Multi-Scale Simulations of Graphene for Energy Applications

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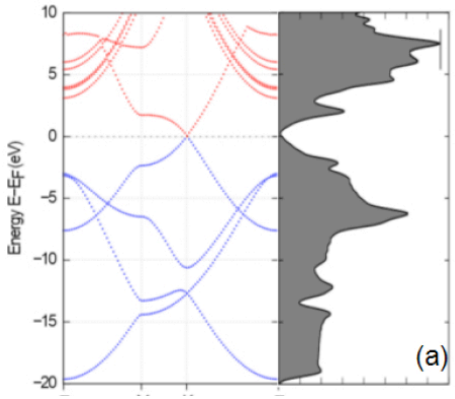
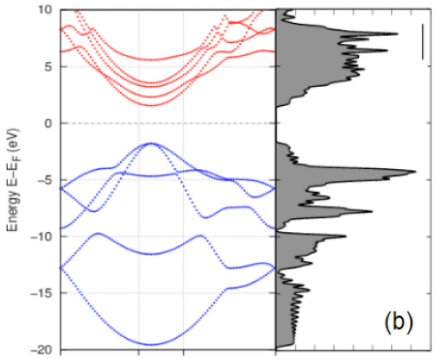
Layout

- Hydrogen and graphene: applications
- The method: Multi-scale simulations
- Results and perspectives

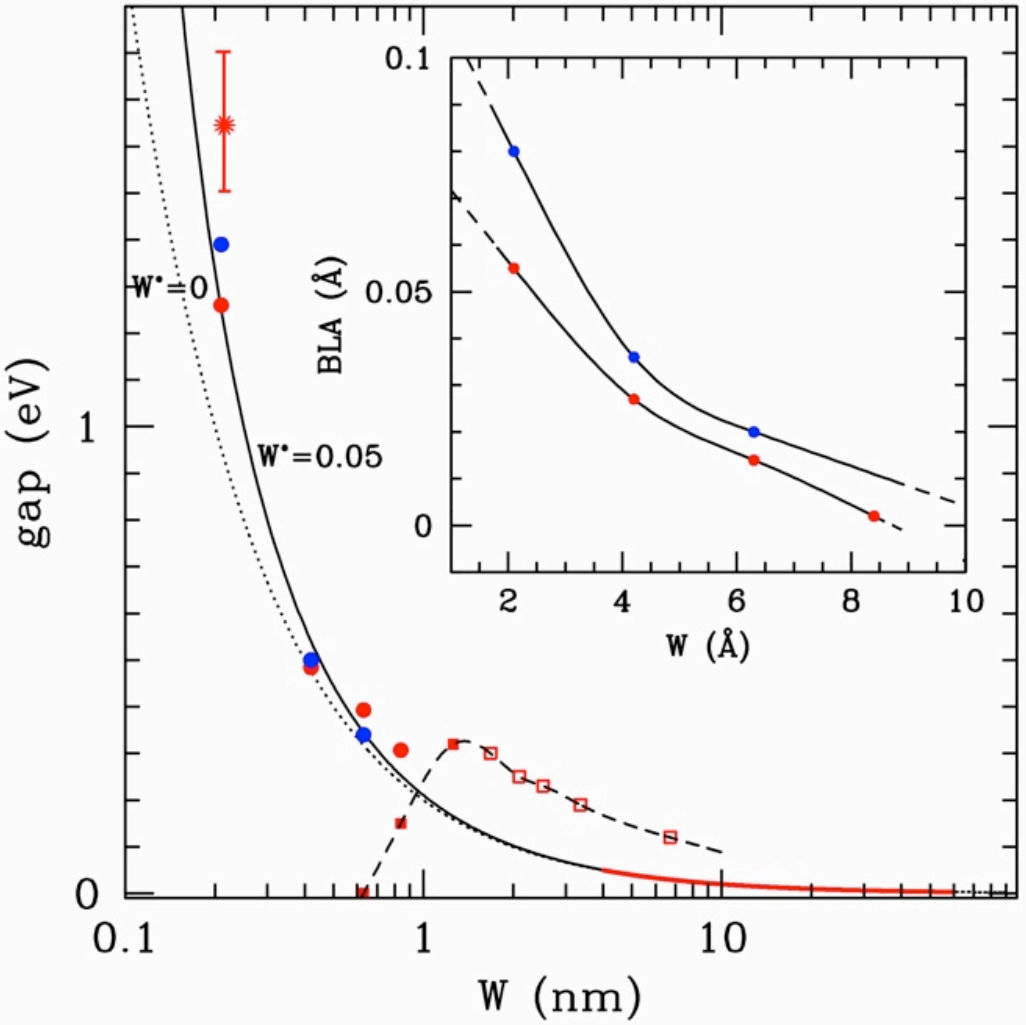
Hydrogenated graphene and nanoelectronics

Graphene is a conductor





"graphane", is an insulator
~3.5 eV gap



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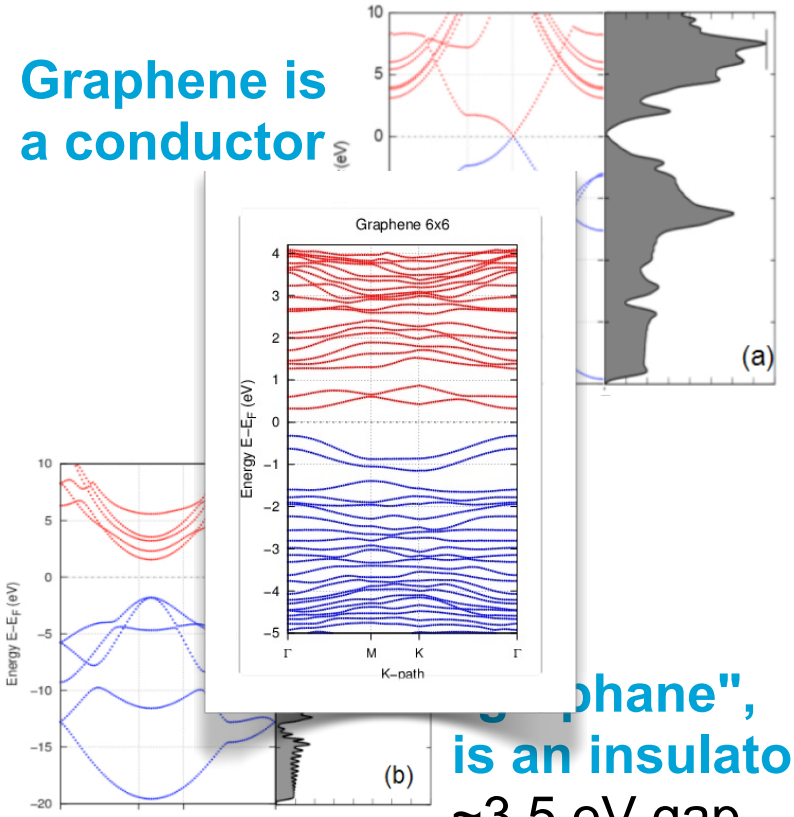

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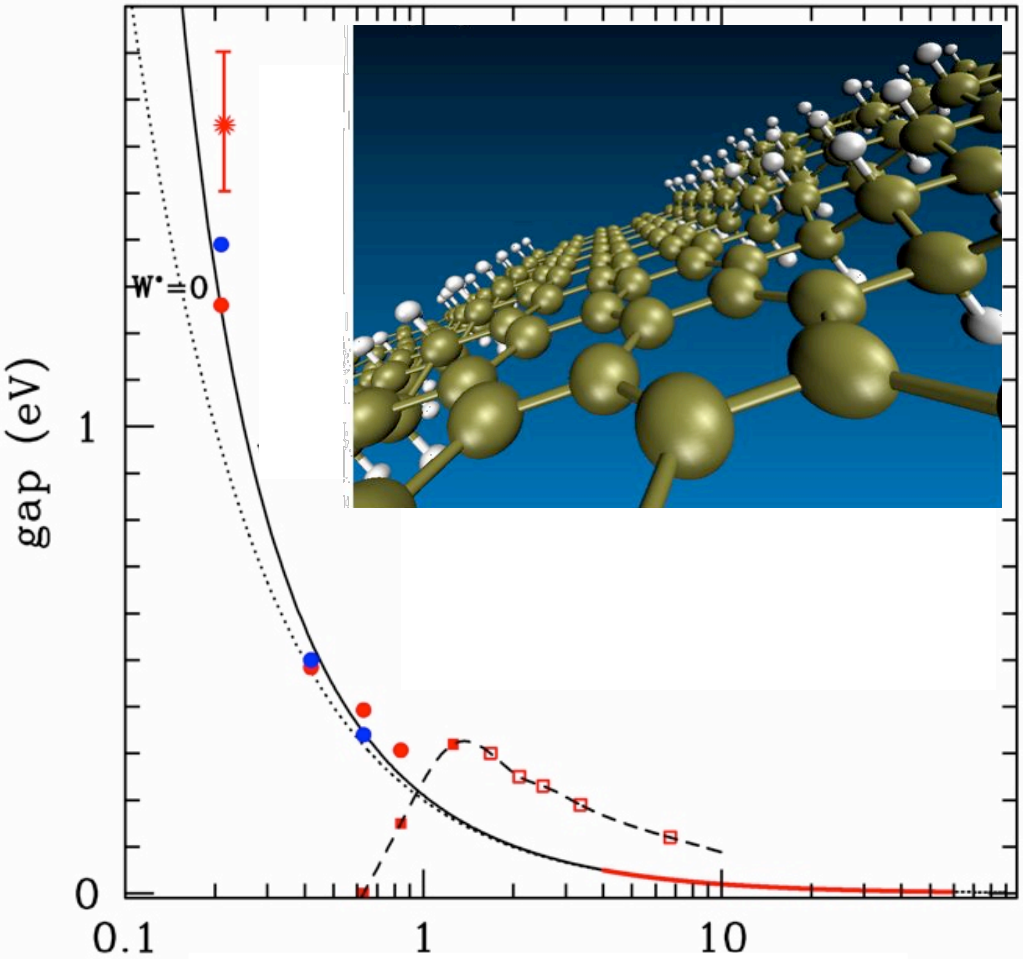


partially hydrogenated graphene is a tunable semiconductor, provided hydrogenation amount and decoration is controllable

Electronic structure and Peierls instability in graphene nanoribbons sculpted in graphane

V Tozzini, V Pellegrini PRB 81 (2011), 113404

Hydrogen & energy

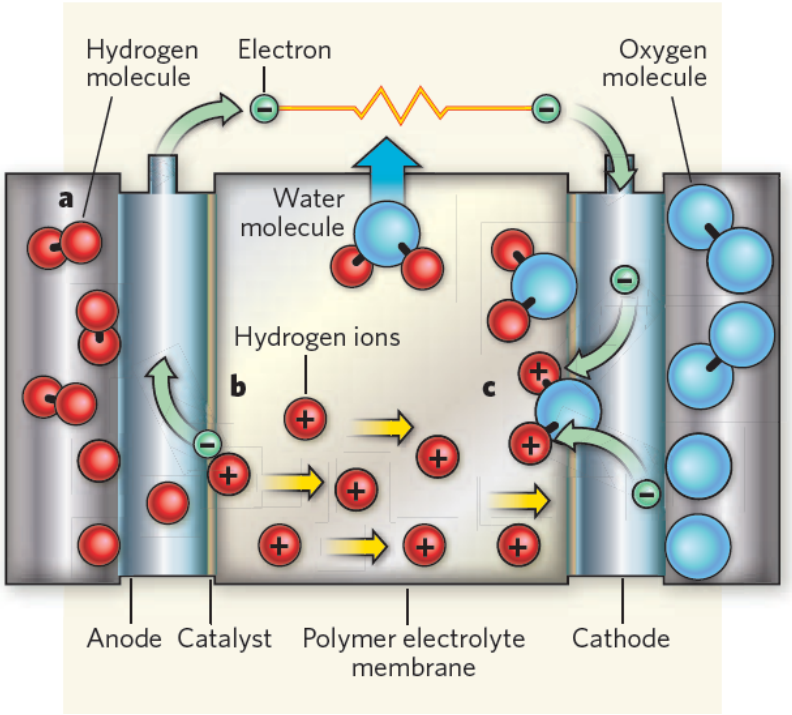
As a fuel, hydrogen has advantages

- high energy-to-mass ratio

  $H_2 + 1/2\ O_2 \rightarrow H_2O \quad \Delta H = -2.96eV$

- Non-toxic, “clean” (product = water) and renewable

Hydrogen fuel cell



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However, hydrogen is NOT an energy source: it must be produced e.g. by electrolysis, needing +2.96 eV, with zero balance with respect to energy production

