Supporting information

Suzuki-Miyaura reaction of C-F bond in fluorographene

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Materials

The graphene was obtained from the Sixth Elementary Materials Technology Co., Ltd (Changzhou). Fluorinated graphene was prepared by direct heat fluorination of graphene according to our early work. In the initial stage of the reaction, the fluorine content increases with exposure time to F_2/N_2 mixed gas, thus we can obtain FG with F/C 0.348 by shorting reaction time. 3-thiopheneboronic acid (TBA), 5-Pyrimidinylboronic acid (PyBA), phenylboronic acid (PBA), tripotassium orthophosphate (K_3PO_4) and tetrakis(triphenylphosphine) palladium (0) [$Pd(PPh_3)_4$] were purchased from the Adamas Reagent, Ltd.   Commercial analytical grade 1,4-dioxane was purchased from Kelong Chemical Reagent Co., Ltd (Chengdu). All reagents were employed without further purification.

Preparations

In the Suzuki coupling reaction, K_3PO_4 (0.4288g, 2mmol) and organic boric acid (1mmol) were solubilized in 20ml 1,4-dioxane. Subsequently, FG (31mg, ~1mmol) was added to the above solution and the mixture was sonicated, follwed by degassed by a stream N_2. Afterward, $Pd(PPh_3)_4$ (57.8mg 5%mmol) was quickly added to the solution and the suspension was vacuum-degassed and back-filled with N_2 three times. The reaction mixture was stirred at 100 °C for 22h. Finally, the mixture was separated by PTFE membrane (0.22μm), the filter cake sample was respeatedly washed with copious water/ethyl alcohol, dichloromethane to remove excess K_3PO_4 and unreacted organic boric acid. In order to remove the residues of Pd, the material was re-suspended in mixed solvents containing hydrochloric acid (HCl) aqueous solution and ethyl alcohol and the solution was filtered as previously. Finally, the precipitate was repeatedly suspended in water/ethyl alcohol and separated by centrifugations, the desired product was collected after centrifugation and was dried in a vacuum at 80°C for 6h.

To ensure adequate purification of the washed black precipitate, the UV-vis absorption spectra of the supernatant were recorded. The washing was repeated until there is no detectable difference in the spectrum of the supernatant after two consecutive washes. In addition, the product was then subjected to Soxhlet extraction 2 days with ethyl alcohol, its sulphur content is approximate to that of product without Soxhlet extraction. Take all into consideration, the products wased by our procedures were considered to be pure, without the absorbed organic boric acid.

Characterizations

X-ray photoelectron spectroscopy (XPS) was performed with a Kratos ASAM 800 spectrometer at a base vacuum pressure higher than 10^{-6} Pa, equipped with a non-monochromatized Al Ka (1486.6 eV) X-ray source (a voltage of 15 kV and a wattage of 250 W) radiation. Elemental analysis (EA) measurement was performed with the ELEMENT vario EL cube (German). The Fourier transform infrared (FT-IR) measurements were carried out on a Nicolet 560 Fourier transform spectrometer. The Raman spectra were recorded on a LabRAM HR Raman spectrometer

with an excitation wavelength of 532 nm. Thermogravimetric analysis (TGA) was performed using a Netzsch 209 TG instrument in N_2 flow at a heating rate of 5 °C/min from 30 to 800 °C. Wide angle X-ray powder diffraction data (XRD) were recorded at room temperature with an Ultima IV powder diffractometer (Rigaku Corporation) using Cu Ka radiation (λ=0.154 nm, U = 40 kV, I = 40 mA) over the angular range 10-80° with a step size of 0.02°. Microscopic images were obtained by TEM (Tecnai G2 F20 S-TWIN) with an accelerating voltage of 200 kV. STEM-HAADF (high-angle annular dark-field imaging) analyses for EDS (energy-dispersive X-ray spectroscopy) mapping of elemental distributions on the products were performed with a FEI Titan HRTEM microscope operating at 80 kV. The radical signals were captured using Electron paramagnetic resonance (EPR) with Bruker EPR EMX Plus spectrometer (Bruker Beijing Science and Technology Ltd, USA), operating at frequency of 9.842 GHz and 2 mW microwave power. ESI-MS were performed with Shimadzu LCMS-IT-TOF.

Electrochemical measurements were performed in a conventional three-electrode cell with a plate-like Pt counter electrode using a CHI 602E Potentiostat and Jiangfen's Rotating Disk Electrode (ATA-1B). The cyclic voltammetry (CV) curves of the sample were recorded in alkaline solution with a Hg/HgO reference electrode or Hg/Hg_2SO_4 (MSE) as the reference electrode in acid solution. The methanol tolerance of FG-TBA was measured with a rotating disk electrode (RDE) in 0.1M $HClO_4$ solution with 0.5 M methanol using the MSE reference electrode. The working electrode was prepared by casting 20 μL of 2 mg/ml ink onto a pre-polished glassy carbon disk (GC, 4 mm in diamete). Based on the integrated peak area of Pd 3d from XPS measurements, mtal loading of FG-TBA samples on the electrode surface was 46 μgcm^{-2}.

