Deterministic Graphene organic functionalization: a controlled functionalization for energy storage and sensing

The outstanding properties of graphene rely on its perfect 2D hexagonal crystal. However, this perfection represents a limit in its use for sensing and storage applications, due to the weak interactions and chemical reactivity. Performance can be improved by increasing the useful surface in 3D arrangements or via functionalization. We achieved organic functionalization of graphene nanosheets and reduced graphene oxide. Next, we induced defects by electron irradiation, in order to control the functionalization. A deterministic functionalization at defect sites has thus been obtained, opening the way towards the controlled synthesis of graphene-based complex structures and devices at the nanoscale.

Organic functionalization of graphene represents a flexible solution for the realization of a platform selectively sensitive to target molecules or atoms, which provides a perspective for a large-scale use in sensing and storage applications. Among the possible routes for an organic functionalization, the use of cycloaddition reaction is one of the most appealing, due to its reversibility and the high controllability of the reaction. This research moves from the random functionalization of graphene, to optimize the reaction parameters, toward a high quality substrate and a fully controlled functionalization. In this framework, organic functionalization of graphene nanosheets (GNS) and reduced graphene oxide (RGO) is successfully performed via 1,3-dipolar cycloaddition of azomethine ylide in the liquid phase [1], and confirmed using various techniques.

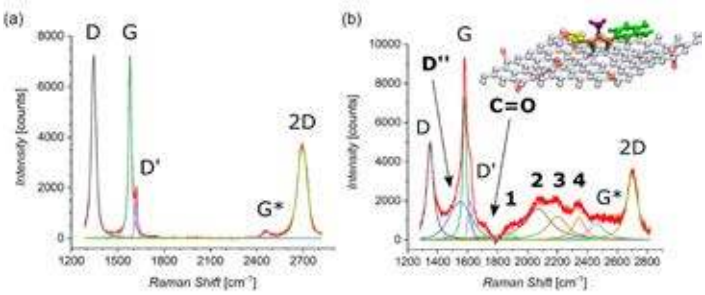

Fig. 1
Raman spectra of (a) pristine GNS and (b) functionalized GNS. The fit of each spectrum is shown and all peaks are labeled (the peaks that appear only after the functionalization of GNS by 1,3-DC of azomethine ylide in N,N-dimethylformamide (DMF) are in bold).

Among them, energy-dispersive X-ray spectroscopy allows to map the pyrrolidine ring of the azomethine ylide on the surface of functionalized graphene, while micro-Raman spectroscopy detects new features arising from the functionalization (Fig. 1), in agreement with the power spectrum obtained from ab initio molecular dynamics simulations. Moreover, XPS of functionalized graphene allows the quantitative elemental analysis and the estimation of the surface coverage, showing a higher degree of functionalization for RGO. This more reactive behavior originates from the localization of partial charges on its surface due to the presence of oxygen defects, as shown by the simula-

tion of the electrostatic features. This behavior suggests the use of defect engineering to control the functionalization (Fig. 2). Therefore, a further step is to induce defects by electron irradiation [L. Basta et al., Surfaces and Interfaces 28, 101694 (2022)] on a high quality exfoliated graphene in order to selectively functionalize the irradiated area with high lateral resolution, obtaining a deterministic functionalization [L. Basta et al., arXiv:2202.06609] (Fig. 3). Deterministic functionalization of graphene using 1,3-dipolar cycloaddition is shown to be a significant step towards the controlled synthesis of graphene-based complex structures and devices at the nanoscale.

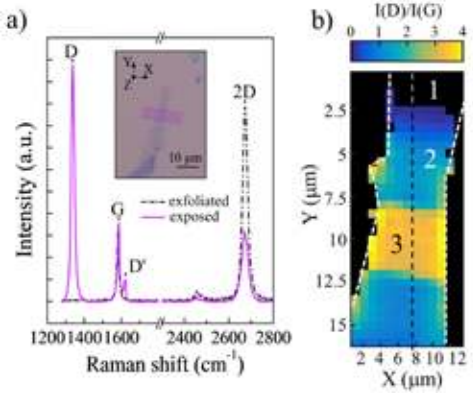

Fig. 2
a) Representative Raman spectrum of as-exfoliated (black dash-dotted curve) and e-beam exposed graphene (violet curve). Inset shows the optical microscopy image of the graphene flake, where the violet area indicates the exposed area. b) Two-dimensional spatial distribution of I(D)/I(G). The white dashed lines indicate the flake edges.

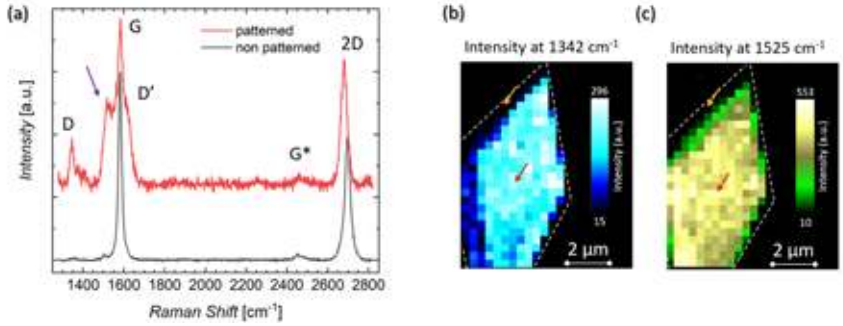

Fig. 3
(a) Raman spectra of a functionalized flake collected in the non-patterned (black line) and patterned (red line) areas of the flake (shifted in height). New Raman features are visible only in the spectrum of patterned functionalized graphene. The arrow indicates the peak used to obtain (c). Raman maps of (b) D peak intensity and (c) intensity at 1525 cm^{-1} collected on the same flake after the functionalization procedure (the white dashed line follows the edges of the flake).

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Reference

[1] Covalent organic functionalization of graphene nanosheets and reduced graphene oxide via 1,3-dipolar cycloaddition of azomethine ylide. L. Basta, A. Moscardini, F. Fabbri, L. Bellucci, V. Tozzini, S. Rubini, A. Griesi, M. Gemmi, S. Heun, and S. Veronesi. Nanoscale Advances 3, 5841 (2021).