

Tuning the hydrogen adsorption on hydroxyl functionalized graphene with titanium

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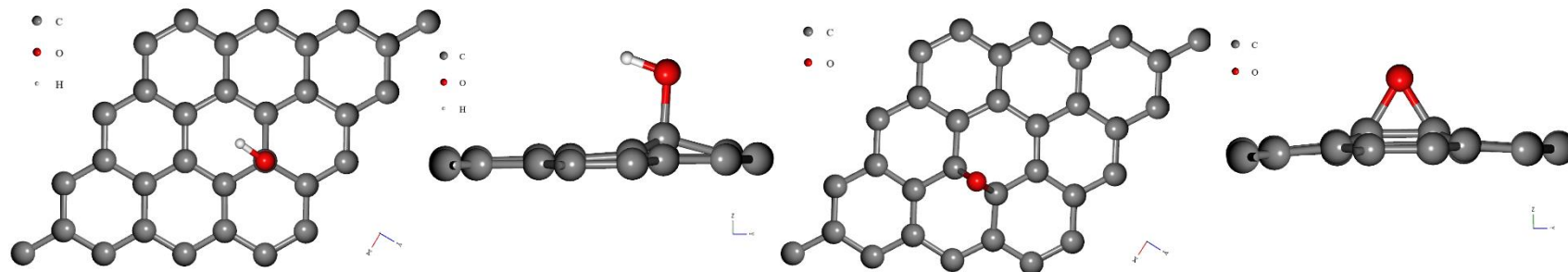


Abstract

Fossil fuels are the main source of energy for the world economy, but they are non-renewable and polluting. The use of hydrogen as a fuel is a good alternative due to its high energy density and low pollution. However, the development of a hydrogen-based economy demands an efficient medium for its storage. The best option is solid-state storage. Carbon based materials are attractive for hydrogen storage because of their low density, high porosity, and high surface area[1]. However, only at cryogenic temperatures, they are able to achieve efficient storage due to the low physisorption energy. We investigate, using DFT, the interaction of titanium with the graphene functionalized with hydroxyl group. We describe structural properties, evaluate the hydrogen adsorption mechanisms and energies.

Computational details

Our numerical approach is based on DFT using the Quantum ESPRESSO code. We use the GGA approximation for the term and exchange and correlation. We set the kinetic energy cutoff at 50 Ry for the wave functions and 600 Ry for the charge density. And we use a 4x4 supercell for graphene with a vacuum of 20 Å.