In order to estimate the functionalization degree, we analyse the information providied from XPS techniques. The molar % of the functional groups [mol_{fn}] was calculated from at% in S/N (from XPS), the molar % of the lattice carbons [mol_{graph}] was considered equal to the total at% in carbon minus the molar % of the carbons of the functional groups (calculated from mol_{fn}). According, degree of functionalization (D.F) was calculated based on the formula:

$$D.F = \frac{mol_{fn}}{mol_{graph}} = \frac{mol_{fn}}{mol_C - 4mol_{fn}}$$

The utilization of F (η) was estimated based on the the formula:

$$\eta = \frac{mol_s/(mol_C - 4mol_S)}{mol_F^i/mol_C^i - mol_F/(mol_C - 4mol_S)}$$

where $[mol_F^i]/[mol_C^i]$ is F/C of initial FG.

Supplementary Figures

Table. S1 Elemental composition of FG, FPG and hFG from XPS

	FG	FPG	hFG
C	66.22	68.09	52.26
F	23.04	22.36	47.08
O	10.75	9.55	0.66

	F/C	0.348	0.328	0.901

	EA (wt%)				XPS(at%)				
	N (%)	C (%)	H (%)	S (%)	F (%)	C (%)	O (%)	S/N (%)	F.D
FG-TBA	1.21 (1.57)	55.56 (56.07)	1.17 (1.52)	4.01 (4.15)	4.63	78.43	13.86	1.94(S)	2.7%
FG-PBA		73.30	2.20		4.32	85.83	8.98		
FG-PyBA					4.34	85.30	9.25	1.03(N)	0.63%
FPG-S	3.31	74.08	3.33	1.00					

Table. S2 Elemental composition of FG and its derivatives based on XPS and EA data

