## Graphene Functionalization

## One-Step Double Covalent Functionalization of Reduced Graphene Oxide with Xanthates and Peroxides

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Abstract: Radical functionalization of reduced graphene oxide has been achieved by reaction with a xanthate in the presence of peroxide as a radical initiator. X-ray photoelectron spectroscopy, bulk elemental analyses, and thermogravimetric analyses showed that the xanthate grafting is covalent and efficient. The synthesis and use of seven xanthates and three peroxides showed that the highest grafting yield is obtained when xanthate and peroxide are introduced in stoichiometric amounts. It also revealed that the peroxide used as radical initiator is grafted at the graphenic surface during the functionalization. The method presented in this contribution therefore allows bifunctionalized reduced graphene oxide samples to be easily obtained in one single step. This method leads to undamaged graphene sheets with higher dispersibility than the pristine sample.

The isolation of graphene, an atom-thick layer of sp<sup>2</sup> carbon atoms arranged in a honeycomb lattice, is one of the significant scientific events of the last decade. Since then, graphene has attracted much interest in various fields<sup>[1]</sup> such as material sciences,<sup>[2]</sup> electronics,<sup>[3]</sup> and biomedical sciences.<sup>[4]</sup> This infatuation is due to its unique physical and electrical properties. Three main methods of graphene synthesis exist: Exfoliation of graphite with scotch tape, epitaxial growth/CVD, and reduction of graphene oxide (GO) to rGO (reduced graphene oxide). The first two allow high-quality graphene to be obtained whereas the latter is simple and allows large-scale production of powder samples.<sup>[1,5]</sup> A critical limitation is nevertheless worth noting: as in the case of carbon nanotubes (CNTs), graphene is insoluble in water and common organic solvents and hardly reacts with common organic reagents. A preliminary functionalization step is thus usually necessary to benefit from its full potential in most applications.<sup>[5a,6]</sup> Fortunately, research in the field of carbon nanotubes has speeded-up the development of graphene functionalization methods. Indeed, in spite of the rel-

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ative flatness of its structure, several examples of successful graphene derivatizations performed by methods initially developed for CNTs functionalization have been reported.<sup>[7-13]</sup> Among all of these methods, the use of radicals arising from, for example, diazonium salts<sup>[14]</sup> is presented as one of the best ways to chemically modify graphene sheets.<sup>[8]</sup>

In this context, we have developed a method of reduced graphene oxide (rGO) radical functionalization using xanthates as radical precursors. Xanthates are indeed known in organic methodology to react with activated and non-activated olefins in the presence of peroxides as initiator.<sup>[15]</sup> In addition, we have recently shown that xanthates react at CNT surfaces.<sup>[16]</sup>

The use of xanthates is beneficial compared to other radical precursors for various reasons. The main reason is that the grafting mechanism implies a degenerative equilibrium that self regulates the radical production and avoids excessive deactivation.<sup>[15]</sup> Moreover, xanthates bearing diverse functional groups can easily be synthesized at multi-gram scale. A wide range of functionalities can therefore be anchored at the graphenic surface. The derivatization reaction is also easy to carry out as no gaseous reactants nor high temperature or long reaction times are required.

In addition, we present here the concomitant radical covalent grafting of both xanthate and peroxide initiator fragments at the reduced graphene oxide surface (Figure 1). Indeed, per-



**Figure 1.** Schematic representation of rGO (oxygen groups not shown) double functionalization with  $R^1$  from a xanthate and  $R^2$  from a peroxide (minor S-containing functions omitted for clarity).

oxides, as radicals themselves, could also be grafted at the graphene surface. This has been shown extensively on CNTs, in particular by thermal activation of dilauroyl peroxide,<sup>[17]</sup> and also only once on graphene by photochemical activation.<sup>[18]</sup> In judiciously choosing the peroxide, a second useful function could therefore be grafted at the carbonaceous surface. Nevertheless, peroxide-derived radicals were also used as radical initiators on graphene without indication of its grafting.<sup>[19]</sup> To our knowledge, this is the first report of graphene double covalent



Figure 2. Structures of the synthetized xanthates (X1–X7) and peroxides (P1–P3) and the commercial dilauroyl peroxide (DLP)

functionalization by two different partners in a single chemical reaction.

First rGO functionalization experiments were carried out with a xanthate molecule bearing a pentafluorophenol activated ester group (**X2**, Figure 2) and dilauroyl peroxide (DLP, Figure 2) as radical initiator. These choices have been dictated by the presence of fluorine atoms in the R<sup>1</sup> fragment of the xanthate **X2** that permits a reliable quantification of its grafting rate and the absence of any functional moiety in the R<sup>2</sup> aliphatic chain of the peroxide. This absence allows the xanthate behavior to be studied as clearly as possible.

