Supporting Information

From ZIF-8 Polyhedron to Three-Dimensional Nitrogen Doped Hierarchical Porous Carbon: An Efficient Electrocatalyst for Oxygen Reduction Reaction

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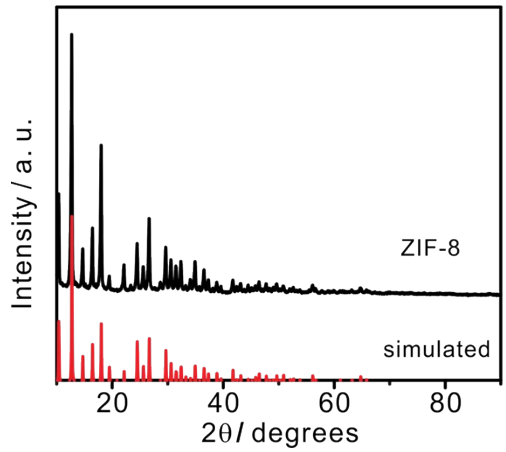

Figure S1 XRD patterns of ZIF-8.

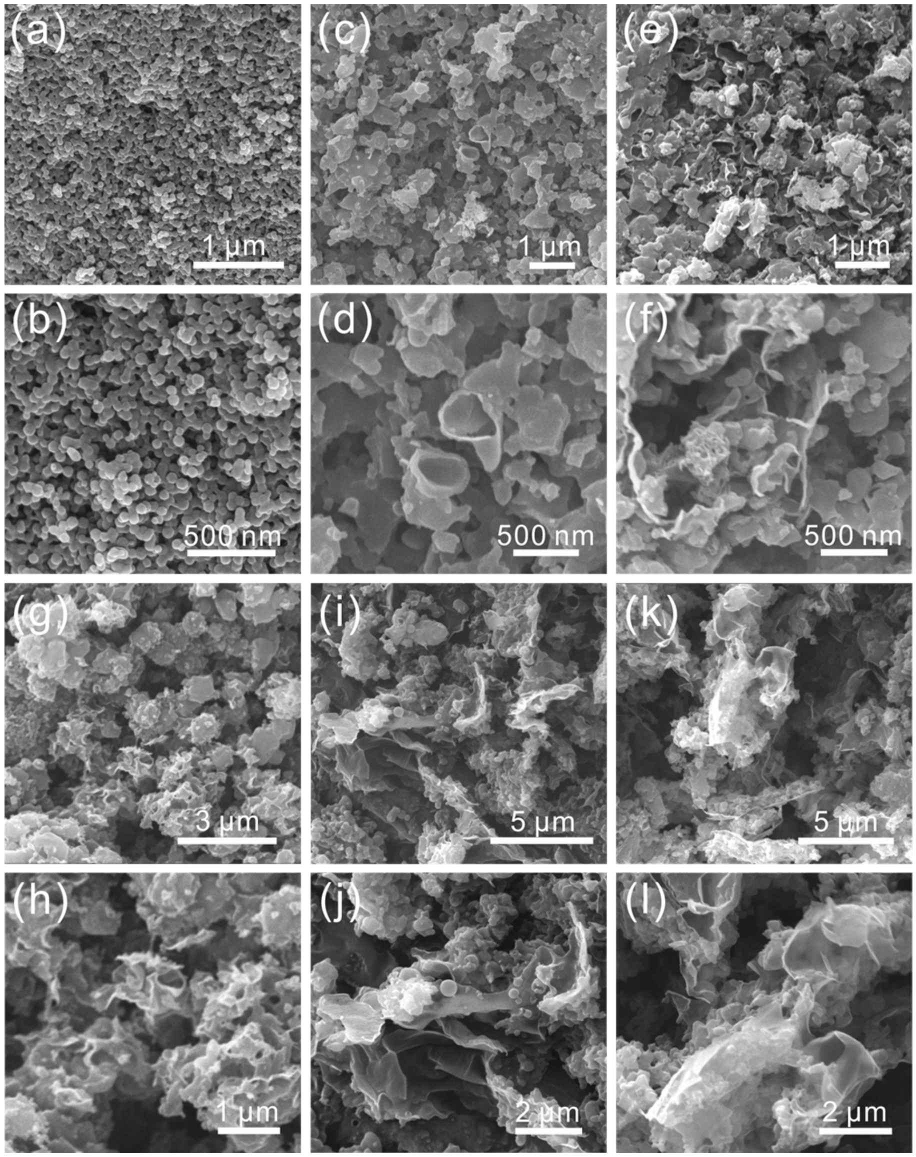

Figure S2 SEM images of NC-900 (a, b) and the materials prepared at different NaCl/ZIF-8 ratio of 1:20 (c, d), 1:10 (e, f), 1:5 (g, h), 1:3 (i, j), 1:1 (k, l) when annealing at 900 °C.

