Supporting Information

Nanoporous bimetallic Zn/Fe-N-C for efficient oxygen reduction in acidic and alkaline media

Jinling Xue[1], Yinshi Li[1,*], Jue Hu[2,*]

[1]Key Laboratory of Thermo-Fluid Science and Engineering of Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

[2]Faculty of Science, Kunming University of Science and Technology, Kunming, Yunnan, 650500, China

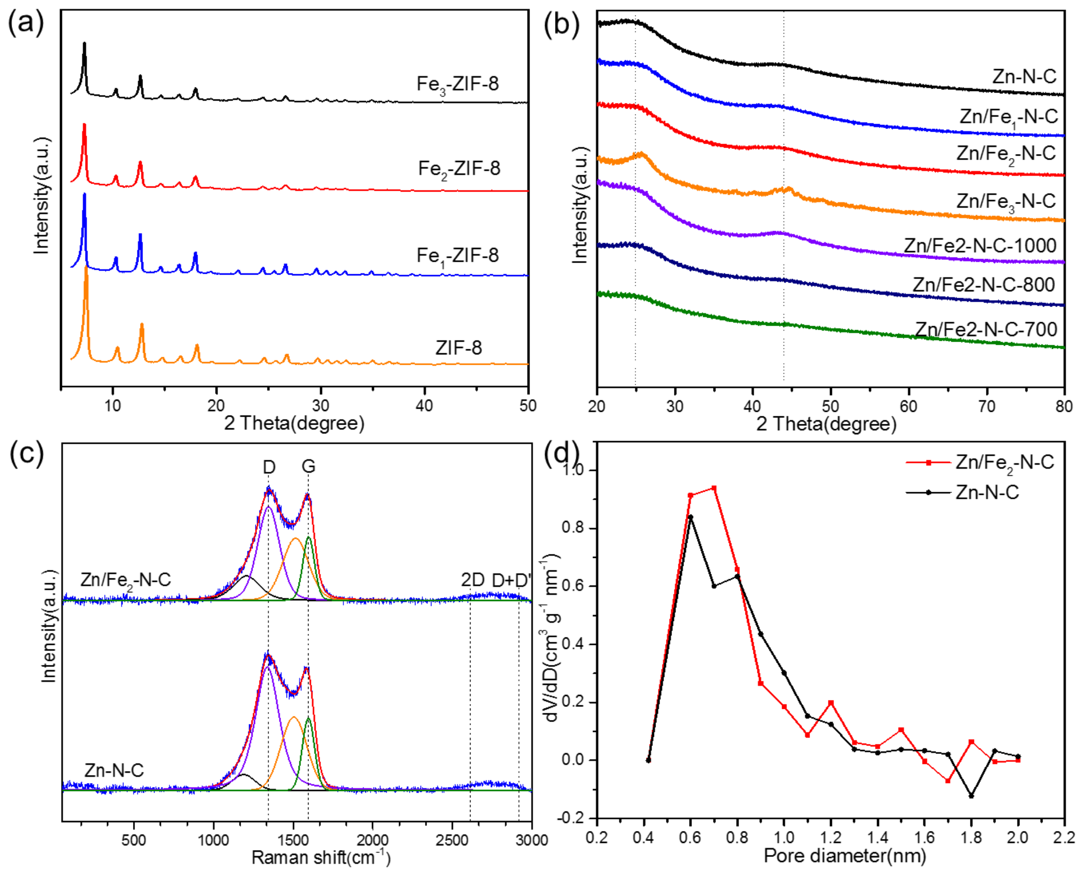

Fig. S1. (a) XRD pattern of pure ZIF-8, Fe_x-ZIF-8 with different densities of hemin; (b) XRD pattern of as-prepared catalysts; (c) Raman spectra of Zn/Fe_2-N-C and Zn-N-C; (d) micropore size distribution determined by H-K method of Zn/Fe_2-N-C and Zn-N-C.

*Corresponding author.

E-mail addresses: ysli@mail.xjtu.edu.cn (Y.L.); hujue@kust.edu.cn (J.H.)

