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), sulpiric acid (95-97%), hydrogen peroxide (30 wt.%), potassium permanganate, sodium nitrate, BF$_3$-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-Kα 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 sulpiric 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 BF$_3$-etherate solution and 1-heptanethiol/n-butylamine under N$_2$ 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 BF$_3$-etherate and 1-heptanethiol/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 BF$_3$-etherate.$^2$

**Fig. S2** Postulated mechanism for fluorination of GO using BF$_3$-etherate and 1-heptanethiol/n-Butylamine.
### Table S1 Comparison of fluorine coverage with different methods

<table>
<thead>
<tr>
<th>Journal</th>
<th>Starting material</th>
<th>Method</th>
<th>F-coverage</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small 2010, 6, 2877-2884</td>
<td>i) Graphite fluoride ii) Graphene and XeF₂</td>
<td>i) Mechanical cleavage ii) Exposure of atomic fluorine</td>
<td>They prepared fluorographene (fully fluorinated graphene) and also partially fluorinated graphene</td>
<td>Atomic exposure is high energy process</td>
</tr>
<tr>
<td>RSC Adv. 2012, 6, 2877-2884</td>
<td>Graphite fluoride</td>
<td>Exfoliation by Arc discharge</td>
<td>10% fluorine coverage</td>
<td>Arc discharge is not suitable</td>
</tr>
<tr>
<td>RSC Adv. 2013, 3, 6327-6330</td>
<td>Graphene oxide and HF</td>
<td>UV irradiation</td>
<td>50 % fluorine coverage</td>
<td>HF is highly corrosive reagent</td>
</tr>
<tr>
<td>RSC Adv. 2013, 3, 3881-3884</td>
<td>Graphene oxide and HF</td>
<td>Using nickel tube</td>
<td>Not mentioned (It is cleared from XPS that F-coverage is very low)</td>
<td>HF is highly corrosive reagent</td>
</tr>
<tr>
<td>Nano letters 2010, 10, 3001-3005</td>
<td>Graphene</td>
<td>Exposure of XeF₂ gas</td>
<td>25 % F-coverage</td>
<td>Not convenient</td>
</tr>
<tr>
<td>Nano letters 2012, 12, 2374-2378</td>
<td>Graphene and Fluoropolymer</td>
<td>Laser irradiation</td>
<td>CₓFᵧ, n &gt; 1 i.e. not fluorographene</td>
<td>Not convenient</td>
</tr>
<tr>
<td>Our method</td>
<td>Graphene oxide and BF₃ (as a fluorinating agent)</td>
<td>Simply solution based method</td>
<td>~67% F-coverage</td>
<td>More convenient, solution based and more greener way</td>
</tr>
</tbody>
</table>
**Fig. S3** XPS spectra of rGO<sub>T</sub> and F-doped reduced GO such as F-rGO<sub>BS-8</sub> (entry no. 8 in Table 1), F-rGO<sub>B-3</sub> (entry no. 3 in Table 1), prGO<sub>S-4</sub> (entry no. 4 in Table 1), F-rGO<sub>BS-5</sub> (entry no. 5 in Table 1), and F-rGO<sub>BS-6</sub> (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 \( \approx 3409 \text{ cm}^{-1} \) (broad, O–H stretching), 2948 cm\(^{-1}\), (CH\(_2\), 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 spectra 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.

![FT-IR Spectra of F-doped reduced GO](image)

**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 BF\(_3\)-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

![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.](image)

**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}.

![SEM images of a) GO, b) F-rGO_{BN-9}, c) F-rGO_{B-2} and d) F-rGO_{BS-1}.](image)

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


