

Sulfur Addition to Graphene Surfaces Invalidated via Isotopically Pure ^{13}C Graphene

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Sulfur Addition to Graphene Surfaces Invalidated via Isotopically Pure ^{13}C Graphene

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Abstract

Covalent addition and incorporation of sulfur to sp^2 carbon surfaces by radical reaction in the gas phase have been reported by a number of studies to explain property changes, such as doping, enhanced mechanical strength and phase changes in graphite superlattices. Here, we investigate the reaction of sulfur radicals to pristine graphene surfaces in the gas phase using advanced surface-sensitive techniques. Consistent with previous works, sulfur bonding is observed at moderate temperature in a gas phase on both few-layers graphene and highly oriented pyrolytic graphite (HOPG). The presence of covalent bonds between carbon and sulfur is confirmed by Raman, photoemission spectroscopies and advanced microscopy. The reaction products are consistent with a stable graphene episulfide structure obtained by DFT calculations, in which the sulfur adatoms are adsorbed at the bridging sites between pairs of sp^2 carbons. The covalent bonding to graphene is, however, invalidated by a control experiment using isotopically pure ^{13}C graphene samples. The analysis shows that adsorbed species are rather due to species deposited during the reaction involving residual carbon species introduced during the experiments. Consistent with organo-sulfur deposition at the graphene surface, these experiments reveal no evidence of direct reaction of sulfur with the graphene surfaces. More generally, the use of isotopically pure graphene samples is presented as a general method for future work on graphene functionalization.

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Introduction

Targeting applications often requires to modify the properties of graphene-based materials (GBMs) using chemical functionalization [1]. Functional surface groups grafted covalently to graphene has been used, for instance, to stabilize colloidal graphene in solution, improve adhesion in composite materials, tailor selectivity and doping in sensing devices, reduce interface states, etc. The low reactivity of graphene restricts, however, the number of chemical pathways for covalent functionalization, requiring activation of the sp^2 carbon lattice before bonding. For that purpose, two main strategies have been adopted : i) Inducing defects as a precursor state of covalent bonding and ii) generating in situ reactive species that can directly bond to the carbon lattice without altering the honeycomb structure. For examples, the use of strong oxidants generates defects that facilitates the exfoliation and oxidation of multilayered graphene and form in batches the so-called graphene oxides (GO), an important industrial precursor for GBMs [2]. The synthesis conditions are however harsh and acidic, which gives rise to a plethora of various surface groups (*e.g.* epoxide, hydroxyl, carbonyl) having mixed chemical behaviours [3, 4]. Radical coupling, such as diazonium [5, 6] and cycloaddition [7], uses reactive intermediate species that can directly bond to the sp^2 carbon lattice and form well-define functional grafts bonded either as a monovalent or a divalent adduct to the carbon lattice. The latter strategy provides, however, coverages of surface adducts that rarely exceed 1% [8]. Such low coverages makes the analysis of the reaction products challenging and prone to errors since only indirect measurements can be obtained, such as a property change after reaction or a modification of the Raman response assigned to graphene disorders (*e.g.* the relative D-band intensity due to sp^3 defects).[9–11]

Graphene reactions with sulfur is of particular interest for application. For example, studies on graphene and graphite functionalization have shown that sulfur can induce doping [12–16], enhance chemical sensing [17–19], and improve composite materials for lithium-sulfur batteries [20–23]. More importantly, a sulfur incorporation has been obtained by a simple thermal activation of elemental sulfur. The thermal annealing forms polysulfur radicals at 160-300 °C that can then react with graphite nanoplatelets. As evidences of sulfur-sulfur bonding between graphene flakes, past work has shown a significant changes of mechanical properties of GBM aerogels following the reaction [24]. Similar conditions involving elemental sulfur and highly oriented pyrolytic graphite (HOPG) have also been used at 500 °C to produce new Raman bands in 1200-1400 cm^{-1} region and induce a partial annihilation of ferromagnetic signal from hexagonal Moiré superlattices [13, 25–28]. Past works have highlighted the presence of new Raman bands and convincing photoemission results on covalent bonding. Combined with property changes, the literature results appear consistent with covalent bonding between sulfur and graphene materials upon annealing.

Here, we explore further the sulfur functionalization of graphene in well-controlled conditions to generate sulfur radical in the gas phase. Exfoliated multilayer graphene as well as monolayers graphene on copper alumina substrates are used to identify the reaction products and test the reaction mechanism using control experiments and supported by theory. The thermal treatments are performed in one pot under mild conditions of pressure and temperature. Following the current best practices in studying the graphene covalent functionalization, we characterized the reaction products using optical (Raman) spectroscopy, surface analysis, and density functional (DFT) calculations. Initially, the results showed that the sulfur reaction induces sulfur-carbon covalent bonding at the surface of graphene. When compared to theory, the analysis points to an episulfide bridge, whose structure appears analogous to that of a graphene epoxide. On the basis of a comparison between theory and experiments, the graphene episulfide (GS) is identified as the most probable product of what appears as a [2+1] cyclo-addition reaction between sulfur diradicals and graphene. However, a validation of the Raman response using isotopically pure ^{13}C graphene invalidates this assignment. The gas phase sulfurization of graphene is rather due to a coating of the surface with organo-sulfur contaminants formed in the gas phase. This contamination layer is selectively deposited onto the hydrophobic surfaces of graphene.

Results

The main evidence of graphene functionalization by elemental sulfur reaction is presented in Figure 1 using few-layer graphene (FLG) flakes mechanically exfoliated from a large and freshly cleaved HOPG crystal (see Methods) and then dry-transferred onto a Si/SiO₂ substrate. An optical image of the flake (see the arrow) is shown in panel A and the main evidences of sulfurization are given by photoluminescence (PL) and Raman spectra in panels B and C, respectively. The spectra of pristine graphene (black curve) are compared with those of reacted graphene (red curve). Note that these results are representative of what was obtained from a large number (more than 20) of samples and other experiments carried out on graphite nanoplatelets.

After reaction, the PL spectra in Fig. 1B of the flake (8 nm thick) show a broad (550-750 nm) and weak visible luminescence (see also Figure S4), which undoubtedly indicates a significant modification in the electronic structure of the sample. The PL spectra before and after reaction show multiple Raman peaks among which the G band (1590 cm⁻¹) and the 2D band (2700 cm⁻¹) of graphene can be identified. These bands are signatures of sp² carbon lattice. Interestingly, several new Raman bands highlighted in Figure 1C are detected after reaction. Two peaks recorded at 400 cm⁻¹ and 495 cm⁻¹ are readily attributed to the C-S and S-S stretching modes, respectively; the latter is probably due to intercalated S_n chains (2 ≤ n ≤ 4) between layers [29] (see also Figure S2A). In the G-band region, two main features are observed at 1260 and 1450 cm⁻¹ along with a broad contribution in the sp³-like carbon band region (1200-1500 m⁻¹). [10]

The most prominent peak at 1450 cm⁻¹, hereafter called the GS band, has been previously reported in sulfur-doped HOPG [25, 26], sulfur-doped carbon nanotubes [30], and is also present in α-sexithiophene [31]. This Raman mode is tentatively

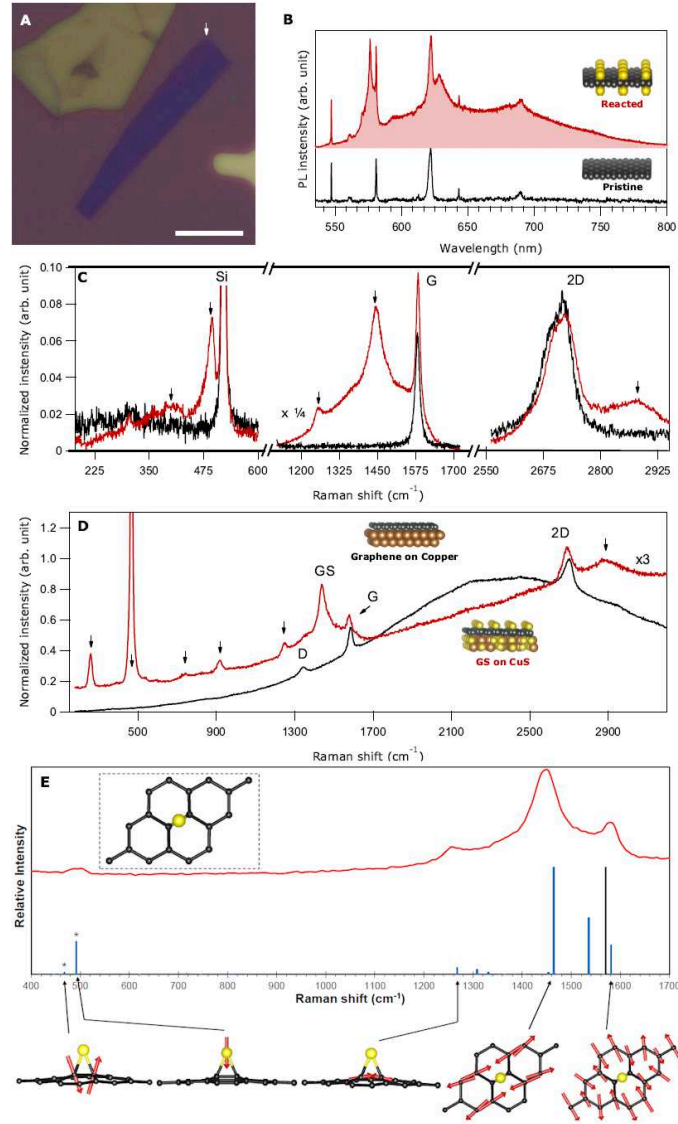


Fig. 1: Optical signatures of graphene functionalization with elemental sulfur. **A.** Optical image of a few-layer graphene (FLG) flake mechanically exfoliated onto a Si/SiO₂ substrate. Scale bar: 5 μ m. **B.** Photoluminescence and **C.** Raman spectra of the FLG sample recorded before (black) and after (red) reaction with elemental sulfur under 532 nm (2.33 eV) laser excitation. Note that the Raman intensity is normalized by the Si peak intensity at 520 cm^{-1} and a baseline is removed for better clarity. New peaks highlighted by the arrows are at 400 cm^{-1} , 1260 cm^{-1} , 1445 cm^{-1} and 2890 cm^{-1} . **D.** Raman spectra of a graphene monolayer grown by Chemical Vapor Deposition (CVD) on a thin layer of copper before (black) and after (red) reaction. **E.** Experimental and calculated first-order Raman spectra of graphene episulfide. The experimental spectrum (red) is compared with the static spectra of GS (blue) and pristine graphene (black). Intensities are normalized to the maximum, and asterisks indicate modes involving S-C bonds. The graphene episulfide model is shown in the inset.

attributed in Figure 1E to the tangential displacement of the C–C(sp²) bonds of an episulfide bridge, i.e., a sulfur atom located at a bridge site between two carbons (see inset). This assignment is further discussed in the following section along with first principles DFT calculations of models of episulfide adducts. The first and second overtones of the GS band are also detected at 2890 cm^{−1} (Figure 1C) and 4335 cm^{−1} (Figure S5). Finally, the G and 2D bands remain present after reaction, but they are systematically blue shifted (here by a few cm^{−1}), a behaviour likely related to doping and/or strain effects [32] introduced during the sulfuration process. The 2D band also decreases in intensity and generally gets broader, and this is especially clear in thinner samples (Figure S6B). These features are normally assigned to spectroscopic signatures of a high level of covalent functionalization [33].

Figure 1D presents additional sulfuration results on a graphene monolayer grown by chemical vapor deposition (CVD) on a thin layer (~1 μm) of copper deposited on a sapphire substrate (Cu/Al₂O₃), see Methods. Performing this reaction directly on freshly prepared graphene was used to rule out reaction with traces of polymer left due to the aqueous phase transfer of monolayer graphene. The sapphire substrate was necessary because the sulfur reaction transforms copper into copper sulfide (CuS), which is brittle and impossible to manipulate. To avoid any other surface contaminants, the sample was quickly transferred to the sulfur reactor after CVD growth, see Methods. The results show similar PL and Raman spectra as before, which can also be assigned to the formation of graphene episulfide. That is, we identify after reaction the presence of the GS bands at 1450 cm^{−1} and 1260 cm^{−1} and of the GS overtone at 2898 cm^{−1}. Additional Raman peaks are also observed at 260 cm^{−1}, 467 cm^{−1}, 746 cm^{−1}, 917 cm^{−1} and ascribed to CuS vibrations [34]. Note that the background emission before reaction is due to emission from the copper substrate.

Figure 1E shows that the calculated Raman spectrum of the GS model reproduces the main features of the experimental spectrum. Sulfur functionalization produces a blue shift of the graphene G mode and introduces a characteristic GS vibration near 1471 cm^{−1}. Additional low-frequency modes around 500 cm^{−1} are associated with vibrations involving S–C bonds. More calculated Raman spectra of another GS model are shown in the supplemental materials in Figure S22.

The spatial distribution of the reaction was investigated by hyperspectral Raman imaging on a large graphene flake (Figure 2A) where two distinct regions of thicknesses of 5.0 and 2.5 nm have been identified by atomic force microscopy (AFM, Figure 2B). Raman images recorded before the reaction first confirm the good quality of the exfoliated sample, namely a uniform G-band signal on the entire flake and no clear signal of a D-band. Figure 2C displays the Raman image of the intensity of the GS band at 1450 cm^{−1} recorded after the reaction. A constant and spatially homogeneous signal is detected on the flake, while no signal could be measured on the Si/SiO₂ substrate (see Figure S3 for confocal Raman data). This key experiment first allows one to rule out the presence of a uniform coating of sulfur-carbon species formed during the reaction. It also indicates that the reaction occurs uniformly throughout the flake, as further evidenced by low surface roughness and homogeneous topography in the AFM line scan (inset Figure 2B). Surprisingly, the position of the G band (Figure 3C) shows a stronger blue shift (ΔG ~19 cm^{−1}) in the thinnest regions of

the flake compared to the value before reaction (1580 cm^{-1}). Note that the same trend is observed for the 2D band (see Figure S6). Hence, sulfur reaction under these conditions appears to take place everywhere on the surface of the graphene flake, but the impact of the reaction on the spectral shifts, often associated to layer doping or strain, appears to be more extensive in thinner regions.

