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**Covalent modification of exfoliated fluorographite with nitrogen functionalities**Concha Bosch-Navarro,<sup>\*,a,b</sup> Marc Walker,<sup>a</sup> Neil R. Wilson,<sup>a</sup> Jonathan P. Rourke<sup>b</sup><sup>a</sup> *Department of Physics, University of Warwick, Coventry, CV4 7AL, UK*<sup>b</sup> *Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK*

Fluorographene, as a completely fluorinated counterpart of graphene, holds great promise for applications in high performance materials such as batteries, dielectrics or biosensors. However, its chemical inertness and low solubility hinders its use in practical devices. Here, water-soluble exfoliated fluorographite is obtained by covalent modification with amino groups. The simplicity of our method may be easily extended to study the effect that chemical modification has on the properties of single layer fluorographene, which have not yet been studied. Moreover, we have further employed the new nitrogen functionalities to selectively bind gold nanoparticles, which may enable novel or enhanced sensing, catalytic or electrochemical applications.

## Introduction

The unique physical properties of graphene (G) mean it is one of the most exciting materials of the present century.<sup>1,2</sup> It is a semi-metal, with zero band gap in its electronic structure,<sup>3,4</sup> but the absence of a band gap, together with its low dispersability and reactivity, also limits its applications. Consequently, there is substantial research activity into chemically modified graphene derivatives which could complement the exciting properties that G itself offers.<sup>5,6</sup> In this regard, graphene oxide (GO) has been the most well studied counterpart of G: it is easy to make and easy to disperse and process, and hence appealing for testing and developing applications. However, the functionalization in GO induces disorder and hence the electronic and mechanical properties are degraded relative to pristine graphene.<sup>7-9</sup> In fact, there are only very few examples where ordered functionalization of graphene derivatives is expected. Of these, fully hydrogenated graphene, or graphane,<sup>10</sup> has proven difficult to realise experimentally and so the most prominent is fluorinated graphene (FG) which can be formed in a variety of stable and ordered stoichiometries such as double-side, fully functionalised CF, and single-side functionalised C<sub>2</sub>F.<sup>11-13</sup> In fully functionalized FG a fluorine is attached to each carbon atom, meaning the carbon atoms no longer have sp<sup>2</sup> hybridization but rather exhibit an sp<sup>3</sup> configuration,<sup>11,13</sup> with alternating fluorine atoms on either side of the basal plane. This distinctive ordered chemical structure is responsible for its band insulating behaviour,<sup>14</sup> while keeping a very similar mechanical strength and elasticity to that shown by graphene,<sup>12,15,16</sup> and an extremely high thermal stability that resembles that of Teflon.<sup>17</sup> These unique physical characteristics make FG suitable for a plethora of applications, such as batteries, dielectrics, lubricants or biosensors.<sup>11</sup>

Despite the potential of FG, its direct application is hampered by its low solubility in both aqueous and organic solvents. By analogy to graphene, in which such solubility problems have been addressed through the development of chemically modified graphenes (CMGs),<sup>18-20</sup> the processability limitations of FG could be overcome by chemical modification of FG with suitable groups. In turn this would lead to chemically modified fluorographenes (CMFGs), in which the new functionalities could be employed for both increasing the solubility and as new anchoring points for further chemical alterations. To the best of our knowledge there is just one report on CMFG.<sup>21</sup> In this work, Urabanova and co-workers chemically modified FG with sulphur functionalities, and subsequently employed it as a biosensor for DNA.

