Electronic Supporting Information

Synthesis of Fe_3C@porous Carbon Nanorods via carbonization for Oxygen Reduction Reaction and Zn-air Battery

Yijie Zhang, Yong Zhao, Muwei Ji, Han-ming Zhang, Minghui Zhang, Hang Zhao, Mengsi Cheng, Jiali Yu, Huichao Liu, Caizhen Zhu* and Jian Xu

China Institute of Low-dimensional Materials Genome Initiative, College of Chemistry and Environmental Engineering of Shenzhen University, Shenzhen 518060, China

Figure S1-S4.

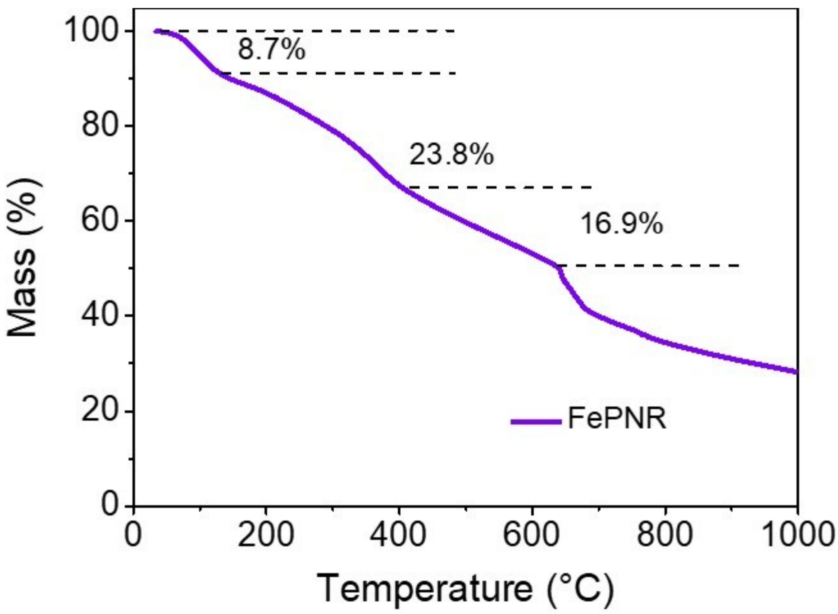

Figure S1. TG analysis of the FePNR.

