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Photochemical functionalization of graphene oxide by thiol-ene click chemistry

Alexis Piñeiro-García^{†§}, Sofia M. Vega-Díaz[†], Ferdinando Tristán[†], David Meneses-Rodríguez[‡], Gladis Judith Labrada-Delgado[‡], Vincent Semetey^{§*}

[†]Departamento de Ingeniería Química, Tecnológico Nacional de México/Instituto Tecnológico de Celaya, Avenida Tecnológico esq., A. Garcia Cubas S/N, CP 38010, Celaya, Guanajuato, Mexico

[‡]Cátedras-CONACYT CINVESTAV – Mérida Km 6, Carretera Antigua a Progreso, Cordemex, CP 97310, Mérida, Yucatán, México

[‡]LINAN-IPICYT, Camino a La Presa San José 2055. Col. Lomas 4 Sección, CP 78216, San Luis Potosí S.L.P, Mexico

[§]Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, 11 Rue Pierre et Marie Curie, 75005 Paris, France

Corresponding author's email: vincent.semetey@chimieparistech.psl.eu

Abstract

Graphene oxide (GO) is an important platform that can be functionalized due notably to its wide variety of functional groups. The functionalization is a critical step leading the production of GO based materials for promising applications in many fields ranging from biomedicine, depollution or energy storage. Defects introduced into the graphitic domain during the graphite oxidation allow to obtain alkene groups which can be functionalized *via* thiol-ene click reactions (TER). Usually for GO functionalization by TER, thermal radical initiators have been used with disadvantages such as high reaction times and the subsequent GO reduction, losing possible oxygen functional groups that can be further used for a second functionalization. Hence, we introduce the photochemical functionalization of GO by TER with cysteamine as probe molecule using a photoinitiator. The reaction was characterized by ATR-FTIR, UV spectroscopy, fluorimetry, XPS and Raman spectroscopy. This new

perspective of photoinduced TER provides advantages such as short reaction time using mild conditions avoiding a subsequent GO reduction, associated with efficient orthogonal functionalization.

Introduction

Graphene oxide (GO) has attracted an important attention due to its great surface area, the wide variety of functional groups, the electronic, thermal and mechanical properties that can be obtained once C-O species are eliminated.^{1,2} In order to produce graphene-based materials with exceptional properties, the GO functionalization with different molecules constitutes an important and critical step.²⁻⁵ This functionalization has been used to improve the performance of GO for a wide range of applications such as energy storage,^{6,7} wastewater treatment,⁸ biomedicine,⁹ catalysis,¹⁰ among others. The conventional methods for GO functionalization involves epoxy or carboxylic acid groups since they are the most abundant species on GO.^{11,12} Generally, the functionalization has been carried out using nucleophilic agents such as amines and thiol compounds.¹³ However, those compounds can interact with different oxygen functional groups losing selectivity.^{11,13} Indeed, some reactions methods include to heat the system leading to GO reduction.¹⁴⁻¹⁶ Thus, new approaches of orthogonal functionalization of GO must be considered in order to generate multi-functionalized materials.

After the oxidation of graphite, a great quantity of defects can be found, including vacancies which reduce the graphitic domain and more alkene groups (C=C) are obtained.¹⁷ In order to take advantage of alkene groups of GO, thiol-ene click reactions (TER) can be applied as a powerful tool for achieving orthogonal reactions under mild conditions, with high yields and avoiding by-products.¹⁸⁻²¹ The first application reported of TER on GO was published by Luong *et al.*,²² where cysteamine was used in presence of 2,2'-azobis(isobutyronitrile) as

thermal radical initiator and then, several efforts have been reported to apply TER on GO a wide range of applications.²³⁻³⁰ Nevertheless, TER has been carried out using systematically 2,2'-azobis(isobutyronitrile) as thermal radical initiator. As a consequence of applying thermal initiators, a simultaneous GO reduction can be produced losing functional groups such as epoxide, that could be used for a second derivatization.²²⁻³⁰ In this context, TER can be carried out by exposing the reaction to UV-light radiation for the production of thiyl radicals ($R-S^{\bullet}$). Nonetheless, the yield depends of the S-H bond dissociation energy (BDE) in order to form thiyl radicals.^{18,19,21} Therefore, a photoinitiator (PI) can be added during the reaction for increasing the production of thiyl radicals and increase the degree of functionalization.³¹ The application of TER under UV-light using a PI possesses several advantages such as extremely rapid reactions, not need to heat the system and thus less reduction of GO leading to a better control of the reaction.^{18,19}

