

§19. Quantum Chemical MD Simulations of Graphene Hydrogenation

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The purpose of this project was to study the hydrocarbon yield from hydrogen chemisorption on the edges of graphite sheets at high temperatures. However, in collaboration with the experimental group of Prof. Alexander Grüneis at Vienna University, we found an interesting hydrogen absorption pattern on graphite (0001) surfaces that appears only at low incident energies (around 0.4 eV incident energies, barely enough to overcome the entrance channel barrier). We therefore performed extensive collaborative simulations on this low energy hydrogen absorption and compared it with higher energy (~1 eV) hydrogen chemical sputtering.

We modified the C-H parameter set of the spin-polarized self-consistent-charge density-functional tight-binding (sSCC-DFTB) method to faithfully reproduce a CCSD(T)-based potential energy curve of hydrogen chemical absorption on graphite (0001) at a tiny fraction of the computational cost. Using this highly accurate quantum chemical potential, we performed direct Born-Oppenheimer MD simulations while “shooting” H atoms in 0.5 ps intervals with incident velocity of 0.4 eV aimed at a periodic graphite target with randomly selected spin. This approach will produce occasionally spin carriers on the graphene, however, on the average and over longer simulation times, the total spin remains zero due to the random selection. Most interestingly, we noticed a difference between high-spin and low-spin situations: Given favorable nuclear configurations, up and down spins on graphene can couple to yield energetically more favorable low-spin electronic structure (closed-shell singlet). This is only the case when hydrogen atoms are separated by an odd number of carbon bonds. If the separation involves an even number of carbon bonds, low- and high-spin states are energetically nearly degenerate. Such a behavior cannot be described by classical force field potentials such as REBO.

The simulations were carried out at a constant temperature of 300 K, using a Nose-Hoover chain thermostat. Chemisorption may occur in principle in random positions on the graphite with little preference for the adsorption site, causing H-frustrated adsorption patterns over time [1] as reported by Flores *et al.* [2]. However, during prolonged exposure to H bombardment, a *para*-adsorption pattern at 25% coverage (see Figure 1), proposed previously by Boukhvalov *et al.* [3], emerges as a consequence of repeated surface reorganization due to associative H₂ elimination [1]. We found that the reason for the existence of this C₄H polymer with long-range order are isolated aromatic sextets with high intrinsic stability towards further hydrogenation, reflected in

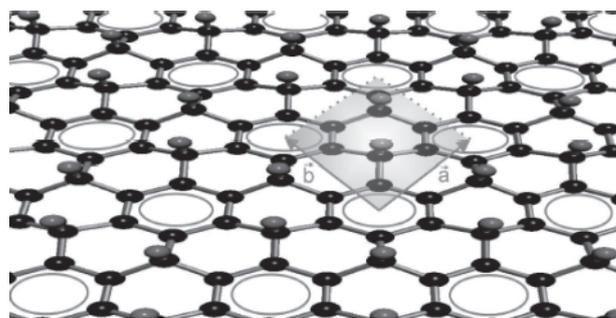


Fig. 1. All-para hydrogenated graphene corresponding to 25% coverage as observed in experiment [1] and during our QM/MD simulations. Black spheres represent carbon, while purple spheres represent hydrogen. Green circles indicate aromatic hexagons.

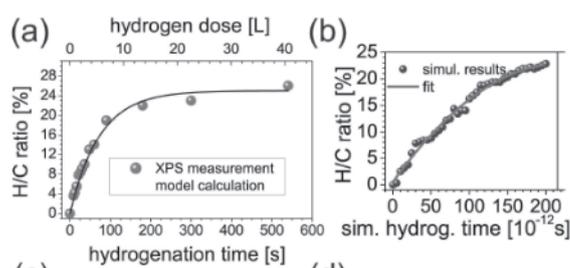


Fig. 2. (a) The H/C ratio as determined by XPS (points) along with a calculated chemisorption curve from an analytical model. The lower scale is the hydrogenation time (normalized for 10⁻⁷ mbar partial pressure) and the upper scale the exposure in Langmuir. (b) Time dependence of the H/C ratio up to equilibrium concentration from our MD simulations.

shallower absorption wells and higher adsorption barriers. Higher incident energies around 1 eV increase the fraction of frustrated hydrogen absorption sites and lead to an absorption pattern without such a long-range order. The latter structure is characterized by 2D ripples, where “hills” associated with positive curvature are hydrogenated due to the higher reactivity of the carbon atoms, while “valleys” with negative carbon curvature remain non-hydrogenated.

In summary, we have shown that self-organized hydrogenation patterns can be induced on graphene, and one may be able to utilize this self-patterning to produce novel graphene-hydrogen polymers with finely tuned electronic band-gaps for electronic devices.

- 1) Haberer, D.; Guisca, C. E.; Wang, Y. *et al.* submitted (2011).
- 2) Flores, M. Z. S.; Autreto, P. A. S.; Legoas, S. B.; Galvao, D. S. *Nanotechnol.* **20** (2009) 465704.
- 3) Boukhvalov, D. W.; Katsnelson, M. I. *Phys. Rev. B* **78** (2008) 085413.