

# Designing graphenes for energy applications (in different environments)

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## Graphene

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## Bio-systems

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Francesco Tavanti

Anna Bochicchio

Marco Galimberti

# Multi-scale modeling

atomistic

super-atomistic

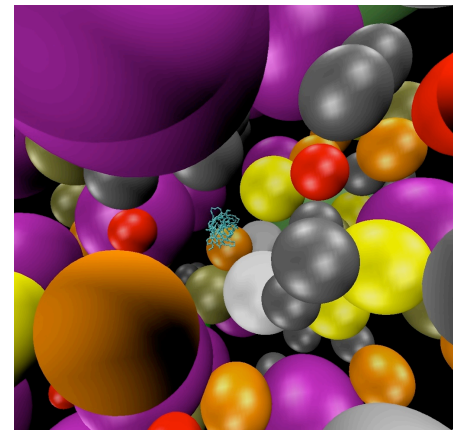
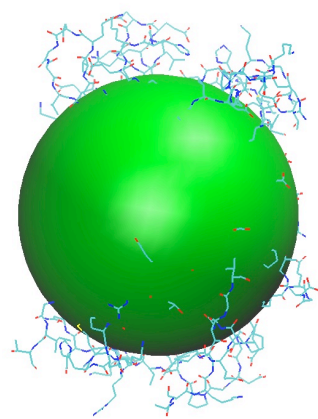
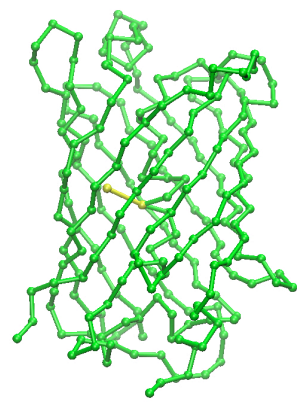
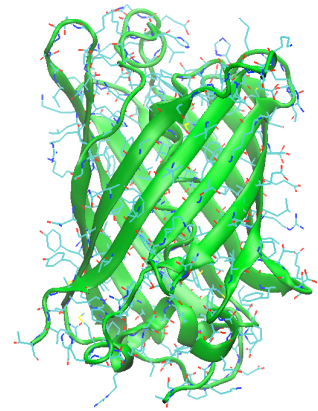
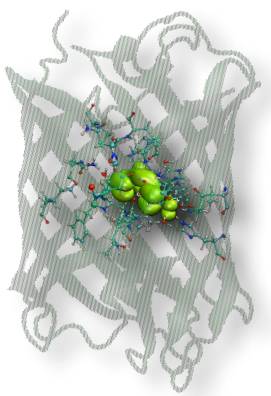
continuum

QM

MM

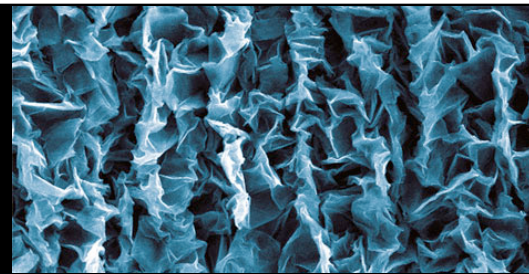
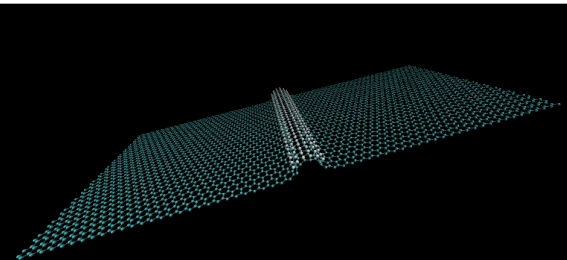
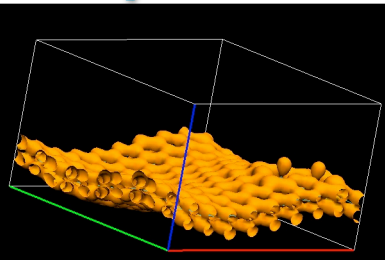
CG

MS

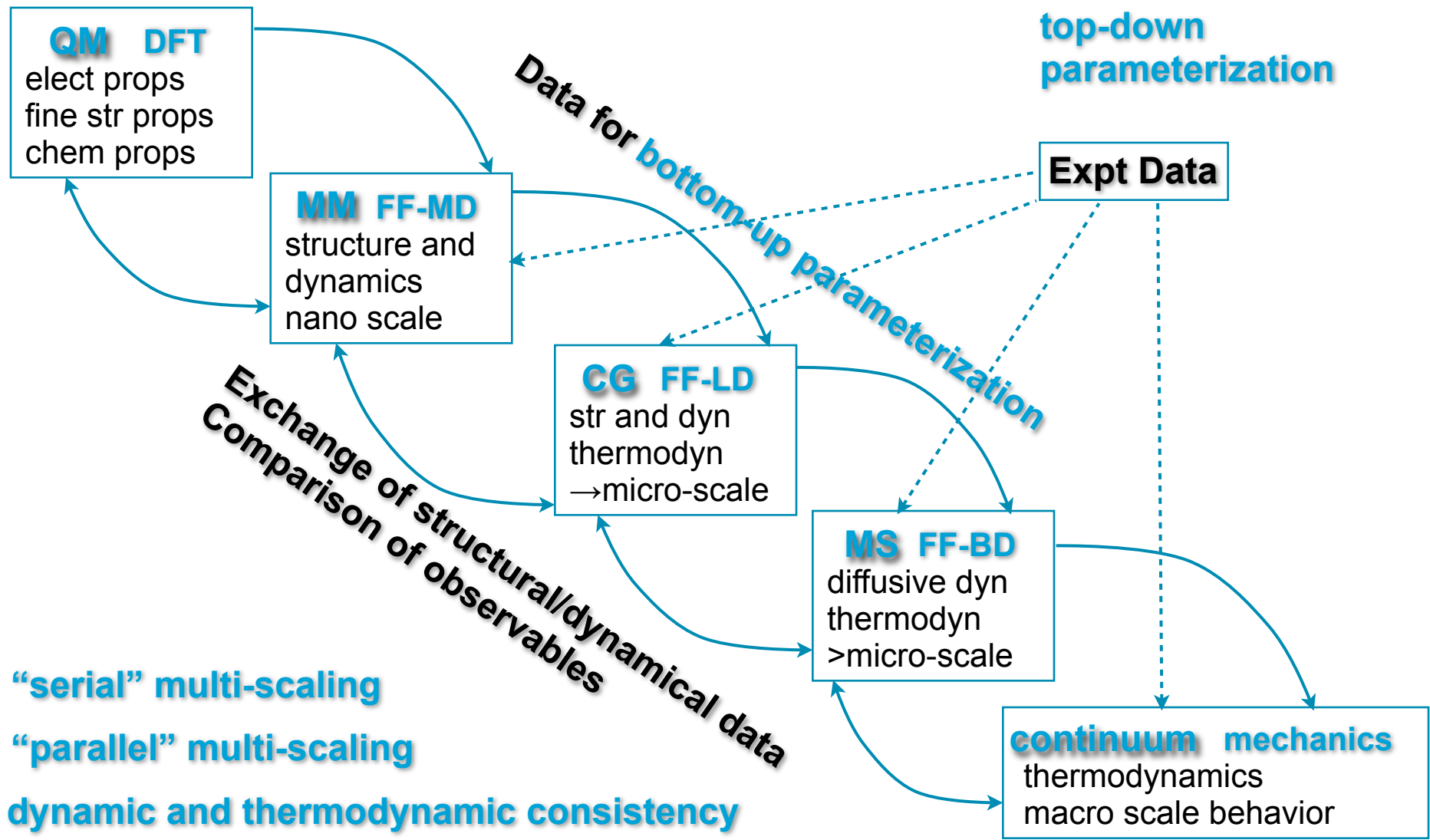


Bio-systems

Graphene



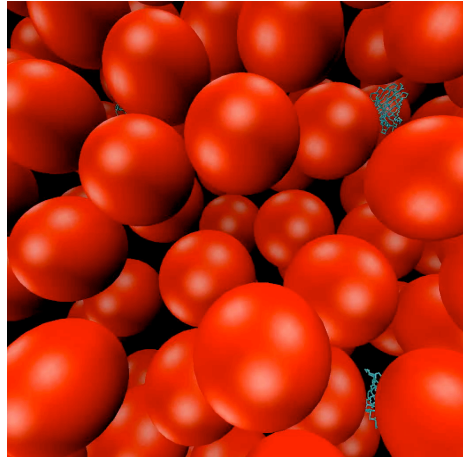
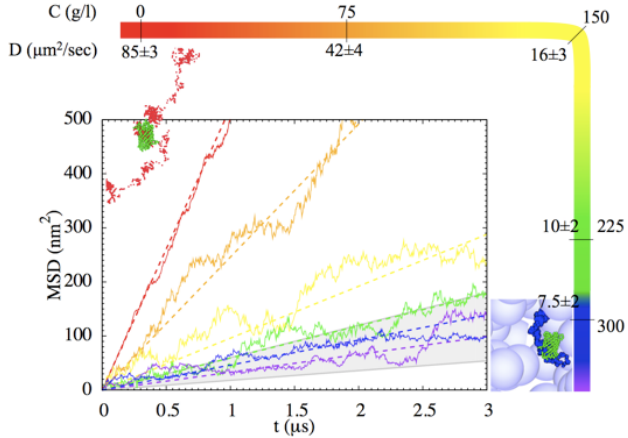
# Multi-scale modeling



