MORPHING GRAPHENE FOR ENERGY APPLICATIONS

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Graphene "real" properties

graphene monolayer

- ✓ Exceptional el mobility
- ✓ Large conductivity
- ✓ Peculiar optical properties
- ✓ Extreme flexibility, strength
- ✓ Large surface to mass ratio
- ✓ 2-Dimensionality

- ✓ Null band gap
- ✓ Null carrier density

Bad for electronics applications

- ✓ Low reactivity
- ✓ Weak interactions
- ✓ No 3-Dimensionality

Bad for storage, sorting and energy applications

Applications require manipulating graphene

This usually imply disrupting its symmetry. This can be done by

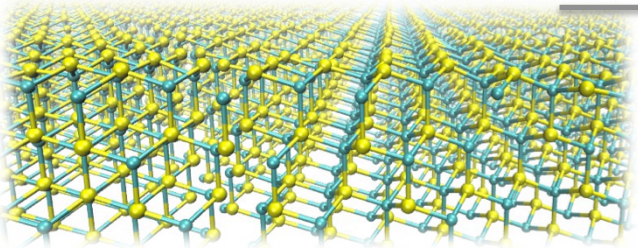
- ✓ Exploit substrates properties
  - ➢ Polarization → Doping
  - ➢ Corrugation, patterned structure → Specific transport props, control of reactivity
- ✓ Introduction of defects
  - ➢ Substitutional → Doping
  - ➢ Conformational (curvature) → Control of reactivity and interactions
  - ➢ Structural (vacancies) → Control of reactivity and interactions
- ✓ Chemical functionalization
  - ✓ Decoration with atoms (e.g. H) → Band gap opening, storage
  - ✓ Adhesion of chemical anchors → Design of 3D frameworks

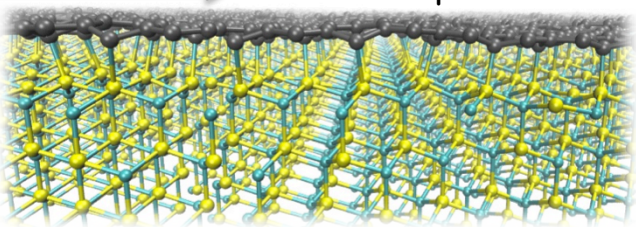
Substrate: not just a support for graphene

Growth of graphene on SiC

SiC bulk (0001) Si rich face

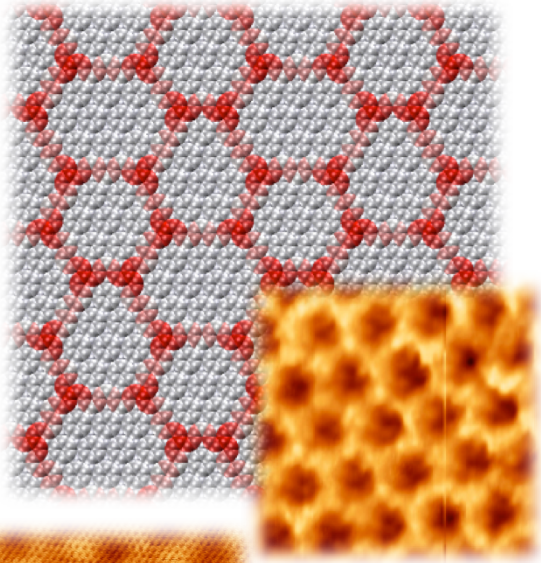
Si evaporation





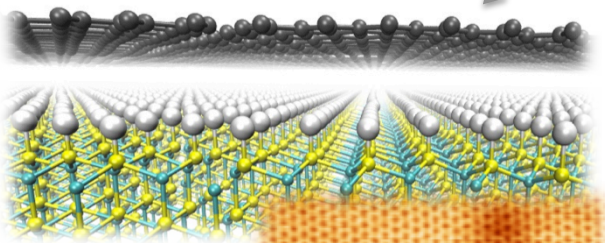
buffer layer

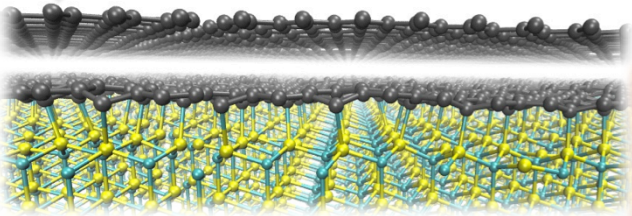
Hoyneycomb structure, but covalently bond to SiC, partially sp^3 hybridized, with sharp ripples following a moiré pattern

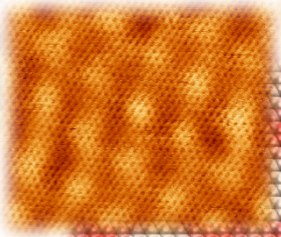


H_2 (or metal) intercalation

Si evaporation

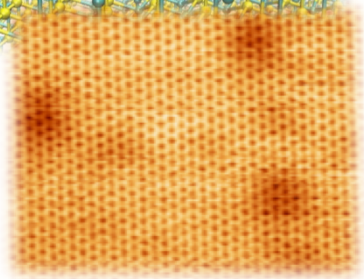






graphene monolayer

Fully sp^2 hybridized, still regular but less enhanced rippling



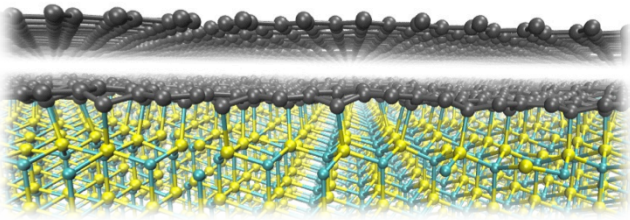
quasi free standing graphene

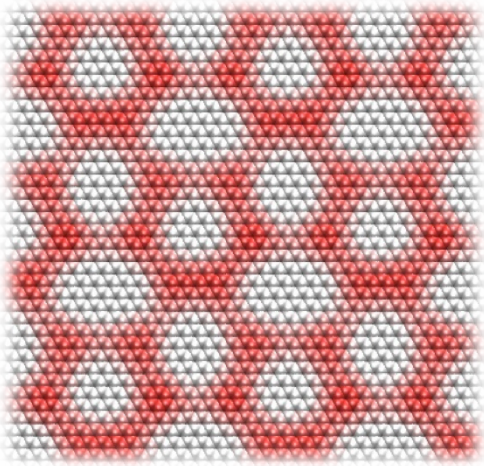
sp^2 hybridized, almost flat, with structural irregularities

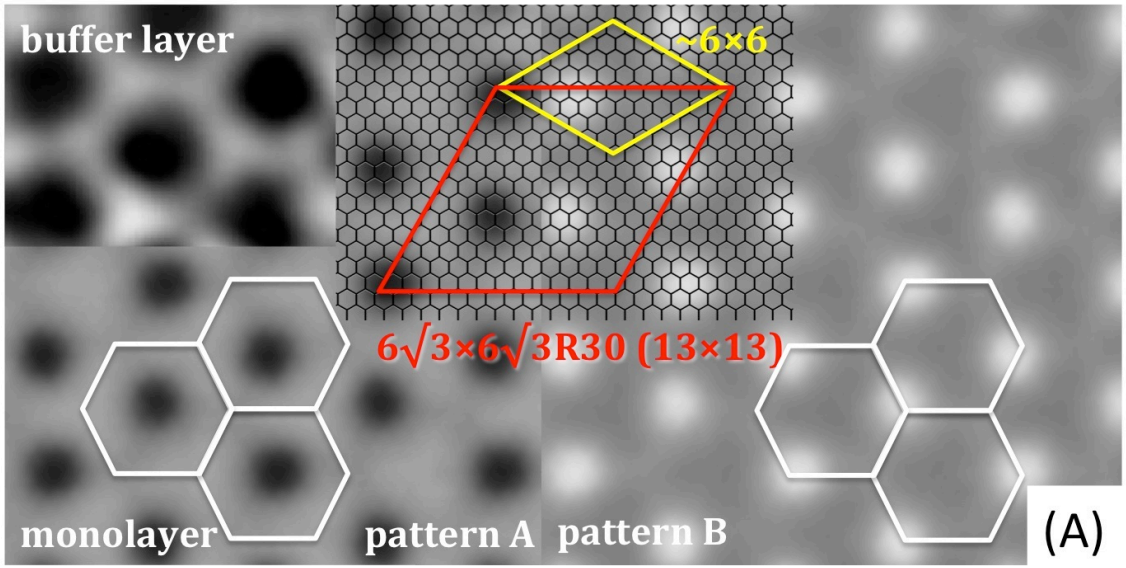
Substrate: not just a support for graphene

