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Supporting Information

Friedel-Crafts reaction of fluorinated graphene for high-yield arylation of graphene

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Experimental section

Materials

The graphene (G) were purchased from The Sixth Elementary (Changzhou) Materials Technology Co., Ltd. The preparation method of fluorinated graphene (FG) was referred to our early work[1, 2] by fluorination of G using F_2/N_2 mixed gas. Methylbenzene (MB), chlorobenzene (CB), commercial polystyrene (PS), aluminium trichloride anhydrous ($AlCl_3$) and tetrachloromethane (CCl_4) were purchased from the Adamas Reagent, Ltd with commercially analytical grade. All other chemical reagents were commercially analytical grade and used without further purification.

Preparations

The aryl molecules that would react with FG were chosen as methylbenzene (MB), chlorobenzene (CB) and polystyrene (PS, M_n=47659 g/mol, M_w/M_n=2.73). The Friedel-Crafts reaction of FG with aromatic molecules was performed in aryl solvent itself for MB and CB. For PS group, 0.5 g commercial PS was first dissolved in 30 mL CCl_4 in the aid of sonication and stirring. Typically, 1.33 g of $AlCl_3$ (10 mmol) was added into 30 mL of MB, CB, or CCl_4 containing PS, followed by 1 h of stirring under nitrogen atmosphere for adequate dissolution or dispersing. After that, 60 mg of FG (2 mmol) was respectively added into three mixtures to perform the reactions at 80 °C for 12 h. As reactions proceeded, all mixtures became black gradually, and the possibly generated acidic gases were removed through condenser pipe, $CaCl_2$ drying tube and alkaline absorbent. When reactions were terminated, the mixtures were subsequently transferred into a suction filtration apparatus (0.22 μm, PTFE membrane). The filter cake samples were repeatedly washed with copious amounts of chloroform to remove the absorbed aromatic agents. Subsequently, the cakes were re-dispersed in 100 mL of mixed solution that contained hydrochloric acid, water and ethanol. The mixed solutions were filtered to removel impurities related to $AlCl_3$. Finally, the filtered powder samples were dried in a vacuum at 80 °C for 6 h. The products were named as FG-MB, FG-CB and FG-PS, corresponding to reactions of FG with MB, CB and PS. For a comparison, graphene (G) were also employed for reaction with MB, CB and PS, obtaining corresponding samples G-MB, G-CB and G-

PS. For aother control group, FG reacted with only $AlCl_3$ in CCl_4 under same conditions, obtaining FG-$AlCl_3$ sample.

Characterizations

X-ray photo-electron spectroscopy (XPS) which was carried out on a Kratos ASAM 800 spectrometer (Kratos Analytical Ltd, UK) at a base vacuum higher than 10^{-6} Pa under non-monochromatized Al Ka (1486.6 eV) X-ray source (a voltage of 15 kV and a wattage of 250 W) radiation. The Fourier transform infrared (FT-IR) spectrum was recorded using a Nicolet 560 Fourier transform spectrometer in the range 4000-400 cm^{-1}. The Raman spectrum was obtained by using a LabRAM HR Raman spectrometer with an excitation wavelength of 532 nm. Elemental analysis (EA) was performed with the ELEMENT vario EL cube (German). Thermo-gravimetric analysis (TGA) was performed on a Netzsch 209 TG instrument under a N_2 atmosphere or air atmosphere at a heating rate of 5 °C/min from 30 to 800 °C. Wide angle X-ray powder diffraction data (XRD) were collected at room temperature with an Ultima IV powder diffractometer (Rigaku Corporation) using Cu Ka radiation (k = 0.154 nm, U = 40 kV, I = 40 mA) over the angular range 5-50° with a step size of 0.02°. The fine microstructures of sample were characterized by using scanning electron microscopy (SEM; FEI Co., Hillsboro, OR, USA), high-resolution transmission electron microscopy (Tecnai G2 F20 S-TWIN) with an accelerating voltage of 200 kV, and AFM carried out with a NanoScopeMultiMole & Explore from Vecco Instruments, using tapping mode. Electron paramagnetic resonance (EPR) measurements were carried out on Bruker EPR EMX Plus spectrometer (Bruker Beijing Science and Technology Ltd, USA) with an ER4119HS resonator type, operating at frequency of 9.842 GHz. EPR spectra were recorded at 2 mW microwave power with 1 G modulation amplitude and 100 kHz frequency modulation at room temperature.

