

High-yield Production of Highly Fluorinated Graphene

by Direct Heating Fluorination of Graphene-oxide

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Experimental section

1.1 Preparation of honeycomb graphene oxide (GO)

GO was prepared by the modification of Hummers's method from flake graphite (average particle diameter of 4 μ m, 99.95% purity, Qingdao Tianhe Graphite Co. Ltd., Qingdao, China)^{1,2}. 5 g of graphite and 3.75 g of NaNO₃ (A.R.) were placed in a flask. Then, 375 mL of H₂SO₄(A.R.) was added with stirring in an ice-water bath, and 22.5 g of KMnO₄(A.R.) were slowly added over about 1 h. Stirring was continued for 2 h in the ice-water bath. After the mixture was stirred

vigorously for 5 days at room temperature, 700 mL of 5 wt % H₂SO₄ aqueous solution was added over about 1 h with stirring, and the temperature was kept at 98 °C. The resultant mixture was further stirred for 2 h at 98 °C. The temperature was reduced to 60 °C, 15 mL of H₂O₂ (30 wt % aqueous solution) was added, and the mixture was stirred for 2 h at room temperature. To remove the ions of oxidant and other inorganic impurity, the resultant mixture was purified by repeating the following procedure cycle 2 times: centrifugation, removal of the supernatant liquid, addition of 2 L of a mixed aqueous solution of 3 wt % H₂SO₄/0.5 wt % H₂O₂ to the bottom solid, and dispersing the solid using vigorous stirring and bath ultrasonication for 30 min at a power of 140 W. Then a similar procedure was repeated: two times using 3 wt % HCl aqueous solution (2 L) and one time using H₂O (2 L). The final resultant water solution was dialyzed for two weeks to further remove the remaining HCl acid and other impurity. After centrifugation, water in the resultant solide was removed by freeze drying for 48 h.

A 2 wt% GO suspension in water was prepared. The aqueous solution of GO was loaded into square aluminum molds. The specimens were then plunged into liquid nitrogen, then dried in a freeze drier for two days. Finally, the samples were further dried at 80 °C for two hour. The honeycomb GO was prepared, as shown in Figure S1.

1.2 Direct heating-fluorination of GO

The fluorination was carried out in closed stainless steel (SUS316) chamber (10 L) equipped with vacuum line. 100 mg GO was put in the chamber. After exchanging nitrogen for three times, we removed residual oxygen and moisture in the chamber. 90 KPa F₂/N₂ mixed gas was introduced in to the chamber at room temperature (RT). The F₂ concentration was adjusted to obtain products with different degree of fluorination. The corresponding product was denoted as FGO-1, FGO-2 and FGO-3 for 2 %, 5% and 10% F₂ concentration, respectively. Fluorination processed with temperature increasing from RT to a certain temperature (room temperature, 100 °C, 180 °C or 250 °C) at rate of 4 °C/min, and steady at this temperature for 20 min. Residual F₂ and by-products in the chamber were removed at once by vacuum and absorbed by alkali aqueous solution. Then fluorinated samples were taken out and preserved in dry atmosphere. The chemical composition and structure were characterized by XPS, FTIR, XRD, Raman, AFM, TEM and UV-vis spectra.

1.3 Characterization

The surface chemical composition of fluorinated and non-fluorinated samples was examined by XPS with monochromatized Al K α rays (1486.6 eV) under the circumstance of 12 kV \times 15 mA, Kratos, Inc., at RT and at 2×10^{-7} Pa. Binding energies were referenced to the hydrocarbon peak at 284.8 eV. The take-off angle was 20° with sampling depths of approximately 6~10 nm. FTIR was recorded by a Nicolet 560 Fourier transform spectrometer. TGA was performed on Netzsch 209 TG instruments. TEM was performed on Tecnai G2 F20 S-TWIN. Raman spectroscopy measurements were performed on LabRamHR instruments. AFM was carried out with a NanoScope MultiMole & Explore from Veeco Instruments, using tapping mode. Raman spectroscopy was carried out using a backscattering geometry. The wavelength of 785 nm line of laser was used to excite the sample. Contact angle of Water were tested using drop sharp analysis with 100 Krüss auto-visual contact angle test equipment. The resistance is measured by a Keithley 6487 picoammeter (Keithley Instruments Inc. Ohio, USA) at a constant voltage of 10 V. Two points method was used. The results were recorded after the voltage had been exerted for 5 seconds.