Graphene monolayer on SiC: multistable rippling

- ✓ In the literature (both experimental and theoretical) two different curvature pattern are observed depending on environmental conditions: one following the buffer layer, one quite opposite, with protruding hills







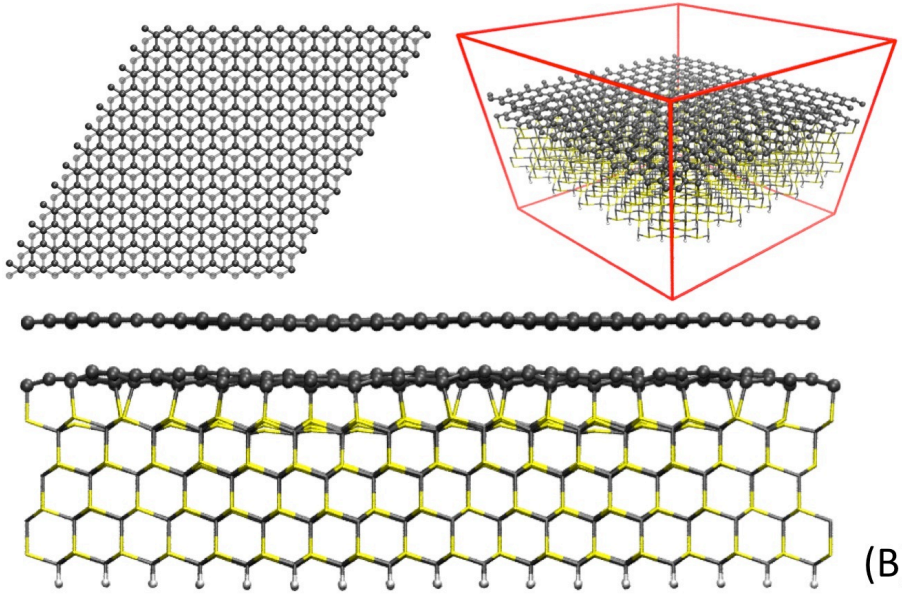
We investigated the relative stability of those patterns and the possibility of switching between them

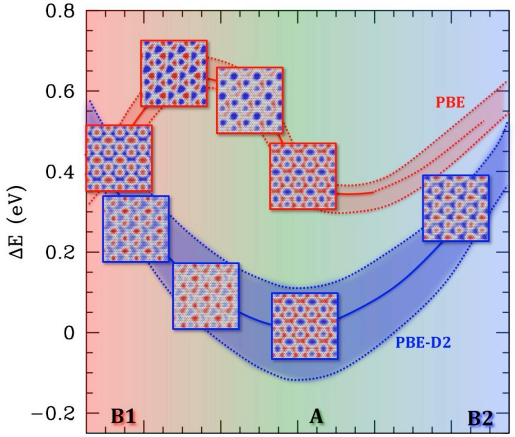
Substrate: not just a support for graphene

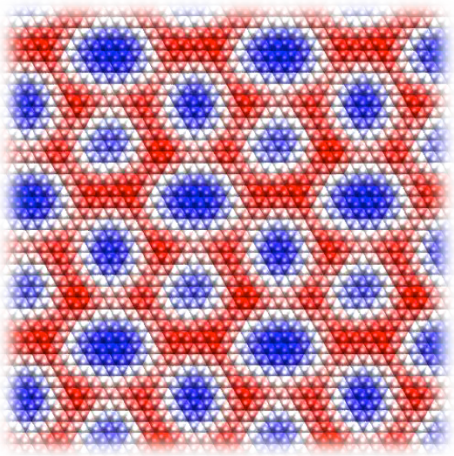
Graphene monolayer on SiC: multistable rippling

Methods

- ✓ DFT calculation on the 13x13 SiC+buffer layer +monolayer (1648 atoms)
- ✓ PW-RRKJUS PP, LDA, PBE, vdW corections
- ✓ Calculations on HCP@CINECA







Results

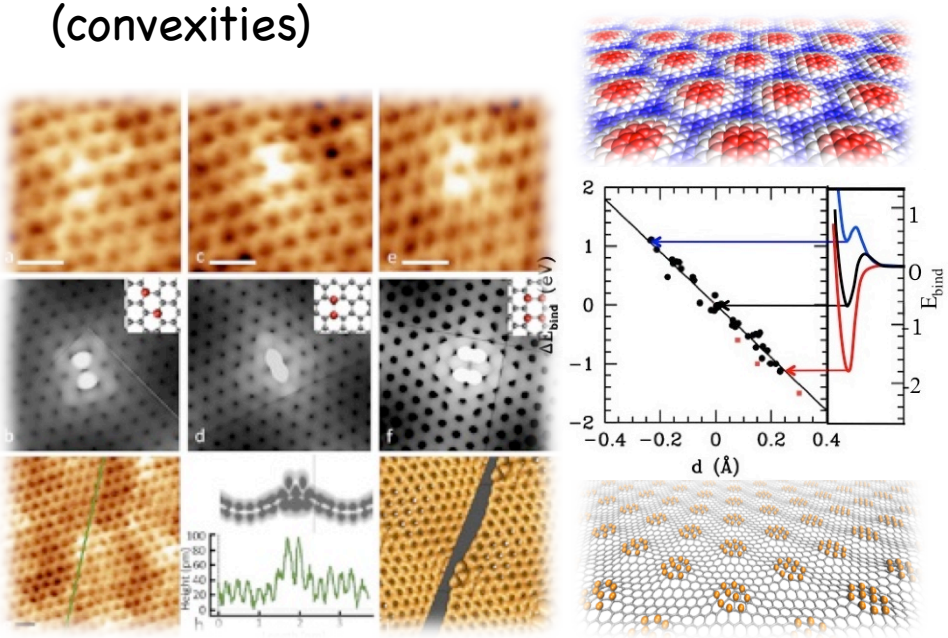
- ✓ Different corrugation pattern can be stabilized by altering the buffer-monolayer interactions

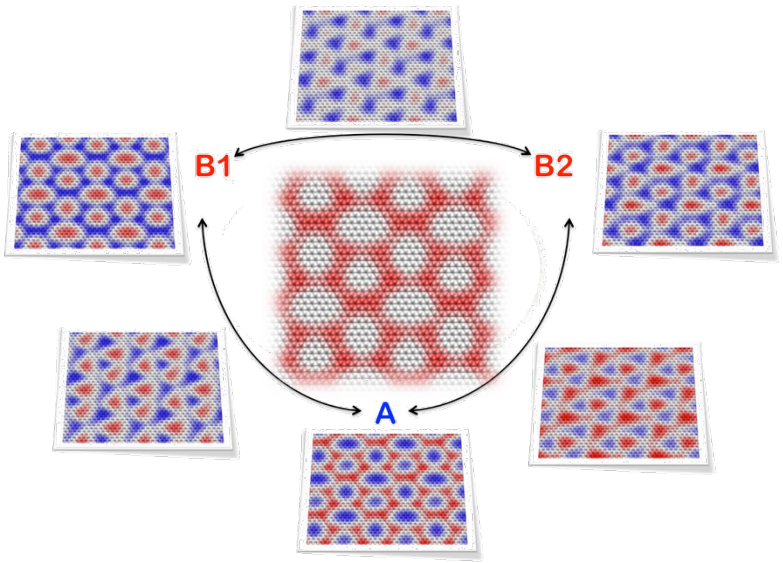
→ The transitions could be driven by changing environmental conditions (e.g. temperauture or Electric Fields)

Substrate: not just a support for graphene

Graphene monolayer on SiC: controllable H adhesion

✓ Reactivity and stability of ad-atoms are strongly dependent on local curvature: H adhesion is enhanced on hot-spots (convexities)

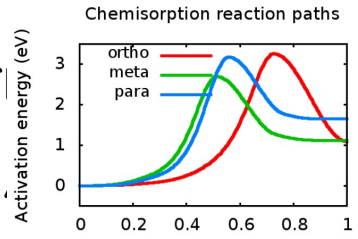




⇒ Decoration with ad-atoms could be driven by the curvature control

✓ **Currently in progress:**

➢ Quantification of chemisor Barriers as a function of Curvature and EF (K Kakhiani, talk 15th ,PM1)