# Multi-scale modeling

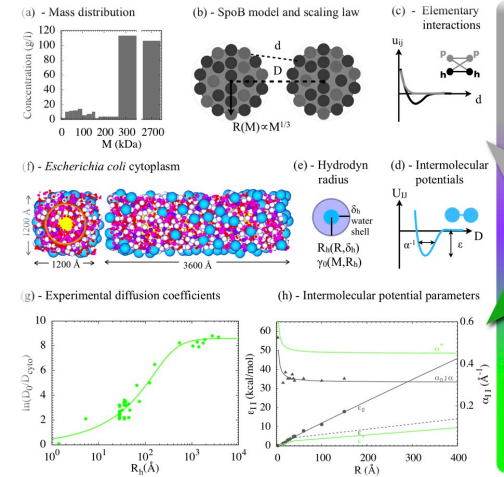
MM

CG



## bottom-up parameterization

MS



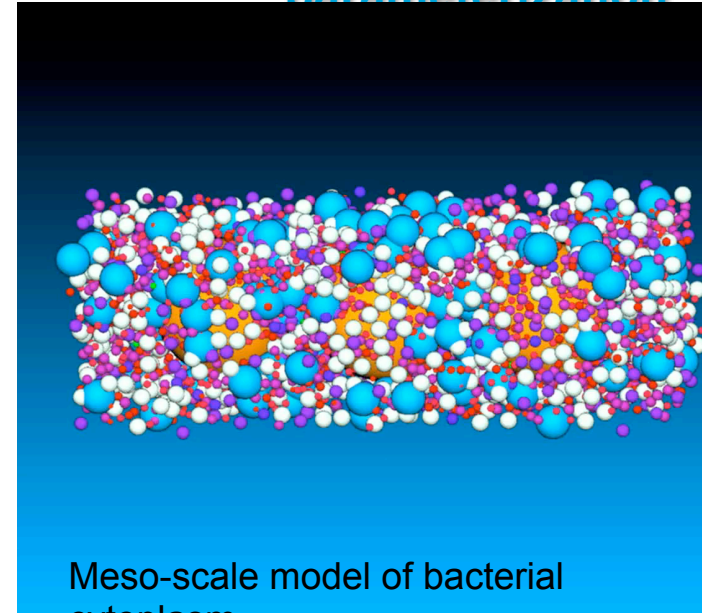
## top-down parameterization

### “parallel” multi-scaling

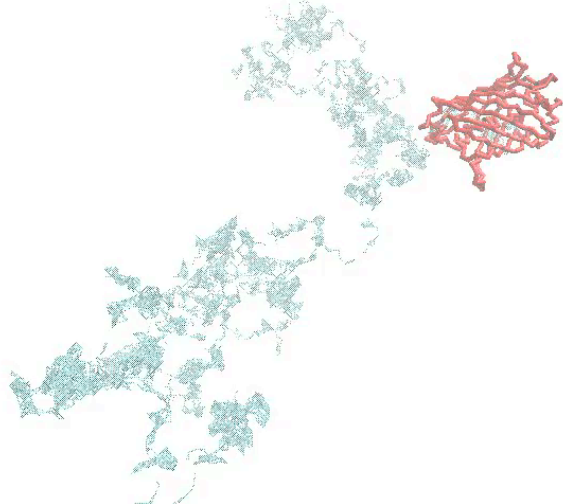
Diffusive dynamics of GFP within the cytoplasm

Results quantitatively comparable with expt diffusion data

F Trovato, R Nifosì, A Di Fenza, V Tozzini, *Macromol* (2013)  
F Trovato, V Tozzini, submitted



Meso-scale model of bacterial cytoplasm



### “serial” multi-scaling

diffusive dynamics of GFP in dilute solution



	atomistic		super-atomistic		continuum
	QM	MM	CG	MS	
modeling	<b>grap_builder</b> (nano/rippled graphe(a)ne builder) multi_graph multi-cells and multi-layer generation  parameterization: <b>ConGra</b> connective graphe(a)ne FF		<b>poly_builder</b> parameterization: <b>SecStAnT</b> (statistical) <b>CGautopar</b> (IBI MC)	<b>cyto_builder</b> parameterization: <b>bottom_up</b> <b>top_down</b>	
input	Molden  Crysdn	Amber DL_FIELD  <b>prepareGRAPH</b>	<b>prepareMINI</b>	<b>prepareMESO</b>	
sim	CPMD QE Gaussian	Amber Gromacs  DL_POLY LAMPPS	<b>+ modules for non standard FFs and dyn</b>		
analysis	<b>2cube</b> orbitals and elec density manipulation  <b>2struct</b> <b>SecStAnT</b> structural and statysical analysis of trajectories <b>2vibr</b> vibrational analysis		biopolymers structural analysis		<b>under development</b>

biopolymers (proteins, NAs)

graphene based systems (nano-structured and nano-functionalised/decorated)

generic

## Contacts

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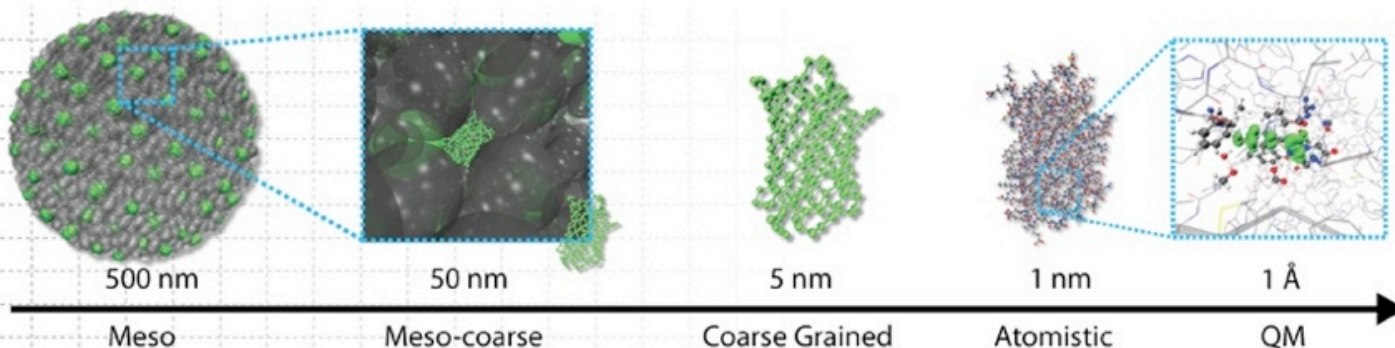
Giuseppe Maccari  
iit etc

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Silvestro 12 56127 Pisa Italy



## News

# MuScaDe

[Home](#)[The Project](#)[Software](#)[Publications](#)[People](#)[Events](#)

## MuScaDe - lab:



### A (virtual) laboratory for Multi-Scale modeling and simulation Devices development

Modeling and simulation of complex molecular systems requires a multi-scale and multi-methodological approach. This is particularly evident in **bio-systems**, whose hierarchical organization naturally suggests addressing them at different levels of resolution (e.g. atomistic and super atomistic), and it has also become clear in the field of **materials science**, where often different approaches needs to be combined (e.g quantum and classical molecular dynamics, but also continuous mechanics).

