Electronic Supplementary Information

A Facile Synthesis of Porous N-Doped Carbon with Hybridization of Fe₃C Nanoparticle-Encased CNT for an Advanced Oxygen Reduction Reaction Electrocatalyst

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Figure. S1 SEM image (a) and TEM (b) image of the sample FeNC-700 obtained at the initial 0.5h.



Figure S2. Powder X-ray diffraction pattern of FeNC-X samples: (a) FeNC-700; (b) FeNC-800; (c) FeNC-900.



Figure S3. TEM image of FeNC-800.



Figure S4. XPS spectrum of (left) FeNC-700; (middle) FeNC-800; (right) FeNC-900: (a-c)

Survey pattern; (d-f) high-resolution spectrum of N; (g-i) high-resolution spectrum of Fe.

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Figure S5. Impedance data for FeNC-X samples and FeNC-ZIF-800.



Figure S6. Impedance data for FeNC-X samples and FeNC-ZIF-800.



Figure S7. TEM image of the interface of N-doped carbon and carbon nanotubes in FeNC-ZIF-

800.



Figure S8. ORR polarization curves before and after 1000 cycles charge-discharge process of FeNC-ZIF-800 (a) and Pt/C (b) in O_2 -saturated 0.1 M KOH solution.



Figure S9. ORR polarization curves before and after 1000 cycles charge-discharge process of FeNC-ZIF-800 in O_2 -saturated 0.5 M H_2SO_4 solution.



Figure S10. XRD pattern of FeNC-1000.



Figure S11. SEM image of FeNC-1000.



Figure S12. ORR polarization curve of FeNC-1000 in O_2 -saturated 0.1 M KOH solution.



Figure S13. XRD pattern of samples obtained at 700 °C. (FeNC-2ZIF-800 means the amount of ZIF in the precursors are 200% of that in FeNC-ZIF-700).



Figure S14. ORR polarization curves of samples obtained at 700 $^{\circ}$ C in O₂-saturated 0.1 M KOH solution.



Figure S15. XRD pattern of samples obtained at 800 °C. (FeNC-2ZIF-800 and FeNC-0.5ZIF-800 mean the amount of ZIF in the precursors are 200% or 50% of that in FeNC-ZIF-800)



Figure S16. ORR polarization curves of samples obtained at 800 $^{\circ}$ C in O₂-saturated 0.1 M KOH solution.

Catalyst	Onset potential	Half-wave potential	Ref.
	(V vs. RHE)	(V vs. RHE)	
FeNC-ZIF-800	1.0	0.86	This work
Fe-N/C-800	0.923	0.809	1
Fe ₃ C/NG-800	1.03	0.86	2
Fe-N/C-800	0.98	1	3
Co ₃ O ₄ @CMWCNT	0.89	0.81	4
Co-N-HPC	0.91	0.83	5
GNPCSs-800	0.957	0.82	6
Fe/N/CNT	1.04	0.86	7
Fe-N-GC-900	1.01	0.86	8
Fe ₃ C/C-800	1.05	0.83	9
GFe-800a	-0.087	-0.29	10
	(vs. Ag/AgCl)	(vs. Ag/AgCl)	
Fe-N/G	0.87	0.78	11
ZIF-67-900	0.95	0.85	12
FePhen@MOF-ArNH ₃	1.03	0.86	13
N-Fe-CNT/CNP	/	0.87	14
NCNT/CoO-NiO-NiCo	1.0	0.83	15
N-CNT/N-G	/	0.85	16
Fe-N ₄ /C	-	0.87	17
Fe-N-CNS	0.98	0.85	18
Fe ₃ C/C-800	1.03	0.86	19

Table S1. Comparison of ORR catalytic performances in 0.1 M KOH solution between FeNC-ZIF-800 and other non-precious metal-based catalysts reported previously.

Catalyst	Onset potential	Half-wave potential	Electrolyte	Ref.
	(V vs. RHE)	(V vs. RHE)		
FeNC-ZIF-800	0.85	0.74	H_2SO_4	This work
pPMF-800	0.89	0.71	HClO₄	20
CPANIFe-NaCl	0.91	0.74	HCIO ₄	21
PpPD-Fe-C	0.83	0.72	H_2SO_4	22
Fe-N-GC-900	1	0.74	HCIO ₄	8
Fe-AAPyr	0.9	0.75	H_2SO_4	23
H–Fe@N–C/RGO	0.89	0.67	HCIO ₄	24
Fe-N/C-800	0.80	0.68	HCIO ₄	1
Fe-g-C ₃ N ₄ @C	1	0.75	HCIO ₄	25
Fe-N-HCMS	0.81	0.60	H_2SO_4	26
FeNC-70	0.8	/	HCIO ₄	27
PANI-Fe	0.85	/	H_2SO_4	28
ZIF-67-900	0.85	0.71	H_2SO_4	12
Fe ₃ C/NG-800	0.92	0.77	HCIO ₄	2
Fe ₃ C/C-700	0.90	0.73	HCIO ₄	9
Fe-N-CNFs	0.55	0.37	H_2SO_4	29
	(vs. Ag/AgCl)	(vs. Ag/AgCl)		

Table S2. Comparison of ORR catalytic performances in acid solution between FeNC-ZIF-800 and other non-precious metal-based catalysts reported previously.