➢ Manipulation of curvature by means of electric fields (Tommaso Cavallucci, PhD)

Nano-Scale Corrugations in Graphene: A Density Functional Theory Study of Structure, Electronic Properties and Hydrogenation A Rossi, S Piccinin, V Pellegrini, S de Gironcoli, and Vtozzini JPCC, 2015

Influence of Graphene Curvature on Hydrogen Adsorption: Toward Hydrogen Storage Devices Goler, C Coletti, V Tozzini, V Piazza, T Mashoff, F Beltram, V Pellegrini, and S Heun *JPC C*, 2013

H-storage in graphene

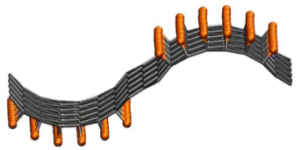
controllable H adhesion

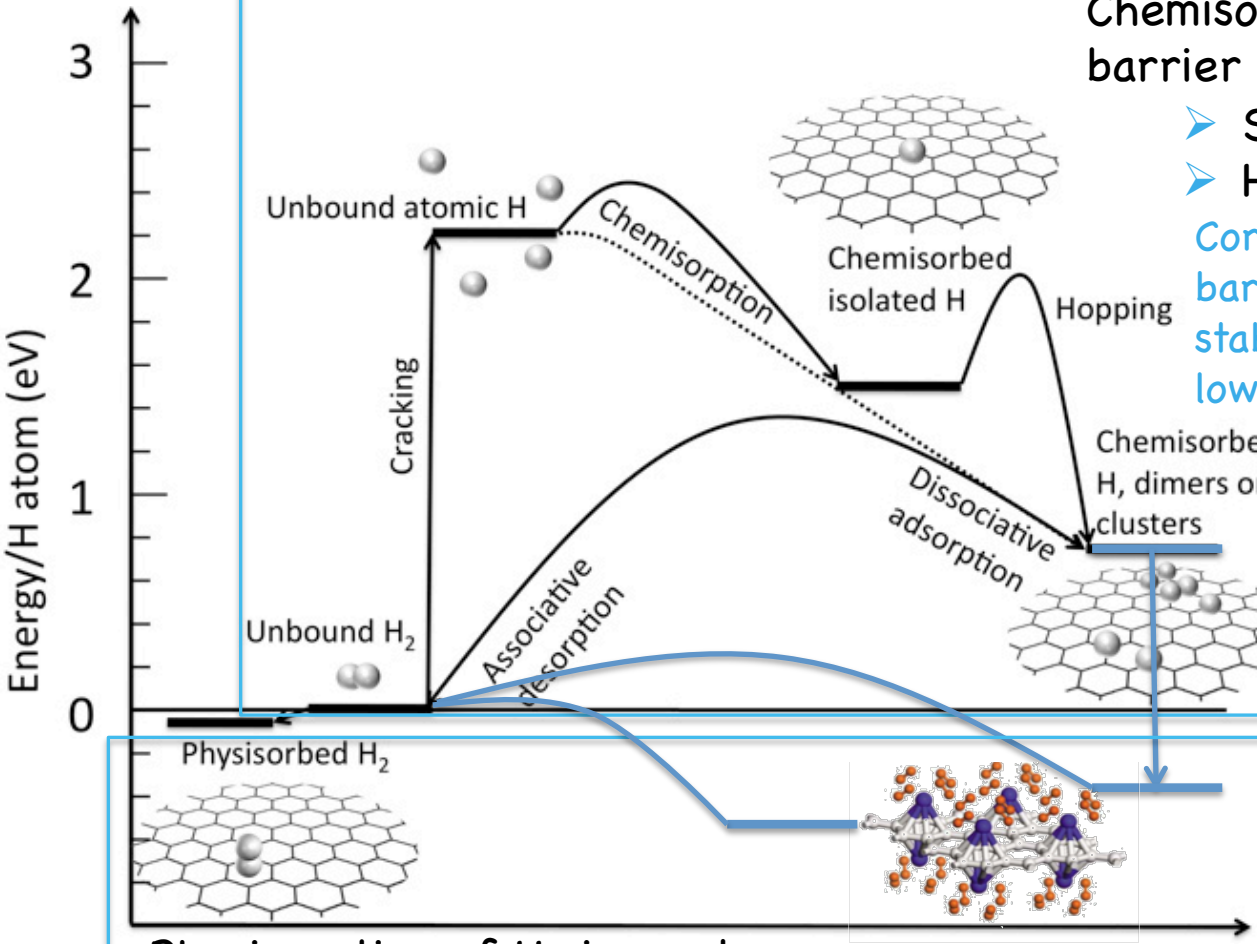
Chemisorption of H_2 has a high barrier

- Slow kinetics
- High operation temp

Corrugation lowers the barrier and enhances stability favoring adhesion at low temp

The process can be inverted





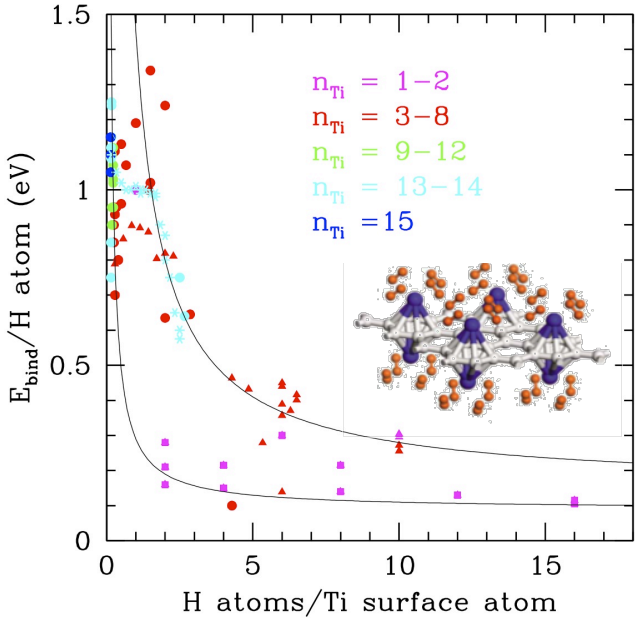
Metal mediated adsorption enhances stability

Physisorption of H_2 is weak

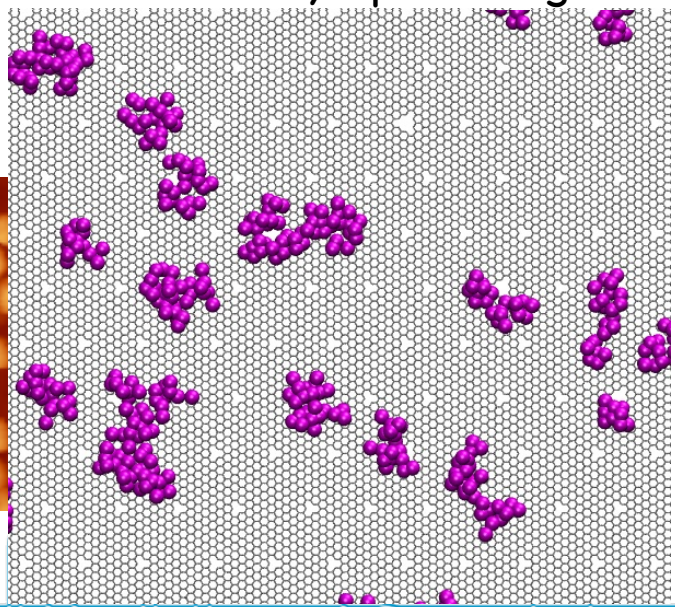
- Limited gravimetric density
- Low temp and/or high press needed

H-storage in graphene

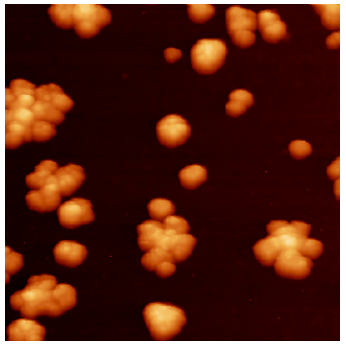
Enhanced H adhesion by multi-modal binding in Ti decorated graphene

