Curvature-dependent reactivity of graphene for storage applications

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Graphene's strength and extreme flexibility allow sustained ripples in a wide range of amplitudes and wavelengths [1]. Ripples produce a modulation of the local curvature, which is strongly correlated with the stability of chemisorbed hydrogen atoms [2]. Curvature induced local pyramidalisation, i.e. pushing a carbon site towards the sp3 configuration, contributes to the increase of graphene's reactivity [3]. Thus, the functionalization of curved graphene with hydrogen, or other adatoms, gives the possibility to tune its chemical and adsorption properties for storage and other applications [4].

While atomic hydrogen adhesion is a spontaneous process with a very small barrier, molecular hydrogen (H2) chemisorption process is characterized by a barrier high on the order of ~1.5ev/atom [5], making the kinetics of loading very slow. Moreover, H tends to stick onto convexities [2,5] and to detach from concavities on the curved graphene. In this work, we address the H2/graphene interaction useful for H-storage applications [4] as well as for the general understanding of graphene morphology/reactivity relationship. We propose that curvature manipulation could be used to improve the adhesion kinetics. To this aim, we perform a systematic density functional theory (DFT) based study to evaluate the dependence of chemi(de)sorption barriers on curvature. We use different density functionals and dispersion corrections to DFT [6] on the model systems with various levels of corrugation generated by lateral compression of the isolated sheet [3], chosen to approximate the symmetry of natural rippling of graphene grown on SiC. We evaluate the chemi(de)sorption profiles by means of nudged elastic band technique [7] with and without effects of an external electric field to estimate the levels of curvature needed to use this effect in a real device [8]. An electric field orthogonal to the graphene sheet is likely to enhance the effect of curvature [9]. Calculations are ongoing.

References

[1] Z F Wang et. al., Phys Rev B 83 (2011) 041403(R)
[2] V Tozzini, V Pellegrini J Phys Chem C 115 (2011) 25523
[3] A Rossi et. al., J Phys Chem C 119 (2015) 7900
[4] F Bonaccorso et. al., Science 347 (2015) 1246501
[5] S Goler et. al., J Phys Chem C 117 (2013) 11506
[6] a) M Dionet et. al., Phys Rev Lett 92 (2004) 246401 b) K. Leeet. et. al., Phys Rev B 82 (2010) 081101 c) S Grimme J Comp Chem 27 (15) (2006) 1787
[7] G Henkelman et. al., J Chem Phys 113 (22) (2000) 9978
[8] K Kakhiani, V Tozzini in preparation
[9] Z M Ao and F M Peeters App Phys Lett 96 (2010) 253106