

Morphing graphene at the nano-scale: from simulations to applications

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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, storage applications require building 3D graphene based frameworks with specific structural properties[3]. In order to endow graphene with necessary properties, one needs controlling its structure at the nanometric level. This in principle can be done in several ways: the “chemical way” includes substitutions of graphene carbon with other elements (usually with B or N), adhesion of atoms or chemical groups, deposition of molecular clusters, usually metallic[4]. The “structural way” includes creation of defects and (static or dynamical) corrugation.

Our work is devoted to address the issues of nano-scale graphene morphing for specific applications in energy (hydrogen) storage. We first show the existence of a quantitative relationship between the “chemical way” and the “structural way”: not only the presence of defects, but also the corrugation is related to the local reactivity of graphene, which is enhanced on convexities[5-7]. While the possibility of using this property as a way to overcome the problem of slow kinetics of operation in chemisorbed based H-storage systems was already proposed and demonstrated in dynamical simulations[6], a systematic study on the dependence of activation barriers for chemisorption on the local graphene curvature is in progress[8]. This will lead to the possibility of controlling the concentration and location of chemically ad-groups (e.g. anchors for pillars molecules) onto the graphene surface to subsequently build 3D frameworks with specific structural properties. In addition, we show that controlled decoration of graphene with H leads to tailored electronic properties: we specifically found a quantitative relationship between the electronic band gap and the H coverage, which could be used to tailor the graphene for nano-electronics applications, or, the other way round, to measure the H coverage by means of an STS measurement [6].

All mentioned results rely on the possibility of controlling the local curvature. We show that while dynamical rippling control such as that allowed by flexural phonons can create nano-cavities capable of transporting and pumping gases through graphene multilayers [9,10], the substrates onto which graphene is grown can also be used to manipulate curvature. For instance, we will show that opposite corrugation patterns of graphene on SiC are almost degenerate in energy and can be selectively stabilized by changing environmental conditions[11] such as temperature and electric fields[12] allowing a controllable curvature manipulation and inversion. Finally, the morphology of the quasi free standing graphene layer obtained by substrate passivation can be changed by environmental dependent induction of defects in the H passivation layer[13]. We will show preliminary simulation results illustrating the relationship between structure and electronic properties in this system.

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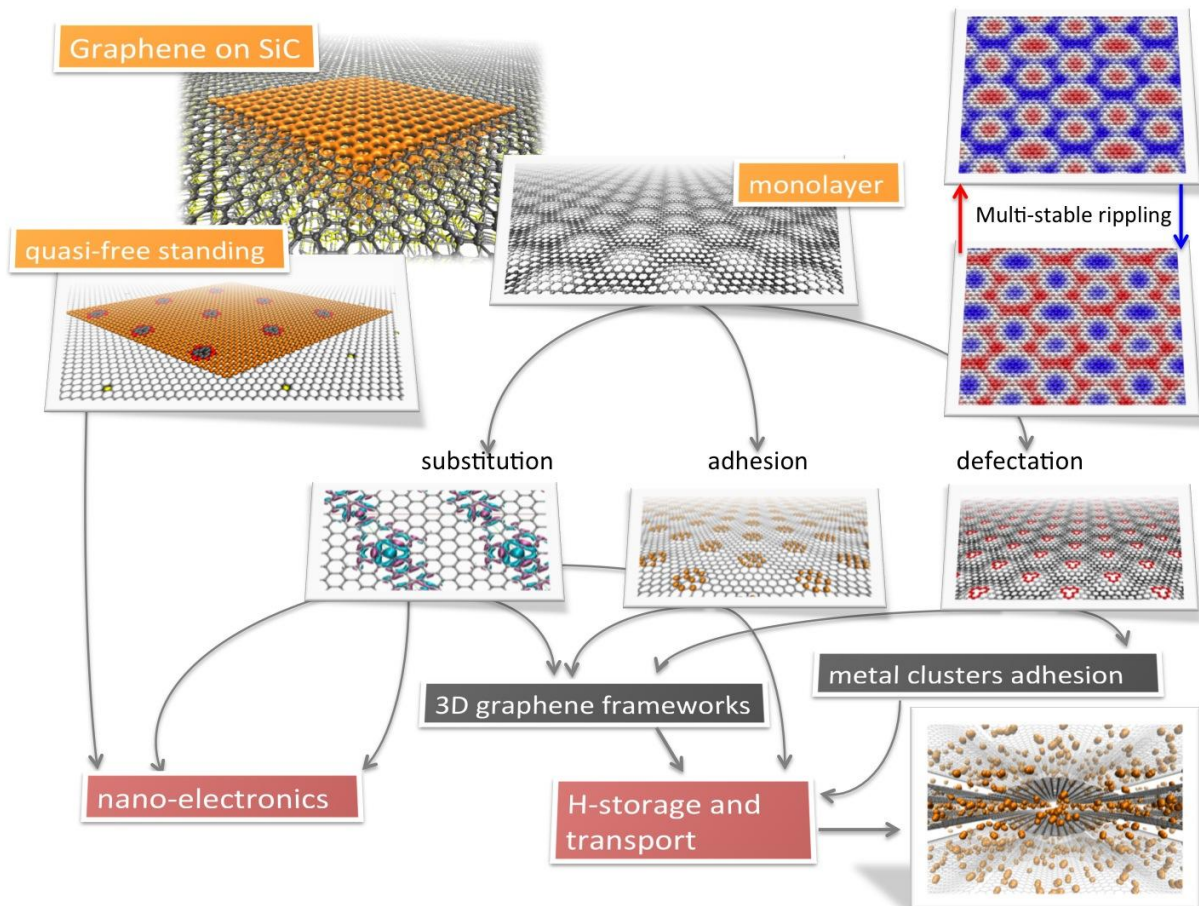


Fig 1 Schematic representation of possible morphological manipulation of epitaxial graphene. Rippled, defected substituted and H decorated graphene are represent. Rippling is either directly shown or represented with color coding (red/blue for protruding/intruding). Carbon is generally represented in gray, H in white or in orange. Charge density surfaces are represented in orange or in cyan-pink.