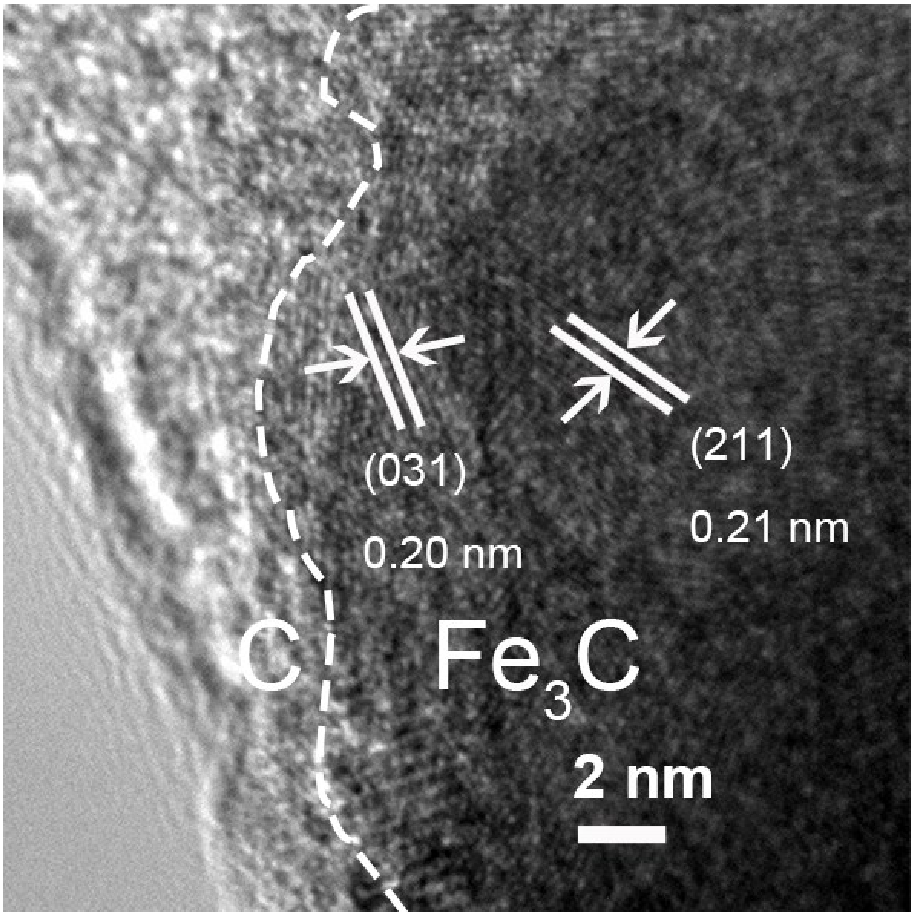

Figure S2. The HRTEM image of Fe_3C/C hetero-structures.

