

Hydroxyl Functional Groups on Pristine, Defected Graphene, and Graphene Epoxide: insights from first principles calculations

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Oxygen-containing functional groups can be present in considerable amount intentionally or unintentionally on graphene, and a complete reduction of graphene oxide is difficult to achieve. To address the origin of this behavior, we have performed pseudopotential density functional theory calculations to investigate in particular the adsorption of hydroxyl (OH) on perfect and defected graphene, individually and in presence of other coadsorbed functional groups. Structural, electronic, and magnetic properties and reactivity of the systems studied have been investigated, with the aim of understanding why complete deoxygenation of graphene oxide is not easy to achieve.

We found that hydroxyl groups weakly adsorb on perfect graphene, with adsorption energy of 0.54 eV, and induces magnetization on graphene. They can diffuse with rather low barriers, less than 0.35 eV, and easily aggregate. Aggregation of hydroxyl groups give an energy gain of about 0.75 eV per each adsorbed OH in the case of pairs and even more in the case of triplets, quadruplets, and larger aggregates. Aggregation with coadsorbed epoxy groups is also energetically favored. Water formation from adsorbed hydroxyl groups can occur at the pristine surface with energy barriers of the order of 0.5 eV or slightly larger in the case of OH initially bonded to epoxy.

The adsorption of hydroxyl on defected graphene is much stronger than that at pristine, with adsorption energy of 1.80 eV at Stone-Wales (SW) defects and 4.23 eV at single vacancies. However, single vacancies and SW defects play different roles. Hydroxyl adsorption at a single vacancy is dissociative, with a low barrier of about 0.2 eV, leading to the formation of stable ether groups with a strong magnetic character. At variance, SW defects could stabilize the hydroxyl groups on the graphene basal plane, with a stronger binding energy than pristine, and, even more important, higher barriers (more than 1 eV) for diffusion [Fig. 1], recombination of neighboring hydroxyl groups and water formation [Fig. 2].

This suggests that SW defects could be responsible for the stabilization of the hydroxyl groups which are also present at graphene oxide after reduction.

References

[1] N. Ghaderi and M. Peressi, J. Phys. Chem. C **114** (2010) 21625.

Figures

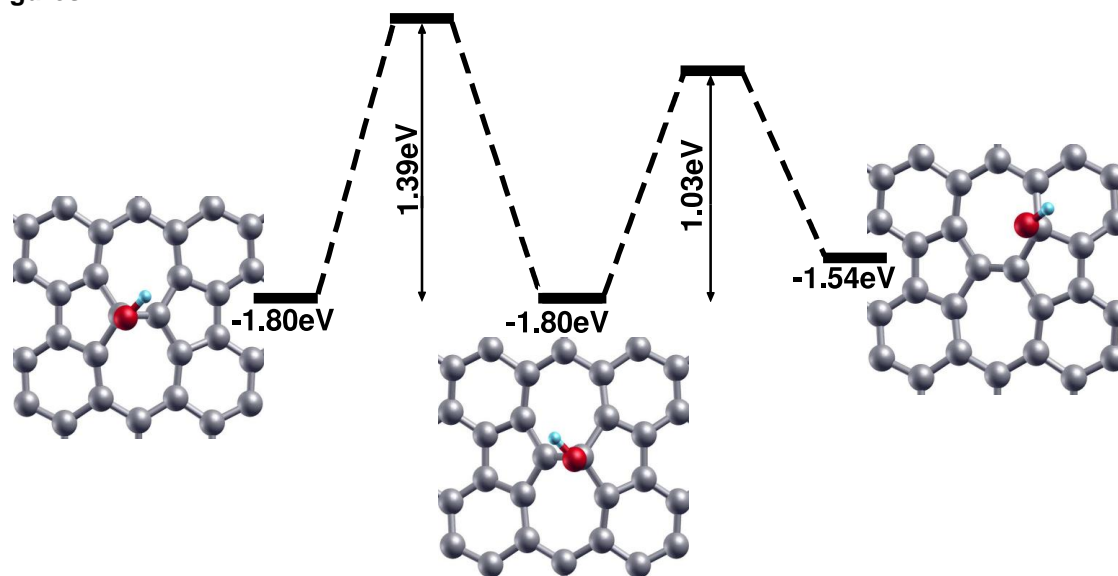


Fig. 1: Optimized structural models and energies in the diffusion process of an hydroxyl group individually adsorbed on a SW defect. Adsorption energies of OH in the initial and final states are reported, together with the diffusion barriers.

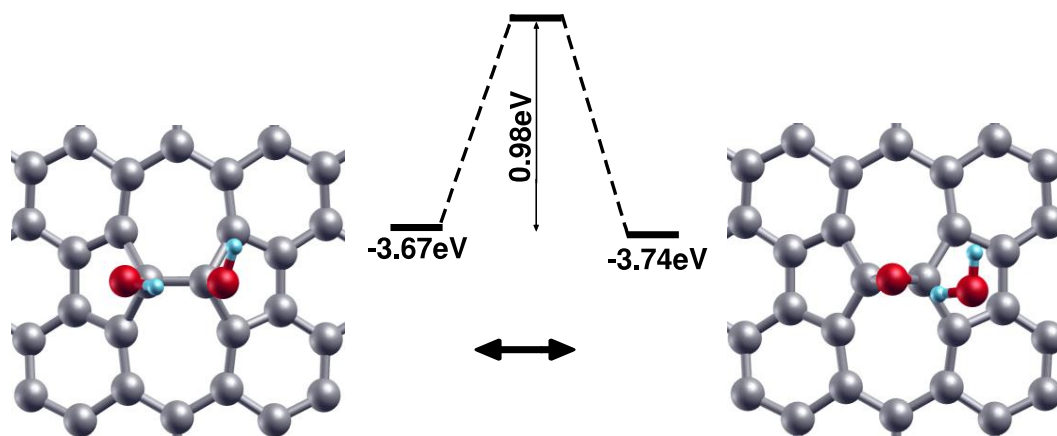


Fig. 2: Optimized structural models and energies in the process of water formation from hydroxyl aggregates on a SW defect.