Computational details

DFT calculations of aryl molecule were performed in DMol3 module implemented in Materials Studio 8.0 to calculate Mulliken and ESP charges. Geometry optimization and population analysis were performed by using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE), and the basis was set as DNP with basis file 3.5. The self-consistent-field calculation had convergence criteria of 10^{-5} Hartree.

Supplementary Figures

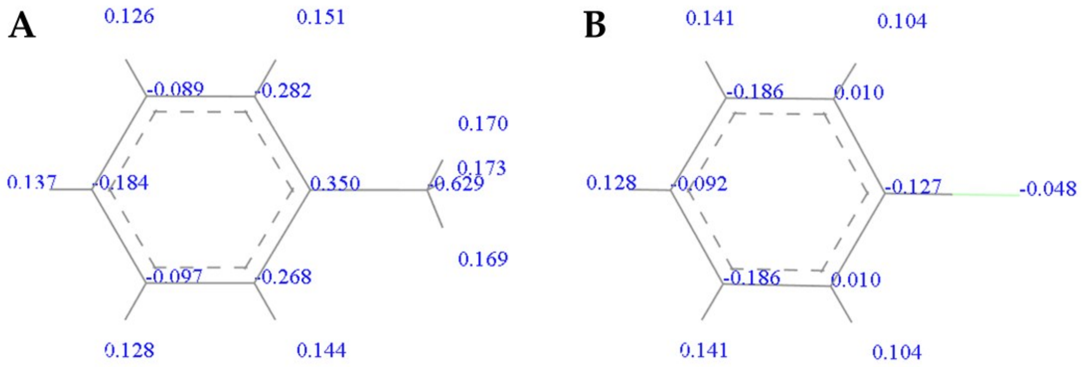

Fig. S1 ESP charges of aryl molecule methylbenzene (A) and chlorobenzene (B).