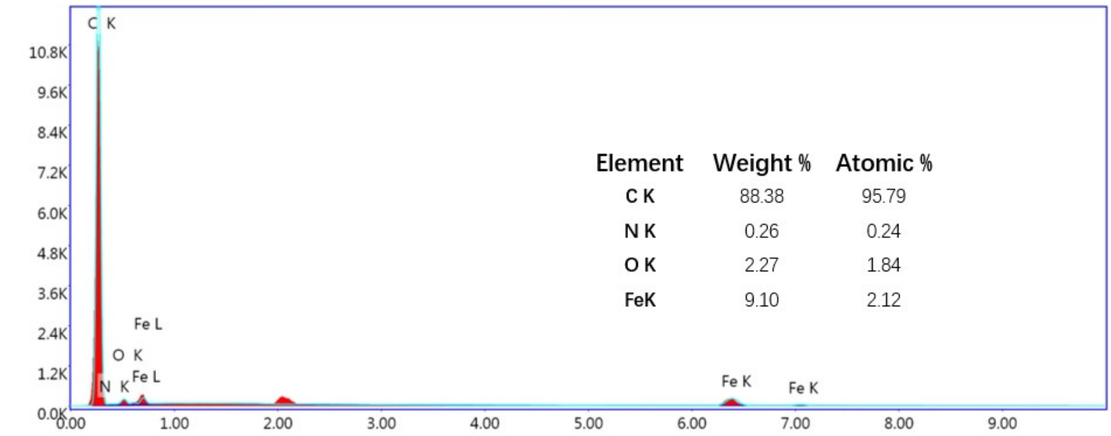

Figure S3. The EDX spectra of as-prepared of FeCNR-750

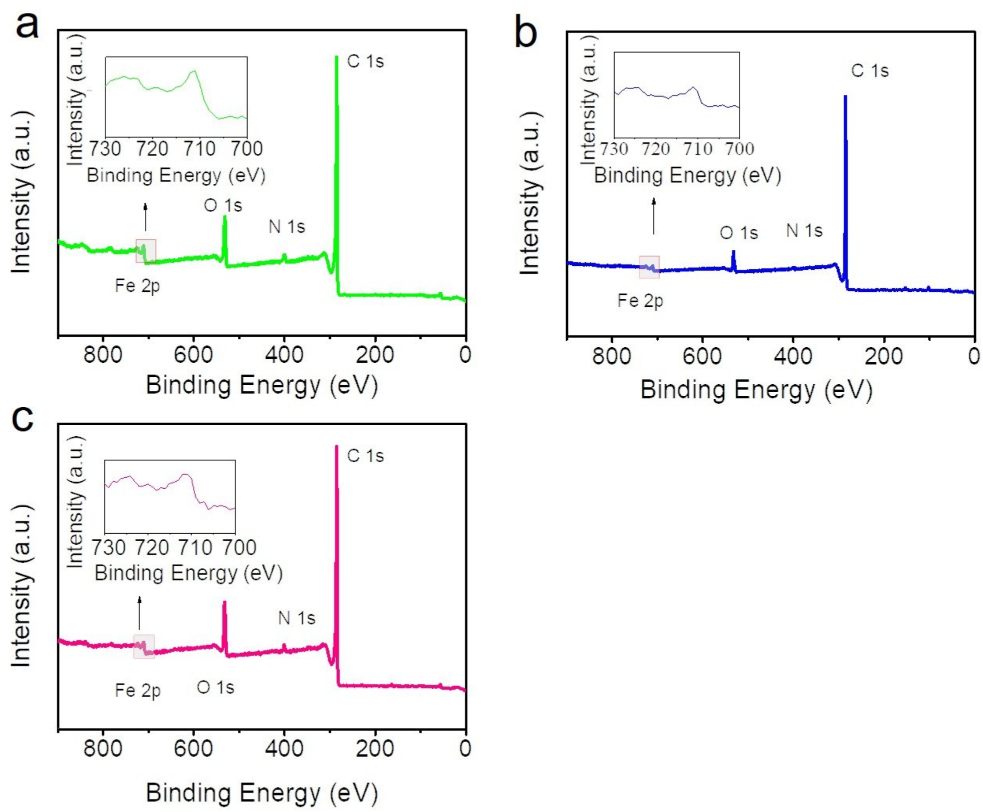

Figure S4. XPS survey spectrum of the FeCNR-700, FeCNR-750 and FeCNR-800.

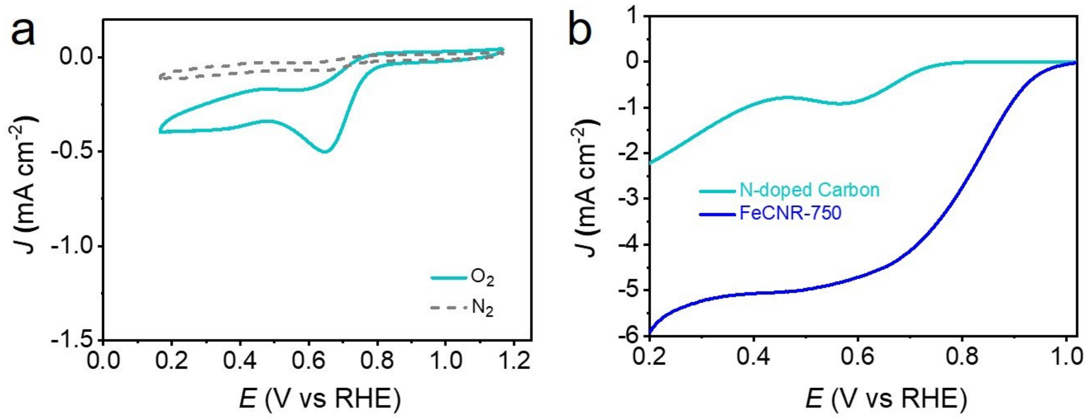

Figure S5. (a) The CV plot and (b) LCV curve of as-prepared N-doeped carbon prepared by following the method of synthesizing FeCNRs without adding Fe(acac)$_3$.

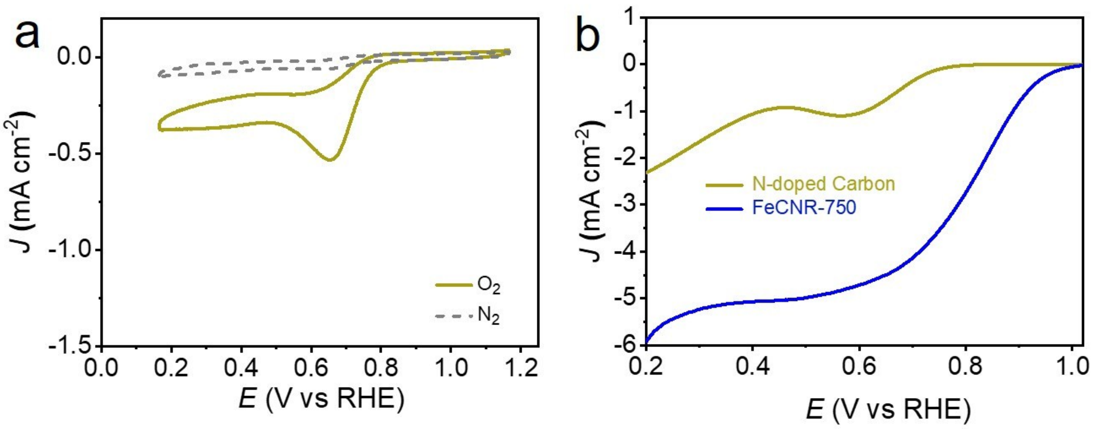

Figure S6. (a) The CV plot and (b) LCV curve of as-prepared N-doeped carbon prepared by removing the Fe_3C nanopartilces.

