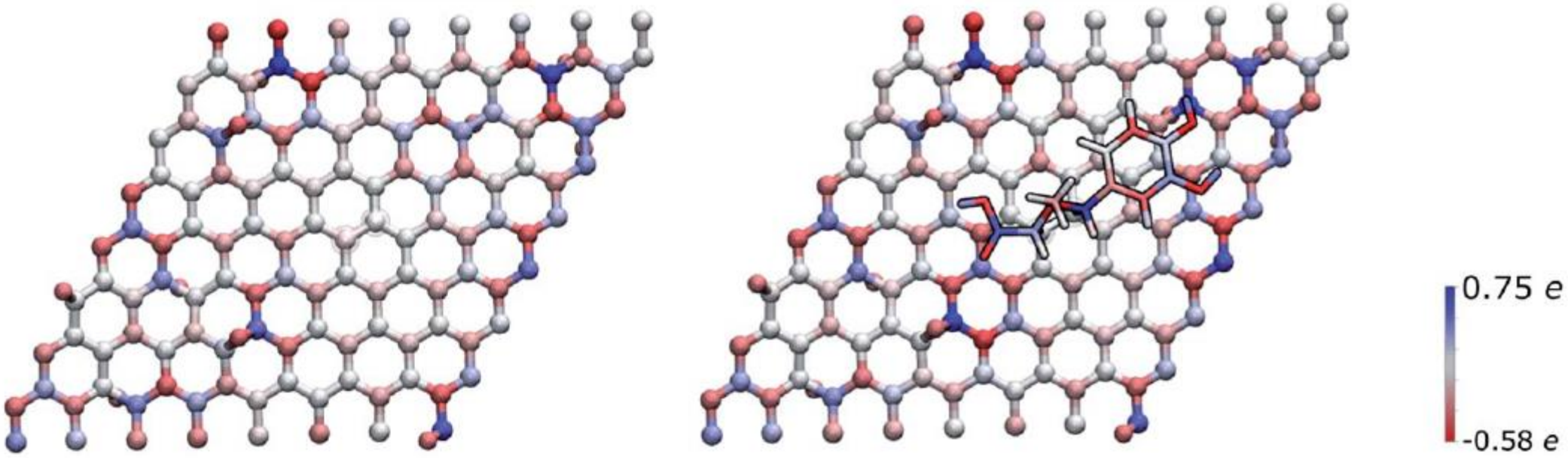


RESP (restrained electrostatic potential) derived partial atomic charges

DFT – Charge localization

pristine rGO

f-rGO



RESP (restrained electrostatic potential) derived partial atomic charges

Conclusions – 1)

- 1,3-DC of GNS and rGO in the liquid phase

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- Solvent comparison:
  - NMP → better dispersion
  - DMF → higher functionalization

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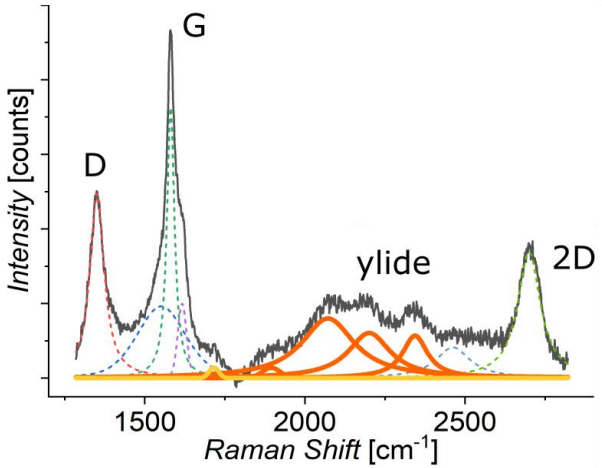
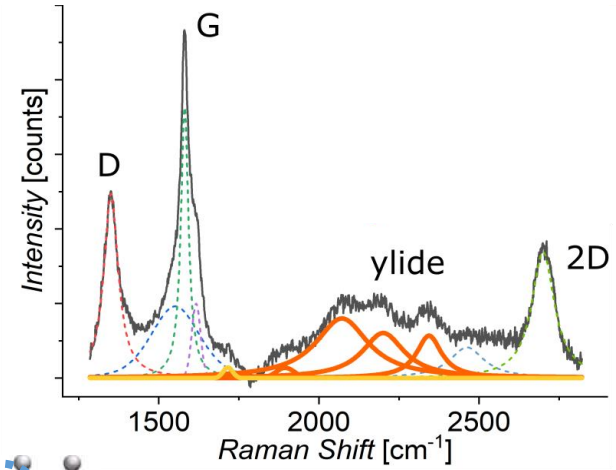
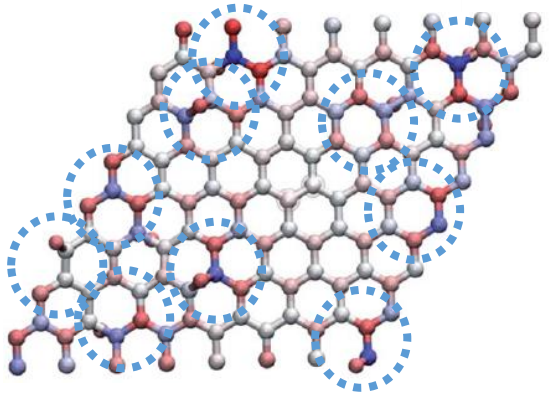
- Raman ***signature*** of the functionalization



Conclusions – 1)

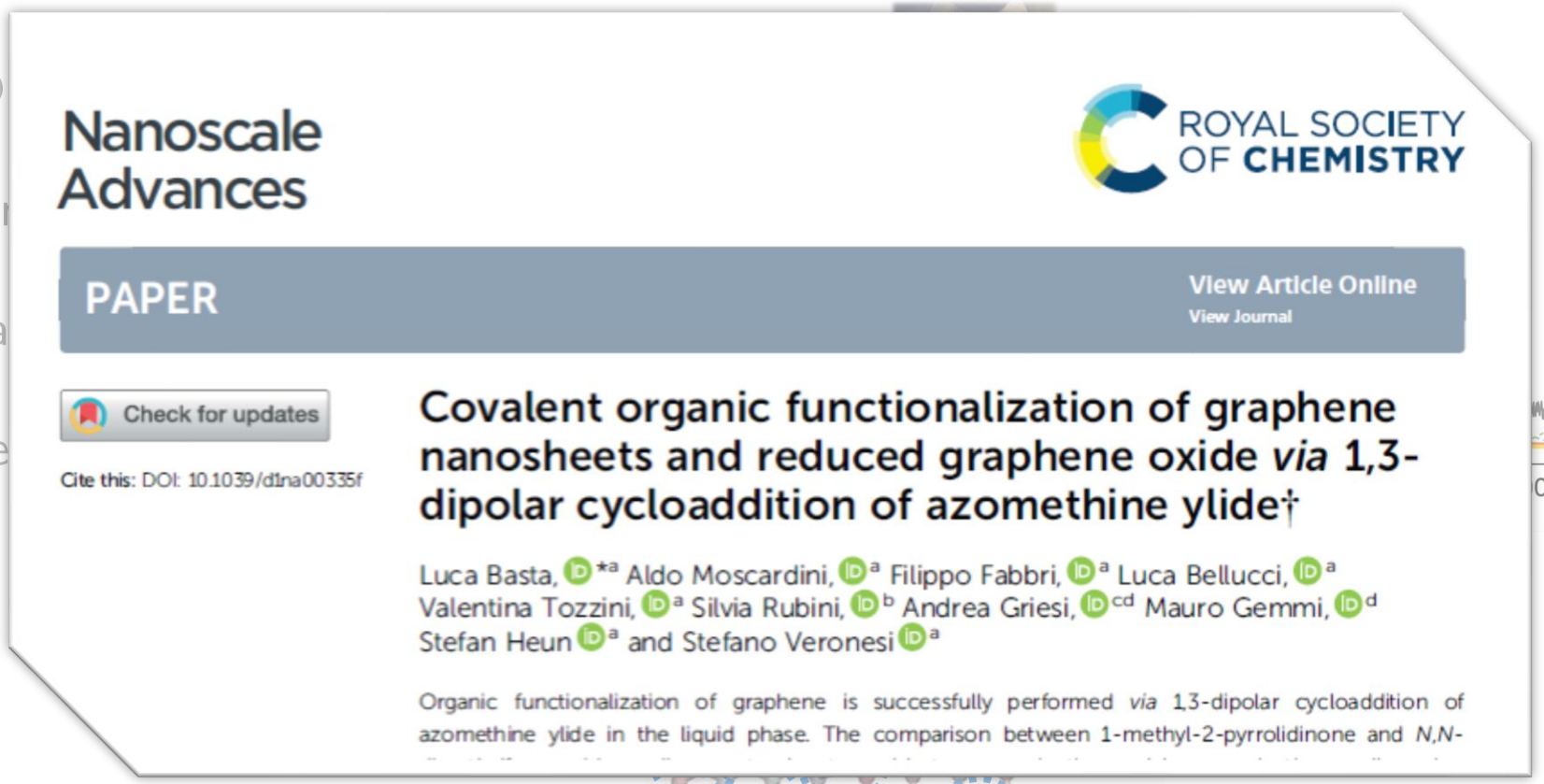
- 1,3-DC of GNS and rGO in the liquid phase
- Solvent comparison (NMP vs DMF)
- Raman ***signature*** of the functionalization
- Higher reactivity of rGO due to the presence of ***defects***





Conclusions – 1)

- 1,3-D
- Solver
- Rama
- Highe



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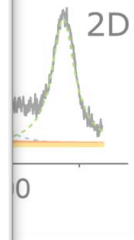
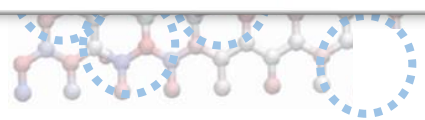
Covalent organic functionalization of graphene nanosheets and reduced graphene oxide *via* 1,3-dipolar cycloaddition of azomethine ylide†

Luca Basta, *[a] Aldo Moscardini, [a] Filippo Fabbri, [a] Luca Bellucci, [a] Valentina Tozzini, [a] Silvia Rubini, [b] Andrea Griesi, [cd] Mauro Gemmi, [d] Stefan Heun [a] and Stefano Veronesi [a]

Organic functionalization of graphene is successfully performed *via* 1,3-dipolar cycloaddition of azomethine ylide in the liquid phase. The comparison between 1-methyl-2-pyrrolidinone and *N,N*-





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Experimental Results

1) Functionalization of dispersed GNS and rGO → ***defects*** for chemical reactivity
2) ML graphene flakes → ***defects engineering*** via EBI
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Mechanically exfoliated graphene

intrinsic defects → engineered defects

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SUBSTRATE PREPARATION: Si/SiO_2

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no O_2-plasma

O_2-plasma

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SUBSTRATE PREPARATION: Si/SiO_2

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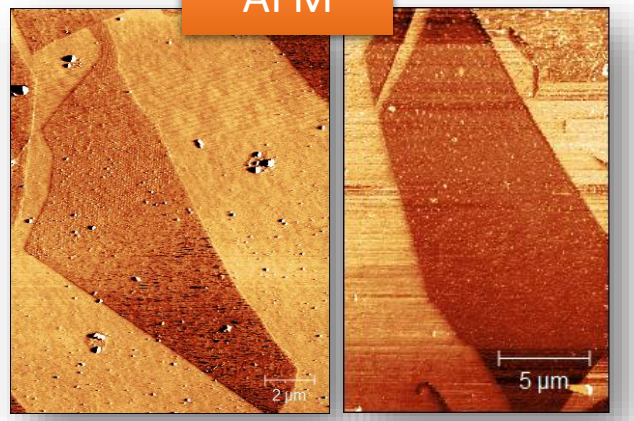
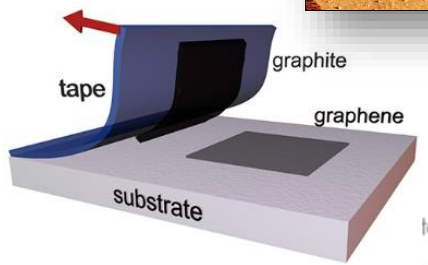
resist remover

no O_2-plasma → graphene EXFOLIATION

O_2-plasma → graphene EXFOLIATION

AFM



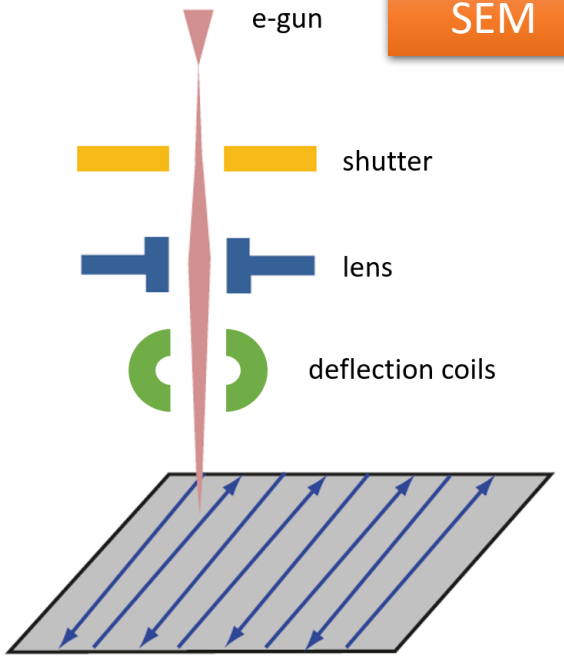


terprise for nanoScience and nanoTechnology

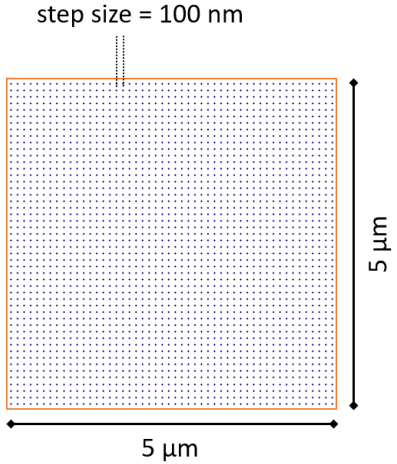
[*F. Bianco* @ NEST]

Defect patterning

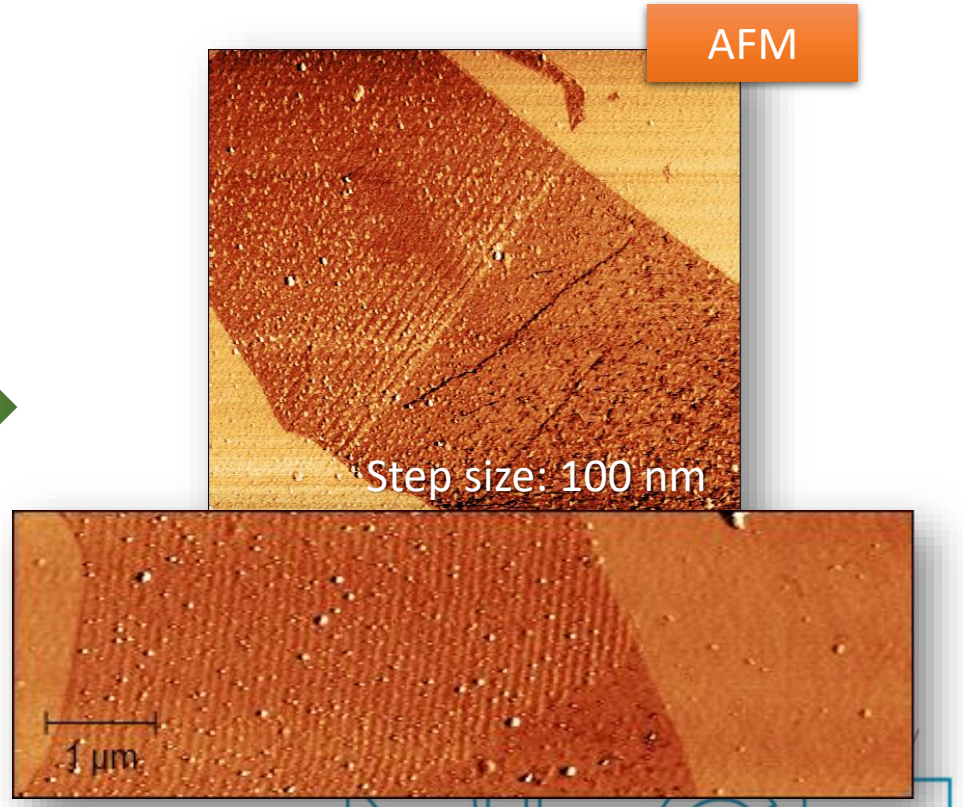
Via electron beam irradiation (EBI, the exposure of graphene sheet to focused beams of energetic electrons) structural defects are patterned into graphene:



SEM



AFM



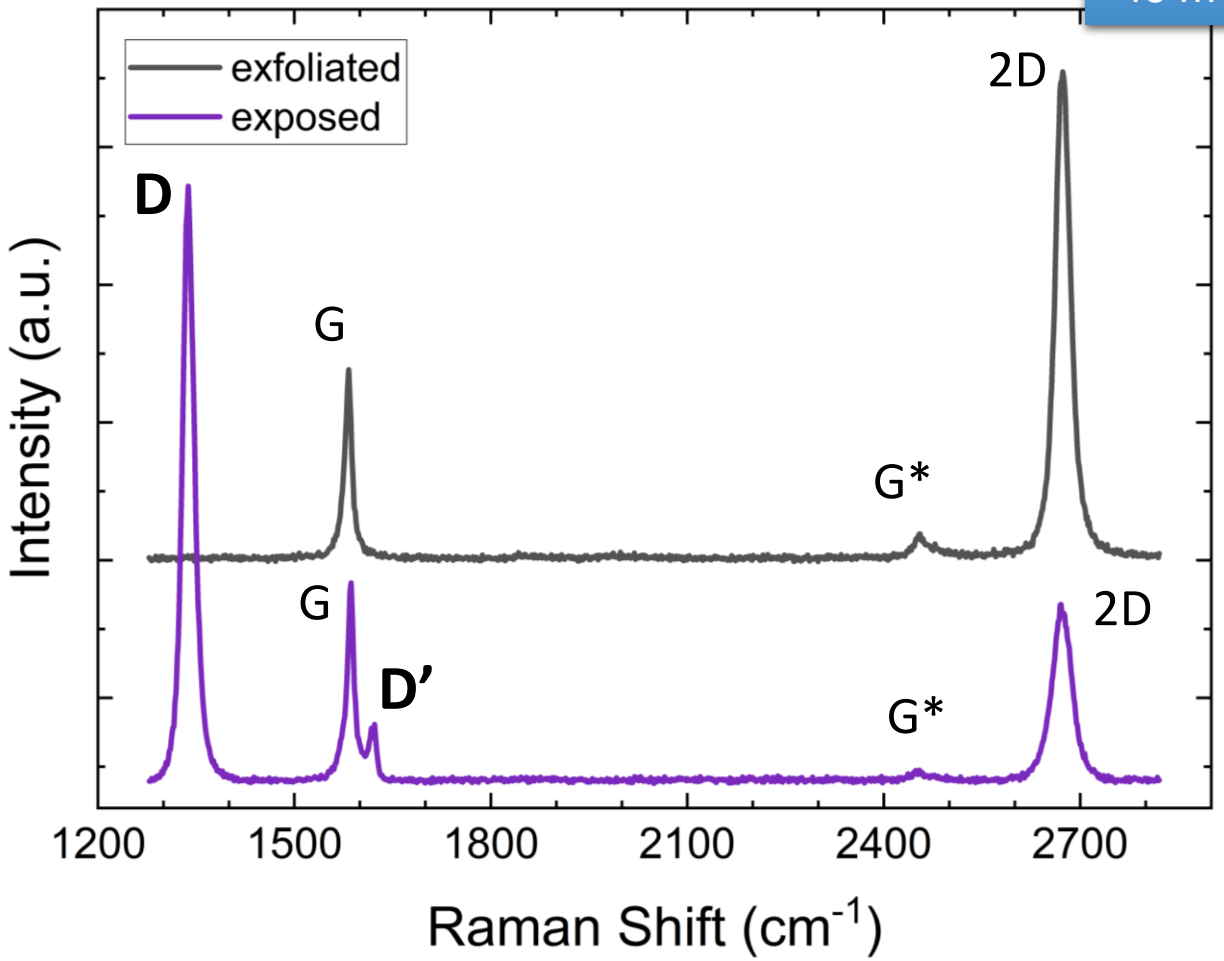
LATERAL RESOLUTION (~ 10 nm)

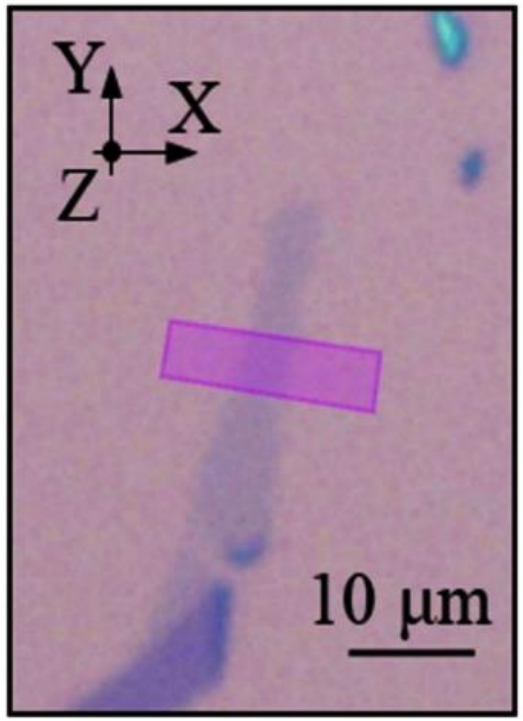
CONTROLLED DESIGN

[EBL, *Encyclopedia of Nanotechnology*, **2012**]

Raman analysis

30 keV
40 mC/cm²





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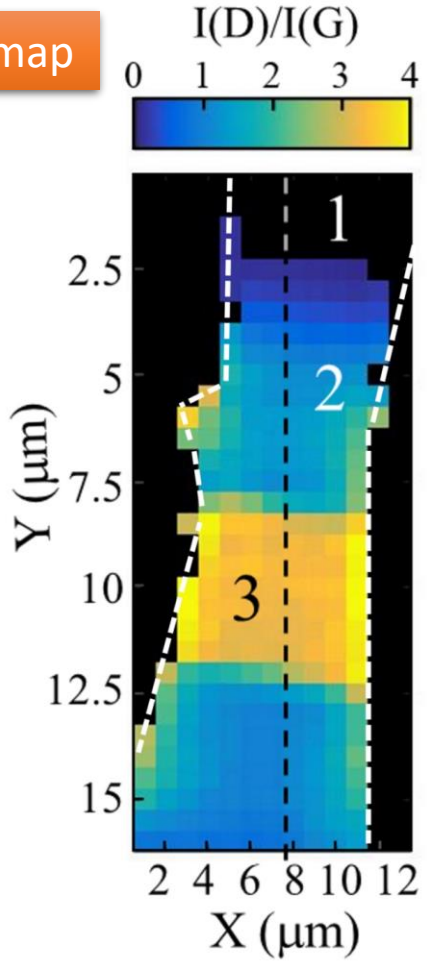
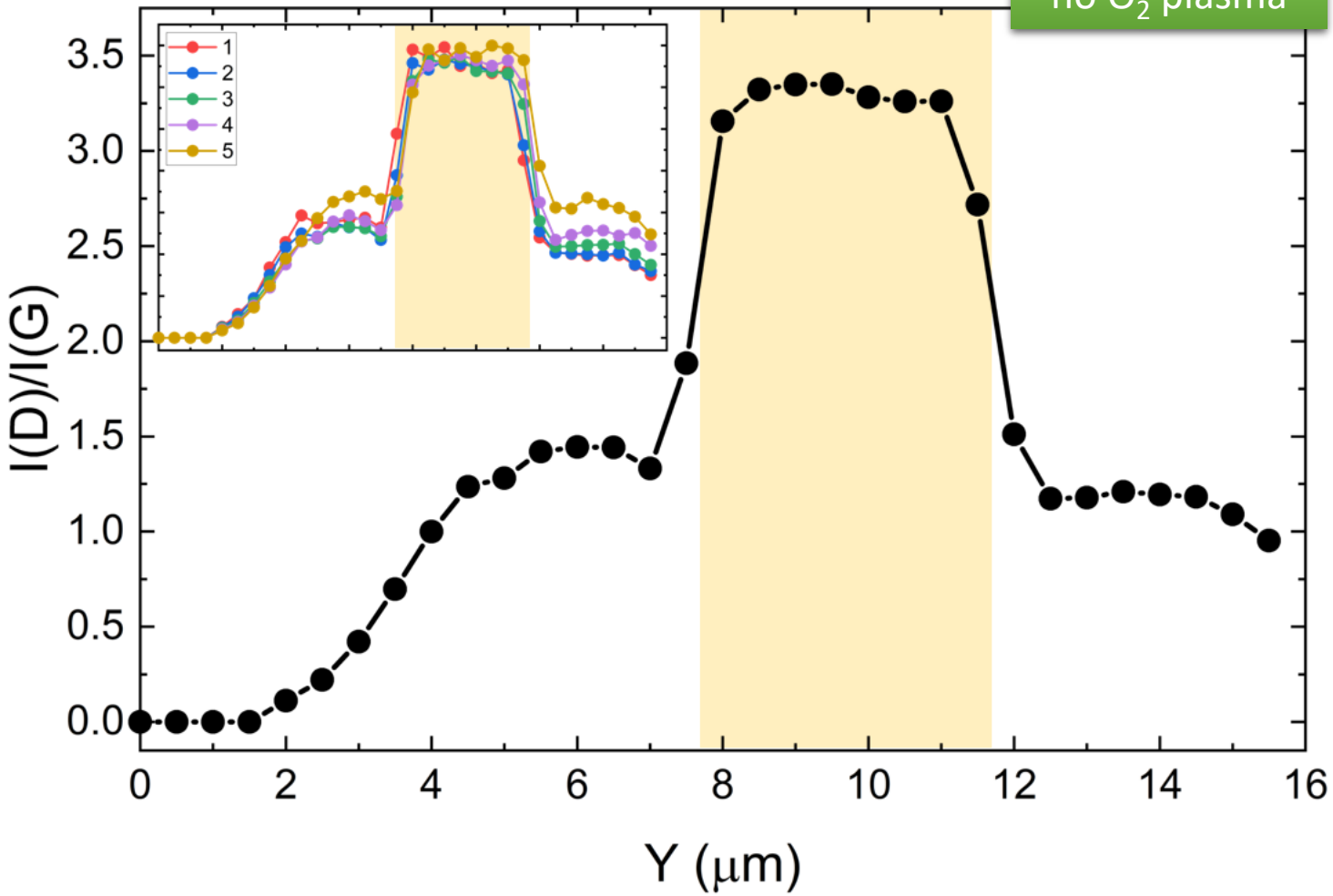
Raman analysis

Raman map



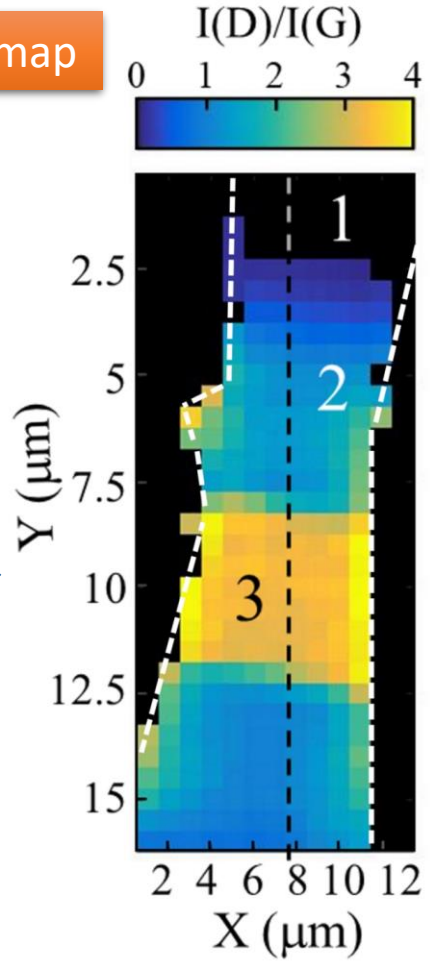
no O_2 plasma



Raman analysis

Raman map

irradiated zone
I(D)/I(G) ~ 3.5



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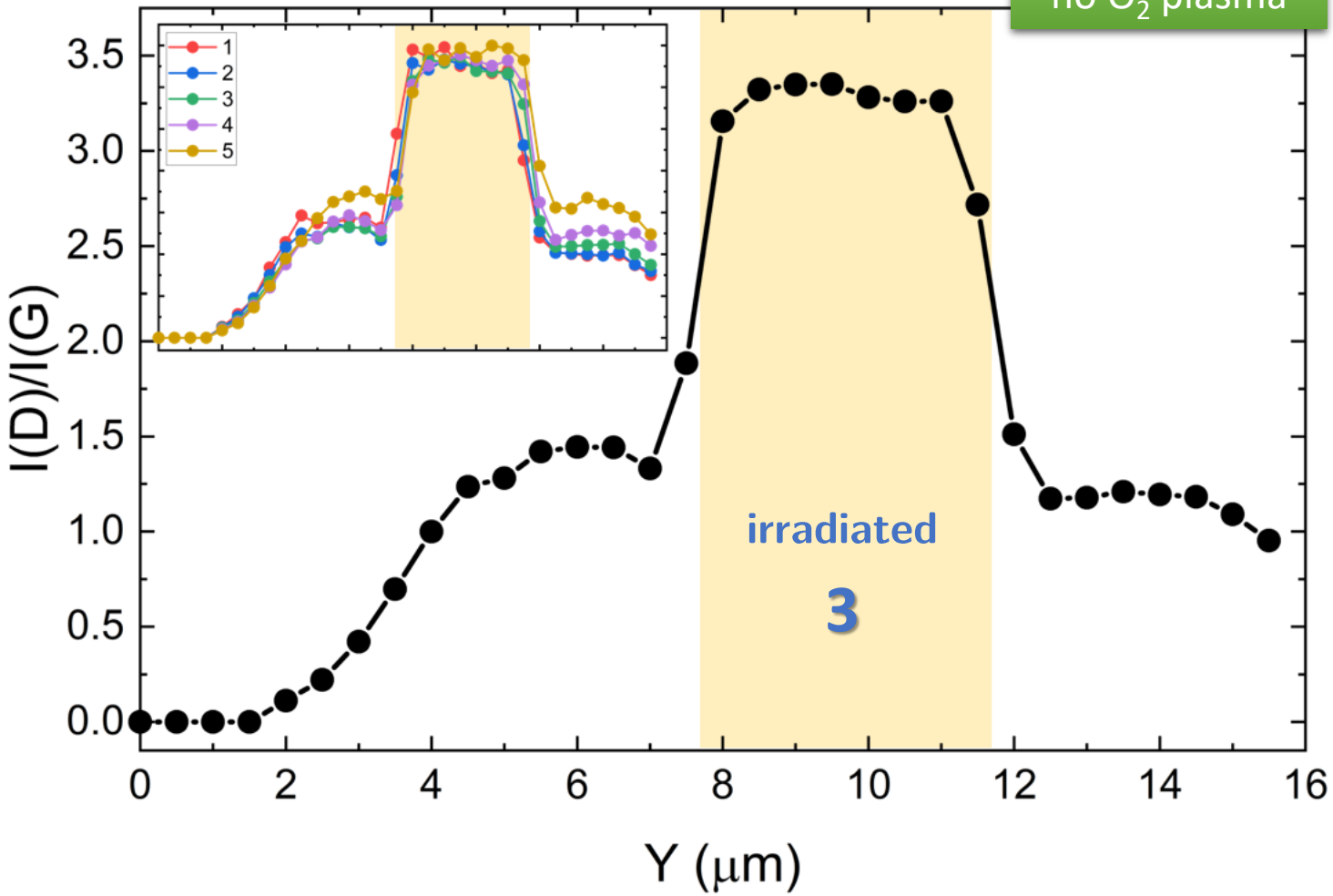
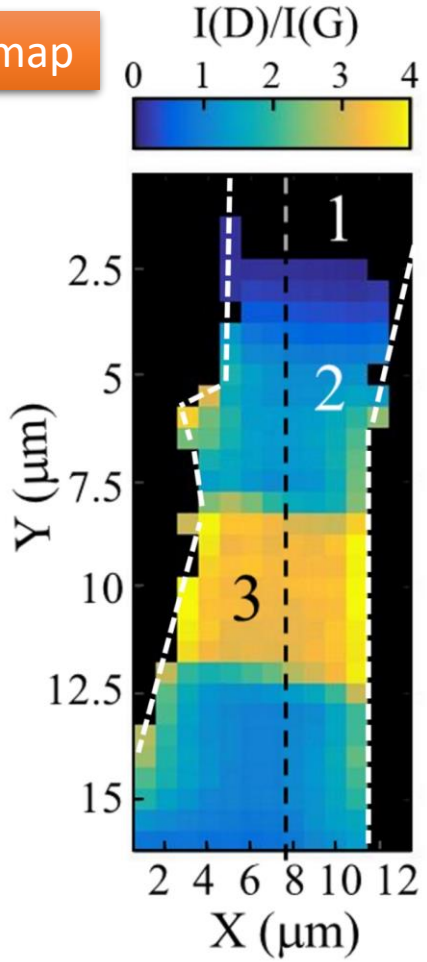


