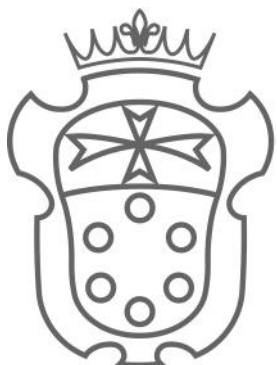

NANOSCIENCES

~ 2nd year PhD report ~

PhD student: **Luca Basta**

Supervisor: **Dr. Stefano Veronesi**



SCUOLA
NORMALE
SUPERIORE

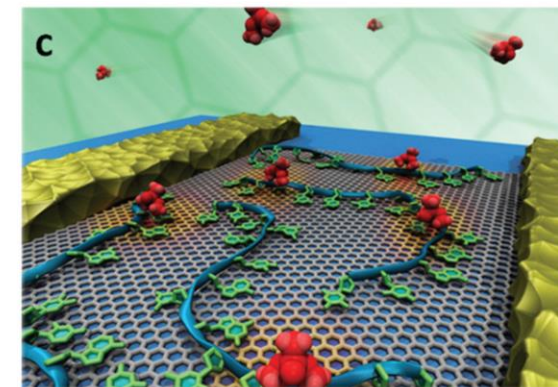
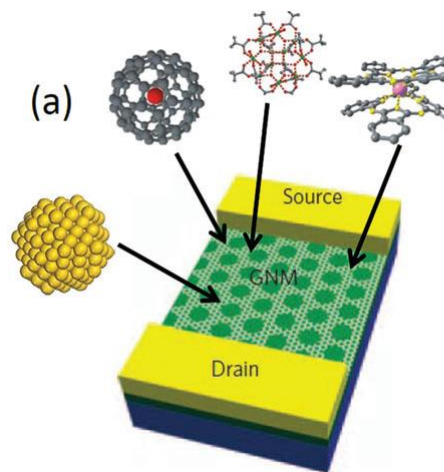
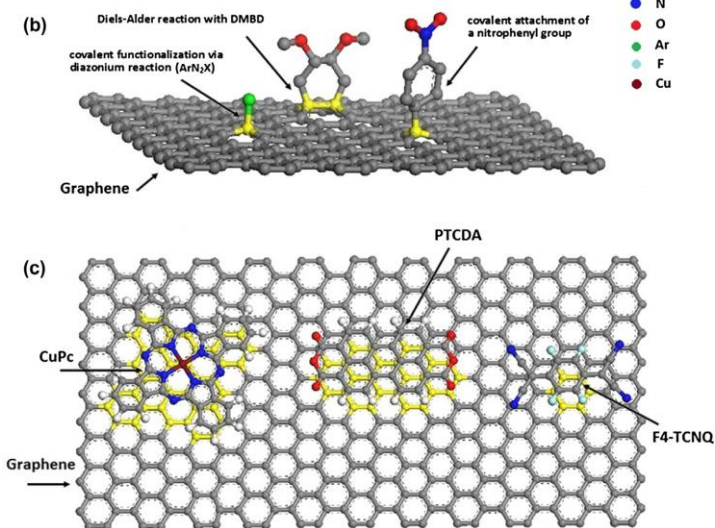
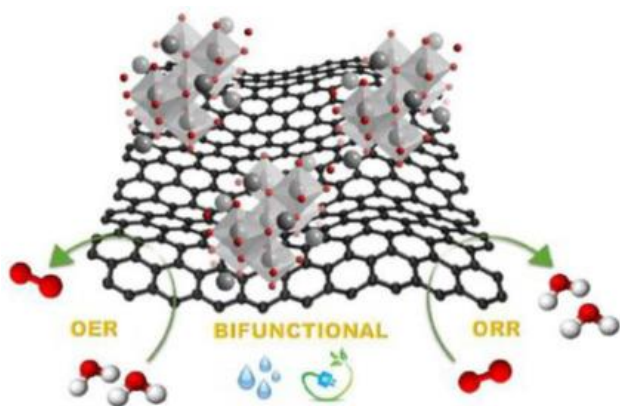
PERFEZIONAMENTO IN NANOSCIENZE

National Enterprise for nanoScience and nanoTechnology

NINEST

RESEARCH MOTIVATION

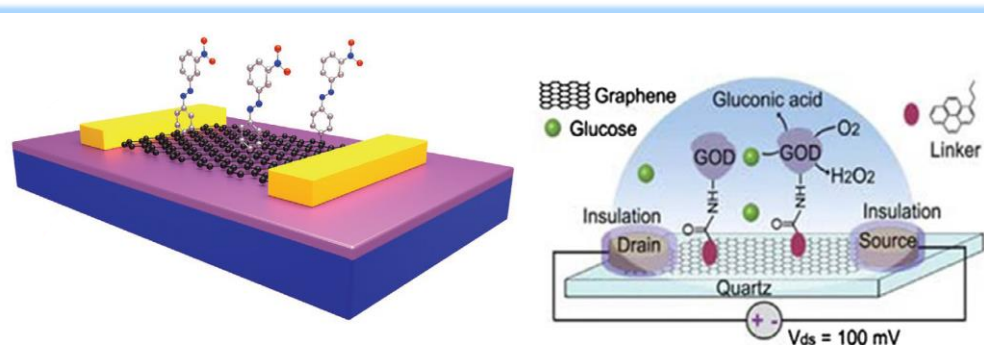
The principal aim of my research is the **covalent functionalization** of graphene with organic molecules. This would allow to finely tune or enhance the system's physical and chemical properties, resulting in a valuable synergistic combination.



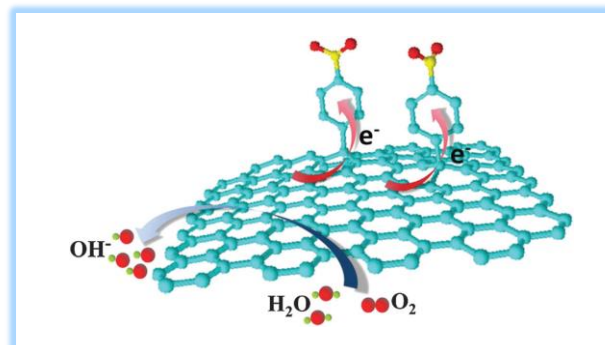
RESEARCH APPLICATION

Covalent functionalization of nanocomposite graphene systems, aimed at achieving:

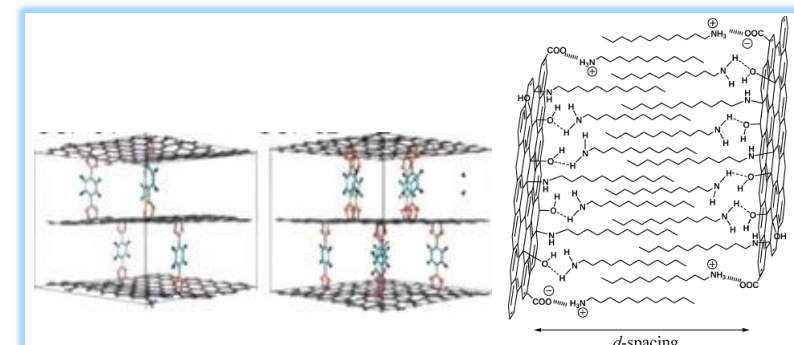
- realization of *new sensors* exploiting organic molecules as active sites onto graphene surface (selective interaction with *target* molecules);
- implementation of *nano-catalyst materials* (nanoparticle bonding or metal-free configuration);
- fabrication of *graphene/molecule/graphene* heterostructures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

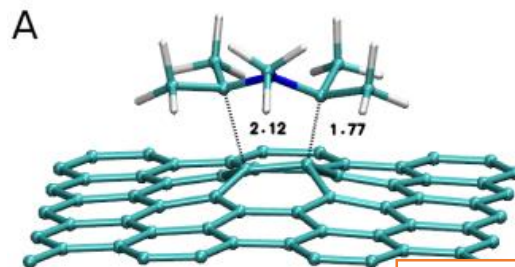
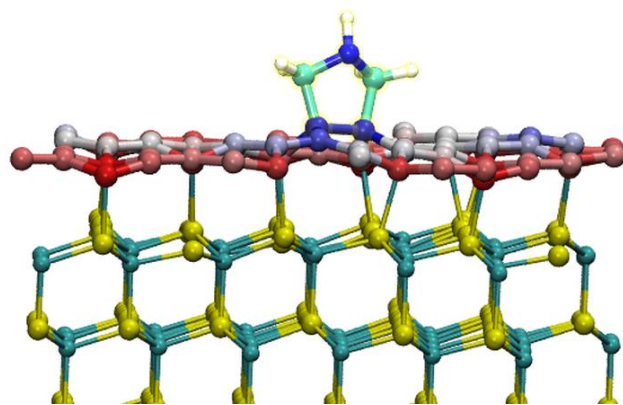
CYCLOADDITION REACTION

