Supporting Information

Well-dispersed Ni_3Fe nanoparticles with N-doped porous carbon shell for highly efficient rechargeable Zn-air batteries

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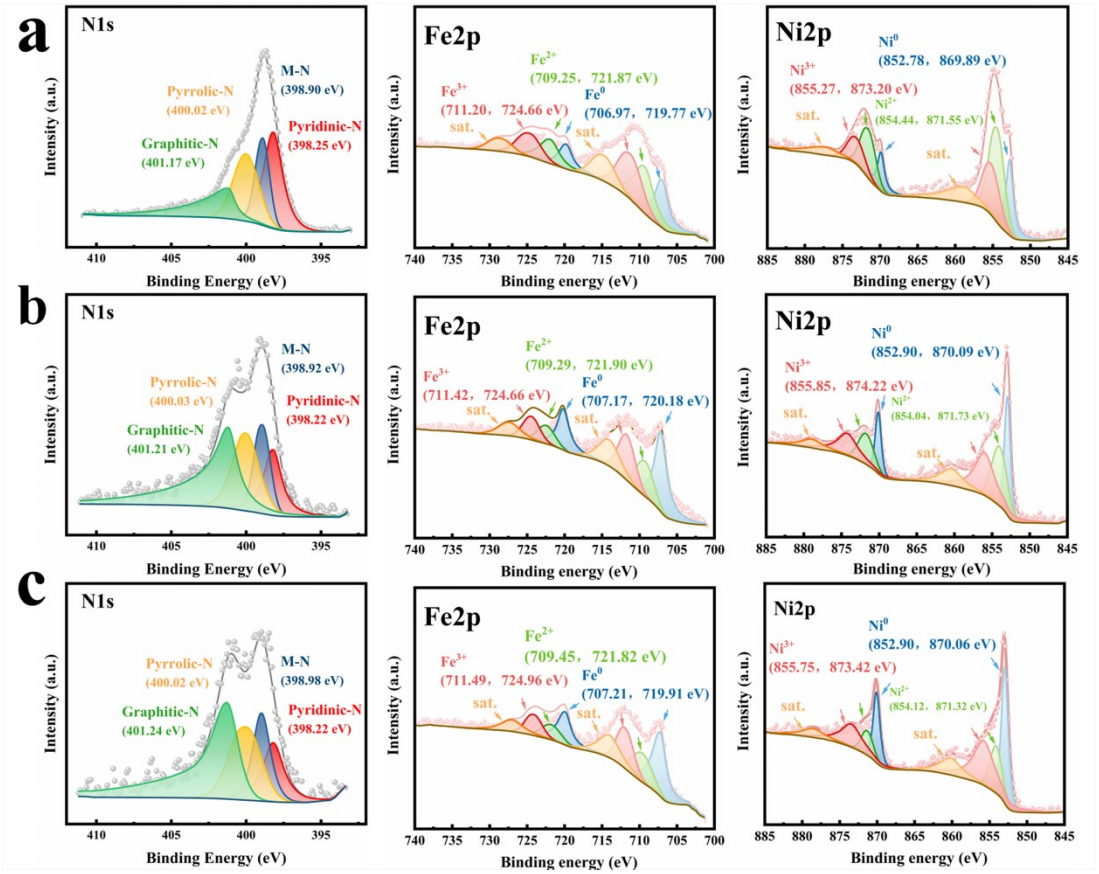

Fig. S1 XPS spectra of N1s, Fe2p, Ni2p for (a) Ni_3Fe@NC-500, (b) Ni_3Fe@NC-700, (c) Ni_3Fe@NC-800.

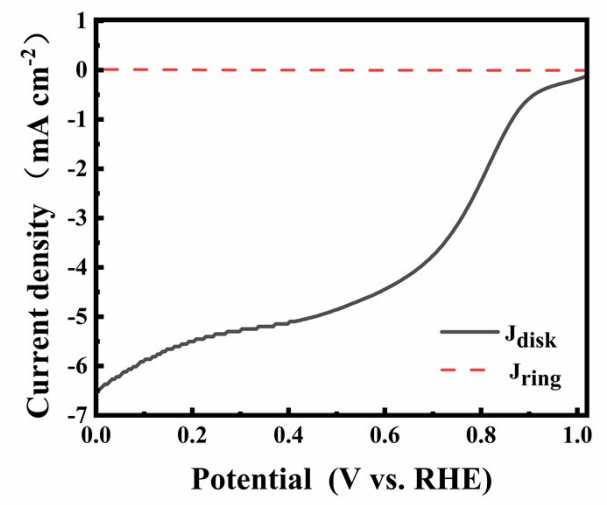

Fig. S2 RRDE voltammogram of Ni_3Fe@NC-600 in O_2-saturated 0.1 M KOH at 1600 rpm.

