Supporting Information:

Hierarchical N-Doped Porous Carbons for Zn–Air Batteries and Supercapacitors

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Preparation of Ni-Fe layered double hydroxide (NiFe-LDH)

The Ni-Fe layered double hydroxide (NiFe-LDH) was fabricated by a hydrothermal method reported previously [S1]. Typically, 3.6 mmol Ni $(NO_3)_2 \cdot 6H_2O$, 1.8 mmol $Fe(NO_3)_3 \cdot 9H_2O$ and 126 mmol $CO(NH_2)_2$ were dissolved in 50 mL of deionized wate and stirred for 15 min. subsequently, the mixtures were hydrothermal treatment at 120 °C for 10 h. The resulting products were washed with deionized water and ethanol 3 times, and dried at 60 °C for 12 h.

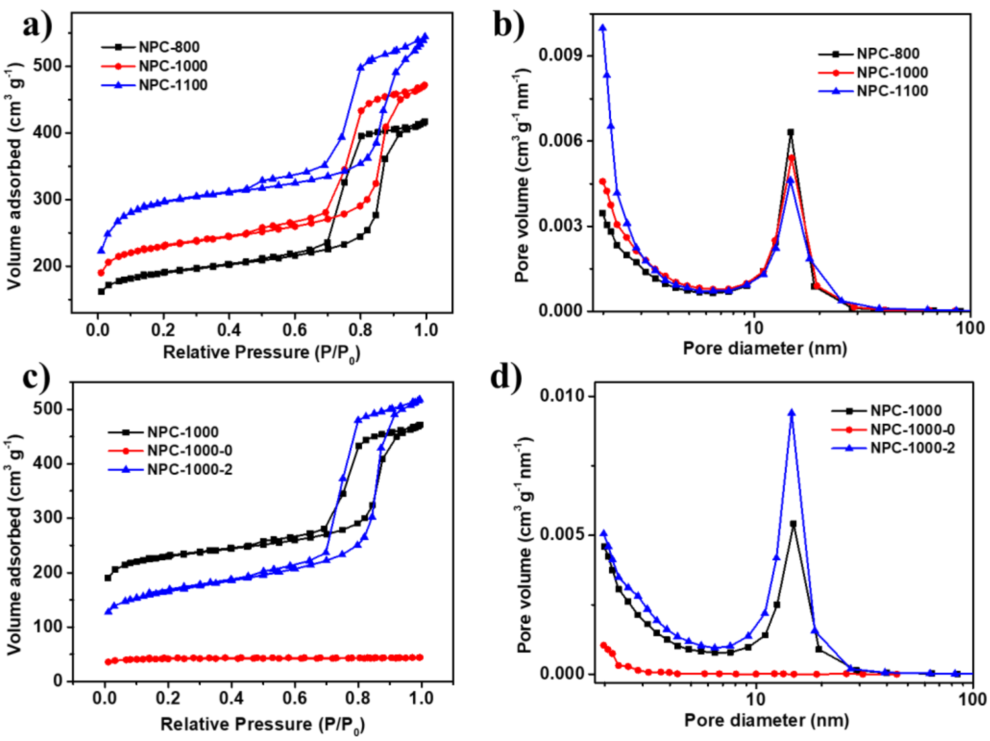

Fig. S1 a) Nitrogen adsorption-desorption isotherms and b) pore-size distribution of NPC-800, NPC-1000 and NPC-1100, indicating that surface area (S_{BET}) and micropore area were gradually improved with the increasing of temperature; c) Nitrogen adsorption-desorption isotherms and b) pore-size distribution of NPC-1000, NPC-1000-0 and NPC-1000-2, implying that the introduction of SiO_2 template greatly increased the specific surface area of NPC, but excessive SiO_2 would lead to collapse of pore structure.