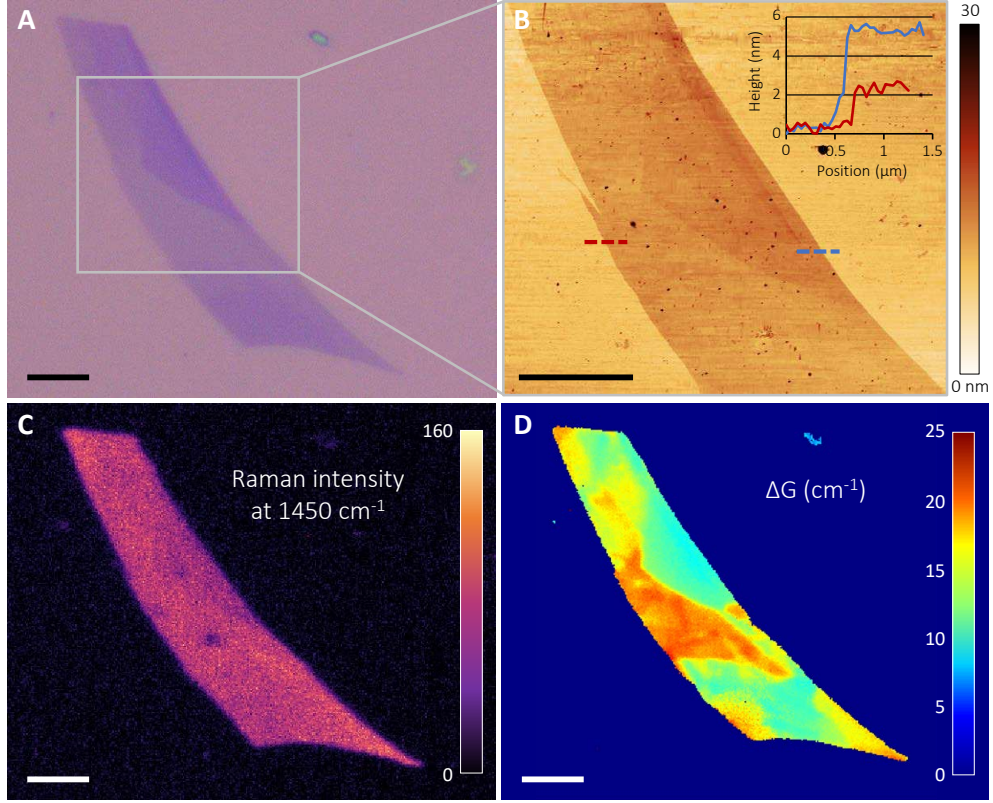


Fig. 2: Homogeneous graphene functionalization identified by hyperspectral Raman imaging. **A.** Optical and **B.** AFM (height) images of a GS flake with two distinct regions of 2.5 nm and 5 nm thickness as shown in Inset (panel **B**). **C.** Hyperspectral image of the Raman intensity of the GS-band at 1450 cm^{-1} . **D.** Hyperspectral image of the G-band shift (ΔG) with respect to its position in the pristine unreacted material (1580 cm^{-1}). Scale bar: $5\text{ }\mu\text{m}$.

X-ray photoelectron spectroscopy (XPS) was used to gain further information about this surface functionalization, thanks to specific signals in the regions of sulfur S(2p) and carbon C(1s) core levels. To minimize air contaminants, the sulfur reaction was performed on a bulk HOPG crystal (1 cm^2) that was freshly cleaved on both sides just before insertion into the reaction chamber (see Methods). The XPS spectra are

shown in Figure 3A-B (see additional results in Figures S11 and S12). As expected, the pristine spectrum is dominated by the C(1s) peak at a binding energy (BE) of 284.4 eV, which is due to the sp^2 carbon lattice of graphene. Minor carbon impurities are detected before reaction at 287.1 and 288.9 eV, which are probably due to some adsorbates containing C–O and O–C=O groups [35]. The S(2p) region exhibits no signal before reaction and a strong doublet at 164 and 165.2 eV after the reaction, which can be assigned to S(2p_{1/2}) and S(2p_{3/2}) of elemental sulfur (S₈) or other sulfur-based species. A very small peak at BE = 161.6 eV also suggests the presence of C=S containing species, similar to thioureas, (di)thiocarbamates, or short sulfur chains [36, 37]. Because elemental sulfur and sulfur covalently bonded to carbon C–S are indistinguishable in XPS (*i.e.* the same chemical shift) [38–40], this S(2p) spectrum alone cannot be used to identify more precisely which reaction products are present. However, the sulfur signal after reaction can be correlated to a significant modification of the C(1s) region in Figure 3B. After reaction (top), the XPS spectrum shows two peaks of comparable intensity at 284.4 and 285.1 eV, which are due to C- sp^2 and C-*quasi*- sp^3 sites, respectively. This change in the C(1s) region is therefore consistent with a covalent bonding between carbon and sulfur on the surface of graphene. The XPS results also show a uniform sulfur content of approximately 24 atomic % relative to carbon throughout the sample, *i.e.* multiple locations have been measured. The sulfur and C-*quasi*- sp^3 content varies from 19 to 27 % atomic and 38 to 51 % atomic, respectively (Figure 3B-C). About half of the total carbon remains unreacted in the sp^2 configuration. These results demonstrate that the detected sulfur has mostly reacted to carbon and forms C-S bonds instead of S-S bonds. Many other elements support this conclusion. First, the concentration of elemental sulfur is very low because the synthesis conditions are kept in a temperature gradient that prevents S deposition. Second, the partial pressure of sulfur is fairly low at the temperature of the reaction, which does not favor S intercalation into the bulk. Third, the Raman signal of S-S stretching modes at 400 and 495 cm^{-1} (see Fig. S7) is weak. In fact, the AFM results show that the detected free sulfur tends to form clusters near step edges (see Fig. S16 D).[19] Finally, the peak integration indicates an average C/S ratio of 1.8, which is consistent with a very large coverage of sulfur. The assignment of sulfur species in the episulfide configuration is further discussed below using DFT calculations.

To investigate the depth profile of the reaction products, angle-resolved XPS measurements were performed at different collection angles, giving a depth analysis ranging from 9 nm (normal incidence, 0°) to 1 nm (high angle). As seen in Figure 3C (see also Figure S13), the relative intensity of the C- sp^2 peak at 284.4 eV decreases as the depth analysis is reduced (*i.e.* the collection angle is increased) while the assigned C–S bonding contribution at 285.1 eV increases. The same trend is observed for the percentage of sulfur, which goes from 21 to 31 % atomic at a high collection angle (75°). These results strongly indicate that a functionalization is either located at the surface or limited to the topmost few layers. This suggests either a slow diffusion of the reactive sulfur species into the bulk or rapid quenching at the surface because of reactant recombinations or self-passivation. As a complementary result, the surface roughness of the sample, measured by AFM, increases from 0.25 ± 0.05 Å to 1.67 ± 0.05 Å after reaction (Figure S16). Although the surface topology has been uniformly

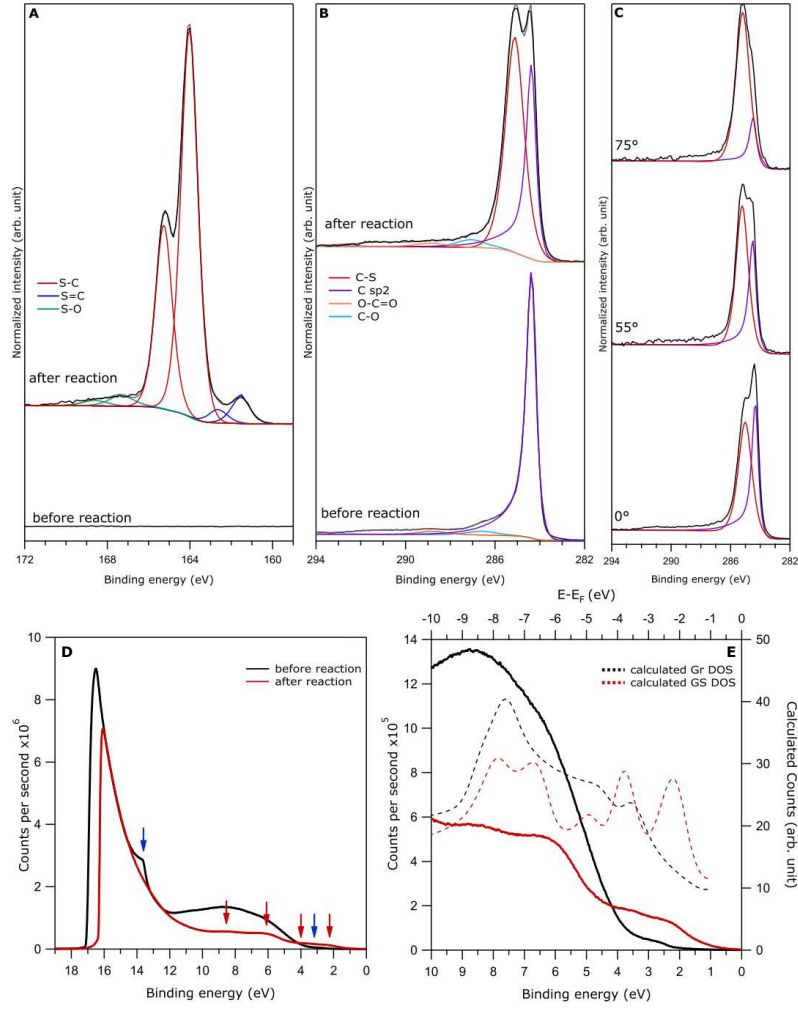


Fig. 3: Formation of carbon-sulfur covalent bonds investigated by photoelectron spectroscopy. High resolution XPS spectra recorded in the core level regions of **A.** sulfur S(2p) and **B.** carbon C(1s) atoms on a freshly cleaved HOPG crystal before (bottom) and after (top) reaction. **C.** Angle-resolved XPS spectra recorded after the reaction in the C(1s) region recorded at various collection angles : 0° (normal incidence, bottom), 55° (middle) and 75° (top). Note that spectra in C are taken at a different location compared to A and B. Ultraviolet photoemission spectroscopy **D.** UPS spectra recorded on a freshly cleaved HOPG crystal before (black) and after (red) reaction with elemental sulfur. **E.** DFT-calculated density of states (DOS) of pristine graphene and graphene episulfide, compared with the UPS spectrum in panel D over the 0–10 eV energy range.

modified, the induced roughness remains relatively low. This is consistent with the XPS data that only the topmost layers do react with sulfur.

To complement the Raman results in Fig. 1D on a graphene monolayer grown on a Cu/Al₂O₃ substrate, XPS (Figures S14) and scanning electron microscopy (SEM) (Figure S17) were acquired before and after reaction. The SEM images show the presence of clusters along the grain boundaries, which is assumed to be due to excess sulfur.[19] The spectral deconvolution of the C(1s)-sp² and -sp³ peaks gives, however, a 4:1 ratio, which is consistent with a sulfur coverage of about 12%. This is lower than what is reported above on HOPG.

The impact of the functionalization on the electronic structure was further studied by ultraviolet photoemission spectroscopy (UPS) using a HeI (21.22 eV) source. Figure 3D (see also Figure S15) displays the UPS spectrum of the same sample as in Figure 3. Before reaction, several features are observed at 13.7 eV, 9.0 eV and 3.0 eV. These peaks are tentatively assigned to π -electrons, σ -electrons, and $\pi \rightarrow \pi^*$ transitions of pristine HOPG, respectively [41]. After reaction, the UPS spectrum is significantly modified. The shoulder at 13.7 eV is no longer observed and provides the first evidence that the upper layers are chemically distinct from the bulk HOPG [42, 43]. In the low energy region below 12 eV, four contributions are identified at 2.3 eV, 3.4 eV, 6.2 eV, and 8.3 eV (red arrows). This result indicates the presence of new electronic states after reaction. The spectra before and after reaction are consistent with the density of states of the pristine graphene and a episulfide graphene model obtained by DFT calculations (Figure 3E). Furthermore, both UPS and DFT data show an increase of the work function (ϕ) of $\Delta\phi \approx +0.6$ eV (Figure S15), a strong evidence of a surface modification induced by the sulfur reaction.

Finally, the reaction products were also analyzed by Transmission Electron Microscopy (TEM) and mapping using Energy Dispersive X-ray Spectroscopy (EDS). The TEM samples were prepared from a powder of graphene nanopellets collected after sulfur reaction and dispersed in ethanol and from a reacted sample graphene monolayer grown on a Cu/Al₂O₃ substrate. Moreover, elemental mappings depicted in Figure S19 indicate that sulfur and carbon atoms are co-localized throughout the samples. These maps confirm the spatial homogeneity of the reaction previously observed by XPS and Raman imaging.

Discussion

All of the measurements above provide clear evidences of a chemical functionalization of graphene with the formation of covalent bonds between sulfur and the carbon (sp²) atoms of the graphene lattice. Raman combined with angle-resolved XPS measurements further indicate that the reaction product are mostly confined to the top layers. Because the Raman signal is proportional to the number of atoms, a surface-limited reaction should lead to GS-band signals that are independent of the number of layers considered. This is consistent with the results presented in Figure 2C. That is, the confocal Raman spectra acquired in regions of various thicknesses (Figure S6 and S8) do show that the G band intensity relative to the GS band is significantly higher on thicker regions. This is in good agreement with a surface-limited reaction as in thicker

regions a larger quantity of unreacted carbon atoms appears present below the surface. Thickness-related effects in Figure 2D show a significant variation of ΔG after reaction from 10 to 19 cm^{-1} for the thinnest regions. At first sight, this may point to different reaction kinetics, but, as discussed above, this cannot be the case. Because ΔG is indicative of graphene doping or strain [32, 44], this shift cannot be simply related to the coverage of reaction products. Although strain may play an important role, the shifting behavior is rather consistent with a doping effect. That is, a doping reaction limited to the topmost layers should redistribute the transferred charges towards the unreacted carbon atoms underneath. This implies that a higher doping level per atom is expected for thinner flakes, as observed, although strain induced by the top layers can also relax down to the sublayers of the flake. Interestingly, results obtained on a suspended exfoliated sample (Figure S9) show a significant increase of the GS-band intensity on the freestanding part of the flake. This suggests a higher degree of functionalization, which is not surprising since both sides of the flake are directly exposed to the gas phase. Combined with the above evidence by XPS (Figure 3C), these experiments point again to a surface-limited reaction with quenching or passivation at the surface.

Considering these strong evidences of covalent addition of sulfur to graphene, we evaluated the first-order static Raman spectra of probable GS configurations of episulfide species located in the bridge position (Z-axis direction) of the graphene sheet (Figure 1E). This model, called hereafter GS_1 , corresponds to a periodic structure containing one sulfur atom in a small graphene cell. The stability of this cell, as well as that of the C-S episulfide, is assessed using both *ab initio* molecular dynamics (MD) simulations and vibrational analyses of the geometries corresponding to the lowest energy structures, as detailed in the Supplementary Information. The model demonstrates high stability for the considered phases and provide consistent results. Figure 1E presents a direct comparison between the simulated (blue) and experimental (red) Raman spectra of the reaction products. The calculated Raman spectrum of a pristine graphene layer is also added for reference. A blue shift the G band of the graphene with episulfide bridge is noted. As shown in Table S6, new Raman active modes associated to the GS_1 structure appear in three distinct regions: (1) the low energy ($400\text{-}1100\text{ cm}^{-1}$), (2) the D-band ($1100\text{-}1550\text{ cm}^{-1}$), and (3) the G-band ($1550\text{-}1650\text{ cm}^{-1}$) regions. The intensity profile of the calculated Raman spectra qualitatively matches the experimental profile. Notably, the calculated GS band exhibits a strong relative intensity and it is only slightly blue-shifted by about 3 cm^{-1} compared to the experimental value.

