Electronic Supporting Information

In–Situ Tunable Pillaring Compact and High–Density Graphite Fluoride with Pseudocapacitive Diamines for Supercapacitors of Combined Predominance in Gravimetric and Volumetric Performances

Fu-Gang Zhao,*[†] Yu-Ting Kong,[†] Bingyige Pan,[†] Cheng-Min Hu,[†] Biao Zuo,[†] Xiaoping Dong,[†] Benxia Li,[†] and Wei-Shi Li*[‡]

[†]Department of Chemistry, Zhejiang Sci-Tech University, 928 Second Street, Hangzhou 310018, China

[‡]Key Laboratory of Synthetic and Self-Assembly Chemistry for Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

*Corresponding authors: zhaofugang85@163.com (Z.F.G.), liws@mail.sioc.ac.cn (W.S.L.)

Experimental section

1. Material Synthesis.

1.1 Chemicals.

Bulk graphite fluoride (bGF) was purchased from Shanghai CarFluor chemicals corporation. Ethylenediamine (EDA), *p*−phenylenediamine (PDA), *4,4'*−oxydianiline (ODA), sodium amide (NaNH$_2$), *N,N*-dimethyl formamide (DMF) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Anhydrous *N,N*-dimethyl formamide was obtained by refluxing with CaH$_2$ under *vacuo* for 12h and freshly distilled prior to use. Tetrahydrofuran was dried by refluxing with sodium using benzophenone as an indicator. Once the solution turned deep blue, tetrahydrofuran was collected.

All other chemicals were used as received, without any further purification.

1.2 Synthesis of diamine pillared graphene materials

1.2.1 Optimization of prototype reaction between bulk graphite fluoride (bGF) and ethylenediamine (EDA)

Detailed procedure:

In view of the chemically inert reactivity of bGF and weak nucleophilicity of EDA, we performed their reactions under various conditions as the following Table S1:

Entry 1: To a 200 mL flask, 1.05 g bGF (F%: 52.8%, 29.2 mmol F) was added. After vacuum pumping and N$_2$ charging for three rounds, 20 mL neat EDA was injected into the flask using a syringe. The mixture was subject to ultrasonic treatment for 2h (40 KHz, 50W) and then slowly warmed to 80 °C and vigorously stirred for 72h. After that, this reaction was naturally cooled down to room temperature. The mixture was filtered over a 0.22 μm PTFE membrane, and the filter cake was subjected to thorough washing with ethanol (500 mL*3) and deionized water (500 mL*3) for

removing any impurities, affording a crude product. To harvest the fine product, the crude product was re-dispersed in 1000 mL DMF with the assist of ultrasonication for 30 min. The dispersion was subject to centrifugation (3000 rpm, 20 min), collecting upper suspension and abandoning the precipitates. After vacuum evaporation of DMF of all the collected dispersion, the target product was obtained and assigned the name of EDA–G[1] (0.37 g).

Table S1. Optimization on the reaction between pristine bGF and ethylenediamine (EDA).

Entry	Conditions	Samples	Elemental content			
			N	F	H	C
/	/	bGF	< 0.3	52.8	< 0.3	46.5
1	neat EDA, bGF, 80 °C, 72h	EDA-G[1]	8.4	12.9	2.0	69.6
2	bGF+DMF, EDA, 80 °C, 72h	EDA-G[2]	11.8	2.7	2.9	73.5
3	bGF+THF, EDA, 80 °C, 72h	EDA-G[3]	9.6	7.5	2.5	71.7
4	bGF+DMF, EDA+K$_2$CO$_3$, 80 °C, 72h	EDA-G[4]	12.6	1.2	3.2	72.5
5	bGF+THF, EDA+K$_2$CO$_3$, 80 °C, 72h	EDA-G[5]	11.1	2.4	2.8	72.9
6	Step I: EDA+NaNH$_2$+THF, reflux, 24h; Step II: bGF+THF suspension added into the solution of Step I, reflux, 72h	EDA-G[6]	12.9	0.7	3.4	72.1
7	Step I: EDA+NaNH$_2$+DMF, 90 °C, 24h; Step II: bGF+DMF solution added into the solution of Step I, 90 °C, 72h	EDA-G	14.7	1.7	3.9	71.2

Entry 2: To a 200 mL flask, 1.02 g bGF (F%: 52.8%, 28.3 mmol F) was added. After vacuum pumping and N$_2$ charging for three rounds, 100 mL dry DMF was injected into the flask using a syringe. Then, the mixture was subject to ultrasonic treatment for 2h (40 KHz, 50W). After 2.5 mL (2.25g, 37.4 mmol) EDA was injected into the flask, the mixture was slowly warmed to 80 °C and vigorously stirred for 72h. After that, this reaction was naturally cooled down to room temperature. The mixture was filtered over a 0.22 μm PTFE membrane, and the filter cake was subjected to thorough washing with ethanol (500 mL*3), deionized water (500 mL*3) and

methanol (500 mL) for removing any impurities, affording a crude product. To harvest the fine product, the crude product was re-dispersed in 1000 mL DMF with the assist of ultrasonication for 30 min. The dispersion was subject to centrifugation (3000 rpm, 20 min), collecting upper suspension and abandoning the precipitates. After vacuum evaporation of DMF of all the collected dispersion, the target product was obtained and assigned the name of EDA–G^2 (0.45 g).

