NANOSCIENCES

~ 3rd year PhD report ~

PhD student: ***Luca Basta***

Supervisor: ***Dr. Stefano Veronesi***

SCUOLA NORMALE SUPERIORE

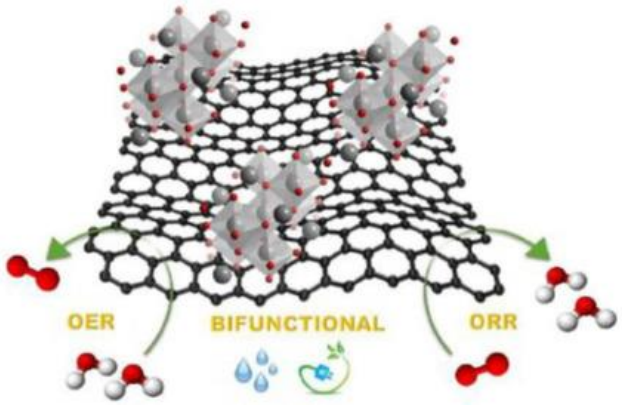
PERFEZIONAMENTO IN NANOSCIENZE

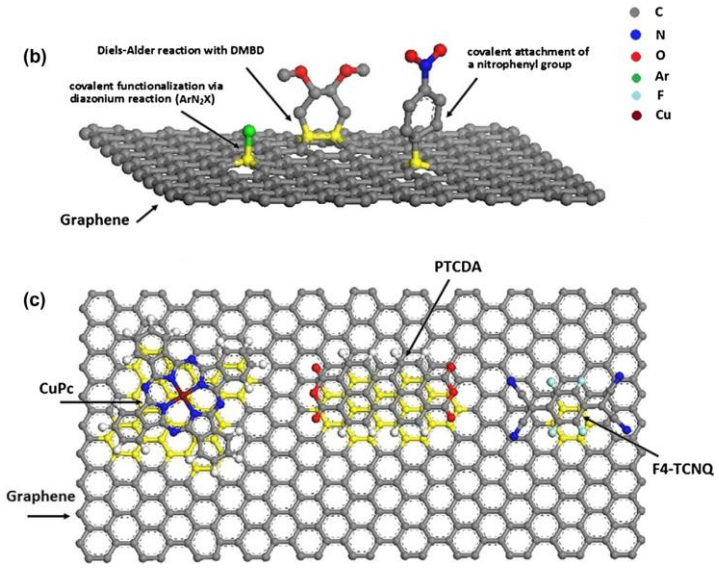
National Enterprise for nanoScience and nanoTechnology

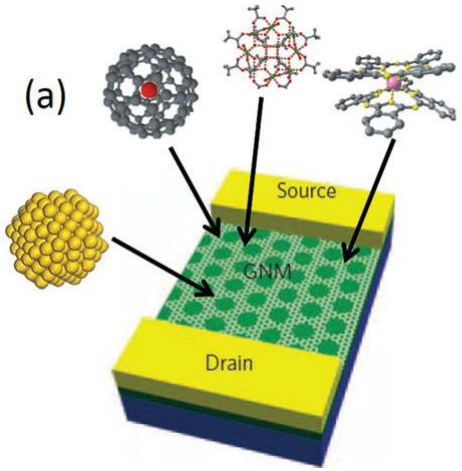
NEST

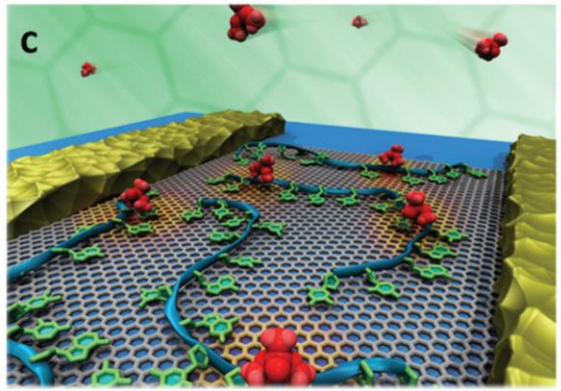
Research Motivation

The principal aim of my research is the ***covalent functionalization*** of graphene with organic molecules. This would allow to finely tune or enhance the system's physical and chemical properties, resulting in a valuable synergistic combination.







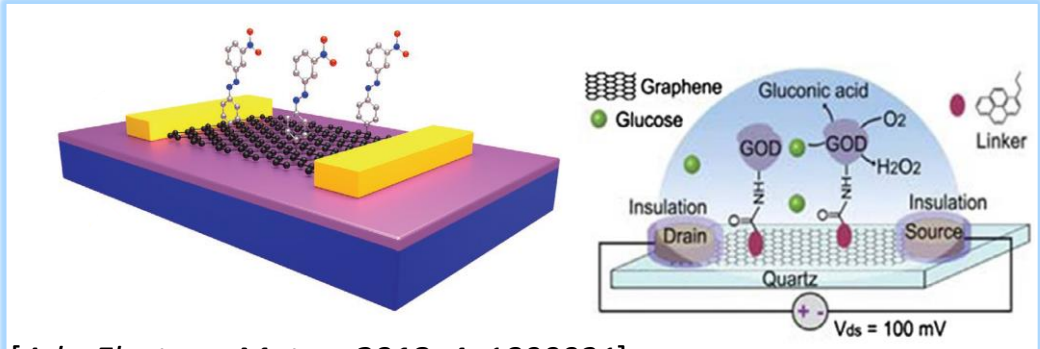


[*Angew. Chem. Int. Ed.*, **2015**, 54, 10734; *Chem. Rev.*, **2012**, 112, 6156]

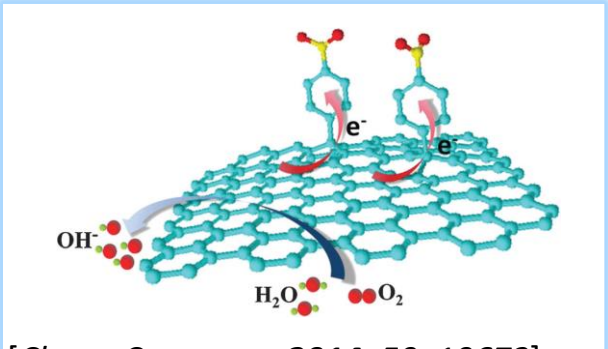
Research Application

Covalent functionalization of nanocomposite graphene systems, aimed at achieving:

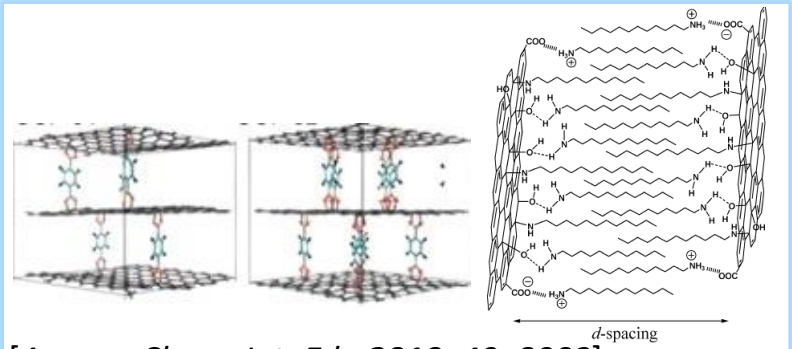
- realization of ***new sensors*** exploiting organic molecules as active sites onto graphene surface (selective interaction with *target* molecules);
- implementation of ***nano-catalyst materials*** (nanoparticle bonding or metal-free configuration);
- fabrication of ***graphene/molecule/graphene*** heterostructures towards multilayer stacking and 3D graphene materials.



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



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

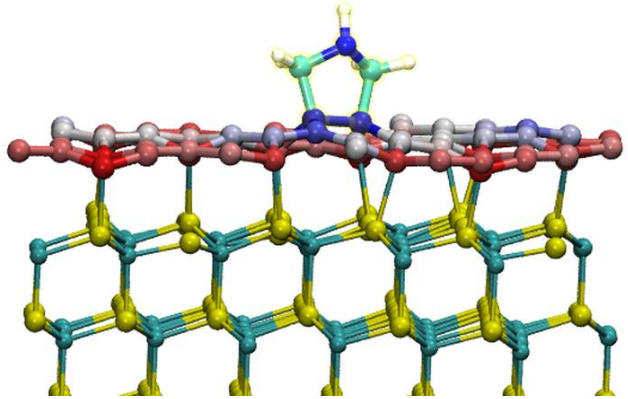


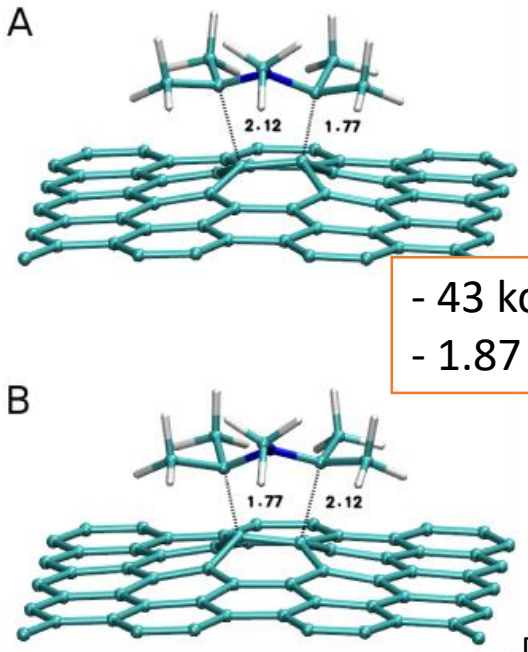
[*Angew. Chem. Int. Ed.*, ***2010***, *49, 8902*]

Cycloaddition reaction

A ***1,3-dipole*** (dienophile) reacts with a π-system (diene/dipolarophile), to form a five-membered ring

- high selectivity (close to the diene)
- reversible process
- stability up to ~300°C

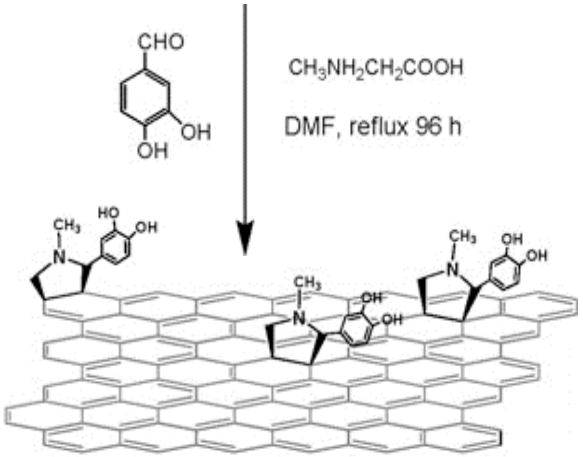


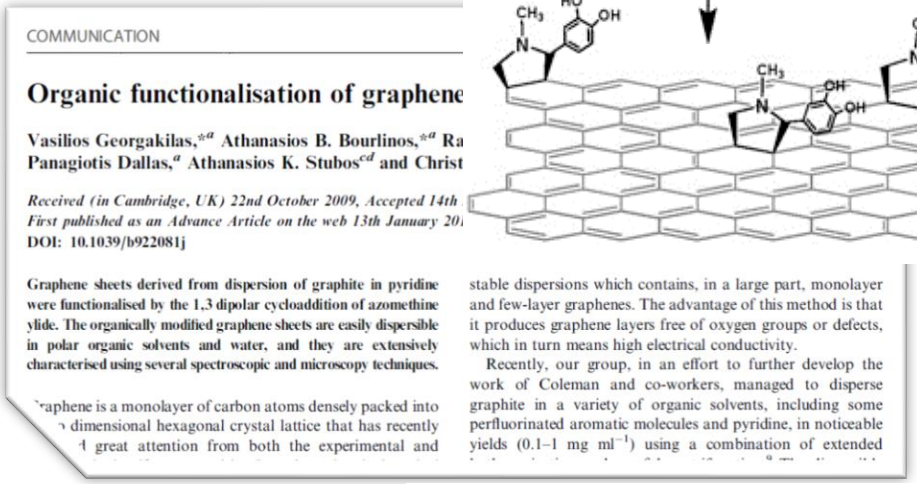


- 43 kcal/mol
- 1.87 eV

[*L. Bellucci* @ NEST]

In collaboration with G. Signore @ NEST we selected the 1,3 dipolar cycloaddition with *azomethine ylide*





COMMUNICATION

Organic functionalisation of graphene

Vasilios Georgakilas,*[a] Athanasios B. Bourlinos,*[a] Ra
Panagiotis Dallas,[a] Athanasios K. Stubos[cd] and Christ

Received (in Cambridge, UK) 22nd October 2009, Accepted 14th
First published as an Advance Article on the web 13th January 20
DOI: 10.1039/b922081j

Graphene sheets derived from dispersion of graphite in pyridine were functionalised by the 1,3 dipolar cycloaddition of azomethine ylide. The organically modified graphene sheets are easily dispersible in polar organic solvents and water, and they are extensively characterised using several spectroscopic and microscopy techniques.

raphene is a monolayer of carbon atoms densely packed into dimensional hexagonal crystal lattice that has recently great attention from both the experimental and

stable dispersions which contains, in a large part, monolayer and few-layer graphenes. The advantage of this method is that it produces graphene layers free of oxygen groups or defects, which in turn means high electrical conductivity.

