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Raman evidence for the successful synthesis of diamane

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Diamane was prepared from the exposure of bi-layer graphene to H radicals produced by the hot-filament process. A sharp sp^3 -bonded carbon stretching mode was observed by UV Raman spectroscopy while no sp^2 -bonded carbon peak was simultaneously detected. This is the first time that Raman spectra of genuine diamane are reported, which, meanwhile, are the very first evidence for the successful synthesis of genuine diamane. First principle calculations support possible full hydrogenation and confirm the hydrogenated AB configuration to be the most stable one. We believe those results constitute a milestone in the path towards the synthesis of high-quality diamane and open the door to large-scale production.

Genuine diamane consists of two crystalline sp^3 -bonded carbon layers for which half of the carbon atoms are hydrogenated while the other half bond the two layers to each other [1,2]. The material stability was first predicted by Chernozatonskii et al in 2009 [1]. The increasing interest in this new 2D wide band-gap semiconducting material comes, in particular, from its potential use in electronics [3]. Recently, the synthesis of stable 2D nanometer-thick and crystalline sp^3 -bonded carbon, was unambiguously shown for the first time [2,4]. This breakthrough was achieved from the chemisorption of H radicals produced by the hot-filament process at low temperature and pressure on the basal planes of few-layer graphene (FLG) and the subsequent interlayer bonding between sp^3 -bonded carbon atoms (sp^3 -C). sp^3 -C stretching peak was detected in visible and UV

Raman spectra. However, these reports cannot claim having evidenced genuine diamane, because of the poor suitability of the starting graphene material with too many layers, thereby inducing the formation of diamanoïd/graphene hybrids instead, and because of the lack of lateral resolution of Raman spectroscopy [4]. Following that work, the synthesis of F-diamane, where carbon atoms are fluorinated rather than hydrogenated as in genuine diamane, was claimed from the fluorination, at low pressure, of AB-stacked bi-layer graphene [5], the latter having been shown to be the most favorable configuration for the sp^2 -C to sp^3 -C conversion [1,2]. However, notably, no sp^3 -C related peak was observed in Raman spectra [5]. Also, the method based on the intensity of the electron diffraction spots to discriminate between the graphite and the diamond structures is known to be unreliable because of the “interference error” effect which can occur in the case of ultrathin films that can be easily distorted [4,6]. Hence, to the best of authors’ knowledge, evidences of diamane synthesis are missing.

Raman spectroscopy is a critical technique to characterize carbon materials, including hydrogenated graphene, graphane [7] and diamanoïds [2,4]. However, in the case of those nanomaterials, since for visible energies, the Raman scattering of sp^2 -C is a resonant process between 50 and 230 times more effective than that of sp^3 -C [8], it is necessary to employ UV excitation to obtain a more evenly weighted probe of sp^3 -C and sp^2 -C sites. This critical point has not been considered in most reports on hydrogenated graphene and 2D sp^3 -C nanomaterials [2].

Therefore, in this work, we studied the hydrogenation of bi-layer graphene by the chemisorption of H generated from the dissociation of H_2 in a hot filament reactor at low temperature and low pressure, and the subsequent structure conversion into highly hydrogenated genuine diamane. UV Raman spectroscopy was used to track the structure conversion, which is unprecedented in the literature in the field but in our own work [2,4]. First principle calculations and electronic diffraction are used to explain our findings. In addition, ultra-low voltage (5 kV) transmission electron microscopy (TEM) analysis was carried-out, mostly in electron diffraction mode.

As-received suspended bi-layer (2LG) graphene films grown by chemical vapor deposition and deposited on 3 mm diameter gold Quantifoil TEM grids were obtained from *Graphenea* and used as starting graphene materials. Each film is polycrystalline, with a maximum grain size of 20 μm . Coverage of the grid is ~98%. 2LG films were obtained from the successive transfer of two individual single-layer graphene (1LG), hence the resulting 2LG stacking is random. However,

considering the dimension of the 1LG layers (~ 3 mm in diameter) and their polycrystalline nature (20- μm -large grains for the most), chances for locally getting the favorable AB or AA stacking configurations [1,2] at micrometer scale are high and can be actually observed as reported in Fig.1b. A commercial hot filament reactor (BWI 1000 model from Blue Wave Semiconductors) was used for the hydrogenation process [9]. The specific experimental details related to the synthesis of diamanoïds were previously disclosed [2]. 2LG grids were placed vertically on the substrate holder. The samples studied here were prepared at a pressure of 50 Torr and using a H_2 flux of 1 sccm. The duration was of 6 minutes and 30 seconds. Filament temperature was within the range of 2350–2590 °C while the maximum 2LG temperature was around 400 °C.

