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# Unexpected reactivity of graphene oxide with DBU and DMF<sup>†</sup>

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An unusual reaction between GO, DBU and DMF, that typically uses base and solvent, has been thoroughly analyzed providing valuable basic knowledge about the reactivity of GO, which is essential to control functionalization and therefore the properties of graphene derivatives. A combination of characterization techniques, experiments and theoretical calculations allowed us to propose a structure for the materials and a plausible mechanism. The catalytic activity of the new basic materials was also analyzed.

Graphene and its derivatives are currently promising materials for the development of heterogeneous catalytic systems, both metallic and organic, as they display a large surface area and unique physicochemical characteristics.<sup>1-6</sup> Most research in this field involves functionalization of the surface or edges of graphene oxide (GO) through its multiple oxygen-based groups (alcohol, epoxide, ketone and carboxylic acid).<sup>7-9</sup> After functionalization, the reduction of GO to reduced graphene oxide (rGO) partially restores the electronic properties of graphene.<sup>10,11</sup>

We recently described an rGO material decorated with piperazine rings (**rGO-NH**, **A**), which was assembled through nitrogen epoxide-opening in GO by treatment with piperazine followed by reduction with hydrazine (Scheme 1).<sup>12</sup> Material **A** presented excellent catalytic activity as a bifunctional heterogeneous organocatalyst in several processes through iminium and basic activation. The Lewis basic role of the electron-rich graphene layer served to stabilize the iminium and ammonium intermediate species, triggering a higher performance of this amino- and carbocatalyst compared to piperazine alone.

As a continuation of our research, and in order to avoid the presence of a basic nitrogen that could potentially interfere in the catalytic process, we decided to study the anchoring of different catalysts through the opening of epoxides in GO by reaction with suitably functionalized alcohols. To our knowledge, this transformation has not been described thus far. As a consequence, we carried out a control experiment consisting of the reaction of GO with 2-(methylthio)ethanol in the presence of 1,8-diazabicycloundec-7-ene (DBU) and using N,N-dimethylformamide (DMF) as solvent (Scheme 2). These conditions were chosen as they are typically used for epoxide-ring-opening and also because DMF features excellent dispersion properties.<sup>‡13</sup> Nevertheless, the elemental analysis of the resulting material revealed an unexpected increase of the nitrogen content (8.5%) instead of the incorporation of the sulfurcontaining moiety.

Although far from our initial objective, but conscious of the importance of understanding the chemistry of graphene derivatives for future applications, we decided to perform a deep study of this unexpected high ratio of nitrogen obtained, which must be attributed to DBU and/or DMF. Therefore, to fully explore the nature of the aforementioned transformation, we carried out a systematic research by preparing different materials arising from the reaction of GO with DMF (material **B**), DBU (material **C**), and DBU/DMF (material **D**). These materials have been characterized by different techniques, and a reasonable mechanistic explanation for their formation was established from experimental results as well as a detailed DFT calculation study. The catalytic activity of materials **B** and **D** and a greener method to produce **rGO-NH** (**A**) avoiding the undesirable use of hydrazine are also presented herein.

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<sup>‡</sup> It is known that dispersions of GO in DMF and THF last for at least 3 weeks after sonication for 1 h (see ref. 13).





Scheme 2 Unexpected result with introduction of nitrogen in the material.

## **Results and discussion**

Table 1 shows the elemental analysis of the obtained materials after submitting GO to different conditions. Material **B** was prepared by heating a suspension of GO in DMF at 120  $^{\circ}$ C for 4 days in a sealed tube, followed by filtration and successive washings with water and acetone (entry 1). Elemental analysis of

material **B** showed a significant increase in the carbon content (77.4%) compared to the starting GO (49.8%), indicating a high degree of deoxygenation of GO. On the other hand, the amount of nitrogen was 2.8%. This result agrees with the literature as the use of DMF for the solvothermal reduction of GO and concomitant introduction of nitrogen has been described,<sup>14-16</sup> due to the generation of dimethylamine by cleavage of DMF under the reaction conditions.<sup>17,18</sup> Nevertheless, some discrepancies on the structure of the resulting materials as well as the possible mechanism will be revisited below.

