

Supplementary data

A facile and rapid preparation of highly crumpled nitrogen-doped graphene-like nanosheets toward high-performance supercapacitors

Hui Peng^a, Guofu Ma^{*a}, Kanjun Sun^b Zhiguo Zhang^a, Qian Yang^a, Feitian Ran^a and Ziqiang Lei^{*a}

^aKey Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

Fax/Tel: +86-931-7975121;

E-mail: magf@nwnu.edu.cn; Leizq@nwnu.edu.cn

^bCollege of Chemistry and Environmental Science, Lanzhou City University, Lanzhou 730070, China

Experimental section

Materials

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

Synthesis of highly crumpled nitrogen-doped graphene-like nanosheets (CN-GLSs)

Before the experiments, the macroporous anion exchange resins (AER) were pretreated by

washings with 2 M HCl and 2 M NaOH solutions alternately to remove the mechanical impurities. The final step of the conditioning consisted in percolating resins by 2 M NaOH solution through the column in order to convert the resins to OH⁻ form.^{S1} The excess of OH⁻ or Cl⁻ groups were removed from the AER by rinsing with deionized water, and then dried in an oven at 60 °C.

The typical preparation of CN-GLSs is as following: the pretreated AER (4.0 g), urea (3.0 g) and calcium chloride (4.5 g) were added into 50 mL ethanol solution and stirred at 80 °C until the mixture solution became a viscous solution. After that, the viscous solution was dried in porcelain boat at 80 °C to form carbon precursor mixtures and then put in a tube furnace. After vacuum extraction, the quartz tube was filled with high-purity nitrogen by connecting the nitrogen gas bag. The carbon precursor mixtures were firstly activated at 450 °C for 1 h in N₂ atmosphere at a heating rate of 5 °C min⁻¹. Finally, the mixtures were heated to the ultimate temperatures of 800 °C for 2 h with a heating rate of 5 °C min⁻¹ in a slow flow N₂. After cooling down to room temperature, the resulting sample was thoroughly washed with 2 M HCl to remove any inorganic salts. Afterwards, the sample was repeatedly washed by distilled water until neutral pH was reached and dried at 60 °C in ambient for 24 h. The sample is named as CN-GLSs.

For comparison purpose, AER (4.0 g) mixed with urea (3.0 g) or calcium chloride (4.5 g) were placed in porcelain boat and put in a tube furnace, respectively. The other process for preparation is the same as that of the CN-GLSs. The as-obtained samples were denoted as N-GLSs (urea treatment) and C-GLSs (calcium chloride treatment), respectively.

Materials characterization

The morphologies of the as-prepared 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, FEI Tecnai G² F20 S-Twin, USA). The elemental microanalysis (C, H and N) was carried out using the Elemental Analyzer Vario EL. 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. X-ray diffraction (XRD) of samples was performed on a diffractometer (D/Max-2400, Rigaku) advance instrument using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) 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 K α radiation source (ThermoVG Scientific).

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 the reported literature.^{S2} Typically, 4 mg of as-prepared products was ultrasonically dispersed in 0.4 mL of 0.25 wt% Nafion (DuPont, USA) ethanol solutions. 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, high purity carbon rod serves as the counter electrode, and Hg/HgO (1 mol L⁻¹ KOH) as the reference electrode.

The capacitive performance of CN-GLSs was investigated using a two-electrode testing device. The working electrode was prepared by mixing the CN-GLSs with commercial conductive carbon

black and polymer binder (polyvinylidene fluoride) (80:10:10, mass ratio) in N-methyl-2-pyrrolidone (NMP) solution until it forms a homogeneous slurry. The slurry was coated on nickel foam with a working area of 1.0 cm² and the electrodes were dried at 120 °C for 12 h and then weighted and pressed into sheets under 15 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 CN-GLSs 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, CN-GLSs electrodes and separator were immersed in 0.5 mol L⁻¹ Na₂SO₄ electrolytes for 12 h to make aqueous electrolyte solutions homogeneously diffuse into the CN-GLSs 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 760E electrochemical workstation (Chenghua, Shanghai China). 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.