While a few explicitly multi-scale software packages exist, a considerable number of specialized codes for several of the single tasks involved in the Multi-Scale approach are available, which are popular, well equipped with utilities and optimized. In order to address Multi-Scale modeling without losing the specialization advantage, we designed **MuScaDe**, a web-lab specifically aimed at **collecting and adapting available software for different resolution molecular modeling, developing specific methods and codes for coarser resolutions, and integrating all in a coherent platform.**

The platform is **modular**, thought to be continuously updated and integrated with new functionalities. Single software modules are freely distributed and, when possible, provided with **user friendly web interfaces.**

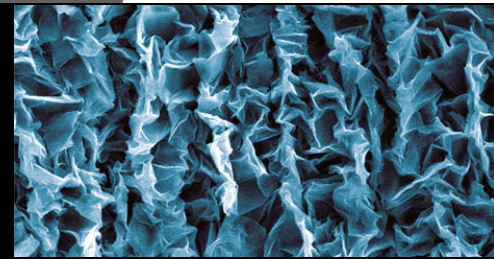
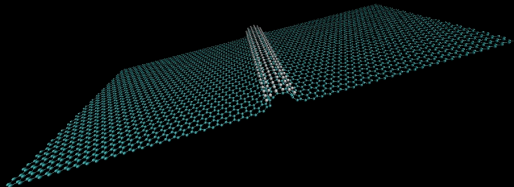
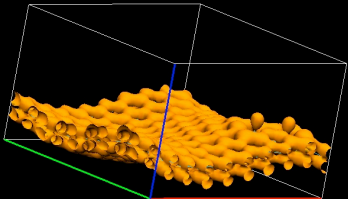
The two main applications lines are **biomolecular systems** and **graphene-based materials.**

## To appear soon on the web!

Graphene Week, Gothenburg, June 2014



	atomistic		super-atomistic		continuum
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modeling	<b>grap_builder</b> (nano/rippled graphe(a)ne builder) multi_graph multi-cells and multi-layer generation  parameterization: <b>ConGra</b> connective graphe(a)ne FF				
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# Multi-Scale Simulations of graphene

## QM

### Scheme 1 DFT-CPMD

- ❖ **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

### Scheme 2 DFT-QE

- ❖ **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

## MM

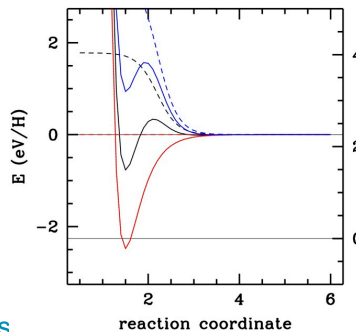
### Scheme 1: "Tersoff-like" potentials

- Capable of describing the sp2 and sp3 hybridization and the interaction with Si
- Good representation of the mechanical/energetic properties
- BUT...
- not capable of accurately treating the corrugation dependent hydrogenation and the structural transitions

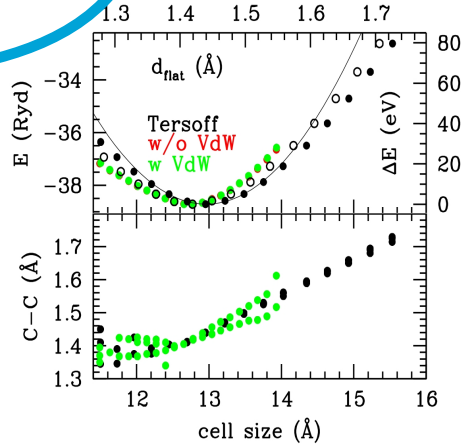
### Scheme 2: hybrid "connective-reactive" FF

- 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 work in progres



Mechanical and dynamical consistency





# Our Methods: Multi-Scale Simulations

## QM

### Scheme 1 DFT-CPMD

#### ❖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 =  $\sim 0.1$ fs
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## MM

### Scheme 1: “Tersoff-like” potentials

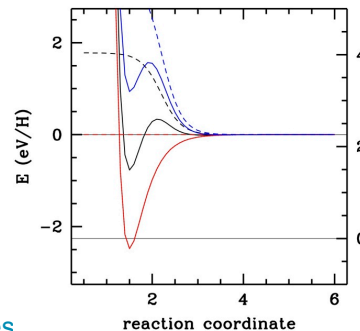
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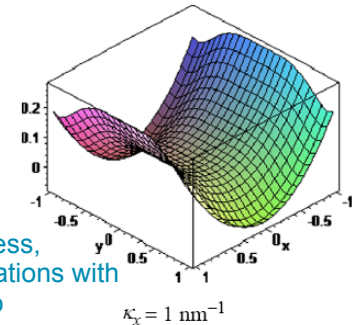
R Farchioni, D Camiola, V Tozzini work in progress



## Continuum

### Mechanicistic approach

- elasticity
- plate theories
- theory of adhesion
- mapping properties on the surface

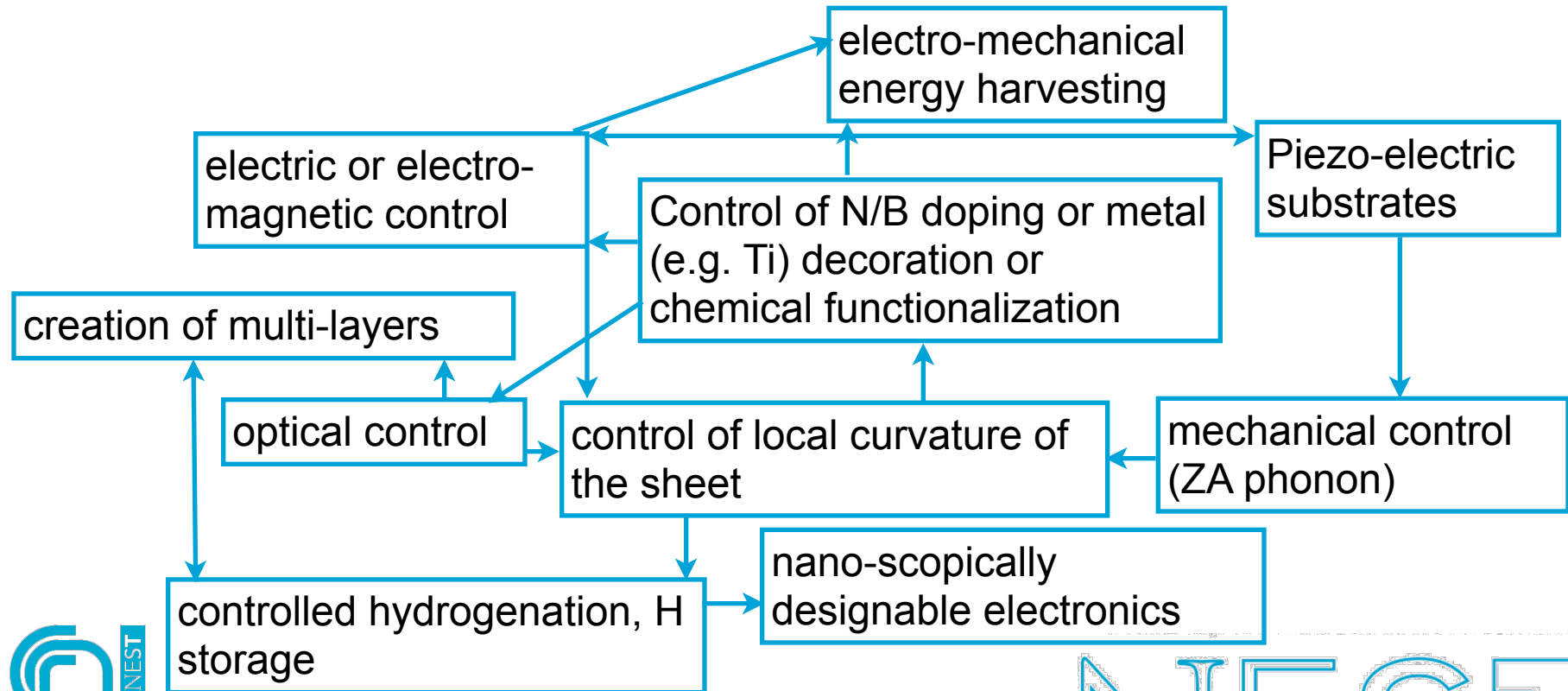


# Applications: graphene based systems

**Aim:** Control nano-structuring and nano-functionalization of graphene for

- ❖ Energy applications
  - Hydrogen storage
  - Energy production
- ❖ Advanced nano-electronics
  - **Flexibility** → Wearability
  - Biocompatibility → Advanced nano-medicine

: Possibility of locally change the curvature sheet without changing the material properties **in reversible way**