Entry 3: The same procedure as that of *Entry 2* except for changing the solvent from DMF to THF. Product: EDA–G^3 (0.39 g).

Entry 4: To a 200 mL flask, 1.04 g bGF (F%: 52.8%, 28.9 mmol F) and 10.4 g K_2CO_3 (75.4 mmol) were added. After vacuum pumping and N_2 charging for three rounds, 100 mL freshly distilled DMF was injected into the flask using a syringe. Then, the mixture was subject to ultrasonic treatment for 2h (40 KHz, 50W). After 2.5 mL (2.25g, 37.4 mmol) EDA was injected into the flask, the mixture was slowly warmed to 80 °C and vigorously stirred for 72h. After that, this reaction was naturally cooled down to room temperature. The mixture was filtered over a 0.22 μm PTFE membrane, and the filter cake was subjected to thorough washing with deionized water (500 mL*3), ethanol (500 mL*3), deionized water (500 mL*3) and methanol (500 mL) for removing any impurities, affording a crude product. To harvest the fine product, the crude product was re-dispersed in 1000 mL DMF with the assist of ultrasonication for 30 min. The dispersion was subject to centrifugation (3000 rpm, 20 min), collecting upper suspension and abandoning the precipitates. After vacuum evaporation of DMF of all the collected dispersion, the target product was obtained and assigned the name of EDA–G^4 (0.48 g).

Entry 5: The same procedure as that of *Entry 4* except for changing the solvent from DMF to THF. Product: EDA–G^5 (0.42 g).

Entry 6:

Step I: To a 500 mL two-necked flask, 1.46 g (37.4 mmol) $NaNH_2$ plates were added. After vacuum pumping and N_2 charging for three rounds, 200 mL freshly distilled THF and 2.5 mL EDA (2.25 g, 37.4 mmol) were injected into the flask using a syringe, respectively. The mixture was slowly warmed to reflux and vigorously stirred for 24h.

Careful attention should be paid to the increasing pressure of the system due to NH_3 release as the reaction is proceeding. After that, the mixture was cooled to room temperature, affording an anionic EDA solution;

Step II: To another 200 mL flask, 1.08 g bGF (F%: 52.8%, 30.0 mmol F) was added. After vacuum pumping and N_2 charging for three rounds, 100 mL freshly distilled THF was injected into the flask using a syringe. Then, the mixture was subject to ultrasonic treatment for 2h (40 KHz, 50W). Afterwards, the bGF/THF suspension was dropwisely injected into the flask charged with EDA anion under ice/water bath using a syringe while vigorously stirring in 2h. After taking the ice/water bath away, the mixture was slowly warmed to reflux and vigorously stirred for 72h. Finally, this reaction was naturally cooled down to room temperature and carefully quenched with 50 mL methanol. The mixture was filtered over a 0.22 μm PTFE membrane, and the filter cake was subjected to thorough washing with ethanol (500 mL*3), deionized water (500 mL*3), ethanol (500 mL) and deionized water (500 mL) and methanol (500 mL) for removing any impurities, affording a crude product. To harvest the fine product, the crude product was re-dispersed in 1000 mL DMF with the assist of ultrasonication for 30 min. The dispersion was subject to centrifugation (3000 rpm, 20 min), collecting the upper suspension and abandoning the precipitates. After vacuum evaporation of DMF of all the collected dispersion, the target product was obtained and assigned the name of EDA–G[6] (0.56 g).

Entry 7:

Step I: To a 500 mL two-necked flask, 1.58 g (40.5 mmol) $NaNH_2$ plates were added. After vacuum pumping and N_2 charging for three rounds, 200 mL freshly distilled DMF and 2.7 mL EDA (2.43 g, 40.4 mmol) were injected into the flask using a syringe, respectively. The mixture was slowly warmed to 90 ℃ and vigorously stirred for 24h. Careful attention should be paid to the increasing pressure of the system due to NH_3 release as the reaction is proceeding. After that, the mixture was naturally cooled to room temperature, affording an anionic EDA solution;

Step II: To another 200 mL flask, 1.17 g bGF (F%: 52.8%, 32.4 mmol F) was added. After vacuum pumping and N_2 charging for three rounds, 100 mL freshly distilled