Motivated by the idea of producing new approaches for GO functionalization, we systematically studied the GO functionalization by TER using a PI coupled to UV radiation in order to have a rapid and selective functionalization under mild conditions, avoiding a GO reduction and opening the possibility to develop double functionalizations in a subsequent step. In this context, we expect to preserve most of the oxygen functional groups in GO for further chemical modification, promoting a pathway to develop materials with outstanding properties for applications in many fields ranging from materials science to biomedicine.^{23,30,32,33}

Materials & methods

Materials

Asbury natural graphite of 1 μm was used for GO synthesis. The reagents used during GO synthesis were sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), potassium permanganate (KMnO_4), phosphorus pentoxide (P_2O_5), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), hydrogen peroxide (H_2O_2) and hydrochloric acid (HCl), all were analytical grade and purchased from Sigma Aldrich. For GO functionalization by TER, 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (97%) was used as photoinitiator (PI), cysteamine hydrochloride (CA, $\geq 98\%$), 2-(dimethylamino)ethanethiol hydrochloride (MEDA, $\geq 95\%$), *N,N*-Dimethylformamide (DMF, for HPLC, $\geq 99.9\%$) and sodium tetraborate decahydrate (sodium borate, $\geq 99.5\%$) were purchased from Sigma-Aldrich, whereas L-cysteine (LC, 98%) was acquired from Alfa Aesar. Fluorescamine ($\geq 98\%$) was used for fluorescence labelling and was purchased from Sigma-Aldrich. All the reagents were used as received without any additional purification.

Instruments

For the photochemical functionalization of GO with CA by TER a UVP CL-1000L Longwave Crosslinker was used and operated at 5.2 mW/cm^2 using UV-lamps of 365 nm. Characterization of chemical species was performed using attenuated total reflection-Fourier transform infrared (ATR-FTIR) conducted in a Nicolet Magna-IR 550 FTIR spectrometer using 50 scans; a Micro-Raman spectrometer confocal Renishaw model DM 2500M operated at laser power of 5%, an exposure time of 3 s and 4 accumulations with a 488 nm laser; a X-Ray photoelectron spectroscopy (XPS) K-ALPHA from Thermo Scientific, with a monochromatic X-ray beam using a k-alpha aluminum line operated at 40 watts irradiating an area of $400 \mu\text{m}^2$. Also, it was used a lambda 800 UV-Vis spectrometer from Perkin Elmer and all the samples were prepared in water at concentrations of 0.05 mg/mL. For the fluorescence characterization a FluoroMax (Jobin-Yvon/Horiba) was used; all the samples

were prepared at concentrations of 0.05 mg/mL with sodium borate as buffer with 5 mM of fluorescamine. The fluorescence was taken at excitation wavelength (λ_{ex}) of 390 nm as reported elsewhere.³⁴ STEM images were taken in a UHR-SEM model DUAL Beam Helios Nanolab 600 from FEI.

