Two-Dimensional Hallmark of Highly Interconnected Three-Dimensional Nanoporous Graphene

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ABSTRACT: Scaling graphene from a two-dimensional (2D) ideal structure to a three-dimensional (3D) millimeter-sized architecture without compromising its remarkable electrical, optical, and thermal properties is currently a great challenge to overcome the limitations of integrating single graphene flakes into 3D devices. Herewith, highly connected and continuous nanoporous graphene (NPG) samples, with electronic and vibrational properties very similar to those of suspended 2D graphene layers, are presented. We pinpoint the hallmarks of 2D ideal graphene scaled in these 3D porous architectures by combining the state-of-the-art spectromicroscopy and imaging techniques. The connected and bicontinuous topology, without frayed borders and edges and with low density of crystalline defects, has been unveiled via helium ion, Raman, and transmission electron microscopies down to the atomic scale. Most importantly, nanoscopy unravels a 3D NPG structure with preserved 2D electronic density of states (Dirac cone-like) throughout the porous sample. Furthermore, the high spatial resolution brings to light the interrelationship between the topology and the morphology in the wrinkled and highly bent regions, where distorted sp² C bonds, associated with sp³-like hybridization state, induce small energy gaps. This highly connected graphene structure with a 3D skeleton overcomes the limitations of small-sized individual graphene sheets and opens a new route for a plethora of applications of the 2D graphene properties in 3D devices.

INTRODUCTION

Graphene is undoubtedly emerging as one of the most promising nanomaterials with high electron mobility, high thermal conductivity, and high tensile strength, opening a new perspective for technological applications ranging from electronics to optics, plasmonics, sensors, and biodevices. Recent years have witnessed many breakthroughs in research on graphene, as well as a significant advance in its mass production. Graphene can revolutionize industrial applications when large-area sheets with the same outstanding performance as the ideal suspended graphene are realized. It maximizes the surface area per weight but, for many devices, it is useful to pack the individual two-dimensional (2D) flakes into a three-dimensional (3D) arrangement to minimize the volume while increasing its surface area. The employment of a single graphene sheet in 3D devices is not straightforward, and a strong research effort is oriented toward the design of such 3D architectures, preserving the remarkable electronic, optical, and transport properties of suspended 2D sheets. The design challenges of 3D nanoporous graphene (NPG) structures are focused on enhancing the surface active areas and on ensuring a topological structure with highly connected layers and negligible density of lattice and edge defects, to engineer physical and chemical properties for the desired functionalities. A number of methods have been employed to prepare graphene in 3D architectures, but the undesired density of...
crystal and topological defects may strongly reduce the electrical and thermal conductivities and influence the operation of electronic devices.

High interconnectivity, low defect density, and tunable nanopore sizes can be obtained by growing high-quality 3D NPG by means of Ni-based chemical vapor deposition (CVD). These NPG samples are not constituted by an assembly of graphene flakes, but they contain thousands of suspended graphene planes stacked in a small volume, with a high crystalline order, continuously interconnected in the 3D space, and decorated with pores in the 0.2−2 μm scale, and they can be an ideal prototype to engineer highly responsive electronic devices.

The realization of 2D graphene millimeter-sized samples with a large surface area (1200 m²/g) into a 3D devices. The hexagonal moiré superstructure (e) and the parallel straight bands (top-left corner of panel d) found in some regions of the NPG sample, depicted by helium ion microscopy (HIM) and transmission electron microscopy (TEM) images reported in Figure 1d,e, where the hexagonal graphene crystal lattice is well visible over a large scale with a well-defined diffraction pattern (f). The hexagonal moiré superstructure (e) and the parallel straight bands (top-left corner of panel d) found in some regions of the NPG sample suggest the presence of misoriented bilayers.

The hexagonal moiré superstructures singled out in the TEM images have periodicities of about 1.4 and 2.4 nm and can be explained by assuming misoriented non-Bernal-stacked AB

### RESULTS AND DISCUSSION

The NPG sample, prepared as detailed in Section 1 of the Supporting Information, after mild annealing in ultrahigh vacuum (UHV) shows high purity and absence of residual contaminants and/or doping, as detected by core-level photoemission spectroscopy (Section 3 of Supporting Information). The free-standing nanoporous 3D graphene sample, depicted by helium ion microscopy (HIM) and transmission electron microscopy (TEM) images reported in Figure 1a−c, presents large flat areas decorated by pores with diameters in the range 0.5−1.0 μm, appearing like a pierced sheet folded in layers with convex and concave curvatures, wrinkles, and interconnected channels without frayed edges. It is worth noticing that the very high surface sensitivity of HIM allows the probing of few graphene layers, thus revealing in detail the 3D and complex nature of the sample morphology of the outermost layer. The high crystalline quality of the sample is deduced by high-resolution TEM images taken at different spatial scales, shown in Figure 1d,e, where the hexagonal graphene crystal lattice is well visible over a large scale with a well-defined diffraction pattern (f). The hexagonal moiré superstructure (e) and the parallel straight bands (top-left corner of panel d) found in some regions of the NPG sample suggest the presence of misoriented bilayers.

