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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 was 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 graphite,[1] chemical vapour deposition,[2] epitaxial growth,[3] thermal annealing of SiC,[4] unzipping of carbon nanotubes,[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.

Chemical functionalisation of graphene is an important strategy to tune its electronic properties and to increase its 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 of 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, only very active organic species, such as radicals 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 the 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 a diene or a dienophile in Diels–Alder reaction in a reversible manner under mild conditions.[22] Graphene can also be functionalised by substitution reaction.[23] Despite this, the number of organic reactions that can be employed for chemical modification of graphene is still very limited (Table 1). Exploring new reactions of 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	Ref.
Radical reaction	Aryl radicals, carbon radicals, 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

In this communication, we use a ferric salt, *e.g.*, $Fe(ClO_4)_3\cdot xH_2O$, as a 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 also be 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**), and 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 °C. After 30 min, graphene dispersion was added and the resulting solution was

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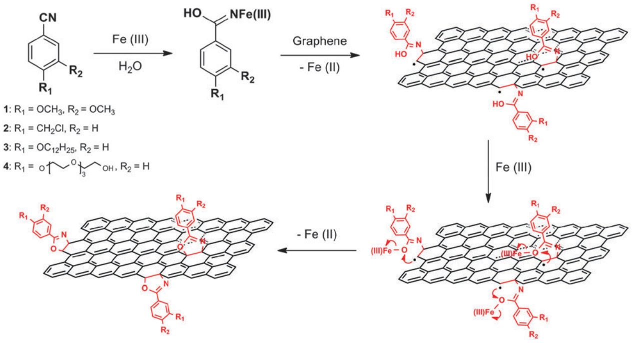

Scheme 1 Functionalisation of graphene with benzonitrile derivatives catalysed by ferric perchlorate. The proposed mechanism is based on the use of fullerene as the substrate.[24]

heated with stirring at 120 °C under a 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 spectra of pristine graphene and FGs, which were recorded using 633 nm laser excitation. While pristine graphene shows a sharp G band and a very weak D band due to the defects at the edges of the graphene plane, all FGs show obvious D and G bands that correspond to sp^3 and sp^2 hybridization states of the C atoms on graphene, respectively. The intensities of D bands of FGs at 1330 cm^{-1} are much higher than that of pristine graphene, indicating a partial change of C atoms from the 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]

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 spectrum 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 shifts to 402.3 eV corresponding to N atoms in the formed oxazole. The full spectra of 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 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 the low miscibility of the ferric salt and the hydrocarbon chain.

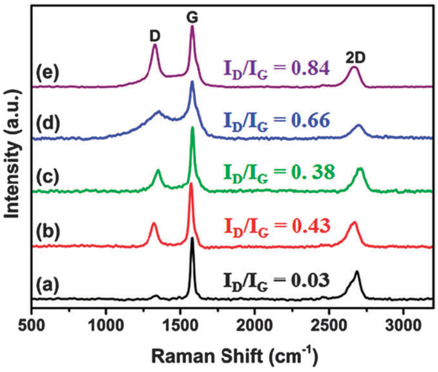

Fig. 1 Raman data of (a) pristine graphene, (b) FG-1, (c) FG-2, (d) FG-3, (e) FG-4.

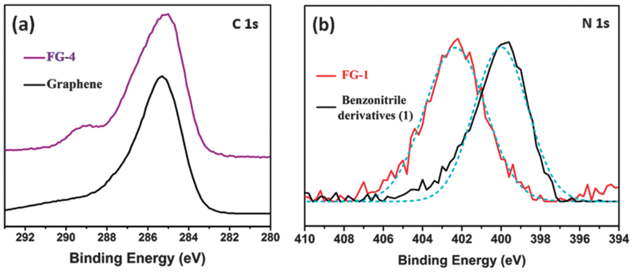

Fig. 2 (a) High-resolution XPS C 1s core level spectrum of graphene and FG-4. (b) High-resolution XPS N 1s core level spectrum of benzonitrile derivative **1** and FG-1.