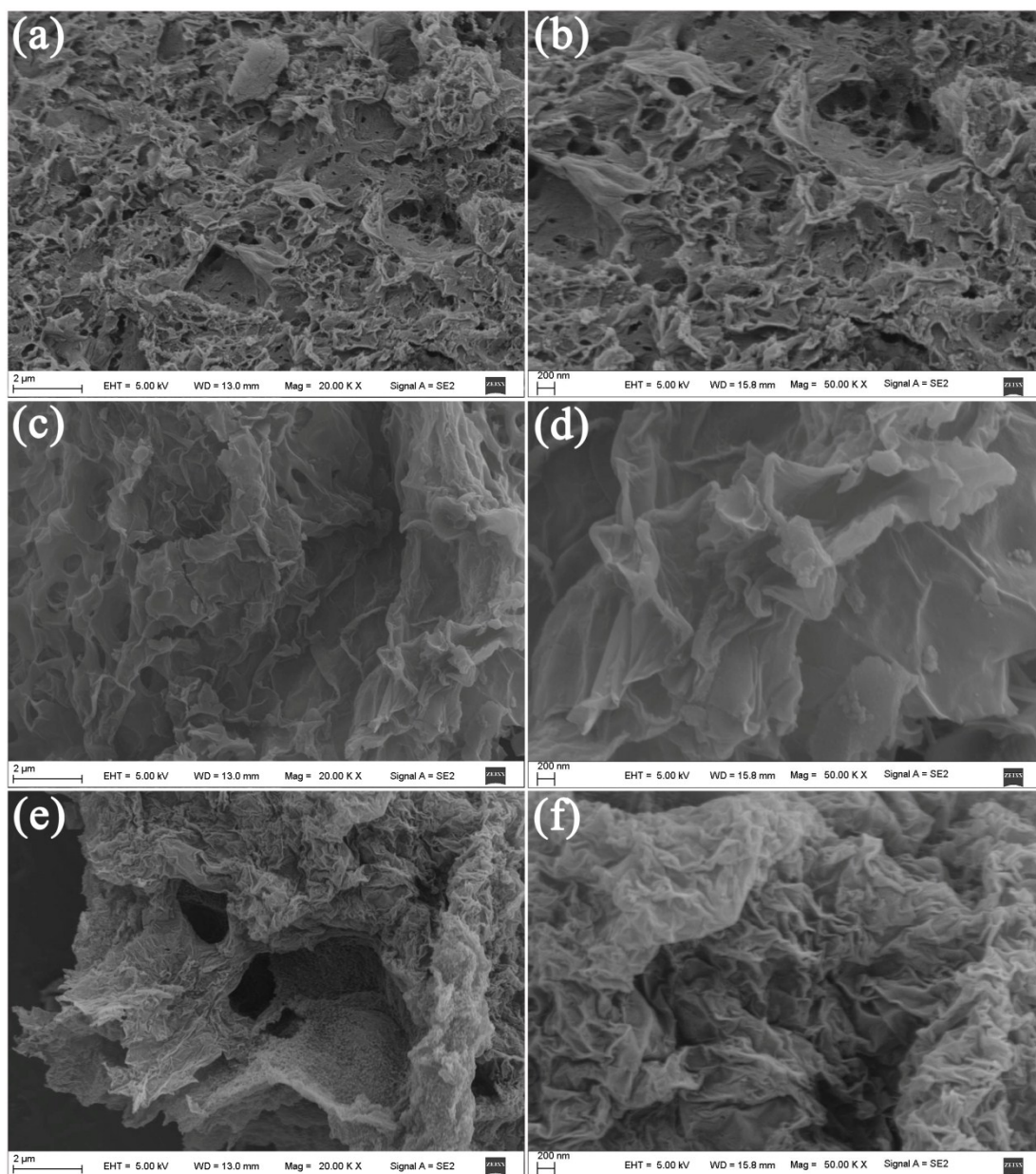


Fig. S1 SEM images of the (a,b) N-GLSs; (c,d) C-GLSs; (e,f) CN-GLSs.

