Effect of the Oxygenic Groups on the Mechanism of Fluorination of Graphene Oxide and its Structure

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Supporting Information

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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 μm, 99.95% purity, Qingdao Tianhe Graphite Co. Ltd., Qingdao, China). 5 g of graphite and 3.75 g of $NaNO_3$ (A.R.) were placed in a flask. Then, 375 mL of H_2SO_4(A.R.) was added with stirring in an ice-water bath, and 22.5 g of $KMnO_4$(A.R.) were slowly added over about 1 h. Stirring was continued for 2h in the ice-water bath. After the mixture was stirred vigorously for 5 days at room temperature, 700 mL of 5 wt % H_2SO_4 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 2h at 98 °C. The temperature was reduced to 60 °C, 15 mL of H_2O_2 (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 2L of a mixed aqueous solution of 3wt% H_2SO_4/0.5wt% H_2O_2 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 3wt% HCl aqueous solution (2L) and one time using H_2O (2L). 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.

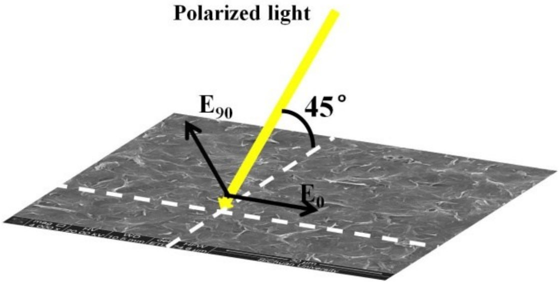

Figure S1. The scheme of polarized ATR-FTIR.

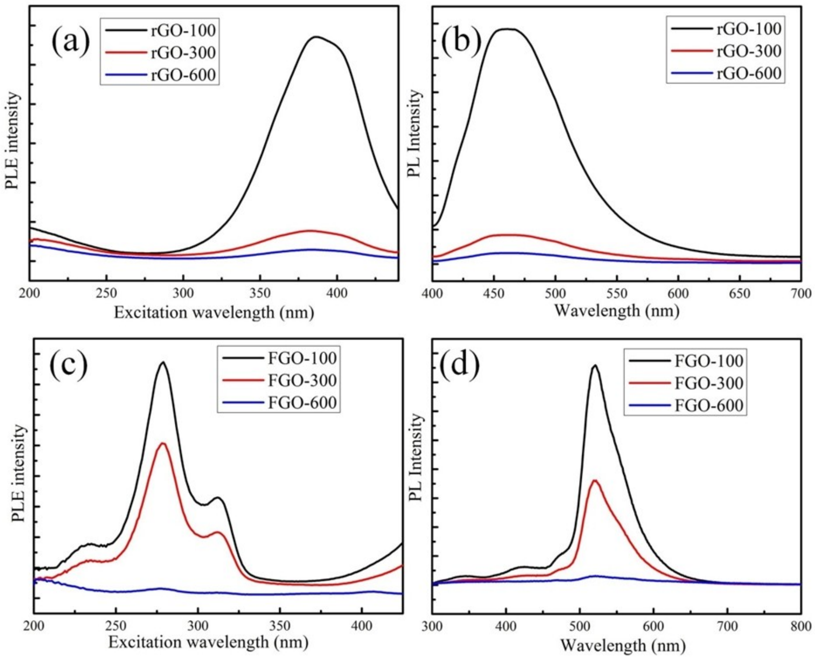

Figure S2. PLE spectrum from rGOs (rGO-100, rGO-300 and rGO-600) (a). PL spectrum from rGOs with the detection wavelength of 386nm (b). And PLE spectrum (c) and PL spectrum with the detection wavelength of 278nm (d) of their corresponding FGOs.