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

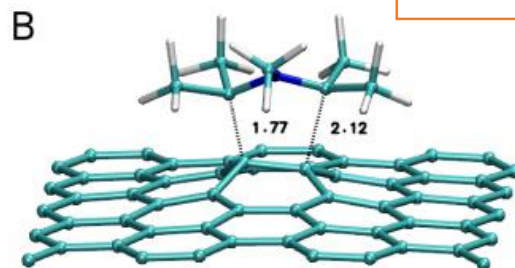
➤ high selectivity (close to the diene)

➤ reversible process

➤ stability up to $\sim 300^\circ\text{C}$



- 43 kcal/mol
- 1.87 eV



[L. Bellucci @ NEST]

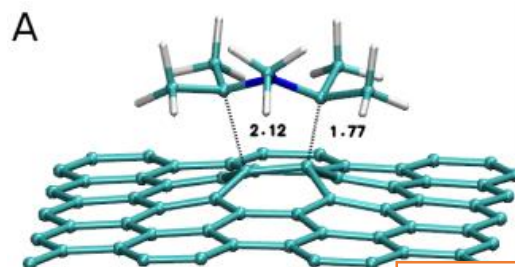
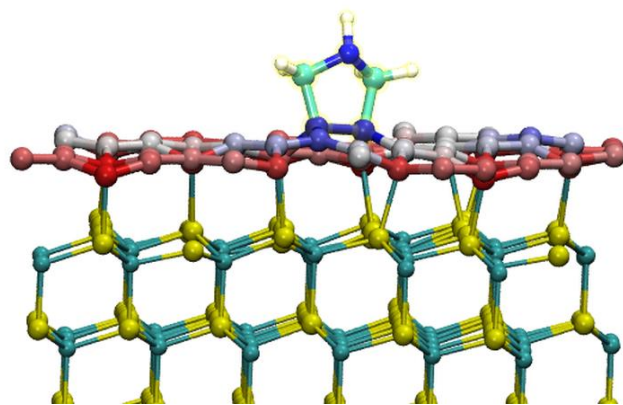
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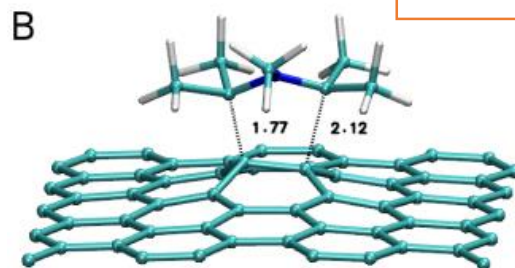
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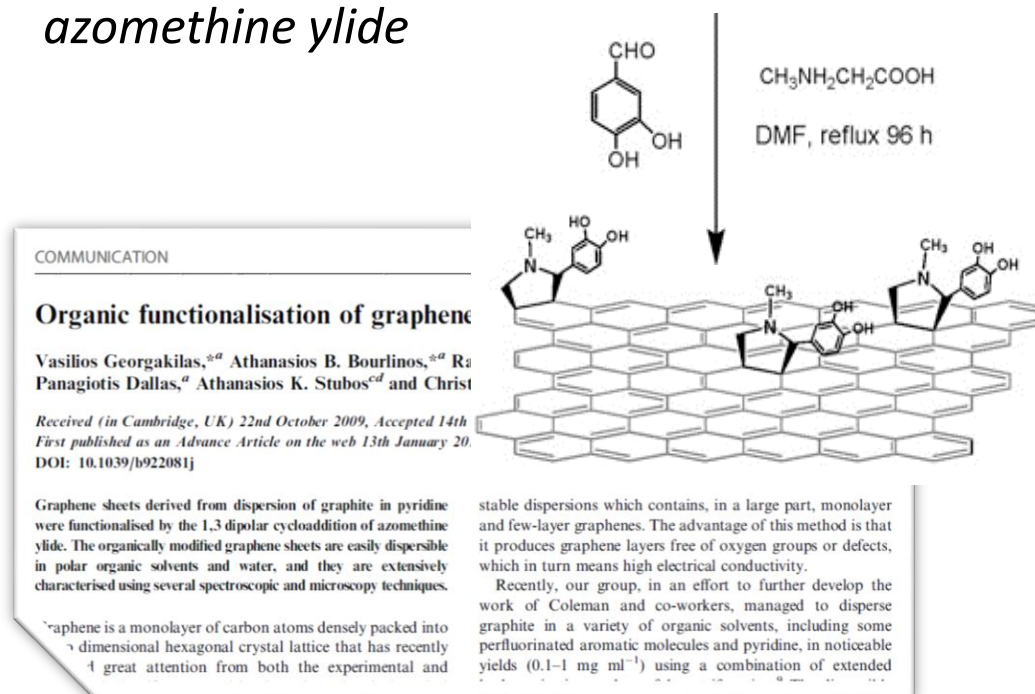


- 43 kcal/mol
- 1.87 eV



[L. Bellucci @ NEST]

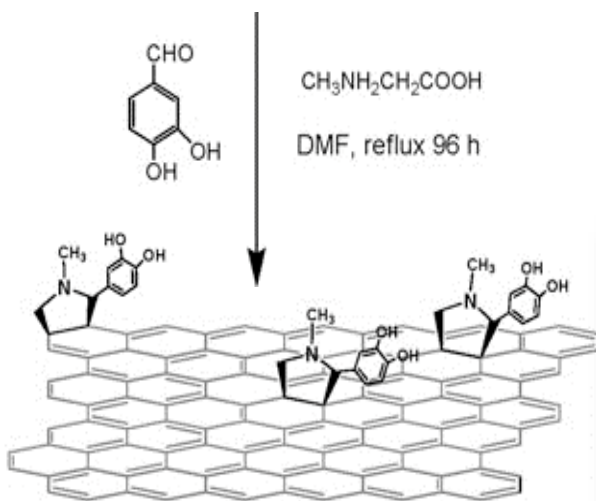
In collaboration with G. Signore @ NEST we selected the 1,3 dipolar cycloaddition with *azomethine ylide*



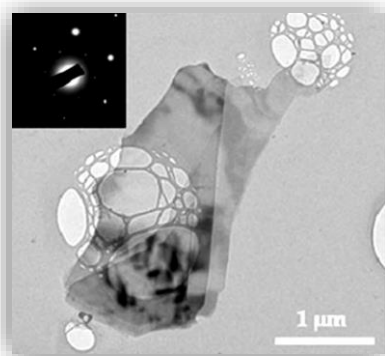
[Chem. Commun., 2010, 46, 1766]

FUNCTIONALIZATION PROCEDURE OPTIMIZED

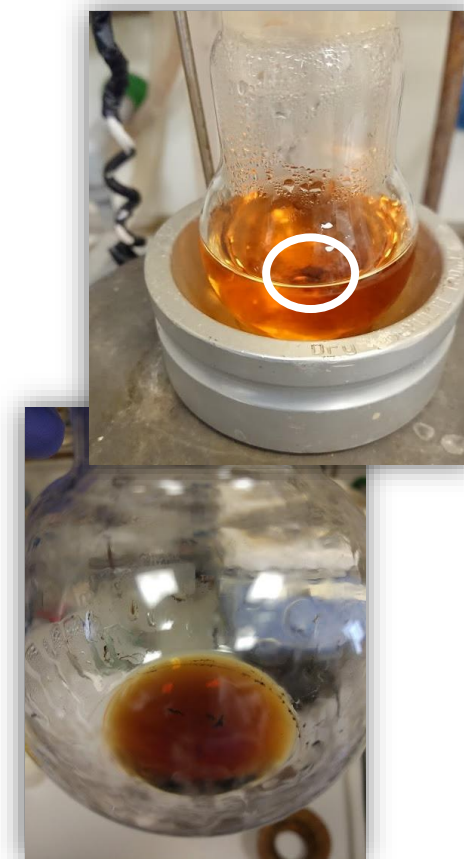
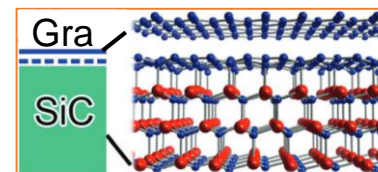
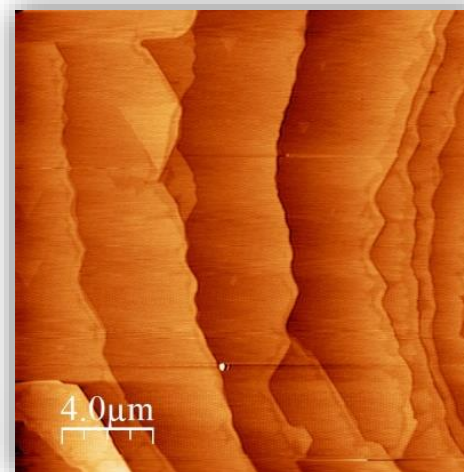
1,3 dipolar cycloaddition (with *methylpyrrolidine*)