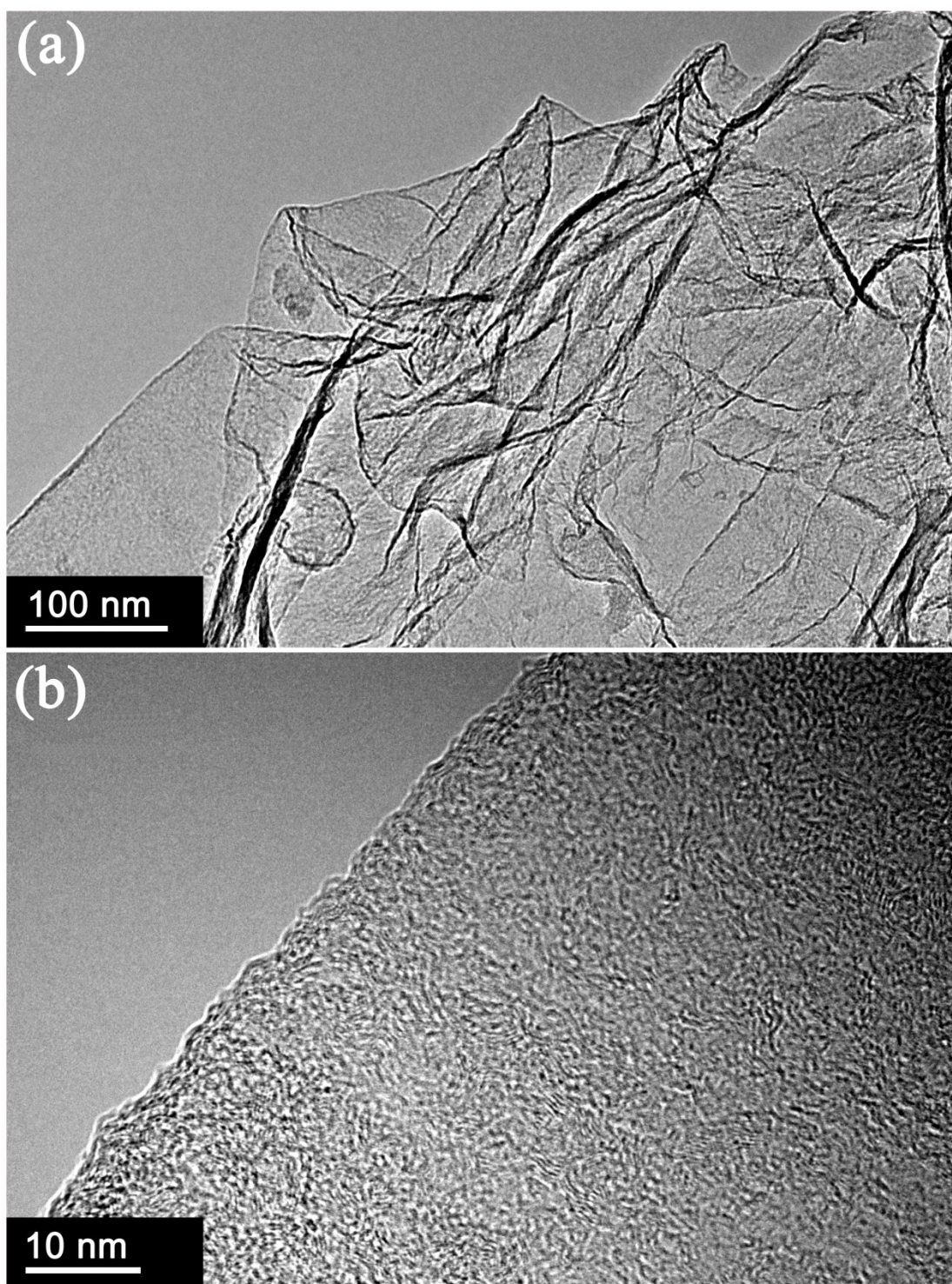


Fig. S2 HRTEM images (a, b) of the CN-GLSs.