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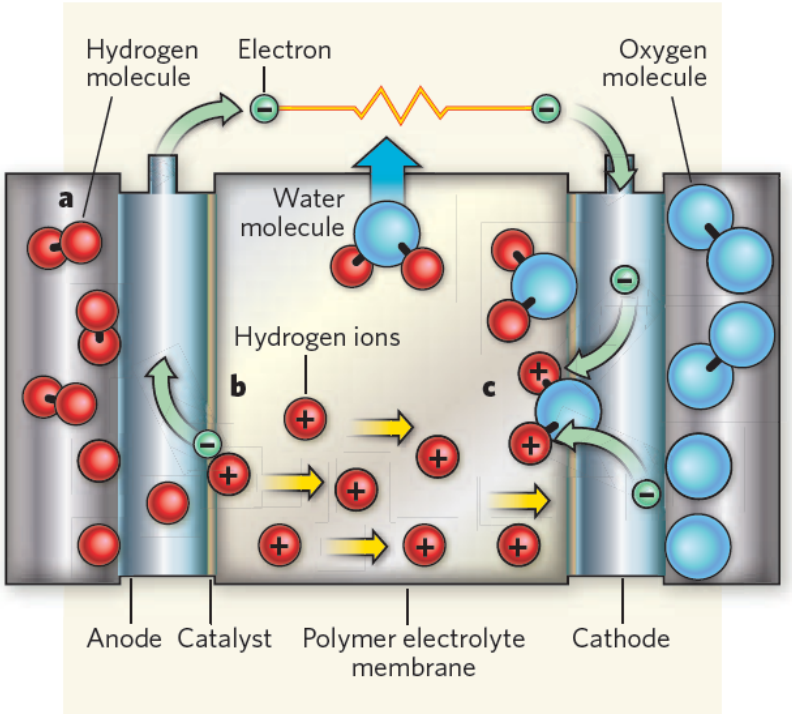
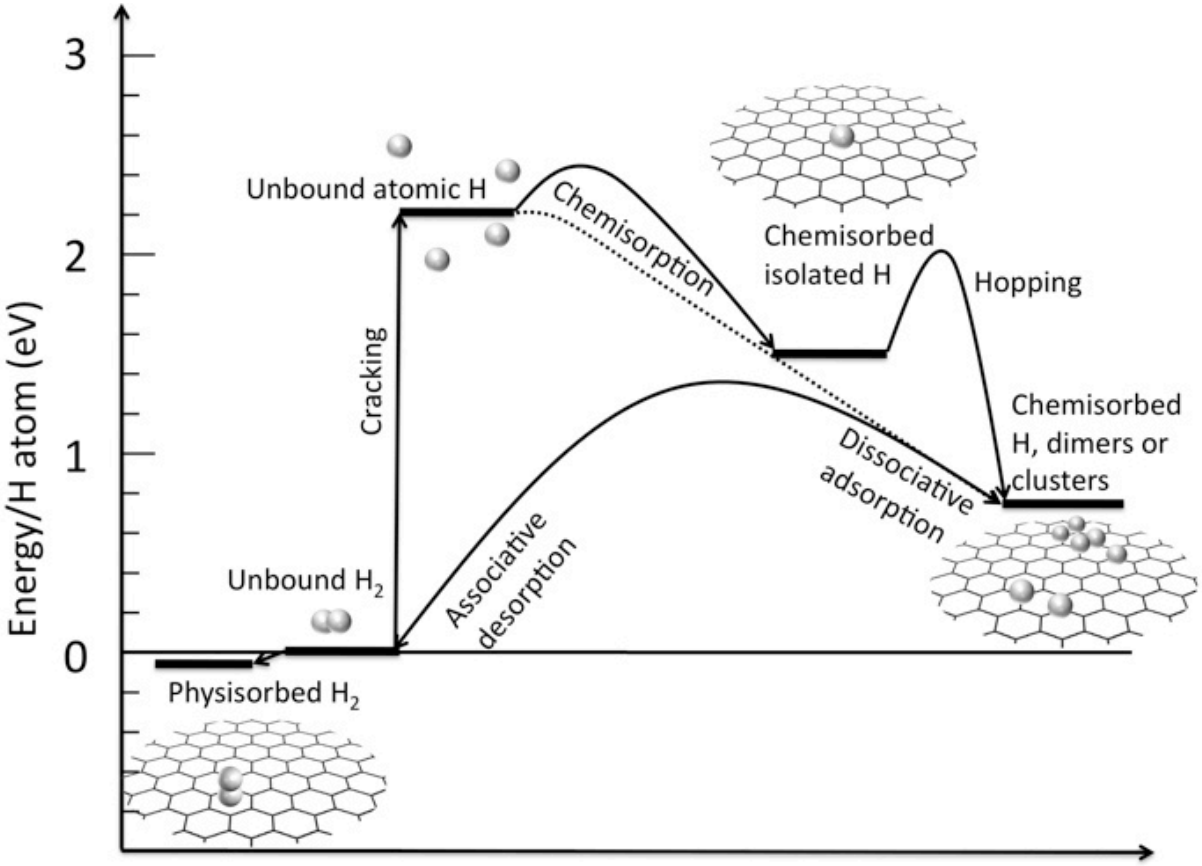


Hydrogen is an energy carrier (as electricity) and its advantages must be considered with respect to storage and transportation devices

- High energy storage capacity ✓
- Low dispersion (✓)
- Easy and practical use in standard conditions (✓)
- Safety (✓)

graphene has potentially all of these properties

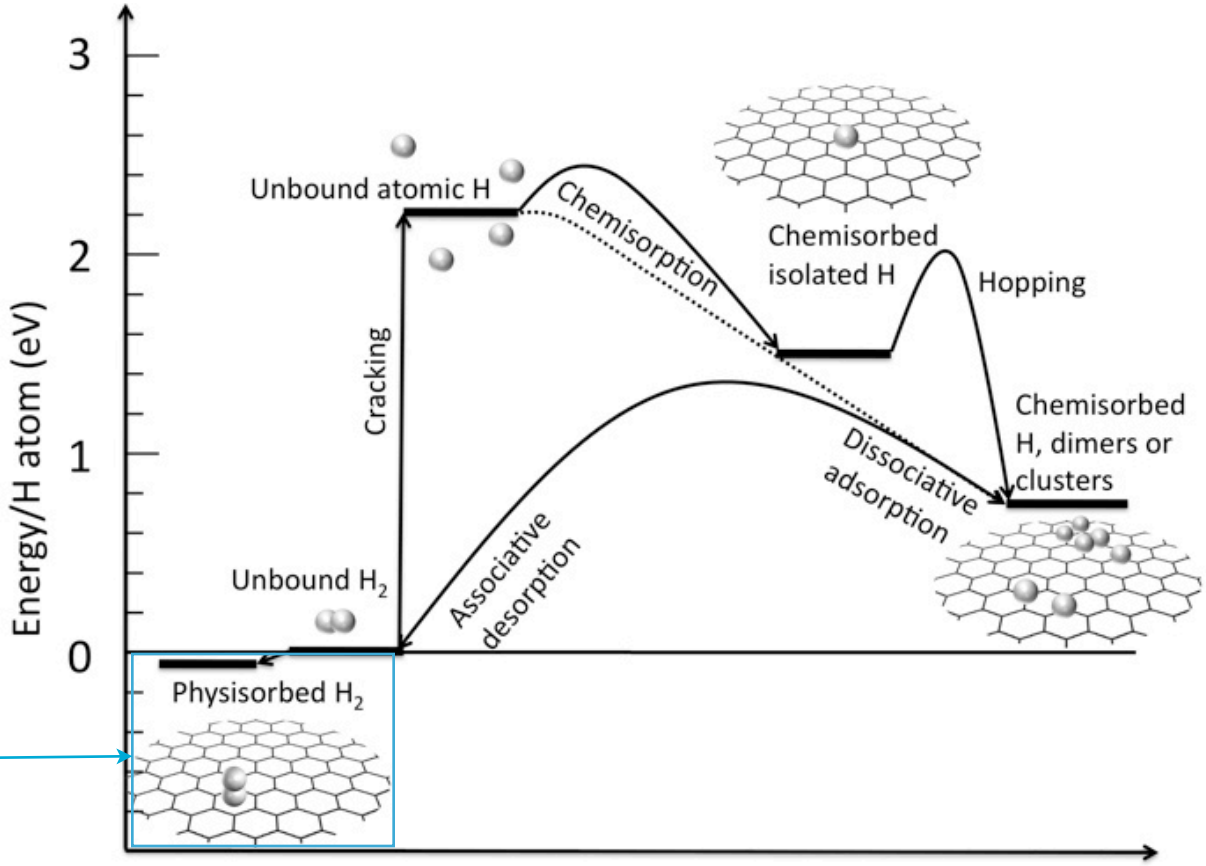
H storage in graphene



H storage in graphene

❖ Physisorption weakly bounds hydrogen ⇒

acceptable storage densities only at low temperatures and/or high pressure



H storage in graphene

- Atomic hydrogen chemisorption has a small or negligible chemisorption barrier ⇒

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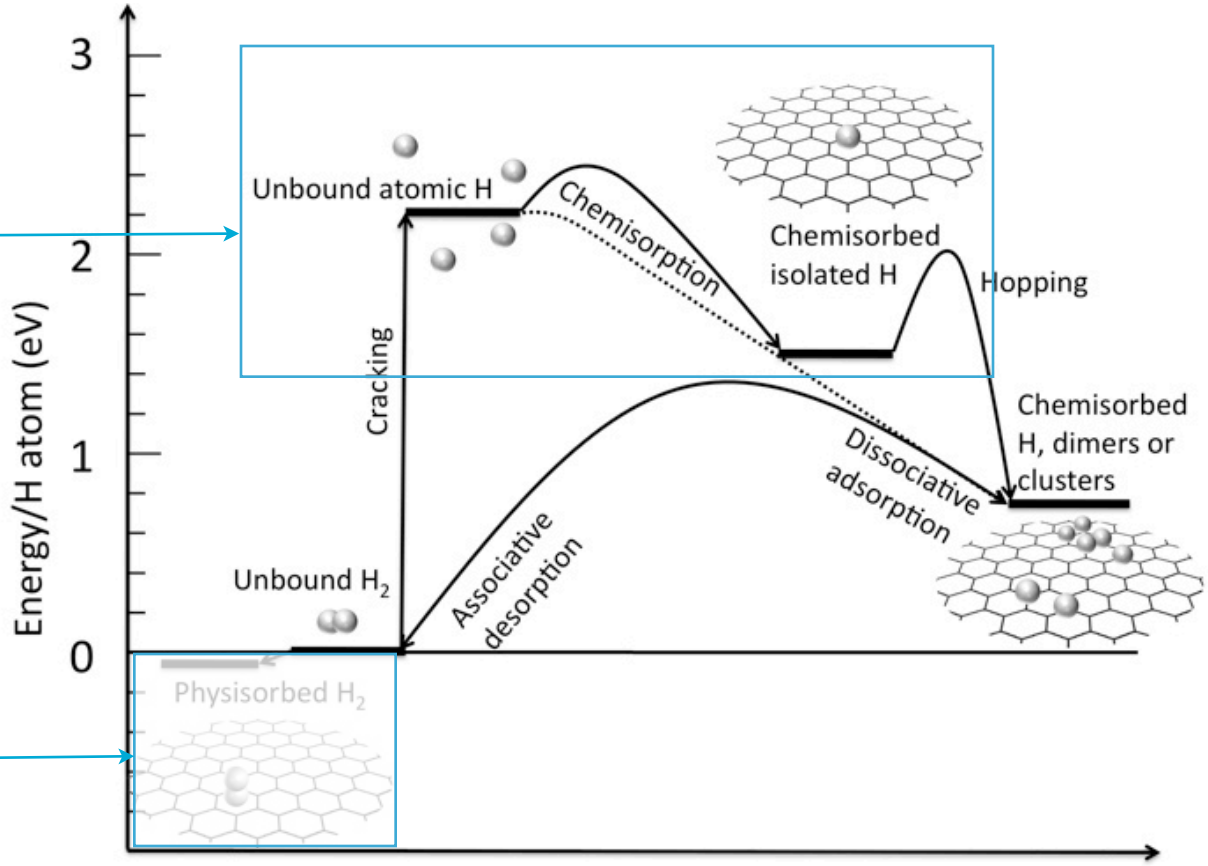