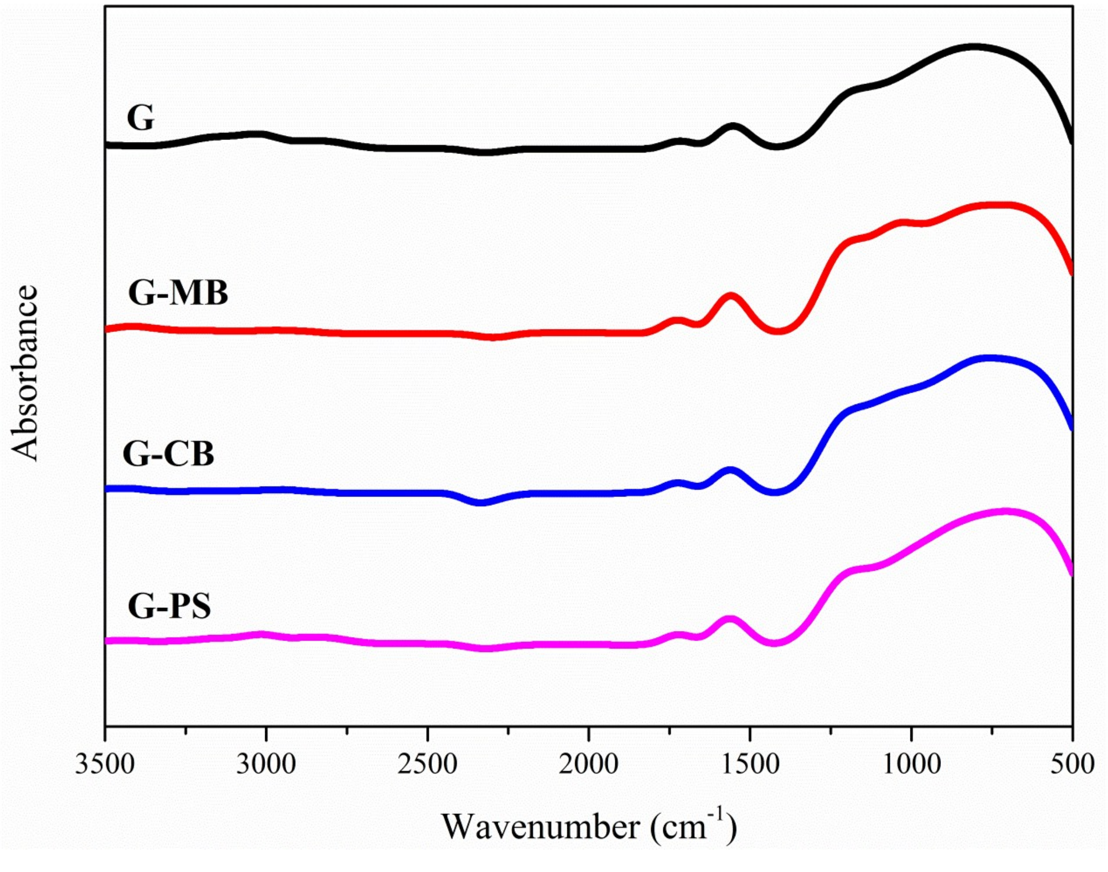

Fig. S2 FT-IR spectra comparison of G and G derivatives after reactions.

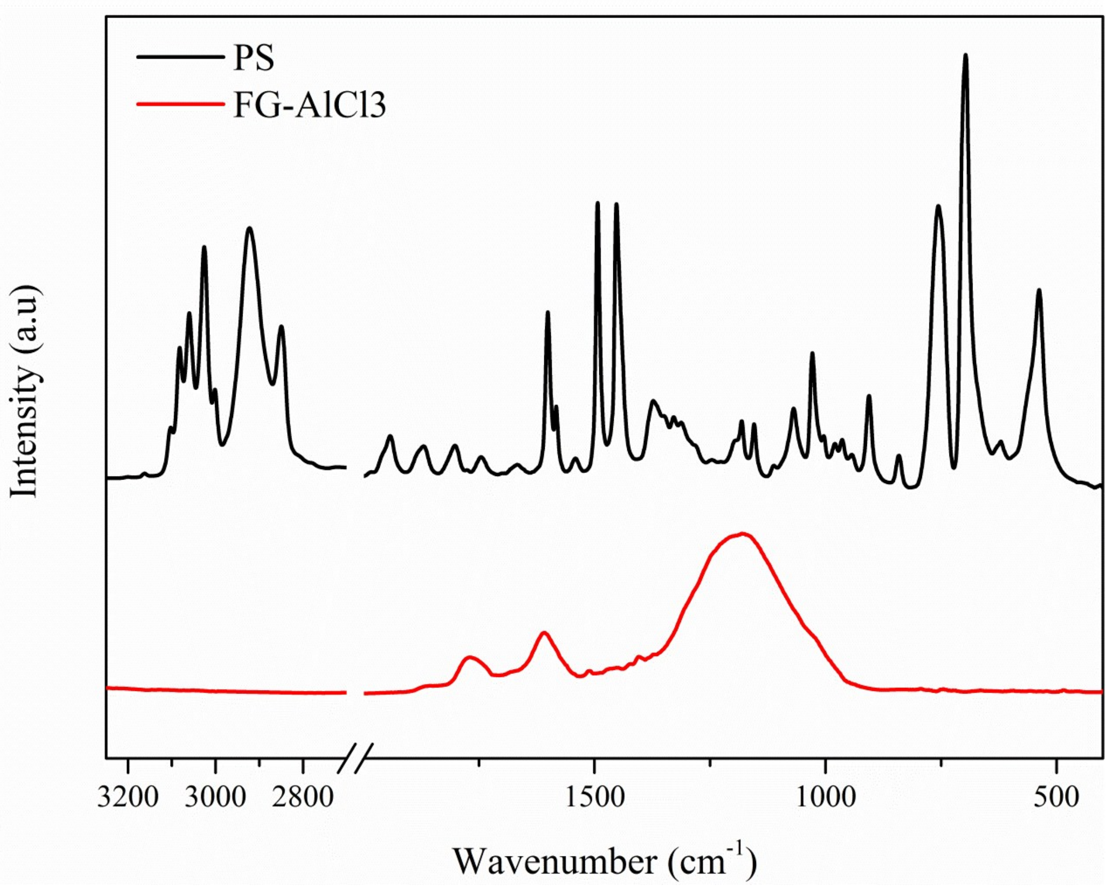

Fig. S3 FT-IR spectra of polystyrene (PS) and FG-$AlCl_3$.

