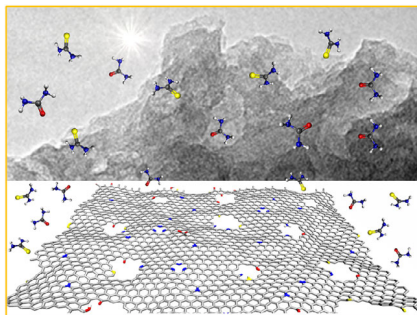


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## RESEARCH ARTICLES

- 3 R. Sánchez-Salas, E. Muñoz-Sandoval,  
4 M. Endo, A. Morelos-Gómez,  
5 F. López-Urías\* ..... 2001444  
6 **Nitrogen and Sulfur Incorporation into**  
7 **Graphene Oxide by Mechanical Process**



Ball-milling (BM) method is used for nitrogen and sulfur-doping graphene oxide (GO). Urea or thiourea are mixed and subjected to a solid-state grinding process. The elemental composition of BM-GO-urea exhibits 7.7 at% of nitrogen, whereas BM-GO-thiourea displays 6 at% of sulfur with 5.6 at% of nitrogen. Urea and thiourea interacting with graphene-sheets are investigated by density functional theory (DFT) calculations.

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# Nitrogen and Sulfur Incorporation into Graphene Oxide by Mechanical Process

Roque Sánchez-Salas, Emilio Muñoz-Sandoval, Morinobu Endo, Aarón Morelos-Gómez, and Florentino López-Urías\*

Graphene oxide (GO) is one of the carbon nanomaterials used most in novel applications. Due to its easy synthesis, easy exfoliation, doping potential performance, and good compatibility in composites, GO has attracted the attention of several research groups. The introduction of foreign atoms into this nanomaterial can enhance its chemical and physical properties. The milling method is used for reducing and doping of GO during the mechanochemical process, using urea and thiourea as dopant agents and solid grinding molecule assistant. The elemental composition of BM-GO-urea exhibits 7.7 at% of N, whereas BM-GO-thiourea displays 6 at% of S with 5.6 at% of N. Using density functional calculations, urea, and thiourea molecules are covalently joined to the carboxyl-functional groups. After structure optimization, the density of states, highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO) wave functions are analyzed. It is shown that nitrogen doping favors a HOMO energy decrement when the molecules are directly attached to graphene sheets in the absence of carboxyl groups, making it energetically less expensive to share electrons in undoped nanomaterials. In contrast, the urea and thiourea molecules joined to graphene sheets via carboxyl groups show deep HOMO energies and low nitrogen-doping variations. Our results demonstrate the viability of the high-energy ball milling (HEBM) technique for reduction and N/S doping-functionalization of GO and a mechanochemical methodology to exfoliate and dope-functionalize graphite.

## 1. Introduction

The physical and chemical properties of graphene oxide (GO) have been widely studied.<sup>[1–3]</sup> One important characteristic of GO, after its fabrication, is its covalent or noncovalent functionalization. As GO shows good biocompatibility, it has been used as a drug-delivery system.<sup>[4]</sup> For environmental remediation, the oxygen functional groups of GO help to remove heavy metals in the liquid media.<sup>[5,6]</sup> Further, GO has been decorated with nanoparticles as hybrid materials for catalyst performance.<sup>[7]</sup> For water treatment, GO has been used as a membrane, exploiting its antifouling properties, facile, and large-scale production.<sup>[8]</sup> GO has been proposed as an ideal candidate for nanomedicine applications and a biomolecule nanocarrier.<sup>[9]</sup>

Recently, the incorporation of foreign atoms or molecules on GO has been suggested as an anode for lithium-ion batteries.<sup>[10]</sup> Nitrogen and phosphorus dual-doped reduced GO has been synthesized by heating GO, urea, and 1,2-bis(diphenylphosphino) methane. Their

lithium-ion storage performance was tested, resulting in a better material for the charge and discharge process. Urea and thiourea are excellent candidates for incorporating nitrogen into graphitic materials via the milling method, using GO or graphite materials. Both urea and thiourea are water-soluble and environmentally-friendly, with a mild chemical reduction activity on GO via deoxygenation of the two amine  $\text{-NH}_2$  groups at the oxygen functional groups. Earlier investigations reported covalent cross-linking when thiourea and urea are included between the GO sheets due to the weak interlamellar interaction and stacked 2D channels with potential molecule selectivity on aqueous GO dissolutions and paper-like membrane.<sup>[11,12]</sup>

Other groups investigated mixing solid N-containing organic molecules in the graphite grinding process as a simultaneous N doping and solid grinding agent during the milling process, known as solid-state dope/functionalized graphitic sheets, via dry milling with a post-purification step, as the molecule was water-soluble. Xue et al.<sup>[13]</sup> used melamine ( $\text{C}_3\text{H}_6\text{N}_6$ ) and graphite in a 10:1 mass proportion to obtain by milling N-doped graphene nanoplatelets with a C/N ratio of 7.4 and evidence 47

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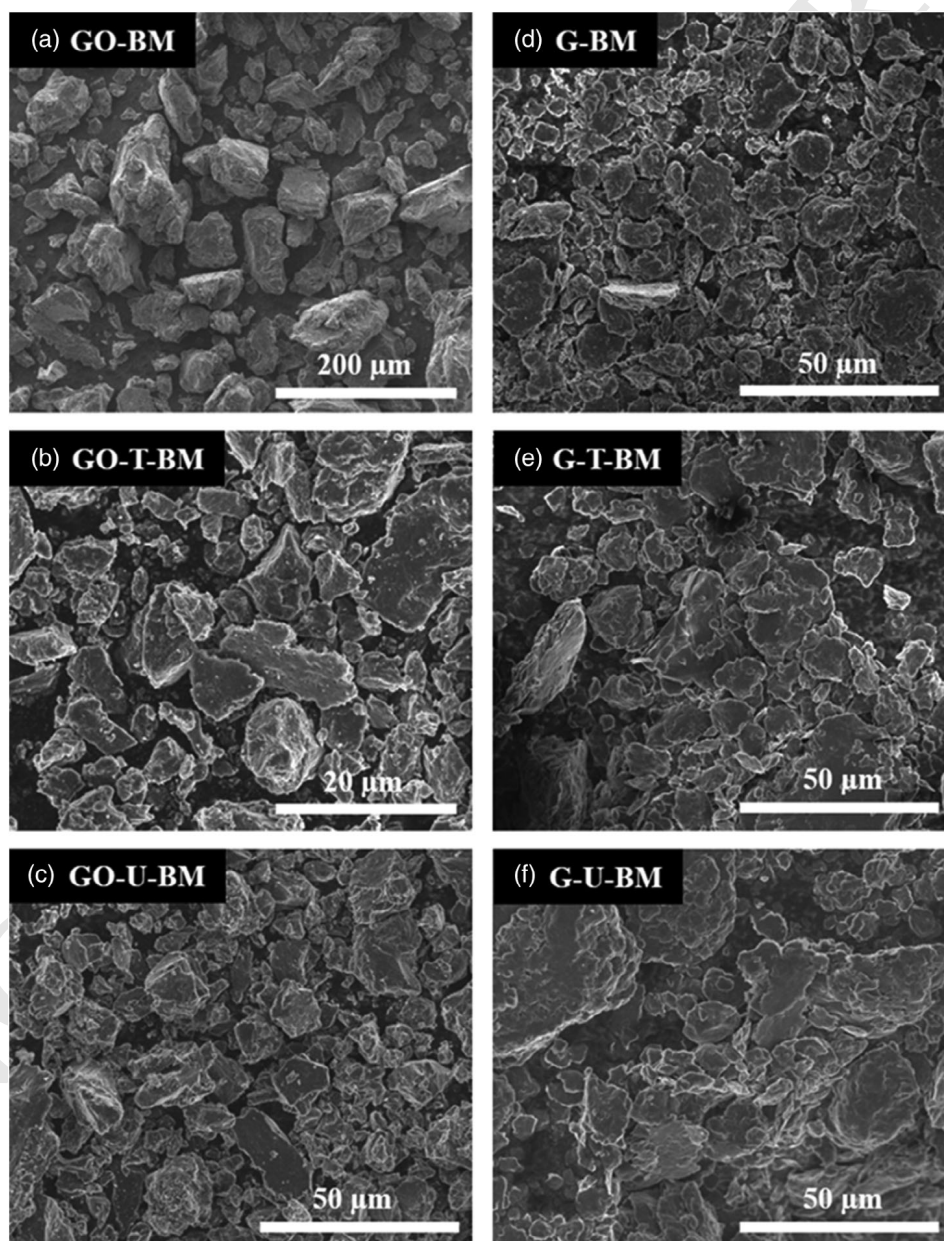
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1 of N-pyridinic, N-quaternary, and N-pyrrolic doping. Further, Liu  
2 and co-workers<sup>[14]</sup> used solid urea ( $\text{CH}_4\text{N}_2\text{O}$ ) and graphite in a  
3 20:1 mass proportion in the milling process, to obtain nitrogen-  
4 doped graphene nanosheets with a C/N ratio of 28.7, also with  
5 evidence of nitrogen doping into the hexagonal plane with a  
6 majority part of N-pyrrolic.

7 In this work, an inexpensive process has been implemented  
8 to fabricate GO with attached nitrogen and sulfur-containing  
9 molecules at the surface. By a simple mixing of GO with urea  
10 and thiourea using a ball-milling (BM) process, we obtained a  
11 novel nanomaterial with interesting chemical and physical  
12 properties.

## 2. Results and Discussion

1 The morphology of the samples after BM was observed by scan-  
2 ning electron microscopy (SEM); **Figure 1a–c** shows the SEM  
3 images of GO-BM, GO-T-BM, and GO-U-BM samples. Sample  
4 GO-BM exhibited grain size with diameters ranging from  
5 10 to  $960\ \mu\text{m}^2$  (Figure S4a, Supporting Information), GO-T-BM  
6 showed grain sizes of  $5\text{--}46\ \mu\text{m}^2$  (Figure S4b, Supporting  
7 Information), and GO-U-BM grain sizes of  $1\text{--}172\ \mu\text{m}^2$   
8 (Figure S4c, Supporting Information), with an average of 119,  
9 16, and  $26\ \mu\text{m}^2$ , respectively. SEM images for G-BM, G-T-BM,  
10 and G-U-BM are shown in Figure 1d,f with respective average  
11



**Figure 1.** SEM images of a) GO-BM, b) GO-T-BM, c) GO-U-BM, d) G-BM, e) G-T-BM, and f) G-U-BM. The grain size distribution can be seen in Figure S4, Supporting Information. All samples exhibited a polydispersity in grain size and morphology. The GO-T-BM showed the smallest grain size area down to  $5\ \mu\text{m}^2$  in diameter. Notice that the use of urea and thiourea influence the grain size and morphology of the grains.

