Deterministic organic functionalization of exfoliated monolayer graphene *via* high-resolution surface engineering

L. Basta,[1] F. Bianco,[1] A. Moscardini,[2] F. Fabbri,[1] L. Bellucci,[1] V. Tozzini,[2] S. Heun[1] and S. Veronesi[1]

[1]NEST Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza S. Silestro 12, 56127 Pisa, Italy
[2]NEST Laboratory, Scuola Normale Superiore, Piazza San Silvestro 12, 56127, Pisa, Italy

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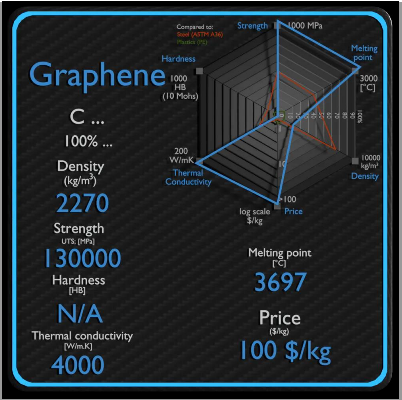
Outline

Why graphene

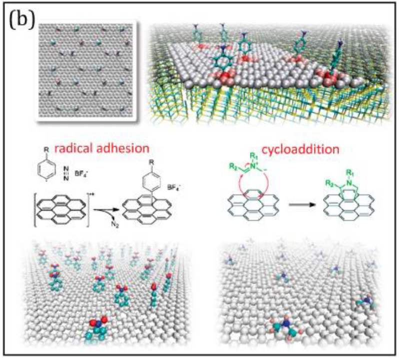
Graphene has an high specific surface area and excellent mechanical, electrical, optical and thermal properties. These features make graphene an actractive material for high performnce devices.

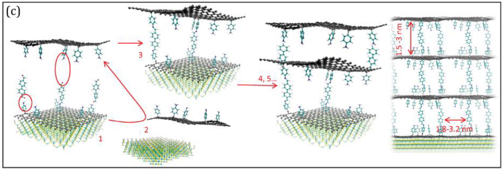
- Sensors
- Catalyzers
- Biochemical applications
- Gas-Storage devices



Chemical Functionalization

Covalent Functionalization of graphene with organic molecules, commonly in wet chemistry environment, offers an appealing possibility to finely tune the material's physical and chemical properties.

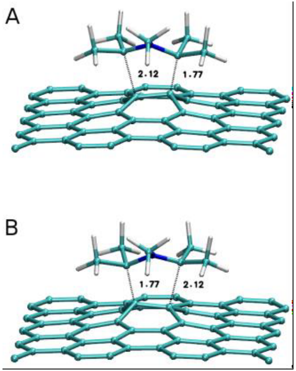


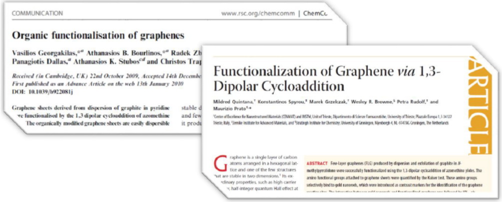


Molecules, 2020, 25, 339.

1,3 dipolar cycloaddition reactions

1,3 DC of azomethine ylide features selectivity, thermal stability (up to 300 C), reversibility





ChemComm 2010, 46, 1766; ACSnano 2010, 4, 6

-43 kcal/mole
-1.87 eV

1,3 DC of GNS and rGO

1,3 DC of azomethine ylide was successfully performed and characterized on graphene nanosheets and reduced graphene oxide

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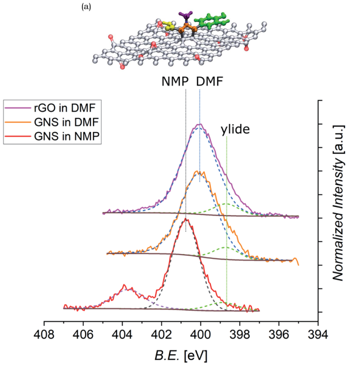
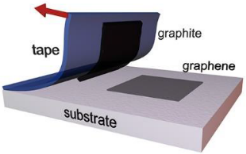
Covalent organic functionalization of graphene nanosheets and reduced graphene oxide *via* 1,3-dipolar cycloaddition of azomethine ylide†