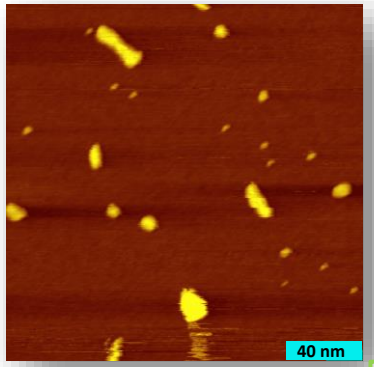
Recently, our group, in an effort to further develop the work of Coleman and co-workers, managed to disperse graphite in a variety of organic solvents, including some perfluorinated aromatic molecules and pyridine, in noticeable yields (0.1–1 mg ml^{-1}) using a combination of extended

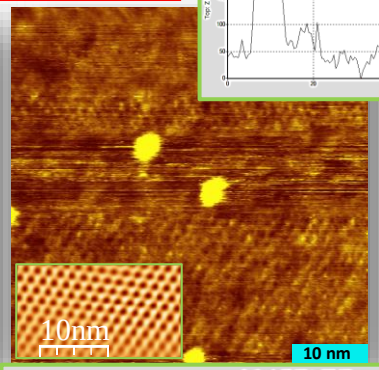
[*Chem.Commun.*, **2010**, 46, 1766]