*The data in ( ) are from the product washed by Soxhlet extractor again
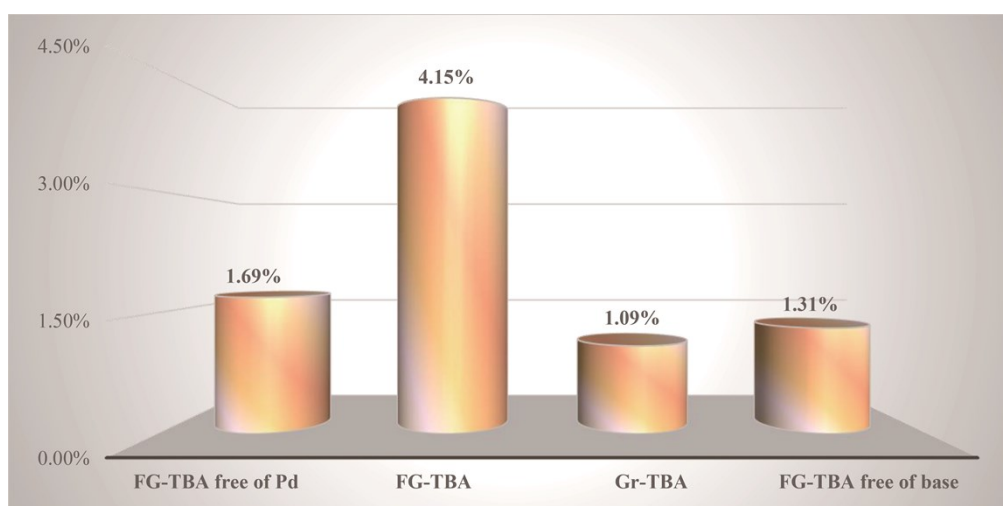
Fig. S1 sulphur content of FG-TBA and materials in control groups from EA
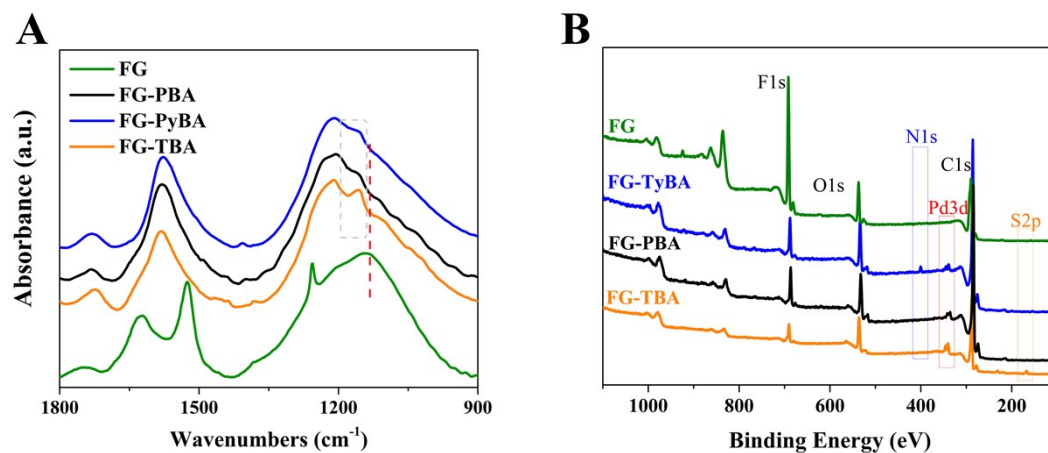
Fig. S2 A) FTIR and B) XPS survey spectra of FG and its derivatives
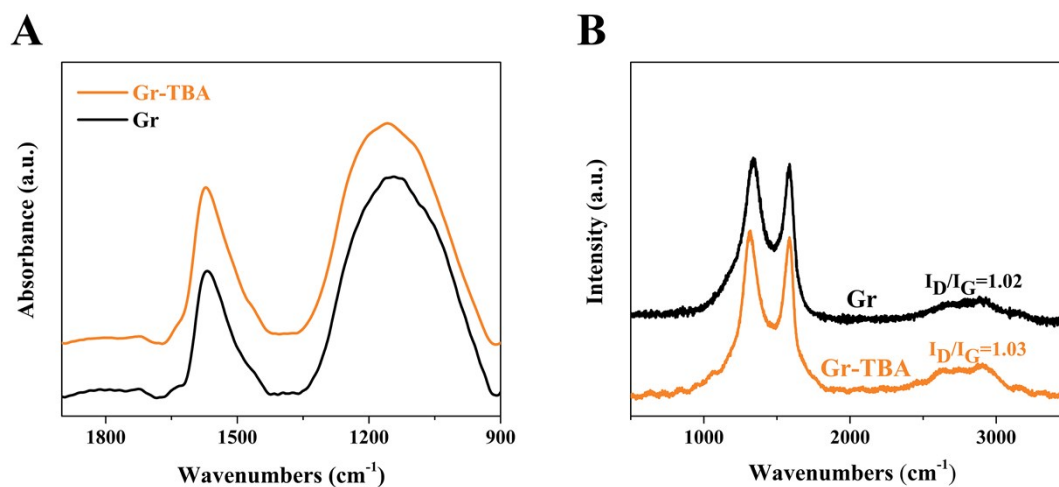
Fig. S3 A) FTIR spectra and B) Raman spectra of Gr and Gr-TBA
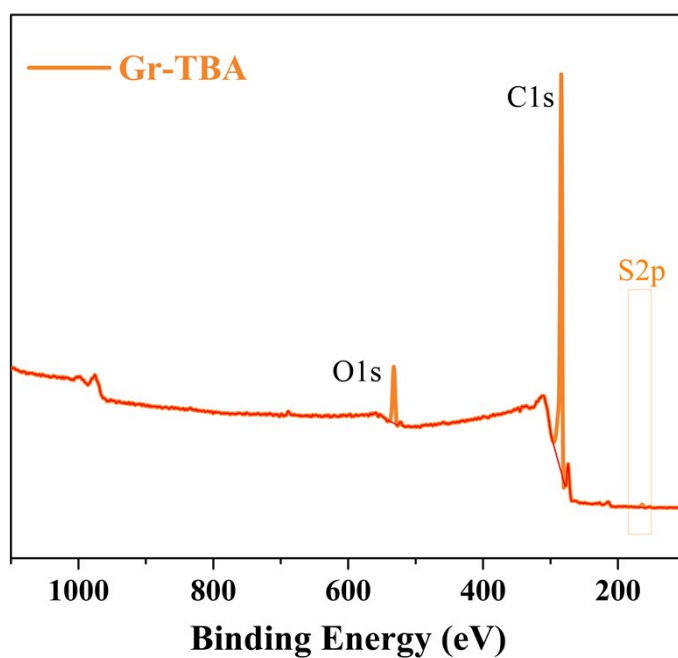
Fig. S4 XPS survey spectrum of FG, and the content of carbon, oxygen and sulfur are 94.4 at%, 5.2 at% and 0.4 at% respectively.