The hexagonal moiré superstructures singled out in the TEM images have periodicities of about 1.4 and 2.4 nm and can be explained by assuming misoriented non-Bernal-stacked AB
bilinear with a relative angular shift of about $10^\circ$ and $6^\circ$, respectively, in agreement with the angular difference between the local multi-spot diffraction pattern reported in Figure 1f (see Section 2 of Supporting Information). The straight band modulation seen in a few zones of the sample (see the top-left zone of Figure 1d) can also be attributed to the moiré modulation induced by parallelogram misfit bilayers, owing to the tilted projection as observed by TEM, intrinsic to the warped geometry of NPG.

The sample appears as constituted by a suspended, interconnected, and continuous graphene layer with misoriented bilayers in some regions. The presence of layers with various distances, stacking, orientations, and degree of π-orbital hybridization can be confirmed by spectromicroscopy analysis. A selected micro-Raman spectrum on the NPG sample taken in 300 nm sized pixels is shown in Figure 2d. At first sight, the low intensity of the “D” Raman peak and the high intensity of the “2D” band suggest the presence of a high-quality graphene sample constituted by a majority of interconnected single layers (SLs). In fact, the “G” band (sp$^2$ C–C stretching mode) is at 1580.6 cm$^{-1}$ over the whole sample, the “2D” band (double-resonant second-order mode activated by in-plane breathing of the hexagonal rings) is at 2693.0 cm$^{-1}$, slightly blue-shifted with respect to SL graphene, and the very small “D” band (activated by the presence of lattice defects) is at 1356 cm$^{-1}$, as determined by the fitting analysis (detailed in Section 4.1 of the Supporting Information). The symmetric line shape of the “2D” band rules out effects of π-orbital hybridization between adjacent AB Bernal-stacked graphene sheets, which would induce splitting into four components and a definite band asymmetry.\(^{13,18}\)

A quality proof of the NPG sample can be obtained by mapping the $I_{2D}/I_G$ and $I_D/I_G$ intensity ratios, whose imaging over a $12 \times 12$ μm$^2$ area constituted by $300 \times 300$ nm$^2$ pixels is presented in Figure 2a,b. Large flat areas of hundreds of nanometers are clearly identified for $I_{2D}/I_G$ in agreement with the HIM/TEM images at the same scale. The histogram of the $I_{2D}/I_G$ ratio estimated over the whole probed area (Figure 2c) assesses the high average quality of the sample, with a mean value of the distribution of 2.6 and a width ($\sigma = 0.6$) reflecting the variety of morphological configurations/orientations in this undoped and contaminant-free NPG sample. This high value of the $I_{2D}/I_G$ ratio is consistent with the presence of one-to-two layers of planar graphene, though curvatures in NPG may influence its absolute value.

Uniaxial and biaxial strain effects in the hexagonal lattice in graphene-based systems have been proposed to justify variations of the Raman peak positions associated with the hexagonal lattice change.\(^{19,20}\) Tensile (compressive) strain can induce a phonon softening (stiffening), leading to a red (blue) shift and broadening of the “2D” and “G” bands. We observe a small stiffening of the “2D” band, compatible with a slight compressive strain on the order of 0.3%, likely to be attributed to the drying process after NPG growth. Different orientations between adjacent misoriented bilayers can induce Raman band broadening, in very good agreement with the high-resolution TEM images (Figure 1d,e). Thus, the symmetric line shape of the “2D” band with a wider width (54 cm$^{-1}$) than that expected at SL graphene can be associated with the coexistence of continuous SL graphene with some regions of disoriented non-Bernal-stacked bilayers,\(^{16,22−25}\) owing to NPG preparation on Ni below 1000 °C,\(^{26}\) that can generate turbostratically stacked bilayers.\(^{12,26−28}\)