The maximum wavelength of excited light for rGOs was 386nm and the corresponding PL wavelength was about 460nm in NMP solvent, which was similar to the previous reports. The intensities of PL spectrum and PLE spectrum of rGOs decreased with the decrease of oxygen content. The PLE spectrum of FGOs showed three peaks at 232nm, 278nm and 312nm, respectively. And the corresponding PL spectrum also showed two peaks at 421nm and 520nm, the intensities depended on the fluorine content.

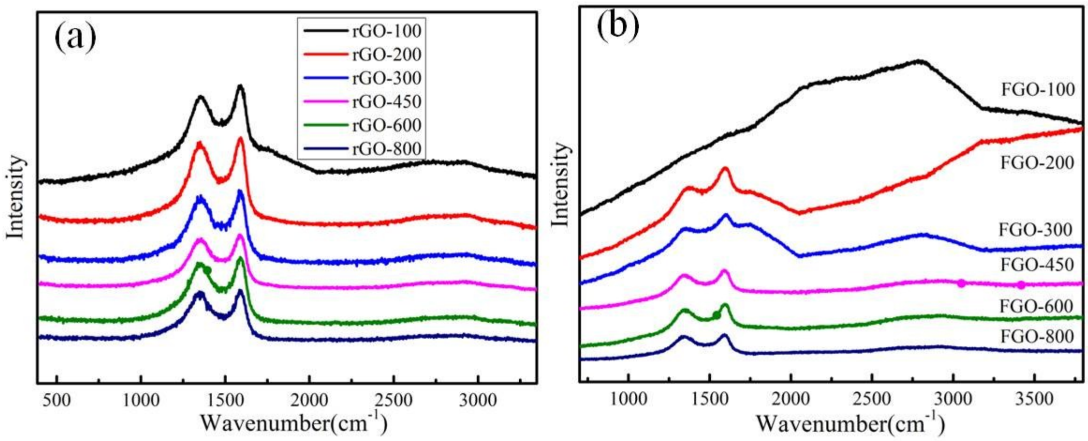

Figure S3. The Raman spectrum of rGOs thermal reduction at different temperatures and their corresponding FGOs.

The Raman spectrum of rGO with different oxygen content and their corresponding FGOs was shown in Figure s6. The I_D/I_G ratio of rGO-100, rGO-200, rGO-300, rGO-450, rGO-600 and rGO-800 were 0.872, 0.956, 0.926, 0.914, 0.919 and 0.909. The I_D/I_G ratio of rGO decreased with the increase of thermal reduction temperature, which indicated the content of sp3 carbon decreased and the recover of conjugation structure. After fluorination, the I_D/I_G ratio of FGO-800 was 0.99, which indicated the defects increased and parts of conjugation structure was destroyed. However, the I_D/I_G ratio of FGO-600 and FGO-450 were 0.87 and 0.83, respectively. With the increase of fluorine content, the I_D/I_G ratio of fluorinated graphene always decrease and then D peak and G peak gradually disappear.

Table S1. Chemical composition of rGOs reduced at different temperature and the corresponding FGOs measured by XPS.

Sample	C	O	sample	C	O	F
rGO-800	0.931	0.069	FGO-800	0.835	0.080	0.084
rGO-600	0.867	0.133	FGO-600	0.750	0.110	0.140
rGO-450	0.820	0.180	FGO-450	0.639	0.124	0.237
rGO-300	0.804	0.196	FGO-300	0.624	0.124	0.252
rGO-200	0.781	0.219	FGO-200	0.597	0.120	0.283
rGO-100	0.751	0.249	FGO-100	0.579	0.113	0.309

