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Supplementary Information

Multi-layered zeolitic imidazolate frameworks engaged self-templated synthesis of nitrogen-doped hollow porous carbon dodecahedrons as robust substrate for supercapacitor

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Experimental

Materials and chemicals

All chemicals were used as received without further purification.

Synthesis of ZIF-8 crystals and ZIF-67 crystals

In a typical synthesis, ZIF-8 crystals were synthesized by mixing zinc nitrate hexahydrate methanol solution (2 mmol, 5 mL) and 2-methylimidazole (MeIm) methanol solution (8 mmol, 20 mL) with magnetic stirring for 2 hours and the reaction was aged for another 12 hours at room temperature (RT). ZIF-67 crystals were synthesized by mixing cobalt nitrate hexahydrate methanol solution (2 mmol, 5 mL) and MeIm methanol solution (40 mmol, 100 mL) at the same protocol. The obtained products were washed with ethanol twice and collected by centrifugation, and finally dried in a vacuum oven at 60 °C for 12 hours.

Synthesis of multi-layered core-shell ZIFs

Taking the synthesis of three-layered core-shell ZIF-67@ZIF-8@ZIF-67 crystals for example, core seeds of ZIF-67 synthesized by the aforementioned method were dispersed in MeIm methanol solution (80 mmol, 400 mL) by sonication for 30 min, then zinc acetate tetrahydrate methanol solution (20 mmol, 100 mL) was injected into ZIF-67 methanol dispersion to fabricate ZIF-8 shell on the surface of ZIF-67. Subsequently, the reaction was kept stirring for 2 hours, aged for 12 hours at RT. Finally, the as-synthesized core-shell ZIF-67@ZIF-8 crystals were used as core seeds, three-layered core-shell ZIF-67@ZIF-8@ZIF-67 crystals were synthesized according to the same protocol by adopting the MeIm methanol solution (80 mmol, 400 mL) and the cobalt acetate tetrahydrate methanol solution (20 mmol, 100 mL) to prepare the ZIF-67 shell.

Similar with preparations of three-layered core-shell ZIF-67@ZIF-8@ZIF-67 crystals, five-layered core-shell ZIF-67@ZIF-8@ZIF-67@ZIF-8@ZIF-67 crystals could be prepared by using as-synthesized ZIF-67@ZIF-8@ZIF-67 crystals as cores and adopting the above synthetic methods to fabricate the next ZIF-8 shell and ZIF-67 shell. Two-layered core-shell ZIF-8@ZIF-67 and four-layered core-shell ZIF-8@ZIF-67@ZIF-8@ZIF-67 could also be prepared by using ZIF-8 crystals as the innermost core seeds via epitaxial growth.

Synthesis of N-doped porous hollow carbon dodecahedrons

The prepared multi-layered core-shell ZIFs including two-layered core-shell ZIF-8@ZIF-67, four-layered core-shell ZIF-8@ZIF-67@ZIF-8@ZIF-67, three-layered core-shell ZIF-67@ZIF-8@ZIF-67, and five-layered core-shell ZIF-67@ZIF-8@ZIF-67@ZIF-8@ZIF-67 were carbonized under nitrogen atmosphere at 500 °C for 1 h and 750 °C for 1h, with a heating rate of 2 °C·min⁻¹. Subsequently, all the

as-prepared porous carbons were washed by HNO₃ solution (3 M) at 80 °C for 12 h to remove the residual Zn and Co species. Finally, N-doped single-shell hollow porous carbon dodecahedrons (N-SS-HPCDs), N-doped double-shell hollow porous carbon dodecahedrons (N-DS-HPCDs), N-doped yolk-shell hollow porous carbon dodecahedrons (N-YS-HPCDs), and N-doped yolk-double-shell hollow porous carbon dodecahedrons (N-YDS-HPCDs) were obtained from the precursors of two-layered core-shell ZIF-8@ZIF-67, four-layered core-shell ZIF-8@ZIF-67@ZIF-8@ZIF-67, three-layered core-shell ZIF-67@ZIF-8@ZIF-67, and five-layered core-shell ZIF-67@ZIF-8@ZIF-67@ZIF-8@ZIF-67, respectively. In addition, ZIF-8 crystals and ZIF-67 crystals were carbonized by the same protocol as control experiments.