GO synthesis

Graphene oxide was synthesized through a modified Hummer's method. In the first step graphite intercalation was carried out, for this H_2SO_4 was heated under stirring until 90 °C, and then of $\text{K}_2\text{S}_2\text{O}_8$ and P_2O_5 was added keeping the stirring. The mixture was cooled at 80 °C and then graphite was added. The reaction was let for 4.5 h keeping the temperature at 80 °C. After that, the mixture was diluted with water ($18.2\text{M}\Omega\cdot\text{cm}$) and the mixture was let overnight for the precipitation of the graphite. The intercalated graphite was filtered and dried at 40 °C in an oven for 24 h. For the oxidation, the intercalated graphite was added to 7:1 of a mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$, under bath ice and stirring. Then, KMnO_4 was added avoiding that the temperature increased more than 10 °C. Subsequently, the reaction was heated at 65 °C keeping the stirring for 2 h. Thereafter, the mixture was cooled at 30 °C and water aliquots were added avoiding that the temperature went up 50 °C. The reaction was let for another 45 min and heated at 65 °C, during this time the mixture turned to violet color. Then, the reaction was cooled at 30 °C and more water was added. After 2 h, H_2O_2 was added to finish the reaction resulting an intense yellow color. The mixture was let overnight in order to precipitate the GO. In the next day the supernatant was decanted and HCl 10 % v/v was added for the elimination of the impurities. Finally, the GO was washed by centrifugation using a 1:3 mixture of water/methanol until increase the pH at 4.5 approximately. In the final wash, the GO precipitated was dispersed only in water.

Thiol-ene reaction on GO using PI

For the photochemical functionalization of GO using PI, the GO (10 mg) was dispersed in 10 mL of DMF using ultrasonic bath until obtaining a well dispersed solution. After that, the GO was kept under sonication another 30 min to exfoliate the GO. On the other hand, two solutions were prepared: the first of CA (10 mg dissolved in 5 mL of DMF) and the second of PI (10 mg dissolved in 5 mL of DMF, this correspond to 2.7×10^{-5} mol). The solutions were deposited in falcon tubes wrapped with aluminum foil and kept at 4 °C until they were used. Subsequently, the three solutions were mixed in a beaker and put inside of the UV-camber during 60 min, under stirring. This experiment was labeled as GO-CA-PI. Two additional experiments were carried out following the same procedure that GO-CA-PI sample: the first without PI (labeled as GO-CA) and the second without PI and carrying the reaction under darkness and stirring (GO-B). These experiments are the respective blanks in order to follow the impact of the UV radiation and then the addition of the PI.

The materials were purified adding 25 mL of ethanol, then they were centrifuged and the supernatant was removed. This wash step was repeated four times. After this, the materials were washed with a solution of NaCl (2 M) with pH~2 (the pH was adjusted using HCl). The solid materials obtained in the step of the purification with ethanol were dispersed with 2 mL of NaCl using an ultrasonic bath. Subsequently, using a microcentrifuge tube of 2 mL the materials were centrifuged for 2 min at 23900 g. The supernatant was removed and enough NaCl solution was added until made them up to 2 mL. This wash step was repeated six times and for each step the ultrasonic bath was used for the materials redispersion. Finally, all the materials were washed with water ($18.2 \text{ M}\Omega \cdot \text{cm}$), made them up to 2 mL, centrifuging at 23900 g for 10 min and removing the supernatant. This process was repeated five times. The centrifugation time increased during the wash step with water because the suspensions

became more stable as the reaction residues were eliminated. At the end, all the materials were dispersed in 2 mL of water.

Thiol-ene reaction using thermal initiator

TER between GO and CA using AIBN was carried out under the reaction conditions described elsewhere.³⁰ Briefly, GO was dispersed in DMF under ultrasonic bath for 30 min. Then, the GO was purged with argon gas for 30 min. A mixture containing AIBN (3×10^{-5} mol) and cysteamine hydrochloride (mass ratio of GO:CA 1:1) was ultrasonicated for 30 minutes and then added to the GO solution. The reaction mixture was purged for another 30 min with argon and was let for 12 h at 70 °C in oil bath. This experiment was labeled as GO-CA-AIBN and the purification was done as described in the section **Thiol-ene reaction on GO using PI**

Analysis of Thiol-ene reaction using different thiol compounds

TER was carried out using another two thiol compounds: LC and MEDA. The functionalization and purification were conducted as described in **Thiol-ene reaction on GO using PI** section. All the experiments developed in this work are summarize in Table 1 with the respective conditions and labels.