Raman analysis

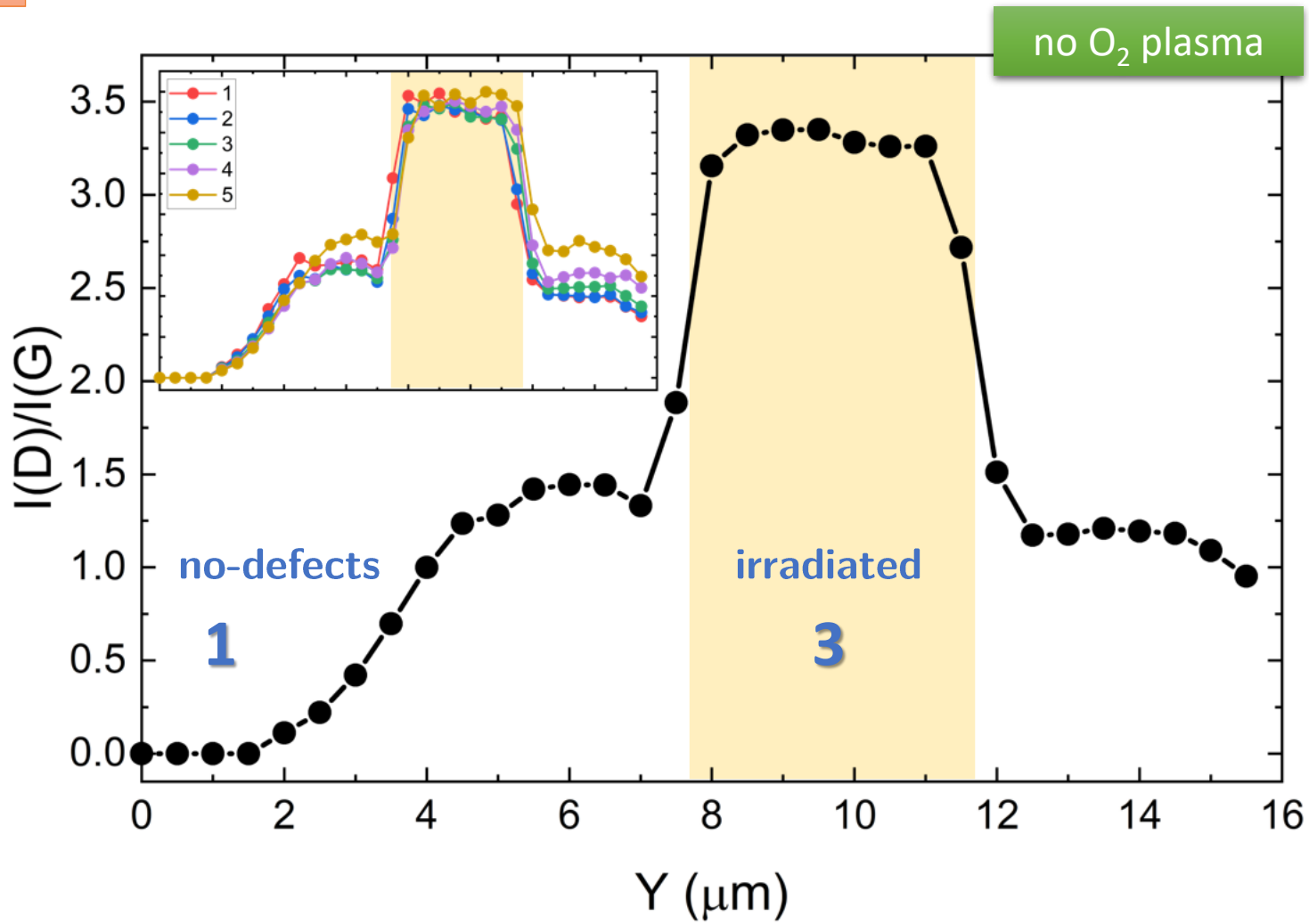
Raman map

no-defects zone
$I(D)/I(G) \sim 0$

irradiated zone
$I(D)/I(G) \sim 3.5$



no O_2 plasma



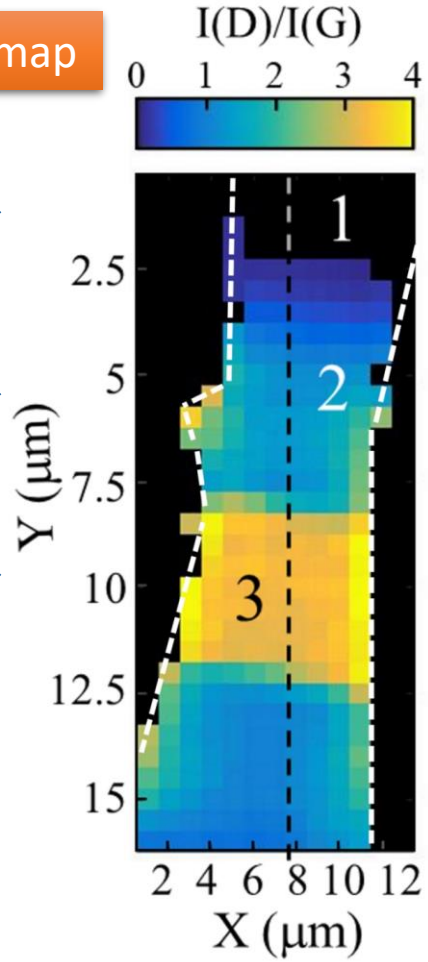
Raman analysis

Raman map

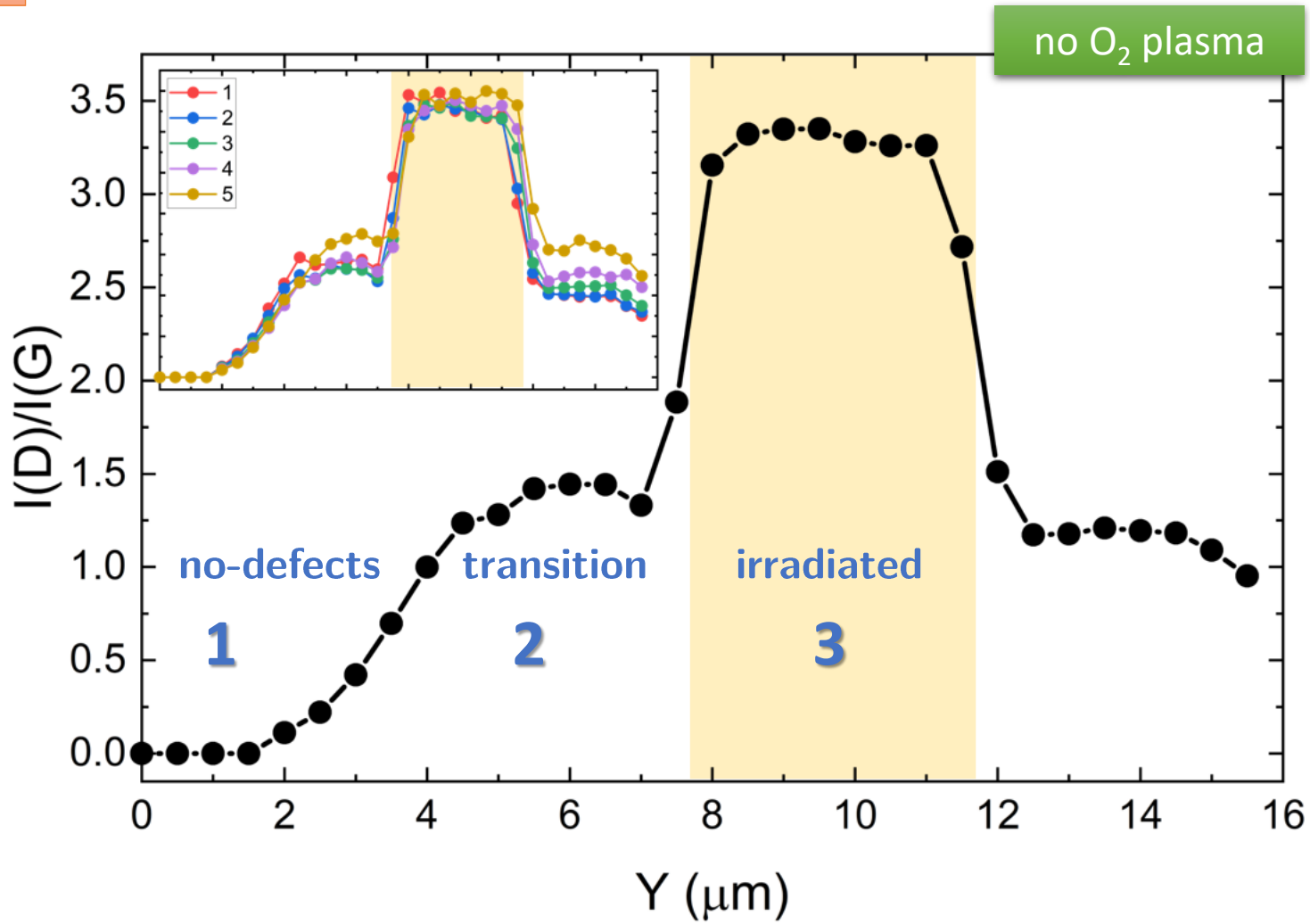
no-defects zone
$I(D)/I(G) \sim 0$

transition zone
$I(D)/I(G) \sim 1.5$

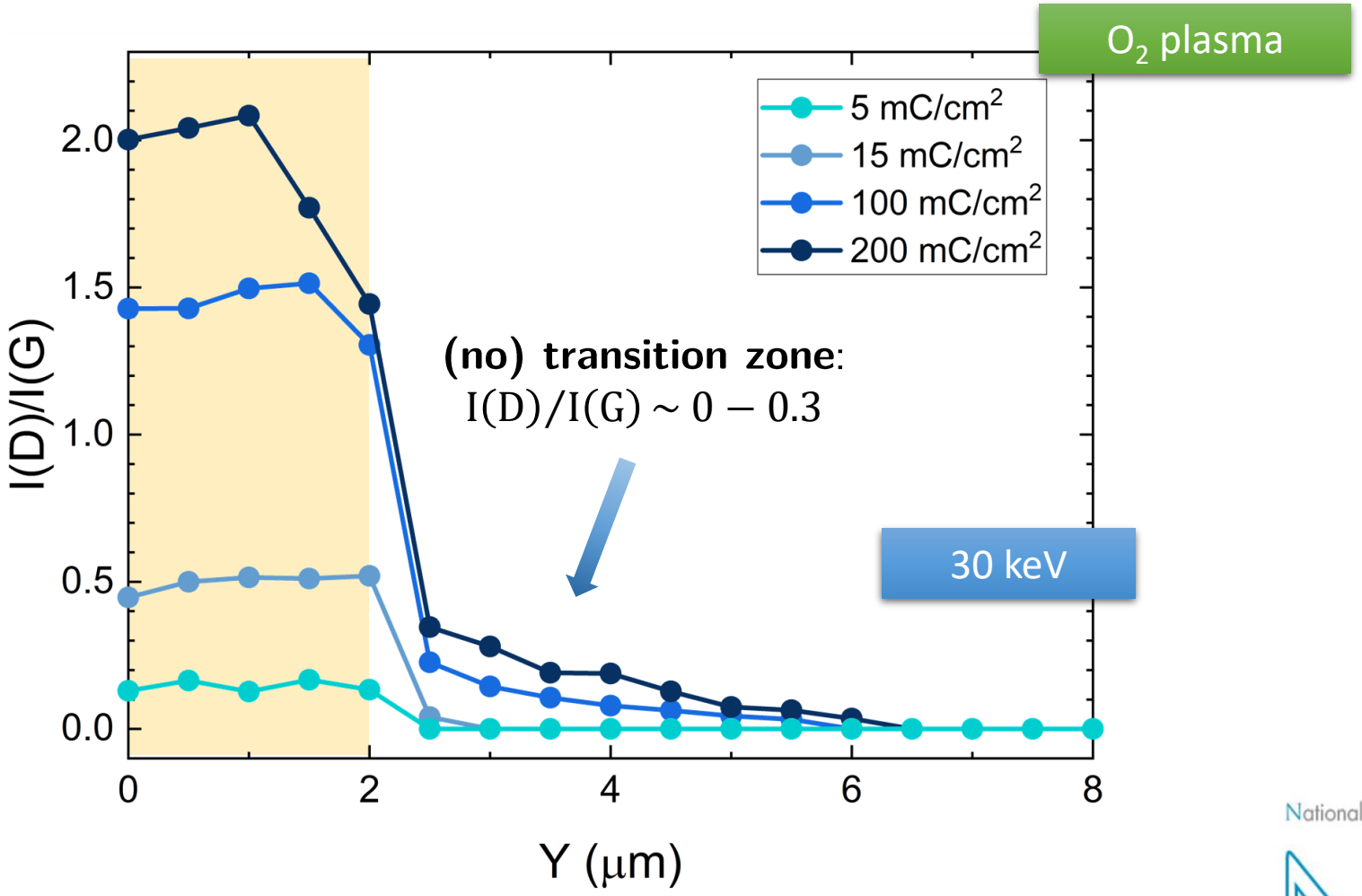
irradiated zone
$I(D)/I(G) \sim 3.5$



no O_2 plasma



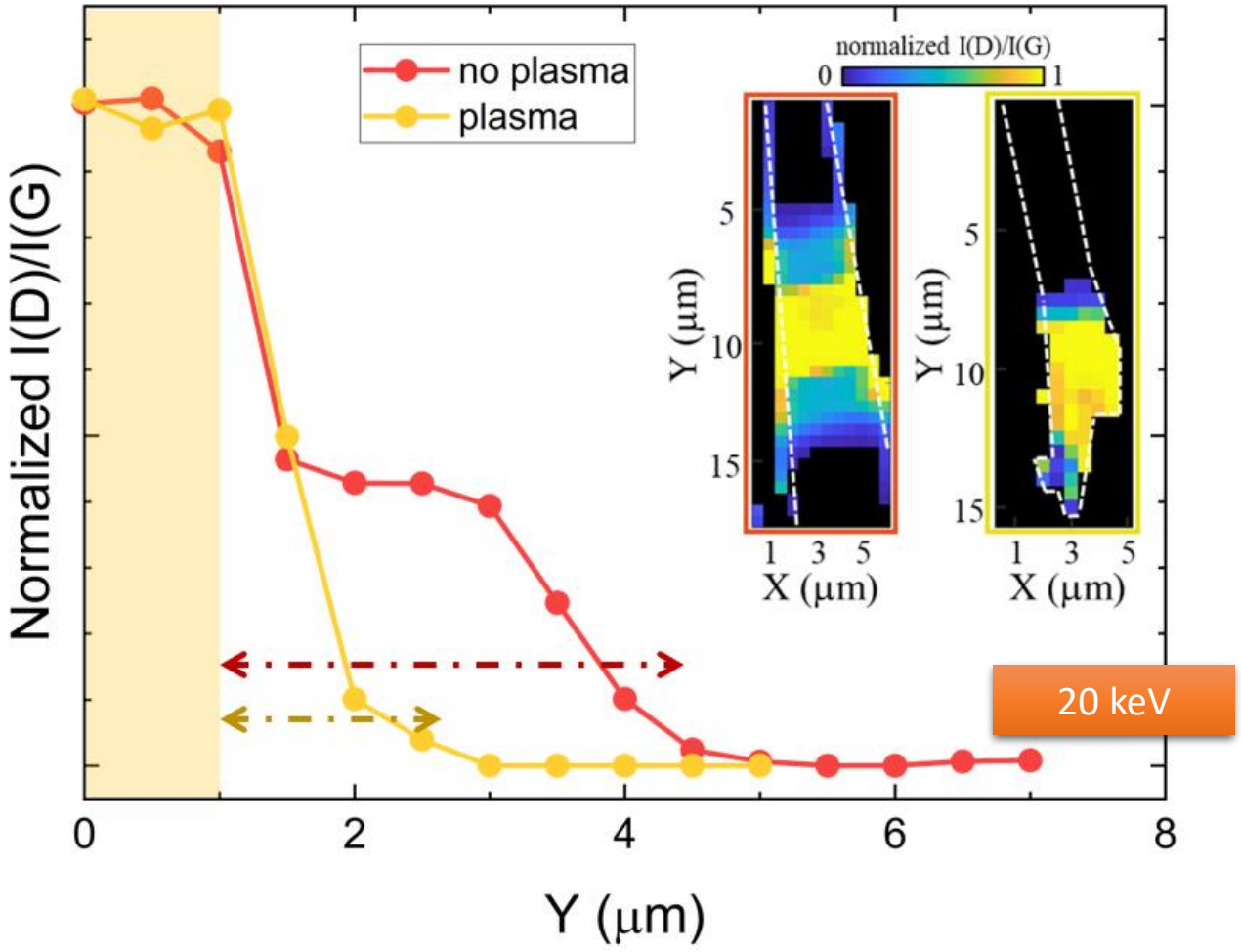
Substrate surface treatments



Monte Carlo

[*F. Bianco* @ NEST]

Substrate surface treatments



- EBI generates radicals at the interface
  - D peak and charge transfer
- O_2-plasma removes organic adsorbates
  - no transition zone

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Transition zone Doping

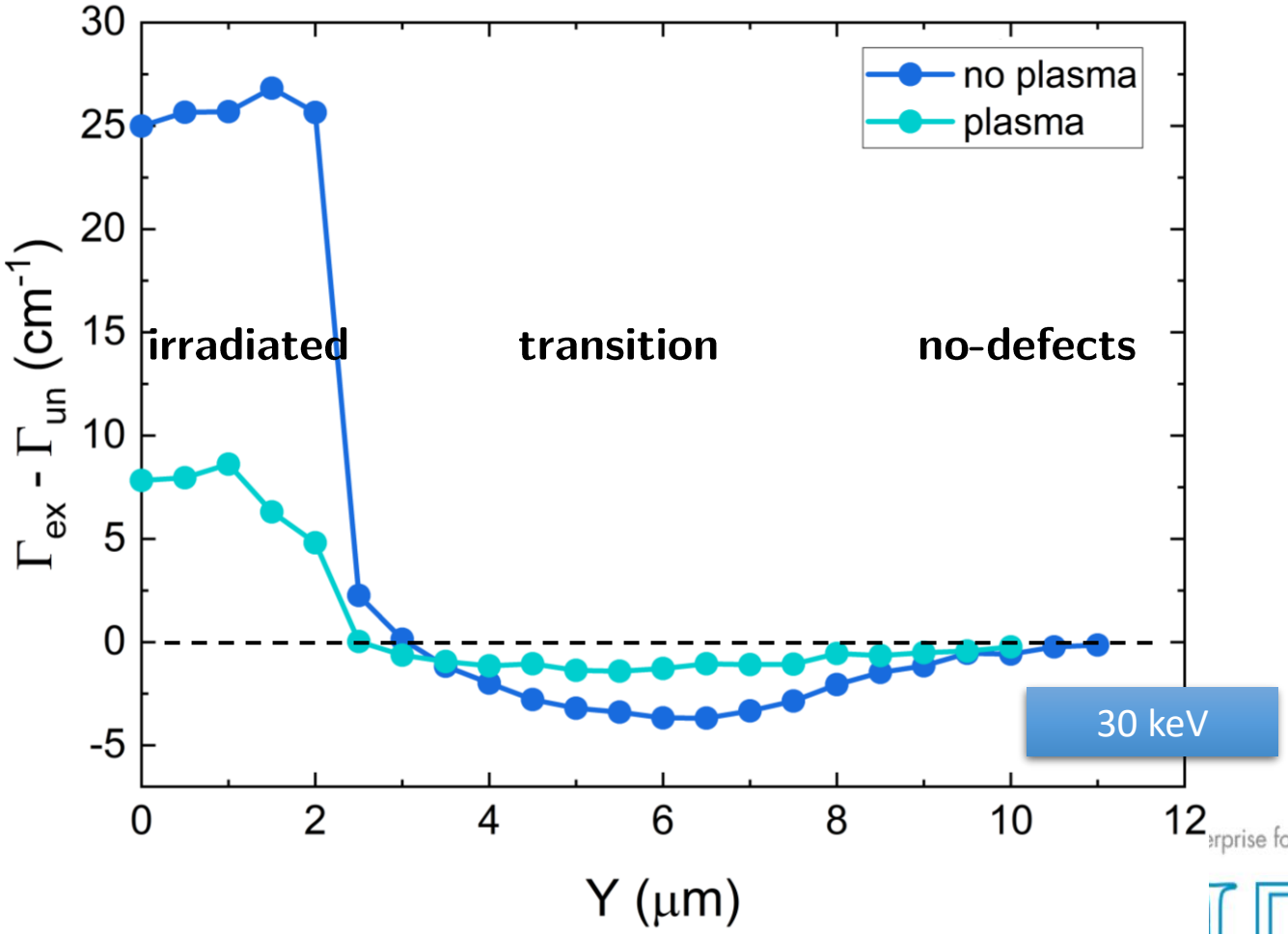
$\Gamma(G)$:

Carrier concentration (doping)

→ **narrowing**

Defect density

→ **broadening**



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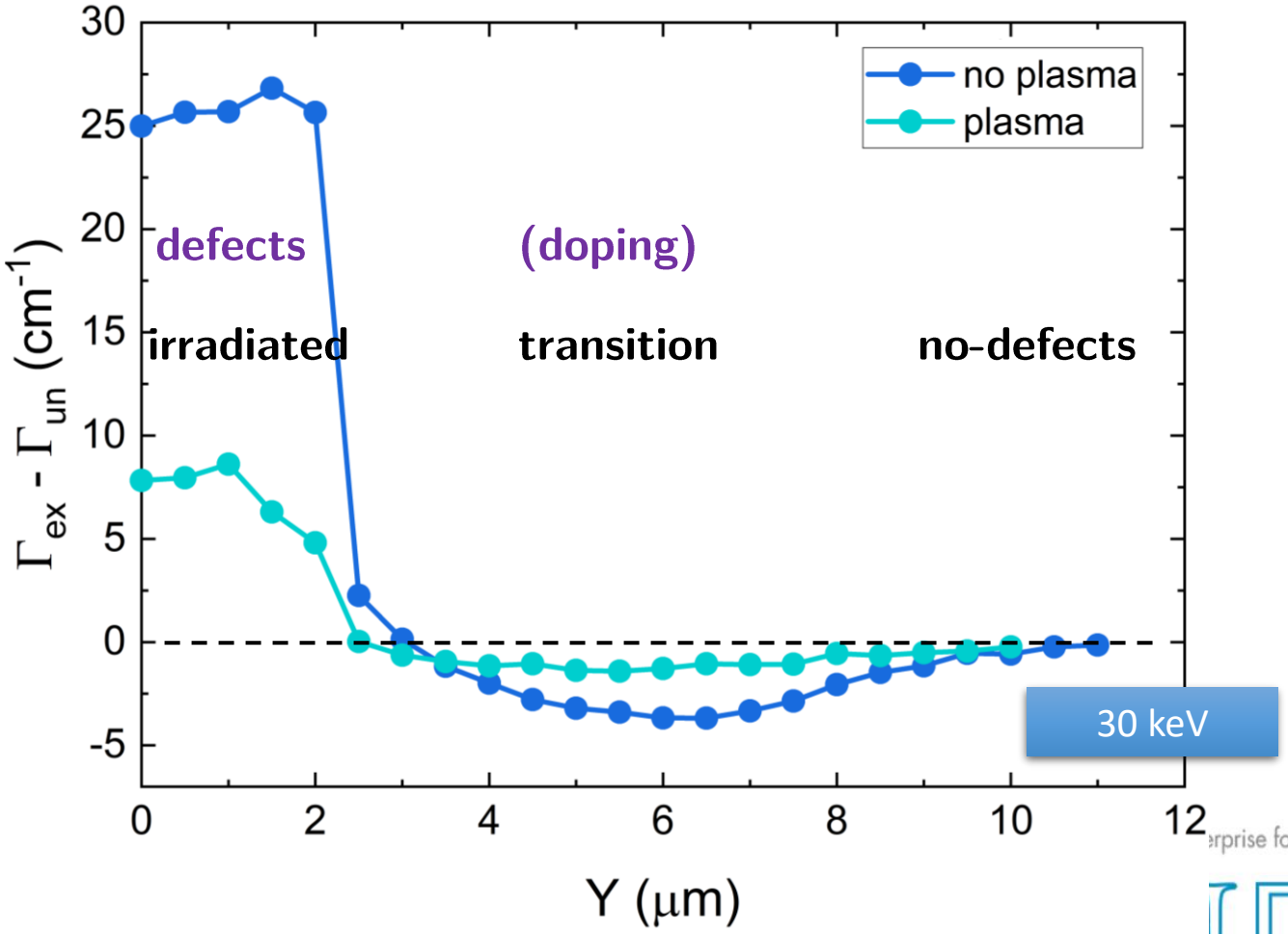

Conclusions – 2)

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  - O_2-plasma → no transition zone for low/medium doses
- In no-plasma-treated: wide defects zone and ***doping***
- In plasma-treated: almost no defects zone and no doping

Conclusions – 2)

- Desig
- Subst
- In no
- In pla

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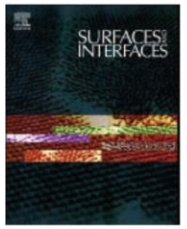


Substrate surface effects on electron-irradiated graphene

Luca Basta [a], Aldo Moscardini [b], Stefano Veronesi [a], Federica Bianco [*,a]

[a] NEST Laboratory, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza San Silvestro 12, 56127, Pisa, Italy
[b] NEST Laboratory, Scuola Normale Superiore, Piazza San Silvestro 12, 56127, Pisa, Italy

ARTICLE INFO

Keywords:
Graphene
ubstrate effect
tron-irradiation

ABSTRACT

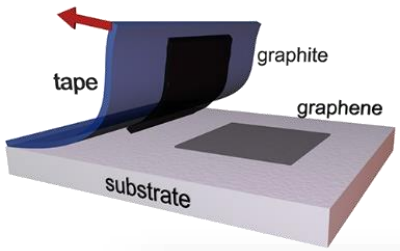
Chemical, mechanical, thermal and/or electronic properties of bulk or low-dimensional materials can be engineered by introducing structural defects to form novel functionalities. When using particles irradiation, these defects can be spatially arranged to create complex structures, like sensing circuits, where the lateral resolution of the defective areas plays a fundamental role. Here, we show that structural defects can be patterned by low-

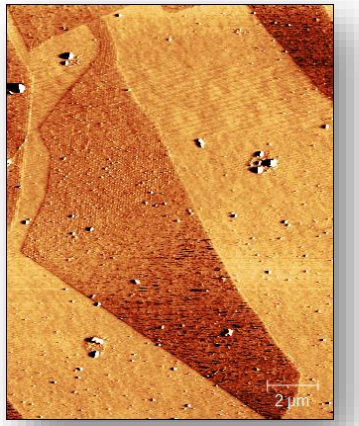
Experimental Results

1) Functionalization of dispersed GNS and rGO → ***defects*** for chemical reactivity
2) ML graphene flakes → ***defects engineering*** via EBI
3) Patterned ML graphene flakes → ***deterministic*** functionalization
4) Epitaxial graphene → functionalization and patterning of ***higher quality graphene***

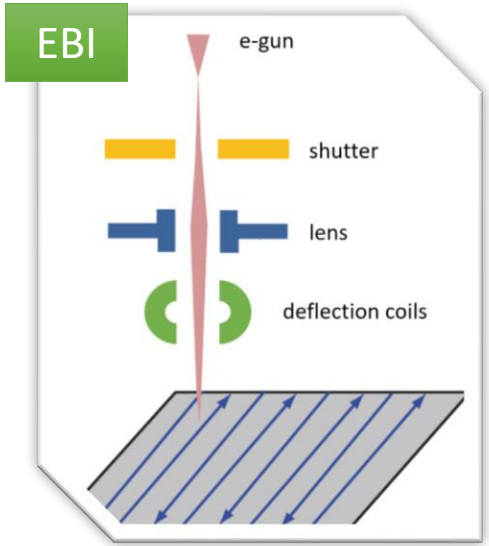
Defect patterning of ML flakes

Designed defect patterning via EBI → tailoring of the surface chemistry of graphene





EBI



20 keV
40 mC/cm^2
step size: 100 nm

STRUCTURAL DEFECTS

+

LATERAL RESOLUTION (~ 10 nm)

CONTROLLED DESIGN

↓

SELECTIVELY ENHANCED SURFACE REACTIVITY?

