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Supporting Information

Superior Oxygen Reduction Electrocatalysis Enabled by Integrating Hierarchical Pores, Fe_3C Nanoparticles and Bamboo-like Carbon Nanotubes

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Figures

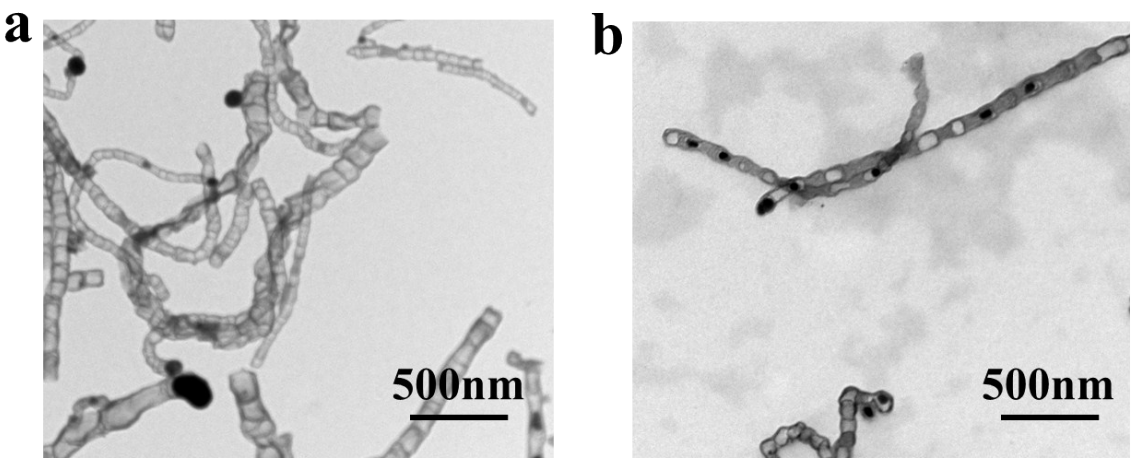

Figure S1. TEM images of the resultant (a) PMF and (b) pPMF-800.

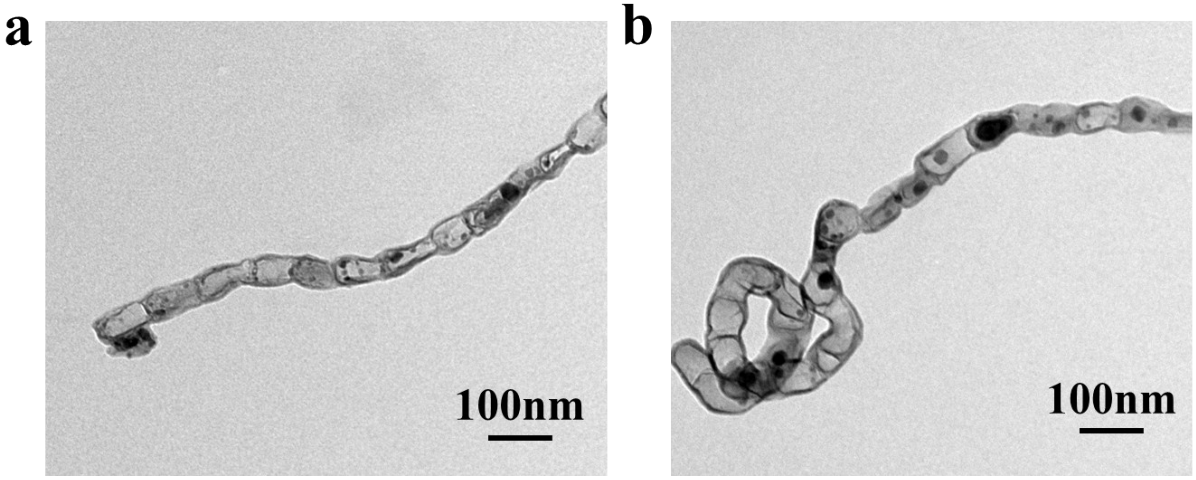

Figure S2. TEM images of the resultant (a) pPMF-600 and (b) pPMF-700.