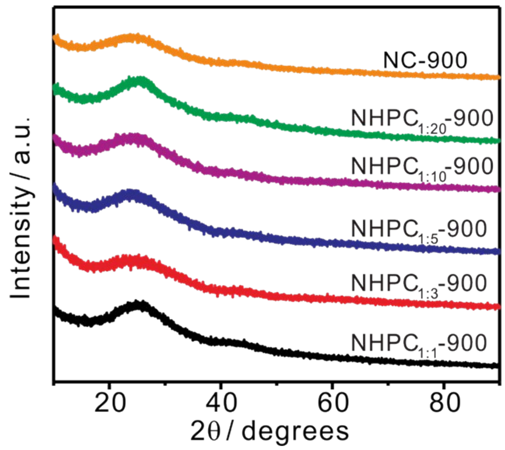

Figure S3 XRD patterns of NC-900 and the materials obtained at different mass ratio of NaCl and ZIF-8 (1:20, 1:10, 1:5, 1:3, 1:1) when annealing at 900 °C.

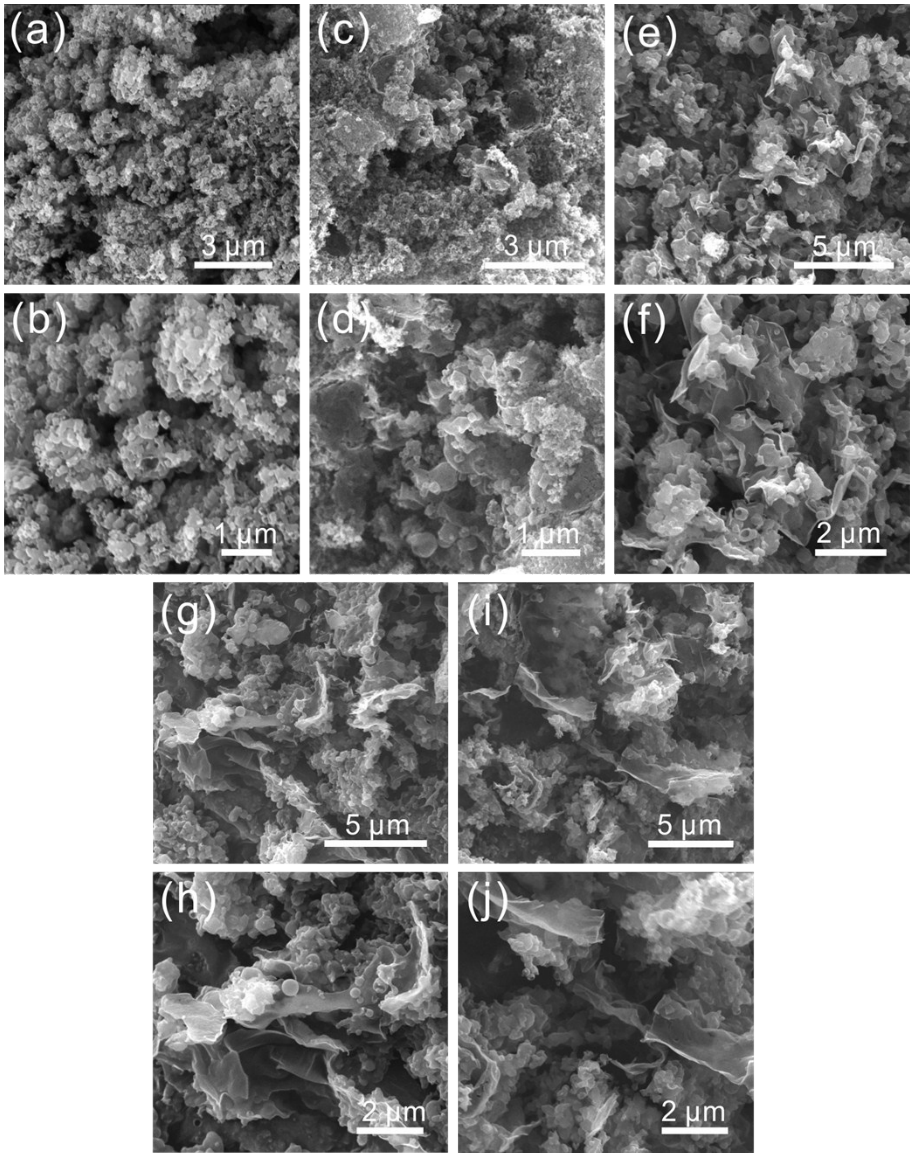

Figure S4 SEM images of the materials synthesized at the NaCl/ZIF-8 ratio of 1:3 when calcining at 600 °C (a, b), 700 °C (c, d), 800 °C (e, f), 900 °C (g, h), and 1000 °C (i, j).