The Raman scattering measurements were performed in the backscattering configuration using 244 nm line and analyzed using a $\times 40$ objective micro-Raman spectrometer system (inVia Reflex, Renishaw). The resolution was of 3.5 cm^{-1} . Typically, laser power was in the range of 1 mW with 1s exposure time. No visible damage and no change of the spectral shape during measurements have been observed. Highly-oriented pyrolytic graphite (HOPG) was used for peak position calibration. Raman mapping was employed using high-speed encoded mapping stage to generate high definition 2D chemical images over typically around 140,000 μm^2 . Step size was set at 3 μm .

TEM (mostly electron diffraction) was employed to further examine the material structure before and after hydrogenation. The converted material, as opposed to the behavior of graphene or diamond, appeared to be electron sensitive, possibly because of the high hydrogenation degree of the surface, even for electron energy as low as 80 keV [2]. This is consistent with the photon sensitivity observed under certain conditions [2] and the reported electron sensitivity of F-diamane [5]. This is the reason why an ultra-low-voltage (5 kV) benchtop transmission electron microscope from America DeLong was used. The instrument includes a Schottky-type field emission gun and a 2560 \times 2160 pixel Front Illuminated Scientific CMOS (6.5 μm^2 pixel size). Electron diffraction patterns were obtained in selected area mode from 100 nm-large areas.

DFT calculations were performed with the VASP package [10,11] with the same conditions than in our previous work [4]: Perdew-Burke-Ernzerhof (PBE) functional [12], cut-off energy of 400 eV, force convergence below 0.005 eV/Å, vacuum height of 20 Å and supercell of (7 \times 7) with a 7 \times 7 \times 1 grid for k-points sampling. VESTA software was used to generate optimized structure pictures [13].

Selected area electron diffraction of the starting 2LG films (Fig.1b-d) exhibited various features depending on the location of the area analyzed, i.e., the evidence for (i) single graphenic domains (supposedly 2LG with AB or AA stacking) (Fig.1b); (ii) two randomly stacked superimposed graphenic domains (supposedly 1LG each) (Fig.1c) (iii) four randomly stacked graphenic domains (Fig.1d), showing that the material is not 2LG only all over the grid.

Micro-Raman mapping was performed before and after exposure to the hot-filament-promoted hydrogenation process, to track any structure conversion change induced by the above-mentioned process. Before hydrogenation process, the spectra of 2LG are characterized by a regular sharp G peak at around 1582 cm^{-1} which is due to bond stretching of all pairs of $\text{sp}^2\text{-C}$ in graphene sheets. After the hydrogenation process, drastic changes can be observed in Raman spectra of various regions of the 2LG samples. Fig.2a presents a typical spectrum of such a region, which exhibits specific features: (i) the G peak is no longer detected; (ii) the D peak which originates from defects in graphene sheets [7] is not observed either; (iii) a sharp peak (FWHM of around $10\text{--}33\text{ cm}^{-1}$) at around $1344\text{--}1367\text{ cm}^{-1}$ has occurred. This type of spectrum can be observed over extended regions of several μm width and in various areas probed by the laser, as illustrated in Fig.2b which displays a map of the intensity of this peak. The peak at around $1344\text{--}1367\text{ cm}^{-1}$ is not the D peak, since the G peak is not simultaneously observed; also, it is too sharp anyway and its spectral position does not correspond to the value observed in the UV spectra of nanocrystalline graphite [14]. It is supposed to be due to bond stretching between $\text{sp}^3\text{-C}$, even if the peak was predicted at near 1320 cm^{-1} from *ab initio* calculations for diamane, and found at lower wavenumber in diamanoïds ($1319.5\text{--}1337\text{ cm}^{-1}$) [2,4] and diamond (1332 cm^{-1}). Therefore, Figs 2a and 2b show that full $\text{sp}^2\text{-C}$ to $\text{sp}^3\text{-C}$ conversion, that is to say full conversion of 2LG into genuine diamane, can be obtained over $20\text{ }\mu\text{m}$ large region. It is assumed that the conversion takes place in regions where graphene sheets are AB- or possibly AA-stacked, which are the most energetically favorable configurations [1,2]. But because of the variability in the stacking sequence all over the polygranular film, many other configurations should appear which lack of symmetry makes them out of the range of calculation. Therefore, the presence of stress or strain is expected in hydrogenated yet randomly stacked layers for which C-C interlayer bonding cannot occur, or only partially, and at the grain boundaries between graphenic and diamane domains. The local modifications induced by the variety of interlayer bonding situation are probably at the origin of the variety of up-shifted positions of the $\text{sp}^3\text{-C}$ peak (Fig.2c). Cracks which have appeared in the