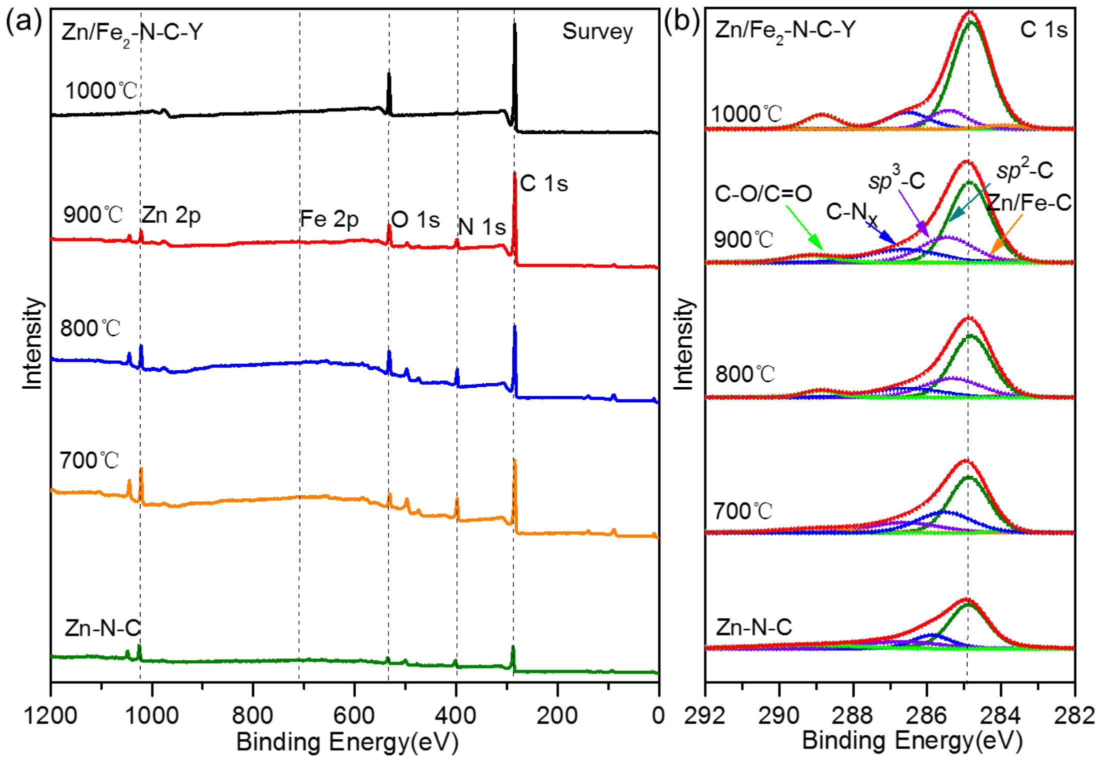

Fig. S2. (a) XPS survey spectrum and (b) high-resolution C 1 s spectra of Zn/Fe_2-N-C prepared at different annealing temperatures and spectra of Zn-N-C.