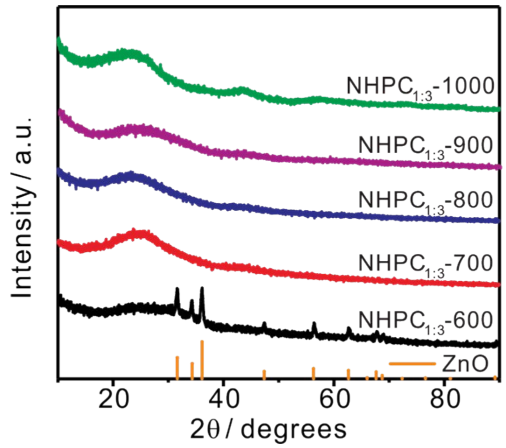

Figure S5 (a) XRD patterns of the materials synthesized at the NaCl/ZIF-8 ratio of 1:3 when calcining at different pyrolysis temperature (600, 700, 800, 900, 1000 °C).

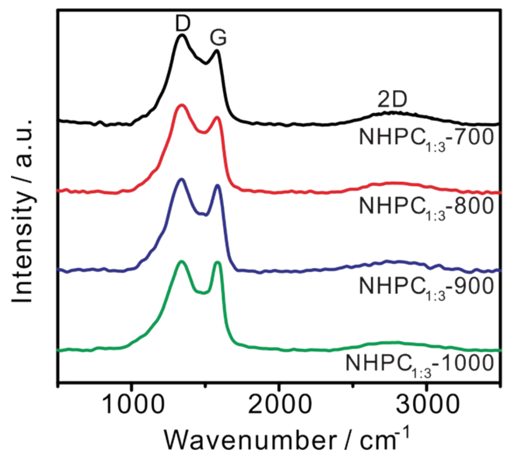

Figure S6 Raman spectra of the samples synthesized at the NaCl/ZIF-8 ratio of 1:3 by annealing at different pyrolysis temperatures (700, 800, 900, 1000 °C)..

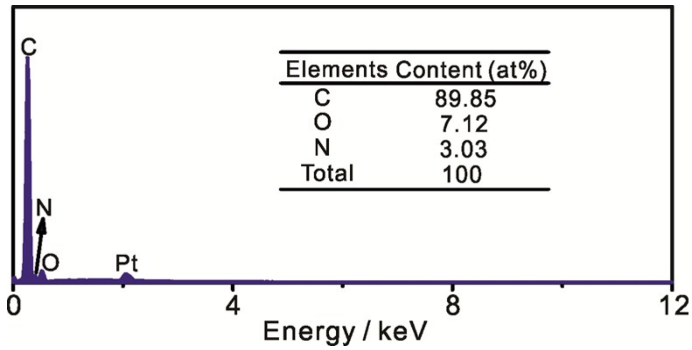

Figure S7 SEM-EDX spectrum of NHPC$_{1:3}$-900 materials. Before measurements, the NHPC$_{1:3}$-900 powder was glued to an electrically grounded sample holder using a double-face conducting tape and then was sputter-coated with platinum, leading to the observation of Pt in Figure S7.

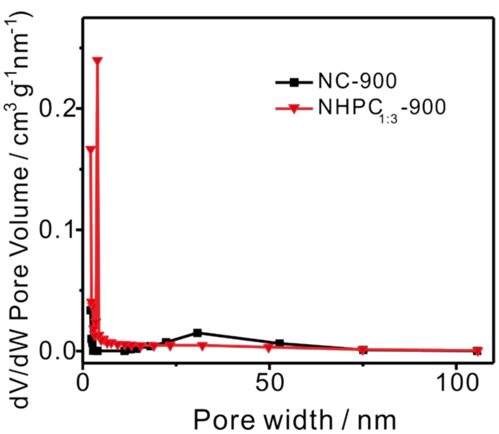

Figure S8 Pore size distribution of NHPC$_{1:3}$-900 and NC-900.