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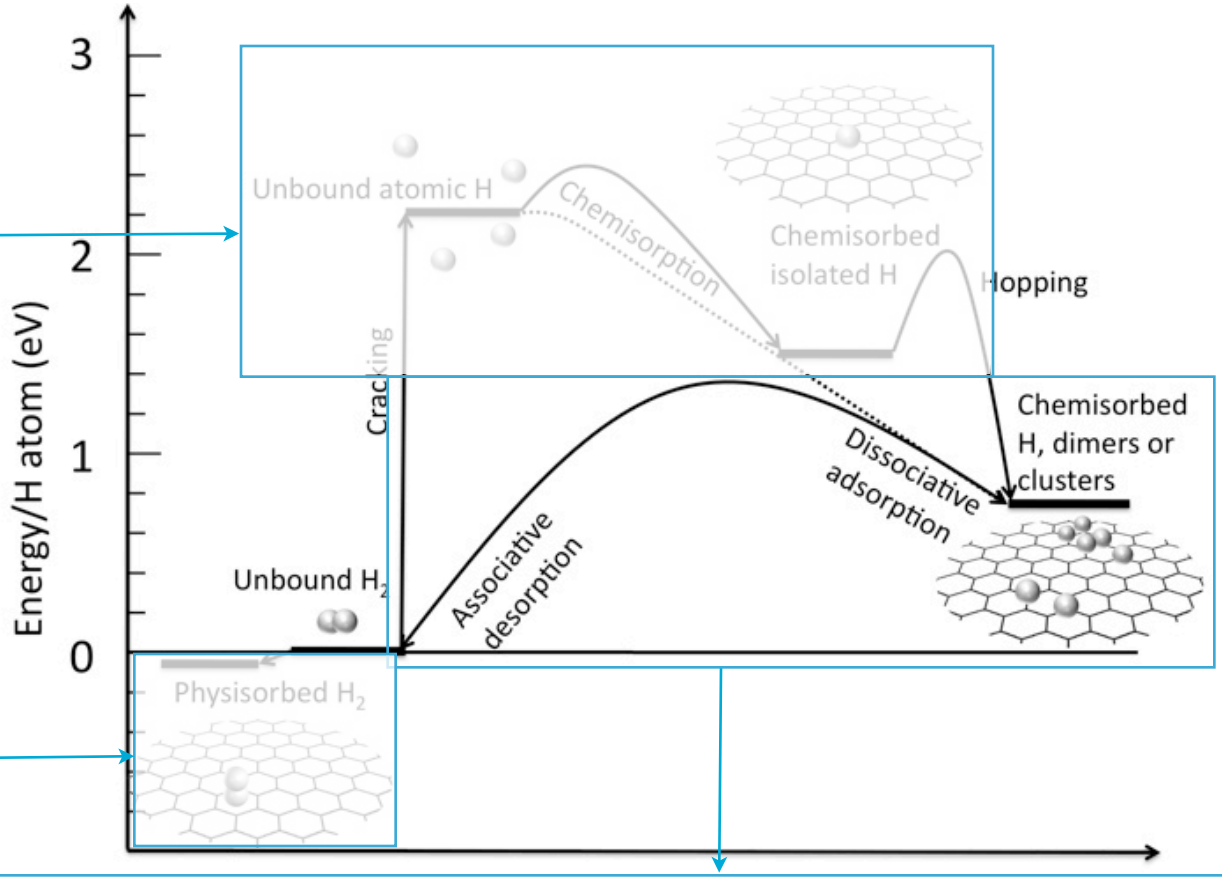


❖ Molecular hydrogen chemi(de)sorption has high barrier (theoretical estimate ~eV) ⇒

chemisorbed H is stable for transportation etc, but catalytic mechanisms are necessary in the loading-release phases

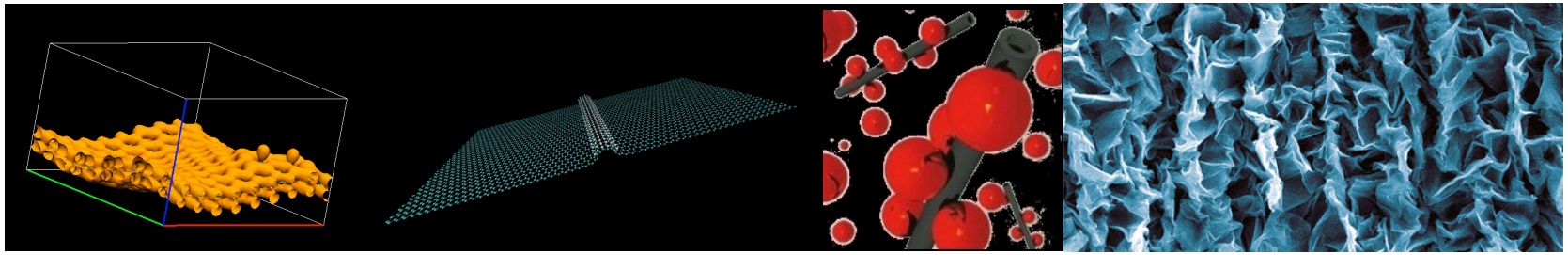
⇒ **Chemi(de)sorption is preferable to physisorption** but it is a process with a slow kinetics and difficult to control

(Partial) summary:

❖**Controlling chemi(de)sorption** (or physisorption) of hydrogen is crucial for energetics and nanoelectronics applications, but it requires deep control on the material and innovative catalytic strategies

❖ **Theoretical and simulations studies** can help designing these strategies, but the processes involve different length and time scales

The multi-scale simulation approach

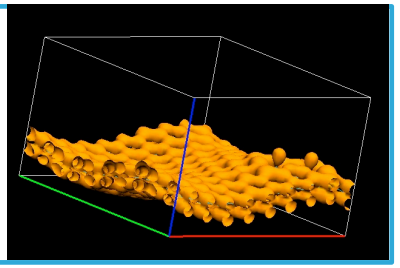


QM-DFT calculations/simulations	Classical MD modeling/simulations	Continuum mechanicistic approaches
electronic props fine structure hydrogenation chemistry	structure and dynamics on the nano-micro scale	statistical behavior thermodynamics large scale mechanical/ chemical props

The multi-scale simulation approach

DFT-QM

Electronic properties
Fine structural props
Hydrogenation chemistry

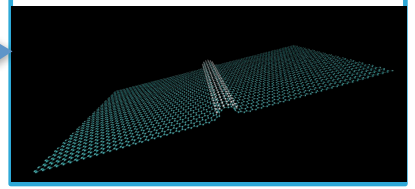


Data for FF params optimization (struct, enrgies, barriers)

Sample structs for electronic calculations

Empirical MM

Structure and hydrogenation of sheets and/or with substrate

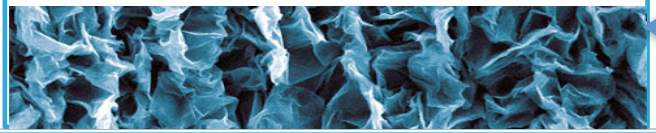


Data for model params

Global structures

Elastic continuum

Curvature and H distribution, global mechanical props



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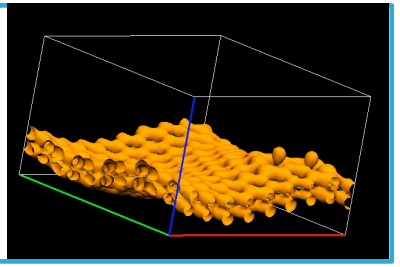

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"Parallel" combination
The methods are used in the same simulation/calculation ("hybrid" approach)

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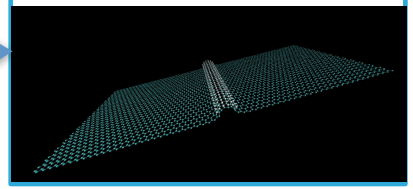

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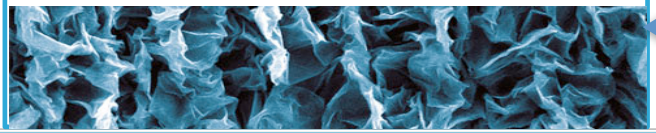

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DFT-QM

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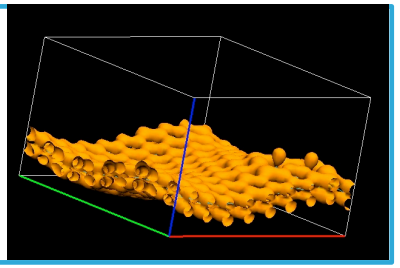

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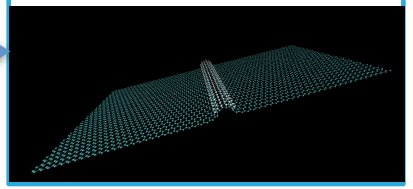

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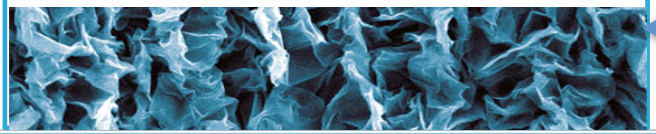


"Serial" combination

- The different representations are used in separate simulations/ calculations
- Coherency among level is maintained in two ways
  - Higher levels are parameterized based on lower level data
  - Structures and other local data are deduced and used at the lower levels from the higher ones

QM-DFT: study of reactivity vs rippling

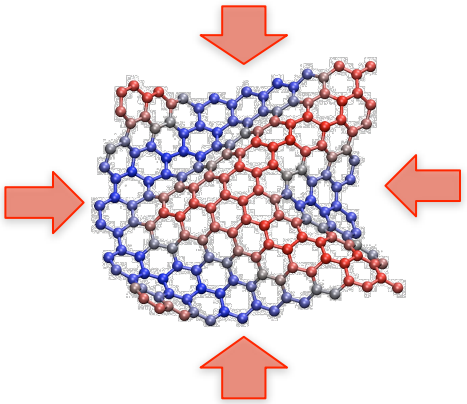
Scheme 1 DFT-CPMD (CPMD 3.13)

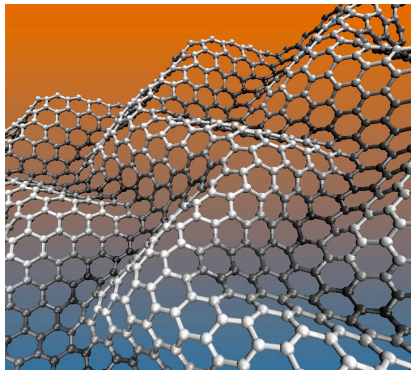
- **Systems: ~Squared cells**
  - Large cell: 180 C atms, 22.13x21.30x15 Å (and contracted) Γ point
  - Small cell: 24 C atms, 7.28x8.41x14.6 Å, 40 K points MP
- **DFT**
  - TM pseudo-potentials + VdW (Grimme, 2006)
  - plane waves (60 Ryd cutoff), Davidson diag
  - PBE functional (checks with BLYP)
- **System Relaxation and dynamics**
  - CP dyn, electron mass preconditioning, timestep = ~0.1fs
  - Simulated annealing + local optimization
  - Nosé Thermostat, restrained/damped MD (metadyn in progress)

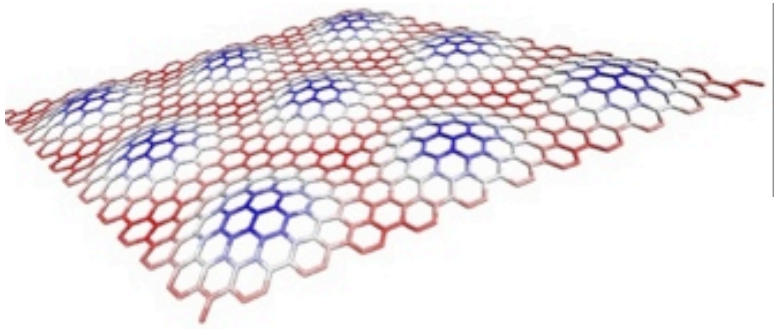
Scheme 2 DFT-QE (QE 5.0.2)

- **Systems: orthorombic cells**
  - 6x6(30deg): 54 C atms, 12.78 Å (and contracted/ expanded), K points 7x7x1
  - 13x13: 338 C atoms, 31.97 Å, Γ point, checks with K points
  - Same on SiC substrate, 1300-1500 atms and with electric field (in progress)
- **DFT**
  - Ultrasoft PPs(RRKJ)+VdW (Grimme, 2006)
  - plane waves (25 ryd), Davidson diag
  - PBE functional (checks with LDA)
- **System Relaxation and dynamics**
  - CP and BO timestep = 0.1-0.5fs
  - Simulated annealing + local optimization
  - Nosé Thermostat, restrained/damped MD

Different patterns and local curvature levels are generated by different boundary or compression conditions