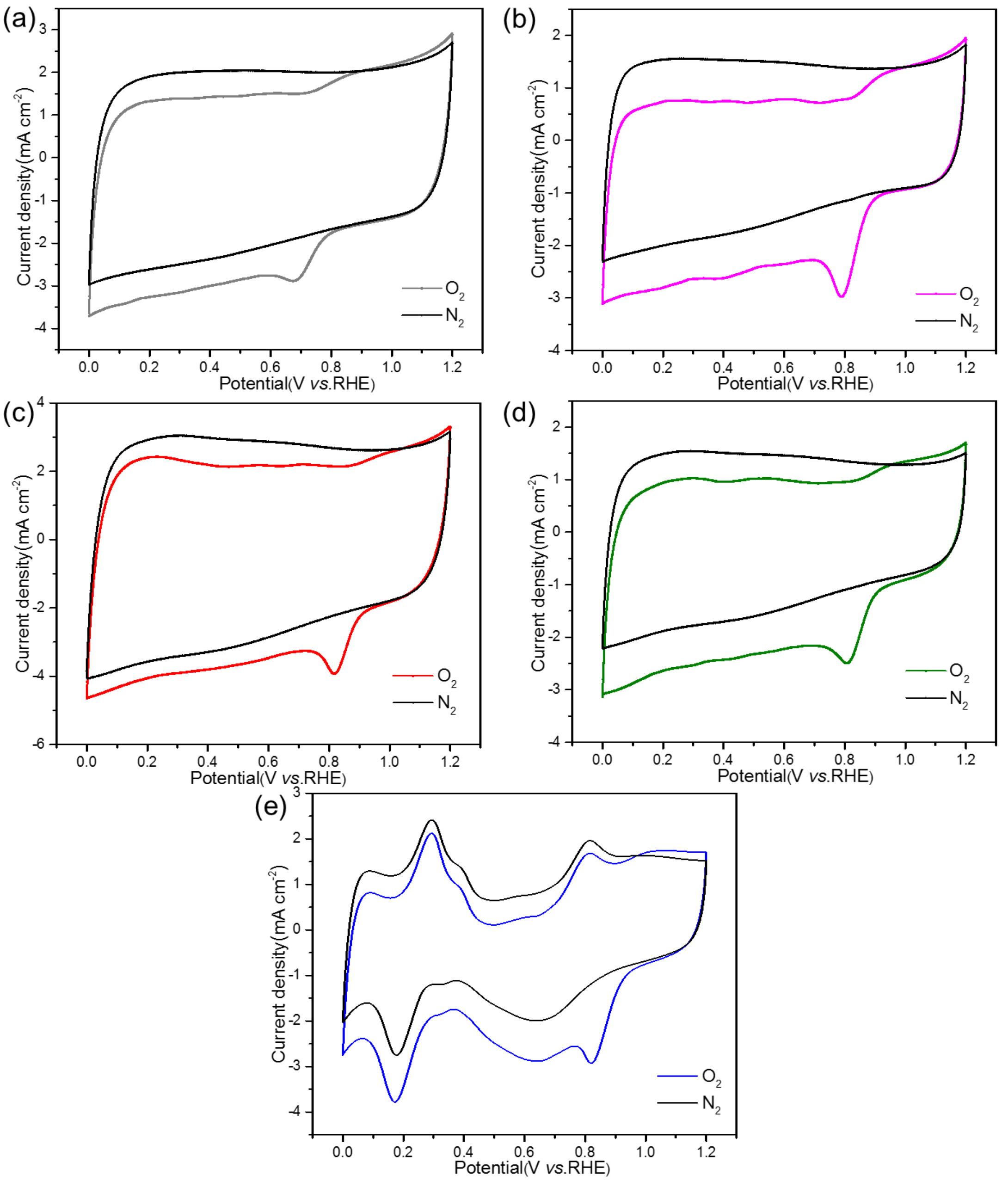

Fig. S3. CV curves of (a) Zn-N-C, (b) Zn/Fe_1-N-C, (c) Zn/Fe_2-N-C, (d) Zn/Fe_3-N-C and (e) Pt/C in O_2-saturated and N_2-saturated 0.1 M KOH solution with cathodic peaks at 0.685, 0.798, 0.810, 0.836, and 0.835 V, respectively.