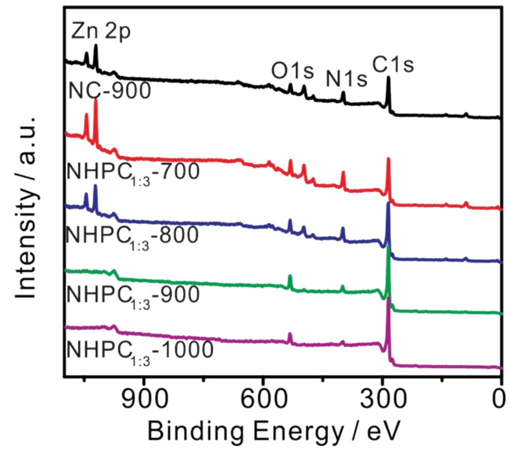

Figure S9 XPS survey spectra of NC-900 and the NHPCs materials obtained at different pyrolysis temperatures.

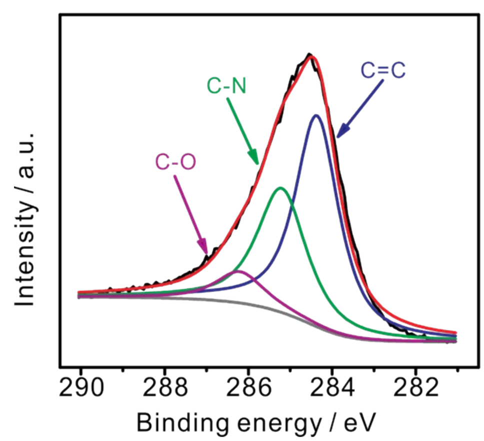

Figure S10 High-resolution C1s XPS spectra of $NHPC_{1:3}$-900.

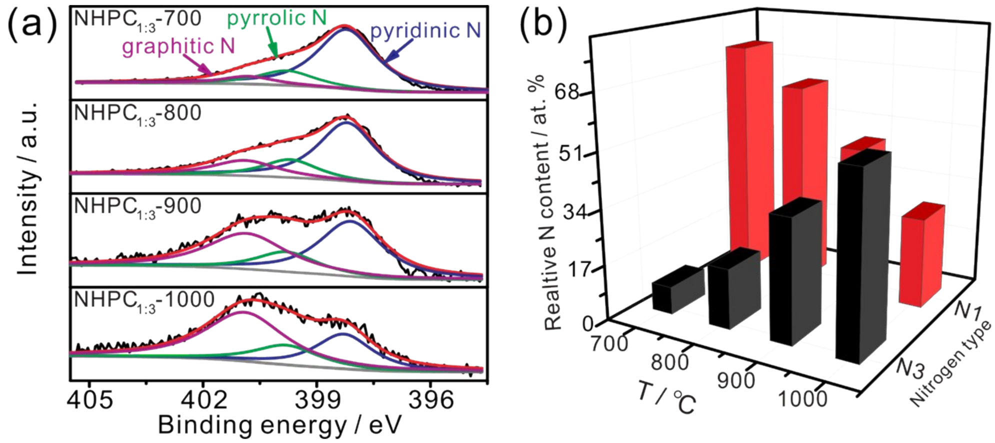

Figure S11 (a) High-resolution N1s XPS spectra of NHPCs obtained at different pyrolysis temperatures, and (b) the corresponding relative content of nitrogen.

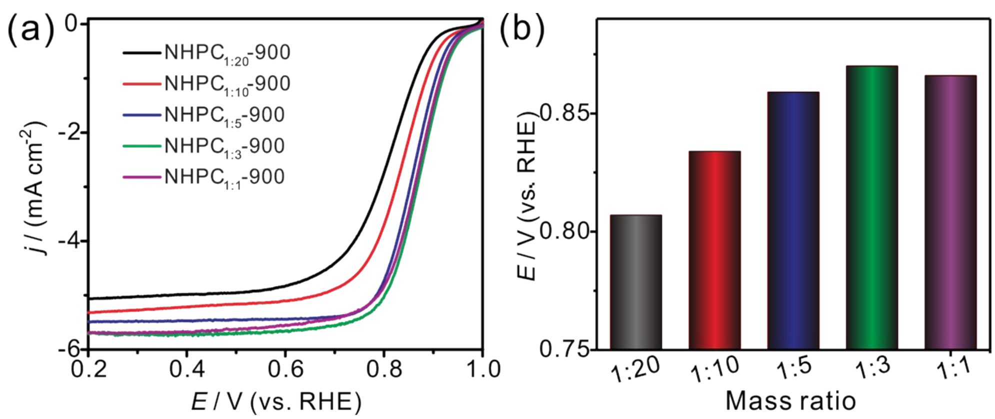

Figure S12 (a) ORR polarization curves of NHPCs obtained at different mass ratio of NaCl and ZIF-8 at a scan rate of 5 mV s^{-1}, and (b) the corresponding half-wave potential.