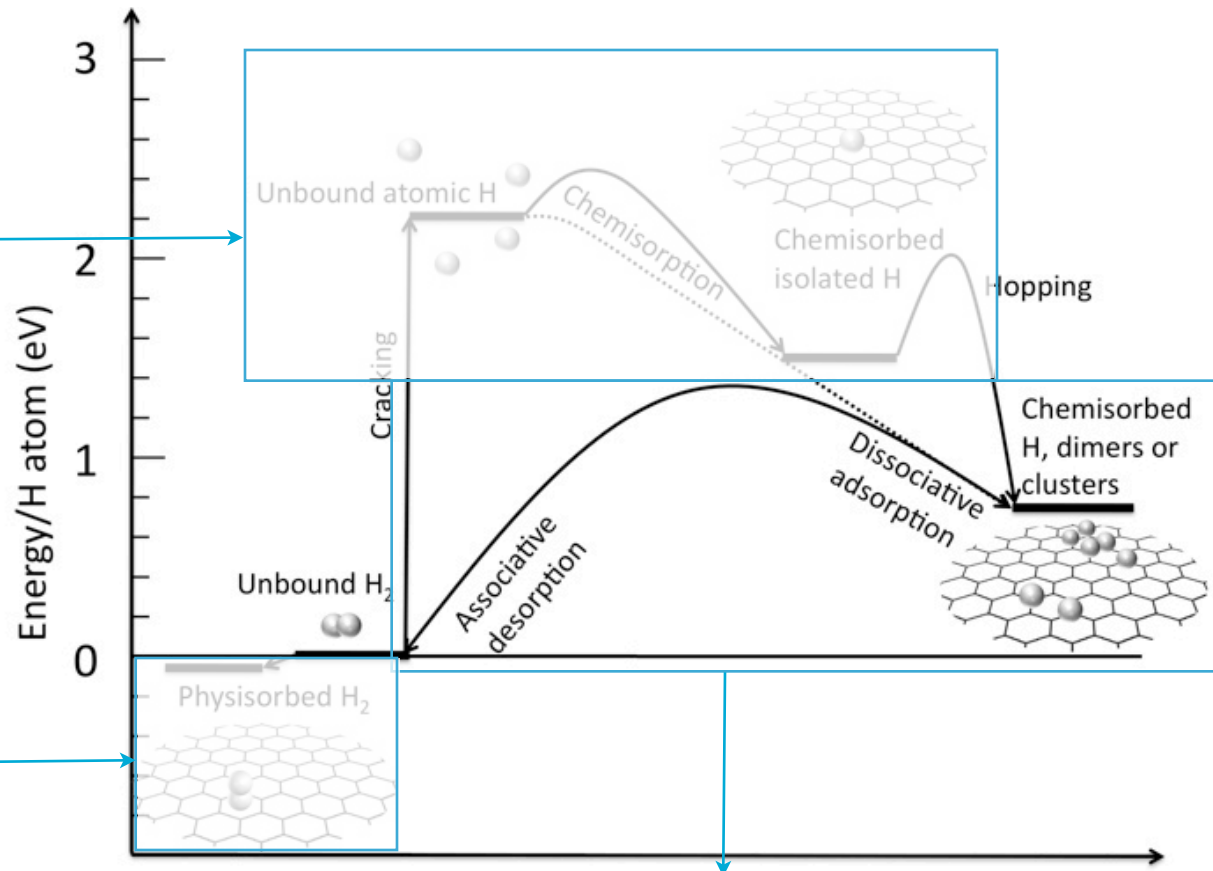
# Hydrogen storage in graphene

❖ Atomic hydrogen chemisorption has a small or negligible chemisorption barrier  $\Rightarrow$

feasible, but  $H_2$  must be cracked

❖ Physisorption weakly binds hydrogen  $\Rightarrow$  acceptable storage densities only at low temperatures and/or high pressure  $\Rightarrow$

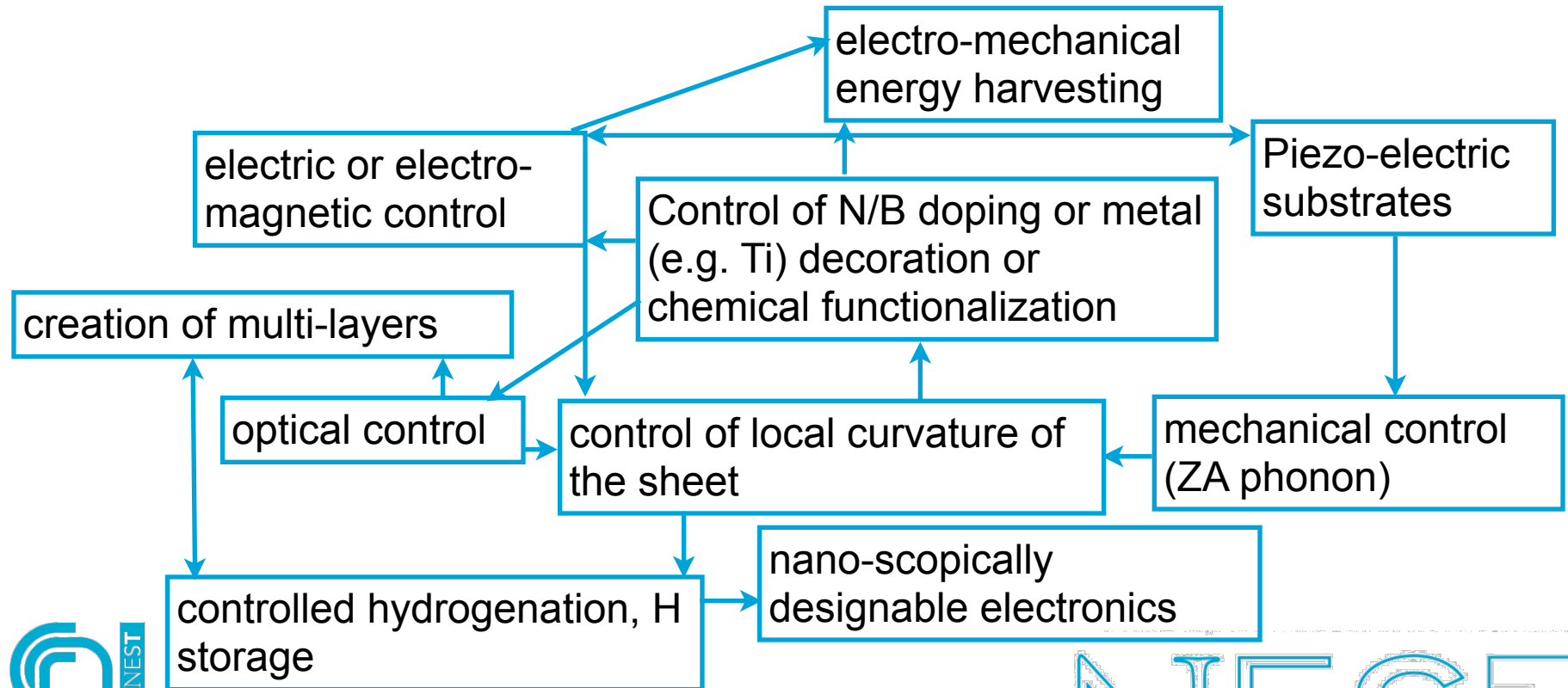
pumping strategies are needed



❖ Molecular hydrogen chemi(de)sorption has high barrier (theoretical estimate  $\sim eV$ )  $\Rightarrow$  chemisorbed H is stable for transportation etc, but catalytic mechanisms are necessary in the loading-release phases

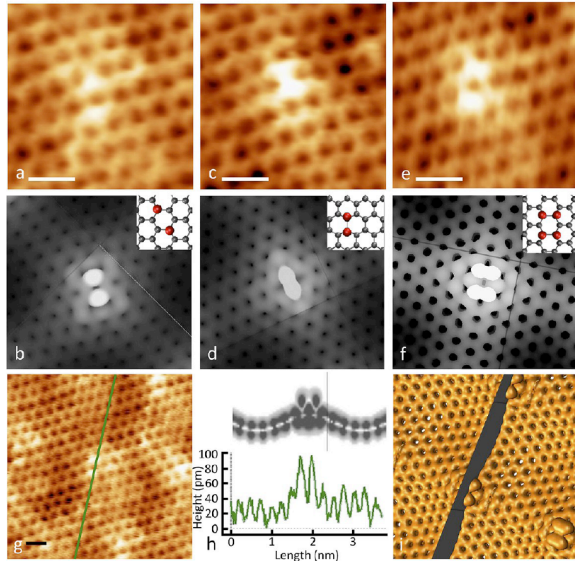
# Hydrogen storage in graphene

Can graphene curvature control help in hydrogen uptake/release?

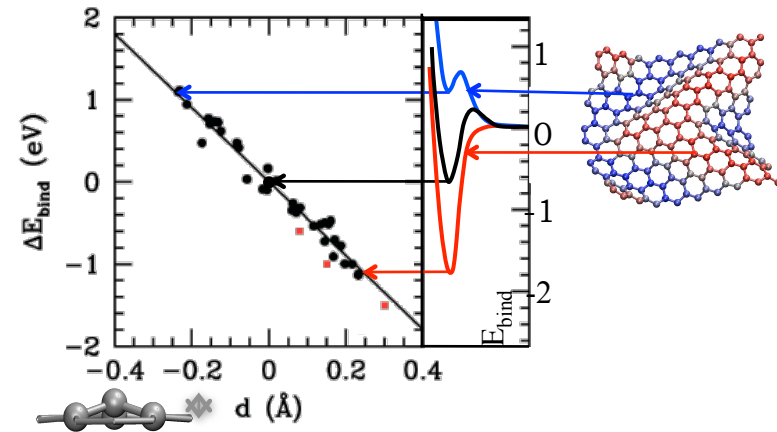


controlled hydrogenation, H storage

control of local curvature of the sheet



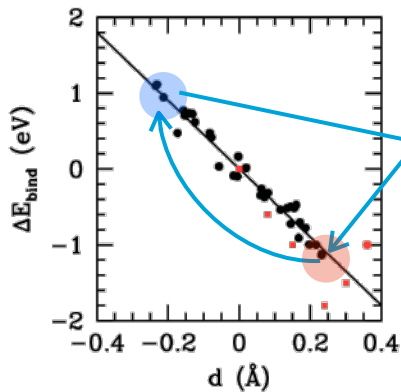
**QM-DFT**  
(verified by expt):  
reactivity (to H or other chemicals) is enhanced on convexities and decreased in concavities