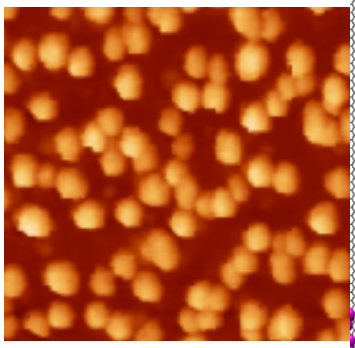


- ✓ Ti is capable of binding hydrogen stably at room temp via a multi-modal d-orbital mediated interaction, half way between chemi- and physisorption
  Revealing the Multibonding State between Hydrogen and Graphene-Supported Ti Clusters K Takahashi, et al *JPCC*, 2016
- ✓ Ti clusterizes, but optimal H loading (ideally 6.8%, reasonably 2.4%) can be obtained with small clusters
- ✓ distributed clusters can be obtained by sputtering N2 onto graphene before exposure to Ti



Ti distribution can be optimized for H-storage
(work in progress)



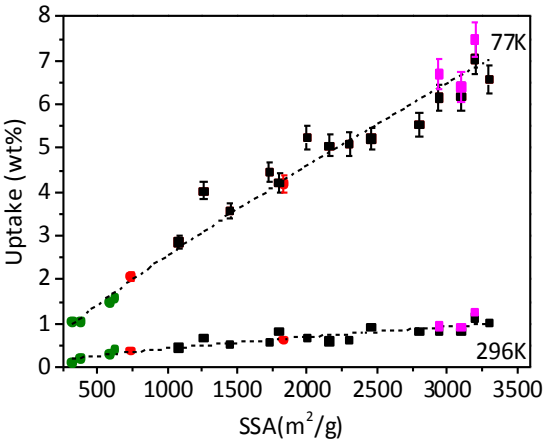


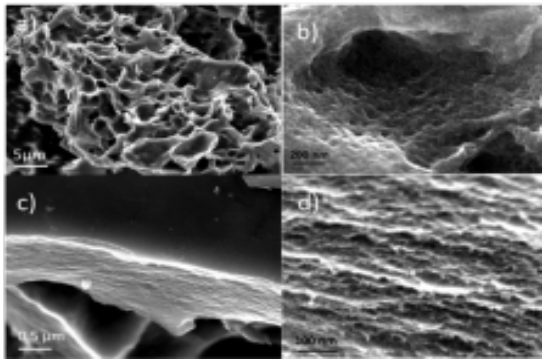
Increasing the active surface of titanium islands on graphene by nitrogen sputtering T Mashoff, et al APL(2015)

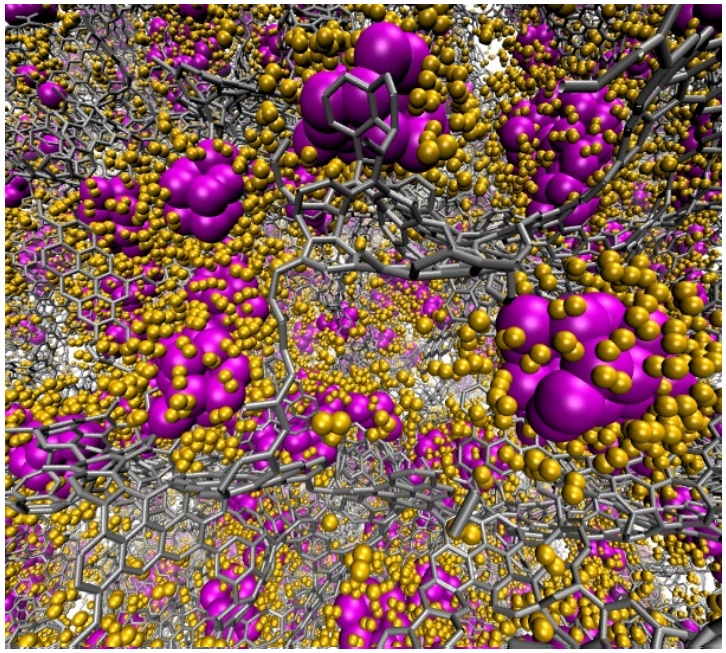
H-storage in graphene – Towards 3D systems

H adsorption in 3D graphene-based scaffolds

- ✓ Esfoliation of GO followed by reduction and activation by KOH leads to a number of graphene based materials characterized by different porosity and defectivity







- ✓ The amount of physisorbed H_2 is only dependent on the specific surface area (SSA), which is therefore a physical limit, due to the weakness of vdW interaction

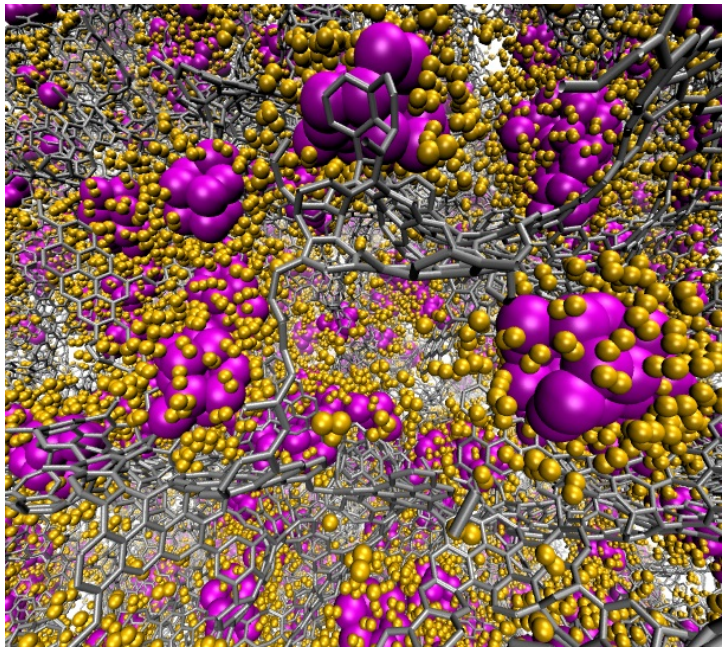
Hydrogen storage in bulk graphene-related materials A G. Klechikov, et al micr Mes Mater 2015

Ti decoration could overcome this limit. Work in progress (Luca Bellucci)

- ✓ Modeling of pristine and Ti decorated graphene scaffolds
- ✓ Simulation of diffusion of H2 within the system
- ✓ Evaluation of H2 loading at different P and T
- ✓ Optimization of Ti decoration

H-storage in graphene – Towards 3D systems

H adsorption in 3D graphene-based scaffolds



Methods

- ✓ Empirical FF based simulations - Combination of different FFs – QM/MM approaches
- ✓ Optimization for an algorithm to generate scaffolds with given porosity and density
- ✓ Evaluation of SSA by means of surface generation algorithms
- ✓ Empirical valuation of H_2 adsorption isotherms (BET)
- ✓ Evaluation of diffusion of H_2 diffusion in the structure by simulations

Preliminary results are encouraging:

- ➢ Ti stably binds to structural defects
- ➢ H2 molecules stably bind and can lead to high GD at RT

Problems to solve:

- ➢ how to tune the size of Ti clusters and their density into the 3D str

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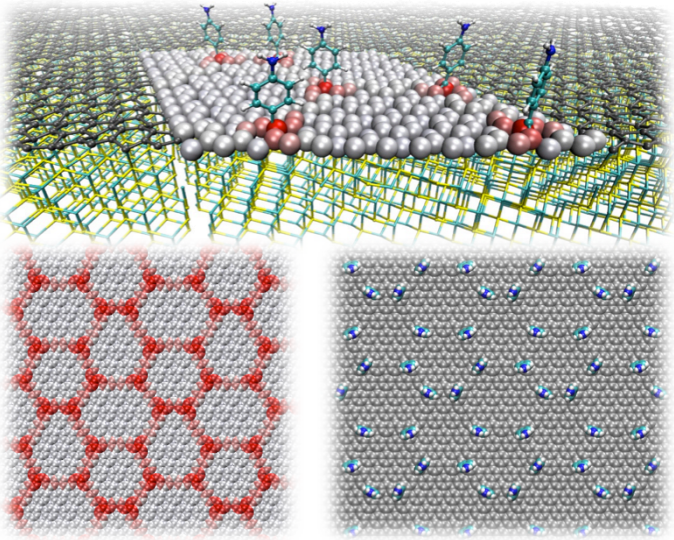
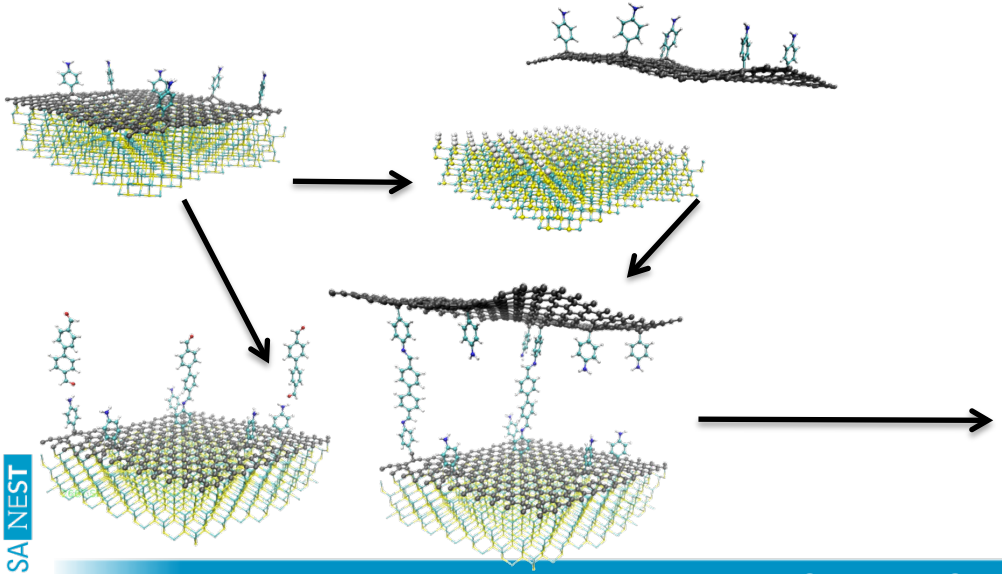
H-storage in graphene – Towards 3D systems

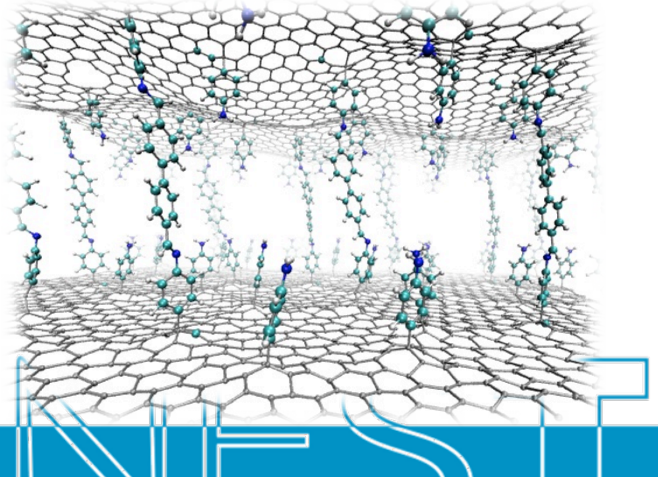
Design of 3D graphene-based pillared frameworks: How to exploit the properties of epitaxial graphene

Limit of graphene scaffolds: very difficult to manipulate or design structure

- ✓ Graphene on SiC corrugation creates hot spots of reactivity which could be exploited to drive the chemical adhesion of anchor molecules
- ✓ The anchors will be regularly spaced
- ✓ Pillar molecules can be added and will be regularly spaced as well
- ✓ The formation of stacked structures will be favored



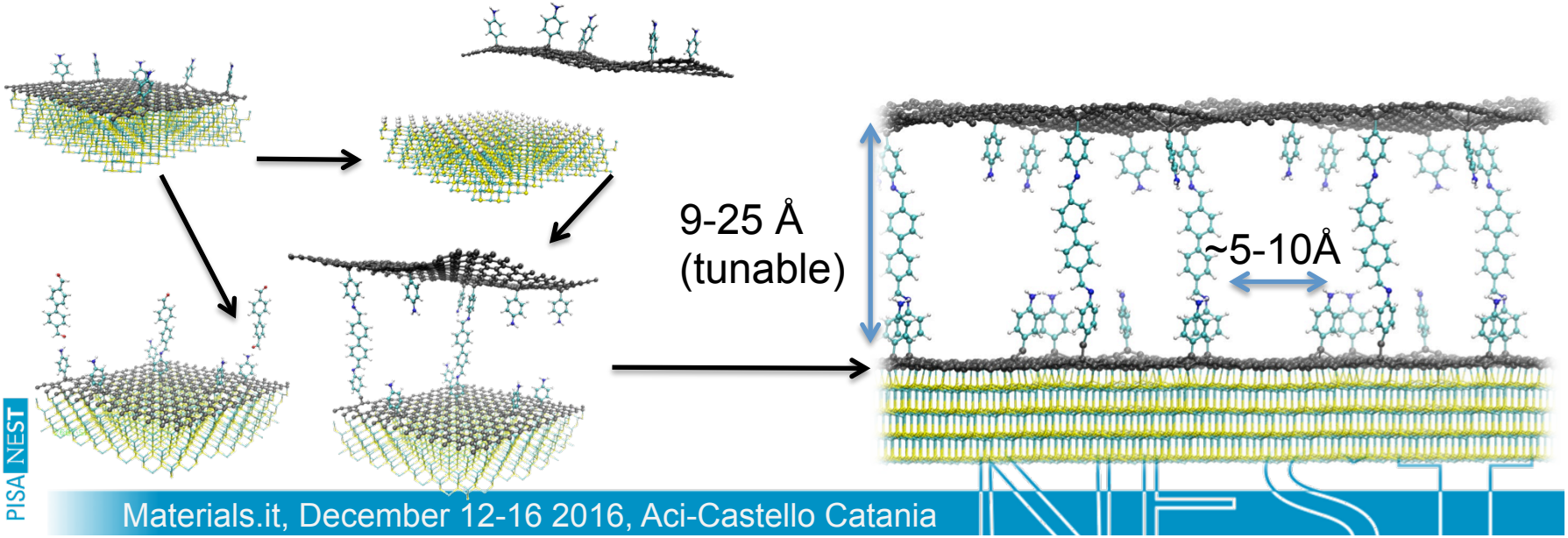




H-storage in graphene – Towards 3D systems

Design of 3D graphene-based pillared frameworks: How to exploit the properties of epitaxial graphene

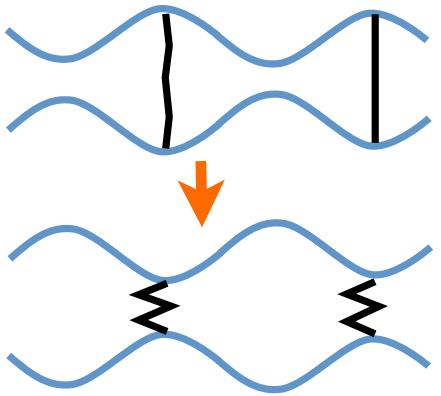
- ✓ Advantages with respect to scaffolds: structural properties can be tuned! Pillars length, rigidity and shape determine the average density, mechanical properties and porosity of the framework
- ✓ Where are we
  - ➢ Modeling: preliminary structures are available, and their properties under evaluation; simulation of reactivity of buffer and moolayer is in progress Luca Bellucci (Cnr-NANO Pisa)
  - ➢ Experiment: Anchor adhesion is being tried (Cnr-NANO and iit-CNI Pisa S Heun, C Coletti, and iit Genoa, Silvia Giordani)