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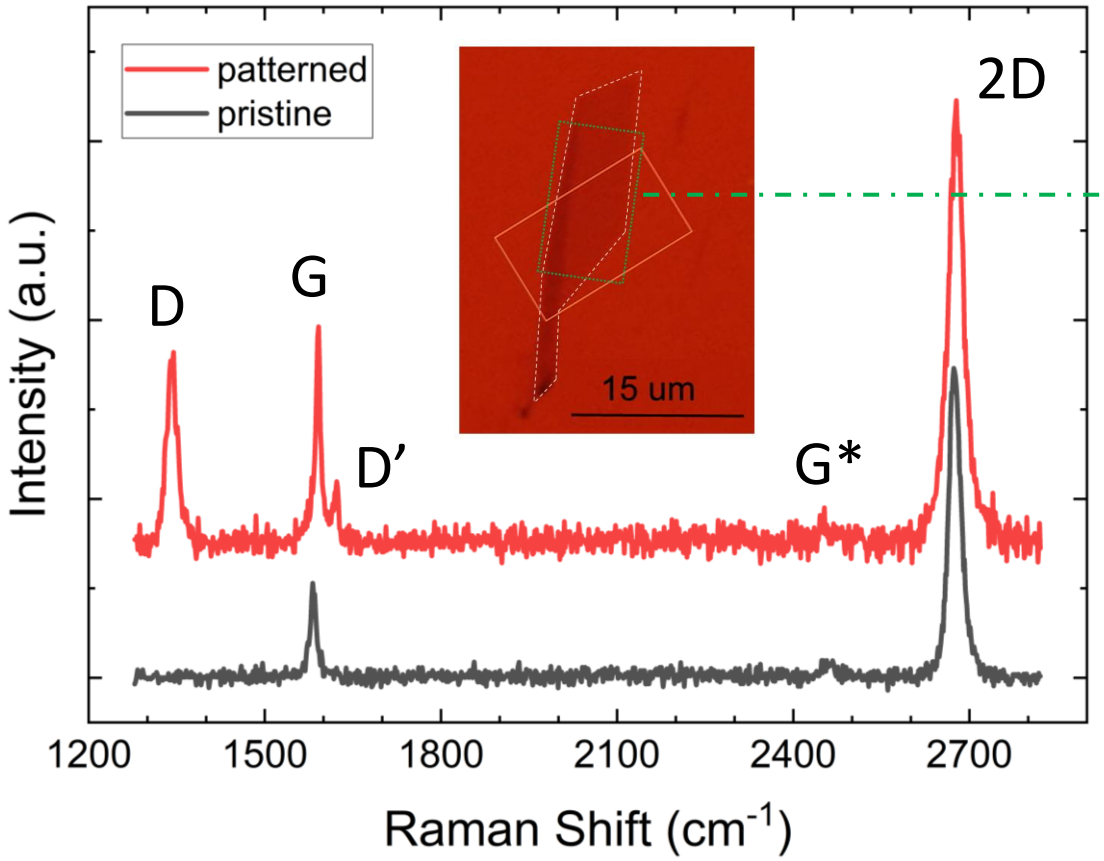
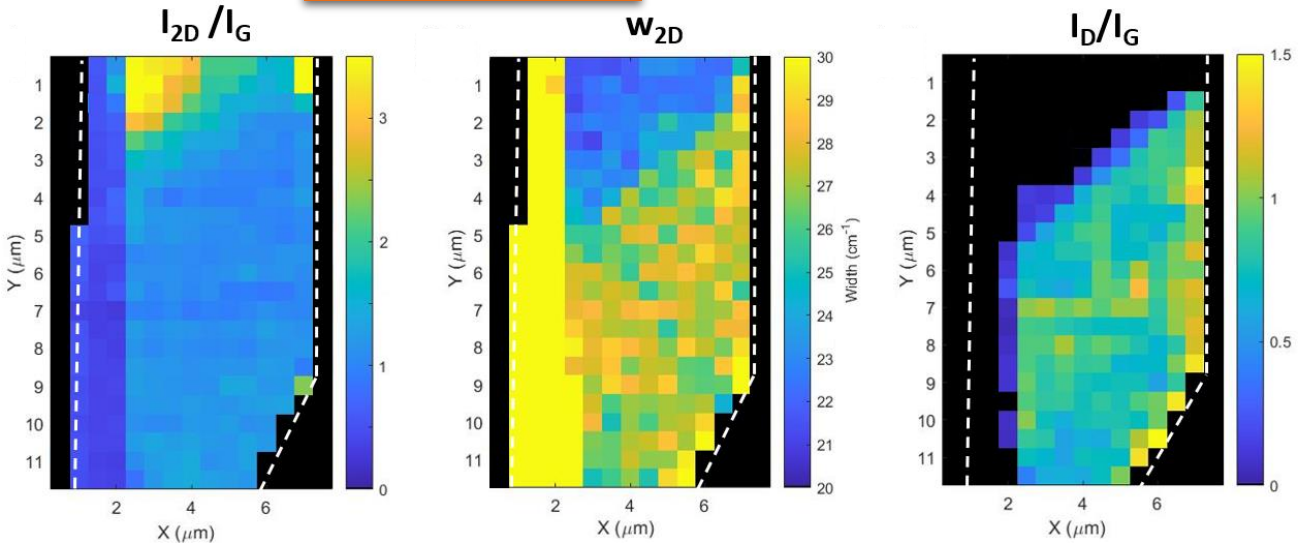
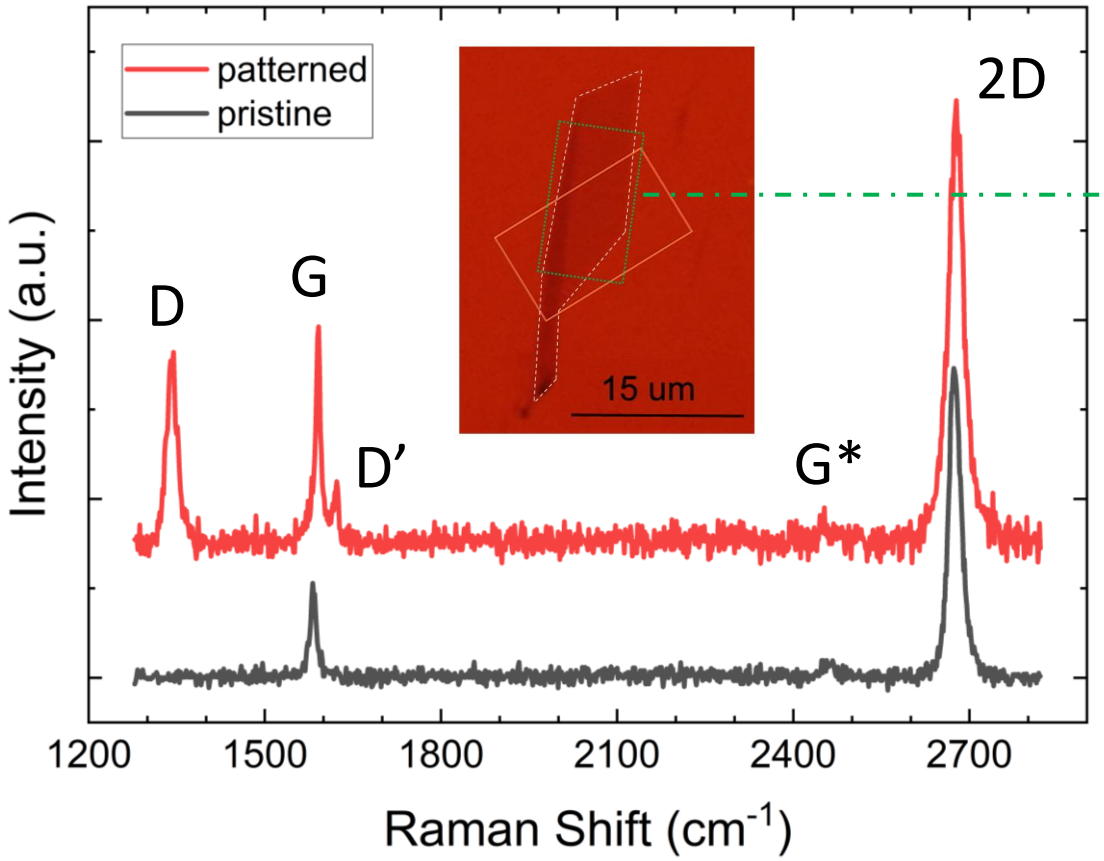
Raman analysis



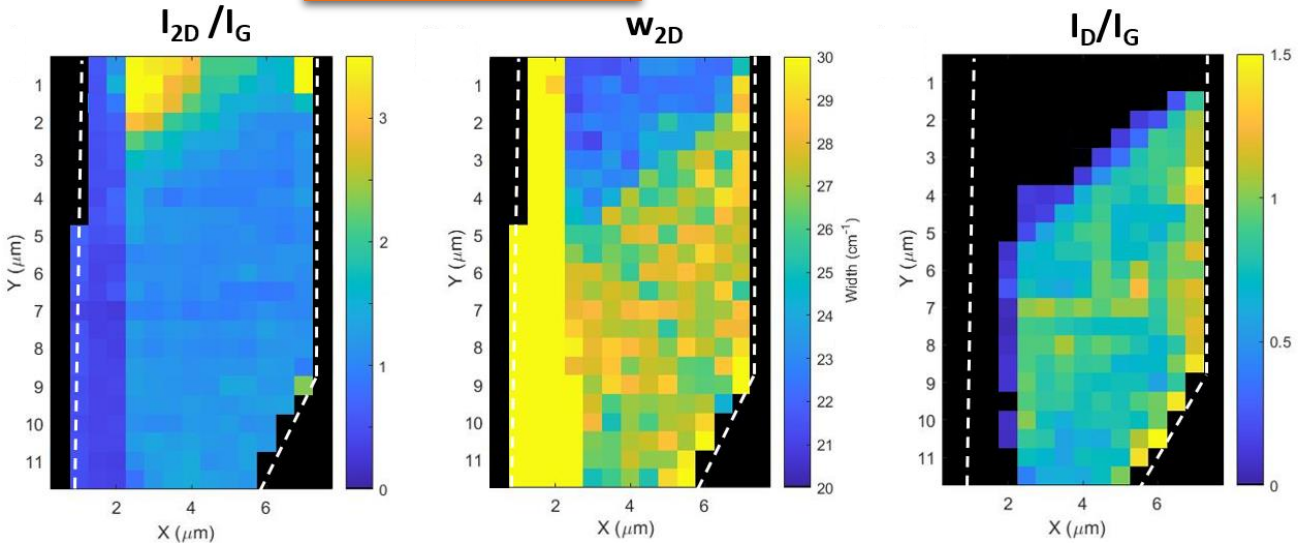
Raman maps



Raman analysis



Raman maps



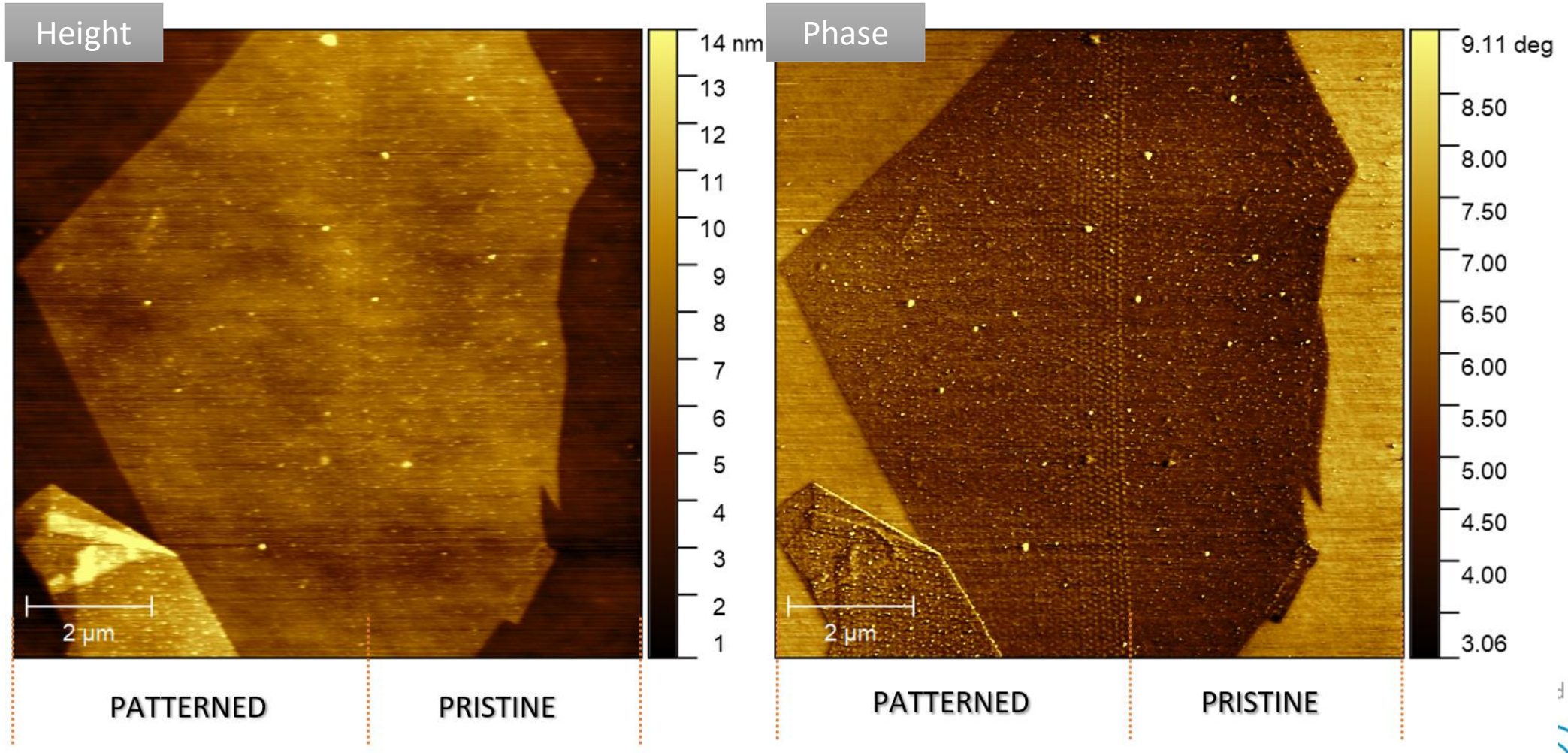
$I(2D)/I(G)$: 3 → 2

$w(2D)$: 24 cm^{-1} → 31 cm^{-1}

$I(D)/I(G)$: 0.9 (**low-defect** regime)

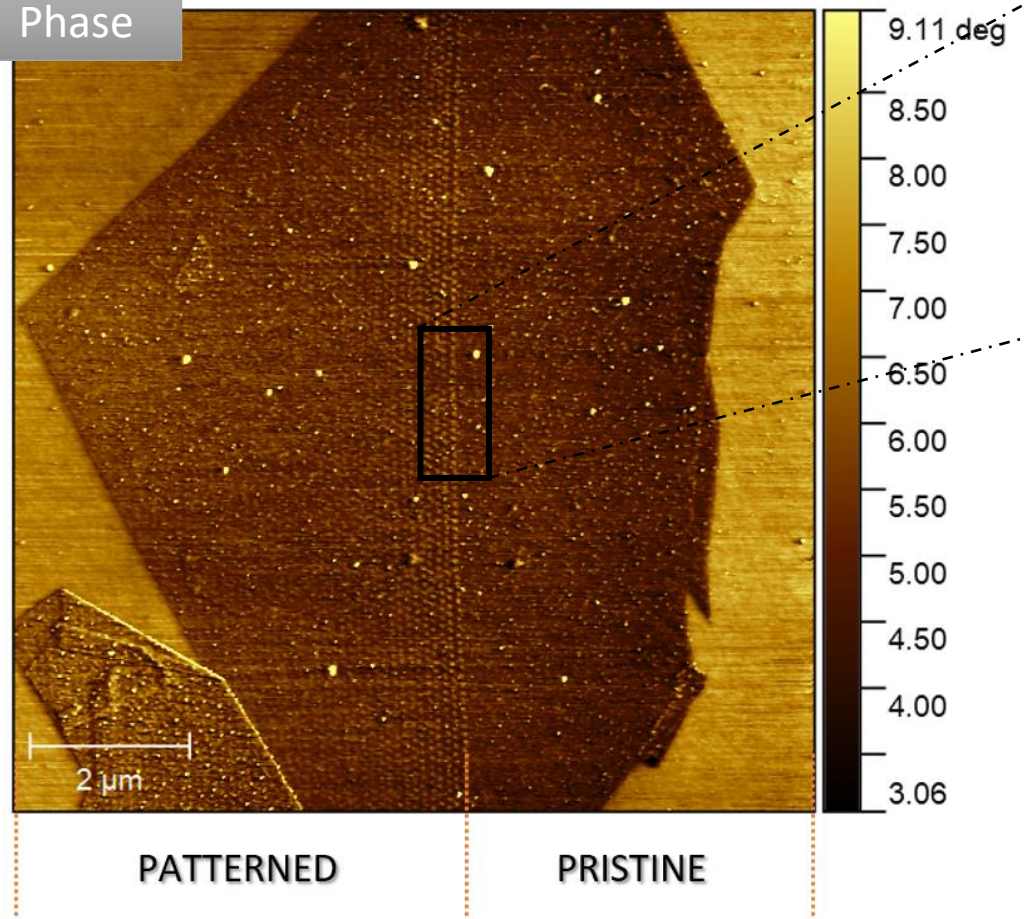
$I(D)/I(D') \sim 4.5$ (**boundary-like** defects)

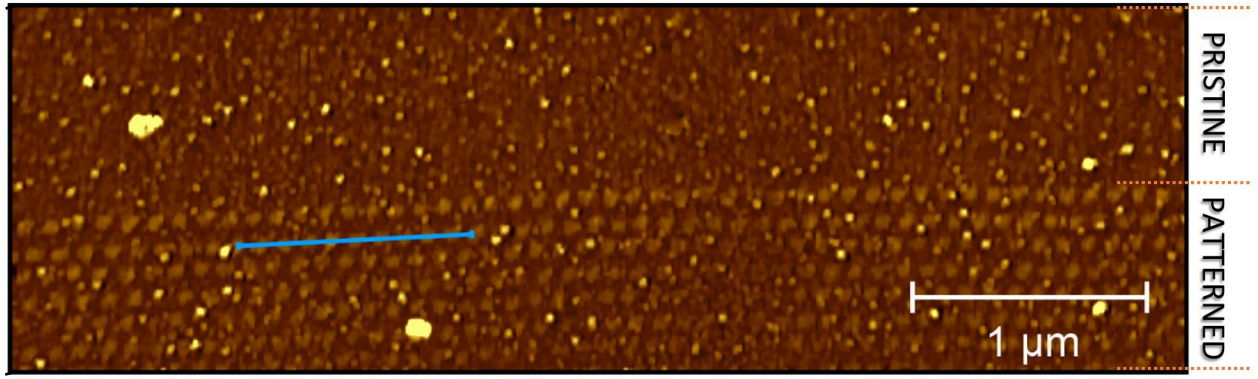
AFM of patterned graphene



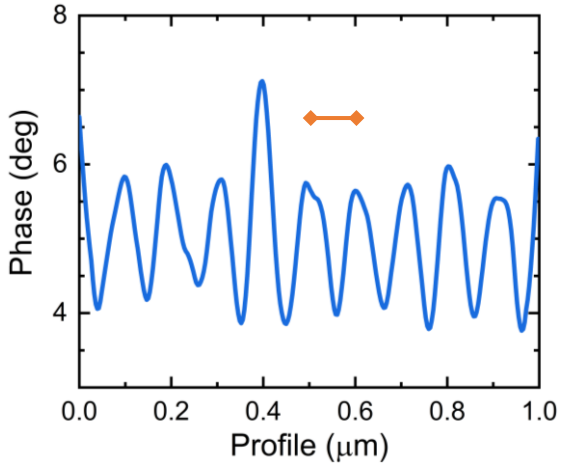
AFM of patterned graphene

Phase





Step size: 100 nm



CONTROLLED DESIGN!

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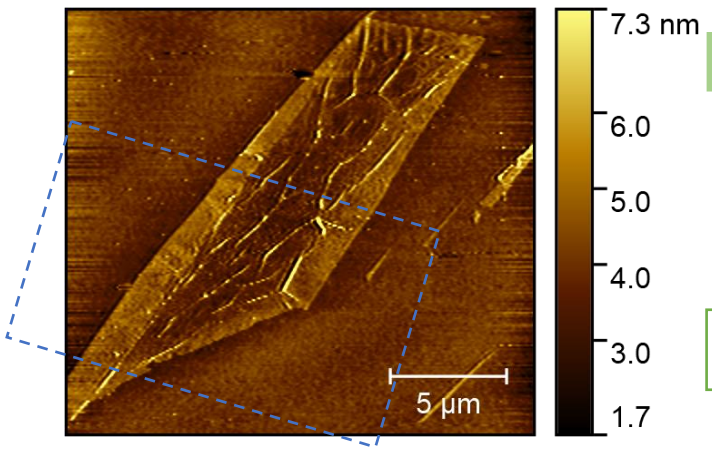
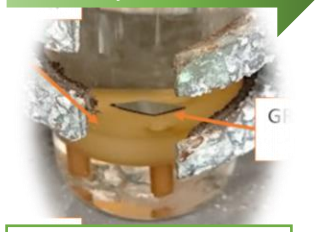
AFM of functionalized graphene

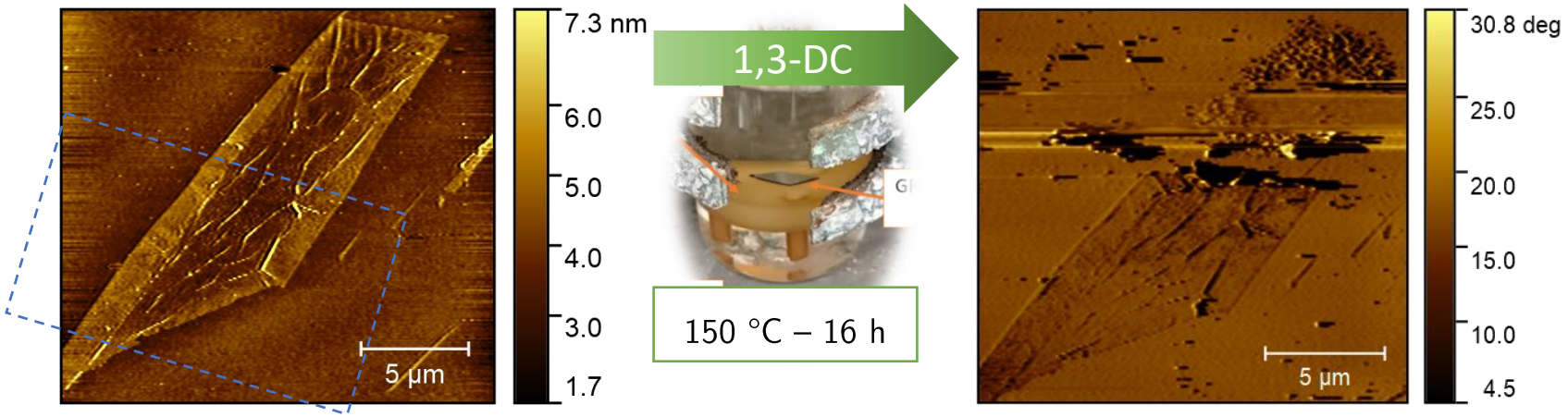


1,3-DC



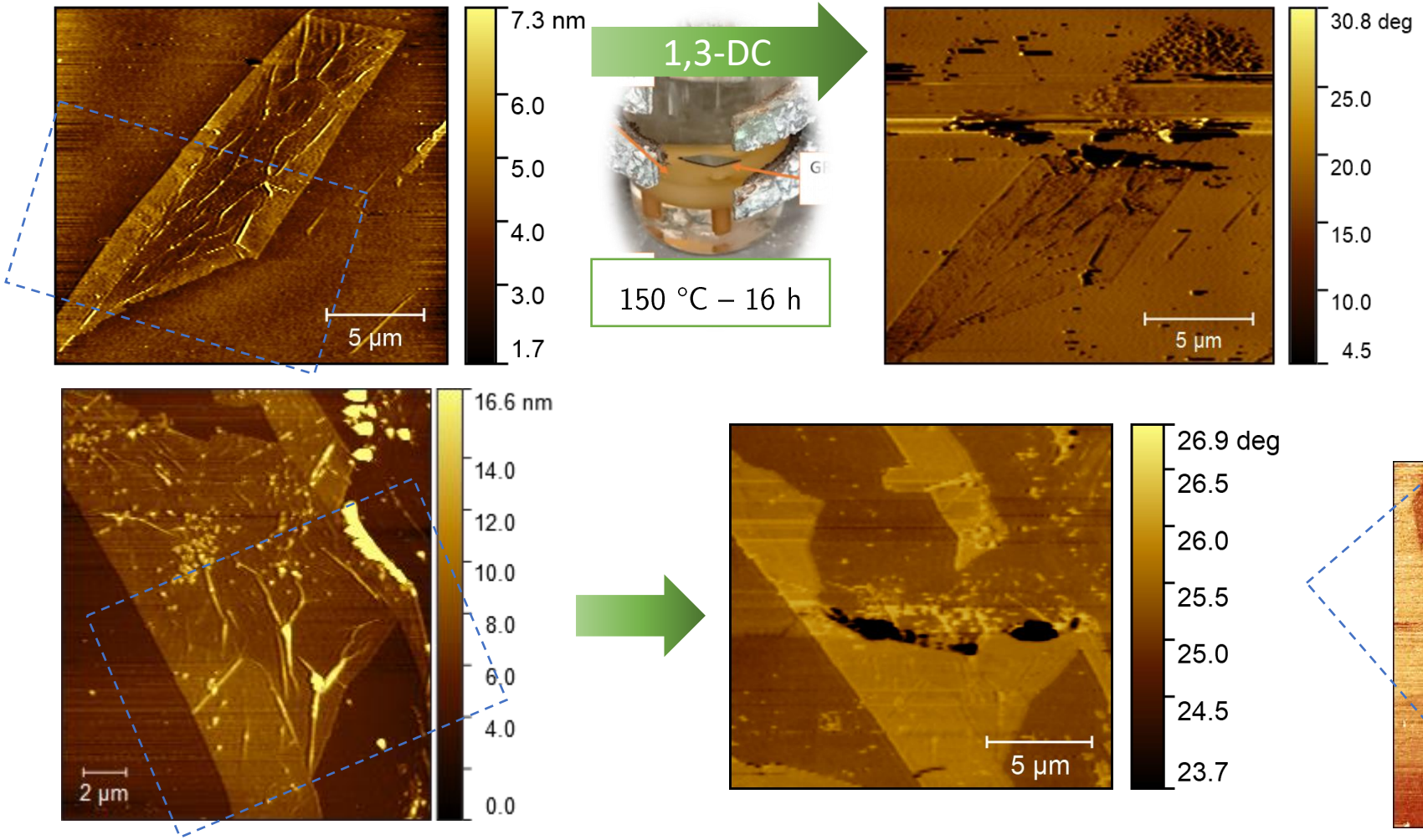
150 °C – 16 h

AFM OF FUNCTIONALIZED GRAPHENE

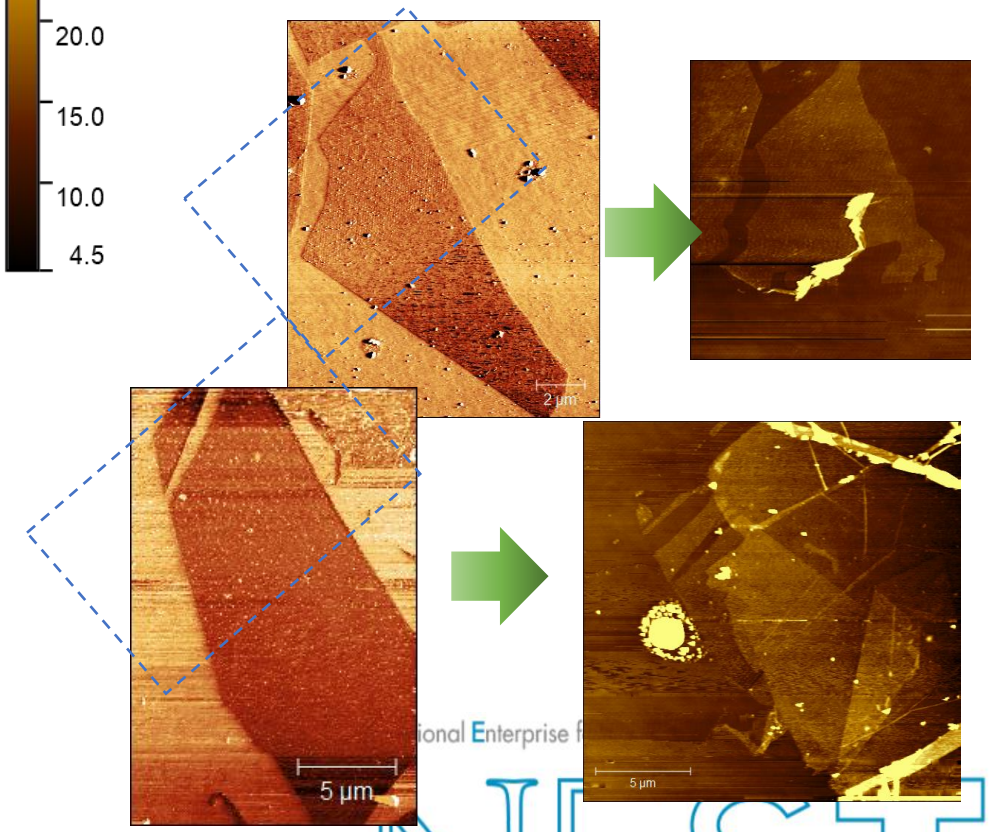


ADHESION ENHANCEMENT!

