Substrate induced defects in graphene as opportunities for advanced applications

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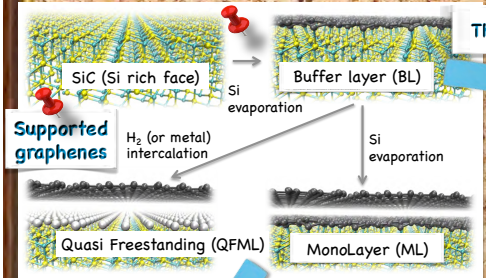
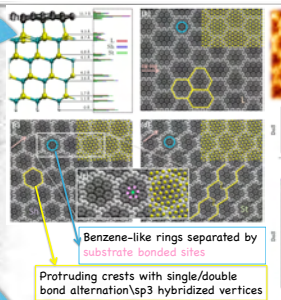
CNRNANO PISA NEST — NEST SCUOLA NORMALE SUPERIORE PISA

All graphene amazing properties – large charge carriers mobility, extreme robustness combined with flexibility, broad band transmittance, huge surface to mass ratio, lubricity – rely on its being a perfect 2D crystal with the specific honeycomb symmetry[1]. However this status brings also some drawbacks [2]: its null density of states at the Fermi level limits its conducting properties; it is weakly interacting, which limits its potentialities as medium for gas storage. In addition, storage applications require building 3D media. On the other hand, perfect graphene is an ideal abstraction rather than a reality: epitaxially grown macroscopic 2D crystals display electronic doping, corrugations or localized defects [3], while using graphene flakes as precursors one can obtain nano-porous scaffolds with extremely complex and little ordered structure[4].
In this poster, it is shown that the deviations from perfection of graphene are in fact opportunities for specific applications. Density Functional Theory calculations show that the multi-stable corrugation of SiC supported epitaxial monolayer graphene[5] and the steady-state rippling of its buffer carbon layer [6] could be exploited for chemical functionalization. Conversely, the quasi free-standing monolayer graphene obtained by H intercalation has with localized electronic states, with potential applications in optoelectronics[7,8]. These systems offer advantages over disordered nano-porous graphene, whose porosity is more difficult to control, and to model[9].

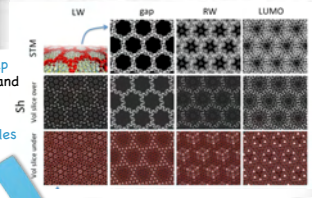
Supported graphenes



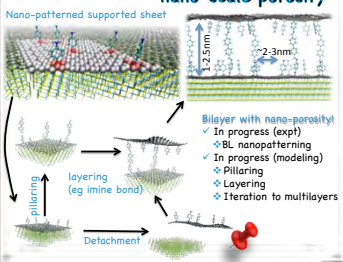
The BL displays regularly patterned and diverse local morphologies



The DoS displays near or in-gap states localized on the crests and in specific "hot spots", which offers te possibility of nano-patterning with anchor molecules and possible subsequent building of 3D structures

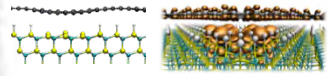


Building 3D-scaffolds with nano-scale porosity

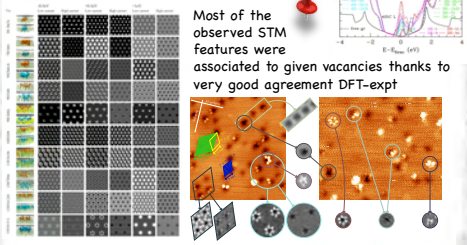


In QFML, vacancies in the H-layer generate localized states

Vacancies appear to be localized on a ~6x6 super-lattice, produce inward bending of the sheet and localized electronic states at the Fermi Level

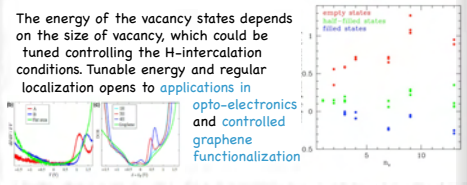


The variety of different contrasts and shapes in the STM images is explained by the existence of vacancies of different shapes and size

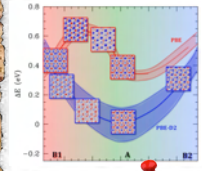


Most of the observed STM features were associated to given vacancies thanks to very good agreement DFT-expt

The energy of the vacancy states depends on the size of vacancy, which could be tuned controlling the H-intercalation conditions. Tunable energy and regular localization opens to applications in opto-electronics and controlled graphene functionalization

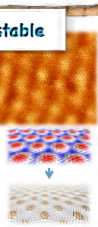


The pattern of corrugation of ML is multi-stable

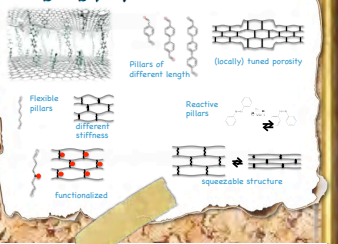


Calculations reveals the presence of different (opposite) corrugation patterns whose relative stability depends on the vdW interaction strength