➤ Dispersed graphene

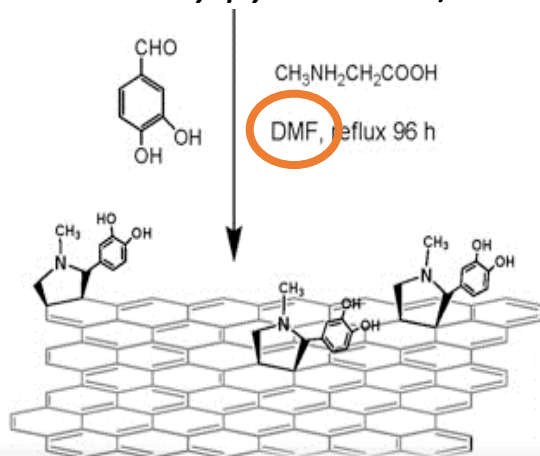


➤ High quality epitaxial graphene (buffer/mono layer)

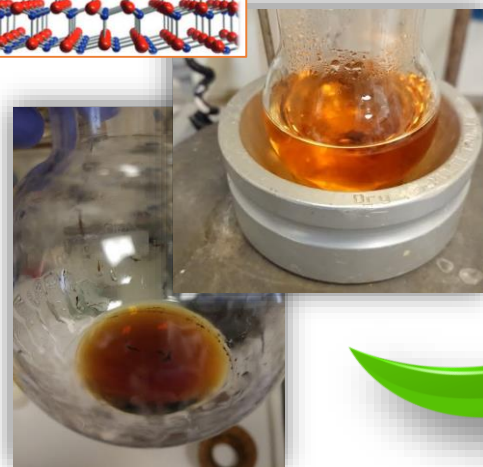
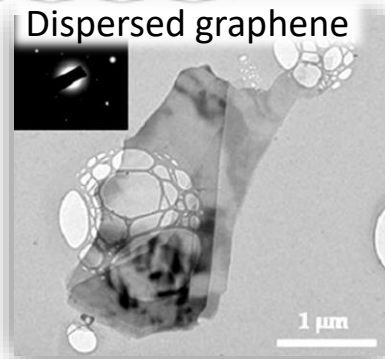
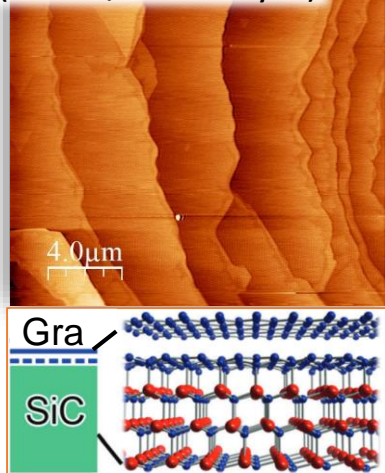


FUNCTIONALIZATION PROCEDURE OPTIMIZED

1,3 dipolar cycloaddition
(with *methylpyrrolidine*)



Epitaxial graphene
(buffer/mono layer)



- NMP as solvent
(increases thermal stability up to 10 days)
- Nitrogen flux
(reduces oxidation and degradation)
- Magnetic stirring
(increases kinetics)

[A. Moscardini @ NEST]