To study the reaction of GO with DBU in the absence of DMF, we performed the reaction using THF as solvent in a sealed tube. After the same time (4 days) material C, which contained around 4% of nitrogen, was obtained (entry 2). As the most reasonable hypothesis could be an acid-base equilibrium between DBU and the acids of GO, material C was treated with basic media and the new material C' subjected again to elemental analysis (entry 3). It showed a decrease in the amount of C, H and N which agrees with an exchange of DBUH<sup>+</sup> by the not detectable Na<sup>+</sup> and a low incorporation of N on the surface (N/C ratio = 0.012) (see ESI<sup>†</sup> for more details). Conversely, the simultaneous use of DBU and DMF incorporated more nitrogen-containing moieties in the resulting material D(N/C =0.117, entry 4) than the sum of both reagents separately (entries 1-3), thus indicating a probable synergistic effect between DBU and DMF.

It is well-known that DBU could undergo hydrolysis of the imidamide moiety in refluxing water to provide amido amine 1.<sup>19</sup> Moreover, the reaction of GO with DBU in water as solvent was previously described, and the incorporation of amine 1 was proposed.<sup>20</sup> Although we did not run the reaction in water, we reasoned that DBU could be partially hydrolyzed under the reaction conditions and the resulting amino group of 1 would attack the epoxides of GO. To demonstrate this hypothesis, we

Table 1 Reaction of GO with different reagents and evaluation of the nitrogen content

		GO	Conditions	► Materials	B-F			
		( <b>GO (%):</b> C 49.8; H	H 2.5; N 0.05; S 1	1.1)				
				Elem. anal. (%wt)			Ratio	
Entry	Conditions <sup>a</sup>		Mat.	С	Н	Ν	H/C	N/C
1	DMF, 120 °C, 4	days	В	77.4	1.5	2.8	0.019	0.036
2	DBU, THF, 80 $^\circ$	C, 4 days	С	60.2	4.5	4.5	0.074	0.075
3	b		$\mathbf{C}'$	40.0	2.2	0.5	0.055	0.012
4	DBU, DMF, 120	$^{\circ}$ C, 4 days <sup>c</sup>	D	68.1	3.9	8.0	0.057	0.117
5	H <sub>2</sub> N H <sub>3</sub> N 1	DMF, 120 °C, 1 day	Е	72.9	3.9	7.2	0.053	0.116
6	$H_2N$ $H_3N$ 1	EtOH, H <sub>2</sub> O 80 °C, 1 day	F	65.0	2.1	5.1	0.032	0.078

<sup>*a*</sup> Reactions performed in sealed tubes. <sup>*b*</sup> Material C was washed with a 2 M NaOH solution. <sup>*c*</sup> When the reaction was performed at 80  $^{\circ}$ C (see ESI), a lower content of nitrogen was observed (N, 6.3%; N/C, 0.09).

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reacted **1** with GO during 1 day, which is considered as enough time for the amines to attack to the epoxides.<sup>21</sup> Both DMF and EtOH were used as solvents as the comparison of the subsequent materials **E** and **F** (entries 5 and 6, respectively) would give information about the possible introduction of nitrogen from DMF. It was found that material **E** presented slightly lower percentage of nitrogen than material **D** (compare entries 4 and 5) but material **F** that was formed in the absence of DMF (entry 6) had a significantly lower nitrogen content than **E** and **D**.

The evolution of the reactions and the structural differences among these materials were inferred from their characterization data employing several analytical techniques. Fig. 1 gathers TGA plots for materials **B**, **D**, **E** and **F**. We could observe that the mass loss in sample **B**, presumably due to NMe<sub>2</sub> groups is quite constant. According to the mass loss in **D**, **E** and **F** (200–550 °C) their degree of functionalization should be quite similar. The maximum of the derivative displaced towards higher temperatures in the order **F**, **E** and **D** indicates that the chains anchored to the graphene are more thermally stable in **E** and **D** than in **F**. This could fit with the assumption that materials **D** and **E** are functionalized with both chain **1** and NMe<sub>2</sub> groups.

Fig. 2 shows a comparison between the <sup>13</sup>C NMR spectra in solid state of GO and of materials **B**, **D**, **E**, and **F**, which turned out very diagnostic and certainly illustrates the reduction of the graphitic structure. The disappearance of broad peaks at 72 and 60 ppm was a clear indication of the removal of oxygen functionalities (hydroxyls and epoxides, respectively), whereas the peak at 132 ppm corresponding to sp<sup>2</sup> carbons was displaced towards higher field due to the increased level of conjugation. In material **B**, the presence of a new peak at 32 ppm could be attributed to the introduction of Me<sub>2</sub>N groups. The presence of the hydroxyl groups in material **E** and not in material **D** could be a consequence of the longer reaction times in the second case that would favor water elimination. Despite this difference, the similar features displayed by **D** and **E** led us to suspect the introduction of compound **1** in material **D**.