Characterization

D/MAX 2500 powder X-ray diffractometer (XRD) with Cu-K α radiation (0.15418 nm) from Rigaku was used for the crystal phases measurements. The morphology of multi-layered core-shell ZIFs and N-doped porous hollow carbon dodecahedrons were observed by SU8020 field-emission scanning electron microscopy (FESEM) from Hitachi and JEM-2100F high resolution transmission electron microscopy (HRTEM) from JEOL. The electronic states of N in the carbon matrix were also studied with an ESCALAB250Xi X-ray photoelectron spectroscopy (XPS) with its energy analyzer working in the pass energy mode at 50 eV, and the Mg K α line was used as the excitation source. Raman spectra of obtained N-doped porous hollow carbon dodecahedrons were collected from a Micro-Raman spectrometer (LabRAM HR Evolution). N₂ adsorption/desorption isotherm and Brunauer-Emmett-Teller (BET) surface areas of multi-layered core-shell ZIFs and N-doped porous hollow carbon dodecahedrons were collected using a Quantachrome Autosorb IQ instrument with liquid nitrogen at 77 K.

Electrochemical measurements

About 10 mg obtained N-doped porous hollow carbon dodecahedrons were mixed with poly(vinylidene difluoride) (1 mg), then the mixture was dissolved and homogenized by ultrasonication in N-methylpyrrolidinone solvent (0.5 mL). Subsequently, about 0.05 mL slurry was smeared and dried (in a vacuum oven at 80 °C for 4 hours) on a graphite paper (1 cm²). The electrochemical properties were carried out in a standard three-electrode electrochemical cell on an electrochemical workstation (Autolab PGSTAT 302N). Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were measured in 2 M KOH solution with the Ag/AgCl (3 M KCl) as the reference electrode, and Pt rod as the counter electrode. Electrochemical impedance spectra (EIS) measurements were carried out in the frequency range from 0.01Hz to 100 kHz at open circuit potential with an ac perturbation of 5 mV. The capacitance (C , F g⁻¹) was calculated from GCD plots according to the following equation :

$$C = \frac{I\Delta t}{m\Delta V}$$

Where I is the discharge current (A), m is the mass of the active materials (g), ΔV is the potential drop excluding the IR drop (V) and Δt is the total discharge time (s).

A symmetrical supercapacitor device was assembled for measurement of N-YDS-HPCDs. Two prepared electrodes with same size and loading mass were soaked in 2 M KOH aqueous solution for 8 h. Subsequently, two electrodes separated by a KOH aqueous solution soaked cellulose paper were placed into a pair of glass plates, which were fixed by two stainless steel clamps. The specific capacitance (C , $F g^{-1}$) was calculated from GCD plots, where m is total mass of active materials of two electrodes, the specific energy density (SE , $W h kg^{-1}$) and specific power density (SP , $W kg^{-1}$) were calculated using the following equations, respectively:

$$C = \frac{4I\Delta t}{m\Delta V}$$

$$SE = \frac{C\Delta V^2}{28.8}$$

$$SP = \frac{3600 * SE}{\Delta t}$$

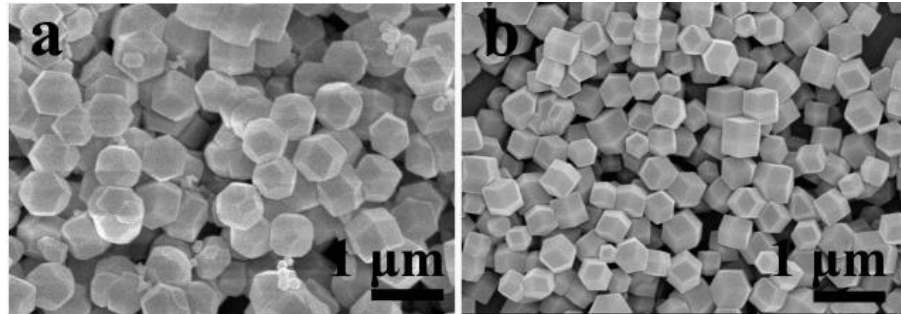


Fig. S1 SEM images of ZIF-8 crystals (a) and ZIF-67 crystals (b).