DMF was injected into the flask using a syringe. Then, the mixture was subject to ultrasonic treatment for 2h (40 KHz, 50W). Afterwards, the bGF/DMF suspension was dropwisely injected into the flask charged with EDA anion under ice/water bath using a syringe while vigorously stirring in 2h. After taking the ice/water bath away, the mixture was slowly warmed to 90 ℃ and vigorously stirred for 72h. Finally, this reaction was naturally cooled down to room temperature and carefully quenched with 50 mL methanol. The mixture was filtered over a 0.22 μm PTFE membrane, and the filter cake was subjected to thorough washing with ethanol (500 mL*3), deionized water (500 mL*3), ethanol (500 mL) and deionized water (500 mL) and methanol (500 mL) for removing any impurities, affording a crude product. To harvest the fine product, the crude product was re-dispersed in 1000 mL DMF with the assist of ultrasonication for 30 min. The dispersion was subject to centrifugation (3000 rpm, 20 min), collecting the upper suspension and abandoning the precipitates. After vacuum evaporation of DMF of all the collected dispersion, the target product was obtained and assigned the name of EDA–G (0.67 g). *Elemental analysis (%), C: 71.6; H: 3.9; N: 14.7; F: 1.7; O (subtraction method): 8.1*

By comparison, it was found that the product EDA-G prepared from the conditions of entry 7 had the highest N contents, implying the highest functionalization degree of EDA. Besides, a high yield of EDA-G fine product was obtained under these conditions. Therefore, this EDA-G product was systematically investigated, and PDA-G and ODA-G products were synthesized following this procedure.

1.2.2   Synthesis of *p−*phenylenediamine (PDA) pillared graphene (PDA-G)

Step I: To a 500 mL two-necked flask, 1.64 g (42.04 mmol) NaNH$_2$ plates and 4.54 g (41.98 mmol) PDA were added. After vacuum pumping and N$_2$ charging for three rounds, 200 mL freshly distilled DMF was injected into the flask using a syringe. The mixture was slowly warmed to 90 ℃ and vigorously stirred for 24h. Careful attention should be paid to the increasing pressure of the system due to NH$_3$ release as the reaction is proceeding. After that, the mixture was naturally cooled to room temperature, affording an anionic PDA solution;

Step II: To another 200 mL flask, 1.26 g bGF (F%: 52.8%, 35.0 mmol F) was added.

After vacuum pumping and N_2 charging for three rounds, 100 mL freshly distilled DMF was injected into the flask using a syringe. Then, the mixture was subject to ultrasonic treatment for 2h (40 KHz, 50W). Afterwards, the bGF/DMF suspension was dropwisely injected into the flask charged with PDA anion under ice/water bath using a syringe while vigorously stirring in 2h. After taking the ice/water bath away, the mixture was slowly warmed to 90 ℃ and vigorously stirred for 72h. Finally, this reaction was naturally cooled down to room temperature and carefully quenched with 50 mL methanol. The mixture was filtered over a 0.22 μm PTFE membrane, and the filter cake was subjected to thorough washing with ethanol (500 mL*2), THF (500 mL*2), deionized water (500 mL*3), DMF (500 mL), acetone (500 mL) and deionized water (500 mL) and methanol (500 mL) for removing any impurities, affording a crude product. To harvest the fine product, the crude product was re-dispersed in 1000 mL DMF with the assist of ultrasonication for 30 min. The dispersion was subject to centrifugation (3000 rpm, 20 min), collecting the upper suspension and abandoning the precipitates. After vacuum evaporation of DMF of all the collected dispersion, the target product was obtained and assigned the name of PDA–G (0.81 g). *Elemental analysis (%), C: 75.9; H: 3.6; N: 12.5; F: 1.5; O (subtraction method): 6.5*

% and 3.6

1.2.3 Synthesis of 4,4'-oxydianiline (ODA) pillared graphene (ODA-G)

Step I: To a 500 mL two-necked flask, 1.72 g (44.1 mmol) $NaNH_2$ plates and 8.96 g (44.75 mmol) ODA were added. After vacuum pumping and N_2 charging for three rounds, 200 mL freshly distilled DMF was injected into the flask using a syringe. The mixture was slowly warmed to 90 ℃ and vigorously stirred for 24h. Careful attention should be paid to the increasing pressure of the system due to NH_3 release as the reaction is proceeding. After that, the mixture was naturally cooled to room temperature, affording an anionic ODA solution;

Step II: To another 200 mL flask, 1.21 g bGF (F%: 52.8%, 33.63 mmol F) was added. After vacuum pumping and N_2 charging for three rounds, 100 mL freshly distilled DMF was injected into the flask using a syringe. Then, the mixture was subject to

ultrasonic treatment for 2h (40 KHz, 50W). Afterwards, the bGF/DMF suspension was dropwisely injected into the flask charged with ODA anion under ice/water bath using a syringe while vigorously stirring in 2h. After taking the ice/water bath away, the mixture was slowly warmed to 90 ℃ and vigorously stirred for 72h. Finally, this reaction was naturally cooled down to room temperature and carefully quenched with 50 mL methanol. The mixture was filtered over a 0.22 μm PTFE membrane, and the filter cake was subjected to thorough washing with ethanol (500 mL*2), THF (500 mL*2), deionized water (500 mL*3), DMF (500 mL*2), acetone (500 mL*2), $CHCl_3$ (500 mL*2), deionized water (500 mL) and methanol (500 mL) for removing any impurities, affording a crude product. To harvest the fine product, the crude product was re-dispersed in 1000 mL DMF with the assist of ultrasonication for 30 min. The dispersion was subject to centrifugation (3000 rpm, 20 min), collecting the upper suspension and abandoning the precipitates. After vacuum evaporation of DMF of all the collected dispersion, the target product was obtained and assigned the name of ODA–G (1.18 g). *Elemental analysis (%), C: 76.4; H: 3.7; N: 8.7; F: 2.1; O (subtraction method): 9.1*

1.2.4 Calculation details for the functionalization degrees of EDA, PDA and ODA using EA data

It is widely accepted that EA provides much more real and accurate element content in comparison with other analysis methods, such energy dispersive spectrometer, X-ray photoelectron spectroscopy, *etc*.

