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Supplementary data

One-step preparation of ultrathin nitrogen-doped carbon nanosheets with ultrahigh pore volume for high-performance supercapacitors

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Experimental details

Materials: Anion exchange resin (AER; 717, granularity: 0.3-1.2 mm, Sinopharm Chemical Reagent Co., Ltd, China), calcium hydroxide, ammonium chloride and potassium hydroxide were purchased from Aladdin Ltd. (Shanghai, China). All chemical reagents were in analytical grade.

Synthesis of nitrogen-doped graphene-like carbon nanosheets (N-CNSs): In a typical process, the pretreated macroporous strongly basic quaternary ammonium-type polystyrene type AER (4.0 g), calcium hydroxide (3.7 g) and ammonium chloride (5.4 g) mixed placed in porcelain boat and put in tube furnace. After vacuum extraction, the quartz tube was filled with high-purity nitrogen by connecting the nitrogen gas bag. The mixtures were firstly activation at 450 ^{o}C for 1 h in N_2 atmosphere at a heating rate of 5 ^{o}C min^{-1}. Finally, the mixtures were increased to the ultimate temperatures of 700, 800 and 900 ^{o}C for 2 h, respectively, with a heating rate of 5 ^{o}C min^{-1} in a slow N_2 flow. After cooling down to room temperature, the resulting sample were then thoroughly washed with HCl (2 mol L^{-1}) to remove any inorganic salts, and then with distilled water until neutral pH and dried at 60 ^{o}C in ambient for 24 h. The samples at different carbonization temperature were named as N-CNSs-700, N-CNSs-800 and N-CNSs-900, respectively.

For comparison purpose, we adopt calcium hydroxide activation method without ammonium chloride for preparation of AER base carbon materials. The pretreated AER (4.0 g) and calcium hydroxide (3.7 g) are mixed placed in porcelain boat and put in tube furnace. The other preparation process is the same as the N-CNSs-800. The sample was denoted as NC-800.

Materials Characterization

The morphologies of the N-CNSs products were examined with field emission scanning electron microscopy (FE-SEM, Ultra Plus, Carl Zeiss, Germany) at an accelerating voltage of 5.0 kV. The structure of the samples was characterized by a transmission electron microscopy (TEM, JEM-2010 Japan). The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of the powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (U.S.A.). All samples were degassed at 200 °C prior to nitrogen adsorption measurements. The elemental microanalysis (C, H and N) was carried out using the Elemental Analyzer Vario EL. X-ray diffraction (XRD) of samples was performed on a diffractometer (D/Max-2400, Rigaku) advance instrument using Cu Kα radiation (k =1.5418 Å) at 40 kV, 100 mA. The 2θ range used in the measurements was from 5 to 80°. X-ray photoelectron spectroscopy (XPS) measurement was performed on an Escalab 210 system (Germany) using a monochromatic Al Kα radiation source (ThermoVG Scientific).

Three-electrode fabrication

For conventional three-electrode system, the glassy carbon electrode with a diameter of 5 mm was used as the working electrode. The working electrodes were fabricated similar to our previous reported literature [S1]. Typically, 4 mg of N-CNSs was ultrasonically dispersed in 0.4 mL of 0.25 wt% Nafion (DuPont, USA). The above suspension of 8 μL using a pipet gun was dropped onto the glassy carbon electrode and dried at room temperature. The three-electrode system was test in 6 mol L^{-1} KOH aqueous solutions, platinum electrode serves as the counter electrode, and Hg/HgO as the reference electrode.

Two-electrode cell fabrication

The capacitive performance of N-CNSs-800 was investigated using a two-electrode testing cell. The working electrode was prepared by mixing the N-CNSs-800 with polyvinylidene fluoride (PVDF) and commercial carbon black (8:1:1) in N-methyl-2-pyrrolidone (NMP) until homogeneous slurry. The slurry was coated on nickel foam with a working area of 1.0 cm2 and the electrodes were dried at 120 ^{o}C for 12 h and then weighted and pressed into sheets under 20 MPa. The total mass was between 3 and 5 mg of each electrode and two electrodes with identical or very close weight were selected for the measurements.