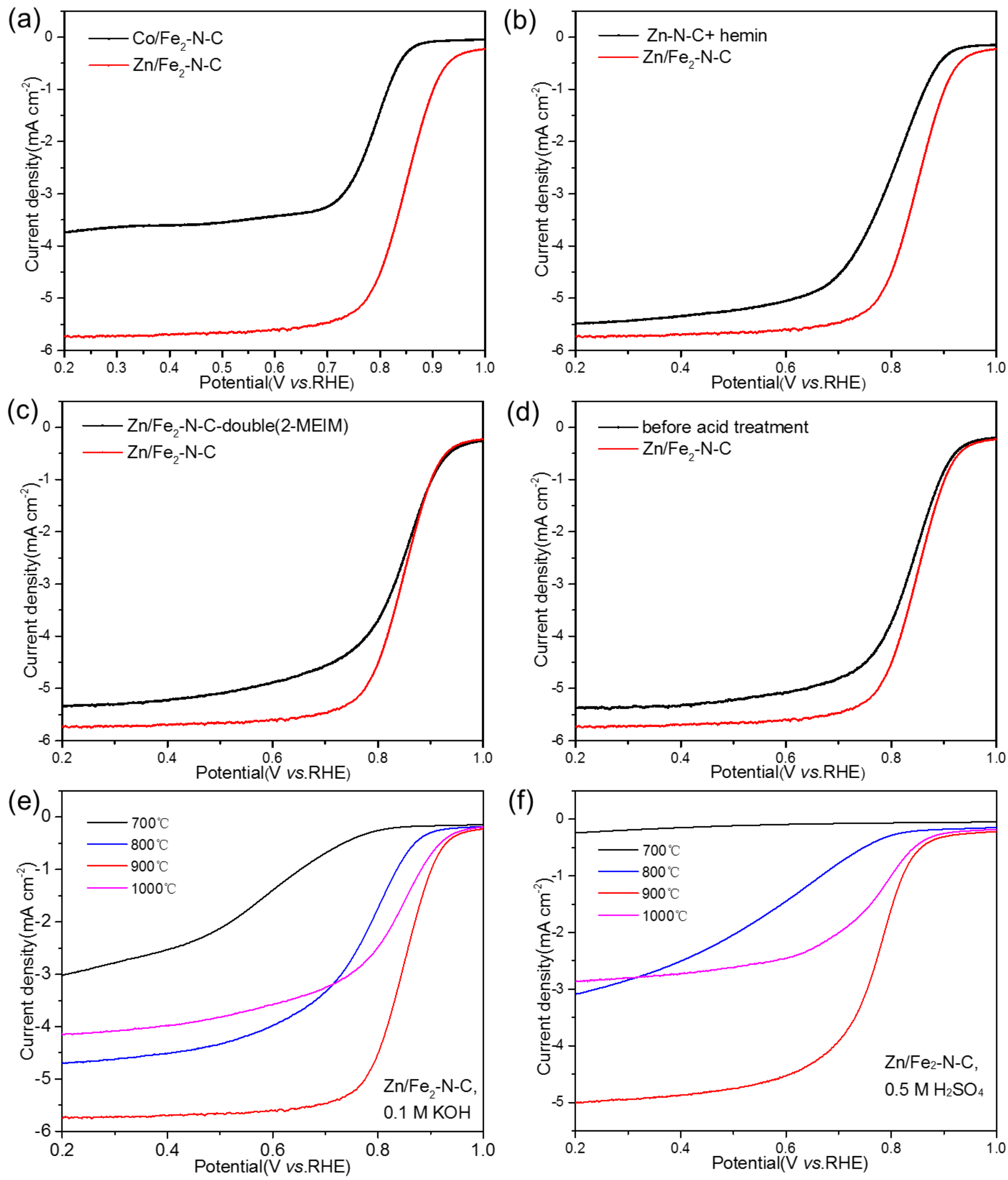

Fig. S4. (a-d) LSV curves of different preparation process catalysts in O_2-saturated 0.1 M KOH with a rotation rate of 1600 rpm; (e-f) LSV curves of Zn/Fe_2-N-C prepared at different annealing temperatures in 0.1 M KOH and 0.5 M H_2SO_4

Table S1. Raman spectra parameters of Zn/Fe_2-N-C and Zn-N-C samples.

	Carbon structures				
Samples	*sp*^{2}-C outside graphene network 1220 cm^{-1}	D-band 1350 cm^{-1}	Heteroatoms 1500 cm^{-1}	G-band 1600 cm^{-1}	I_G/I_D
Zn/Fe_2-N-C	14.39%	40.67%	30.97%	13.97%	0.34
Zn-N-C	4.21%	54.02%	28.61%	13.16%	0.24

Table S2. Pore characteristics of Zn/Fe_2-N-C and Zn-N-C samples.

Samples	S_{BET} (cm^2/ g)	$V_{Micropore}$ (cm^3/ g)	$V_{Mesopores}$ (cm^3/ g)	$V_{Macropore}$ (cm^3/ g)	$R_{p,\ peak}$ (nm)
Zn/Fe_2-N-C	772.65	0.3452	0.3392	0.1694	34
Zn-N-C	770.94	0.3172	0.8959	0	19

Table S3. Atomic percentage of the samples determined by XPS

Samples	C 1s	N 1s	O 1s	Fe 2p	Zn 2p
Zn/Fe_2-N-C-1000	83.88	1.25	14.62	0.09	0.16
Zn/Fe_2-N-C	80.79	7.16	9.74	0.25	2.06
Zn/Fe_2-N-C-800	73.04	11.32	10.31	0.18	4.19
Zn/Fe_2-N-C-700	71.87	15.25	6.69	0.08	6.11
Zn-N-C	74.86	13.36	8.08	--	3.70

Table S4. XPS atomic percentage of different types of C of the applied samples

Samples	**C 1s**				
	C-O/C=O	C-N_X	sp^3-C	sp^2-C	C-Fe
Zn/Fe_2-N-C-1000	8.07	11.72	11.59	66.47	2.15
Zn/Fe_2-N-C	5.84	15.79	22.45	54.38	1.54
Zn/Fe_2-N-C-800	5.25	14.40	24.75	54.51	1.09
Zn/Fe_2-N-C-700	8.09	15.84	25.57	49.56	0.94
Zn-N-C	8.14	19.57	20.61	51.68	--