Table 1. Summary of the reaction conditions for the different samples prepared

Label	Description	GO (mg/mL)	Thiol ^a	Radical initiator ^b	UV radiation (min)
GO-CA-PI	GO functionalized with CA adding PI	1	CA	PI	60
GO-CA	GO functionalized with CA without PI	1	CA	/	60
GO-B	GO functionalized with CA without PI and under darkness	1	CA	/	/
GO-CA-AIBN	GO functionalized with CA adding AIBN	1	CA	AIBN ^c	/
GO-MEDA	GO functionalized with MEDA adding PI	1	MEDA	PI	60
GO-LC	GO functionalized with LC adding PI	1	LC	PI	60

^aThiols were used at concentration of 2 mg/mL giving a final GO : thiol mass ratio 1:1

^b 3×10^{-5} mol of photoinitiator or and thermal initiator were used

^cThermal radical initiator was used heating at 70 °C during 12 h.

Results & Discussion

GO functionalization by Thiol-ene reaction

Scheme 1. a) Reaction of the functionalization of GO with CA by TER, b) detection of CA on GO by fluorescence labelling.

We studied the photochemical functionalization of graphene oxide by cysteamine using thiol-ene reaction (Scheme 1a). This reaction involves the formation of radicals, generated by PI subjected to light, that in turn are transferred to CA leading to the formation of thiyl radicals ($R-S\cdot$) due to the low S-H bond dissociation energy of CA.^{21,35} The thiyl radicals are highly reactive species which can attack C=C of the GO producing an alkylthiyl radical on GO.

Then, the alkylthiyl radical is stabilized by the addition of one hydrogen or another CA molecule through a chain transfer process.^{18,19}

Characterization of the functionalization by TER of GO with CA

Figure 1 presents STEM images of GO and GO-CA-PI were taken in order to observe the morphological difference before and after the photochemical functionalization. In Figure 1a, 1b and 1c, GO exhibited extended, interconnected and translucent layers due to low staking. After the chemical functionalization, the GO-CA-PI displays separated structures, that could be formed by stacked sheets functionalized with CA (Figure 1d, 1e and 1f). However, no apparent defects on GO layers were detected suggesting that the mild conditions allowed to preserved the GO layers structure.^{22,30}

Figure 1. STEM images of GO at amplifications: a) 10000x, b) 50000x and c) 100000x.

STEM images of GO-CA-PI at amplifications: d) 5000x, e) 40000x and f) 100000x.

The characterization of the chemical species of samples GO-CA-PI, GO-CA, GO-B and GO prepared was carried out by ATR-FTIR, Raman spectroscopy, UV spectroscopy, fluorimetry

and XPS. The ATR-FTIR results are presented in Figure S1 and GO exhibited the follow bands: O-H stretching vibrations (3312 cm^{-1}), C=O vibrations from carboxylic acid groups (1732 cm^{-1}), C=C bonds and O-H bending vibrations (1622 cm^{-1}), C-O vibrations (1218 cm^{-1}), C-OH vibrations from phenol and alcohol groups (1056 cm^{-1}) and C-O-C asymmetric vibration from epoxy groups (968 cm^{-1}).^{36,37} GO-CA-PI sample showed the most significant changes with two new bands at 1441 cm^{-1} and 710 cm^{-1} attributed to C-S and C-S-C vibrations, respectively.^{26,30,38} This information confirmed the presence of CA moieties bonded on GO.

Figure 2. Characterization of GO, GO-B, GO-CA and GO-CA-PI samples by: a) UV spectroscopy, b) Raman spectroscopy and b) fluorescence spectrometry ($\lambda_{\text{ex}}=390\text{ nm}$).