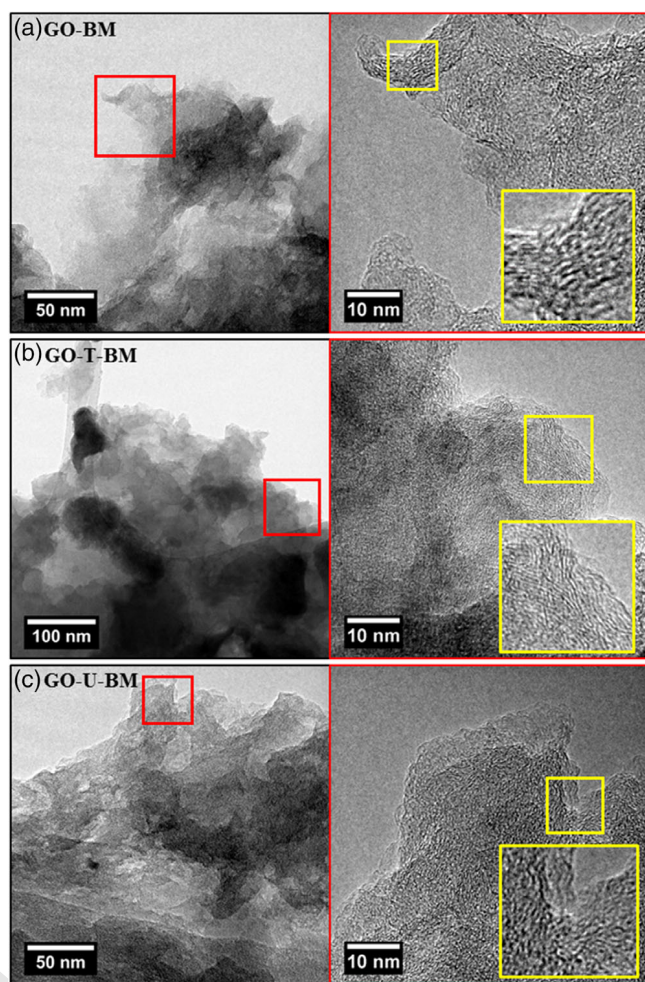


1 sizes of 22, 23, and 24  $\mu\text{m}^2$ , with similar size, ranging between  
2 1 and 150  $\mu\text{m}^2$ . Energy-dispersive X-ray spectroscopy (EDS) of  
3 the samples is shown in Figure S5, Supporting Information, with  
4 their respective atomic concentration. As expected, the GO-based  
5 samples showed the highest oxygen contents concerning  
6 graphite-based samples; see Figure S5a–c, Supporting  
7 Information. The use of urea provided the highest nitrogen con-  
8 centrations for samples GO-U-BM and G-U-BM (Figures S5c and  
9 S5f, Supporting Information). In contrast, with thiourea, the  
10 highest sulfur content was found for the sample GO-T-BM, fol-  
11 lowed by sample G-T-BM (Figures S5b and S5e, Supporting  
12 Information). The sulfur traces in sample GO-BM and GO-U-  
13 BM come from the GO preparation (Figures S5a,c, Supporting  
14 Information). **Figure 2** shows the transmission electron micro-  
15 scopy (TEM) and HRTEM images of GO. The structural damages  
16 are notable in the TEM images of GO-based materials. Hole-like  
17 structures were observed in GO-T-BM and G-T-BM samples, due  
18 most likely to the mechanochemical decomposition of thiourea  
19 into graphitic carbon nitride nanocomposites between 500 and

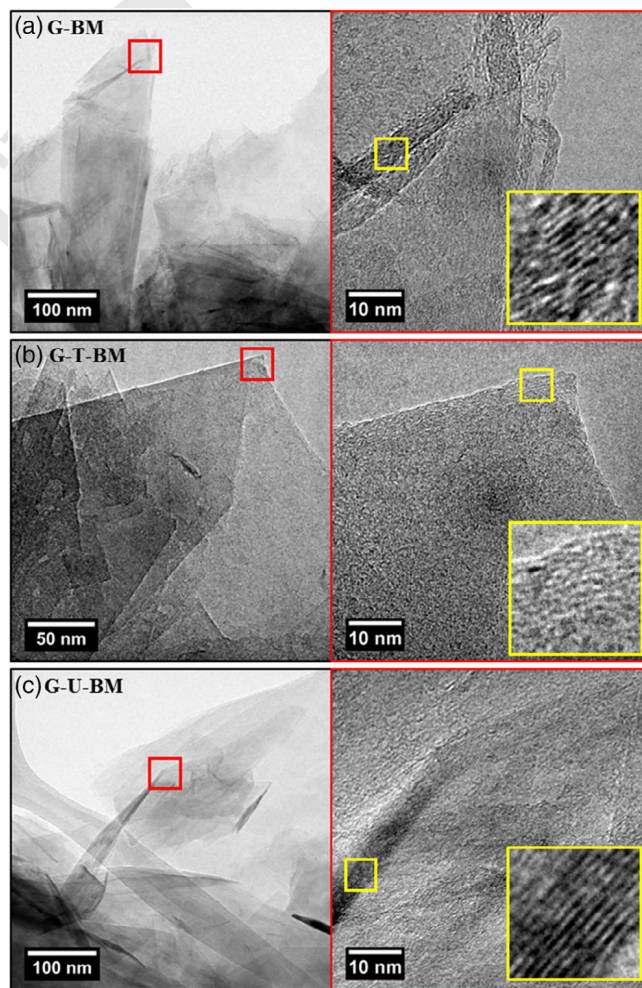
–600 °C under air or inert atmosphere;<sup>[15–19]</sup> moreover, hole dam- 1  
ages were observed in graphite milled sample with thiourea 2  
(Figure S7–S8, Supporting Information). 3

The BM process for graphitic-based materials (G-BM, G-T- 4  
BM, and G-U-BM) causes other structural damage compared 5  
to GO, due to the higher mechanical properties of the graphite 6  
layers, as shown in **Figure 3**, exhibiting usual top-to-down 7  
graphite exfoliation with few-layered sheet nanostructures and 8  
well-graphitized stacked-layer planes with similar layered 9  
distance stacking. Figure S6, Supporting Information, shows 10  
HRTEM images and interatomic distance profiles of the (002) 11  
crystallographic plane. 12

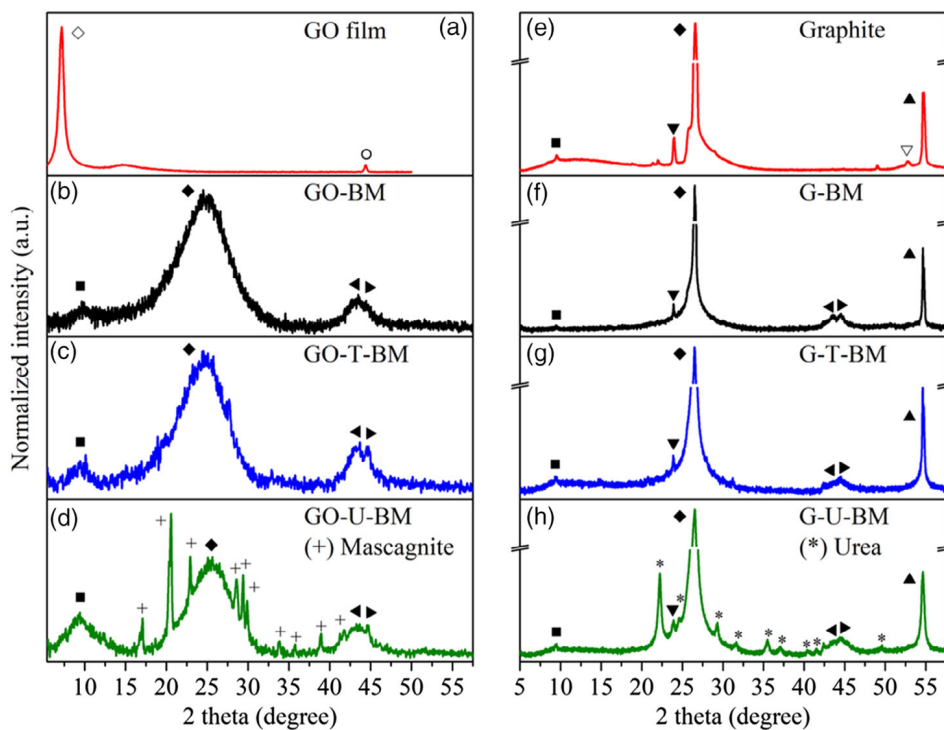
The sample's crystal structure was characterized by X-ray 13  
diffraction (XRD). **Figure 4a–d** shows the XRD patterns for 14  
milled GO-based samples. The graphitic (002) peak for GO-BM, 15  
GO-T-BM, GO-U-BM was found at  $2\theta = 24.7 \pm 0.46^\circ$ , with an 16  
interlayer distance of 3.59, 3.58, and 3.49 Å, respectively. The 17  
GO (001) area peaks were 9.6%, 14.8%, and 31.6%, compared 18  
to their respective graphitic (002) peak. We identified the 19



**Figure 2.** TEM and HRTEM images of a) GO-BM, b) GO-T-BM, and c) GO-U-BM. The corresponding enclosed areas in red color are shown on the right side. All samples exhibited corrugated reduced GO sheets with irregular edges. Complementary TEM images for GO milled samples can be seen in Figure S7, Supporting Information.



**Figure 3.** TEM and HRTEM images of a) G-BM, b) G-T-BM, and c) G-U-BM. In (a–c) the graphitic structures exhibits few layered graphenic sheets. The square yellow insets show stacked graphitic layers. Complementary TEM images for graphite-milled samples can be seen in Figure S8, Supporting Information.



**Figure 4.** XRD patterns for a–d) GO materials and e–h) graphite materials. The symbols refer to different crystallographic planes: left triangle (001), square and empty rhomb (001), full rhomb (002), down triangle  $K_{\beta}$ (002), left triangle (001), right triangle (101), up triangle (004), and empty down triangle  $K_{\beta}$ (004). For (f–h), the crystalline sizes  $L_{C(002)}$  were 34, 32, and 15 nm, respectively. Additionally, ammonium sulfate (Mascagnite) peaks (ICDD #40-0660) and urea peaks (ICDD #08-0822) were found in GO-U-BM and G-U-BM samples with a residual percentage of 7.3% and 8.6%, respectively.