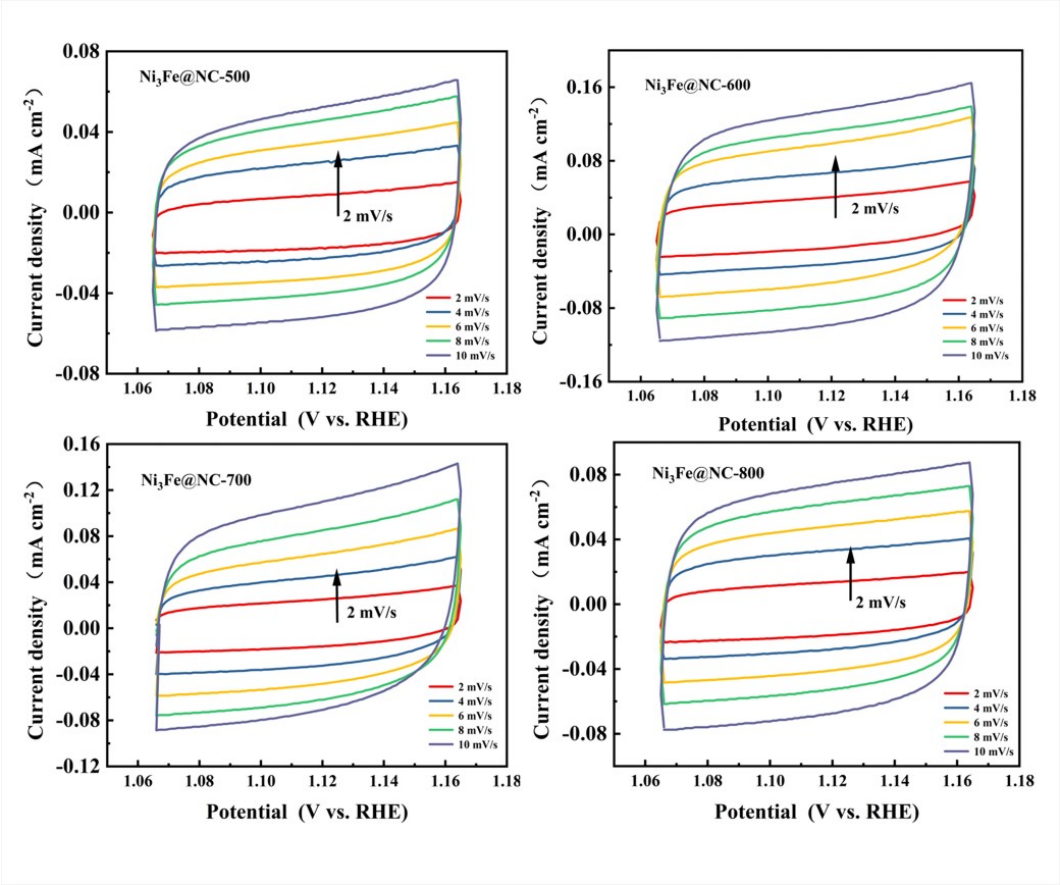

Fig. S3 The CV cures of Ni_3Fe@NC series samples with scan rates from 2 mV s^{-1} to 10 mV s^{-1} in 0.1 M KOH.

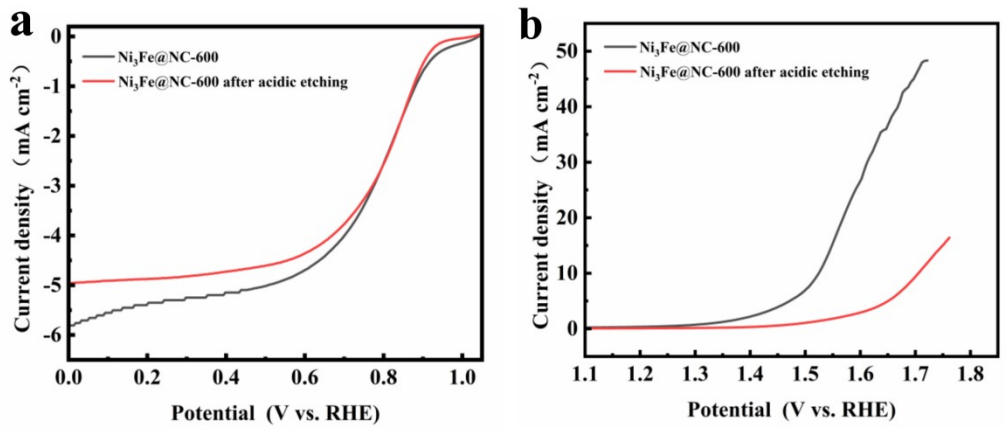

Fig. S4 (a) ORR performances and (b) OER performances of the Ni_3Fe@NC-600 before and after acidic etching.

