

Selective edge functionalization of graphene layers with oxygenated groups by means of Reimer-Tiemann and domino Reimer-Tiemann/Cannizzaro reactions

Original

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1 **Selective edge functionalization of graphene layers with oxygenated groups by means of**
2 **Reimer-Tiemann and domino Reimer-Tiemann / Cannizzaro reactions**

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11
12 **Abstract**

13 Graphene layers were selectively edge-functionalized with oxygenated functional groups,
14 maintaining their bulk structure essentially unaltered. A reaction was performed between
15 polyhydroxylated graphene layers (G-OH) and CHCl₃/KOH/H₂O. When the reaction with
16 KOH/H₂O was performed at 0°C, by adding successive portions of CHCl₃, the functionalization
17 occurred with aldehydic functional groups. When G-OH was reacted with CHCl₃/KOH at room
18 temperature, benzylic alcohol and carboxy groups were introduced. XPS, IR, Raman, WAXD
19 analyses indicated that the graphene layers were chemically modified with the abovementioned
20 functional groups, without intercalated and/or absorbed molecules. It can be thus assumed that
21 functionalization of G-OH with aldehydic groups occurred through Reimer-Tiemann reaction and
22 that domino Reimer-Tiemann / Cannizzaro reaction led to aldehyde disproportion. As a further
23 evidence and a first viable usage of the functionalization with aldehydic functional groups, chitosan
24 was crosslinked with the graphene layers, obtaining flexible and electrically conductive carbon
25 papers.

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34 **1. Introduction**

35 Graphene [1-3] has indeed exceptional properties: it features high charge-carrier mobilities [4,5], its
36 in-plane thermal conductivity is among the highest for known materials [6], the theoretical elastic
37 modulus is over 1 TPa and the Young modulus is about 1060 MPa [7]. Thanks in particular to their
38 electrical properties, graphene and graphene related materials find application for energy storage
39 devices [8-10] and in fuel cells [11].

40 Such outstanding graphene properties are essentially due to its six atoms aromatic ring core. Any
41 synthesis [7-15] and functionalization [7, 16-22] has therefore the objective to obtain and preserve
42 such structure. In particular, the control of size, shape, and edge structure of graphene layers is a
43 challenging task.

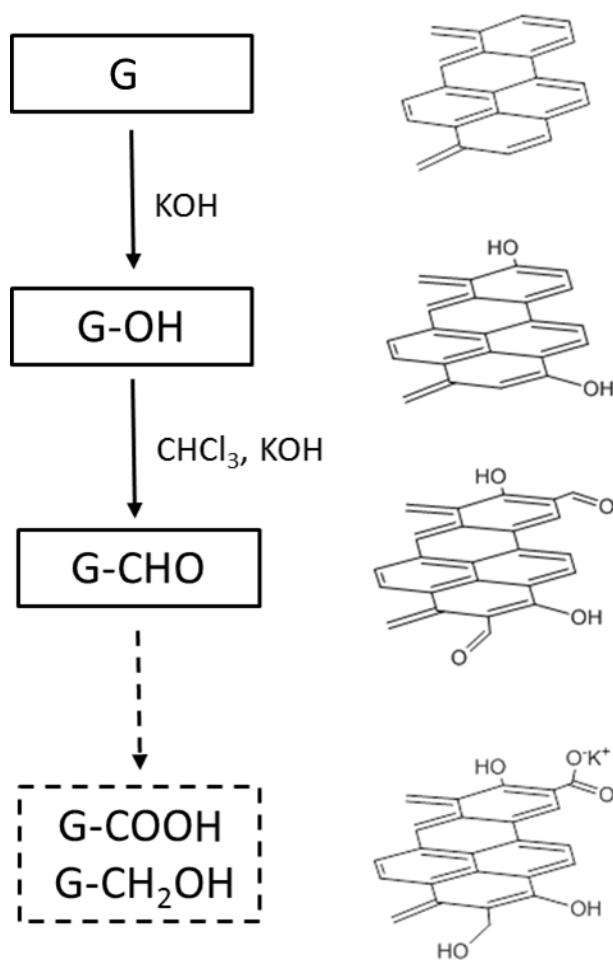
44 Graphene functionalization has great importance. Functional groups affect electronic and solubility
45 properties, self-assembly and phase forming behaviour and can promote further reactions. Over the
46 last years, research has been focused on edge functionalization [3-21], so as to preserve the ideal
47 structure of the graphene core. Edge functionalization has been reported with halogen atoms,
48 [20,21,23-26] converted to nitrile [27] or arylthio [28] groups and used for various metal-catalyzed
49 coupling reactions [29]. Iridium-catalysed direct borylation reaction [30], direct palladium-
50 catalyzed C–H arylation [31] and double C–H activation [32], initializing the construction of novel
51 aromatic structures [33], have also been reported.

52 Great interest is shown for graphene layers with oxygenated functional groups. The chemistry of
53 carboxylic acids has been much explored in the case of carbon nanotubes (CNT) [34]: amidation
54 and esterification reactions have been applied in order to achieve solubility in different solvents, to
55 perform the so-called grafting from polymerizations, to prepare biocompatible sensors. Moreover,
56 graphene and oxygenated derivatives, such as graphene oxide (GO), are being increasingly applied
57 in the field of catalysis [35]. The chemical or thermal reduction of graphene oxide is considered the
58 best practice for large-scale production of graphene [14].

59 However, the introduction of carboxylic groups on CNT and, in particular, the preparation of GO
60 require strong acidic, harsh and even dangerous oxidative conditions [36-46]. The structure of GO
61 has been investigated for decades, but it is still substantially unknown [7,13]. It has been reported
62 [47] that carbonyl and carboxylic groups are on the edges and hydroxy and epoxy groups are on
63 basal planes. Hence, the chemistry that leads to GO cannot be used for the selective edge
64 functionalization of graphene layers. Alternatively, Friedel–Crafts acylation reaction with 4-
65 aminobenzoic acid was performed: it is a one-pot reaction, but requires acidic substances, which
66 could hardly be removed from a graphitic substrate. Another approach reported in the literature for
67 the edge carboxylation is ball milling with carbon dioxide [48]: ~~the~~ this method is environmentally

68 friendly, but does not appear ideal for large-scale development. This work describes a new
 69 procedure for the edge functionalization of graphene layers with oxygenated functional groups, in
 70 particular aldehydes and carboxylic acids or their ester derivatives. It is worth clarifying that
 71 reactions were designed to occur on peripheral positions of graphene layers, independently of their
 72 organization as single layers or as stacks of few or many layers. Nanosized high surface area
 73 graphite (G) with high shape anisotropy (i.e. with a high ratio between the size of crystallites
 74 parallel and perpendicular to the structural layers [49]) was chosen as a starting material and the
 75 synthetic strategy shown in Figure 1 was adopted.

76



77

78 **Figure 1.** Synthetic strategy for the introduction of oxygenated functional groups on the edges of
 79 graphene layers G.

80

81

82 As reported in previous works [50,51], G can be easily functionalised with hydroxyl groups in
 83 peripheral position and polyhydroxylated graphene layers are obtained, with substantially unaltered
 84 bulk structure. G-OH layers can be considered as a polycyclic aromatic compound, suitable for
 85 reactions able to introduce oxygenated functional groups on phenolic substrates. Besides Friedel-