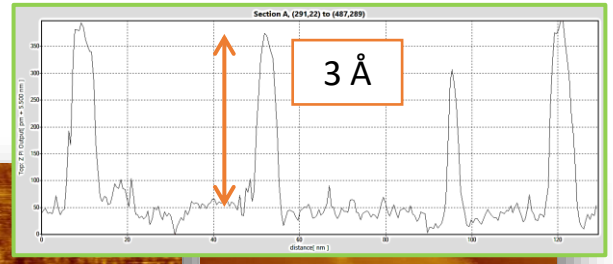
STM/STS Results on EG

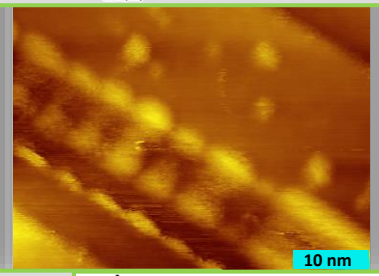
STM

Clusters

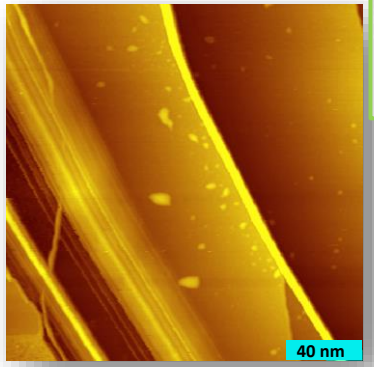


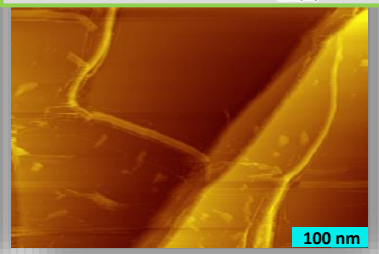


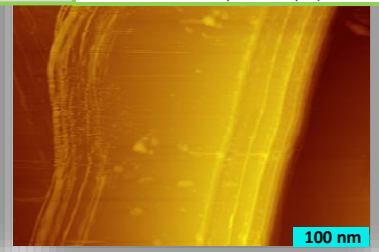


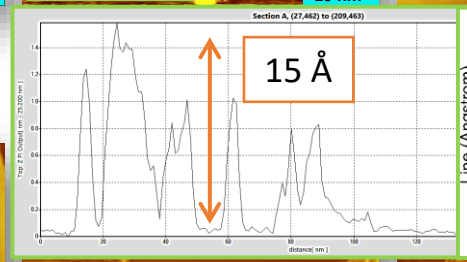


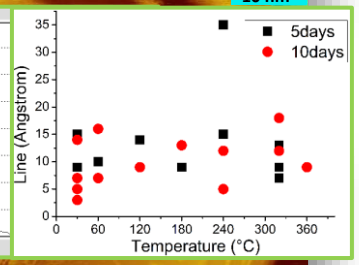
Lines



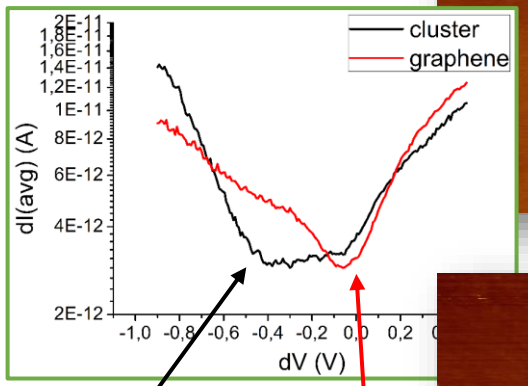






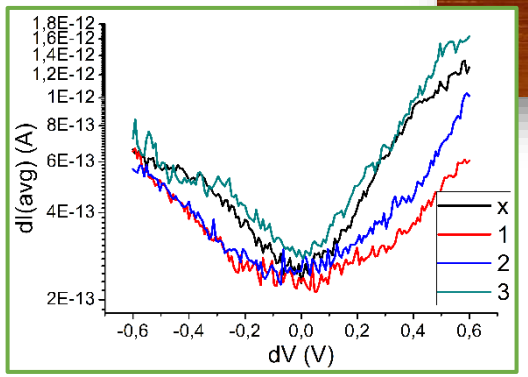


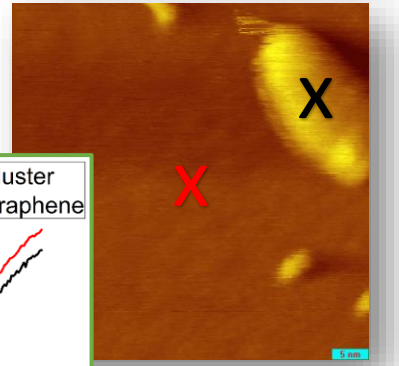
STS

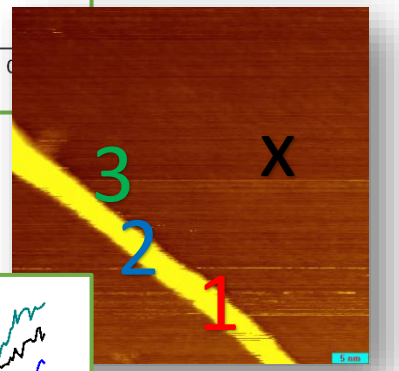


Molecules

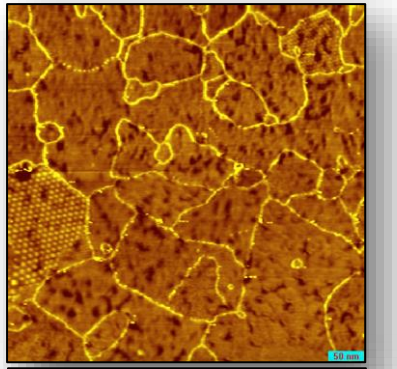
Graphene

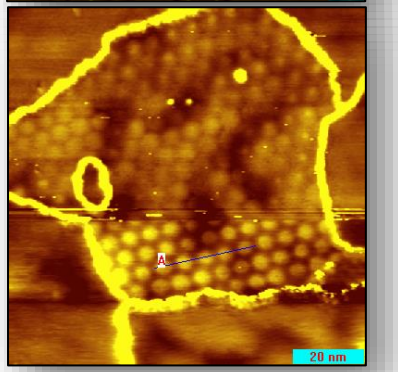


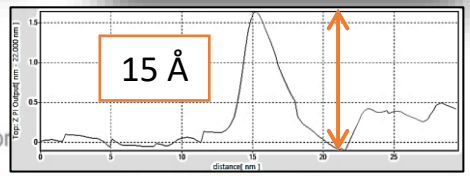




Total coverage





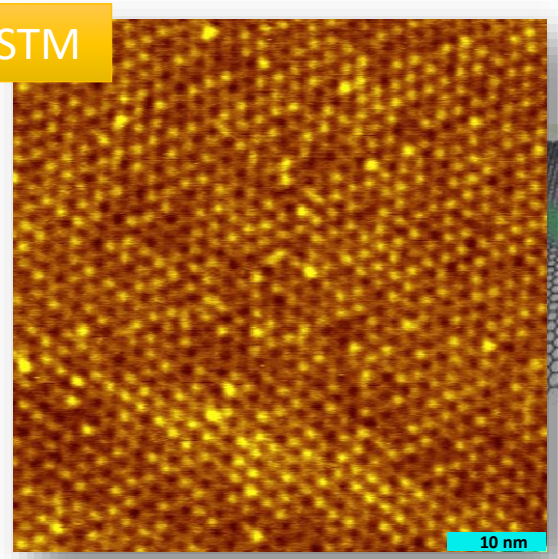


Defects introduction

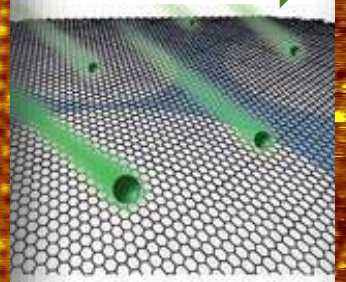
Defects introduction

Ion bombardment (N^+) on EG

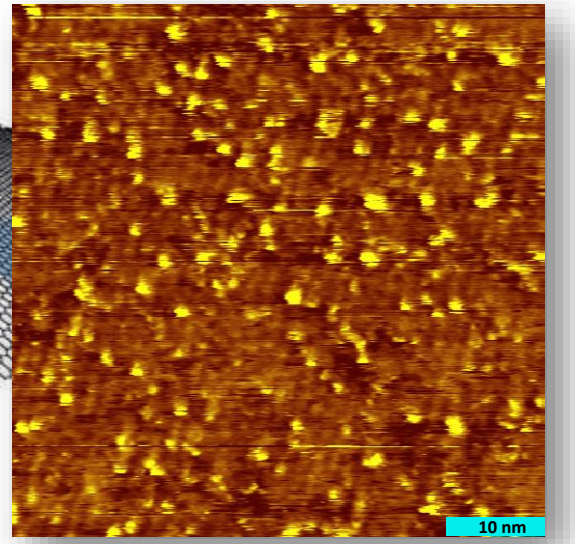
STM



500eV, 150s



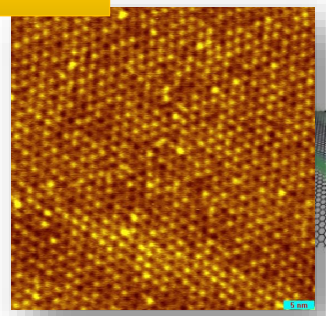
~ 2 def / 100 nm^2

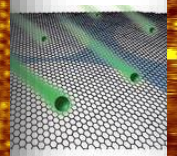


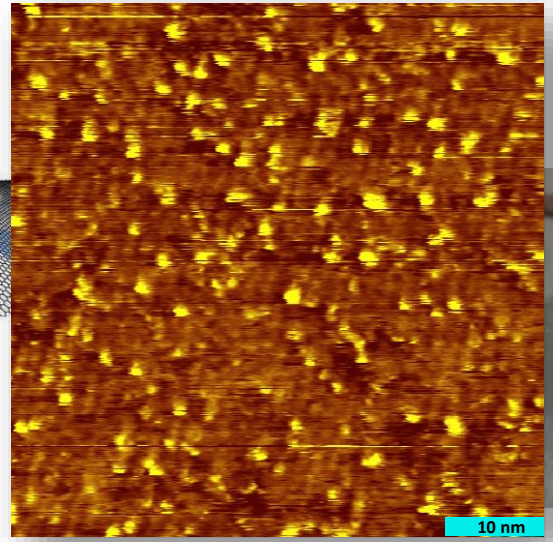
Defects introduction

Ion bombardment (N^+) on EG

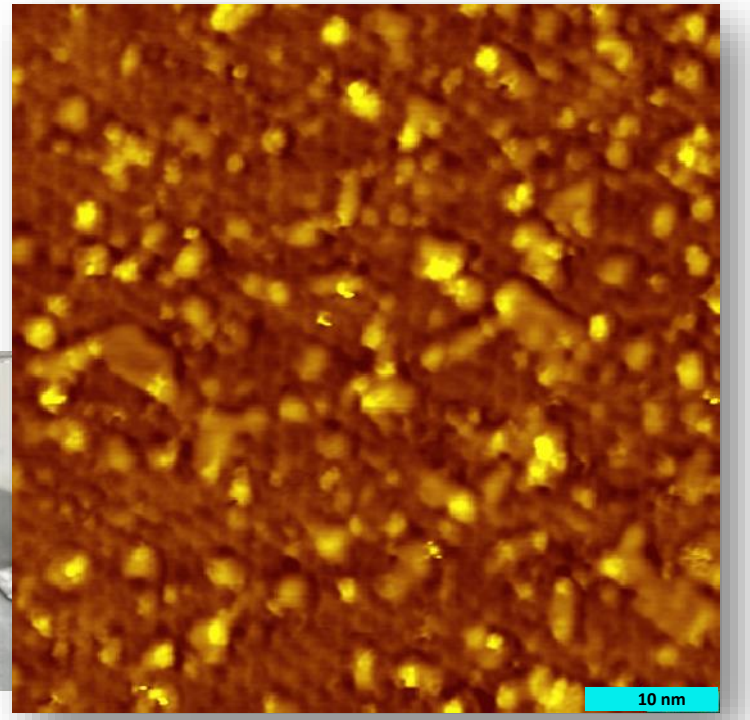
STM

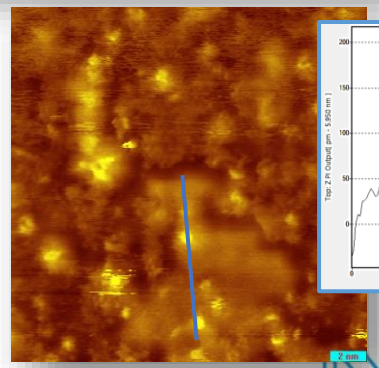


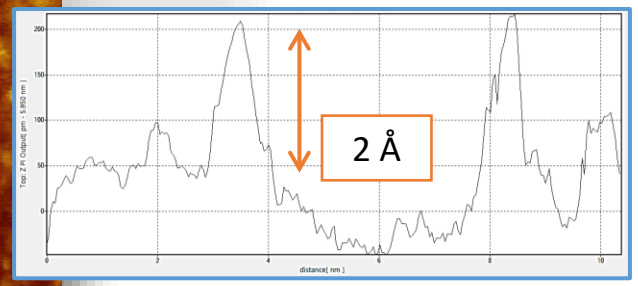




~ 45 % coverage



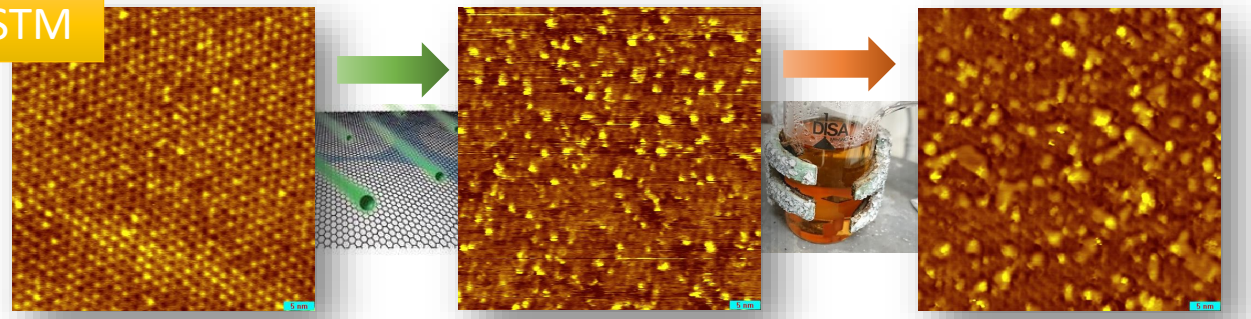




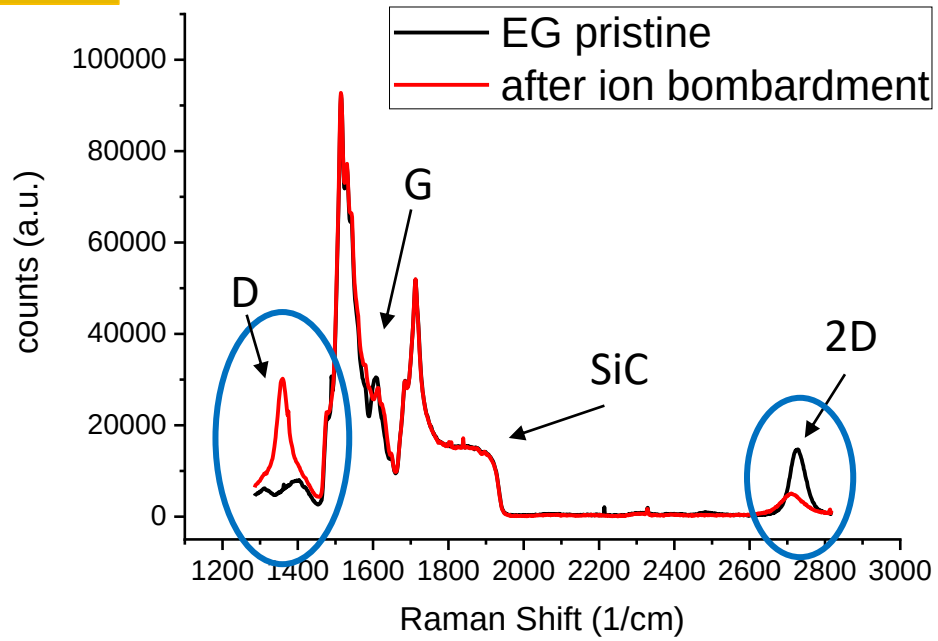
Defects introduction

Ion bombardment (N^+) on EG

STM



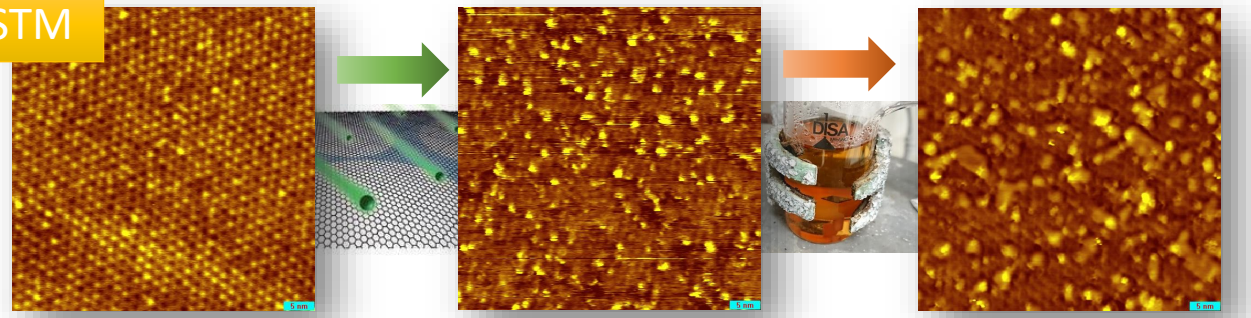
Raman

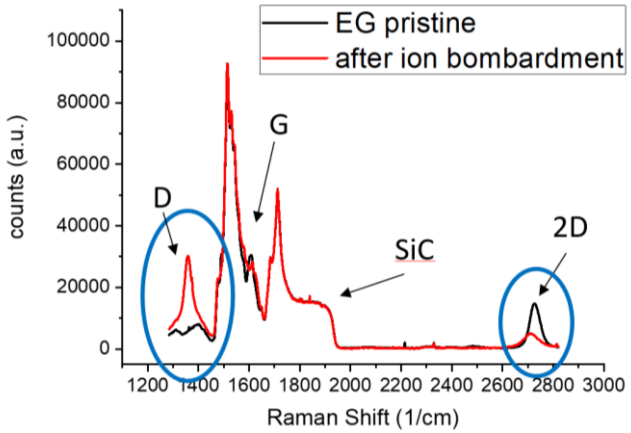


Defects introduction

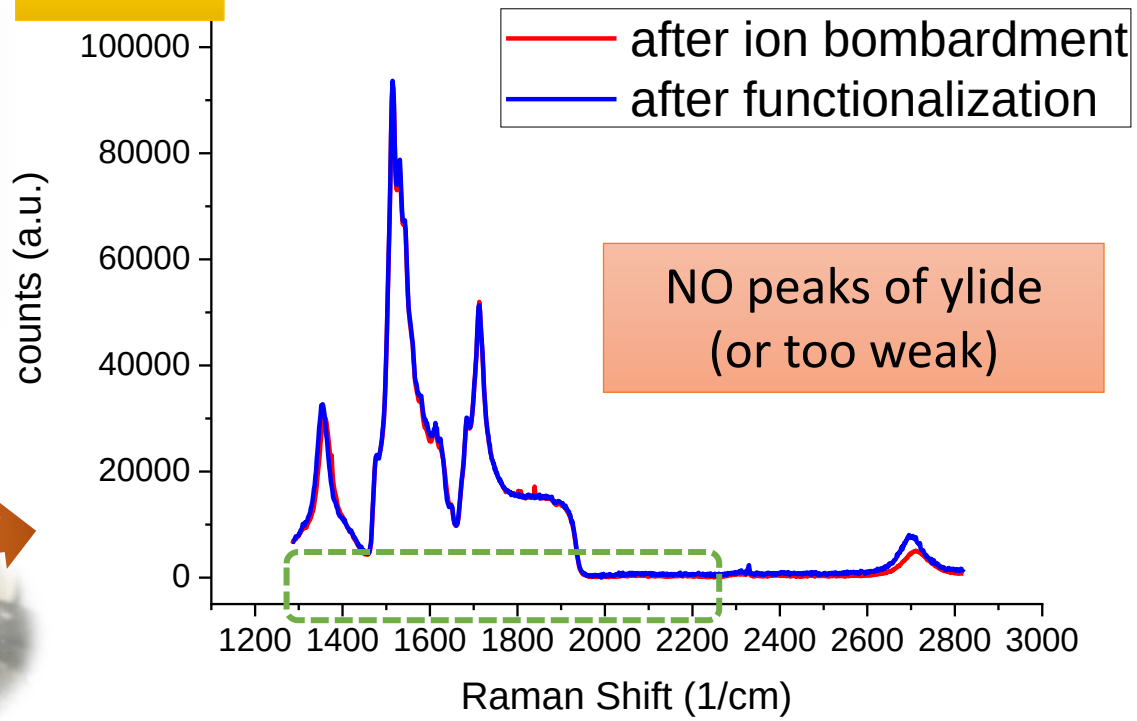
Ion bombardment (N^+) on EG

STM





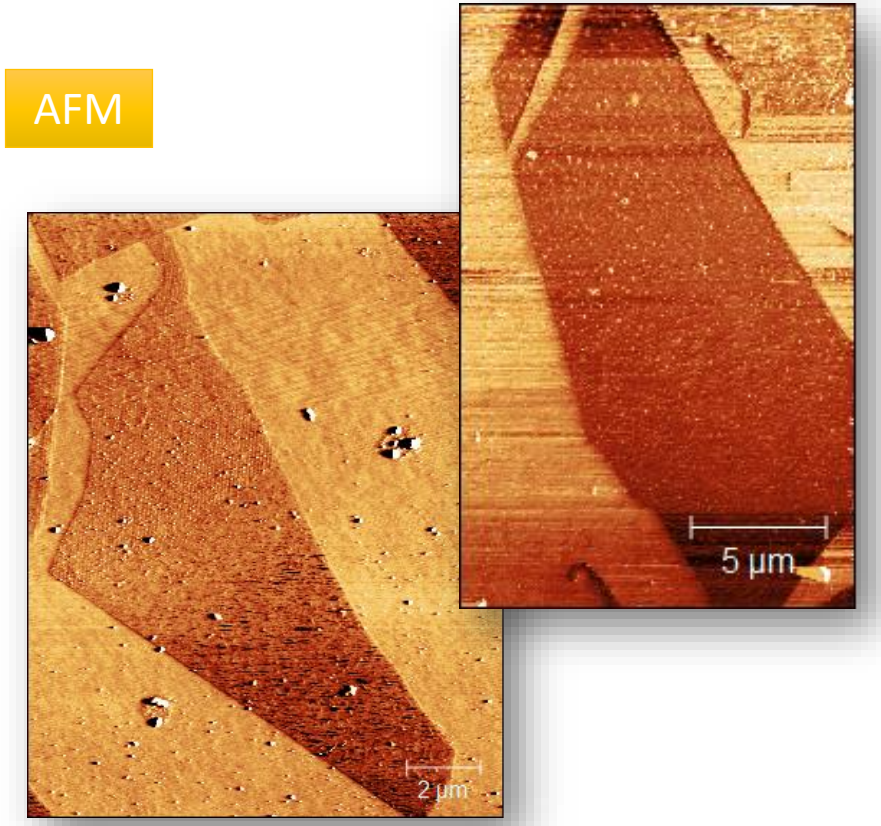
Raman

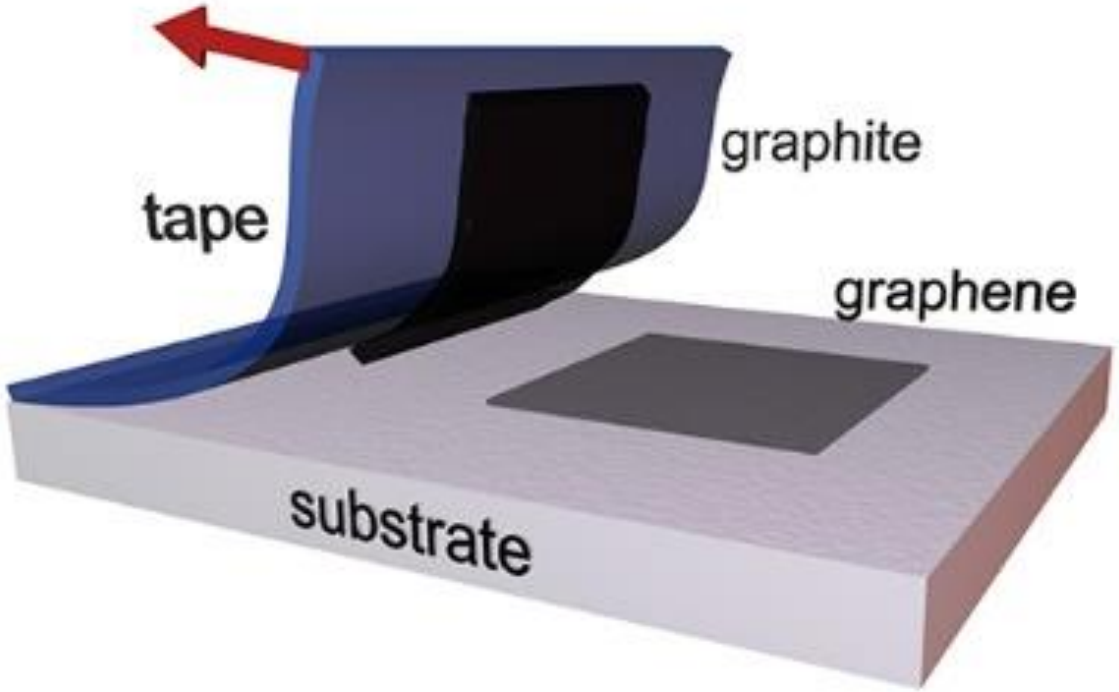


NO peaks of ylide
(or too weak)

Exfoliated graphene flakes

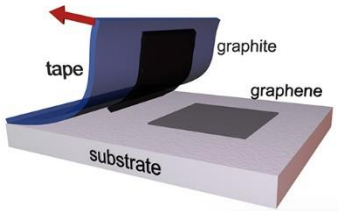
AFM



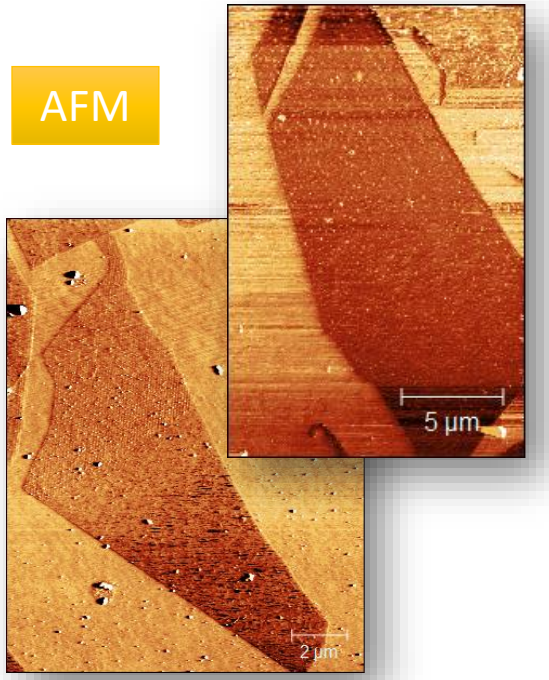


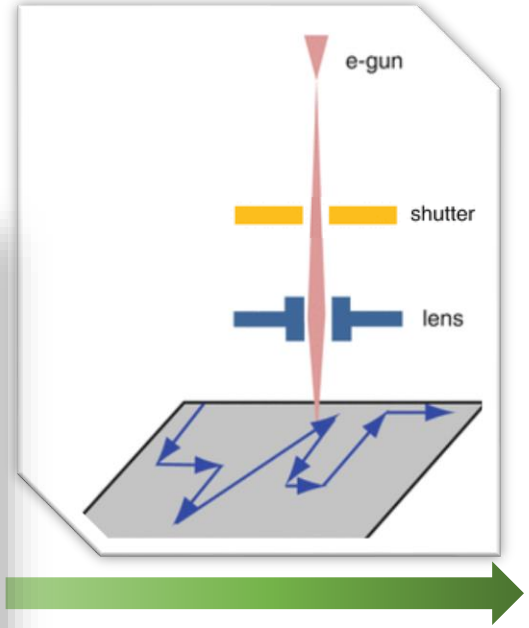
Defects introduction

Electron bombardment (EBL) on flakes



AFM



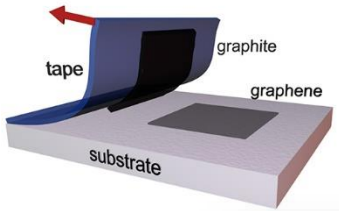


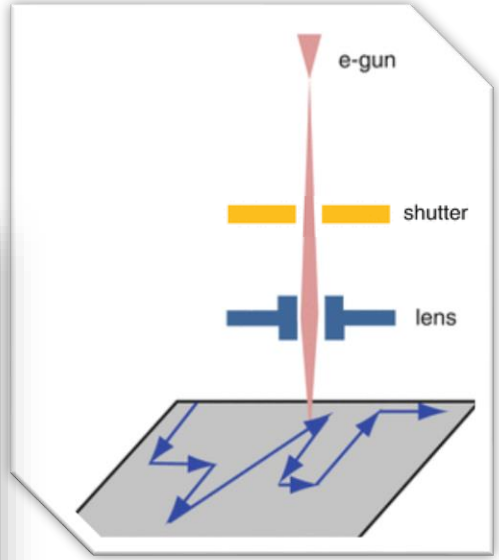
30 kV, 40.000 µC/cm^2
Step size: 100 nm

[*F.Bianco* @ NEST]