It is detected that bGF contains C element of 46.5% and F of 52.8%, and no N element. Therefore, N element in EDA–G, PDA–G and ODA–G samples only stems from the functionalized diamine moieties in the case that diamine residues are thoroughly washed away. In this end, the N mass/molar amounts are 0.147 g/0.0105 mol for 1 g EDA–G sample according to N content of 14.7%; that are 0.125 g/0.00893 mol for 1 g PDA–G sample according to N content of 12.5%; that are 0.087 g/0.00621 mol for 1 g ODA–G sample according to N content of 8.7%. Taking double amines into account, the loading mass/molar amounts of EDA, PDA and ODA

functionalities are 0.31g/0.00525 mol, 0.48 g/0.00446 mol and 0.62 g/0.00311 mol, respectively, for each 1 g EDA–G, PDA–G and ODA–G samples.

Furthermore, according to their molecular formulas of EDA, PDA and ODA, together with the N contents of EDA–G, PDA–G and ODA–G products (14.7%, 12.5% and 8.7%), it can be readily calculated the C contents of EDA, PDA and ODA functionalities with 12.6%, 32.1% and 44.7%, respectively. By easy subtracting, the C contents contributed from graphene scaffolds are 59% (71.6%-12.6%), 43.8% (75.9%-32.1%) and 31.7% (76.4%-44.7%). Therefore, the molar amounts of graphene sheets are 0.0492, 0.0365 and 0.0264 mol for each 1 g EDA–G, PDA–G and ODA–G samples. The functionalization degrees (per mol graphene containing x mol functional species) for EDA, PDA and ODA are 0.11, 0.12 and 0.12, respectively.

2.   Material Characterizations.

Elemental analysis (EA) on carbon, hydrogen and nitrogen contents was carried out with an Elementar vario EL III elemental analyzer. The content of fluorine element was measured by using a typical oxygen flask combustion method, in which the sample was totally burned in an oxygen atmosphere, thereafter the produced inorganic fluorine was collected, and titrated with thorium nitrate. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Avatar-360 Fourier transform infrared spectrophotometer using a potassium bromide pellet. Raman spectra were performed on a Renishaw inVia Reflex micro-Raman spectrometer using a 100-fold objective lens and crystal laser excitation at 514.5 nm with a power of 0.1 mW. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI-5000 VersaProbe spectrometer under 10^{-7} Pa using a monochromatic Al K_α X-ray source operating at 100 W. The thermogravimetric analysis (TGA) was carried out in N_2 on a TA instrument with a heating rate of 10 °C min^{-1}. Atomic force microscopy (AFM) images were acquired under ambient conditions on a Veeco instrument Nanoscope IIIa Multimode apparatus operating in a non-contact mode with a silicon tip and

cantilever operating at a frequency of 325 kHz and a scanning speed of 1 Hz. Samples were prepared by placing a drop of their dilute DMF dispersion on a fresh mica substrate and dried in a vacuum oven at room temperature. The morphology of products was investigated using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operating at 3 kV. The samples were fiercely exfoliated with ultrasonication (40 KHz, 800 W, 60 °C, 1h × 6). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL JEM-2010 microscope operating at 120 kV. The exfoliated samples were prepared by placing a drop of their dilute DMF dispersion on a holey-carbon-coated copper grid. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance with Cu K_α radiation (1.5406 Å). Nitrogen adsorption-desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020 analyzer after being vacuum-dried at 120 °C for 12 h. The specific surface area (*SSA*) was calculated using the Brunauer-Emmett-Teller (BET) method.

3. Electrochemical Measurements.

The electrochemical performances of EDA–G, PDA–G and ODA–G samples based supercapacitor cells were measured in a two-electrode symmetric configuration with 1 M Na_2SO_4, which showed high ionic conductivity as electrolyte, using a CHI660D electrochemical workstation at room temperature.   To fabricate EDA–G, PDA–G and ODA–G electrodes, the pasty mixtures of 90 wt% of their powders and 10 wt% of poly(vinylidene fluoride) (PVDF) as a binder in ethanol were pre–prepared, followed by coating the slurries on 1×1 cm^2 nickel foam as the current collector. Prior to suffering from hydraulic pressing between two stainless steel plates under a compression of 20 MPa for 30 s, the electrodes were vacuum dried overnight at 120 °C. After weighing, the areal loading mass of active materials on each nickel foam was in the range 3~5 mg cm^{-2}. Thereafter, a sandwich structure was assembled by placing a piece of a porous polypropylene (PP) membrane as a separator between