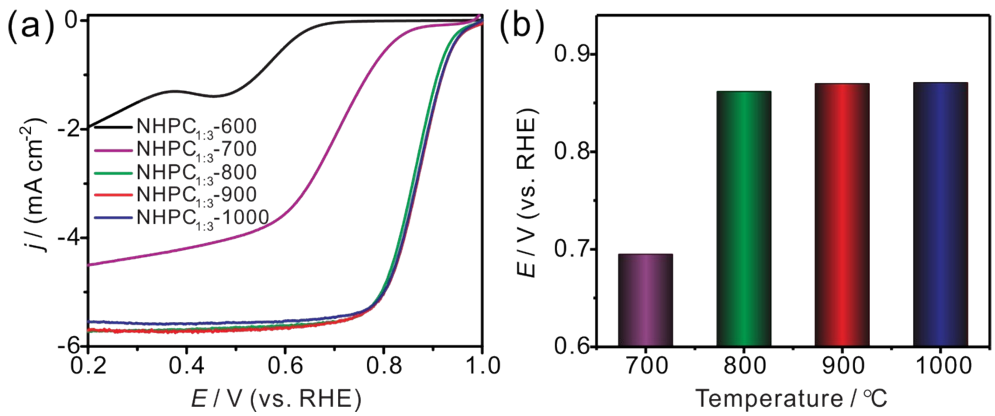

Figure S13 (a) ORR polarization curves of NHPCs obtained at different pyrolysis temperatures at a scan rate of 5 mV s^{-1}, and (b) the corresponding half-wave potential.

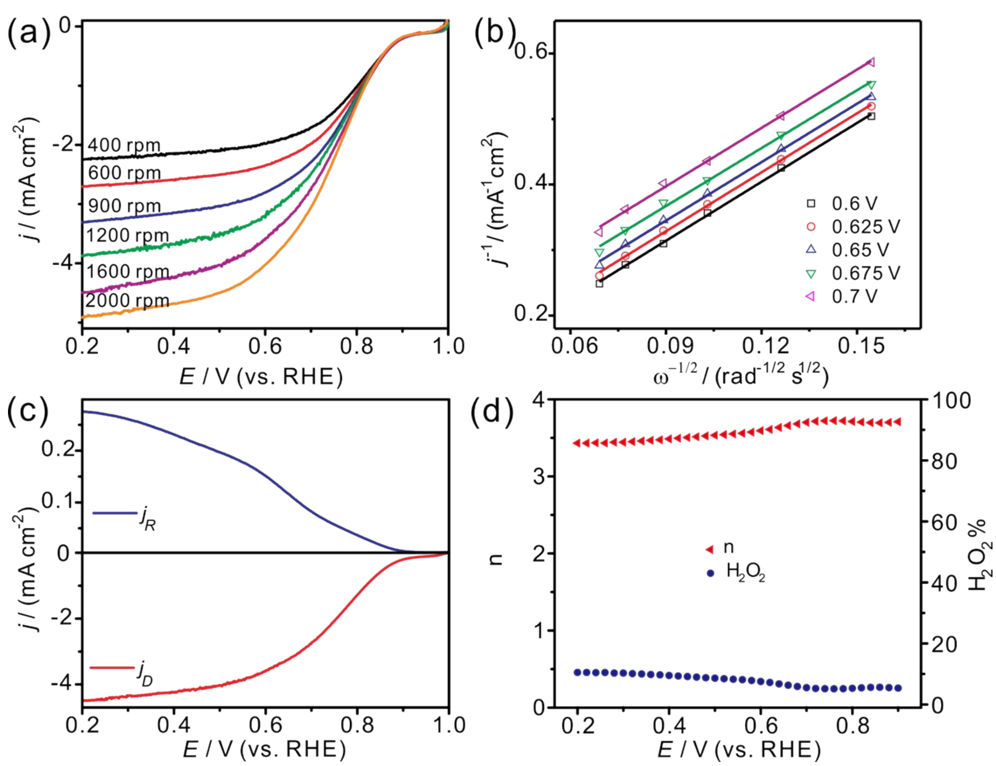

Figure S14 (a) ORR polarization curves of NC-900 at various rotating speeds with a scan rate of 5 mV s^{-1}, and (b) the corresponding Koutecky-Levich plots of under potentials of 0.6 V, 0.625 V, 0.65 V, 0.675 V, and 0.7 V. (c)The electron-transfer number n and H_2O_2 yield and (d) RRDE voltammograms for NC-900.

