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# Journal Name

## COMMUNICATION

# Organic Functionalisation of Graphene Catalysed by Ferric Perchlorate

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We have developed a method to prepare covalently functionalised graphene using ferric perchlorate as the catalyst. The resulting functionalised graphene were characterised by Raman spectroscopy, TGA, XPS, AFM, and dispersibility tests in organic or aqueous media.
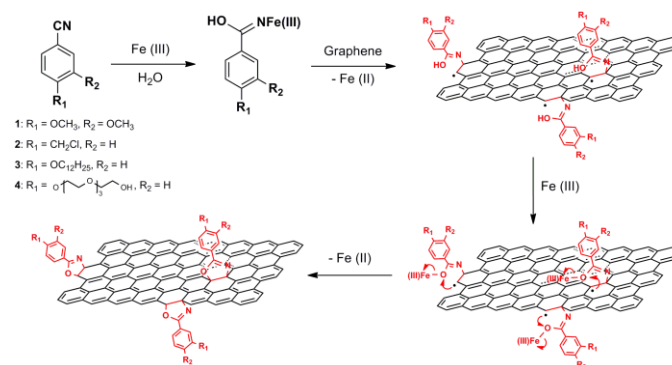
Graphene is a two-dimensional carbon material that can be prepared by mechanical exfoliation of bulk graphites,[1] chemical vapour deposition,[2] epitaxial growth,[3] thermal annealing of SiC,[4] unzipping of carbon nanotube,[5] as well as bottom-up organic synthesis.[6] These preparation approaches have been remarkably improved with the assistance of laser,[7] microwave[8] and sonication[9] with respect to size controllability, homogeneity and the ability for pattern formation.

only very active organic species, such as radical or carbene, can be used in the functionalisation reaction. For instance, carbon radicals derived from benzoyl peroxide,[11] diazonium salts,[12] alkyl iodides,[13] or α-naphthylacetic acid,[14] as well as halogen radicals generated by laser irradiation of chlorine[15] or fluoropolymers,[16] can be readily added to graphene basal plane. Halogenation of graphene was also achieved by heat treatment in the presence of $XeF_2$.[17] Nitrene is another active organic species which has been used for efficient functionalisation of graphene and fabrication of graphene/silicon hybrid materials.[18] The basal plane of graphene may also serve as a substrate for cycloaddition of aryne,[19] azomethine ylide[20] as well as malonate derivatives.[21] In addition, graphene can act as either diene or dienophile in Diels-Alder reaction in a reversible style under mild conditions.[22] Graphene can be also functionalised by substitution reaction.[23] Despite of this, the number of organic reactions that can be employed for chemical modification of graphene is still very limited (Table 1). Exploring new reactions on graphene will undoubtedly facilitate the research and application of graphene based materials.

**Table 1** Summary of Graphene Functionalisation Reactions in the literature

| Type of Reactions | Examples | References |
|---|---|---|
| Radical reaction | Aryl radical, Carbon radical, Halogen radicals | 11-17 |
| Cycloaddition | Nitrene addition, Bingel reaction, Aryne cycloaddition, Diels-Alder reaction, 1,3-dipolar cycloaddition | 18-22 |
| Substitution | Friedel-Crafts acylation, Hydrogen-lithium exchange | 23 |

Chemical functionalisation of graphene is an important strategy to tune its electronic property and to increase the dispersibility in water or organic solvents and compatibility with matrix materials. Graphene can be functionalised either through harsh oxidation by $H_2SO_4/HNO_3$[10] or through mild organic reactions. Oxidation of pristine graphene into graphene oxide (GO) may cause severe disruption to the π-conjugation. Organic reactions may be used to introduce functional groups without significant damage to the basal plane. Regarding the high stability of the fused π-conjugated system,



**Scheme 1** Functionalisation of graphene with benzonitrile derivatives catalysed by ferric perchlorate. The proposed mechanism is based on that using fullerene as the substrate.[24]

In this communication, we use a ferric salt, e.g., $Fe(ClO_4)_3 \cdot xH_2O$, as catalyst to activate benzonitriles that makes them active enough to functionalize graphene (Scheme 1). It has been shown by Wang and

coworkers that fullerenes react with various nitriles to afford corresponding fullerooxazoles in the presence of $Fe(ClO_4)_3 \cdot xH_2O$.[24] In the present work, we demonstrate that graphene can be also functionalised using benzonitrile derivatives with various **R** groups.