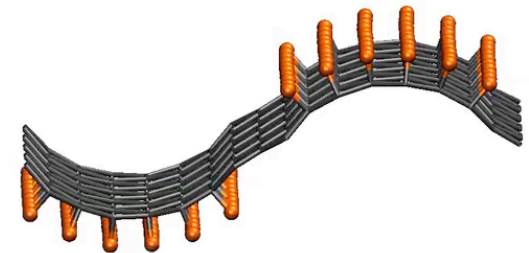
S. Goler, V Tozzini et al. JPCC (2013)

V Tozzini, V Pellegrini JPCC (2011)

## Using curvature to control chemi(de)sorption



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



“mechanical catalysis”

V Tozzini V Pellegrini JPCC 2011

controlled hydrogenation, H storage

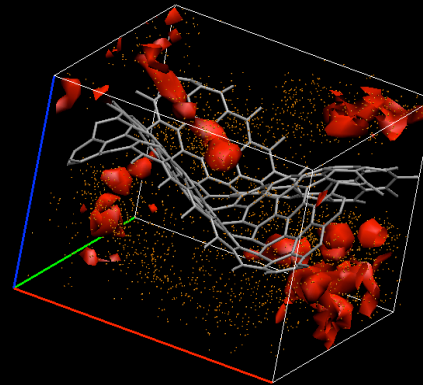
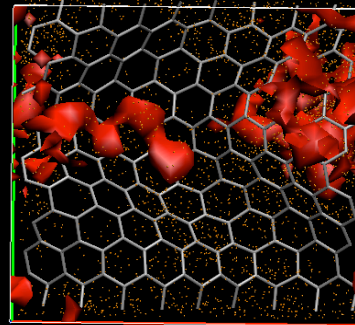
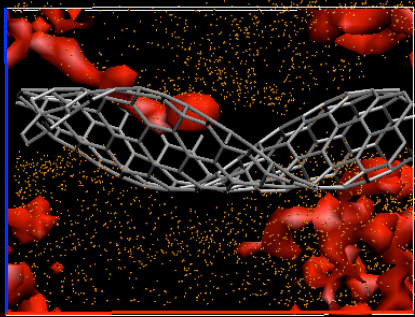
control of local curvature of the sheet

mechanical control (ZA phonon)

## Physisorption of molecular hydrogen

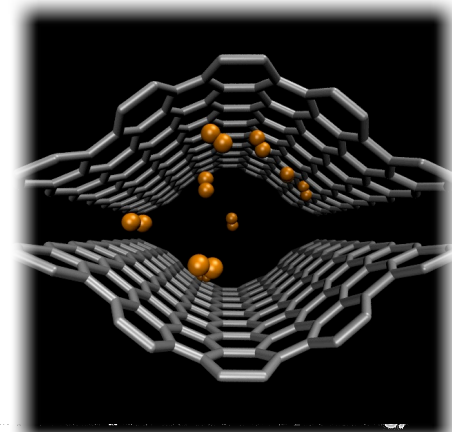
Reasonable gravimetric densities in nanostructured graphenes can be achieved at low temperatures and high pressures

Mechanisms are needed to pump hydrogen into the nanocavities



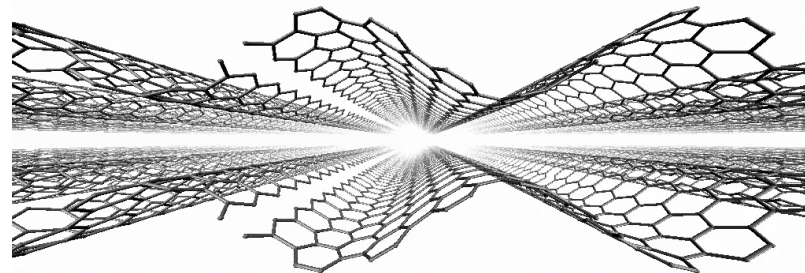
### Preliminary results

❖ DFT based simulations show accumulation of  $H_2$  within concavities (at  $\sim 100K$ )



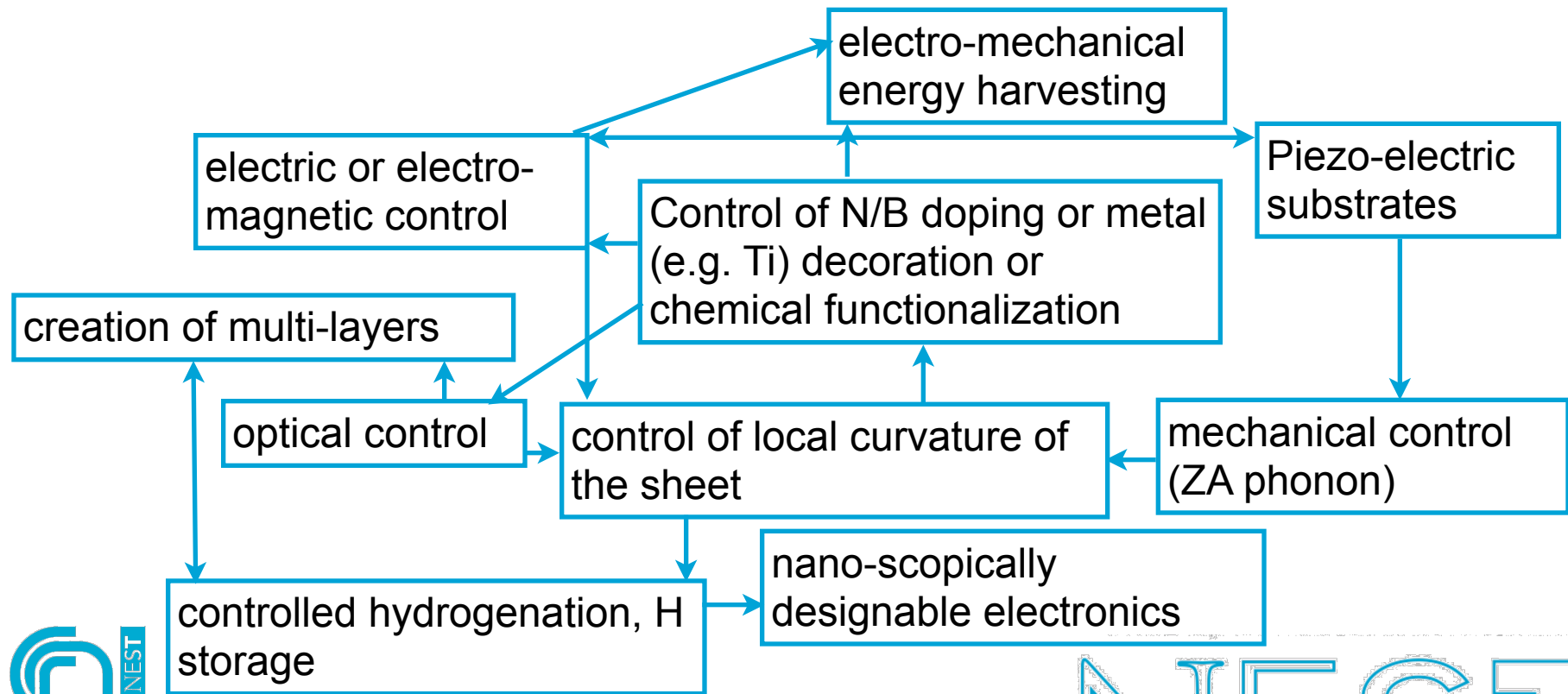
### In progress

❖ evaluate the possibility of using this for hydrogen transportation and pumping



D Camiola, R Farchioni, V tozzini, in progress

Graphene Week, Gothenburg, June 2014



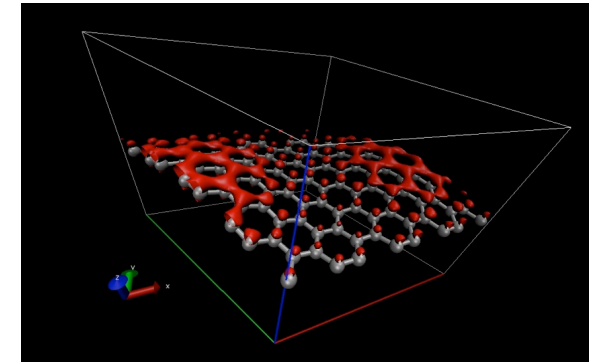
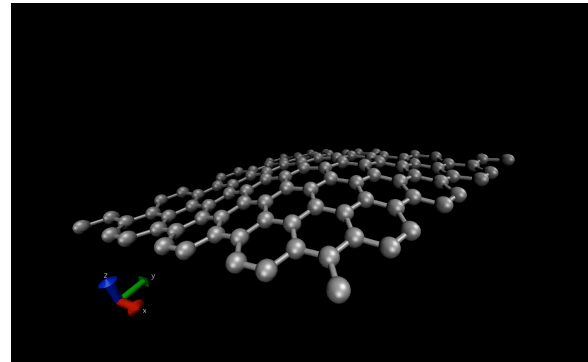
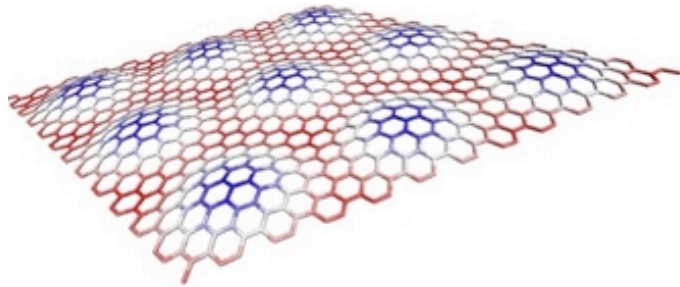
Control of N/B doping or metal (e.g. Ti) decoration or chemical functionalization

