Nitrogen-Enriched Hierarchically Porous Carbons Fabricated by Graphene Aerogel Templated Schiff-base Chemistry for High Performance Electrochemical Capacitors

Electronic Supplementary Information

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1. Experimental Section

Materials

Natural flake graphite was purchased from Aldrich. 1,4-Phthalaldehyde (99%) was purchased from Energy Chemical (Shanghai, China) and used without further purification. All other chemicals (~99%) were purchased from Aladdin Reagent (Shanghai) and used without further purification. Organic solvents were distilled before use.

Preparation of monolithic graphene aerogels (GAs)

To produce three-dimensional (3D) GAs, graphene oxide (GO) was initially prepared from natural graphite flakes by a modified Hummer's method.¹ 3D GAs were obtained through a combined hydrothermal and freeze-drying process.² First, the as-prepared GO was dispersed in deionized (DI) water by sonication reaching a concentration of 1.5 mg mL⁻¹. Second, 80mL GO aqueous dispersion was sealed in a Teflon-lined autoclave and then hydrothermally treated at 180 \degree for 12 h. Finally, the resultant samples were freeze-dried for 2 days to yield 3D GAs.

Synthesis of aminated graphene aerogels (AGAs)

AGAs were prepared through amidation of residual carboxylic acid groups of 3D GAs. First, 50mg GAs were repeatedly infiltrated in dry DMF with *N*-hydroxysuccinimide (NHS, 342 mg) and *N*-(3-(dimethylamino)propyl)-*N*²-ethylcarbodiimide hydrochloride (EDC•HCl, 575mg) at 0 °C under mild stirring for 4h; then, 1,3-diaminopropane (0.38mL) was added. The mixture was gently stirred for 24 h at room temperature, yielding black bulk products. AGAs were obtained after washing the bulk products with DI water and ethanol for at least 3 times, followed by vacuum drying at ca. 40 °C overnight. The carbon and nitrogen contents of the AGAs measured by elemental analysis are 65.9 wt% and 4.8 wt%, respectively.

Synthesis of 3D Graphene-Coupled Schiff-base Hierarchically Porous Polymers (GS-HPPs)

AGAs (3 equiv. by weight) were immersed in dry DMSO followed by the addition of melamine and 1,4-phthalaldehyde (57, 27, and 17 equiv. by weight for GS-HPP-5, GS-HPP-10, GS-HPP-15 respectively; the molar ratio of melamine to 1,4-phthalaldehyde is 2:3). After nitrogen bubbling for 0.5 h and then gentle stirring for about 2h, the mixture was incubated at room temperature for 3 days for the complete infiltration of the monomers into the interior space of the AGAs. Subsequently, the mixture was heated to 180 °C followed by reflux for 3 days under a nitrogen atmosphere. The resultant black bulk products were collected, washed with excess DMF and acetone, and then purified by Soxhlet fraction for 3 days using THF as the solvent. Finally, the solid products were filtered and then dried in vacuum at room temperature overnight, yielding GS-HPPs. The control sample, porous polymers (PP) without GA as a template, was synthesized under the similar conditions except the addition of AGA.

Pyrolysis of the GS-HPPs

The GS-HPP samples were placed in a quartz boat and heated to 800 $^{\circ}$ C (for GS-HPP-10, heated to 700, 800, and 900 $^{\circ}$ C) at a heating rate of 5 $^{\circ}$ C/min under a nitrogen atmosphere. The samples were held at the corresponding temperatures for 2 h. After cooling to room temperature, the pyrolyzed samples (N-HPCs) were collected for subsequent characterizations.

Characterizations

Fourier transform infrared spectroscopy (FT-IR). The IR spectra were obtained on a Spectrum 100 (Perkin Elmer, Inc., USA) spectrometer with a frequency range of 4000–400 cm⁻¹. The sample powders were pulverized with KBr, and pressed into disks.

Thermogravimetric analysis (TGA). TGA of the samples were carried out on a Q5000IR (TA Instruments, USA) thermogravimetric analyzer with a heating rate of 20 $^{\circ}$ C min⁻¹ under nitrogen flow with temperature range of 0 $^{\circ}$ C-800 $^{\circ}$ C.

Elemental analysis (EA). Elemental analysis was performed using a Vario ELIII/Isoprime (Elementar Co., Germany) isotope ratio mass spectrometer.

X-ray photoelectron spectroscopy (XPS). XPS was measured on an AXIS Ultra DLD system (Kratos Co., Japan) with Al Kα radiation as the X-ray source.