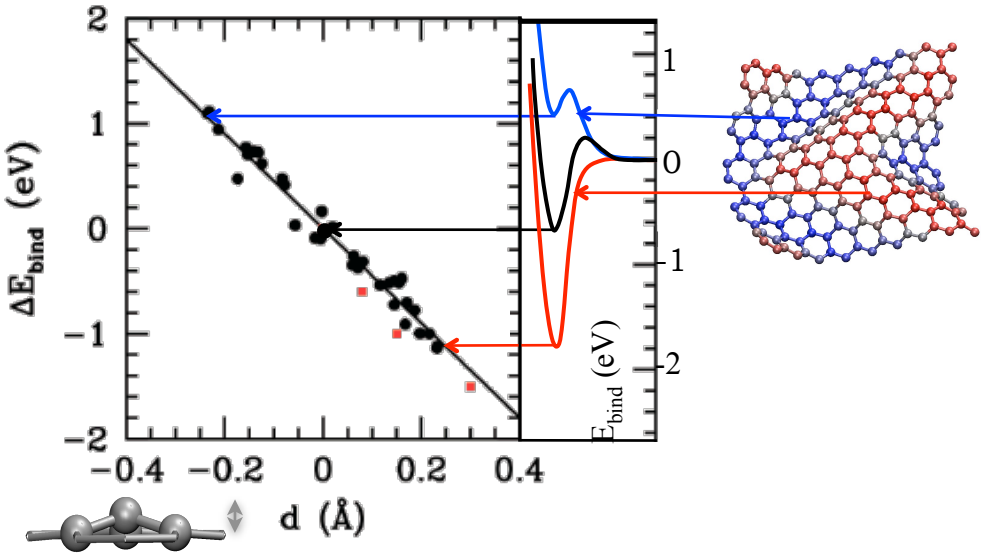


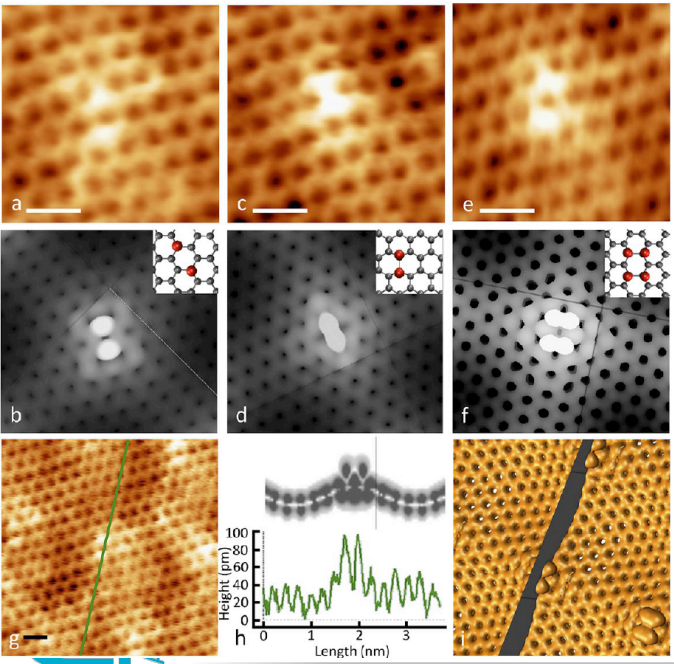
QM-DFT: study of reactivity vs rippling

The relationship between curvature and H binding energy is linear

The reactivity towards H is enhanced on convexities and decreased in concavities ⇒

the curvature can be used to control H adsorption



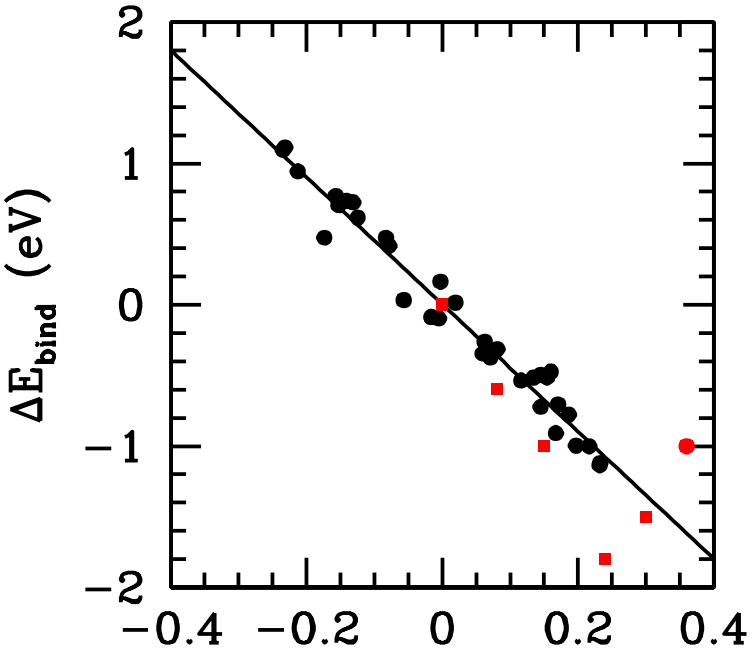


This was experimentally verified by hydrogenation of naturally curved graphene grown on SiC

S. Goler et al. The influence of graphene curvature on H adsorption JPCC (2013)

V Tozzini,V Pellegrini Reversible H storage by controlled buckling of graphene Layers JPCC (2011)

QM-DFT: study of reactivity vs rippling



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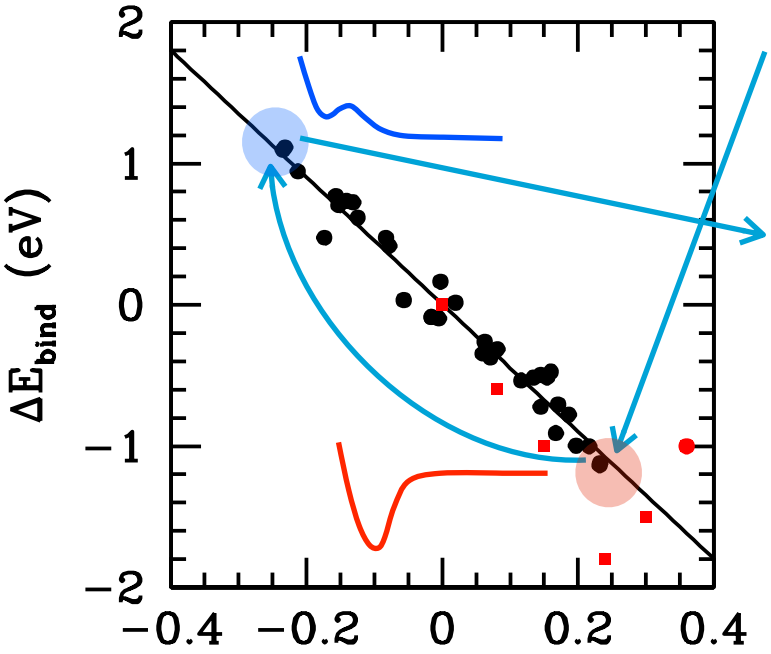

1. H is adsorbed on convex sites
2. Inverting the curvature, H is found on concave sites: unstable adsorbate...
3. ... and H dissociation

⇒ Curvature inversion could be used as H release mechanism

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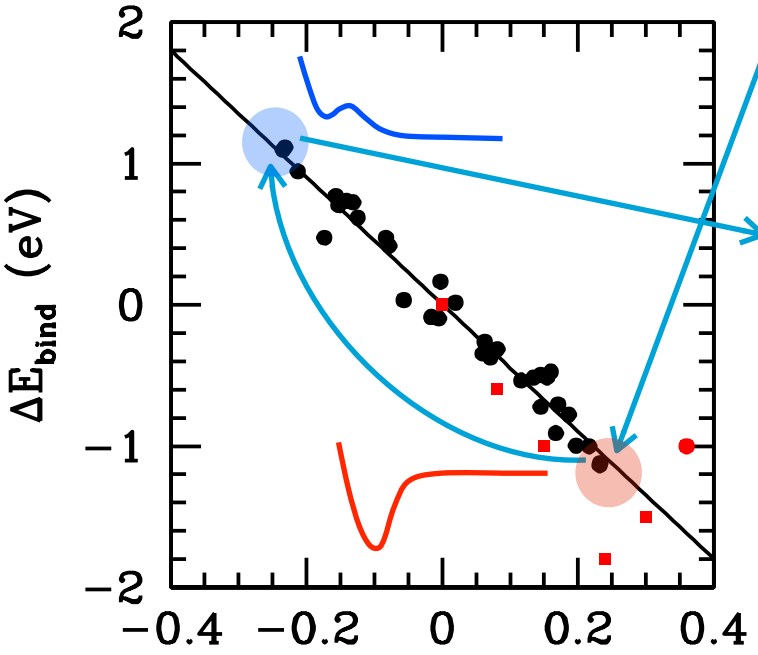

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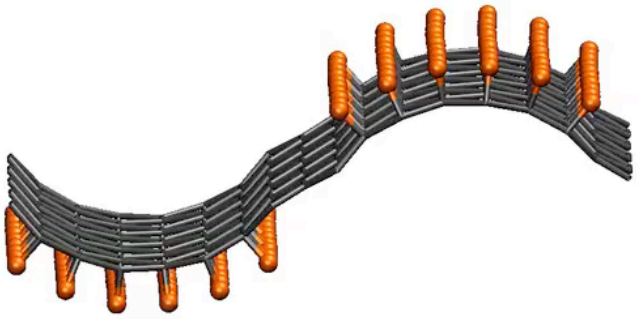
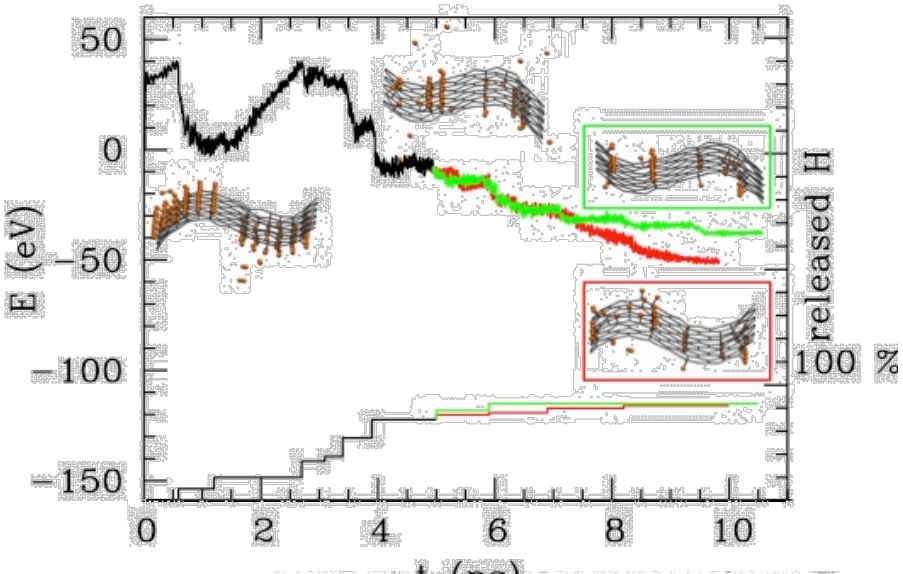
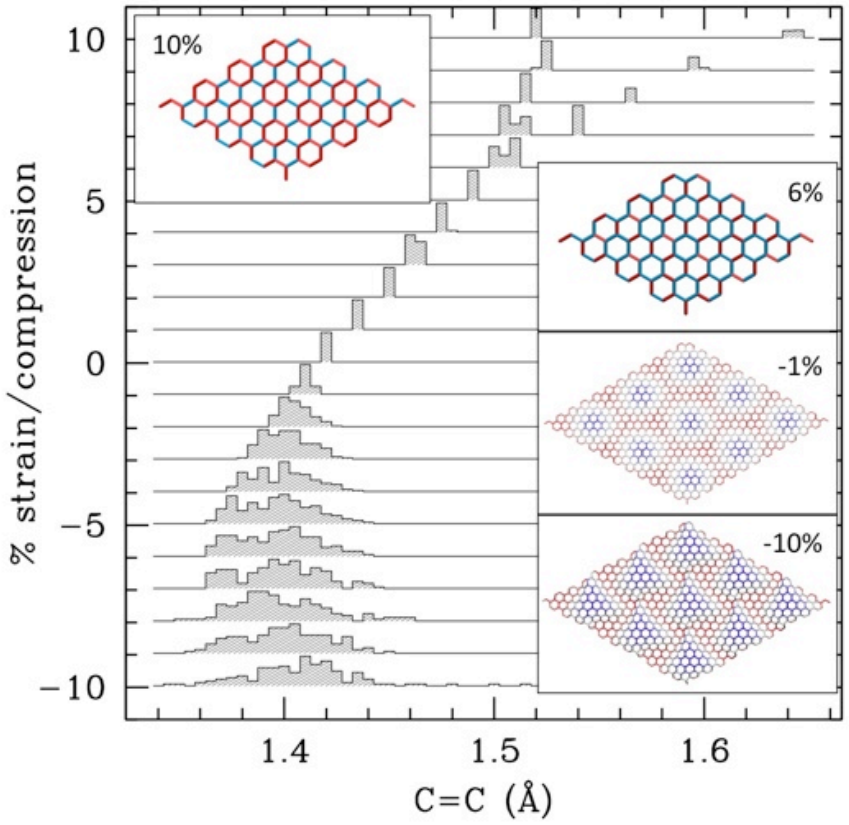
Curvature inversion by mechanical wave





⇒ Application to H storage

QM-DFT: study of reactivity vs rippling



- Strain generate a bond distortion with a formation of isolated “benzenes” separated by single bonds

- Contraction induces pyramidalization and enhances reactivity

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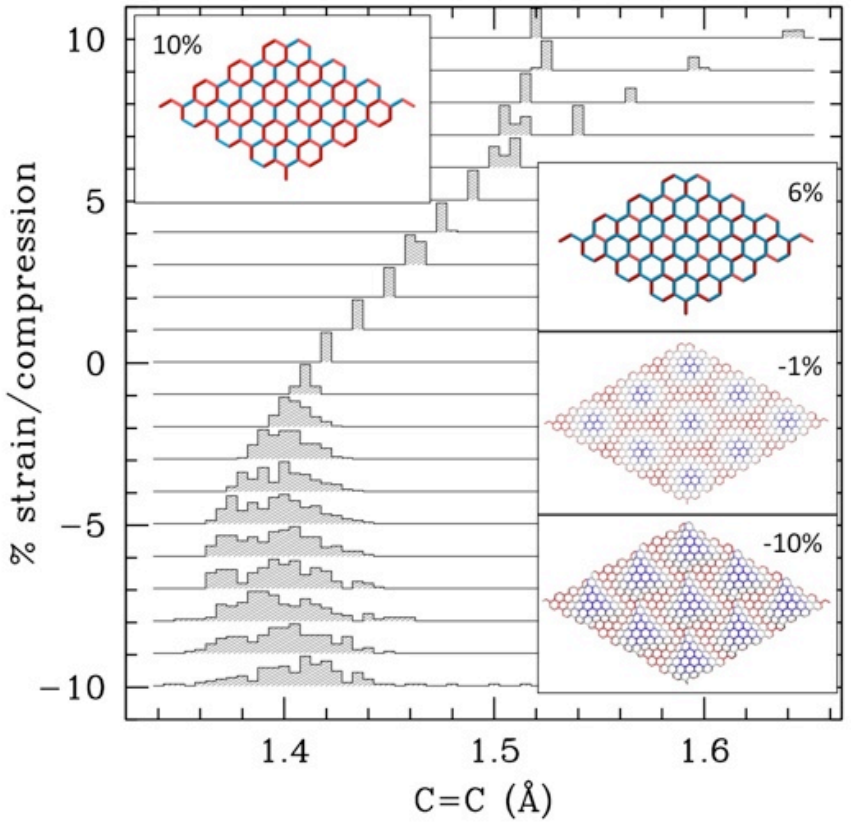