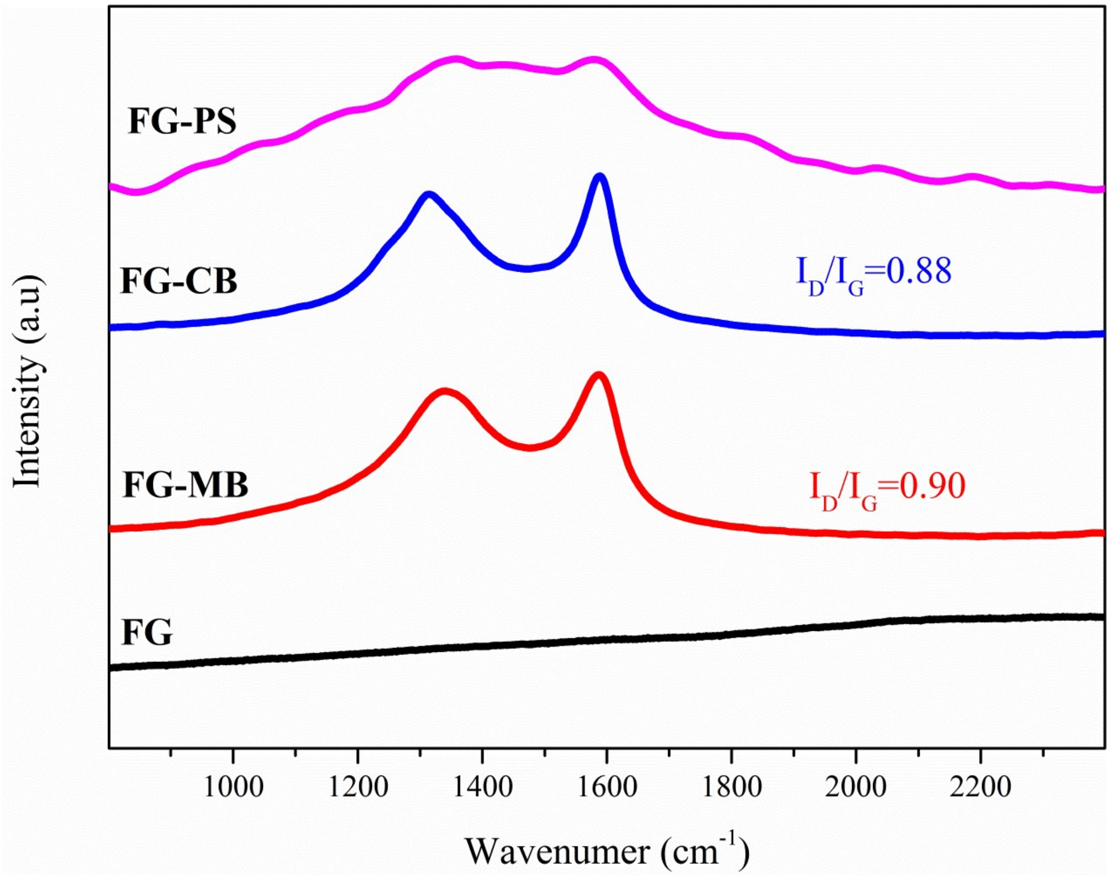

Fig. S4 Raman spectra of FG and graphene derivatives.