Two as-prepared N-CNSs-800 electrodes fitted with the separator (thin polypropylene film) and electrolyte solution were symmetrically assembled into sandwich-type cells construction (electrode/separator/electrode). Before assembling the supercapacitor configuration, N-CNSs electrodes and separator were immersed in 0.5 mol L^{-1} Na_2SO_4 electrolytes for 12 h to make aqueous electrolyte solutions homogeneously diffuse into the N-CNSs electrodes.

Electrochemical measurements

The electrochemical properties of the samples were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge measurements in three-electrode cell and two-electrode configuration using a CHI 660D electrochemical workstation. The cycle-life stability was performed using computer controlled cycling equipment (LAND CT2001A, Wuhan China). Electrochemical impedance spectroscopy (EIS) measurements were performed with the Autolab PGSTAT 128N equipped (Eco-chemie, Netherland) with FRA module, the frequency ranging from 10 mHz to 100 kHz and an impedance amplitude of ±5 mV at open circuit potential.

The gravimetric capacitance from galvanostatic charge/discharge was calculated by using the formula of $C_s=4I\Delta t/(m\Delta V)$ for the two-electrode cells, while, $C_s^*=I\Delta t/(m\Delta V)$ for the three-electrode system, where I is the constant current (A) and m is the mass (g) of electrode material (For the two-electrode cells, m is the total mass of positive and negative electrodes), Δt the discharge time and ΔV the voltage change during the discharge process.

The specific energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) for a supercapacitor cell can be calculated using the following equations: $E=1/2CV^2$ and $P=E/t$, where C is the specific capacitance of supercapacitor cell, V is voltage change during the discharge process after IR drop in V-t curve, and t is the discharge time.