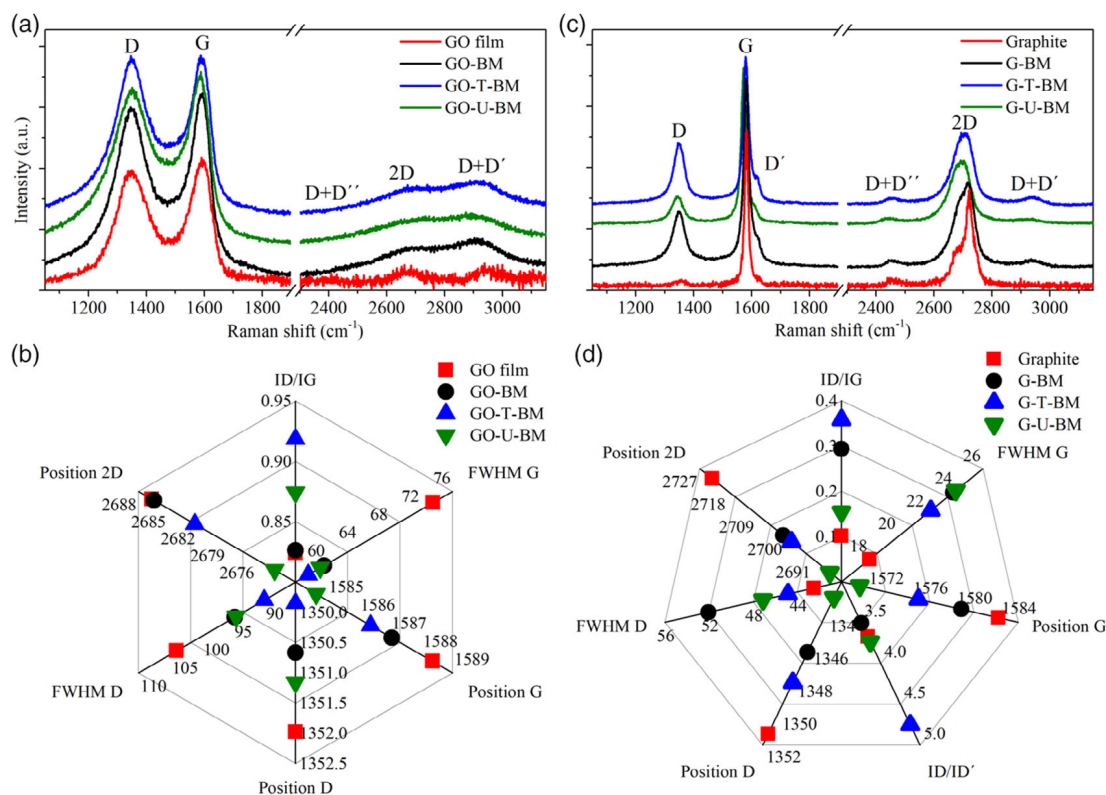
1 ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$  diffraction peaks in GO-U-BM,  
 2 called Mascagnite, suggesting that amino groups might be  
 3 reduced to ammonium  $(\text{NH}_4^+)$  and be made salts with sulfate  
 4 ions  $(\text{SO}_4^{2-})$  from residual GO synthesis during the milling pro-  
 5 cess. XRD results for milled graphite-based samples are shown  
 6 in Figure 4f–h, revealing the (002) diffraction peak at  
 7  $2\theta = 26.51^\circ \pm 0.02$  with an interlayer distance of 3.36 Å but full  
 8 width at half maximum (FWHM) of 0.20, 0.25, and 0.43 for  
 9 G-BM, G-T-BM, and G-U-BM, respectively. For GO-U-BM, the  
 10 additional diffraction peaks coincide with those of urea. This fact  
 11 could be due to the higher energy decomposition of the urea  
 12 molecule. The average crystallite size for the graphite-based  
 13 BM samples was estimated using the Scherrer's Equation  
 14  $D(hkl) = K\lambda/\beta\cos\theta$  at the (002) graphitic peak, where K is a con-  
 15 stant taken as 0.89,  $\lambda$  is the X-ray wavelength (nm), and  $\beta$  is the  
 16 FWHM of the considered diffraction peak. Then, crystalline sizes  
 17 were 34, 32, and 15 nm for G-BM, G-T-BM, and G-U-BM, respec-  
 18 tively, which confirmed that urea remains to act as a solid grind-  
 19 ing agent. Raman spectrum was adopted to study the graphitic  
 20 nature of the samples; the D, G,  $G'$ ,  $D + D''$ , 2D, and  $D + D'$   
 21 bands for GO-based and graphitic-based samples are shown  
 22 in Figure 5a,c. Furthermore, the pristine reference was added.  
 23 It is noteworthy that all the GO-based samples showed less than  
 24 one  $I_D/I_G$  ratio (see Figure 5b). The corresponding Raman shift  
 25 band positions and FWHM dispersions are shown in Figure 5b,  
 26 d. In GO-based materials, GO-T-BM showed the lowest graphiti-  
 27 zation ratio  $I_D/I_G$ , lowest FWHM of D and G bands, and shorter  
 28 down-Raman shift for G and 2D bands, compared to GO-BM.

These findings suggest a higher density from concurring defects  
 1 as an indicator of an N, N–S doping, or functionalized edges  
 2 due to thiourea. In addition, GO-BM had the highest graphiti-  
 3 zation quality ratio  $I_D/I_G$ . The highest FWHM for the D and G  
 4 bands from milled GO-based samples could indicate different  
 5 border disorders or defect differences at graphitic defects and  
 6 active sites.  
 7

Alternatively, milled graphite-based samples showed an incre-  
 8 ment in their D band due to the structural exfoliation damage  
 9 (Figure 5c). Top-to-down exfoliated graphite displays an increase  
 10 in the  $D'$  band at  $\approx 1620\text{ cm}^{-1}$  (just next to G-band), usually  
 11 indicating the presence of edge defects in the graphitic lattice,<sup>[20]</sup>  
 12 as well as an N doping contribution in the G-T-BM and G-U-BM  
 13 cases.<sup>[21]</sup> Therefore, the  $I_D/I_G$  ratio could be used as a parameter  
 14 of defects at the borders in the exfoliated graphitic material  
 15 related to  $sp^3$ -like vibration modes.<sup>[22,23]</sup> The G-T-BM sample  
 16 presents the lowest graphitization ratio  $I_D/I_G$ , lower FWHM  
 17 of the D and G bands, with a down-Raman shift position of  
 18 the G and 2D bands, compared to the G-BM sample. Finally,  
 19  $I_D/I_G$  ratio shows the highest value in Figure 5d for G-T-BM  
 20 and matched in the conjecture of higher density from concurring  
 21 defects or incorporation of N, N-S doping borders concerning  
 22 G-U-BM. However, after the milling process, the FWHM for  
 23 the D band had the highest value for G-BM, followed by G-T-BM  
 24 and the lowest for G-U-BM as an indication of higher to smaller  
 25 active sizes, respectively.  
 26

The thermal decomposition of the samples was studied by  
 27 thermal gravimetry analysis (TGA). Figure 6 shows the TGA  
 28



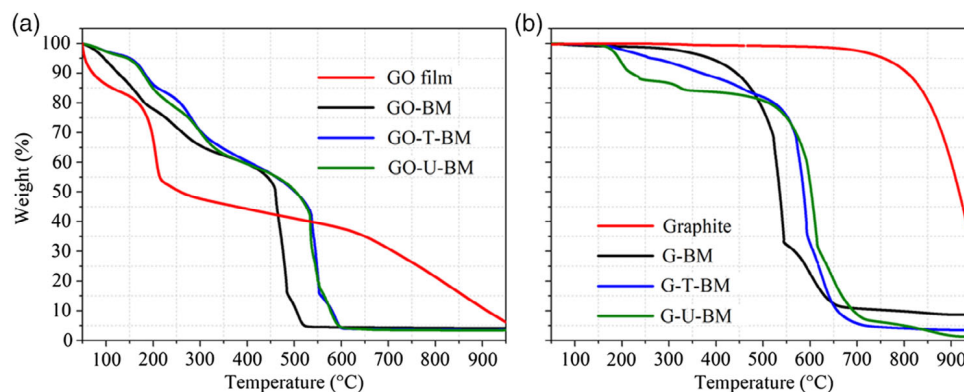


**Figure 5.** Raman spectra for a) GO and c) graphite materials (pristine and BM). b,d) Radar plots showing the ratio of intensities between the D- and G-bands ( $I_D/I_G$ ) with their FWHM and peak position of D, G, and 2D bands for GO and graphite samples, respectively.  $I_D/I_G$  ratios were estimated from graphitic-based samples. Values shown in (b) and (d) can be seen in **Table 1**.

1 curves for milled graphite-based and GO-based samples. The  
 2 onset point for GO-BM, GO-T-BM, and GO-U-BM samples  
 3 was found at 484, 533, and 552 °C, respectively (Figure 6a) with  
 4 weight losses over four intervals: 1) 50–130 °C due to the water  
 5 evaporation on the surface and inter/intralayer due to their  
 6 hygroscopic nature derived from the oxygen functionalities,  
 7 2) 130–220 °C corresponds to the residual decomposition of oxy-  
 8 genated functional groups (carbonyl and carboxyl), 3) 220–420 °C  
 9 due to the decomposition in more complex oxygenated func-  
 10 tional groups (lactone-ester, carboxylic-anhydride, phenol,  
 11 ether, carbonyl),<sup>[24]</sup> 4) 420–650 °C, which is assigned to the  
 12 decomposition of turbostratic reduced-GO and finally graphitic  
 13 decomposition after 650 °C.<sup>[25–27]</sup> The thermogram exhibits  
 14 water desorption below 160 °C, with a weight loss of 18% regard-  
 15 ing the GO-film. Then, between 160–226 °C, we found an onset  
 16 point at 206 °C. The sample underwent an accumulative weight  
 17 loss of 29% due to the decomposition of oxygenated groups, then  
 18 a gradual decomposition of more stable oxygenated functional  
 19 groups of  $\approx 4$  wt% every 100 °C up to 600 °C, and finally, the  
 20 graphitic decomposition  $\approx 9$  wt% every 100 °C up to 950 °C.  
 21 Finally, due to the premixture of the urea and thiourea with  
 22 the GO, their mild chemical reduction potential enhanced the  
 23 thermal oxidation stability compared to GO pristine milling.  
 24 On the other hand, we found that milled graphite-based samples  
 25 exhibited a weight loss of less than 1 wt% before 160 °C.  
 26 The samples G-BM, G-T-BM, and G-U-BM showed an onset  
 27 temperature of 544, 592, and 614 °C (Figure 6b), respectively.