We used commercially available graphene (multi-layer graphene) (Xiamen Knano Graphene Technology Corp., Ltd) and four benzonitrile derivatives as the starting materials. The benzonitriles contain methoxy (**1**), chloromethyl (**2**), dodecyl (**3**), oligo(ethylene oxide) (**4**) as functional groups, respectively. First, pristine graphene (24 mg) was dispersed in *o*-dichlorobenzene (ODCB, 100 mL) and sonicated for 1 hour to obtain graphene dispersion.[13] A mixture of nitrile **1** (or **2**, **3**, **4**, 10 mmol) and ferric perchlorate hexahydrate (46.0 mg, 0.10 mmol) was placed in a 250 mL round-bottom flask and melted in an oil bath at 120 ℃. After 30 min, the graphene dispersion was added and the resulting solution was heated with stirring at 120 ℃ under nitrogen atmosphere for 2 days. After completion of the reaction, the functionalised graphene (FG) was separated from the mixture by filtration using a PVDF filter (pore size 0.45 μm), washed thoroughly with tetrahydrofuran (THF), ethanol and acetone, and then collected and dried under vacuum. Raman spectroscopy, TGA, XPS and AFM were utilized to confirm the attachment of these functional groups to graphene.

Fig. 1 shows the Raman spectroscopy of the pristine graphene and FGs which were measured using 633 nm laser excitation. While the pristine graphene shows a sharp G band and a very weak D band due to the defects at the edges of graphene plane, all FGs show obvious D and G bands that corresponds to $sp^3$ and $sp^2$ hybridization state of the C atoms on graphene, respectively. The intensities of D bands of FGs at 1330 $cm^{-1}$ are much higher than that of the pristine graphene, indicating partial change of C atoms from $sp^2$ to $sp^3$ state after functionalisation. The ratio of the intensities of D and G bands also reflects the degree of functionalisation.[25]
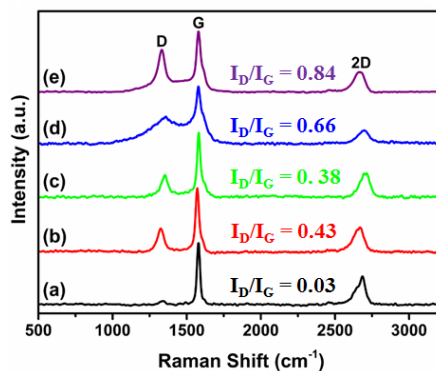


**Fig. 1** Raman data of (a) pristine graphene, (b) FG-1, (c) FG-2, (d) FG-3, (e) FG-4.

X-Ray photoelectron spectroscopy (XPS) was utilized to determine the surface elemental composition of all the FGs. Fig. 2 shows the high-resolution XPS scans for C 1s peaks of pristine graphene and FG-4. The peak at 285.2 eV is due to the C=C bonds of graphene. After functionalisation reaction, a new shoulder peak appears at 289.3 eV in C1s core level spectra of FG-4, corresponding to the presence of C-O and C-N bonds. Moreover, the N 1s core level spectrum of benzonitrile derivative **1** shows a peak at 398.8 eV due to its nitrile group. After reaction with graphene, the peak moves to 402.3 eV corresponding to N atoms in the formed oxazole. The full spectra for all the FGs are presented in the electronic supplementary information (Fig. S1, ESI†). From the intensities of all the elements, the atomic percentages can be calculated as shown in the Table 2. According to FGs' nitrogen content, the degree of functionalisation is estimated to be one functional group in 40 (FG-

1), 50 (FG-2), 110 (FG-3) and 60 (FG-4) graphene carbon atoms, respectively. The notably low functionality of FG-3 is possibly due to low miscibility of ferric salt and the hydrocarbon chain.
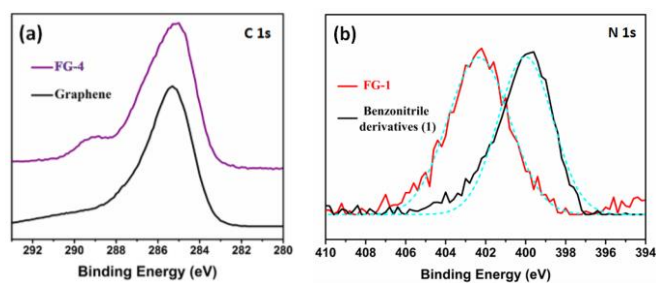


**Fig. 2** (a) High-resolution XPS C 1s core level spectrum of graphene and FG-4. (b) High-resolution XPS N 1s core level spectrum of benzonitrile derivative **1** and FG-1.

**Table 2** Elemental Contents of Pristine and Functionalised Graphenes

| Sample | C (%) | O (%) | N (%) | Cl (%) | $F^a$ |
|--------|-------|-------|-------|--------|-------|
| G | 92.5 | 7.5 | - | - | - |
| FG-1 | 74.9 | 23.1 | 2.0 | - | 1/40 |
| FG-2 | 83.1 | 13.4 | 1.8 | 1.7 | 1/50 |
| FG-3 | 86.5 | 12.8 | 0.7 | - | 1/110 |
| FG-4 | 74.8 | 23.9 | 1.3 | - | 1/60 |

[a]Functionality (*F*) is presented as number of functional groups divided by the number of graphene carbon atoms.