The IR analysis also confirmed a restoration of the sp<sup>2</sup> carbon network (or removal of oxidative debris) when comparing with GO.<sup>22</sup> For example, in material **B** the peaks



Fig. 1 Thermograms of material B (GO + DMF); material D (GO + DBU + DMF); material E (GO + 1 in DMF) and material F (GO + 1 in EtOH/  $H_2O$ ).



Fig. 2 Solid <sup>13</sup>C NMR of (a) GO; (b) material B (GO + DMF); (c) material D (GO + DBU + DMF); (d) material E (GO + 1 in DMF); (e) material F (GO + 1 in EtOH/H<sub>2</sub>O).

corresponding to C=O and C=C stretches shifted to lower wavenumbers, 1713 and 1563 cm<sup>-1</sup>, respectively (Fig. 3). Conversely, intense peaks around 1085–1250 cm<sup>-1</sup> that could correspond to C–N stretching from the NMe<sub>2</sub> groups were observed in materials **B**, **D** and **E**. These data are reinforced by DFT calculations (see ESI†). These peaks are wider for materials **B** and **D** but narrower for material **E**, probably due to the smaller



Fig. 3 FTIR spectra of GO and materials B-F.

amount of NMe<sub>2</sub> in material E. For E and F the peak is narrow and shifted to higher wavenumbers, this could correspond to the C–N stretching from compound **1**. Spectra of samples C', D, E and F showed a reduction in intensity for the C=O stretching and a new peak around 1640 cm<sup>-1</sup> that could correspond to the formation of the carboxylate salt. Assignment of this peak as possible C=O stretching of amides was excluded since this would appear as a more intense peak around 1634 cm<sup>-1</sup> (amide I) together with a second peak around 1585 cm<sup>-1</sup> (amide II).<sup>23</sup> Finally, the spectrum of material C displayed an intense peak around 1645 cm<sup>-1</sup> corresponding to C=N stretch of DBU, but after washing with a NaOH solution (material C') the peaks corresponding to DBU disappeared, in agreement with an exchange of DBUH<sup>+</sup> by Na<sup>+</sup> as previously observed by elemental analysis.

Next, we performed additional experiments in order to understand the process by which materials **D** and **E** incorporate  $NMe_2$  groups. First, we analyzed the nature of the resulting supernatant solution when GO was treated with DMF or *N*,*N*dimethylacetamide (DMA) (Table 2). We could isolate some unaltered DBU along with compounds 2. When using DMF, a mixture **2a**/DBU in 62 : 38 ratio was obtained (entry 1). Due to the anchoring process, only around 65% of the mass of the initial DBU was recovered. This result is consistent with the breakdown of the amide, the anchoring of dimethylamine (blue) to the GO surface and a concurrent transamidation of the acyl group (red) to the amine residue. The formation of compounds **2** also confirms that DBU was partially hydrolysed.

We reasoned that the low conversion and slow evolution towards **2a** (after two days the ratio **2a**/DBU was 44 : 56, entry 2) could be a consequence of the relatively low amount of water in the reaction media, presumably produced from the elimination of the hydroxyl groups of GO. Indeed, we observed a faster reaction using one equivalent of water, and after 2 days only **2a** was detected (entry 3). When using DMA as solvent, acetamide **2b** was isolated in 36% yield (entry 4). This hypothesis is reinforced by the fact that when the nonvolatile 4-phenylbutylamine was treated with DMF under the conditions of entry 1 (Table 3) about only 67% of the mass was recovered but the formylated amine 3 was isolated in 64% yield from a very clean mixture. In the absence of DBU the yield was somewhat lower (entry 2), suggesting a role of DBU in the reaction mechanism. Nevertheless, the latter is an important point to consider as DMF could interfere when used as solvent in the amine functionalization of GO *via* ring opening of the epoxides by lowering the yield and incorporating NMe<sub>2</sub> groups to GO. This transamidation would also explain that the reaction of 1 with DMF after only 1 day also incorporated NMe<sub>2</sub> to provide material E (Table 1, entry 5). The low yield obtained in the experiment shown in entry 3, that uses K<sub>2</sub>CO<sub>3</sub> instead of DBU, put forward that DBU is not acting as a simple base.

