## 1.3.11 Hydrogen storage in functionalized graphene

Owing to its large surface-to-mass ratio, graphene is a promising candidate for hydrogen storage. However, hydrogen is weakly physisorbed by graphene so that useful storage densities can be achieved only at low temperature/high pressure. Conversely, chemisorption leads to stable loading at room temperature, but with slow kinetics. We have investigated both physi- and chemisorption of hydrogen on functionalized graphene in the perspective of improving its performance for applications.

All amazing properties of graphene – high carrier mobility, robustness and flexibility, broadband transmittance, large surface to mass ratio, lubricity – rely on its being a perfect 2D hexagonal crystal. However, this brings also some drawbacks, such as zero density of states at the Dirac point, weak interactions and reactivity, limiting its potential both in nanoelectronics and in storage applications. These, in addition, require functionalization or building 3D graphene-based scaffolds. We combine Density Functional Theory (DFT), classical Molecular Dynamics (MD), Scanning Tunneling Microscopy (STM), Low Energy Electron Diffraction (LEED), and nanocalorimetry to the aim of functionalizing and morphing graphene for energy applications. To these aims, graphene imperfections acquire a new significance: the crystal symmetry breaking through chemical defects, structural deformations, or other types of disorder creates electron density inhomogeneities with an enhancement of reactivity and new interaction capabilities.

Our work focuses mainly on epitaxial monolayer graphene grown on SiC. Both the buffer layer on SiC [1,2], obtained by Si evaporation and partially covalently bound to the substrate, and quasi free-standing monolayer graphene (QFMLG) [2-5], obtained by metal [6] or H intercalation [2,5], show possible "hot spots" of chemical reactivity located on nanosized super lattices, which could be exploited for chemical nanopatterning. On the other hand, grain boundaries of supported nanocrystalline graphene are shown to pin Ti clusters more efficiently than single-crystalline graphene [7].

In the last years we have performed combined Density Functional Theory (DFT) and Scanning Tunneling Microscopy (STM) studies of graphene with different kinds of irregularities. Starting from carbon layers epitaxially grown on silicon carbide (SiC) by Si evaporation, the covalently bond buffer layer (BL) can be viewed as extremely distorted graphene, because its structures includes a large portion of sp^3 hybridized sites, organized on a nanosized superlattice. Our DFT studies [1] reveal the space-resolved electronic structure of the system as well as the location and shape of localized states, and give indications on the reactivity of the different sites to additive or substitutive reactions, which could be exploited for controlled nanopatterning. Conversely, quasi free-standing monolayer graphene QFMLG, formed by hydrogen intercalation under the BL, is completely sp^2 hybridized, but the regularity of the electronic structure is disrupted by the presence of localized states in correspondence to H vacancies. By means of a combined STM-DFT [3,4] study we have completely characterized these states, which appear to locate on a regular nanosized super lattice [5] and have various shapes and tunable energy depending on their size, opening opportunities in optoelectronics and controlled chemical nanopatterning (Fig. 1) [8].