This explains the ambiguity in measurements and offers a way to corrugation driven patterning



Designing properties of scaffolds



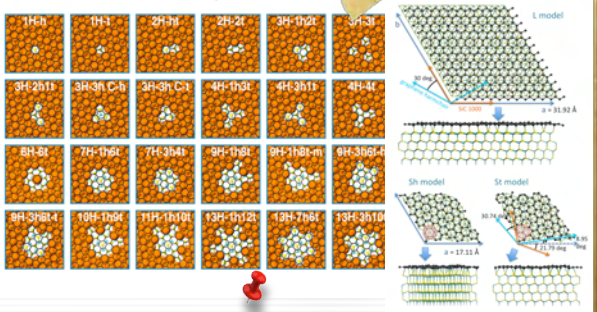
Summary & Conclusions

- ✓ Defects are useful effects* to optimize graphene for applications
- ✓ Epitaxial "graphenes" display defects following precise symmetries and periodicity due to the interaction with the substrate
- ✓ These alters locally the reactivity, allowing chemical nano-patterning
- ✓ Nano-patterned sheets can be used to build 3D scaffolds with tailored properties

** ... and now it remains that we find. out the cause of this effect; or rather say, the cause of this defect; for this effect, defective, comes of cause.*
W. Shakespeare, *Hamlet*, 2, 2.

Methods

- ✓ Two model systems (Large and Small) with sligthly different SiC-graphene rotation/translation; 300-1800 atoms; S one order of magnitude "cheaper" than L; 2-4 layers of SiC
- ✓ Models for BL obtained by superposition /translation/optimization of ML on SiC
- ✓ Models for ML obtained by superposition /optimization
- ✓ Models for QFML obtained by H saturation/superposition/optimization; ~30 models of H vacancies
  PW-RRRKJUS PP, LDA and XDM in selected cases
- ✓ Calculations performed with QE on FERMI/MARCONI@CINECA, ~10⁴ cores



People & Collaborations

Theory, formerly in the group:
Khatuna Kakhiani, MCSA Fellow NANO-Cnr (now at Tbilisy Univ)
Vito Dario Camiola, Post-Doc NANO-Cnr (now at MOX poliMi)
Experiment
Camilla Coletti (iit-CNI, Pisa)
Vittorio Pellegrini (iit-Graphene labs Genoa)
Keisuke Takahashi, Shigehito Isobe, Kengo (Omori Hokkaido University, Japan)
Niko Pavliček, Leo Gross, Gerhard Meyer (IBM Research-Zurich Rüschlikon Switzerland)

Projects & support

MusCaDe — Multi-scale modeling and simulation Devices — http://www.muscade-lab.it
PRACE
MARIE CURIE ACTIONS
GRAPHENE FLAGSHIP
CINECA SCAI — SuperComputing Applications and Innovation

This work is supported by EU-H2020, Graphene-Core1 (agreement No 696656) and Core2 (agreement No 725219), MCSA (agreement No 657070), by CINECA awards IsB11_flexogra (2015), IsC36_ElMaGRe (2015), IsC44_QFSGvac (2016), IsC44_ReIMCGr (2016) and PRACE "Tier0" award Pra13_ 2016143310 (2016), IsC61_MGchpDFA (2017)
Calculations were performed on FERMI and MARCONI national HPC facility @CINECA

Publications

[1] E Quesnel, et Graphene-based technologies for energy applications, challenges and perspectives al 2D Mater 2, 030204 (2015)
[2] T Cavallucci, K Kakhiani, R Farchioni, V Tozzini Morphing graphene-based systems for applications: perspectives from simulations GraphITA. Carbon Nanostructures., 87-111 (2017)
[3] A Rossi, S Piccinin, V Pellegrini, S de Gironcoli, V Tozzini Nano-Scale Corrugations in Graphene: a Density Functional Theory Study of Structure, Electronic Properties and Hydrogenation JPC C 119, 7900-7910 (2015)
[4] G Mercier, A Klechikov, et al Porous Graphene Oxide/Diboronic Acid Materials: Structure and Hydrogen Sorption JPCC 119, 49, 27179-27191 (2015)
[5] T Cavallucci, V Tozzini Multistable Rippling of Graphene on SiC: A Density Functional Theory Study JPCC 120, 7670 (2016)
[6] T Cavallucci and V Tozzini Intrinsic structural and electronic properties of the Buffer Layer on Silicon Carbide unraveled by Density Functional Theory Sci Rep 8, 13097 (2018)
[7] T Cavallucci, Y Murata, M Takamura, H Hibino, S Heun, V Tozzini Unraveling localized states in quasi free standing monolayer graphene by means of Density Functional Theory Carbon 130, 466 (2018)
[8] Y Murata, T Cavallucci, V Tozzini, et al Atomic and Electronic Structure of Si Dangling Bonds in Quasi-Free-Standing Monolayer Graphene Nano Res 11, 864-873 (2018)
[9] L Bellucci, and V Tozzini In Silico design, building and deconstruction of nano-porous graphene scaffolds, in preparation