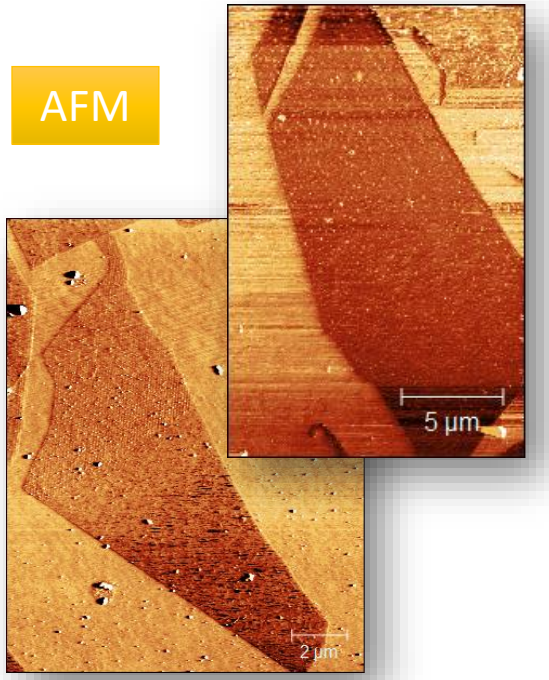
Defects introduction

Electron bombardment (EBL) on flakes



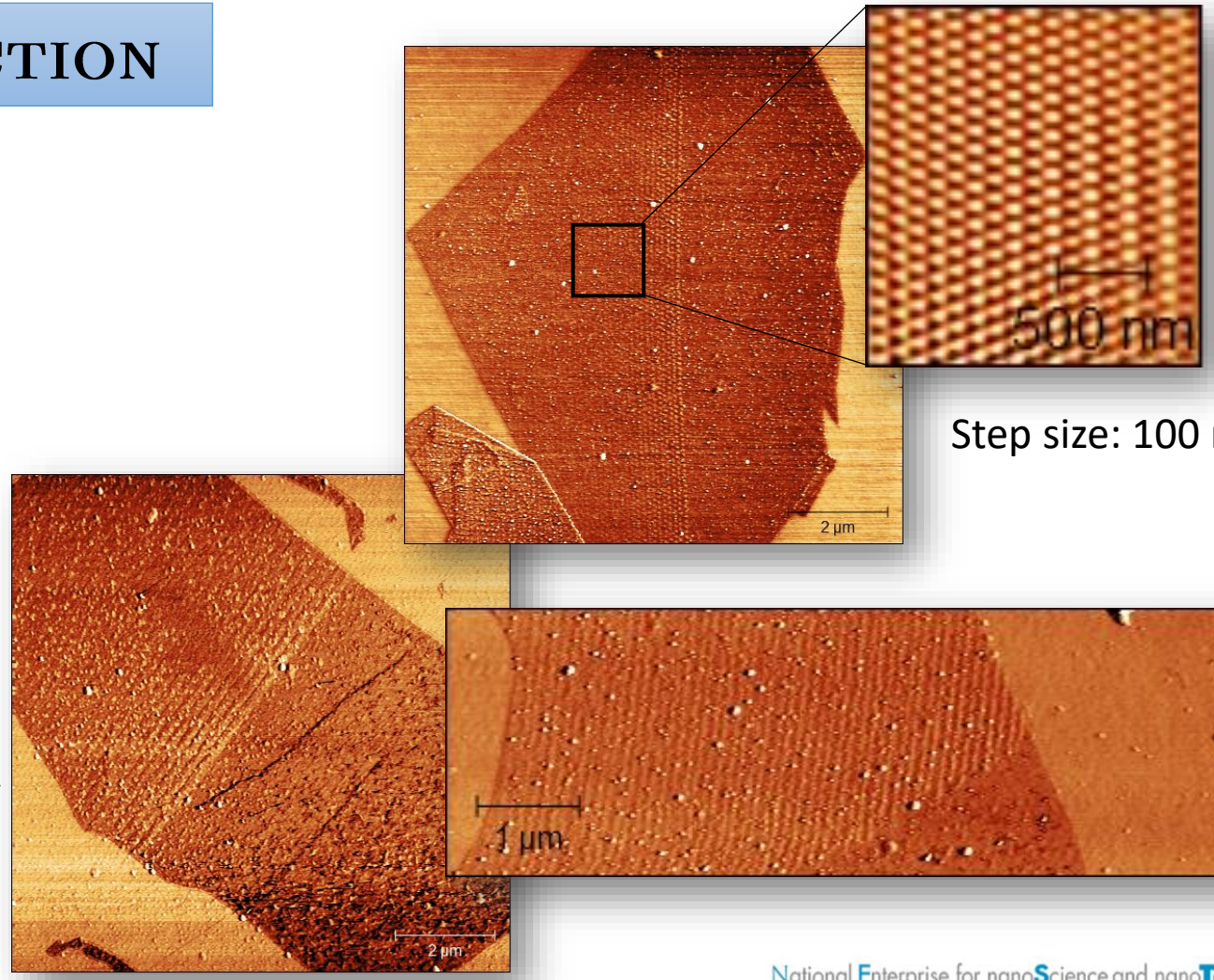


AFM



30 kV, 40.000 µC/cm^2
Step size: 100 nm

[*F.Bianco* @ NEST]



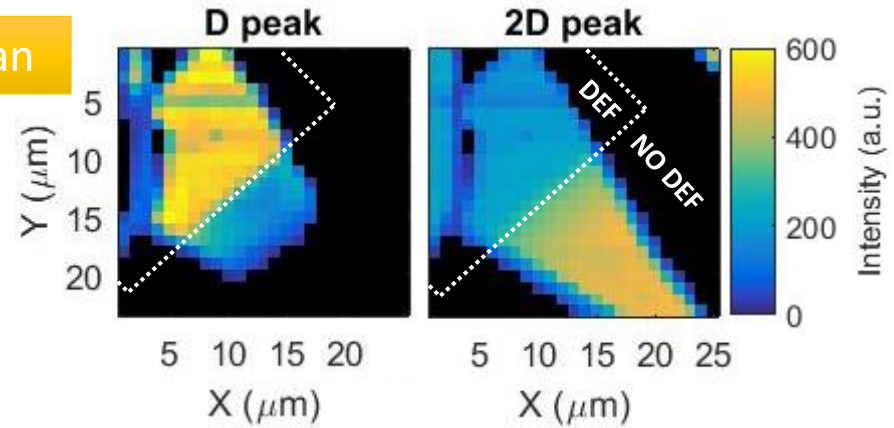
Step size: 100 nm

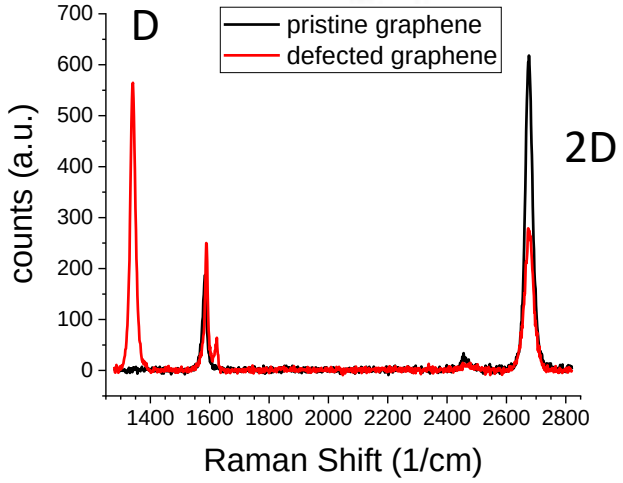
National Enterprise for nanoScience and nanoTechnology