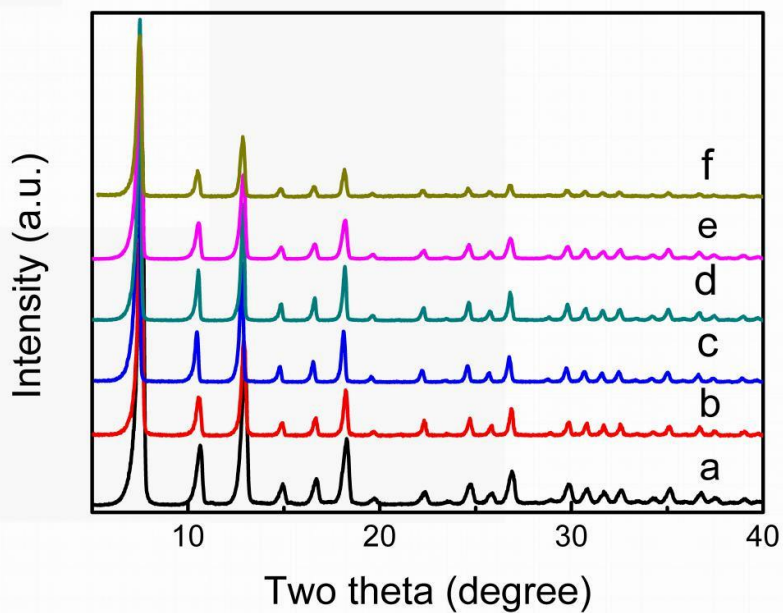


Fig. S2 XRD patterns of ZIF-8 crystals (a), ZIF-67 crystals (b), ZIF-8@ZIF-67 crystals (c), ZIF-67@ZIF-8@ZIF-67 crystals (d), ZIF-8@ZIF-67@ZIF-8@ZIF-67 crystals (e), and ZIF-67@ZIF-8@ZIF-67@ZIF-8@ZIF-67 crystals (f).

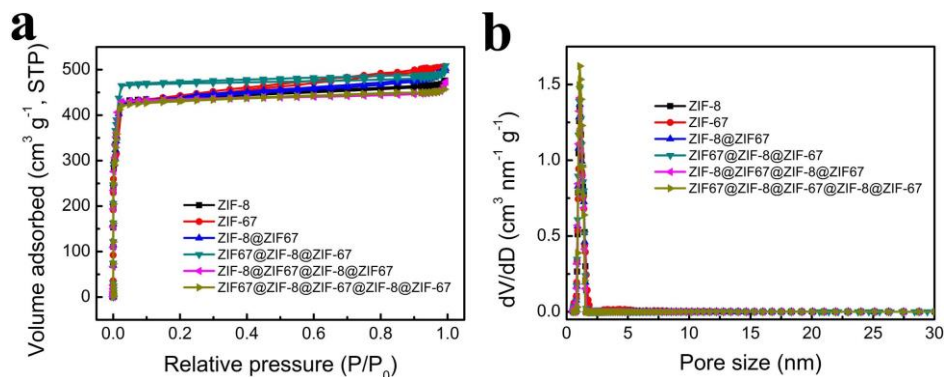


Fig. S3 The N₂ adsorption/desorption isotherms (a) and the pore-size distribution curves (b) of ZIF-8, ZIF-67, ZIF-8@ZIF-67, ZIF-67@ZIF-8@ZIF-67, ZIF-8@ZIF-67@ZIF-8@ZIF-67, and ZIF-67@ZIF-8@ZIF-67@ZIF-8@ZIF-67.

Table. S1 Summary on the surface areas, total pore volumes, and pore sizes of ZIF-8, ZIF-67, ZIF-8@ZIF-67, ZIF-67@ZIF-8@ZIF-67, ZIF-8@ZIF-67@ZIF-8@ZIF-67, and ZIF-67@ZIF-8@ZIF-67@ZIF-8@ZIF-67.

Sample	S_{BET} (m ² g ⁻¹)	V_{pore} (cm ³ g ⁻¹)	Pore size (nm)
ZIF-8	1948	0.736	1.076
ZIF-67	1871	0.785	1.076
ZIF-8@ZIF-67	1953	0.777	1.076
ZIF-67@ZIF-8@ZIF-67	2092	0.787	1.076
ZIF-8@ZIF-67@ZIF-8@ZIF-67	1949	0.732	1.076
ZIF-67@ZIF-8@ZIF-67@ZIF-8@ZIF-67	1947	0.724	1.076