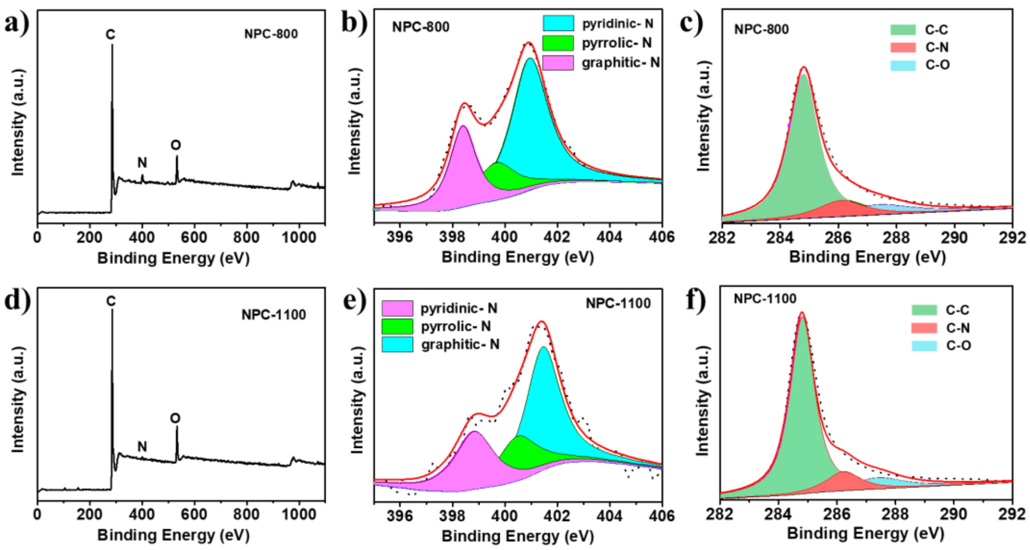

Fig. S2 a) The XPS full spectrum, b) high-resolution N 1s, and c) C1s of NPC-800; d) The XPS full spectrum, e) high-resolution N 1s, and f) C1s of NPC-1100.

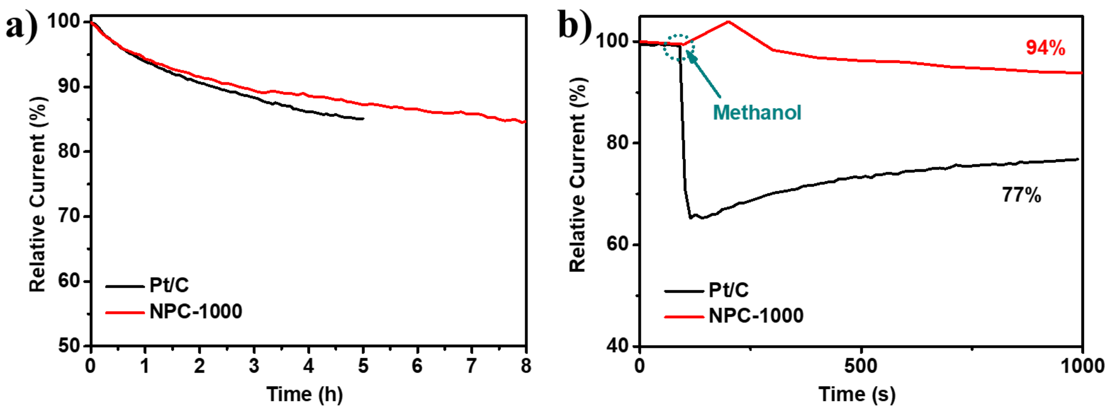

Fig. S3 a) Current–time (i-t) chronoamperometric responses for NPC-1000 and 20% Pt/C at 0.4 V (vs. RHE) for the ORR at a rotating speed of 1600 rpm; b) comparison of chronoamperometric responses for NPC-1000 and commercial Pt/C in O_2-saturated 0.1 M KOH electrolyte with 3 M methanol added at 100 s.

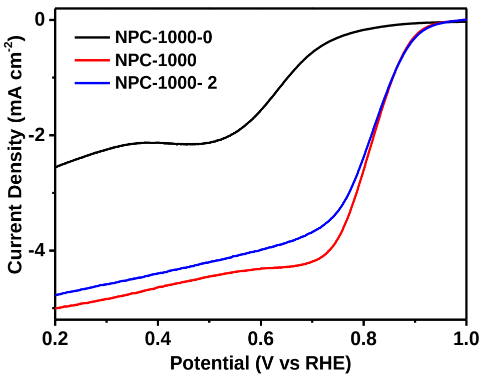

Fig. S4 ORR polarization curves in O_2-saturated 0.1 M KOH (rotation rate: 1600 rpm).

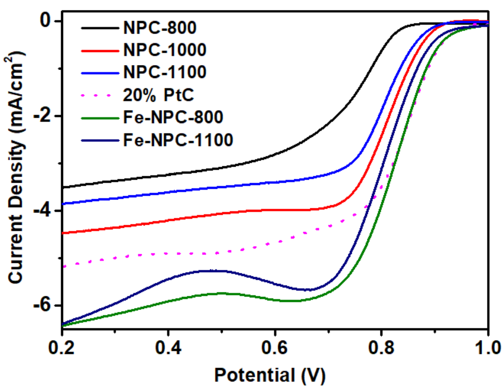

Fig. S5 ORR polarization curves in O_2-saturated 0.1 M KOH (rotation rate: 1600 rpm) indicating the porous carbon prepared by ball-milling and pyrolysis is also a good metal carrier.

