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Thermal stability of C-F/C-F_2 bonds in fluorinated graphene detected by in-situ heating infrared spectroscopy

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Details about in situ Fourier transform infrared (FTIR) spectroscopy combining with moving-window two-dimensional (MW2D) technique and 2DCS software

The FG powder is sandwiched between two BaF_2 slides, which are cleaned and dried, and then put into an in-situ cell. The prepared sample is subjected to in-situ infrared spectroscopy analysis under nitrogen atmosphere. The temperature range from 30 °C to 650 °C and the heating rate was 5 °C/min. The obtained infrared spectra are corrected by OMNIC software, and then analyzed by two-dimensional correlation infrared software, which is developed by Tao Zhou. Before calculation, we use OMNIC software to perform a linear baseline correction for the infrared spectra in the range of 1610 cm^{-1} - 1495 cm^{-1} and 1400 cm^{-1} -1000 cm^{-1}.

The 2DCS software we use was developed by Professor Tao Zhou from Sichuan University. To ensure the credibility of results, the baseline of spectra in the regions of 1350-1020 cm^{-1} and 1620-1480 cm^{-1} were corrected by linear baseline correction. The window size of PCMW2D spectra was chosen as 11 (2m+1). In the PCMW2D correlation spectra, the red and blue areas represent positive and negative correlations, respectively.

F/C ratio and I_{1219}/I_{1528} datas of FGs

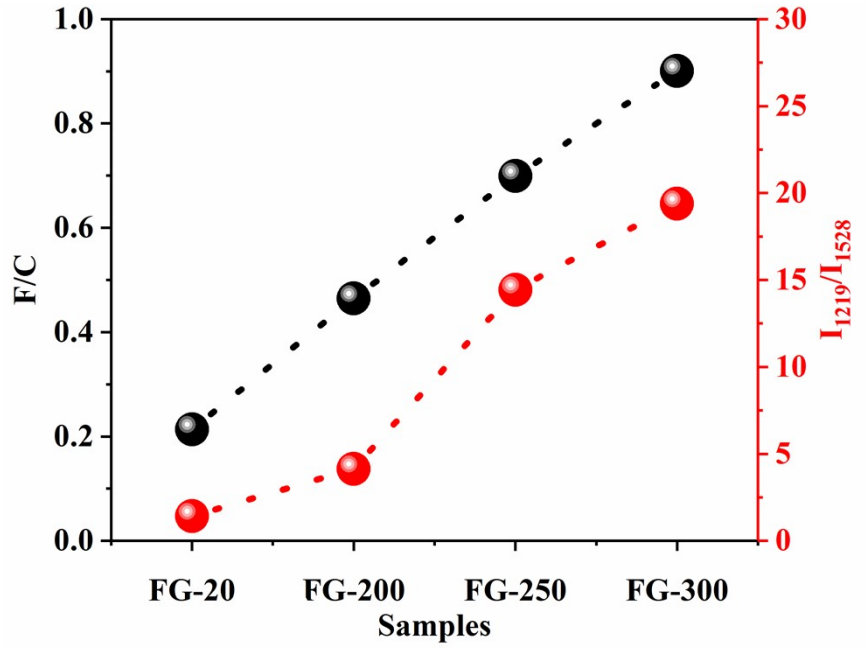

Figure S1. The F/C ratio calculated from XPS spectra and I_{1219}/I_{1528} calculated from FTIR spectra of FG samples with different fluorination temperature.

TGA and DTG data of graphene raw materials

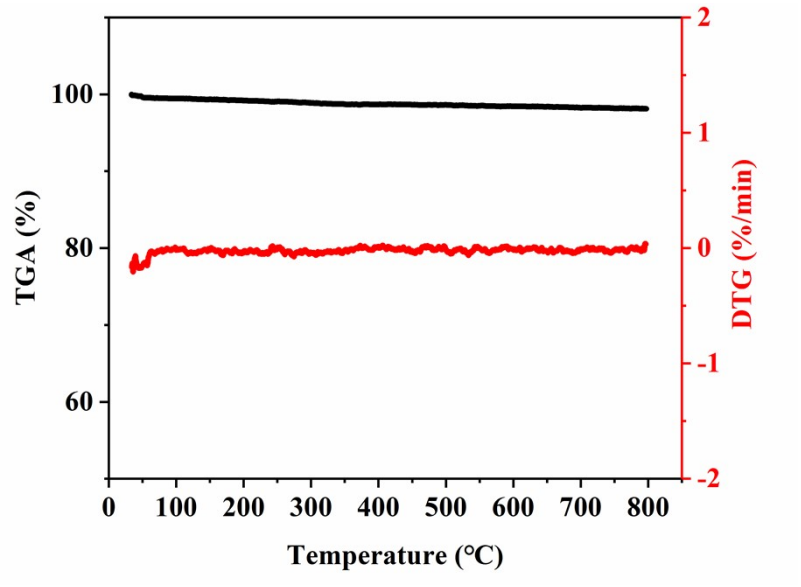

Figure S2. TGA and DTG curves of G.

