Morphing graphene at the nano-scale: from simulations to applications

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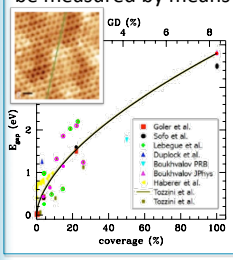
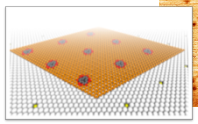
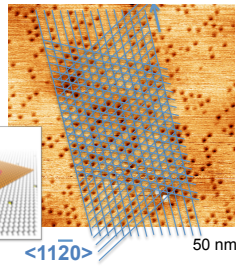
Introduction In spite of its exceptional properties, for many applications bare graphene is not optimal. For instance, it is a conductor with exceptional mobility, but with null density of states at the Fermi level, therefore it requires either doping to create charge carriers, or gap opening to become semiconductor[1,2]. Its low weight and exceptional resistance makes it an optimal candidate as a medium for gas storage, but it is physically and chemically rather inert, implying either a too slow kinetics of loading/release or a low gravimetric density at room temperature. In addition, storage applications require building 3D graphene based frameworks with specific structural properties[3]. In order to endow graphene with necessary properties, one needs controlling its structure at the nanometric level. This in principle can be done in several ways: the "chemical way" includes substitutions of graphene carbon with other elements (usually with B or N), adhesion of atoms or chemical groups, deposition of molecular clusters, usually metallic[4]. The "structural way" includes creation of defects and (static or dynamical) corrugation. Our work is devoted to address the issues of nano-scale graphene morphing for energy applications (gas storage) and nanoelectronics.

Nano-electronics

The gap opening is quantitatively related to hydrogenation[6,7]. GD can be measured by means of STS expt



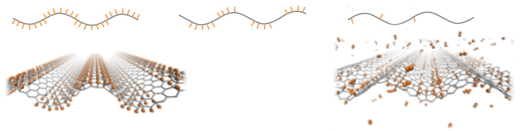




Quasi Free Standing graphene on SiC with H coverage defects displays altered transport properties[10]

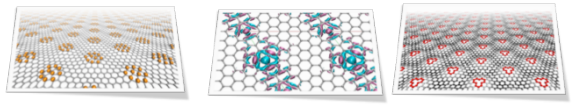
Hydrogenation-dehydrogenation control

In simulations, chemisorbed H is released at room temperature by a curvature inversion induced e.g. by flexural phonons[2]



Controlling metal adsoprtion

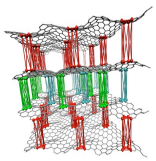
Reactivity and defectation control allows in turn controlling metals (e.g. Ti) adhesion and avoid their clusterization [8]. This in turn favors H adsorption, onto Ti clusters



Controlling morphology, i.e. concentration and location of defects, substitutions and ad-atoms (groups)

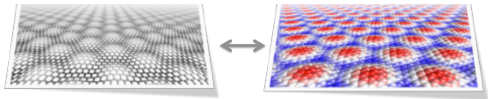
Building 3D graphene networks

Reactivity manipulation can aid controlling the concentration and location of chemically ad-groups (e.g. anchors for pillars molecules) to build 3D frameworks with specific structural properties. [8]



Connection between structure and reactivity

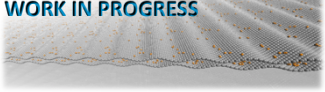
the corrugation is related to the local reactivity of graphene, which is enhanced on convexities [5-7] (see also **poster n. 248**)



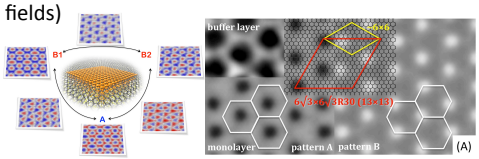
Strategies for curvature control

2. Flexural phonons can dynamically control the local curvature. The goal is to generate and control coherency of phonons (**see also poster n. 230**)

WORK IN PROGRESS



1. The curvature pattern of graphene on SiC is multistable[9] (**see also poster n. 248**) ⇒ switching between rippling states might be driven by environmental changes (temperature, elec fields)



Methods

***Ab initio* calculations and simulations**

- DFT+PW, PBE+vdw corr, RRKYUS pp
- Model systems: graphene monolayer, graphene on SiC (100-1700 atoms per cell)

Classical MD simulations

- Tersoff-like FF optimized: monolayers and multilayers (up to 2000 atoms)

Experiment

- Buffer + monolayer graphene on SiC (by Si evaporation)
- QFSG obtained by H intercalation between buffer and SiC
- Analysis by: STM, STS, EM, LEED, TDS

Conclusions

- Advanced applications require controlled graphene hydrogenation or functionalization in general
- This could be achieved by curvature controlled reactivity
- Curvature control could also directly allow manipulating electronic properties and gas transportation and storage
- Therefore curvature control assumes a key role, which must be considered in creating 3D graphene based frameworks or in functionalizing sheets
- Strategies for curvature control are currently under consideration, involving optical, mechanical and electro(dynamical) stimuli

Publications

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[7] A Rossi, S Piccinin, V Pellegrini, S de Gironcoli, V Tozzini JPCC 119, (2015) 7900
[8] K Kakhiani, V Tozzini, in preparation (See poster n. 248)
[9] T Cavallucci, V tozzini J Phys Chem 2016 (in press)
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