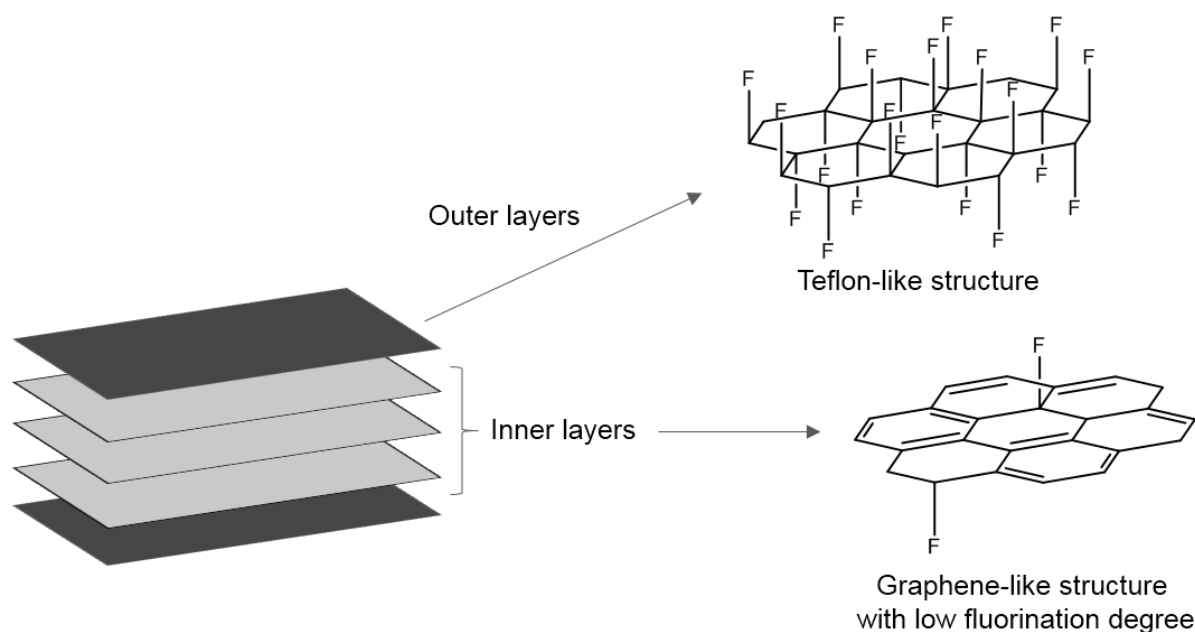
Amino-functionalized CMGs have been widely explored due to the biocompatibility of nitrogen moieties, and because they offer a convenient platform to further functionalization with different active molecules.<sup>22-24</sup> Therefore, the introduction of amino groups into the lattice of FG should pave the way for future applications and will increase its processability in aqueous media. Herein, we show how amino groups can be easily introduced by reaction of exfoliated fluorographite with sodium amide (NaNH<sub>2</sub>). In brief, sodium amide acts as a source of nucleophilic amine, replacing some of the fluorine groups across the fluorographite lattice. We demonstrate that the amino groups do indeed

increase the solubility of CMFGs and also increase their reactivity, illustrated here by the selective binding of gold nanoparticles (AuNPs) which act as contrast markers of the new functionalities.<sup>22–27</sup>

It is worth highlighting that, so far, the synthesis of FG has been achieved either by direct fluorination of G using expensive  $\text{XeF}_2$ ;<sup>11</sup> by direct chemical modification of GO with toxic hydrofluoric acid<sup>28</sup> or elemental fluorine;<sup>29</sup> or by liquid phase exfoliation of fluorographite in organic solvents.<sup>30–33</sup> The first method leads to the highest quality FG, but its high cost and low yield limits its use in real devices, and hampers its proper use towards CMFGs. Although the latter two methods can lead to reasonably good FG yields, the use of GO as starting material results in a non-stoichiometric FG compound having some oxygen functionalities that could interfere with the chemical process. Therefore, liquid phase exfoliation of fluorographite offers a convenient way to obtain few-layer FG in reasonable yields and quality, with which to perform further chemical modifications. Hence, here fluorographite (FGr) was exfoliated by sonication in N,N-dimethylformamide (DMF) to yield few-layer FG for our investigations.

