Epitaxial graphene growth on porous 4H-SiC(0001): a versatile platform for gas storage and sensing

The outstanding properties of graphene rely on its perfect 2D hexagonal crystal structure. However, several applications, such as sensing, energy applications, catalysis, drug delivery, and many others, require a high surface-to-volume ratio and a three-dimensional structure. The growth of epitaxial graphene in a 3D arrangement on the contours of a porous backbone of 4H-SiC(0001) allows the realization of high-quality graphene with a three-dimensional structure (3DG). Indeed, the synergy between the outstanding properties of graphene and a 3D porous structure, circumventing the limits of the 2D nature of graphene, constitutes a breakthrough for many fields.

The porous 4H-SiC material is obtained via a sequence of metal-assisted photochemical and photoelectrochemical etching in hydrofluoric acid-based electrolytes [1]. The fabrication allows the control of the local definition of the pores as well as the degree of porosity with depth. Moreover, the porosification technique allows obtaining stacked layers of different porosity, increasing the versatility of this material. Epitaxial graphene is successively grown on this porous substrate via thermal annealing in an ultra–high vacuum environment. Fig. 1a shows the scanning electron microscopy (SEM) image of a 3DG sample top surface, Fig. 1b the transmission electron microscopy (TEM) image of the cross-section. The role of chemisorption and physisorption, in the hydrogen uptake of 3DG, is investigated by exposing samples to atomic and molecular hydrogen at room temperature and at low temperature (100 K) [2]. We demonstrate, for the first time, the adsorption of molecular hydrogen in 3DG samples (Fig. 1c). Indeed, while the ability of epitaxial graphene to bind atomic hydrogen is well documented, the binding of molec-

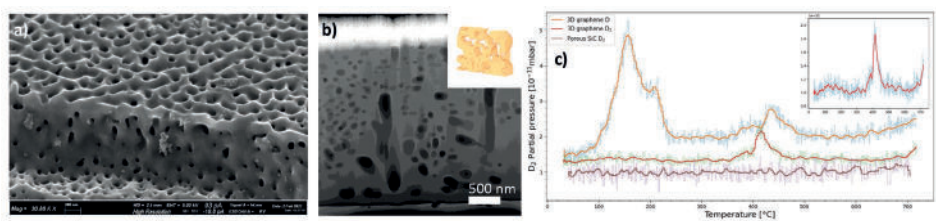

Fig. 1
a) SEM image of the top surface and edge of a 3DG sample after epitaxial growth of graphene at 1370 °C under ultra-high vacuum conditions. b) TEM cross section of a 3DG sample. The inset shows the electron tomographic reconstruction of the porous structure. c) Thermal desorption spectra after hydrogenation of 3DG with atomic and molecular hydrogen. Orange and red curves show the hydrogen desorption peaks after the exposure to atomic (orange) and molecular (red) hydrogen, demonstrating the hydrogen uptake. The lower flat curve is the hydrogenation of the porous SiC before the graphene growth, showing a negligible hydrogen uptake.

ular hydrogen at room temperature has never been reported before. This feature highlights the peculiar characteristics of 3DG in the molecular hydrogen uptake, suggesting that catalytic sites able to split hydrogen molecules are active in 3DG. In view to enhance hydrogen storage efficiency, 3DG samples have been functionalized with metal nanoparticles (Fig. 2a), in particular Au and Pd nanoparticles. Besides, we have utilized a 3DG sample as sensor of the Volatile Organic Compounds related to the degradation of hazelnuts, demonstrating the ability to discriminate between healthy and damaged hazelnuts (Fig. 2b) [3]. Our results open the perspective of sensor development utilizing specific functionalization for the target molecules.

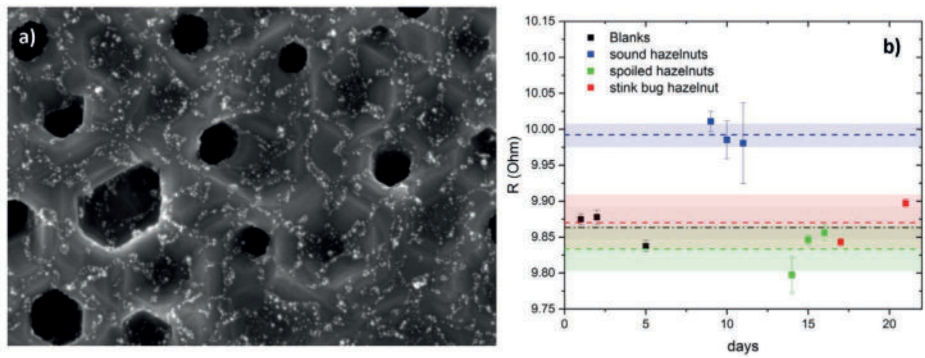

Fig. 2
a) SEM image of the top surface of a 3DG sample after functionalization with Pd nanoparticles. b) Sensor resistance in a series of measurements covering several days. The sensor ability to discriminate between healthy and damaged hazelnut is evident.

Contact persons
Stefan Heun (stefan.heun@nano.cnr.it)
Stefano Veronesi (stefano.veronesi@nano.cnr.it)

References

[1] 3D arrangement of epitaxial graphene conformally grown on porousified crystalline SiC. S. Veronesi, G. Pfusterschmied, F. Fabbri, M. Leitgeb, O. Arif, D. A. Esteban, S. Bals, U. Schmid, and S. Heun. Carbon 189, 210 (2022).
[2] Study of hydrogen absorption in a novel three-dimensional graphene structure: Towards hydrogen storage applications. A. Macili, Y. Vlamidis, G. Pfusterschmied, M. Leitgeb, U. Schmid, S. Heun, and S. Veronesi. Applied Surface Science 615, 156375 (2023).
[3] Three-dimensional graphene on a nano-porous 4H-SiC backbone: a novel material for food sensing applications. S. Veronesi, Y. Vlamidis, L. Ferbel, C. Marinelli, C. Sanmartin, I. Taglieri, G. Pfusterschmied, M. Leitgeb, U. Schmid, F. Mencarelli, and S. Heun. J. Sci. Food Agric. http://doi org/10.1002/jsfa.13118 (2023).