AFM images of graphene and FG-300

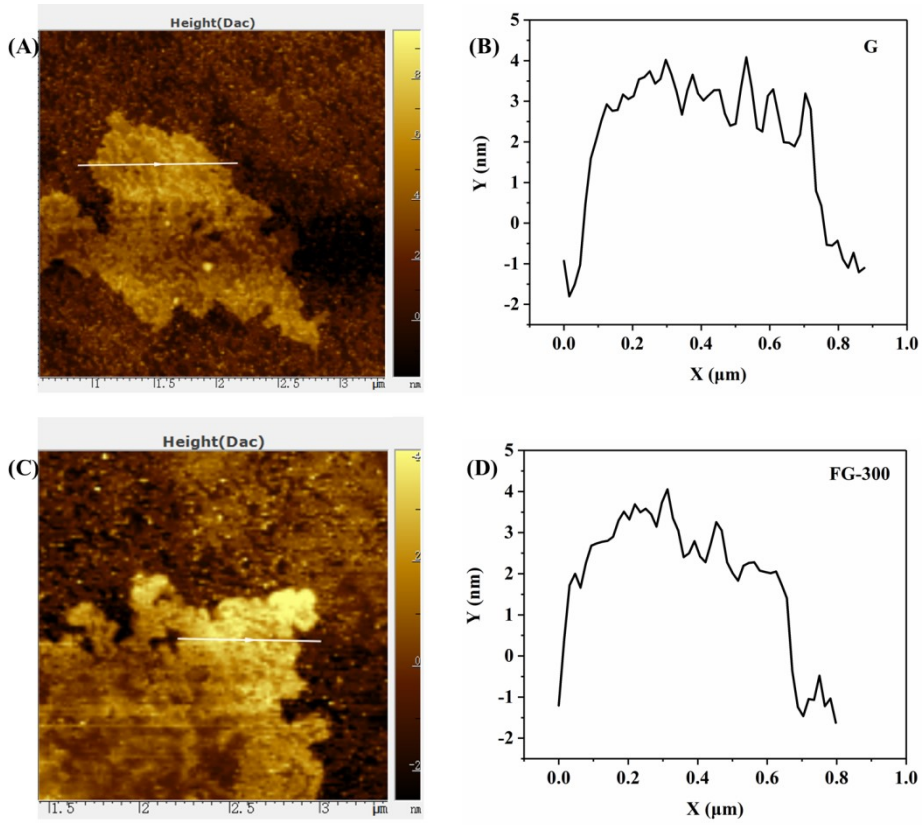

Figure S3. AFM images of graphene (A, B) and FG-300 (A, B).

Atomic Force Microscopy (AFM) test is carried out by using the SmartSPM instrument (AIST-NT, Inc., Novato CA, USA). For AFM test, 1 mg graphene or fluorinated graphene is ultrasonically dispersed in 20 ml ethanol, and then centrifuged at 8000 rpm for 1 minute. The cleaned Si wafer is immersed in the supernatant for seconds. Finally, the prepared silicon wafer loaded with CNFs was tested using the AFM tapping mode.

TEM images of FG-20, FG-200 and FG-300

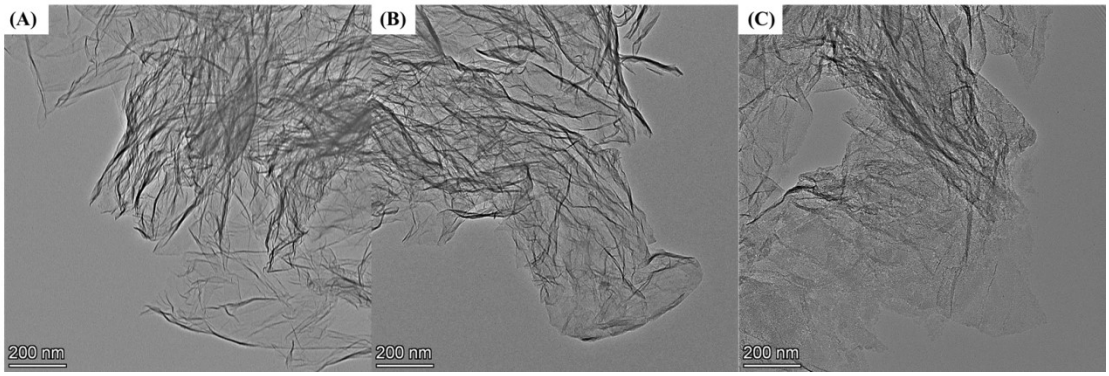

Figure S4. TEM images of FG-20 (A), FG-200 (B) and FG-300 (C).