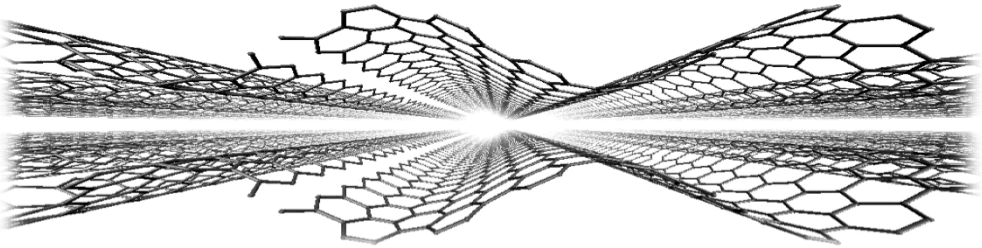


H-storage in graphene – Towards 3D systems

Design of 3D graphene-based pillared frameworks
Perspectives

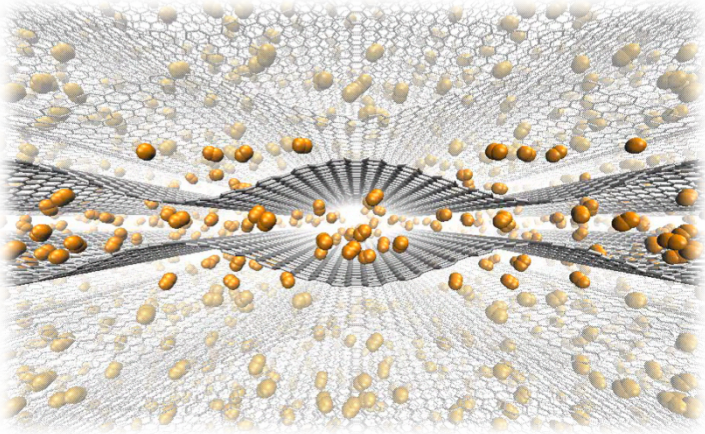
- ✓ The system could be enriched with special properties, e.g, by using optically active pillars: the network could be squeezed or expanded by means of an optical pulse
- ✓ Depending on the distribution of pillars and frequency of pulse, this could generate and sustain flexural phonons…

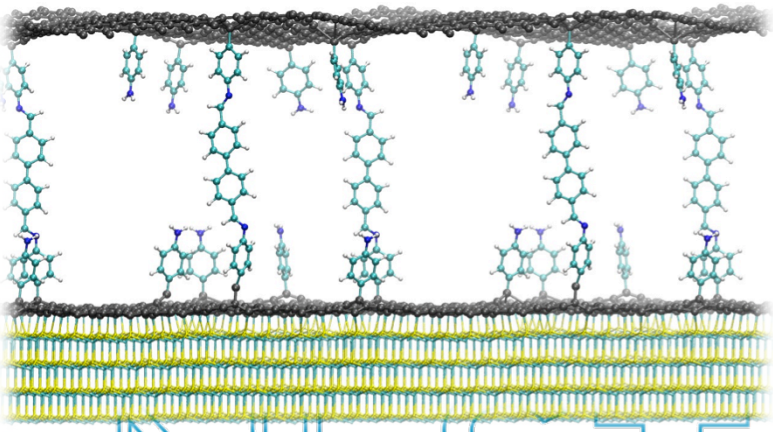




V D Camiola et al 2015 2D Mater. 2 014009

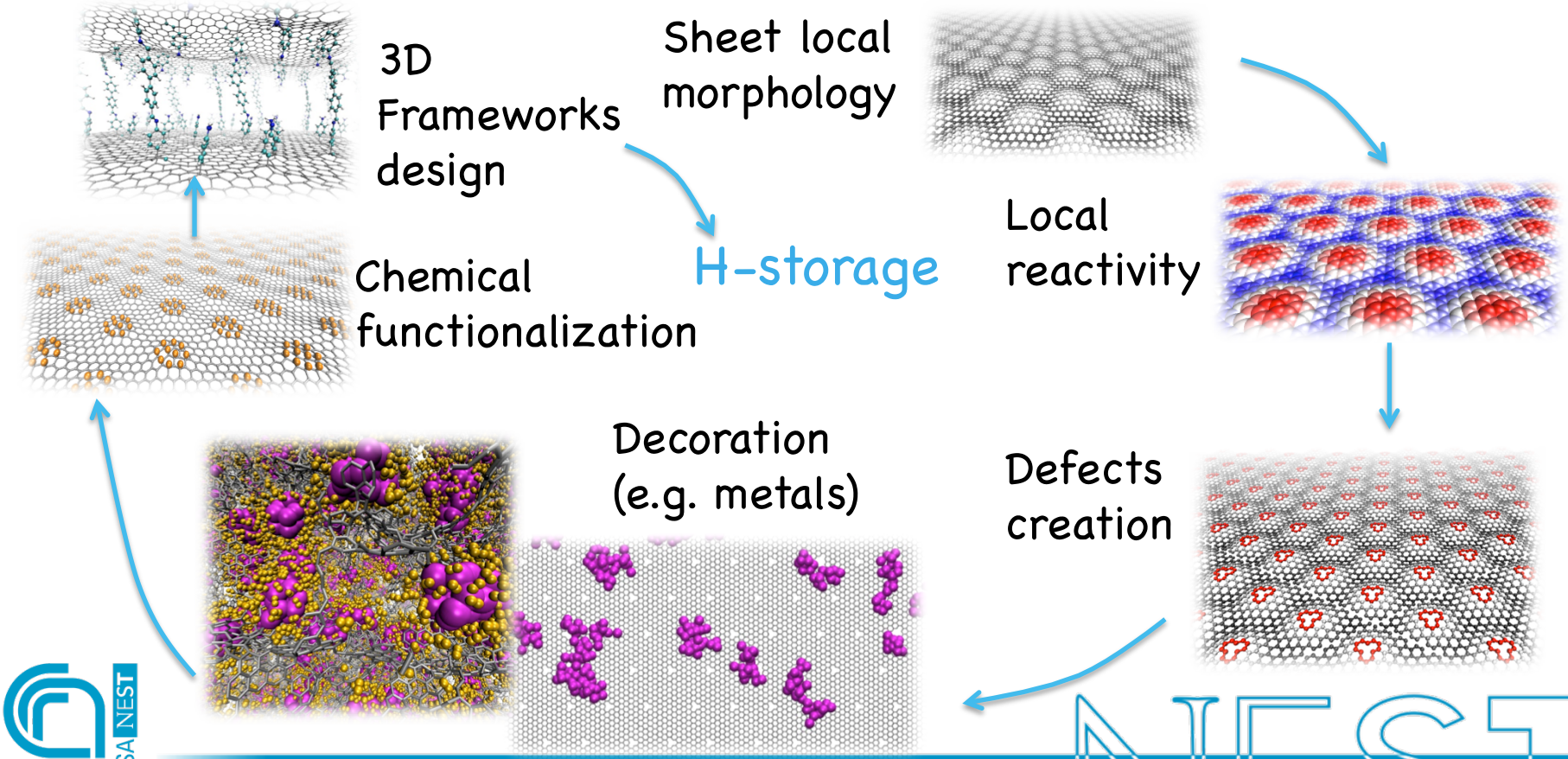
… which could be used to move or pump gases through the structure





Conclusions on graphene for H-storage

- ✓ Graphene for H-storage requires its morphology manipulation to
  - ➢ Optimize the interaction with hydrogen
  - ➢ Buld 3D systems
- ✓ Epitaxial graphene natural properties can be exploited to drive the nano-scale functionalization and design 3D frameworks



"Side results": Nano-electronics

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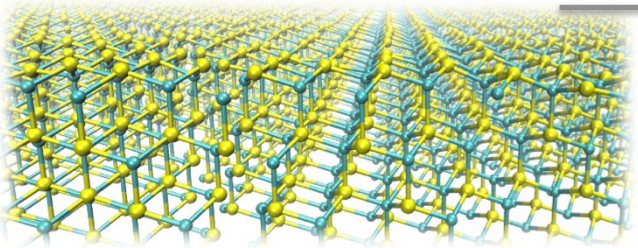
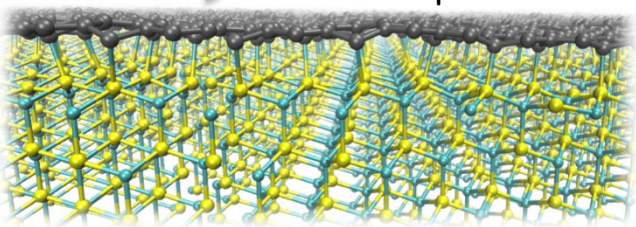
SiC bulk (0001) Si rich face

Si evaporation





buffer layer

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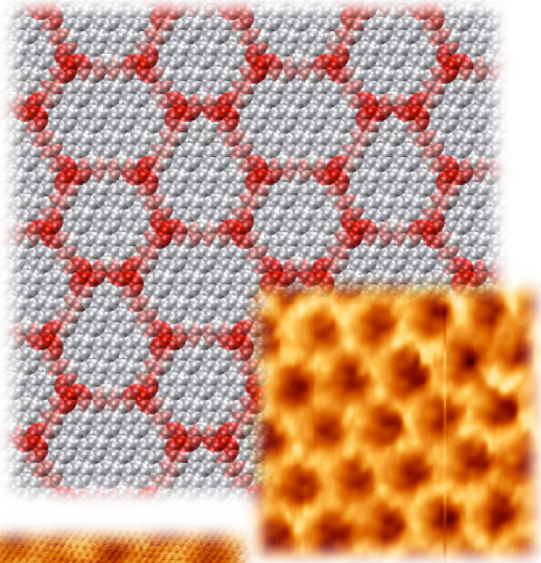