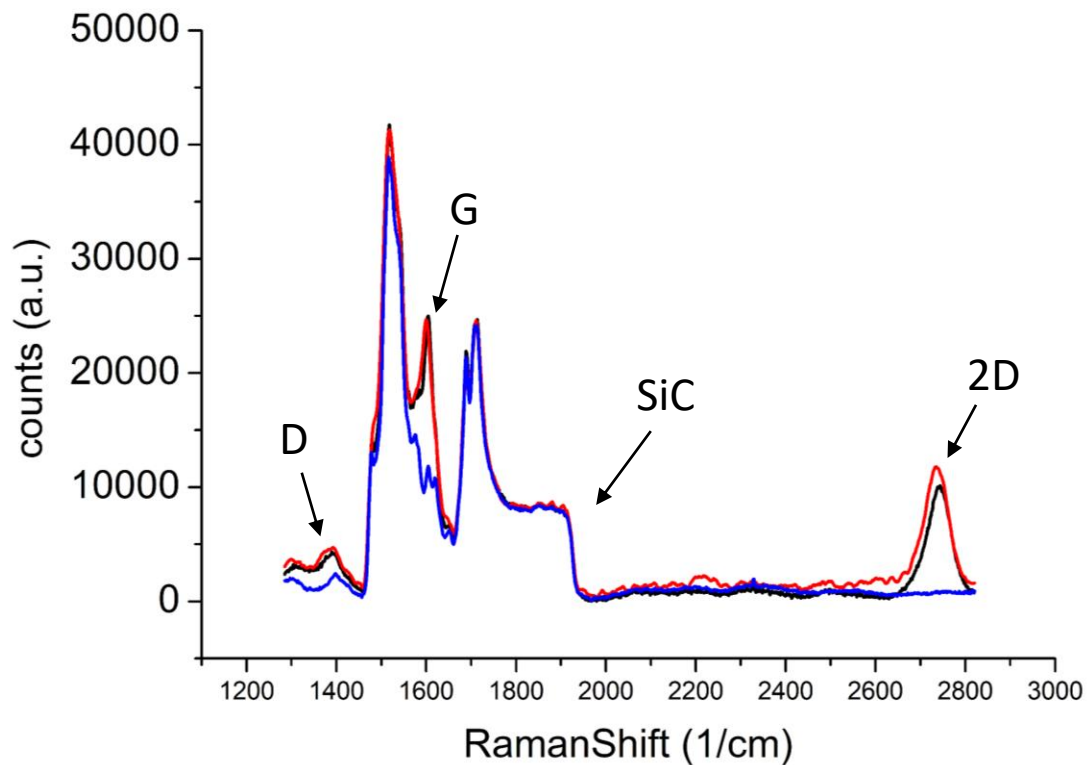


National Enterprise for nanoScience and nanoTechnology

RAMAN/AFM RESULTS

Raman spectroscopy

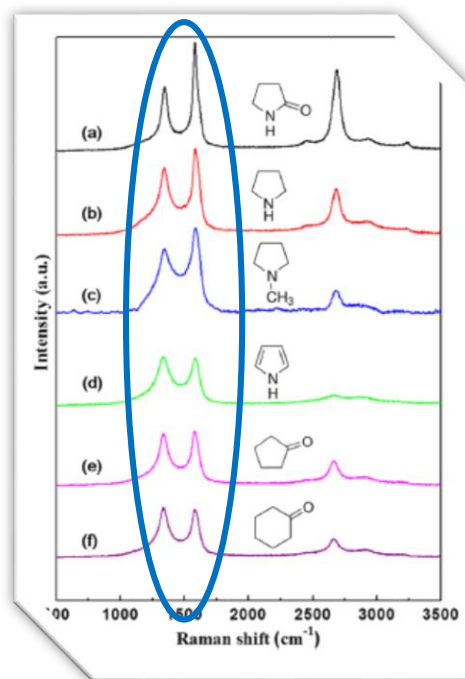
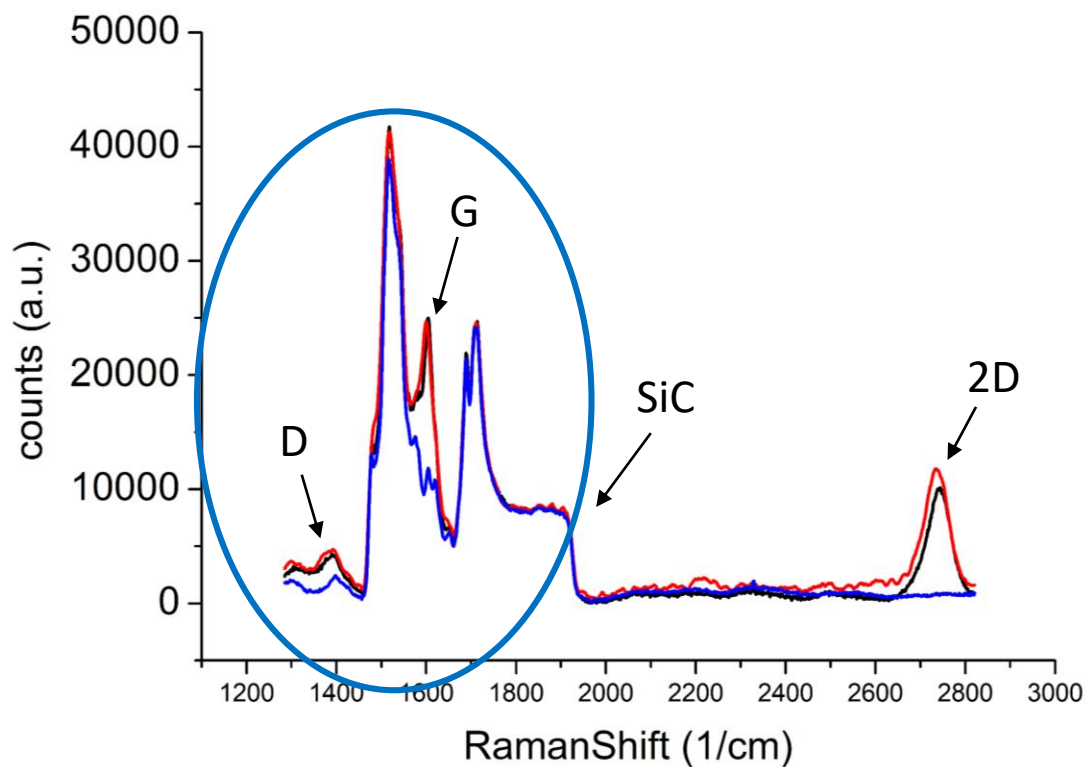
- Substrate (SiC)
- Pristine Graphene
- Functionalized graphene



RAMAN/AFM RESULTS

Raman spectroscopy

- Substrate (SiC)
- Pristine Graphene
- Functionalized graphene

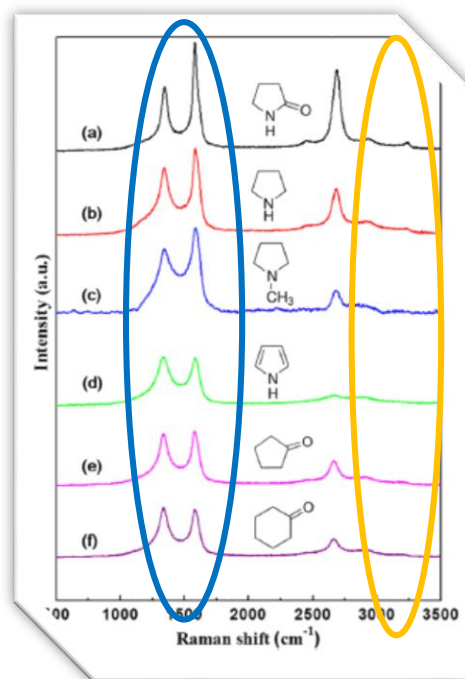
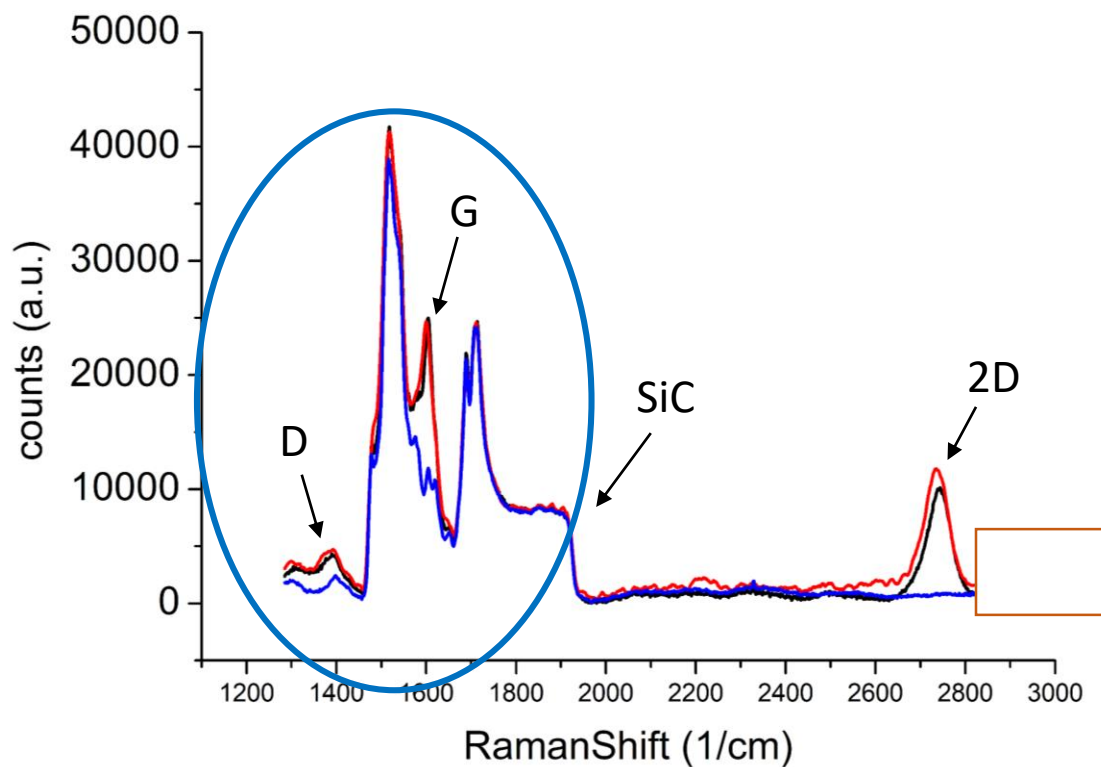


[*Scientific Rep.*, 2017, 7, 3825]

RAMAN/AFM RESULTS

Raman spectroscopy

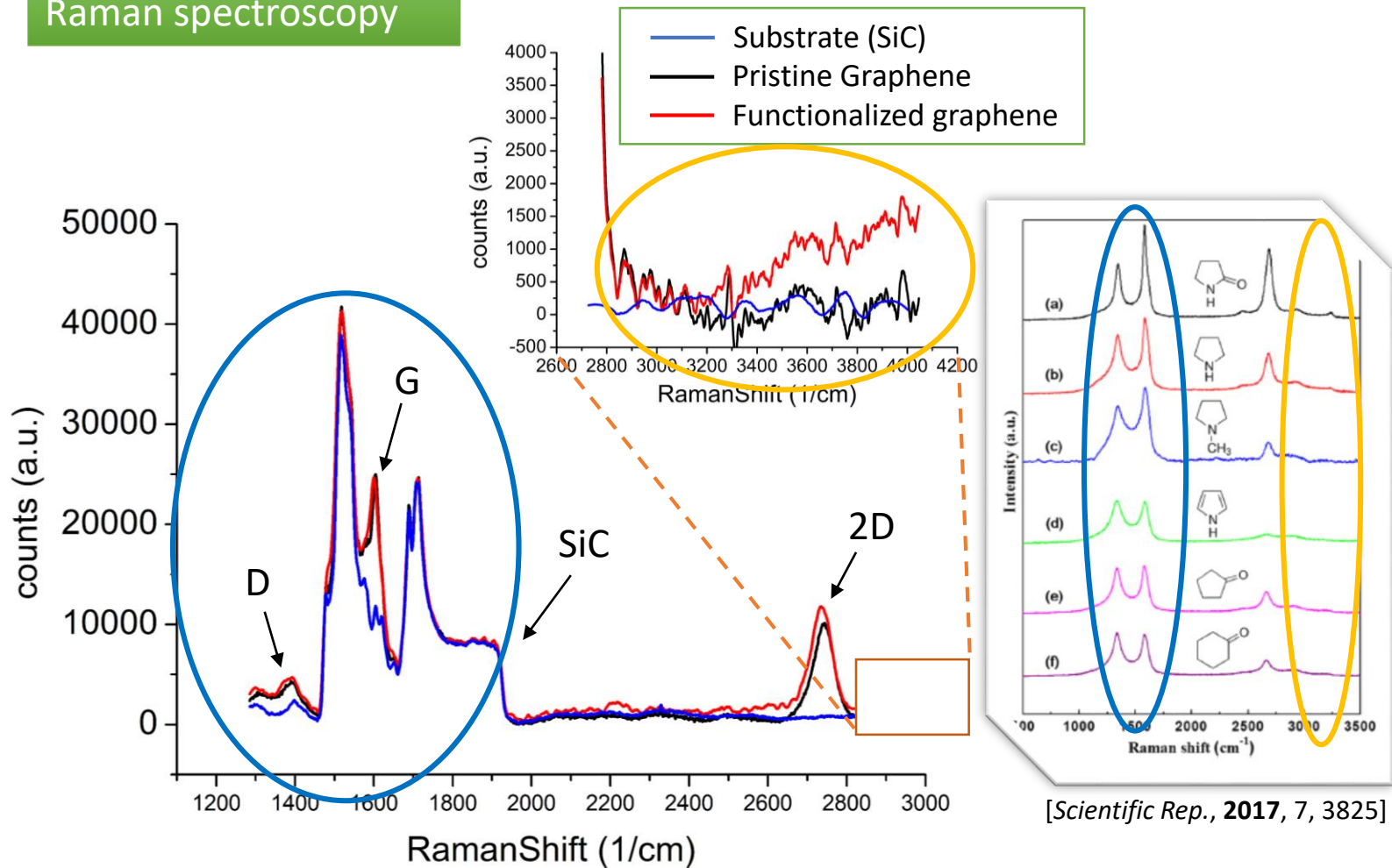
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- Functionalized graphene



