Supporting Information

Atomically Dispersed Fe/Zn Synergy on Sulfur-Modified Nitrogen-Doped Carbon for Boosting Oxygen Reduction Activity

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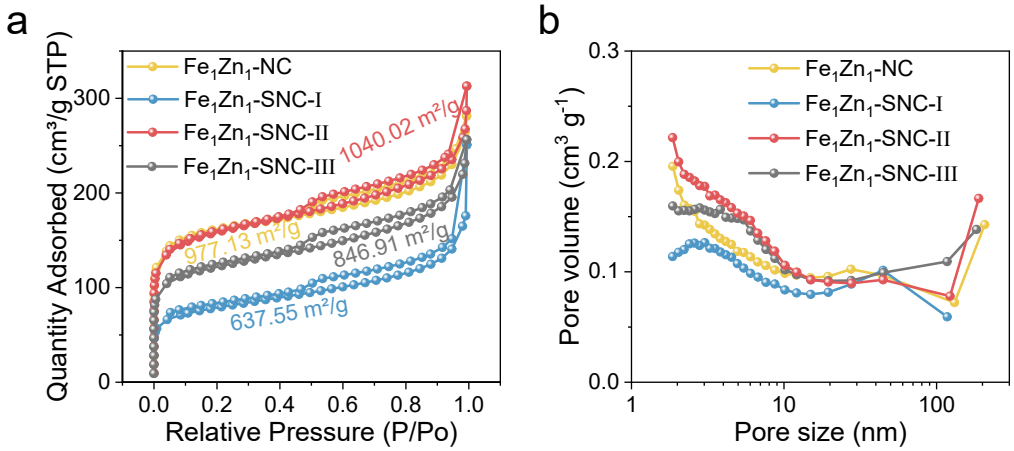

Fig. S1. (a) The surface area and (b) pore size of Fe_1Zn_1-NC, Fe_1Zn_1-SNC-I, Fe_1Zn_1-SNC-II and Fe_1Zn_1-SNC-III.

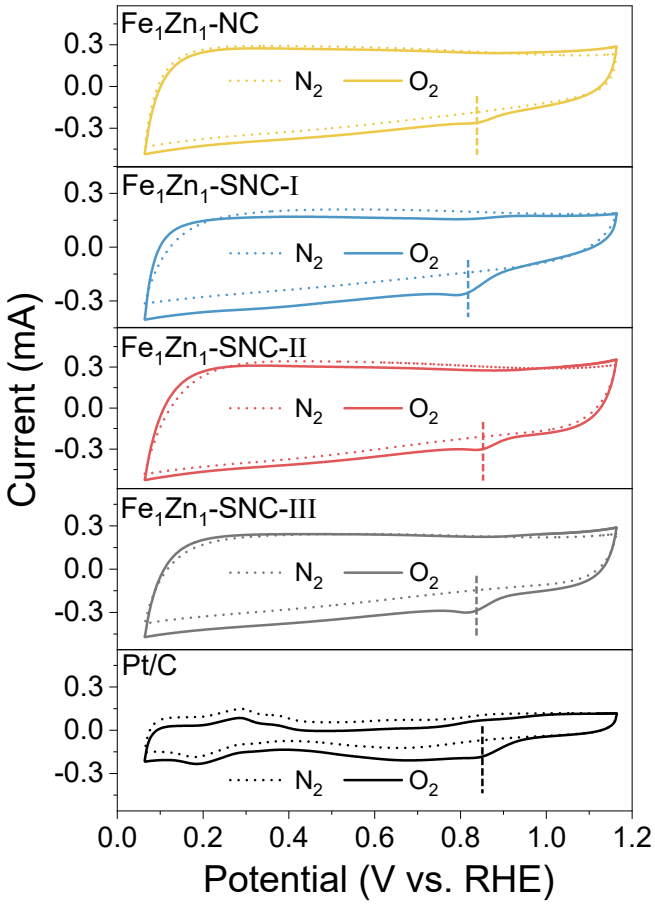

Fig. S2. CV curves in N_2 and O_2 of Fe_1Zn_1-NC, Fe_1Zn_1-SNC-X (X = I, II, III) and Pt/C.