Table S5. XPS atomic percentage of different types of N of the applied samples

Samples	**N 1s**				
	Oxidized-N	Graphitic-N	Pyrrolic-N	Zn/Fe-N	Pyridinic-N
Zn/Fe_2-N-C-1000	12.71	28.98	12.95	5.78	39.58
Zn/Fe_2-N-C	13.66	14.41	9.03	20.31	42.58
Zn/Fe_2-NC-800	2.38	3.34	22.54	12.11	59.63
Zn/Fe_2-NC-700	5.92	10.40	17.11	1.04	65.53
Zn-N-C	4.34	5.08	29.54	8.10	52.94

Table S6. A list of noble-metal ORR catalysts with derivative precursors showing preparation conditions, active sites and performance. The potentials below are relative to RHE.

preparation conditions							ORR performance					
										Testing conditons		
Catalysts	**Precursors**	**Metal species**	**Synthesis routine**	**Annealing temperature (°C)**	**Active sites**	**Cat loading [mg cm^{-2}]**	**E_{onset} [V]**	**$E_{1/2}$ [V]**	**j_L [mA cm^{-2}]**	**Alkaline media**	**Acidic media**	**Ref**
Fe-SilkPNC	Silk fibers or silk textile, $FeCl_3/ZnCl_2$	Fe, Zn	Silk fibroin precursor, programmed heating procedure, acidic leaching (HCl)	120 - 220 - 320 - 900	Fe-N_x-C	0.60	N.A.	0.853	5.25	0.1 M KOH	N.A.	S1
Fe-N_x-C	ZIF-8, $FeSO_4\cdot 7H_2O$, 1,10-phenanthroline	Fe, Zn	Hydrothermal treatments, pyrolysis	900	FeN_x	0.31	1.05	0.91	5.44	0.1 M KOH	N.A.	S2
FeN_x-PNC	ZIF-8, graphene, pyrrole, $FeCl_3$, bipyrodine	Fe, Zn	Two-step synthetic precursor, pyrolysis, acidic leaching (H_2SO_4)	1000	FeN_x	0.14	1.00	0.86	5.95	0.1 M KOH	N.A.	S3
$Fe_{0.5}$-N/CDC-2	Carbide-derived carbon powders, 1,10-phenanthroline, iron(II) acetate	Fe, Ti, Zr	Ball-milled, pyrolysis	800	FeN_xC_y	0.80	N.A.	0.81	6.40	N.A.	0.5 M H_2SO_4	S4
20Mn-NC-second	Mn-doped ZIF-8, cyanamide	Mn, Zn	Calcination- acid etching (H_2SO_4) - calcination	900, 1100	MnN_4	0.40	0.96	0.80	3.85	N.A.	0.5 M H_2SO_4	S5
20Co-NC-1100	ZIF-8, $Co(NO_3)_2\cdot 6H_2O$	Co, Zn	Pyrolysis	1100	CoN_4	0.80	0.93 V, 0.1 mg/c	0.80	4.20	N.A.	0.5 M H_2SO_4	S6

							m^2					
ZIF/MIL-10-900	ZIF-8, MIL-101(Fe)	Fe, Zn	Two-MOF precursor synthetic, physical grinding mixture, pyrolysis, acidic leaching (HCl)	900	FeN_4	0.50	N.A.	0.78	5.90	N.A.	0.1 M $HClO_4$	S7
Fe-N-C	ZIF-8, $Fe(acac)_3$	Fe, Zn	Pyrolysis, acidic leaching (HCl)	950	FeN_4	0.40	0.92	0.78	5.80	N.A.	0.1 M $HClO_4$	S8
Fe, N-HPCC	$FeSO_4 \cdot 7H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, benzimidazole	Fe, Zn	Pyrolysis	1000	FeN_4	0.79	0.97	0.90	5.50	0.1 M KOH		S9
							0.90	0.76	5.00		0.1 M $HClO_4$	
Fe_{SA}-N-C	20% Fe-TCPP, 80% H_2-TCPP, Zr^{4+}	Fe, Zr	Two-MOF precursor synthetic, pyrolysis, acidic leaching (HF)	800	FeN_4	0.28	1.00	0.89	6.00	0.1 M KOH		S10
							0.93	0.78	5.75		0.1 M $HClO_4$	
C-FeZIF-1.44-950	ZIF-8, ferrocene	Fe, Zn	Physical mixture, pyrolysis, acidic leaching (H_2SO_4), second pyrolysis	950	FeN_x	0.50	0.99	0.86	6.35	0.1 M KOH		S11
							0.91	0.78	6.20		0.1 M $HClO_4$	
Fe_3C@NP-PCFs	3D polyvinylpyrrolidone (PVP), cyanamide, $Fe(C_2H_3O_2)_2$, H_3PO_4	Fe	Fe_3C@NP-PCFs homogeneous precursor solution, precursor membranes, pyrolysis	800	Fe_3C, Fe-P, P-C	0.46	0.90	0.80	5.68	0.1 M KOH		S12
							0.86	0.74	5.59		0.5 M H_2SO_4	
N-HPCNSs-800	Water hyacinth		Two-step pyrolysis, acidic leaching (HCl)	500 - 800	Pyridinic-, graphitic-	N.A.	1.00	0.887	6.15	0.1 M KOH		S13