86 Crafts acylation, Reimer-Tiemann reaction [52,53] has been known for a long time as an efficient
87 tool for the preparation of 2-hydroxyaryl aldehydes [52], and is used on an industrial scale for the
88 preparation of salicylic aldehyde (2-hydroxybenzaldehyde)salicylaldehyde, an important
89 intermediate in the chemical industry for the production of fragrances, perfumes, dyes and
90 pharmaceuticals. Studies on Reimer-Tiemann reaction [54] have demonstrated that dichlorocarbene,
91 formed by mixing chloroform with KOH, interacts with the potassium salt of the phenolic substrate
92 in the aqueous phase. By using the same reaction mixture, CHCl_3 in alkaline medium, in the
93 presence of a phase transfer catalyst, cyclopropanation reaction occurs on alkenylic substrates [55]
94 and at the edges of graphene layers [56]. These reagents are not the preferred ones, as
95 cyclopropanes are traditionally formed by adding the methylene-zinc-iodide complex, generated
96 from diethyl zinc and diiodomethane [57-59], or by transition metal-catalyzed decomposition of
97 diazo compounds [60]. As G-OH forms stable water dispersions [51] it could thus be a suitable
98 substrate and graphene layers bearing 2-hydroxy aldehyde as functional group should be obtained.
99 However, the selectivity of the Reimer-Tiemann reaction on G-OH cannot be taken for granted.
100 Indeed, it is well known that a strong base, such as KOH, can induce disproportionation of aromatic
101 aldehydes lacking a hydrogen atom in the α -position, promoting the Cannizzaro reaction and
102 leading to benzyl alcohol and potassium benzoate. However, to obtain disproportionation of
103 aldehyde with vanillin as substrate, a catalyst had to be used [61,62] and electrocatalytic effects
104 have been reported to enhance the efficiency of the Cannizzaro reaction [63]. It has to be taken into
105 account that carbon nanostructured materials such as carbon fibers and carbon nanotubes have been
106 used as catalysts for phenol oxidation [64]. Hence, the occurring of Cannizzaro reaction, indicated
107 with the dotted line in the block diagram in Figure 1, cannot be ruled out. Moreover, the
108 introduction of aldehydes in other positions of the graphene layers, which are indeed electron rich,
109 could also be hypothesized. Rather than stretching too far inferences not supported by experimental
110 facts, in this work G-OH was subjected to the Reimer-Tiemann reaction, performed under ~~with~~
111 different experimental conditions: at nominal room temperature, reproducing the experimental
112 conditions usually adopted in the prior art, and at 0°C by adding chloroform in three portions, with
113 the aim of preventing the Cannizzaro disproportionation. Mechanisms for the formation of
114 functionalized graphene layers are proposed.
115 Moreover, reaction of chitosan (CS) with graphene layers bearing aldehydic groups was performed
116 ~~for preparing~~ to prepare bionanocomposites.

117

118 **2. Experimental**

119 *2.1 Materials and methods*

120 Reagents and solvents were commercially available and were used without further purification:
121 KOH pellets (Carlo Erba Reagenti), chloroform (Aldrich).

122 High surface area graphite (HSAG) was Synthetic Graphite 8427[®] (Asbury Graphite Mills Inc.).
123 Characterization of HSAG has been reported by some of the authors in previous works [49,
124 51,65,66]. Analyses have been repeated on the sample used for the present work, to confirm the
125 reproducibility of what already published.

126 The Fourier-Transform Infrared (FT-IR) spectra were recorded in transmission mode (128 scan and
127 4 cm⁻¹ resolution) in a diamond anvil cell (DAC) using a ThermoElectron Continuum IR
128 microscope coupled with a FT-IR Nicolet Nexus spectrometer.

129 PHI 5000 VersaProbe instrument (Physical Electronics) was used for survey scan and high
130 resolution X-ray photoelectron spectroscopy (XPS). The powder was dried in oven at 100°C for 24
131 h at atmospheric pressure before analysis and thereafter placed in the XPS pre-chamber overnight,
132 in order to avoid anomalous outgassing during the XPS characterization, performed in UHV
133 condition (10⁻⁸ Pa). A monochromatic Al K-alpha X-ray source (1486.6 eV energy, 15 kV voltage
134 and 1 mA anode current) and a power of 25.2 W were used for analysis. Different pass energy
135 values were employed: 187.85 eV for survey spectra and 23.5 eV for high resolution peaks.
136 Analyses were carried out with a take-off angle of 45° and with a 100 µm diameter X-ray spot size
137 on a square area of 1400×1400 µm², with the aim to have a good average and better statistics of
138 powder behavior. A double beam (electron and argon ion gun) neutralization system, dedicated to
139 reduce the charging effect on samples, was also employed during data acquisition. All binding
140 energies (B.E.) were referenced to the C1s line at 284.8 eV. Spectra were analyzed and peak
141 deconvolution was performed using Multipak 9.6 software.

142 Raman spectra were recorded on powdered samples deposited on a glass slide by using an Horiba
143 Jobin Yvon Labram HR800 dispersive Raman spectrometer equipped with Olympus BX41
144 microscope and a 50X objective. The excitation line at 632.8 nm of a He/Ne laser was kept at 0.5
145 mW in order to prevent samples degradation. The spectra were obtained as the average of four
146 acquisitions (30 seconds each) with a spectral resolution of 2 cm⁻¹. The Raman spectra reported in
147 this work are the average of spectra recorded in five different points of the samples.

148 Wide-angle X-ray diffraction (WAXD) patterns were obtained in reflection, with an automatic
149 Bruker D8 Advance diffractometer, with nickel filtered Cu-Kα radiation. Patterns were recorded in
150 10° – 100° as the 2θ range, being 2θ the peak diffraction angle. Distance between crystallographic
151 planes was calculated from the Bragg law. The D_{hkl} correlation length, in the direction

152 perpendicular to the hkl crystal graphitic planes, was determined applying the Scherrer equation
153 (equation (1)).

$$154 \quad D_{hkl} = K \lambda / (\beta_{hkl} \cos\theta_{hkl}) \quad (1)$$

155 where: K is the Scherrer constant, λ is the wavelength of the irradiating beam (1.5419 Å, Cu-K α),
156 β_{hkl} is the width at half height, and θ_{hkl} is the diffraction angle. The instrumental broadening, b , was
157 determined by obtaining a WAXD pattern of a standard silicon powder 325 mesh (99%), under the
158 same experimental conditions. The width at half height, $\beta_{hkl} = (B_{hkl} - b)$ was corrected for each
159 observed reflection with $\beta_{hkl} < 1^\circ$ by subtracting the instrumental broadening of the closest silicon
160 reflection from the experimental width at half height, B_{hkl} .

161

162 *2.2 Preparation of polyhydroxylated graphene layers (G-OH)*

163 ~~G-OH was prepared by reacting HSAG and KOH in a planetary ball mill S100 from Retsch,~~
164 ~~with 0.3 L grinding jar moving on a horizontal plane. The jar was loaded with 6 ceramic balls~~
165 ~~having a diameter of 20 mm. HSAG (1g), KOH powder (20 g) and H₂O (6.5 mL) were put into the~~
166 ~~jar, that was allowed to rotate at 300 rpm, at nominal room temperature, for 10 hours. After this~~
167 ~~time, the mixture was placed in a Büchner funnel with a sintered glass disc and repeatedly washed~~
168 ~~with distilled water (6 x 100 mL) under vacuum. Finally, the obtained solid was put in an oven to~~
169 ~~remove excess water. 1.1 g of black powder were obtained.~~

170

171 *2.2 Reimer-Tiemann reaction performed at nominal room temperature (Procedure 1)*

172 In a round bottomed flask equipped with magnetic stirrer and condenser, KOH powder (3.12 g, 55
173 mmol), CHCl₃ (1.12 mL, 14 mmol) and H₂O (0.5 mL) were added in sequence. G-OH (0.500 g)
174 was added to such mixture after few seconds, to avoid chloroform decomposition by alkaline ions,
175 well known problem in Reimer-Tiemann reaction performed on phenol ring. The mixture was
176 stirred at room temperature, for 12 hours. After this time, solvent was removed at reduced pressure.
177 The solid was reduced in fine grains in a mortar with a pestel, transferred into a Falcon™ tube
178 (15mL) and water (10 mL) was added. The suspension was sonicated for 10 minutes and
179 centrifuged at 4000 rpm for 10 minutes (3 times). 0.7 g of black powder were obtained.

180

181 *2.3 Reimer-Tiemann reaction performed at nominal 0°C (Procedure 2).*

182 The procedure reported in the previous paragraph was adopted also for the reaction performed at
183 0°C, keeping the round bottomed flask in an ice bath. 0.67 g of black powder were obtained.