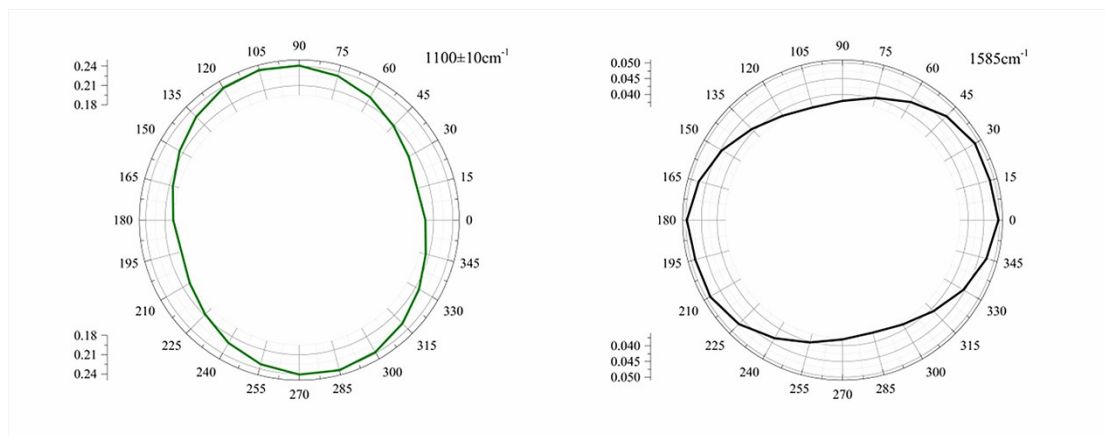
Fig. S5 Polar diagrams of IR absorbance at different positions as a function of angle of polarization, obtained using linearly polarized ATR-IR spectra: 1100±10 cm^{-1}, 1585 cm^{-1}.
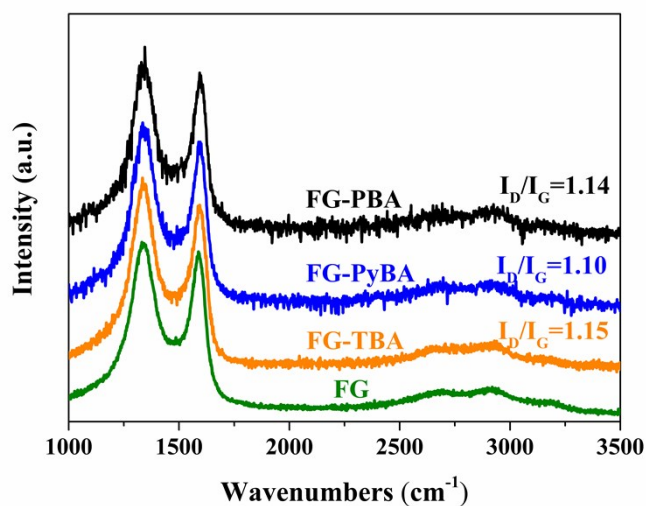
Fig. S6 Raman spectra of FG and its derivatives
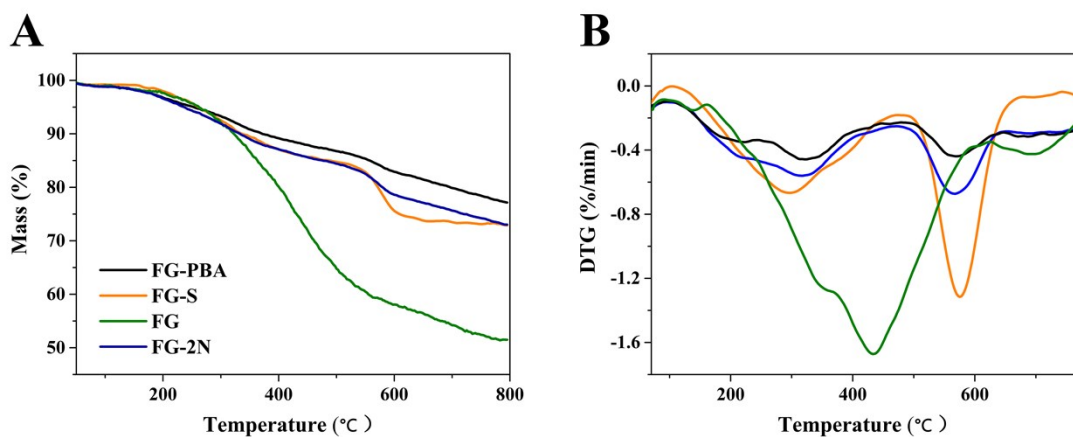
Fig. S7 TGA (A) and DTG (B) curves of FG and its derivatives
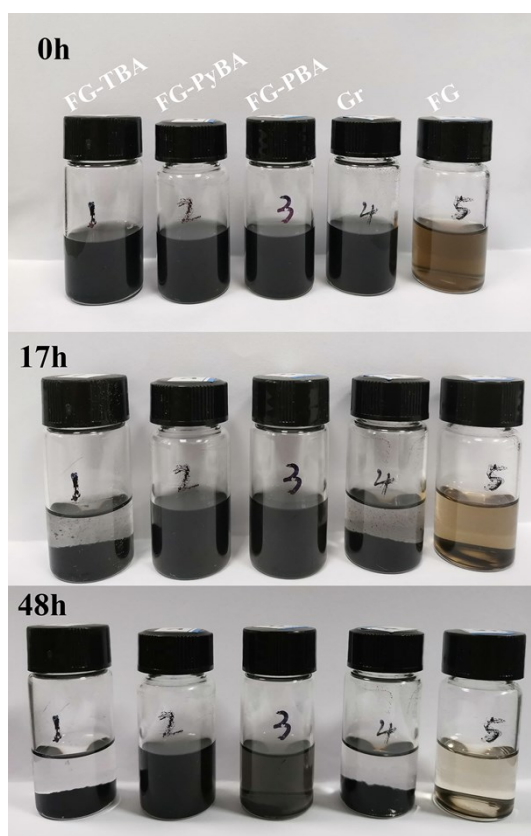
