

Graphene engineering: new opportunities for controlled functionalization and energy storage

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 null density of states at the Dirac point, weak interactions and reactivity, limiting its potential both in nano-electronics 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 Nano-calorimetry to the aim of functionalizing and morphing supported graphene for energy applications.

To these aims, graphene imperfections acquire a new significance: the crystal symmetry breaking by chemical defects, structural deformations, or other types of disorder creates electron density inhomogeneities with an enhancement of reactivity and new interaction capabilities [1]. This is the case both for the buffer layer on SiC [1], obtained by Si evaporation and partially covalently bound to the substrate (Figs. 1a,b) and for quasi free-standing monolayer graphene (QFMLG) [2,3] obtained by metal or H intercalation (Figs. 1a,c). Both show possible “hot spots” of chemical reactivity located on nano-sized super lattices, which could be exploited for chemical nano-patterning.

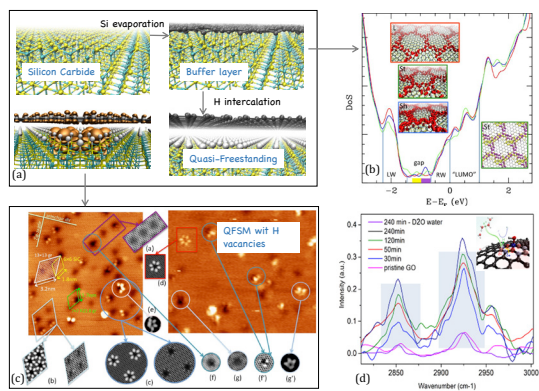


Fig. 1

(a) A scheme illustrating the production of different types of graphene on SiC and their main structural characteristics. From the SiC bulk (upper left) one obtains the buffer layer by Si evaporation. Intercalating metals or H, one obtains QFMLG. If the H coverage is not complete, localized electronic states form between the substrate and the graphene layer (orange surfaces in the bottom left image). The color-coding for atoms in structures is: yellow = Si, cyan = C in the substrate, grey = C in graphene, white = H. (b) Details of the total and local density of states of the buffer layer (from [2]). The total DoS is

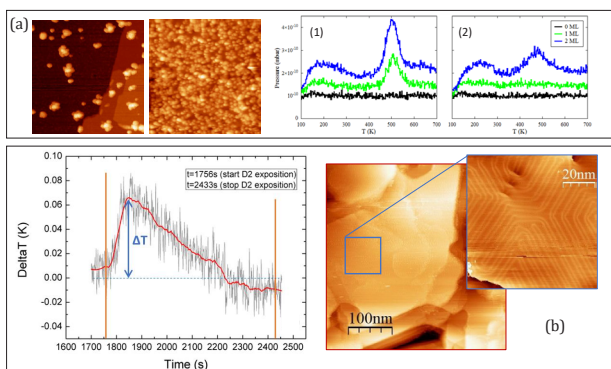
reported at the top for three slightly different model systems and shaded up to the Fermi level. The system appears a doped semiconductor with some localized states in the ~ 1 eV gap. The electronic density of the in-gap states is reported as insets in the enlarged DoS plot at the bottom, as red isosurfaces (total DoS integrated in the gap, for the three different models), and in yellow-purple, for two separated sets of in-gap states. (c) An illustration of the different types of localized vacancy states that can be found in QFSMG (orange = STM images, grey = STM simulated images). The experimental images show that vacancies are located over a nano-sized lattice, although not all sites are occupied. However, the sizes, shapes, and contrasts are various. The simulations show that these differences depend on the number and relative location of the H-vacant sites, allowing at the same time to classify a large number of different vacancy types. From [3,4]. (d) Raman spectrum of the C-H peak to determine the amount of chemisorbed H (images from [5]), as per the water splitting reaction path illustrated in the inset.

On the other hand, grain boundaries of supported nano-crystalline graphene are shown to pin Ti clusters more efficiently than single-crystalline graphene (Fig. 2a) [4]. Besides, electric 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 (Fig. 1d) [5], so to allow the combination of H-storage with water splitting for new concept devices in the clean energy field.

Calorimetry is a powerful tool to investigate the energy exchange due, e.g., to chemisorption, but it usually requires macroscopic sample quantities. We have developed an original experimental setup able to detect temperature variations as low as 10 mK in a sample of ~10 ng using a thermometer device having physical dimensions of 5x5 mm², and used it to measure the enthalpy release during the adsorption process of D₂ on a Ti-decorated monolayer graphene, involving an enthalpy release of ~ 23 μJ [6]. Further upgrades and combination with atomically resolved microscopy techniques show an improvement of sensitivity up to 4 mK at room temperature (Fig. 2b).

Fig. 2

H adhesion on graphene of different types. (a) STM images of single-crystalline graphene (1-left) and nano-crystalline graphene (2-left) after Ti deposition of 0.55 ML. TDS on (1-right) single-crystalline graphene and (2-right) nanocrystalline graphene, with Ti coverage of 0 ML (black), 1 ML (green), and 2 ML (blue). Hydrogen uptake is higher in single crystalline graphene [4]. (d) Heat release during the hydrogenation of a Ti-graphene sample (left) and surface analysis of a gold on mica thermometer (right) [6]. Zoom-in shows the gold “herringbone” reconstruction.



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