The non-homogeneous grainy $I_D/I_G$ imaging, mirroring the defect distribution density, is inversely proportional to the $I_{2D}/I_G$ image in terms of brighter versus darker regions (Figure 2a,b).\(^{26}\) This mapping unveils a very low defect intensity, with the presence of $5−7$ lattice distortions from pure hexagons only in the complementary regions where the $I_{2D}/I_G$ intensity ratio is lower, confirming the high-spatial-resolution TEM images.\(^3\) These defects, despite appearing with a very low density, are intrinsically associated with the curvature necessary to warp graphene into the 3D NPG structure, as previously reported in refs 2, 3, and 9. The D/G intensity ratio can also be directly related to the average crystallite size (i.e., average distance between two defects/edges), according to the Tuinstra–Koenig relation:\(^{40}\) $L_s (\text{nm}) = 2.4 \times 10^{-10} \times \lambda^4 / I_D / I_G$. In this NPG sample, average $L_s$ results about 225 nm ($\lambda$ being 532 nm), in agreement with the typical size of the structures as observed in the aforementioned microscopy data.

The Raman spectra demonstrate that the NPG 3D architecture is indeed very similar to that of ideal decoupled and suspended graphene layers, with a low density of defects over all of the NPG sample. These results have been verified also for NPG samples with smaller nanopore size, although the intensity of the “D” Raman peak is slightly higher in this case because of a larger curvature gradient in the pore regions (see Section 4.2 of Supporting Information).\(^5,18\) The topology as observed by HIM, TEM, and Raman microspectroscopy allows us to define this 3D NPG architecture as composed by highly interconnected graphene sheets, where only a slight compressive strain and the presence of rotational misoriented bilayer graphene are observed. These lines of evidence and the absence of interface interactions, frayed borders, and edge defects could provide a novel route to exploit this 3D NPG with the desirable electronic properties of an ideal suspended 2D graphene. However, only a spatially resolved analysis of the electronic states via the very surface-sensitive nanoscanning photoelectron
Spectroscopy can verify whether NPG presents the properties of 2D graphene and whether we can associate different hybridization states and electronic spectral DOS with the different spatial zones of the actual NPG samples, namely, at flat and at bent/wrinkled regions.

The precise topological and structural description obtained by HIM and TEM together with Raman mapping does not give univocal hallmarks of the electronic properties of 2D NPG. The spatially integrated C 1s and valence band spectra of the NPG sample compared with those taken on HOPG are shown in Figure 3a,b. The C 1s centroid (Figure 3a) is located almost at the same binding energy (BE; 284.4 eV) attained at HOPG (284.3 eV), with a broader lineshape likely to be attributed to the presence of C 1s multicomponent at higher BE. The angle-integrated photoelectron spectroscopy valence band data (Figure 3b) allow the identification of both the σ-band, at about 7.7 eV BE, the π-band, centered at about 3.1 eV BE, and a linear spectral density toward the Fermi level, reflecting the typical lineshape measured on suspended graphene. It is worth noting that these data are very surface sensitive, owing to the chosen photon energy (\(h\nu = 350\) and 100 eV, for the C 1s and VB data, respectively) guaranteeing a photoelectron kinetic energy at the minimum escape depth (only few Å). The photoemission data are therefore related to non-interacting graphene layers at the surface of the NPG sample.

Although the averaged spatial signal shows the dominant 2D signatures of suspended graphene, the spatial distribution of the hallmarks of graphene is essential to disentangle the chemical, optical, transport, and electronic properties of NPG structures. In the following, both chemical imaging and electronic imaging, using high energetic and spatial resolution nanoscanning photoemission, have been combined to determine directly the \(sp^2/sp^3\) degree of hybridization throughout the sample as well as its relation with the DOS at the Fermi level. Recently, high energy and angular resolution nanoscanning photoemission measurements of core levels and valence band at a given momentum, with a spatial resolution of a few hundred nanometer scale, have been made possible, combining information on the chemical sensitivity and hybridization state (core levels), with the spectral density close to the Fermi level (valence band) at the same scale. In the last decade, disentangling the actual carbon chemical state in \(sp^2\)-based nanostructures (such as C nanotubes) with a resolution down to few hundred nanometers has been a great challenge. This innovative spectromicroscopy approach applied to the NPG sample paves the way for imaging electronic states at new frontiers because a combined analysis of both the C 1s and the spectral density close to \(E_F\) for graphene structures at the nanoscale is still lacking.