When material F was treated with DMF at 120 °C for 72 h, the ratio of nitrogen did not increase (C, 71.5; H, 3.1; N, 4.8; S, 0.03; N/C, 0.067). This experiment supports the idea that a previous reaction between DMF and DBU enables the introduction of different nitrogen-containing groups on GO. Moreover, when the GO was treated with DBU and DMF at 120 °C for 4 days (conditions of entry 4, Table 1) in the presence of BHT as a radical inhibitor, the material also contained a high ratio of nitrogen (C, 73.7; H, 3.7; N, 6.0; S, 0.06; N/C, 0.081), thus supporting a non-radical mechanism.

At this point, we evaluated the basicity of the differently functionalized materials (Fig. 4). The similarity in pH values of materials **A** and **B** in aqueous dispersions suggests that most of the amino groups must be located on the surface of GO, instead of forming amides by reaction with the acid groups sited at the edges as it has been proposed.<sup>15</sup> IR analyses (see above) and other reports<sup>24</sup> also support the absence of amides. Moreover,





Table 2 Reaction of DBU with DMF and DMA in the presence of GO

Solvent	t (days)	2/DBU ratio <sup>a</sup>	Product	Yield (%)
$\mathrm{DMF}^b$	4	62:38	2a	38
DMF	2	44:56	2a	ND
DMF	2	>95:5	2a	ND
DMA	4	$\mathrm{ND}^d$	2b	36
	Solvent DMF <sup>b</sup> DMF DMF DMA	$\begin{array}{c} t\\ \text{Solvent} & (\text{days}) \end{array}$ $\begin{array}{c} \text{DMF}^b & 4\\ \text{DMF} & 2\\ \text{DMF} & 2\\ \text{DMF} & 2\\ \text{DMA} & 4 \end{array}$	$\begin{array}{c} t\\ \text{Solvent} & (\text{days}) & 2/\text{DBU ratio}^a \end{array}$ $\begin{array}{c} \text{DMF}^b & 4 & 62:38\\ \text{DMF} & 2 & 44:56\\ \text{DMF} & 2 & >95:5\\ \text{DMA} & 4 & \text{ND}^d \end{array}$	$\begin{array}{c} t\\ \text{Solvent} & (\text{days}) & 2/\text{DBU ratio}^a & \text{Product} \end{array}$ $\begin{array}{c} \text{DMF}^b & 4 & 62:38 & \mathbf{2a}\\ \text{DMF} & 2 & 44:56 & \mathbf{2a}\\ \text{DMF} & 2 & >95:5 & \mathbf{2a}\\ \text{DMA} & 4 & \text{ND}^d & \mathbf{2b} \end{array}$

<sup>*a*</sup> Determined by <sup>1</sup>H NMR. <sup>*b*</sup> When the reaction was performed at 80 °C 2 was not detected. <sup>*c*</sup> 1 equiv. of H<sub>2</sub>O was added. <sup>*d*</sup> Ratio not determined due to overlapping of signals.



Entry	Reagents/conditions	Yield (%)
1	GO, DBU, 120 °C, 4 days	64
2	GO, 120 °C, 4 days	54
3	GO, $K_2CO_3$ , 120 °C, 4 days	<20



Fig. 4 pH measurements of the suspension of materials in water.



Scheme 3 Plausible mechanism that explain formation of materials D and E though a synergistic effect of DBU and DMF and transamidation reaction.

the higher pH of material **D** is consistent with a higher amount of basic nitrogens.

With all this information we are in position to propose two possible pathways that explain the formation of materials **D** and **E**. Under the non-anhydrous conditions and the continuous formation of water by heating GO, DBU could be easily hydrolyzed to afford **1**, which could evolve by attacking both the epoxide groups of GO as well as DMF to provide 2 as a result of the transamidation reaction (Scheme 3, route A).

According to the observed cooperative effect of both DBU and DMF in this transformation, we reckon that route B must be also operative to some extent. In this route B, DBU could react with DMF to evolve though intermediate I (left bottom side in Scheme 3) towards hydrolysis and provide compound 2. Intermediate I has been suggested in several examples that proposed that DBU could promote the transfer of acyl groups.§<sup>25–29</sup> Therefore intermediate I (route B) could promote other transamidation reactions of DMF if a suitable nucleophile is present (see Table 3, entry 1). Nevertheless, as it will be shown below, some considerations have to be made regarding this intermediate I.