1 It was noticed that under 350 °C, the TGA curves were different  
 2 due to the raw thiourea/urea residue. For instance, the mass  
 3 losses of G-T-BM matched with the thiourea molecule at 180,  
 4 220, and 250 °C.<sup>[28,29]</sup> Furthermore, sample G-U-BM exhibited  
 5 two mass losses at 200 and 320 °C attributed to the urea  
 6 molecule.<sup>[30]</sup> To conclude, the BM decreases the thermal oxida-  
 7 tion stability of graphite. Interestingly, urea and thiourea exhibit  
 8 higher stability than without these dopant/reducing precursors  
 9 from the TGA observations; urea and thiourea aid to increase  
 10 the chemical stability of GO with BM.

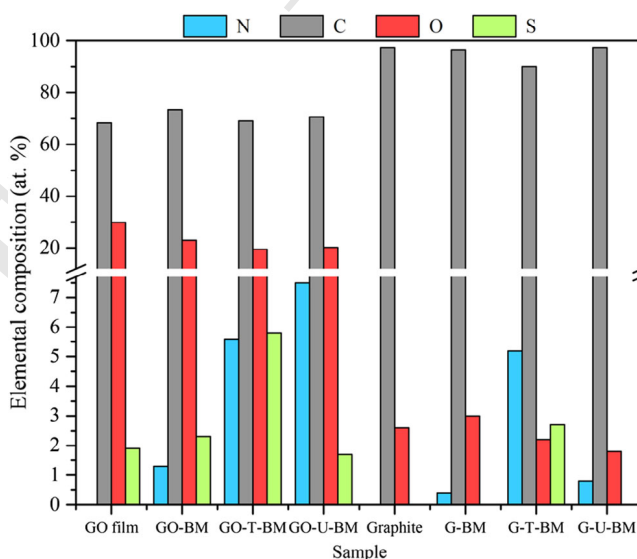
11 We now discuss the XPS characterizations to study the surface  
 12 chemistry. **Figure 7** shows the atomic percent derived from the  
 13 XPS survey spectra (see also Figure S9, Supporting Information).  
 14 **Figure 8** shows the high-resolution XPS for pristine and milled  
 15 GO-based samples. The C1s spectra for GO-BM showed remarka-  
 16 ble changes, compared to the as-produced GO (Figure 8a).  
 17 The milled GO-based samples exhibited an attenuated peak  
 18 around 286.7 eV related to C–O and C=O bonds (epoxy, car-  
 19 bonyl, and carboxyl groups). This indicates a partial reduction  
 20 process of GO by mechanochemical processes, combined with  
 21 urea and thiourea, were observed in peaks attributed to C=C  
 22 and C–C bond ( $sp^2$  and  $sp^3$  carbon hybridization). The GO-film  
 23 showed a broader peak due to the high concentration of  $sp^3$   
 24 hybridization, and the BM samples exhibited narrow graphitic  
 25 peaks. The C=O/C–C peak for GO-BM showed a peak centered  
 26 C=C energy. Those milled with urea or thiourea exhibited a bind-  
 27 ing energy shift toward the C–C bond, larger for the GO-U-BM



**Figure 6.** TGA curves for a) pristine GO and BM GO materials. The onset temperature for GO-BM, GO-T-BM, and GO-U-BM samples are located at 484, 533, and 552 °C, respectively. The GO pristine exhibited a significant loss of weight ( $\approx 25\%$ ) at  $\approx 200$  °C. b) TGA curves for pristine graphite and BM graphite materials; the onset temperatures are 544, 592, and 614 °C for G-BM, G-T-BM, and G-U-BM, respectively. The pristine graphite exhibited an onset temperature of  $\approx 935$  °C.

**Table 1.** Raman characterization data from radar plots (see Figure 5).

Sample	Band	FWHM	Position	$I_D/I_{D'}$ ratio	$I_D/I_G$ ratio
GO film	D	103.9 $\pm$ 17.1	1351.9 $\pm$ 0.1		0.82 $\pm$ 0.03
	G	73.5 $\pm$ 8.1	1588.3 $\pm$ 1.5		
	2D	170.5 $\pm$ 11.7	2686.6 $\pm$ 3.8		
GO-BM	D	94.6 $\pm$ 0.9	1350.6 $\pm$ 0.8		0.83 $\pm$ 0.03
	G	59.6 $\pm$ 0.9	1587.0 $\pm$ 0.5		
	2D	227.8 $\pm$ 20.8	2686.4 $\pm$ 4.5		
GO-T-BM	D	89.9 $\pm$ 1.0	1349.8 $\pm$ 0.8		0.93 $\pm$ 0.02
	G	57.6 $\pm$ 0.7	1586.3 $\pm$ 1.6		
	2D	218.5 $\pm$ 2.8	2682.2 $\pm$ 6.9		
GO-U-BM	D	94.4 $\pm$ 7.4	1351.1 $\pm$ 1.0		0.87 $\pm$ 0.10
	G	59.1 $\pm$ 2.8	1584.6 $\pm$ 4.1		
	2D	227.1 $\pm$ 14.9	2674.1 $\pm$ 4.5		
Graphite	D	42.5 $\pm$ 0.0	1351.3 $\pm$ 0.5	3.7 $\pm$ 0.1	0.10 $\pm$ 0.04
	G	17.9 $\pm$ 1.3	1582.2 $\pm$ 0.3		
	2D	38.5 $\pm$ 2.2	2723.0 $\pm$ 1.7		
G-BM	D	52.0 $\pm$ 4.1	1346.3 $\pm$ 2.9	3.5 $\pm$ 0.5	0.29 $\pm$ 0.02
	G	23.8 $\pm$ 4.3	1578.8 $\pm$ 4.7		
	2D	89.5 $\pm$ 7.2	2700.4 $\pm$ 4.6		
G-T-BM	D	44.8 $\pm$ 0.8	1348.1 $\pm$ 1.5	4.7 $\pm$ 0.4	0.36 $\pm$ 0.07
	G	22.3 $\pm$ 0.1	1574.9 $\pm$ 2.4		
	2D	85.8 $\pm$ 0.9	2697.8 $\pm$ 2.9		
G-U-BM	D	47.0 $\pm$ 0.3	1342.9 $\pm$ 0.5	3.7 $\pm$ 0.1	0.15 $\pm$ 0.02
	G	24.0 $\pm$ 4.6	1569.6 $\pm$ 3.6		
	2D	83.6 $\pm$ 0.1	2685.6 $\pm$ 6.2		

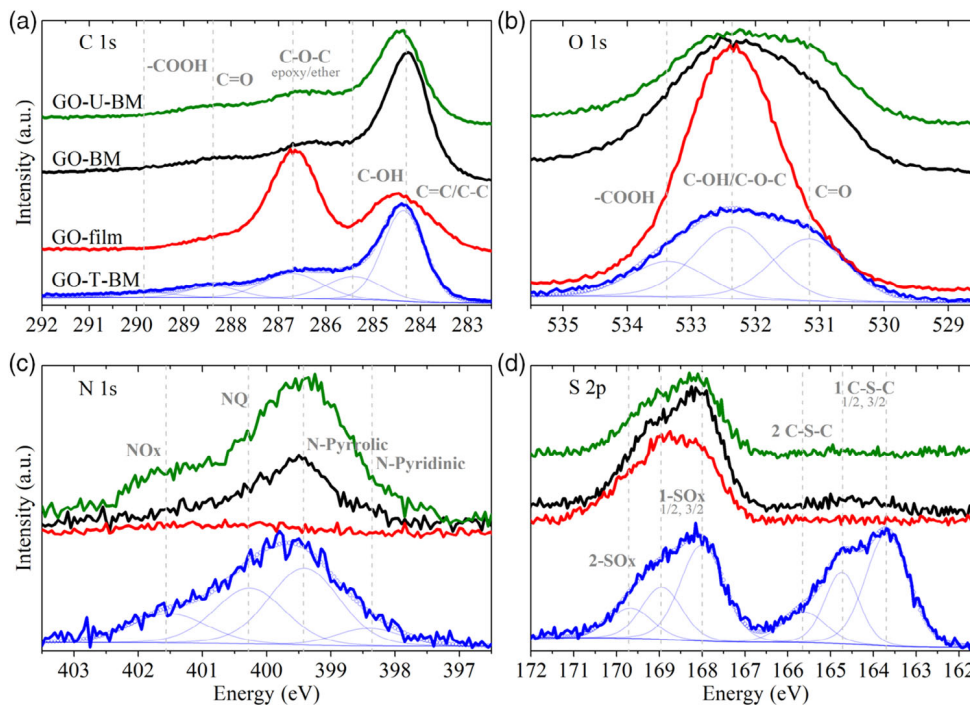


**Figure 7.** Estimated atomic percent concentration for elemental composition (at%) derived from the XPS survey spectra. In gray (carbon), red (oxygen), green (sulfur), and blue (nitrogen). The XPS survey spectra can be seen in Figure S9, Supporting Information.