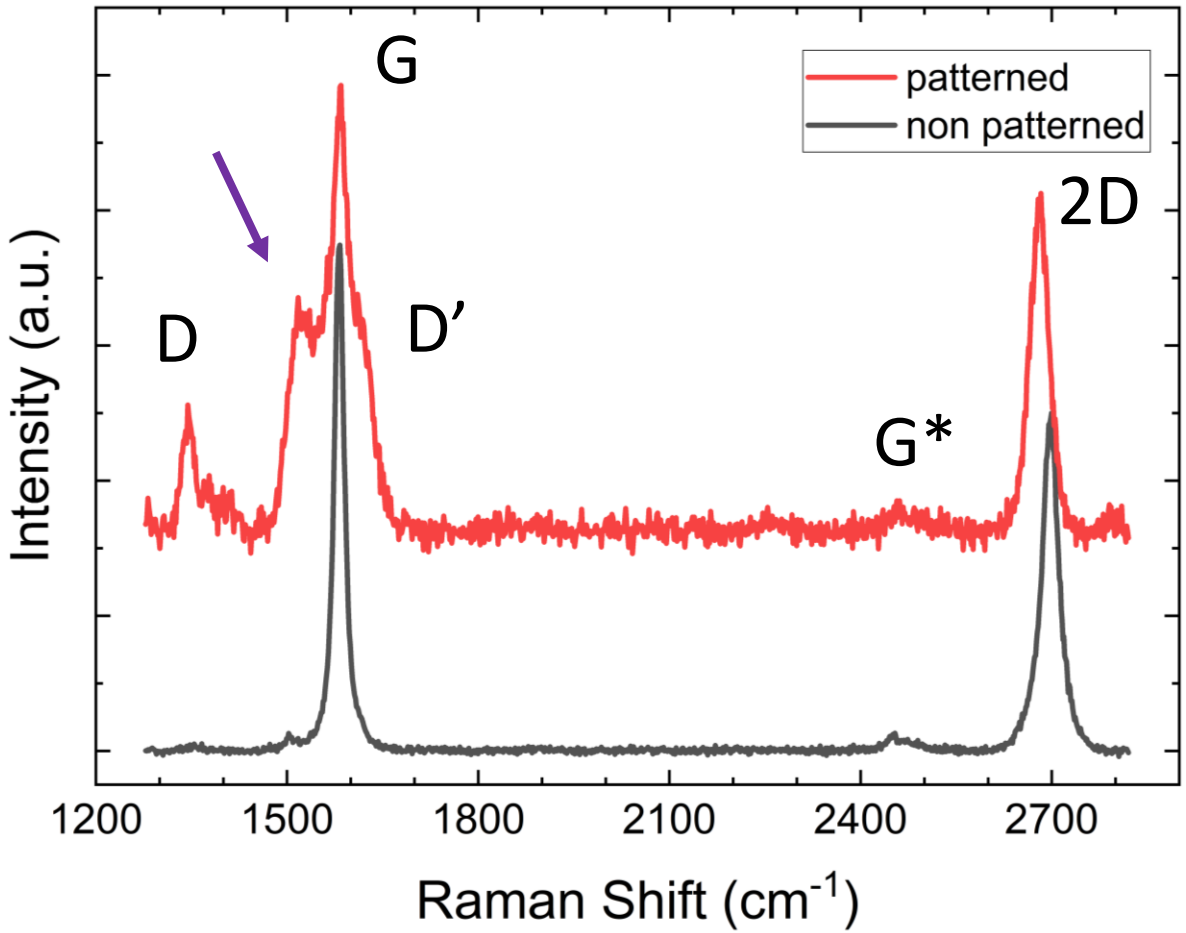
AFM OF FUNCTIONALIZED GRAPHENE



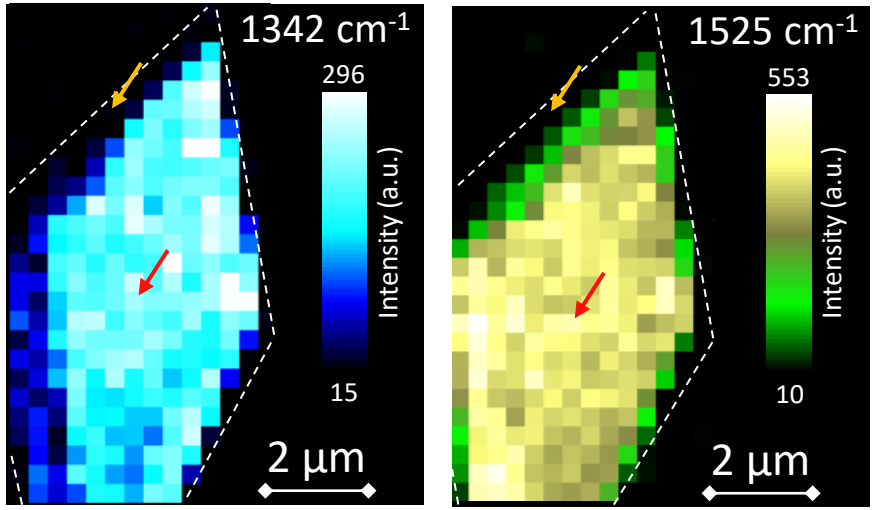
ADHESION ENHANCEMENT!



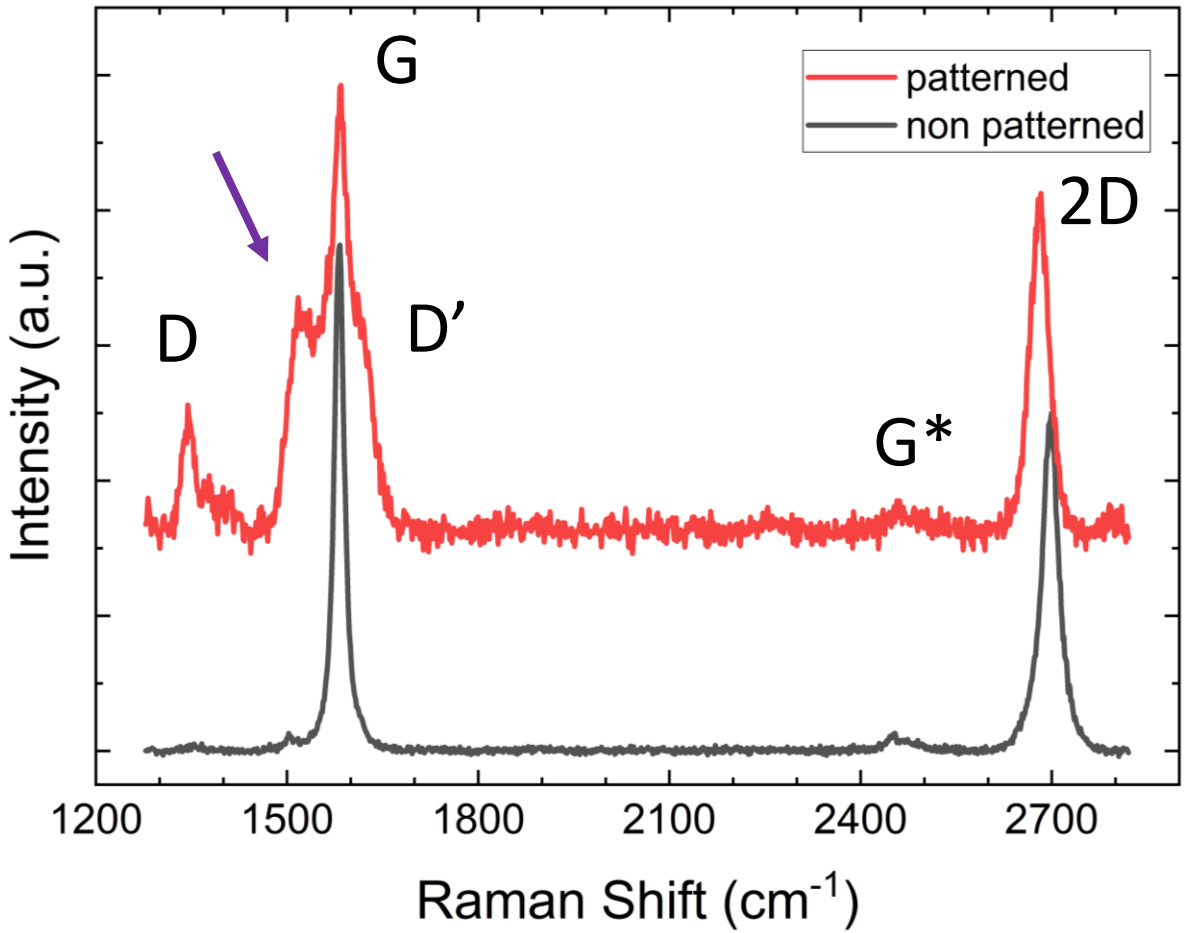
Raman of functionalized graphene



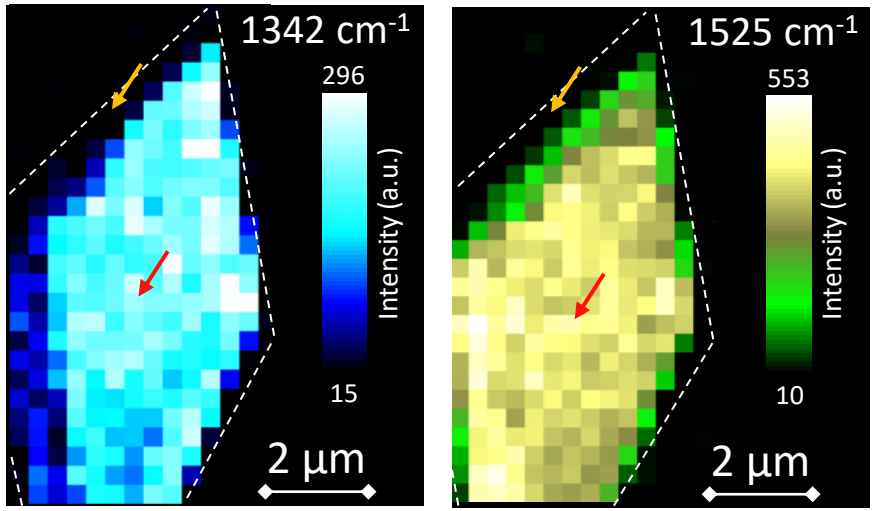
Raman maps



Raman of functionalized graphene



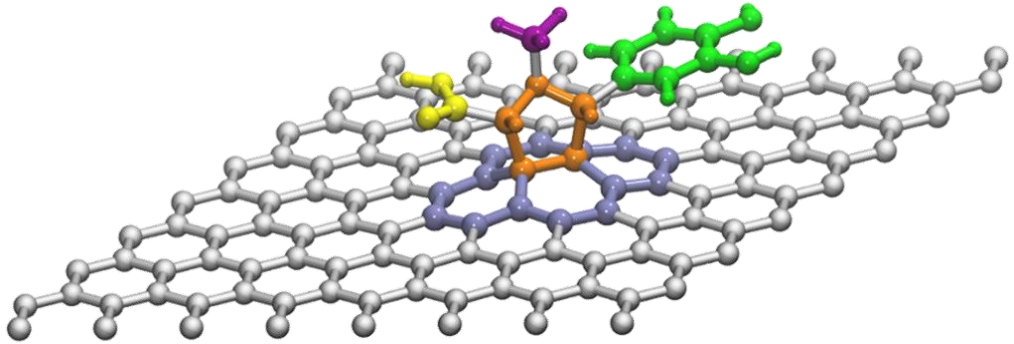
Raman maps

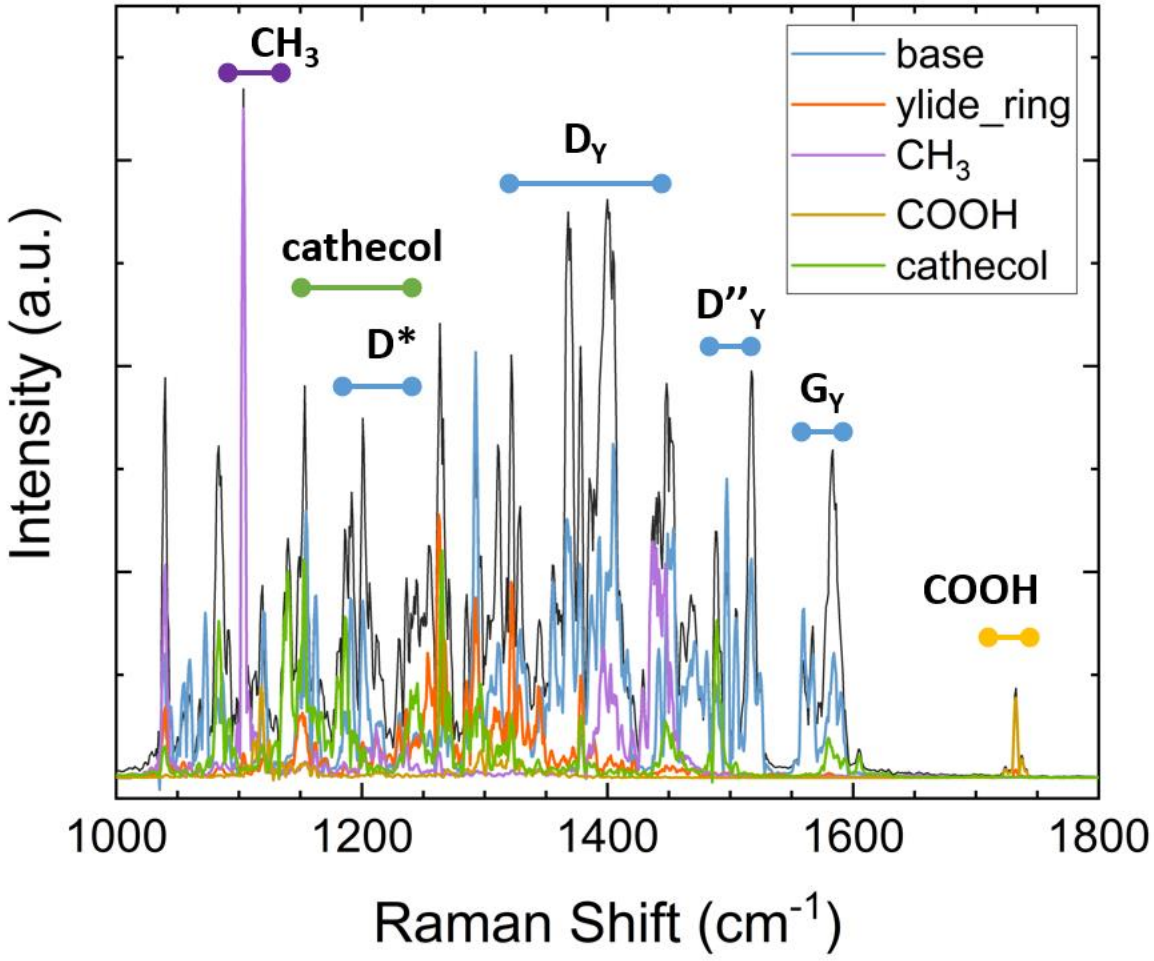


SELECTIVITY!

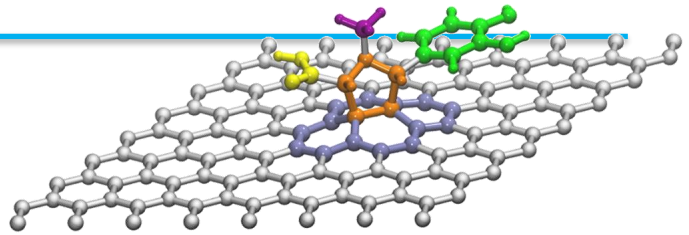
[*L. Bellucci* @ NEST]