References:

- 1 M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara and M. Ohba, Carbon 2004, 42, 2929.
- 2 H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao and Y. Chen, ACS Nano 2008, 2, 463.

Additional Figures and Tables

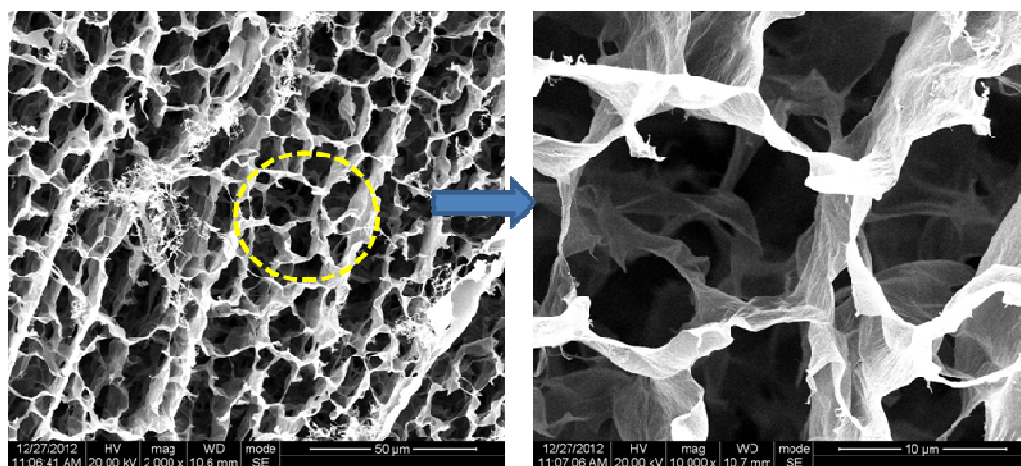


Figure S1. SEM pictures of honeycomb GO

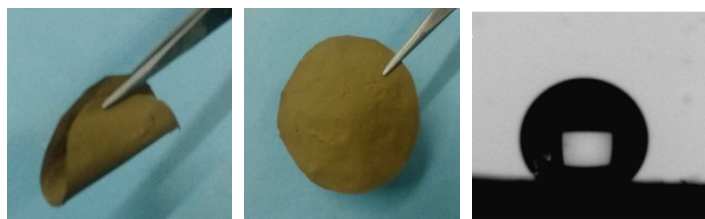


Figure S2. Photograph of a 15- μm -thick FGO-3 film

Figure S2 shows a 15- μm -thick FGO-3 film or paper prepared on a membrane filter by vacuum filtration of the FGO-3 dispersion of alcohol. The film exhibits a wheat color, which implies the poor conductivity. Its resistivity is found to be $1.3 \times 10^{12} \Omega$ at room temperature. This paper exhibits excellent hydrophobic properties (water contact angle $> 135^\circ$, Figure 3c).

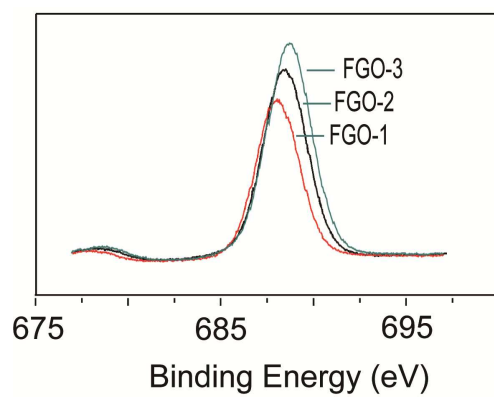


Figure S3. F 1s spectra of fluorinated samples

Figure S3 shows the increasing of F content results in the position of F peak shifts from 687.9 eV to 688.9 eV, which implies the enhancing of C-F covalence. This results is consistent with the results of FTIR analysis.