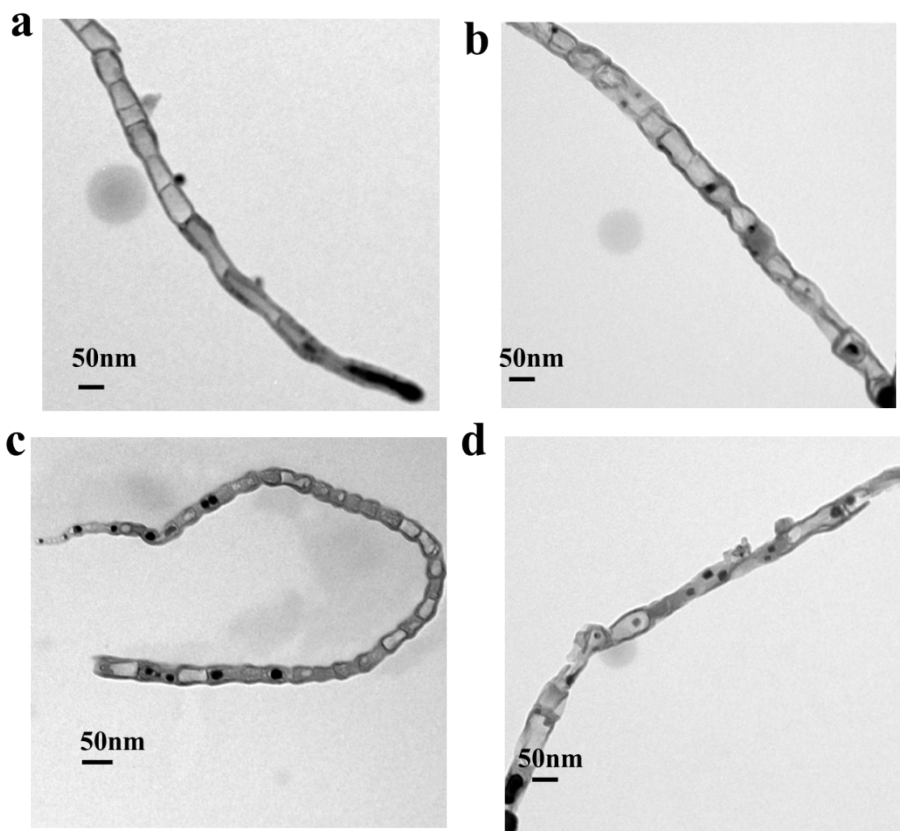

Figure S3. TEM images of the resultant (a) PMF-800-0.2, (b) PMF-800-0.5, (c) PMF-800-1, and (d) PMF-800-3.

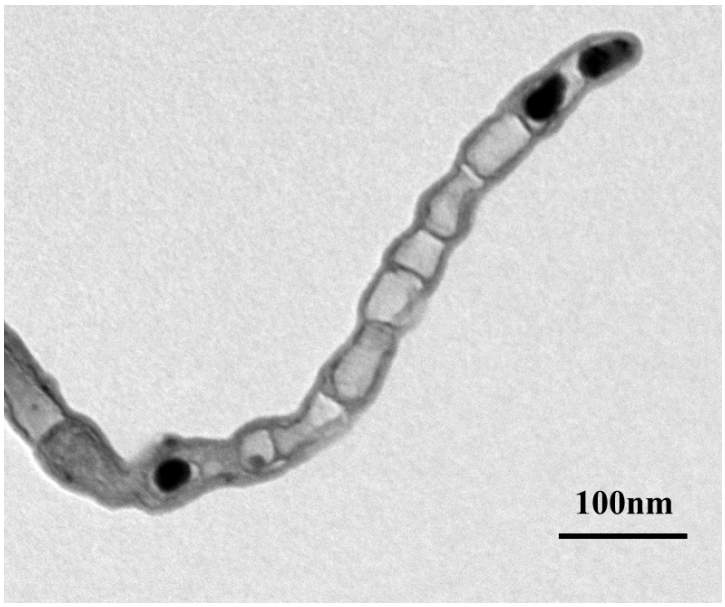

Figure S4. TEM image of the resultant PMF-800-Cl.