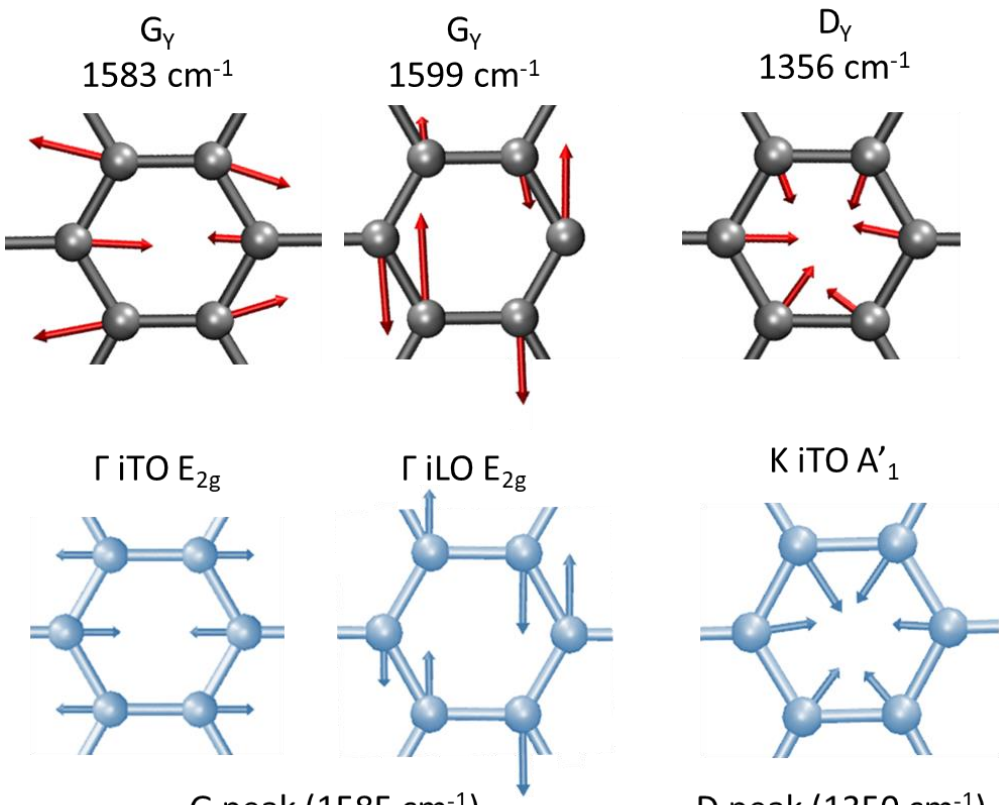
DFT – Power Spectrum

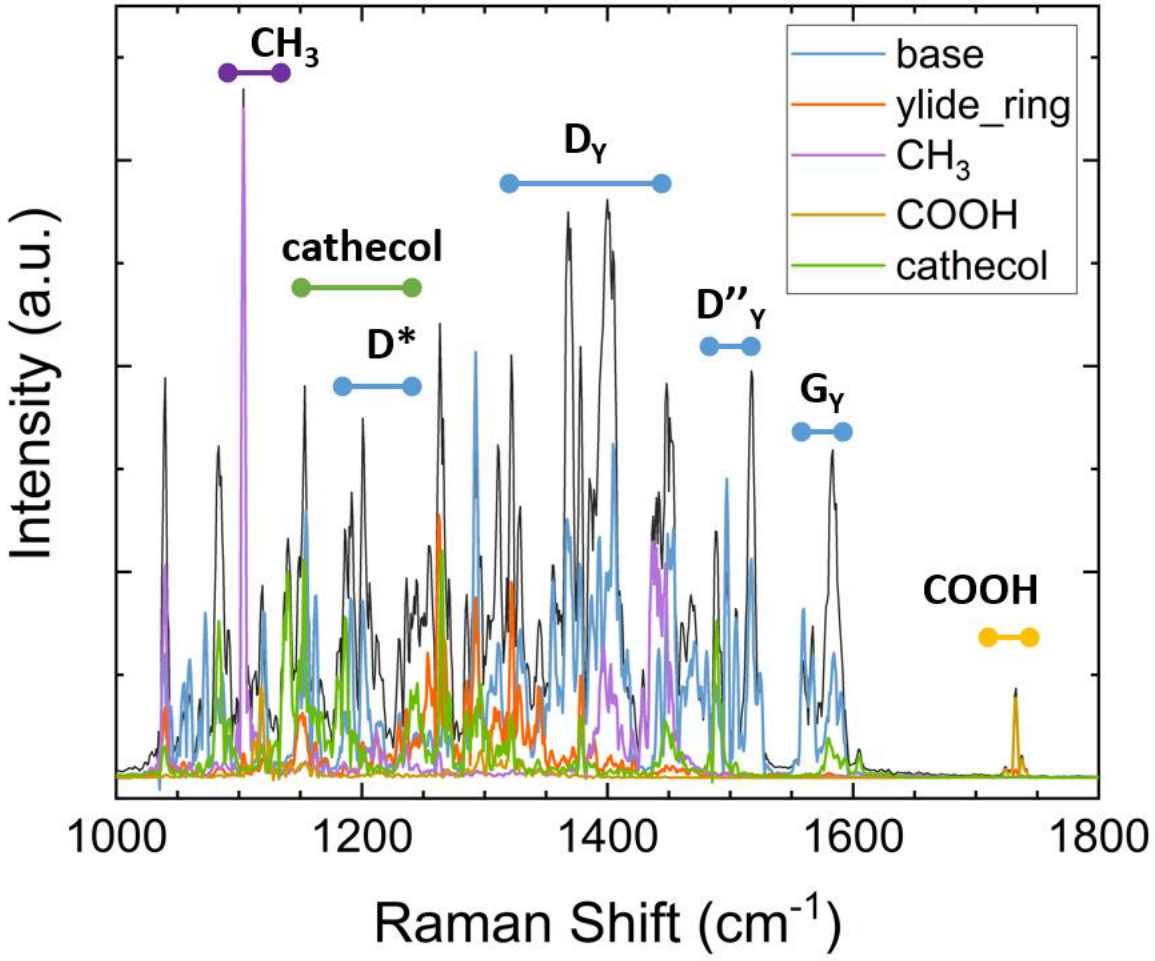




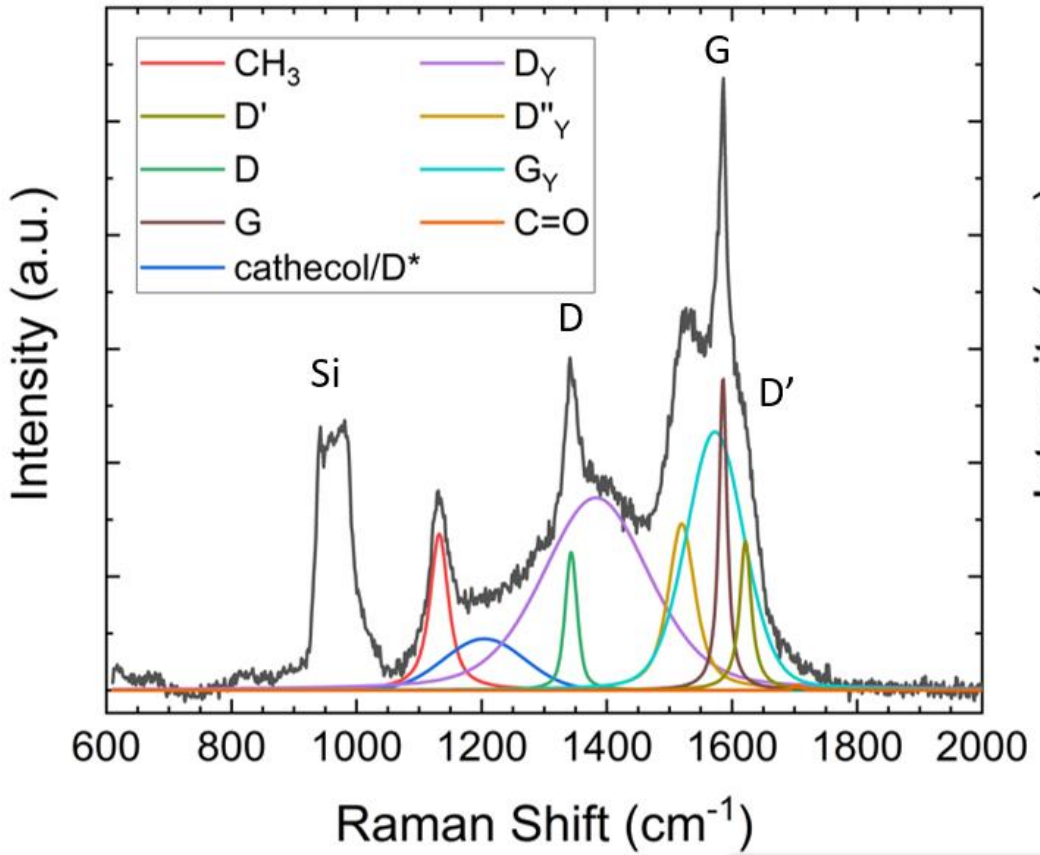
DFT – Power Spectrum

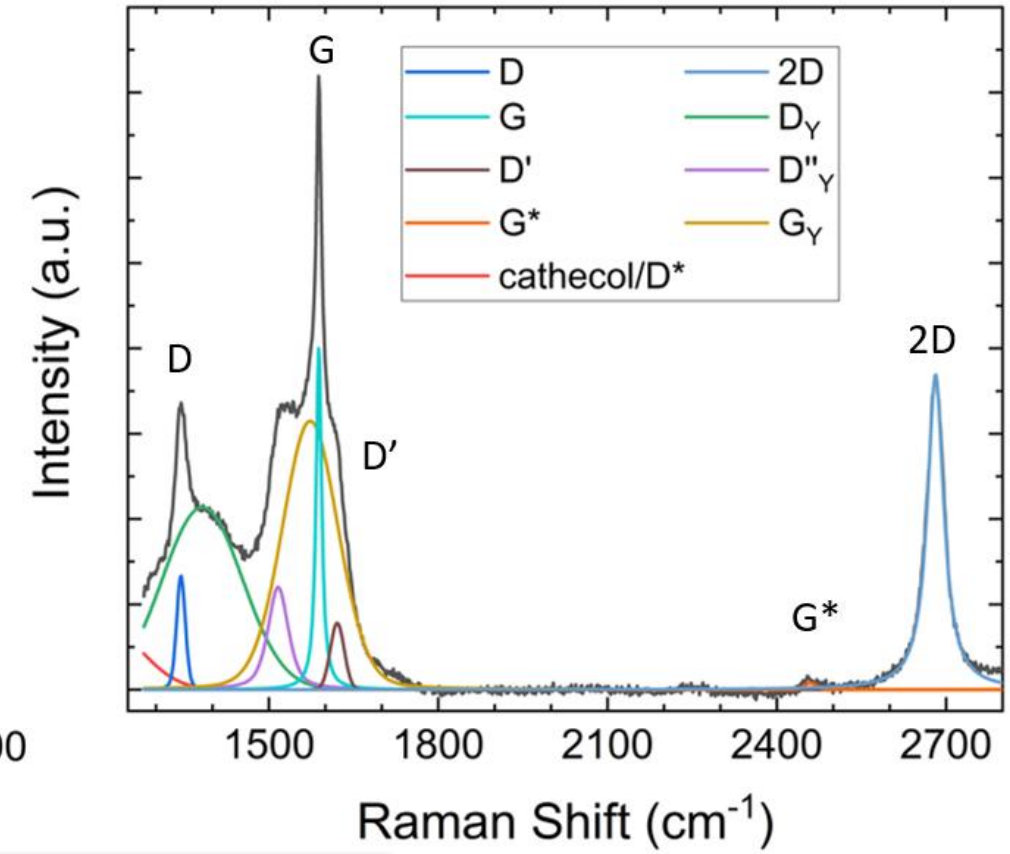






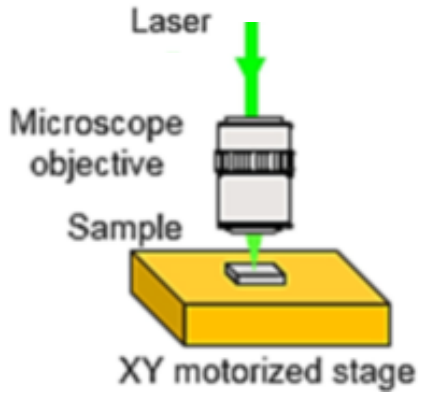
Raman of functionalized graphene

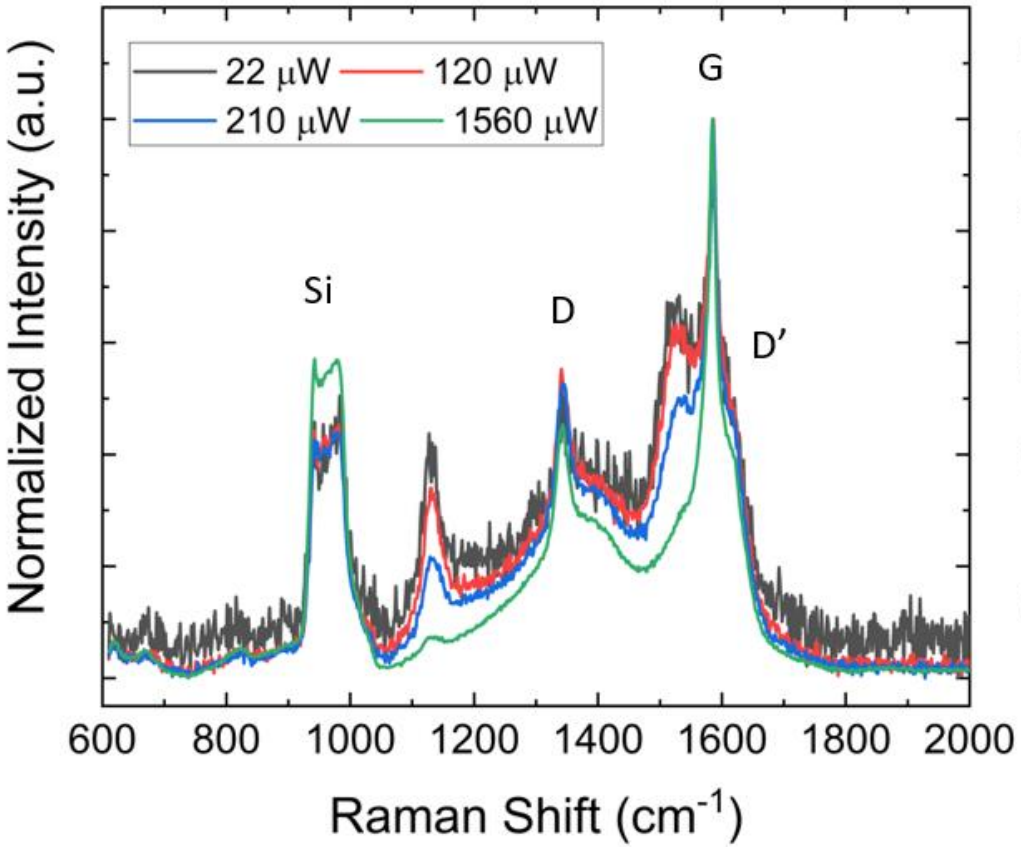


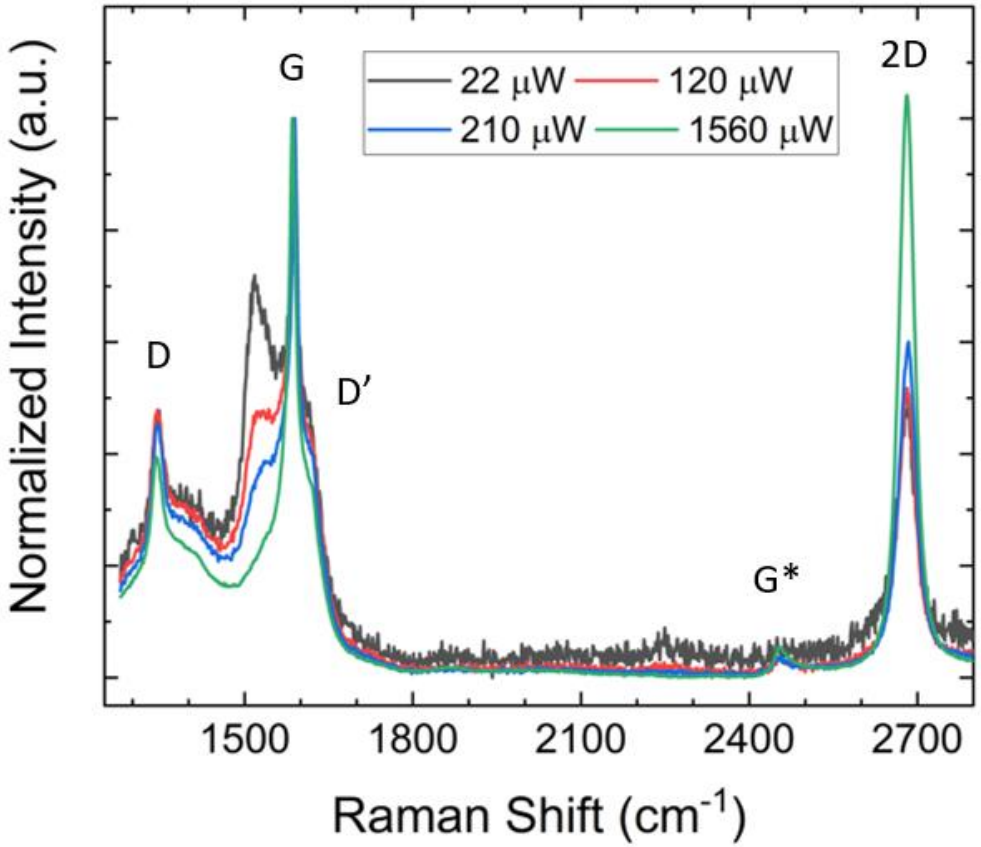


peaks from DFT-PS

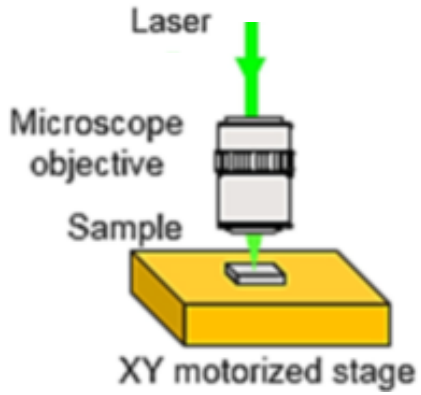
Laser-induced desorption

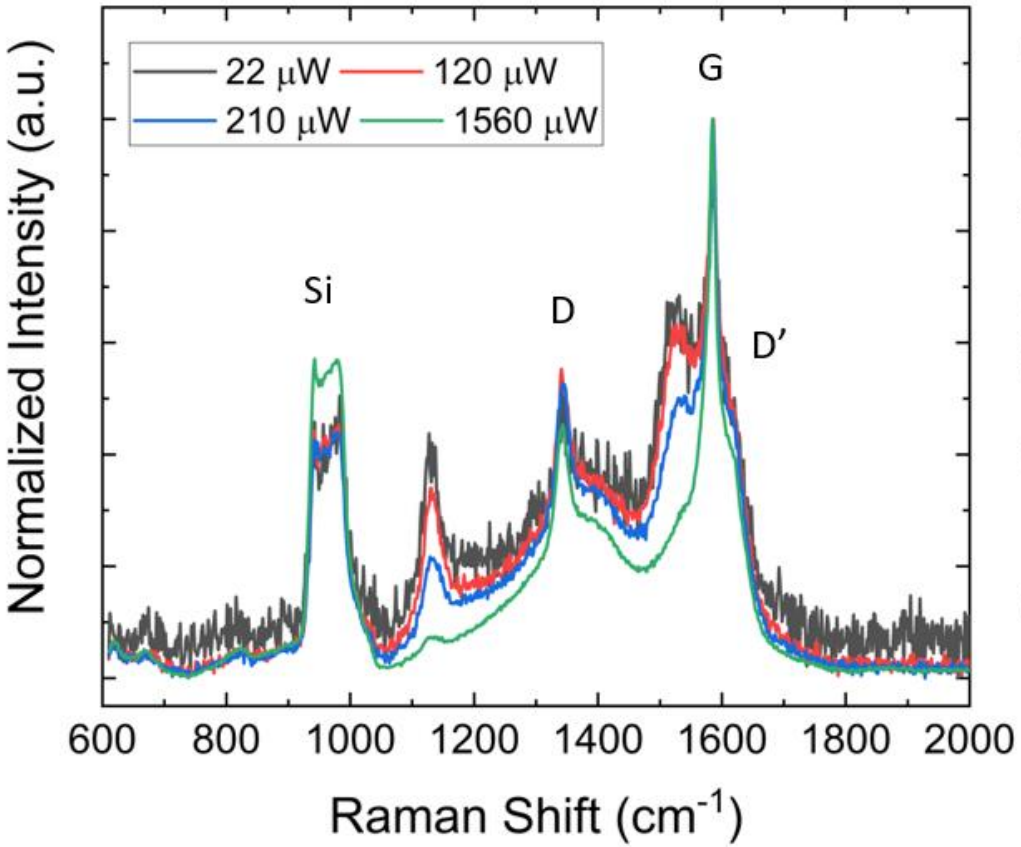


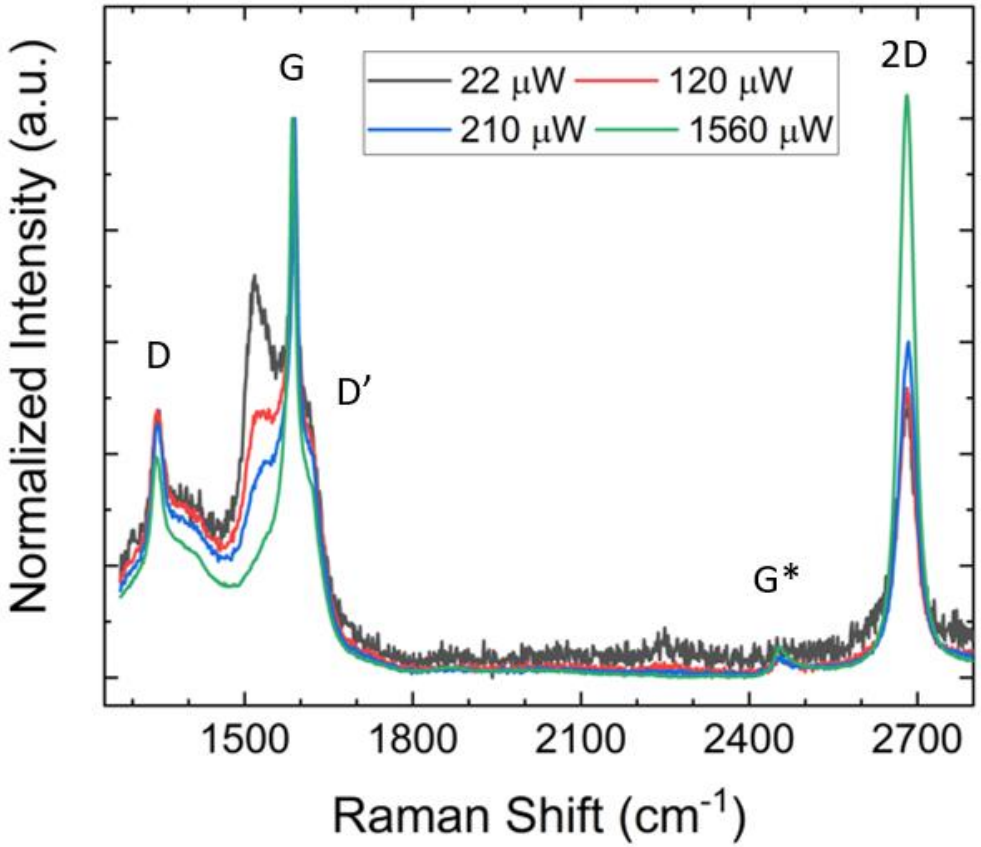




Laser-induced desorption







REVERSIBILITY!

Conclusions – 3)

- Controlled and laterally-resolved ***defects engineering*** via EBI (step size: 100 nm)

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Conclusions – 3)

- Controlled and laterally-resolved ***defects engineering*** via EBI (step size: 100 nm)
- Patterned graphene shows ***enhanced adhesion*** and ***selectivity*** towards 1,3-DC
- DFT simulation of the PS in agreement with the Raman spectra
- Recovery of clean defected graphene indicates ***reversibility*** of the functionalization

Conclusions – 3)

- Cont
- Patt
- DFT
- Reco

arXiv ***preprint*** (under review on JMC C)

Condensed Matter – Materials Science
arXiv.org

Deterministic Covalent Organic Functionalization of Monolayer Graphene with 1,3-Dipolar Cycloaddition Via High Resolution Surface Engineering

Luca Basta[1]*, Federica Bianco[1], Aldo Moscardini[1], Filippo Fabbri[1], Luca Bellucci[1], Valentina Tozzini[1], Stefan Heun[1], Stefano Veronesi[1]‡

Abstract
Spatially-resolved organic functionalization of monolayer graphene is successfully achieved by combining low-energy electron beam irradiation with 1,3-dipolar cycloaddition of azomethine ylide. Indeed, the modification of the graphene honeycomb lattice obtained via electron beam irradiation yields to a local increase of the graphene chemical reactivity. As a consequence, thanks to the high-spatially resolved generation of structural defects (~ 100 nm), chemical reactivity patterning has been designed over the graphene surface in a well-controlled way. Atomic force microscopy and Raman spectroscopy allow to investigate the two-dimensional spatial distribution of the structural defects and the new features that arise from the 1,3-dipolar cycloaddition, confirming the spatial

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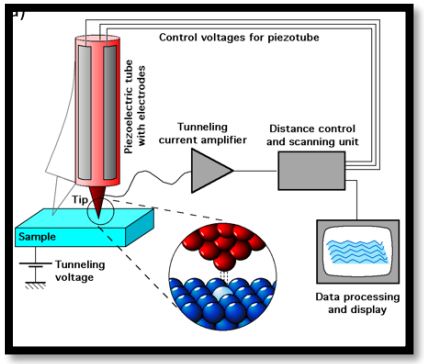
Experimental Results

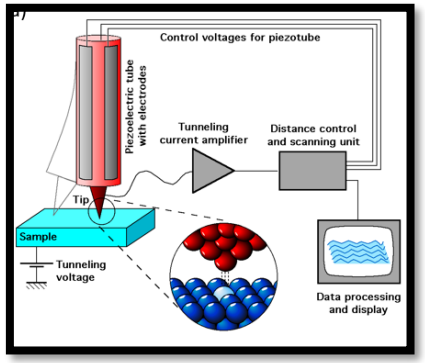
1) Functionalization of dispersed GNS and rGO → ***defects*** for chemical reactivity
2) ML graphene flakes → ***defects engineering*** via EBI
3) Patterned ML graphene flakes → ***deterministic*** functionalization
4) Epitaxial graphene → functionalization and patterning of ***higher quality graphene***

Epitaxial graphene

EG on SiC allows for direct STM and STS measurements → atomic resolution



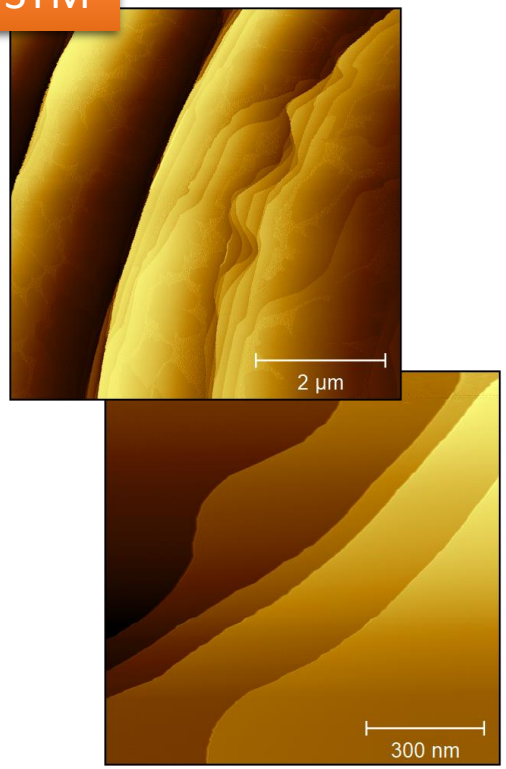
Epitaxial graphene

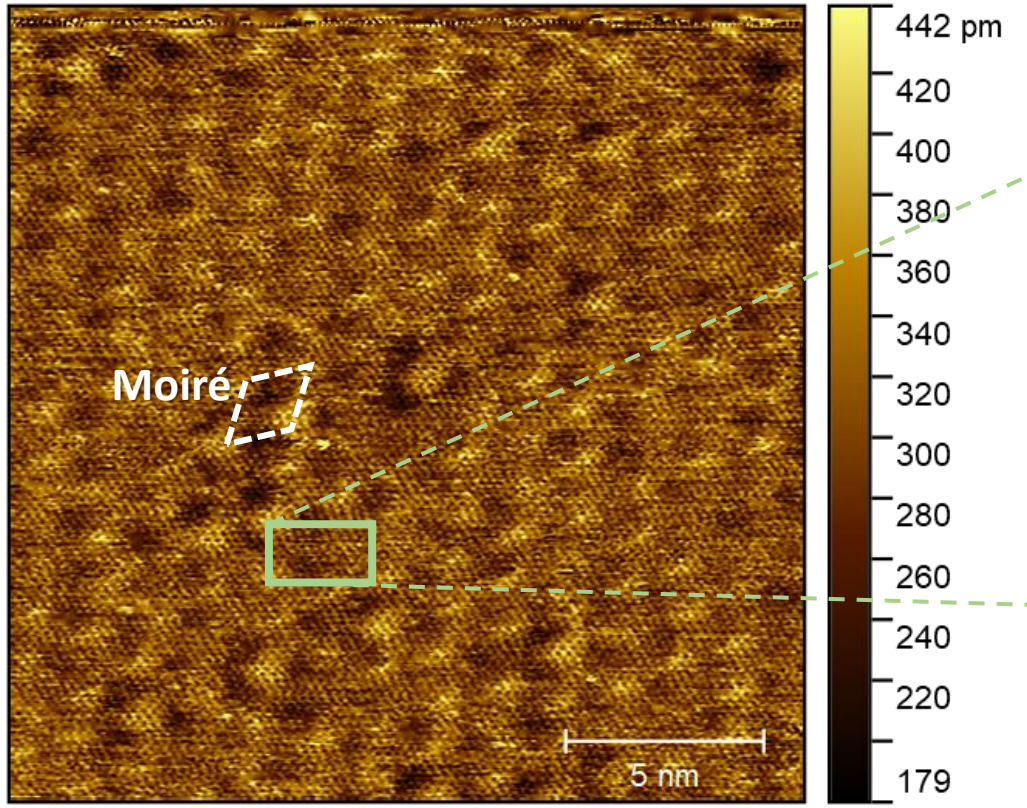


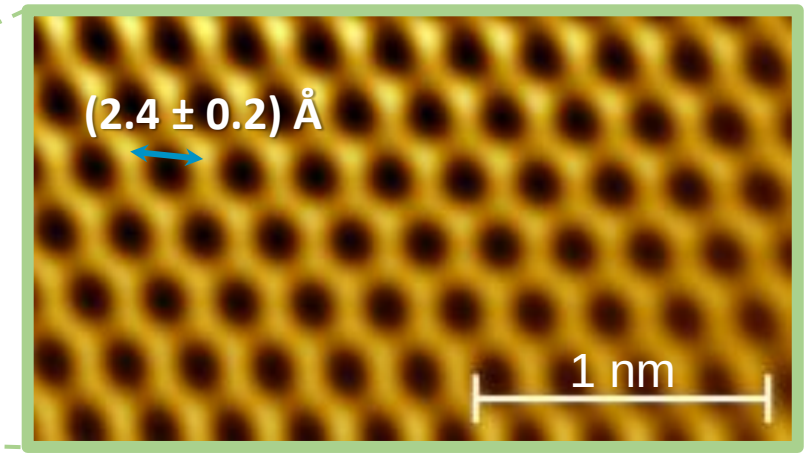
EG on SiC allows for direct STM and STS measurements → atomic resolution

MLEG: 60 - 80 %

STM







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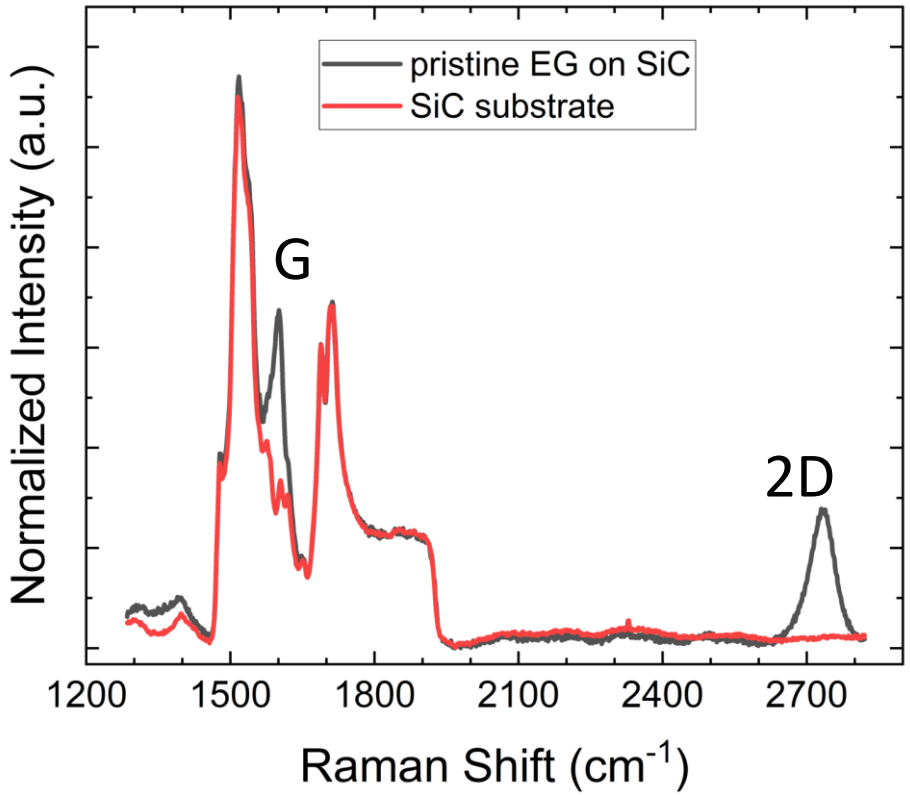
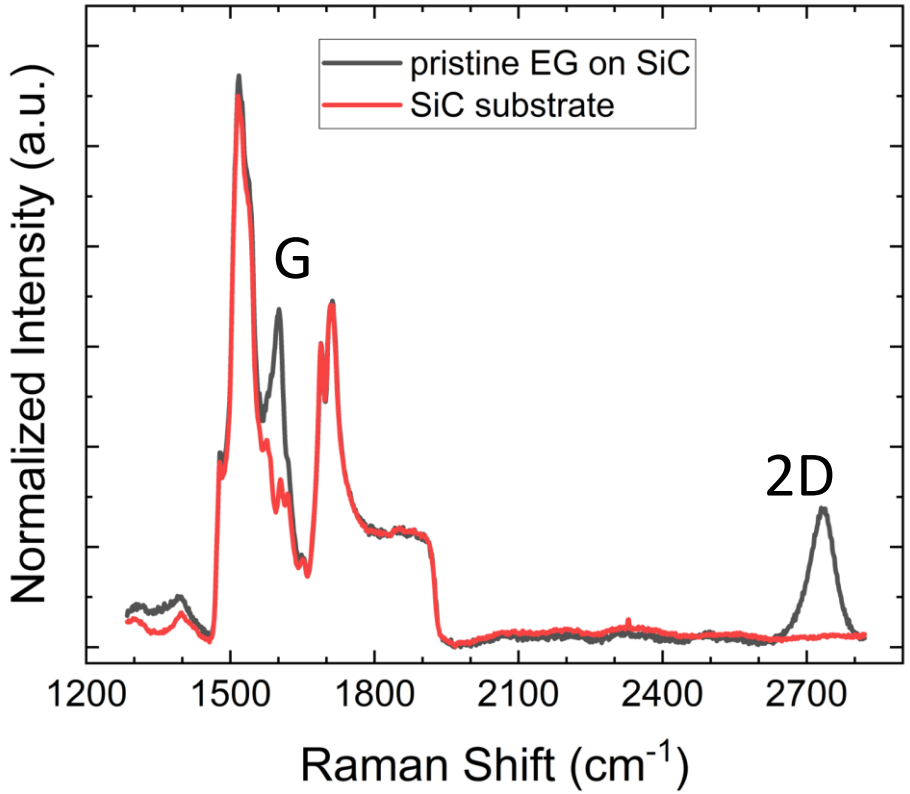
Raman of pristine EG

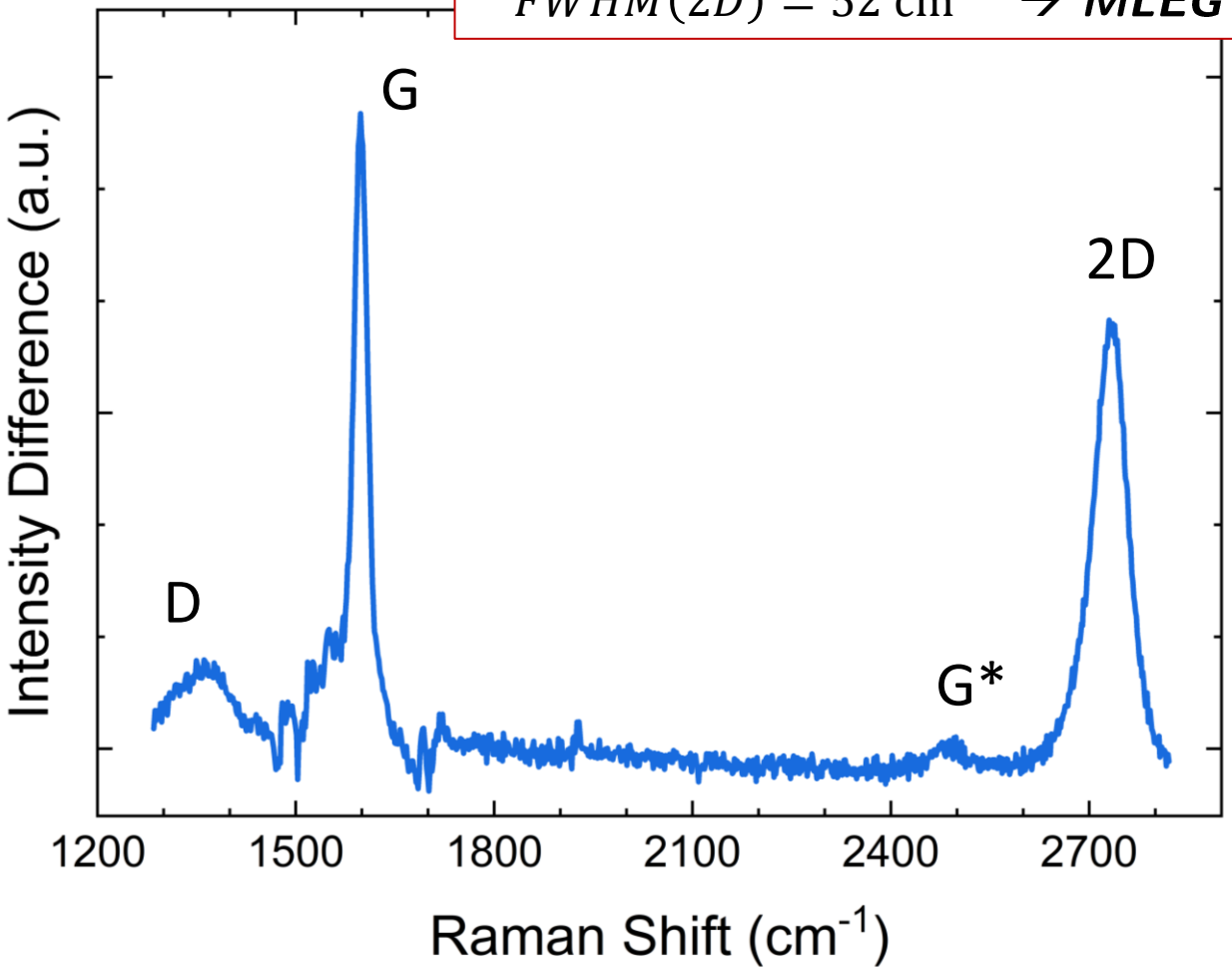


Raman of pristine EG

$I(D)/I(G) \sim 0.1$

$FWHM(2D) = 52\ \mathrm{cm}^{-1}$ → ***MLEG***



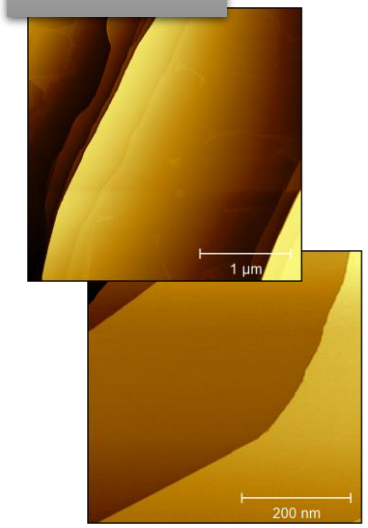


STM of functionalized EG

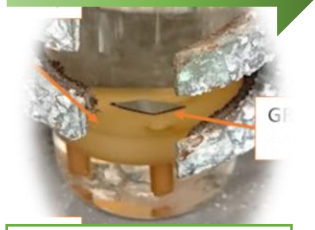
New structures!

Coverage: 5% – 14%

Pristine

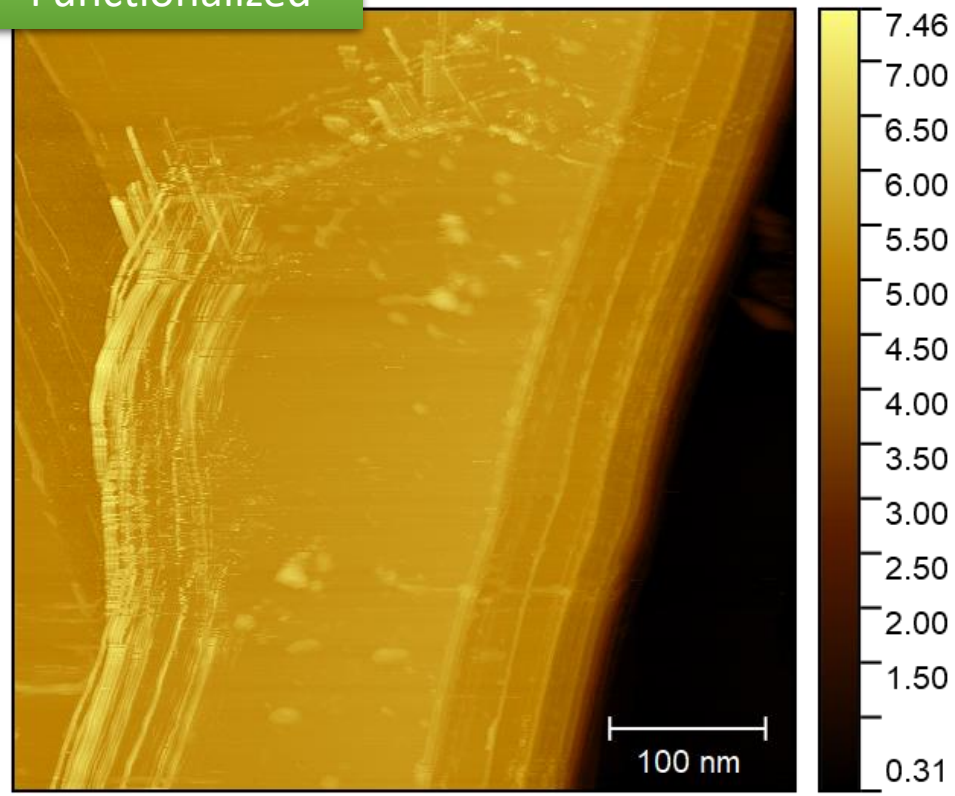


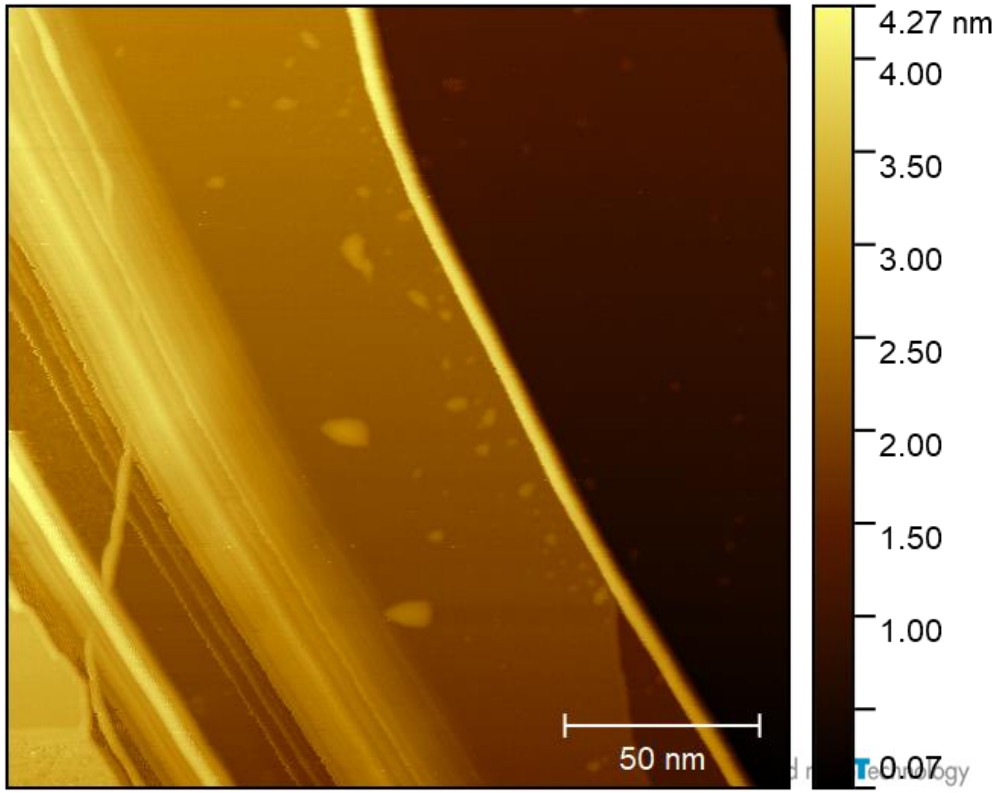
1,3-DC



150 °C – days

Functionalized

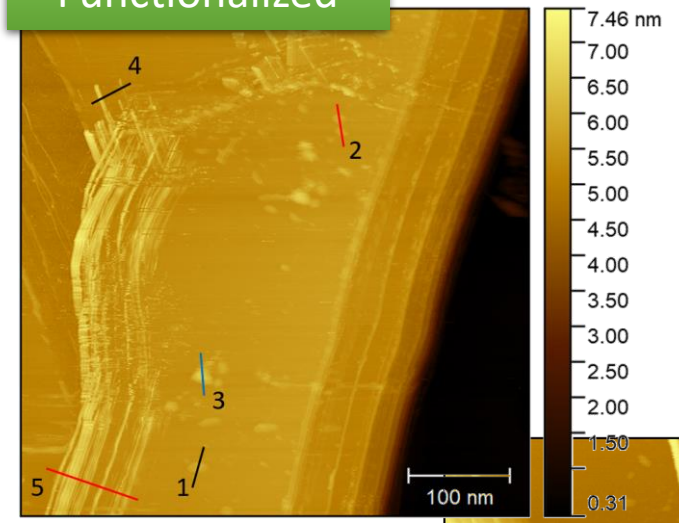


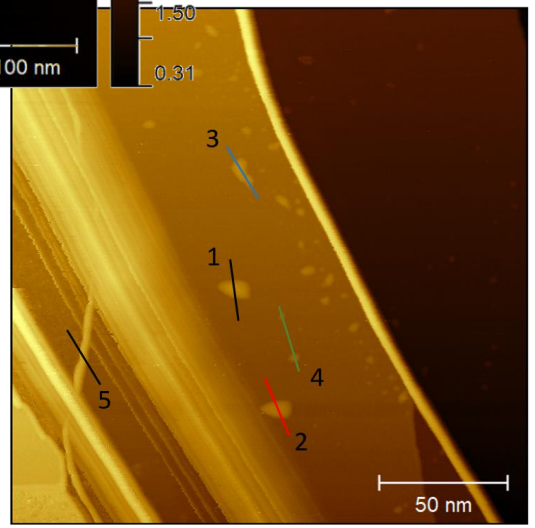


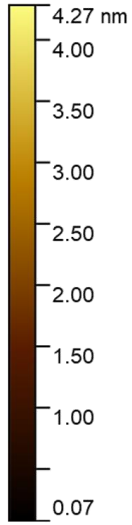
STM OF FUNCTIONALIZED EG

New structures!