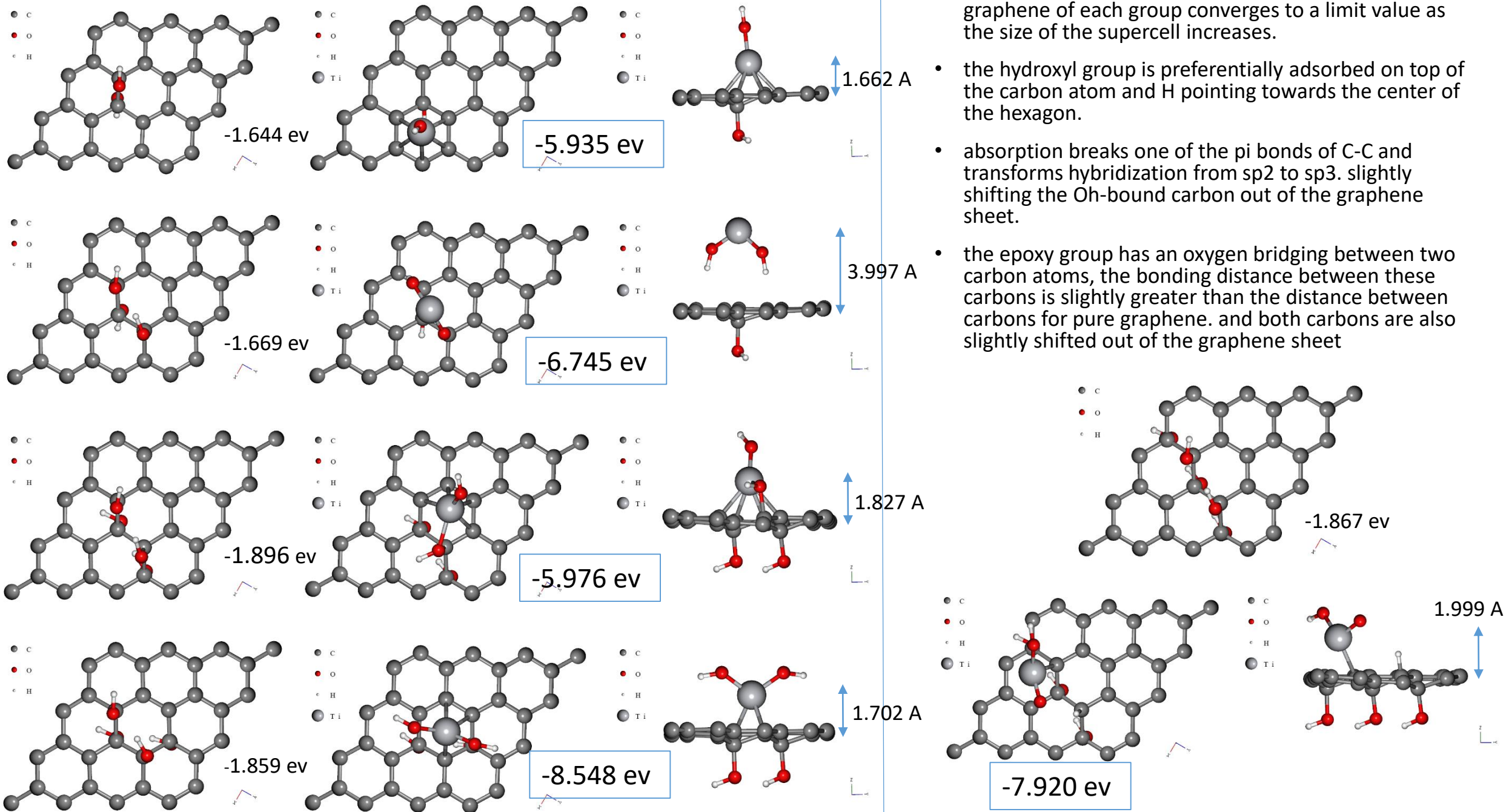


Results and discussions

Individual OH and O on pristine graphene

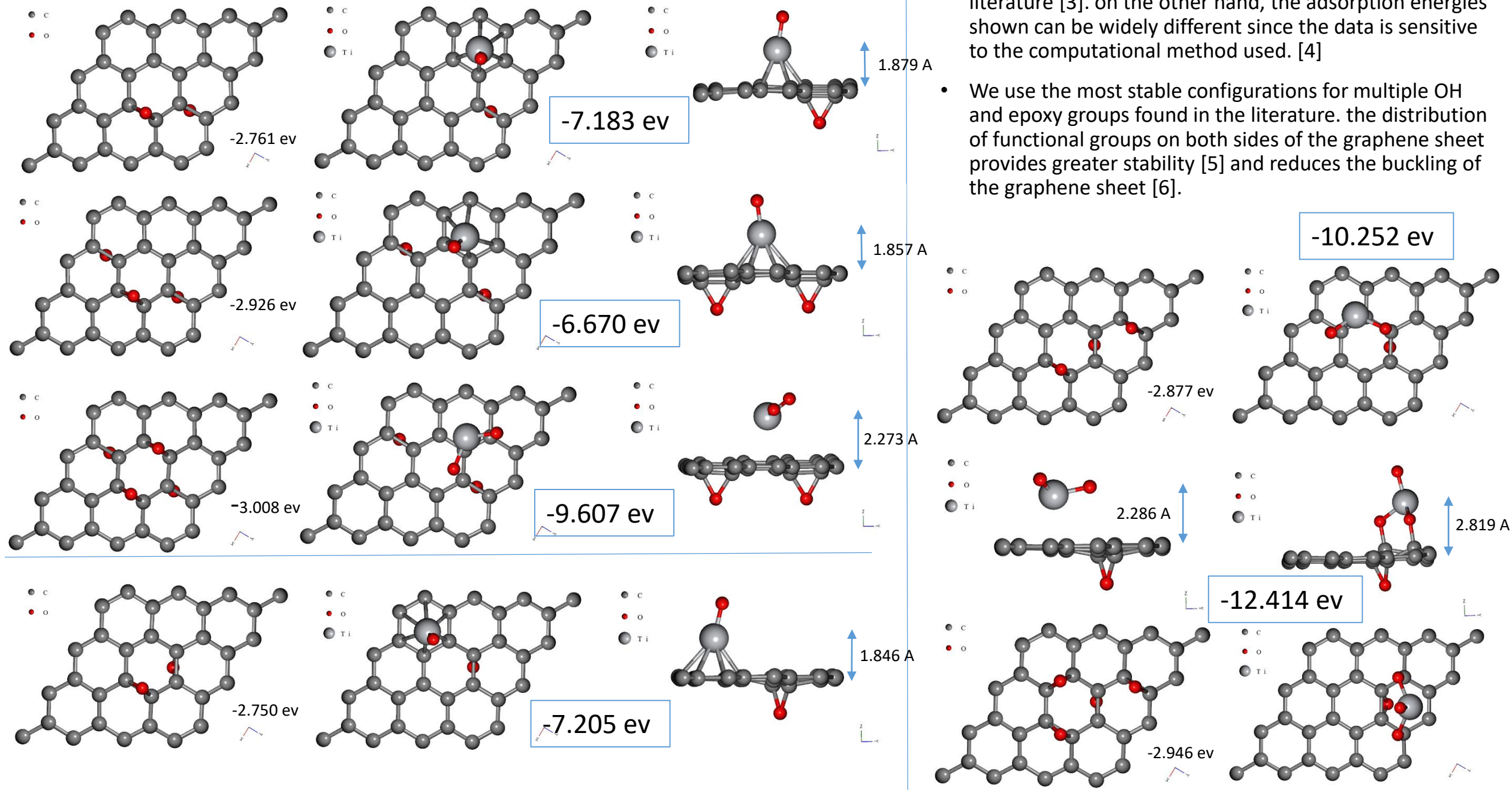
OH/graphene					
	2x2	3x3	4x4	5x5	6x6
Energy (ev)	-0.733	-0.8	-0.9	-0.884	-0.924
C-O (Å)	1.513	1.506	1.505	1.504	1.504
O-H (Å)	0.977	0.976	0.976	0.976	0.976
O/graphene					
	2x2	3x3	4x4	5x5	6x6
Energy (ev)	-2.375	-2.447	-2.467	-2.436	-2.487
C-O (Å)	1.472	1.460	1.462	1.460	1.461
C-C (Å)	1.477	1.506	1.512	1.519	1.518

Ti on nOH/graphene



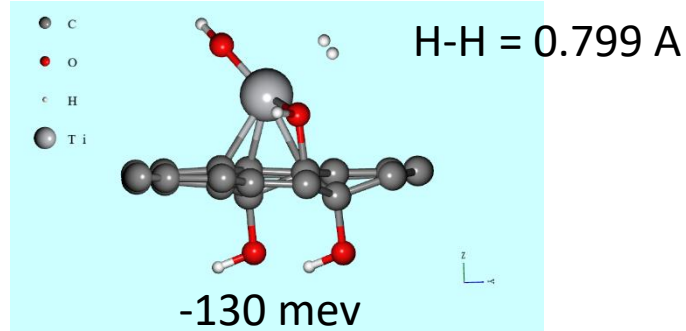
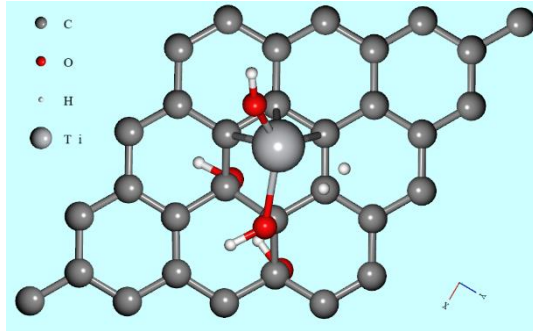
- the adsorption energy with respect to the pure graphene of each group converges to a limit value as the size of the supercell increases.
- the hydroxyl group is preferentially adsorbed on top of the carbon atom and H pointing towards the center of the hexagon.
- absorption breaks one of the pi bonds of C-C and transforms hybridization from sp² to sp³. slightly shifting the Oh-bound carbon out of the graphene sheet.
- the epoxy group has an oxygen bridging between two carbon atoms, the bonding distance between these carbons is slightly greater than the distance between carbons for pure graphene. and both carbons are also slightly shifted out of the graphene sheet