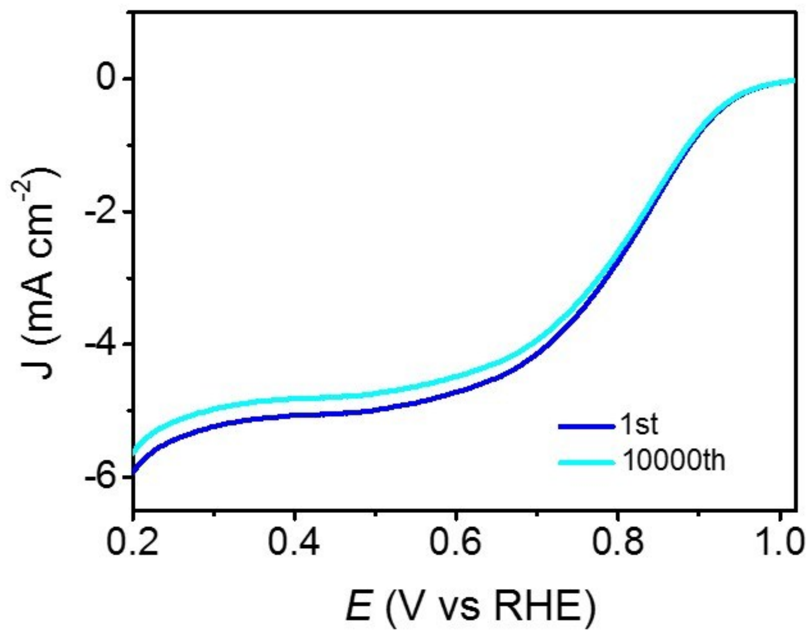

Figure S7. LSV curves of FeCNR-750 in 0.1 M KOH at 1600 rpm before and after 10000 cycles.

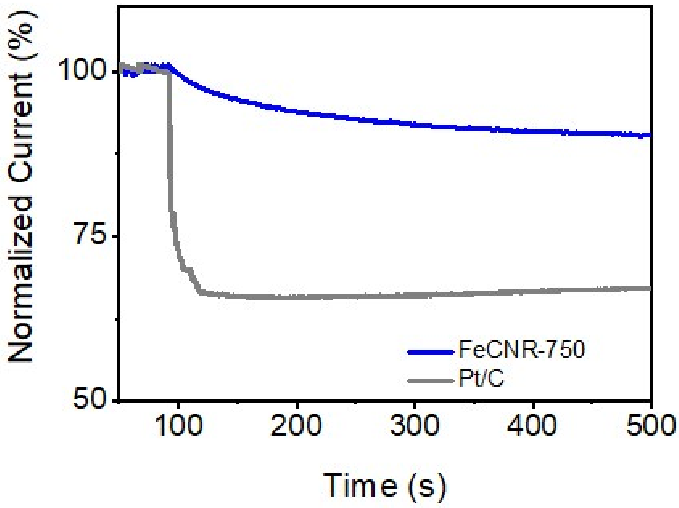

Figure S8. The methanol tolerance of FeCNR-750.

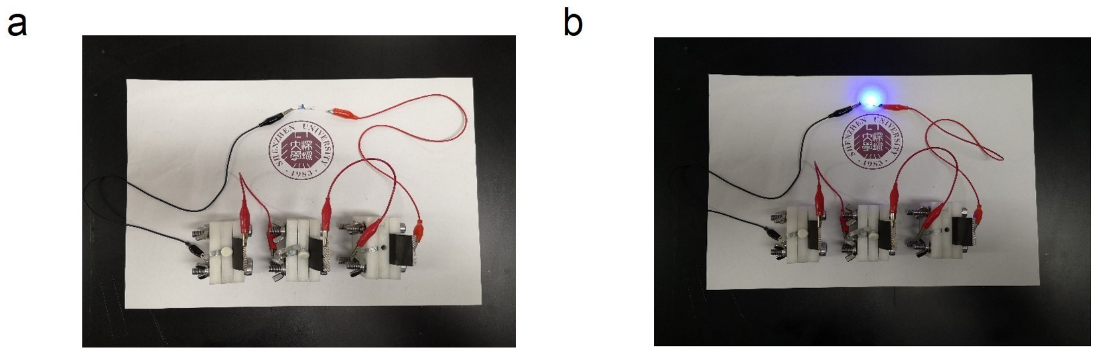

Figure S9. There is a photograph of three Zn-air batteries connected in series with FeCNR-750 as the catalysts before (a) and after (b) connecting.