film (Fig.1e, to be compared to Fig.1a), and layers stacked with a very slight twist angle (Fig.1f) are probably related to this occurrence of stress and strain.

In Fig.2c, one can note a coarse correlation of the sp^3 -C peak width with its position, which ranges from 1340 to 1370 cm^{-1} . An upshift can be associated to strain due to the presence of several phases (diamane, graphene) in equilibrium, or to an inhomogeneous layer hydrogenation, or to a distorted bonding between two hydrogenated twisted layers. The Gruneisen parameter for optical phonon is around $1cm^{-1}/GPa$ [15] leading to a conversion factor of 3 cm^{-1}/GPa for hydrostatic pressure. For biaxial strain, a splitting between singlet and doublet is expected and not observed, which is consistent with an average hydrostatic strain, which is an acceptable yet rough hypothesis. The in-plane lattice parameter of lonsdaleite is 0.249 nm, and 0.252 nm in diamond, while it is 0.246 nm in graphene, leading to a strain of -1 to -2%. In graphene or diamond, -1% is associated to a hydrostatic stress of about 10 GPa. Consequently, a wavenumber shift of 30 cm^{-1} is possible and corresponds to the range of the shift observed.

To test this hypothesis, we have performed first principle calculations on modified diamane structures. First, starting from the genuine diamane structure (one hydrogen atom every two carbon atoms), and then subsequently moving a hydrogen or a pair of hydrogen atoms to the neighboring C atoms, a spontaneous relocation of the hydrogen atoms to the right sites to form diamane is observed. So, hydrogen atoms self-organize when reacting with a graphene layer. Second, by adding extra hydrogens on C atoms already coordinated to 3 others carbon atoms so that two first-neighbor carbon atoms both wear a hydrogen, the excess H atoms always desorb spontaneously to reform H_2 molecules. Over-hydrogenation is thus not favorable. Finally, while testing the case of under-hydrogenation by removing 7 H atoms from the top layer, a strong structural reorganization occurs, see Fig.3a and Fig.3b. The 19 C atoms involved in the extended defect tend to lose their sp^3 character to recover a sp^2 one, implying reductions of several C-C bond-lengths, confirmed by the histogram given in Fig.3c. The phonon polarization imposed by the light polarization is in the plane, activating phonons without physical limitation. In such a case, the linewidth is not broadened and the wavenumbers of the optical modes calculated by DFT are close to the bulk value within the uncertainty range of the calculations. Thus, the lattice parameter remains the same while very local distortions can be present which could be at the origin of both linewidth broadening and frequency changes. Therefore, our calculations show that full hydrogenation for AB stacking is the most stable, final material, and that significant distortions can occur upon partial hydrogenation. Thus, sp^2 -C to sp^3 -C conversion induces huge stresses, specifically at the

grain boundaries, either when the 2LG involved does not exhibit the AB or AA stacking needed for allowing the optimized hydrogenation of the layers (in case of turbostratic or commensurate stacking indeed, only partial hydrogenation may occur, locally promoted when carbon atoms happen to locally superimposed), or in case of under-hydrogenation. This is also consistent with the stress estimated in diamanoïd/graphene hybrids [4].