electric or electro-magnetic control

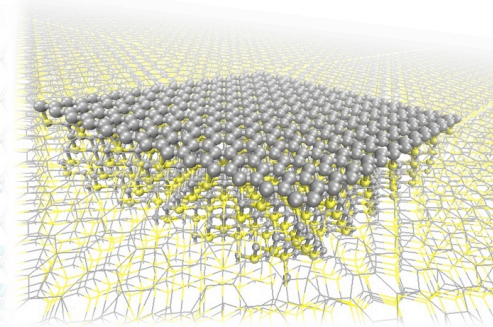
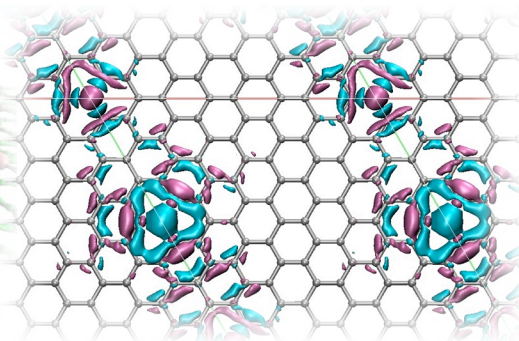
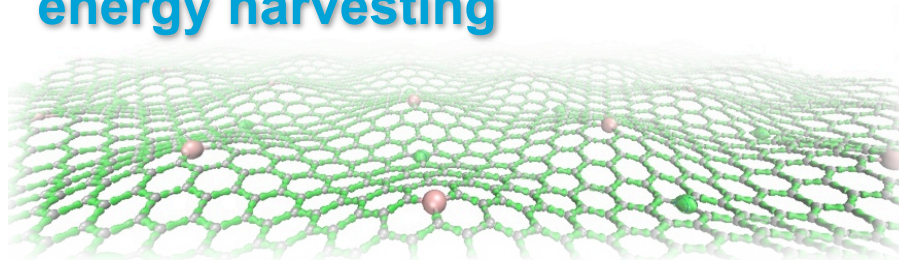
electro-mechanical energy harvesting

Piezo-electric substrates

Ripples in graphene are enhanced by an orthogonal electric field due to an anisotropic charge displacement effect...

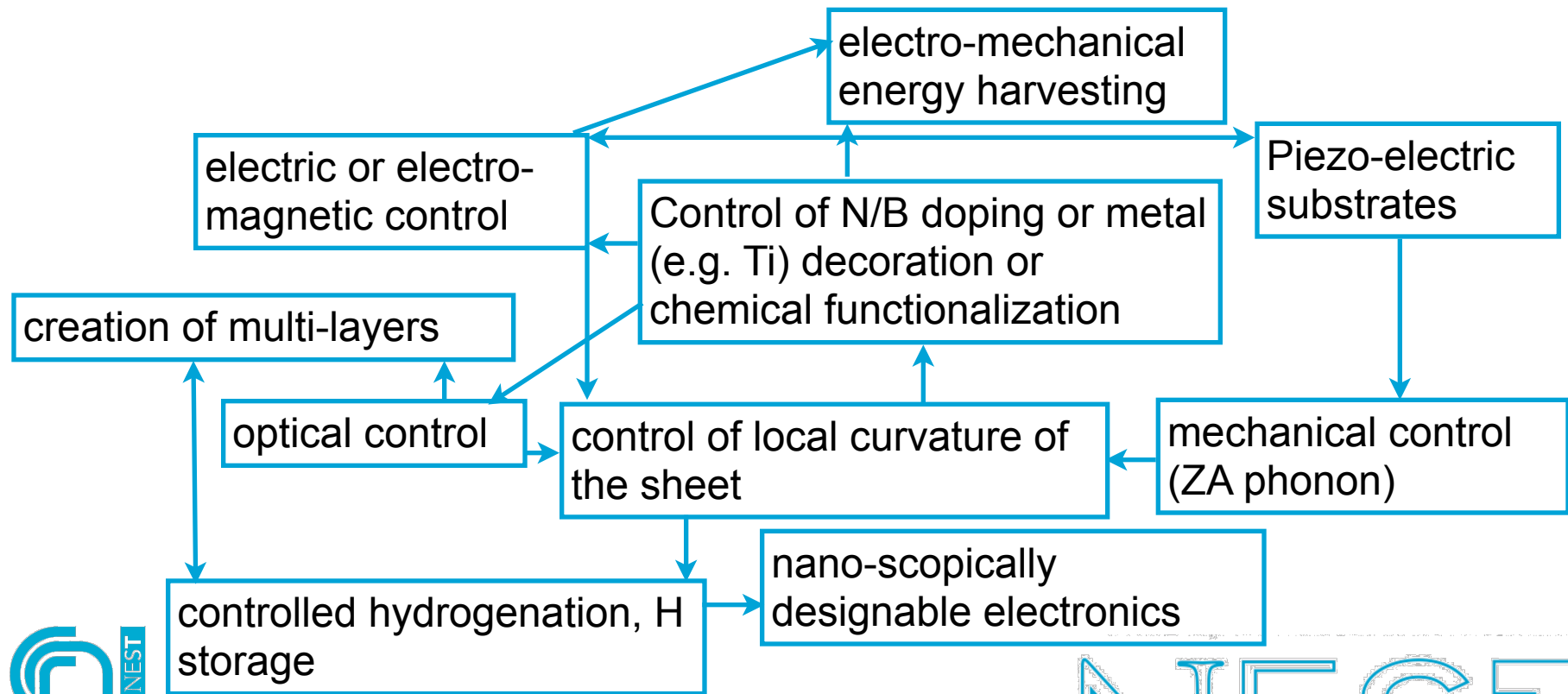


Enhance the effect and use it for **curvature control** and **electro-mechanical energy harvesting**



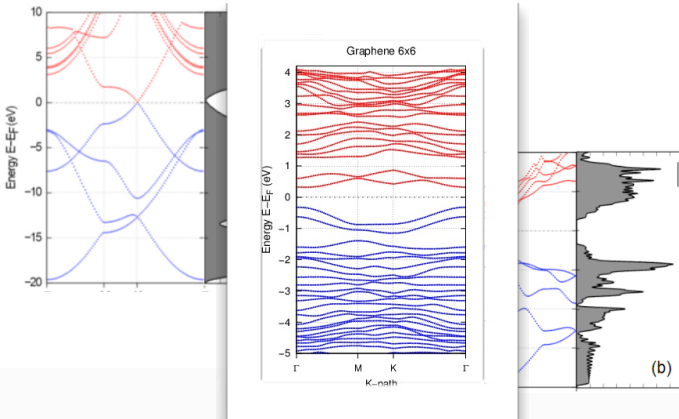
DFT simulations are currently in the course to evaluate its effect on free standing layer and on the substrate and the possibility of exploiting it