184

185 *2.4 Reimer-Tiemann reaction performed at nominal 0°C with sequential addition of CHCl₃*
186 *(Procedure 3)*

187 In a round bottomed flask equipped with magnetic stirrer and condenser, KOH powder (3.12 g, 55
188 mmol), G-OH (0.5 g) and H₂O (0.5 mL) were added in sequence. CHCl₃ (1.12 mL, 14 mmol) was
189 added to such mixture after few seconds in three parts (3 x 0.37 mL). The mixture was stirred at
190 0°C for 12 hours. After this time, solvent was removed at reduced pressure. The solid was reduced
191 in fine grains in a mortar with a pestel, transferred into a Falcon™ tube (15mL) and water (10 mL)
192 was added. The suspension was sonicated for 10 minutes and centrifuged at 4000 rpm for 10
193 minutes. This procedure was repeated three times. Byproduct such as KCl was extracted by water.
194 0.50 g of black powder were isolated. The pH was measured to be 14 immediately after the
195 dispersion of KOH in the reaction medium and 13.8 shortly before the work-up.

196

197 *2.5 Preparation of chitosan based nanocomposites*

198 G-CHO (0.4 g) and chitosan (0.4 g) were mixed for 5 minutes in a mortar with the help of a pestle.
199 The mixture was dispersed in water (8 mL) and 4 drops of an aqueous solution of acetic acid 99.7%
200 (0.010 g, 9.9 10⁻³ mol) were added, obtaining a homogenous suspension. Acetic acid was used in
201 such an amount to lead to the protonation of about 7% of chitosan amino groups.

202 The so obtained water suspension was sonicated for 15 minutes. Casting of G-CHO/CS suspension
203 was performed on a glass plate in which an adhesive tape was used to delimit the area. Sheets were
204 formed after water evaporation, at room temperature and at atmospheric pressure (24 hours).

205

206

207 **3. Results and discussion**

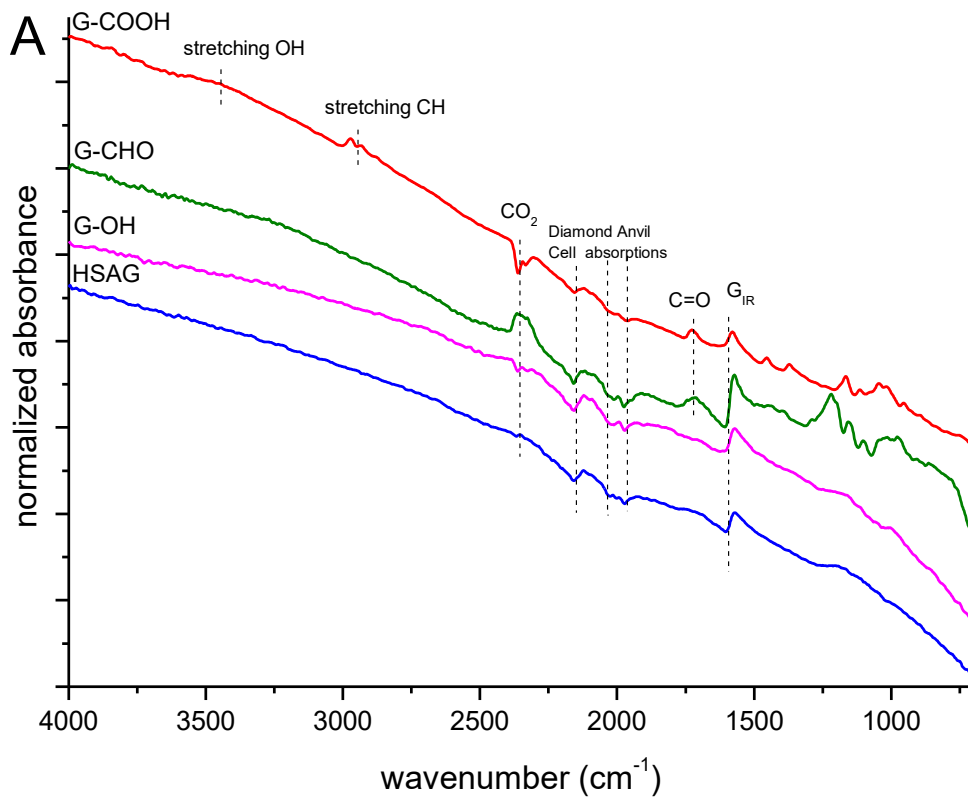
208 *3.1 Preparation and characterization of graphene layers with oxygenated functional groups*

209 Prior to functionalization, the graphitic sample used in this work (HSAG) was duly characterised.
210 Chemical composition, determined by elemental analysis, was (mass %): carbon 99.5, hydrogen
211 0.4, nitrogen 0.1, oxygen 0.0. TGA revealed the following mass loss: 3.2% below 700°C. Surface
212 area was determined by BET according to ASTM D6556 method and was found to be 330.3 m²/g.
213 Average size of HSAG particles was evaluated by means of dynamic light scattering [65], obtaining
214 values representing the hydrodynamic radius of HSAG particles in water dispersions. Average
215 values were 500 nm in the as prepared dispersion and 190 nm after centrifuging the dispersion for
216 30 min centrifugation at 9000 rpm. Transmission electron micrograph taken on supernatant
217 suspension after 60 min centrifugation at 9000 rpm revealed graphite stacks randomly arranged,

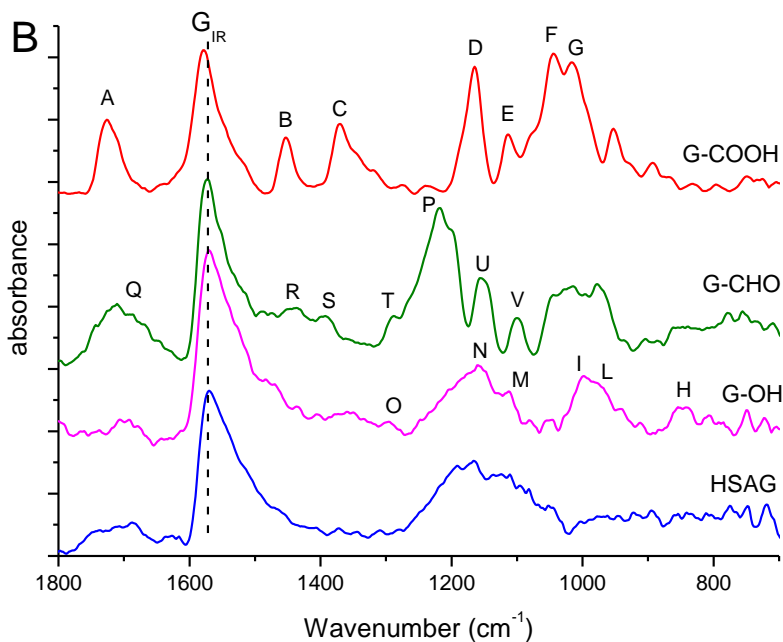
218 with lateral size between about 300 nm and 500 nm [51]. FT-IR, XPS and Raman characterization
219 showed that no oxygenated functional group was present prior functionalization (see below).
220 In the first step of the reaction pathway of Figure 1, the high surface area graphite (HSAG) was
221 reacted with KOH, with the help of mechanical energy (through ball milling, details in [51]),
222 obtaining G-OH. Elemental analysis confirmed the results already reported [51]. Elements other
223 than carbon, oxygen, hydrogen and nitrogen were not found. The oxygen content was found to
224 increase to about 6 mass%. A larger mass loss was found for G-OH, below 700° C, than for HSAG.
225 Data are reported in [51]. XPS analysis, commented below in the text, revealed also the presence of
226 potassium. Size of G-OH nanoparticles was evaluated by means of dynamic light scattering and
227 High-Resolution Transmission Electron microscopy (HRTEM). As already reported [51], treatment
228 of HSAG with KOH via ball milling led to the reduction of HSAG aggregates size: from about 190
229 nm (HSAG) to about 150 nm, for particles in supernatant suspensions (centrifugation at 9000 rpm
230 for 60 min). TEM micrographs confirmed that the lateral size of HSAG and G-OH were of the same
231 order of magnitude, in samples isolated after centrifugations [51]. These data suggest that the
232 milling step does not cause appreciable breaking of the graphitic layers. Micrographs taken at
233 higher magnification on graphene layers disposed perpendicularly to the beam allowed to visualize
234 stacks with thickness of about 1.7 – 4.8 nm, hence with 6 to 15 stacked graphene layers. Stacks with
235 low number of layers were frequently observed [51].