Table S1. Comparison of properties of Fe derivatives for Zn-air batteries in alkaline electrolytes

Catalysts	Mass Loading mg cm^{-2}	Specific Capacity mAh·g-1 Zn	Maximum Power Density mW·cm^{-2}	Open Circuit Voltage V	Reference
FeCNR-750	1	825.77	126.4	1.42	This work
Fe@C–NG/NCNTs	1	682.6	101.3	1.37	[1]
FeNC-850		790.0	186	1.46	[2]

Fe–N-CNBs-600		880	257	1.53	3
$F_{0.2}N_{0.2}M_{0.2}$-900		637.4	95.3	1.414	4
Fe–Phen–N-800	0.5	708		1.55	5
HP-Fe-N/CNFs		701	135	1.42	6
Fe-N_4 SAs/NPC			232		7
Fe-NC-900-M-AW			271	1.5	8
Fe-N-CNFs		614			9
N–P–Fe–C		625		1.52	10

References

1. Q. Wang, Y. Lei, Z. Chen, N. Wu, Y. Wang, B. Wang and Y. Wang, Fe/Fe_3C@C nanoparticles encapsulated in N-doped graphene–CNTs framework as an efficient bifunctional oxygen electrocatalyst for robust rechargeable Zn–air batteries, *J.Mater. Chem. A,* 2018, **6**, 516-526.
2. J. Yang, J. Hu, M. Weng, R. Tan, L. Tian, J. Yang, J. Amine, J. Zheng, H. Chen and F. Pan, Fe-Cluster Pushing Electrons to N-Doped Graphitic Layers with Fe_3C(Fe) Hybrid Nanostructure to Enhance O_2 Reduction Catalysis of Zn-Air Batteries, *ACS appl. mater. inter.,* 2017, **9**, 4587-4596.
3. L. Cao, Z.-h. Li, Y. Gu, D.-h. Li, K.-m. Su, D.-j. Yang and B.-w. Cheng, Rational design of N-doped carbon nanobox-supported Fe/Fe_2N/Fe_3C nanoparticles as efficient oxygen reduction catalysts for Zn–air batteries, *J. Mater. Chem.y A*, 2017**, 5**, 11340-11347.
4. W. Yang, Y. Zhang, X. Liu, L. Chen and J. Jia, In situ formed Fe–N doped metal organic framework@carbon nanotubes/graphene hybrids for a rechargeable Zn–air battery, *Chem. Commun.,* 2017, **53**, 12934-12937.
5. Z. K. Yang, Z.-W. Zhao, K. Liang, X. Zhou, C.-C. Shen, Y.-N. Liu, X. Wang and A.-W. Xu, Synthesis of nanoporous structured iron carbide/Fe–N–carbon composites for efficient oxygen reduction reaction in Zn–air batteries, *J. Mater. Chem. A,* 2016, **4**, 19037-19044.
6. Y. Zhao, Q. Lai, Y. Wang, J. Zhu and Y. Liang, Interconnected Hierarchically Porous Fe, N-Codoped Carbon Nanofibers as Efficient Oxygen Reduction Catalysts for Zn–Air Batteries, *ACS appl. mater. inter.,* 2017, **9**, 16178-16186.
7. Y. Pan, S. Liu, K. Sun, X. Chen, B. Wang, K. Wu, X. Cao, W. C. Cheong, R. Shen and A. Han, A Bimetallic Zn/Fe Polyphthalocyanine-Derived Single-Atom Fe-N_4 Catalytic Site:A Superior Trifunctional Catalyst for Overall Water Splitting and Zn–Air Batteries, *Angew. Chem. Int. Ed.,* 2018, **57**, 8614-8618.
8. Z. Liu, J. Liu, H. B. Wu, G. Shen, Z. Le, G. Chen and Y. Lu, Iron-decorated nitrogen-rich carbons as efficient oxygen reduction electrocatalysts for Zn–air

batteries, *Nanoscale*, 2018, **10**, 16996-17001.

9. Z. Y. Wu, X. X. Xu, B. C. Hu, H. W. Liang, Y. Lin, L. F. Chen and S. H. Yu, Iron Carbide Nanoparticles Encapsulated in Mesoporous Fe-N-Doped Carbon Nanofibers for Efficient Electrocatalysis, *Angew.Chem. Int. Ed.,* 2015, **54**, 8179-8183.

10. W. Wan, Q. Wang, L. Zhang, H.-W. Liang, P. Chen and S.-H. Yu, N-, P- and Fe-tridoped nanoporous carbon derived from plant biomass: an excellent oxygen reduction electrocatalyst for zinc–air batteries, *J. Mater.Chem. A,* 2016, **4**, 8602-8609.