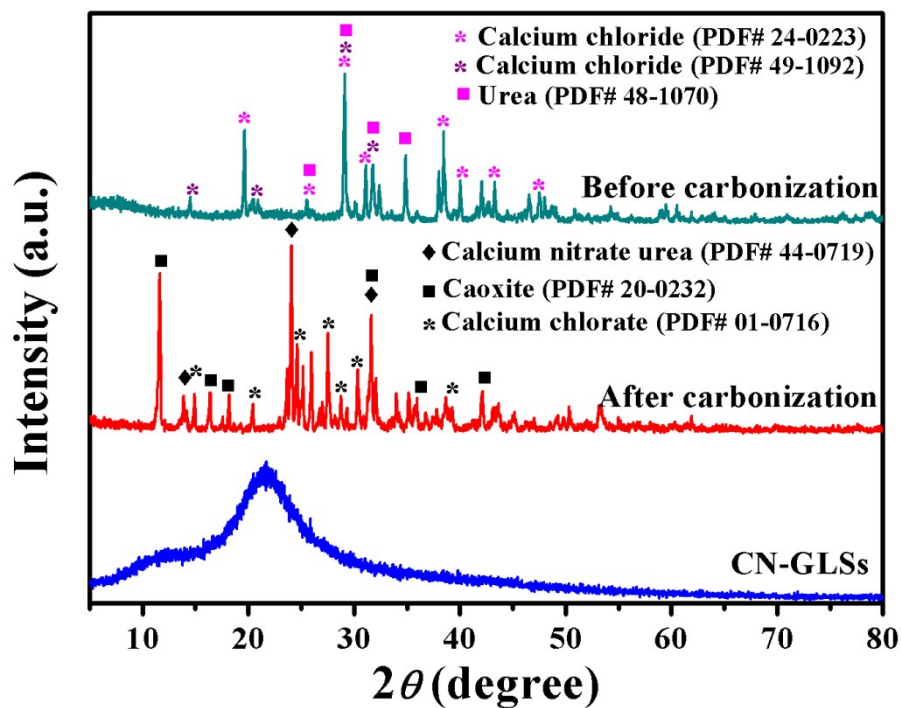


Fig. S3 X-ray powder diffraction (XRD) of hybrid materials in the stages before and after carbonization.

Table S1 Elemental analysis, BET surface area and pore structure characterization parameters of N-GLSs, C-GLSs and CN-GLSs.

Samples	Elemental analysis			$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \text{g}^{-1}$)	$V_{\text{total}}^{\text{b}}$ ($\text{cm}^3 \text{g}^{-1}$)	D^{c} (nm)
	C %	N %	H %			
N-GLSs	82.47	4.36	1.35	346	0.25	2.71
C-GLSs	80.96	0.91	1.43	502	1.33	7.56
CN-GLSs	82.54	4.25	1.32	1169	2.58	5.45

