

# Curvature-dependent chemisorption onto graphene for storage applications: a Density Functional Theory study

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## Abstract

Besides its special electronic properties, graphene also has peculiar mechanical properties. Its strength and extreme flexibility allow sustaining ripples in a wide range of amplitudes and wavelengths[1]. This circumstance can be exploited for applications: ripples produce a modulation of the local curvature in a considerable range, which in turn was shown to be strongly correlated with the stability of hydrogen chemisorbed atoms[2]. This is due to the fact that curvature induces the local pyramidalisation, i.e. pushes a carbon site towards the  $sp^3$  configuration, making it more reactive[3].

Having demonstrated by Density Functional Theory (DFT) and confirmed experimentally that atomic H tends to stick onto convexities[4] and detaches from concavities, we now address the issue of the behavior of molecular hydrogen  $H_2$ , more relevant for H-storage applications[5]. In fact, while in the case of atomic hydrogen the adhesion is rather spontaneous, with a very small barrier, for molecular hydrogen the process is limited by the high chemisorption barrier of the order of  $\sim 1.5\text{eV/atom}$  [4], making the kinetics of loading very slow.

We propose that curvature manipulation could be used to improve the adhesion kinetics. To this aim, we perform a systematic DFT based study to evaluate the dependence of chemi(de)sorption barriers on curvature. We use different kinds of functionals with different levels of corrections for electronic density gradient and for London dispersion[6]. We use model systems with various levels of corrugation generated by lateral compression of the isolated sheet[3], chosen however to approximate the symmetry of natural rippling of graphene grown on SiC. We evaluate the chemi(de)sorption profiles by means of nudged elastic band technique[7]. Our results implies that the barrier can be manipulated by changing the curvature, and give indications on the levels of curvature needed to use this effect in a real device[8].

However, applications require the capability of controlling the local curvature. The naturally curved graphene grown on SiC is a natural platform to study this issue. In fact, different and sometimes opposite determination of the curvature of graphene on SiC are available in the literature, both from experiment and theoretical studies[9,10]. The moiré pattern of curvature of the graphene monolayer, grown by Si evaporation and generated by the mismatch between graphene and SiC lattice parameters, is either described as hills surrounded by valleys or, conversely, by wells surrounded by crests. This suggests the idea that rippling of graphene on SiC may be multi-stable, and therefore prone to be manipulated. We studied this hypothesis by means of a model system reproducing the graphene grown on SiC with high fidelity, including  $\sim 1700$  atoms and with different energy density functionals, to evaluate the effect of simulation setup[11]. We show that a number of rippling patterns with different (and opposite) curvature exist, among which the system can switch. Their relative stability is driven by the strength of the van der Waals forces, and therefore is possibly manipulated by environmental conditions, such as temperature or external electric fields[12].

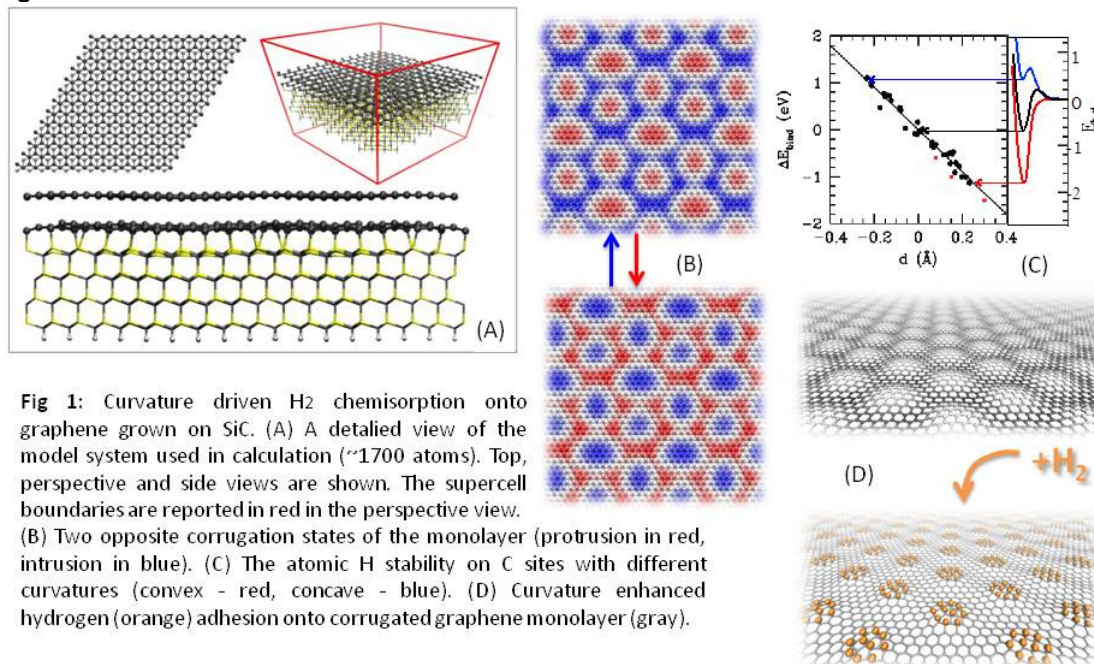
This is key in manipulating the local curvature, and therefore the local reactivity could be directly exploited for storage applications based on chemisorption. In addition, it could be a way to control not only the amount of adatoms but also their location. Because reactivity depends on graphene properties instead of those hydrogen, this reasoning is extendable to other substances and chemical groups, e.g. anchors for pillar molecules. This drives the functionalization of graphene to build 3D networks.

## References

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## Figures



**Fig 1:** Curvature driven H<sub>2</sub> chemisorption onto graphene grown on SiC. (A) A detailed view of the model system used in calculation (~1700 atoms). Top, perspective and side views are shown. The supercell boundaries are reported in red in the perspective view. (B) Two opposite corrugation states of the monolayer (protrusion in red, intrusion in blue). (C) The atomic H stability on C sites with different curvatures (convex - red, concave - blue). (D) Curvature enhanced hydrogen (orange) adhesion onto corrugated graphene monolayer (gray).