Electronic Supporting Information

Highly hydrophilic and insulating fluorinated reduced graphene oxide

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1. Experimental methods

1.1 Materials

Natural graphite (Bay Carbon, SP-1 graphite), sulpuric acid (95-97%), hydrogen peroxide (30 wt.%), potassium permanganate, sodium nitrate, BF₃-etherate, 1-heptanethiol, and n-butylamine were obtained from commercial sources and used as received.

1.2 Characterization

Raman spectroscopy measurements were taken using a micro-Raman system (Renishaw, RM1000-In Via) with an excitation energy of 2.41 eV (514 nm). All X-ray photoemission spectroscopy (XPS) measurements were made by a SIGMA PROBE (ThermoVG, U.K.) with a monochromatic Al-K α X-ray source at 100 W. FT-IR spectra was collected using a Thermo Nicolet AVATAR 320 instrument. The microstructure was observed by field emission scanning electron microscopy (FE-SEM; JSM-6701F/INCA Energy, JEOL). The thermal properties of the rGO were characterized by TGA (Polymer Laboratories, TGA 1000 plus). All UV-vis absorption spectra were recorded using a double-beam UV-1650PC spectrophotometer (Shimadzu).

1.3 Preparation of Graphene oxide (GO)

Graphene oxide (GO) was prepared from natural graphite powder by the modified Hummers and Offenman's method using sulpuric acid, potassium permanganate, and sodium nitrate.¹

1.4 Preparation of Fluorinated reduced Graphene Oxide (F-rGO)

The GO (200 mg) prepared following the above method was dispersed in 100 mL dry tetrahydrofuran (THF) and followed by the addition of BF₃-etherate solution and 1-hepatnethiol/n-butylamine under N₂ atmosphere. Then the temperature was increased to 60 °C and the reaction was carried out for 24 hours. Then the reaction mixture was filtered and first washed with THF to remove excess BF₃-etherate and 1-hepatnethiol/n-butylamine and then with deionised water for several times to wash away by-products formed during the reaction. It was then dried under vaccum at 60 °C.



Fig. S1 Postulated mechanism for ring opening hydrofluorination with BF3-etherate.²



Fig. S2 Postulated mechanism for fluorination of GO using BF₃-etherate and 1-heptanethiol/n-Butylamine.

Journal	Starting material	Method	F-coverage	Remarks
Small 2010, 6, 2877-2884	i) Graphite fluorideii) Graphene and XeF₂	i) Mechanical cleavageii) Exposure of atomic fluorine	They prepared fluorographene (fully fluorinated graphene) and also partially fluorinated graphene	Atomic exposure is high energy process
RSC Adv. 2012, 6, 2877- 2884	Graphite fluoride	Exfoliation by Arc discharge	10% fluorine coverage	Arc discharge is not suitable
RSC Adv. 2013, 3, 6327- 6330	Graphene oxide and HF	UV irradiation	50 % fluorine coverage	HF is highly corrosive reagent
RSC Adv. 2013, 3, 3881- 3884	Graphene oxide and HF	Using nickel tube	Not mentioned (It is cleared from XPS that F-coverage is very low)	HF is highly corrosive
Nano letters 2010, 10, 3001-3005	Graphene	Exposure of XeF ₂ gas	25 % F-coverage	Not convenient
Nano letters 2012, 12, 2374-2378	Graphene and Fluoropolymer	Laser irradiation	C_nF , $n > 1$ i.e. not fluorographene	Not convenient
Our method	Graphene oxide and BF_3 (as a fluorinating agent)	Simply solution based method	~67% F-coverage	More convenient, solution based and more greener way

Table S1 Comparison of fluorine coverage with different methods



Fig. S3 XPS spectra of rGO_T and F-doped reduced GO such as F-rGO_{BS-8} (entry no. 8 in Table 1), F-rGO_{B-3} (entry no. 3 in Table 1), prGO_{S-4} (entry no. 4 in Table 1), F-rGO_{BS-5} (entry no. 5 in Table 1), and F-rGO_{BS-6} (entry no. 6 in Table 1), which was produced by the reaction of GO with BF3-etherate solution and 1-heptanethiol/n-Butylamine at different condition.

The characteristic peaks in the IR spectra of GO (Fig. 2a) were ~3409 cm⁻¹ (broad, O–H stretching), 2948 cm⁻¹, (CH₂, stretching), 1728 cm⁻¹ (C=O stretching), 1632 cm⁻¹ (C=C stretching), 1404 cm⁻¹ (O–H bending), and 1065 cm⁻¹ (C–O–C stretching from epoxide and/or ester groups).³ IR spectrua of F-rGO_{BS-1} and F-rGO_{BN-9} showed no peak at 1728, 1404, 1065 cm⁻¹ and very low intensity at 3409 cm⁻¹, but a new peak arose at 1196 cm⁻¹ (C-F stretching),⁴ which indicated that with the incorporation of fluorine atom, -COOH, >C=O, and epoxide functional groups were absent and –OH group decreased. IR spectra of other compounds were given in the Fig. S4. This observation was a good evidence for fluorination and *in-situ* reduction.



Fig. S4 FT-IR Spectra of F-doped reduced GO such as $F-rGO_{B-2}$ (entry no. 2 in Table 1), F-rGO_{B-3}, prGO_{S-4}, F-rGO_{BS-5}, F-rGO_{BS-6}, and F-rGO_{BS-7} (entry no. 7 in Table 1), which was produced by the reaction of GO with BF₃-etherate solution and 1-heptanethiol/n-Butylamine at different condition.



Fig. S5 Raman spectra of F-doped reduced GO such as $F-rGO_{B-2}$, $F-rGO_{B-3}$, $prGO_{S-4}$, $F-rGO_{BS-5}$, $F-rGO_{BS-6}$, $F-rGO_{BS-7}$, $F-rGO_{BS-8}$, which were produced by the reaction of GO with BF3-etherate solution and 1-heptanethiol /n-Butylamine at different condition.

TGA plots of GO, F-rGO_{BS-1} and F-rGO_{BN-9} were shown in Fig. S6b. In the GO sample prepared, the maximum weight was lost between 100 and 200 °C, indicating CO, CO₂ and steam release from the most labile functional groups. At temperatures below 700 °C, the total weight lost in the GO was about 77%. In contrast, the fluorine functionalized rGO sample showed very high thermal stability. The total weight lost was only 20% and 23% for F-rGO_{BS-1} and F-rGO_{BN-9} respectively at temperatures below 700 °C. This minor weight-loss could be attributed to the absence of most oxygen functional groups.⁵



Fig. S6 a) Resistivity as a function of amount of fluorination, b) TGA Data of GO, F-rGO_{BS-1} and F-rGO_{BN-9}.



Fig. S7 SEM images of a) GO, b) F-rGO_{BN-9}, c) F-rGO_{B-2} and d) F-rGO_{BS-1}

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