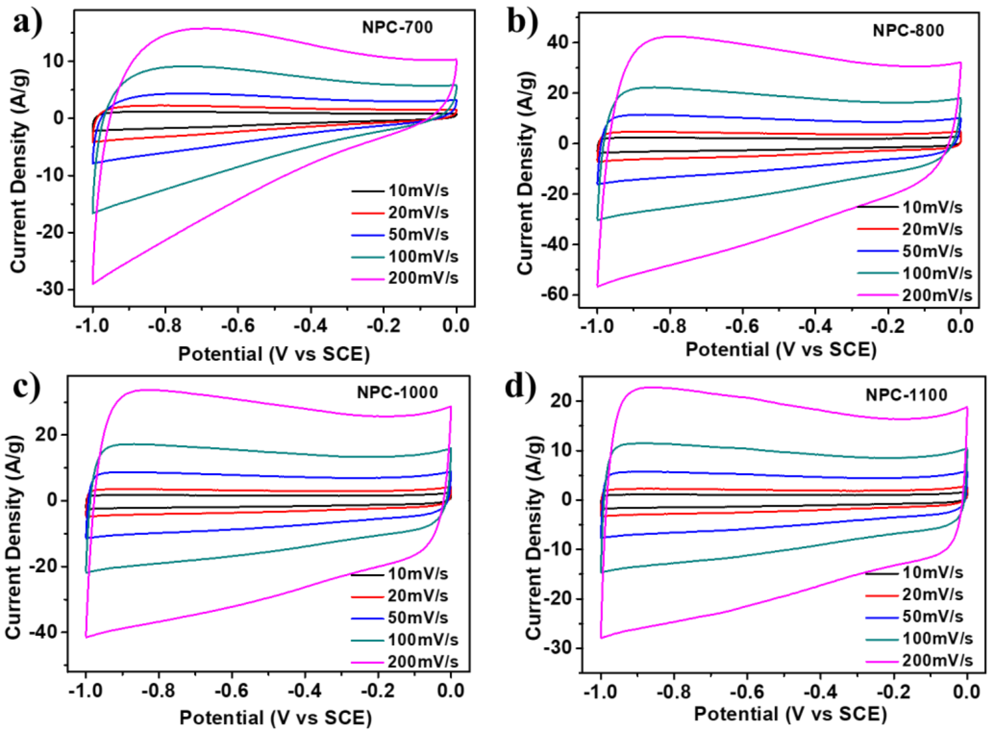

Fig. S6 CV curves of a) NPC-700, b) NPC-800, c) NPC-1000 and d) NPC-1100 at different scan rates in 6M KOH solution.