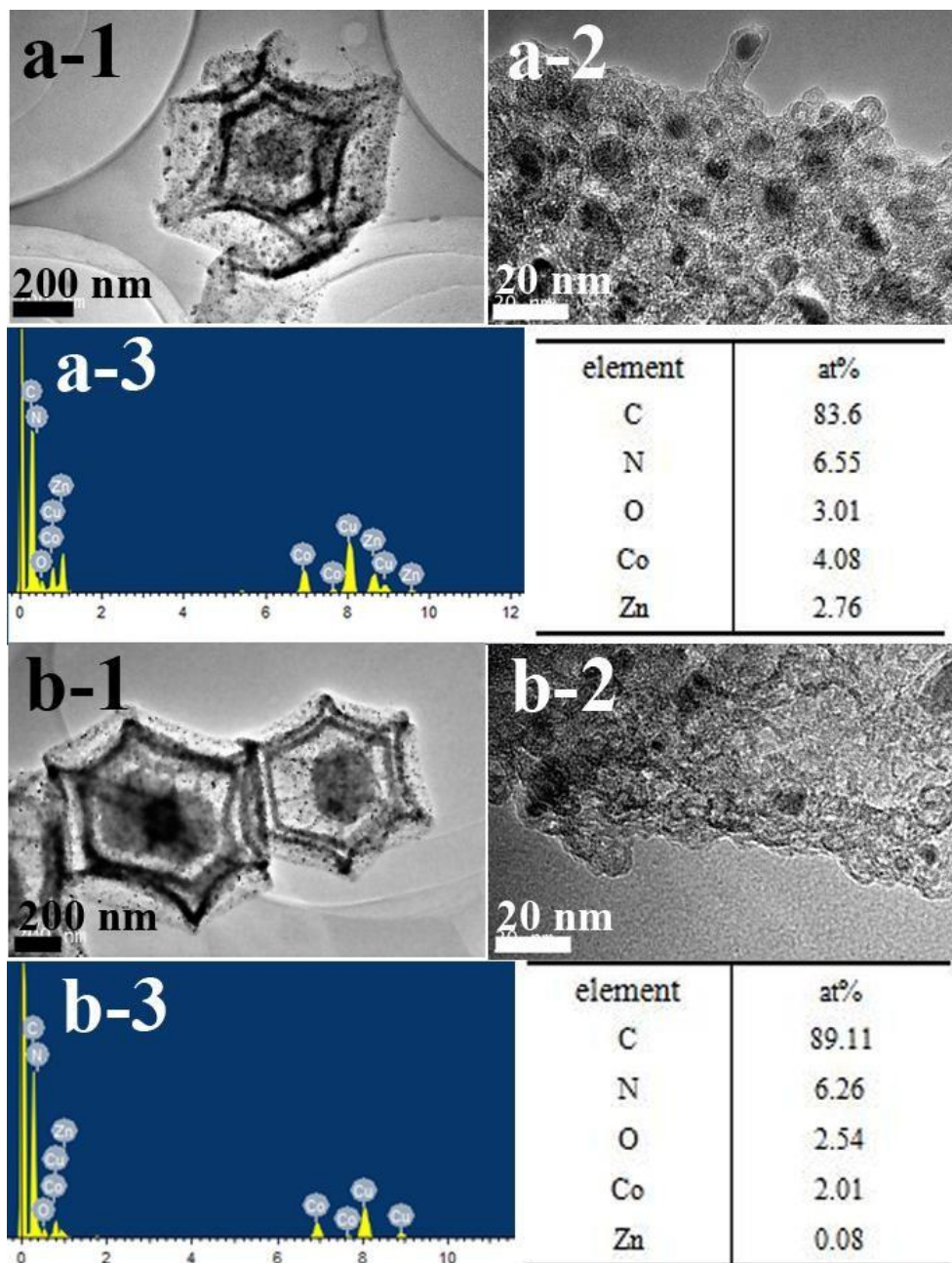


Fig. S4 TEM images and EDX data of N-YDS-HPCDs before (a) and after (b) HNO_3 solution treatment.