In addition, UV-Vis spectroscopy characterization was carried out and GO-CA-PI showed a red shift until 250 nm in the broad peak attributed to the plasmon C=C (labeled as $\pi-\pi^*$) as compared to GO (see Figure 2a). The change in the maximum position of the plasmon C=C can be attributed to the alkyl chains of CA which can interact with the GO graphitic domain leading to a red shift as reported elsewhere.²⁶ Besides, GO-B preserved the position of the peak at 228 nm confirming that there was no reaction between the GO and CA under darkness by TER.

On the other hand, Figure 2b shows the Raman spectrum for the different samples where GO exhibited the characteristics *D* and *G* band at 1364 cm⁻¹ and 1593 cm⁻¹, respectively. *D* band arises due to the defects in the graphene sheets in this case due to change in the hybridization from sp² to sp³.^{39,40} Raman information was extracted as well as the A_D/A_G was calculated for all the samples and the results are presented in Table 2. The change in A_D/A_G allows to observe the contribution of interbands located under *D* and *G* bands attributed to the introduction of defects such as change in the hybridization from sp² to sp³.^{39,41} GO-CA-PI sample exhibited a blue shift in *G* band, whereas a slight shift was detected for GO-CA and GO-B samples (see Table 2). The blue shift can be attributed to the presence of amine groups from CA on GO layers which produces N-type doping.^{42,43}

Table 2. Information of Raman spectra of Figure 1b.

Material	G (cm ⁻¹)	A _D /A _G
GO	1593	1.15
GO-B	1591	1.16
GO-CA	1589	1.3
GO-CA-PI	1583	1.47

Besides, it was found a similar A_D/A_G ratio in GO and GO-B samples indicating that minimum defects were introduced in the blank experiment. However, GO-CA showed an increased in A_D/A_G ratio confirming that UV radiation induced a slight introduction of CA moieties on GO. More important, GO-CA-PI exhibited the strongest A_D/A_G ratio corroborating a higher change in the hybridization by the presence of PI. This information is consistent with the UV spectrum results.^{39,41}

After the functionalization, the free primary amine that resulted from the grafting of CA onto GO can be, as well, detected by fluorescence labelling (Scheme 1b). Indeed, fluorescamine reacts in picoseconds with primary amines in order to form a fluorophore with an excitation wavelength (λ_{ex}) of 390 nm and a maximum emission (λ_{em}) in 475 nm.³⁴ The GO-CA-PI

sample exhibited the strongest fluorescence signal followed by GO-CA>GO-B>GO samples. GO exhibited a minor fluorescent contribution meaning fluorescence signal of GO-CA-PI and GO-PI came from CA moieties on GO (see Figure 2c). The sequence of the fluorescence intensity found in the different samples followed the same order that UV and Raman results confirming the photochemical functionalization of GO with CA by TER.

In order to confirm the chemical bonds formed after the functionalization, XPS characterization was carried out. Figure 3 shows the XPS survey scans for GO, GO-B, GO-CA and GO-CA-PI where was possible to detect nitrogen (N) and sulfur (S) contribution in GO-CA and GO-CA-PI samples. Table S1 presents a summary of the survey XPS information and GO-CA-PI exhibited the strongest S contribution with an atomic percentage around 1.7% followed by GO-CA>GO-B. This result is consistent with the fluorescence labelling and the UV and Raman spectroscopy results. Besides, the low N and S contributions detected for GO-B sample confirmed that no reaction was carried out between GO and CA under darkness.

Figure 3. XPS survey scan of the samples: a) GO, b) GO-B, c) GO-CA and d) GO-CA-PI.

Furthermore, the S2p high resolution XPS deconvolution was performed to confirm the chemical bonds formed after the functionalization. In Figure 4, GO-CA and GO-CA-PI were fit in the respective doublet peak at 163.5 eV and 164.8 eV attributed to $S2p_{3/2}$ and $S2p_{1/2}$ due to C-S-C and C-S bonds.^{22,26,30,44} This information confirms that CA was covalently bonded to GO by TER using a PI. It should be highlighted that this functionalization was achieved with just one hour of reaction whereas classical thermal initiator needs over 12 h of reaction.²²⁻³⁰

Figure 4. S2p deconvolution of XPS high resolution spectrums of a) GO, b) GO-B, c) GO-CA and d) GO-CA-PI.