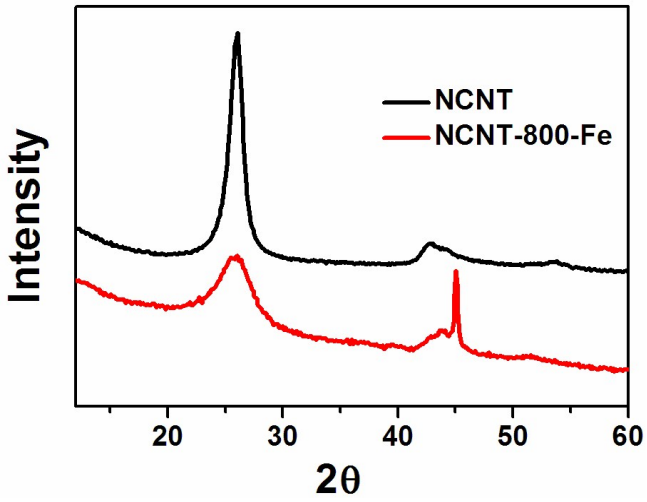

Figure S5. XRD survey of the resultant NCNT and NCNT-800-Fe.

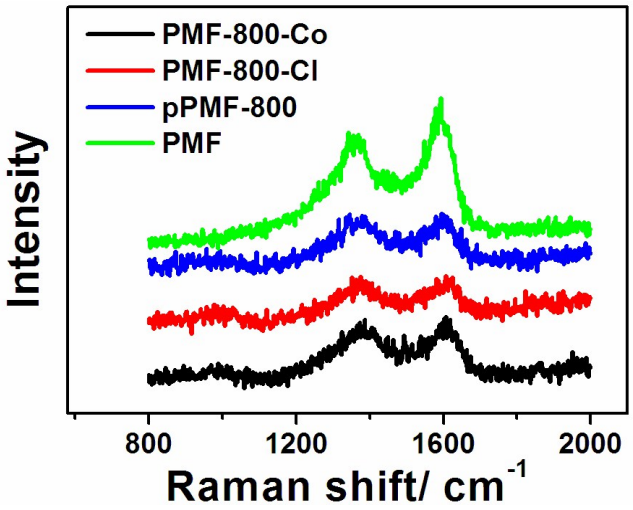

Figure S6. Raman spectra of the resultant PMF-800-Co, PMF-800-Cl, pPMF-800, and PMF.

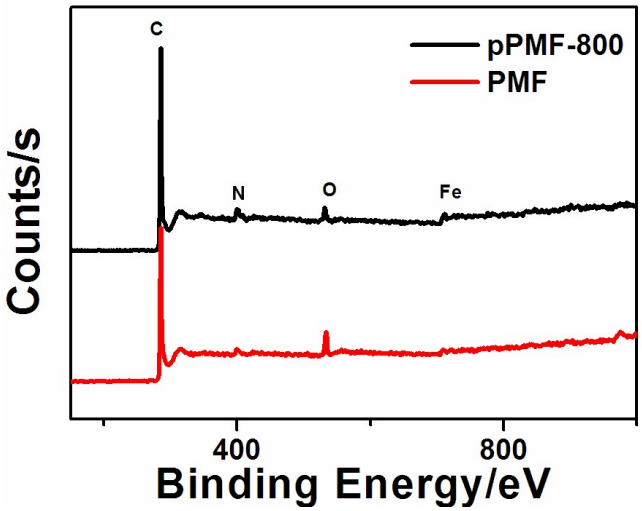

Figure S7. XPS spectra of the resultant pPMF-800 and PMF.

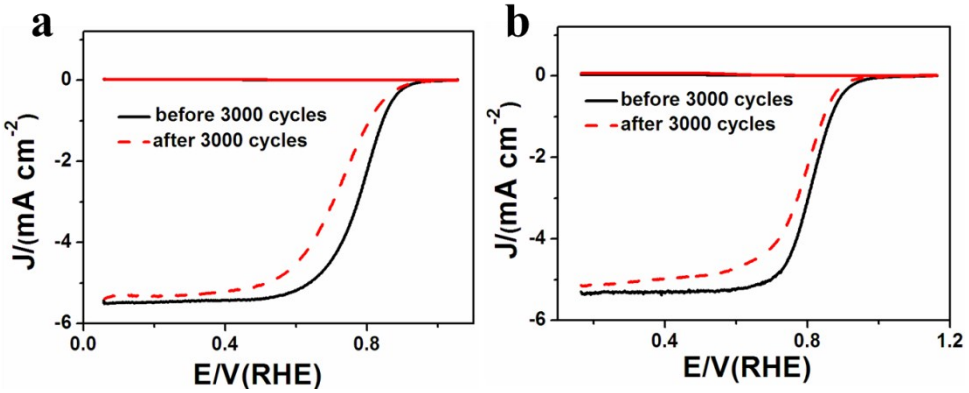

Figure S8. Representative ORR polarization curves for Pt/C catalyst in O_2-saturated (a) 0.1 M $HClO_4$ and (b) 0.10 M KOH aqueous solutions before and after 3000 cycles with a scan rate of 5 mV/s and a rotation rate of 1600 rpm.