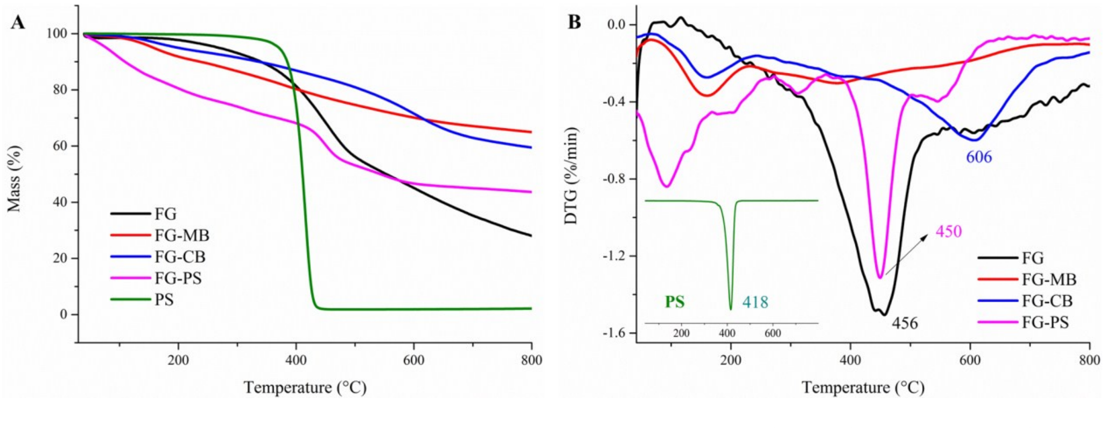

Fig. S5 TGA (A) and DTG (B) curves of pristine FG, graphene derivatives and PS.

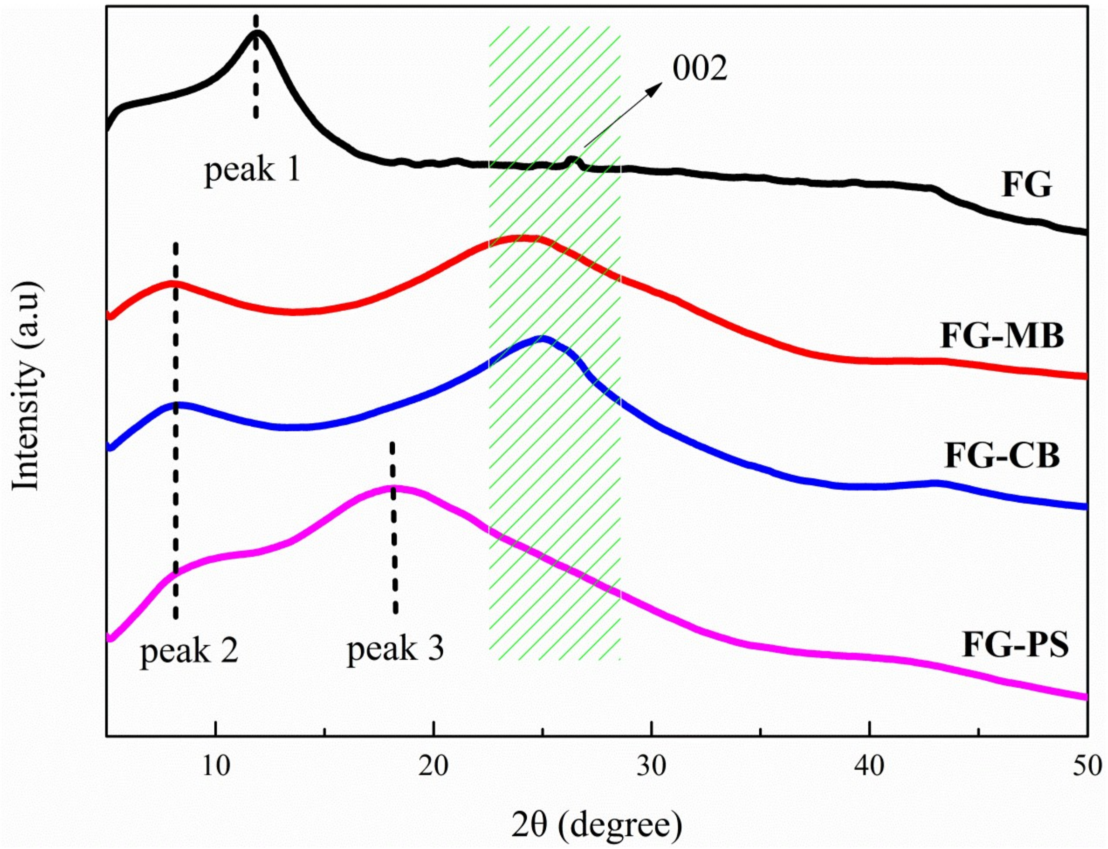

Fig. S6 XRD patterns of FG and FG derivatives.