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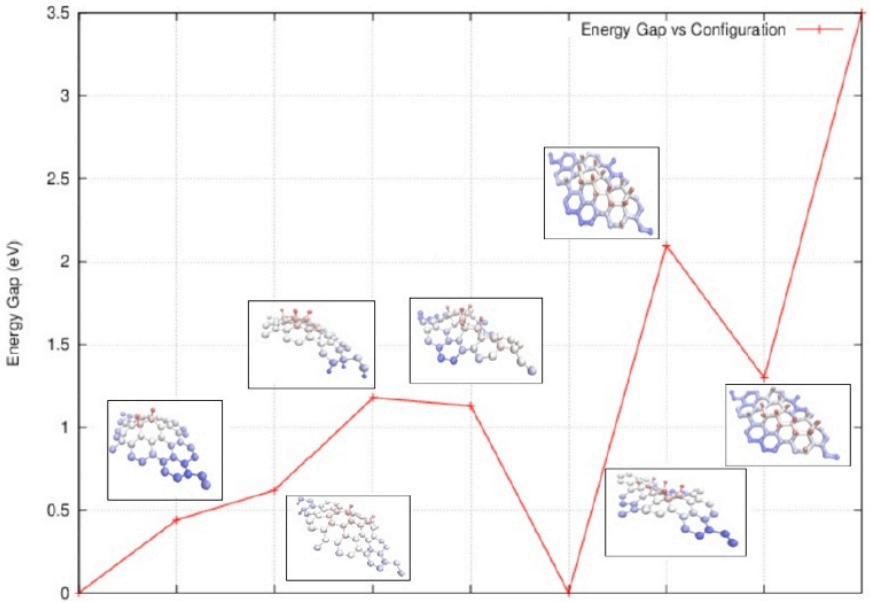

- When hydrogen is added on convexities, different pattern and level of hydrogenation generate systems with different band structure and gap

A Rossi, V tozzini Structure, electronic properties and stability of nano-scopically corrugated/hydrogenated graphene: a Density Functional Theory study in preparation

Towards real devices

- Create and maintain an extended multilayer structure

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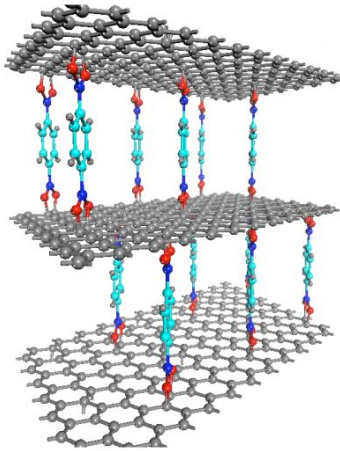
  “Spacers” molecules are currently under consideration to create “pillared” multilayer structure



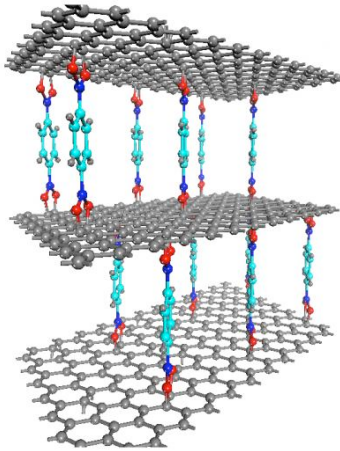
Towards real devices

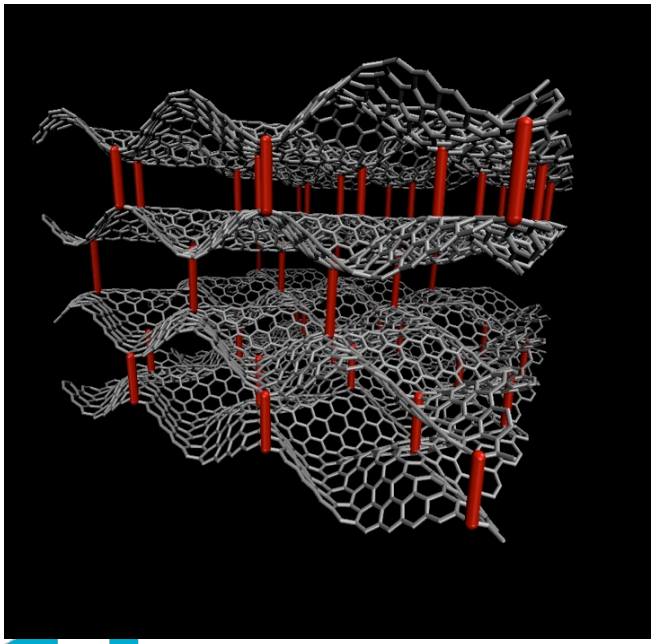
- Create and maintain an extended multilayer structure

  "Spacers" molecules are currently under consideration to create "pillared" multilayer structure

- Control the curvature

  if designed sensitive to external stimuli (e.g. light or E/M fields) pillars could also serve to create and control the curvature





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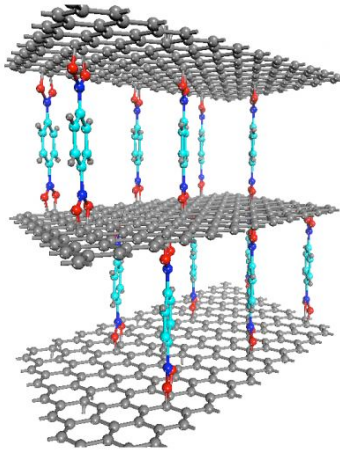

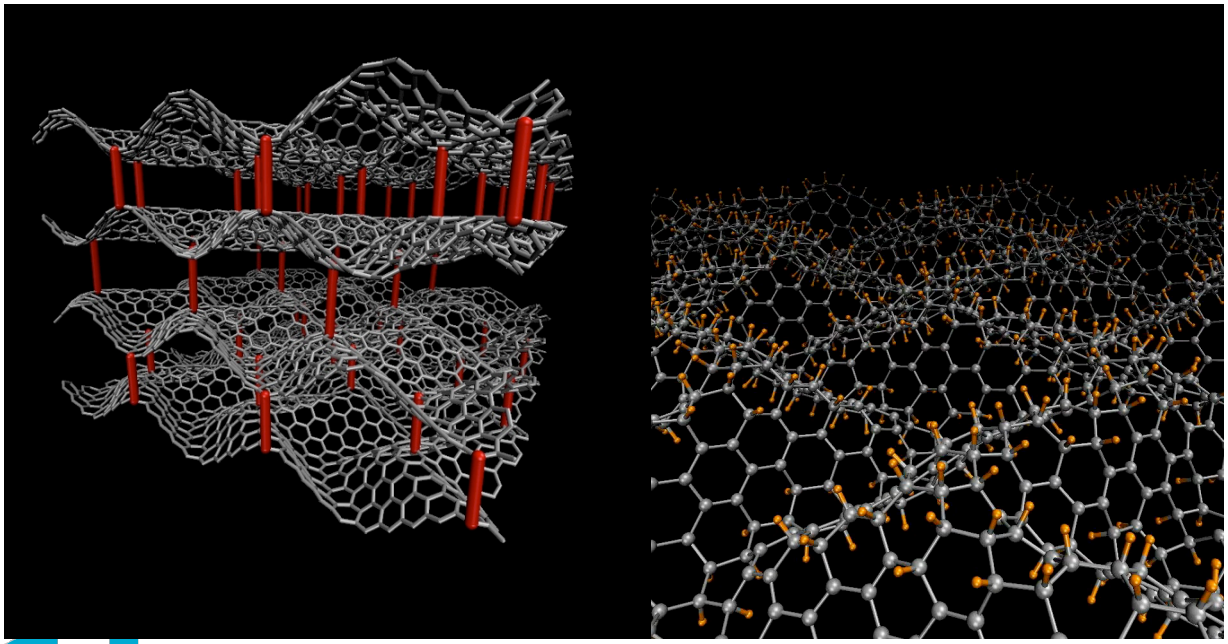

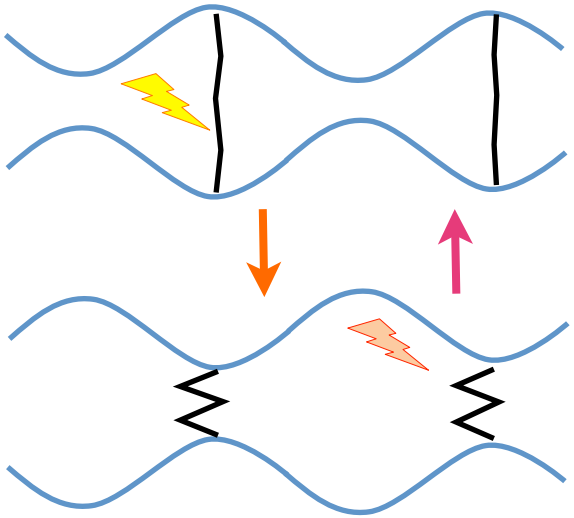

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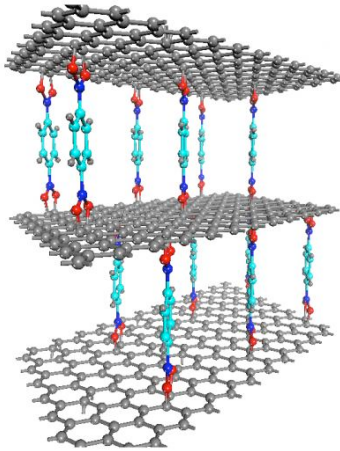
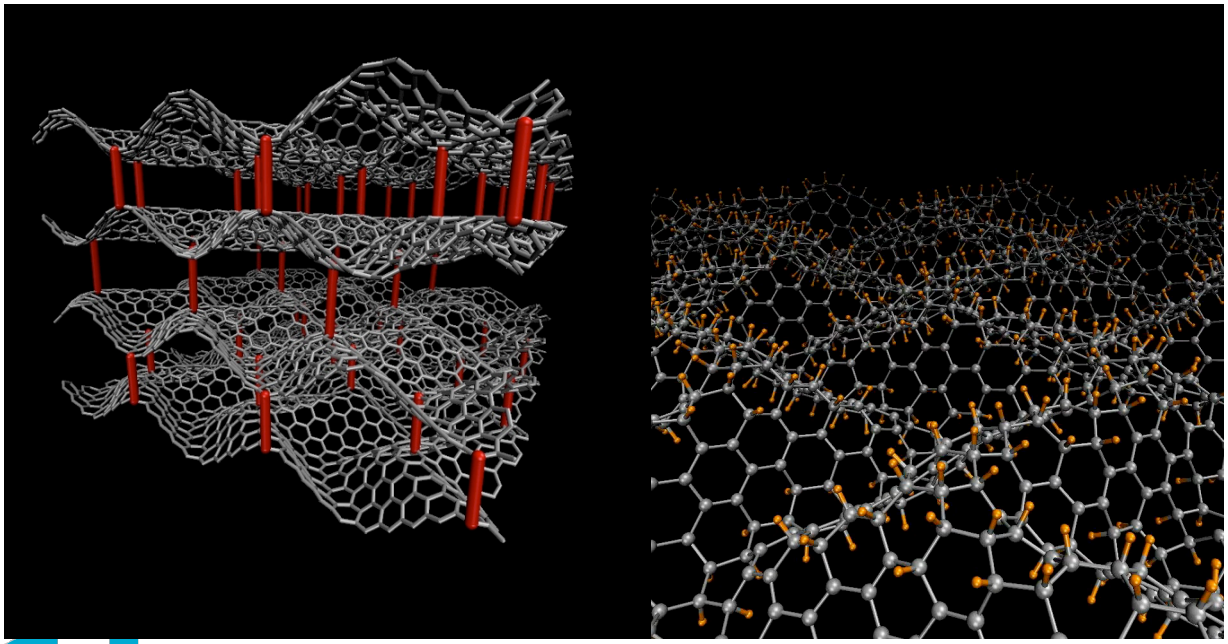
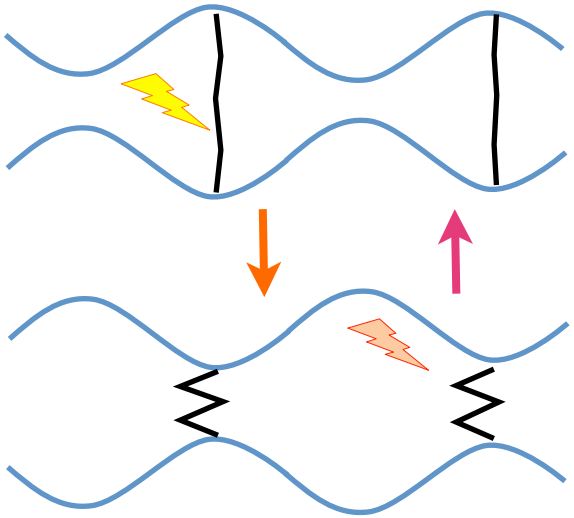
- Evaluate the effects on the macroscopic scales







