

Graphene Manipulation for Energy Applications

Graphene's exceptional structural and mechanical properties make it potentially applicable in many high tech fields, especially those related to energy and environmental applications. Cnr Nano activity in the last two years was involved in fundamental studies related to the possibility of using graphene in energy storage devices. These require in any case some sort of manipulation. For instance, Hydrogen storage via chemisorption was shown to be enhanced by rippling on SiC due to interaction with the substrate; Hydrogen adsorption can be mediated by transition metal clusters such as Ti. Finally, Li intercalation was also considered as a possible way to functionalize graphene because light-weight metals mediate H_2 adsorption, or to use graphene in batteries.

In this decade after its first observation, it has become clear that for most applications graphene needs some sort of manipulation [1]. Substitutional doping can increase the density of carriers, while any kind of defects (substitutional, structural, or adatoms) can be used to open the band gap. Both of these features are needed for applications in nano-electronics. In the field of substance storage for energy applications (e.g., hydrogen storage or electrolytes adsorption), the problem is the low physisorption level of graphene, which can be enhanced either by structural manipulation (curvature, creation of porosity), or by decorating graphene with metals. Finally, the manipulation of the local reactivity is important for the chemical functionalization with anchor molecules, useful to attach pillars for building 3D superstructures [1].

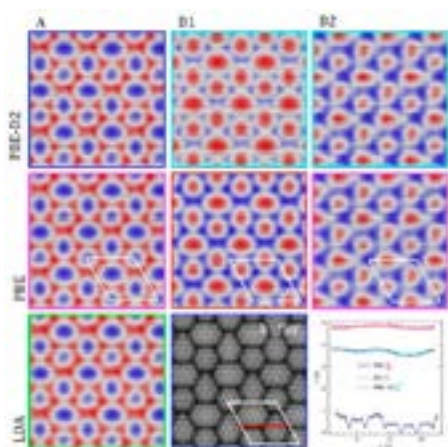


Fig. 1

Graphene monolayer on SiC(0001) with different corrugation patterns color-coded according to height (red protrusion, blue intrusion) as obtained with DFT simulations of the monolayer model system including the full symmetry of moiré pattern and 4 layers of substrate (~1800 atoms). Configurations are evaluated with different functionals (LDA, PBE, and PBE-D2, as indicated) and differ between each other by ~0.2-0.6 eV. In the lower row, the configuration of the buffer layer is also reported (black to grey, protrusion to intrusion), displaying a more pronounced corrugation and more evident moiré pattern. The structural profile of buffer and monolayer with different functionals is reported in the plot.

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 (see Fig. 1) and can be manipulated by changing environmental conditions [2] (e.g., temperature, external fields). This in turn opens the possibility of manipulating reactivity, which is shown to be larger on convexities. Corrugation and other kinds of structural defects can favor the adhesion of metal clusters (e.g., Ti). This increases the adhesion of hydrogen, both in atomic and molecular form, capable of different kinds of binding modes with the Ti clusters [3]. Finally, graphene on SiC was shown capable of efficiently adsorbing Li by intercalation (see Fig. 2), opening the possibility of applications for batteries [4]. The future developments of these studies include their extension to – less ideal but more feasible – nanoporous graphene, a widely studied material currently considered the most viable 3D version of graphene.

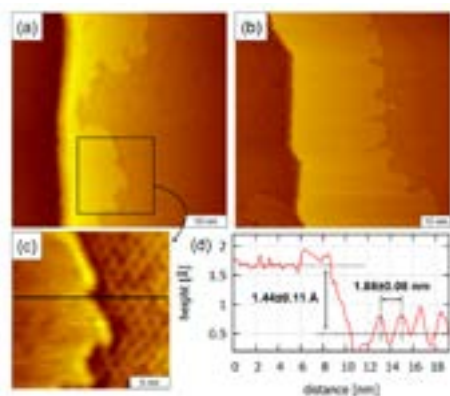


Fig. 2

(a) STM topographical image taken after deposition of 0.031 ML Li on. In the middle there is a flat and not reconstructed region which is identified as the Li-intercalated region. Scan area: 50 x 50 nm². (b) STM topographical image taken after deposition of 0.047 ML Li. The image shows that the Li-intercalated area has grown as compared to (a). The images suggest that Li-intercalation starts from the step edges of the substrate. Scan area: 72 x 72 nm². (c) Magnification taken from the area indicated by the solid square in (a). Scan area: 20 x 20 nm². (d) Cross-sectional plot taken along the black line in (c). From the step height we can calculate by how much the graphene film is lifted up by the Li-intercalation. Image parameters: (a) –500 mV, –170 pA; (b) 1 V, 1 nA; (c) –500 mV, –170 pA.

Contact persons

Valentina Tozzini (valentina.tozzini@nano.cnr.it)
Stefan Heun (stefan.heun@nano.cnr.it)

References

- [1] Morphing Graphene-Based Systems for Applications: Perspectives from Simulations. T. Cavallucci, K. Kakhiani, R. Farchioni, and V. Tozzini. GraphITA. Carbon Nanostructures, 87-11 (2017).
- [2] Multistable Rippling of Graphene on SiC: A Density Functional Theory Study. T. Cavallucci and V. Tozzini. J Phys Chem C 120, 7670-7677 (2016).
- [3] Revealing the Multibonding State between Hydrogen and Graphene-Supported Ti Clusters. K. Takahashi, S. Isobe, K. Omori, T. Mashoff, D. Convertino, V. Miseikis, C. Coletti, V. Tozzini, and S. Heun. J Phys Chem C 120, 12974-12979 (2016).
- [4] Li-intercalated graphene on SiC(0001): An STM study. S. Fiori, Y. Murata, S. Veronesi, A. Rossi, C. Coletti, and S. Heun Phys. Rev. B 96, 125429 (2017).