Defects introduction

Electron bombardment (EBL) on flakes

Raman

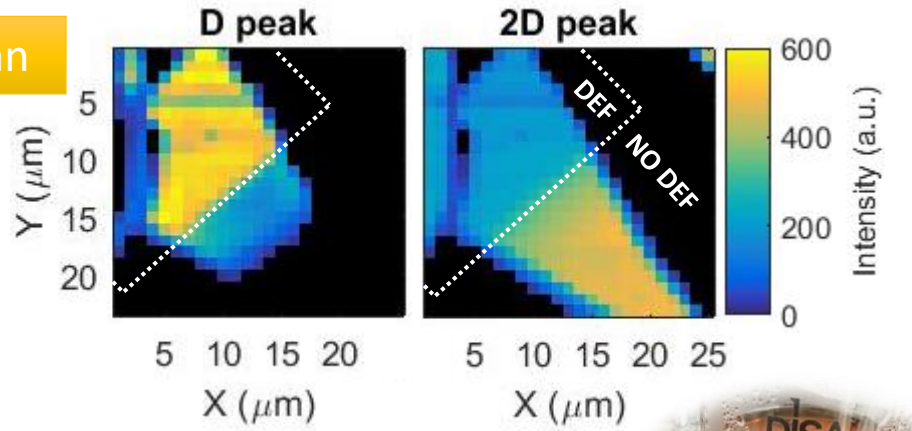


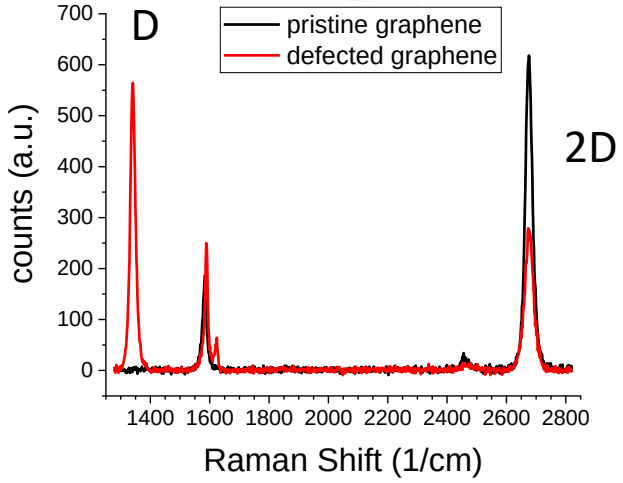


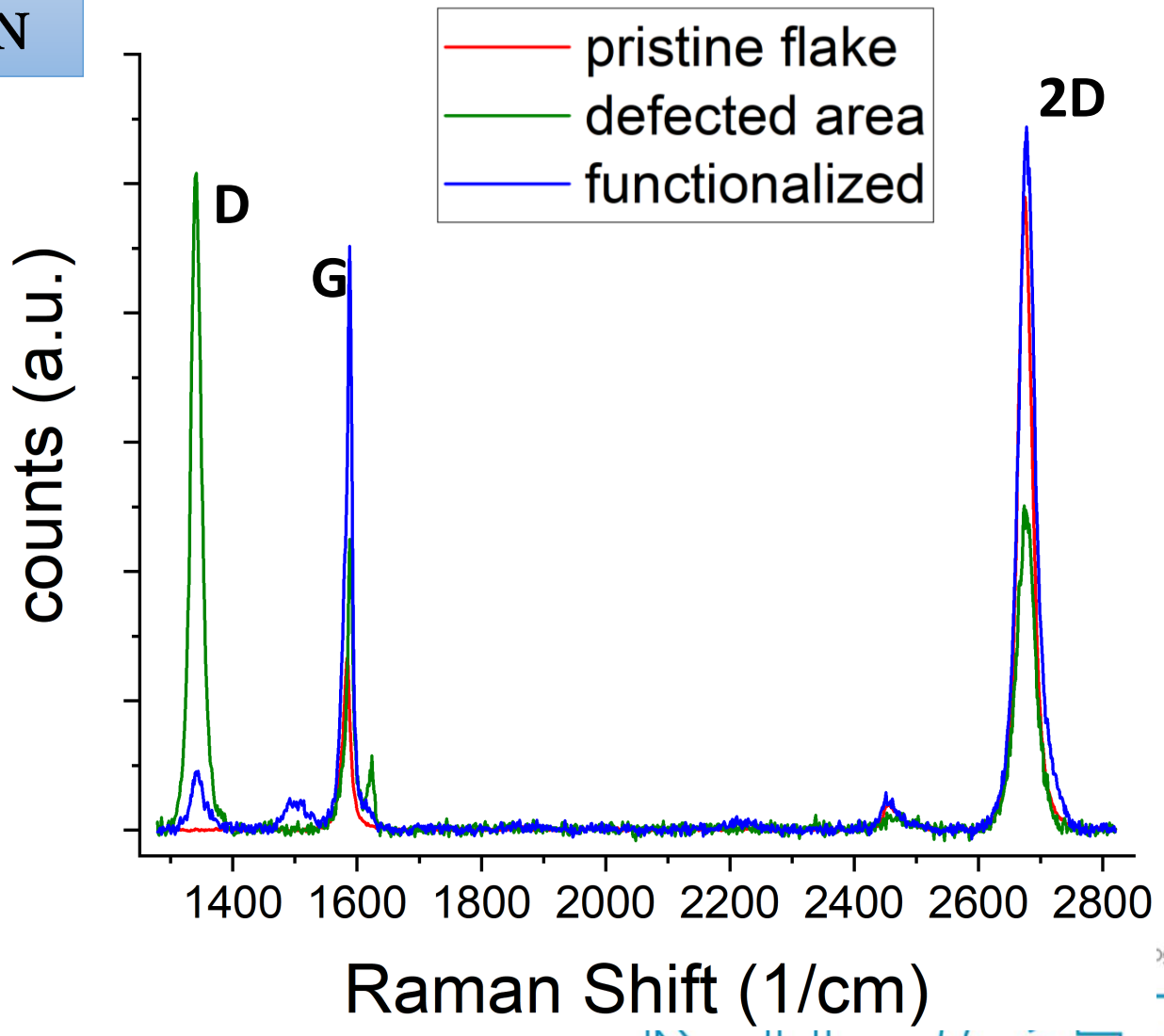
Defects introduction

Electron bombardment (EBL) on flakes

Raman



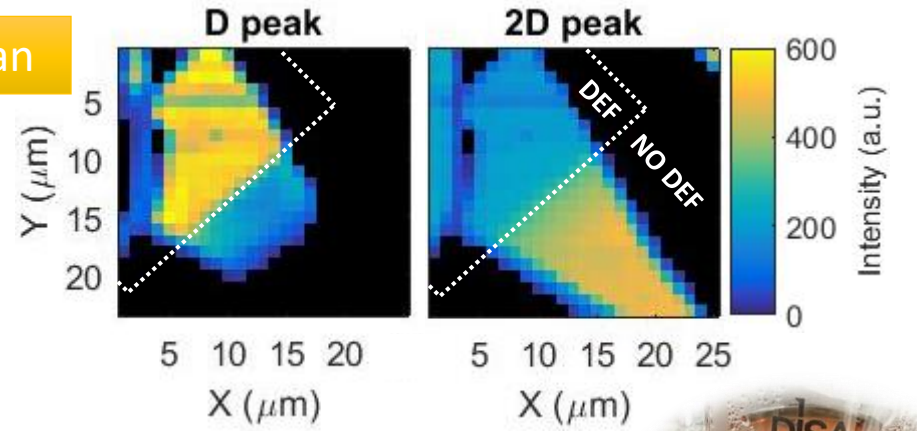


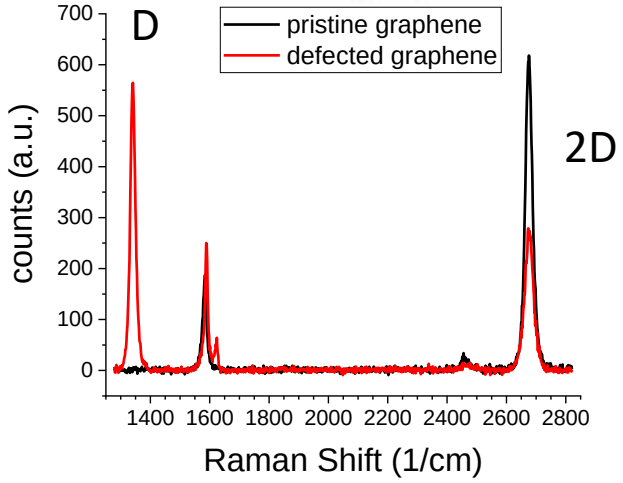


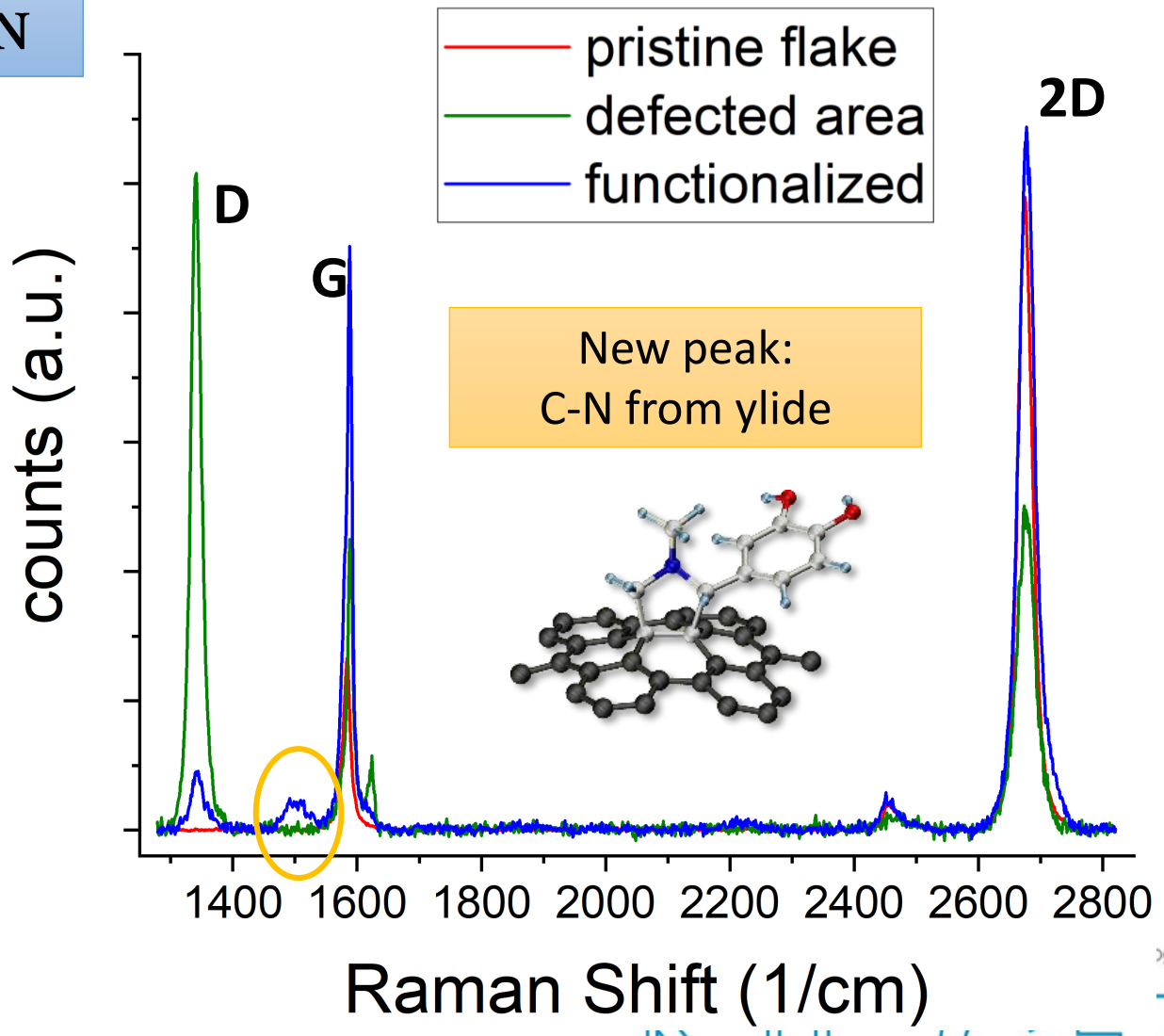
Defects introduction

Electron bombardment (EBL) on flakes

Raman



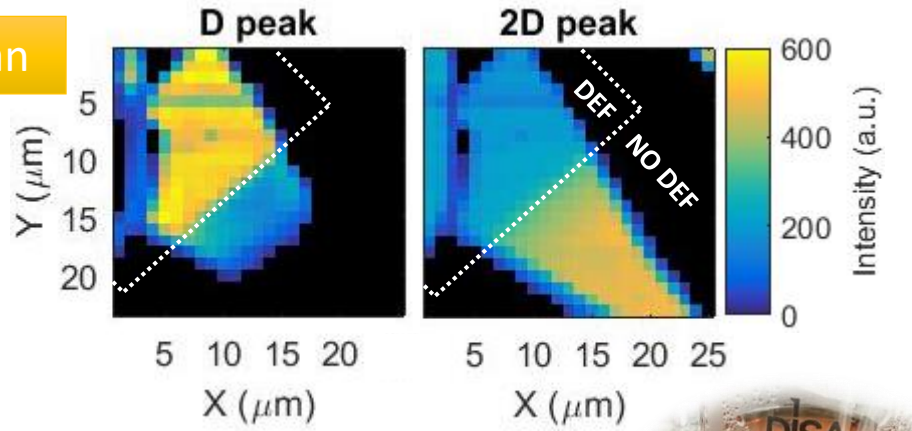


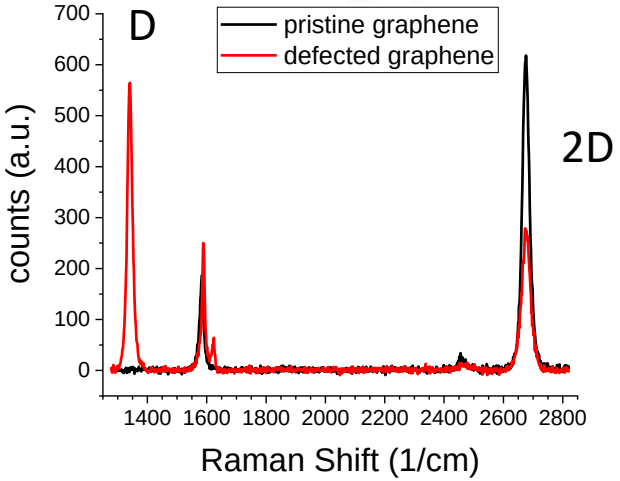


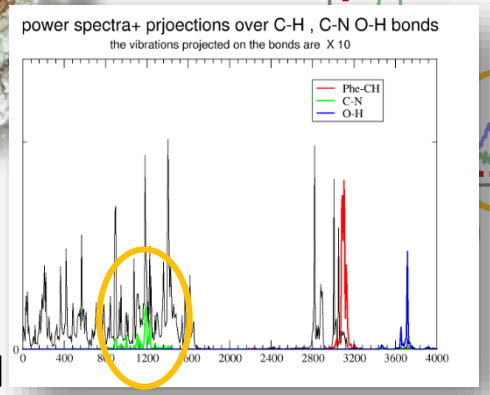
Defects introduction

Electron bombardment (EBL) on flakes

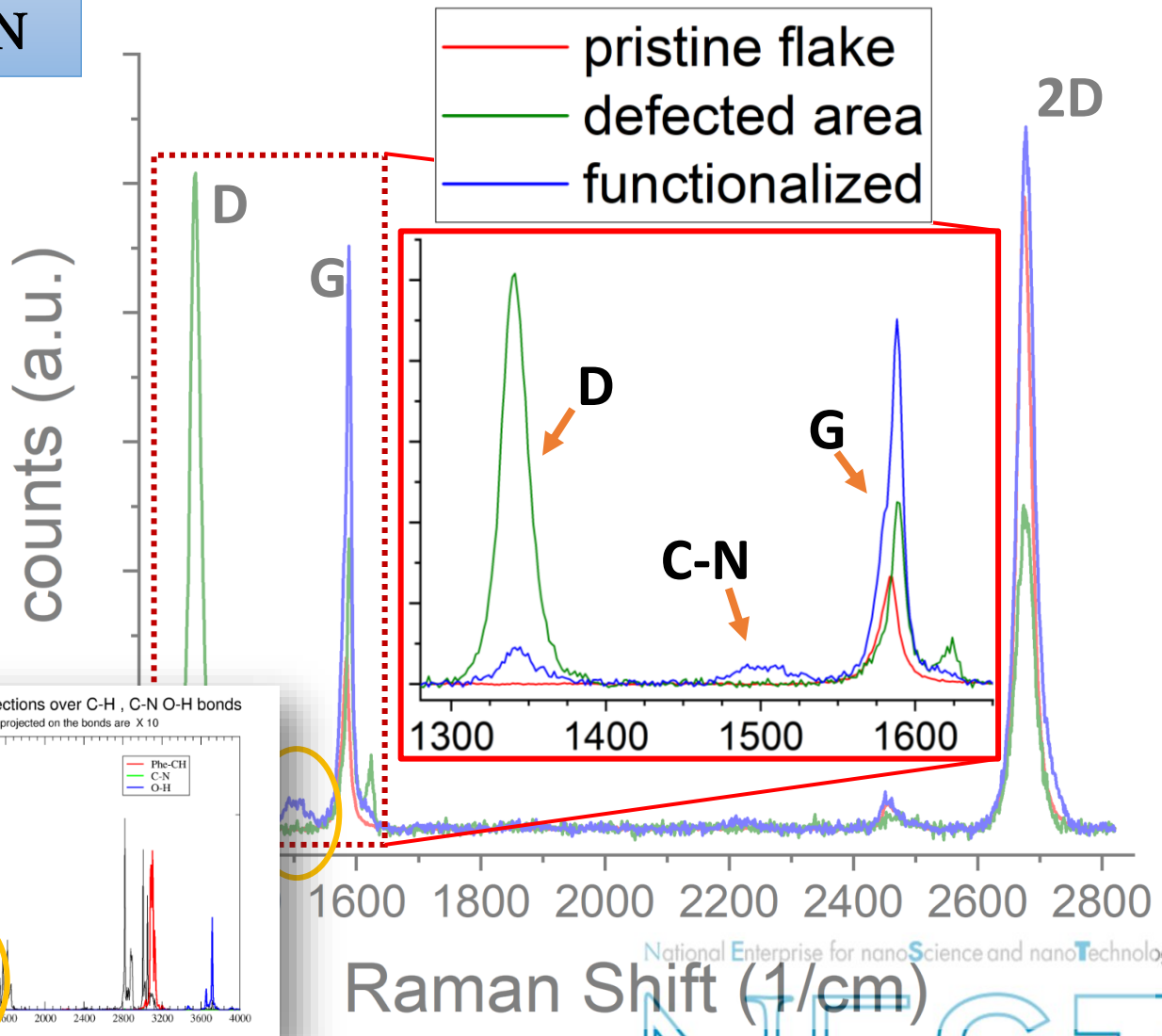
Raman







[L.Bellucci @ NEST]

