Hydrogen interaction with statically and dynamically rippled graphene

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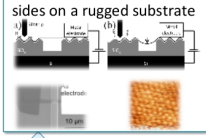
Hydrogen can be either physisorbed in graphene, interacting with carbon by Van der Waals, forces or chemisorbed by chemically bonding to it[1]. Physisorption is often considered as a mean for H storage, but the gravimetric density (GD, related to gas internal pressure) reaches reasonable values only at low temperatures[1,2]. H chemisorption allows modulating the electronic properties of graphene with possible applications in nano-electronics. In addition, it leads to acceptable GD and stable binding, but the loading and release kinetics are slow at room temperature, due to high chemi-de-sorption barriers[1,3].
We propose that rippling in graphene could be exploited to enhance its interaction with hydrogen[4]. By means of experimental measurements on naturally corrugated graphene grown on SiC[5] combined with multi-scale simulations[6,7] we show that hydrogen preferentially binds on convex areas and is unstable within concavities. We demonstrate by simulations that a curvature interchange mechanically induced by e.g. by coherent flexural phonons can be used to enhance the desorption kinetics and actively transport physisorbed molecular hydrogen eventually increasing the internal pressure of the gas[6]. We are currently evaluating the possibility of obtaining curvature control by mean of external electric fields, exploiting the flexoelectric properties of the pristine or N/B substituted graphene, or by mechanical pulling of graphene sheets on corrugated substrates. These results can be used to design devices for hydrogen storage and in advanced nano-electronics.

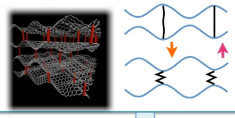
Suspended sheet electro-mechanical bending

The sheet is bent and pulls the sides on a rugged substrate



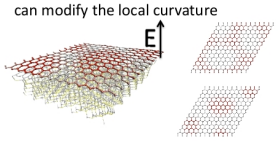
Multilayers optical control

Optically sensitive pillars could control local corrugation in response to optical stimuli



Electro(dynamic) fields

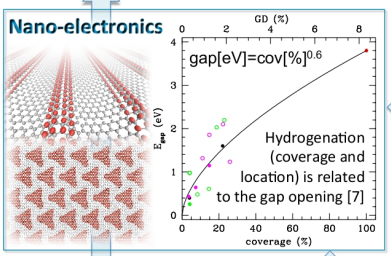
An electric field orthogonal to the sheet can modify the local curvature



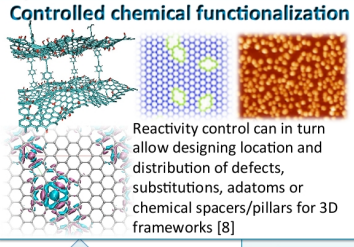
Strategies for curvature control

All of these strategies are currently under consideration, analysed by mean of a combined simulation-experimental approach

Nano-electronics



Controlled chemical functionalization



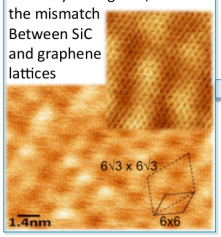
Reactivity control can in turn allow designing location and distribution of defects, substitutions, adatoms or chemical spacers/pillars for 3D frameworks [8]

Hydrogen storage

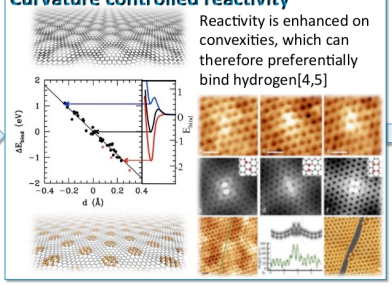
Curvature controlled adsorption/desorption and transport could be used in graphene based storage devices

Graphene corrugation

Graphene grown on SiC is naturally corrugated, due to the mismatch Between SiC and graphene lattices



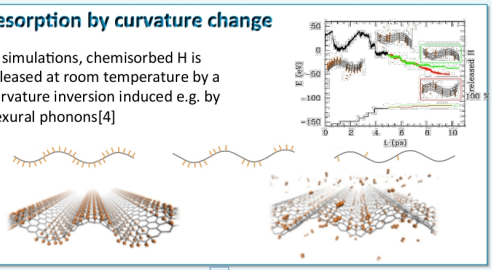
Curvature controlled reactivity



Reactivity is enhanced on convexities, which can therefore preferentially bind hydrogen[4,5]

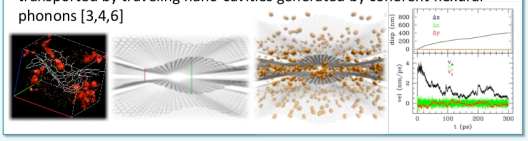
Desorption by curvature change

In simulations, chemisorbed H is released at room temperature by a curvature inversion induced e.g. by flexural phonons[4]



Hydrogen transport through multilayers

Once desorbed, H_2 tends to cumulate within concavities, and can be transported by traveling nano-cavities generated by coherent flexural phonons [3,4,6]



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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2. F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini *et al.* - Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage *Science (2015)*
3. V D Camiola, R Farchioni, T Cavallucci, A Rossi, V Pellegrini, V Tozzini - Hydrogen Storage in Rippled Graphene: Perspectives from Multi-Scale Simulations *Front Mat (2015)*
4. V Tozzini, V Pellegrini - Reversible Hydrogen Storage by Controlled Buckling of Graphene Layers *JPCC (2011)*
5. S Goler, C Coletti, V Tozzini, *et al.* - The Influence of Graphene Curvature on Hydrogen Adsorption: Towards Hydrogen Storage Devices *JPCC (2013)*
6. V D Camiola, R Farchioni, V Pellegrini, V Tozzini - Hydrogen transport within graphene multilayers by means of flexural phonons *2D Mat (2015)*
7. A Rossi, S Piccinin, V Pellegrini, S de Gironcoli, V Tozzini - Nano-Scale Corrugations in Graphene *JPCC (2015)*
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Methods

Ab initio calculations and simulations

- DFT, plane waves expansion, PBE functional, TM pseudopotential
- Car-Parrinello dynamics
- Model systems: graphene monolayer, graphene on SiC substrate (100-1500 atms)

Classical MD simulations

- Tersoff-like FF optimized for phonons [J Tersoff, *PRB* (1988), DA Broido L Lindsay, *PRB* (2010)]
- Model systems: monolayers and multilayers (orthorombic super cells ~500-2000 atms)

Experiment

- Graphene grown by Si evaporation from SiC → buffer layer + monolayer graphene on SiC
- Analysis by: STM, STS, EM, LEED, TDS

Software

MusCaDe
Multi-scale modeling and simulation Devices
http://www.muscade-lab.it

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