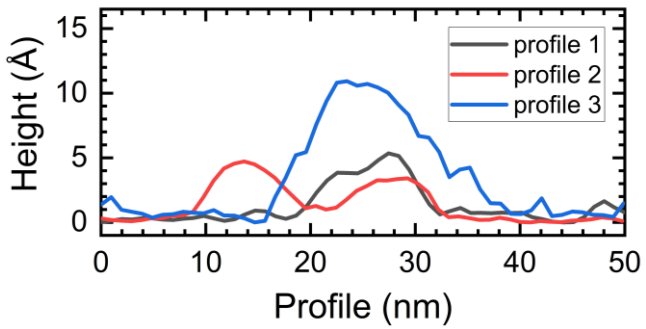
Functionalized



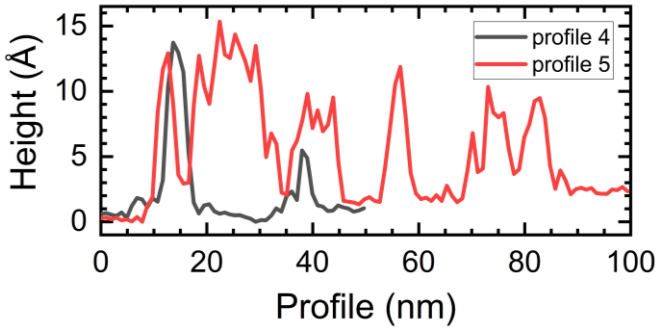




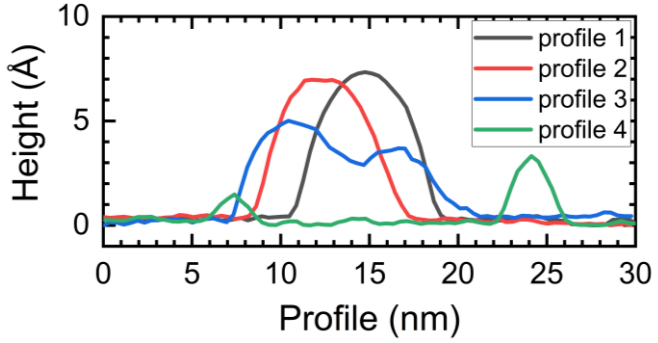
clusters



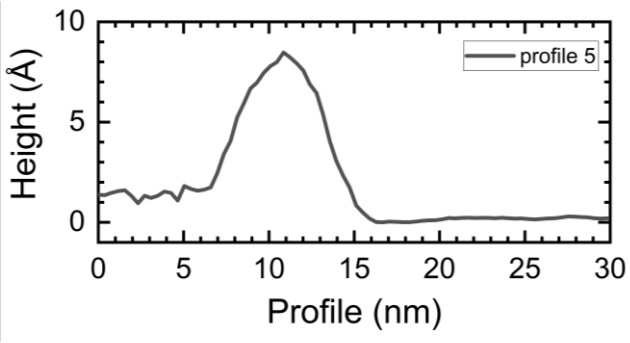
filaments



clusters



filaments

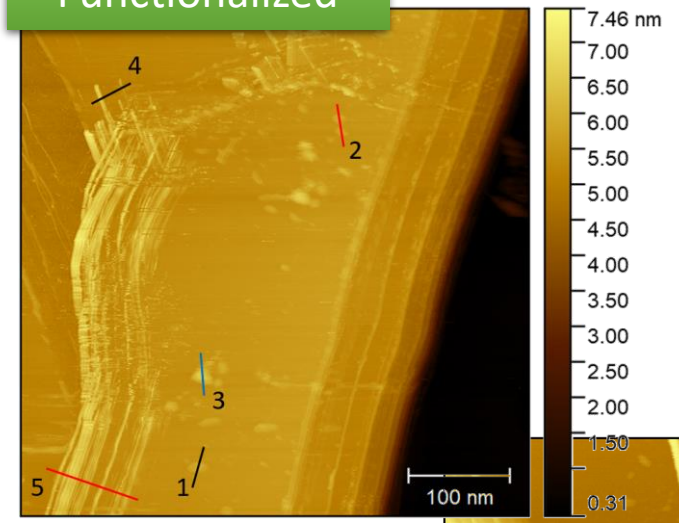


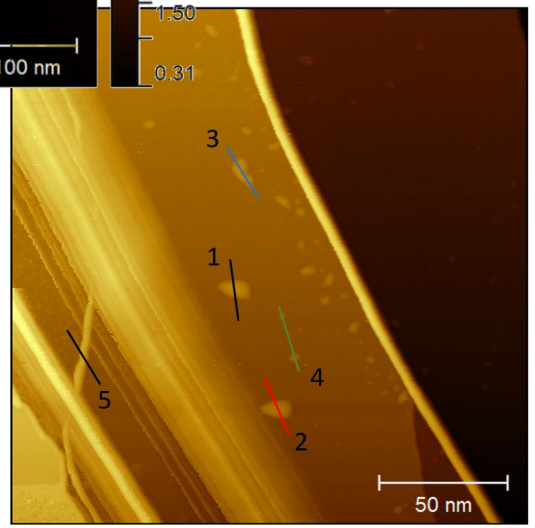
STM OF FUNCTIONALIZED EG

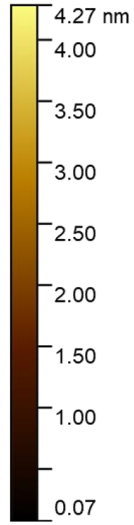
New structures:

- clusters → 2 – 10 Å
- filaments → 5 – 15 Å

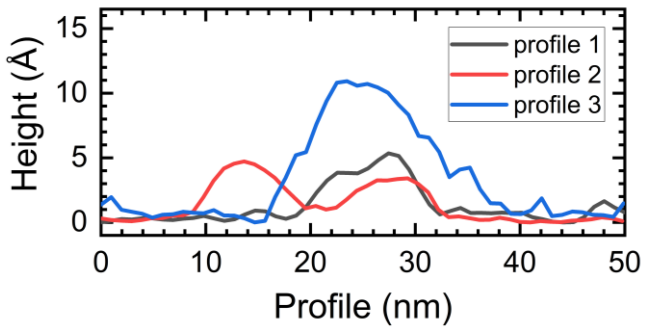
Functionalized



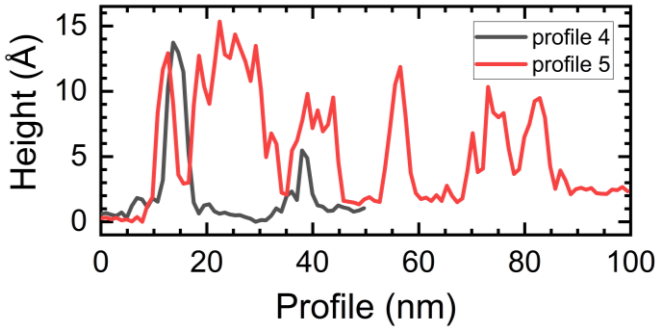




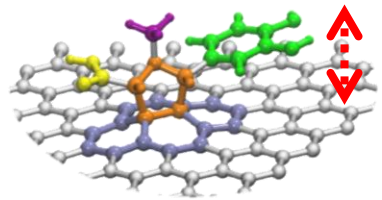
clusters



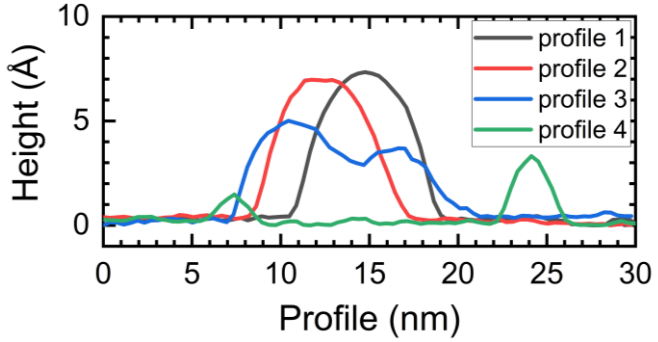
filaments



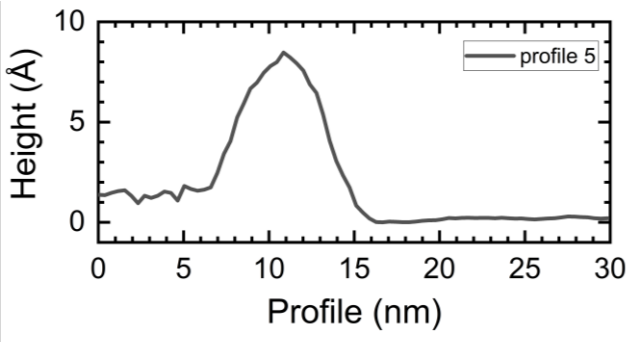
5 Å



clusters



filaments

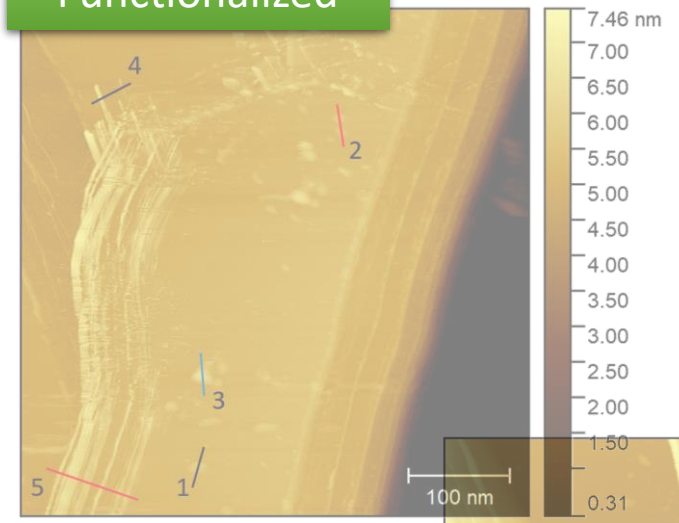


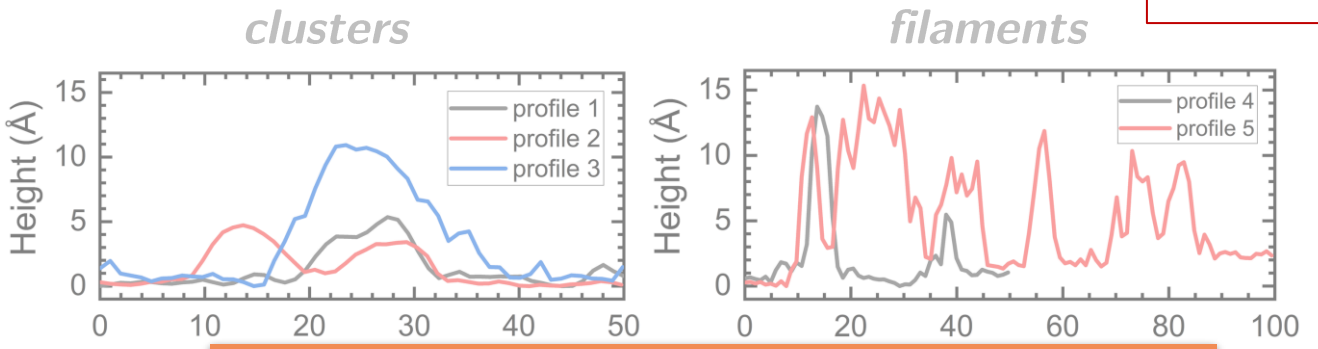
STM OF FUNCTIONALIZED EG

New structures:

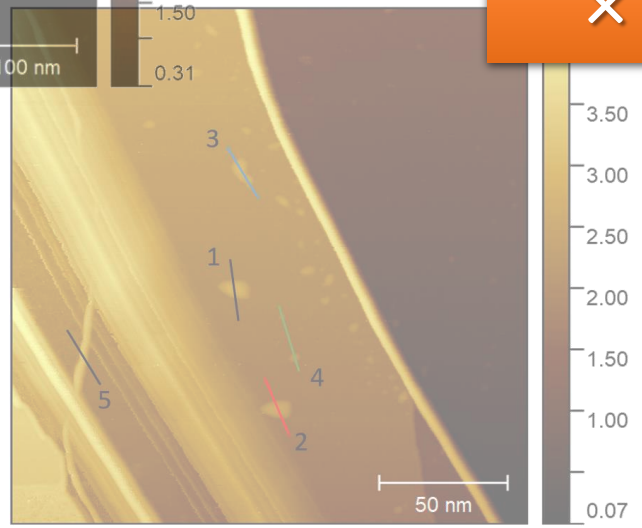
- clusters → 2 – 10 Å
- filaments → 5 – 15 Å

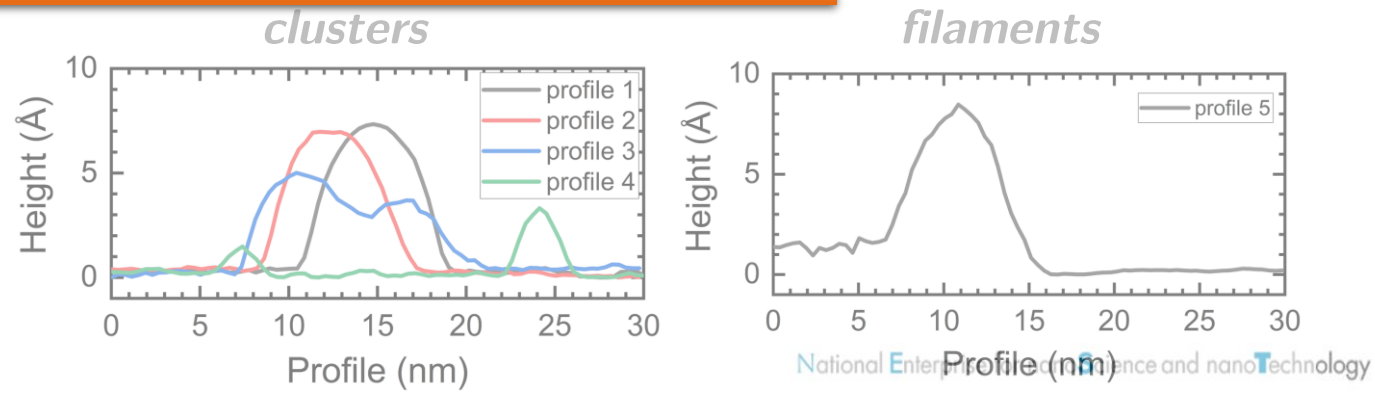
Functionalized





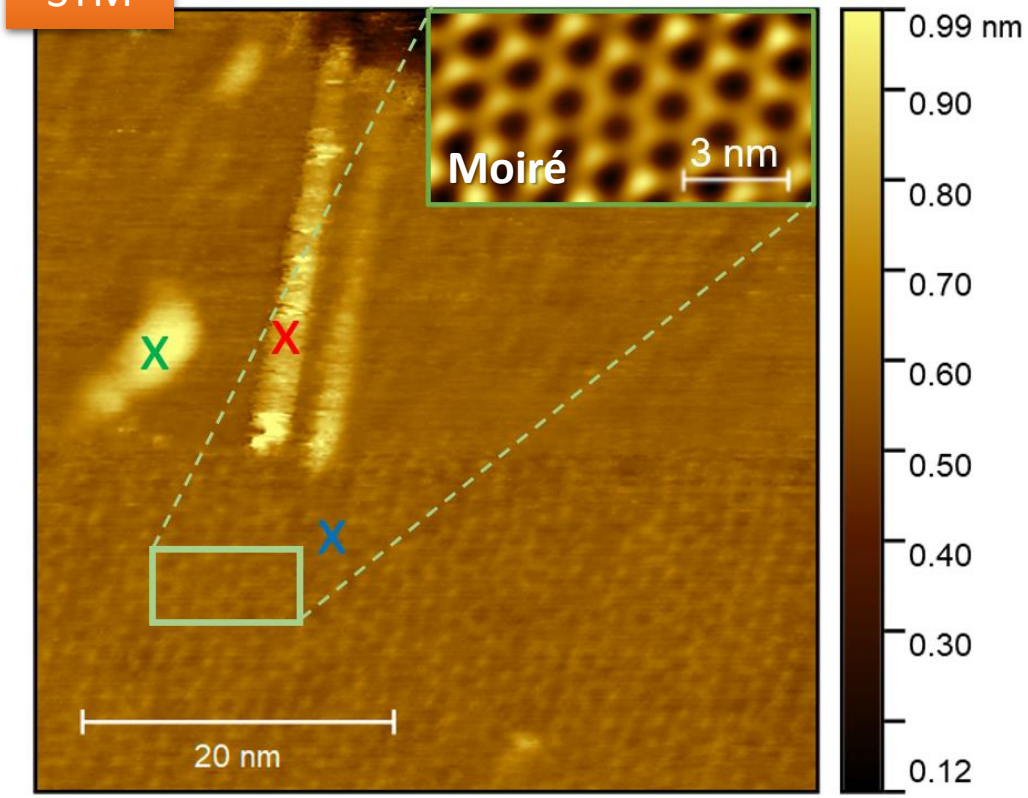
× NO atomic resolution



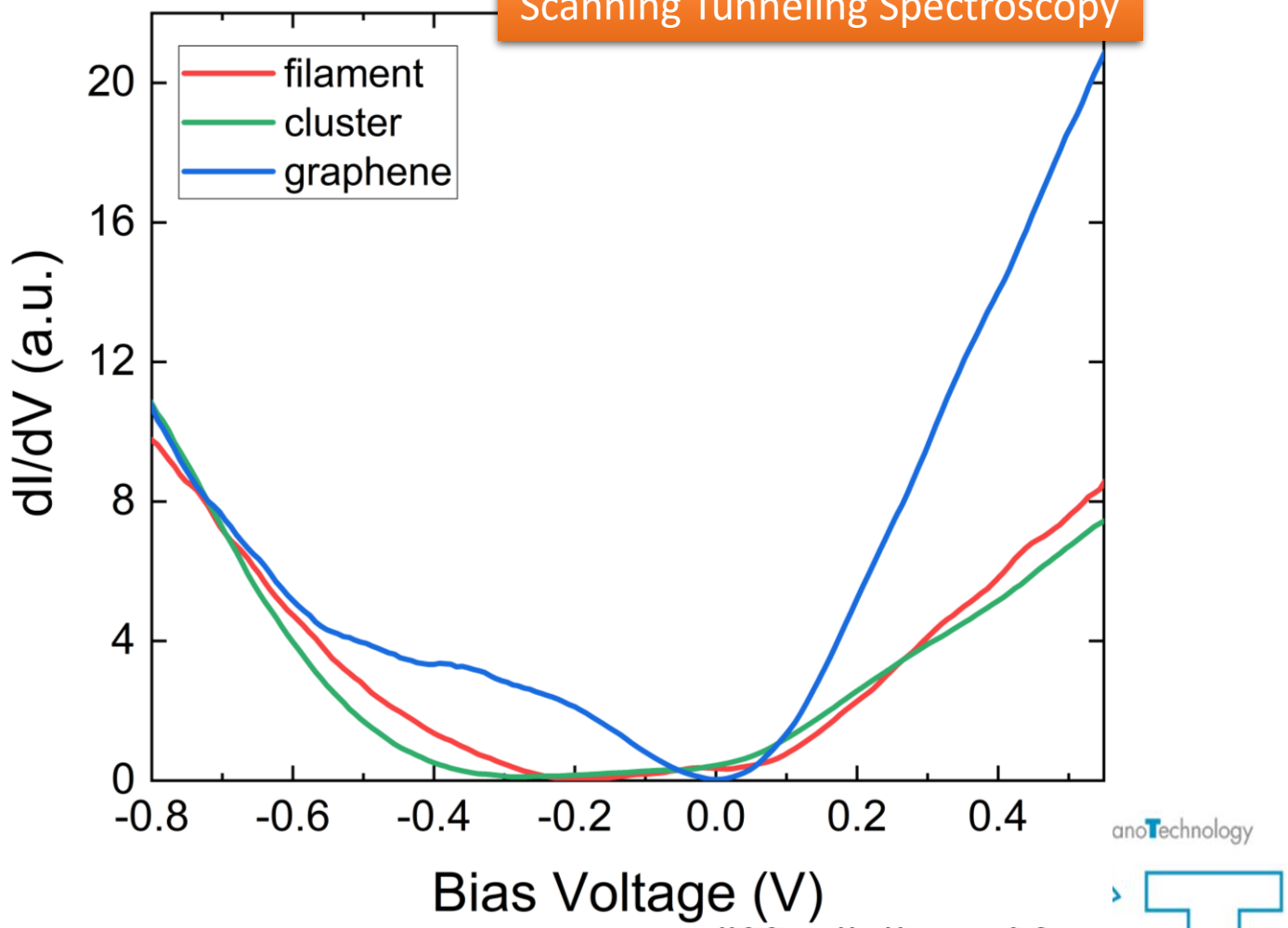


STS of functionalized EG

STM



Scanning Tunneling Spectroscopy



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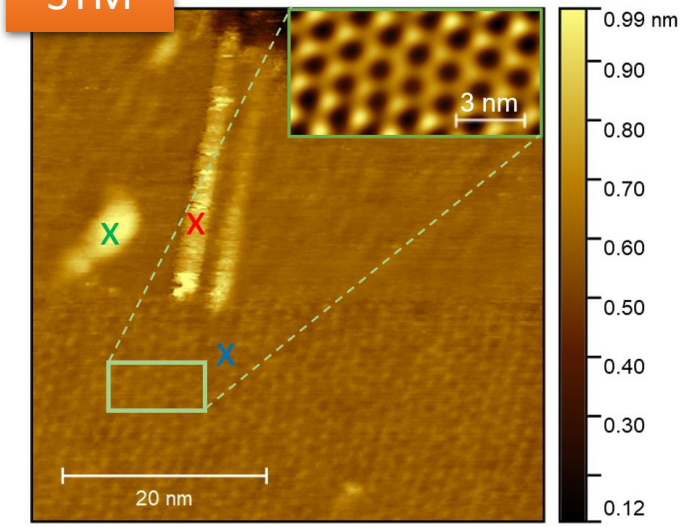
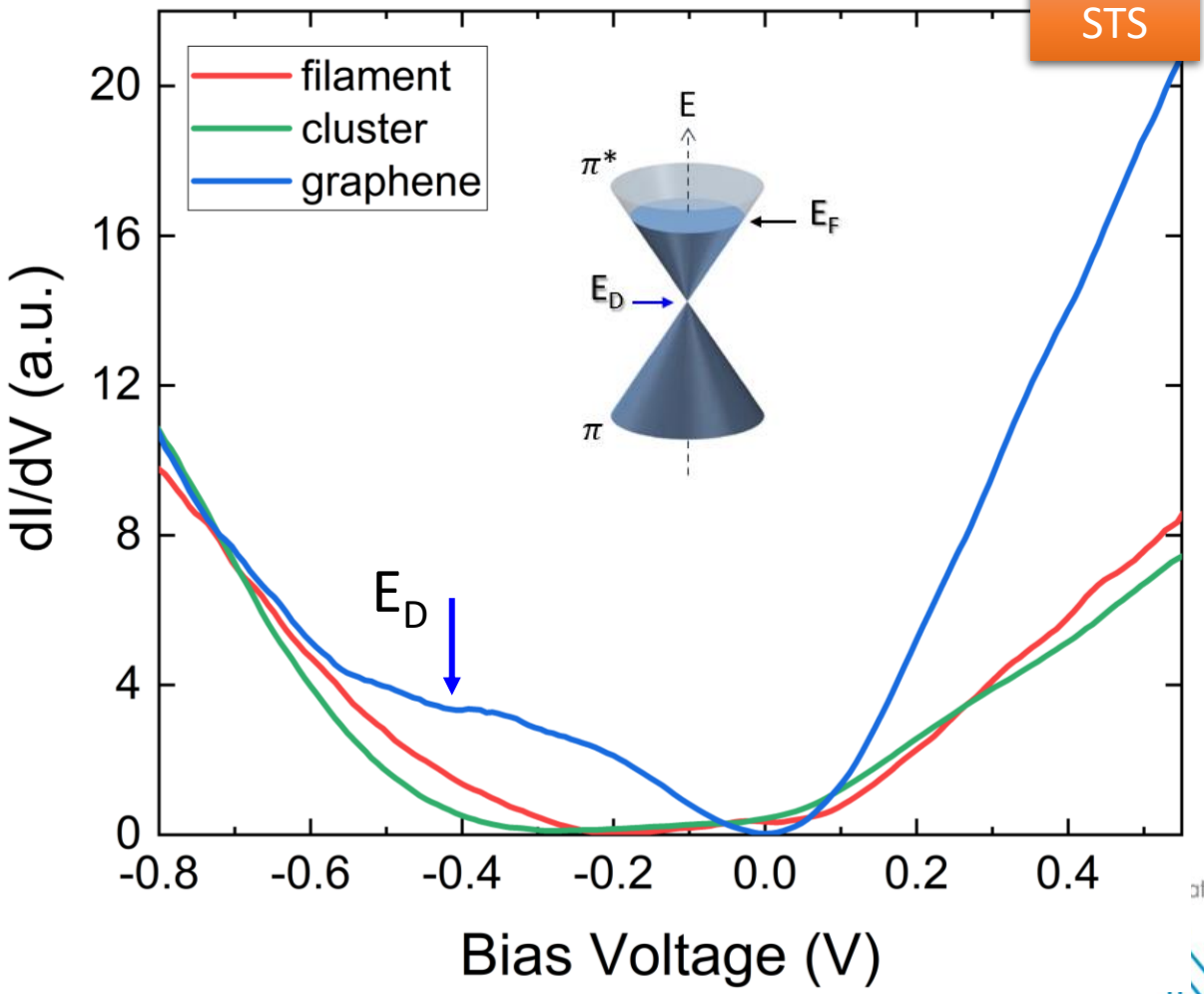
STS OF FUNCTIONALIZED EG

STM



STS



GRAPHENE:

- n-doping (from n-SiC)
- no bandgap

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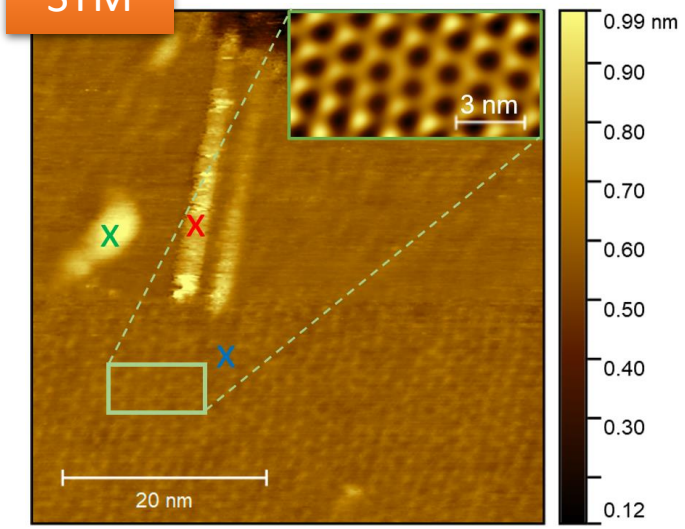
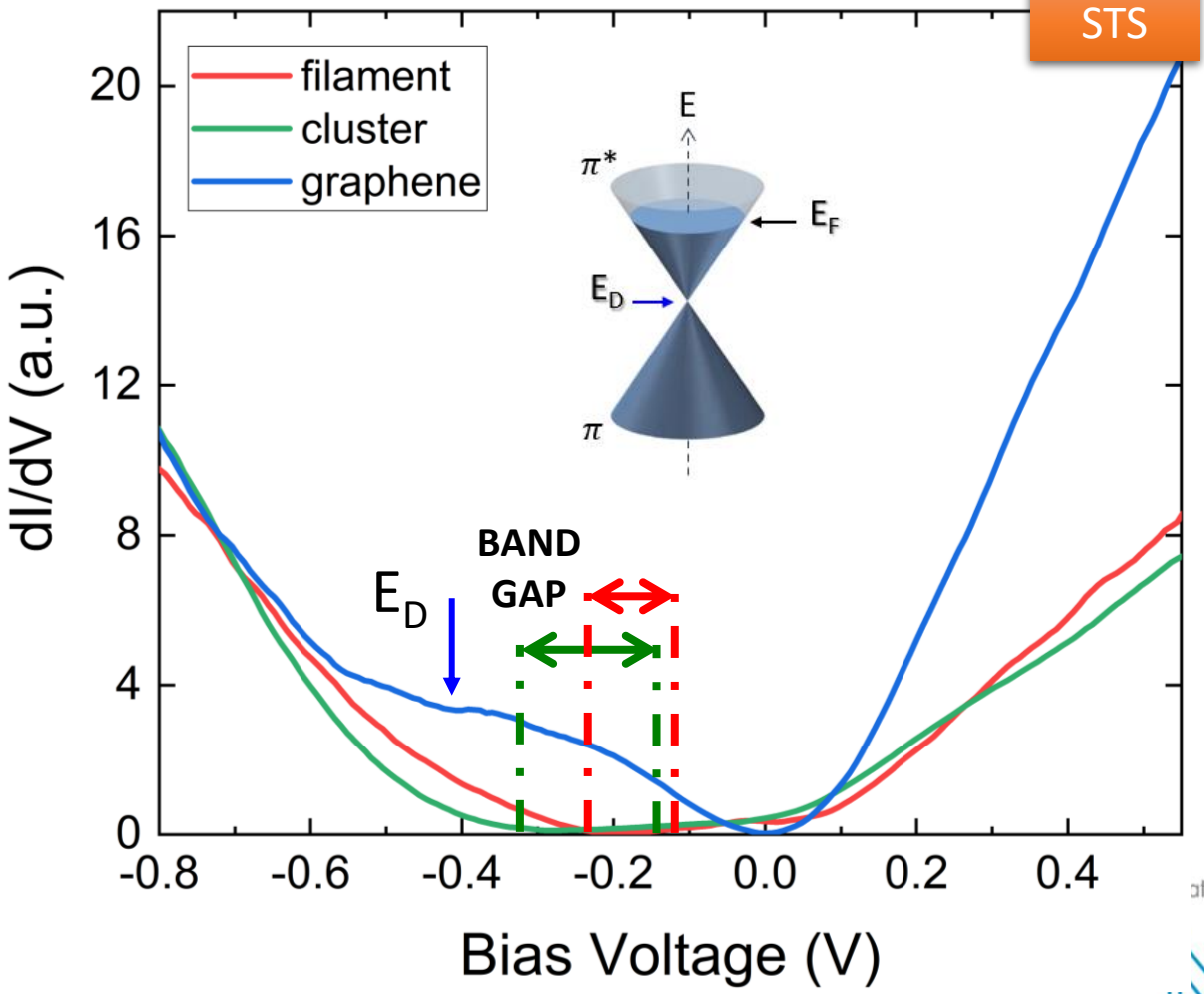
STS OF FUNCTIONALIZED EG