The sulfur atom of this GS_1 model is that of a divalent adduct positioned off-plane relative to graphene. According to these Raman calculations, the sulfur configuration should lead to multiple C-C modes in the broad region between 1200 and 1600 cm^{-1} . The stable configuration sits near a slightly deformed graphene sheet, which breaks the symmetry of the C-C stretching modes in the vicinity of the adduct. This induces, for instance, local modes near 1250 cm^{-1} , which is far down below the position of the G band of pristine graphene near 1590 cm^{-1} and additional C-C modes between 1420 and 1500 cm^{-1} , identified as stretching and breathing combination modes of C-C movements out of the graphene plane. Also, some breathing deformations of the

deformed graphene sheet appear at around 1300-1360 cm^{-1} , near the D band. Table S6 directly compares the experimental and calculated Raman shifts for the GS₁ model. Overall, the calculated bands are in good agreement with the experiments. The relative intensities of the peaks show, however, only few discrepancies, which is surprising considering the simplicity of the harmonic approximation used here (*i.e.* anharmonic effects not included [45]). Another element is the finite size of the supercell for periodic calculations, which can also induce spectral shifts. 310

The best practice in studying covalent functionalization often calls for many characterization methods to probe the graphene functionalization. Another evidence of covalent bonding was therefore acquired using comparative experimental UPS spectra with calculated DOS of graphene and GS₁ models (Figure 3). The calculated transition at 3.0 eV is, for instance, transformed into two new states at 2 eV and 3.5 eV, while the experimental spectra is substantially modified in the 0-4 eV region with a new peak at 2 eV. Moreover, the DFT-DOS of the graphene states near 9 eV also split into two bands at 6.5 eV and 8 eV, which is consistent with the peaks detected experimentally in UPS at 6 eV and 8.5 eV, respectively (Figure 3E). Intensity variations observed around 4 eV also suggest a redistribution of the DOS after sulfur reaction. It is important to note here that the DFT-DOS results do not consider any photoemission cross-section, and differences in intensity with the UPS experimental data are therefore expected. 315 320 325

Combining these classical experimental and theoretical results argue in favor a GS configuration in which the sulfur is chemisorbed on the graphene surface into a bridge configuration (Figure 1E). XPS measurements in Figure 3 further indicate that the sulfur content saturates near 25-30 % atomic, given the uncertainty of the depth profile. This is about half of the surface carbon bonded to sulfur, an experimental stoichiometry that clearly points towards the episulfide structures, as predicted by DFT calculations. That is, a maximum sulfur incorporation of 25 % atomic is expected at saturation when a complete layer of episulfide bridges is formed as main functional groups. Finally, TEM results indicate that the integrity of the graphene lattice is preserved after extended reaction time, which implies that the formation of this sulfur-carbon phase at the surface is not limited to graphene defects or edges, but covers the whole honeycomb lattice (see Figures S18 and S19). 330 335

The formation of episulfide has previously been observed when elemental sulfur is reacted with alkenes in the presence of steric hindrance [46, 47]. A chemisorption of sulfur on the planar sp^2 lattice of graphene brings similar steric hindrance by the surface. Different available sites for sulfur chemisorption have therefore been considered by DFT calculations, and the results confirm the higher stability of the bridge site, with a total energy of roughly 500 meV lower than that of the top site. In addition, all the multi-sulfur GS structures considered converge towards a bridge configuration. In effect, the top site converges only when the S atom is placed at exactly the local minimum in the potential energy surface; all the other initial positions migrate towards the bridge site. 340 345

While all of the results presented above converge towards a direct covalent bonding scheme between sulfur and graphene, it is noted, however, that the experimental evidence remains indirect, as none of these measurements has revealed the exact nature 350

of the reaction products. Although compelling is the case for the episulfide species, one cannot completely rule out other species, such as surface contaminants adsorbed selectively onto the graphene surfaces. Albeit extensive, the experimental results remain inconclusive, as extrinsic organo-sulfur species, that share for instance similarity with
 355 episulfides, can also be accounted for in this reaction scheme. To clarify this important point, we devised an additional control experiment using CVD graphene grown with ultrapure ^{13}C methane and reacted the freshly grown ^{13}C labeled graphene sample in the same conditions as presented before. The results are presented in the Figure 4. Isotopically pure graphene with ^{13}C is first confirmed by the red shifted G and 2D
 360 bands, which values are now at 65 and 122 cm^{-1} away from that of regular graphene, respectively. These redshifts of the G and 2D bands are consistent with a reduced effective mass of the graphene carbons, now enriched with ^{13}C at a concentration of about 100% [48]. After the sulfur treatment, the photoluminescence of the copper decreased to levels typical for such samples on a SiO_2 substrate. As expected, the Raman peaks of CuS after reaction are observed at 260 cm^{-1} , 467 cm^{-1} , 746 cm^{-1} and 917 cm^{-1} ,
 365 which confirms that a reaction with sulfur took place and consumed the copper substrate underneath the graphene layer, as in Figure 1D. Surprisingly, the graphene sample grown with isotopically pure ^{13}C transforms with similar bands as that of ^{12}C graphene. The peaks of the reaction products are observed in both graphene samples at around 1260 and 1455 cm^{-1} , and hence, no Raman shift is observed for those bands
 370 on the isotopically pure ^{13}C graphene sample. Considering the change in reduced mass of the ^{13}C atoms, reaction products such as episulfides involving direct bonding to the carbon lattice would normally exhibit red shifted bands by at least tens of cm^{-1} , as predicted by DFT calculations (Table S7). The result of this control experiments is
 375 therefore negative and reveals that the sulfur-carbon bonds formed by the reaction are from extrinsic source of carbon. More importantly, it shows that the graphene lattice is not involved in this reaction.

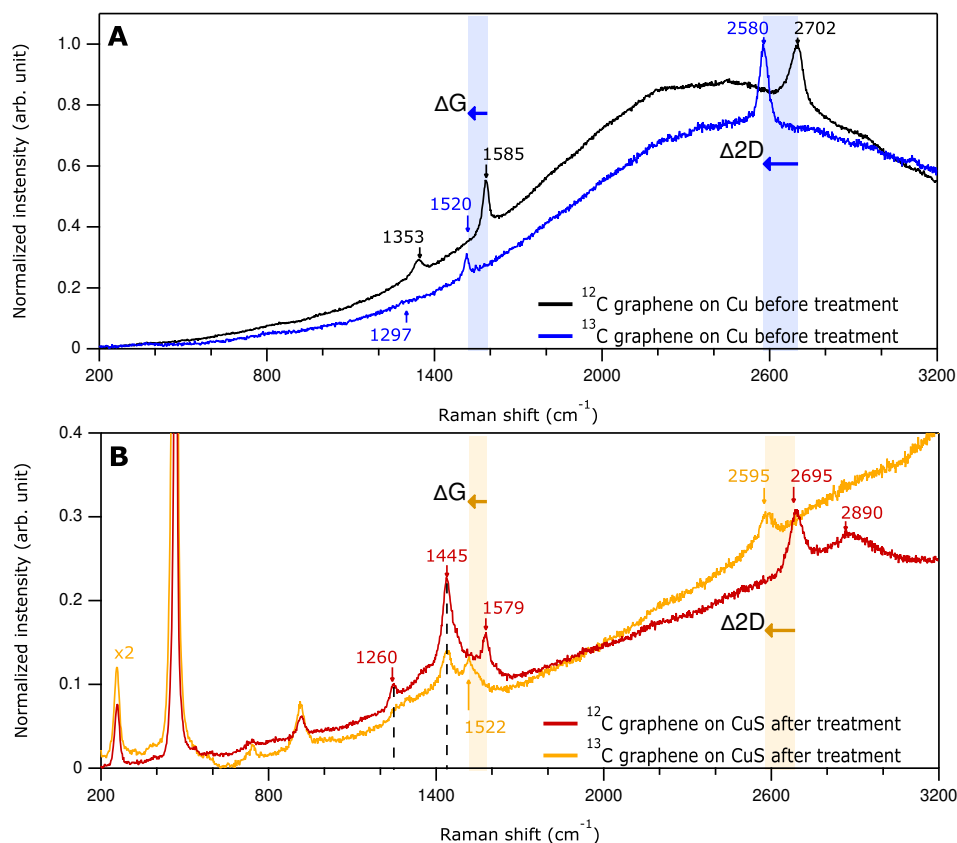


Fig. 4: Raman spectra comparison of ^{12}C and ^{13}C graphene monolayers on copper before and after sulfur treatment. ^{12}C graphene before and after treatment are respectively in black and red. ^{13}C graphene before and after treatment are respectively in blue and orange. Redshift have been highlighted with arrows. Spectra couples were normalized respectively on their 2D band and the CuS main peak at 467 cm^{-1} .

This last control experiment calls for a significant change of the spectroscopic assignments of the Raman results. The representative peaks of the reaction products at 1445 and 1260 cm^{-1} remain unshifted after isotope labeling, which is a clear proof that extrinsic carbons, such as organo-sulfur compounds, are adsorbed onto the graphene surfaces, as highlighted by both Raman and XPS spectra. To fully explained the experimental results, one could consider both: i) organo-sulfur species produced in the gas phase and then deposited on the graphene and ii) organic contaminants already present at the graphene surface [49, 50] followed by a reaction with sulfur radicals. The presence of hydrocarbon contaminants is ubiquitous in graphene research and recognized as being problematic and responsible of reproducibility issues in the field.

It is therefore not surprising that contaminants is present. The surprise comes from the consistency of the results with what is expected for an addition reaction of sulfur on graphene, with selectivity and doping effects limited to the graphene layers, not the oxide substrates. Based on Raman evidences, the species are undoubtedly related to episulfide species and should therefore present sulfur located in a bridge site between two sp^2 carbon atoms. Organic and polymeric contaminants are particularly difficult to eliminate from hydrophobic graphene [51] and it is therefore likely that such impurities could not be completely removed in our experiments, even when extreme precautions were taken (*e.g.* avoiding polymer transfer, rapid transfer of freshly cleaved or grown samples to the reaction chamber, etc.).

As for the identification of the species involved in this coating reaction, Figure 1D and Figure 3D shows that the reacted monolayer exhibits a weak luminescence emission near 650 nm wavelength and charge transfer feature leading to p-doping, which is often the case with organo-sulfur compounds[15]. Moreover, the peaks at 1260, 1445, and 1530 cm^{-1} can also be assigned to stretching modes of substituted thiophene compounds.[52]. Because the coating is not observed on the hydrophilic SiO_2 surfaces, as in Figure S3, the contaminants are likely hydrophobic species deposited selective from the gas phase. To verify the deposition hypothesis, we performed measurements in the same exact conditions but using exfoliated hexagonal boron nitride, h-BN, as a replacement of graphene. h-BN is a non-reactive hydrophobic substrate [53] on which a deposition from the gas phase of organo-sulfur compounds is possible. Indeed, the Raman results in Figure S10 shows the appearance of the characteristics bands 495, 1260 and 1445 cm^{-1} along with the typical photoluminescence emission of the compounds. This result confirms the hydrophobicity of the deposited species and confirms the presence of a gas phase reaction to form the organo-sulfur species.

While the nature of the species formed by the reaction remains unclear, some insight can be deduced from the pressure and temperature conditions of the synthesis. At 0.75 atm, sulfur evolves with temperature from a rhombic solid phase to a monoclinic structure. The latter reaches its fusion point at around 392 K and liquid sulfur vaporizes near 700 K [54]. In its liquid phase, sulfur chemistry is peculiar and interesting because the most stable form, the cyclo-octasulfur or S_8 , breaks down into thiyl diradicals ($\cdot\text{S}_8\cdot$) and other polymeric diradicals ($\cdot\text{S}_n\cdot$, where $n = 8$ to 35) at around 432 K [55, 56]. As described in Methods, the chamber temperature is clearly above the homolytic fragmentation, where free radicals are formed in liquid sulfur. Hence, a smaller proportion of thiyl radicals that enters the gas phase can be carried in the gas phase via chemical vapor transport across the dumbbell chamber and temperature gradient. This condition favors radical addition reactions to organic contaminants, and this is therefore the most probable reaction mechanism for the formation of organo-sulfur species deposited onto the graphene surfaces.

Current state-of-the-art in graphene characterization performed after a functionalization experiment is today perceived as strong support of covalent bonding, even if the species produced at the surface have not been resolved structurally. No matter how sophisticated the analysis can be, most current surface techniques provide only indirect evidences of covalent bonding, a situation that is prone to premature conclusions. The use of additional control experiments that can disentangle reaction products

covalently attached to the graphene carbons from physisorbed species is therefore an important step to include in functionalization papers. As demonstrate here, an isotopically pure graphene sample provides spectroscopic signatures of the origin of the carbon involved in chemical bonding. Replacing the ^{12}C carbons of graphene by ^{13}C has resolved the issue of contaminants in this case and allowed us to conclude that graphene layers do not undergo addition reaction with sulfur radicals in the conditions explored. The same methodology is likely to be useful in most experiments involving covalent bonding to graphitic structures such as graphene, carbon nanotubes, carbon foams, nanohorns, etc.

Spectroscopic methods based on isotope labeling have been popular in the past to assign vibrational modes of molecules, a task that is nowadays mostly replaced by DFT calculations, avoiding by the latter costly experiments and syntheses. In the specific case of 2D materials, this methodology also requires expansive sources of ^{13}C and special implementation into the growth systems. As demonstrated here, this investment is fully compensated by the unambiguous evidence of covalent bonding, which cannot be supplied by any other known techniques. This approach unambiguously determines from spectral shifts the presence or not of graphene carbons and helps to support vibrational modes assignments of the reaction products. As an example, the method has been recently applied by some members of our team to settle the controversial debate on the graphene edge modes in Raman [57]. As seen in Figure 4, the modes at 1260, 1445 cm^{-1} and the overtones cannot be assigned anymore to a sulfur functionalization of graphene, and this case study therefore serves as another good example that can guide future direction to adopt for the best practice in reports on nanocarbon functionalization.

To conclude, this work presents a comprehensive study on a sulfur radical reaction in the gas phase with graphene materials. The classical experiments are mostly consistent with covalent bonding involving sulfur atoms bonded on a bridge site between two carbon atoms of the lattice, called episulfide grafts. This analysis is also supported by DFT calculations. However, the use of isotopically pure ^{13}C graphene samples has invalidated the formation of covalent bonds to the graphene lattice and revealed instead the role of organo-sulfur contaminants produced in the gas phase and deposited selectively onto the graphene surfaces.