On the other hand, C/O ratio was calculated to estimate the GO reduction when PI was used. This was calculated as the ratio of the total area of C1s to the total area of O1s, as reported elsewhere.⁴⁵ The results are presented in Table 3 where GO and GO-B showed similar C/O ratio indicating that no reduction was induced. GO-CA and GO-CA-PI exhibited a slight increase in the C/O ratios suggesting that some oxygen functional groups were lost during the reaction. This can be attributed to the radicals formed from the PI which could lead in a slight GO reduction. Nevertheless, when thermal initiators are used the C/O ratios observed are around 4.2 until 10.1 values.^{22,30} This information is a clear evidence that the use of PI as radical initiator offers a better control of the functionalization, with short reaction time, while

minimizing GO reduction and keeping similar atomic percentage in comparison with classical thermal radical initiators.

Table 3. C/O ratios calculated from survey XPS of Figure 2.

Material	C/O
GO	2.4
GO-B	2.4
GO-CA	2.5
GO-CA-PI	2.8

GO functionalization with CA using AIBN by TER

When GO has been functionalized by TER a thermal radical initiator was used to promote thiyl radicals ($R-S^{\bullet}$).²²⁻³⁰ Since the optimal conditions for TER using AIBN as thermal initiator have been reported,³⁰ this experiment allowed the comparison againsts the application of PI. GO-CA-AIBN experiment was carried out according to previous reports and such conditions of GO:CA mass ratio and radical initiator concentration are similar to the experiment GO-CA-PI presented in this work. Morphological characterization was conducted and Figure S2 shows STEM images of the functionalized material. GO-CA-AIBN displays a similar behavior that GO-CA-PI where interconnected and aggregated layers were detected due to the presence of CA moieties. Figure 5 presents the XPS characterization of GO-CA-AIBN where the XPS survey revealed an atomic percentage of 74.7, 19.2, 2.8 and 2.8 for C, O, N and S, respectively. This represents a C/O ratio of 3.9 which is higher than GO-CA-PI sample indicating that a stronger GO reduction associated to loss of oxygen was obtained with thermal initiators. It is worth noting that a S atomic percentage of 2.8 was stronger even when the experiment conditions used were taken from previuos reports and they found only a 1.7 of S atomic contribution.³⁰ In addition, S2p deconvolution revealed the peaks at 163.5 eV, 164.6 eV and 168.1 eV attributed to S2p_{3/2} and S2p_{1/2} of C-S and C-S-C

bonds as well as SO_3 moieties (see Figure 5b).^{22,26,30,44} The C-S-C bonds detected confirm the GO functionalization with CA using AIBN as thermal initiator.

Figure 5. a) XPS survey of GO-CA-AIBN, b) S2p deconvolution of XPS high resolution of GO-CA-AIBN and c) Raman spectrum of GO, GO-CA-PI and GO-CA-AIBN

On the other hand, Raman characterization was performed and the results are presented in Figure 5c. Notably, *G* and *D* bands were broader for GO-CA-AIBN than GO and GO-CA-PI indicating that a greater functionalization and more defects were introduced.⁴¹ Moreover, the Raman information was extracted from Figure 5c and A_D/A_G ratio was calculated as can be seen in Table 4. A_D/A_G was lower than GO-CA-PI and this can be attributed to the strong change in the hybridization from sp^2 to sp^3 .⁴⁶ This change is mainly observed with a widening of *G* band and together to the fact that *D* band was broader the A_D/A_G ratio can be mitigated.⁴¹ In order to observe the whole process in GO-CA-AIBN sample the I_D/I_G was calculated and the results showed a significant difference when is compared to GO-CA-PI sample.⁴⁷ The strong intensity of *D* band can be associated to an increase in the oxygen functional groups released.⁴⁸ This is consistent with the higher C/O ratio of XPS survey calculated for GO-CA-AIBN sample.

Table 4. Information of Raman spectra of Figure 5b.