As a proof for the feasibility of these mechanisms, a density functional theory (DFT) calculation was performed at B3LYP/6-311G(d,p) level of theory.<sup>30,31</sup> Our main target was to highlight the different steps that could take place and the intermediates formed in the reaction between DBU and DMF in the presence of water to explain the formation of HNMe<sub>2</sub>, compound 2, and materials D and E. Therefore, if the reaction between water and DBU takes place first (route A, Scheme 3), the initial intermediate is a hydrogen bond complex between both species (minA-1 in Fig. 5, green pathway). This interaction is exergonic by a release of  $\sim -41$  kJ mol<sup>-1</sup> in energy. This complex is transformed into compound 1 in two steps, namely the addition of the hydroxyl group which occurs as a consequence of hydrogen transfer from a water molecule to DBU (TsA-12) involving an energy activation of ~174.7 kJ mol<sup>-1</sup>, and a second intramolecular hydrogen transfer in minA-2 from the OH group to the nearest nitrogen atom (TsA-21) with an estimated activation barrier of  $\sim$ 149.7 kJ mol<sup>-1</sup>. The resulting compound **1** is highly stable in the potential energy surface, about -63.6 kJ mol<sup>-1</sup>

below the entrance channel. The following step (transamidation reaction, in red) starts with a new hydrogen bond interaction between DMF and **1** leading to complex minA-3. In this case, the stabilization energy is around -17.8 kJ mol<sup>-1</sup>. Finally, the latter complex needs to overpass an energy barrier of  $\sim 201$  kJ mol<sup>-1</sup> to get the transamidated product **2** and HNMe<sub>2</sub>, thus accounting for the lack of compound **2** if the reaction is performed at 80 °C (see Table 2 and ESI†).

On the other hand, if DMF interacts first with DBU (route B, Scheme 3) the complex formed is again a hydrogen bond-based structure (minB-1 in Fig. 5, red pathway). In this case, the stabilization energy is less than the previous one observed in route A ( $\sim$ -18.5 kJ mol<sup>-1</sup>). The process towards compound 2 and HNMe<sub>2</sub> would begin by a reaction between DBU with DMF that, in the first step, presents a high activation barrier ( $\sim$ 280 kJ mol<sup>-1</sup>).

Since DFT calculations were performed in gas phase, the formation of the cationic intermediate I is not probable due to the high energy that should be needed to break DMF homolitically. Nevertheless, DFT calculations by hydrogen transfer between both entities led us to compound 4. This could be an intermediate to take into account when studying other related processes, as its formation should be very favored in solution under the basic conditions used (DBU).

The second step is the hydrolysis followed by a double hydrogen transfer between the involved species to obtain 2 and HNMe<sub>2</sub>. Although according to DFT calculations, route A is more favored than route B, both pathways could be possible under the experimental conditions applied to the systems under study (T = 120 °C).

In both routes the HNMe<sub>2</sub> liberated to the reaction media is easily trapped by the GO shifting the equilibrium. In fact, the interaction of HNMe<sub>2</sub> with a GO model (containing an epoxide, a hydroxyl and a carboxylic group) shows a great electrostatic linkage between both species (Fig. 6). The estimation of the binding energy by means of ONIOM model<sup>32</sup> reveals an energy value about -57 kJ mol<sup>-1</sup>, which is in the range of strong hydrogen bonds.<sup>33</sup> This has been ratified by a non-covalent interaction (NCI) analysis which has shown a great attractive character in the region where HNMe<sub>2</sub> is attached to the GO epoxide group (see structure (c) in Fig. 6).

<sup>§</sup> DBU is considered non nucleophilic but it can also act as a nucleophile.



Fig. 5 Energy profile of the DBU and DMF reaction in presence of water to get HNMe<sub>2</sub>. The colours code follow-up the same reasoning as in Scheme 3 (all values are in kJ mol<sup>-1</sup>).



Fig. 6 Structures of the complex between a GO-model and HNMe<sub>2</sub>. (a) On the plane interaction (b) on the side Interaction. (c) NCI-plot analysis of structure. The values presented are the binding energies at B3LYP//6-311G\* level of theory in kJ  $mol^{-1}$ .

Once the generation of  $HNMe_2$  under the experimental conditions has been established by the mechanism depicted above (Fig. 5), and considering the ability of amines to get attached to the GO surface,<sup>21</sup> we can next propose a pathway for this insertion. This can occur through a hydrogen transfer from  $HNMe_2$  to GO-epoxide oxygen which is possible by overpassing an activation barrier of about 177 kJ mol<sup>-1</sup> (Fig. 7). It is worth noting that other possible pathways could take place under the same conditions as deprotonation by DBU or the reduction of rGO by DMF to produce  $HNMe_2$  as pointed out by Kim *et al.*<sup>34</sup>