This study paves the way to benchmarking covalent functionalization reactions on graphene materials and can serve as a guide to assess different addition reaction schemes reported so far. The use of high purity ^{13}C methane is however expensive, but the studies shows that it cannot be replaced by either DFT calculations or other characterization techniques available for graphene. The method is quick and reliable, and can be used to validate the presence of covalent bonds to the graphene materials. Furthermore, the isotopic method combined with FTIR or Raman spectroscopy can be adapted to many other reaction schemes involving different adatoms, including boron, oxygen, nitrogen, halogens and other chalcogens. A new methodology is therefore proposed to unambiguously conclude about the bonding nature of the surface species formed after reaction onto graphene-like surfaces.

Methods

Experiments

Preparation of few and multilayers of graphene. A dry transfer method was used to produce a large number of clean (free of polymer residues) graphene flakes of thicknesses between 2 and 10 nm on Si/SiO₂. The Si/SiO₂ (300 nm oxide) was previously cleaned with acetone, isopropanol, then a PIRANHA acid bath (1:3 hydrogen peroxide 30% and sulfuric acid for 20 min), and finally rinsed in DI water. PDMS was prepared by mixing together a SYLGARD TM 184 Silicone elastomer base with a curing agent in a 1:6 catalyst:polymer proportion. The mixture was then heated at 85°C for 30 min. Few layers graphene samples were extracted using freshly prepared PDMS directly from a HOPG sample (Advanced Ceramics Corporation, Grade ZYA).

Thin layers for Raman studies were obtained by selecting optically flakes in the range from 6 layers to 30 layers. The samples used for XPS measurements were produced from a bulk 1 mm thick HOPG (Pelco, Ted Pela), which was mechanically cleaved with a razor blade into four 0.25 mm thick samples. Each surface was peeled with tape and tweezers right before insertion in the reaction chamber.

Additional hexagonal boron nitride, h-BN, samples have been prepared for the hydrophobicity tests of deposited species by the sulfur treatment. Flakes, from previously grown CVD h-BN [58], in DMF solution were dropcasted onto Si/SiO₂ in order to obtain thin films of h-BN of various thicknesses.

Preparation of graphene monolayer on thin deposition of copper. A copper film of 1.5 μm was deposited on a sapphire (Al₂O₃) substrate using magnetron sputtering (Denton Vacuum, DESK TOP PRO) at 100 V. Graphene growth was carried out by chemical vapor deposition (CVD) on this copper film in a tube furnace using the procedure described in our previous work [59]. In short, the procedure consists of increasing the temperature of the Cu/Al₂O₃ substrate from RT to 1000°C in Argon (50 mTorr - 7 sccm), followed by a short reducing step in H₂ (50 mTorr - 8 sccm). Finally, the graphene growth was obtained using ¹²C or ¹³C CH₄, (450 mTorr - 70 sccm) exposure for 10 min, followed by rapid cooling from 1000°C to 250°C in under 5 minutes in Ar (50 mTorr).

Synthesis. A silica (quartz) glass tube of 1.6 cm in diameter and 16-20 cm in length was successively cleaned using acetone, isopropanol, left to dry overnight at room temperature and then reheat at 600°C for 4h. The reaction chamber is then prepared by melting one end of the tube and the middle section to form a local constriction or bottleneck. The other end is left open and serves to connect the tube to a dry pump. A vacuum of about 1 mTorr is generally obtained while pumping the chamber. Multiple steps of heating and purging with argon are used to remove traces of humidity. The sulfur (99.9 % Aldrich) and graphene samples were then placed in their corresponding compartment, and the reaction chamber was purged three more times by vacuuming and filling with argon. The reactor is finally sealed in about 0.75 atm of argon using an hydrogen torch. Therefore, this reaction chamber has the shape of a dumbbell, which can be inserted between two cylindrical ovens. Each oven is separately controlled to ensure a tight control over the reaction temperature and over the temperature gradient across the reaction chamber. The furnace temperatures are

continuously monitored using three built-in thermocouples strategically placed along the double oven right next to the main compartments of the reaction chamber. 520

For Raman spectroscopy and imaging, samples made of few layers of graphene deposited on a Si/SiO₂ (300 nm) wafer are first placed on one side of the chamber and then 50 mg of elemental sulfur powder was placed on opposite ends of the tube chamber. For XPS studies, a freshly cleaved HOPG sample (Pelco, Ted Pela) of 5 525 mm × 5 mm is used with 5 g of sulfur. In both experiments, a temperature gradient is applied between the graphene and sulfur compartments with T_{Sulfur} inferior to $T_{Graphene}$ at all times. T_{Sulfur} was raised to 473 K and $T_{Graphene}$ to 643 K, respectively. The reaction time is 1 day for few-layer graphene samples and 6 days for a larger piece of bulk HOPG. After reaction, the oven was slowly cooled while maintaining a higher 530 temperature in the graphene/HOPG compartment. These temperature conditions help maximize the production of sulfur radicals in the saturated vapor phase, and the gradient favors sulfur transport from one compartment to the other.

Raman Spectroscopy. Raman spectra were acquired using a home-built Raman set-up under 532 nm and 488 nm laser excitation in backscattering geometry with a 535 100× (NA=0.9) objective, a 55 cm focal length monochromator and a nitrogen-cooled charge-coupled device camera. The laser power density was kept at $95 \mu W \cdot \mu m^{-2}$. Before data acquisition, the spectrometer was calibrated using the Raman line of the silicon substrate at $520 cm^{-1}$. Other confocal Raman spectra were acquired with an excitation wavelength of 514 nm using a Renishaw spectrometer (InVia) using a 540 maximum power of $150 \mu W \cdot \mu m^{-2}$ and an acquisition time of 60 s. Raman images were recorded using a hyperspectral Raman Imaging system (RIMATM, Photon Etc.) under 532 nm laser excitation and a 100× (NA=0.9) objective. The laser power density was $80 \mu W \cdot \mu m^{-2}$ and the integration time was 20 s.

Atomic Force Microscopy. AFM images were obtained using a Dimension 3100 545 scanning probe microscope in ambient conditions. Height profiles of $20 \times 20 \mu m$ selected areas were acquired in tapping mode using a silicon probe with a nominal spring constants of $42 N \cdot m^{-1}$, a resonance frequency of 320 Hz, and a tip radius curvature of less than 10 nm.

X-Ray and UV Photoemission Spectroscopy. XPS measurements were performed on a VG ESCALAB 250 Xi device from Thermo-Fisher Scientific. A Al K α 550 source at 1486.68 eV of 218.8 W (14.7 kV, 14.9 mA) was used. The base pressure was 1.0×10^{-8} Torr. The measurements were acquired on a surface of $1300 \mu m$ in diameter, at different electron emission angles 0, 55, 65, 75 and 85°, giving depth analysis from 8.94 nm to 0.78 nm for C(1s), 8.46 nm to 0.74 nm for S(2p) and 7.41 nm to 555 0.65 nm for O(1s). Distances are calculated from: $I = I_0 \exp(-d/\lambda \cos \theta)$ where I and I_0 are the intensities of the photoelectron signal from an element in specific chemical state and from a specific transition and the same element from a thick layer of material, respectively, λ is the attenuation length within a uniform material and θ is the collection angle. Global spectra and high-resolution spectra were measured with 560 acquisition steps of 1.0 eV and a passing energy of 150 eV and 20 eV, respectively. The UPS measurements were acquired on the same device with a Helium I (21.22 eV) source, acquisition steps of 0.02 eV and a passing energy of 2.0 eV.

Computations

Geometry optimization and electronic structure. Electronic structure calculations were performed within density functional theory (DFT) using SIESTA [60]. Exchange–correlation effects were treated with the PBEsol functional [61], previously applied to covalently bonded heteroatoms on graphene [62], together with Grimme’s D3 van der Waals correction [63]. Double- ζ polarized basis sets and norm-conserving Troullier–Martins pseudopotentials [64] were employed, with a real-space mesh cutoff of 500 Ry. Structures were relaxed at the Γ point until the forces and total-energy changes were below 0.02 eV/Å and 10^{-4} eV, respectively. Electronic calculations used a $(22 \times 22 \times 1)$ Monkhorst–Pack mesh, and a 40 Å vacuum layer was introduced perpendicular to the graphene plane to suppress interactions between periodic images.

Vibrational The fully relaxed geometries were used for the vibrational and Raman calculations. Γ -point vibrational modes were evaluated using the VIBRA package with a DZP basis set, a $(3 \times 3 \times 1)$ Monkhorst–Pack mesh, and a maximum atomic displacement of 0.01 Å. No significant imaginary frequencies were observed. Raman calculations were subsequently performed within density-functional perturbation theory using Quantum ESPRESSO [65]. The self-consistent calculations employed an $(8 \times 8 \times 1)$ Monkhorst–Pack mesh, norm-conserving scalar-relativistic pseudopotentials for carbon and sulfur, and wavefunction and charge-density cutoffs of 80 and 320 Ry, respectively. Denser k -point meshes produced no significant changes in the vibrational frequencies. Phonons were calculated at the Γ point using a convergence threshold of 10^{-12} Ry [66]. Raman intensities were obtained from derivatives of the dielectric polarizability tensor with respect to the phonon normal coordinates. Vibrational modes and structural models were visualized using the VESTA software [67].

Supplementary information

See Supplementary Information for further information on Raman, XPS, AFM and TEM measurements of of graphene before and after sulfur treatment, as well as the control measurements.

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Conflict of interest/Competing interests

All authors declare that they have no conflicts of interest.

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Supplementary information

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systems.

Experiments

For a better understanding and reproducibility of the sulfur treatment, an example of dumbbell reaction chamber with reactants is shown in Figure S1. In order to validate the necessity of having both reactants for the synthesis of the product and its location, control measurements were performed. Firstly, the process was done with only sulfur, as seen in Figure S2, the only differences seen between the Raman spectra before and after reaction can be attributed to a quenching when the sample is taken out the ovens and a resulting phase transition of the sulfur. Secondly, the process was done with only HOPG, no modifications of the Raman spectra were observed in the low frequencies near the 520 cm^{-1} peak. Near the G band region, some phenomena are observed, a small and wide D band appears as well as a D' band possibly due to the heat treatment, however no traces of the graphene episulfides peaks. Concerning the 2D band area, the 2D peak decreases and shifts, and again there are no traces of the product. Finally, during the Raman measurements of the process with both sulfur and HOPG, measurements were taken on the surface of the substrate (see Fig S3) before and after the reaction, in this case, no graphene episulfides or contaminants peaks were seen.

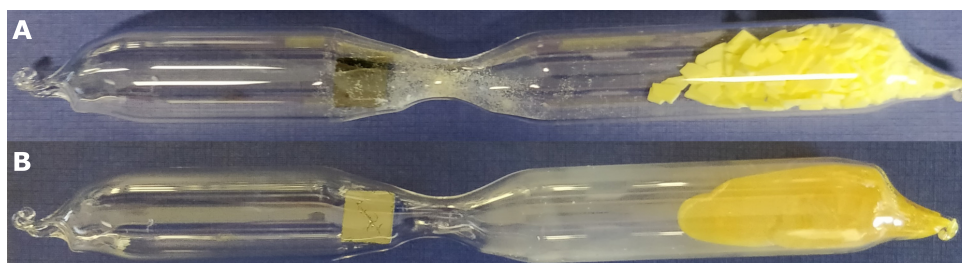


Fig. S1: Picture of dumbbell shaped chamber before and after reaction. A. Reaction chamber with freshly cleaved 1 by 1 cm HOPG sample and pristine sulfur before reaction. Thin sulfur powder can be seen near the bottleneck and the HOPG, it is due to the introduction of sulfur pellets in the glass tube however due to the size and geometry of the cleaved sample within the cylindrical part of the chamber no powder was in direct contact with the sample. **B.** Reaction chamber with reacted cleaved HOPG sample and quenched sulfur after reaction. Due to the temperature decrease conditions and the induced chemical vapor transport, one can see that no sulfur is in the graphene compartment and all the sulfur condenses within its compartment.

Control Raman measurements

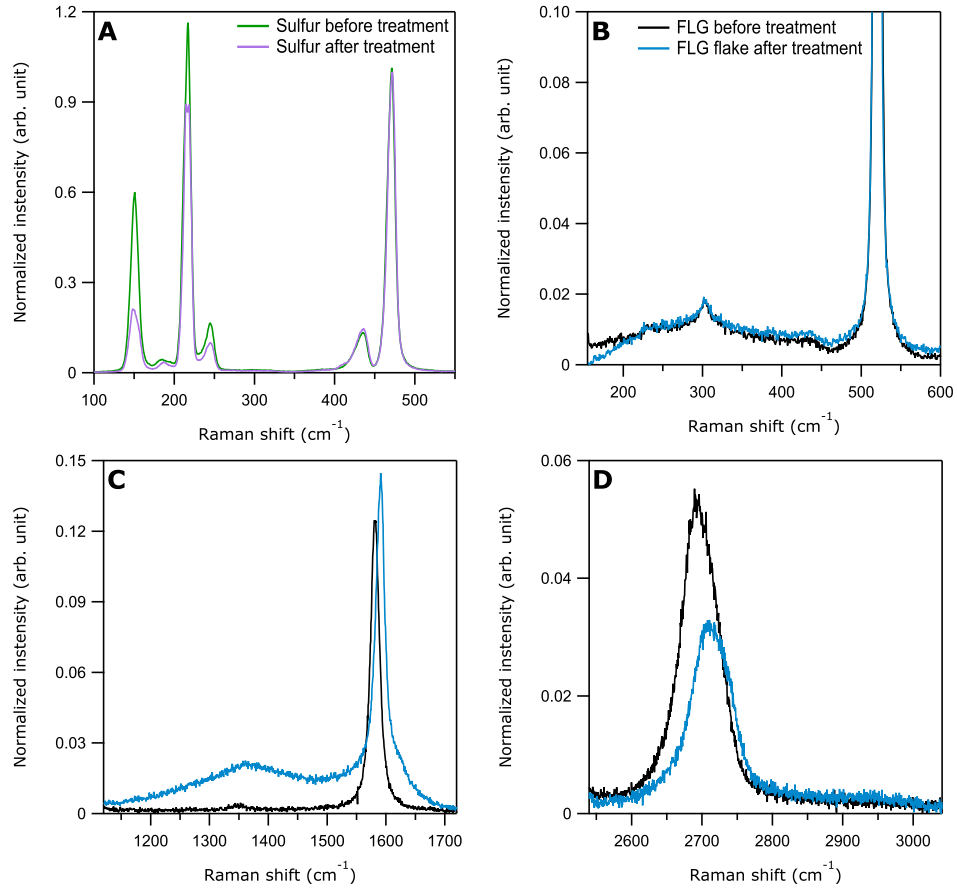


Fig. S2: Raman control experiments (I). **A.** Raman spectra of elemental sulfur before and after treatment without the presence of multilayer graphene. **B-D** Raman spectra of a few-layer graphene flake (3 nm, about 9 layers) in the Si, G and 2D bands regions before (black) and after (blue) treatment without the presence of sulfur reactant. Duration and conditions of temperature, pressure and atmosphere composition were kept the same as the synthesis protocol, respectively 24 h, 473 K and 643 K, 0.75 atm of Argon.