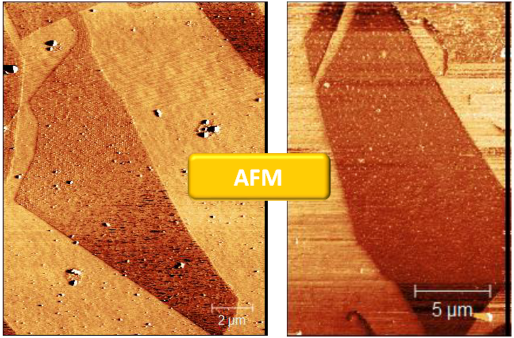
Luca Basta,[*a] Aldo Moscardini,[a] Filippo Fabbri,[a] Luca Bellucci,[a] Valentina Tozzini,[a] Silvia Rubini,[b] Andrea Griesi,[cd] Mauro Gemmi,[d] Stefan Heun[a] and Stefano Veronesi[a]



Mechanically exfoliated graphene

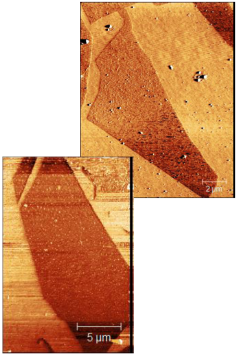
Pristine graphene flakes are widely utilized in optoelectronic applications thanks to their excellent transport properties and low defect concentration.

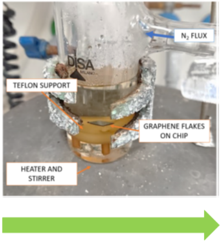


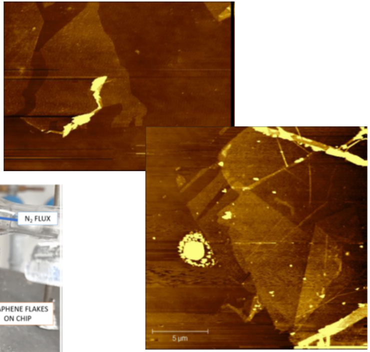


Mechanically exfoliated graphene

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

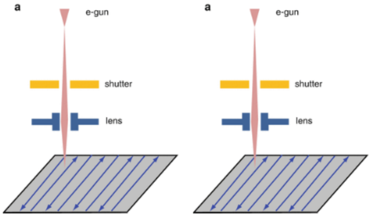






e-beam defects pattern

precise control in defects patterning allows a fine tailoring of the surface chemistry of graphene → electron irradiation via EBL



EBL, Encyclopedia of Nanotechnology, 2012

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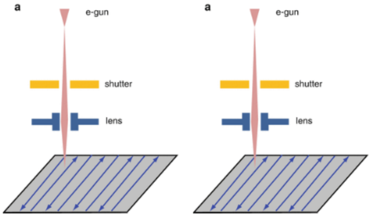
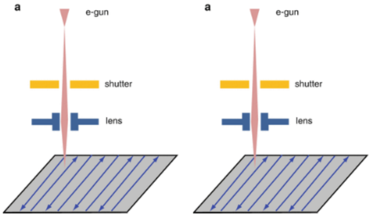


EBL, Encyclopedia of Nanotechnology, 2012

Lateral Resolution
Controlled Design

e-beam defects pattern

precise control in defects patterning allows a fine tailoring of the surface chemistry of graphene $\rightarrow$ electron irradiation via EBL



EBL, Encyclopedia of Nanotechnology, 2012

Lateral Resolution
Controlled Design

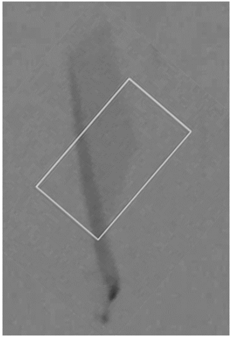
$\Downarrow$

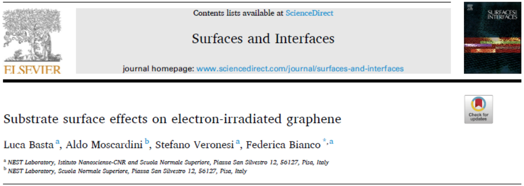
Enhanced surface chemical reactivity

Patterned graphene flakes

30 kV, 40.000 μC/cm^2

Step size: 100 nm





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Substrate surface effects on electron-irradiated graphene

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

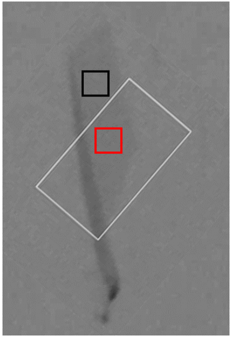
[a] NEST Laboratory, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza San Silvestro 12, 56127, Pisa, Italy
[b] NEST Laboratory, Scuola Normale Superiore, Piazza San Silvestro 12, 56127, Pisa, Italy