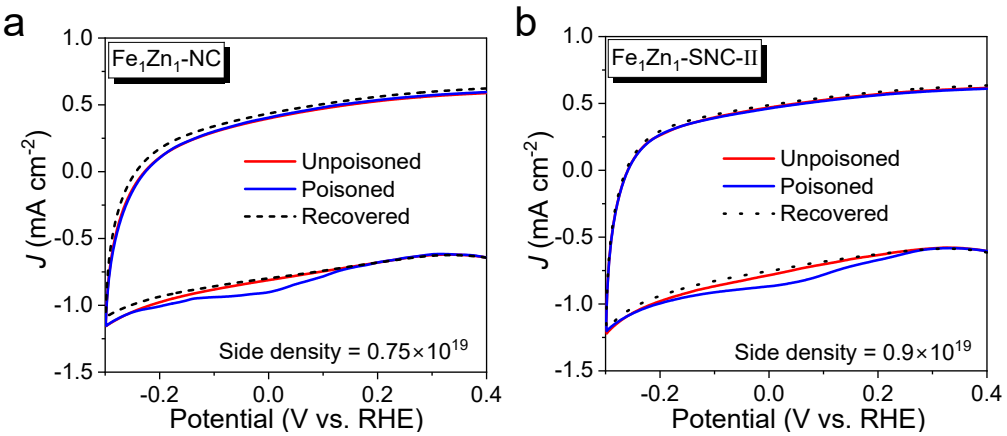

Fig. S3. Site density of (a) Fe_1Zn_1-NC and (b) Fe_1Zn_1-SNC-II through reversible nitrite poisoning in a 0.5 M acetate buffer at pH=5.4.

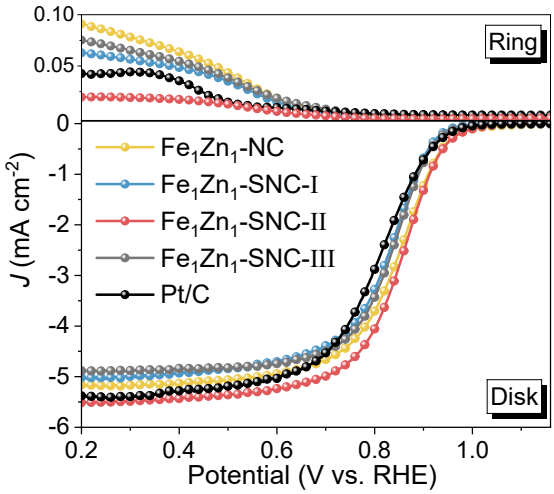

Fig. S4. LSV curves tested on the RRDE for all catalysts in an O_2-saturated 0.1 M KOH at 1600 rpm.