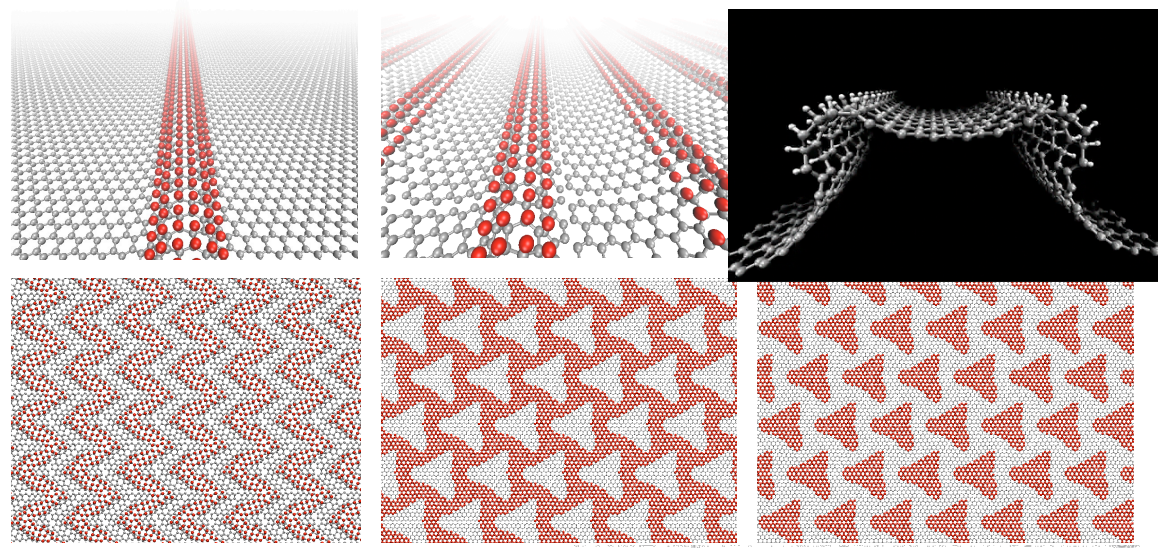
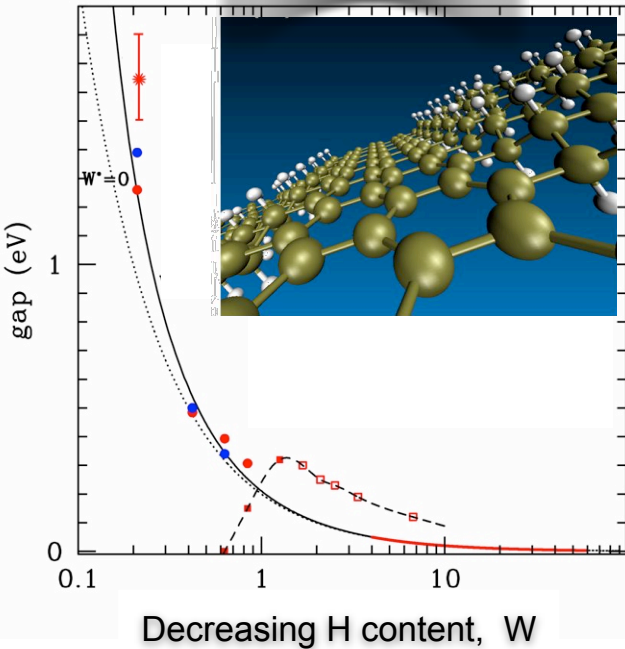
# controlled hydrogenation, H storage

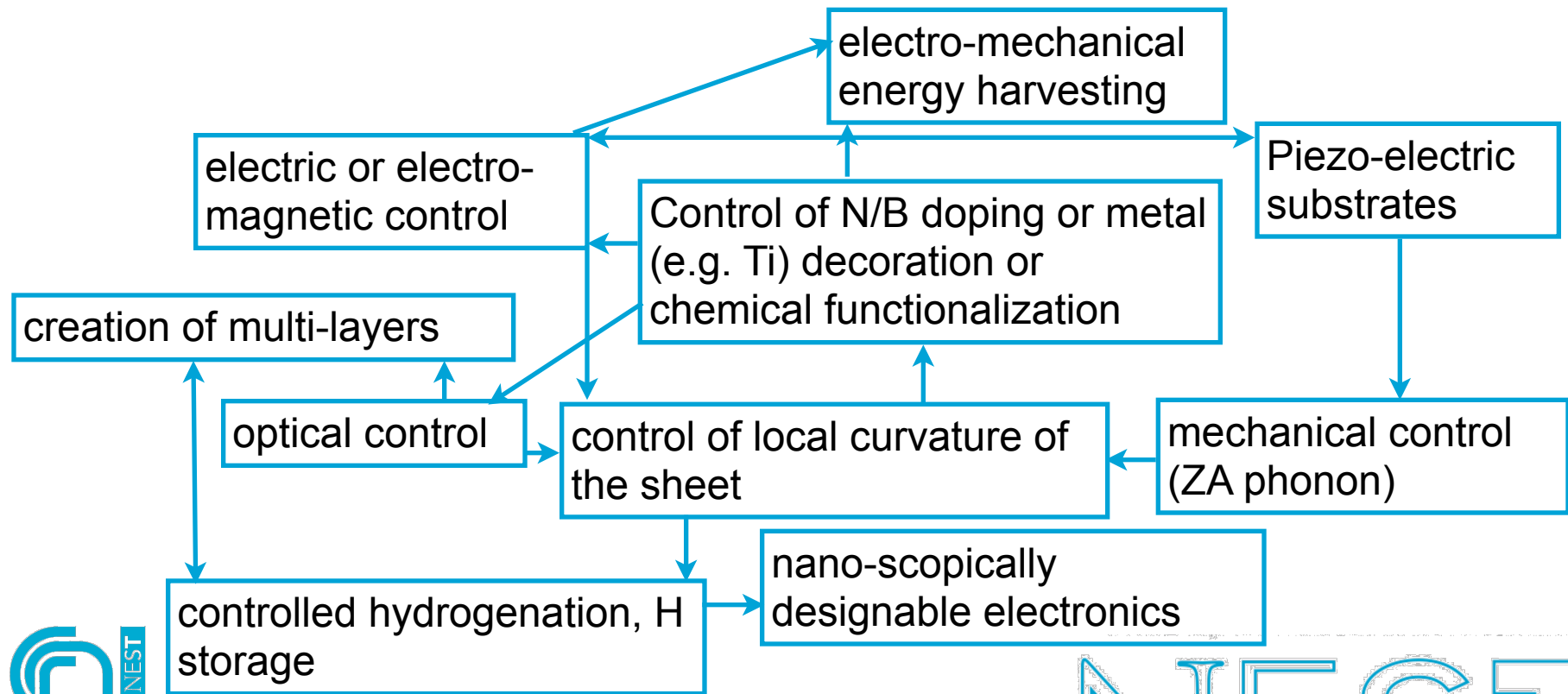
# nano-scopically designable electronics



- ❖ Graphene is a high mobility conductor
- ❖ Its completely hydrogenated counterpart, graphane, is a high gap insulator (~3.5eV)

⇒ partially hydrogenated graphene with decoration controlled by rippling can potentially have interesting nano electronic properties, depending on the H amount and distribution



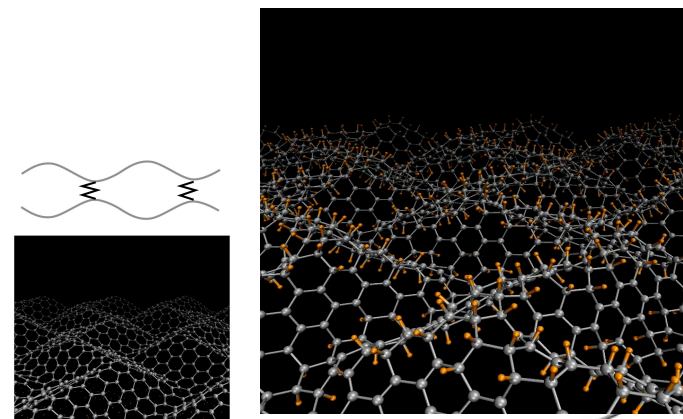
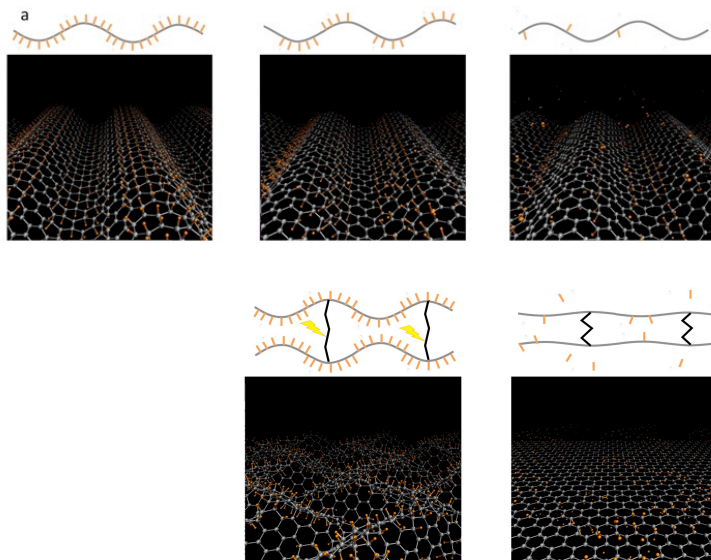
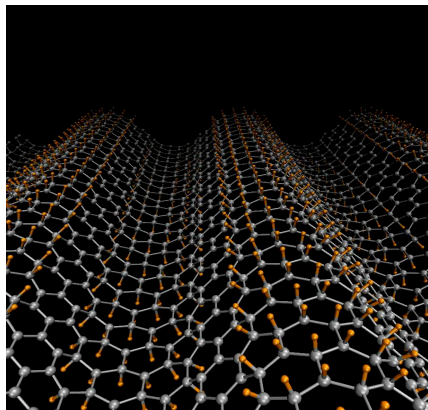