Brunauer–Emment–Teller (BET) specific areas were measured on an Autosorb-iQA3200-4 sorption analyzer (Quantatech Co., USA) based on N2

adsorption.

Scanning electron microscopy (SEM). SEM observations were performed using an FEI Sirion-200 (FEI Co., USA) field emission scanning electron microscope. The 3D samples were directly put on copper tables without other treatment.

Transmission electron microscopy (TEM). TEM studies of samples were performed using a JEOL-2100 (JEOL Ltd., Japan) electron microscope at an operating voltage of 200 kV. Before the TEM measurement, GS-HPP and N-HPC samples were dispersed in ethanol and sonicated for 2h. TEM samples were prepared by dropping a drop of the ethanol dispersion on copper grids, followed by drying at 60 °C overnight.

Electrochemical capacity measurements: Performance of supercapacitor was evaluated on an EG & potentiostat/galvanostat Model 2273 advanced electrochemical system. CV measurements and charge-discharge galvanostatic tests were performed in a three-electrode system. Working electrodes for supercapacitor were prepared by mixing 80 wt% powdered active materials (~ 2 mg), 10 wt% carbon black (Mitsubishi Chemicals, Inc.), and 10 wt% polytetrafluoroethylene (PTFE) binder. Nickel foam was applied as a counter electrode with a Ag/AgCl electrode as a reference electrode. The experiments were carried out in 6 M KOH solution. The potential range was between -1 to 0 V (Ag/AgCl) at different scan rates and different current densities at the ambient temperature. Nyquist plots of the samples were recorded by applying a sine wave with amplitude of 5.0 mV over the frequency range of 100 kHz ~ 1 Hz.

2. Figures and Tables



Figure S1. FT-IR spectra of GA and GS-HPPs.



Figure S2. SEM (a and b), TEM (c) images and nitrogen adsorption-desorption isotherm and PSD curve (d) of GS-HPP-5.



Figure S3. SEM (a and b), TEM (c) images and nitrogen adsorption-desorption isotherm and PSD curve (d) of GS-HPP-15.



Figure S4. Representative scanning TEM (STEM) images (a1 and b1) and the corresponding elemental mapping images of carbon (a2 and b2, blue) and nitrogen (a3 and b3, red). (a1-a3) for GS-HPP-5; (b1-b3) for GS-HPP-15.



Figure S5. TEM image of Schiff-base porous polymer (PP) prepared from the polymerization of melamine and 1,4-phthalaldehyde without a GA template.



Figure S6. TGA curves of GS-HPPs and PP. The curves were obtained under nitrogen atmosphere



Figure S7. SEM (a, b), TEM (c) images and nitrogen adsorption-desorption isotherm and PSD curve (d) of N-HPC-5.



Figure S8. SEM (a, b), TEM (c) images and nitrogen adsorption-desorption isotherm and PSD curve (d) of N-HPC-15.



Figure S9. CV curves of N-HPCs, GA and PC as electrodes recorded at a scan rate of 5 mV/s in 6 M KOH electrolyte solution.



Figure S10. Equivalent circuit and complex impedance spectrum of N-HPC based capacitor (Red: received data; green: calculated data). According to the equivalent circuit, the ohmic resistance values (R_t) of the samples are obtained and listed below.

Samples	$R_{\mathrm{t}}\left(\Omega\right)$
N-HPC-5	0.54
N-HPC-10	0.30
N-HPC-15	0.48
GA	1.10
PC	1.21

Samples	N _{wt%}	N _{atom%}	$\mathbf{N}_{\mathbf{graphitic}}{}^{a}$	$\mathbf{N}_{\mathrm{Pyridinic}}{}^{a}$	N _{Pyridinic} / N _{graphitic}
GS-HPP-10	36.1	33.2	NA	NA	NA
N-HPC-10 (700°C)	8.1	7.2	16,670	9,730	0.58
N-HPC-10 (800°C)	6.0	5.1	17,780	7,050	0.40
N-HPC-10 (900°C)	2.8	2.4	7,190	1,220	0.17

Table S1. Data obtained from the XPS spectra of GS-HPP-10 and N-HPC-10 prepared at different pyrolysis temperatures

^{*a*} the values were obtained from the integration areas of the corresponding peaks in the XPS spectra in Figure 3d in the main text.

3. Reference

[1] S. Yang, X. Feng, L. Wang, K. Tang, J. Maier, K. Müllen, *Angew. Chem. Int. Ed.* **2010**, 49, 4795.

[2] Z. Wu, Y. Sun, Y. Tan, S. Yang, X. Feng, K. Müllen, J. Am. Chem. Soc., 2012, 134, 19532.