Fig. S8 Digital images of aryl graphene derivatives (e.g. FG-TBA, FG-PyBA, FG-PBA), graphene and FG dispersed in ethanol. The samples were sonicated in the solvent for 10 min and rested for 17 h and 48h before capturing the images.
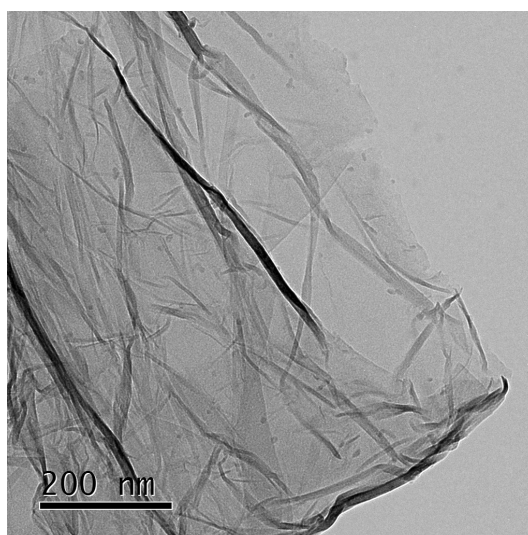
Fig. S9 TEM image of a graphene flake.
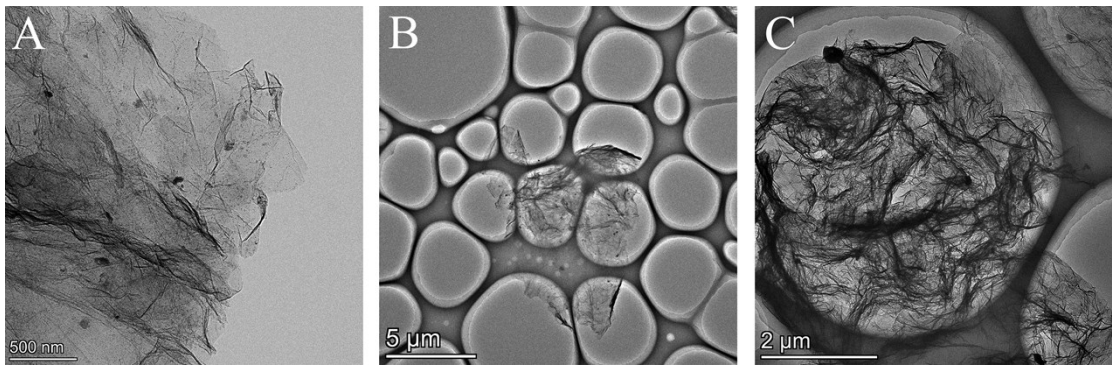
Fig. S10 TEM image of FG-TBA (A）, FG-PyBA (B) and FG-PBA (C)
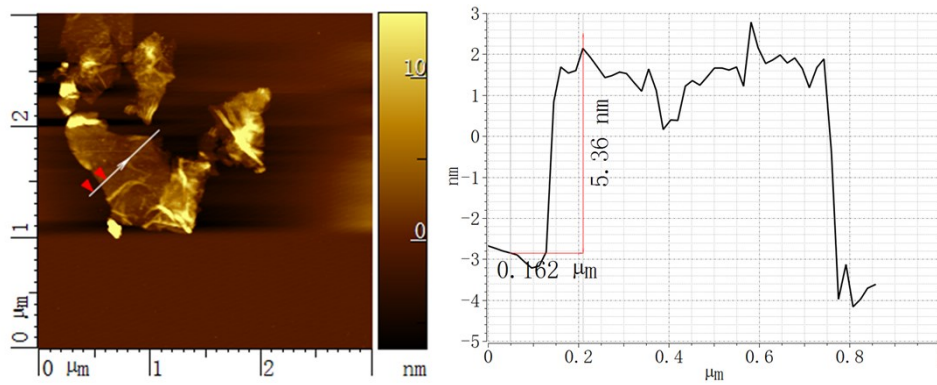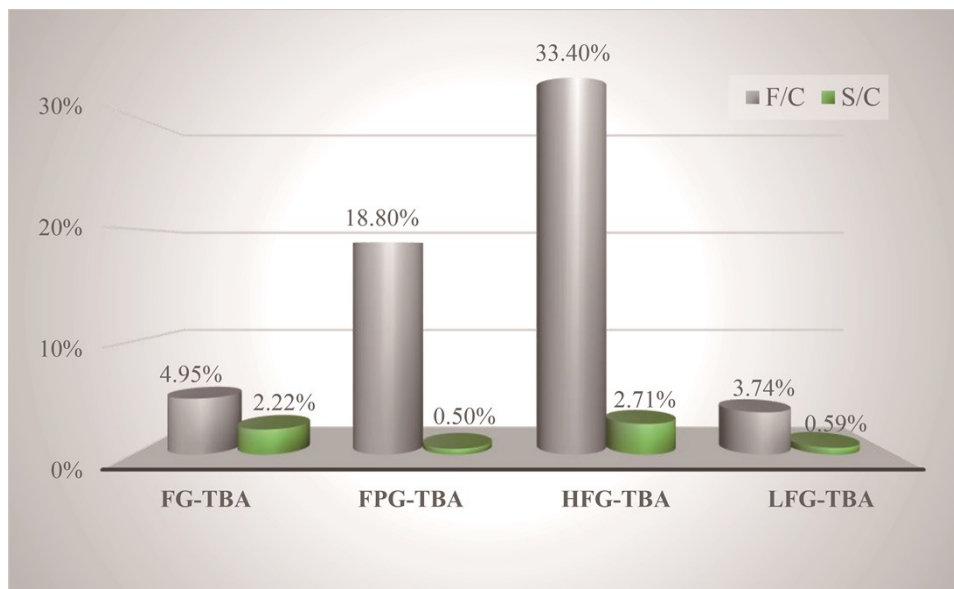

