§14. Quantum Chemical MD Simulations of Graphite Edge Reactions with Hydrogen

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This project focuses on the isotope effect in chemical sputtering of hydrogen and deuterium on a graphene surface by quantum-chemical molecular dynamics (QM/MD), based on the self-consistent-charge density-functional tight-binding (DFTB) method. Chemical sputtering is a process where bombardment by ions, atoms or molecules induces a chemical reaction producing volatile particles which are transported to the surface, and ejected or desorbed into the gas phase. It is expected that different hydrogen isotopes will damage the graphite surface by a different amount. However, experimentally, such isotope effects are difficult to study in actual fusion devices. Therefore, we decided to perform a comparative study in collaboration with the experimental group of Alexander Grüneis, University of Vienna, Austria.

In order to obtain an atomic-level understanding of the H/D isotope effect in graphene hydrogenation/deuteration, we performed nonequilibrium MD simulations. On the basis of the Born-Oppenheimer (BO) approximation, we computed total electronic energy and forces on the nuclei on the fly at each time step of the trajectories, and performed the time propagation of the position of the nuclei using Newton's classical equation of motion. The simulations are a direct extension of our previous simulations of graphene hydrogenation, reported in ref. [1], where details of the spin-polarized density-functional tight-binding (SDFTB) quantum chemical potential, time propagation, and nuclear thermostat were given. Briefly, our graphene model system consisted of 32 carbon atoms, forming a plane within a cuboid unit cell $(9.856 \times 8.596 \times 100 \text{ Å}^3)$ for the periodic boundaries. In ten trajectory replica for each isotope, H or D atoms were placed in randomly chosen positions at a distance of 4 Å with initial velocities corresponding to 0.4 eV kinetic energy, aimed perpendicularly to the target graphene surface. The spin on each H or D atom was randomly selected, and total spin of the system during the QM/MD simulations was defined at all times as the cumulative sum of projectile spins. The "shooting rate" was one H/D projectile every 0.5 ps. In the case of graphene hydrogenation, we extended the previously reported simulations[1] up to 250 ps (500 H atoms), while in the case of deuteration, a new set of ten trajectory replicas was generated, also up to 250 ps simulated time (500 D atoms). The incident kinetic energy of 0.4 eV is just barely enough to overcome the chemisorption barrier for H/D on the BO potential energy surface (PES), according to refs.[2, 3]. Our modified SDFTB potential correctly reproduces this barrier and the energy of the chemisorption well, estimated for infinite graphene at around -0.7 to -0.8
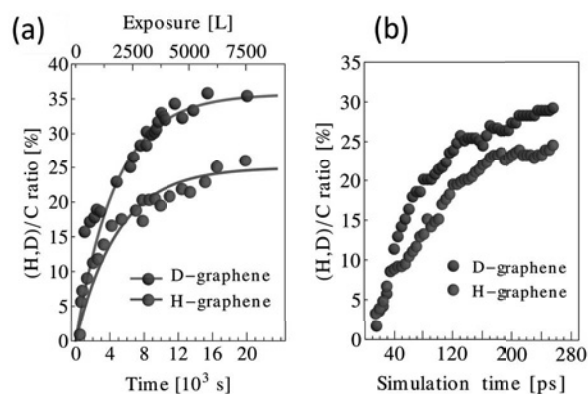

Fig. 1. Comparison of hydrogenation/deuteration of graphene according to a) experiment, b) QM/MD simulations.

eV.[3, 4]

Our theoretical investigation has shown that the kinetic isotope effect is consistent higher deuteration rates. In particular, we find the following three factors affecting the adsorption/desorption rates:

a) higher reaction probability of D vs H due to longer contact times with the surface,

b) higher barrier for D than for H towards escape to the vacuum,

c) smaller probability for tunneling through this barrier in the case of D,

d) higher recapture probability for D than for H during escape to the vacuum.

Since H is more easier lost to the vacuum than D [factors b) through d)], it is easier for H to form a superlattice pattern such as C_4H, which possesses highly non-reactive, isolated, aromatic hexagons. In the case of D, once the C-D bond is made, loss to the vacuum is less likely, and the greater persistence of a random adsorption pattern with more "frustrated" hydrogen pairs makes the formation of the C_4H pattern difficult.

The presented experimental and theoretical results suggest that an equilibrium H/D coverage rate is established in experiment, according to which the overall reaction rates for chemisorption ($k_{forward}$) and desorption ($k_{backward}$) reach identical values after long-enough exposure. Since $k_{backward}$ is larger for H than for D due to factors b) through d), and $k_{forward}$ is larger for D than for H due to factor a), we have established that the use of deuterium allows higher surface coverage than hydrogen.

[1]   D. Haberer et al., Adv. Mat. **23** (2011).

[2]   M. Bonfanti et al., J. Chem. Phys. **135** (2011).

[3]   Y. Wang et al., J. Phys. Chem. A (2012).

[4]   L. F. Huang et al., J. Phys. Chem. C **114** (2010)