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

RAMAN/AFM RESULTS

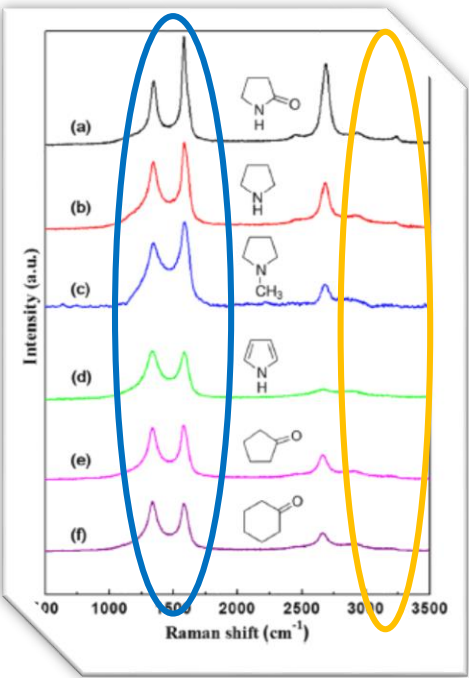
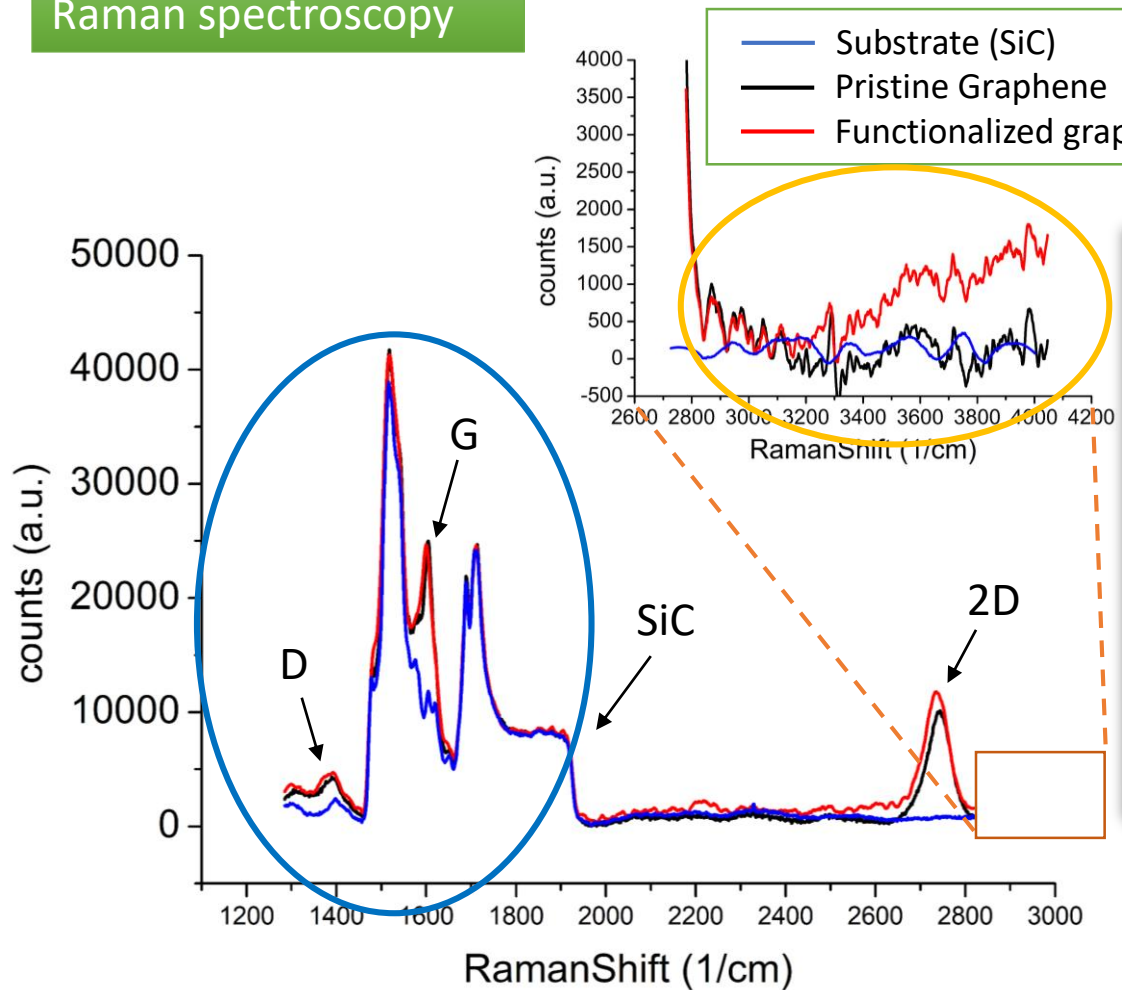
Raman spectroscopy



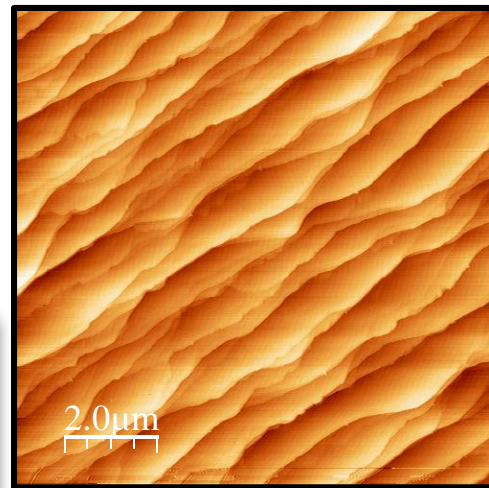
RAMAN/AFM RESULTS

AFM

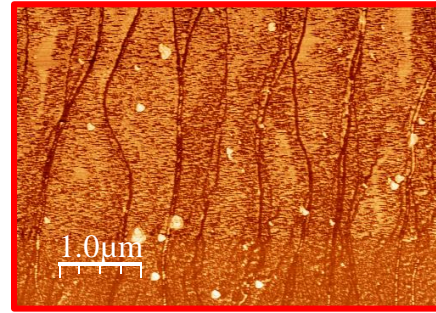
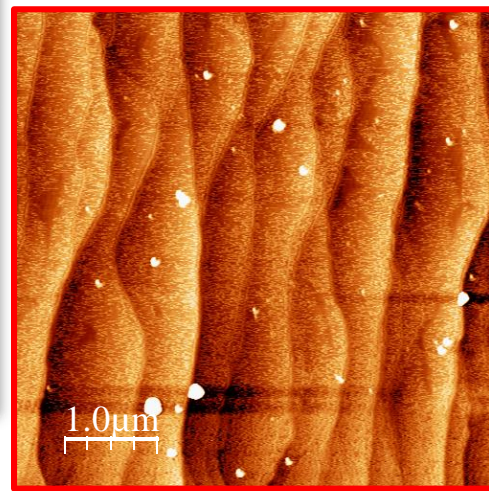
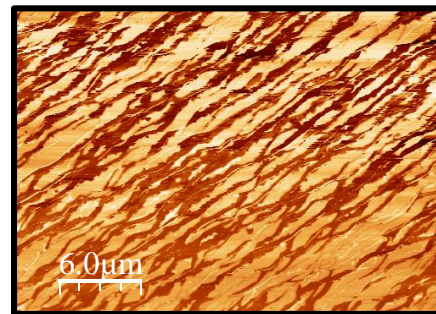
Raman spectroscopy