					N		0.858	0.75	6.36	0.5 M H_2SO_4	
P12-900	Ethylenedioxythiophene, $FeCl_3 \cdot 6H_2O$	Fe	Pyrolysis, acidic leaching (H_2SO_4), second pyrolysis	900	FeS_x, FeN_x	0.50	1.016	0.86	7.20	0.1 M KOH	S14
							0.92	0.78	5.70	0.5 M H_2SO_4	
HCS-A	Polyaniline, polypyrrole, triton X-100, $Fe(CH_3COO)_2$, pyrrole, aminothiophenol	Fe	Three-step pyrolysis	400 - 800 - 900	FeN_x	0.50	N.A.	0.87	4.70	0.1 M KOH	S15
								0.75	4.30	0.5 M H_2SO_4	
PBE2PB	$Fe(NO_3)_2$, nicarbazin, Stöber spheres, fumed silica, fumed silica	Fe	Batch, 1st pyrolysis, 1st ball milling, acidic leaching (HF and NNO_3), 2nd pyrolysis	975	FeN_x	0.175	N.A.	0.825	4.35	0.1 M KOH	S16
								0.70	3.80	0.5 M H_2SO_4	
Fe-N-DSC	$FeCl_3 \cdot 6H_2O$, ammonium acetate, pyrrole	Fe	Solvothermal reaction, pyrolysis	900	FeN_x	0.102	1.03	0.84	4.50	0.1 M KOH	17
							0.81	0.65	4.50	0.5 M H_2SO_4	
Fe-SN-C@800	$FeCl_3$, methyl orange	Fe	Pyrolysis, acidic leaching (HCl)	800	FeN_x	0.180	0.935	0.848	4.60	0.1 M KOH	S18
							0.747	0.640	3.60	0.5 M H_2SO_4	
Fe/N/S-CNT	$FeCl_3$, methyl orange pyrrole	Fe	Pyrolysis, acidic leaching (HCl)	800	Fe-N-C, C-S-C	0.10	0.96	0.84	5.00	0.1 M KOH	S19
							0.80	0.62	4.60	0.5 M	

										H_2SO_4	
D-PC-1(900)	Sodium alginate, $NH_3 \cdot H_2O$		Solvothermal reaction, acidic dialysis (HCl), pyrolysis	900	N-doping--removal	0.40	1.01	0.827	5.43	0.1 M KOH	S20
							0.82	0.60	4.60	0.5 M H_2SO_4	
B,N-carbon	$ZnCl_2$, ethyl cellulose, 4-(1-naphthyl)benzeneboronic acid	Zn	Pyrolysis, acidic leaching (HCl)	800	BN_x	0.146	0.98	0.84	5.50	0.1 M KOH	S21
							0.81	0.52	N.A.	0.5 M H_2SO_4	
N/3D-GNS	Graphene oxide, Cab-O-Sil L90		Thermal reduction, etching, pyrolysis	850	Graphitic-, hydrogenated- and pyridinic-N	0.20	0.90	0.80	208	0.1 M KOH	S22
							0.71	0.51	N.A.	0.5 M H_2SO_4	
1MIL/40ZIF-1000	ZIF-8, MIL-100(Fe)	Fe, Zn	Pyrolysis, acidic leaching (H_2SO_4)	1000	Fe-Fe_3C, FeN_x	0.50	1.07	0.88	4.66	0.1 M KOH	S23
							0.93	0.79	4.38	0.5 M H_2SO_4	
Fe-N-S CNN	ZIF-8, $FeSO_4$, $N_2H_4 \cdot H_2O$	Fe, Zn	Pyrolysis	900	FeN_x, C-S-C	N.A.	N.A.	0.91	5.75	0.1 M KOH	S24
								0.78	6.00	0.5 M H_2SO_4	
Cu@Fe-N-C	ZIF-8, copper foil, $Fe(NO_3)_3 \cdot 9H_2O$	Fe, Cu, Zn	Pyrolysis	900	Fe/Cu-N_x	0.50	1.01	0.89	5.75	0.1 M KOH	S25
							0.88	0.76	5.20	0.5 M	