The usefulness of the newly prepared GO-derived materials was next tested on some C–C bond-forming processes, such as the Knoevenagel condensation that has also been performed recently in the presence of other graphene-derived catalysts.<sup>12,35–39</sup> Thus, both materials **B** and **D** were able to promote

the reaction between aromatic aldehydes and nucleophiles such as malononitrile or ethyl 2-cyanoacetate to furnish Knoevenagel adducts **5a**, **5b** in high yields and reasonable reaction times (Table 4, entries 1–3). Furthermore, the analogous condensation employing ketones was also successful when longer reaction times were applied, albeit material **D** proved much more effective than material **B** (entries 4 and 5). Leaching of functional groups from the catalyst was ruled out as the elemental analysis of material **D** after the Knoevenagel reaction (entry 2) showed comparable results (C, 68.4; H, 3.7; N, 8.2; N/C, 0.120) as those included in Table 1.

Compounds 5a, 5b served as excellent Michael acceptors in the subsequent addition of nucleophiles. This transformation could be also conducted in a one-pot Knoevenagel–Michael sequence and hence nitroderivatives 6a, 6b were readily obtained in the presence of excess of nitromethane in moderate



**Fig. 7** Energy profile of a possible HNMe<sub>2</sub> insertion in graphene oxide achieved with ONIOM model where the high layer is optimized at B3LYP/6-311G(d,p) and low layer at B3LYP/STO-3G levels of theory.

Table 4 Synthetic processes catalyzed by GO-derived materials



Entry	Х	R	R′	Catalyst	5 (reaction time, yield)	<b>6</b> (reaction time, <sup><i>a</i></sup> yield <sup><i>b</i></sup> )	
1	Cl	Н	CN	В	5a (6 h, 90%)	<b>6a</b> (36 h, 67%)	
2	Cl	Н	CN	D	5a (2.5 h, 99%)	<b>6a</b> (20 h, 66% <sup>c</sup> )	
3	Cl	Н	$CO_2Et$	D	5 <b>b</b> (18 h, 97%)	<b>6b</b> (20 h, 36% <sup>c</sup> )	
4	Br	Me	CN	В	<b>5c</b> (96 h, $38\%^d$ )		
5	Br	Ме	CN	D	5c (96 h, 90%)		

<sup>a</sup> Reaction time of the Michael addition step. <sup>b</sup> Overall yield of the Knoevenagel-Michael sequence. <sup>c</sup> After 72 h, 20-30% of compound 7 was also formed. <sup>d</sup> Conversion.

overall yields (Table 4, entries 1-3). It should be noted that variable amounts of dinitro compound 7 were produced, arising from a retro-Michael reaction followed by the addition of a second molecule of nitromethane.

These excellent results prompted us to reevaluate the preparation method of our former material A,<sup>12</sup> but avoiding the use of hydrazine as reducing agent. Thus, GO was first reacted with piperazine as in Scheme 1, and further treatment with DMF produced a rearomatization to provide reduced material A' (Scheme 4).

Interestingly, the elemental analysis showed an almost identical ratio of nitrogen for both materials A (C, 66.5; H, 2.8; N, 5.2; N/C, 0.078) and A' (C, 66.1; H, 2.1; N, 5.1; N/C, 0.077). Similarly to material **B**, FTIR analysis for material **A**' also shows the shifting of C=O and C=C stretches peaks when comparing with GO (restoration of the sp<sup>2</sup> carbon network or removal of oxidative debris). Material A' also showed the appearance of an intense and wide peak around 1200 cm<sup>-1</sup> that could correspond to C-N stretching from both NMe2 groups and piperazine (Fig. 8). Comparison of TGA plots for materials A and A' shows different profiles and weight losses that could be assigned to the NMe<sub>2</sub> groups that have been incorporated during DMF treatment (see ESI<sup>†</sup>).

The catalytic performances of A and the newly prepared material A' were compared by performing several reactions



Scheme 4 Preparation of material A'.

which could occur via different mechanisms and could provide valuable information about the nature of both catalysts. The Knoevenagel reaction could work either via iminium or basic activation and the subsequent Michael addition must occur via basic activation. In this case, both catalysts A and A' behaved in a very similar way to provide compound 6d (Scheme 5, path a).

On the contrary, the reaction of cinnamaldehyde and nitromethane via iminium ion activation produced a mixture of 1,2and 1,4-addition products 8 and 9, respectively, in different ratios depending on the catalyst employed (Scheme 5, path b). It is expected that compound 9 was formed via iminium activation whereas compound 8 could be formed via both mechanisms, namely iminium and basic activation. The higher ratio of 8 when using catalyst A' corroborated the presence of  $Me_2N$ moieties as additional basic centers that modulate the catalytic activity of the material, showing a decrease of the iminium pathway only possible through the piperazine moiety.