Fig. S11 AFM image and the height profile of FG-TBA.

Fig. S12 Elemental composition of derivatives of FG, FPG and HFG from EDS
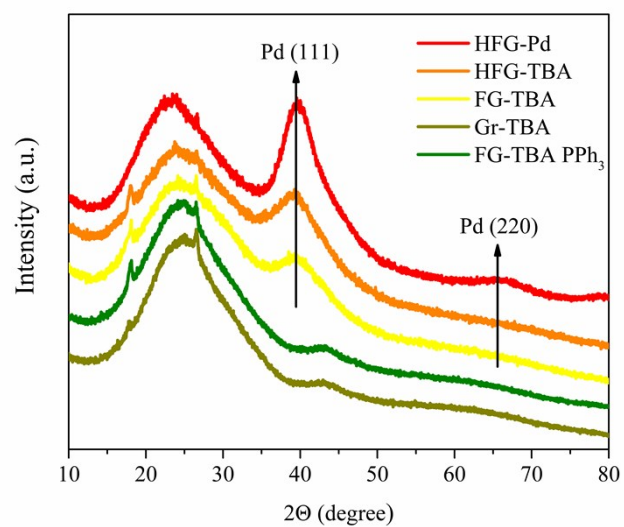
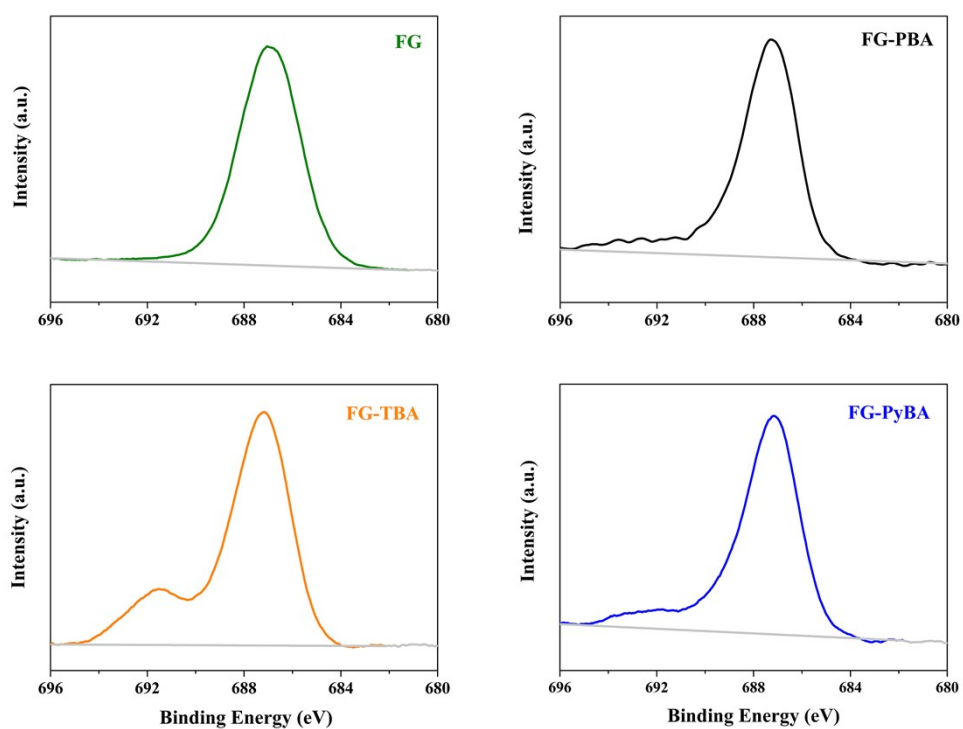**Fig. S13** XRD patterns of FG-TBA, HFG-TBA, HFG-Pd, Gr-TBA and FG-TBAwith excess PPh$_3$