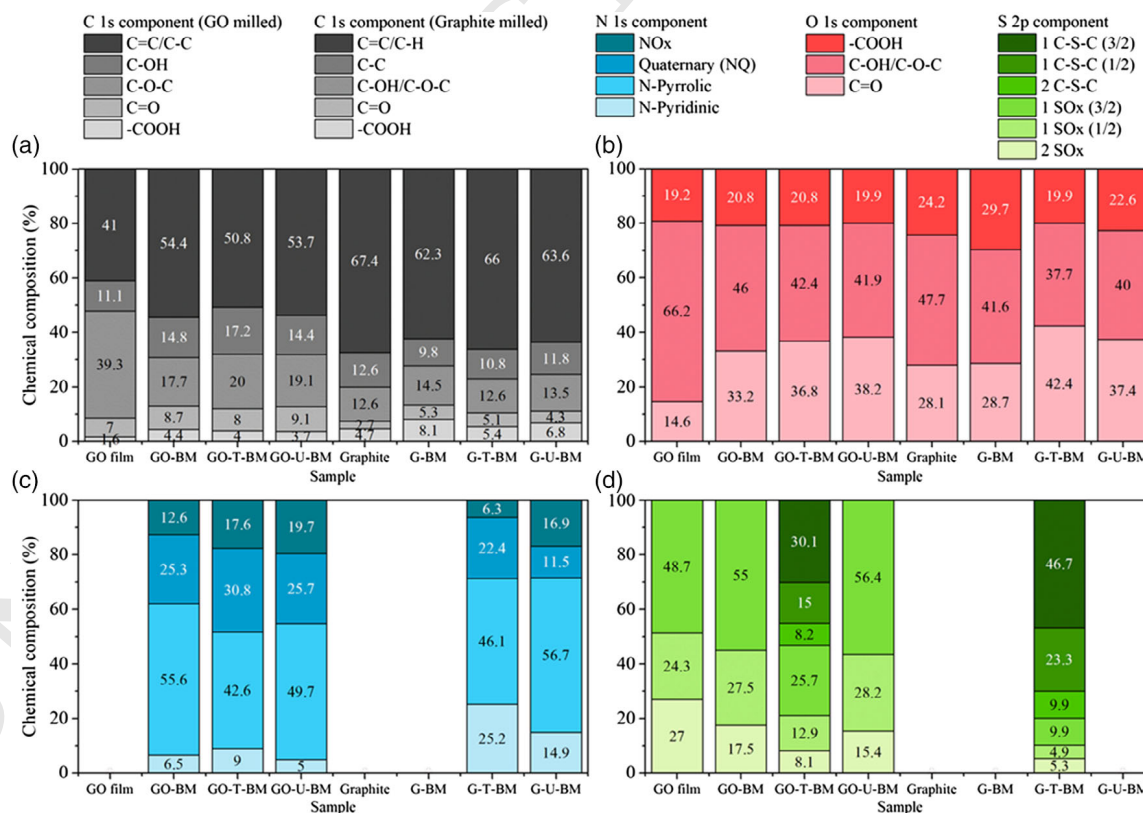
1 sample. This binding energy shift could result from urea and  
2 thiourea or chemical species derived therefrom being anchored  
3 to the surface or edges of graphite sheets. Many aspects and  
4 trends of the C1s spectra can be supported by the O1s spectra  
5 (Figure 8b). The GO-film displayed an O1s peak centered at  
6 532.4 eV attributed to C–O bonds due to carboxyl and epoxy

groups with two more peak contributions of –OH (hydroxyl 1  
groups) at 533.3 eV and C=O (carbonyl, carboxyl, amide groups) 2  
at 531.1 eV. The GO-milled samples showed O1s peak asymmetry 3  
broadness. The irregular width shape observed in milled GO 4  
samples could be due to a wide variety of oxygen, nitrogen, or 5  
sulfur functional groups attached to the edges, probably due to 6  
amides (C–NH<sub>2</sub>), ammonia (C–NH<sub>3</sub><sup>+</sup>), nitrogen oxide 7  
(NO<sub>x</sub>), and sulfur oxide (SO<sub>x</sub>). For N1s spectra (Figure 8c), 8  
the GO-film did not exhibit a nitrogen signal (red line); however, 9  
the GO-BM sample yielded a signal centered at the N-pyrrolic 10  
position (Figure 9c). GO-U-BM showed an N1s peak centered 11  
at the N-pyrrolic position with significant NO<sub>x</sub> traces. Similar 12  
behavior was observed for GO-T-BM, where the maximal peak 13  
intensity corresponded to N-pyrrolic and, subsequently, to quar- 14  
ternary nitrogen (NQ). C–NH<sub>2</sub> could be found at  $\approx 399.5$  eV and 15





**Figure 8.** High-resolution XPS spectra for pristine GO-films and BM-GO materials, with thiourea (GO-T-B) and urea (GO-U-BM). Results for a) C1s, b) O1s, c) N1s, and d) S2p. The pristine GO film (red lines) exhibited the typical C1s and O1s peaks suggesting the presence of hydroxyls (C—OH), carbonyl (C=O bonds), and carboxyl groups (C=O and C—O bonds), and likely epoxy groups (C—O—C bonds). For all samples, we identified the sulfur oxide (SOx) in S2p spectra; here, the sulfur comes from the GO fabrication.



**Figure 9.** Estimation of the different chemical species derived from the deconvolution analysis of high-resolution XPS spectra (the percentage is indicated). Chemical species containing a) carbon, b) oxygen, c) nitrogen, and d) sulfur.

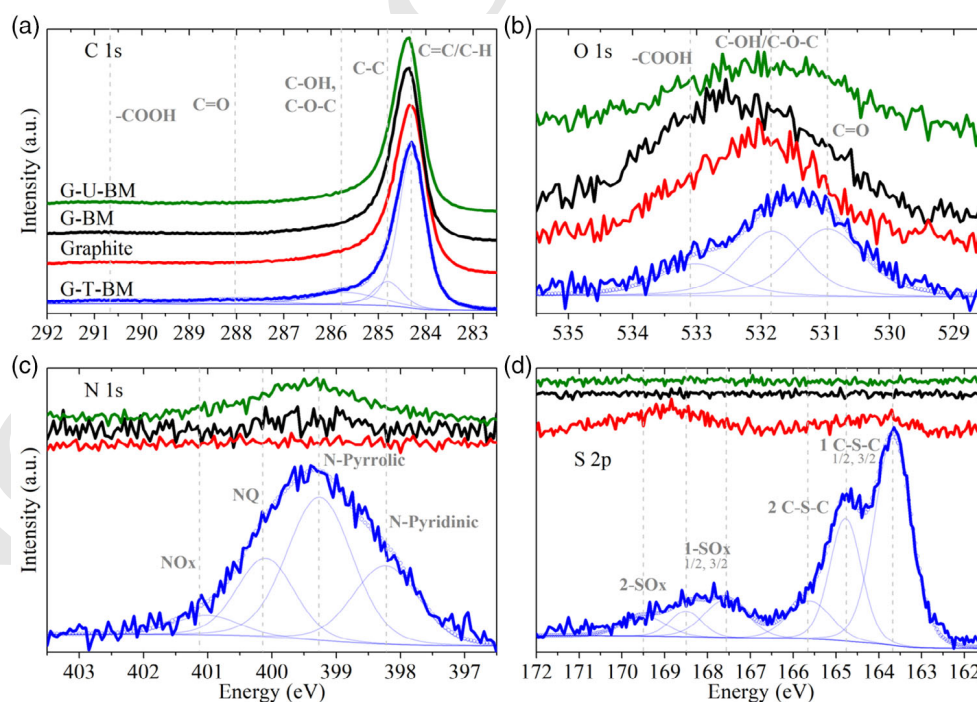
1 C-NH<sub>3</sub><sup>+</sup> at ≈401.6 eV.<sup>[31]</sup> The S2p spectra showed two signal  
2 distributions, one of them related to a group of oxidized sulfur  
3 groups signals (-SOx-) ≈168-170 eV, which were found for all  
4 samples, suggesting its origin from the GO synthesis process.  
5 The second group at binding energies ≈164 eV was found for  
6 GO-T-BM, attributed to sulfur bridge species C-S-C bonds.

7 **Figure 10** shows the high-resolution XPS for milled graphite-  
8 based samples. The narrow C1s peaks centered at ≈284.4 eV  
9 associated with the C=C bonds reveal the dominance of sp<sup>2</sup>  
10 hybridizations (Figure 10a). The low concentration of sp<sup>3</sup> bonded  
11 carbons (C-C) indicates nonsubstantial structure damages. O1s  
12 spectra (Figure 10b) of graphite showed a high binding energy  
13 shift toward -OH and C-O functionalities. The O1s peak  
14 (sample G-T-BM) is more centered at the C-O and C=O bonds.  
15 These samples should not have oxygen (G-BM, G-T-BM, and  
16 graphite). However, it could be due to the unavoidable oxygen  
17 from the environment reacting with the carbon-dangling bonds  
18 produced during BM or physisorbed. Figure 10c shows the N1s  
19 spectrum with remarkable peaks for G-U-BM and G-T-BM  
20 samples. These peaks were centered at N-pyrrolic binding ener-  
21 gies with an essential NQ and N-pyridinic contribution, as the  
22 deconvolution analysis showed. We observed significant signals  
23 associated with SO<sub>x</sub> and C-S-C chemical species, only for sample  
24 G-T-BM (Figure 10d).

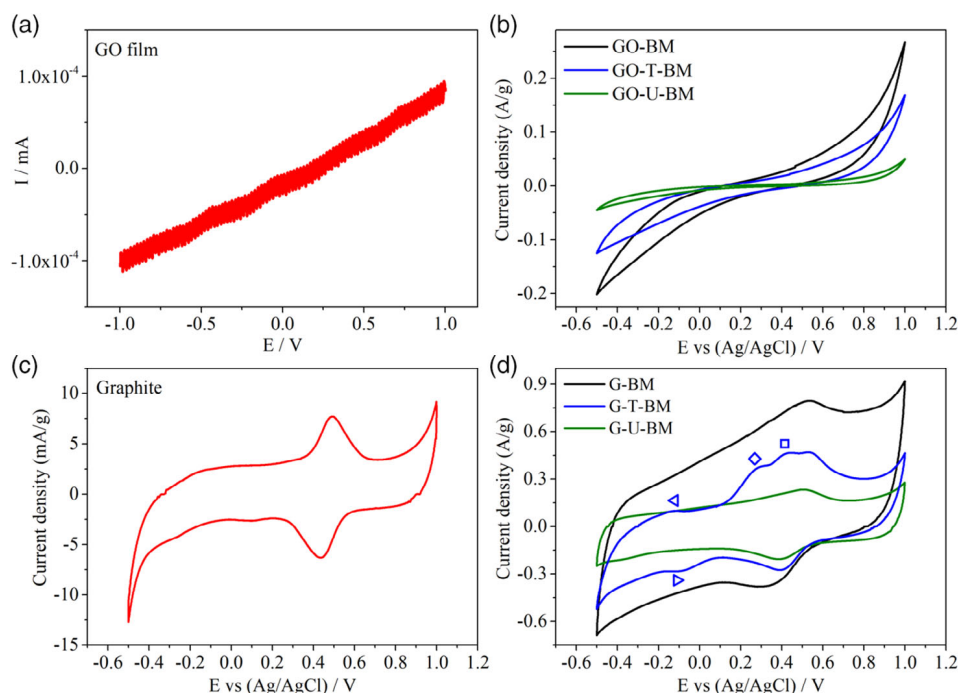
25 The electrochemical characterizations were evaluated by  
26 the cyclic voltammetry (CV) technique. **Figure 11a** shows the  
27 GO-film I-V curve, and a ≈10 kΩ Ohmic resistance signature  
28 by the two-probes method was obtained.<sup>[32]</sup> We estimated the  
29 specific capacitance from the charge and discharge model  
30  $C_p = A/2mk(V_2 - V_1)$  from the CV curve, where A is the area

enclosed by the CV loop, m the mass of material at the working 1  
electrode, k the scan rate, and (V<sub>2</sub> - V<sub>1</sub>) is the potential window. 2  
Table S1, Supporting Information, shows the estimated specific 3  
capacitance of all the milled samples. Figure 11b shows the 4  
electrochemical response of the milled GO samples; the 5  
GO-BM sample showed the largest specific capacitance due to 6  
the higher density of active sites in concordance with their 7  
TGA results. Interestingly, the specific capacitance of the 8  
GO-T-BM sample was nearly 4.4 times larger than GO-U-BM, 9  
due to the difference in double-layer capacitance in the grain size 10  
area, residue of pristine GO, and water-soluble residues 11  
as mascagnite urea. 12