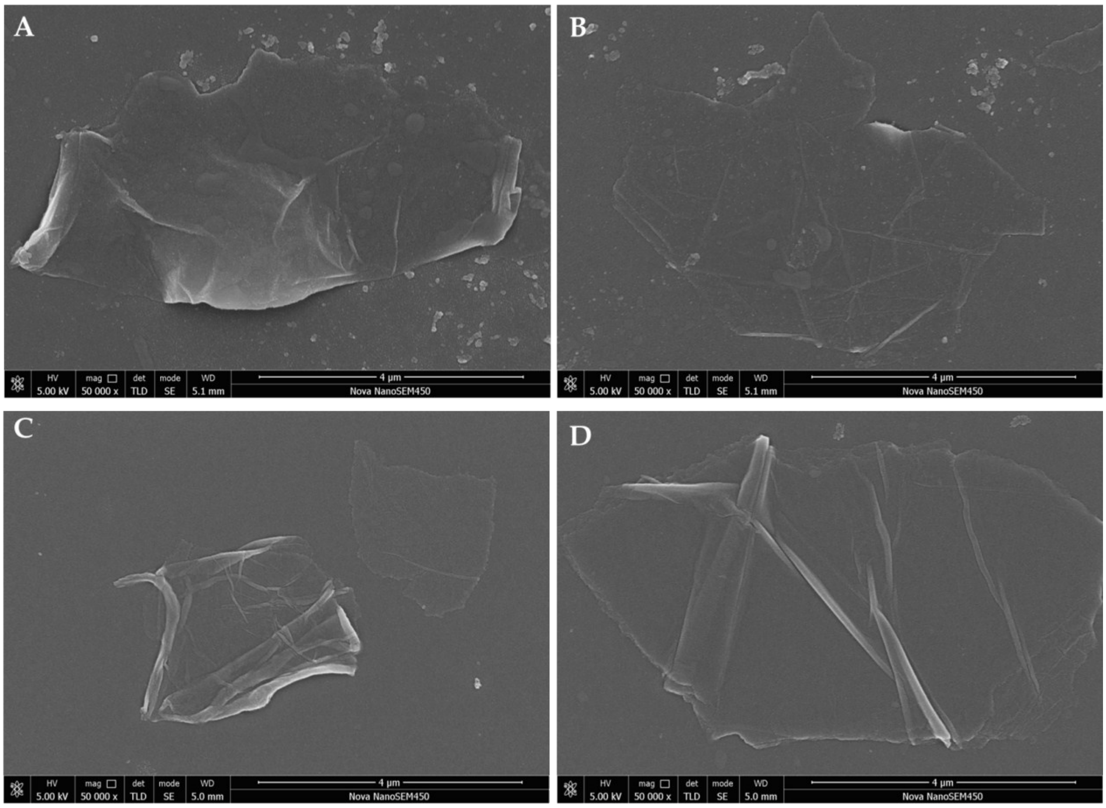

Fig. S7 SEM images of FG (A, B) and FG-CB (C, D) samples.