STM



STS



GRAPHENE:

- n-doping (from n-SiC)
- no bandgap

CLUSTER:

- 0.2 eV bandgap

FILAMENT:

- 0.13 eV bandgap

Literature: 0.15 – 0.5 eV

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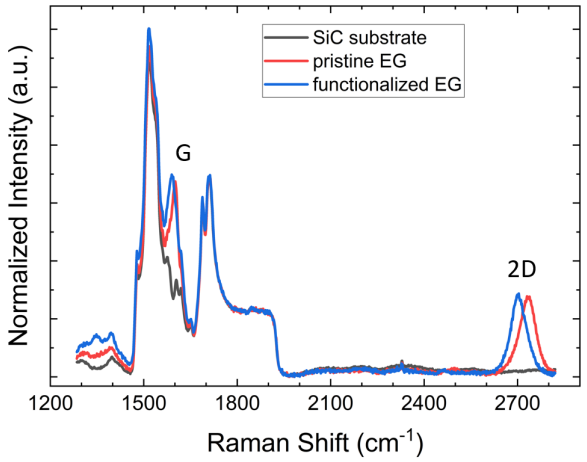
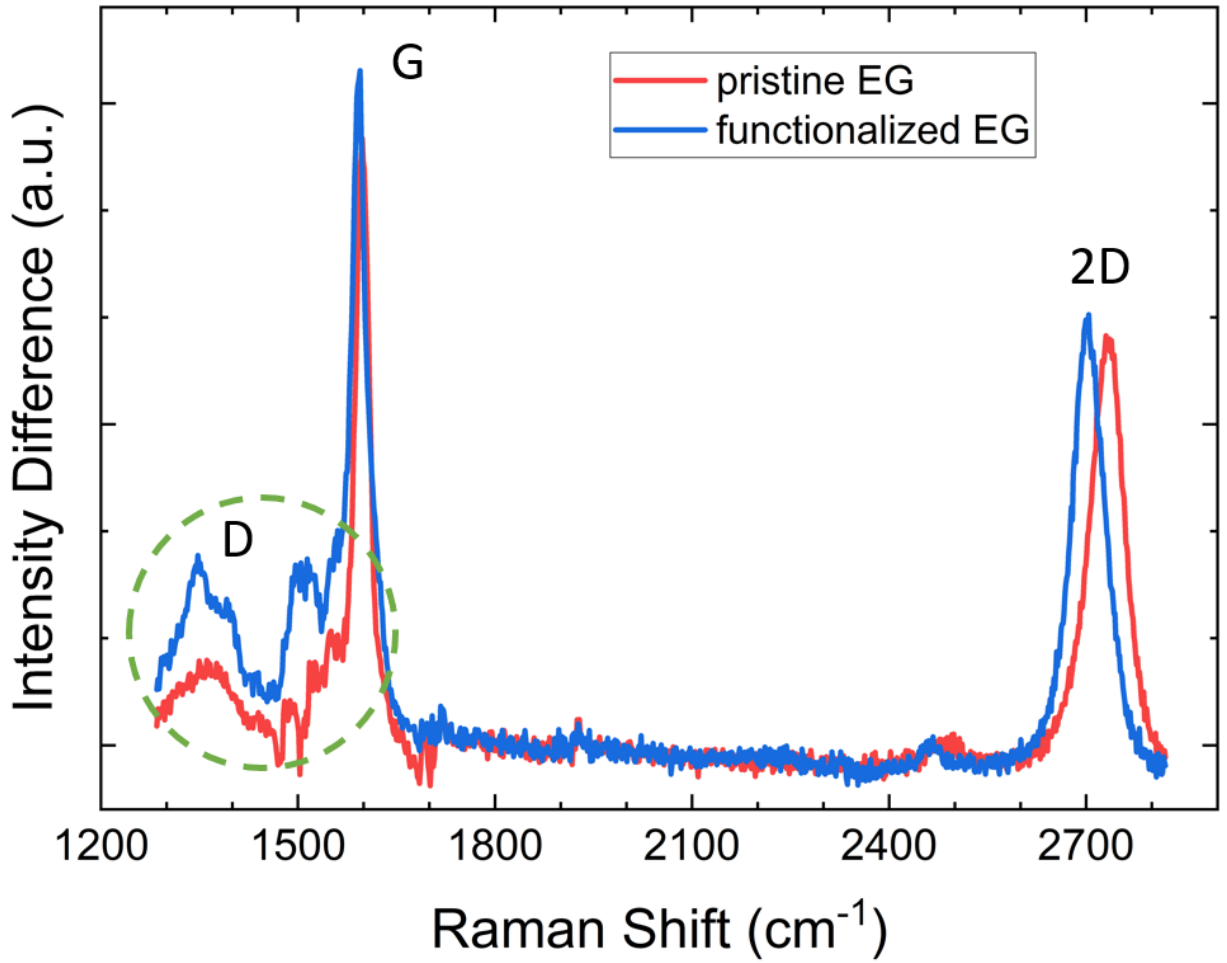
Raman of Functionalized EG





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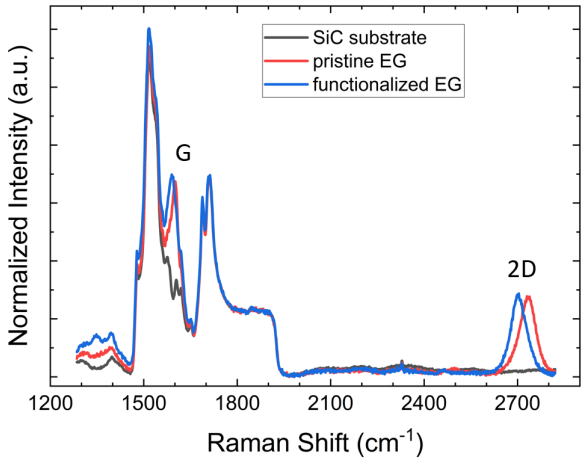
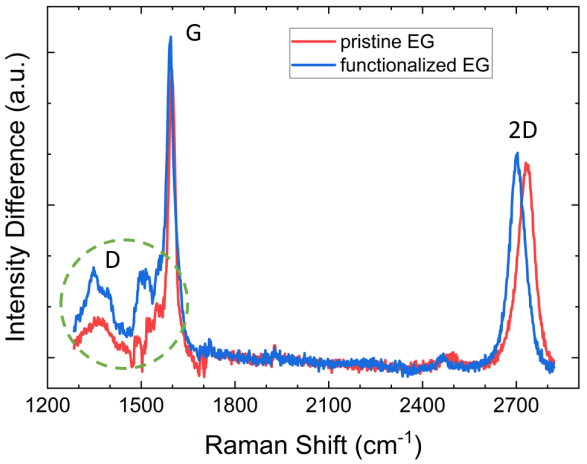
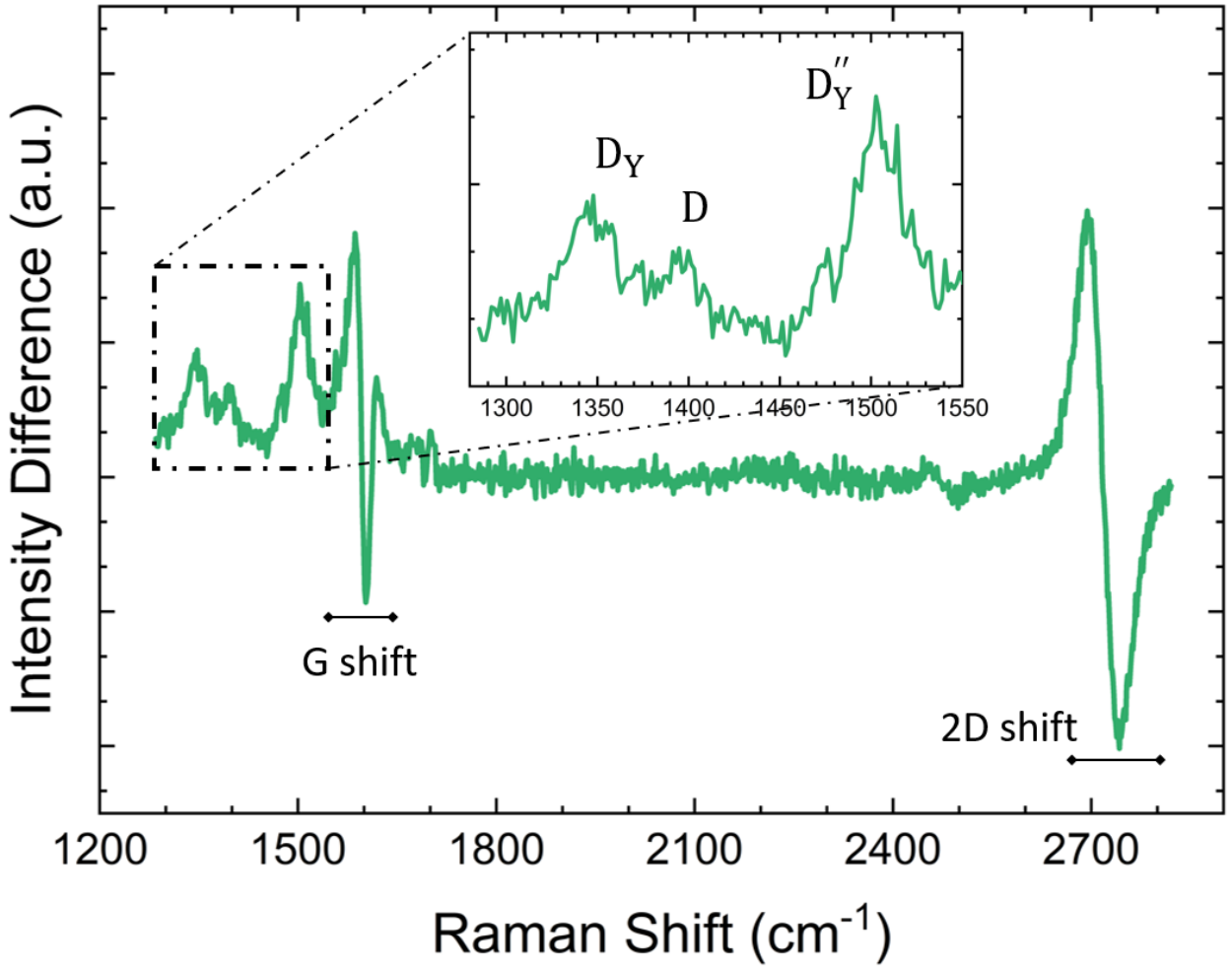
Raman of Functionalized EG







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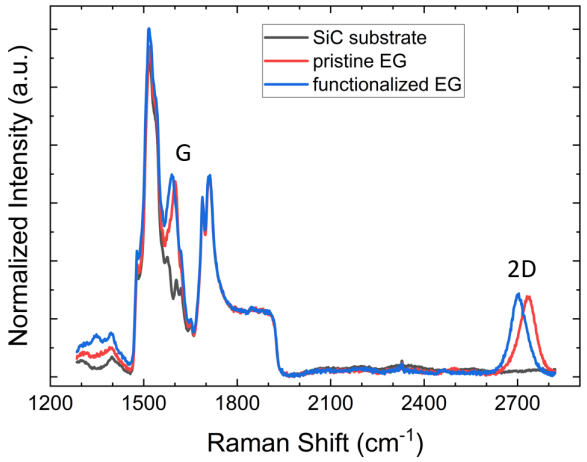
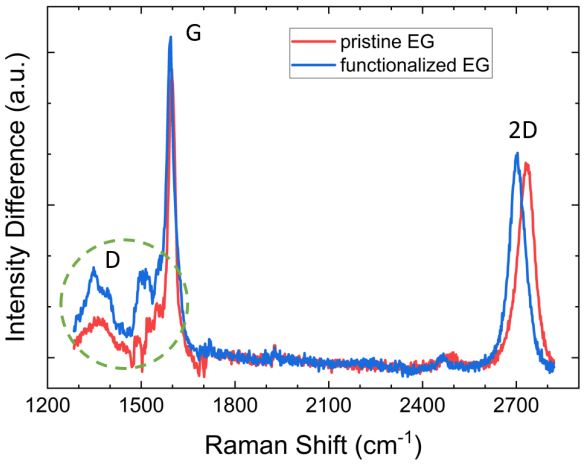
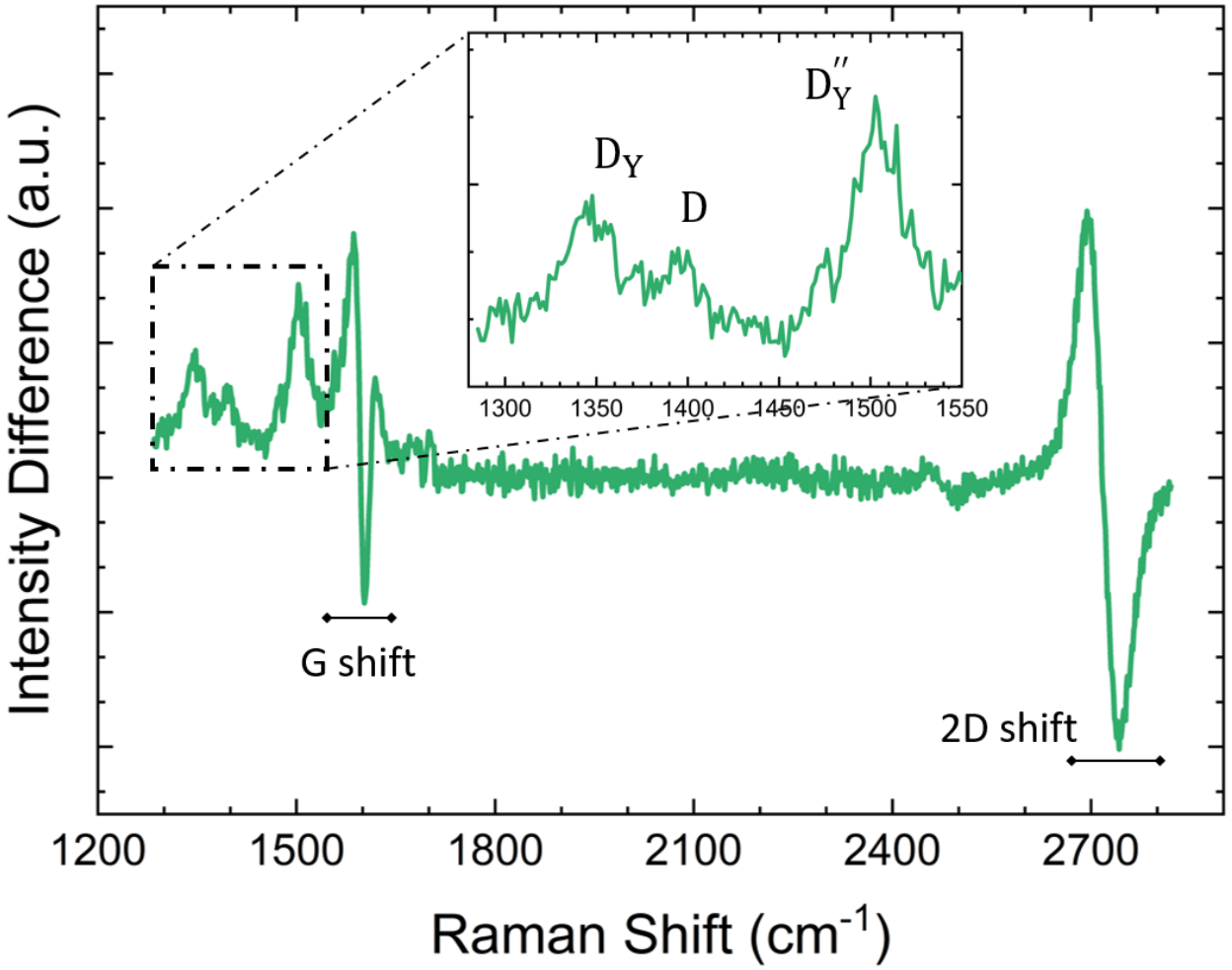
Raman of Functionalized EG







- G shift
- 2D shift

(doping + strain)

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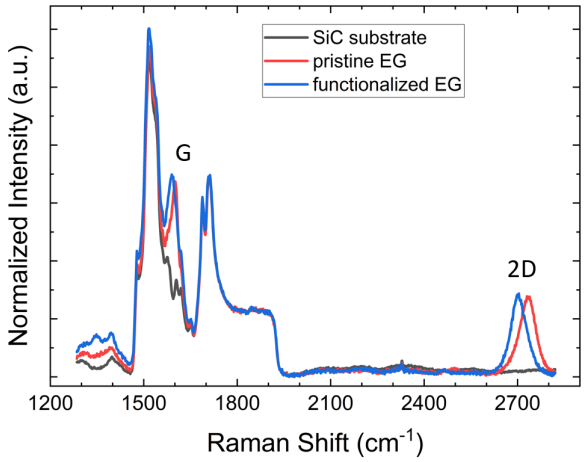
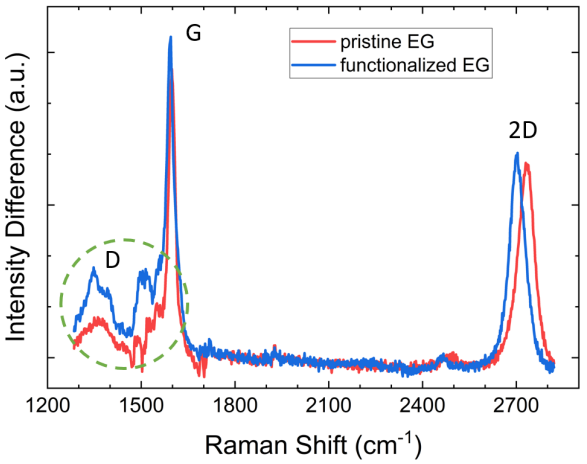
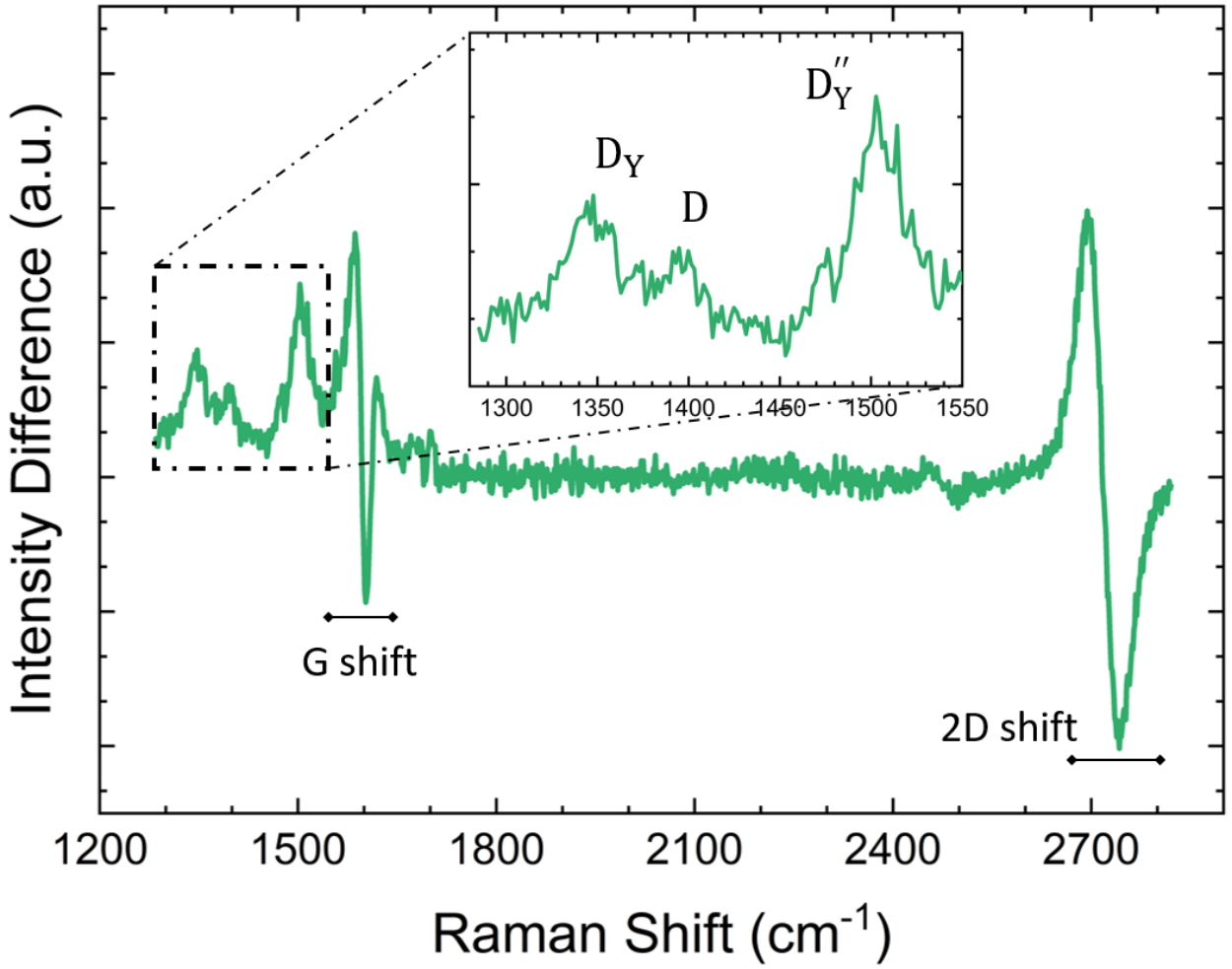
Raman of Functionalized EG





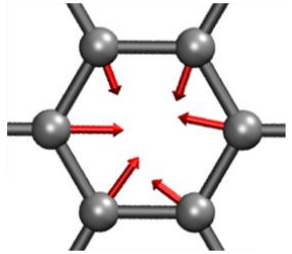


- G shift
- 2D shift

(doping + strain)

- New peaks!

D_Y
1356 cm^{-1}



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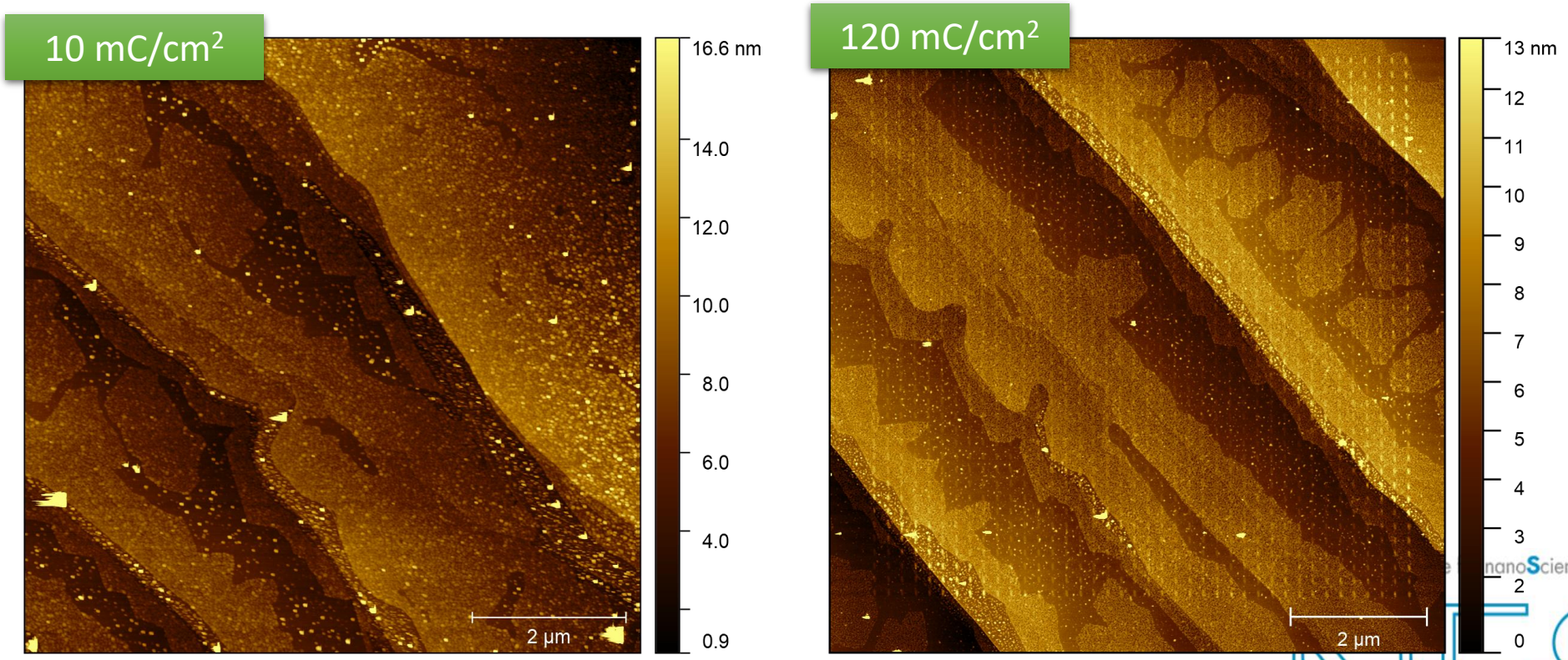
AFM of Patterned EG

Defects patterning on EG via low-energy (20 keV) EBI:

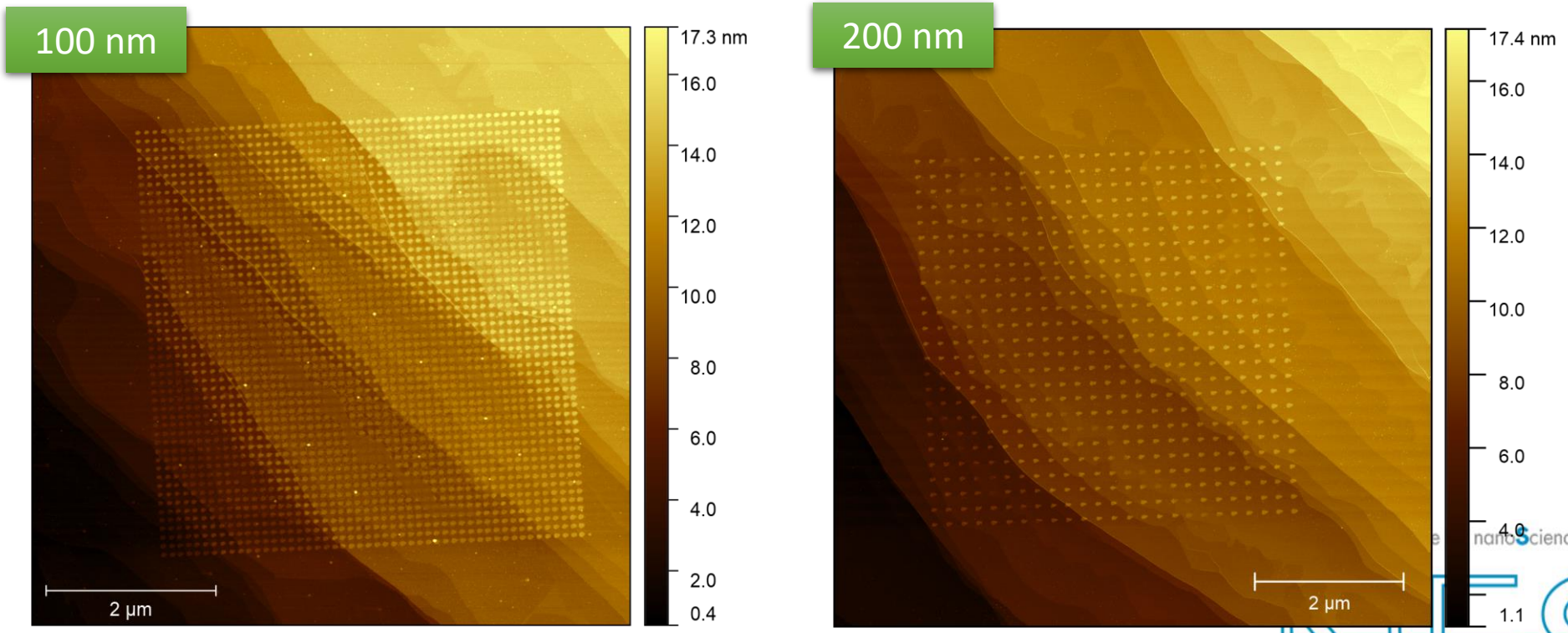
- dose array (from 10 to 120 mC/cm^2)