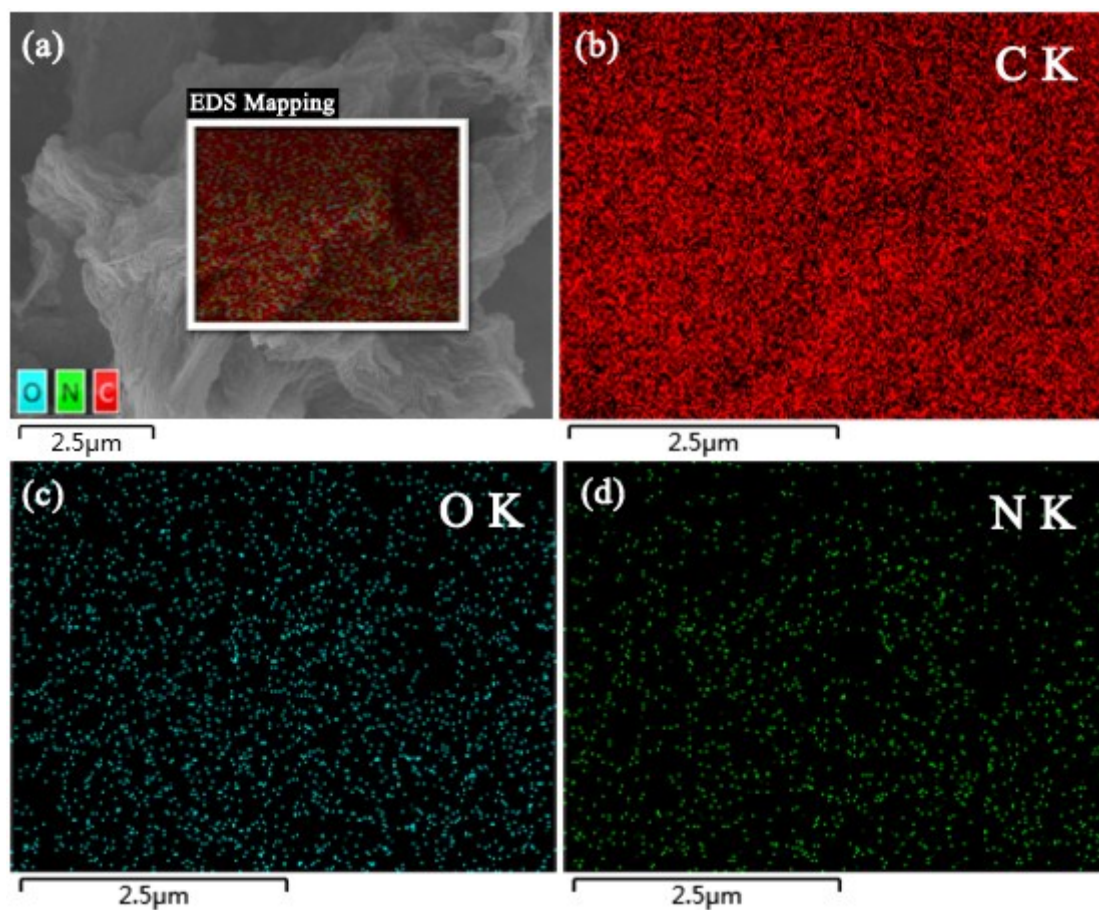


Fig. S4 (a) SEM image of CN-GLSs; (b) carbon, (c) oxygen, and (d) nitrogen element mapping images of CN-GLSs taken in the square region in Fig. S4a.

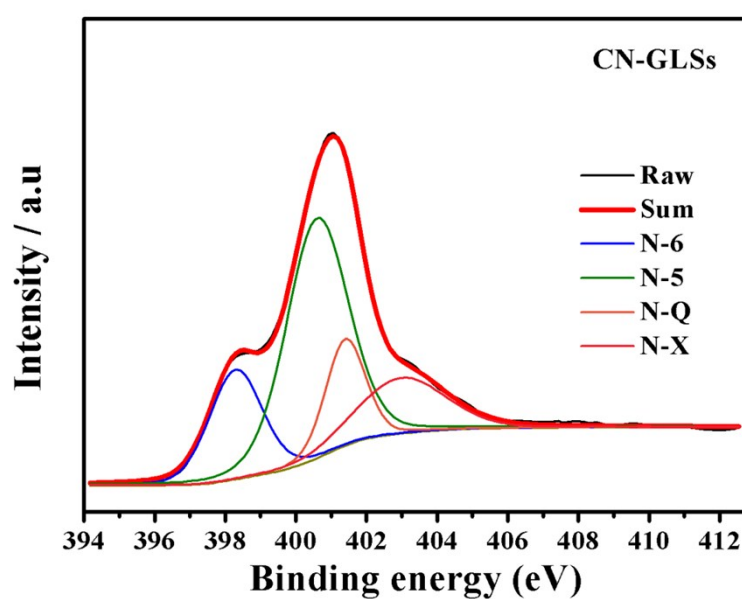


Fig. S5 X-ray photoelectron spectroscopy (XPS) of N1s regions for CN-GLSs.

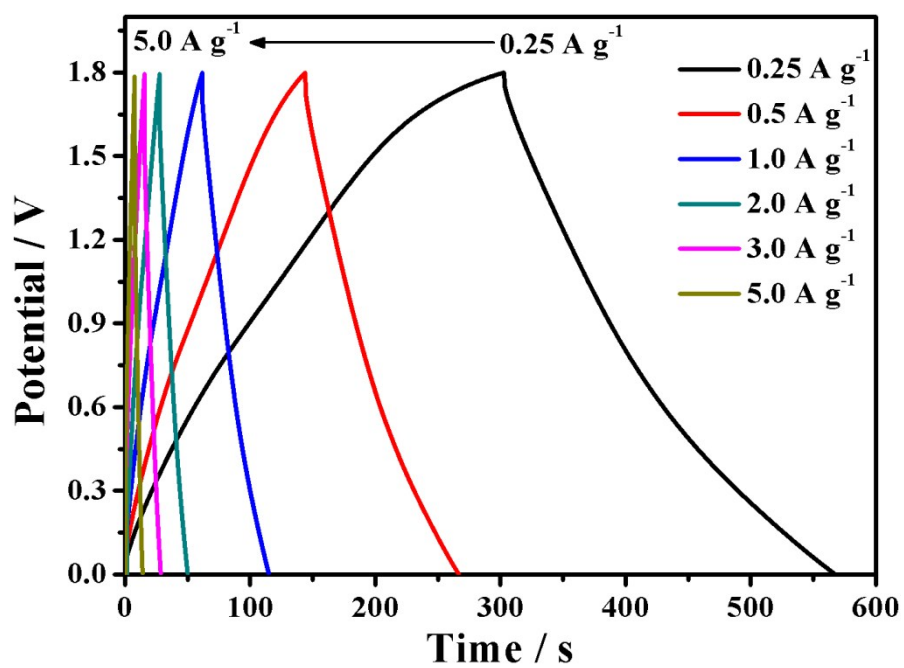


Fig. S6 Galvanostatic charge/discharge curves of CN-GLSs symmetric cell at various current densities.