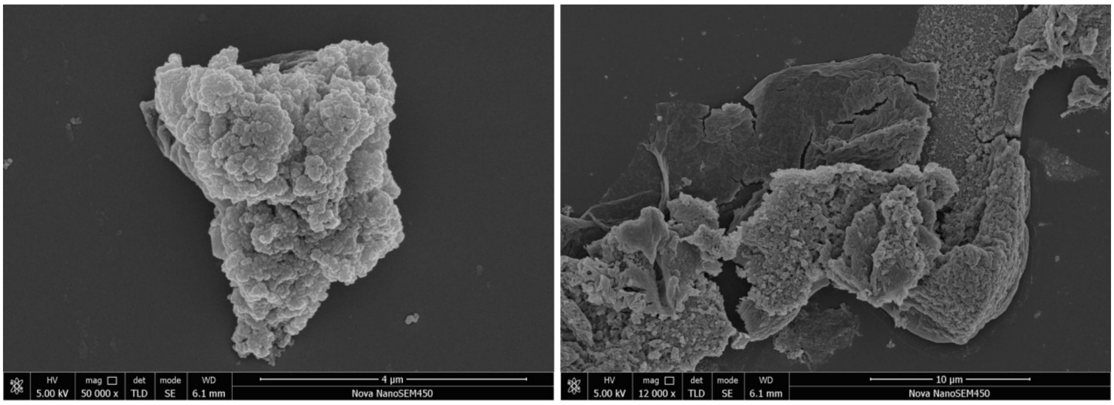

Fig. S8 SEM images of FG-PS sample.

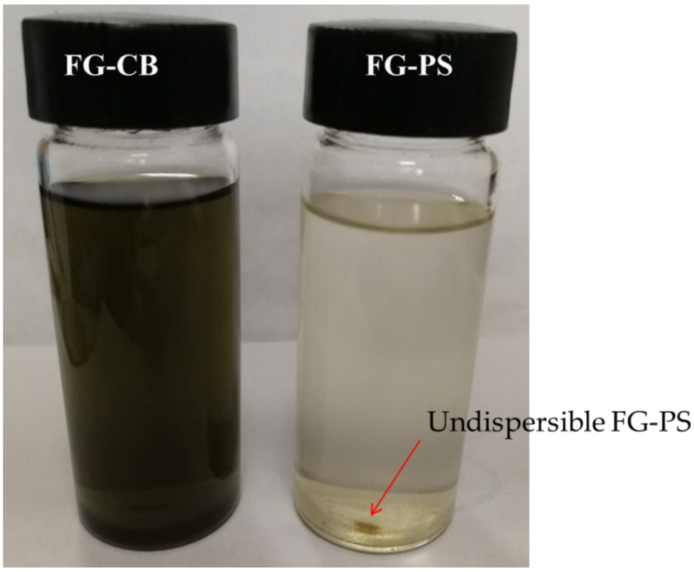

Fig. S9 Dispersibility of FG-CB and FG-PS materials in tetrahydrofuran after sonication.