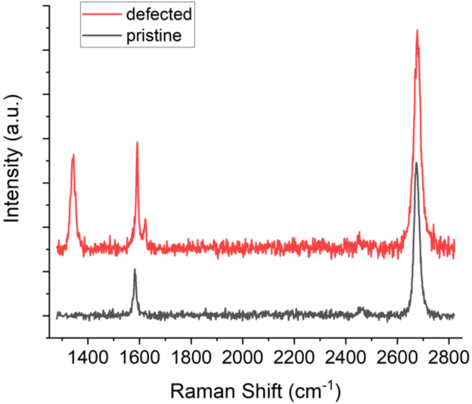
F. Bianco@NEST

Patterned graphene flakes

30 kV, 40.000 μC/cm^2

Step size: 100 nm





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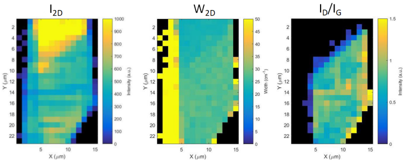
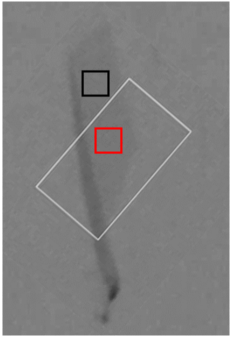
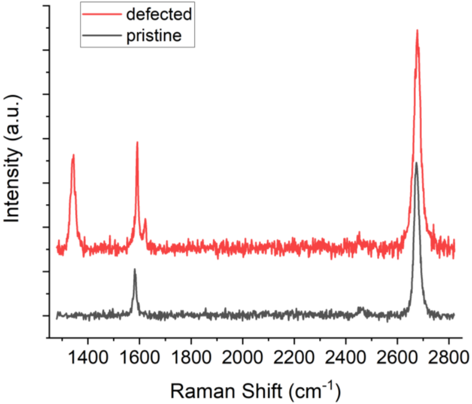
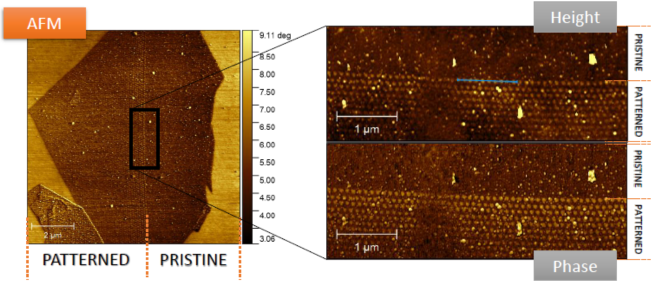






Patterned graphene flakes



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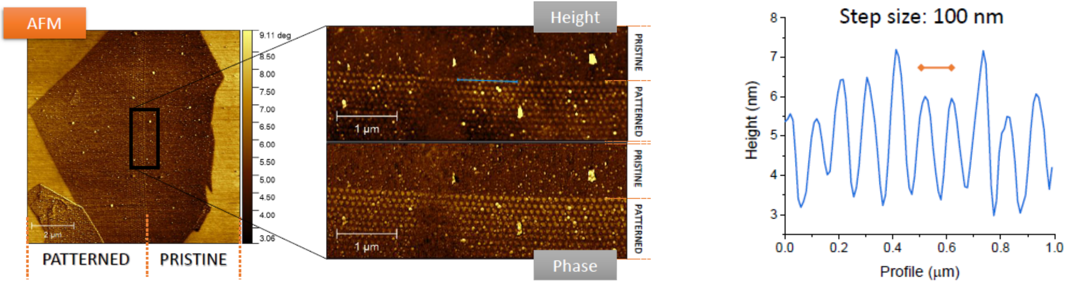
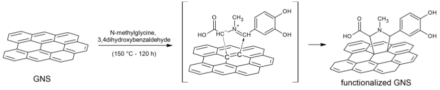
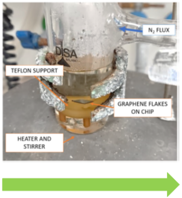
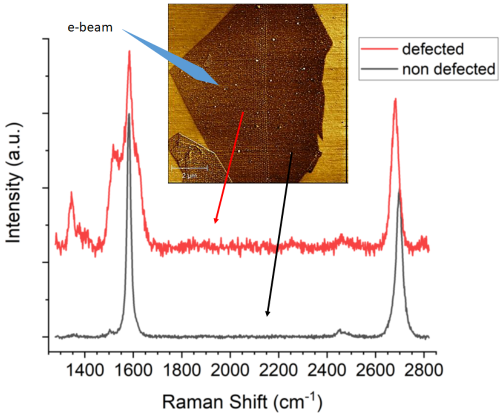