										H_2SO_4	
Fe/N/S-CNTs	ZIF-8, $FeSO_4 \cdot 7H_2O$, hydrazine hydrate,	Fe, Zn	Pyrolysis, acidic leaching (HCl)	900	FeN_x, C-S-C	0.815	0.987	0.887	6.00	0.1 M KOH	S26
							N.A.	0.767	5.85	0.5 M H_2SO_4	
Fe/S-NC	ZIF-8, $FeCl_3$, KSCN	Fe, Zn	Pyrolysis-adsorption-pyrolysis, acidic leaching (HCl)	900	Fe-N_x-C, C-S-C	0.764	1.003	0.859	4.40	0.1 M KOH	S27
							0.877	0.757	4.30	0.5 M H_2SO_4	
NPSpC	ZIF-8, sodium phytate, dodecyl mercaptan	Zn	Pyrolysis	900	N, P and S -doping	N.A.	0.923	0.821	4.40	0.1 M KOH	S28
							0.899	0.757	4.60	0.5 M H_2SO_4	
ES-CNCo-5	ZIF-8, ZIF-67	Zn, Co	Electrospinning, pyrolysis	800	CoN_x	0.30	0.79	0.71	4.82	0.1 M KOH	S29
							0.73	0.64	4.25	0.5 M H_2SO_4	
MSZIF-900	ZIF-67, melamine sponge	Co	Pyrolysis	900	CoN_x	0.286	0.91	0.84	5.00	0.1 M KOH	S30
							0.92	0.72	3.50	0.5 M H_2SO_4	
Zn/Fe_2-N-C	ZIF-8, hemin	Fe, Zn	Pyrolysis	900	FeN_x	0.34	1.08	0.86	5.67	0.1 M KOH	This work
							1.06	0.81	4.90	0.5 M H_2SO_4	

Note: "-" represents being not available in the references.