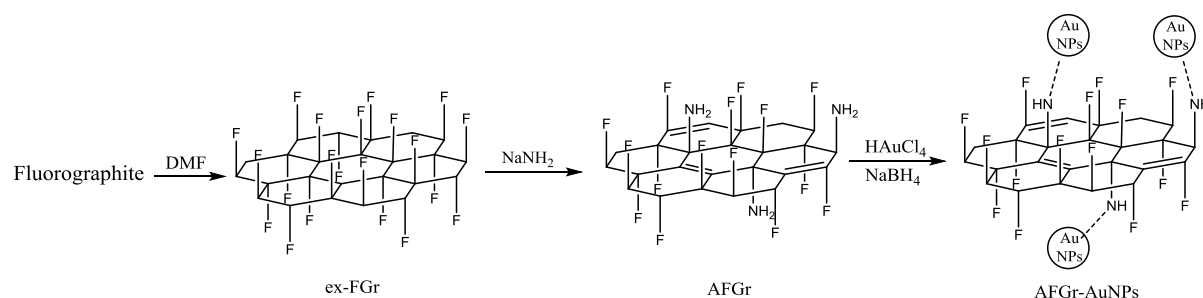
## Results and discussion

First, the nature of pristine fluorographite (FGr) and exfoliated fluorographite in DMF (ex-FGr) were analysed by energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). The atomic composition obtained by both EDX and XPS is summarized in Table SI2 and Table SI3b. As shown, important differences are observed in the C/F atomic content for pristine FGr (C/F = 1.3 calculated from EDX; C/F = 1.4 calculated from XPS) when compared to ex-FGr (C/F = 3.2 calculated from EDX; C/F = 0.7 calculated from XPS). Investigation of the morphology of the sample by SEM shows a significant change after exfoliation (see supporting information Figure SI4): ex-FGr has more plate like material without the smaller particles and debris that are apparent in the initial FGr. The large difference in the C/F ratio obtained for ex-FG when using EDX (C/F = 3.2) and XPS (C/F = 0.7) arises because the two techniques are measuring different parts of the FGr: XPS is surface sensitive, with typical inelastic mean free paths of the low energy electrons of no more than a few nanometres, and thus the measurements are dominated by the first few atomic layers of the FGr, whereas under typical acquisition conditions EDX signals come from sample depths up to a micrometre and hence is representative of the average of the whole volume of the FGr flakes. The discrepancy in the relative fluorine content can thus be accounted for by a model that has a much greater degree of fluorination on the outermost layers of the ex-FGr, with the innermost regions of the sample being less functionalized (Scheme 1).



Scheme 1. Depiction of a possible structural model of ex-FGr as deduced from EDX and XPS compositional analysis. The nucleophilic attack with  $\text{NaNH}_2$  would take place over the outermost layers.

This leads to the conclusion that ex-FGr must be composed of stacks of multiple layers (see TEM in supporting information Figure SI5) which are more heavily fluorinated near the surface (Scheme 1). It is important to highlight that as ex-FGr is composed of multiple layers, it is better described as “exfoliated fluorographite” rather than “fluorographene”. This feature will have implications in the functionalization process, as the substitution with amino groups is expected to take place preferentially in the outermost layers. However, we expect the chemical process described here to be equally relevant for fluorographene.



Scheme 2. Representation of the steps followed for the synthesis of amino-fluorographite (AFGr) and its further decoration with gold nanoparticles (AuNPs). Note that to simplify the scheme a single layer of FG has been considered.

ex-FGr was chemically modified by employing sodium amide as nucleophile, to yield a material we refer to as amino-fluorographite (AFGr), Scheme 2. Thermogravimetric analysis (TGA) provides the first evidence of chemical modification. As shown in Figure 1, ex-FGr shows a single weight loss at *ca.* 580 °C which corresponds to the decomposition of the C-C-F structure.<sup>30</sup> After functionalization with NaNH<sub>2</sub> some distinctive features appear, giving rise to four different steps. The weight loss observed in the region 200-500 °C may be assigned to both the new amino functionalities and the desorption of the ionic fluoride groups that appear during the chemical process (see XPS analysis below).<sup>34</sup> Unfortunately, these two decomposition processes take place in the same temperature range, which precludes determination of the degree of functionalization of amino groups by TGA. A new small decomposition step (*ca.* 25%) appears at around 520°C and can be assigned to CF<sub>3</sub> groups that are formed during the synthesis process (see XPS analysis below). As a consequence of the structural changes, the C-C-F content (45% weight loss at ~580°C) clearly decreases after functionalization. Still, the high thermal stability of AFGr points to a Teflon-like behaviour.<sup>17,30</sup> In addition, AFGr seems to be more hygroscopic as suggested by the small weight loss shown at around 100 °C. This is also apparent from the change in solubility after functionalization. As shown in Figure 2, ex-FGr is completely insoluble in water, while AFGr shows a great affinity for water and suspensions (~1 mg/ml) remained stable for weeks.