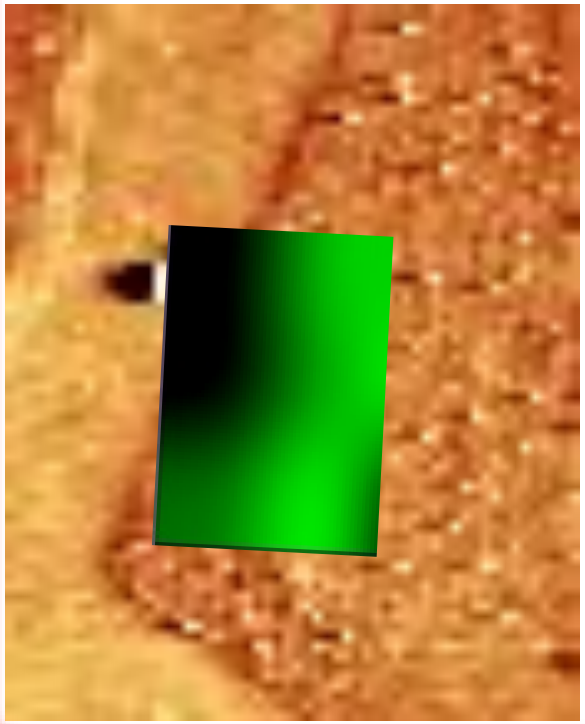


Defects introduction

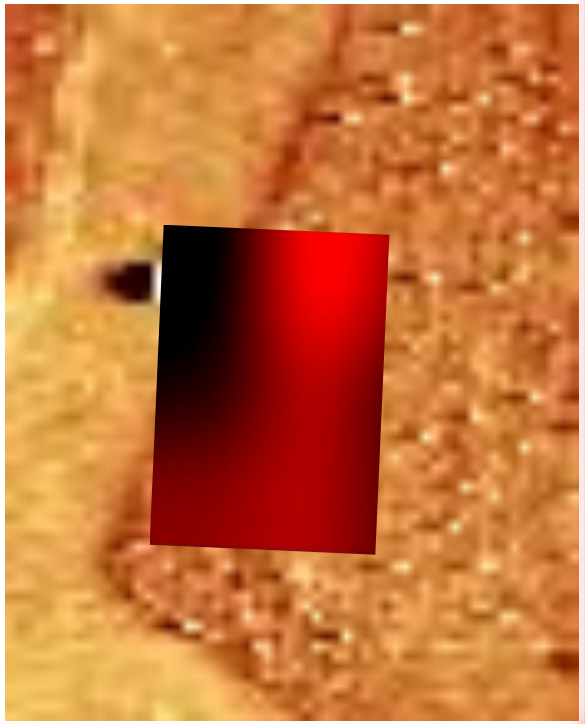
Electron bombardment (EBL) on flakes

Raman

Intensity at 1345 cm^{-1}



Intensity at 1499 cm^{-1}

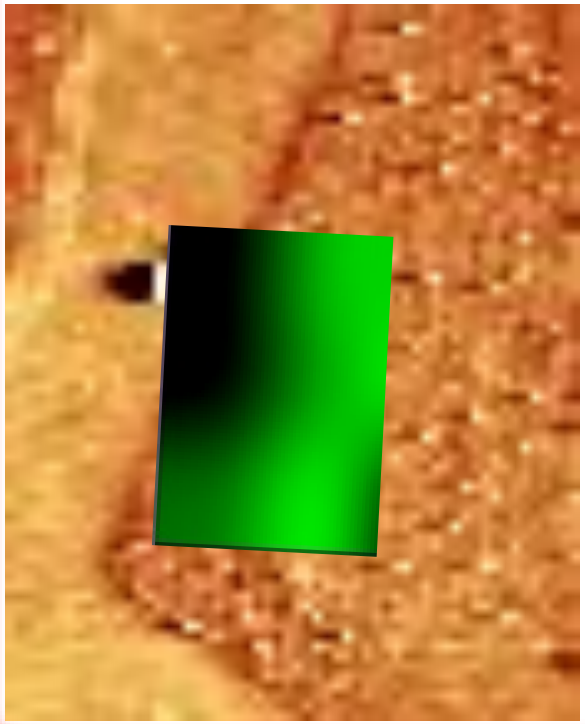


Defects introduction

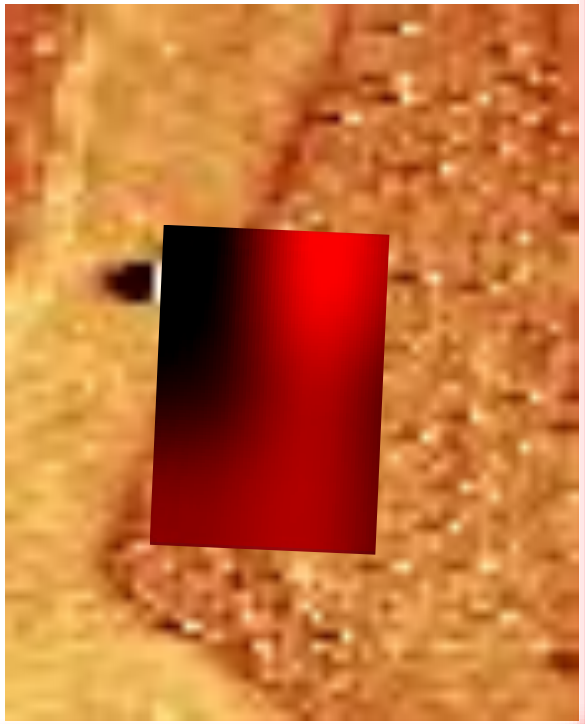
Electron bombardment (EBL) on flakes

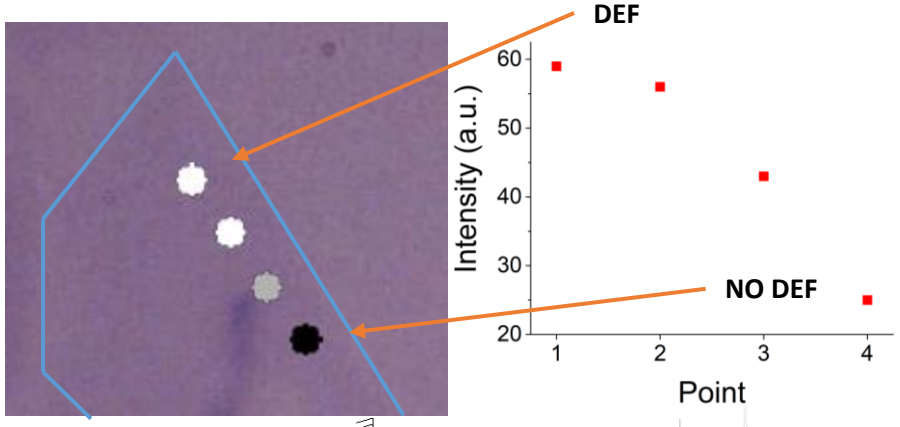
Raman

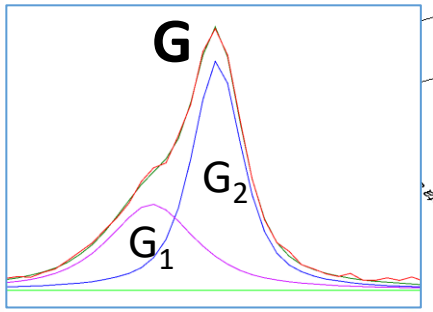
Intensity at 1345 cm^{-1}



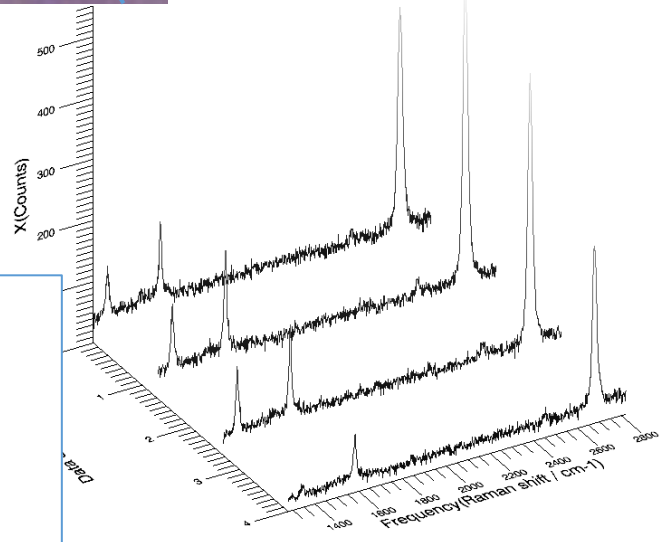
Intensity at 1499 cm^{-1}







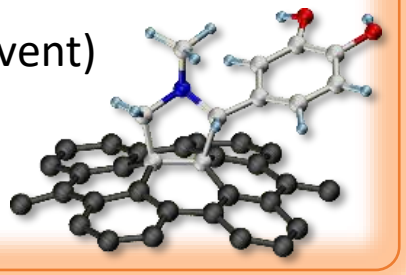
Splitting of G peak



National Enterprise for nanoScience and nanoTechnology

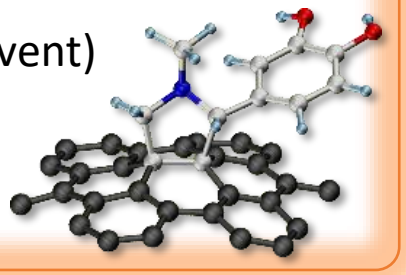
Functionalization Optimization

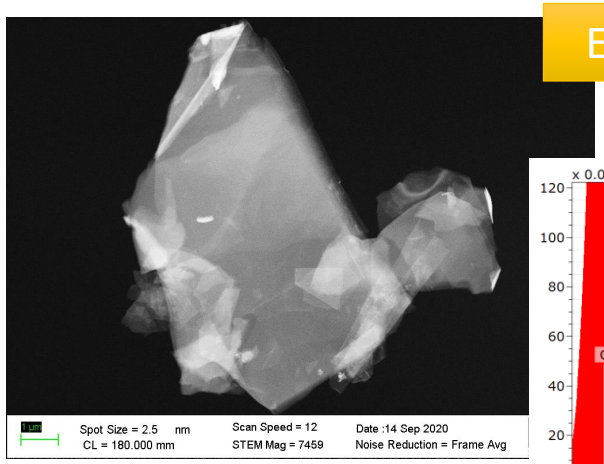
- Sonicator dispersion VS Homogenizer dispersion
- NMP VS DMF (as dispersion solvent)
- Dispersed graphene VS rGO



Functionalization Optimization

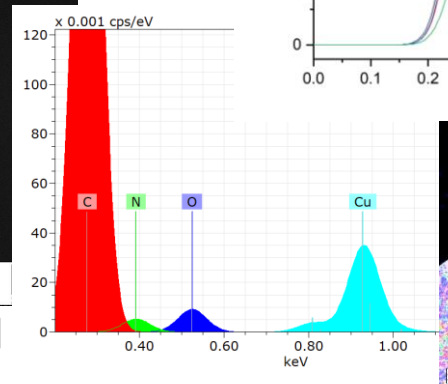
- Sonicator dispersion VS Homogenizer dispersion
- NMP VS DMF (as dispersion solvent)
- Dispersed graphene VS rGO

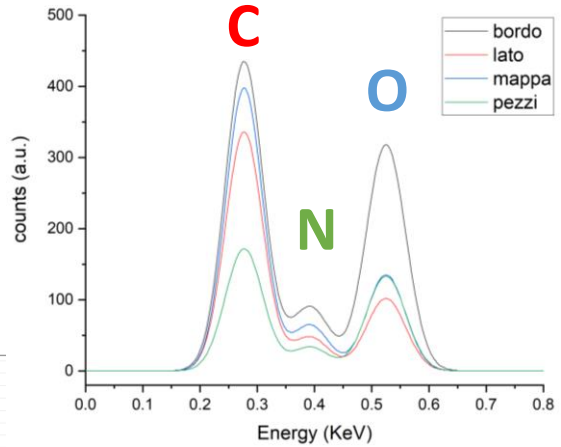


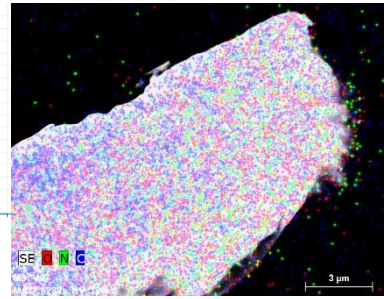


[*A.Griesi* @ NEST]

EDX



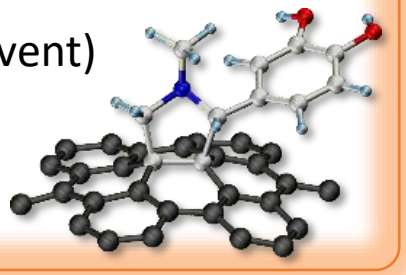




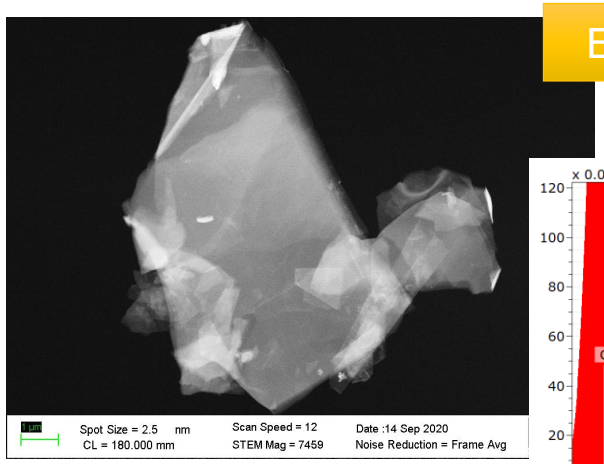
[*Scientific Rep.*, **2017**, 7, 3825]

Functionalization Optimization

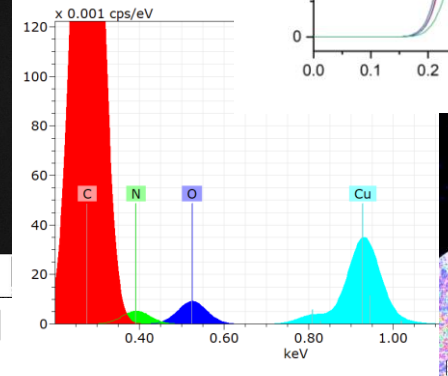
- Sonicator dispersion VS Homogenizer dispersion
- NMP VS DMF (as dispersion solvent)
- Dispersed graphene VS rGO