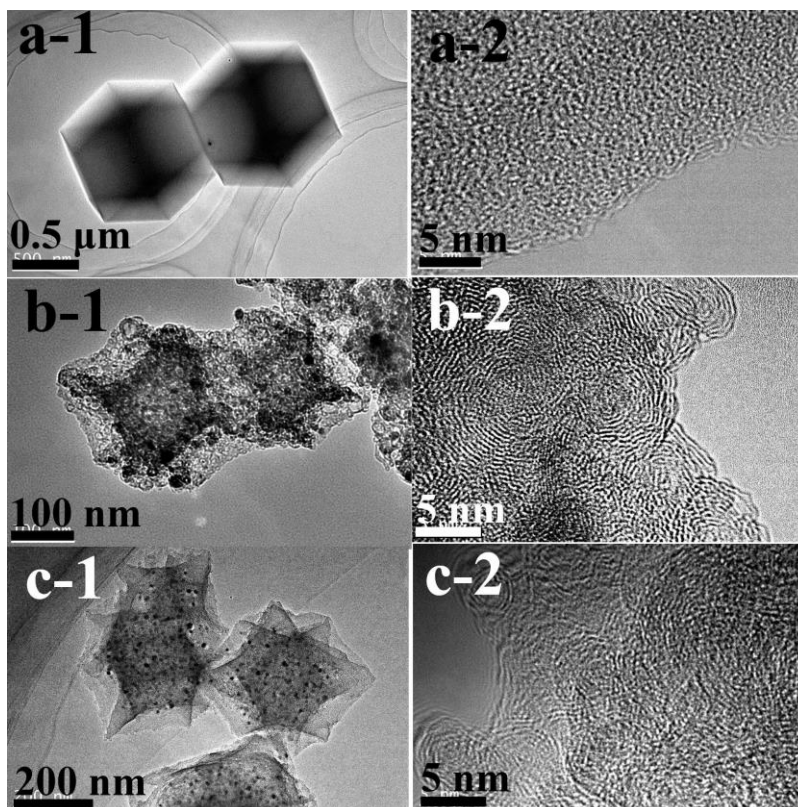


Fig. S5 TEM images and HRTEM images of the amorphous carbon particles derived from ZIF-8 (a-1, a-2), the graphitic carbon particles derived from ZIF-67 (b-1, b-2), and the solid carbon dodecahedrons derived from core-shell ZIF-67@ZIF-8 (c-1, c-2).

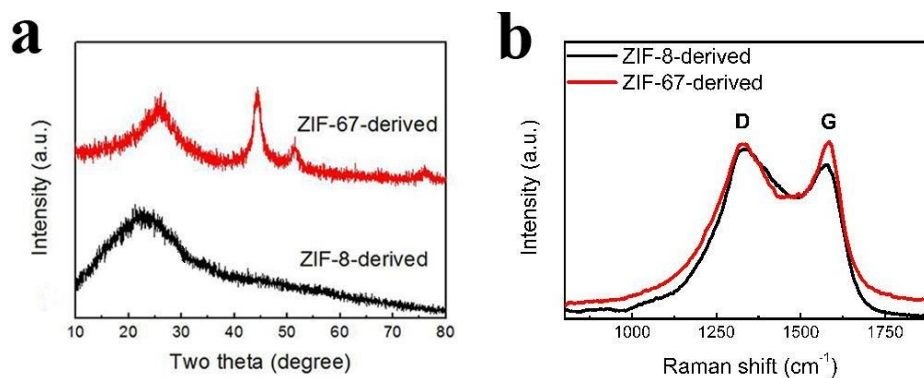


Fig. S6 XRD patterns (a) and Raman spectra (b) of ZIF-8-derived and ZIF-67-derived carbon dodecahedrons.