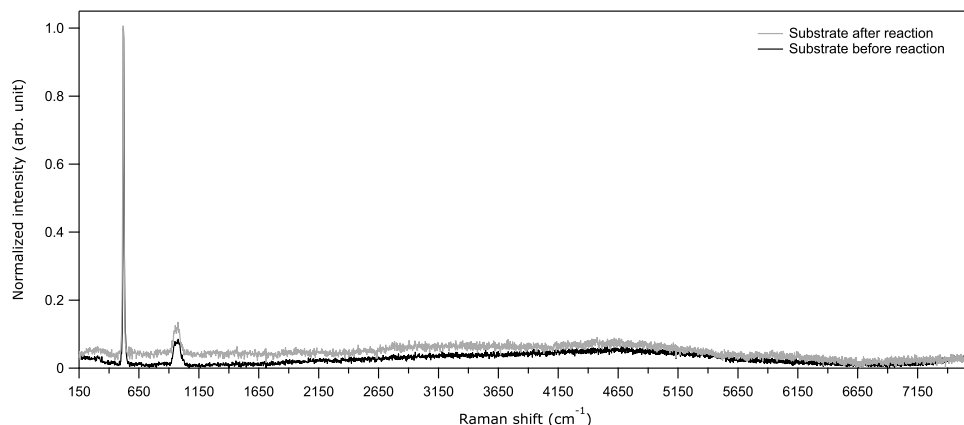


Fig. S3: Raman control experiments (II). No peak of graphene episulfide can be detected on the substrate after 24h reaction indicating that sulfur species react only with graphene.

PL - Raman spectroscopy

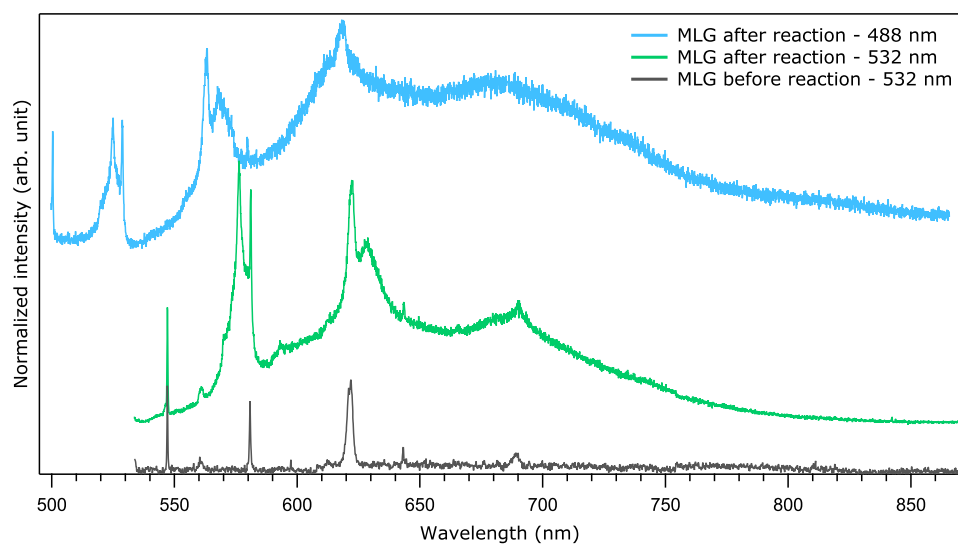


Fig. S4: Visible luminescence of graphene episulfide under two laser excitation wavelengths. PL spectra of a pristine few-layer graphene flake (black) and the reacted compound recorded under 488 nm (blue) and 532 nm (green) laser excitation.

Supplementary Raman measurements

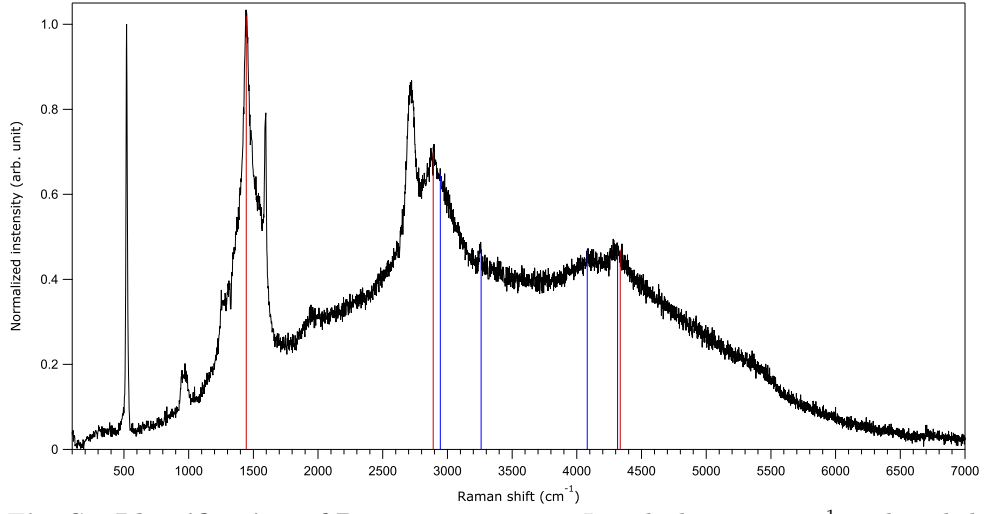


Fig. S5: Identification of Raman overtones. In red, the 1445 cm^{-1} peak and the first and second overtones at 2890 and 4335 cm^{-1} . In blue, pristine graphene peaks: D+G, $2D'$, D+2D and G+2D respectively at 2945 , 3260 , 4080 and 4315 cm^{-1} [68].

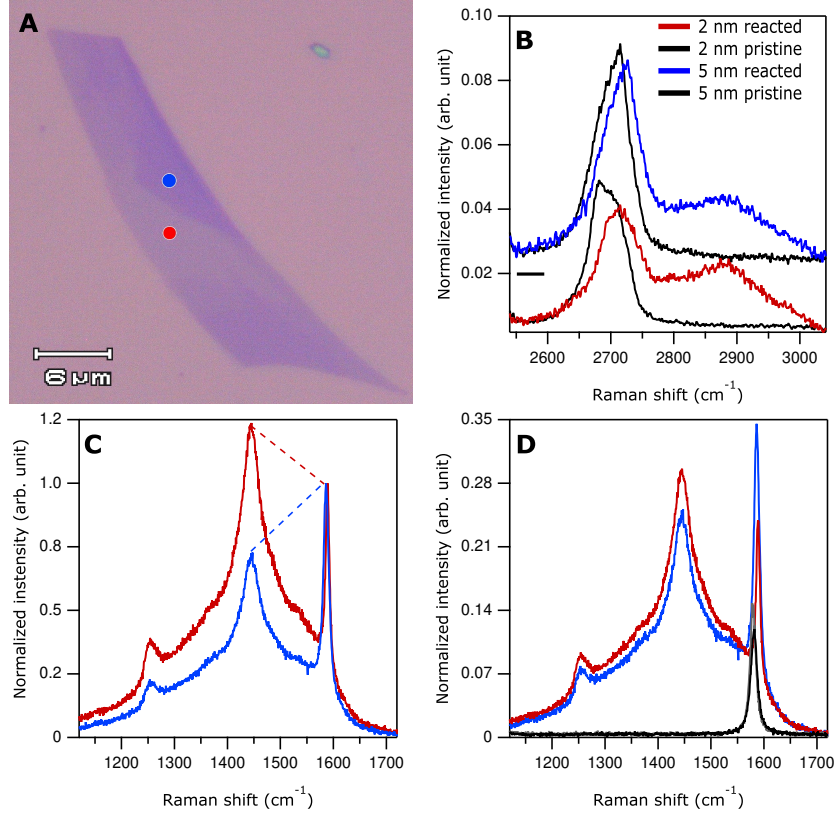


Fig. S6: Confocal Raman spectra recorded in two distinct regions of the GS flake presented in Figure 2. **A.** Optical image of the flake indicating the locations of the selected regions for Raman measurements corresponding to plateaus of 2 nm (red) and 5 nm (blue) in thickness. **B.** Raman spectra in the 2D band region normalized with the integrated Si band intensity (I/I_{Si} ratio) before (black) and after (red: 2nm and blue: 5nm) reaction. Note: for better clarity an offset of 0.02 is applied to the 5-nm region spectra. **C and D.** Raman spectra of selected regions (see panel A) after reaction in the G band region. The spectra are normalized relative to the integrated G band intensity (I/I_{G} ratio) in panel C and relative to the integrated Si band intensity (I/I_{Si} ratio) in panel D. The shifts before and after reaction are $\Delta G = +8 \text{ cm}^{-1}$ and $\Delta 2D = +15 \text{ cm}^{-1}$ for 2 nm region and $\Delta G = +6 \text{ cm}^{-1}$ and $\Delta 2D = +10 \text{ cm}^{-1}$ for the 5 nm region.

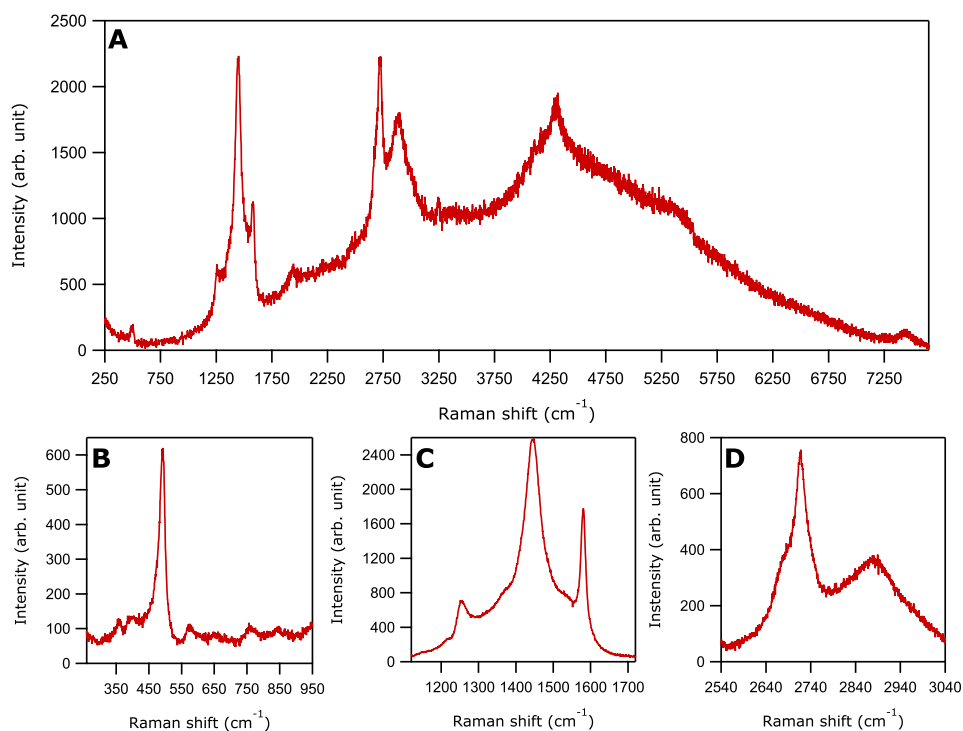


Fig. S7: Raman spectra of the cleaved HOPG sample after reaction analyzed by XPS. A. Full Raman spectrum recorded under 532 nm laser excitation. **B-D** Zooms of the Raman spectra taken after reaction in the S-band, G-band and 2D-band regions. The Raman responses are strong despite the large thickness (in microns) due to a longer reaction time (7 days) suggesting a slow diffusion process into the bulk.

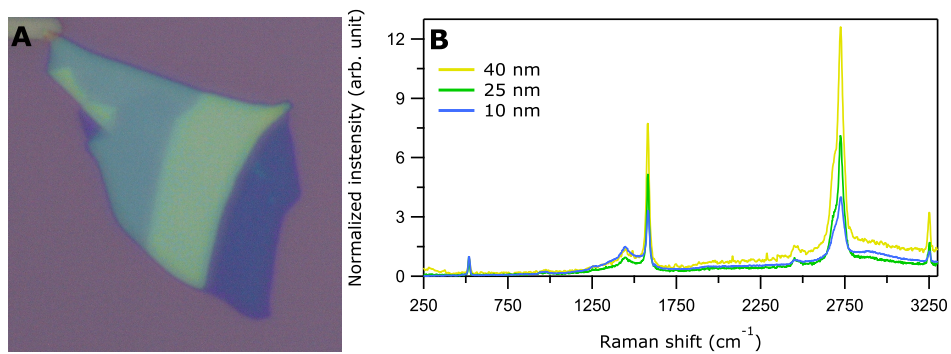


Fig. S8: Thickness-dependent Raman spectra of GS materials. **A.** Optical image ($23 \times 23 \mu\text{m}$) of a GS flake showing three distinct regions of 10 nm (right), 25 nm (left) and 40 nm (middle) thickness. **B.** Raman spectra measured on the three regions after reaction with sulfur. Clarification: on the 40 nm sample, signals can be seen before 400 cm^{-1} however they are just enhanced noise due to the normalization via the Si peak intensity and not elemental sulfur residue peaks.

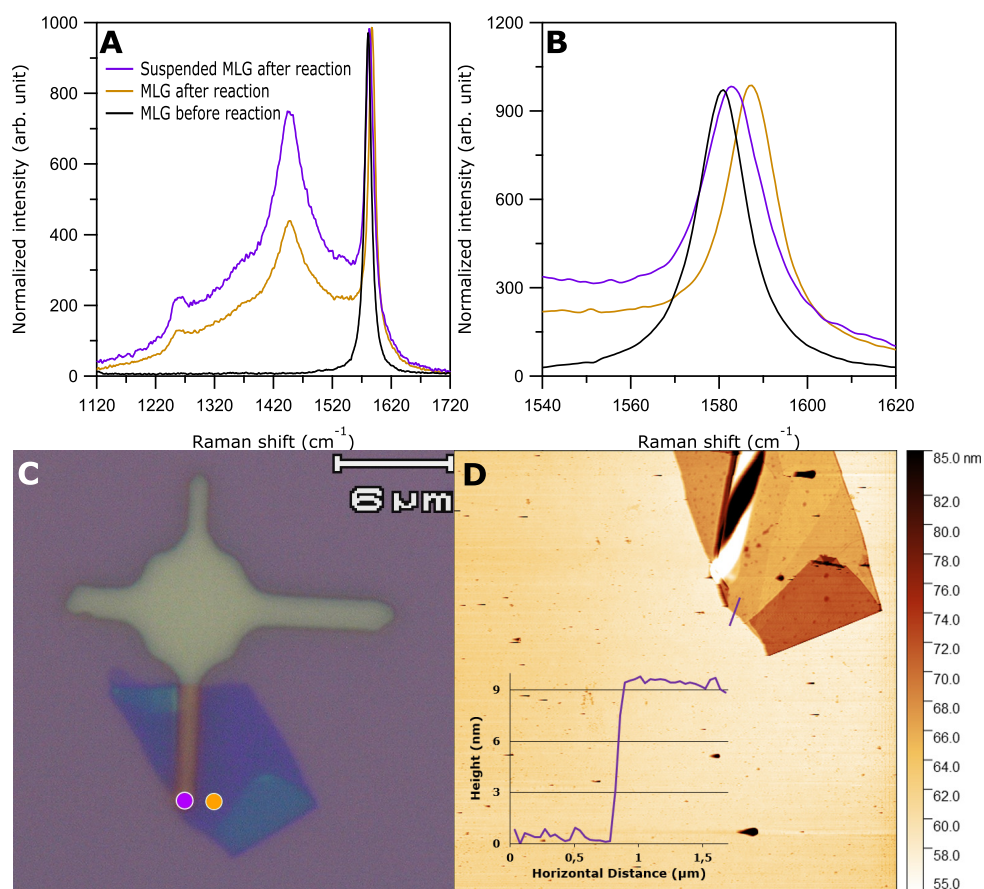


Fig. S9: Preliminary results obtained on a suspended GS flake. **A.** Comparison of the Raman spectra measured before reaction (black) and after reaction on a suspended (purple) and non-suspended (yellow) area of the reacted sample. **B.** Normalized Raman intensities highlighting different values of the G-band shift between the freestanding (purple) and supported (yellow) parts of the GS flake. **C.** Optical image of a partially suspended few-layer graphene flake. **D.** AFM image (20 $\times$ 20 μm) of the FLG flake recorded after the reaction.