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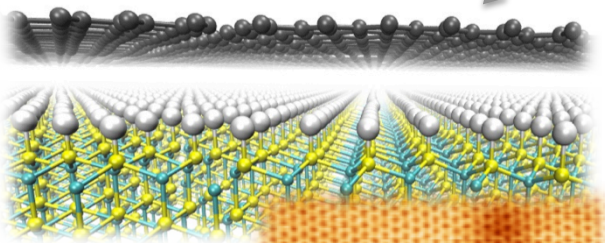

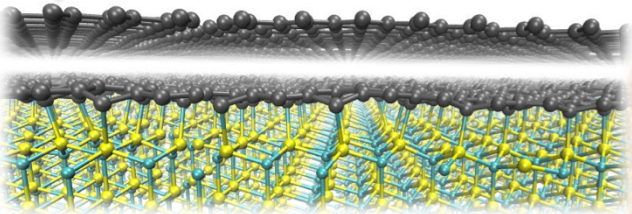

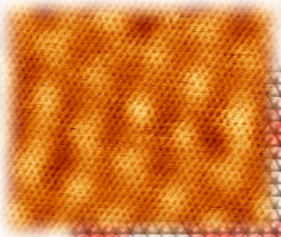

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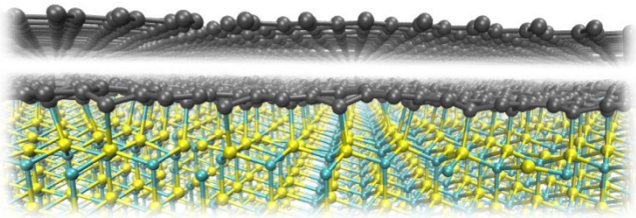
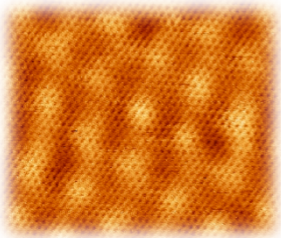
quasi free standing graphene

sp^2 hybridized, almost flat, with structural irregularities

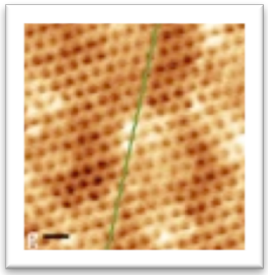
"Side results": Nano-electronics

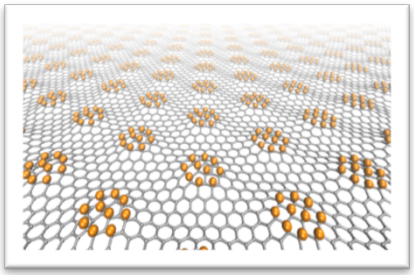
graphene monolayer



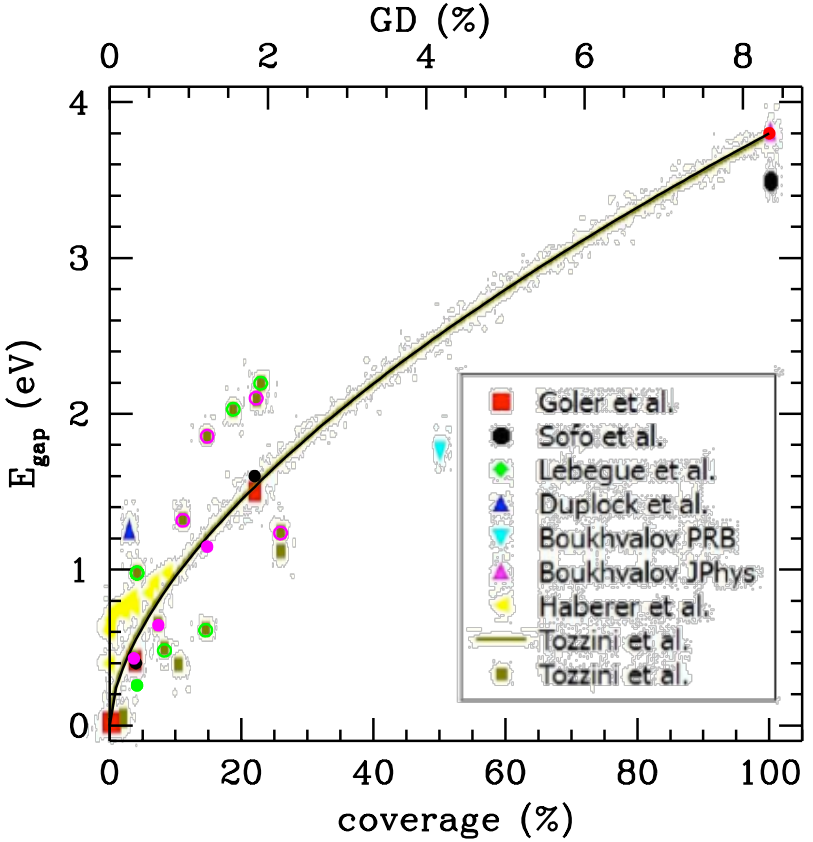


+H





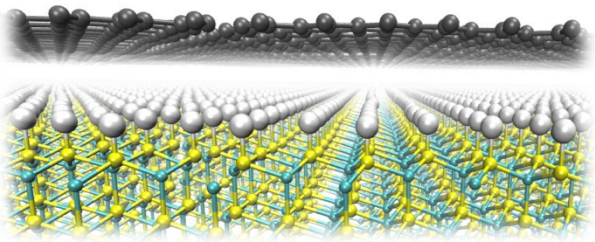
- ✓ A regular band gap increasing as a function of H coverage is found with DFT calculations
- ✓ The spread of data is due to different decoration
- ✓ This relationship could be used to measure the coverage by STS
- ✓ The band gap can be tuned by H decoration

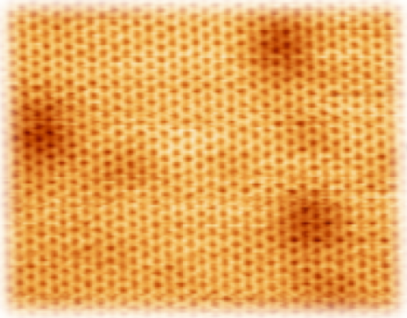


Nano-Scale Corrugations in Graphene: A Density Functional Theory Study of Structure, Electronic Properties and Hydrogenation A Rossi, S Piccinin, V Pellegrini, S de Gironcoli, and Vtozzini JPCC, 2015