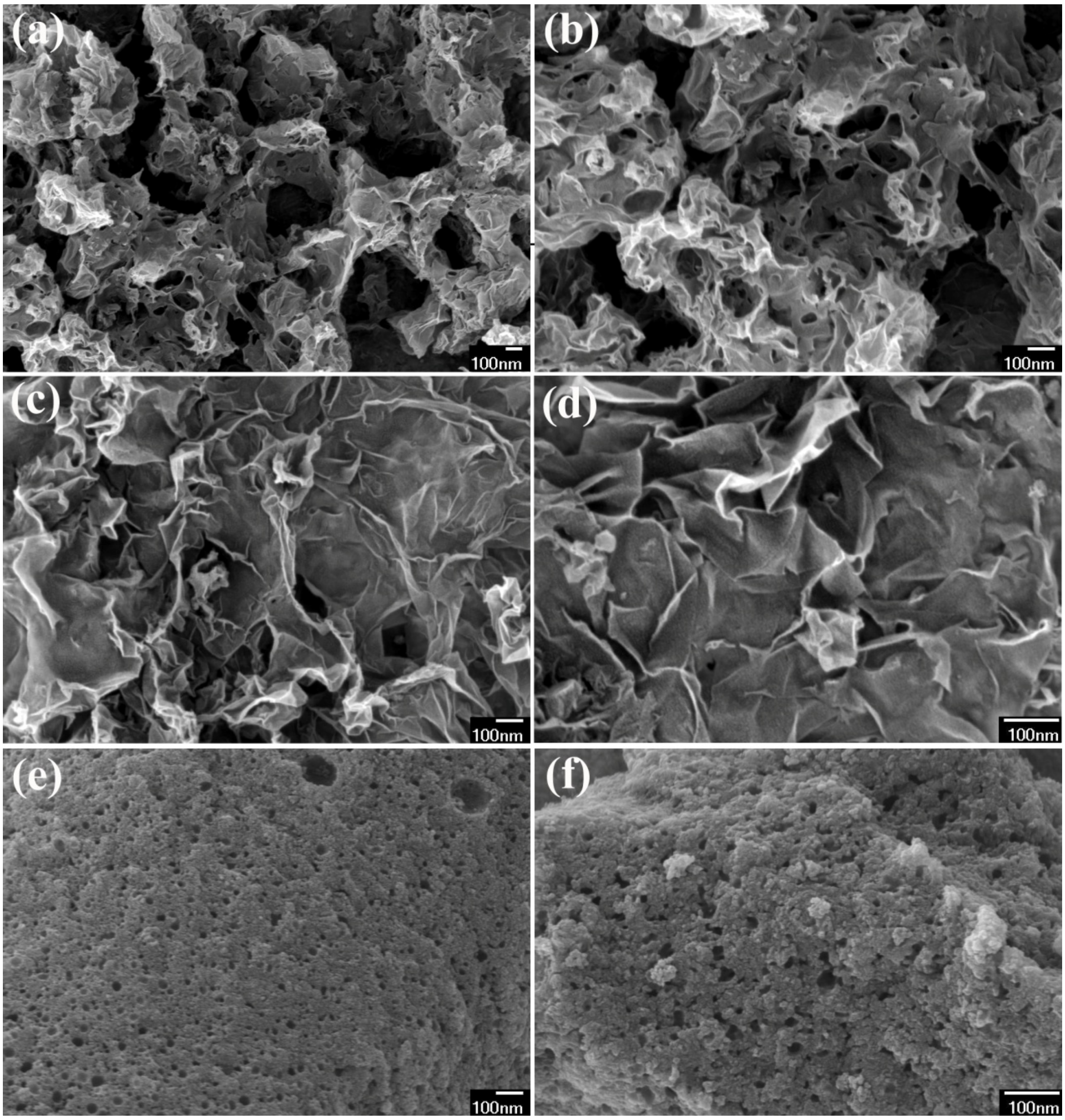

Fig. S1 SEM images of the (a,b) N-CNSs-700; (c,d) N-CNSs-900; (e,f) NC-800

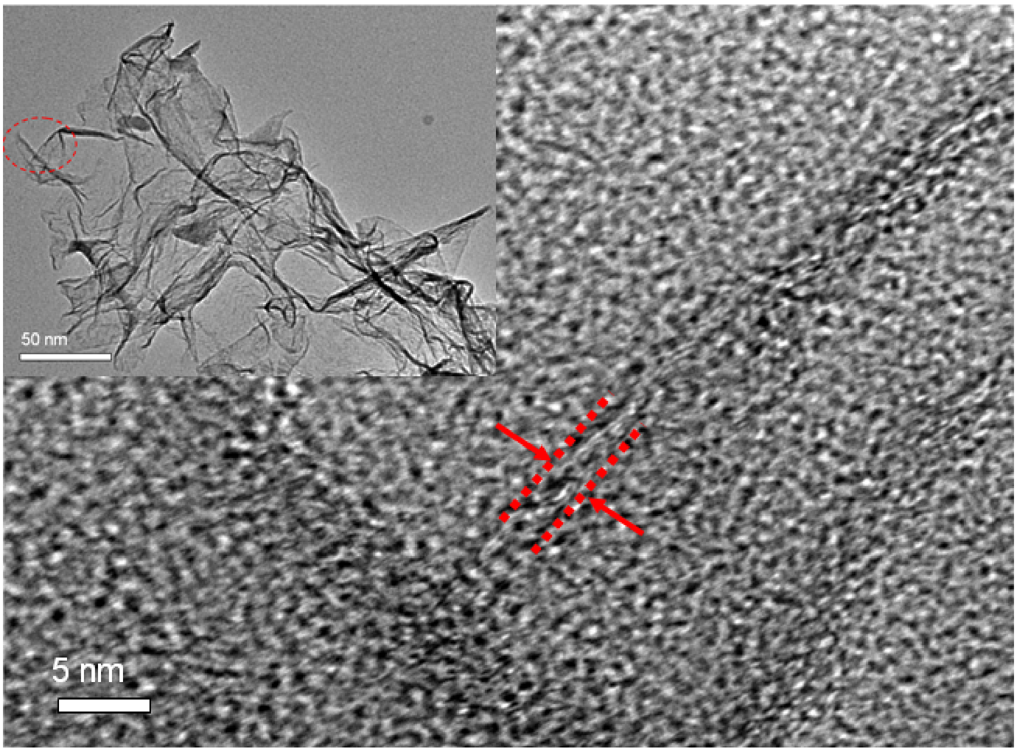

Fig. S2 HRTEM images of the edge of the graphene-like ultrathin carbon nanosheets.

Table S1 Elemental analysis, BET surface area and pore structure characterization parameters of N-CNSs from different carbonization temperature and NC-800.

Samples	Elemental analysis			BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