PCMW2D synchronous spectra in the regions of 1300-1220 cm^{-1} of FG-300

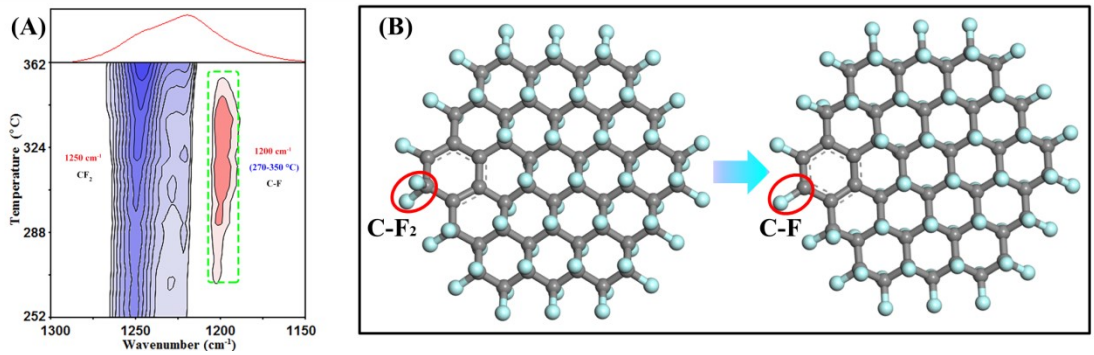

Figure S5. (A) The PCMW2D synchronous spectra in the regions of 1300-1150 cm^{-1} calculated from the dynamic FTIR spectra of FG-300; (B) schematic diagram of the transition of C-F_2 bond adjacent to the congjugated structure transforming into C-F bond.

It can be seen that after the blue correlation peak appears at 1250 cm^{-1}, red correlation peak appears at 1200 cm^{-1} (270-350 °C). This indicates that the C-F bonds are formed in the defluorination process of C-F_2. Therefore, the C-F2 bonds will release an F atom during the annealing process and form an edge C-F bond (Fig S5B). The DFT calculation results show that the bond energy of C-F in the C-F2 adjacent to the conjugated structure is 76.3 Kcal/mol, while the bond energy of the edge C-F bond adjacent to the conjugated structure is as high as 102.1Kcal/mol. This further proves the speculation of the transition from C-F_2 to C-F.

Structures of FGs with different kinds of C-F bonds

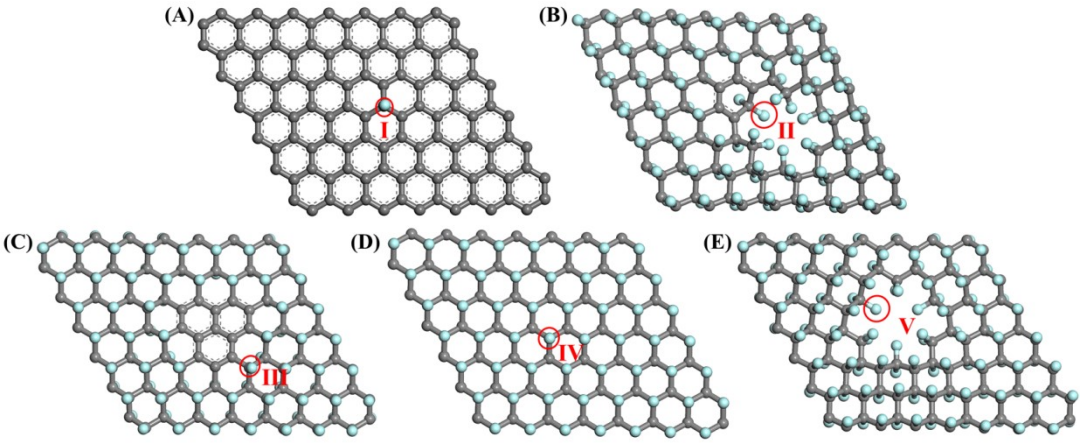

Figure S6. The structures of FGs with five kinds of C-F bonds after optimization.