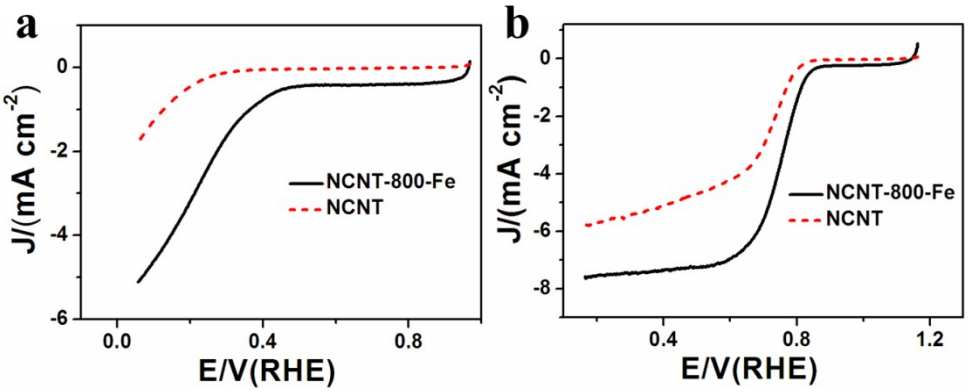

Figure S9. Representative ORR polarization curves for NCNT-800-Fe and NCNT in O_2-saturated (a) 0.1 M $HClO_4$ and (b) 0.10 M KOH aqueous solutions with a scan rate of 5 mV/s and a rotation rate of 1600 rpm.

Table S1 The I_D/I_G values of the PMF, pPMF-800, PMF-800-Cl, and PMF-Co-800 determined by Raman spectroscopy.

Materials	PMF	pPMF-800	PMF-800-Cl	PMF-Co-800
I_D/I_G	0.81	1.01	1.00	1.005

Table S2 Comparison of ORR performance in basic and acidic media for pPMF-800 with other non-precious metal carbon electrocatalysts.

Catalyst	**E^b_{onset}/ V**	**$E^b_{1/2}$/ V**	**E^a_{onset}/ V**	**$E^a_{1/2}$/ V**	**Reference electrode**	**References**
S-graphene	-0.15	-0.37	-	-	*vs* SCE	1
BP-NFe	0.045	-0.089	0.6	-	*vs* SCE	2
Fe-N-CNFs	-0.02	-0.140	0.55	0.365	*vs* Ag/AgCl	3
NOSCs	0.96	0.74	-	-	*vs* RHE	4
S_2N_2-GN1000	-0.052	-	-	-	*vs* Ag/AgCl	5
N,S-RGO/GQDs	-0.10	-	-	-	*vs* Ag/AgCl	6
CNT/HDC-1000	0.92	0.82	-	-	*vs* RHE	7
C-PANI/NSA	0.84	0.67	-	-	*vs* RHE	8
Fe−P-900	0.95	-	0.84	-	*vs* RHE	9
Fe_3C/C-700	1.05	0.83	0.90	0.73	*vs* RHE	10
Fe−N-CNS	0.98	0.85	-	-	*vs* RHE	11
Fe/C/N	0.94	0.83	-	-	*vs* RHE	12
Fe-N/C-800	0.98	-	0.77	-	*vs* RHE	13
BCNFNHs		0.861		0.575	*vs* RHE	14
pPMF-800	1.05	0.879	0.89	0.71	*vs* RHE	this work

Notes:

E^b: potential in basic solution; **E^a**: potential in acidic solution; **BP**: cheap chemicals BP2000; **S_2N_2-GN**: N and S dual doped graphene; **RGO:** reduced graphene oxide; **GQDs**: graphene quantum dots; **HDC**: heteroatom-doped carbon; **PANI**: polyaniline; **NSA**: b-naphthalene sulfonic acid; **OMMC**: ordered macro/mesoporous carbon; **Fe-N-CNFs**: Fe-N-doped carbon nanofibers; **BCNFNHs**: bamboo-like carbon nanotube (b-CNT)/Fe_3C nanoparticle (NP) hybrids; **CNS**: carbon nanoshells.