Table S1 Comparison of the ORR electrocatalytic performance of $NHPC_{1:3}$-900 and other metal-free nitrogen-doped carbon electrocatalysts.

Catalysts	Loading (mg cm^{-2})	Electrolyte	Half-wave potential ($E_{1/2}$)	$E_{1/2}$-$E_{1/2}$(Pt/C) (mV)	j_L(mA cm^{-2})	Refs.
Nitrogen-Doped Porous Carbon Nanosheets	0.2	0.1 M KOH	-0.210 V vs. Ag/AgCl	-3	5.79	[1]
Nitrogen containing mesoporous carbon	0.245	0.1 M KOH	0.75 V vs. RHE	—	~4.3	[2]
Nitrogen-doped carbon nanofiber (N-CNF) aerogel	0.1	0.1 M KOH	0.80 V vs. RHE	-50	~5.35	[3]
Nitrogen containing mesoporous carbon	0.245	0.1 M KOH	0.75 V vs. RHE	—	~4.3	[4]
Nitro Lignin-Derived Nitrogen-Doped Carbon	0.29	0.1 M KOH	0.85 V vs. RHE	—	~5.4	[5]
Nitrogen-doped hierarchical porous carbons	0.42	0.1 M KOH	0.83 V vs. RHE	0	~4.6	[6]
N-doped carbon nanoplatelets	0.4	0.1 M KOH	-0.15 V vs. SCE	30	6.50	[7]
Hybrids of nitrogen-doped graphitic porous carbon and carbon nanotube	0.102	0.1 M KOH	-0.171 V vs. Ag/AgCl	1	~5.1	[8]
Nitrogen doped carbon nanoribbons	0.191	0.1 M KOH	0.864 V vs. RHE	-39	~3.5	[9]
Nitrogen-doped Graphene-Wrapped Carbon Nanoparticles	0.15	0.1 M KOH	—	-131	~5.1	[10]
N-doped porous carbon@graphene	0.408	0.1 M KOH	0.80 V vs. RHE	20	—	[11]
Hierarchically tubular nitrogen-doped carbon	0.137	0.1 M KOH	0.76 V vs. RHE	—	~4.9	[12]
N doped three dimensional few-layer porous carbon nanosheets	0.3	0.1 M KOH	-0.17 V vs. SCE	30	~5.4	[13]
N,P-doped porous carbon	0.306	0.1 M KOH	~ -0.20 V vs. Ag/AgCl	—	~5.4	[14]
Nitrogen-doped carbon nanoscale networks	0.425	0.1 M KOH	-0.0.171 V vs. Ag/AgCl	-10	5.8	[15]
$NHPC_{1:3}$-900	0.42	0.1 M KOH	0.87 V vs. RHE	50	5.7	This work

Table S2 Comparison of the Zn-air battery performance of non-precious metal based electrocatalysts extracted from literature.

Catalysts	Loading ($mg\ cm^{-2}$)	Peak power density ($mW\ cm^{-2}$)	Electrolyte	Refs
NCNF-1000	2.0	185	6 M KOH + 0.2 M zinc acetate	[16]
MnO_2-2h/KB	1.0	133.17	6 M KOH	[17]
FeCo@NC-750	1.0	132	6 M KOH + 0.2 M zinc acetate	[18]
NiFe@NCX	1.0	83	6 M KOH	[19]
C-CoPAN900	1.0	125	6 M KOH + 0.2 M $ZnCl_2$	[20]
CoFe@NCNTs	1.0	150	6 M KOH + 0.2 M zinc acetate	[21]
$NiCo_2S_4$/N-CNT	1.0	147	6 M KOH + 0.2 M $ZnCl_2$	[22]
Mn_3O_4/Ti_3C_2 MXene	1.0	150	6 M KOH	[23]
Mo-N/C@MoS_2	1.0	194.6	6 M KOH + 0.2 M zinc acetate	[24]
N-GCNT/FeCo	2.0	89.3	6 M KOH + 0.2 M zinc acetate	[25]
Cu-N/C	1.0	132	6 M KOH	[26]
3D actiniae-like carbon nanotube assembly	2.0	157.3	6 M KOH + 0.2 M zinc acetate	[27]
bicontinuous hierarchical porous carbon	0.5	197	6 M KOH	[28]
Co/N/O tri-doped graphene mesh	0.5	152	6 M KOH + 0.2 M $ZnCl_2$	[29]
$CuCo_2O_4$/N-CNTs	2.0	90.50	6 M KOH + 0.2 M zinc acetate	[30]
Co_4N/CNW/CC	—	174	6 M KOH + 0.2 M zinc acetate	[31]
Nanoporous carbon fiber Film	2.0	~185	6 M KOH + 0.2 M zinc acetate	[16]
N,P codoped carbon	0.3	~93	6 M KOH	[32]
N-doped hollow carbon nanospheres	1.0	76	6 M KOH	[33]
carbon nanotube arrays	—	190	6 M KOH + 0.2 M zinc acetate	[34]
macro-porous N, S-doped carbon	2.0	151	6 M KOH + 0.2 M zinc acetate	[35]
hierarchically porous iron and nitrogen-codoped carbon nanofibers	1.0	135	6 M KOH	[36]
Co_3O_4 nanosheets/carbon cloth	0.74	107	6 M KOH + 0.2 M zinc acetate	[37]
FeNC-850	2.4	186	7 M KOH	[38]
Core-Shell NiFe@N-Graphite	2	85	6 M KOH + 0.2 M zinc acetate	[39]
N,P-codoped nanoporous carbon	1	146	6 M KOH	[40]
Co@N-C	0.5	105	6 M KOH	[41]
$NHPC_{1:3}$-900	1.0	207	6 M KOH + 0.2 M zinc acetate	This work