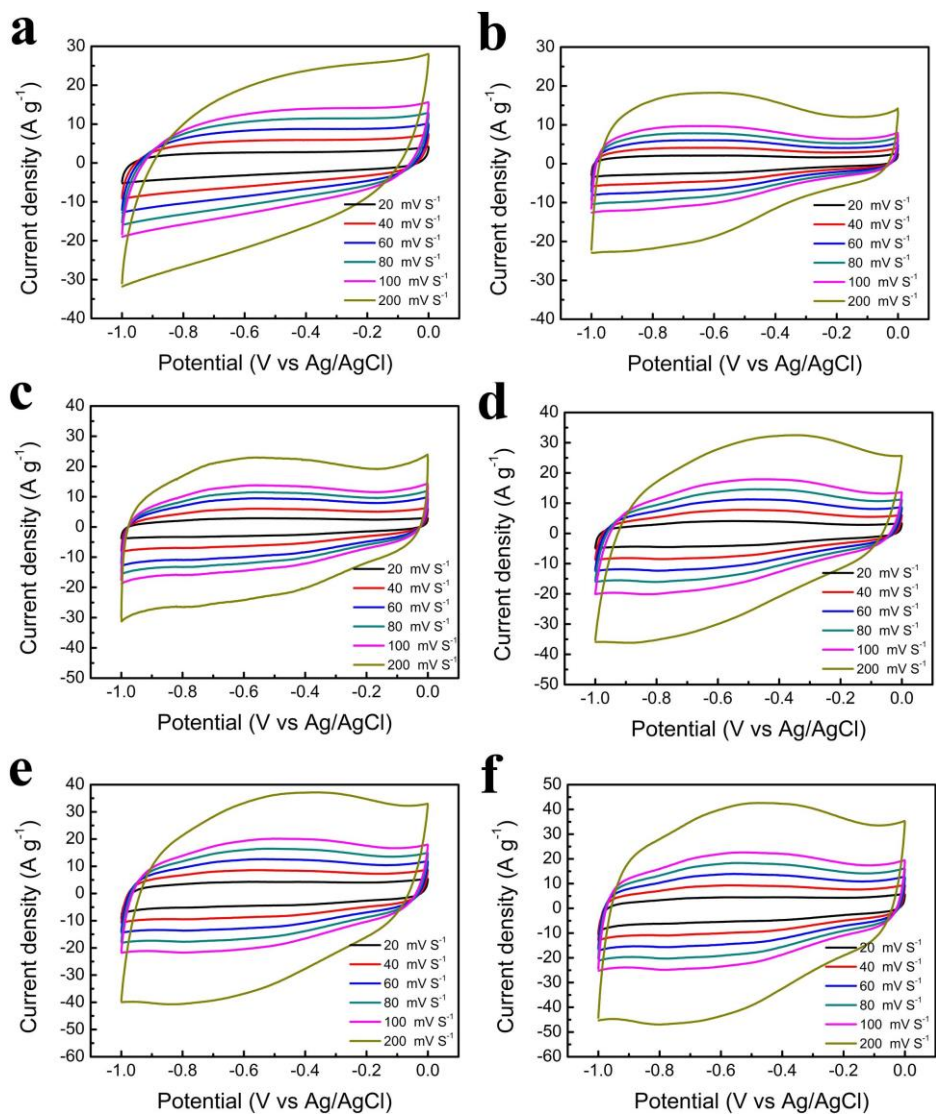


Fig. S7 The CV curves of ZIF-8-derived carbon dodecahedrons (a), ZIF-67-derived carbon dodecahedrons (b), N-SS-HPCDs (c), N-DS-HPCDs (d), N-YS-HPCDs (e), and N-YDS-HPCDs (f) at the potential scan rate of 20, 40, 60, 80, 100, and 200 mV S^{-1} .

