Selective Covalent Organic Functionalization Of Patterned Graphene Via 1,3-Dipolar Cycloaddition

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The outstanding mechanical, optical, and transport properties of graphene are of great interest for a plethora of applications. However, these often require graphene manipulation, while preserving its exceptional properties has proved to be extremely complex. A promising strategy to finely tune graphene's physical and chemical properties consists in the covalent functionalization of graphene with organic molecules, resulting in a synergistic combination of the individual features of each component. We report here the selective graphene surface functionalization via electrons irradiation, which allows both a controlled enhancement of the chemical reactivity of high quality graphene flakes and the precise design and engineering of the functionalized area. Pristine exfoliated monolayer graphene flakes are characterized by AFM and Raman spectroscopy, and then exposed to electron beam irradiation with energy of 30 kV and dose of 40.000 µC/cm^2 (as previously reported[1]). Subsequent AFM images clearly resolve the pattern designed by the electron beam, with 0.1 µm step size (Fig. 1a). Raman maps show a homogeneous defects coverage in the exposed area, with the emergence of the characteristic D peak only in the patterned region. Graphene is functionalized via 1,3-dipolar cycloaddition of azomethine ylides. This reaction in-situ involves the localization of a C=C bond, which is favorable in presence of the defects[2], hence introducing a selective control of the chemical modification of graphene. The Raman analysis on the functionalized flakes exhibits new features in the region 1050 – 1750 cm^{-1}, only in the patterned area. Ab initio DFT simulation of the power spectrum of functionalized graphene (model in Fig. 1b) allows to identify the vibrational contribution both of the functional groups of the azomethine ylides grafted on the graphene surface and of the modified vibrational modes of the graphene sheet (Fig. 1c). Finally, under laser irradiation (up to 1.6 mW) the recovering towards the Raman spectrum of non-functionalized defected graphene indicates the desorption of the ylide and the reversibility of the functionalization. Functionalization of patterned 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.

References

[1] L. Basta, et al., arXiv:2103.15725 (2021)

[2] L. Basta, et al., submitted to Nanoscale Advances (2021)
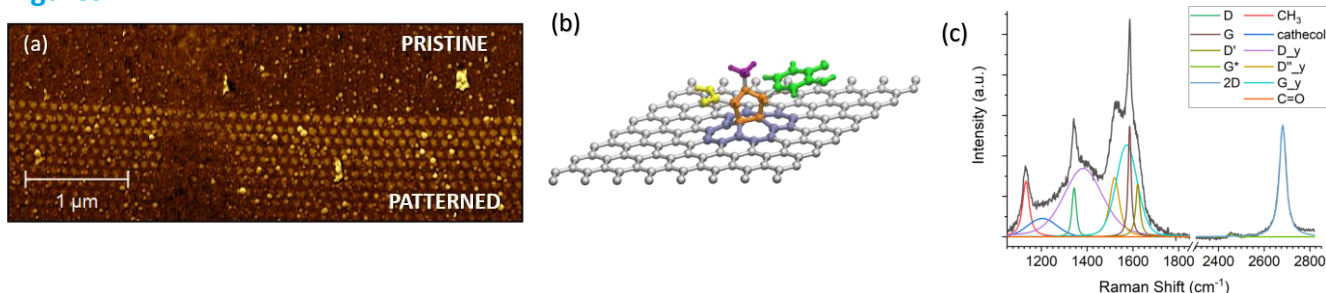
Figures

Figure 1: (a) AFM image showing the defects pattern after electrons irradiation; (b) DFT model of the azomethine ylide attached to graphene (the functional groups of interest are highlighted with different colors); (c) Raman spectrum of functionalized patterned graphene, showing the fit of the new features.