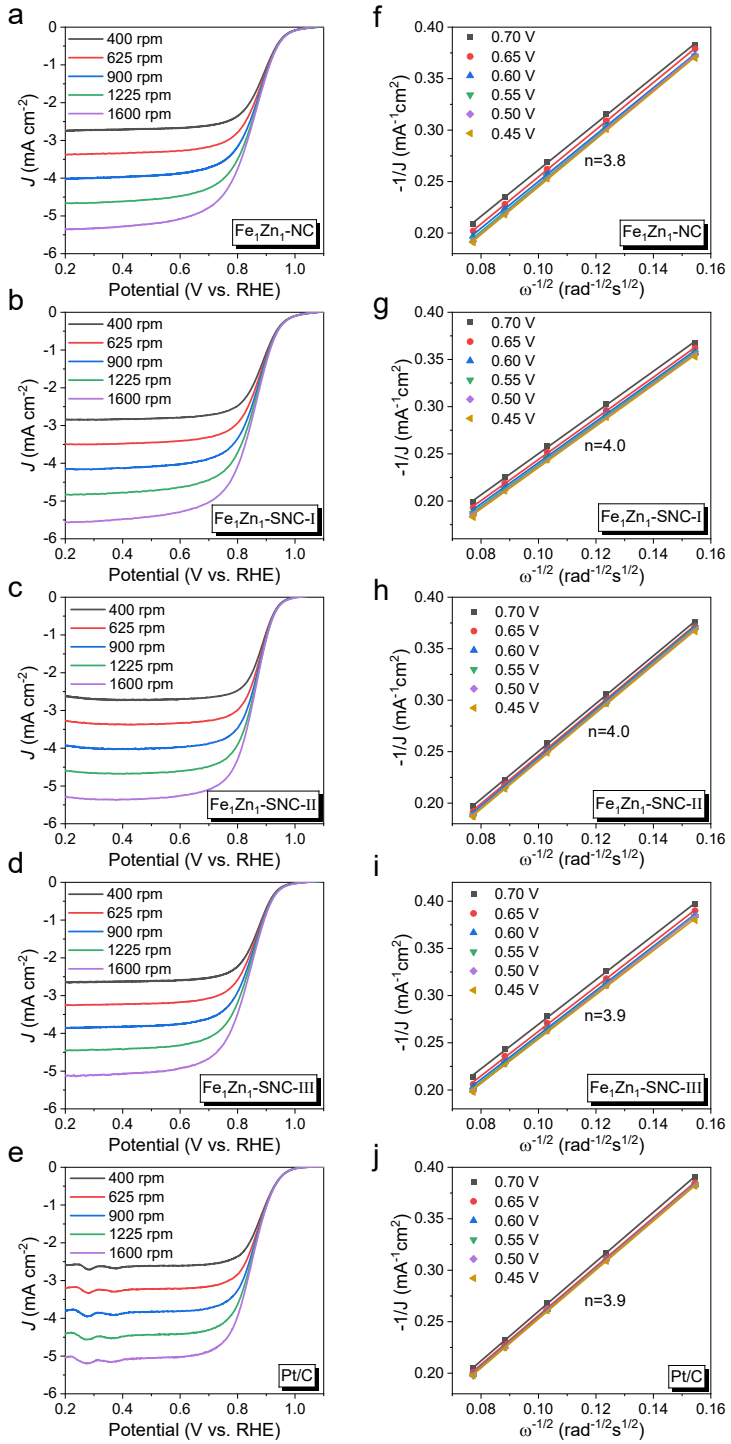

Fig. S5. LSV curves of (a) Fe_1Zn_1-NC, (b) Fe_1Zn_1-SNC-I, (c) Fe_1Zn_1-SNC-II, (d) Fe_1Zn_1-SNC-III and (e) Pt/C at different rotation speeds. Corresponding K-L plots of (g) Fe_1Zn_1-NC, (h) Fe_1Zn_1-SNC-I, (i) Fe_1Zn_1-SNC-II, (j) Fe_1Zn_1-SNC-III and (j) Pt/C.

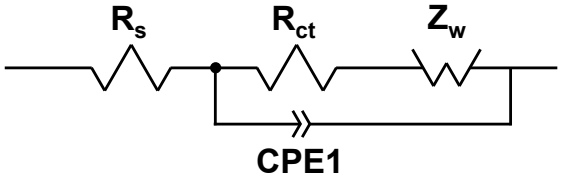

Fig. S6. Equivalent circuit corresponding to the EIS spectra.

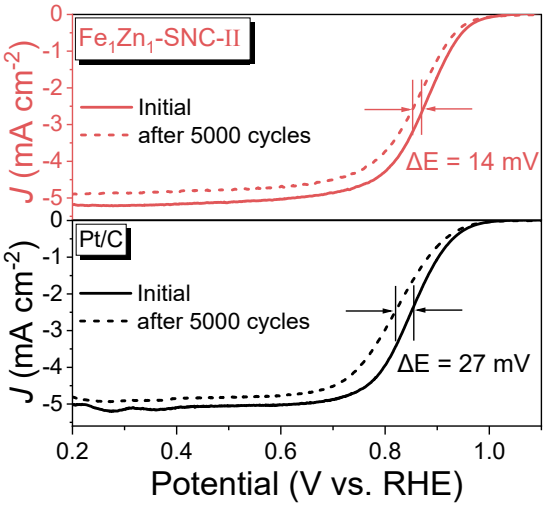

Fig. S7. Long-term cycling stability via an accelerated durability test (ADT).