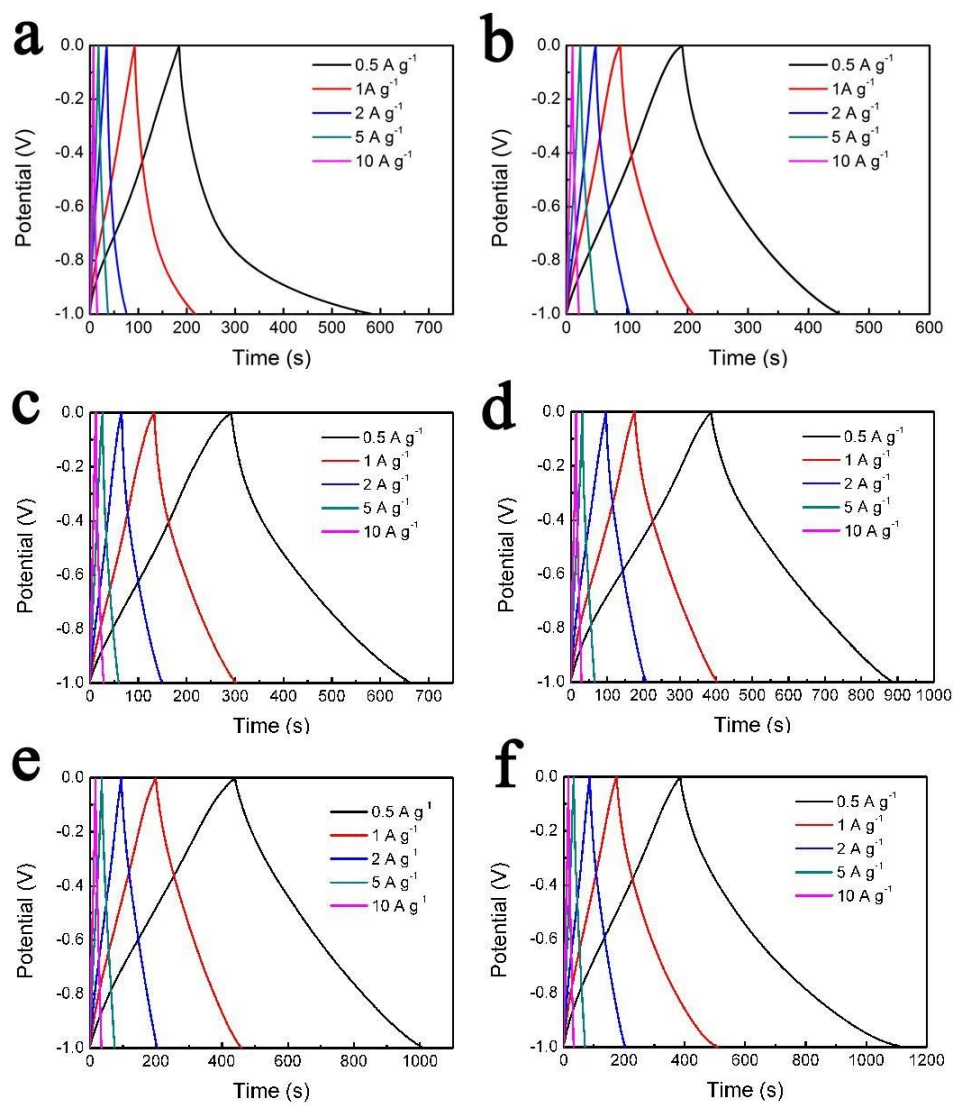


Fig. S8 The GCD plots of ZIF-8-derived carbon dodecahedrons (a), ZIF-67-derived carbon dodecahedrons (b), N-SS-HPCDs (c), N-DS-HPCDs (d), N-YS-HPCDs (e), and N-YDS-HPCDs (f) at different current densities.

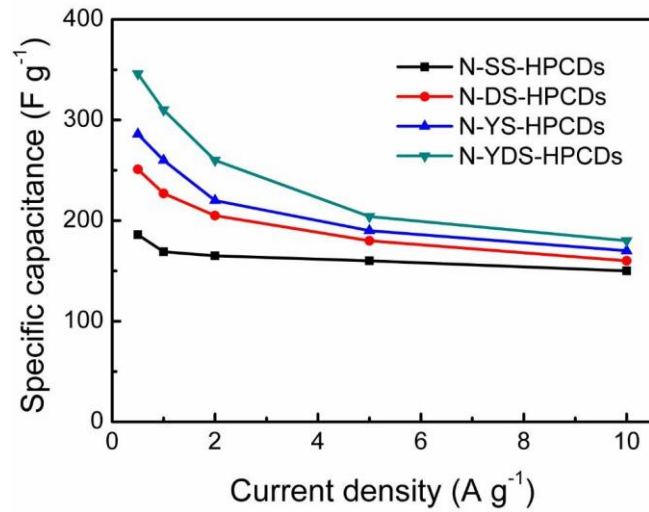


Fig. S9 The specific capacitances of N-SS-HPCDs , N-DS-HPCDs , N-YS-HPCDs , and N-YDS-HPCDs at different current densities.