Thermal gravimetric analysis (TGA) also provides an indirect evidence of organic group on graphene sheet. All the samples were heated to 600 ℃ at a rate of 20 ℃ $min^{-1}$ under $N_2$. The results are given in Fig. 3. While the pristine graphene shows remarkable thermal stability, FGs undergo degradation in the temperature range 200–420 ℃, which is attributed to the pyrolysis of the covalently grafted organic groups on graphene. The weight loss of all FGs till 420 ℃ is 24% (FG-1), 16% (FG-2), 13% (FG-3) and 35% (FG-4), respectively. These values fall in the range of functionalities calculated from XPS results shown in Table 1. Further weight loss above 420 ℃ is due to the thermal decomposition of defects formed at sites where functionalisation occurred.[21] Similar behaviour was also observed for functionalised carbon nanotubes.[26]
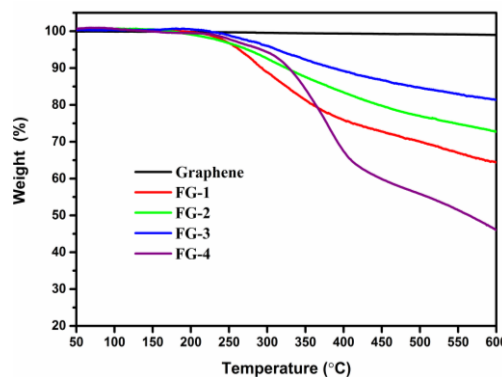


**Fig. 3** TGA of pristine graphene and functionalised graphenes.

Fig. 4 shows the AFM images of pristine graphene, FG-3 and FG-4. Sonicating the purchased graphene in ODBC led to the formation of multi-layer graphene, with the height of ~ 3 nm measured by AFM. After functionalisation, single-layer graphene is easily

obtained with the thickness of less than 1 nm. Thus, it seems that the functional groups with short aliphatic hydrocarbon or ether chains prevent graphene sheets from agglomerating. Furthermore, the side chains render the graphene sheet hydrophilic and hydrophobic nature, respectively (Figure 4d and 4e). FG-3 disperses well in toluene or ODCB, whereas FG-4 forms stable dispersion in water. This macroscopic evidence demonstrates that graphene was indeed functionalised.
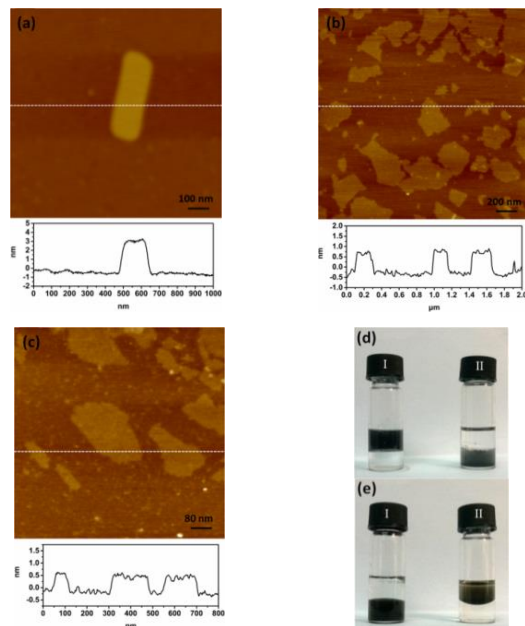


**Fig. 4** AFM images of (a) pristine graphene, (b) FG-3 and (c) FG-4, and photographs of (d) FG-3 and (e) FG-4 in the mixed solvents. (I: Top layer is water; Bottom layer is ODCB; II: Top layer is toluene; Bottom layer is water).

Benzonitriles with electron-withdrawing groups such as 4-nitro-benzonitrile did not react with graphene. XPS showed no signal of nitrogen on the collected graphene species by filtration (after washing thoroughly with organic solvents) (Fig. S2, ESI†). This also indicates that the product purification process used in this work is efficient to remove any physically adsorbed organic molecule.

The mechanism of the reaction is proposed according to Wang and coworkers.[24] Thus, benzonitriles first react with one molecule of $H_2O$ in the presence of $Fe(ClO_4)_3 \cdot xH_2O$ to form a hydroxylimine-Fe(III) complex. The complex then undergoes a stepwise addition towards graphene at N and O atoms involving the release of Fe(II) and combination of the intermediate radicals, resulting in the formation of oxazole bridge between graphene and the incoming phenyl ring bearing the functional groups.

## Conclusions

In conclusion, we have, for the first time, functionalised graphene using $Fe(ClO_4)_3 \cdot xH_2O$-catalysed cycloaddition between benzonitrile and unsaturation in graphene. The products were analyzed using Raman, XPS, TGA and AFM. The analytical results proved the successful covalent attachment of the organic molecules to graphene. By changing the R groups in benzonitrile derivatives, we obtained functionalised graphene with methoxy, chloromethyl, dodecyl and oligo(ethylene oxide) functionalities, respectively. Therefore, the present reaction can be used as a novel tool for the organic functionalisation of graphene under mild conditions.

## Notes and references

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