	C %	N %	H %			
NC-800	86.14	0.93	0.75	352.1	0.37	3.71
N-CNSs-700	83.00	4.50	1.18	486.5	2.23	18.39
N-CNSs-800	86.26	2.87	0.86	549.5	3.19	23.20
N-CNSs-900	91.11	1.81	0.59	511.7	2.69	21.06

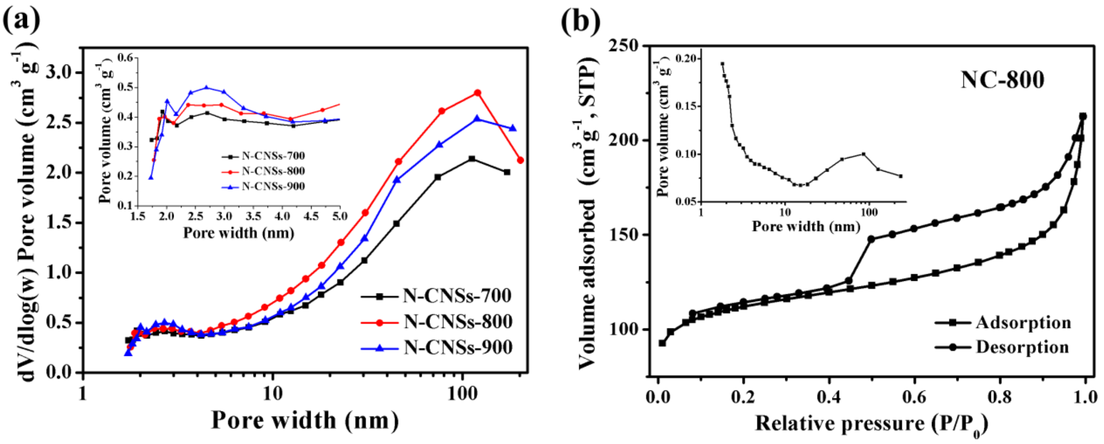

Fig. S3 (a) Pore diameter distribution curves of N-CNSs from different carbonization temperature; (b) N_2 adsorption-desorption plots and pore diameter distribution curves (inset) of NC-800.