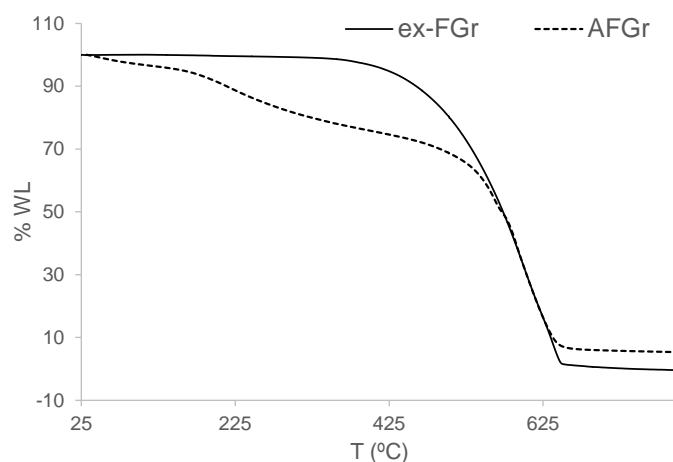


Figure 1. TGA under air of ex-FGr (solid line) and AFGr (dashed line).

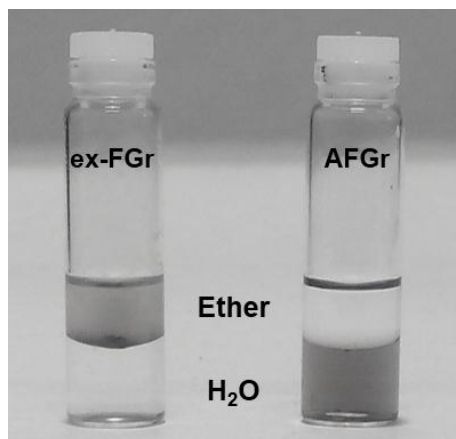


Figure 2. Photograph showing the change in solubility of ex-FGr after functionalization to AFGr.

FT-IR gives the first insight into chemical modification. As shown in Figure SI7, the FT-IR of AFGr is characterized by the appearance of a new band at *ca.*  $1150\text{ cm}^{-1}$  corresponding to the stretching of the C-N and a broad band at *ca.*  $3440\text{ cm}^{-1}$  which corresponds to the stretching of the N-H bonds together with O-H stretches from the presence of some water. Moreover, a new band at *ca.*  $1620\text{ cm}^{-1}$  points to the formation of some C=C bonds. This distinctive features suggest that some structural changes have also occurred during the reaction with sodium amide, and further confirms that the resulting AFGr has enhanced water affinity.

Both EDX (SI2) and XPS (Figure 3 and SI3) confirm the presence of carbon, fluorine and nitrogen in AFGr, thus giving unequivocal proof of the introduction of amine functionalities across and within the layers. Table SI2 and Table SI3b summarize the detailed atomic composition of ex-FGr and AFGr as obtained from EDX and XPS, respectively. As already alluded to, the differences between the inner and outer layers of ex-FGr suggest that the introduction of the amino groups should take place preferentially in the outer layers. This is confirmed by the fact that the change in the fluorine content is more pronounced in the XPS measurements (56.6% of F before functionalization; 34.6 % F after functionalization) than in the EDX results (22% F before functionalization; 19% F after functionalization). Hence XPS, as a predominantly surface sensitive technique, appears to be the most accurate for addressing the structural and compositional changes that take place through the chemical process. According to XPS, after completion of the reaction, the amount of N is 2.1 %, which can be attributed to the amino functionalities introduced. An increase in the oxygen content (from 1.2 % in ex-FGr to 8.9 % in AFGr) was also observed. We believe that this increase in the oxygen content may come from the aqueous work up, and hence is related to the increased water affinity shown by AFGr.