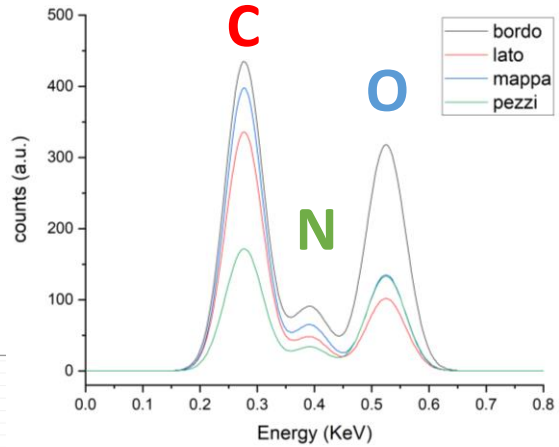


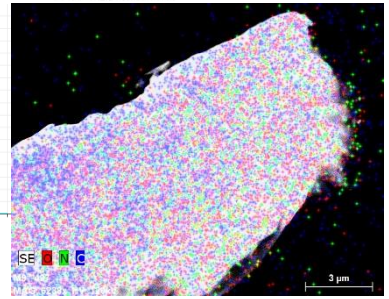
EDX



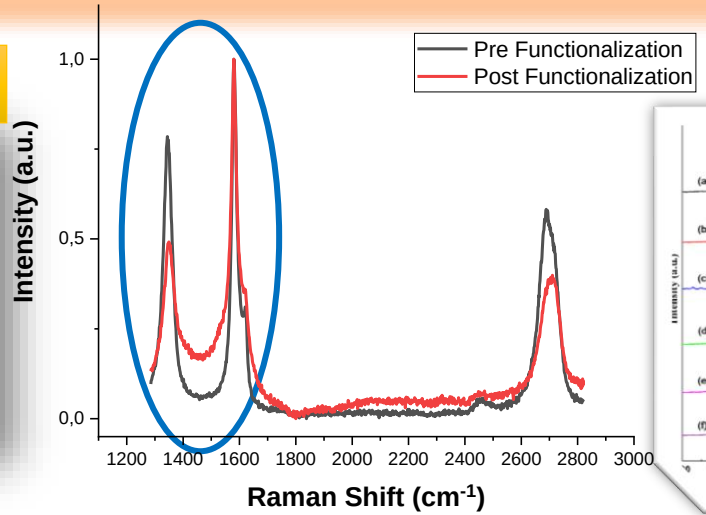
[*A.Griesi* @ NEST]

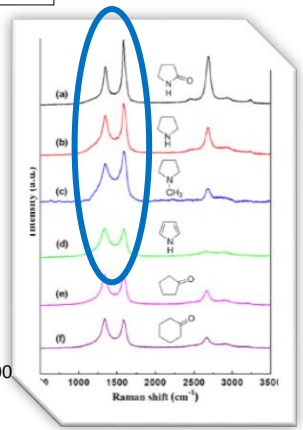






Raman

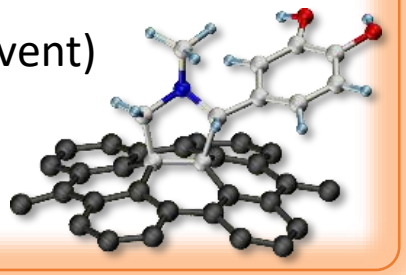




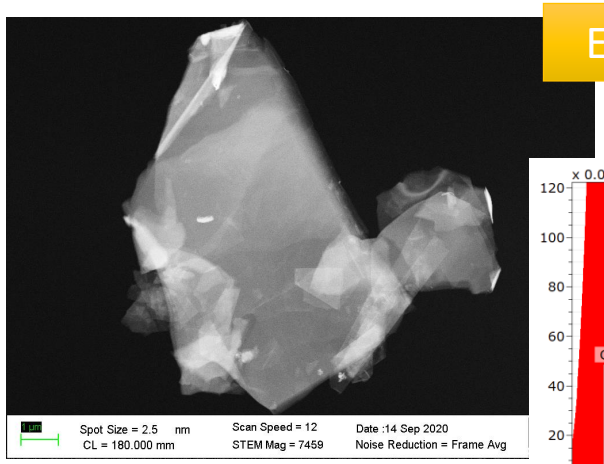
[*Scientific Rep.*, **2017**, 7, 3825]

Functionalization Optimization

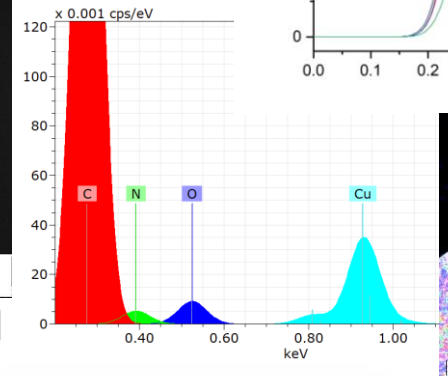
- Sonicator dispersion VS Homogenizer dispersion
- NMP VS DMF (as dispersion solvent)
- Dispersed graphene VS rGO

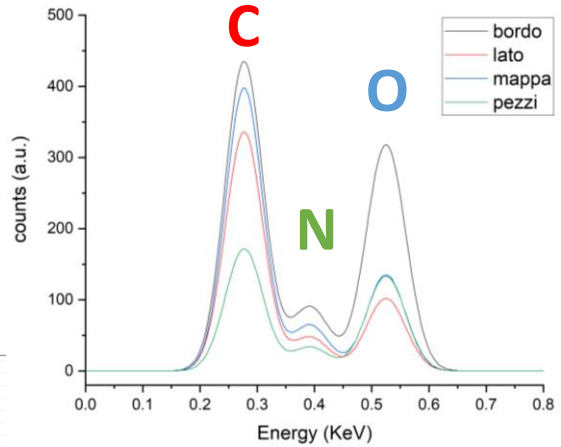


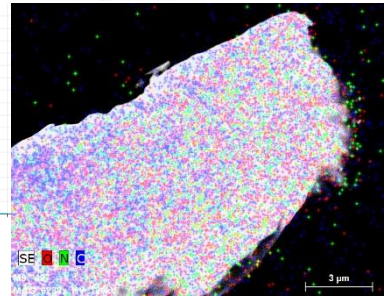
EDX



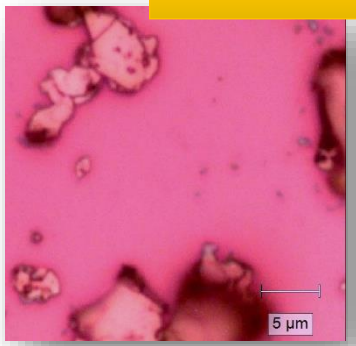
[*A.Griesi* @ NEST]

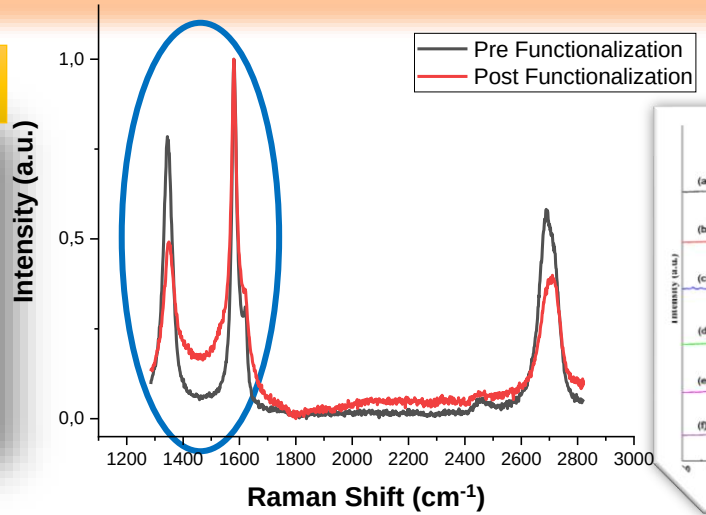


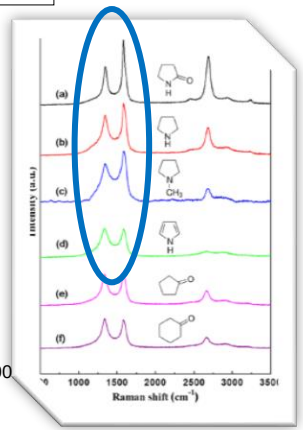




Raman

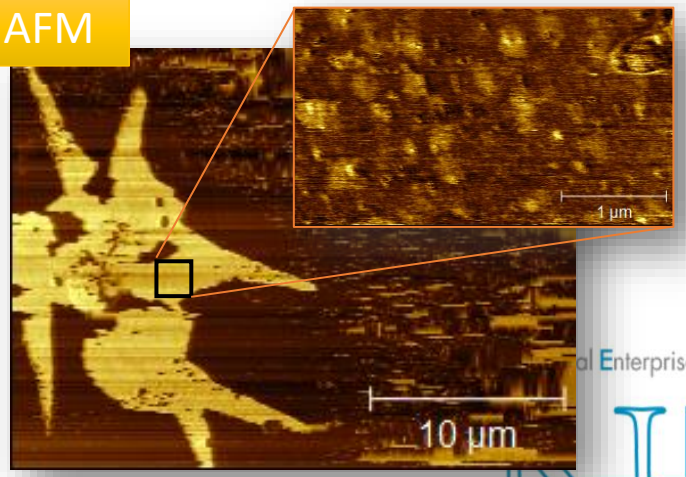






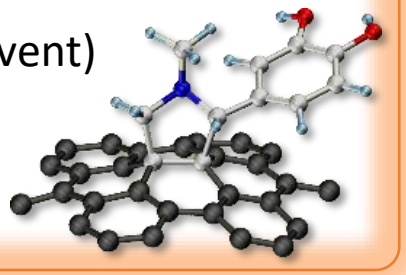
[*Scientific Rep.*, **2017**, 7, 3825]

AFM

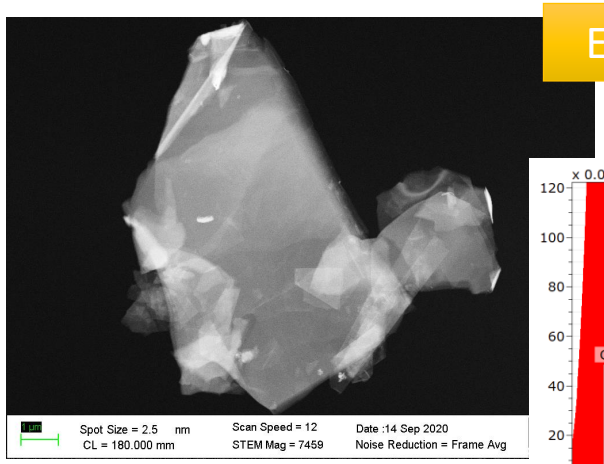


Functionalization Optimization

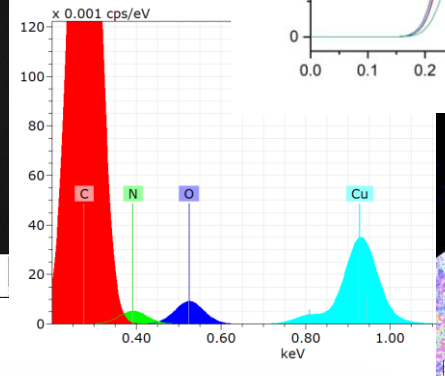
- Sonicator dispersion VS Homogenizer dispersion
- NMP VS DMF (as dispersion solvent)
- Dispersed graphene VS rGO

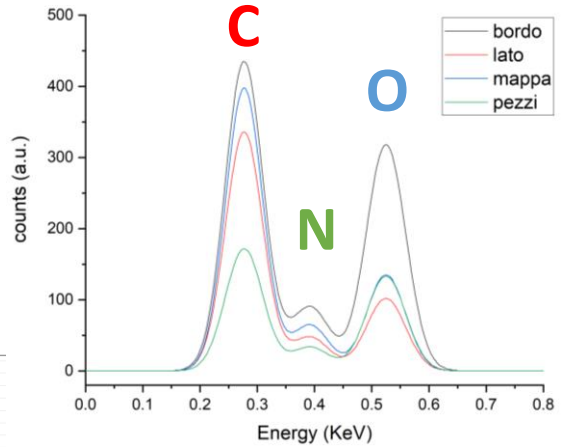


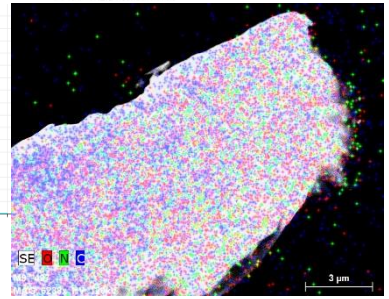
EDX



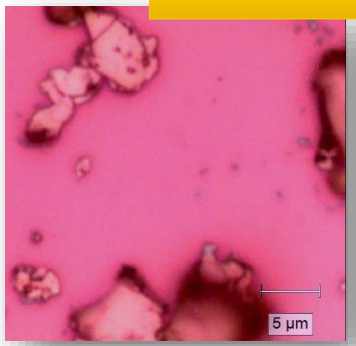
[*A.Griesi* @ NEST]

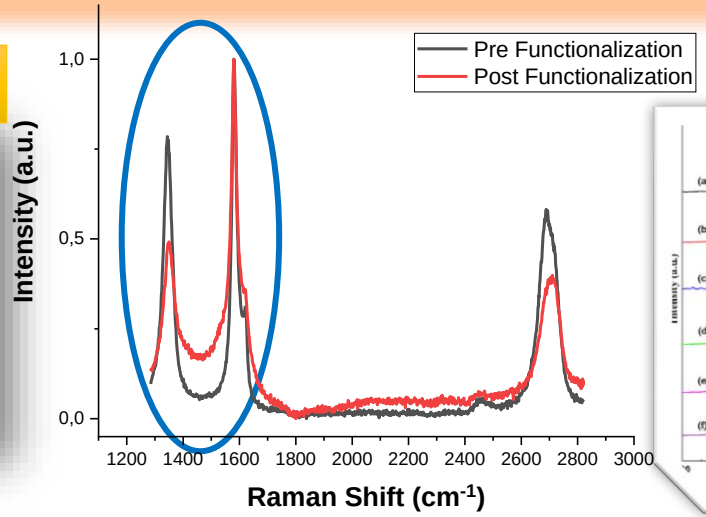


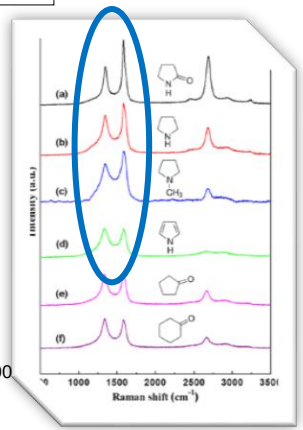




Raman

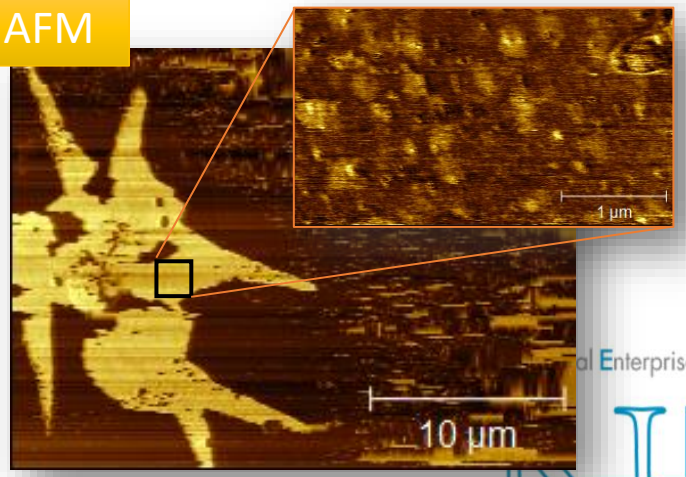






[*Scientific Rep.*, **2017**, 7, 3825]

