Water at the Interface Between Defective Graphene and Cu or Pt (111) Surface

Daniele Perilli,[a] Lara Ferrighi,[a] Daniele Selli[a] and Cristiana Di Valentin[a]

[a]*Università di Milano-Bicocca, Dipartimento di Scienza dei Materiali, Via R. Cozzi, 55 Milano - ITALIA*

e-mail: d.perilli@campus.unimib.it

The presence of defects in the graphenic layers deposited on metal surfaces[1] modifies the nature of the interaction.[2] Unsaturated carbon atoms, due to vacancies in the lattice, form strong organometallic bonds with surface metal atoms that highly enhance the binding energy between the two materials. We investigate by means of a wide set of dispersion-corrected density functional theory calculations how such strong chemical bonds affect both the electronic properties of these hybrid interfaces and the chemical reactivity with water, which is commonly present in the working conditions. We compare different metal substrates (Cu vs Pt) that present a different type of interaction with graphene and with defective graphene. This comparative analysis allows us to unravel the controlling factors of water reactivity, the role played by the carbon vacancies and by the confinement or "graphene cover effect".[3,4] Water is capable of breaking the C–Cu bond by dissociating at the undercoordinated carbon atom of the vacancy, restoring the weak van der Waals type of interaction between the two materials that allows for an easy detachment of graphene from the metal, but the same is not true in the case of Pt, where C–Pt bonds are much stronger. These conclusions can be used to rationalize water reactivity at other defective graphene/metal interfaces.[5]

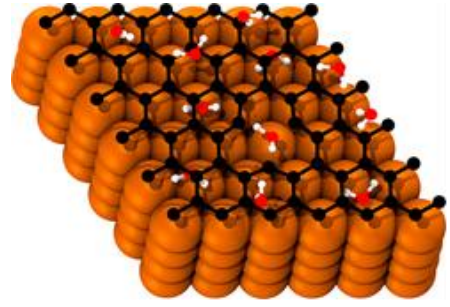

Figure 1: H_2O reactivity on top and at the graphene/metal interfaces.

1. M. Batzill, *Surf. Sci. Rep.* **2012**, 67, 83−115
2. E. N. Voloshina, Y. Dedkov, *Mater. Res. Express* **2014**, 1, 035603
3. H. Li, J. Xiao, Q. Fu, X. Bao, *Proc. Natl. Acad. Sci. USA* **2017**, 114, 5930-5934
4. L. Ferrighi, M. Datteo, G. Fazio, C. Di Valentin, *J. Am. Chem. Soc.* **2016**, 138, 7365-7376
5. L. Ferrighi, D. Perilli, D. Selli, C. Di Valentin, *ACS Appl. Mater. Interfaces* **2017**, 9, 29932-29941