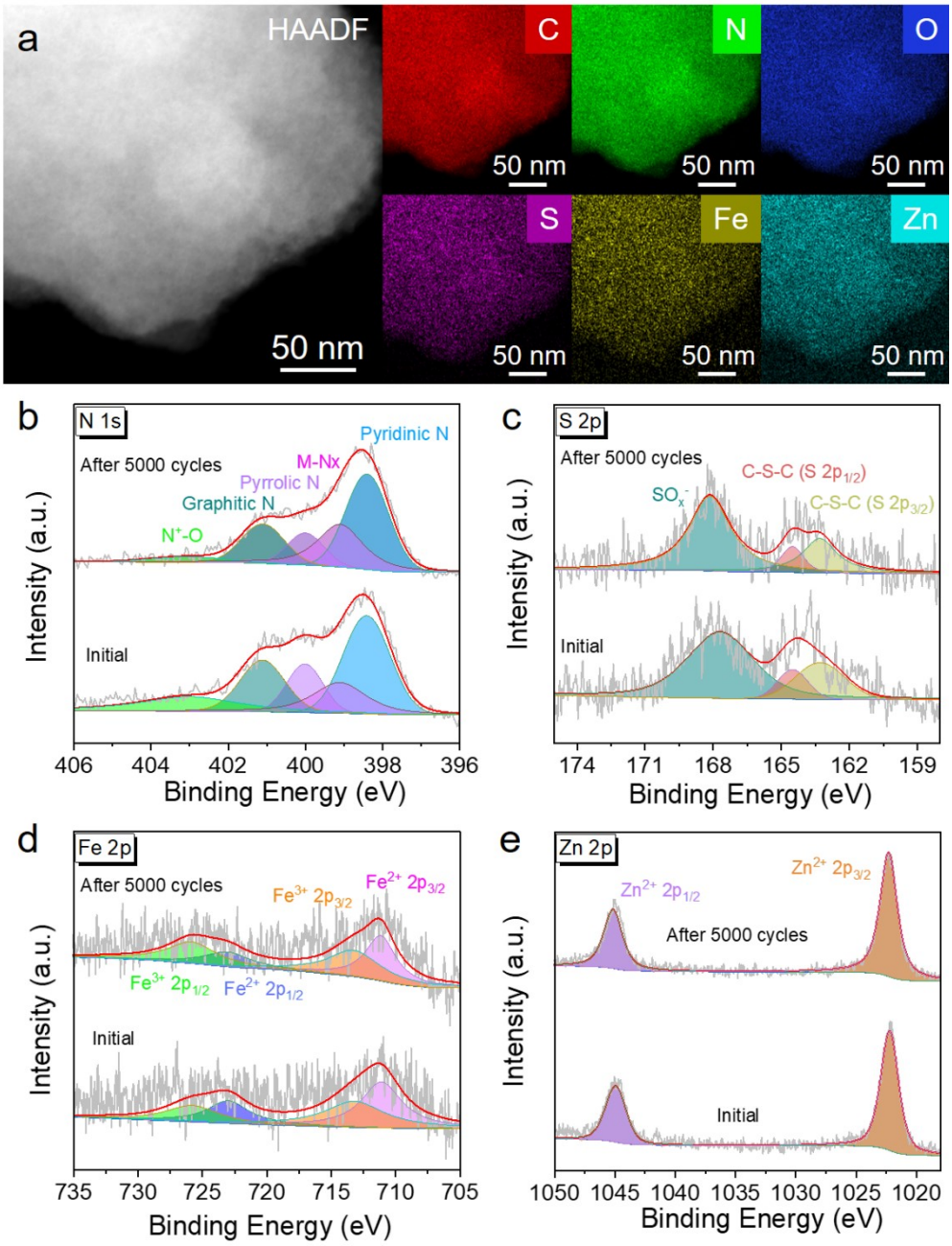

Fig. S8. (a) EDS mapping, (b) XPS N 1s spectra, (c) S 2p, (d) Fe 2p and (e) Fe 2p were examined after 5000 cycles of Fe_1Zn_1-SNC-II.

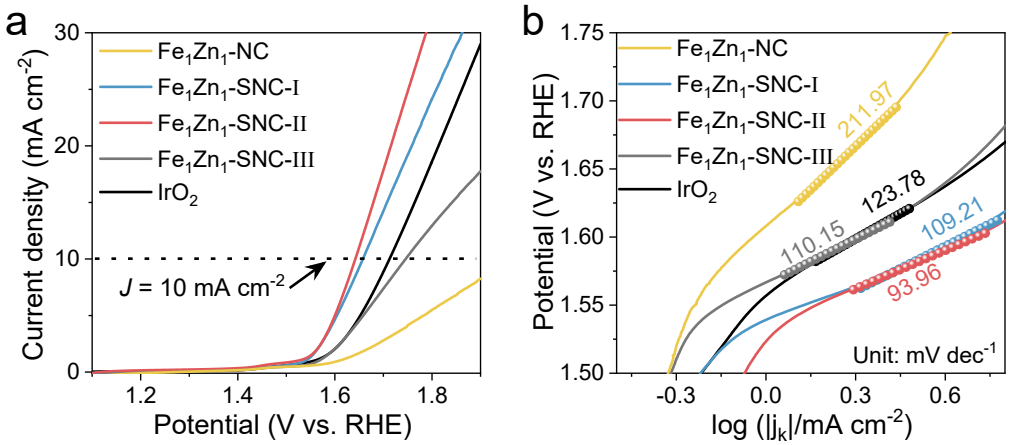

Fig. S9. (a) OER polarization curves and (b) Tafel plots of Fe_1Zn_1-NC, Fe_1Zn_1-SNC-I, Fe_1Zn_1-SNC-II, Fe_1Zn_1-SNC-III, and IrO_2.