[Scientific Rep., 2017, 7, 3825]



Pristine EG –
buffer/mono layer

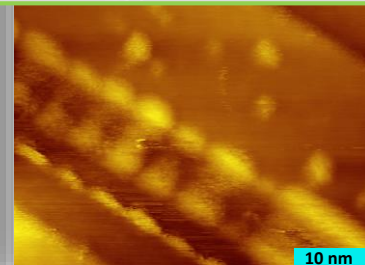
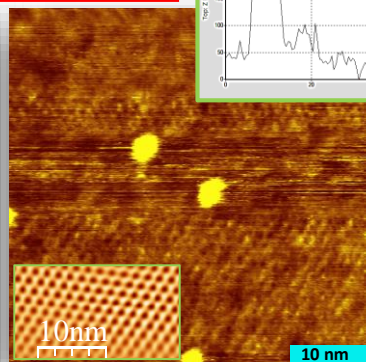
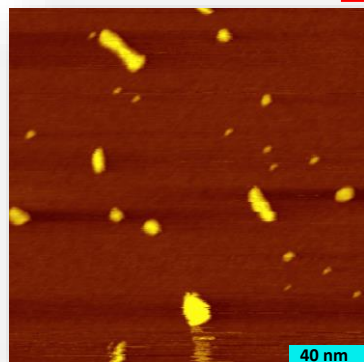
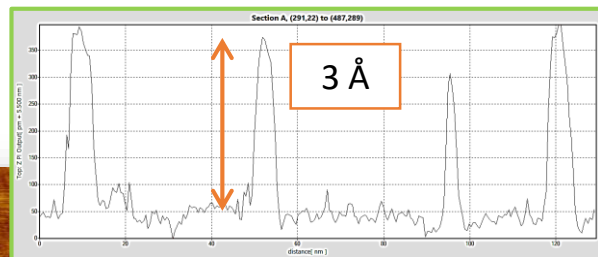


Functionalized EG

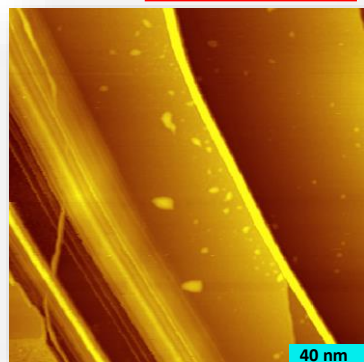
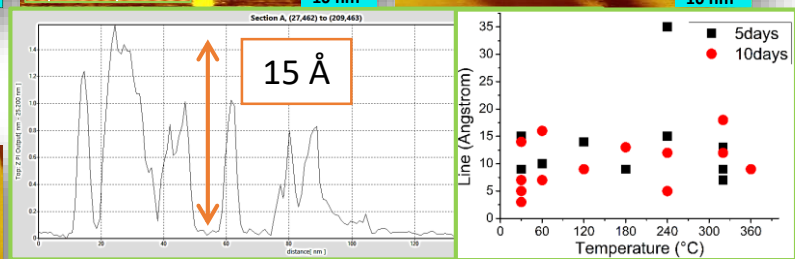
STM/STS RESULTS

STM

Clusters



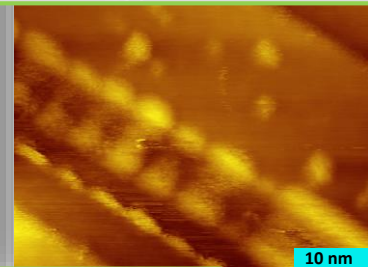
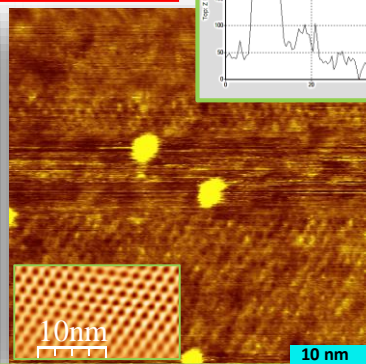
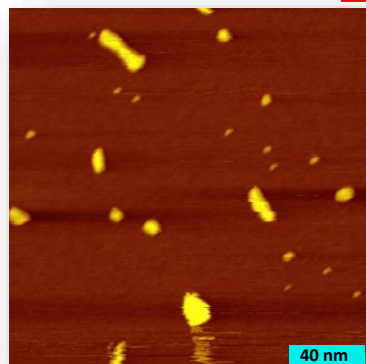
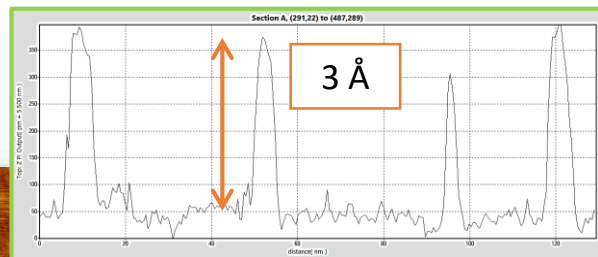
Lines



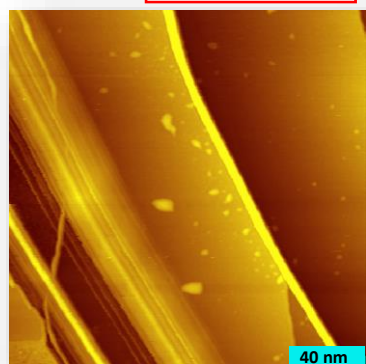
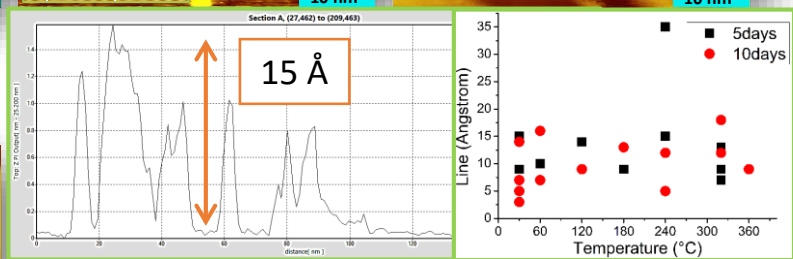
STM/STS RESULTS

STM

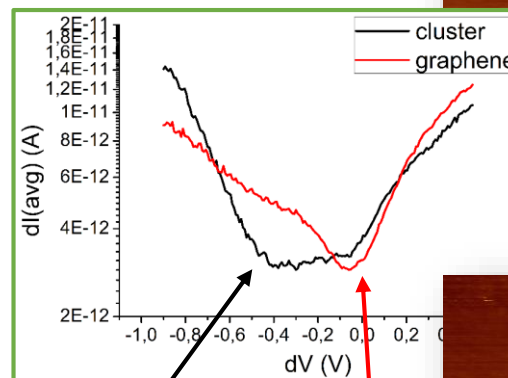
Clusters



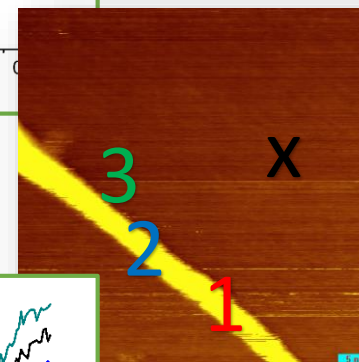
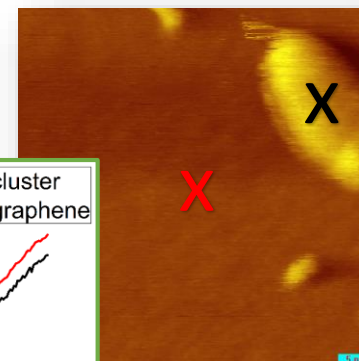
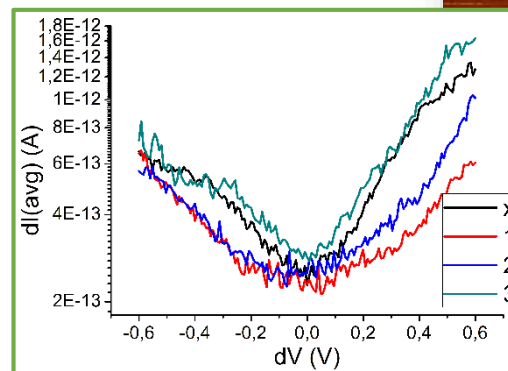
Lines