X-ray photoelectron spectroscopy (XPS) analysis of the pristine reduced graphene oxide (p-rGO) shows the presence of carbon, oxygen and nitrogen atoms. The high oxygen content in the p-rGO sample indicates that the reduction of the GO in rGO is incomplete. After functionalization (f-rGO), XPS spectra show the expected apparition of both sulfur and fluorine peaks belonging to the xanthate anchored at the carbonaceous surface (Figure 3; for reproducibility, see Table S1 and S2 in the Supporting Information). This result is further confirmed



**Figure 3.** XPS spectra of *p*-rGO (——) and *f*-rGO (----). Inset: Magnification of the sulfur peaks.

by the presence of fluorine and sulfur in bulk elemental analyses (Table S3 in the Supporting Information). Moreover XPS measurements show that, as previously reported in the case of carbon nanotubes,<sup>[16]</sup> the grafting yield of the sulfur-containing moiety is far lower than that of the R<sup>1</sup> fragment.

To highlight the covalent nature of the bond between xanthate and the rGO surface, three samples were analyzed by thermogravimetric analysis (TGA): rGO before and after functionalization with xanthate **X2** and a physical mixture of p-rGO and xanthate **X2**. Figure 4 shows that p-rGO suffers a weak



**Figure 4.** Thermogram derivatives of *p*-rGO (——), *f*-rGO (-----) and physical mixture of *p*-rGO and xanthate **X2** (-----). Inset: Corresponding thermograms.

mass loss attributable to the decomposition of oxygenated functions remaining from the GO. After reaction with xanthate **X2**, the thermogram exhibits a larger mass loss corresponding to the decomposition of the grafted fragments, strengthening the idea of xanthate grafting at the rGO surface. Beyond the extent of the mass loss, its position in the thermogram also gives useful information: the higher decomposition temperature visible in the derivative of *f*-rGO thermogram compared with that of the physical mixture is indicative of the presence of a covalent bond between rGO and xanthate in the case of *f*-rGO.

Notably, *f*-rGO forms a longer-lasting stable suspension in DMF compared with *p*-rGO samples (stable after 7 days and 3 months; see Figure S1 in the Supporting Information). The methodology is thus appropriate for the preparation of samples usable in applications in which good graphene dispersions are required. The colloidal nature of the *f*-rGO dispersion is also exhibited by the appearance of the Tyndall effect (Figure S2).<sup>[20]</sup> The rGO integrity after treatment with xanthate and peroxide has been verified by TEM (Figure S3). Micrographs of *p*- and *f*-rGO reveal the presence of both graphene sheets and nanoplatelets. The *f*-rGO sample has suffered no visible damage during functionalization.

To increase the grafting efficiency, several optimization experiments have been carried out. The choice of the parameters to vary was facilitated by a preceding study concerning the behavior of xanthates towards carbon nanotubes.<sup>[16]</sup> It was demonstrated that the two relevant parameters regulating the xanthate grafting yield are xanthate and peroxide concentrations. A maximum in the R<sup>1</sup> moiety grafting rate was indeed observed when both xanthate and peroxide were introduced in stoichiometric amounts on CNTs. Optimization reactions have then been carried out here by varying both parameters. XPS results show that, in accordance with previous results on CNT, a maximum of R<sup>1</sup> grafting is reached at the stoichiometric point where the xanthate concentration equals the peroxide one (Figure 5). Moreover, the grafting of the sulfur-containing part is less effective than that of the R<sup>1</sup> fragment and barely influenced by external parameters, as previously observed in the case of CNTs.



**Figure 5.** Evolution of fluorine (——) and sulfur (----) concentrations determined by XPS as a function of DLP (left) and xanthate **X2** (right) concentrations. In both cases, the concentration of the non-varying parameter is 1 equivalent with respect to the C content of rGO.

To demonstrate the versatility of the method, xanthates **X1** to **X7** (Figure 2) bearing different R<sup>1</sup> fragments have been synthesized and grafted at the rGO surface using the function-free DLP as radical initiator. In each case, the xanthate was successfully grafted at the rGO surface as shown by XPS (Table 1). For each xanthate, the peak corresponding to the heteroatom in the R<sup>1</sup> fragment is detected in the XPS spectrum. Reduced graphene oxide samples bearing activated ester, phthalimide, succinimide, nitro, acetamide and phosphonate functionalities were therefore obtained. It is worth mentioning that the sulfur concentration remains low in each case, meaning that the grafting yield of the sulfur-containing fragment is still lower than that of the R<sup>1</sup> fragment, except for **X4**.