two electrodes having the identical composition and mass, and were tightly clipped, then soaked in 1 M Na_2SO_4 aqueous solution as an electrolyte. Cyclic voltammetry (CV), galvanometric charge/discharge curves (GCD), and electrochemical impedance spectroscopy (EIS) over a frequency range of 0.01 Hz to 100 kHz at an open-circuit potential with an alternating current (AC) amplitude of 10.0 mV were acquired using a CHI660D electrochemical workstation. The gravimetric specific capacitance (C_{wt}) in a two-electrode cell was calculated from the galvanometric charge/discharge curves. The following formula was used: $C_{wt} = 4I\Delta t/(m\Delta V)$, where I is the constant discharge current, Δt is the discharging time, m is the total mass of the active material in both electrodes and ΔV represents voltage drop on discharging (excluding the V_{drop}). The corresponding volumetric specific capacitances (C_{vol}) were calculated using: $C_{vol} = C_{wt} \times \rho$, where ρ is the bulk density of EDA–G, PDA–G and ODA–G samples. The gravimetric (E_{wt}) and volumetric (E_{vol}) energy densities against two electrodes in device were calculated using the following formula: $E_{wt} = 0.125C_{wt}(\Delta V)^2$ and $E_{vol} = E_{wt} \times \rho$, respectively. The gravimetric (P_{wt}) and volumetric (P_{vol}) power densities were calculated using the following formula: $P_{wt} = 3600E_{wt}/\Delta t$ and $P_{vol} = P_{wt} \times \rho$, respectively.