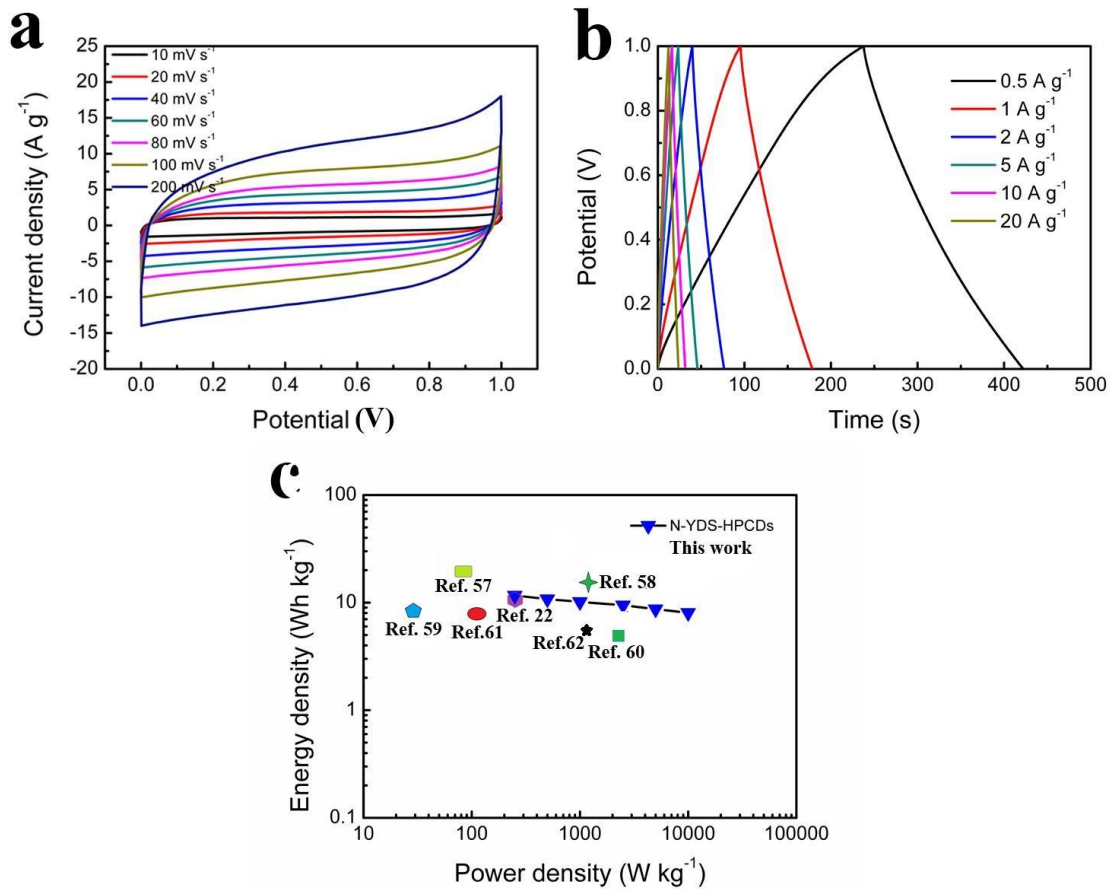


Fig. S10 The CV curves (a), GCD plots (b) and Ragone plots (c) of N-YDS-HPCDs based on a symmetrical supercapacitor device.

Table. S2 Comparison of specific capacitances of N-doped porous carbon materials reported in the representative literatures.

Materials	Nitrogen content (wt%)	Electrolyte	Potential range (V)	Loading mass of active materials	Testing condition	Current density (A g ⁻¹)	Capacitance (F g ⁻¹)	Ref.
N-YDS-HPCDs	12.8	2 M KOH	1.0	1.0 mg cm ⁻²	three-electrode	0.5	346 F g ⁻¹	This work
Nanoporous NC@GC	10.6	1 M H ₂ SO ₄	0.8	1.0 mg cm ⁻²	three-electrode	2.0	270 F g ⁻¹	<i>J. Am. Chem. Soc.</i> , 2015 , 137 , 1572.
Double-shells hollow carbon spheres	5.6	1 M H ₂ SO ₄	0.8	0.7 mg cm ⁻²	three-electrode	1.0	381 F g ⁻¹	<i>ACS Appl. Mater. Interfaces</i> , 2015 , 7 , 18609.
Nitrogen-doped porous nanofibers	7.2	6 M KOH	1.0	5.0-6.0 mg cm ⁻²	three-electrode	1.0	202 F g ⁻¹	<i>ACS Nano</i> , 2012 , 6 , 7092.
Hetroatom-doped carbon	0.7	1 M H ₂ SO ₄	1.0	Not reported	three-electrode	2.0	245 F g ⁻¹	<i>Adv. Funct. Mater.</i> 2013 , 23 , 1305.
Nitrogen-doped hollow carbon spheres	6.0	2 M H ₂ SO ₄	0.8	1.88 mg cm ⁻²	three-electrode	2.0	245 F g ⁻¹	<i>J. Mater. Chem.</i> 2012 , 22 , 13464.
Hierarchically flower-like N-doped porous carbon	1.9	6 M KOH	1.0	1.0 mg cm ⁻²	three-electrode	0.5	149 F g ⁻¹	<i>Inorg. Chem.</i> 2016 , 55 , 6552.
Exfoliated Carbon Nanosheets	6.13	6 M KOH	1.0	1.57 mg cm ⁻²	three-electrode	0.5	265 F g ⁻¹	<i>ACS Appl. Mater. Interfaces</i> 2017 , 9 , 17317.
Hollow particle-based nitrogen-doped carbon nanofibers	9.39	2 M H ₂ SO ₄	1.0	1.0 mg cm ⁻²	two-electrode	1.0	307.2 F g ⁻¹	<i>Energy Environ. Sci.</i> , 2017 , 10 , 1777.