The graphite's CV plot showed a redox process corresponding 13  
to the oxidation and reduction reaction of the quinone functional 14  
group at 0.49 and 0.43 V, respectively (Figure 11c). After the 15  
mechanochemical process, considering crystallite size differ- 16  
ences for G-BM, G-U-BM, and G-T-BM, the double-layer effect dif- 17  
ference in the specific capacitance was between 1.9 and 2.7 times 18  
larger for G-BM, compared to G-T-BM and G-U-BM, respectively. 19  
Figure 11d is in concordance with their chemical stability 20  
temperature, graphitic crystallite size, and the graphitization 21  
quality Raman I<sub>D</sub>/I<sub>G</sub> ratio. We found that the milled graphite 22  
samples showed an oxidation reaction of quinone at 0.53, 23  
0.54, and 0.51 V with their corresponding hydroquinone pair 24  
at 0.31, 0.40, and 0.38 V for G-BM, G-T-BM, and G-U-BM, 25  
respectively. Finally, G-T-BM samples exhibited electrocatalytic 26  
processes related to sulfur functionalization groups with N, O 27  
at the graphitic edges.<sup>[33-35]</sup> Based on previous reports, the 28  
G-T-BM electrocatalytic processes (blue line in Figure 11d) could 29  
be related to pyrrolic-N-sulfide, sulfhydryl oxidation (thiol) to 30



**Figure 10.** High-resolution XPS spectra for pristine graphite and graphite BM materials, with thiourea (G-T-BM) and urea (G-U-BM). Results for a) C1s, b) O1s, c) N1s, and d) S2p. The samples exhibited the typical C1s graphite materials dominated mainly by C=C bonds. Notice that the width, shape, and peak position of O1s spectra depended strongly on the material involved suggesting the presence of different functional groups. Notice that only G-T-BM showed S2p signals, suggesting the presence of C-S-C bonds.

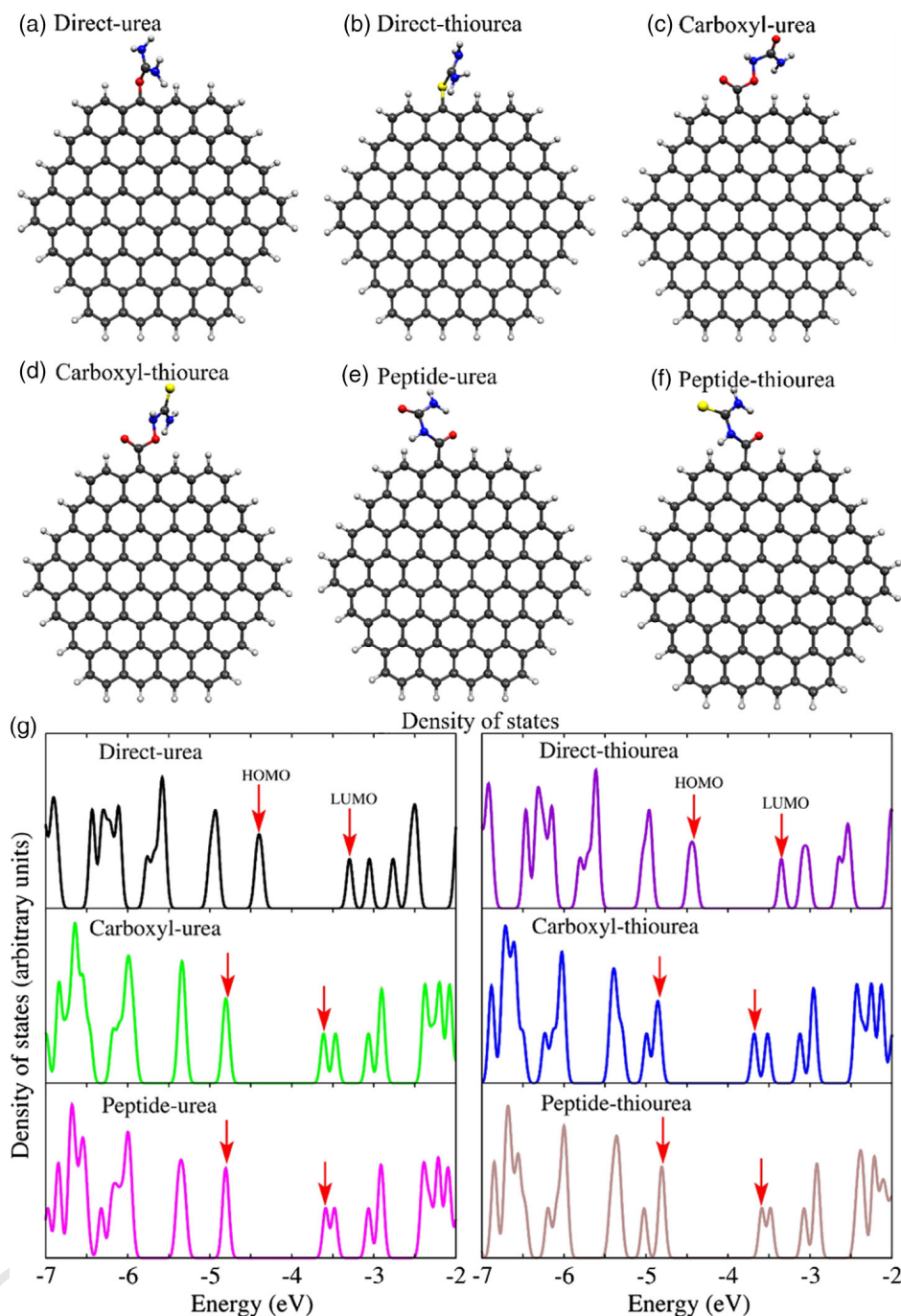


**Figure 11.** LSV for a) GO film, and CV measurements for b) milled GO materials with thiourea (T), urea (U), c) pristine graphite (G), and d) milled graphite materials with thiourea and urea. The GO-film exhibited almost negligible currents for this particular voltage window due to the isolator feature of GO materials.

1 thiolate reduction (thioketone), thiophene-like dioxide, and other  
 2 oxidized sulfur –SO functional groups.<sup>[36–41]</sup>  
 3 To elucidate the role of urea and thiourea in the electronic  
 4 properties of  $sp^2$  carbon materials, we performed first-principles  
 5 density functional theory (DFT) calculations on  $C_{96}H_{24}$  graphene  
 6 sheets with zigzag edges. We considered three different paths of  
 7 anchoring urea and thiourea molecules on the graphene sheets.  
 8 The molecules were anchored to the edge via the oxygen or sulfur  
 9 atoms labeled as direct-urea and direct-thiourea systems, as  
 10 shown in **Figure 12a,b**. The molecules were joined through their  
 11 amine group and carboxylic group, using two routes for function-  
 12 alized graphene sheets. For the first route, in the anchoring  
 13 mechanism, the system releases two hydrogens, labeled as  
 14 carboxyl–urea and carboxyl–thiourea, as in **Figure 12c,d**. In  
 15 the second route, the systems were labeled as peptide–urea  
 16 and peptide–thiourea; the anchoring was carried out via the pep-  
 17 tide bond, as in **Figure 12e,f**. Here, the systems release  $H_2O$  in  
 18 the anchoring process. **Figure 12g** shows the density of states of  
 19 urea and thiourea molecules joined to the edges of the graphene  
 20 sheets discussed earlier. The highest occupied molecular orbital  
 21 (HOMO) and the lowest unoccupied molecular orbital (LUMO)  
 22 energies showed a downshift for carboxyl-molecule and peptide-  
 23 molecule systems, compared to direct-molecule systems, as in  
 24 **Figure 12g**. **Figure 13** shows the HOMO and LUMO wave func-  
 25 tions and their associated energies. In general, the systems  
 26 showed delocalized HOMO wave functions at the entire gra-  
 27 phene sheet and localized LUMO wave functions mainly at  
 28 the urea and thiourea molecules. A significant localization of  
 29 LUMO wave functions was observed in direct-urea and direct-  
 30 thiourea systems (**Figure 13a,b**).

Now, the nitrogen-doping effects on the HOMO and LUMO 1  
 energies of the structure shown earlier are discussed. Here, the 2  
 nitrogen is incorporated via substitutional doping, where a carbon 3  
 atom is removed and replaced by a nitrogen atom (**Figure 14a**). 4  
 The nitrogen was moved from position N1 (near the anchoring 5  
 sites) to N8 (away from the anchoring sites). We observed an 6  
 apparent effect of nitrogen doping on the HOMO energies, 7  
 mainly for direct-urea and direct-thiourea systems (**Figure 14b**); 8  
 here, it was observed that monotonic energy decreases as the 9  
 nitrogen atom moves away from the anchoring sites. These 10  
 results suggest that direct-urea and direct-thiourea systems could 11  
 easily donate their electrons when doped with nitrogen. 12  
 Conversely, the urea and thiourea molecules attached via carboxyl 13  
 to peptide bond showed lower HOMO energy with slight changes 14  
 with the nitrogen doping, which should make it much more ener- 15  
 getically expensive to remove their electrons. In electrochemical 16  
 terms, the direct-urea and direct-thiourea are more susceptible to 17  
 oxidation. On the other hand, we observed a low LUMO energy 18  
 for carboxyl–urea, carboxyl–thiourea, peptide–urea, and peptide- 19  
 thiourea systems; thus, a reduction process in these systems 20  
 could be favored. We show more results for urea and thiourea 21  
 molecules chemisorbed through a carboxyl group at the central 22  
 part of the graphene sheets. **Figure 15** shows the optimized struc- 23  
 tures, density of states, and wave functions. In general, the sys- 24  
 tems considered exhibited electronic properties similar to HOMO 25  
 wave functions localized mainly at and around the urea and thio- 26  
 urea molecules. In contrast, the LUMO wave function showed a 27  
 delocalization on the entire body of the graphene sheets. The 28  
 HOMO energies were less than those obtained for molecules 29  
 joined to the ribbon's edges. Additional calculations revealed that 30