STS

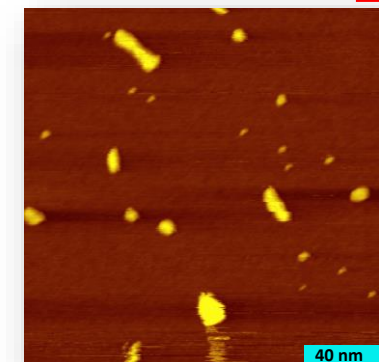


Molecules

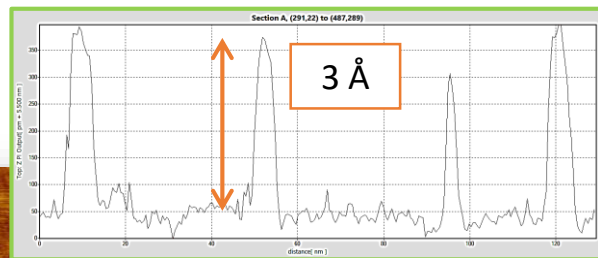
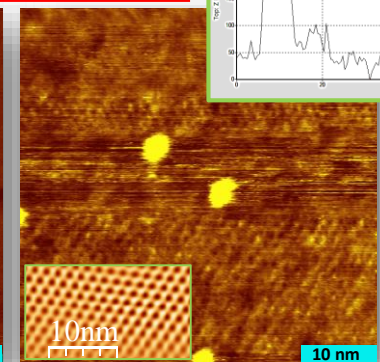


STM/STS RESULTS

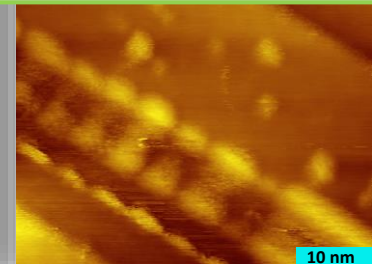
STM



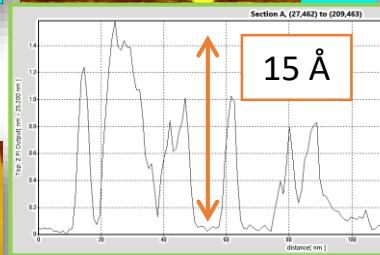
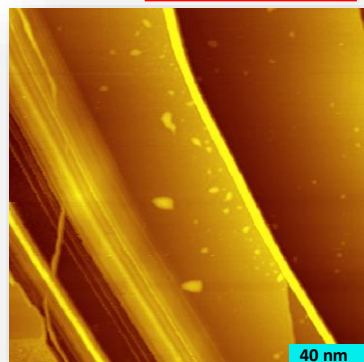
Clusters



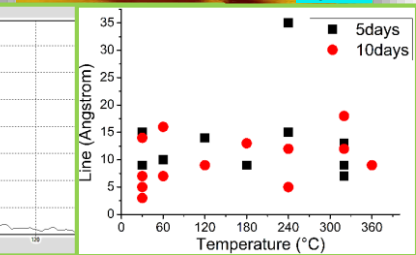
3 Å



Lines



15 Å

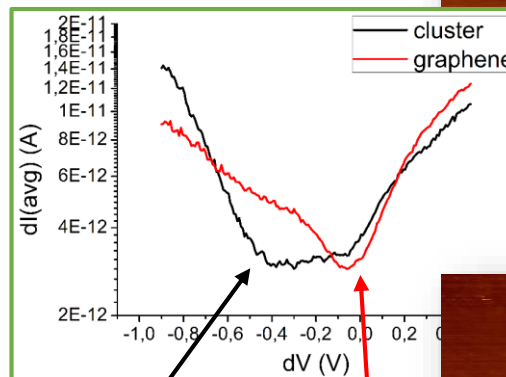


Line (Angstrom)

Temperature (°C)

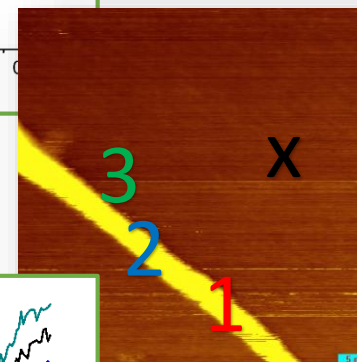
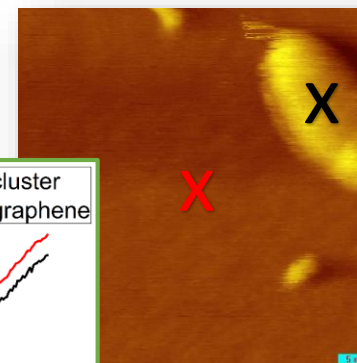
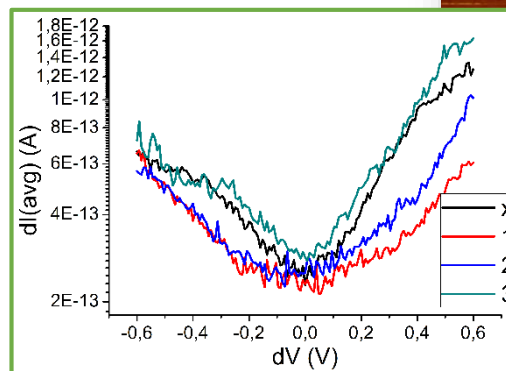


STS

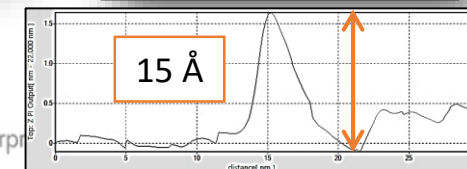
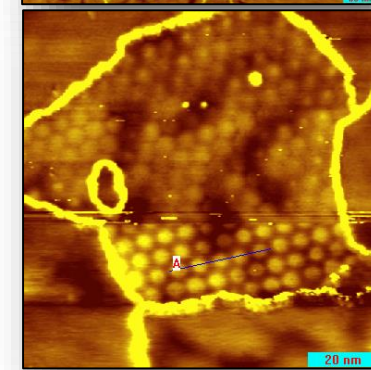
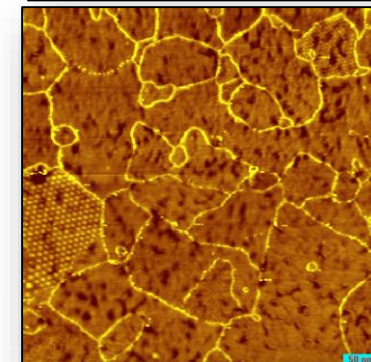


Graphene

Molecules



Total coverage



15 Å

National Enterprise

WHAT'S NEXT

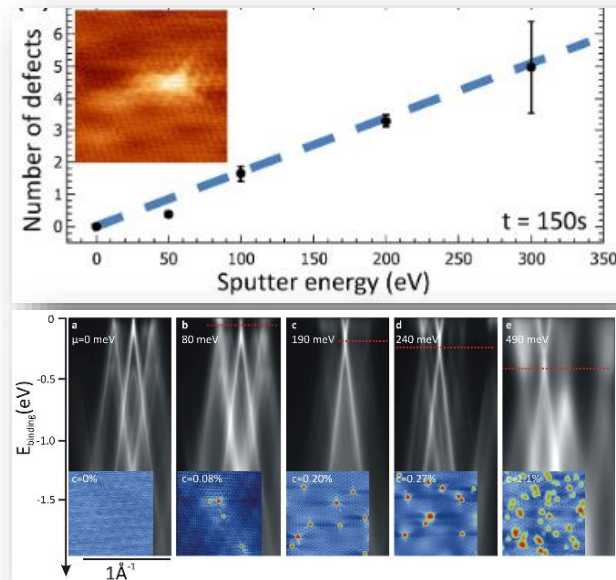
Controlled introduction of defects in the graphene structure

Ion bombardment (N⁺)