236 Reaction of G-OH with CHCl₃ was performed by adopting different procedures, described in detail
237 in the experimental part. In a first approach (Procedure 1), KOH powder, CHCl₃ and H₂O were
238 mixed and G-OH was added after few seconds, to avoid chloroform decomposition by alkaline ions,
239 which is known to occur in the case of Reimer-Tiemann reaction performed on phenolic rings. The
240 reaction was performed at 21°C (room temperature in the text) as usually done in the scientific
241 literature [52,53]. An extraordinary reactivity was observed (see Figure S1 in Supplementary
242 Material). To avoid such uncontrolled behaviour, the reaction was carried out at 0°C (Procedure 2).
243 Moreover, G-OH, KOH powder and H₂O were mixed at 0°C and CHCl₃ was added in three
244 different steps, in smaller portions (Procedure 3).

245 The characterization of the reactions products was performed by means of IR, XPS, Raman,
246 WAXD spectroscopies. In the following text, products from the reaction carried out at room
247 temperature (Procedure 1) and at 0°C with the successive addition of small CHCl₃ portions
248 (Procedure 3) are described. They are labelled G-COOH and G-CHO, respectively. Product from
249 Procedure 2 is described in the Supplementary Material.



250



251

252 **Figure 2.** FT-IR spectra of HSAG (blue), G-OH (purple), G-CHO (green) and G-COOH (red): in
 253 the full region 4000-700 cm^{-1} (A) and zoom in the region 1800-700 cm^{-1} (B). Spectra are displayed
 254 after baseline correction.

255

256 In Figure 2A and 2B the IR spectra of the materials under investigation are reported. As explained
257 in detail in the experimental part, IR spectra have been recorded in transmission using a diamond
258 anvil cell (and not in KBr pellet) in order to avoid the presence of the absorption features due to the
259 water molecules that are typically absorbed by KBr during sample preparation. Spectra were
260 obtained from the absorption of very thin films of HSAG particles, which are not transparent to the
261 IR beam. Indeed, the G_{IR} absorption observed in the spectra at 1590 cm^{-1} is mostly due to the
262 reflection from the graphitic planes as revealed by its shape, which resembles a sigmoid function (as
263 expected in specular reflection IR spectroscopy). The strong light diffusion from the HSAG
264 particles is responsible for the increase of the spectra toward high wavenumbers. Details about the
265 interpretation of the signals coming from HSAG and G-OH can be found in previous publications
266 [51,65,66]. Some comments are also reported in this paper to allow direct comparison. The
267 spectrum of the product of the reaction performed at room temperature between CHCl_3/KOH and
268 G-OH (G-COOH) reveals a variety of strong and structured bands, which can be assigned to
269 vibrations of different oxygenated functional groups. It is worth reminding that this family of
270 functional groups show, in IR spectra, the Lorentzian and/or Gaussian profile of an absorption
271 phenomenon. Such profile is observed also in the spectrum of G-CHO in Figure 2. Bands due to G-
272 CHO in Figure 2 appear very different with respect to the signals present in IR spectra of GO or
273 reduced GO. Due to the complexity of the systems, the proposed assignment of the peaks is based
274 on correlative spectroscopy [67]. In Figure 2A the broad and weak absorption at 3400 cm^{-1} can be
275 assigned to -OH stretching vibrations of hydrogen bonded hydroxy groups already present in G-OH.
276 At 1590 cm^{-1} the signal common to all the samples is assigned to the E_{1u} IR active mode of the
277 collective C=C stretching vibration (G_{IR}) of graphitic materials enhanced for the structural
278 disordered and/or chemically functionalization of the graphitic layers. In the spectrum of G-COOH
279 bands at 2967 cm^{-1} , 2928 cm^{-1} and 2874 cm^{-1} (absent both in HSAG and GOH) can be assigned to
280 the CH stretching vibrations of CH_3 and CH_2 units. Therefore they can be associated to the presence
281 of $-\text{CH}_2\text{-OH}$ functional groups (i.e. benzylic alcohol moiety, absent in the spectrum of G-OH).
282 In Figure 2B the spectrum of G-COOH shows a structured band at 1730 cm^{-1} (A) that can be
283 assigned to $-\text{C}=\text{O}$ stretching vibration of $-\text{COOR}$ functionalities (acid and/or ester). The frequency
284 of the stretching of this vibration is compatible with the possible formation of intramolecular
285 hydrogen bonds between $-\text{C}=\text{O}$ and $-\text{OH}$ groups which are close to each other in aromatic
286 compounds such as salicylic acid and its derivatives. The band at 1450 cm^{-1} (B) can be assigned to
287 bending vibrations of CH_2 and CH_3 groups and the broad and asymmetric band at 1371 cm^{-1} (C) to
288 both the CH_3 symmetric bending and the out of plane vibration of $-\text{OH}$ groups. The strong bands at

289 1164 cm⁻¹ (D), 1111 cm⁻¹ (E), 1042 cm⁻¹ (F), and 1014 cm⁻¹ (G) can be assigned to the stretching
290 vibrations of C-O-C and C-OH functional groups.

291 In the spectrum of G-OH bands at 846 cm⁻¹ (H) and 1000 cm⁻¹ (I) can be assigned to vibrations of
292 aryl-OH groups, and bands at 975 cm⁻¹ (L), 1121 cm⁻¹ (M), 1158 cm⁻¹ (N), and 1290 cm⁻¹ (O) are
293 compatible with vibration of epoxy or ether groups.

294 The spectrum of G-CHO (i.e. the product of the reaction performed at 0°C with successive
295 additions of small CHCl₃ portions) shows many features observed also for G-OH. A relevant
296 difference is the presence of the strong band at 1220 cm⁻¹ (P), and the broad and structured band at
297 1715 cm⁻¹ (Q) which can be assigned to -C=O stretching vibration of aldehydic functionalities.
298 Other bands at 1438 cm⁻¹ (R), 1390 cm⁻¹ (S), 1290 cm⁻¹ (T), 1158 cm⁻¹ (U), and 1100 cm⁻¹ (V) have
299 a good correspondence with the absorptions of benzaldehyde and salicylaldehyde [68] molecules.

300 The IR spectroscopic evidences indicate that the reaction between G-OH and CHCl₃/KOH
301 introduces new functional groups onto the graphene layers. The type of functional groups
302 introduced depend on reactions conditions: -OH, -COOR (acid and/or ester) and -CH₂-OH groups
303 were introduced when the reaction was performed at room temperature and reagents were added in
304 one shot. When the reaction was carried out in milder conditions, at 0°C with successive CHCl₃
305 additions, aldehydic groups were selectively formed. This latter procedure (Procedure 3) seems thus
306 to allow the selective occurring of Reimer-Tiemann reaction. Domino reaction made by Reimer-
307 Tiemann followed by Cannizzaro disproportionation appears instead to occur when the high surface
308 area graphite reacts with KOH/CHCl₃.

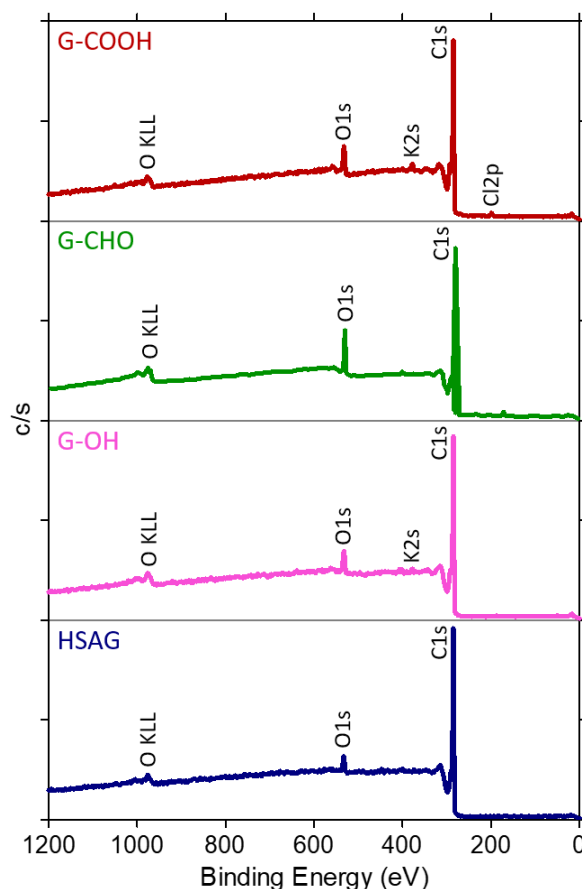
309 XPS spectra of HSAG, G-OH, G-CHO and G-COOH are shown in Figure 3. The main signals of all
310 the samples are due to C_{1s} and O_{1s}. In the case of HSAG, as discussed in [51], a surface oxidation
311 was detected (O_{1s}/C_{1s}=0.04, 4.2% atomic) while elemental analysis did not reveal the presence of
312 oxygen. G-OH presented however a larger amount of oxygen: O_{1s}/C_{1s}=0.07, 6.4% atomic.