Fig. 8 FTIR spectra of GO and materials A and A'.



Scheme 5 Comparison between catalysts A and A' in: (a) Knoevenagel–Michael sequence and (b) Michael *versus* Henry and elimination.

These results demonstrate that DMF is not an innocent solvent when using GO. In this context, it has been published that DMF played a relevant role in the catalytic activity of CuO/ GO composites.<sup>40</sup> Although in this case the metal has been proposed as responsible of the cleavage of DMF, according to our results it cannot be discarded an effect of the GO.

## Conclusions

In conclusion, we have found that the reaction between DBU and DMF triggers the formation of amine 1 and HNMe<sub>2</sub>, and the further covalent bonding of these amines to GO. Some experiments and DFT calculations allowed us to propose a plausible mechanism and reaffirm the characterization of the obtained materials. In addition, our estimations showed a great hydrogen bond interaction between HNMe<sub>2</sub> and GO. Understanding this type of processes is essential to control graphene functionalization, which in turn is fundamental to control the properties and applications of graphene derivatives. We have demonstrated the catalytic potential of the resulting materials and proved that the use of DMF for the solvothermal reduction of functionalized graphene derivatives could be a greener option but it may also change the properties of the material compared to other reduction methods. Moreover, this study reveals that the use of DMF as solvent to introduce amines into GO via epoxide opening would undergo transamidation reactions and introduction of NMe2 groups. Therefore, these results must be considered when DMF and/or DBU are used in reactions promoted by GO as the introduction of basic groups might change the properties of the desired materials.

### Experimental and methods

#### Preparation of materials B–F and $\mathbf{A}'$

**Preparation of material B.** A suspension of 100 mg of GO in DMF (5 mL) was sonicated for 30 min. The reaction mixture was stirred at 120 °C in a sealed tube for 96 h. After cooling to room temperature, the material was filtered through a filter plate, washing with deionized water (4  $\times$  15 mL) until neutral pH. Then, the material was washed with methanol (20 mL), acetone (20 mL) and left to stir in a vial tube at 70 °C for 24 h.

**Preparation of material C.** A suspension of 600 mg of GO in THF (100 mL) was sonicated for 30 min, whereupon DBU (900  $\mu$ L, 916 mg, 6 mmol) was added to the suspension. The reaction mixture was stirred at 70 °C in a sealed tube for 96 h. After cooling to room temperature, the material was filtered through a filter plate, washing with deionized water (4 × 15 mL) until neutral pH. Then, the material was washed with methanol (20 mL), acetone (20 mL) and left to stir in a vial tube at 70 °C for 24 h.

**Preparation of material D.** A suspension of 1.5 g of GO in DMF (110 mL) was sonicated for 30 min, whereupon DBU (2.25 mL, 2.29 g, 15 mmol) was added to the suspension. The reaction mixture was stirred at 120 °C in a sealed tube for 96 h. After cooling to room temperature, the material was filtered through a filter plate, washing with deionized water (5  $\times$  20 mL) until neutral pH. Then, the material was washed with methanol (20 mL), acetone (20 mL) and left to stir in a vial tube at 70 °C for 24 h.

**Preparation of material E.** A suspension of 500 mg of GO in DMF (60 mL) was sonicated for 30 min, whereupon amine 1 (ref. 19) (600 mg, 3.53 mmol) was added to the suspension. The reaction mixture was stirred at 120 °C in a sealed tube for 24 h. After cooling to room temperature, the material was filtered through a filter plate, washing with deionized water ( $4 \times 15$  mL) until neutral pH. Then, the material was washed with acetone ( $2 \times 15$  mL) and left to stir in a vial tube at 70 °C for 24 h.

**Preparation of material F.** A suspension of 200 mg of GO in deionized  $H_2O$  (5 mL) was sonicated for 30 min, whereupon a solution of amine 1 (ref. 19) (342 mg, 2 mmol) in EtOH (5 mL) was added to the suspension. The reaction mixture was stirred at 100 °C in a sealed tube for 24 h. After cooling to room temperature, the material was filtered through a filter plate, washing with deionized water (3 × 15 mL) until neutral pH. Then, the material was washed with acetone (2 × 15 mL) and left to stir in a vial tube at 70 °C for 24 h.