Alongside the increase in the nitrogen content there is an increase in the C/F ratio from 0.7 in ex-FGr to 1.5 in AFGr, which points to a partial defluorination and hence graphitization (*i.e.* formation of new C=C bonds) during the reaction. This change also affects the Raman spectra: as shown in SI8, ex-FGr shows a strong fluorescence that makes it difficult to distinguish the peaks due to graphitic carbon, but in AFGr the D ( $1336\text{ cm}^{-1}$ ), G ( $1585.9\text{ cm}^{-1}$ ) and 2D ( $2687.84\text{ cm}^{-1}$ ) bands typical of graphitic materials can clearly be observed,<sup>35</sup> suggesting an increase in  $\text{sp}^2$  conjugation. The D band is more

intense than the G band and both are broad, characteristic of a disordered graphitic material. The increase in C=C bonding is also apparent in the high resolution C 1s XPS (Figure 2 and Table SI3d), up to 21 at% of the carbon content, where other interesting structural changes are also observed. As summarized in Table SI3d, the ex-FGr was largely composed of in-plane C-C-F (69 at%) carbon bonds, with just a residual quantity of terminal CF<sub>2</sub> bonds (1 at%). By contrast, in AFGr the C-C-F carbon content decreases dramatically to 24 at% and is accompanied by the appearance of a component at 291 eV which can be assigned to the new H<sub>2</sub>N-C-F carbon bonding environment (24 at%), and the formation of some terminal CF<sub>3</sub> bonds (7 at%), as already anticipated from the TGA analysis. Interestingly, the F 1s XPS signal shows a single peak for ex-FGr, which can be assigned to covalent C-F (685 eV), but splits into two components for AFGr (685 eV and 687 eV) (SI3b). This indicates that after the chemical reaction some C-F groups have been converted into something that is best described as ionic F intercalated between the layers.<sup>36</sup>

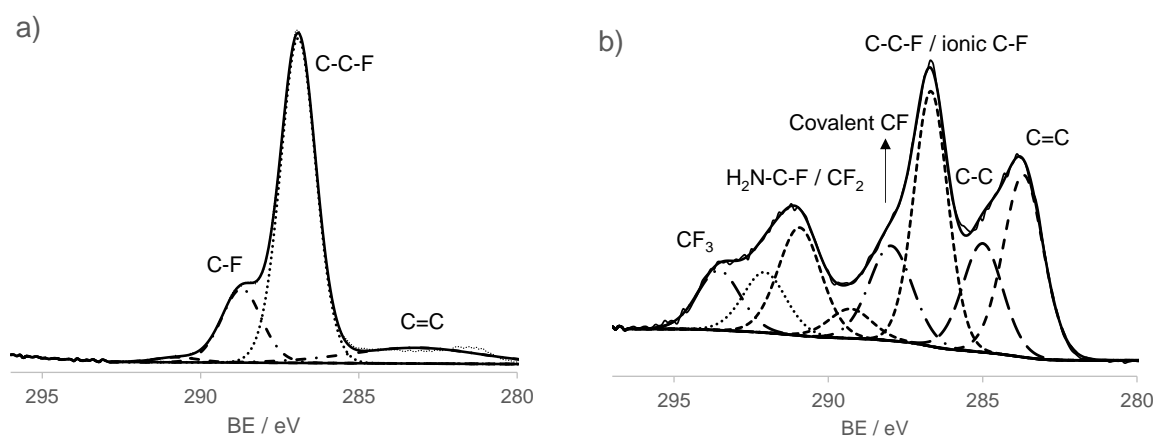


Figure 3. High resolution C1s XPS spectra of (a) ex-FGr and (b) AFGr.

The selective attachment of AuNPs to the amino-functionalized FGr provides further evidence of successful functionalization. AFGr was dissolved in water and mixed with a freshly prepared solution of H<sub>2</sub>AuCl<sub>4</sub>/NaBH<sub>4</sub> which produces AuNPs in-situ. The sample was stirred for 5 minutes and a black precipitate was obtained which was washed with water to remove the excess of AuNPs. The solid was first analysed with EDX, which confirmed the presence of gold. Subsequently, the resulting solid was dispersed in ethanol and deposited over a lacey carbon grid. As a control experiment, ex-FGr in DMF was also mixed with AuNPs in a similar procedure (for further experimental details refer to SI1). Figure 4 and SI9 shows typical TEM images of both exFGr-AuNPs and AFGr-AuNPs. As Figure 4 shows, ex-FGr demonstrated no clear affinity for binding AuNPs. In fact, ex-FGr seemed to be co-precipitated with AuNPs in such a way that aggregated sheets of FGr were observed embedding big bundles of AuNPs (Figure 4a and SI9a). By contrast, for the amino-functionalised material (Figure 4b and SI9b), the gold nanoparticles (apparent as black spots of *ca.* 5 nm diameter (SI10)) homogeneously decorated



the AFGr sheets. This shows that the amine-functionalities were introduced uniformly across the AFGr flakes and retain a much higher reactivity than the fluorine functionalities alone.