References

1. C. Wang, W. Chen, K. Xia, N. Xie, H. Wang and Y. Zhang, *Small*, 2019, **15**, 1804966-1804971.
2. J. Han, X. Meng, L. Lu, J. Bian, Z. Li and C. Sun, *Adv. Funct. Mater.*, 2019, **29**, 1808872-1808879.
3. L. Ma, S. Chen, Z. Pei, Y. Huang, G. Liang, F. Mo, Q. Yang, J. Su, Y. Gao, J. A. Zapien and C. Zhi, *ACS Nano*, 2018, **12**, 1949-1958.
4. S. Ratso, N. Ranjbar Sahraie, M. T. Sougrati, M. Käärik, M. Kook, R. Saar, P. Paiste, Q. Jia, J. Leis, S. Mukerjee, F. Jaouen and K. Tammeveski, *J. Mater. Chem. A*, 2018, **6**, 14663-14674.
5. J. Li, M. Chen, D. A. Cullen, S. Hwang, M. Wang, B. Li, K. Liu, S. Karakalos, M. Lucero, H. Zhang, C. Lei, H. Xu, G. E. Sterbinsky, Z. Feng, D. Su, K. L. More, G. Wang, Z. Wang and G. Wu, *Nat. Catal.*, 2018, **1**, 935-945.
6. X. X. Wang, D. A. Cullen, Y. T. Pan, S. Hwang, M. Wang, Z. Feng, J. Wang, M. H. Engelhard, H. Zhang, Y. He, Y. Shao, D. Su, K. L. More, J. S. Spendelow and G. Wu, *Adv Mater*, 2018, **30**, 1706758-1706768.
7. X. Xu, Z. Xia, X. Zhang, R. Sun, X. Sun, H. Li, C. Wu, J. Wang, S. Wang and G. Sun, *Appl. Catal. B: Envir.*, 2019, **259**, 118042-118050.
8. M. Xiao, J. Zhu, L. Ma, Z. Jin, J. Ge, X. Deng, Y. Hou, Q. He, J. Li, Q. Jia, S. Mukerjee, R. Yang, Z. Jiang, D. Su, C. Liu and W. Xing, *ACS Catal.*, 2018, **8**, 2824-2832.
9. Z. Guo, Z. Zhang, Z. Li, M. Dou and F. Wang, *Nano Energy*, 2019, **57**, 108-117.
10. L. Jiao, G. Wan, R. Zhang, H. Zhou, S. H. Yu and H. L. Jiang, *Angew. Chem. Int. Ed.*, 2018, **57**, 8525-8529.
11. Y. Deng, B. Chi, J. Li, G. Wang, L. Zheng, X. Shi, Z. Cui, L. Du, S. Liao, K. Zang, J. Luo, Y. Hu and X. Sun, *Adv. Energy Mater.*, 2019, **9**, 1802856-1802863.
12. M. Li, Y. Liu, L. Han, J. Xiao, X. Zeng, C. Zhang, M. Xu, P. Dong and Y. Zhang, *J. Mater. Chem. A*, 2019, **7**, 17923-17936.
13. L. Liu, G. Zeng, J. Chen, L. Bi, L. Dai and Z. Wen, *Nano Energy*, 2018, **49**, 393-402.
14. S. N. Bhange, S. M. Unni and S. Kurungot, *ACS Appl. Energy Mater.*, 2018, **1**, 368-376.
15. P. Xu, J. Zhang, G. Jiang, F. Hassan, J. Choi, X. Fu, P. Zamani, L. Yang, D. Banham, S. Ye and Z. Chen, *Nano Energy*, 2018, **51**, 745-753.
16. K. Artyushkova, S. RojasCarbonell, C. Santoro, E. Weiler, A. Serov, R. Awais, R. R. Gokhale and P. Atanassov, *ACS Appl. Energy Mater.*, 2019, **2**, 5406-5418.
17. Z. Huang, H. Pan, W. Yang, H. Zhou, N. Gao, C. Fu, S. Li, H. Li and Y. Kuang, *ACS Nano*, 2018, **12**, 208-216.
18. J. Tong, W. Li, J. Ma, W. Wang, L. Bo, Z. Lei and A. Mahboob, *ACS Appl. Energy Mater.*, 2018, **1**, 5746-5754.
19. Z. Tan, H. Li, Q. Feng, L. Jiang, H. Pan, Z. Huang, Q. Zhou, H. Zhou, S. Ma and Y. Kuang, *J. Mater. Chem. A*, 2019, **7**, 1607-1615.
20. Y. Hao, X. Zhang, Q. Yang, K. Chen, J. Guo, D. Zhou, L. Feng and Z. Slanina, *Carbon*, 2018, **137**, 93-103.
21. T. Sun, J. Wang, C. Qiu, X. Ling, B. Tian, W. Chen and C. Su, *Adv. Sci.*, 2018, **5**, 1800036-1800044.
22. S. Kabir, K. Artyushkova, A. Serov and P. Atanassov, *ACS Appl. Mater. Inter.*, 2018, **10**, 11623-11632.
23. H. Wang, F. X. Yin, N. Liu, R. H. Kou, X. B. He, C. J. Sun, B. H. Chen, D. J. Liu and H. Q. Yin, *Adv. Funct. Mater.*, 2019, **29**, 1901531-1901541.
24. H. Jin, H. Zhou, D. He, Z. Wang, Q. Wu, Q. Liang, S. Liu and S. Mu, *Appl. Catal. B: Envir.*, 2019, **250**, 143-149.
25. Z. Wang, H. Jin, T. Meng, K. Liao, W. Meng, J. Yang, D. He, Y. Xiong and S. Mu, *Adv. Funct. Mater.*, 2018, **28**, 1802596-1802603.
26. H. Jin, H. Zhou, W. Li, Z. Wang, J. Yang, Y. Xiong, D. He, L. Chen and S. Mu, *J. Mater. Chem. A*, 2018, **6**, 20093-20099.
27. P. Zhang, C. Chen, X. Zhang, Z. Jiang, J. Huang and J. Chen, *Electrochim. Acta*, 2019, **298**, 570-579.

28. H. Rong, T. Zhan, Y. Sun, Y. Wen, X. Liu and H. Teng, *Electrochim. Acta*, 2019, **318**, 783-793.
29. C. Zhang, B. Lu, F. Cao, Z. Wu, W. Zhang, H. Cong and S. Yu, *Nano Energy*, 2019, **55**, 226-233.
30. G. Jia, W. Zhang, G. Fan, Z. Li, D. Fu, W. Hao, C. Yuan and Z. Zou, *Angew. Chem. Int. Ed.*, 2017, **56**, 13781-13785.