Table S1 Atomic percentages of C, N, O, Fe, and Ni, and relative surface concentration of nitrogen species obtained from XPS.

Sample	C1s	N1s	O1s	Fe2p	Ni2p	Pyridinic-N	M-N	Pyrrolic-N	Graphitic-N
Ni_3Fe@NC-500	68.07 %	18.95 %	6.75 %	3.76 %	2.47 %	32.87 %	20.04 %	26.50 %	20.59 %
Ni_3Fe@NC-600	79.25 %	9.10 %	6.35 %	2.71 %	2.60 %	22.70 %	26.39 %	25.96 %	24.95 %
Ni_3Fe@NC-700	83.29 %	5.80 %	6.20 %	2.25 %	2.46 %	19.51 %	19.29 %	24.81 %	36.39 %
Ni_3Fe@NC-800	84.49 %	3.69 %	6.47 %	2.50 %	2.85 %	17.80 %	18.49 %	25.58 %	38.13 %

Table S2 Surface relative content of Fe in different valence states in Fe2p energy spectrum and surface relative content of Ni in different valence states in the Ni2p energy spectrum for each sample.

Sample	Fe^0	Fe^{2+}	Fe^{3+}	Ni^0	Ni^{2+}	Ni^{3+}
Ni_3Fe@NC-500	27.37 %	36.28 %	36.35 %	24.92 %	46.33 %	28.75 %
Ni_3Fe@NC-600	35.73 %	28.68 %	35.59 %	26.59 %	31.11 %	42.30 %
Ni_3Fe@NC-700	41.10 %	26.44 %	32.46 %	28.60%	30.31 %	41.09 %
Ni_3Fe@NC-800	47.62 %	24.08 %	28.30 %	36.58 %	22.51 %	40.91 %

Table S3 Structural parameters of different samples.

Sample	SBET[a] (m^2g^{-1})	VT[b] ($cm^3\ g^{-1}$)	Vmicro[c] ($cm^3\ g^{-1}$)	Vmeso[d] ($cm^3\ g^{-1}$)	Dap[e] (nm)
Ni_3Fe@NC-500	50.06	0.14	0.002	0.14	12.65
Ni_3Fe@NC-600	51.41	0.22	0.008	0.21	18.47
Ni_3Fe@NC-700	50.87	0.29	0.006	0.28	24.70
Ni_3Fe@NC-800	59.01	0.28	0.008	0.27	20.36

Table S4 Comparison of bifunctional ORR/OER catalytic activity of the Ni_3Fe@NC-600 presented in this work with other well-developed FeNi-based electrocatalysts tested in 0.1 M KOH.

Materials	Loading (mg cm^{-2})	Eonset (V vs.RHE)	$E_{1/2}$ (V vs.RHE)	$E_{j=10}$ (V vs. RHE)	ΔE/V ($E_{j=10}$ - $E_{1/2}$)	RZABs Peak power density (mW cm^{-2})	Ref.
NiFe-LDH	1	/	0.862	1.57	0.71	97	1
TA-NiFe@NCNT	0.24	0.93	0.81	1.54	0.73	/	2
NiFe/N-CNT	0.4	/	0.75	1.52	0.77	300.7	3
NiFeMo@N-rGO	0.4	/	0.82	1.56	0.73	120	4
NiFe LDH@Fe-N-CNFs	0.3	0.99	0.8	1.58	0.86	157.6	5
NiFe-ND/FeCo-NC	0.2	0.93	0.85	1.66	0.81	121.1	6
NiFe@N-CFs	/	0.94	0.82	1.53	0.71	102	7
NiFe@NC	0.5	/	0.86	1.51	0.65	159.8	8
Fe_3Pt/Ni_3FeN	0.12	/	0.93	1.6	0.67	/	9
FeNi-NCS-2	0.2	/	0.87	1.63	0.76	109.8	10
Ni_3Fe@NC-600	0.25	1.01	0.79	1.52	0.73	175	this work

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