313 In the XPS wide scan spectrum of G-COOH, besides the two main signals, C_{1s} at B.E.=284.8 eV
314 and O_{1s} at B.E.=533.0 eV, presence of K and Cl is also revealed. The O_{1s}/C_{1s} atomic ratio has a
315 value of 0.09, which is higher than the ratio estimated in G-OH (0.07); the oxygen content is 8.2%
316 atomic. The G-CHO sample presents an oxygen content of 10 % atomic and O_{1s}/C_{1s}=0.12.

317 By the C_{1s} peak deconvolution, three components were detected (see Figure S2 and Table S1 in
318 Supplementary Material). One peak has the same position as that of graphite (284.8 eV), with the
319 characteristic tailing on the high energy side, due to the π bond shake-up satellite, which are clear in
320 the HSAG spectrum [51]. The other two components of C_{1s} are found at higher binding energies,
321 due to the electron withdrawing effect of oxygen. They are attributable to C-O and C=O functions.
322 The C=O/C-O ratio is 0.45 for HSAG, decreases to 0.18 and 0.16 for G-OH and G-COOH

323 respectively. Interestingly the value is 0.55 for G-CHO and this indicates that carbonyl functions are
324 the prevailing ones among the oxidized groups.

325



326

327

Figure 3. Wide scan XPS spectra of HSAG, G-OH, G-CHO and G-COOH.

328

329 To better understand the nature of the oxidized groups, a narrow scan on the O_{1s} peak and its
330 deconvolution was performed (see Figure S3 in Supplementary Material). In fact, analysis of the C_{1s}
331 spectrum does not allow accurate characterization, due to the large contribution of C sp², which
332 tends to mask relative contributions of other groups [69]. Information provided by the analysis of
333 the O_{1s} can therefore better complement the information gathered by the IR spectra. It has however
334 to be taken into account that XPS analysis probes only the outer layer (about 40 Å thick) of the
335 graphitic material and the O_{1s} spectra can be more surface specific than C_{1s} spectra.

336 For G-COOH as for G-OH, there are two main contributions to O_{1s} signal, i.e., at 531.3 eV and
337 533.2 eV, a minor component at 535.2 eV and a negligible signal at 530.4 eV. The main
338 components are located at slightly different energies than G-OH. On the basis of the literature data,
339 one can attribute the signal at 531.3 eV to C=O groups of carbonyl and carboxyl groups (they count
340 for around 50% of the signal intensity) with a shift of 0.2 eV with respect to G-OH. The component

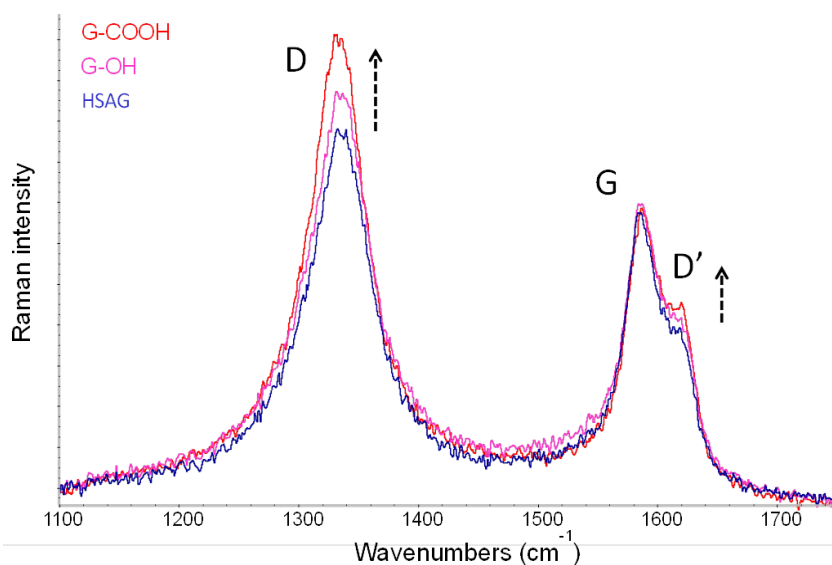
341 at 533.2 eV (again 0.3 eV shifted with respect to G-OH) evidences the presence of C-O groups
342 identified as hydroxyl and ether groups bonded to aromatics. The contribution could account for
343 both phenolic and benzylic OH, but they cannot be separately identified. The minor component at
344 higher binding energy can be attributed to adsorbed water and oxygen.

345 In G-CHO, three components appear by deconvoluting the O_{1s} signal: a negligible peak at 530.2 eV
346 and two main components of similar intensity at 531.5 and 532.9 eV. They could be interpreted as
347 signals due to C=O groups and C-O groups as in G-COOH. However the second peak appears at a
348 lower binding energy (532.9 instead of 533.2 eV): it can account for aliphatic C-O but it could also
349 be a shake-up feature from the C=O peak [70].

350 Both IR and XPS findings indicate the formation of aldehydic derivatives of G-OH, G-CHO, after
351 the reaction with CHCl₃/KOH at 0°C through Procedure 3. Further oxidized species detected by
352 XPS appear to be confined in an outer layer. A different product, G-COOH, is obtained, allowing
353 the occurring of disproportionation Cannizzaro reaction.

354 To demonstrate that the functionalization of the graphene layers does not modify the crystalline
355 structure, Raman spectroscopy analysis was performed on HSAG, G-OH and G-COOH and spectra
356 are shown in Figure 4.

357



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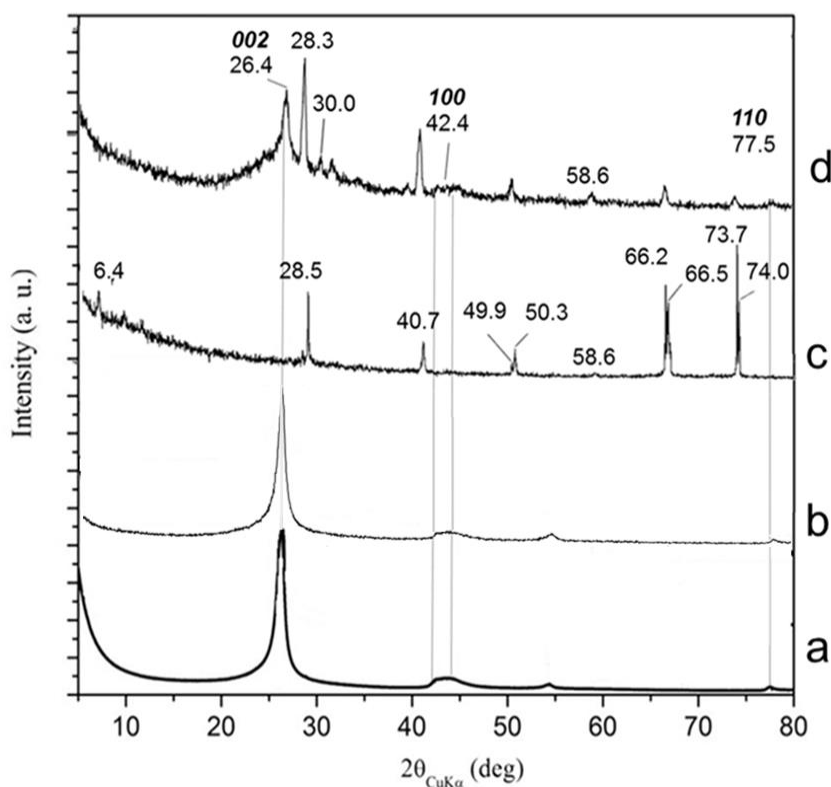
359 **Figure 4.** Raman spectra of HSAG (red), G-OH (blue) and G-COOH (purple) excited at 632.8 nm.

