Multi-Scale Simulations of Graphene for Energy Applications

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Abstract

Graphene is currently considered one of the most promising materials due to its extreme versatility. In its pristine form, it is a high mobility conductor, mechanically resistant and flexible, and was proposed for a number of applications in the field of energy storage and harvesting[1,2]. However, for all of these applications, its interactions with different chemical species and/or with external stimuli must be considered.

The enhanced graphene reactivity of rippled graphene towards adatoms has been theoretically studied within the Density Functional Theory (DFT) framework [3] and proposed as a mean to create partially hydrogenated graphene structures [4] with tunable semiconducting properties [5]. Furthermore, we recently showed by means of DFT calculations and Car-Parrinello simulations that this property could be used as the base of a hydrogen storage-release working at room temperature: hydrogen preferentially chemisorbs on convexities, then, provided the curvature can be controlled and inverted, it spontaneously release from concavities[6] (see Fig 1). The first part of this mechanism (chemisorption) was experimentally confirmed using naturally rippled graphene grown on SiC[7]. However, further investigations are necessary to solve a number of problems, for instance (i) the accurate control of the local curvature, statically and dynamically (ii) the evaluation of behavior of the system at the macroscopic level. We proposed different possible solution to (i), namely optical control by functionalization with photosensitive molecules, electro-mechanical control, exploiting piezo or flexo electricity. In both cases chemisorption [8] or subsitutional doping [9] with different chemical species can be considered to control the electro-mechanical properties of graphene. However both for (i) and for (ii), also the molecular dynamics and thermodynamics of the system at the large size and time scales must be studied.

We propose a multi-scale molecular simulation and modeling approach (Fig 2) to address all the different aspects of the problem. DFT calculations and simulations are used to evaluate the quantum chemical properties of the system at the 1-10 nm scale in different conditions. Specifically we evaluated the hydrogen binding properties as a function of the local curvature and on ripples of different sizes and geometry and the effect of the external electric field and of N and B doping on the mechanical and reactive properties. Subsequently, we transfer the quantitative information obtained at the DFT level into a classical empirical force field. This allows molecular dynamics simulations at the 10-100 nm scale, and, especially, to extend the analysis of the mechanical behavior of the system in the time scale, up to hundreds of ns, enabling evaluation of the statistical behavior. Finally, the knowledge get from the two atomistic levels of analysis is transferred to a continuum mechanicistic model [6-9], representing the system as a 2D membrane, onto which all the properties are mapped. This allows the analysis of the statistical properties of the system on the macroscopic scale.

This approach combines the accuracy of atomistic and quantum calculations with the extensive and large scale view given by the empirical-continuum models, allowing quantitative evaluation of the feasibility of devices for energy applications.

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Fig 1 Left: hydrogen binding energy as a function of the curvature (positive=convex, negative=concave). Right simulation of the hydrogen release upon curvature inversion by a transverse traveling wave.

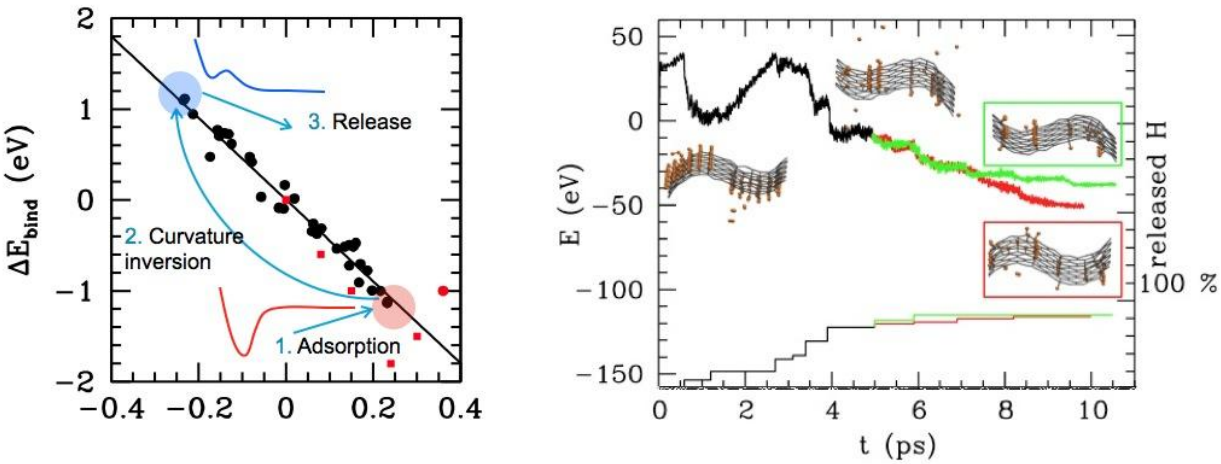
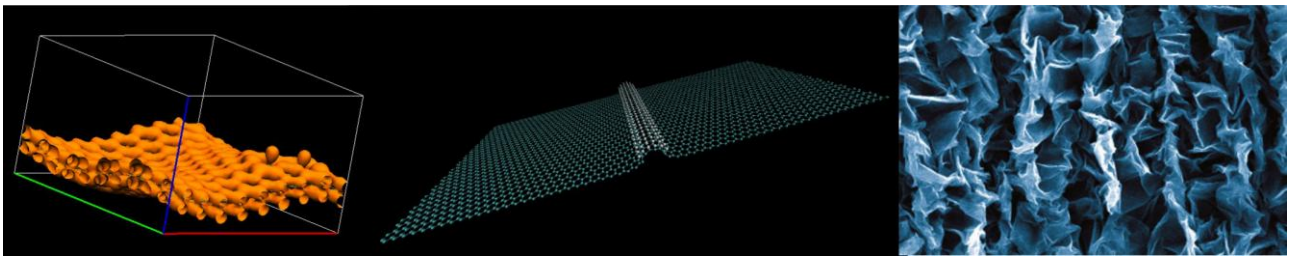
Fig 2
The three levels of the multi-scale representation of graphene. From left to right, a 2nmx2nm supercell of rippled graphene with a dimer of hydrogen atoms attached. A iso-charge surface of energy states near the Fermi level is represented in orange; a ~1000 atoms supercell of graphene with an hydrogenated ripple; a surface representation of buckled graphene.