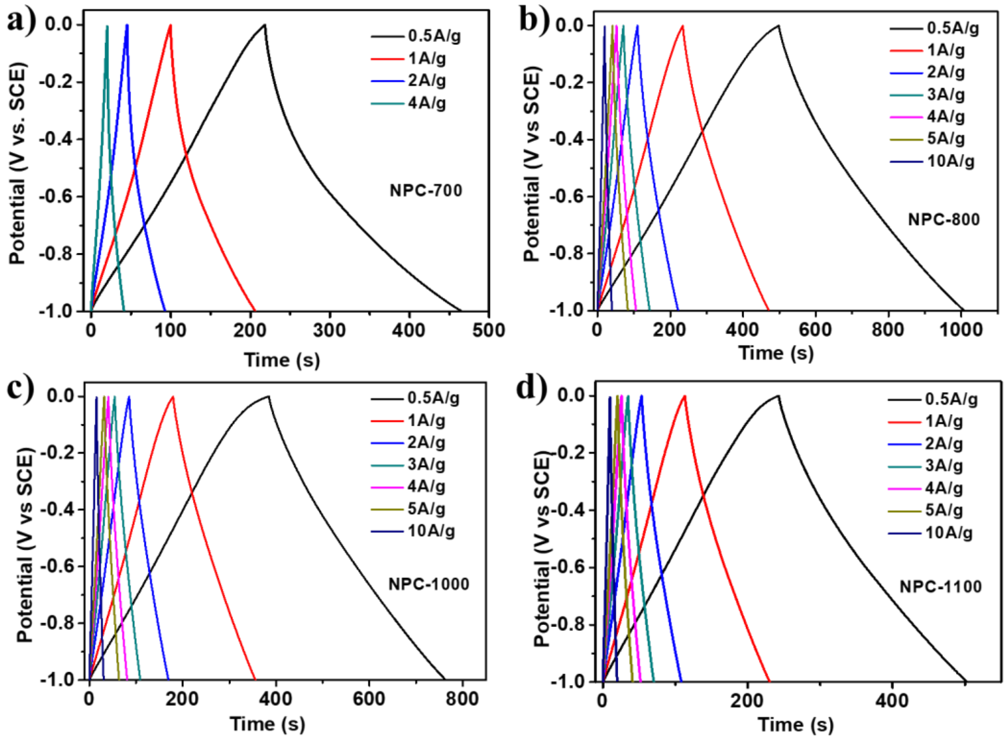

Fig. S7 Galvanostatic charge-discharge (GCD) curves of a) NPC-700, b) NPC-800, c) NPC-1000 and d) NPC-1100 at different current density in 6M KOH solution.

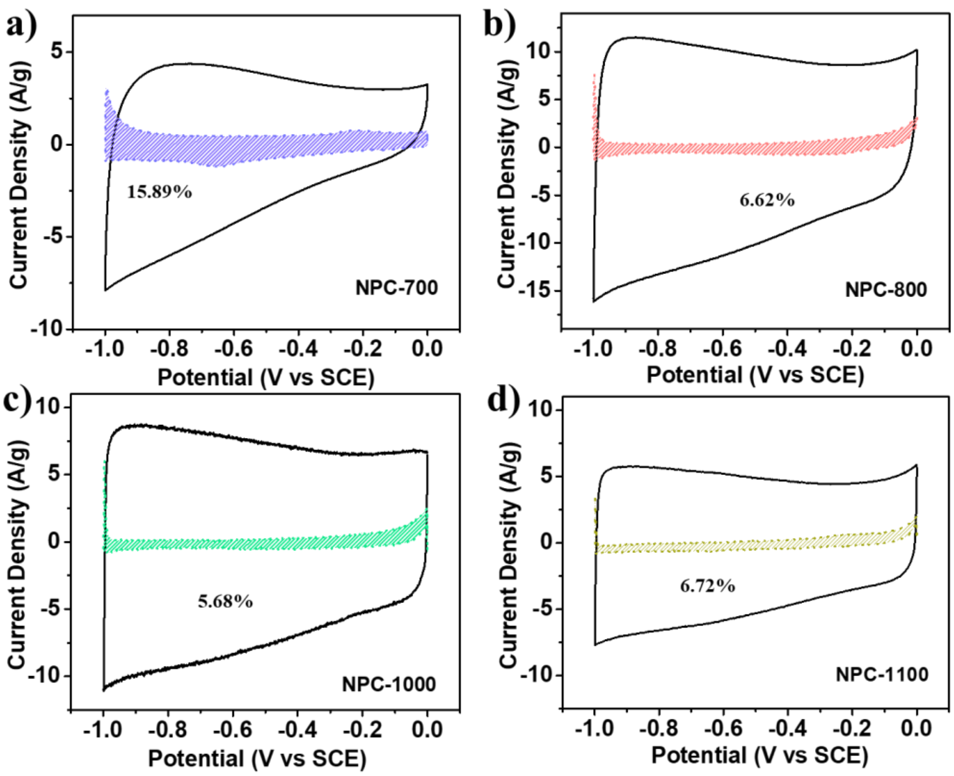

Fig. S8 Deconvolution of diffusion-controlled (shaded area) and capacitive-like capacitance in a) NPC-700, b) NPC-800, c) NPC-1000 and d) NPC-1100 at 50 mV/s.