Thermogravimetric analysis (TGA) also provides indirect evidence of the organic group on graphene sheets. All the samples were heated to 600 °C at a rate of 20 °C min^{-1} under N_2. The results are given in Fig. 3. While pristine graphene shows a remarkable thermal stability, FGs undergo degradation in the temperature range 200–420 °C, which is attributed to the pyrolysis of the covalently grafted organic groups on graphene. The weight loss of all FGs up to 420 °C 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 °C is due to the thermal decomposition of defects formed at sites where functionalisation occurred.[21] A similar behaviour was also observed for functionalised carbon nanotubes.[26]

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, respectively (Fig. 4d and e). FG-3 disperses well in

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 the number of functional groups divided by the number of graphene carbon atoms.

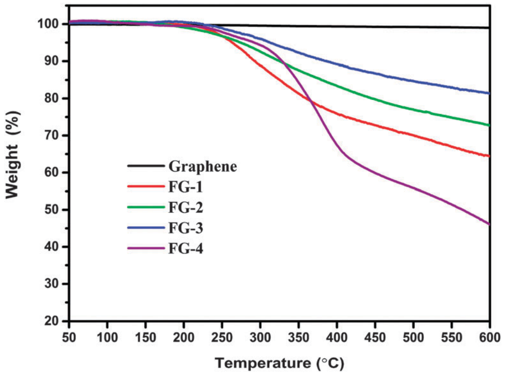

Fig. 3 TGA of pristine graphene and functionalised graphenes.

toluene or ODCB, whereas FG-4 forms stable dispersion in water. This macroscopic evidence demonstrates that graphene was indeed functionalised.

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.

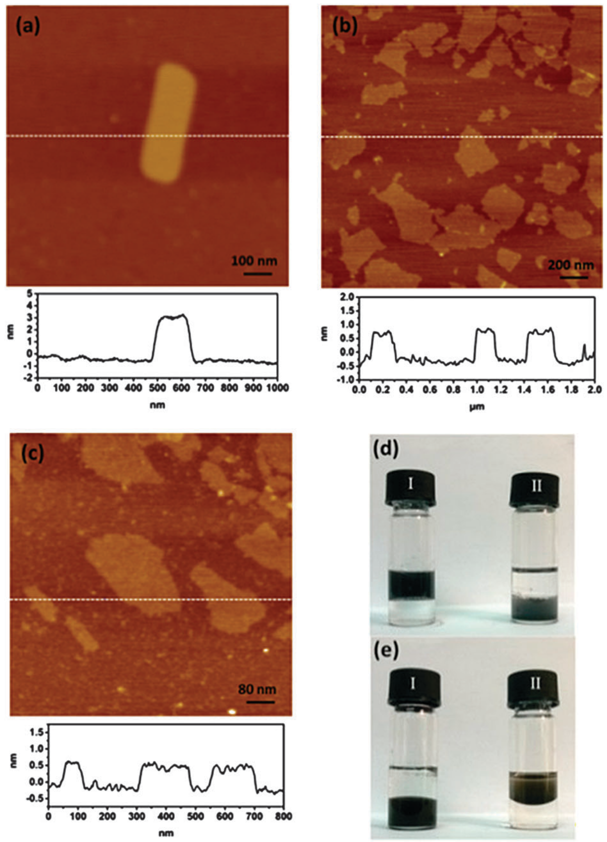

Fig. 4 AFM images of (a) pristine graphene, (b) FG-3 and (c) FG-4, and photographs of (d) FG-3 and (e) FG-4 in the mixed solvents. (I: top layer is water; bottom layer is ODCB; II: top layer is toluene; bottom layer is water).

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 an oxazole bridge between graphene and the incoming phenyl ring bearing the functional groups.

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.

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