PCMW2D synchronous spectra in the regions of 1580-1495 cm^{-1} of FG-300

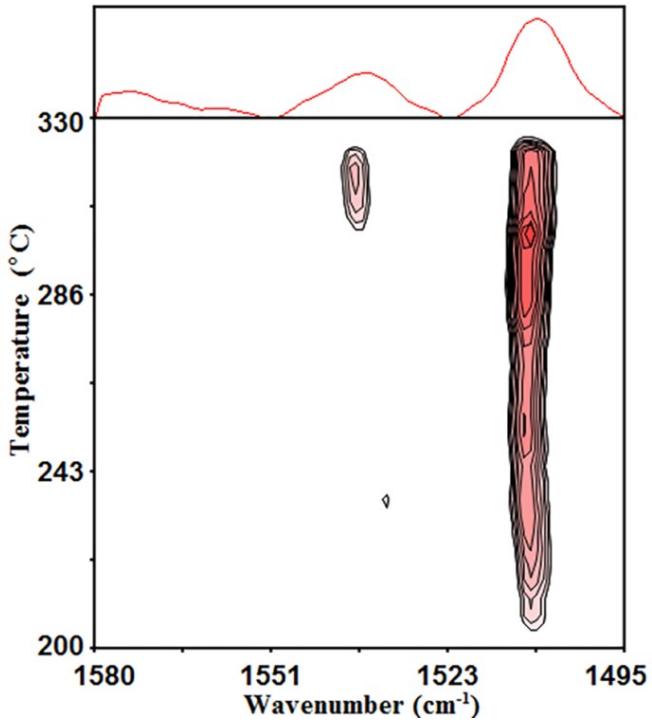

Figure S7. The PCMW2D synchronous spectra in the regions of 1580-1495 cm^{-1} calculated from the dynamic FTIR spectra of FG-300.

FG structures with different sizes of conjugated regions

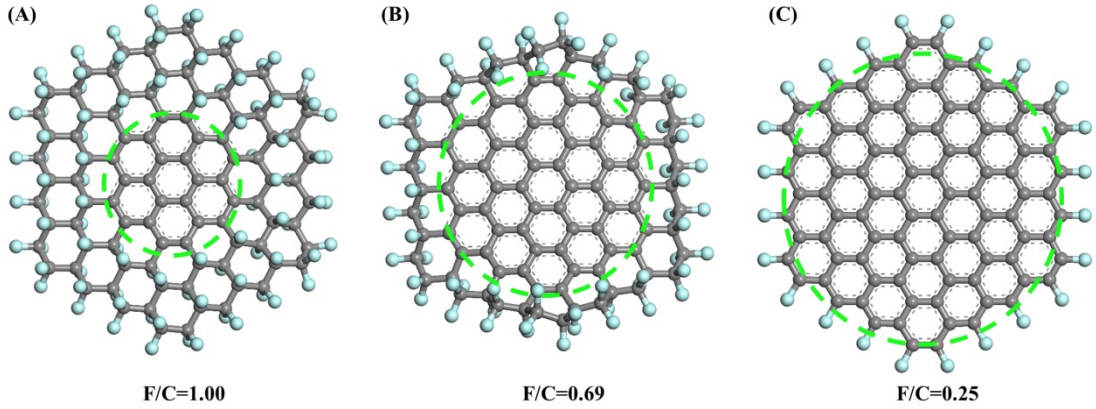

Figure S8. FG structures with different sizes of conjugated regions.

Table S1. C1s data of FGs.

	293.0 eV	291.8 eV	290.0 eV	287.0 eV	285.2 eV	284.4 eV
FG-20	1.43	3.46	20.83	14.00	39.06	21.22
FG-200	1.69	8.37	43.39	12.94	17.41	16.20
FG-250	1.33	8.57	60.98	8.12	11.13	9.87
FG-300	1.32	20.17	71.41	1.77	3.50	1.83

Table S2. Data of peak fitting of infrared characteristic absorption peaks.

	1311 cm^{-1}	1250 cm^{-1}	1219 cm^{-1}	1165 cm^{-1}	1112 cm^{-1}	1050 cm^{-1}
FG-20	0.69	20.16	16.53	19.42	22.98	22.22
FG-200	7.53	23.78	17.56	25.76	11.99	13.38
FG-250	12.16	7.25	52.63	13.13	11.52	3.31
FG-300	12.63	5.79	67.65	6.20	6.37	1.35

Reference:

1. H. Arnolds, *Progress in Surface Science*, 2011, **86**, 1-40.
2. P. Zhang, Y. X. Chen, J. Cai, S. Z. Liang, J. F. Li, A. Wang, B. Ren and Z. Q. Tian, *Journal of Physical Chemistry C*, 2009, **113**, 17518-17526.