360

361 All spectra show a similar pattern with the G band at 1582 cm⁻¹ and evident D and D' bands at 1333
362 cm⁻¹ and 1620 cm⁻¹ respectively. The G peak is assigned to the E_{2g} Raman active mode of collective
363 C=C stretching vibration of crystalline graphite (graphene), whereas the D and D' peaks appear
364 when structural defects, such as holes, sp³ or sp carbon atoms, dangling bonds, distortions from
365 planarity, grafted functional groups or confinement (e.g. by edges), affect the graphitic layers. Finite

366 dimensions of the graphitic platelets lead to larger amount of irregular boundaries and, as a
367 consequence, to larger intensity of D and D' peaks [51]. HSAG consists of platelets with a surface
368 of approximately 500 x 500 nm². Such low size can be attributed to the production via ball milling,
369 which cracks the layers, however without substantially altering the in plane order, as revealed by X-
370 ray analysis. The in plane order was maintained also after ball milling with KOH and after the
371 chemical reactions. The enhancement of D band in the spectrum of G-OH can be thus assigned to
372 the hydroxyl functionalization of graphene edges. A further enhancement of D and D' peaks are
373 observed for G-COOH as consequence of the introduction of additional functional groups after
374 reactions of G-OH with CHCl₃/KOH, while indeed new Raman components between G and D
375 peaks, due to disordered sp³ carbon structures, are not appreciable [71]. One can conclude that the
376 bulk structure of the graphitic layers is essentially unaffected by the functionalization reaction.
377 The essentially unaltered in plane order and interlayer distance allow to assume that
378 functionalization occurred on peripheral positions, reasonably mainly on sites located around the
379 borders of the platelets. This is consistent with the observed stability of the G peak which does not
380 change either the intensity or the frequency. Frequency shifts of the G peak in graphene or the
381 appearance in graphite of a second component at higher Raman shifts are observed for doped
382 graphene, [72-75] and graphite intercalation compounds [72-76].
383 The inspection of Raman spectra leads to exclude the presence of species intercalated between the
384 graphene layers, because their occurrence should generate frequency shifts and/or a second
385 component of the G peak, as normally observed for intercalated Graphite Intercalation Compounds
386 GICs [72-74]. The intercalation of chemical species in between graphene layers is indeed a relevant
387 aspect to be investigated, when graphene layers undergo chemical reactions. Chemical substances
388 could also be absorbed on the carbon material. As discussed in the next paragraph, the presence of
389 absorbed molecule was also investigated and excluded by performing *ad hoc* experiments.
390 The WAXD pattern in Figure 5 reveals that the (002) reflection of G-OH (Figure 5b) and G-COOH
391 after purification (Figure 5d) are at the same 2θ value as in the pristine HSAG sample (Figure 5a).
392 A number of about 22 stacked layers in G-OH (about 35 were in HSAG [51]) was estimated by
393 applying the Scherrer equation. The presence of 100 and 110 reflections, with intensity similar to
394 the one in pristine HSAG, indicates that G-OH and G-COOH remain substantially unaltered: they
395 are thus formed by a low number of stacked graphene layers, the core of which has the ideal
396 graphitic structure. Interestingly, the WAXD profile of G-COOH before purification (Figure 5c) is
397 different: it shows peaks at 28.5 (200), 40.7 (220), 49.9 (222), 58.6 (400), 66.5 (420), 73.7 (422),
398 which can be attributed to KCl. It can be assumed that KCl promotes the exfoliation of the material.
399 In fact, the preparation of exfoliated graphite from hydrothermally synthesized graphite-KCl

400 compounds has been reported [78]. The removal of KCl by the purification procedure (see
401 experimental part) can restore the stacking of graphene layers. WAXD patterns, in particular the
402 (002) reflection at the same 2θ value in HSAG and in the functionalized samples, lead to exclude
403 the presence of intercalated compounds [79].



404 **Figure 5.** WAXD patterns of HSAG (a), G-OH (b), G-COOH before purification (c) and after
405 purification (d).
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407
408 Experimental findings discussed so far indicate that the reactions proposed in this work (Figure 1)
409 preserve the bulk structure of graphene layers through all the processes.

411 3.2 Mechanisms proposed for the functionalization reactions of graphene layers

412 Experimental findings reported above reveal that the reaction of polyhydroxylated graphene layers
413 with $\text{CHCl}_3/\text{KOH}/\text{H}_2\text{O}$ led to the modification of graphene layers with oxygenated functional
414 groups.

415 Results from analytical investigations allow to identify the nature of the functional groups:
416 aldehydic groups were observed when the reaction was performed at 0°C and benzyl alcohol and
417 carboxy groups (prevailingly ester) when the reaction was carried out at nominal room temperature.

418 Below in the text, it is shown the formation of imines from the reaction of G-CHO with chitosan.
419 This appears a support of the presence of aldehydic groups on the graphene layers.

420 The presence of intercalated oxygenated species can be ruled out on the basis of Raman and WAXD
421 results. As anticipated above, the presence of low molar mass oxygenated molecules only absorbed
422 on the graphene layers was also investigated. G-OH was mixed with an excess of formaldehyde
423 (even though it would be hard to justify the presence of formaldehyde) for 12 hours and FT-IR
424 spectrum was immediately recorded, without observing any modification (Supplementary Material
425 S1).

426 In order to elaborate an interpretation of the results so far reported, the scientific literature has to be
427 carefully considered. For example, it was reported that by using the same reaction mixture, CHCl_3
428 in alkaline medium, in the presence of a phase transfer catalyst, cyclopropanation reaction occurs on
429 alkenylic substrates [56] and at the edges of graphene layers [55]. These reagents are not the
430 preferred ones for cyclopropanation, as cyclopropanes are traditionally formed by adding the
431 methylene-zinc-iodide complex, generated from diethyl zinc and diiodomethane [57,58,79], or by
432 transition metal-catalyzed decomposition of diazo compounds [59]. Moreover, cyclopropanation
433 reaction was reported [55] to occur on the graphene layers in the presence of a phase transfer
434 catalyst, which was not used in the work here reported. However, to investigate and, in case, to rule
435 out the formation of cyclopropane ring, pristine HSAG was mixed with KOH powder, CHCl_3 and
436 H_2O . Results of this experiment are reported as Supplementary Material S2. Infrared spectrum is
437 shown in Figure S5. Typical spectral features of cyclopropane rings cannot be detected, confirming
438 that the phase transfer catalyst, as reported in literature [56], is needed.

439 In the light of what discussed so far, the following mechanism can be proposed. The
440 functionalization of graphene layers occurred through Reimer-Tiemann reaction (introduction of
441 aldehydic groups) and domino Reimer-Tiemann / Cannizzaro reaction (benzyl alcohol and carboxy
442 groups). The mechanism for these reactions is presented in Figure S6 of the Supplementary
443 Material and discussed in the following.

444 **Figure 6. Proposed synthetic pathway for the reaction of G-OH with CHCl_3/KOH at room**
445 **temperature: mechanism of Reimer-Tiemann (A) and Cannizzaro (B) reactions.**

446 Figure S6A shows the mechanism for the introduction on graphene layers of aldehyde functional
447 groups, through the Reimer-Tiemann reaction. It is known that chloroform reacts with aqueous
448 potassium phenoxide very slowly at room temperature, but its reactivity remarkably increases in the
449 presence of a strong base such as KOH [54]. KOH deprotonates CHCl_3 , leading to a
450 trichlorocarbanion, and deprotonates the OH groups on the graphene layer as well, forming product
451 **1**. The trichlorocarbanion, through a quick α -elimination, spontaneously loses a chloride ion

452 forming neutral dichlorocarbene, the reactive species that attacks **1**. The negatively charged
453 phenoxide-like rings in **1**, with their negative charge delocalized on many aromatic rings, have a
454 large resonance stabilization. Dichlorocarbene could react with both the phenoxide ion and the
455 carbon atoms in the ortho positions with respect to the oxygenated group. Indeed, both mechanisms
456 are reported in scientific literature [54]. Reactivity with ortho positions is favored by the charge
457 delocalization which increases nucleophilicity of the carbon atoms. As a matter of fact, only this
458 reactivity can account for the formation of an aldehydic species. Moreover, studies on the reactivity
459 of dichlorocarbene in the Reimer-Tiemann reaction [54] demonstrated the quick formation of o- and
460 p-hydroxybenzaldehydes. FT-IR findings suggested that dichlorocarbene attacks carbon atoms in
461 ortho position with respect to aldehyde. Hence, dichlorocarbene gives rise to an attack on the ortho
462 carbon atom of the phenoxide ion, forming product **3**, through the dichloro intermediate **2**. Such
463 regioselective ortho attack, followed by 1,2-proton transfer, is the preferred mechanism [54], even
464 though the intermolecular proton transfer mediated by water cannot be ruled out. Hydrolysis
465 promoted by KOH leads to o-hydroxyformyl graphene layers, i.e. final product **6**, with CHO group
466 in ortho position with respect to OH.