Reference

- 1 L. Lin, Q. Zhu and A.-W. Xu, J. Am. Chem. Soc., 2014, 136, 11027-11033.
- 2 M. Xiao, J. Zhu, L. Feng, C. Liu and W. Xing, Adv. Mater., 2015, 27, 2521-2527.
- 3 W. Niu, L. Li, X. Liu, N. Wang, J. Liu, W. Zhou, Z. Tang and S. Chen, *J. Am. Chem. Soc.*, 2015, 137, 5555-5562.
- 4 X. Li, Y. Fang, X. Lin, M. Tian, X. An, Y. Fu, R. Li, J. Jin and J. Ma, *J. Mater. Chem. A*, 2015, 3, 17392-17402.
- 5 M. Dou, D. He, W. Shao, H. Liu, F. Wang and L. Dai, *Chem. Eur. J.*, 2016, 22, 2896-2901.
- 6 H.-x. Zhong, J. Wang, Y.-w. Zhang, W.-l. Xu, W. Xing, D. Xu, Y.-f. Zhang and X.-b. Zhang, *Angew. Chem. Int. Ed.*, 2014, 53, 14235-14239.
- 7 C. Dominguez, F. J. Perez-Alonso, M. A. Salam, S. A. Al-Thabaiti, M. A. Pena, F. J. Garcia-Garcia, L. Barrio and S. Rojas, *Appl. Catal.*, *B*, 2016, 183, 185-196.
- 8 A. Kong, X. Zhu, Z. Han, Y. Yu, Y. Zhang, B. Dong and Y. Shan, *ACS catal.*, 2014, 4, 1793-1800.
- 9 Y. Hu, J. O. Jensen, W. Zhang, L. N. Cleemann, W. Xing, N. J. Bjerrum and Q. Li, *Angew. Chem. Int. Ed.*, 2014, 53, 3675-3679.
- 10 Q. Dong, X. Zhuang, Z. Li, B. Li, B. Fang, C. Yang, H. Xie, F. Zhang and X. Feng, *J. Mater. Chem. A*, 2015, 3, 7767-7772.
- 11 Q. Lai, Q. Su, Q. Gao, Y. Liang, Y. Wang, Z. Yang, X. Zhang, J. He and H. Tong, *ACS Appl. Mater. Interfaces*, 2015, 7, 18170-18178.
- 12 X. Wang, J. Zhou, H. Fu, W. Li, X. Fan, G. Xin, J. Zheng and X. Li, *J. Mater. Chem. A*, 2014, 2, 14064-14070.
- 13 K. Strickland, E. Miner, Q. Jia, U. Tylus, N. Ramaswamy, W. Liang, M. T. Sougrati, F. Jaouen and S. Mukerjee, *Nat Commun*, 2015, 6, 7343.
- 14 H. T. Chung, J. H. Won and P. Zelenay, *Nat. Commun.*, 2013, 4, 1922.
- 15 X. Liu, M. Park, M. G. Kim, S. Gupta, G. Wu and J. Cho, *Angew. Chem. Int. Ed.*, 2015, 54, 9654-9658.
- 16 S. Zhang, H. Zhang, Q. Liu and S. Chen, *J. Mater. Chem. A*, 2013, 1, 3302-3308.
- 17 N. Ramaswamy, U. Tylus, Q. Jia and S. Mukerjee, J. Am. Chem. Soc., 2013, 135, 15443-15449.
- 18 Y. Wang, A. Kong, X. Chen, Q. Lin and P. Feng, *ACS catal.*, 2015, 5, 3887-3893.
- 19 M. Xiao, J. Zhu, L. Feng, C. Liu and W. Xing, *Adv. Mater. (Weinheim, Ger.)*, 2015, 27, 2521-2527.
- 20 W. Yang, X. Yue, X. Liu, L. Chen, J. Jia and S. Guo, *Nanoscale*, 2016, 8, 959-964.
- 21 W. Ding, L. Li, K. Xiong, Y. Wang, W. Li, Y. Nie, S. Chen, X. Qi and Z. Wei, *J. Am. Chem. Soc.*, 2015, 137, 5414-5420.
- 22 Z. Xiang, Y. Xue, D. Cao, L. Huang, J.-F. Chen and L. Dai, *Angew. Chem., Int. Ed.*, 2014, 53, 2433-2437.
- 23 M. H. Robson, A. Serov, K. Artyushkova and P. Atanassov, *Electrochim. Acta*, 2013, 90, 656-665.
- 24 J. Wang, G. Wang, S. Miao, J. Li and X. Bao, *Faraday Discuss.*, 2014, 176, 135-151.
- 25 M.-Q. Wang, W.-H. Yang, H.-H. Wang, C. Chen, Z.-Y. Zhou and S.-G. Sun, *ACS catal.*, 2014, 4, 3928-3936.
- 26 M. Zhou, C. Yang and K.-Y. Chan, *Adv. Energy Mater.*, 2014, 4, 1400840.
- T. Palaniselvam, B. P. Biswal, R. Banerjee and S. Kurungot, *Chem. Eur. J.*, 2013, 19, 9335-9342.
- 28 H.-W. Liang, W. Wei, Z.-S. Wu, X. Feng and K. Muellen, *J. Am. Chem. Soc.*, 2013, 135, 16002-16005.
- 29 Z. Y. Wu, X. X. Xu, B. C. Hu, H. W. Liang, Y. Lin, L. F. Chen and S. H. Yu, *Angew. Chem. Int. Ed.*, 2015, 54, 8179-8183.