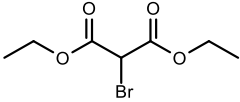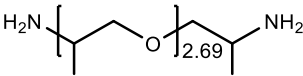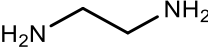
Supporting Figures
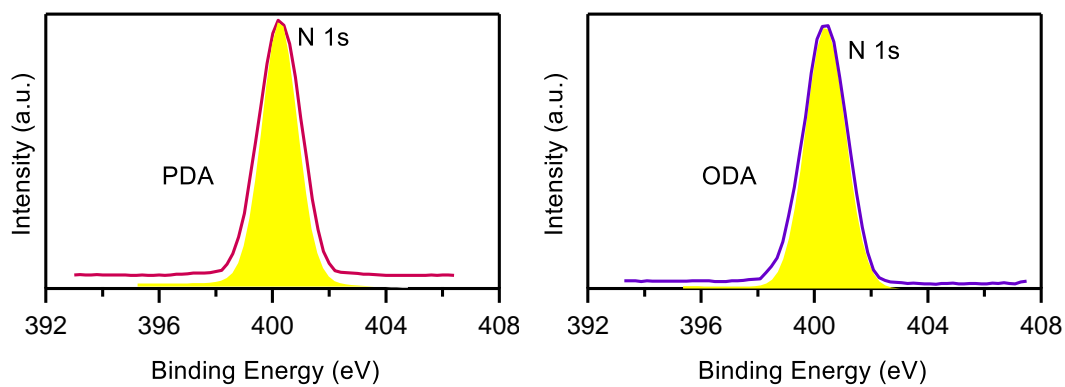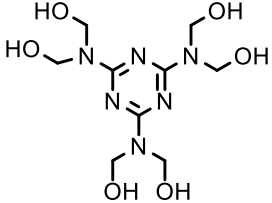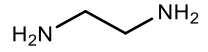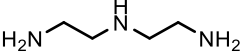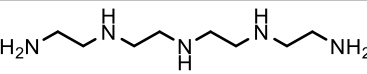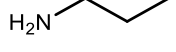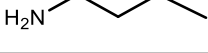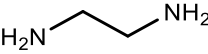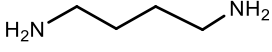
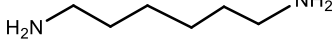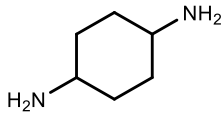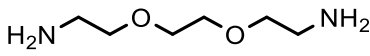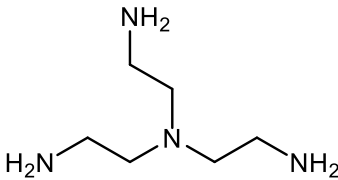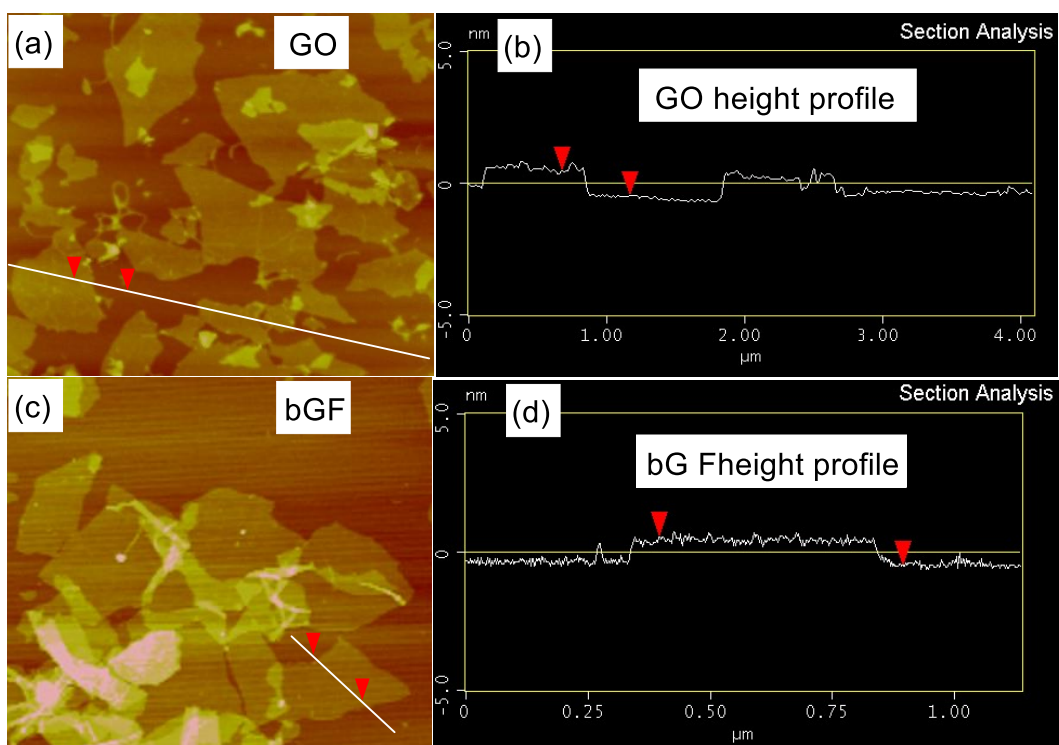**Fig. S1** N 1s XPS spectra of PDA and ODA.
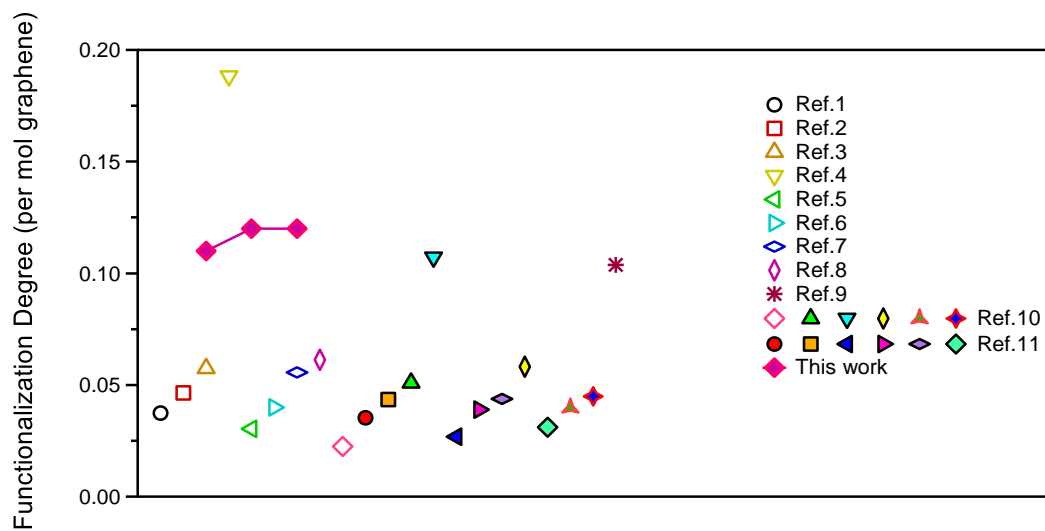
Fig. S2 Comparison plot of the functionalization degree of EDA, PDA and ODA achieved by our strategy with the modifiers listed in **Table S2** using other proposals described in the literatures.
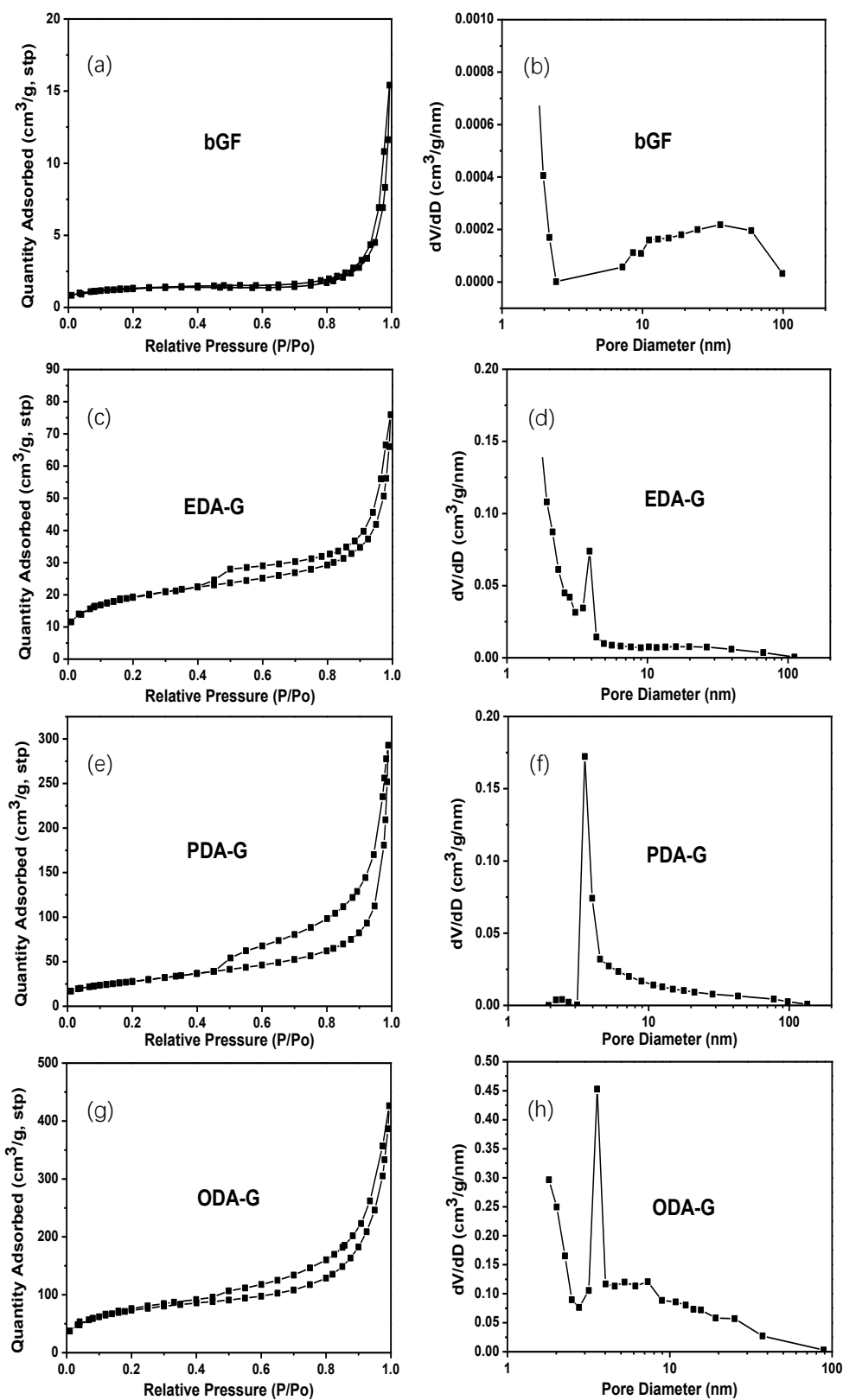
Table S2. The functionalization degree of functional compounds plotted in the above **Fig. S2**.