467 This mechanism suggests that oxygenated functional groups are located on the edges of the
468 graphene layers and that a reaction occurs on graphene layers in the armchair configuration, which
469 have two neighboring reactive sites. The Reimer-Tiemann reaction leads to the formation, for each
470 CHO mole, of three KCl moles, which indeed affect the organization of graphene layers, favoring
471 their impressive exfoliation [29], as shown by WAXD results (Figure 5). The functionalization
472 degree of this reaction is reported in the Supplementary Material S3.

473 Figure S6B of the Supplementary Material shows the mechanism for the Cannizzaro
474 disproportionation reaction, which occurs at room temperature and leads to the introduction of
475 benzyl alcohols and carboxy functional groups on graphene layers. Product **6**, obtained through a
476 Reimer-Tiemann reaction, undergoes a nucleophilic attack of the hydroxide ion on the aldehydic
477 group. The tetrahedral carbon (intermediate **7**) expels a hydride ion becoming a potassium
478 carboxylate group (product **8**). A second molecule of o-hydroxyformyl graphene **6** undergoes a
479 nucleophilic acyl addition by the hydride ion. The benzyloxy intermediate **9** becomes alcohol (**10**)
480 upon washing with water. Therefore, the Cannizzaro reaction can only occur on aldehydes lacking
481 hydrogen atoms in the α positions. In fact, aromatic substrates with α hydrogens undergo instead
482 deprotonation leading to enolates: these species are not detected in the IR spectra of isolated
483 products. Carboxy functional groups could be due to both acids and esters. The presence of esters
484 could be justified if we hypothesize the condensation of benzyl alcohol and acid groups. Indeed, the
485 Cannizzaro reaction is used on an industrial scale for the preparation of esters starting from

486 aldehydes. In order to estimate to what extent esterification reaction occurred, calculations (reported
487 as Supplementary Material S4) have been attempted. They seem to indicate that esterification
488 reaction may occur. Graphene layers with alcohol and acid functional groups could be then be
489 prepared through hydrolysis.

490 The efficiency of the domino process, documented in Figure S1 (Supplementary Material), can be
491 explained taking into account that both Reimer-Tiemann and Cannizzaro are exothermic reactions,
492 in particular the former one. In spite of such efficiency, the bulk structure of graphene layers was
493 substantially unaltered and this is in line with functionalization on peripheral positions. In the
494 Supplementary Material S5, it is reported the characterization of graphene layers obtained from the
495 reaction of G-OH with KOH/H₂O/CHCl₃ at 0°C (Procedure 2). It is worth summarizing that
496 disproportionation reaction was not prevented: indeed, aldehydes were detected together with
497 carboxylic acids.

498 It is definitely important pondering why G-OH allows the occurring of the domino reaction. Only
499 speculations can be attempted. Two key steps characterize Cannizzaro disproportionation: (i) the
500 formation of the carboxy group with the expulsion of a hydride ion, (ii) the addition of the hydride
501 ion to a second mole of aldehyde. The carboxy group in G-OH could have high stability thanks to
502 the conjugation allowed by an infinite polycyclic aromatic hydrocarbon such as graphene. Such
503 stability allows an easy leaving of the hydride ion, which could be adsorbed on the graphene layer,
504 as potassium salt. Indeed, the absorption on graphene of hydrides of electropositive metals is
505 studied as tool for hydrogen storage [80]. Moreover, it could also be hypothesized that electron rich
506 G-OH adsorbs the reagents, acting as a catalyst for oxidation promoted by the oxygen dissolved in
507 the alkaline medium.

508 According to the reported mechanisms, the functionalization should occur on the edges of the
509 graphene layers. This could account for the difference of the IR spectra of the present work with
510 respect to the IR spectra of GO or reduced GO, where functional groups are expected over the entire
511 graphene plane. Moreover, Cannizzaro disproportionation reaction is known to occur moving from
512 aldehydes in the absence of acidic hydrogen on the alpha carbons, as it would be G-CHO. It is not
513 the purpose of this work to stretch inferences too far. However, a good number of experimental data
514 and analytical indications seem to support the plausibility of the above reported mechanisms. More
515 than that, they indicate that graphene layers were chemically modified with oxygenated functional
516 groups.

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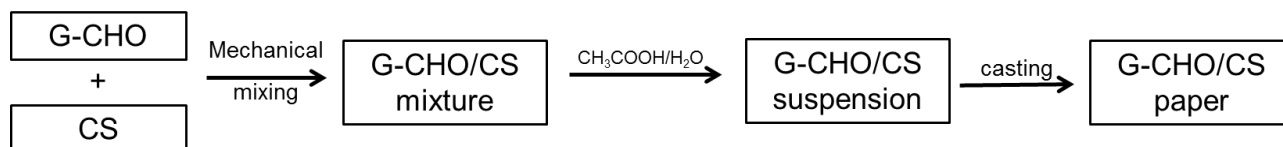
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520 3.3 Nanocomposites based on G-CHO and chitosan

521 With the aim to prove a viable use of functionalized graphene layers, exploiting the aldehydic
522 groups, bionanocomposites were prepared based on G-CHO and chitosan. The objective was to
523 crosslink chitosan with the graphene layers, thanks to the reaction between aldehydes and amino
524 groups. It is well known that chitosan can be crosslinked by dialdehydes and a molecule such as
525 glutaraldehyde is traditionally used [81], in spite of its critical aspects as for the impact on human
526 health. In the scientific literature, nanocomposites based on chitosan and graphene related materials
527 (i.e., graphene oxide or reduced graphene oxide) have been reported for different applications, such
528 as the preparation of highly compatible membranes [82], the detection of human epidermal growth
529 [83] and bone tissue engineering [84]. Improved properties are expected for the bionanocomposite
530 based on chitosan and G-CHO, thanks to the unperturbed nature of the graphene layers. To verify
531 the feasibility of the crosslinking reaction of G-CHO with amino groups, hexamethylenediamine
532 was successfully used as the crosslinking agent. Results are reported as Supplementary Material S6.
533 In this manuscript, reaction of G-CHO with chitosan and main materials molecular features are
534 reported, while the assessment of its physico-mechanical properties will be the focus of a future
535 work.

536 Reaction between G-CHO and CS was performed as described in the experimental part and
537 schematically shown in Figure 6.

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539

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Figure 6. Block diagram for the preparation of G-CHO/CS paper.

541

542 In brief, G-CHO and CS were first premixed in a mortar with the help of a pestle. Water dispersion
543 of the formed adduct was prepared in the presence of acetic acid. These dispersions were stable for
544 at least 1 week. Flexible carbon paper (Figure 7a) was then prepared by simply casting the
545 dispersion on a glass support and waiting for water evaporation. Characterization of G-CHO/CS
546 carbon paper was performed by means of FT-IR (Figure 7b) and XPS (Figure 7c and 7d).