AFM

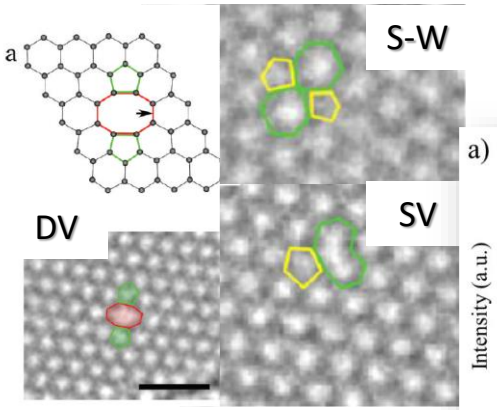


XPS

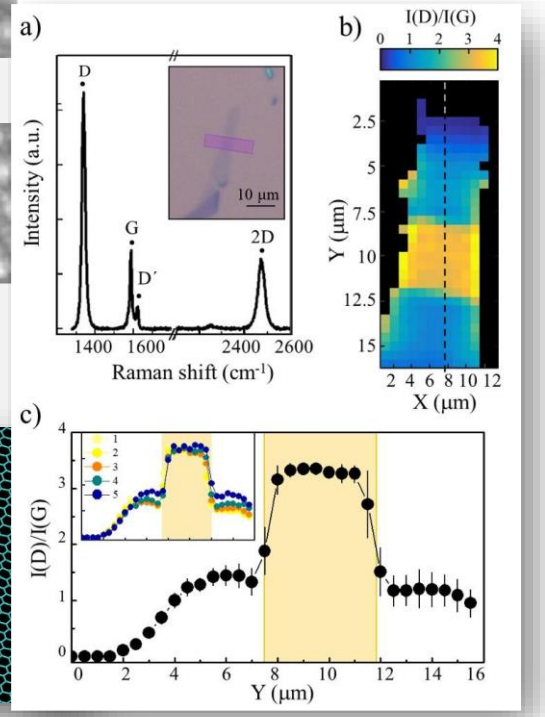
DLS

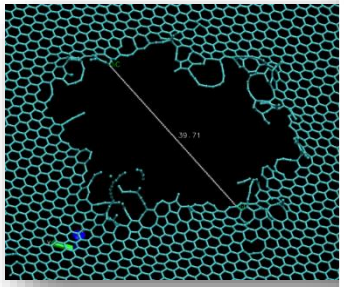
What's Next

Investigation on defects



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

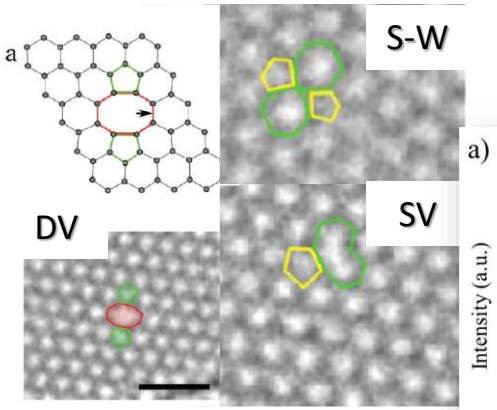




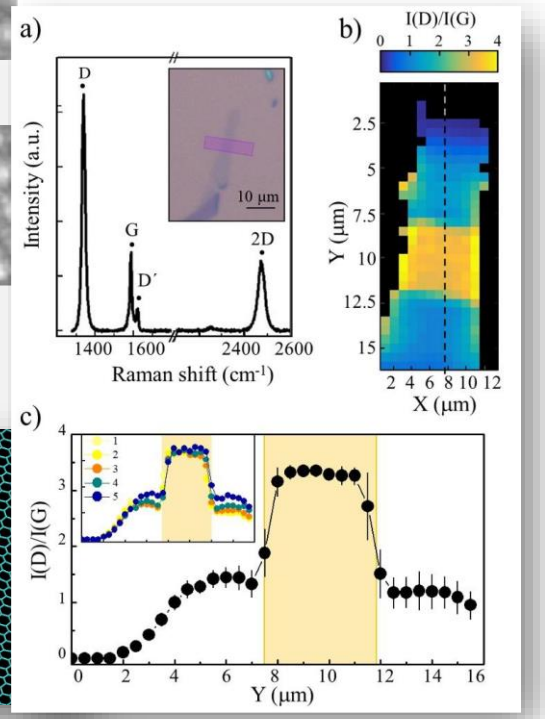
[*F.Bianco, L.Bellucci* @ NEST]

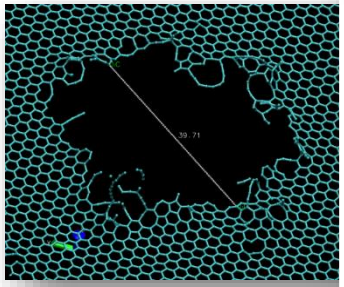
What's Next

Investigation on defects



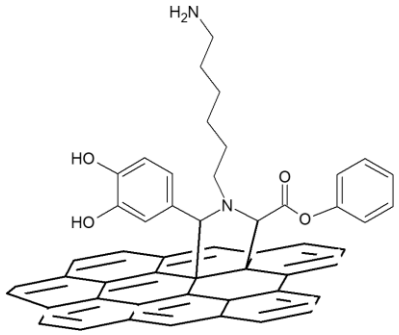
[*ACSNano*, **2015**, 9, 4, 3428
ACSNano, **2011**, 5, 1, 26]





[*F.Bianco, L.Bellucci* @ NEST]

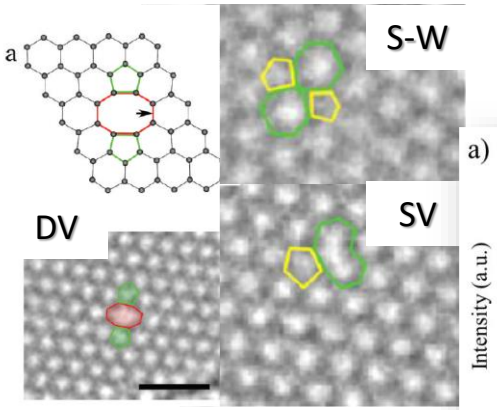
Synthesis of a new ylide



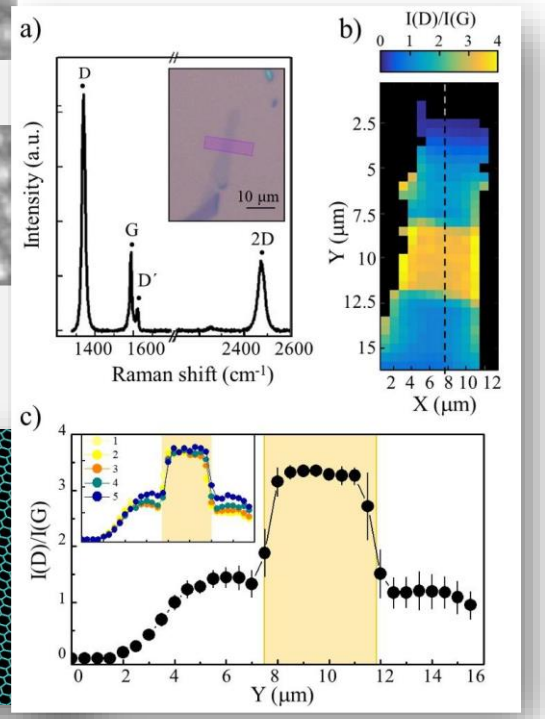
[*A.Moscardini* @ NEST]

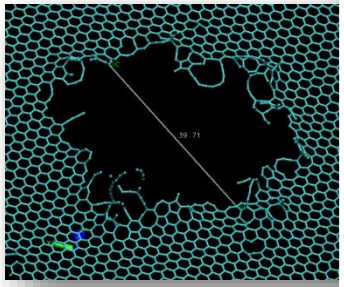
What's Next

Investigation on defects



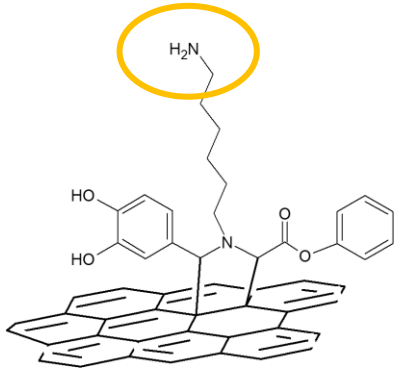
[*ACSNano*, **2015**, 9, 4, 3428
ACSNano, **2011**, 5, 1, 26]





[*F.Bianco, L.Bellucci* @ NEST]

Synthesis of a new ylide



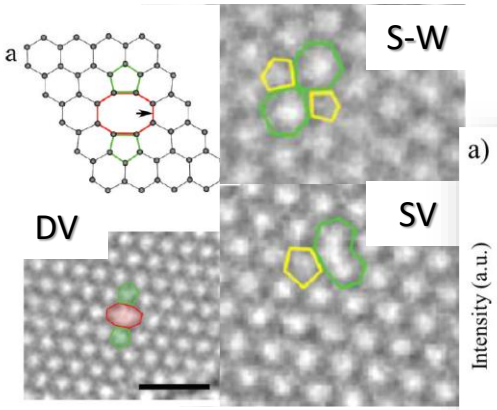
[*A.Moscardini* @ NEST]

Patterned functionalization with:

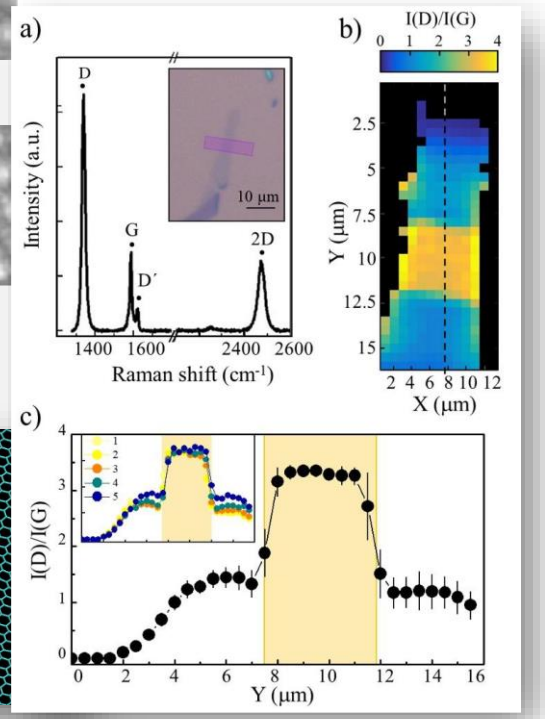
- Fluorophores
- Gold NP (with linker)

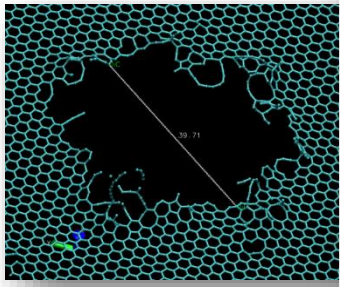
What's Next

Investigation on defects



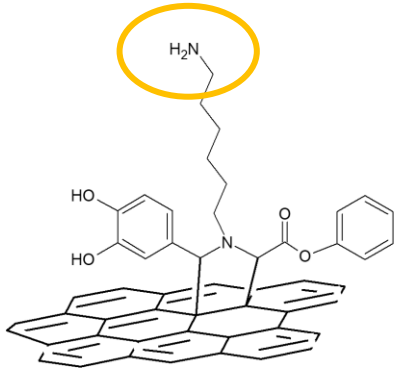
[*ACSNano*, **2015**, 9, 4, 3428
ACSNano, **2011**, 5, 1, 26]





[*F.Bianco, L.Bellucci* @ NEST]

Synthesis of a new ylide

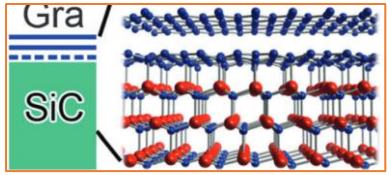


[*A.Moscardini* @ NEST]

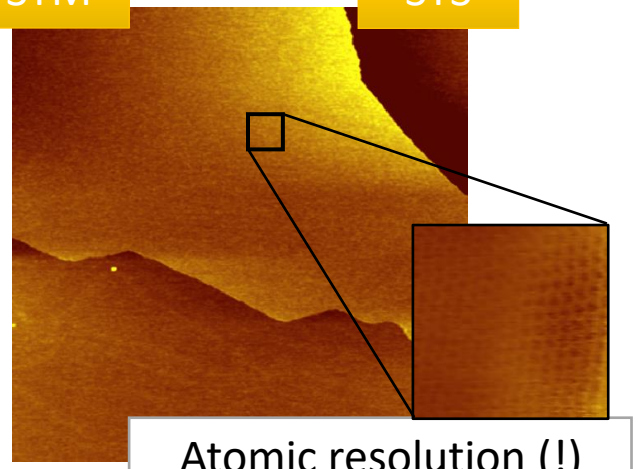
Patterned functionalization with:

- Fluorophores
- Gold NP (with linker)

… back to EG



STM STS



Atomic resolution (!)

National Enterprise for nanoScience and nanoTechnology

Other PhD oriented Activities

- August 2020: abstract submitted to the ECOSS35 in Luxembourg

- July 2020: tutorship as Science Class SNS tutor at the Orientation week (online)

- Seminars & Training