Precursor	Functional Compounds	Functionalization degree (/mol graphene)	
fluorographene	CH₃O–C₆H₄–MgBr (4-methoxyphenylmagnesium bromide)	0.0374 **Ref. [1]**	
exfoliated graphite fluoride	diethyl bromomalonate (EtO_2C–CHBr–CO_2Et)	0.0464 **Ref. 2]**	
few-layer fluorographene	CHCl₃	0.0575 **Ref. [3]**	
graphite fluoride	NaCN	0. 1883 **Ref. [4]**	
fluorinated graphene (graphene+F₂)	H_2N–[CH(CH₃)CH₂O]–[ ]₂.₆₉–CH(CH₃)–NH_2	0.0302 **Ref. [5]**	
exfoliated graphite fluoride	NaNH₂	0.0399 **Ref. [6]**	
fluorinated graphene (graphene+XeF₂)	H_2N–CH₂CH₂–NH_2 (ethylenediamine)	0.0556 **Ref. [7]**	
fluorographene	NaSH	0.0612 **Ref. [8]**	
GO	hexakis(hydroxymethyl)melamine (triazine with N(CH₂OH)₂ groups)	0.1038 **Ref. [9]**	
GO	H_2N–CH₂CH₂–NH_2	0.0581	**Ref. [10]**
	NH₃	0.1071	
	H_2N–CH₂CH₂–NH–CH₂CH₂–NH_2	0.0398	
	H_2N–CH₂CH₂–NH–CH₂CH₂–NH–CH₂CH₂–NH–CH₂CH₂–NH_2	0.0225	
	H_2N–CH₂CH₂CH₃	0.0510	
	H_2N–CH₂CH₂CH₂CH₃	0.0449	
	H_2N–CH₂CH₂–NH_2	0.0435	
	H_2N–CH₂CH₂CH₂–NH_2	0.0437	
	H_2N–(CH₂)₅–NH_2	0.0310	