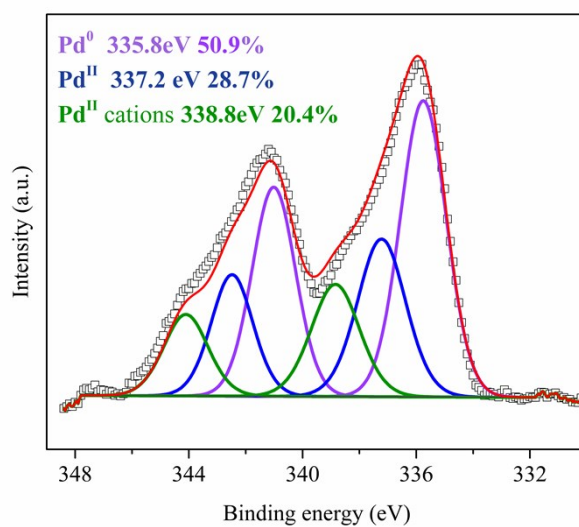**Fig. S14** High-resolution F1s XPS spectra of FG and its derivatives.

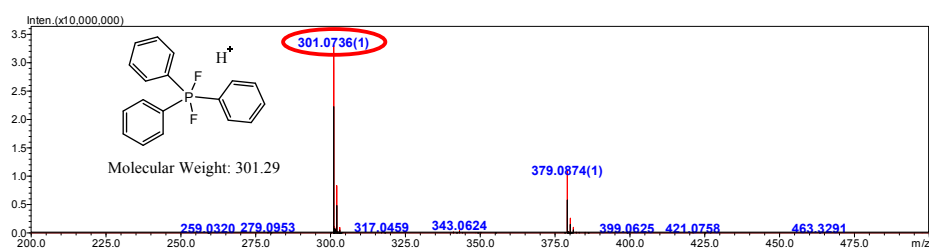**Fig. S15** XPS of Pd 3d core level in FG-PBA.

Fig. S16 ESI-MS data from the supernatant after reaction (positive ion mode)
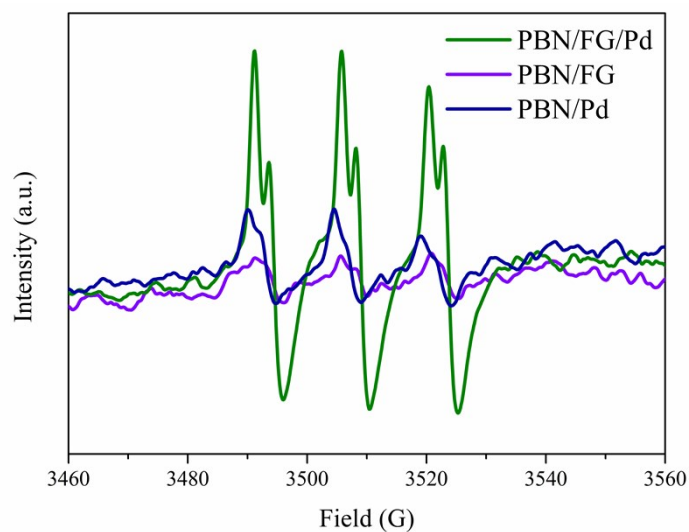

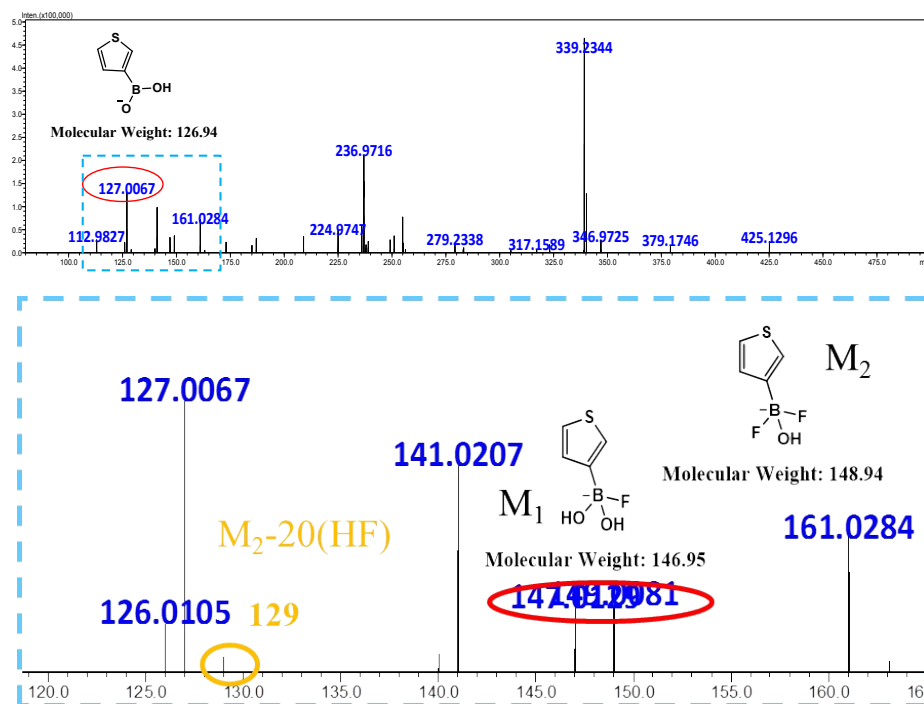**Fig. S17** The PBN spin-tapped EPR spectra with catalyst or FG solely and with catalyst and FG.