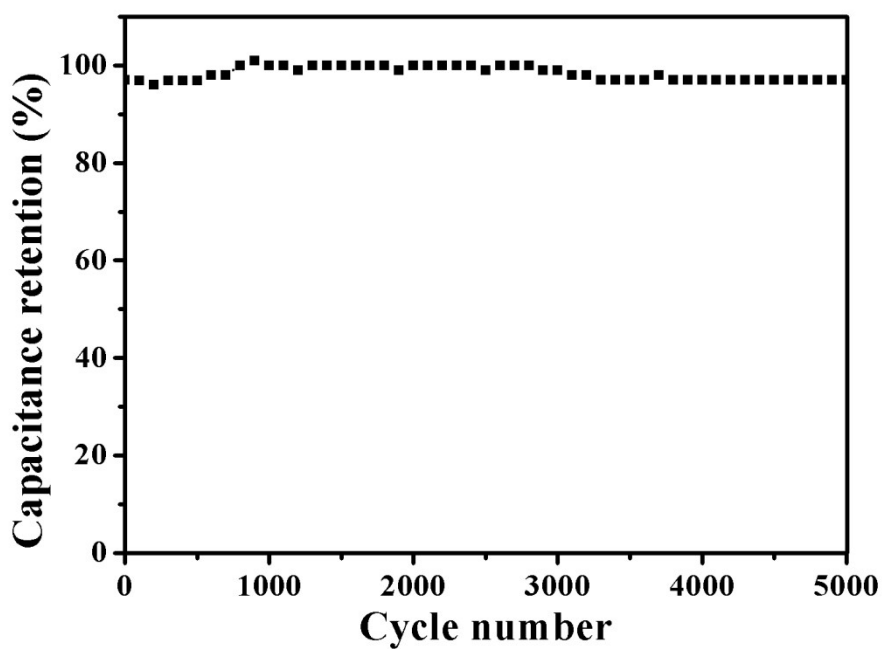


Fig. S7 Cycling stability of CN-GLSs symmetric cell device.

Table S2 Comparison of the BET surface area, pore volume and capacitance values of different crumpled graphene or carbon nanosheets electrode materials in the literature.

Electrode materials	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Specific capacitance (6 M KOH)	Refs.
Crumpled nitrogen-doped graphene-like nanosheets (CN-GLSs)	1169	2.58	294 F g ⁻¹ (0.5 A g ⁻¹)	This work
Highly corrugated graphene sheets (HCGS)	524.0	1.45	227 F g ⁻¹ (1 A g ⁻¹)	S3
Nitrogen-doped graphene nanosheets (C-NGNSs)	465.0	3.42	248.4 F g ⁻¹ (5 mV s ⁻¹)	S4
Highly crumpled graphene sheets (HCGSs)	433.1	0.98	259 F g ⁻¹ (1 A g ⁻¹)	S5
3D hierarchical porous graphene-like (3D HPG)	1810	1.22	305 F g ⁻¹ (0.5 A g ⁻¹)	S6
N-doped graphene fibers mats (NG-FMs-300)	176	0.21	188 F g ⁻¹ (5 mV s ⁻¹)	S7
Nitrogen-doped graphene	1301	0.85	293 F g ⁻¹ (5 mV s ⁻¹)	S8
Nitrogen-doped graphene (NG) sheets	412	-	295 F g ⁻¹ (5 A g ⁻¹)	S9
Nitrogen-doped carbon nanosheets (N-CNSs)	549.5	3.19	249 F g ⁻¹ (1 A g ⁻¹)	S10

Table S3 Performances comparison of symmetric cells used various carbon materials in the references.