1,3 DC of patterned graphene







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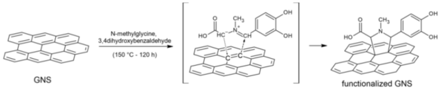
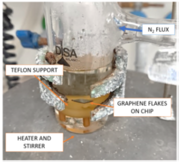
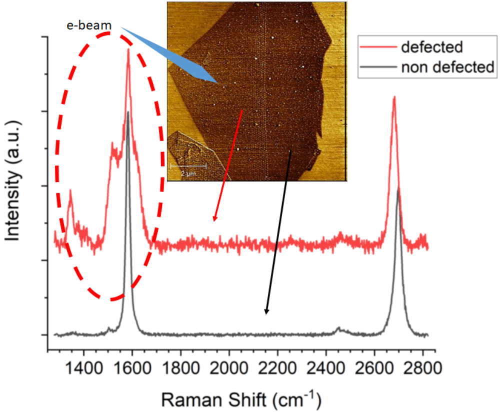
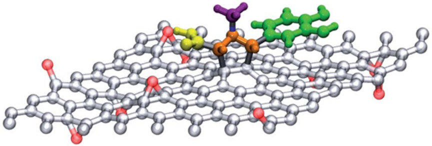




SELECTIVITY

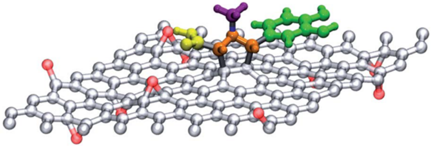


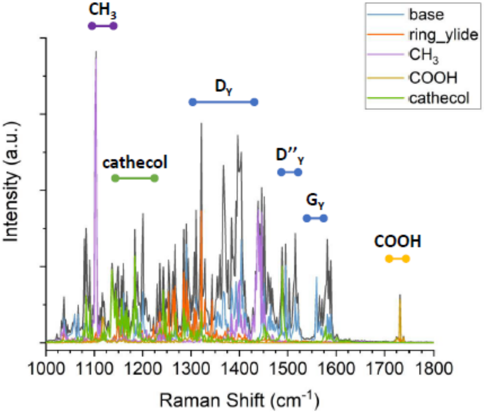
DFT - power spectrum



L. Bellucci@NEST

DFT - power spectrum





L. Bellucci@NEST

Raman analysis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Deterministic organic functionalization of monolayer graphene *via* high resolution surface engineering†

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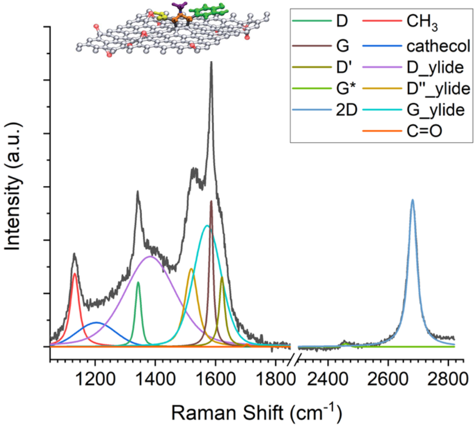
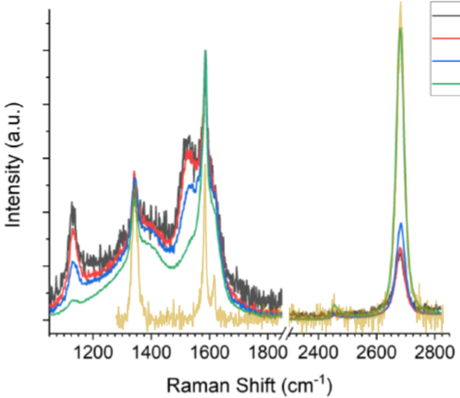


Laser-induced desorption

Laser irradiation produces the recover towards the spectrum of defected graphene, indicating the desorption of the Ylide molecules and the **reversibility** of the functionalization.



Conclusions and Outlook

conclusions

- Controlled and spatial resolved defect engineering via EBL ($\sim$ 100 nm)
- Patterned graphene shows extreme selectivity towards 1,3 DC
- DFT simulation of the Power Spectrum in agreement with the Raman spectra
- Recovery of the Raman spectra of clean defected graphene indicates the reversibility of the functionalization

outlook

- Synthesis of a new Ylide to host fluorophores or gold nanoparticles (with linker)
- Specific sensors demonstration

People


F. Bianco
A. Moscardini
F. Fabbri
L. Basta
S. Heun
V. Tozzini
L. Bellucci

thanks

Thank you for your attention