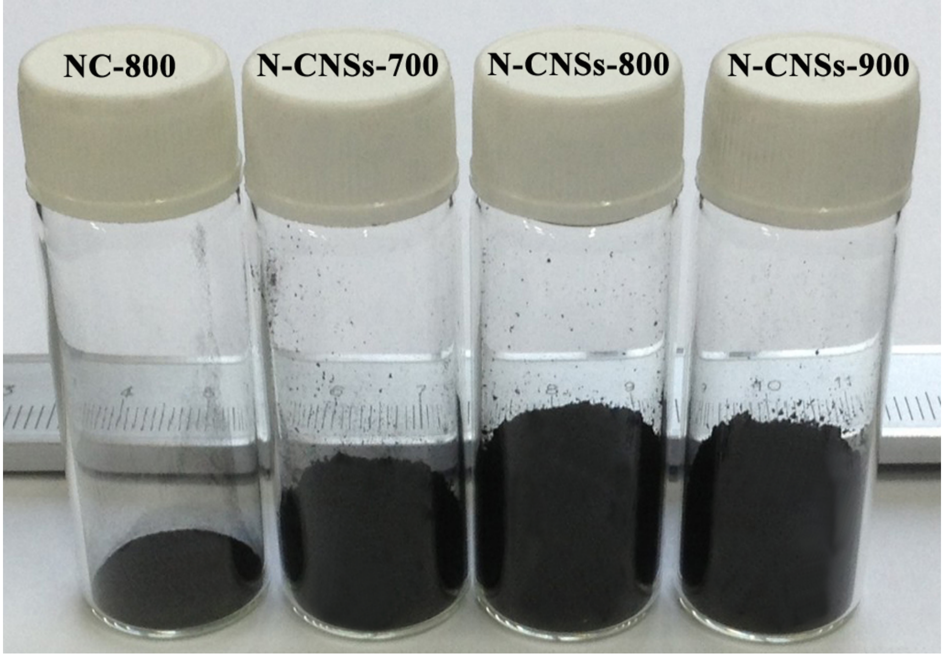

Fig. S4 Photograph of NC-800, N-CNSs-700, N-CNSs-800, and N-CNSs-900 with the same masses (20 mg) in 5 mL vials.

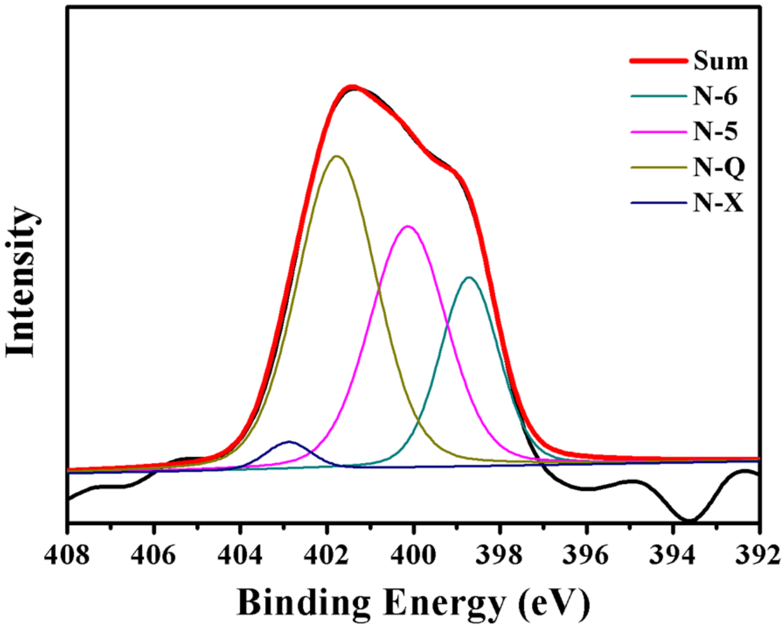

Fig. S5 X-ray photoelectron spectroscopy (XPS) of N1s regions for N-CNSs-800.