References

1. H. Yu, L. Shang, T. Bian, R. Shi, G. I. Waterhouse, Y. Zhao, C. Zhou, L. Z. Wu, C. H. Tung and T. Zhang, *Adv. Mater.*, 2016, **28**, 5080-5086.
2. M. Thomas, R. Illathvalappil, S. Kurungot, B. N. Nair, A. A. P. Mohamed, G. M. Anilkumar, T. Yamaguchi and U. S. Hareesh, *ACS Appl. Mater. Interfaces*, 2016, **8**, 29373-29382.
3. H. W. Liang, Z. Y. Wu, L. F. Chen, C. Li and S. H. Yu, *Nano Energy*, 2015, **11**, 366-376.
4. M. Thomas, R. Illathvalappil, S. Kurungot, B. N. Nair, A. A. P. Mohamed, G. M. Anilkumar, T. Yamaguchi and U. Hareesh, *ACS Appl. Mater. Interfaces*, 2016, **8**, 29373-29382.
5. M. Graglia, J. Pampel, T. Hantke, T. P. Fellinger and D. Esposito, *ACS Nano*, 2016, **10**, 4364-4371.
6. C. Xuan, Z. Wu, W. Lei, J. Wang, J. Guo and D. Wang, *ChemCatChem*, 2017, **9**, 809-815.
7. Y. Zhang, X. Zhang, X. Ma, W. Guo, C. Wang, T. Asefa and X. He, *Scientific Reports*, 2017, **7**, 43366.
8. L. Zhang, X. Wang, R. Wang and M. Hong, *Chem. Mater.*, 2015, **27**, 7610-7618.
9. J. He, Y. He, Y. Fan, B. Zhang, Y. Du, J. Wang and P. Xu, *Carbon*, 2017, **124**, 630-636.
10. R. Ma, Y. Zhou, P. Li, Y. Chen, J. Wang and Q. Liu, *Electrochim. Acta*, 2016, **216**, 347-354.
11. S. Liu, H. Zhang, Q. Zhao, X. Zhang, R. Liu, X. Ge, G. Wang, H. Zhao and W. Cai, *Carbon*, 2016, **106**, 74-83.
12. W. Wei, H. Ge, L. Huang, M. Kuang, A. M. Alenizi, L. Zhang and G. Zheng, *J. Mater. Chem. A*, 2017, **5**, 13634-13638.
13. J. Zhang, C. Zhang, Y. Zhao, I. S. Amiinu, H. Zhou, X. Liu, Y. Tang and S. Mu, *Appl. Catal. B-Environ.*, 2017, **211**, 148-156.
14. M. Borghei, N. Laocharoen, E. Kibena-Põldsepp, L. S. Johansson, J. Campbell, E. Kauppinen, K. Tammeveski and O. J. Rojas, *Appl. Catal. B-Environ.*, 2017, **204**, 394-402.
15. A. Zhang, T. Qu, S. Cao, Y. Li, Y. Zhao and A. Chen, *Adv. Mater. Interfaces*, 2018, **5**, 1701390.
16. Q. Liu, Y. Wang, L. Dai and J. Yao, *Adv. Mater.*, 2016, **28**, 3000-3006.
17. M. Wu, T. Zhao, H. Jiang, L. Wei and Z. Zhang, *Electrochim. Acta*, 2016, **222**, 1438-1444.
18. P. Cai, S. Ci, E. Zhang, P. Shao, C. Cao and Z. Wen, *Electrochim. Acta*, 2016, **220**, 354-362.
19. J. Zhu, M. Xiao, Y. Zhang, Z. Jin, Z. Peng, C. Liu, S. Chen, J. Ge and W. Xing, *ACS Catal.*, 2016, **6**, 6335-6342.
20. B. Li, X. Ge, F. T. Goh, T. A. Hor, D. Geng, G. Du, Z. Liu, J. Zhang, X. Liu and Y. Zong, *Nanoscale*, 2015, **7**, 1830-1838.
21. P. Cai, Y. Hong, S. Ci and Z. Wen, *Nanoscale*, 2016, **8**, 20048-20055.
22. X. Han, X. Wu, C. Zhong, Y. Deng, N. Zhao and W. Hu, *Nano Energy*, 2017, **31**, 541-550.
23. Q. Xue, Z. Pei, Y. Huang, M. Zhu, Z. Tang, H. Li, Y. Huang, N. Li, H. Zhang and C. Zhi, *J. Mater. Chem. A*, 2017, **5**, 20818-20823.
24. I. S. Amiinu, Z. Pu, X. Liu, K. A. Owusu, H. G. R. Monestel, F. O. Boakye, H. Zhang and S. Mu, *Adv.*