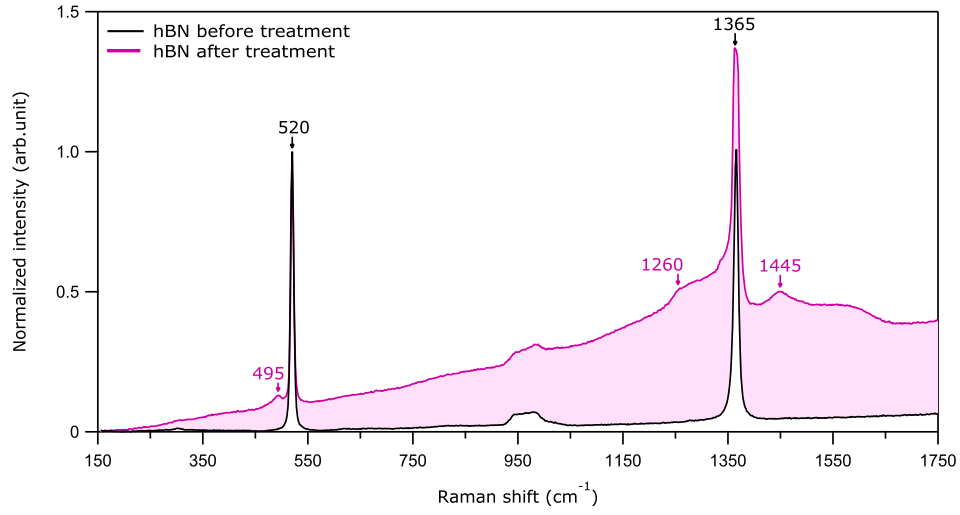


Fig. S10: Sulfur treatment of h-BN flakes. In black, the Raman spectrum of a h-BN flake before treatment with a representative 1370 cm^{-1} peak [69]. In pink, the Raman spectrum of a h-BN flake after treatment with the new peaks and a photoluminescence background. Note that the two squared shoulders to the left of the 1370 cm^{-1} peak are due to instrumental artifacts and the features at 520 and $\sim 960\text{ cm}^{-1}$ are contributions from the silicon substrate. Spectra were normalized on the 520 cm^{-1} peak.

Supplementary XPS and UPS results

960 In order to complete the validation of the necessity of having both reactants for the synthesis of the product, control measurements were performed. In XPS, the process was done with only HOPG, without sulfur, in the same conditions of temperature, pressure and atmosphere composition. As seen in Figure S11, there is no changes between the pristine HOPG and the control HOPG.

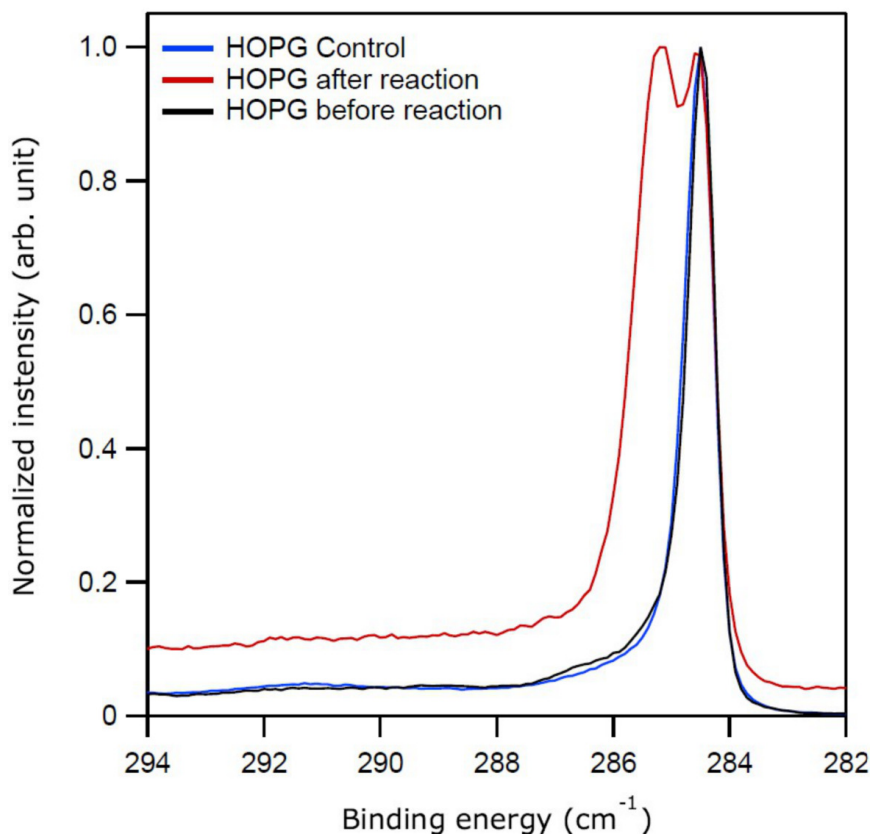


Fig. S11: Comparison of C(1s) XPS spectra of HOPG recorded before and after reaction, and of HOPG under the same treatment without sulfur. Reaction conditions were kept as described in Methods, only sulfur was removed from the reaction chamber for control. In this Figure, XPS peaks are normalized on the C-sp² of graphite before reaction for comparison.

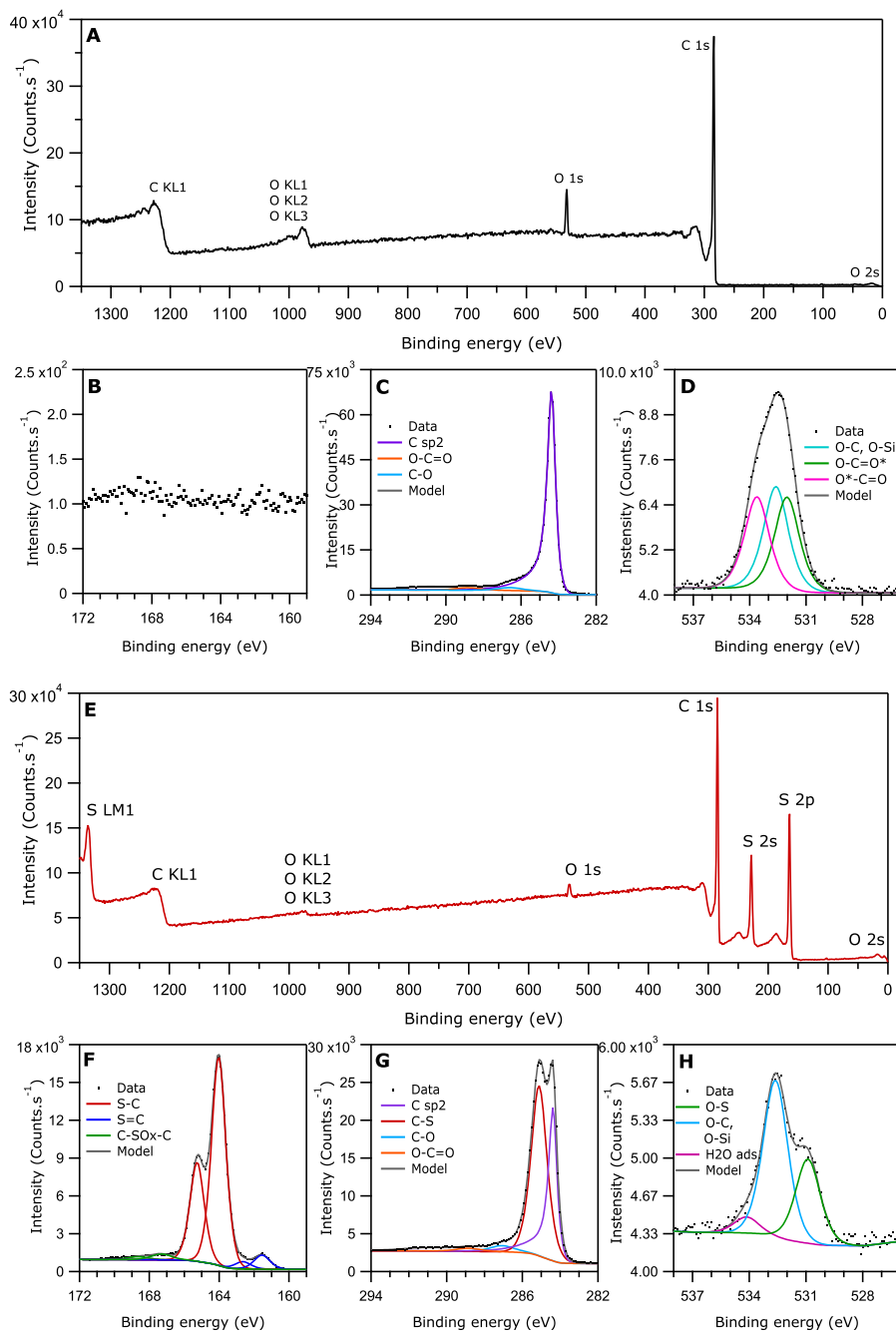


Fig. S12: Complete XPS measurements of freshly cleaved HOPG sample before and after reaction with sulfur. A. XPS spectrum survey of cleaved HOPG before reaction. **B-D.** High resolution spectra of the respective S(2p), C(1s) and O(1s) regions of cleaved HOPG before reaction. **E.** XPS spectrum survey of cleaved HOPG after reaction. **F-H.** High resolution spectra of the respective S(2p), C(1s) and O(1s) regions of cleaved HOPG after reaction. 39

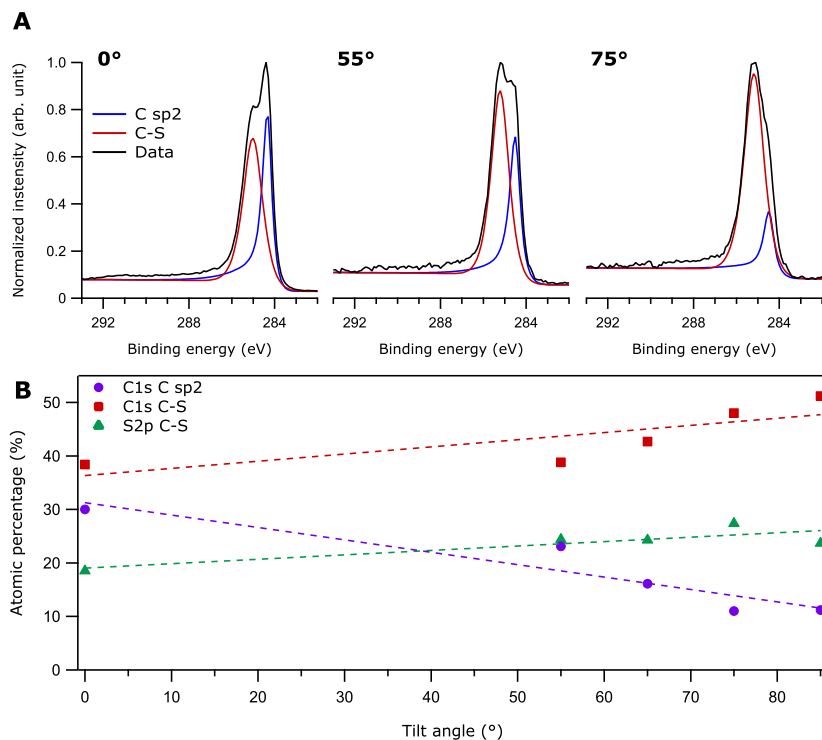


Fig. S13: Angle-resolved XPS measurements of freshly cleaved HOPG taken after a reaction with sulfur. **A.** Angle-resolved XPS measurements of freshly cleaved HOPG from the normal incidence to 75°. Fits to the peaks at 285.5 eV (red) and 284.4 eV (blue) are also shown. **B.** Evolution of the atomic percentage of C-sp² in purple, C-sp³ (C-S) in red and S-C in green with the depth of the XPS measurement. Lines have been added to better appreciate the trend. The angles are determined from the normal incidence and allow progressively an aimed depth of 8.94 to 0.78 nm.