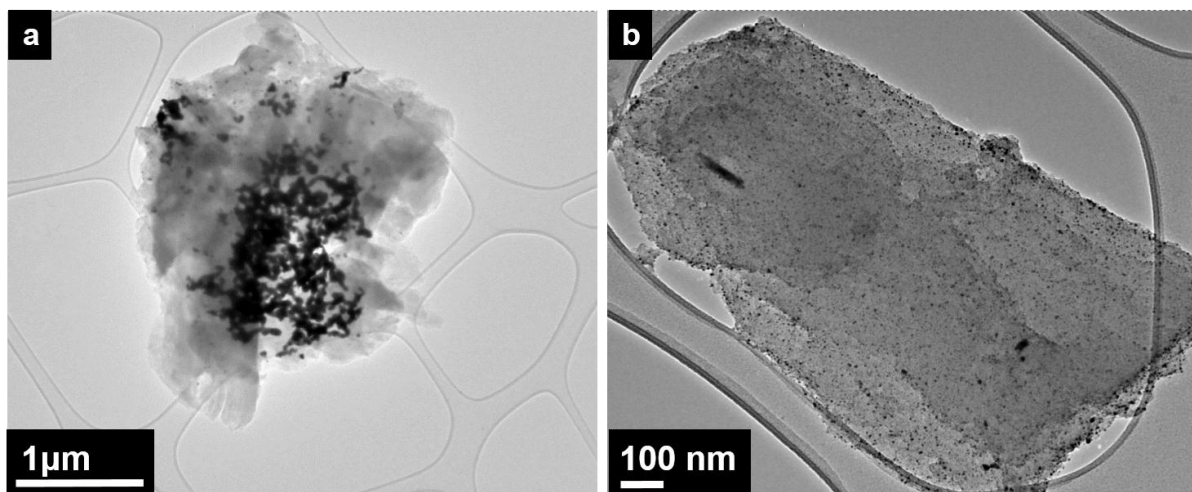


Figure 4. TEM images of AuNPs deposited on (a) ex-FGr and (b) AFGr. On AFGr the AuNPs bind to the amine-functionalities and hence are homogeneously dispersed.

## Conclusions

In conclusion, we have described a straightforward method for the chemical modification of exfoliated fluorographite with amine groups. The resultant material is readily dispersed in water, unlike fluorographene and fluorographite, and the amine groups act as convenient sites for further functionalization. XPS, TEM and EDX clearly demonstrate that the starting material, resulting from exfoliation of as-bought fluorographite, is composed of stacks of layers in which the outer layers are more heavily fluorinated. As a consequence, chemical substitution with amino groups takes place preferentially over the outer layers and, as demonstrated by XPS and Raman spectroscopy, is accompanied by a partial defluorination and graphitization. The chemically modified FGr could be easily decorated with AuNPs. These nano-particles serve as contrast markers for the identification of the functional sites, and are homogeneously distributed across the entire surface of the amino functionalized FGr sheets.

Interestingly, the significant changes in the physical properties occur despite the level of amine functionalization being only  $\sim 2\%$  and suggest that the properties of fluorographene itself could be modified without much affect to its internal structure. The simplicity of our method could also be extended both to synthesize chemically modified FGr with other functionalities and easily extrapolated to other Teflon-like materials including fluorographene. Thus, it opens the door to explore the effects that chemical modification may have on the properties of this new material, which have, so far, not been studied. Finally, the strong affinity between amino groups and a wide variety of metals could be exploited for the anchoring of other nanoparticles to fluorographite/fluorographene, thus enabling novel or enhanced sensing, catalytic or electrochemical applications.

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**Graphical Abstract**

Chemical functionalization of exfoliated fluorographite with amino groups induces a change in the solubility properties and allows further decoration with gold nanoparticles