Towards real devices

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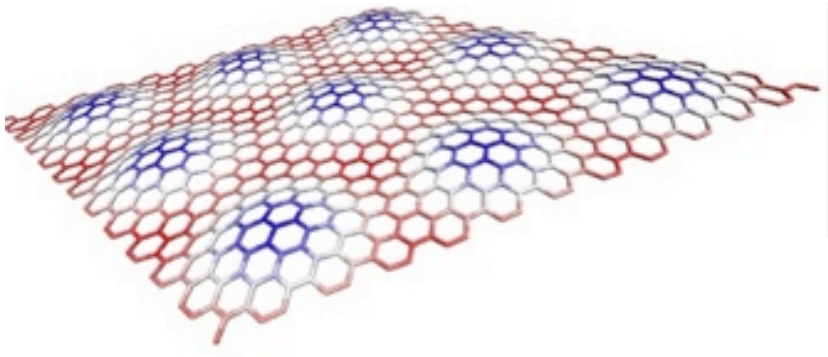
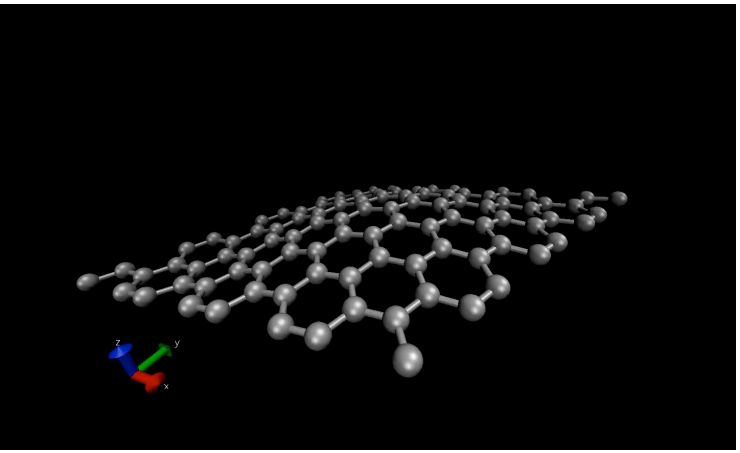
Towards real devices

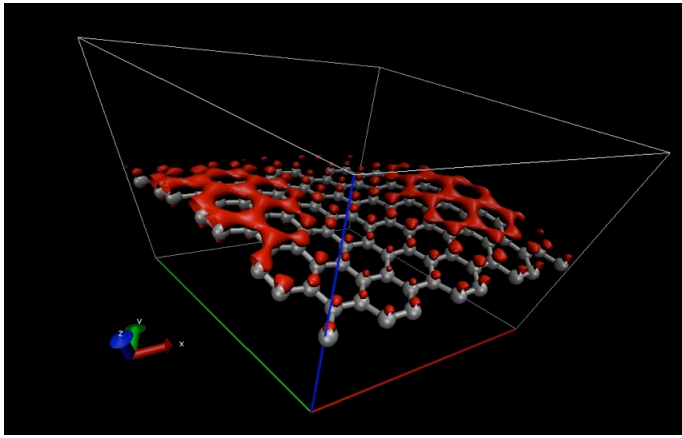
❖Control the curvature



Control by external **electric field** system: corrugated graphene sheet (like graphen on SiC)

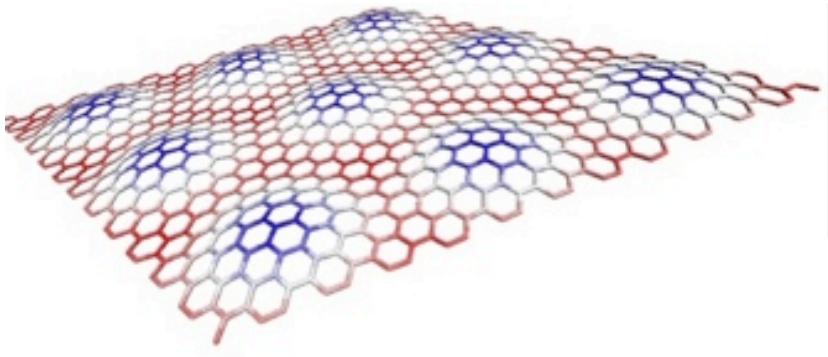


The local curvature is enhanced by an electric field orthogonal to the sheet, due to electronic charge rearrangement



Towards real devices

- Control the curvature



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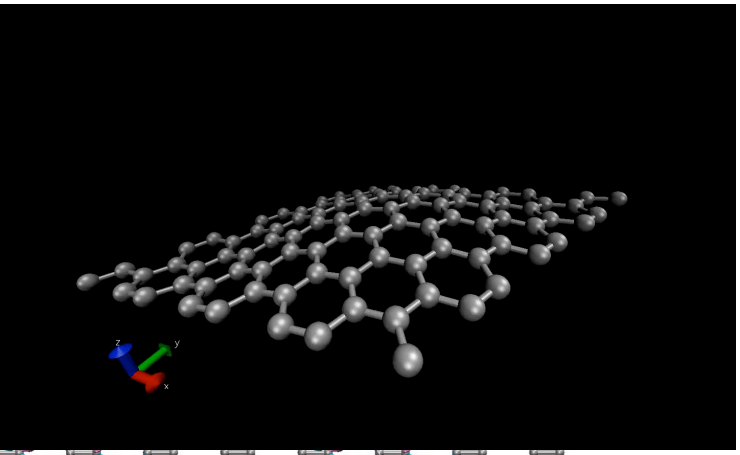

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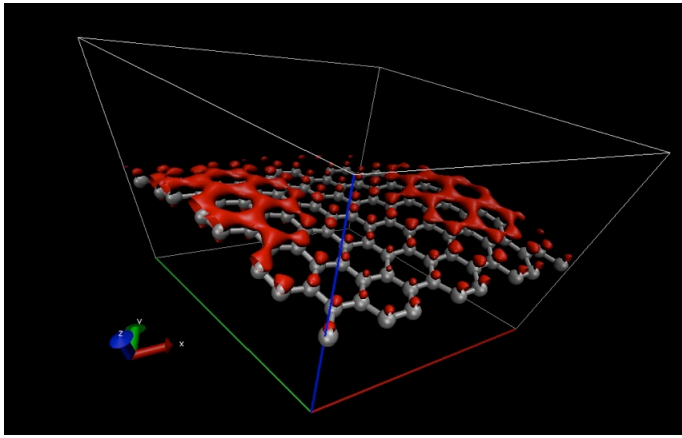
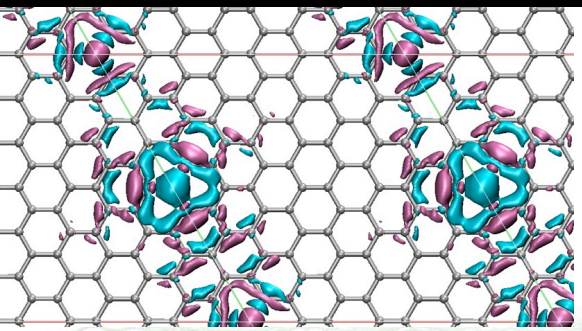
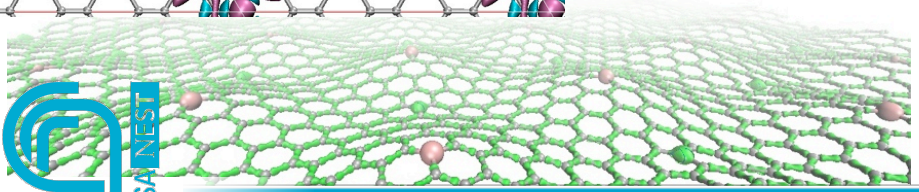
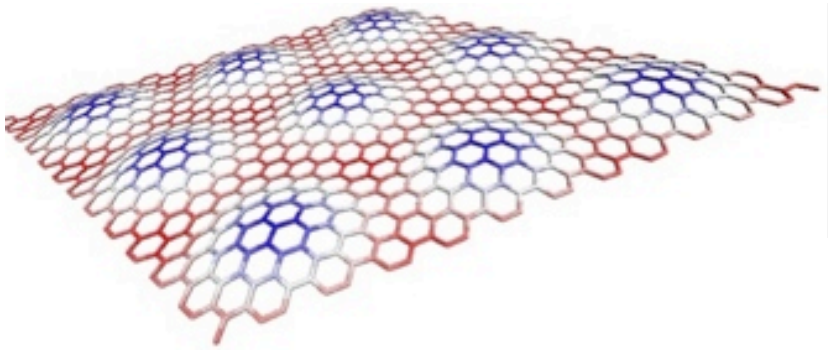




The effect is enhanced by B and N substitutions, creating local charges



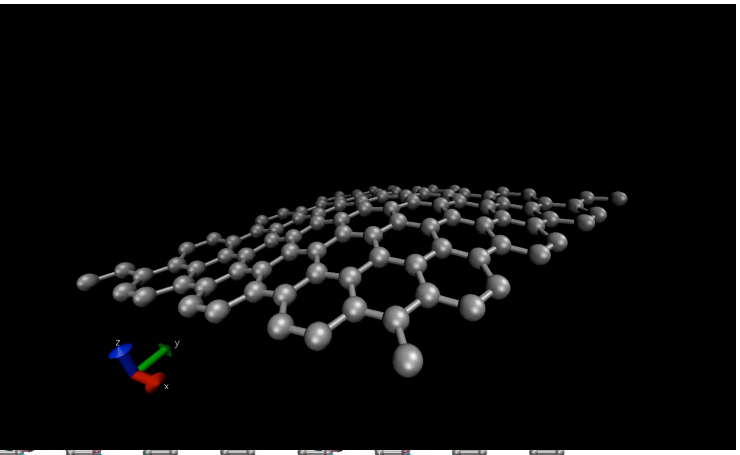
Towards real devices



- Control the curvature

Control by external **electric field**

system: corrugated graphene sheet (like graphen on SiC)



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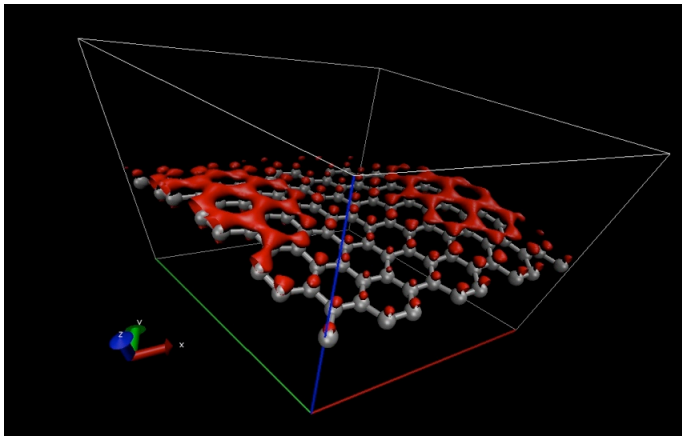

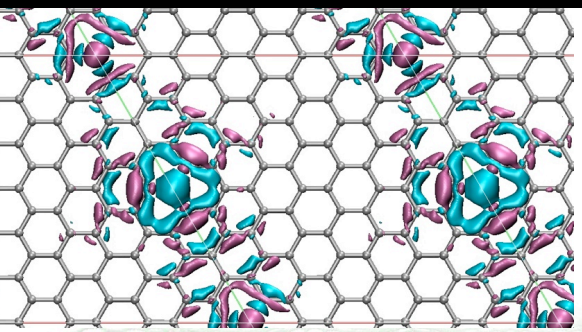

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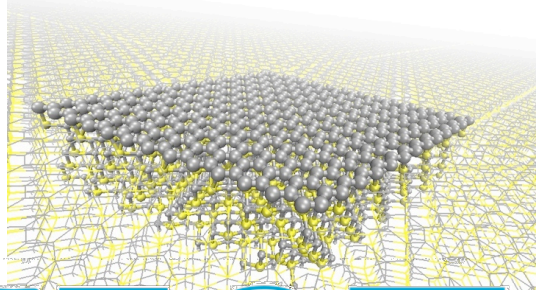
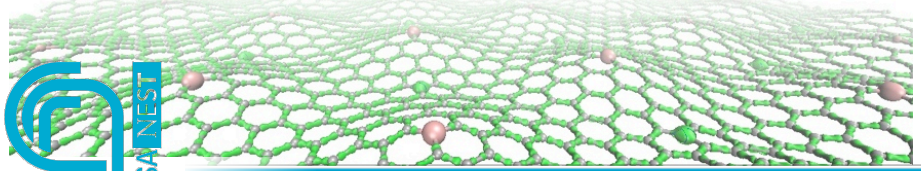
Next: Substrate adding, for direct comparson with experiment