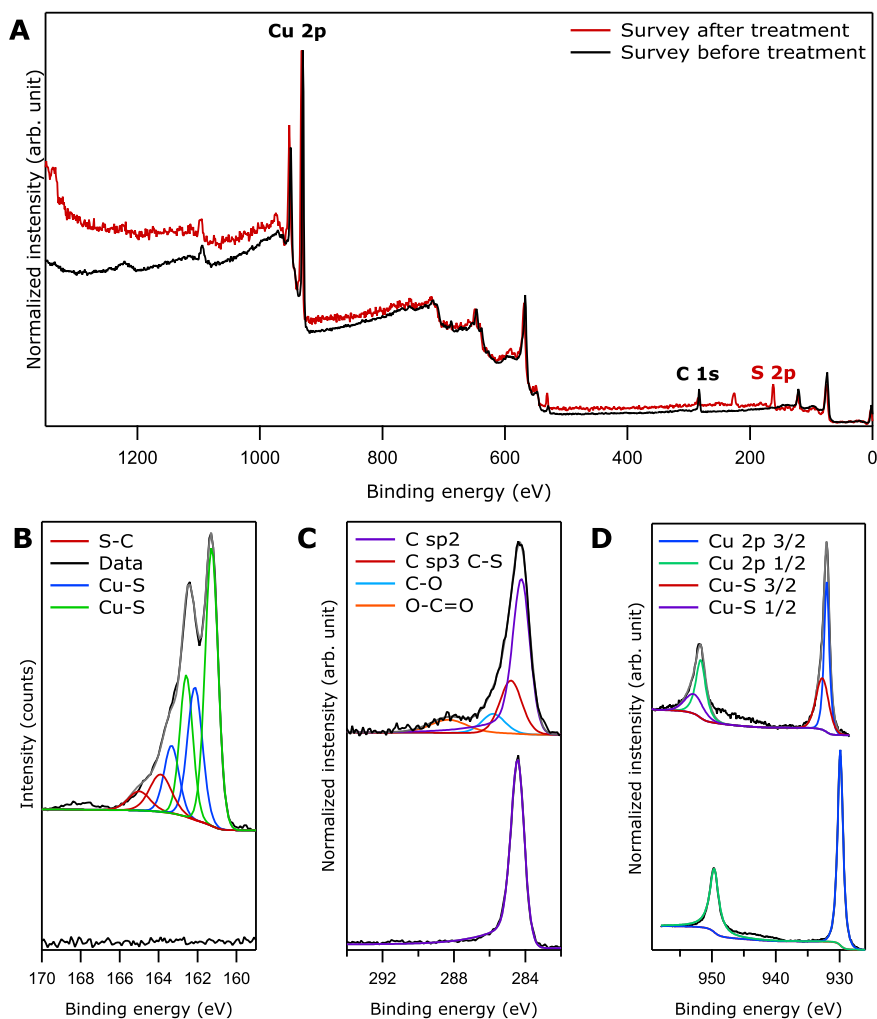


Fig. S14: XPS measurements on Graphene on Copper before and after treatment. **A.** XPS spectrum survey of Graphene on copper before and after treatment. Peaks from the S(2p) and S(1s) core level regions appear after the reaction. High resolution XPS spectra recorded in the core level regions of **B.** sulfur S(2p), **C.** carbon C(1s) and **D.** copper Cu(2p) [70]. Note that the spectra have been vertically shifted for better readability.

In the Figure S14, as in the treated FLG, new peaks appeared after treatment on the GS/CuS sample. In the C(1s) region, C-sp³ C-S appears around 285 eV, the smaller ratio C-S over C-sp² is 1:4 can be explained by the sulfur reacting primarily with copper as seen in S14D. Concerning the S(2p) region, peaks are numerous and

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970 overlapping and make the study difficult, peaks representative of metal sulfides, in this case copper sulfide appeared before 162 eV. Despite this addition, S-C peak can still be observed at 164 eV, confirming again the reaction.

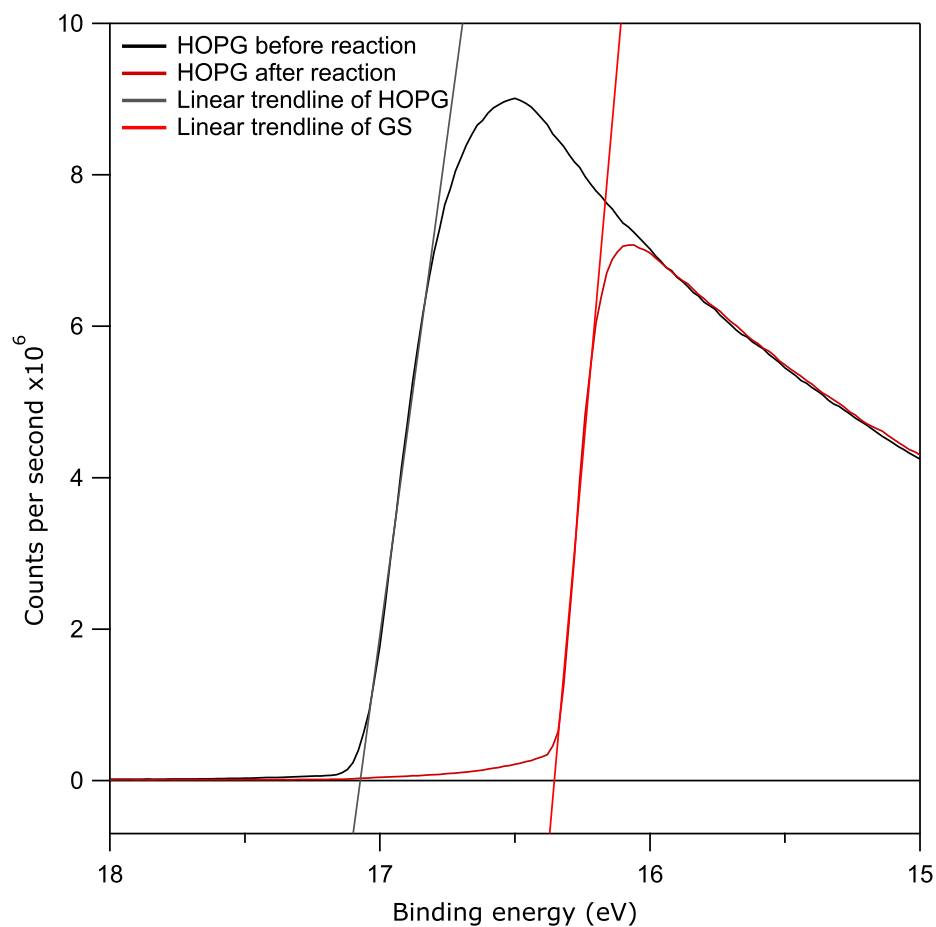


Fig. S15: Zoom in the UPS spectra of a cleaved HOPG sample taken before and after reaction. The extraction via line fits of the workfunction change gives a $\Delta\phi = +0.6$ eV.

Atomic Force Microscopy

In order to remove the hypothesis of a possible of a polymeric coating instead of a compound, AFM measurements have been performed. Figure S16 displays a comparison between the pristine and reacted sample for two samples. Changes in the topography and marbles can be observed after reaction. The increase of roughness can be explained by the strain applied by the episulfidation of graphene domains.

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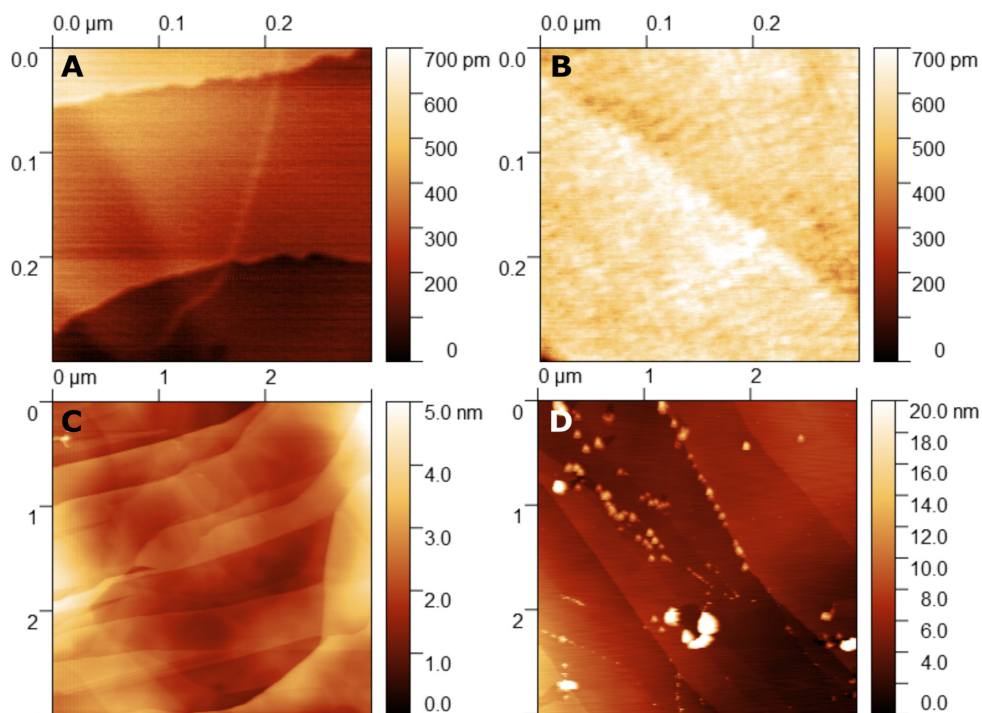


Fig. S16: Atomic Force Microscopy images of HOPG before and after reaction. **A.** AFM image (300×300 nm) of FLG flakes before reaction; **B.** AFM image (300×300 nm) of HOPG after reaction. **C.** AFM image (3×3 μm) of HOPG before reaction. **D.** AFM image (3×3 μm) of HOPG after reaction. The RMS roughness of regions of flat surfaces before (A) and after (B) reaction are 0.27 Å and 0.58 Å, respectively.

Scanning Electron Microscopy

980 The rugosity of CuS made the AFM imaging difficult, as a result, SEM images have been performed on GS/CuS samples instead. The pictures seen below are done with a FEI Quanta 200 from FEIC at an accelerating voltage of 5 kV, a field-emission gun (FEG) as electron source and a secondary electron detector (SED).

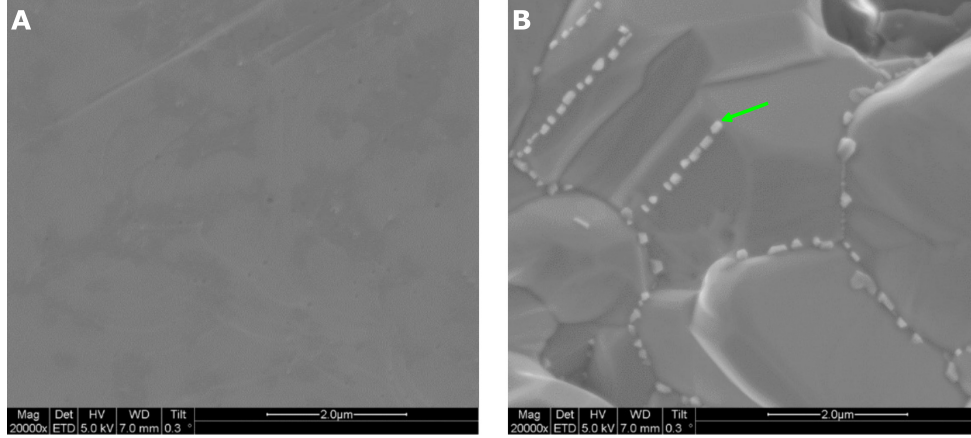


Fig. S17: Scanning Electron Microscopy (SEM) measurements on graphene on copper/ Al_2O_3 before and after sulfur treatment. A. SEM image of graphene/Cu/ Al_2O_3 before reaction; **B.** SEM image after reaction with sulfur. The reaction transforms Cu into large grains of CuS, which layer is rough. Small white polygonal islands are formed at grain boundaries (see arrow), which are assigned to clusters of unreacted sulfur. Scales are 2 μm .

Transmission Electron Microscopy

Transmission electron microscopy (TEM) coupled with energy dispersion spectroscopy (EDS) has been performed on graphene nanopellet flakes and the results are presented in Figure S18. The yellow rectangle in panel C marks the region investigated by EDS images of elemental mapping. To verify the homogeneity of the reaction, we analyzed the carbon and the sulfur distributions and the results in panels D-F show that the distribution is uniform throughout the flakes. This is with the Raman results discussed in the main text. The carbon distribution (green) also shows a good colocalization between the sulfur (in red) and the carbon distribution. The colocalization image in panel F was obtained using COL Finder plugin of IMAGE J software and show that up to 99% of the pixels are correlated.

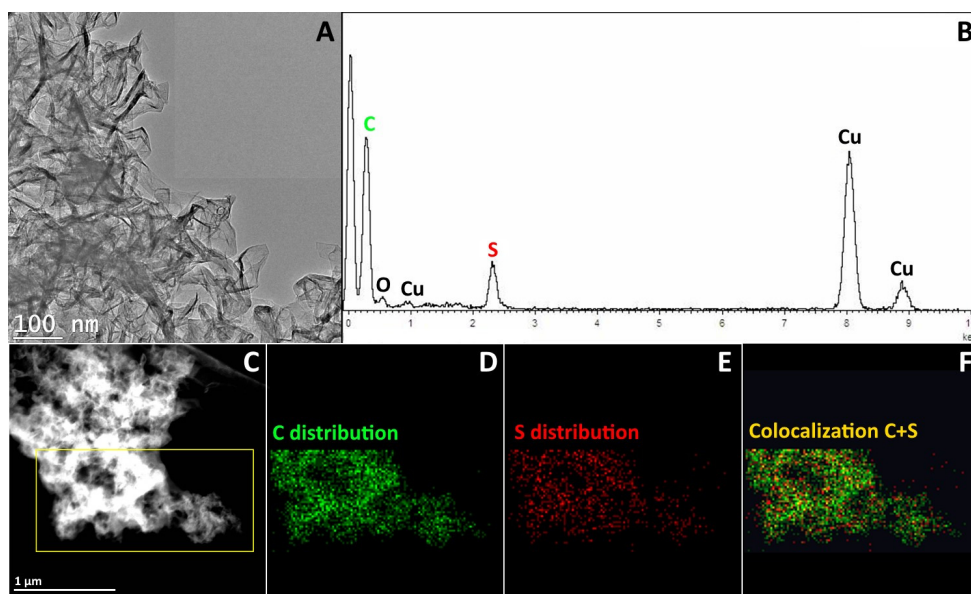


Fig. S18: Transmission Electron Microscopy (TEM) experiments. A. TEM image of graphene flakes after reaction with sulfur; B. EDS spectrum of the reacted sample. C. TEM image displaying the region analysed (yellow) via EDS. D-F. EDS images of carbon (green), sulfur (red) and their superposition, respectively, highlighting the colocalization of carbon and sulfur atoms in the reacted material.

EFTEM images and mapping of the elemental composition of synthesized graphene episulfides on copper sulfide were done in a JEM-F200 TEM (JEOL) at an accelerating voltage of 120 kV coupled with a Gatan Imaging Filter (GIF - Continuum ER System). Energy filtered maps were acquired for carbon, sulfur and copper. The maps of inner shell ionization of the carbon K shell (284 eV), the sulfur L shell (165 eV) and copper L shell (951 eV) were acquired with a slit width of 20 eV.

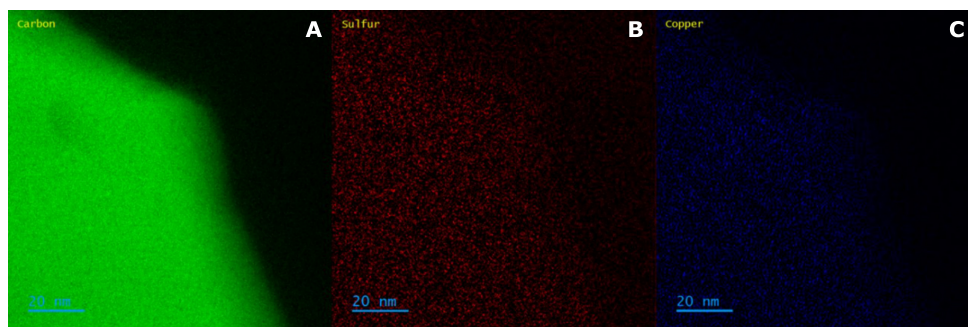


Fig. S19: EFTEM experiments on GS on CuS flakes. EFTEM image of **A.** Carbon ; **B.** Sulfur. **C.** Copper. Sulfur can be primarily seen evenly distributed throughout the Carbon image with few aggregates that could be explained as sulfur nanoparticles due to unavoidable sulfur precipitation. Flakes from Figure S17 sample were dispersed in pure ethanol and then dropcasted onto a TEM grid.