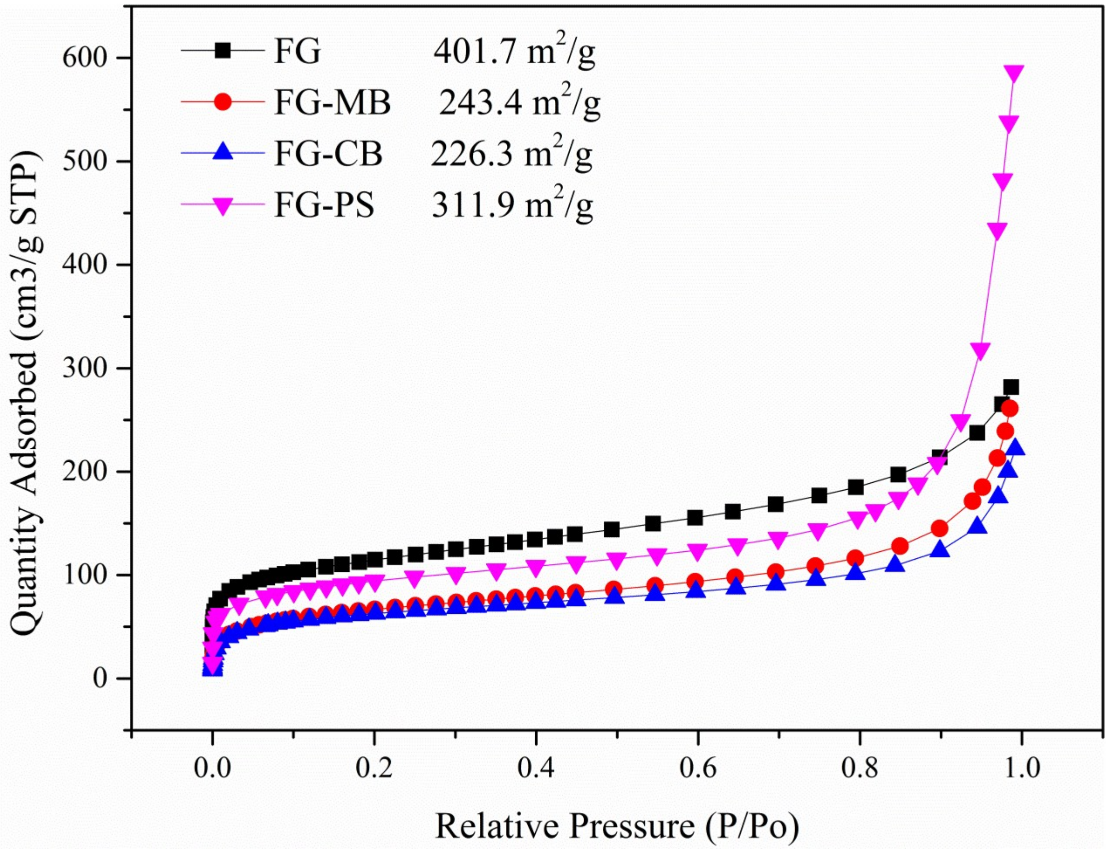

Fig. S10 Nitrogen sorption isotherms curves of FG and three graphene derivatives.

The presented value corresponds to specific surface area of FG or graphene derivatives.

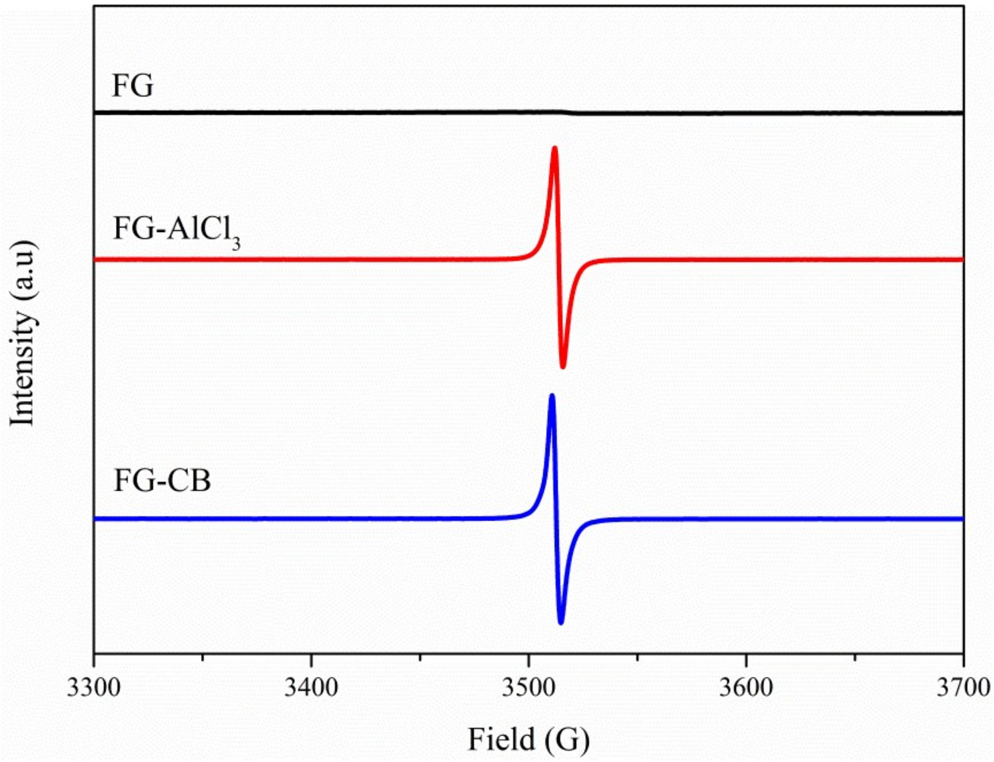

Fig. S11 EPR spectra of FG, FG-AlCl$_3$ and FG-CB samples.

Reference

1. X. Wang, Y. Dai, W. Wang, M. Ren, B. Li, C. Fan and X. Liu, *ACS applied materials & interfaces*, 2014, **6**, 16182-16188.
2. W. Lai, X. Wang, J. Fu, T. Chen, K. Fan and X. Liu, *Carbon*, 2018, **137**, 451-457.