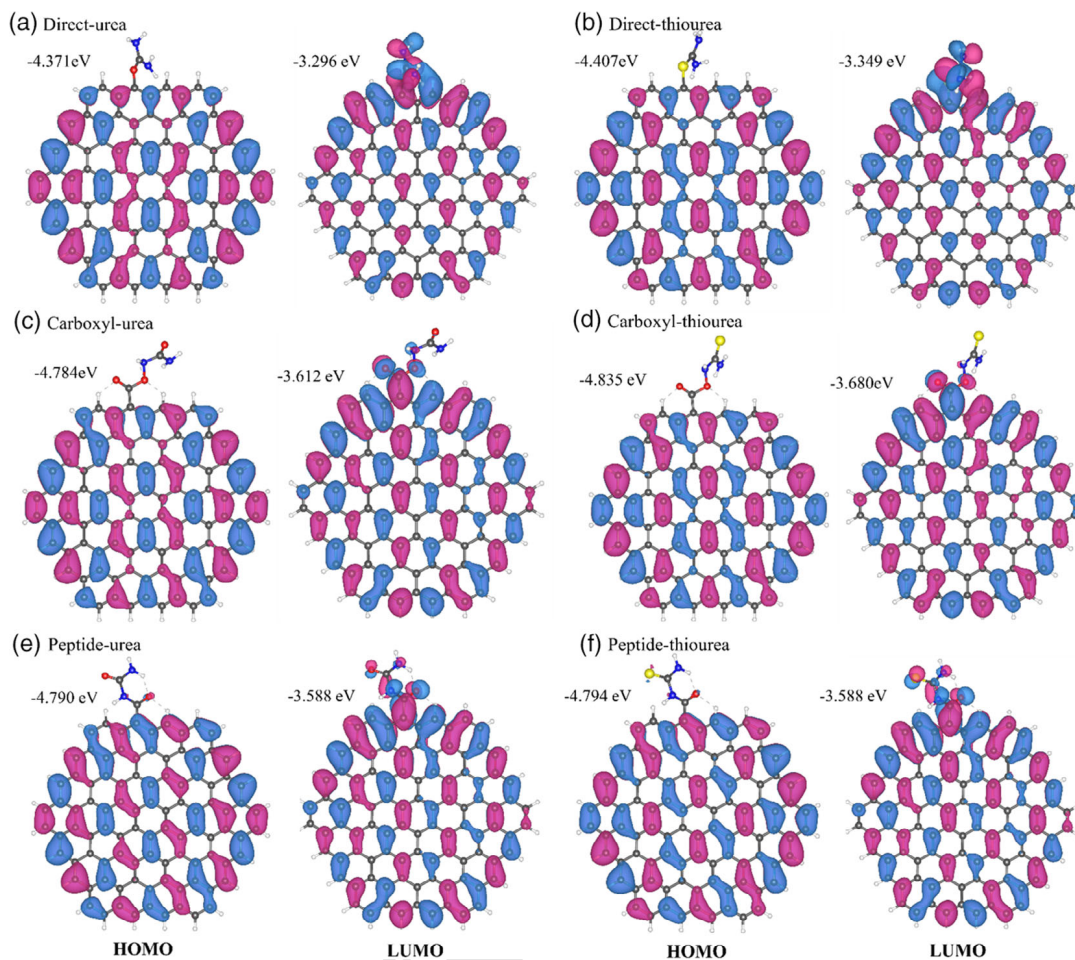


**Figure 12.** a–f) Ball-stick model of the optimized structures of graphene sheets C<sub>96</sub>H<sub>24</sub> with urea and thiourea molecules covalently anchored to the edges. The hydrogen, carbon, nitrogen, oxygen, and sulfur atoms are in gray, black, blue, red, and yellow colors, respectively. g) The corresponding electronic density of states. Arrows indicate the HOMO and LUMO energies.

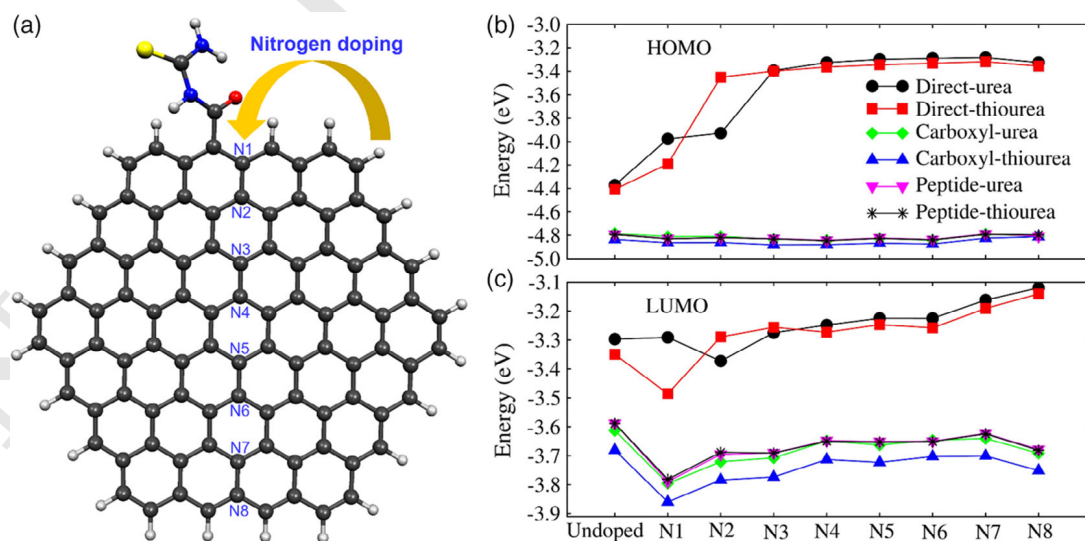
1 the molecules were not chemisorbed in pristine sheets and  
2 carbonyl-functionalized sheets. In sum, the calculations  
3 demonstrated that the carboxyl group plays a crucial role in  
4 the anchoring of urea and thiourea molecules in graphene sheets.  
5 The changes in HOMO and LUMO changes emerged by the  
6 type of anchoring, and nitrogen doping could be reflected in  
7 the voltammetry measurements, as shown earlier.

### 3. Conclusion

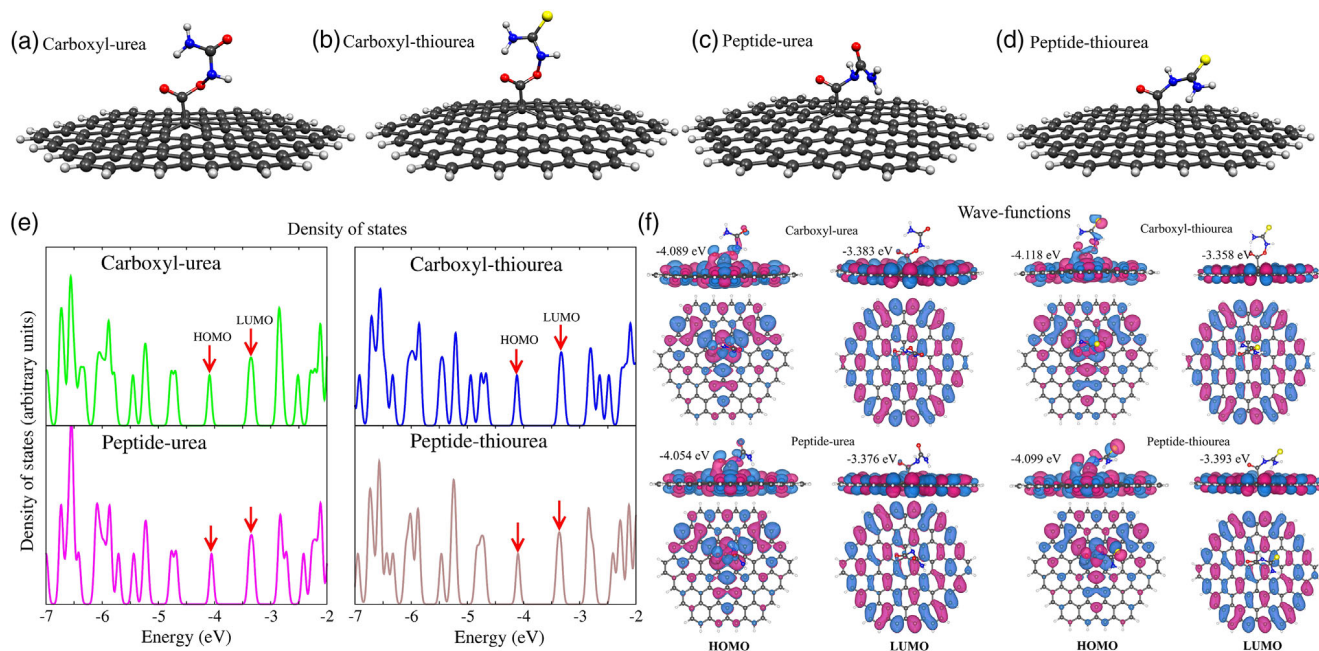
1 We produced carbonaceous materials from GO and graphite. 2  
3 Sulfur and nitrogen were incorporated into the carbonaceous 3  
4 materials by the mechanochemical method. We followed three 4  
5 different routes 1) pristine graphite, and GO subjected to a 5  
6 BM treatment, 2) pristine material (GO or graphite) mixed with 6



**Figure 13.** HOMO and LUMO wave functions and the corresponding energies of urea and thiourea molecules covalently attached to the graphene sheet  $C_{96}H_{24}$  edges. The wave functions were plotted at the isosurface of  $\pm 0.03 \text{ \AA}^{-3/2}$ . The colors refer to the positive (blue) and negative (purple) phase of the wave function.



**Figure 14.** a) Ball-stick model of a particular system (peptide-thiourea) showing how the nitrogen is incorporated in  $C_{96}H_{24}$  graphene sheets. Thus, a single carbon atom indicated by N1, N2, N3, N4, N5, N6, N7, and N8 is removed and replaced by nitrogen. b,c) HOMO and LUMO energies for urea and thiourea for the nitrogen-doped cases. The energies corresponding to undoped cases are also shown.