To summary, we have shown that the hot-filament promoted hydrogenation process can be successfully used to produce genuine diamane from bi-layer graphene. UV Raman spectroscopy reveals the sp^3 -C stretching mode peak in diamane showing that using a UV excitation is critical for the characterization of such sp^3 -C nanomaterials. It is believed that the key for producing homogenous diamane films now only relies on starting from a good quality 2LG material, that is to say, ideally, single-crystal AB flakes as large as possible. The present results open the door to mass-produced diamane by means of the hot-filament-assisted CVD process, as it is employed for the industrial production of other sp^3 -bonded carbon materials, such as diamond films, for about 40 years.

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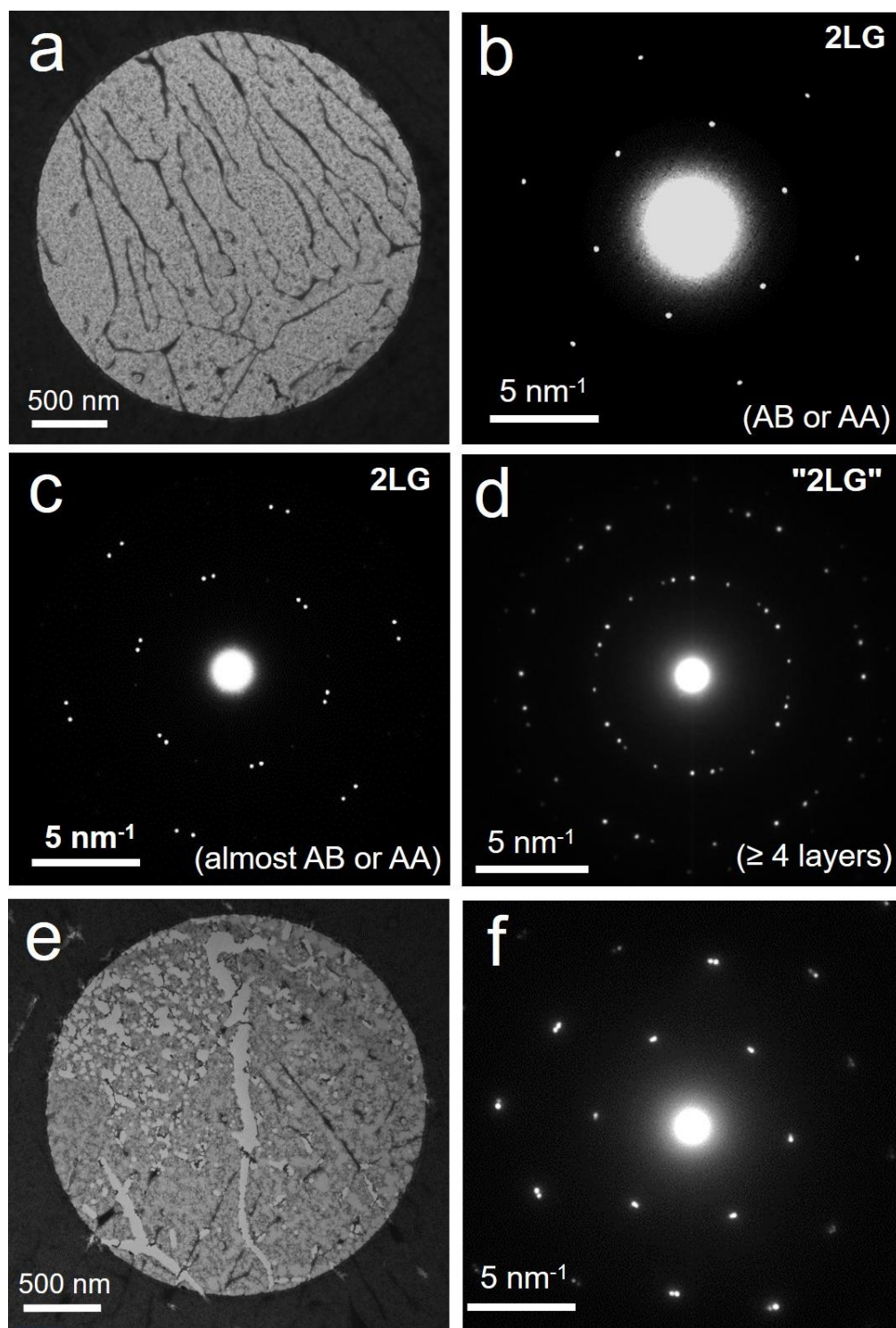