Carbon type	Electrolyte	Operation voltage (V)	<i>E</i> (Wh kg ⁻¹)	<i>P</i> (W kg ⁻¹)	Refs.
Crumpled nitrogen-doped graphene-like nanosheets (CN-GLSs)	Na ₂ SO ₄ (0.5 M)	1.8	17.0	225	This work
Hierarchical porous carbon material (FHPC)	Na ₂ SO ₄ (1 M)	1.8	15.9	317.5	S11
Mesoporous carbon sheet-like framework (MCSF)	Na ₂ SO ₄ (1 M)	1.6	9.6	108.5	S12
Activated carbon (AC)	Li ₂ SO ₄ (1 M)	1.6	16.9	200	S13
Hierarchical porous carbon (HPC)	Li ₂ SO ₄ (1 M)	1.6	11	~100	S14
	TEABF ₄ /PC (1 M)	2.7	20	-	
Phosphorus and oxygen enriched carbons (APP900)	H ₂ SO ₄ (1 M)	1.5	6.5	3410	S15
Porous graphene-like nanosheets (PGNSs)	KOH (6 M)	1.0	9.58	500	S16
Nitrogen-doped carbonaceous nanofibers (N-CNFs)	KOH (6 M)	1.0	7.11	~130	S17
Nitrogen-doped graphene (NG)	KOH (6 M)	1.0	7.6	23	S18
Carbon nanosheets (CNS-750)	Ionic liquid	3.0	19	20K	S19

References

- S1 S. A. Cavaco, S. Fernandes, M. M. Quina, L. M. Ferreira, *J. Hazard. Mater.*, 2007, **144**, 634.
- S2 Z. Li, L. Zhang, B. S. Amirkhiz, X. Tan, Z. Xu, H. Wang, B. C. Olsen, C. M. B. Holt, D. Mitlin, *Adv. Energy Mater.*, 2012, **2**, 431.
- S3 J. Yan, J. Liu, Z. Fan, T. Wei, L. Zhang, *Carbon*, 2012, **50**, 2179.
- S4 Z. Wen, X. Wang, S. Mao, Z. Bo, H. Kim, S. Cui, G. Lu, X. Feng, J. Chen, *Adv. Mater.*, 2012, **24**, 5610.
- S5 J. Yan, Y. Xiao, G. Ning, T. Wei, Z. Fan, *RSC Adv.*, 2013, **3**, 2566.
- S6 Y. Li, Z. Li, P. Shen, *Adv. Mater.*, 2013, **25**, 2474.
- S7 Y. Chang, G. Han, D. Fu, F. Liu, M. Li, Y. Li, *J. Power Sources*, 2014, **252**, 113.
- S8 H. Jin, X. Wang, Z. Gu, Q. Fan, B. Luo, *J. Power Sources*, 2015, **273**, 1156.
- S9 H. Zhang, T. Kuila, N. H. Kim, D. Yu, J. H. Lee, *Carbon*, 2014, **69**, 66.
- S10 H. Peng, G. Ma, K. Sun, J. Mu, Z. Lei, *J. Mater. Chem. A*, 2014, **2**, 17297.
- S11 C. Huang, A. M. Puziy, T. Sun, O. I. Poddubnaya, F. Suárez-García, J. M. D. Tascón, D. Hulicova-Jurcakova, *Electrochim. Acta*, 2014, **137**, 219.
- S12 Q. Wang, J. Yan, T. Wei, J. Feng, Y. Ren, Z. Fan, M. Zhang, X. Jing, *Carbon*, 2013, **60**, 481.
- S13 L. Chen, X. Zhang, H. Liang, M. Kong, Q. Guan, P. Chen, Z. Wu, S. Yu, *ACS Nano*, 2012, **6**, 7092.
- S14 Y. Guo, Z. Shi, M. Chen, C. Wang, *J. Power Sources*, 2014, **252**, 235.
- S15 X. Sun, X. Zhang, H. Zhang, D. Zhang, Y. Ma, *J. Solid State Electrochem.*, 2012, **16**, 2597.
- S16 L. Sun, C. Tian, M. Li, X. Meng, L. Wang, R. Wang, J. Yin, H. Fu, *J. Mater. Chem. A*, 2013, **1**, 6462.

- S17 Q. Wang, J. Yan, Y. Wang, T. Wei, M. Zhang, X. Jing, Z. Fan, *Carbon*, 2014, **67**, 119.
- S18 M. Li, J. Xue, *J. Phys. Chem. C*, 2014, **118**, 2507.
- S19 H. Wang, Z. Xu, A. Kohandehghan, Z. Li, K. Cui, X. Tan, T. J. Stephenson, C. K. King'andu, C. M. B. Holt, B. C. Olsen, J. K. Tak, D. Harfield, A. O. Anyia, D. Mitlin, *ACS Nano*, 2013, **7**, 5131.