Funct. Mater., 2017, **27**, 1702300.

25. C. Y. Su, H. Cheng, W. Li, Z. Q. Liu, N. Li, Z. Hou, F. Q. Bai, H. X. Zhang and T. Y. Ma, *Adv. Energy Mater.*, 2017, **7**, 1602420.
26. Q. Lai, J. Zhu, Y. Zhao, Y. Liang, J. He and J. Chen, *Small*, 2017, **13**, 1700740.
27. S. Wang, J. Qin, T. Meng and M. Cao, *Nano Energy*, 2017, **39**, 626-638.
28. M. Yang, X. Hu, Z. Fang, L. Sun, Z. Yuan, S. Wang, W. Hong, X. Chen and D. Yu, *Adv. Funct. Mater.*, 2017, **27**, 1701971.
29. C. Tang, B. Wang, H. F. Wang and Q. Zhang, *Adv. Mater.*, 2017, **29**, 1703185.
30. H. Cheng, M. L. Li, C. Y. Su, N. Li and Z. Q. Liu, *Adv. Funct. Mater.*, 2017, **27**, 1701833.
31. F. Meng, H. Zhong, D. Bao, J. Yan and X. Zhang, *J. Am. Chem. Soc.*, 2016, **138**, 10226-10231.
32. J. Zhang, L. Qu, G. Shi, J. Liu, J. Chen and L. Dai, *Angew. Chem.*, 2016, **128**, 2270-2274.
33. J. Zhu, H. Zhou, C. Zhang, J. Zhang and S. Mu, *Nanoscale*, 2017, **9**, 13257-13263.
34. Z. Li, M. Shao, Q. Yang, Y. Tang, M. Wei, D. G. Evans and X. Duan, *Nano Energy*, 2017, **37**, 98-107.
35. Z. Pei, H. Li, Y. Huang, Q. Xue, Y. Huang, M. Zhu, Z. Wang and C. Zhi, *Energy Environ. Sci.*, 2017, **10**, 742-749.
36. Y. Zhao, Q. Lai, Y. Wang, J. Zhu and Y. Liang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 16178-16186.
37. Z. Song, X. Han, Y. Deng, N. Zhao, W. Hu and C. Zhong, *ACS Appl. Mater. Interfaces*, 2017, **9**, 22694-22703.
38. J. Yang, J. Hu, M. Weng, R. Tan, L. Tian, J. Yang, J. Amine, J. Zheng, H. Chen and F. Pan, *ACS Appl. Mater. Interfaces*, 2017, **9**, 4587-4596.
39. P. Liu, D. Gao, W. Xiao, L. Ma, K. Sun, P. Xi, D. Xue and J. Wang, *Adv. Funct. Mater.*, 2018, 1706928.
40. H. Luo, W.-J. Jiang, Y. Zhang, S. Niu, T. Tang, L.-B. Huang, Y.-Y. Chen, Z. Wei and J.-S. Hu, *Carbon*, 2018, **128**, 97-105.
41. M. Zhang, Q. Dai, H. Zheng, M. Chen and L. Dai, *Adv. Mater.*, 2018, **30**, 1705431.