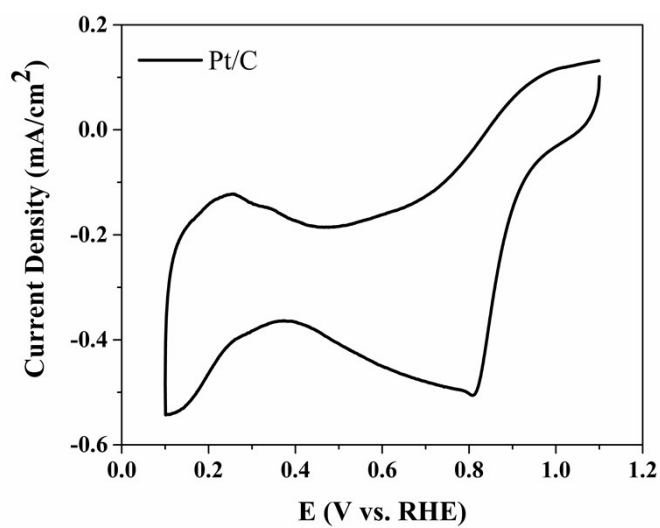**Fig. S18** ESI-MS data from the supernatant after reaction (negative ion mode) and its larger version

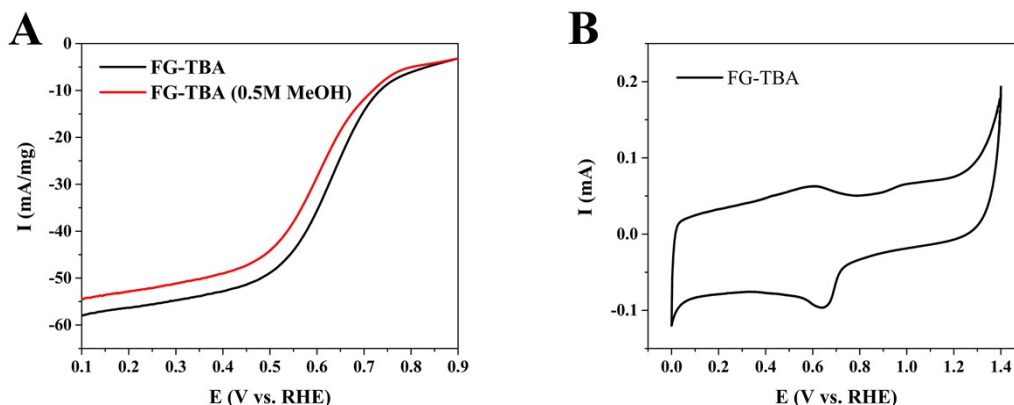**Fig. S19** Voltammogram recorded for Pt/C at a scan rate of 10 mVs^{-1} in an 0.1 M KOH solution saturated with O_2.

Fig. S20 (A) linear scan voltammograms of FG-TBA in 0.1 M $HClO_4$ solution saturated with O_2 and 0.1 M $HClO_4$ solution with 0.5 M methanol saturated with O_2, with a scan rate of 10 mVs^{-1} and a rotation rate of 1600 rpm. The half-wave potential ($E_{1/2}$) of the ORR curves was used to quickly assess the catalyst activity. $E_{1/2}$ is defined as the potential at which the ORR current is the half of that measured at 0.1 V, considering that the diffusion-limited current is practically reached at that potential for the sample discussed in this work. In a solution containing methanol, the half-wave potential of the FG-TBA catalyzed ORR is 96.3% of that without methanol. Therefore, the addition of methanol has almost no effect on its ORR activity. (B) Voltammogram recorded for FG-TBA at a scan rate of 10 mVs^{-1} in an 0.5 M H_2SO_4 solution saturated with N_2. Electrochemically active surface areas (EASA) of Pd nanoparticles in FG-TBA sample is calculated to be 30m^2/g. The formula for electrochemically active specific surface area is as follows:

$$S_{PdO} = Q_{PdO}/(m \cdot 424)$$

Q_{PdO} is the reduction charge of a single layer of PdO, the value of 424 C cm^{-2} is the charge density associated with the reduction of PdO.
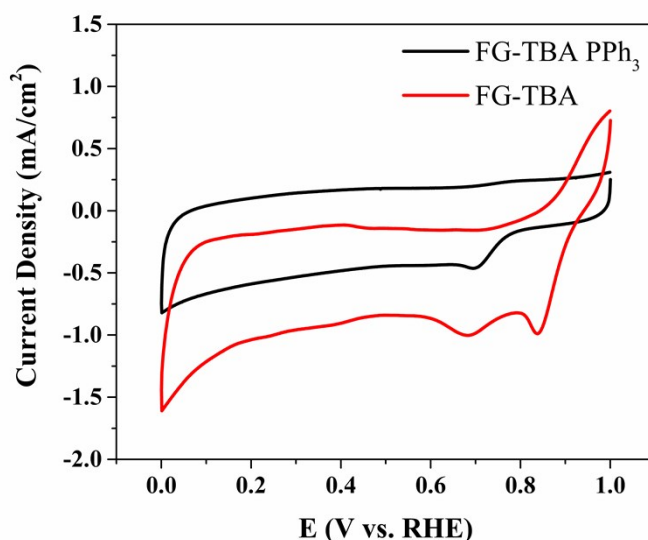

Fig. S21 CVs of FG-TBA with excess PPh$_3$ (FG-TBA PPh$_3$) and FG-TBA in O_2-saturated 0.1 M KOH at a scan rate of 10 mVs^{-1}.