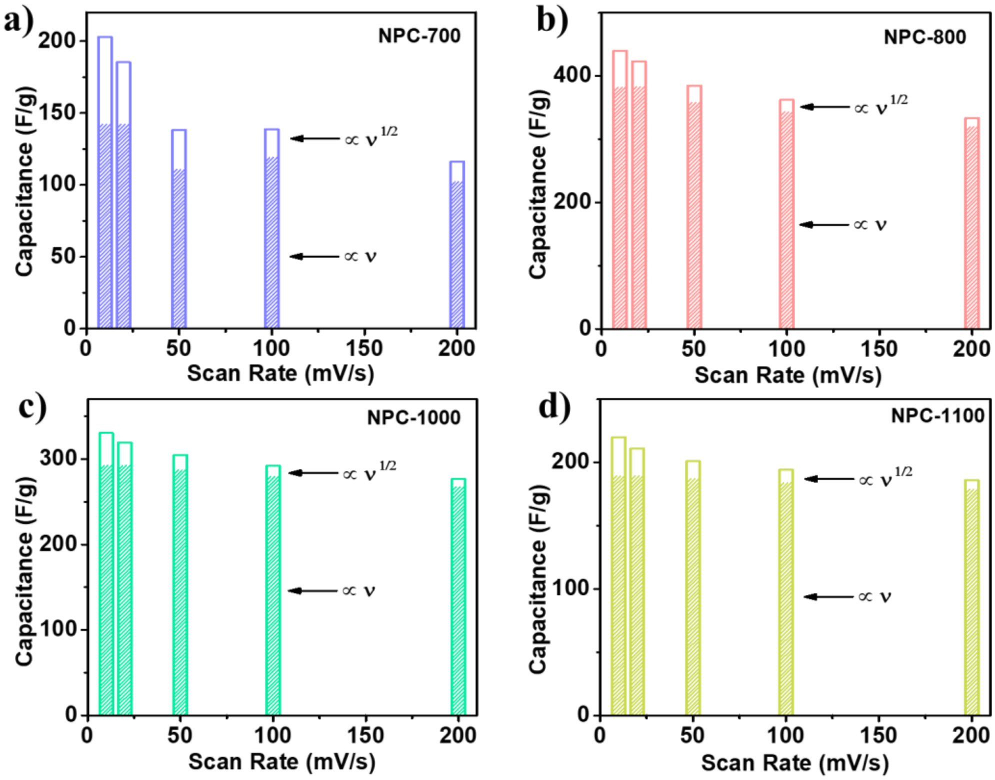

Fig. S9 Deconvolution of charge contribution as a function of scan rates.

Table S1. The surface area, pore volume and pore size of the as prepared catalysts.

Samples	BET Surface Area (m^2/g)	Micropore Area(m^2/g)	Pore Volume (cm^3/g)	Micropore Volume (cm^3/g)	Pore Size (nm)
NPC-800	641.3	464.0	0.64	0.22	3.97
NPC-1000	777.8	564.7	0.72	0.26	3.70
NPC-1100	1013.2	684.0	0.82	0.31	3.23
NPC-1000-0	139.6	118.1	0.07	0.05	1.95
NPC-1000-2	569.1	303.0	0.79	0.14	5.55

Table S2. A comparison in contents of Pyridinic N, Pyrrolic N and Quaternary N species for resultant NPC-800 and NPC-1000 and NPC-1100 catalysts calculated from their N 1s spectra.

Samples	Pyridinic N (at %)	Pyrrolic N (at %)	Quaternarty N (at %)	Total N Content (at %)
NPC-800	0.24	0.16	0.60	4.33
NPC-1000	0.20	0.16	0.64	2.18
NPC-1100	0.27	0.15	0.58	1.08

Table S3. Comparison of the ORR electrocatalyst performances of the prepared catalysts in 0.1 M KOH.

Catalysts	E_{onset} (V)	$E_{1/2}$ (V)
NPC-700	0.83	0.69
NPC-800	0.84	0.73
NPC-900	0.86	0.75
NPC-1000	0.9	0.82
NPC-1100	0.88	0.80
PtC	0.93	0.85

Table S4. Summary of the ORR performances of reported heteroatom-doped porous carbons in 0.1 M KOH.

Catalysts	E_{onset} (V vs RHE)	$E_{1/2}$ (V vs RHE)	References
NPC-1000	0.9	0.82	**This work**
N-doped C/CNTs-1000	0.92	0.82	Angew. Chem. Int. Ed., 2014, 53, 4102-4106
NPMC-1000	0.94	0.85	Nat. Nanotechnol., 2015, 10, 444-452.
CNF@NC	unknown	0.72	Appl. Surf. Sci.,2017, 443,266–273
a-C NH3 900	0.83 (900rpm)	~0.7 (900rpm)	Small, 2019, 1902081
Ultra N-doped carbon nanosheet	0.95	0.82	Energy Environ. Sci.2019, 12,332

Reference for SI

[S1] Zhong H, Liu T, Zhang S, Li D, Tang P, Alonso-Vante N, Feng Y. Template-free synthesis of three-dimensional nife-ldh hollow microsphere with enhanced oer performance in alkaline media. J. Energy Chem. **33**(130-137 (2019). doi:10.1016/j.jechem.2018.09.005