**Preparation of material A**'. A suspension of 500 mg of GO-NH<sup>12</sup> in DMF (50 mL) was sonicated for 30 min. The reaction mixture was stirred at 120 °C in a sealed tube for 72 h. After cooling to room temperature, the material was filtered through a filter plate, washing with deionized water (5 × 20 mL) until neutral pH. Then, the material was washed with acetone (2 × 20 mL) and left to stir in a vial tube at 70 °C for 24 h.

#### **Knoevenagel reactions**

**Reactions with aldehydes.** A suspension of 20 mg of the corresponding material in EtOH (1 mL) was sonicated for 10 min. Then, benzaldehyde or *p*-chlorobenzaldehyde (0.123 mmol) and the corresponding nucleophile (malononitrile or ethyl 2-cyanoacetate, 0.135 mmol) were added. The mixture was stirred at 70 °C until completion, whereupon the crude was filtered to remove the material and the solvent was evaporated at reduced pressure, to afford the corresponding product **5a**, **5b**, **5d**, in the yields and reaction times indicated in Table 4 and Scheme 5. Characterization data of **5a**, **5b**, **5d** were in agreement with those previously reported.<sup>41-43</sup>

**Reactions with ketones.** A suspension of 30 mg of the corresponding material in EtOH (1 mL) was sonicated for 10 min. Then, *p*-bromoacetophenone (19.9 mg, 0.1 mmol) and malononitrile (7.2 mg, 0.1 mmol) were added. The mixture was stirred at 70 °C for 96 h, whereupon the crude was filtered to remove the material and the solvent was evaporated at reduced pressure to afford the corresponding product **5c** in the yields indicated in Table 4. Characterization data of **5c** were in agreement with those previously reported.<sup>44</sup>

#### Knoevenagel-Michael one-pot sequence

**Reaction with nitromethane.** A suspension of 20 mg of the corresponding material in EtOH (1 mL) was sonicated for 10 min. Then, benzaldehyde or *p*-chlorobenzaldehyde (0.123 mmol) and the corresponding nucleophile (malononitrile or ethyl 2-cyanoacetate, 0.135 mmol) were added. The mixture was stirred at 70 °C until completion (TLC analysis), and nitromethane (131  $\mu$ L, 2.45 mmol, 20 equiv.) was then added. The mixture was stirred at 70 °C until completion of the reaction, whereupon the crude was filtered to remove the material and the solvent evaporated at reduced pressure. The crude was purified by flash column chromatography (hexane/EtOAc, 5 : 1) to afford products **6a**, **6b**, **6d** and 7 in the yields and reaction times indicated in Table 4 and Scheme 5. Characterization data of **6a**, **6b**, **6d** and 7 were in agreement with those previously reported.<sup>45-48</sup>

#### Michael/Henry addition of nitromethane to enals

**Reaction with cinnamaldehyde.** A suspension of 50 mg of the corresponding material in MeNO<sub>2</sub> (2 mL) was sonicated for 10 min. Then, cinnamaldehyde (38  $\mu$ L, 0.3 mmol) was added. The mixture was stirred at 60 °C for 72 h, whereupon the crude was filtered to remove the material and the solvent evaporated at reduced pressure. The crude was purified by flash column chromatography (cyclohexane/EtOAc, 10 : 1 to 5 : 1) to afford products 8 and 9 in the yields and reaction times indicated in Scheme 5. Characterization data of 8 and 9 were in agreement with those previously reported.<sup>49,50</sup>

#### **Computational details**

The structure optimization together with the frequencies estimation along the potential energy surface were done at B3LYP/ 6-311G(d,p) level of theory.<sup>30,31</sup> Starting from an asymmetric distribution of the functional groups in the graphene oxide which lead to a non periodic system the Oniom model<sup>32</sup> was choose as implemented in Gaussian 09 series of programs.<sup>51</sup> The optimization of the high layer was achieved at B3LYP/6-311G(d,p) while for the low layer the level of theory was B3LYP/STO-3G. The election of graphene model was conditioned by the active functional groups (epoxide, hydroxyl and carboxylic groups) and the size of the active region (high layer of Oniom calculation) where the interaction could take place. The objective was to reduce the computational cost achieving a reasonable quantum calculation quality. So, we tried different sizes of graphene and different positions of functional groups by comparing the experimental infrared spectrum and theoretical ones. The nice coincidence between the major vibrations was the decisive factor for our choice (see ESI†). As a complement of our exploration a non covalent interaction analysis was done by means of NCI-plot proposed by Yang *et al.*<sup>52,53</sup>

## Conflicts of interest

There are no conflicts to declare.

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