Material	G (cm ⁻¹)	A _D /A _G	I _D /I _G
GO	1593	1.15	0.70
GO-CA-PI	1583	1.47	0.78
GO-CA-AIBN	1595	1.3	0.96

Furthermore, the low I_D/I_G for GO-CA-PI sample confirmed that the use of PI as radical initiator conducts to an efficient functionalization while minimizing GO defects.

Therefore, taking into account the XPS information, the use of UV-light coupled with the addition of PI as radical initiator allows the efficient functionalization of GO, minimizing the GO reduction due to the use of mild condition reactions and opens up the possibility to use the rest of oxygen functional groups of GO for further functionalization.

Functionalization of GO with MEDA and LC by TER

Two additional thiol compounds where tested (MEDA and LC) under the experimental conditions used for GO-CA-PI material. XPS characterization was used in order to corroborate the functionalization. Figure S3 contains the XPS survey scans of GO-MEDA and GO-LC samples an they exhibited a slight N and S contribution. In addition, Figure 6 shows the deconvolution of XPS high resolution of C1s, N1s and S2p for GO-MEDA and GO-LC. Both samples presented the peak at 284.8 eV attributed to C-S/C-N bonds possible from MEDA and LC moieties bonded to GO (see Figure 5a and 5d).^{29,49} Moreover, the N1s deconvolution of GO-LC showed the peaks at 398.5 eV, 399.7 eV and 401.7 eV attributed to C-N-C, C-N and N-H bonds from secondary and primary amines.^{50,51} Furthermore, GO-MEDA exhibited the peaks at 398.5 eV, 400 eV and 402 attributed to secondary and tertiary amines.^{52,53} In addition, S2p deconvolution revealed two peaks at 163.5 eV and 168.5 eV attributed to S2p_{3/2} and S2p_{1/2} of C-S bonds.^{30,54}

It is worth noting that the functionalization using MEDA and LC presented low contributions when they are compared with GO-CA-PI sample. This behavior can be explained as the BDE

of S-H bonds which changes for different thiols. The BDE can be modified for the type of the alkyl chain *i.e.*, thiol phenols have low BDE and thus the hydrogen atom can be extracted easily whereas aliphatic thiols are more difficult to extract the hydrogen atom.^{18,19} CA molecule can release easier the H atom from the S-H bond than MEDA and LC due to its low pKa as well as low BDE. This was confirmed by the XPS survey of Figure 3 and Figure S3 where a stronger sulfur contribution was detected for GO-CA-PI. Moreover, depending of the capability of the thiol to release the hydrogen atom, the charge transfer step can be disturbed. Sulfur compounds with low pKa and highly electronegative alkyl chains can release easily the hydrogen atom.¹⁹ In the case of MEDA and LC, the low stability in the radical R-S• can lead to the dissociation *via* reversible step to obtain the original thiol and alkene group.³⁵

Figure 6. Chemical characterization of GO-LC and GO-MEDA. From a) to c) corresponds to the deconvolution XPS high resolution of GO-LC whereas from d) to f) corresponds to GO-MEDA.

Conclusions

In the present work, the photochemical functionalization of graphene oxide with cysteamine was carried out *via* UV-light coupled with a PI as radical initiator and characterized by ATR-FTIR, UV spectroscopy, fluorimetry, XPS and Raman spectroscopy. The functionalization introduced in this work allows the efficient GO functionalization while keeping most of the oxygen functional groups that can be used for further modification in order to develop multifunctional materials which can be used for many fields. The functionalization by TER using a PI possesses several advantages with respect the typical thermal initiator such as high yield achieved in short reaction time, minimum side reactions and GO reduction can be minimized due to the mild reaction conditions used (no heating). This functionalization can be carried out with a variety of thiol compounds. Finally, this work introduces the use of fluorescamine in order to detect CA moieties by fluorescence labelling.

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Supporting information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxx

ATR-FTIR spectrum, STEM images, XPS survey scan and table (PDF)

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