The spatially resolved C 1s mapping of the NPG sample taken on 300 × 300 nm² size pixels is shown in Figure 4. At this...
scale, we clearly identify everywhere in the probed area two components in the C 1s feature, fitted by two asymmetric pseudo-Voigt (Gaussian and Lorentzian) curves, the dominant component centered at 284.4 eV (sp²-like) and the smaller component centered at 285.1 eV, whose energy value suggests its attribution to a distortion of the perfect sp² bonds of graphene toward an sp³-like hybridization state. The relative intensity ratio of the two components varies in the mapping, depending on the topology of the NPG zone.

To correlate the bond distortion with the morphology of the NPG sample, the intensity spatial mappings generated by selecting the energy regions centered on the main component at 284.4 (sp²-like) and on the component at 285.1 (sp³-like) are reported in Figure 4 (middle and right panels, respectively). The images are obtained by integrating the data in a 0.6 eV energy window around 284.4 and 285.1 eV. While we observe the same general diagonal-shaped structures in both images (dominated by the main sp² component), the sp³-like component prevails in the border areas of the elongated tubular regions.

Wrinkles and highly bent regions are indeed expected to induce some of the carbon atoms to partially warp the sp² bonding and rehybridize toward an sp³-like configuration, generating a high BE weight in the spectra. We exclude everywhere in the sample the presence of contaminants or oxidation, as revealed in the survey photoemission spectrum shown in Section 3 of the Supporting Information. Furthermore, the absence of a low-BE component associated with unsaturated in-plane C bonds points out the irrelevant density of edge defects, in agreement with the low “D” band intensity in the Raman spectra. The absence of frayed contours with armchair and/or zigzag edges confirms the coincident topology, as suggested by Ito et al. The nanospectroscopy images in Figure 4 demonstrate that the very 2D graphene properties dominate in the NPG sample, with the prominent sp² C 1s peak and the presence of a small component owing to distorted bonds. We notice that the same analysis carried out on an NPG sample with smaller pore size and higher curvature gradients reveals a slight intensity increase in the sp³-like component, as reported in Section 4.3 of the Supporting Information, but the dominant planar hybridization state is preserved.

The most important spectroscopic signature of 2D graphene is the linear DOS toward the Fermi level, reflecting the Dirac cone band. A detailed spatial mapping can correlate the sample topology to the DOS close to the Fermi level, which could have consequences on the electrical/thermal conductivities of the NPG. Spatially resolved DOS photoelectron spectroscopy data of the NPG sample taken in the first few electronvolts below the Fermi level (E_F) in a 12 x 12 μm² spot, with a high spatial resolution at the submicrometer scale (300 x 300 nm²), are shown in Figure 5a.

A point-to-point analysis of the spatially resolved spectra reveals the importance of data with the following characteristics: (i) a spectral density with a common linear shape toward E_F, in agreement with the expected DOS for ideal graphene with a Dirac cone dispersion, (ii) a peak at about 3.1 eV owing to the 2p-π states, and (iii) a bump associated with σ-π states at higher BE. In few regions, corresponding to the edges of the tubular-shaped forms of the mapping, we observe a reduction in the 2p-π state, which is more intense in pure sp³ hybridization, and it is expected to be reduced as the distortion toward sp³-like bonds progresses, as in hydrogenated graphene. In Figure 5b,c, we present two exemplary VB spectra taken in flat and bent/wrinkled regions of that spectroscopy mapping. By focusing on the binding energies right below E_F, a linear fit perfectly matches the DOS in the flat regions of the sample (inset of Figure 5b), whereas the same kind of fit does not match appropriately the complementary regions (inset to Figure 5c). We suggest these regions to be related to the wrinkled/highly bent areas of the NPG sample, where the presence of the distortion leads to sp³-like hybridized states. By adding a Gaussian contribution to the linear spectral density and multiplying the curve by the edge-like Fermi–Dirac distribution function calculated at 80 K, we observe a tiny finite DOS contribution at a few tenths of electronvolts below the Fermi level.

In summary, the DOS mapping corroborates the spatial resolved spectroscopic results obtained from the sp²-like and sp³-like bonds in Figure 5. Certainly, the feature at ≈3.1 eV BE, with sp³-like character, shows a dominant distribution with areas of the order of several micrometer size. By mapping the total spectral density, the sp³-like distribution persists, indicating that the DOS of the NPG sample is dominated by the electronic 2D graphene-like character. Interestingly,
mapping regions where that feature is less intense are able to show where the sp$^2$-like bonds are present. Furthermore, these results enlighten the powerful approach of nanoscale photoemission, able to precisely unravel and discriminate the coexistence of even small sp$^3$-like deformations in NPG materials strongly dominated by the 2D hallmark of graphene-like structures. In fact, the continuous topology, the absence of defects and sharp edges, and the linear spectral density can ensure a 2D graphene-like electrical conductivity ($10^4$ S/m)$^3$ and mobility ($5000$ cm$^2$/V/s)$^9$ of these NPG sample.