**Figure 15.** a–d) Ball-stick model of the optimized structures of graphene sheets C<sub>96</sub>H<sub>24</sub> with urea and thiourea molecules covalently anchored through the carboxyl group. e) Corresponding density of states and f) HOMO and LUMO wave functions (top and side views). The HOMO and LUMO energies are indicated. The wave functions were plotted at the isosurface of  $\pm 0.03 \text{ \AA}^{-3/2}$ .

1 thiourea powder and exposed to a BM treatment, 3) pristine  
2 material (GO or graphite) mixed with urea and subjected to a  
3 BM treatment. After the mechanochemical process reduced  
4 the GO samples, the usage of urea and thiourea enhance N,  
5 N–S doping. Different functional groups containing C, N, and  
6 O, and S were hosted at the milled sample surface when urea  
7 and thiourea were introduced into the BM treatment. We have  
8 also shown that all carbonaceous materials exhibited oxidation  
9 temperature intermediates between the GO and graphite pris-  
10 tine. The specific capacitance performance in milled GO samples  
11 was smaller, compared with milled graphite samples.

12 DFT calculations demonstrated that urea and thiourea were  
13 chemisorbed at the graphene sheets' edges and surface through  
14 carboxyl groups. Our results also revealed that urea and thiourea  
15 were covalently joined only to the edges of the graphene sheet  
16 through their oxygen or sulfur and in the absence of carboxyl  
17 groups (direct link). The HOMO energies analysis revealed that  
18 these direct-link cases and those joined to the surface through  
19 carboxyl group cases are energetically more susceptible to oxida-  
20 tion. Further results demonstrated that nitrogen doping in direct-  
21 link cases decreases the HOMO energy; thus, the nitrogen could  
22 improve these oxidization processes.

23 For the first time, a simultaneous N, S doping and GO paper-  
24 like reduction using a dry HEBM methodology was achieved with  
25 a predissolved water-soluble urea/thiourea molecule. Our results  
26 showed a low-cost, environmentally-friendly, practical, and  
27 scalable mechanochemical method for N/S doping graphitic  
28 material that opens a range of possibilities for other heteroatom  
29 dopants and water-soluble molecules. The thiourea molecule  
30 had a higher reducing chemical activity than urea in the GO dis-  
31 persions, which exhibited interlayer cross-linking and sulfur

linkages with the milling process. Our results demonstrated that 1  
the HEBM method was energetically efficient in reducing the 2  
GO, analogous to inert atmosphere heat treatment to remove 3  
or reduce carboxylic and epoxide groups. 4

#### 4. Experimental Section 5

Pristine GO was synthesized by the modified Hummer's method. 6  
This purified GO aqueous suspension reached  $3.6 \text{ mg mL}^{-1}$  fraction of 7  
mas and was then degassed ( $\approx -0.1 \text{ MPa}$ ) for 30 min to avoid gas bubbles 8  
during GO film deposition. Thiourea (CH<sub>4</sub>N<sub>2</sub>S, Sigma-Aldrich, Prod. #62- 9  
56-6,  $\geq 99 \text{ wt\%}$  purity) and urea (CH<sub>4</sub>N<sub>2</sub>O, Sigma-Aldrich, Prod. #57-13-6, 10  
 $\geq 99 \text{ wt\%}$  purity) molecules were used as N, S containing doping source. 11  
For GO synthesis and graphite HEBM experiments, we used raw mineral 12  
graphite mesh #32 + 99% purity from Asbury-Carbons Company. One GO 13  
dissolutions control and two GO doping dissolutions were prepared: all 14  
GO dissolutions–GO film, GO + thiourea, and GO + urea (Table S2, 15  
Supporting Information), were magnetically stirred at 400 rpm for 16  
15 min, and bath sonicated for 15 min, whereafter the urea and thiourea 17  
molecules were dispersed uniformly. 18

Prior to BM process, paper-like GO films were deposited via drop- 19  
casting technique on  $15 \text{ cm} \times 15 \text{ cm}$  mold release over a tempered glass 20  
substrate at  $70^\circ \text{C}$  for 72 h. Thereafter, dried GO films were used to 21  
fabricate pills as a freestanding film, with GO films area density of 4.31, 22  
4.35, and  $4.71 \text{ mg cm}^{-2}$  for GO, GO + thiourea, and GO + urea films, 23  
respectively. In a typical experiment, 800 mg of ground material was introduced 24  
into a 65 mL stainless ball-grinding jar (8007—stainless-steel grinding 25  
vial set) with ten stainless planetary balls mill with diameters 26  
 $12 \text{ mm} \times 3 \text{ pc}$ ,  $6 \text{ mm} \times 4 \text{ pc}$ ,  $5 \text{ mm} \times 1 \text{ pc}$ ,  $4 \text{ mm} \times 1 \text{ pc}$ , and  $3 \text{ mm} \times 1 \text{ pc}$ . 27  
The average ball to powder mass ratio (BPMR) was 36:1 for all grinding 28  
experiments. Milling experiments were run in 8000D Mixer/Mill 29  
equipment at 1725 rpm speed along 80 min under nongas inert 30  
conditions. The BM materials were collected and labeled as GO-BM, 31  
GO-T-BM, and GO-U-BM, corresponding to pristine GO, GO mixed 32  
with thiourea, and GO mixed with urea dissolutions, respectively 33



1 (Figure S1, Supporting Information). On the other hand, the same mecha-  
2 nochemical methodology, contrasting with graphite flakes in dry heteroge-  
3 neous grinding mixes with the same N, N=S containing source molecules  
4 without a post-purification process. Then, we prepared one graphite sample  
5 control and two dry heterogeneous mixed samples: graphite, graphite +  
6 thiourea, and graphite + urea (Table S1, Supporting Information). After  
7 milling, the collected material was labeled as G-BM, G-T-BM, and G-U-  
8 BM, corresponding to graphite, graphite mixed with thiourea, and graphite  
9 mixed with urea, respectively (Figure S2, Supporting Information).

10 SEM images and EDX were characterized on an FEI-Helios Nanolab  
11 600. Raman spectra were carried out with a 514 nm laser wavelength  
12 in a Raman Renishaw Micro-Raman. TEM and HR-TEM techniques were  
13 characterized on FEI Tecnai F30 (300 keV); milled samples were dispersed  
14 on ethanol sonication for 10 min, deposited by drop on lacy carbon 300  
15 mesh copper grids and dried. The post-milled powders were made into  
16 pills in a hydraulic press CARVER 3925 applying 1500 psi for 10 s fit on  
17 14 mm pellet pressing die set. The extracted pills were weighed and sum-  
18 marized in Table S2, Supporting Information, with an average weight of  
19  $80.5 \pm 0.6$  mg. CV and Linear sweep voltammetry (LSV) techniques were  
20 performed in a VSP 300 Potentiostat-Biologic Science Instruments.  $4 \text{ cm}^2$   
21 of 904L stainless #80 mesh was used as an Ohmic sample holder with a  
22 negligible double-layer signal (Figure S13, Supporting Information). Pill  
23 samples (WE) were totally covered by stainless mesh and mechanically  
24 fitted by 500 psi uniform area pressure for 5 s. Ag/AgCl electrode was used  
25 as a reference electrode (RE), and 2 mm OD  $\times$  4 cm Pt wire was used as a  
26 counter electrode (CE). Pill samples were CV measured in a three-  
27 electrode cell configuration with 0.5 M of  $\text{H}_2\text{SO}_4$  electrolyte into a window  
28 potential range from  $-0.5$  to 1 V versus Ag/AgCl at  $10 \text{ mV s}^{-1}$  from the  
29 open circuit to the cathodic direction. The current-potential ( $I$ - $V$ ) curve  
30 of GO-film was measured via a two-electrode configuration electrode  
31 clamped on the opposite and broadside and using LSV technique  
32 within  $-1$  to 1 V potential range at  $10 \text{ mV s}^{-1}$  speed on GO-film strip of  
33  $1 \text{ cm} \times 5 \text{ cm}$ . Thermogravimetric analysis (TGA) measurements were car-  
34 ried out using equipment 6000 Perkin Elmer from 50 to  $950^\circ\text{C}$  under the  
35 heating rate of  $10^\circ\text{C min}^{-1}$  into a dynamic flow of oxygen ( $20 \text{ mL min}^{-1}$ ).  
36 Nevertheless, we used dynamic nitrogen flow ( $20 \text{ mL min}^{-1}$ ) with the same  
37 rate and temperature settings for the GO-film thermogravimetric measure-  
38 ment. X-ray photoelectron spectroscopy (XPS) measurements were carried  
39 out on PHI Quantera II (Al K $\alpha$ ). XRD patterns were carried out with  
40 a Rigaku Smart Lab (Cu, K $\alpha \approx 1.54 \text{ \AA}$ ). Attenuated total reflectance-  
41 Fourier transform infrared spectroscopy (ATR-FTIR) measurement was per-  
42 formed via Thermo Scientific Nicolet 6700 spectrometer.

43 Electronic calculations were performed using DFT.<sup>[42,43]</sup> The general-  
44 ized gradient approximation with the Perdew, Burke, and Ernzerhof  
45 parametrization was chosen for the exchange-correlation functional,<sup>[44]</sup>  
46 as implemented in the SIESTA code.<sup>[45]</sup> The wave functions for the valence  
47 electrons were represented by a linear combination of pseudoatomic  
48 numerical orbitals, using a double- $\zeta$  polarized basis (DZP),<sup>[46]</sup> and the core  
49 electrons by norm-conserving Troullier-Martins pseudopotentials in the  
50 Kleinman-Bylander nonlocal form.<sup>[47,48]</sup> The real-space grid used for  
51 charge and potential integration is equivalent to a plane wave cut-off  
52 energy of 150 Ry. Urea ( $\text{CH}_4\text{N}_2\text{O}$ ) and thiourea ( $\text{CH}_4\text{N}_2\text{S}$ ) molecules were  
53 joined to  $\text{C}_{96}\text{H}_{24}$  graphene sheets and structurally relaxed. Density matrix  
54 and energy tolerances were both taken as  $10^{-5}$  eV. Geometry optimization  
55 was performed by conjugate gradient minimization until the maximum  
56 force was  $<0.03 \text{ eV \AA}^{-1}$ .

## 57 Supporting Information

58 Supporting Information is available from the Wiley Online Library or from  
59 the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Author Contributions

R.S.S. performed the GO synthesis, conducted milling experiments, and  
performed TGA, CV, and XRD characterizations. A.M.G. and M.E. contrib-  
uted to SEM, FTIR, and XRD characterizations. All authors designed the  
research and wrote the manuscript.

## Data Availability Statement

Research data are not shared.

## Keywords

ball-milling, doping, graphene oxide, graphite, nitrogen, sulfur

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