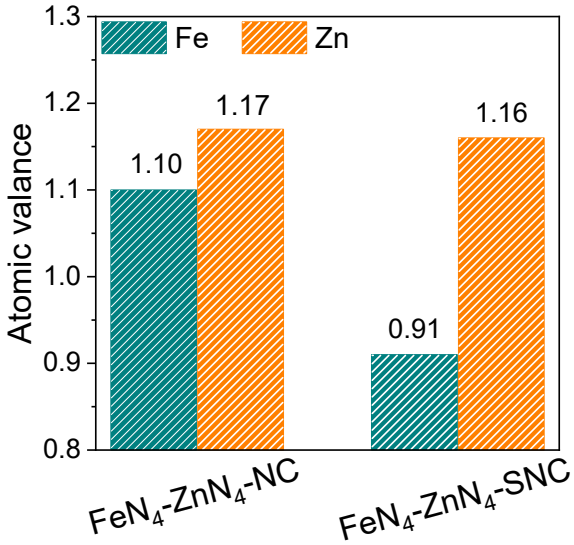

Fig. S10. Bader charge of Fe and Zn atoms in FeN_4-ZnN_4-NC and FeN_4-ZnN_4-SNC.

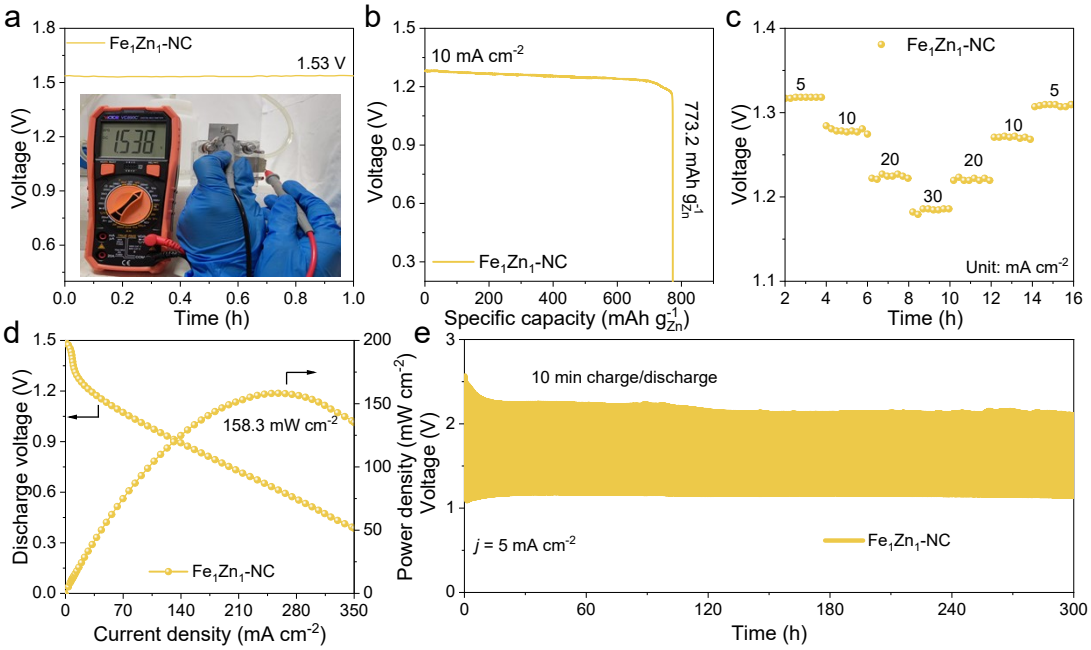

Fig. S11 (a) Open-circuit voltage plots, inset graphic shows voltage values. (b) Specific capacity curves at a current density of 10 mA cm^{-2}. (c) Galvanostatic discharge curves at various current densities. (d) Discharge polarization plots and power density curves and (e) charge–discharge cycling performance of the Zn-air battery assembled with Fe_1Zn_1-NC.

Table S1. Composition of various samples obtained using ICP analysis.

Elements / Catalysts	Fe (wt. %)	Zn (wt. %)
Fe_1Zn_1-NC	0.93	9.23
Fe_1Zn_1-SNC-I	1.24	7.66
Fe_1Zn_1-SNC-II	1.48	7.95
Fe_1Zn_1-SNC-III	1.44	7.77

Table S2. EXAFS fitting parameters at the Fe K-edge for different structures.