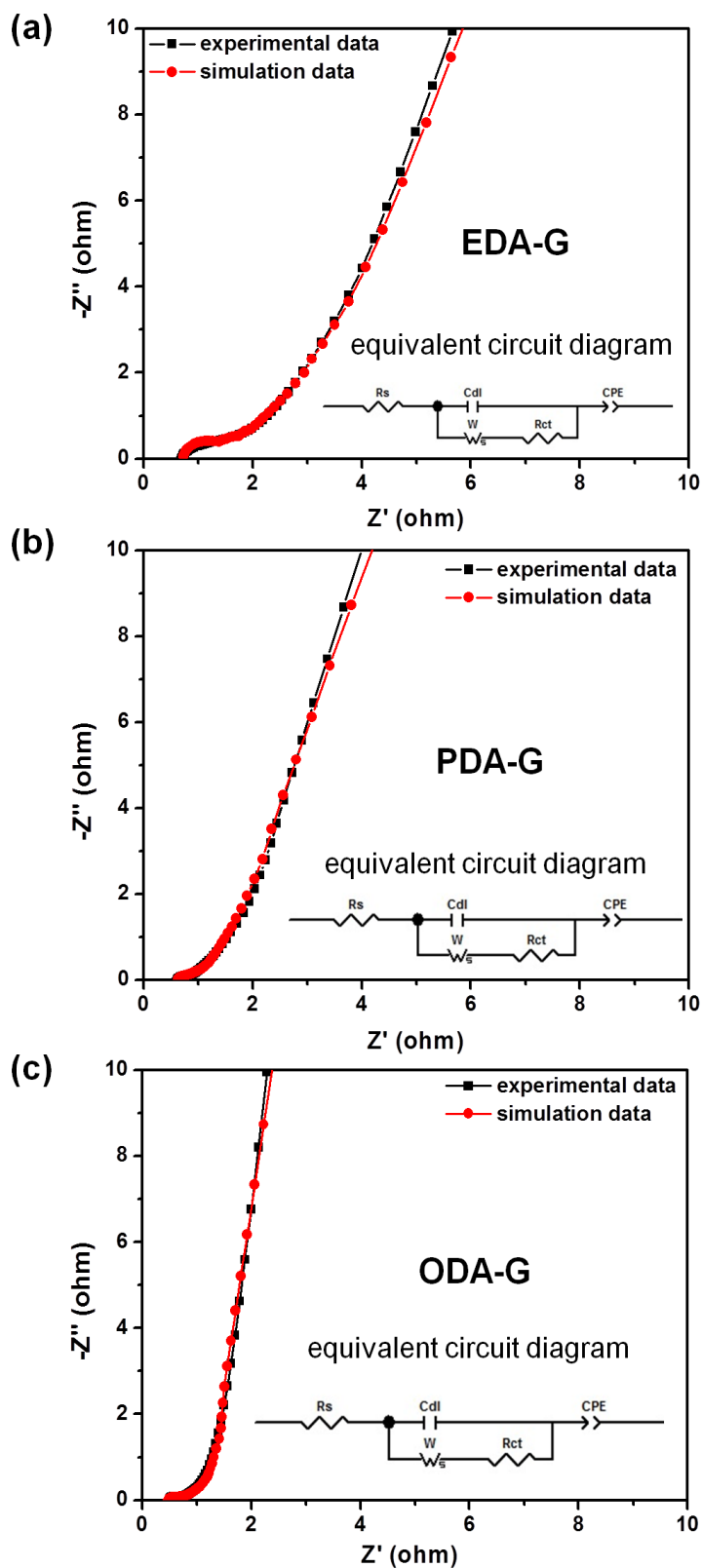| GO	(chemical structure: cyclohexane-1,4-diamine)	0.0353	**Ref. [11]**
	H_2N—CH_2CH_2—O—CH_2CH_2—O—CH_2CH_2—NH_2	0.0389	
	(chemical structure: tris(2-aminoethyl)amine)	0.0268	

Fig. S3   AFM images and corresponding height profiles of GO and bGF sheets.

Fig. S4 (a), (c), (e), (g) N$_2$ adsorption-desorption test and (b), (d), (f), (h) DFT por-size distribution of bGF, EDA-G, PDA-G and ODA-G.

Fig. S5 Nyquist plots of the supercapacitors based on EDA-G (a), PDA-G (b) and ODA-G (c) materials. The insets show the individual equivalent circuits by Z-view software. The fitted curve almost overlaps the original EIS curve, indicating a perfect

fit is obtained. The equivalent circuit consists of the following parts: W, C_{dl}, CPE, R_{ct}, and R_s, where W represents the Warburg impedance of diffusive resistance, C_{dl} means the double-layer capacitance, CPE means the constant phase element, R_{ct} represents the charge transfer resistance and R_s represents the bulk solution resistance. The R_{ct}, R_s and W values are listed in the following **Table S3**.

Table S3. The fitting parameters derived from the equivalent circuits of EDA-G, PDA-G and ODA-G.

Samples	Rs (Ω)	Rct (Ω)	W (Ω)
EDA-G	0.82	1.26	6.483
PDA-G	0.69	0.75	1.616
ODA-G	0.51	0.69	1.044

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