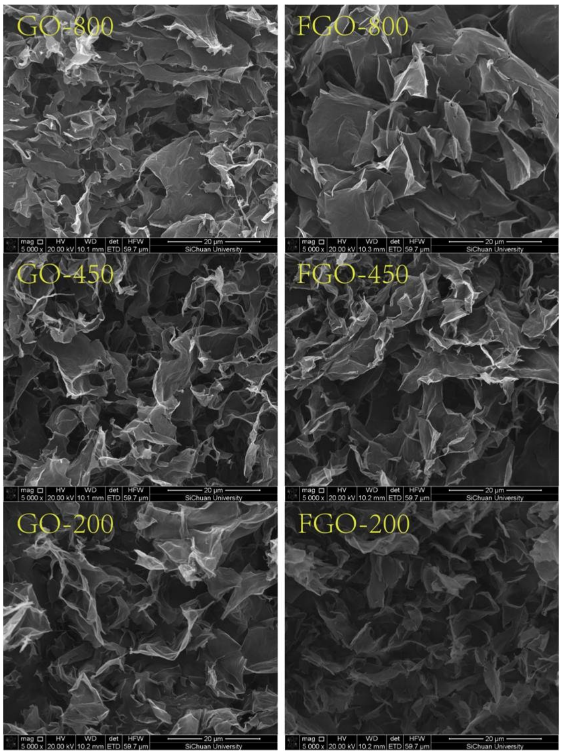

Figure S4. SEM micrographs of sample rGO-800, rGO-450, rGO-200 and their corresponding fluorinated products, FGO-800, FGO-450, FGO-200.

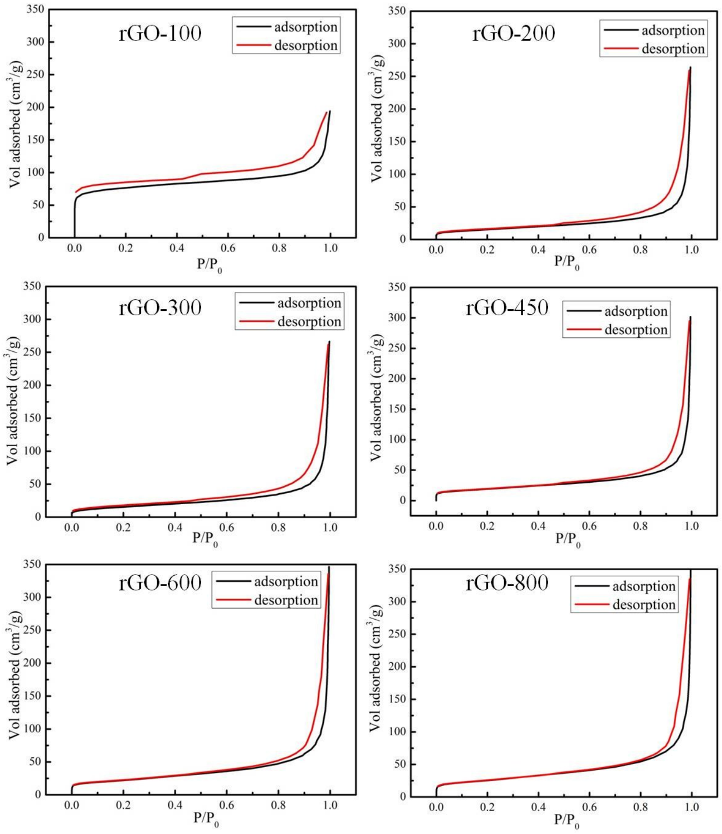

Figure S5. Nitrogen sorption isotherms of rGOs with different oxygen contents.