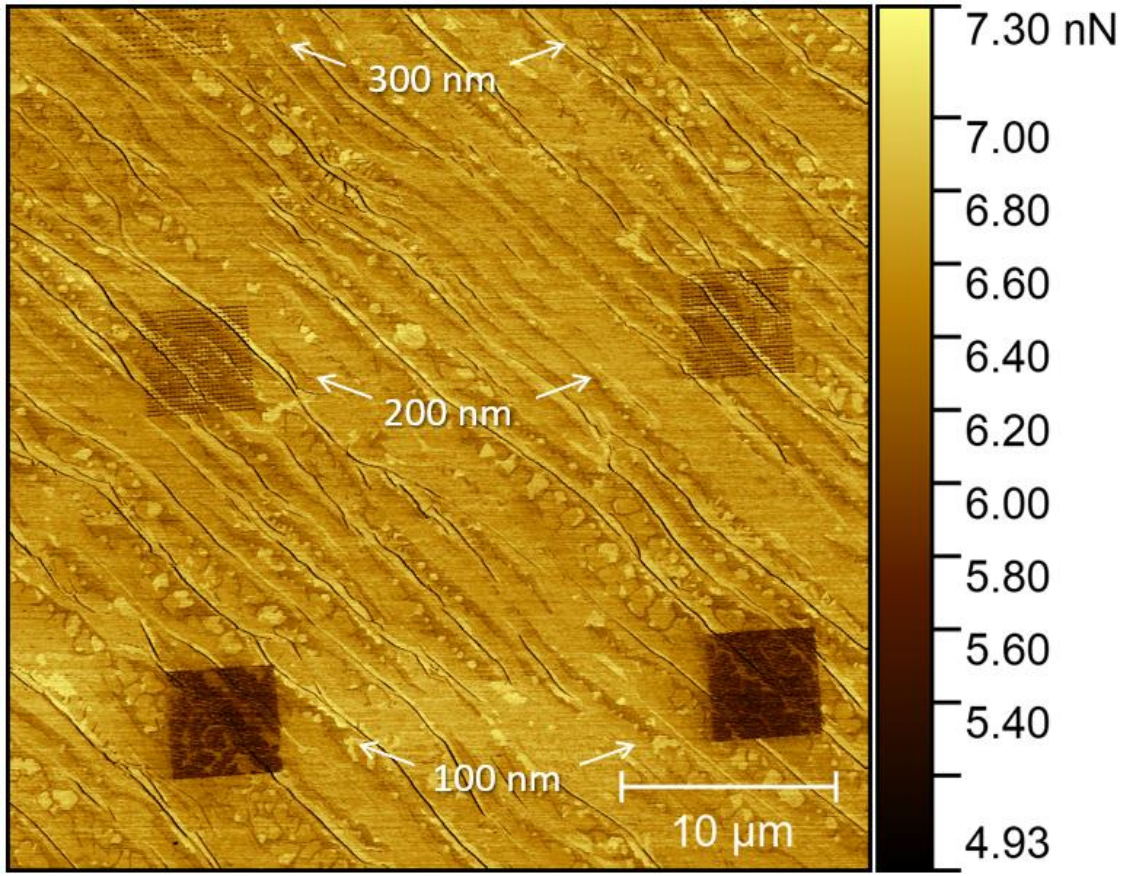
AFM of Patterned EG

Defects patterning on EG via low-energy (20 keV) EBI:

- dose array (from 10 to 120 mC/cm^2)
- step size (from 100 to 500 nm)



QNM of Patterned EG - adhesion



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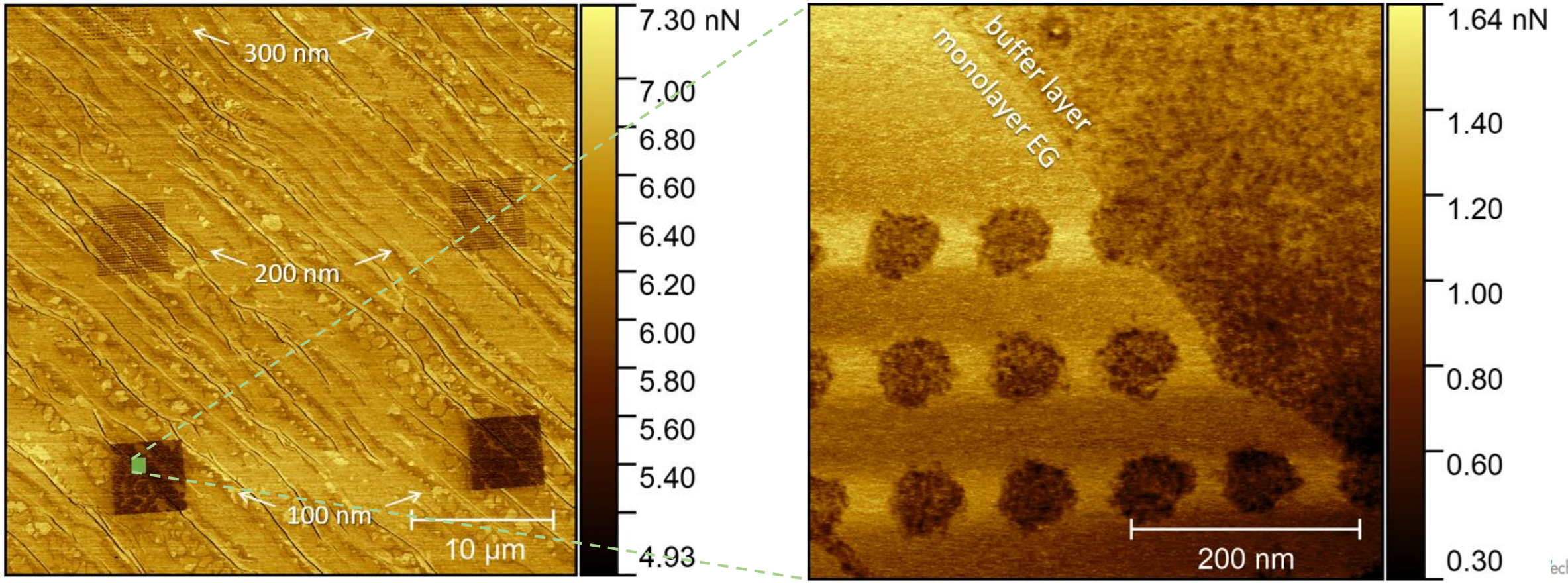
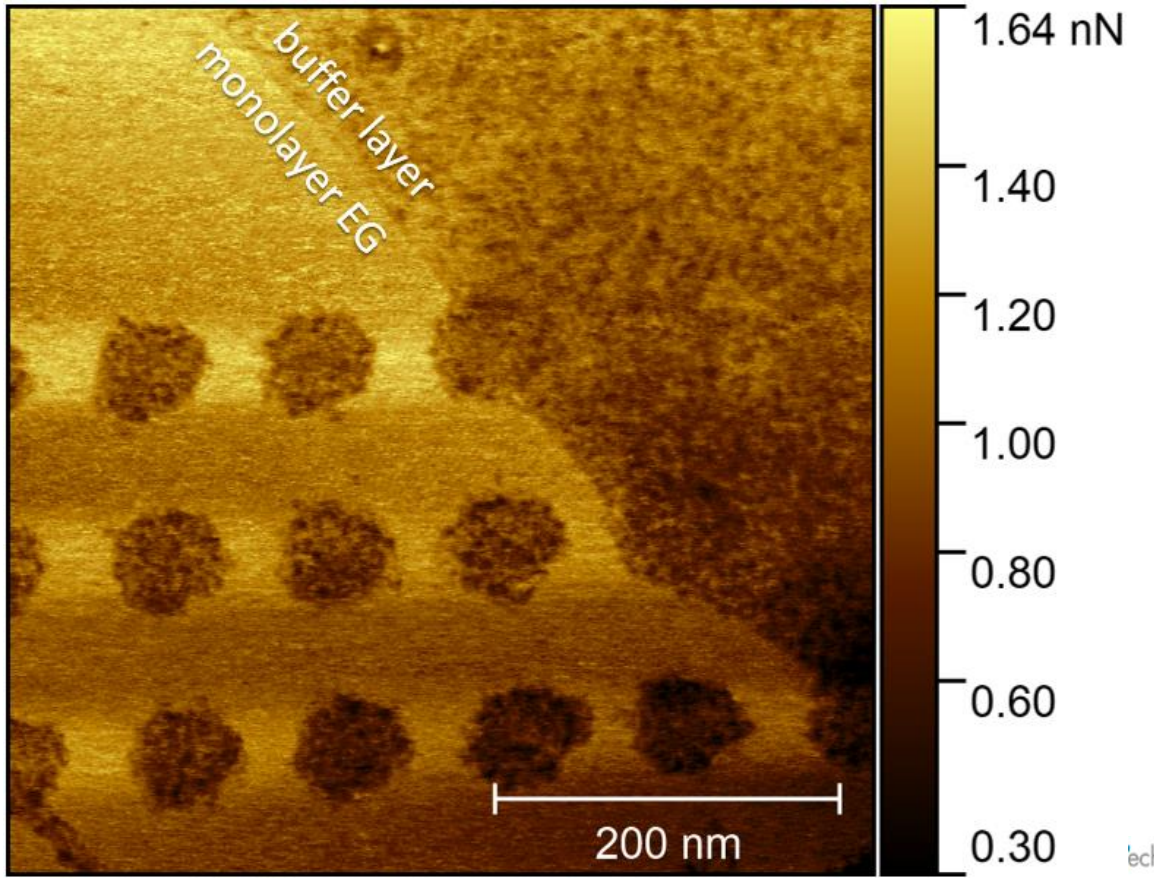


QNM of Patterned EG - adhesion

$$A_{patterned-BL-tip} \approx A_{BL-tip}$$

$$A_{ptr-MLEG-tip} - A_{MLEG-tip} = -0.39\ \text{nN}$$

$$A_{ptr-MLEG-tip} \approx A_{BL-tip}$$



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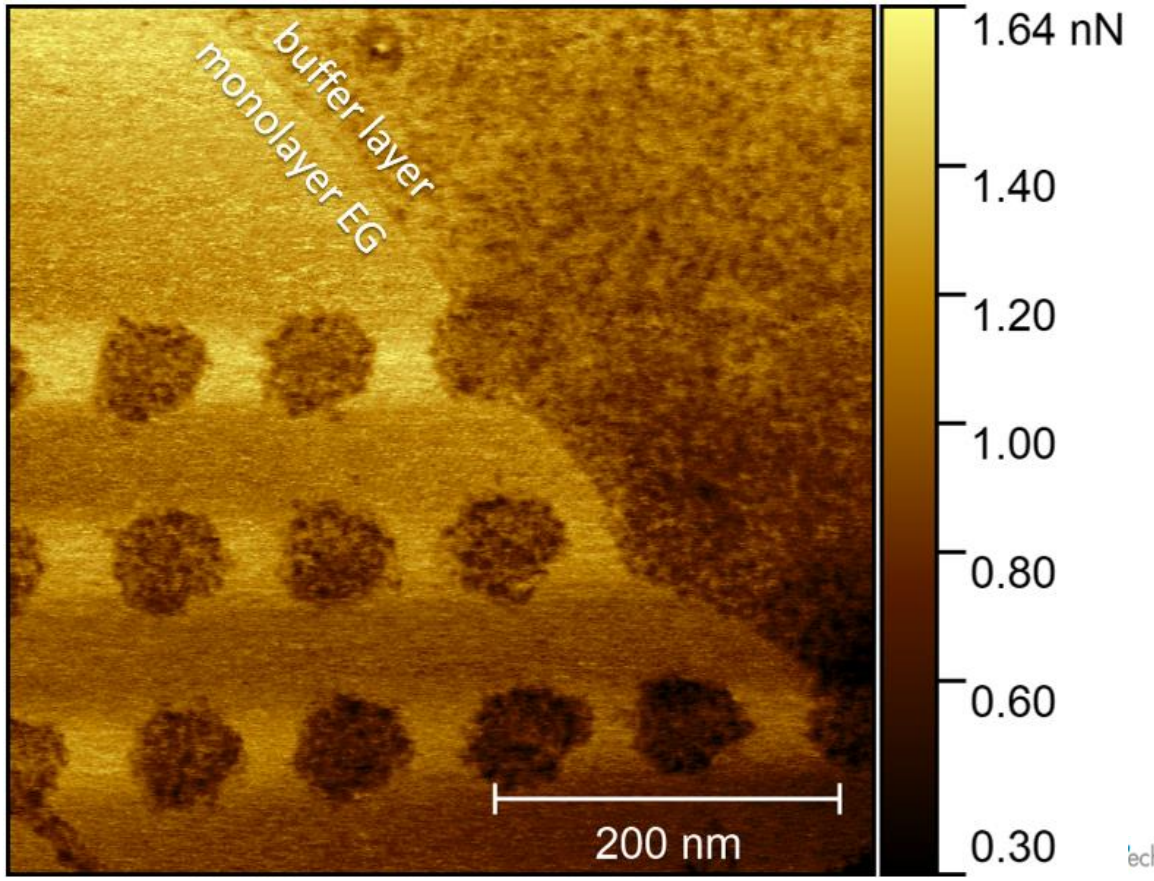
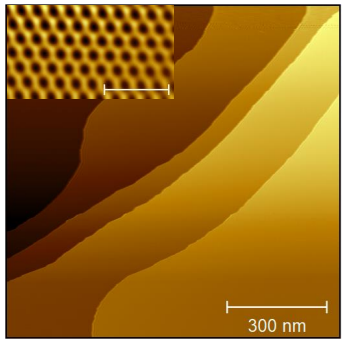
patterned−MLEG ≈ BL

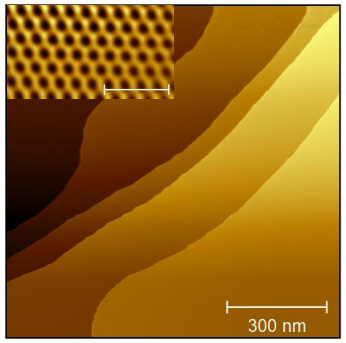


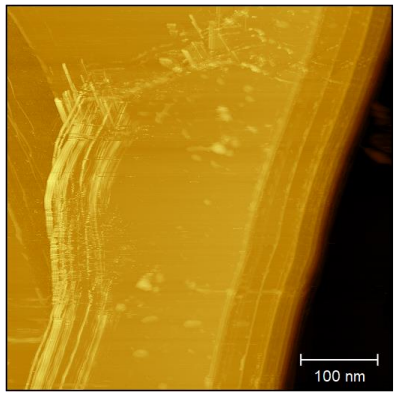
Conclusions – 4)

- 1,3-DC of near defect-free EG:



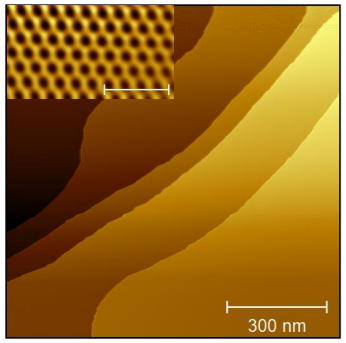
Conclusions – 4)

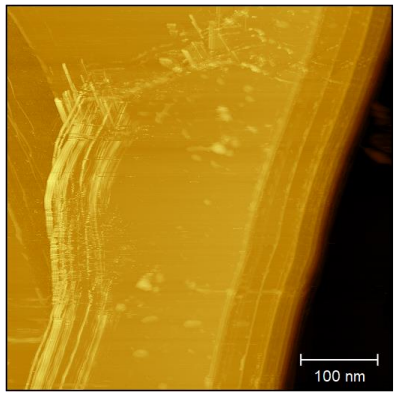




- 1,3-DC of near defect-free EG:
  - STM → new structures with height of 2 – 15 Å
  - STS → new structures with bandgap of 0.13 – 0.20 eV

Conclusions – 4)





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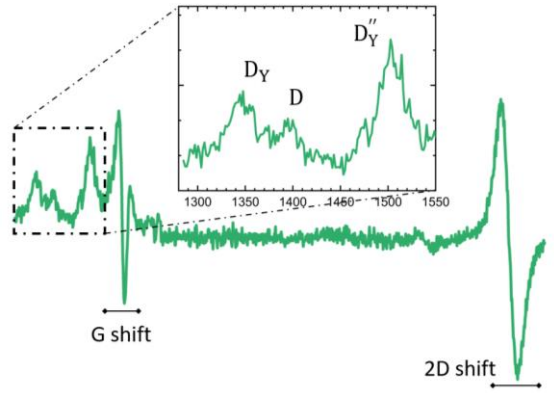

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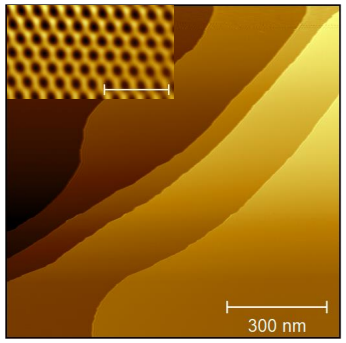

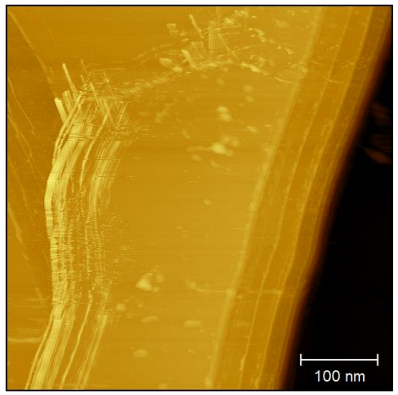

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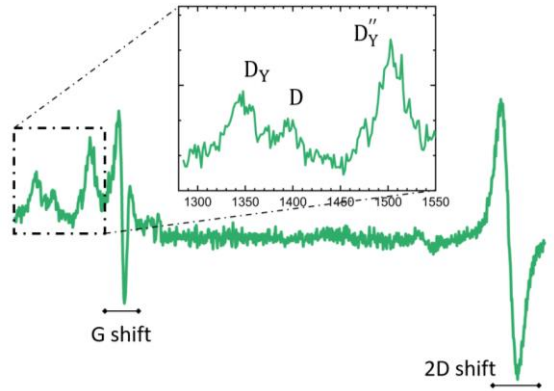

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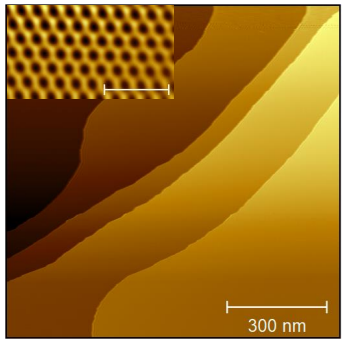

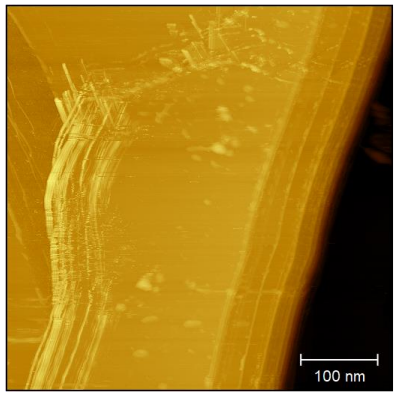

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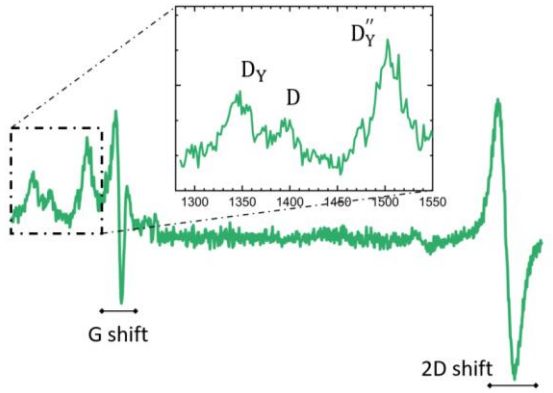
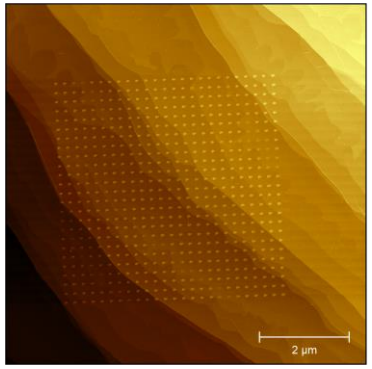
- Defect patterning of EG:
  - AFM → controlled design
  - QNM → enhanced adhesion





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Summary

- 1,3-DC of dispersed, exfoliated and epitaxial graphene systems (towards higher quality)

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- Chemical signature via EDX/EELS and XPS + Raman spectroscopy and DFT-PS
  (new method of detection in case of low coverage)

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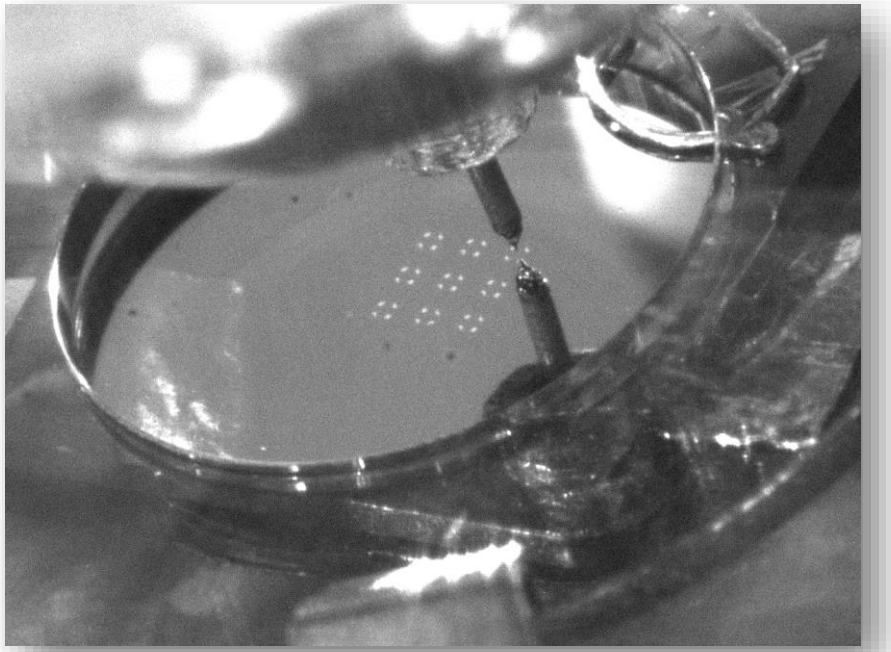
- Adhesion enhancement in patterned graphene

What's Next?

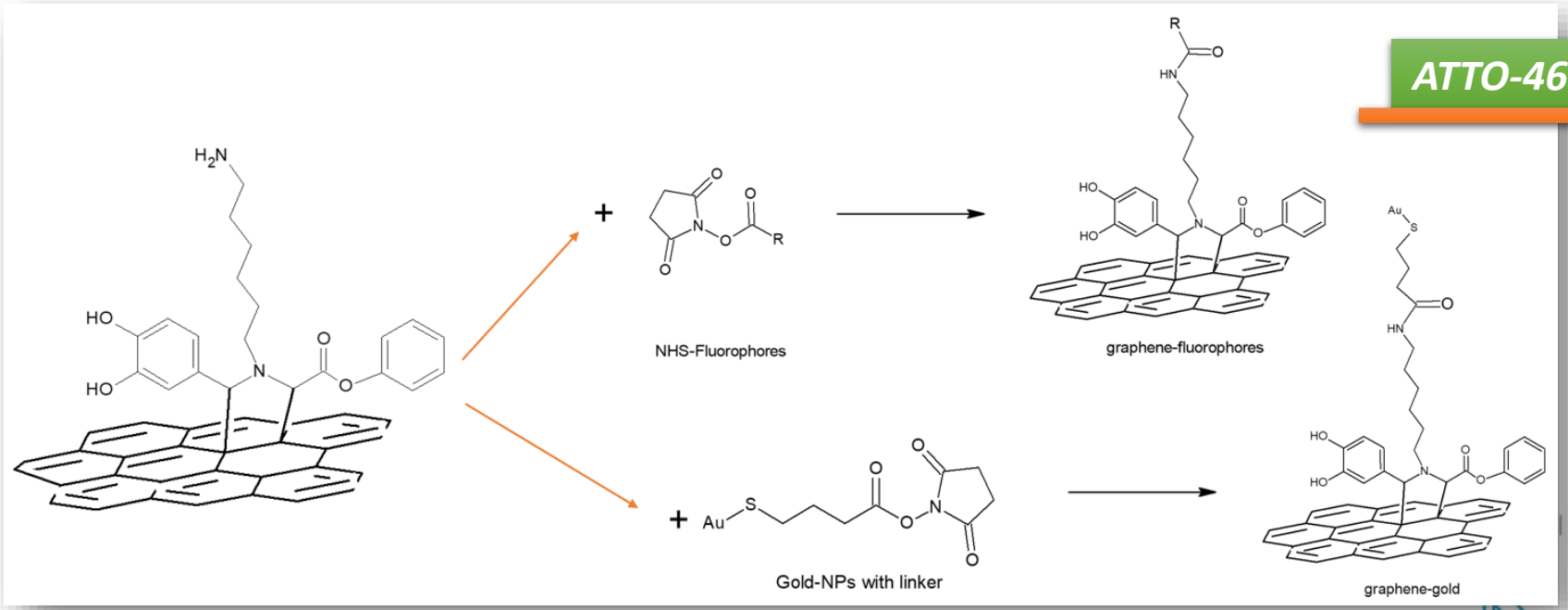
- EG → STM/STS investigation on patterned EG and after 1,3-DC of patterned EG



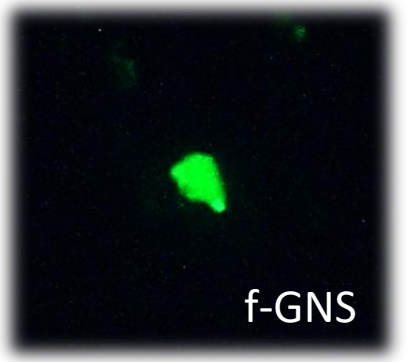
What's Next?

[*Y. Vlamidis, A. Moscardini* @ NEST]

- EG → STM/STS investigation on patterned EG and after 1,3-DC of patterned EG
- New tailored ylide → further functionalization towards applications at the nanoscale



ATTO-465



Enterprise for nanoScience and nanoTechnology

What's Next?

- EG → STM/STS investigation on patterned EG and after 1,3-DC of patterned EG
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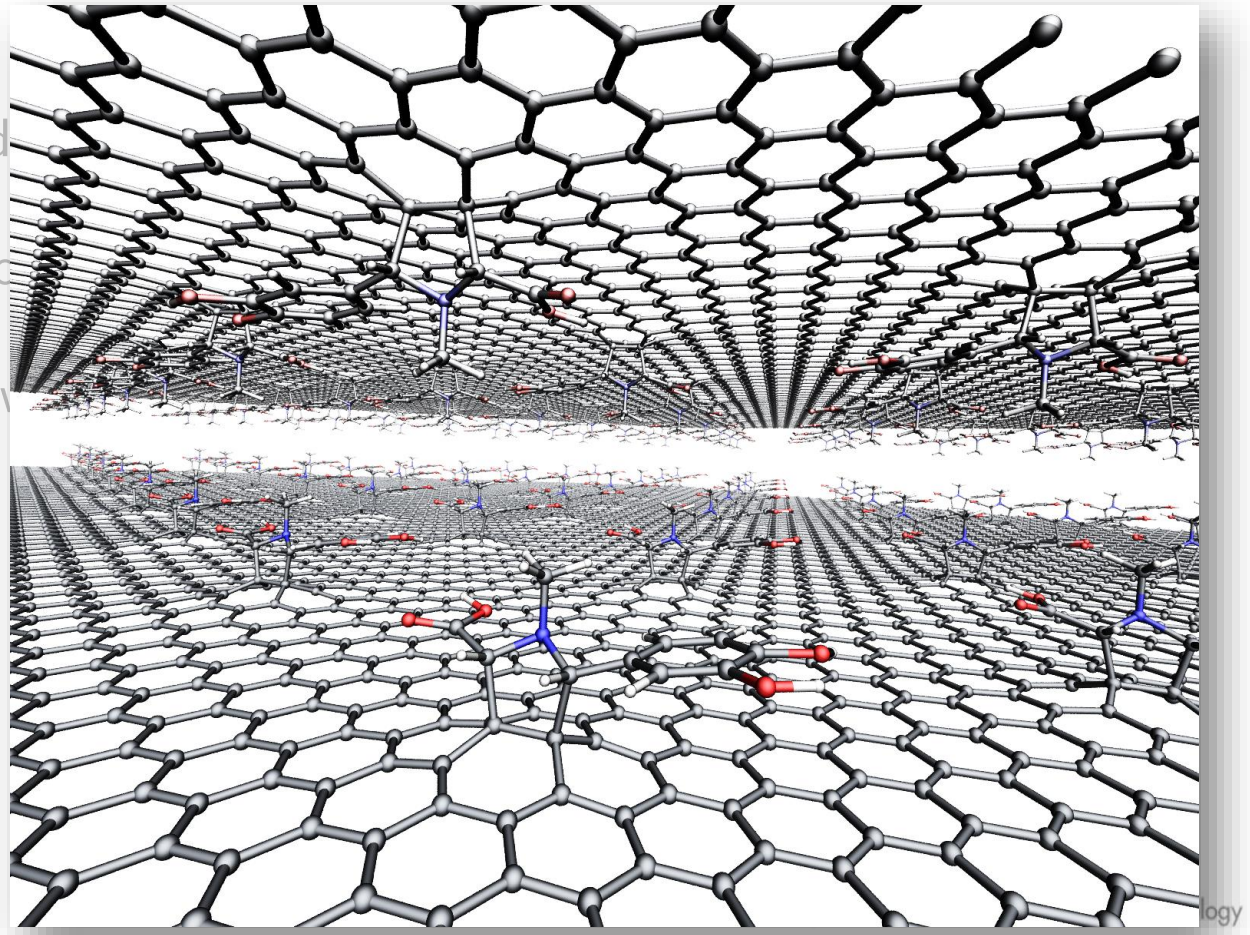
- Raman investigation → doping vs strain, new tailored ylide

What's Next?

- EG → STM/STS investigation on patterned
- New tailored ylide → further functionalizatic
- Raman investigation → doping vs strain, ne
- Positioning of molecular pillars
  - → spaced multilayer graphene systems:
    - gas storage (H_2)
    - sensing



~ People ~


Aldo Moscardini


Giovanni Signore


Filippo Fabbri


Luca Bellucci


Valentina Tozzini


Yuya Murata


Neeraj Mishra


Federica Bianco


Ylea Vlamidis


Andrea Griesi


Luigi Rolandi


Silvia Rubini


Mauro Gemmi

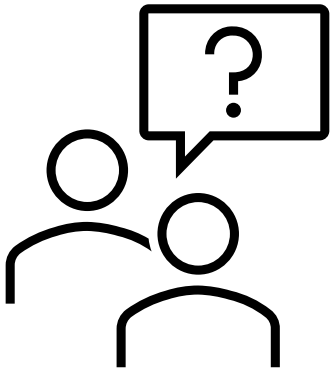

Camilla Coletti


NEST

SNS

Thank You

For Your Attention



"Magnus in magnis, maximus in minimis" - Augustine

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