Figure 1: Examples of TEM characterization of the 2LG films before (from (a) to (d)) and after hydrogenation ((e) and (f)). Diffraction patterns are from 100 nm-large areas. (a) Image of an as-received 2LG film. Contrast variations are due to the presence of amorphous material partially covering the film. (b) Single graphenic domain, as an evidence for two superimposed 1LG in AB or AA stacking; the inner and outer 6 spots correspond to the 100 and 110 spot families in graphite, respectively. (c) Two slightly rotated graphenic domains, as an example of a random stacking of two superimposed 1LG. (d) Evidence for the presence of 4 superimposed graphenic

domains. **(e)** Image of a hydrogenated 2LG film. **(f)** A single domain, as an evidence for the successful conversion of an AB (or AA)-stacked 2LG domain as in (b) into a genuine diamond domain. Therefore, the inner and outer 6 spots correspond to the 111 and 110 spot families in diamond (or 100 and 110 in lonsdaleite), respectively.

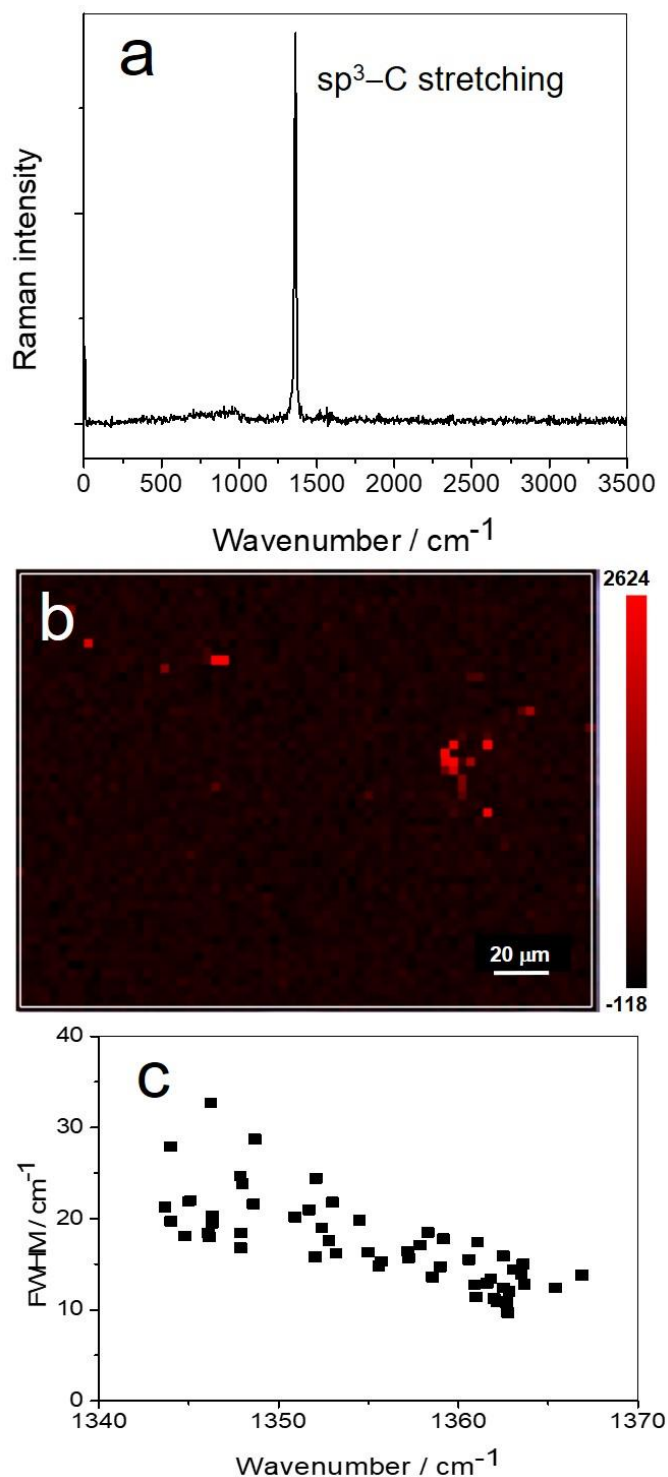


Figure 2: Typical UV (at 244 nm) Raman data. **(a)** Example of a Raman spectrum obtained on a hydrogenated bilayer graphene, as the evidence for the occurrence of genuine diamane, as discussed in the text. **(b)** Example of the Raman map of the intensity of the sp^3 -C stretching mode of 2LG after exposure to the hot-filament-promoted hydrogenation process. **(c)** Full Width at Half Maximum (FWHM) as a function of wavenumber of the sp^3 -C stretching peak for graphene materials exposed to the hot-filament-promoted hydrogenation process.

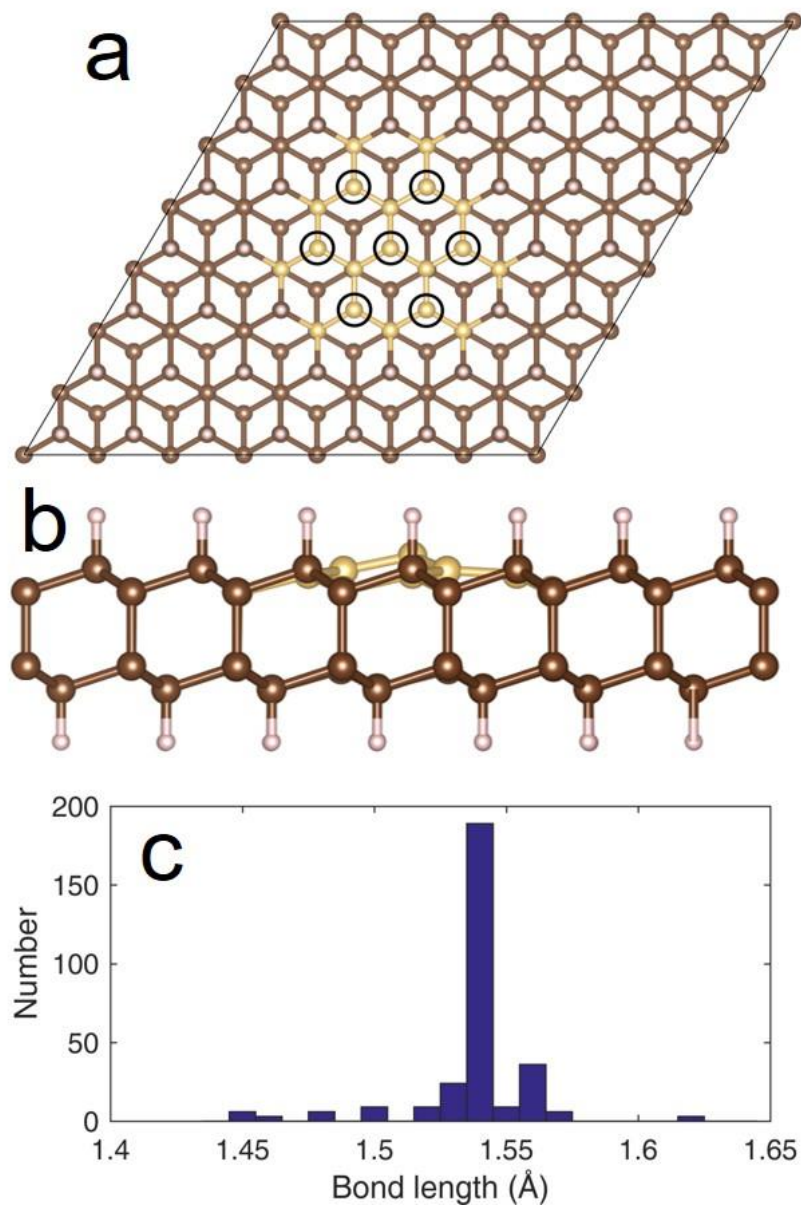


Figure 3: (a) Top view of the reconstructed unsaturated structure, with 7 missing hydrogen atoms on the top layer (position of the missing H atoms is given by the black circles, and (b) side view. Carbon atoms involved in the reconstruction are given in yellow, while the others are brown and H atoms are white. (c) Resulting C-C bond-length distribution.