- substitutional defects
- "hole" defects



- ✓ n-doping of graphene
- ✓ $C = C$ bond localization



WHAT'S NEXT

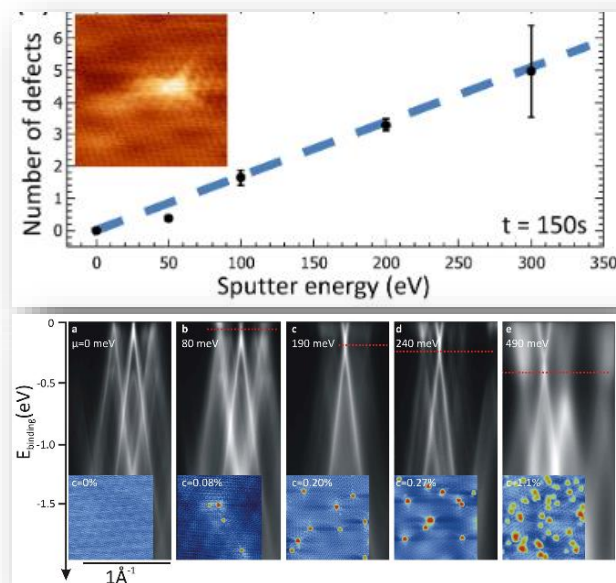
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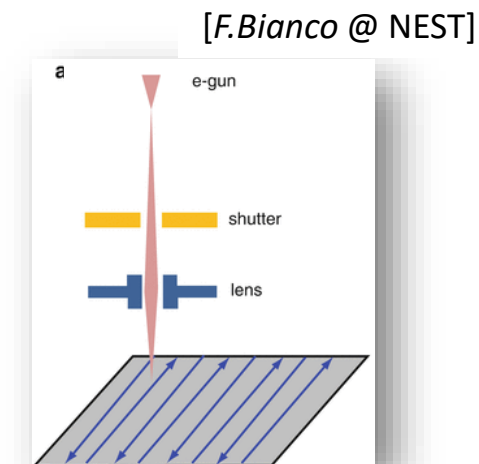
- ✓ n-doping of graphene
- ✓ $C = C$ bond localization



Electron bombardment (EBL)



- ✓ temporary (?) doping
- ✓ design of defects distribution



[F.Bianco @ NEST]

WHAT'S NEXT

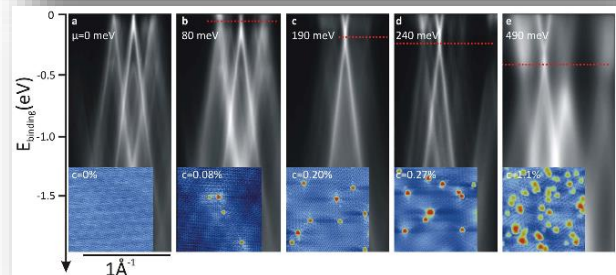
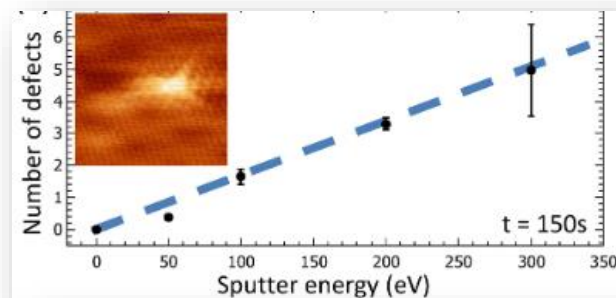
Controlled introduction of defects in the graphene structure

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- "hole" defects



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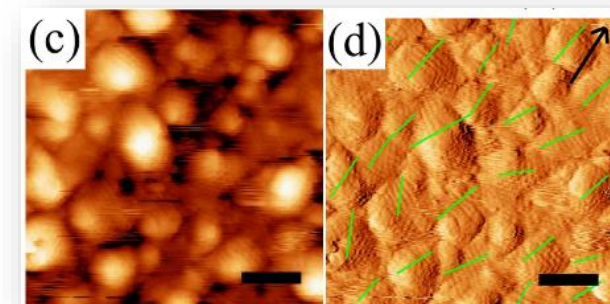
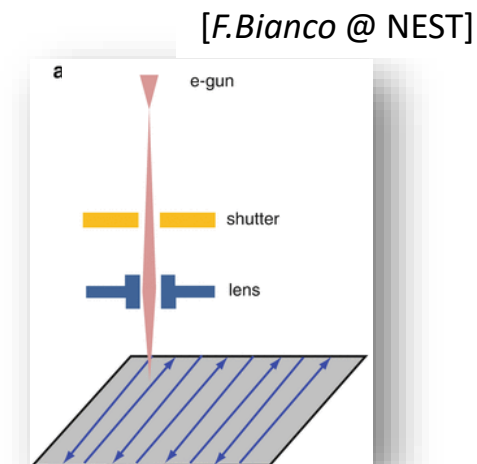


Electron bombardment (EBL)

- ✓ temporary (?) doping
- ✓ design of defects distribution

Nano-crystalline graphene

- edge defects
- ✓ $C = C$ bond localization

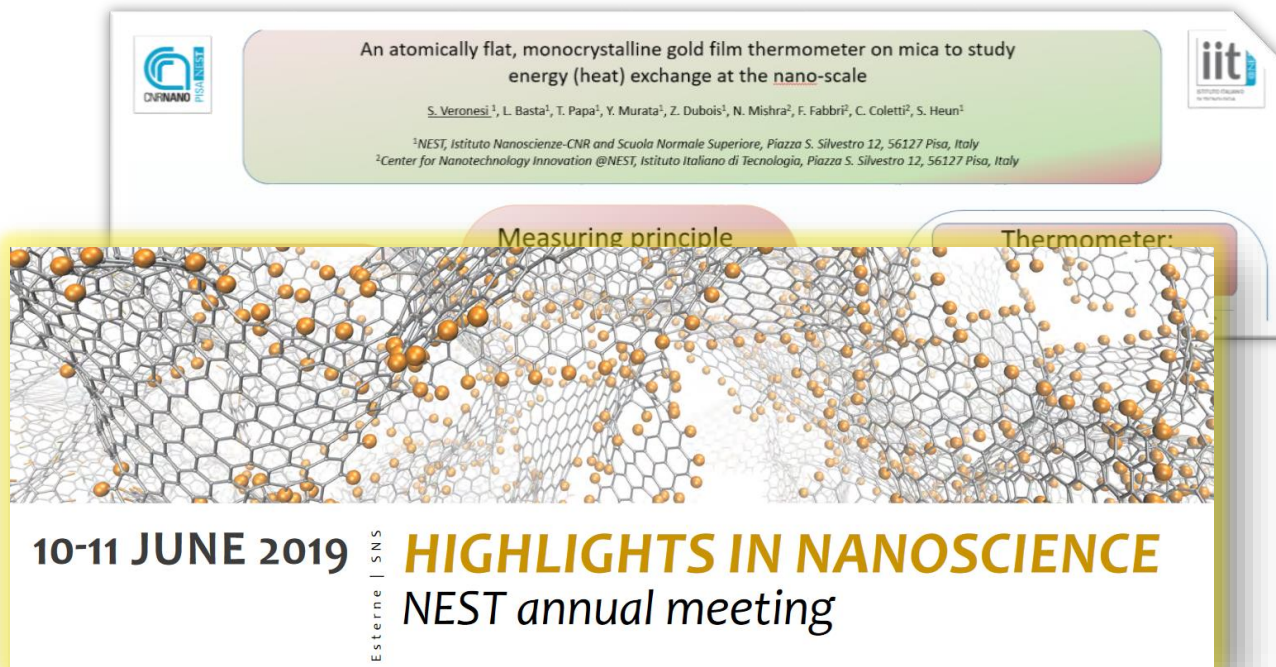


[Y.Murata, *J. Phys. Chem. C*, 2019, 123, 1572 @NEST]

OTHER PHD ORIENTED ACTIVITIES

➤ June 2019: poster presented at the NEST annual meeting in Pisa
Highlights In Nanoscience

➤ July 2019: tutorship as Science Class SNS tutor at the Orientation week in Rome



An atomically flat, monocrystalline gold film thermometer on mica to study energy (heat) exchange at the nano-scale

S. Veronesi¹, L. Basta¹, T. Papa¹, Y. Murata¹, Z. Dubois¹, N. Mishra², F. Fabbrì², C. Coletti², S. Heun²

¹NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza S. Silvestro 12, 56127 Pisa, Italy
²Center for Nanotechnology Innovation @NEST, Istituto Italiano di Tecnologia, Piazza S. Silvestro 12, 56127 Pisa, Italy

Measuring principle Thermometer:

10-11 JUNE 2019 | SNS **HIGHLIGHTS IN NANOSCIENCE**
NEST annual meeting



NANOSCIENZE

~ There's plenty of room at the bottom ~
(C'è un sacco di spazio giù in fondo)

RESPIRARE UN'ALTRA ARIA
Corsi di orientamento universitario | giugno-settembre 2019

Science and nanoTechnology