T Cavallucci, V Tozzini in progress



Towards real devices

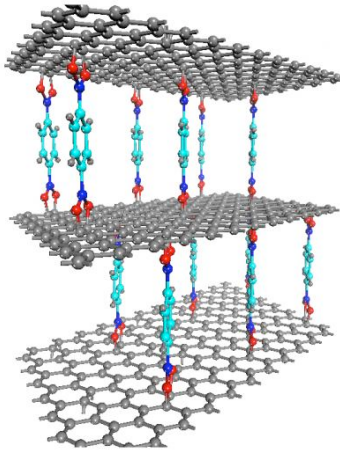
- Create and maintain an extended (multilayer) structure

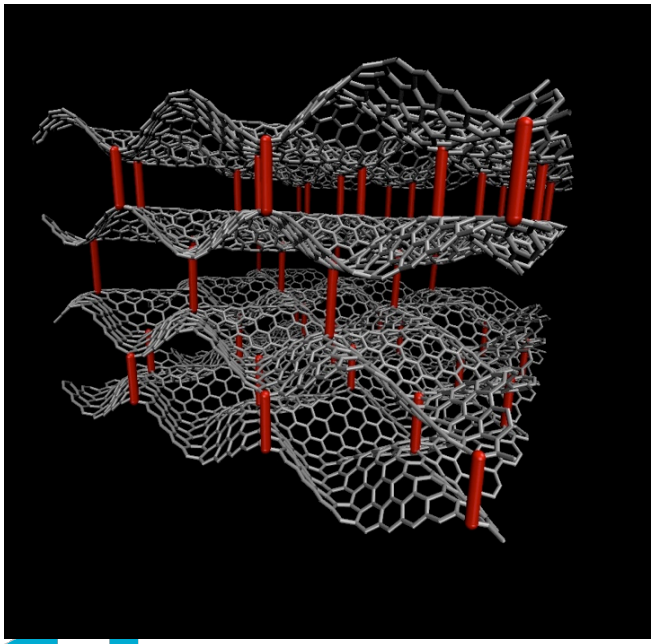
  "Spacers" molecules are currently under consideration to create "pillared" multilayer structure

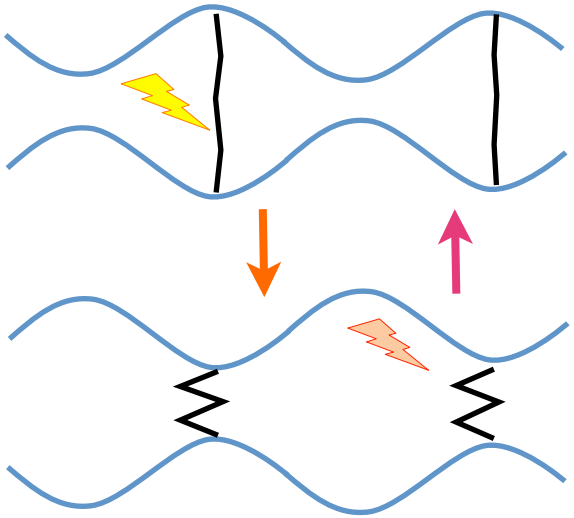
- Control the curvature

  if designed sensitive to external stimuli (e.g. light or E/M fields) pillars could also serve to create and control the curvature

- Evaluate the effects on the macroscopic scales





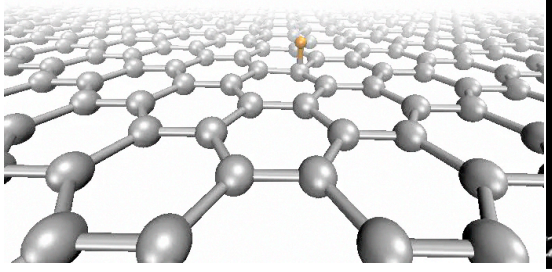


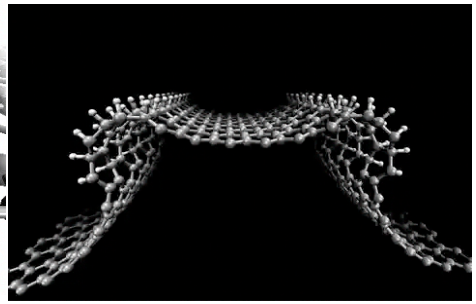
- Create and maintain an extended (multilayer) structure

❖ Create and maintain an extended (multilayer) structure

Classical classical atomistic MD

- **System: 10000-100000 atms (30-50 nm) plus H or substrate**
  - Any periodic boundary conditions
  - Software: DL_POLY, LAMMPS
- System Relaxation and dynamics
  - Classical dynamics, timestep ~1-2fs
  - Simulated annealing + local optimization
  - NVE, NVT, NPT





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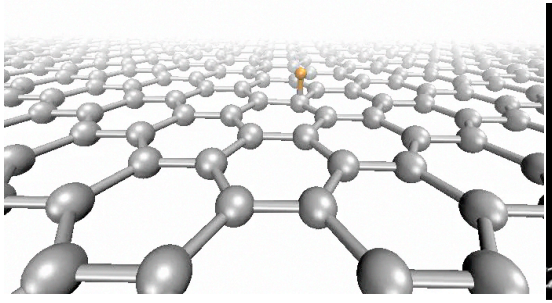

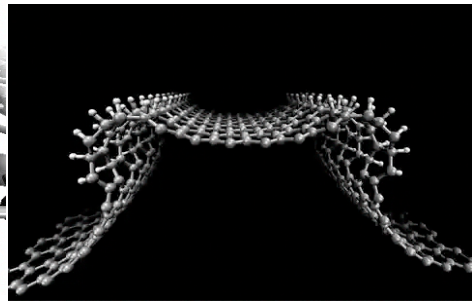

❖ **Force Fields**

❖ **Scheme 1: "Tersoff-like" potentials**
- ◉ Capable of describing the sp2↔sp3 transition and the interaction with Si
- ◉ Good representation of the mechanical/energetic properties

  BUT…
- ◉ not capable of accurately treating the corrugation dependent hydrogenation

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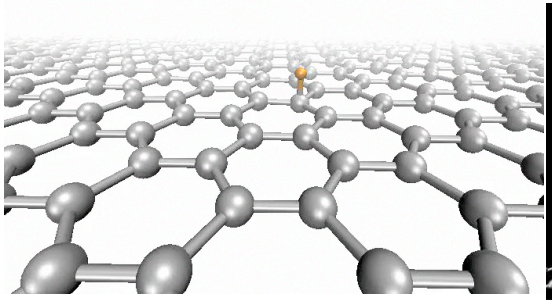

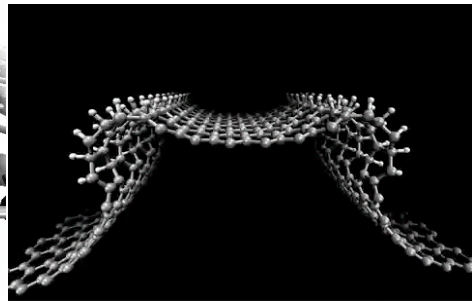

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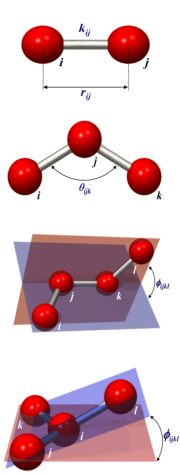
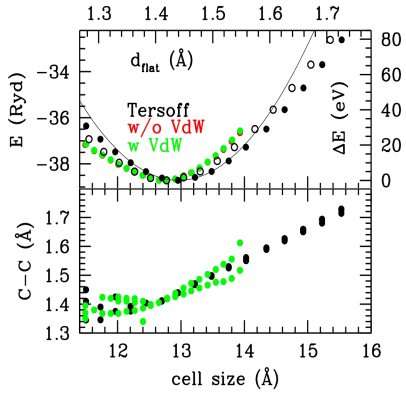
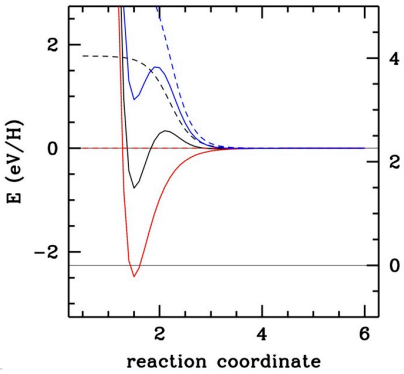
  BUT…
- ◉ not capable of accurately treating the corrugation dependent hydrogenation

❖ Scheme 2: "connective" FF

including
- ◉ energetics of compression/strain
- ◉ sp2-sp3 transition
- ◉ Interplay between curvature and hydrogenation
- ◉ interplay between BN doping, curvature and electric fields

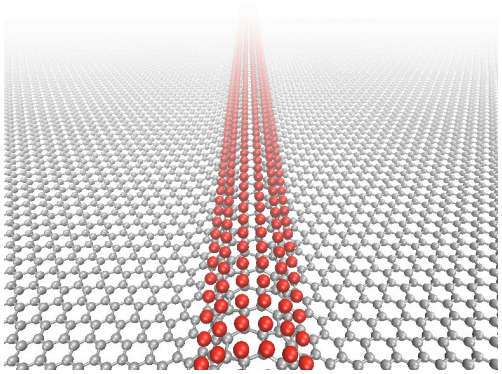


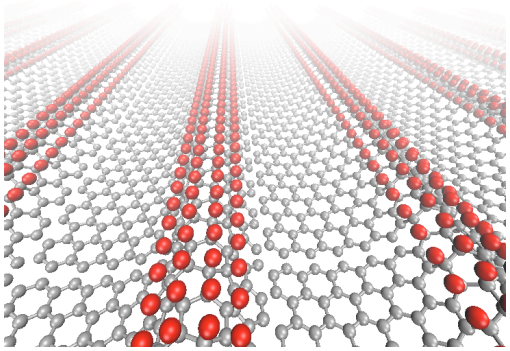


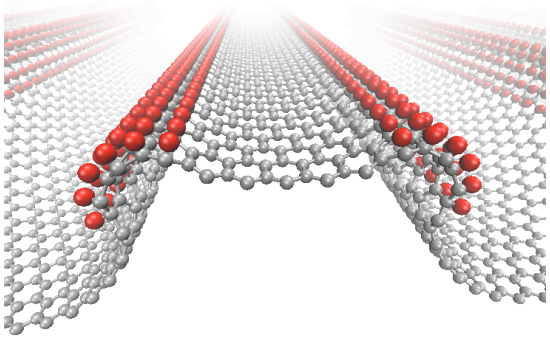


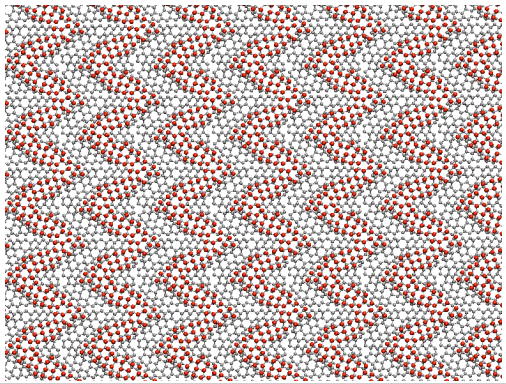
R Farchioni, D Camiola, V Tozzini in progress