1000 **Thermogravimetric analysis (TGA) coupled with Mass spectrometry**

TGA measurements were performed using 50 mg of graphene nanopellets from Raymor industries treated by sulfur reaction for 7 days in the same conditions as exfoliated thin films of HOPG. The TGA instrument is a TGA 8000 - GC (Clarus 690)/MS (Clarus SQ 8 S) from PerkinElmer. The measurements conditions were the following: heating was done under an Ar flow of 20 mL/min from 35 to 1000°C at 60°C/min. As shown in Figure S20, TGA analysis determines a temperature resistance of the material up to 700°C of some representative fragments of graphene episulfide ($m/z = 64$ and 44). The first loss at 300°C is consistent with the loss of elemental sulfur that did not react (around 1 percent). The compound is stable until around 700°C, then loses the C-S bond and then burns at 935°C. Furthermore, no fragments representative of thiophene, at 58 and 84 m/z , have been detected, excluding its possible formation. Finally in the Figures S20 B and C, the temperatures axis are calculated with the observed ramp of temperature during the measurement and the weight loss time seen on Figure S20 A.

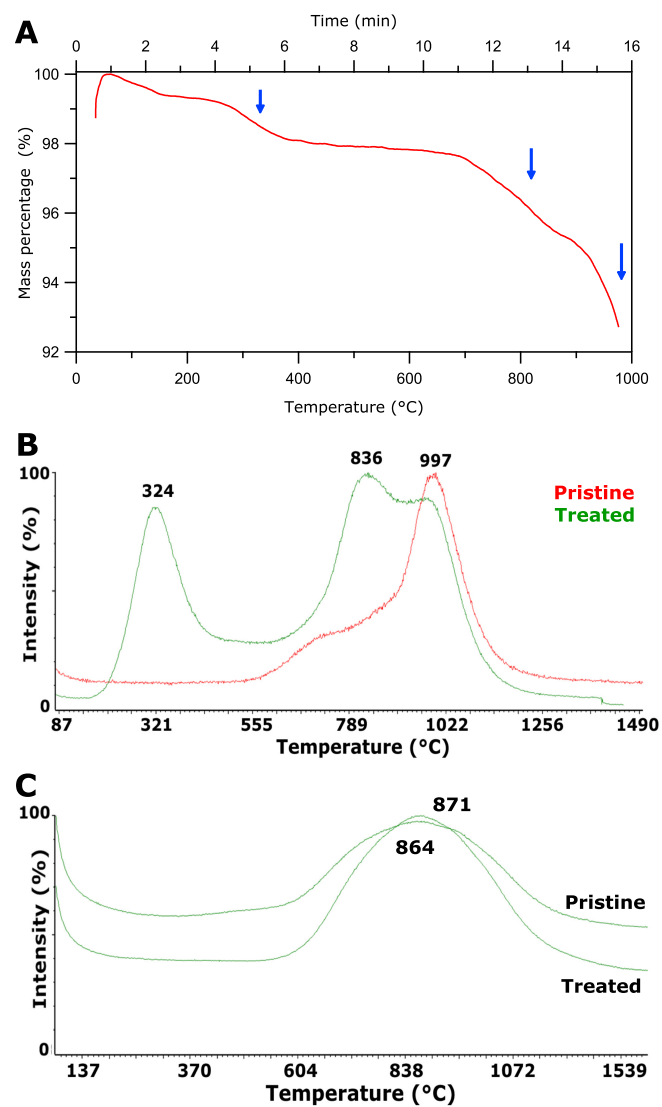


Fig. S20: **A.** Thermogravimetric Analysis (TGA) coupled with mass spectrometry (TGA-MS) of a graphene powder before (pristine) and after reaction (treated). **B.**, **C.** TGA-MS of the intensities of 64 m/z (**B**) and 44 m/z (**C**) fragments, which are consistent of S₂ and CS (or CO₂), respectively.

Table S1: Raman peaks (in cm^{-1}) table of few-layer graphene before and after 24 hours of reaction.

Peak	Before reaction	After reaction	Intensity	Comments	Ref
$\nu(\text{C}-\text{S})$	-	400	Wide and weak	Similar to C-S bondings in graphdiyne sulfide	[29]
$\nu_2: \nu(\text{S}-\text{S})$	-	495	Narrow and weak	Possible small intercalated Sn chains	[29]
$\nu(\text{C}=\text{S})$	-	1260	Medium	Similar to thiocarbonyl	[71]
$\nu_4: \nu(\text{C}(\text{sp}^2)-\text{SC}(\text{sp}^2))$	-	1445	Strong	Similar to observed C-S-C bondings in sulfur doped CNTs, sexithiophene and sulfur thermal reaction on a bilayer of graphene.	[31] [30] [25]
G	1580	1588	Strong	Blueshift due to p-doping and strain	[32]
$\nu_2+\nu_4$	-	1947	Weak	Possible association of (S-S) and $\nu(\text{C}(\text{sp}^2)-\text{SC}(\text{sp}^2))$ modes	
2D	2690	2705	Strong	Blueshift due to p-doping and strain	[32]
$2^*\nu_4$	-	2890	Medium	Possible first overtone	[68]
$3^*\nu_4$	-	4335	Weak	Possible second overtone	[68]

Table S2: XPS values measured on a cleaved HOPG before and after 7 days of reaction. Average values of three measurements performed on cleaved HOPG. The percentage of episulfide sulfur is extracted from the amount of $\text{S}(2\text{p}_{3/2})$ C-S on the amount of $\text{S}(2\text{p}_{3/2})$ C-S, $\text{C}(1\text{s})\text{-sp}^2$ and C-S.

Attribution	Before reaction		After reaction		Ref.
	Average Peak Position (eV)	Average Atomic Percentage	Average Peak Position (eV)	Average Atomic Percentage	
C 1s C sp^2	284.4	80.5	284.4	27.93	[72]
C 1s C sp^3 C-S	-	-	285.1	38.73	[39]
C 1s C sp^2 shake up 1	291.1	6.4	290.967	3.1	[73]
C 1s C sp^2 shake up 2	294.53	0.6	-	-	[73]
C 1s C-O, epoxide	286.63	2.63	287.13	2.23	[35]
C 1s O-C=O	288.83	2.367	288.93	1.2	[35]
O 1s O-C=O	532	2.2	-	-	[72]
O 1s C-O, epoxide, SiO_2	532.53	3.2	532.6	1.8	[72]
O 1s O-C=O	533.567	2.1	-	-	[72]
O 1s sulfone	-	-	530.9	0.67	[72]
O 1s H_2O ads.	-	-	534.23	0.167	[72]
S $2\text{p}_{3/2}$ and $2\text{p}_{1/2}$ C=S	-	-	161.53 and 162.6	1.6	[37]
S $2\text{p}_{3/2}$ and $2\text{p}_{1/2}$ C-S	-	-	164 and 165.2	21.1	[39]
S $2\text{p}_{3/2}$ and $2\text{p}_{1/2}$ C-SO _x -C	-	-	167.3 and 168.6	0.867	[30]
Si 2p SiO_2 Quartz residue from the reaction chamber opening	-	-	103.2	0.67	[72]

Theory

Structural Stability

The addition of sulfur on top, bridge, and hollow sites was tested on a 3×3 graphene sheet. The relaxation of the hollow site consistently converged towards the bridge site configuration, while the top site configuration exhibited an E_{ads} that is 0.5 eV lower than that of the bridge site configuration, as shown in Figure S3. In addition, when two sulfur atoms are added to the 3×3 graphene sheet, the results consistently converge towards the formation of two episulfide bridges, regardless of the initial positions of the sulfur atoms. The average adsorption energy and C-S bond length remain consistent across varying sulfur concentrations added to the graphene sheet, as well as across different cell sizes used in the simulations, as shown in Figures S4 and S5 respectively. This consistency confirms that covalent bonding between graphene and sulfur is robust, even at high sulfur concentrations (average adsorption energy above 2.5 eV). This is further evidenced by the S-C bond length of approximately 1.9 Å, which aligns with experimental episulfide bridge bond lengths.

Table S3: Adsorption energies and S-C bond lengths for Graphene 3×3 systems with one adsorbed Sulfur in Top or Bridge site

	Top	Bridge
C—S bond length (Å)	1.93	1.88
E_{ads} (eV)	2.55	2.03

Table S4: Average adsorption energies and S-C bond lengths of various sized GrS systems at 20% sulfur in atomic percentage

	2×2	3×3	4×4	8×8
Average C—S bond length (Å)	1.89	1.88	1.89	1.88
Average E_{ads} (eV)	3.00	2.77	2.82	2.93

Table S5: Average adsorption energies and S-C bond lengths of various S atomic % in GrS 8×8 systems

Atomic S%	1.56	11.00	20.00	27.00
Average C—S bond length (Å)	1.89	1.89	1.89	1.89
Average E_{ads} (eV)	2.90	2.95	3.16	3.66

Ab initio molecular dynamics

Ab-initio molecular dynamics (AIMD) simulations were performed to verify the time-realized dynamical stability of the proposed GS systems. The temperature was controlled through a Nose thermostat [74] implemented in the SIESTA software package. The simulations were performed over 5 ps at a temperature of 300 K. The energy profiles are shown in Figure S21. The three systems give rise to total energy fluctuations of about twice the baseline thermal energy (~ 50 meV). This is negligible both with respect to the total energy and the adsorption energies of the systems. No bond breaking or major structural changes were observed throughout the MD simulation. As such, the AIMD results support the time-resolved dynamical stability of the systems proposed herein.

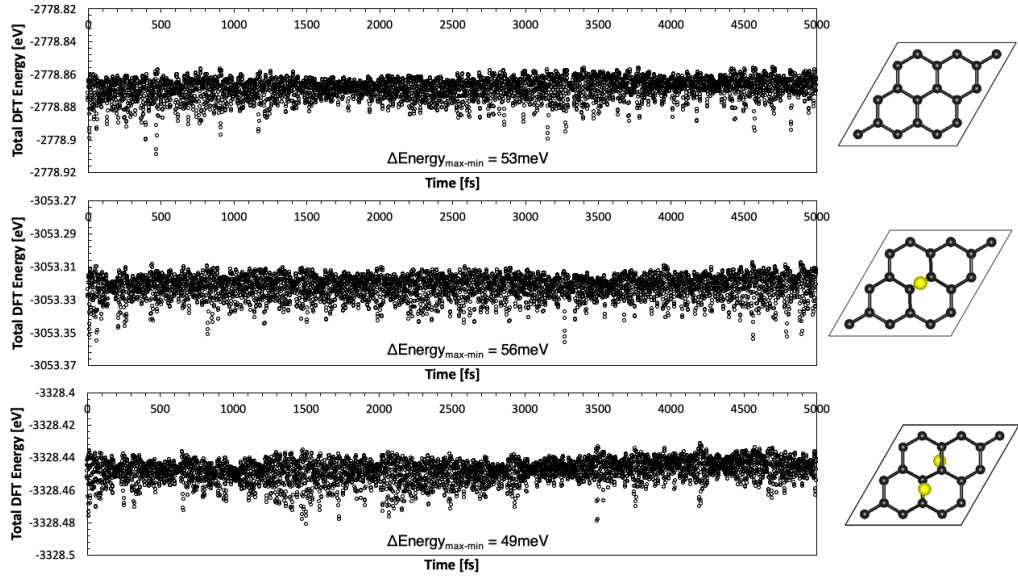


Fig. S21: AIMD variation of total DFT calculated energy of the pristine Gr (top) and two GS systems with 6 and 13% atomic sulfur content over a 5 ps timeframe with a time step of 1 fs and a temperature of 300 K.

Vibrational Calculation Details

The Raman spectrum of a second graphene episulfide model containing two sulfur atoms in a 3×3 graphene supercell, corresponding to a sulfur concentration of 13%, is shown in Fig. S22. The spectrum exhibits the same main features observed in Fig. 1E, including a blue shift of the G mode, the characteristic graphene-episulfide mode at 1471 cm^{-1} , and several low-frequency modes near 500 cm^{-1} . These calculated frequencies are compared with the corresponding experimental modes in Table S6. The persistence of these characteristic features indicates that the vibrational signature of the GS structure is preserved across different sulfur concentrations and remains consistent with the experimental spectrum.

The effect on the Raman spectra by isotopic substitution of ^{12}C by ^{13}C in the GS structures is shown in Table S7. The low-frequency modes associated mainly with sulfur motion exhibit only minor changes upon isotopic substitution. In contrast, the mode above mentioned at approximately 1100 cm^{-1} show a systematic shift toward lower Raman frequencies for the ^{13}C GS structure. The calculated shift is around 3% for the carbon dominated modes, which is a significant value, albeit somewhat smaller than the $\sim 3.9\%$ expected from the harmonic approximation for modes dominated entirely by carbon motions. [75].

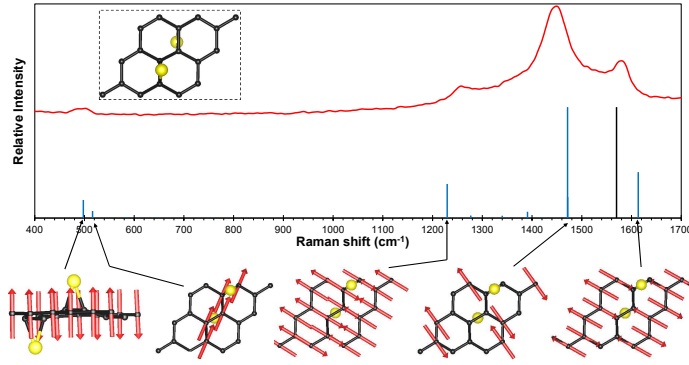


Fig. S22: Experimental first-order Raman spectrum of sulfur-functionalized HOPG (red), compared with the calculated spectra of graphene episulfide (GS; blue) and pristine graphene (black). All intensities are normalized to their respective maxima.

Table S6: Comparison of the experimental and calculated first order Raman peak positions for the GS system with 13% S.

Experimental shift (cm^{-1})	Calculated shift of GS (cm^{-1})
495	508 and 516
1218 to 1260	1229, 1277 and 1340
1450	1471
1580	1613

Table S7: Comparison of the calculated first-order Raman peaks for the GS system and ^{13}C -GS, with the corresponding percentage shift.

GS (cm^{-1})	^{13}C -GS (cm^{-1})	Shift (%)
498	489	1.62
586	576	1.62
1229	1194	2.85
1277	1240	2.89
1340	1300	2.89
1471	1424	3.13
1613	1564	3.13