Manipulating graphene properties at the nano-scale

V.D. Camiola^{1,2}, R. Farchioni^{1,2}, T. Cavallucci², A. Rossi², T Mashoff³, Y Murata^{1,2}, V. Pellegrini^{4,2}, C. Coletti³, S Heun^{1,2}, F Beltram², V. Tozzini^{1,2} *

¹ Istituto Nanoscienze del Cnr, Piazza San Silvestro 12, 56127 Pisa, Italy

² NEST-Scuola Normale Superiore, Pisa, Italy

³CNI@NEST, Istituto Italiano di Technolgia Pisa, Italy

⁴ Graphene labs, Istituto Italiano di Technolgia Genova Italy

In spite of its exceptional properties, for many applications bare graphene is not optimal. For instance, it is a conductor with exceptional mobility, but with null density of states at the Fermi level, therefore it requires either doping to create charge carriers, or gap opening to become semiconductor[1,2]. Its low weight and exceptional resistance makes it an optimal candidate as a medium for gas storage, but it is physically and chemically rather inert, implying either a too slow kinetics of loading/release or a low gravimetric density at room temperature. In addition this task requires building 3D graphene based frameworks with specific structural properties[3]. In order to endow graphene with needed properties, great efforts are devoted to its manipulation, including chemical functionalization, decoration or substitution with different chemical species, or defects creation. Clearly, the rational and efficient functionalization would require controlling location and distribution of defects/adatoms.

To this aim, we recently proposed to explore one of the most peculiar properties of graphene, namely its capability of supporting nano-sized ripples, and their propagating counterpart, i.e. flexural phonons. Starting from the observation that chemical reactivity is enhanced on the convexity and decreased on concavities[4,5], we proposed to use this effect as the basis of a possible device for hydrogen chemisorption and subsequent curvature-inversion induced release. However, manipulating curvature would control reactivity in general. Therefore a static curvature pattern could be used also to drive, metal adhesion or defects creation in specific locations[7], and eventually chemical functionalization e.g. with pillar molecules for 3D graphene base frameworks creation. Furthermore, simulations shows that coherent flexural phonons can create nano-cavities capable of transporting and pumping gases through graphene multilayers, though enhancing the storage capabilities[8,9].

All of these applications rely on the possibility of controlling (statically or dynamically) graphene curvature at the nano-sale. To this aim, we investigated different strategies, namely electromechanical pulling on rugged substrate, interaction with external electric fields (related to flexo-electricity), coupling to piezo-electric substrates, optical control, by means of functionalization with optically active molecules. These concepts are illustrated reporting combined simulation-experimental studies on supported and suspended graphene.

References

[1] F Bonaccorso, L Colombo, G Yu, M Stoller, V Tozzini, A C Ferrari, R S Ruoff, V Pellegrini, Science 347, (2015) 1246501

- [2] V Tozzini, V Pellegrini Phys Rev B 81, (2010) 113404
- [3] V Tozzini, V Pellegrini Phys Chem Chem Phys, 15 (2013) 80
- [4] V Tozzini, V Pellegrini J Phys Chem C, 115 (2011) 25523
- [5] A Rossi, S Piccinin, V Pellegrini, S de Gironcoli, V Tozzini J Phys Chem C 119, (2015) 7900
- [6] S Goler, C Coletti, V Tozzini, et. al. J Phys Chem C 117 (2013) 11506-
- [7] T Mashoff, D Convertino, V Miseikis, C Coletti, V Piazza, V Tozzini, F Beltram, S Heun App Phys Lett 106, (2015) 083901
- [8] V D Camiola, T Cavallucci, A Rossi, V Pellegrini, V Tozzini Front Mat, 2 (2015) 00003
- [9] VD Camiola, R Farchioni, V Pellegrini, V Tozzini 2D Mater 2, (2015) 014009

[10] This work was supported by EU, 7th FP, Graphene Flagship (Contract No. NECT-ICT-604391), by the CINECA Award " ISCRA C" IsC10_HBG, 2013, PRACE " Tier0" Award Pra07_1544, and IIT "Compute platform"



Figure 1: Illustration of the potential applications of graphene rippling. Natural corrugation of graphene on SiC naturally attracts hydrogen, and possibly substitutional and structural defects. These in turn could be seeds for chemical functionalization with pillar molecules. Propagating ripples (i.e. flexural phonons) can detach and transport hydrogen.