### CONCLUSIONS

These Raman and photoemission nanospectromicroscopy studies unveil that the NPG 3D structure is indeed very similar to that of ideal decoupled graphene layers. Thanks to the state-of-the-art nano-photomission spectroscopy, we are able to correlate local electronic structures with the different spatial regions in a single component sample. The bicontinuous topology, imaged by scaling the spatial resolution down to the 300 nm scale, reveals highly interconnected graphene sheets, with only a slight compressive strain and presence of rotational misoriented bilayers. The very low defect density and the absence of frayed borders and edges optimize the 2D properties of this topologically bicontinuous and connected 3D structure. The presence of wrinkled and bent regions, where the distorted sp$^2$-like bonds increase and the Dirac cone is perturbed with a tiny gap opening, does not invalidate the potentialities of these 3D NPG samples. The interconnected graphene sheets retain the structural, vibrational, electronic, and transport responses of the ideal 2D graphene, with a positive cost-benefit ratio to overcome the limitation of integrating graphene in 3D devices.

### MATERIALS AND METHODS

The NPG sample was synthesized by following the procedure described in detail in the Supporting Information: Ni$_{30}$Mn$_{70}$ ingots were used to generate nanoporous Ni and then loaded in a quartz tube for producing graphene by CVD into the template. The as-grown NPG, which inherited the spongy structure of the substrate, was then exfoliated by chemically removing the Ni substrate.

HIM images were collected with the Zeiss Orion Nanofab helium ion microscope (Peabody, USA) located in the CARF Laboratories of the Queensland University of Technology (Brisbane, Australia), with a beam acceleration of 25 kV and a working distance of 14 mm. The secondary electron signal was collected with an Everhart–Thornley detector with 500 V collector bias.

Micro-Raman spectra were acquired in the same facility by using a WITec alpha300R microscope (WITec GmbH, Ulm, Germany) equipped with a diode-pumped Nd:YAG laser, operating at 532 nm, focused through a 50× Zeiss objective (0.7NA) to obtain a spot size of about 250 nm. The Raman maps were collected in pixels of 300×300 nm$^2$, and the laser power was kept at 1.0 mW to avoid beam damage.

TEM images and diffraction patterns were taken with a JEOL JEM-2100F system equipped with two aberration correctors for the image- and probe-forming lens systems. High-resolution TEM observations were conducted at an accelerating voltage of 120.0 and 200.0 kV, both Cs correctors were optimized for image observations, and the point-to-point resolutions of TEM were 1.3 Å. Further details are provided in the Supporting Information.

The spectromicroscopy photoemission experiments were carried out at the ANTARES beamline (SOLEIL synchrotron radiation facility). The nano-X-ray photoelectron spectroscopy (XPS) microscope is equipped with two Fresnel zone plates for beam focusing, whereas higher diffraction orders were eliminated, thanks to an order selection aperture. The sample was placed on a precision positioning stage located at the common focus point of the hemispherical Scienta R4000 analyzer (whose energy resolution is 0.005 eV) and the Fresnel zone plates, and this experimental setup was used both for the collection of point-mode spectra and imaging-mode spectra. In this mode, the photo-emitted electron intensity from the desired energy range is collected over the sample to form a 2D image resolved at the submicrometer range (pixel size of 300×300 nm$^2$). Core-level and valence band spectra were taken with 350 and 100 eV photon energy, respectively. The analyzer pass energy was set to 100 eV (200 eV) for the spatially unresolved (resolved) mode.

After insertion in UHV, the NPG sample was degassed at 500 °C for 2 h to minimize contamination from the environment. The base pressure of the UHV chamber was kept in the range 10$^{-10}$ mbar, whereas the sample was cooled via liquid nitrogen (±89 K) to avoid damaging the sample via radiation pressure.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00706.

NPG synthesis preparation protocols and procedures; a wide-energy XPS spectrum with focus on the potential contamination; and TEM analysis of the moire pattern, Raman fitting curves, and HIM, Raman, and C 1s XPS spectroscopy at the nanoscale on an NPG sample with smaller pore sizes (PDF).

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**Notes**

The authors declare no competing financial interest.

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