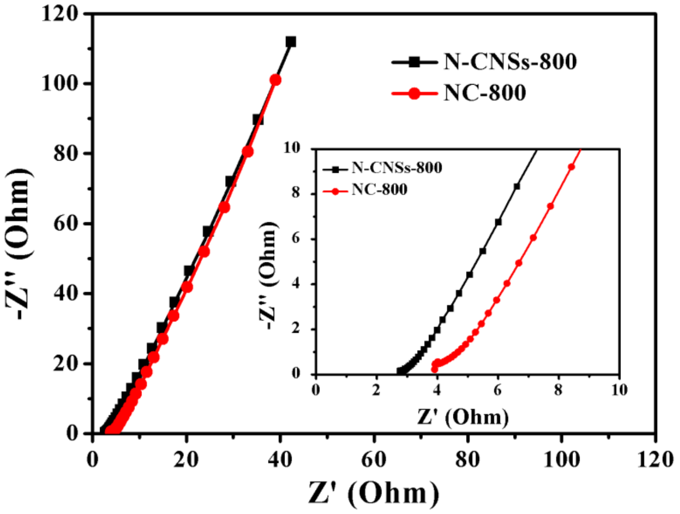

Fig. S6 Nyquist plots of N-CNSs-800 and NC-800 in 6 M KOH. The inset shows the expanded high frequency region of the plot.

Table S2 Comparison of the BET surface area, pore volume and capacitance values of different carbon-based supercapacitors in the literature

Electrode materials	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Specific capacitance (electrolyte)	Refs.
Highly corrugated graphene sheets (HCGS)	524.0	1.45	227 F g^{-1} (1 A g^{-1}) (6 M KOH)	[S2]
Embossed chemically modied graphene (e-CMG)	194.2	-	202 F g^{-1} (1 A g^{-1}) (1 M Na_2SO_4)	[S3]
Hierarchically aminated graphitic honeycombs (AGHs)	247.0	3.40	207 F g^{-1} (3 mV s^{-1}) (6 M KOH)	[S4]
N-doped carbon nanosheets	695.0	-	102 F g^{-1} (25 mV s^{-1}) (0.5 M H_2SO_4)	[S5]
Nitrogen-doped porous nanofibers (N-CNFs-900)	562.5	0.51	202 F g^{-1} (1.0 A g^{-1}) (6 M KOH)	[S6]
N-doped graphene fibers mats (NG-FMs-300)	176.0	0.21	188 F g^{-1} (5 mV s^{-1}) (6 M KOH)	[S7]
Chemically-reduced graphene (CRG)	408.6	0.52	106.3 F g^{-1} (5 mV s^{-1}) (6 M KOH)	[S8]
Nitrogen-doped graphene nanosheets (C-NGNSs)	465.0	3.42	248.4 F g^{-1} (5 mV s^{-1}) (6 M KOH)	[S8]
3D hierarchical porous graphene-like (3D HPG)	1810	1.22	305 F g^{-1} (0.5 A g^{-1}) (6 M KOH)	[S9]
N-CNSs-700	486.5	2.23	158 F g^{-1} (1 A g^{-1}) (6 M KOH)	This work
N-CNSs-800	549.5	3.19	249 F g^{-1} (1 A g^{-1}) (6 M KOH)	This work
N-CNSs-900	511.6	2.69	212 F g^{-1} (1 A g^{-1}) (6 M KOH)	This work

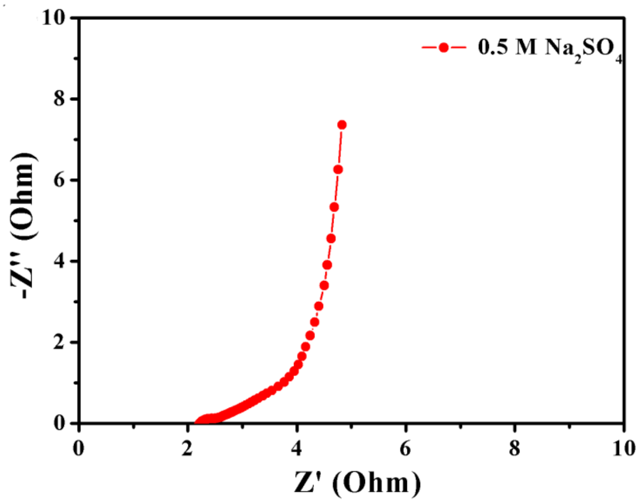

Fig. S7 Nyquist plot of symmetric two-electrode cell**.**

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