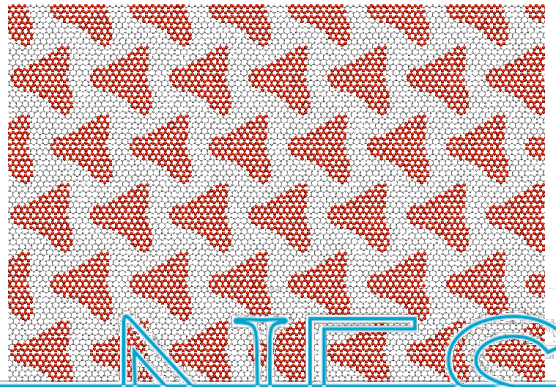
Towards real devices







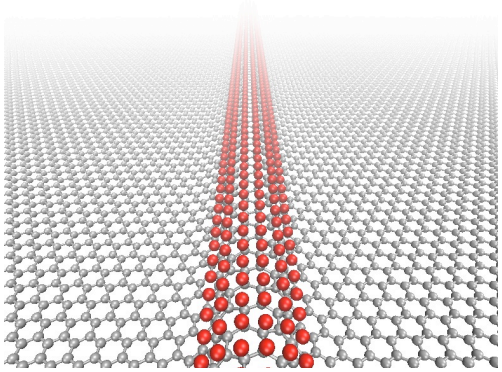
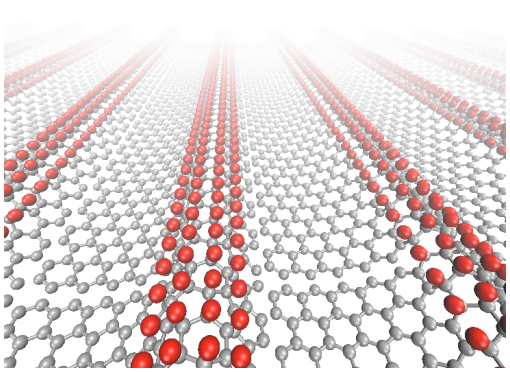
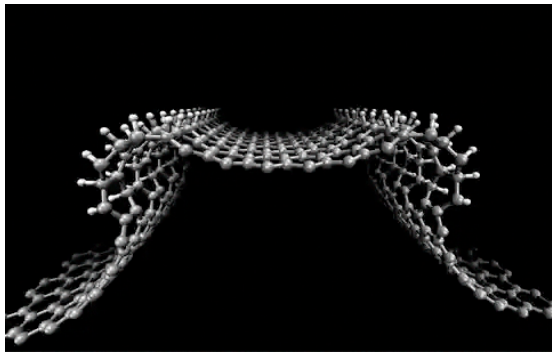
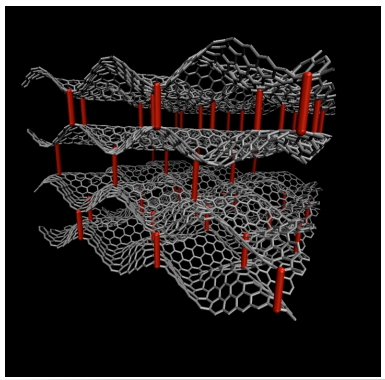
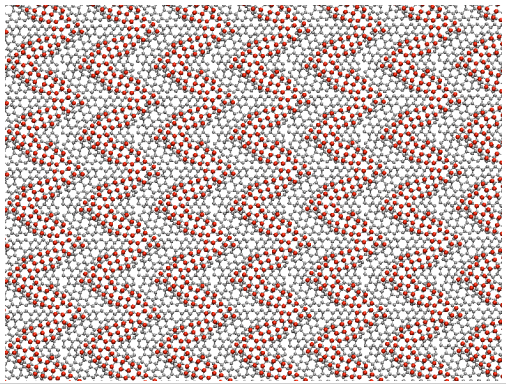
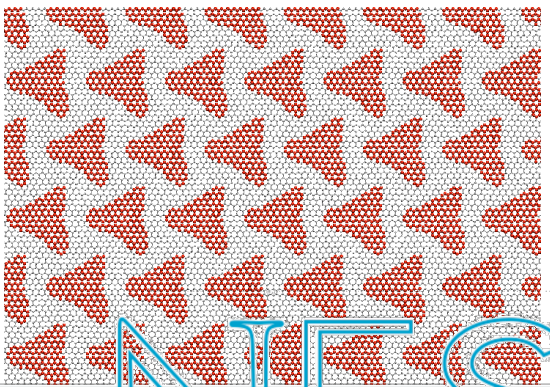




Towards real devices

- Create and maintain an extended (multilayer) structure

  “Spacers” molecules are currently under consideration to create “pillared” multilayer structure

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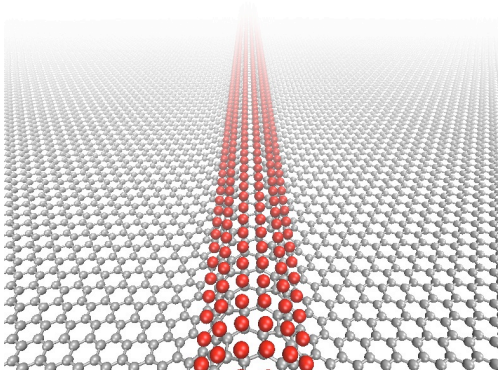
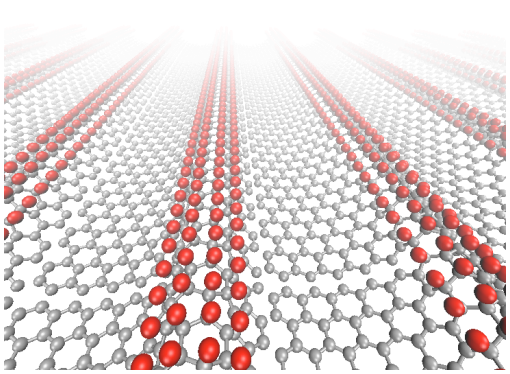
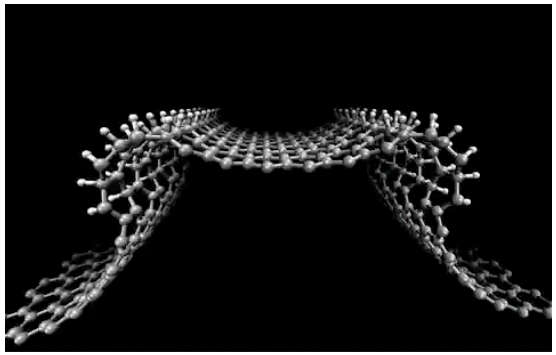
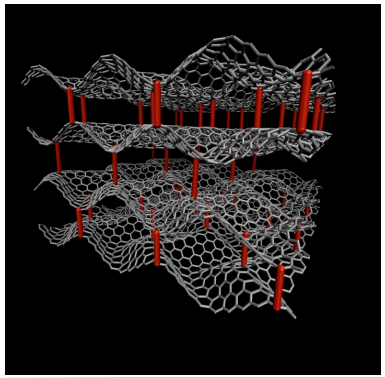
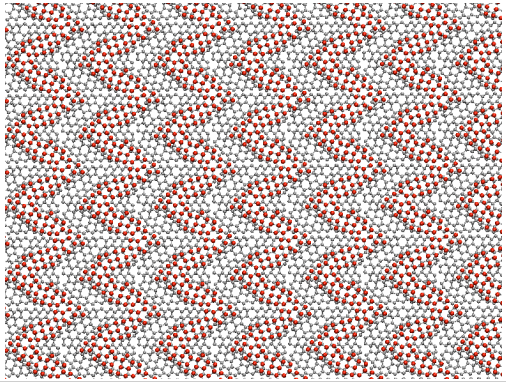
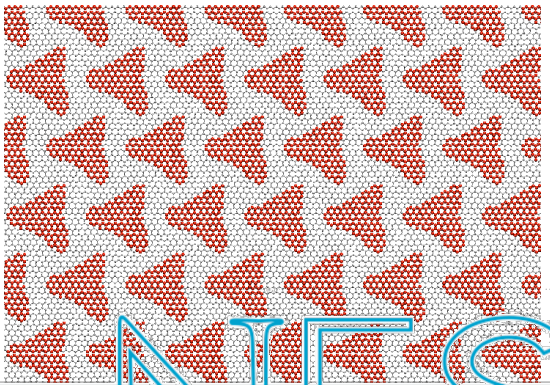

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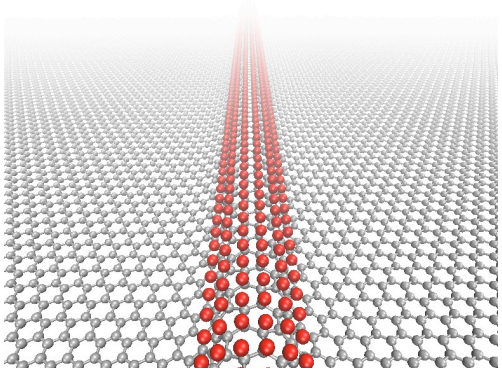
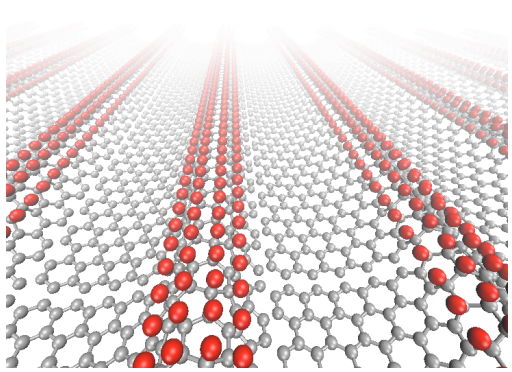
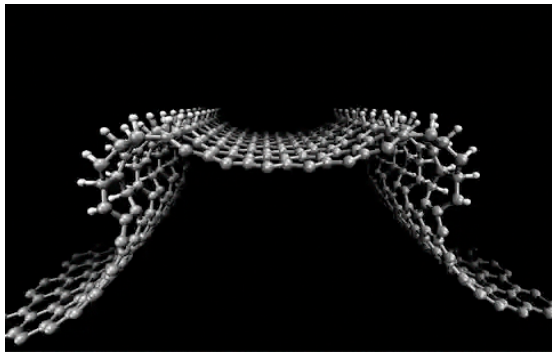
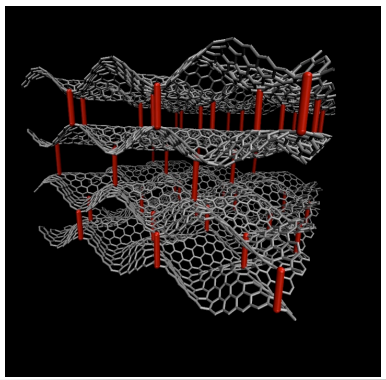
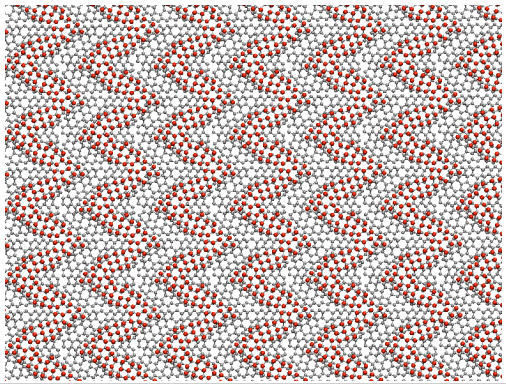
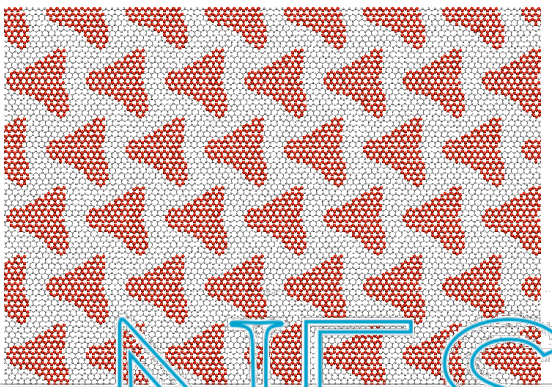
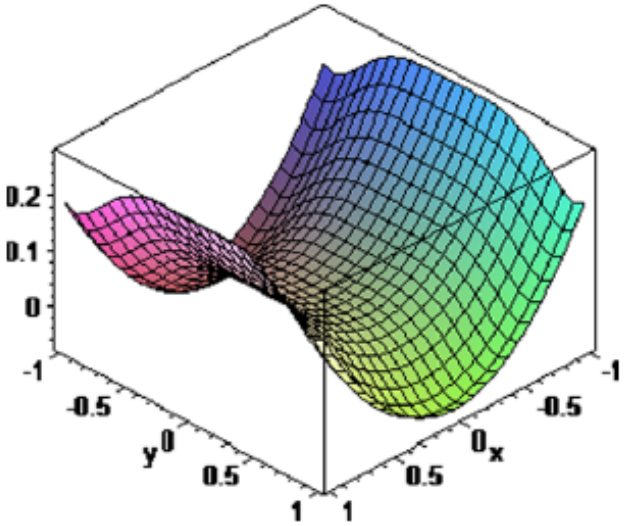







Towards real devices

❖Evaluate the effects on the macroscopic scales

- ❖System: 2D surface, virtually infinite, any geometry
- ❖Linear Elasticity
  - ◉ Bending energy
  - ◉ Theory of plates
- ❖ Interactions
  - ◉ Adhesion energy (theory of adhesion)
  - ◉ H binding
  - ◉ Self-consistent modification of the local curvatures
- ❖ Parameterization based on DFT and MM calculations. The following properties should be mapped onto the surface
  - ◉ Dependence between H binding probability/adhesion and curvature
  - ◉ elasticity and its dependence on H binding
  - ◉ Barriers and other energetics



$\kappa_x = 1\ \mathrm{nm}^{-1}$

This approach will allow to address the thermodynamics of the process and the macroscopic scales in time and space ⇒

- ❖ Direct comparison with experiment
- ❖ Devices design

J. Zang, Q. Wang, Q. Tu, S. Ryu, N. Pugno, M. Buehler, X. Zhao , Nat. Mat ., 12, 321 (2013).
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Conclusions

- Multi-scale approaches are useful to design new devices, since they couple the accuracy and microscopic physics to the macroscopic effects
- We addressed several problems related to the design graphene-based devices for energy and nano-electronics applications
  - control of reactivity by means of control of curvature
  - different means of curvature control (mechanical, electric field, chemical, in progress)
  - how to create stable multi-layers (in progress)
  - how to evaluate macroscopic energetics and thermodynamics (in progress)

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Support