mechanical control  
(ZA phonon)

control of local curvature of  
the sheet

optical control

creation of multi-layers



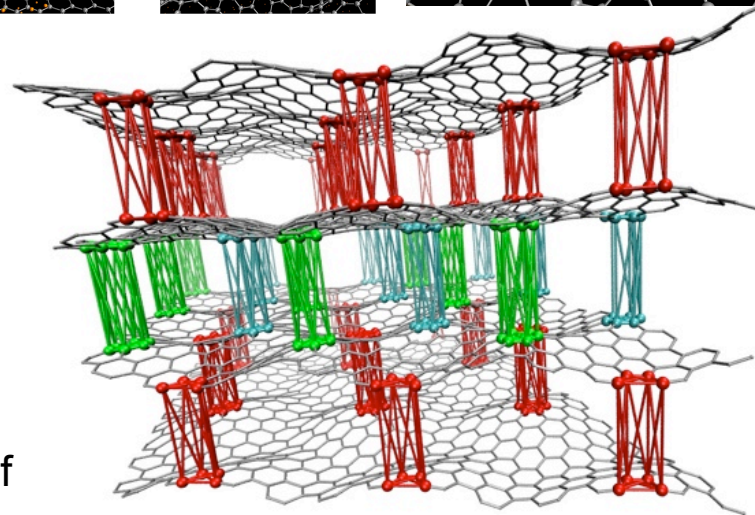
Designing optically controllable molecular pillars to:

- ❖ control curvature
- ❖ control inter-layer spacing

To this aim:

- ❖ Control chemical adhesion by means of the curvature
- ❖ Design optically active proper molecules

Simulation can help designing chemical/physical properties of the molecules and predicting the behavior of the system



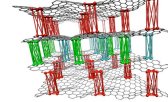
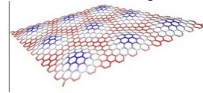
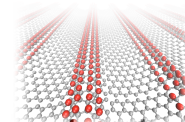
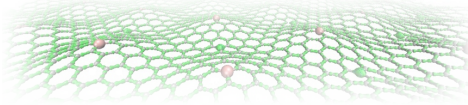
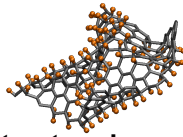
V Tozzini, V Pellegrini Prospects for Hydrogen storage in graphene PCCP (2013)

V Pellegrini, V Tozzini et al Review submitted to Science

D Camiola, R Farchioni and V Tozzini, in progress

# Conclusions

- ❖ Controlling graphene interaction with H and other chemicals would allow designing devices for
  - ⦿ energy storage
  - ⦿ energy production
  - ⦿ nanoelectronics
- ❖ Simulations suggest strategies (mechanical, optical, electro-mechanical) for
  - ⦿ curvature control
  - ⦿ multi-layer creation and control
- ❖ Computer modeling can help designing these strategies, but it must be
  - ⦿ accurate at the atomic level and electronic level, to describe the chemisorption
  - ⦿ able to address the slow kinetics and nano-to-micro scale structural changes
  - ⦿ able to evaluate the thermodynamics and other “macroscopic” properties
- ❖ We proposed a coherent multi-scale approach to graphene (and complex systems)
- ❖ Software platform [MusCaDe](#), currently local, but to be published soon



## Perspective

use multi-scale for graphene-bio hybrids. Applications:  
Biophysics, medical, environment...

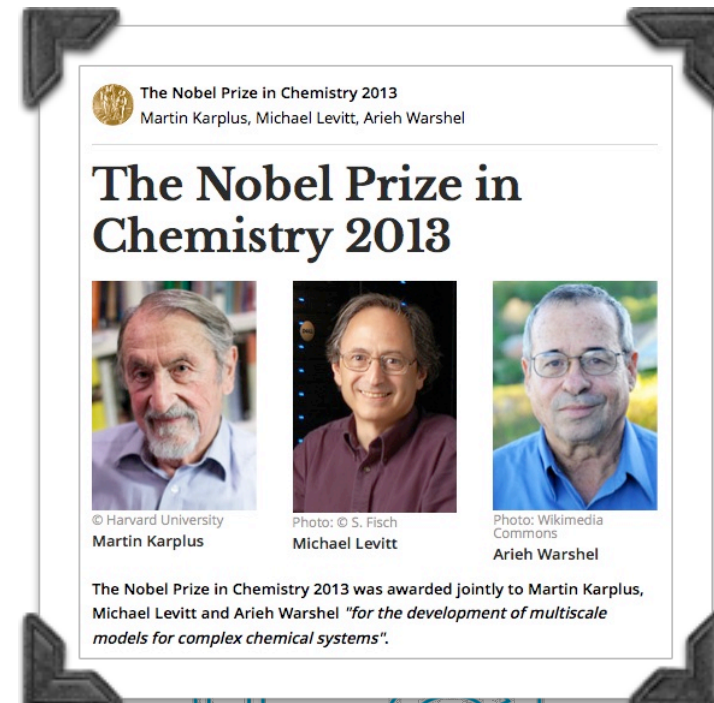
## Support



GRAPHENE FLAGSHIP



Graphene Week, Gothenburg, June 2014



# Consultation for new FET pro-active topics

<http://ec.europa.eu/digital-agenda/en/content/consultation-new-fet-proactive-topics>

New Topic:  
**Multi-Scale Simulations of Complex Systems**

European Commission | Digital Agenda for Europe | A Europe 2020 Initiative

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- The Future and Emerging Technologies Community
  - Consultation for new FET Proactive topics

### Consultation for new FET Proactive topics

Do you have a great idea for a new technology that is not possible yet? Could it become real if Europe's best minds were put on the task? Share your view and the European Commission can make it happen via the Future and Emerging Technologies (FET) programme.

**The consultation is open till 30 June 2014.**

The aim of the public consultation launched today is to identify promising and potentially game-changing directions for future research in any technological domain.

The consultation is organised as a series of discussions, in which contributors can suggest **ideas for a new FET Proactive initiative** or **discuss the 9 research topics** identified in the previous consultation to determine whether they are still relevant today:

- Ideas for new topics (what's new that isn't in the other 9 topics?)
- Bottom-up intelligent construction
- Constructive symbiosis
- Ecological technology
- Global Systems Science
  - Knowing, doing and being
  - Nano-optomechanical technologies
- New possibilities at the nano-bio-chem interface
- Quantum technologies
- Time for time

Group managers

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Project Officer

You can:

- ❖ read more about the proposal
- ❖ express interest with a click
- ❖ write a comment

**Dead-line: June 30th**

Multi-Scale Simulations of Complex Systems

Title: Multi-Scale Simulations of Complex Systems

Keywords:  
QM and MM calculations,  
Classical Molecular Dynamics,  
Coarse Grained models,  
Meso-Scale and continuum models,  
Stochastic dynamics

Topics to be addressed:  
Multi-scale modeling and computer aided design of new-materials  
Biopolymers (Proteins and Nucleic Acids) and other biological macromolecules;  
Bio-inspired and bio/non bio-hybrid materials

Technological applications  
Advanced nano-electronics (flexible, wearable, biocompatible)  
Production and storage of (renewable) energy  
Control of environmental pollution  
Advanced nano-medicine

edit reply

Interesting  
1 user has voted.

<https://ec.europa.eu/digital-agenda/en/comment/15985#comment-15985>

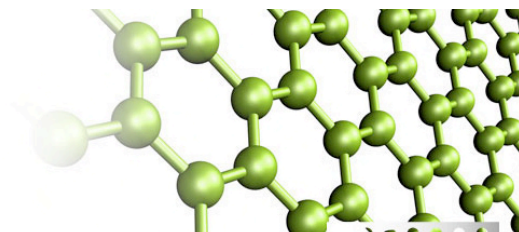
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**PISA NEST | LECS | MNL | MODENA | - 30.06.2014 -** Vote for CnrNano proposed FET Topic!  
At the open consultation for new FET pro-active Topics, some NANO researchers submitted to the scientific community a new topic on **Multi-Scale Simulations of Complex Systems** with the aim of possibly attracting interest and have new specific calls in the next FET pro-active program. If you wish to express interest or support the initiative, please do it on the forum **HERE** by clicking the 'thumbs-up' icon at the bottom and/or posting a comment, **within June 30th**.

Link <https://ec.europa.eu/digital-agenda/en/comment/15985#comment-15985>

30.06.2014 Vote for CnrNano proposed FET Topic!  
At the open consultation for new FET pro-active Topics, som...

11.06.2014 Una finestra con vista: la vita segreta del cervello  
Gian Michele Ratto di CnrNano di Pisa terrà una conferenza pubblica dal titolo Una finestra co...

30.05.2014 Osservato il "big-bang" della luce che si trasforma in elettricità  
Come inizia il processo di trasformazione della luce del sole in corrente elettrica in una cella sol...

<http://www.nano.cnr.it/>  
**NEWS section**