Table 1. XPS characterization of rGO functionalized with xanthate X1–X7.					
Xanthate <sup>[a]</sup>	Surface concentrations [atomic%] Heteroatom from R <sup>1</sup> S 2p				
X1	F 1s	7.85	0.65		
X2	F 1s	5.96	0.43		
X3	N 1s	0.56	0.32		
X4	N 1s	0.17	0.37		
X5	N 1s	0.62 <sup>[b]</sup>	0.39		
X6	F 1s	1.03	0.63		
X7	Р 2р	0.29	0.50		
[a] Xanthate and DLP concentrations are 1 equivalent with respect to the C content of rGO. [b] Only the nitrogen content corresponding to nitro mointing is taken into account.					

Due to the non-negligible concentration of nitrogen in p-rGO samples, a reliable estimation of xanthate X3 and X4 grafting yields is hard to achieve. For this reason, xanthate X5 bearing a nitro moiety was synthetized and grafted at the rGO surface. Indeed, nitrogen signals arising from nitro compounds (N1s peak at 406 eV) can easily be distinguished from the nitrogen content in p-rGO (N1s at 400 eV; see Figure S4 in the Supporting Information).

To prove the covalent grafting of the peroxide in the conditions used for xanthate grafting, a reaction between rGO and DLP without xanthate was performed. The TGA analysis of the solid obtained shows a weight loss with a maximum slope at about 500 °C, attributable to DLP (Figure S5). The importance of the mass loss and the high temperature at which it appears indicates that the peroxide is indeed covalently grafted at the rGO surface.

By modifying the R<sup>2</sup> fragment of the peroxide used for the xanthate grafting initiation, it becomes then possible to obtain bifunctionalized rGO samples. For this purpose, diverse heter-oatom-containing peroxides were synthesized (P1–P3, Figure 2) and grafted at the rGO surface along with diverse xanthates. XPS analyses show the efficiency of the double functionalization as heteroatoms belonging to both xanthate and peroxide are detected in the samples after functionalization (Figure 6 and Table 2). This is, to our knowledge, the only graphene functionalization to be achieved in one single step.

From these results, the degree of functionalization can be estimated to be about 1 functional group for 35-70 rGO carbon atoms depending on the xanthate and peroxide used. Even if the different types of graphene and functionalization methods cannot be directly compared, this falls within the range of values reported in the literature for various derivatization pathways such as the Bingel reaction,<sup>[21]</sup> diazonium grafting,<sup>[22]</sup> cycloadditions,<sup>[23]</sup> and reductive alkylation<sup>[24]</sup> (see Table S4 in the Supporting Information). In addition, as our sample of rGO is constituted of a few layers of graphene, the internal graphene sheets were not functionalized but only the top and bottom faces. Single-layer graphene is known to be more reactive, therefore our values would have been even higher on single-layer graphene.<sup>[18]</sup> It should be noted, however, that rGO presents many defects which might increase its reactivity compared to CVD or exfoliated graphene.

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Figure 6. Bifunctionalized rGO samples (oxygenated and minor sulfured moieties omitted for clarity).

Table 2. XPS characterization of bifunctionalized rGO.							
Sample <sup>[a]</sup>	Xanthate <sup>[b]</sup>	Peroxide <sup>[b]</sup>	Peroxide <sup>(b)</sup> Surface concentrations [atomic %]			nic %]	
			Cl 1s	F 1s	N 1s <sup>[c]</sup>	Р 2р	S 2p
1	X2	P1	3.33	3.11	_	_	0.25
2	X5	P2	_	1.24	0.54	—	0.23
3	X5	P3	—	0.74	0.34	—	0.30
4	X7	P2	—	3.73	—	0.23	0.21
[a] See Figure 6. [b] Xanthate and peroxide concentrations are 0.4 equiva- lents with respect to the C content of rGO. [c] Only the nitrogen content corresponding to nitro moieties is taken into account.							

In summary, the grafting of a xanthate using a peroxide as radical initiator was proven to be an effective method to covalently functionalize reduced graphene oxide sheets. This method easily provides diverse types of functionalized rGO samples and has been proven efficient by XPS, TGA, and bulk elemental analysis. The versatility of the method was highlighted by the grafting of seven different xanthates. The behavior of xanthates toward rGO was proven to be in agreement with what was previously described for the functionalization of carbon nanotubes: i) To obtain a maximal grafting rate of the R<sup>1</sup> fragment, xanthate and peroxide have to be introduced in stoichiometric amounts; ii) the sulfur containing fragment's grafting yield is lower than that of the R<sup>1</sup> fragment. Finally, bifunctionalized rGO was achieved in one single step by using derivatized peroxides as radical initiators. Samples of functionalized rGO exhibited a longer-lasting dispersibility than pristine samples, suggesting that the procedure proposed herein is a good method to prepare doubly-functionalized graphene samples for further applications.

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