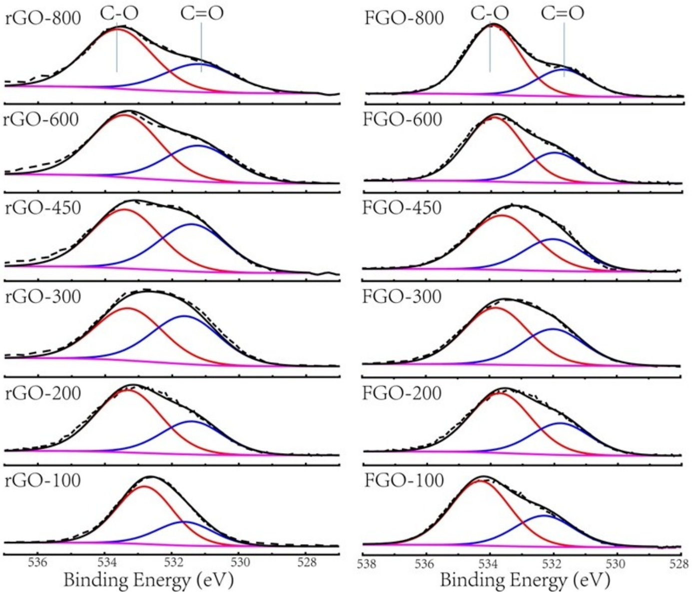

Figure S6. XPS O 1_S spectra of GOs with different thermal reduction temperature and their corresponding FGOs.

The content of C-O bond and C=O bond can be calculated by their corresponding area of curve-fitting peak, as shown in Equation (1) and Equation (2).

$$n(\text{C-O bond}) = n(\text{O/C}) \times A(\text{C-O}) / [A(\text{C-O}) + A(\text{C=O})] \qquad (1)$$

$$n(\text{C=O bond}) = n(\text{O/C}) \times A(\text{C=O}) / [A(\text{C-O}) + A(\text{C=O})] \qquad (2)$$

n(C-O bond): the content of C-O bond in graphene sheet.

n(C=O bond): the content of C=O bond in graphene sheet.

n(O/C): the O/C ratio of sample rGOs and FGOs.

A(C-O): the peak area of corresponding C-O bond in Curve-fitting of XPS O 1s spectra.

A(C=O): the peak area of corresponding C=O bond in Curve-fitting of XPS O 1s spectra.

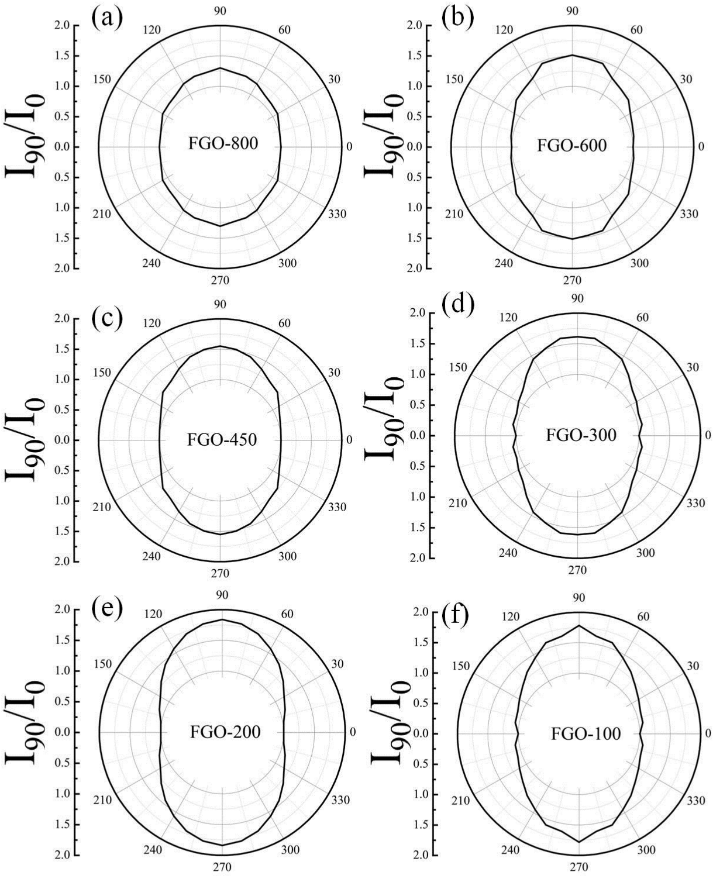

Figure S7. Polar diagrams of absorbance of peaks at 1140cm^{-1} for FGOs.