Ti on O/graphene

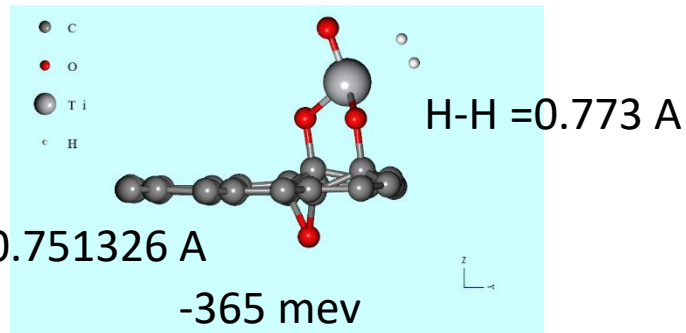
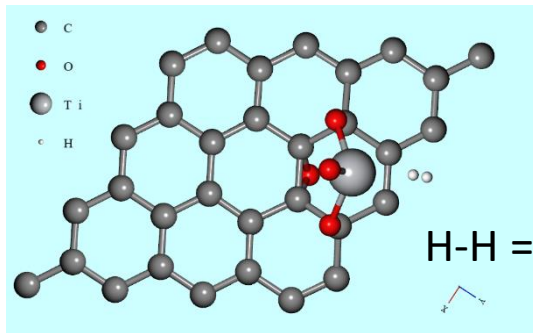


- the structures obtained are in good agreement with the literature [3]. on the other hand, the adsorption energies shown can be widely different since the data is sensitive to the computational method used. [4]
- We use the most stable configurations for multiple OH and epoxy groups found in the literature. the distribution of functional groups on both sides of the graphene sheet provides greater stability [5] and reduces the buckling of the graphene sheet [6].

Ti on O/graphene + H2



Ti on OH/graphene + H2



- the formation of hydrogen bonds is observed, and the increase in the adsorption energy per functional group when the number of functional groups increases for all the arrangements.
- the energy of adsorption of epoxy groups is greater than that of hydroxyl groups. however, stability improves when both groups coexist [6].
- the bond of the hydrogen molecule slowly increases

- there is improved physisorption with adsorption energy within the energy window required for hydrogen storage applications [5]
- the titanium atom is strongly adsorbed in all the arrangements indicating good stability and that in the synthesis of this composite material there will be a low agglomeration of titanium atoms.

References

- [1] V. Jain and B. Kandasubramanian, "Functionalized graphene materials for hydrogen storage," *J. Mater. Sci.*, vol. 55, no. 5, pp. 1865–1903, 2020, doi: 10.1007/s10853-019-04150-y.
- [2] M. Mohan, V. K. Sharma, E. A. Kumar, and V. Gayathri, "Hydrogen storage in carbon materials—A review," *Energy Storage*, vol. 1, no. 2, p. e35, Apr. 2019, doi: 10.1002/est2.35.
- [3] J. A. Yan and M. Y. Chou, "Oxidation functional groups on graphene: Structural and electronic properties," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 82, no. 12, pp. 21–24, 2010, doi: 10.1103/PhysRevB.82.125403.
- [4] K. P. Katin, V. S. Prudkovskiy, and M. M. Maslov, "Chemisorption of hydrogen atoms and hydroxyl groups on stretched graphene: A coupled QM/QM study," *Phys. Lett. Sect. A Gen. At. Solid State Phys.*, vol. 381, no. 33, pp. 2686–2690, 2017, doi: 10.1016/j.physleta.2017.06.017.
- [5] L. Wang *et al.*, "Graphene oxide as an ideal substrate for hydrogen storage," *ACS Nano*, vol. 3, no. 10, pp. 2995–3000, 2009, doi: 10.1021/nn900667s.
- [6] N. Ghaderi and M. Peressi, "First-principle study of hydroxyl functional groups on pristine, defected graphene, and graphene epoxide," *J. Phys. Chem. C*, vol. 114, no. 49, pp. 21625–21630, 2010, doi: 10.1021/jp108688m.