	1H	3H	4H
Dangling bond			
Simulated AFM			
Simulated STM			
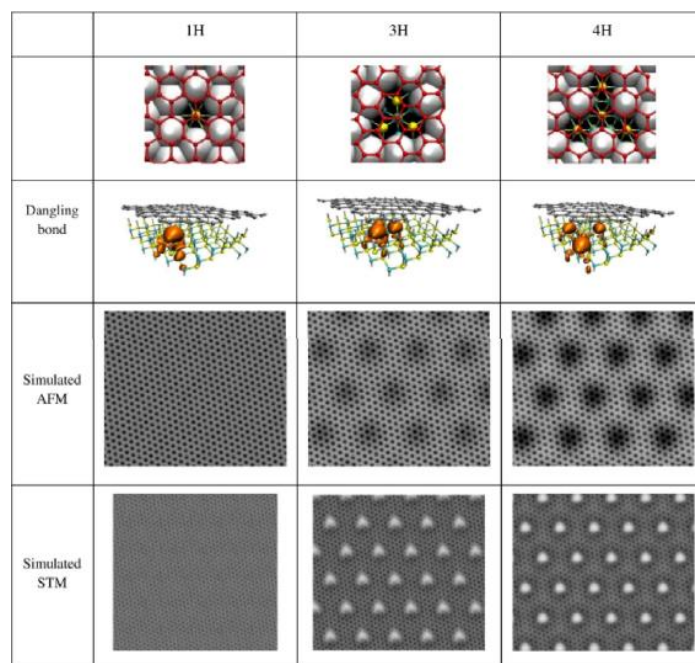
Figure 1. Theoretical analysis of the structure of vacancies with one, three, and four missing H atoms (columns 1H, 3H, 4H). The fully relaxed structure models of the vacancies are represented in the first row, where the graphene lattice, Si, and substrate C atoms are colored red, yellow, and cyan, respectively. H atoms are represented by white spheres. Second and third row are the simulated AFM and STM images, respectively. From Ref. [4].

The graphene functionalization with Ti has been widely investigated in several samples: epitaxial monolayer graphene (EMLG) [9-11], CVD grown graphene [12], and nanocrystalline graphene grown on Ge(110) [7]. Corrugation and other kinds of structural defects can favor the adhesion of metal clusters (e.g. Ti) [11]. We showed that grain boundaries of nanocrystalline graphene are attractors for Ti clusters [7], which form a larger amount of smaller Ti islands on it than on monocrystalline graphene. The hydrogen uptake has been investigated as a function of Ti coverage up to about 1 ML [9]. Hydrogen is capable of different kinds of binding modes with the Ti clusters, both in atomic and molecular form [10]. In other words, hydrogen exploits both physisorption and chemisorption on such samples, but physisorption can be observed at low temperatures only. The physisorption of H_2 on functionalized graphene has been studied by thermal desorption spectroscopy (TDS), utilizing epitaxial monolayer graphene (EMLG) [10] and nanocrystalline graphene (Fig. 2) [7]. In both cases, however, the main feature that has been observed is related to chemisorption. Indeed, the nanocrystalline samples show a lower chemisorption yield than the EMLG samples. This effect is related to the strong bonds between Ti and the defects on the surface, which influences the electronic structure of the Ti clusters.

A particular effort has been made to study the energetics of the hydrogen storage process. Therefore, beside the well-established TDS evaluation of the H_2 binding energy, an original calorimetric technique has been developed [12]. The technique allowed, for the first time, both to measure the heat released during the hydrogenation process in real time and the non-destructive quantification of the hydrogen stored, with an extremely high sensitivity (5 µJ and 0.2 ng). Our

nanocalorimeter is based on a gold film thermometer as detector. The thermometer has been upgraded recently utilizing a mica substrate, which allows for a better performance and has an atomically flat surface, suitable for STM analysis [13].
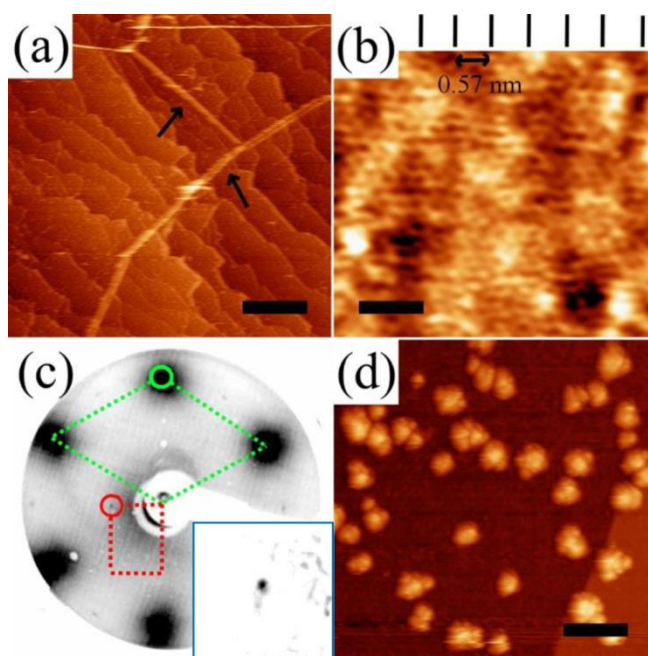
Figure 2. Ti on nanocrystalline graphene. (a) STM image, scan size 1000 nm x 1000 nm. (b) STM image, scan size 5 nm x 5 nm. Vertical lines indicate the periodicity of the Ge(110)-[110] lattice. (c) LEED pattern with electron energy 75 eV. (d) STM image after Ti deposition of 0.55 ML, scan size 100 nm x 100 nm. From Ref. [7].