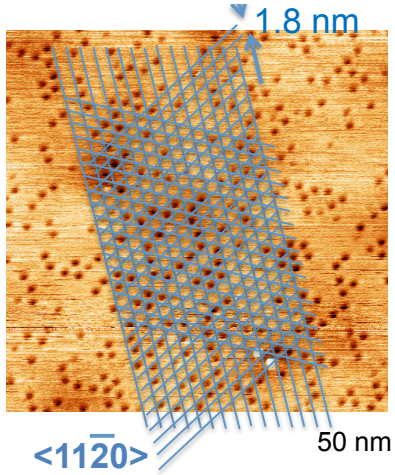
"Side results": Nano-electronics

quasi free standing graphene



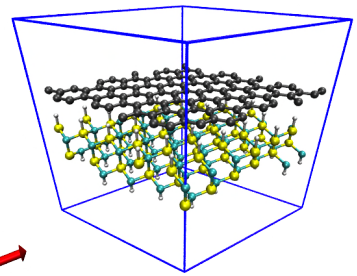


Zoom out



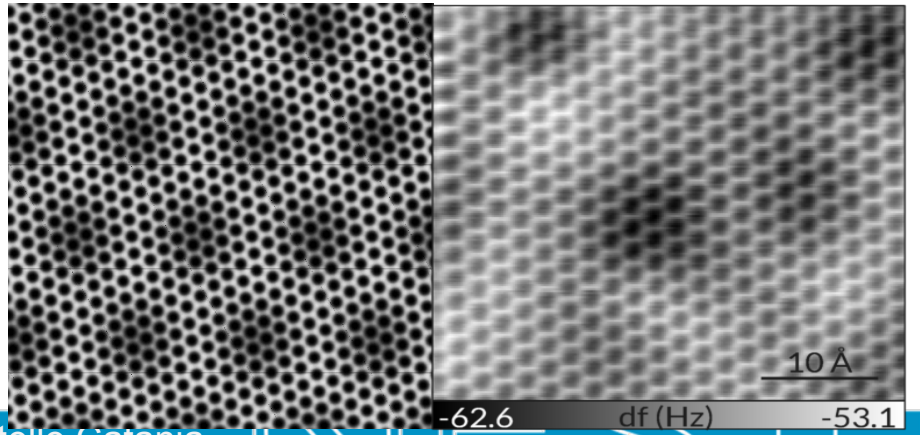
periodicity: 1.8 nm = SiC-6-

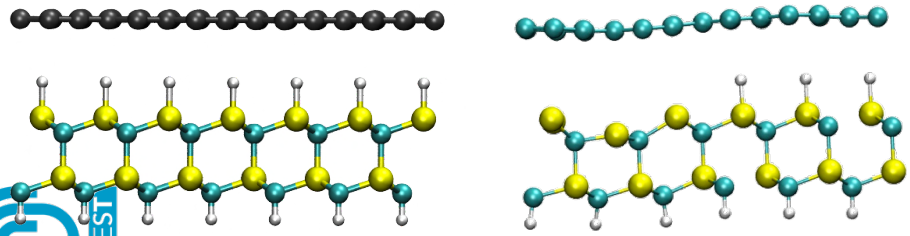
- ✓ The STM images show anomalies whose contrast depends on the voltage bias (Talk by Stefan Heun, 16th)
- ✓ Those anomalies follow a symmetry corresponding to the 6x6 with respect to SiC
- ✓ They were attributed therefore to vacancies in the H coverage
- ✓ DFT Calculations shows that vacancies of 3-7 H atoms can reproduce a deformation whose size and depth is comparable with experiment



Theory

AFM measurement





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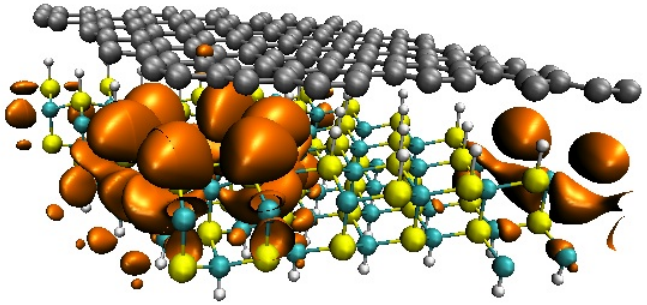
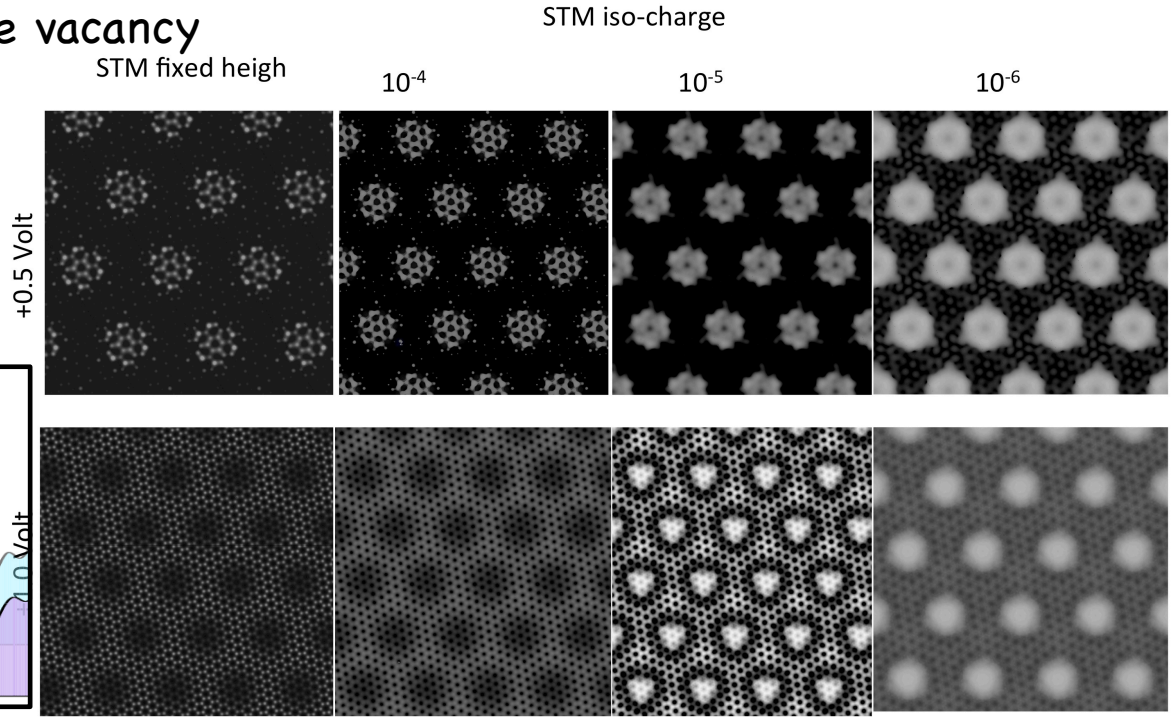
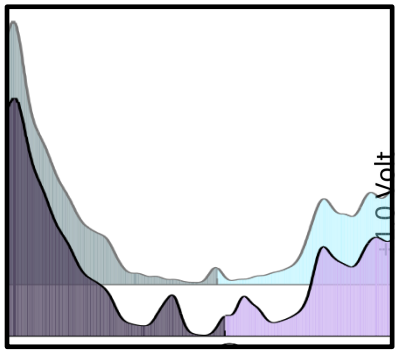
"Side results": Nano-electronics

- ✓ The vacancies create localized electronic states responsible of the features in the STM contrast
- ✓ However he contrast can be either dark or bright, due to two opposite tendencies: the inward bending of graphene and the protruding capacity of the localized orbitals
- ✓ The size and energy of the states depend on
  - ➢ The doping or charge state of the sheet (substrate induced)
  - ➢ The voltage bias
  - ➢ The size and shape of the vacancy



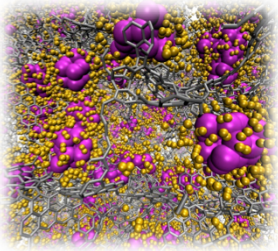
⇒ The electronic properties can be tuned, since distribution, symmetry of vacancies depend on the conditions of H intercalation



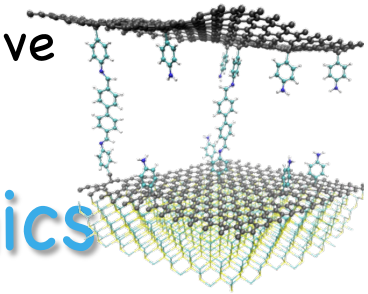


Work in progress

Conclusions: graphene for H-storage

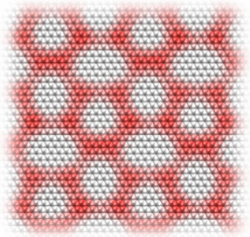


- ✓ Graphene for H-storage requires its morphology manipulation to
  - ➢ Optimize the interaction with hydrogen
  - ➢ Buld 3D systems from a 2D material
- ✓ Epitaxial graphene natural properties can be exploited to drive the nano-scale functionalization and design 3D frameworks



Conclusions: graphene for nanoelectronics

- ✓ Epitaxial graphene can assume different morphologies
  - ➢ Regular patter of curvature (monolayer)
  - ➢ Concavities on a regular lattice, but with tunable size and densities (quasi free standing)
- ✓ Using these properties systems with different electronic properties can be obtained
  - ➢ Tunable band gap
  - ➢ Localized mid-gap states with different energies



Graphene must be manipulated to obtain different "graphenes" for different aplications

Aknowlegements

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Yuya Murata — IA NO-Cnr Pisa
Torge Mashoff — NANO-Cnr Pisa (former)
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THANK YOU FOR YOUR ATTENTION