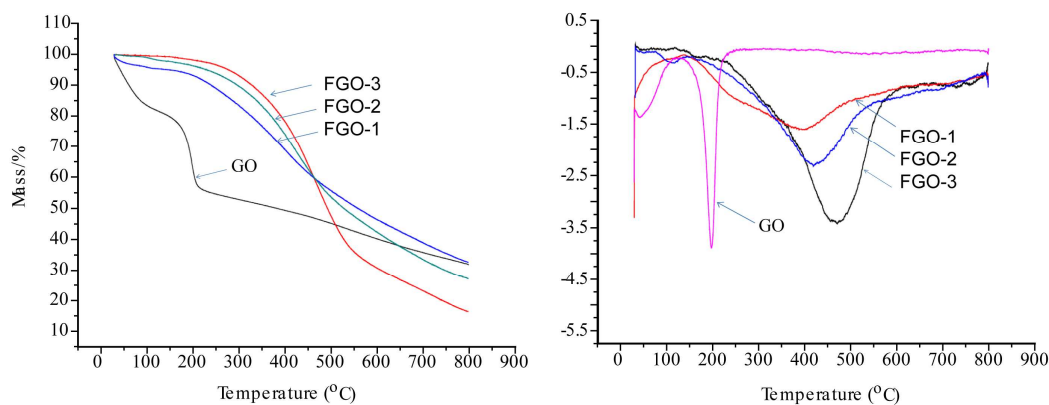


Figure S4. shows the TGA (left) and DTA (right) lines of fluorinated and non-fluorinated samples at heating rate of 10 °C/min under N₂ atmosphere

Table S1. Data of thermal analysis

样品编号	5%失重温度/°C	10%失重温度/°C	失重峰值温度/°C
GO	42.7	61.9	197.3
FGO-1	154.6	241.3	399.1
FGO-2	232.8	298.3	418.5
FGO-3	279.4.	330.0	469.7

Figure S4 and Table S1 show the TGA (left) and DTA (right) lines of fluorinated and non-fluorinated samples and data of thermal analysis. The rapid weight loss observed around 197 °C is attributed to the elimination of oxide related group bonding on the graphene sheets. After fluorination, the thermal stability of samples was improved obviously. The weight loss of FGO-1, FGO-2 and FGO-3 mainly occurred at 399.1, 418.5 and 470 °C, respectively.

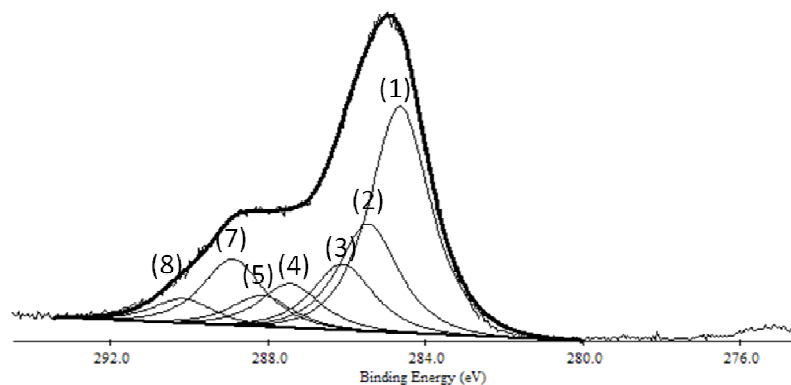


Figure S5. Curve-fitting of XPS C 1s spectrum of sample 1 in table 3 in manuscript

Table S2. Location, ascription and content of sample 1

<i>Peak</i>	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Location (eV)	284.6	285.4	286.1	287.4	288.2	288.9	290.2
Ascription	- <u>C</u> =C-	- <u>C</u> -	<u>C</u> -O	<u>C</u> =O	C _{sp2} -F	C-F	CF ₂
Content (%)	39.9	39.9	39.9	39.9	39.9	39.9	39.9

Figure S4 and Table S1 show the chemical structure of fluorinated samples (sample 1 in manuscript) at RT. The share of -C=C- component, 39.9 5 %, almost has no obvious change, compared with that of GO, 40.6 %.