547 In Figure 7b, spectra of solid CS, G-CHO/CS paper and G-CHO are reported in the region 1800 –
548 800 cm^{-1} . In the spectrum of pure CS (A) the strong and structured band at 1558 cm^{-1} with a
549 shoulder at 1575 cm^{-1} could be assigned to the overlap of the -CN- stretching (amide II) of the
550 C=ONHCH₃ group (chitin units) and of the -NH₂ bending vibration of the primary amine
551 (deacetylated chitin units). The sharp peak at 1378 cm^{-1} is assigned to the symmetric bending of

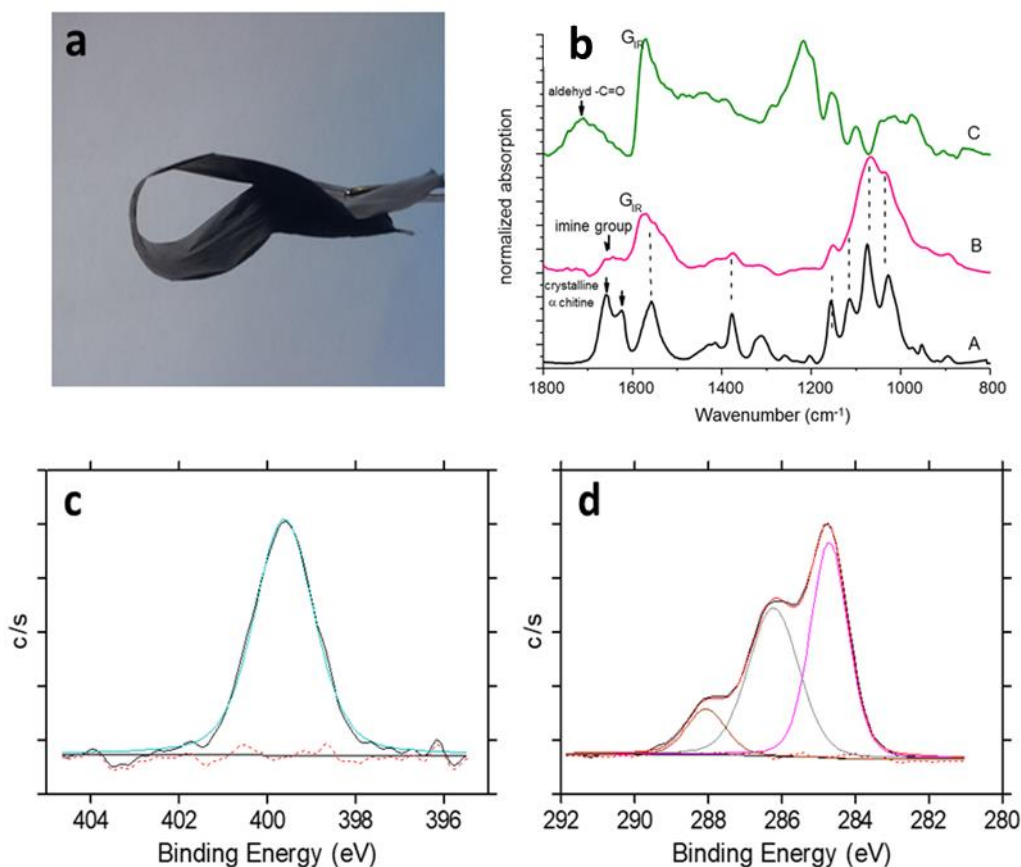
552 methyl groups (“umbrella” motion of chitin groups). The four strong and sharp peaks in the region
553 1200 cm^{-1} - 1000 cm^{-1} could be assigned to CO stretching modes of $-\text{COH}$, $-\text{COC}-$ and $-\text{CH}_2\text{OH}$
554 groups of the glycosidic ring [85]. The occurrence of sharp and well-defined absorption bands and
555 of the doublet at 1659 cm^{-1} and 1625 cm^{-1} (assigned to NH bending in crystalline α -chitin) suggests
556 the presence in the solid of crystalline domains.

557 In the spectrum of the G-CHO/CS paper (B) the G_{IR} peak at 1590 cm^{-1} and the main absorption of
558 CS can be observed. However, all the absorption bands are broader; there is a peak shift and band
559 overlapping. This observation supports the occurrence of structural disorder CS moiety in the
560 carbon paper. Interestingly the well-defined band at 1715 cm^{-1} (observed in the spectrum of G-CHO
561 and assigned to $-\text{C}=\text{O}$ stretching vibration of aldehydic functionalities) is strongly reduced in
562 intensity while a new medium-weak feature at 1656 cm^{-1} appears. Although in this region features
563 due to ammidic functionalities of CS are expected, the contemporary presence of the band at 1656
564 cm^{-1} associated to the strong $-\text{C}=\text{O}$ stretching reduction highly support the formation of imine
565 groups between CS and G-CHO.

566 The wide scan XPS spectrum of G-CHO/CS carbon paper contains signals from C_{1s} , O_{1s} and N_{1s} ,
567 as expected; minor amounts of Na, Si and Ca are present. Deconvolution was attempted for carbon
568 and nitrogen signals, although it is difficult to precisely assign the individual contribution of the
569 several groups in both the C_{1s} and N_{1s} peak. The N_{1s} narrow scan signal (Figure 7c) presents one
570 component at 399.6 eV : it can account for amine and amide belonging to chitosan (partially
571 deacetylized), imine, imide, amide groups resulting from a reaction between chitosan and the
572 oxygen containing groups of the carbon material. Therefore the presence of C-N and C=N groups
573 due to a covalent attachment of the macromolecule to the functionalized graphene can be predicted.

574 The deconvolution of the C_{1s} peak results in three components (Figure 7d). The one at 284.7 eV
575 corresponds to sp^3 carbon and can also be assigned to C-N groups which have been formed by the
576 already commented direct reaction of the polyamines with the $\text{C}=\text{C}$ double bonds of the carbon
577 material. The component at 286.2 eV can be assigned to imine groups (C=N) and C-O. Other
578 carbon-nitrogen and C=O groups cause the component at 288.1 eV . These data can suggest the
579 covalent bonding of G-CHO and the amino groups of chitosan, namely the imino groups coming
580 from the reaction of the carbonyl functions introduced by the Riemer-Tieman functionalization.

581 Comparing the C_{1s} narrow scan XPS spectra of G-CHO/CS carbon paper to those collected on
582 chitosan mixed with HSAG [65], binding energy shifts are observed, which can further prove the
583 covalent linking.



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Figure 7. (a) Image of the flexible G-CHO/CS carbon paper; (b) FT-IR spectra of CS (A), G-CHO/CS carbon paper (B) and C-CHO (C) in the region 1900-700 cm^{-1} ; (c) and (d) XPS narrow scans and peak deconvolution of N_{1s} (c) and C_{1s} (d) signals of G-CHO/CS carbon paper.

4. Conclusions

Polyhydroxylated graphene layers were reacted with KOH/H₂O and CHCl₃. When the reaction was performed at 0°C and CHCl₃ was added sequentially in small portions, aldehydic groups were detected on the graphene layers, as revealed by FT-IR spectra, XPS analysis and by the formation of imine functional groups after the reaction with the primary amines of chitosan. The presence of aldehydic functional groups can be justified with by the occurring of Reimer-Tiemann reaction, which is well known to happen to phenolic substrates reacted with CHCl₃ in alkaline medium. When the reaction was performed ~~done~~ at room temperature, benzyl alcohol and carboxy (prevailingly ester) groups were detected on the graphene layers. The Cannizzaro disproportionation reaction is known to lead to such functional groups moving from aldehydes in the absence of acidic hydrogen on the alpha carbons and could thus occur on the polyhydroxylated graphene layers that underwent Reimer-Tiemann reaction. Therefore it can ~~It could be thus~~ assumed that domino Reimer-Tiemann / Cannizzaro reaction occurred.

602 Graphene layers were thus functionalized with oxygenated functional groups. According to the
603 reaction mechanism proposed, functionalization occurred on the edges of the layers.
604 First proof of concept for a ~~first~~ viable usage of the produced graphene layers bearing aldehydic
605 groups was the crosslinking of chitosan, with the preparation of stable water dispersions and
606 flexible carbon papers, without using graphene oxide or reduced graphene oxide. Graphene layers
607 act as crosslinker for chitosan and ingredient to give ~~for giving~~ mechanical resistance, electrical and
608 thermal conductivities to the composite material. Future objectives of the research are to
609 characterize and fully exploit such properties.

610

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615

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