Hydrogen chemisorption has been widely investigated in structurally deformed graphene [14]. Our idea is to exploit the natural corrugation of graphene grown on SiC to enhance one or more of the mentioned features. The moiré pattern of corrugation is multi-stable and can be manipulated by changing environmental conditions (e.g. temperature, external fields). This in turn opens the possibility of manipulating reactivity, which is shown to be larger on convexities. This increases the adhesion of hydrogen in atomic form (Fig. 3). Besides, electric [15] or electrochemically driven functionalization is shown to be a viable route to control H adhesion, and is enhanced by the presence of structural defects such as epoxy or hydroxyl groups produced by oxidation so to allow the combination of H-storage with water splitting for new concept devices in the clean energy field.
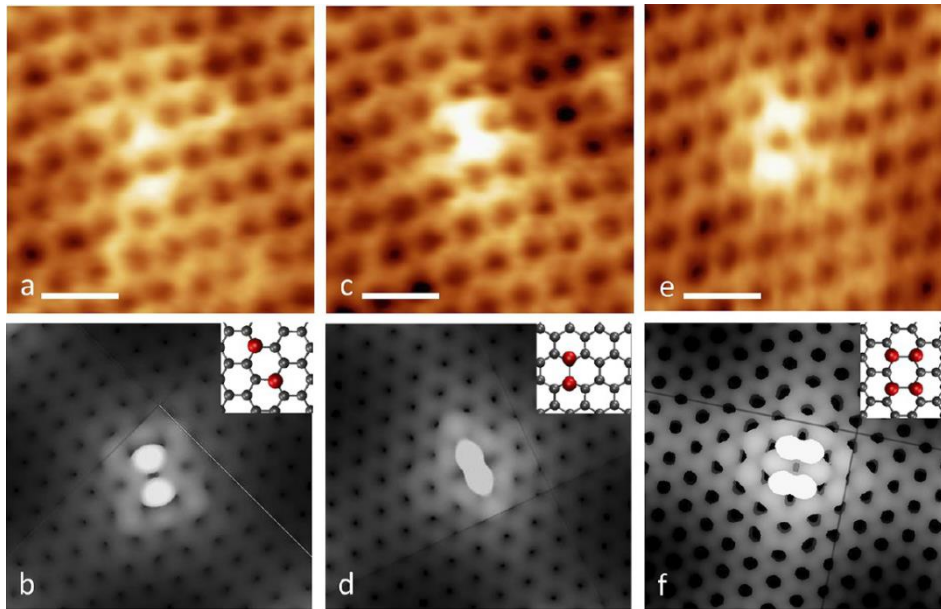
Figure 3. (a) A para dimer observed by STM on EMLG after a dose of 5 s of atomic hydrogen. (b) Simulated STM image by DFT calculation. (c) STM image of an ortho dimer and (d) corresponding simulation. (e) STM image of a tetramer and (f) corresponding simulation. Scale bar in (a), (c), (e) is 0.4 nm. From Ref. [14].

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