	Shell	N^a	R(Å)^b	σ^2(Å^2)^c	ΔE_0 (eV)^d	R factor
Fe foil	Fe-Fe	8.0*	2.48 ± 0.02	0.0069	6.5 ± 2.6	0.0072
Fe_2O_3	Fe-O	5.9 ± 0.2	1.97 ± 0.03	0.0129	4.9 ± 0.4	0.0089
	Fe-Fe	12.8 ± 0.7	3.09 ± 0.04	0.0354		
FePc	Fe-N	4.2 ± 0.3	1.99 ± 0.02	0.0085	3.1 ± 0.7	0.0069
Fe_1Zn_1-SNC-II	Fe-N	4.1 ± 0.2	1.99 ± 0.03	0.0157	3.3 ± 0.2	0.0125

$^a N$: coordination numbers; $^b R$: bond distance; $^c \sigma^2$: Debye-Waller factors; ^{d} ΔE_0: the inner potential correction. R factor: goodness of fit. S_0^2 was set to 1.063, according to the experimental EXAFS fit of metal foil reference by fixing N as the known crystallographic value.

Table S3. EXAFS fitting parameters at the Zn K-edge for different structures.

	Shell	N^a	R(Å)^b	σ^2(Å^2)^c	ΔE_0 (eV)^d	R factor
Zn foil	Zn-Zn	6*	2.64 ± 0.02	0.0124	2.7 ± 1.3	0.0146
ZnO	Zn-O	6.2 ± 0.3	1.95 ± 0.02	0.0034	3.5 ± 0.9	0.0225
	Zn-Zn	12.4 ± 0.2	3.25 ± 0.03	0.0181		
ZnPc	Zn-N	4.1 ± 0.1	1.99 ± 0.01	0.0056	6.9 ± 0.5	0.0167
Fe_1Zn_1-SNC-II	Zn-N	3.8 ± 0.3	2.01 ± 0.02	0.0067	7.9 ± 1.6	0.0157

^{a}*N*: coordination numbers; ^{b}*R*: bond distance; $^c\sigma^2$: Debye-Waller factors; ^{d} ΔE_0: the inner potential correction. *R* factor: goodness of fit. S_0^2 was set to 1.050, according to the experimental EXAFS fit of metal foil reference by fixing *N* as the known crystallographic value.

Table S4. Site density of Fe_1Zn_1-NC and Fe_1Zn_1-SNC-II.

Sample	Site density (mol g^{-1})	Site density (μmol g^{-1})
Fe_1Zn_1-NC	0.75×10^{19}	12.4
Fe_1Zn_1-SNC-II	0.9×10^{19}	14.9

Table S5. The simulated equivalent circuit data of the catalysts.

Catalysts	R_s (Ω cm^{-2})	R_{ct} (Ω cm^{-2})	CPE-T	CPE-P
Fe_1Zn_1-NC	7.098	59.72	5.29E-9	0.990
Fe_1Zn_1-SNC-I	12.12	60.87	2.95E-9	1.019
Fe_1Zn_1-SNC-II	7.277	53.52	4.44E-9	0.970
Fe_1Zn_1-SNC-III	9.623	59.54	2.39E-9	1.010

Table S6. Performance comparison of non-noble metal catalysts reported in recent literature

Catalysts	$E_{1/2}$ (V)	OCV (V)	Power density (mW cm^{-2})	Specific capacity (mAh g_{Zn}^{-1})	Tafel plots (mV dec^{-1})
This work	0.871	1.58	228	804	78.69
Pt/C in this work	0.849	1.49	185	762	91.95
NPS-HPCNF[1]	0.86	1.51	210	795	67.4
Zn/Fe-NC[2]	0.875	1.46	186	815	-
A-MnO2/NSPC-2[3]	0.87	1.54	181	816	91
Fe/Cu-N-C[4]	0.89	1.50	116.6	809.2	69.4
FeCu SACs/NC[5]	0.89	1.48	153	741.0	68.6
Fe–N,O/G[6]	0.86	1.55	164.7	-	90
Co_3S_4/FeS@CoFe/NC[7]	0.872	1.34	170	816.3	45
Fe SAs/NG[8]	0.883	1.51	272.6	798	91.7
Fe@NC-2-900[9]	0.86	1.50	198	867	90.1
Co_3O_{4-x}@N–C-2[10]	0.845	1.524	105.2	799.5	73.1

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