References

1. Ma, Z.; Dou, S.; Shen, A.; Tao, L.; Dai, L.; Wang, S. Sulfur-doped graphene derived from cycled lithium-sulfur batteries as a metal-free electrocatalyst for the oxygen reduction reaction. *Angew. Chem. Int. Edit.* **2015**, *54*, 1888–1892.
2. Liu, J.; Sun, X.; Song, P.; Zhang, Y.; Xing, W.; Xu, W. High-performance oxygen reduction electrocatalysts based on cheap carbon black, nitrogen, and trace iron. *Adv. Mater.* **2013**, *25*, 6879–6883.
3. Wu, Z. Y.; Xu, X. X.; Hu, B. C.; Liang, H. W.; Lin, Y.; Chen, L. F.; Yu, S. H. Iron carbide nanoparticles encapsulated in mesoporous Fe-N-doped carbon nanofibers for efficient electrocatalysis. *Angew. Chem. Int. Edit.* **2015**, 54, 8179–8183.

4. Meng, Y.; Voiry, D.; Goswami, A.; Zou, X.; Huang, X.; Chhowalla, M.; Liu, Z.; Asefa, T. N-, O-, and S-tridoped nanoporous carbons as selective catalysts for oxygen reduction and alcohol oxidation reactions. *J. Am. Chem. Soc.* **2014**, *136*, 13554–13557.
5. You, J.-M.; Ahmed, M. S.; Han, H. S.; Choe, J. E.; Ustundag, Z.; Jeon, S. New approach of nitrogen and sulfur-doped graphene synthesis using dipyrrolemethane and their electrocatalytic activity for oxygen reduction in alkaline media. *J. Power Sources* **2015**, *275*, 73–79.
6. Luo, Z.; Yang, D.; Qi, G.; Shang, J.; Yang, H.; Wang, Y.; Yuwen, L.; Yu, T.; Huang, W.; Wang, L. Microwave-assisted solvothermal preparation of nitrogen and sulfur co-doped reduced graphene oxide and graphene quantum dots hybrids for highly efficient oxygen reduction. *J. Mater. Chem. A* **2014**, *2*, 20605–20611.
7. Sa, Y. J.; Park, C.; Jeong, H. Y.; Park, S.-H.; Lee, Z.; Kim, K. T.; Park, G.-G.; Joo, S. H. Carbon nanotubes/heteroatom-doped carbon core-sheath nanostructures as highly active, metal-free oxygen reduction electrocatalysts for alkaline fuel cells. *Angew. Chem. Int. Edit.* **2014**, *53*, 4102–4106.
8. Zheng, R.; Mo, Z.; Liao, S.; Song, H.; Fu, Z.; Huang, P. Heteroatom-doped carbon nanorods with improved electrocatalytic activity toward oxygen reduction in an acidic medium. *Carbon* **2014**, *69*, 132–141.
9. Singh, K. P.; Bae, E. J.; Yu, J. S. Fe-P: a new class of electroactive catalyst for oxygen reduction reaction. *J. Am. Chem. Soc.* **2015**, *137*, 3165–3168.
10. Hu, Y.; Jensen, J. O.; Zhang, W.; Cleemann, L. N.; Xing, W.; Bjerrum, N. J.; Li, Q. Hollow spheres of iron carbide nanoparticles encased in graphitic layers as oxygen reduction catalysts. *Angew. Chem. Int. Edit.* **2014**, *53*, 3675–3679.
11. Wang, Y.; Kong, A.; Chen, X.; Lin, Q.; Feng, P. Efficient oxygen electroreduction: hierarchical porous Fe–N-doped hollow carbon nanoshells. *ACS Catal.* **2015**, *5*, 3887–3893.
12. Zhao, Y.; Kamiya, K.; Hashimoto, K.; Nakanishi, S. Efficient bifunctional Fe/C/N electrocatalysts for oxygen reduction and evolution reaction. *J. Phys. Chem. C* **2015**, *119*, 2583–2588.
13. Niu, W.; Li, L.; Liu, X.; Wang, N.; Liu, J.; Zhou, W.; Tang, Z.; Chen, S. Mesoporous N-doped carbons prepared with thermally removable nanoparticle templates: an efficient electrocatalyst for oxygen reduction reaction. *J. Am. Chem. Soc.* **2015**, *137*, 5555–5562.
14. Yang, W.; Liu, X.; Yue, X.; Jia, J.; Guo, S. Bamboo-like carbon nanotube/Fe_3C nanoparticle hybrids and their highly efficient catalysis for oxygen reduction. *J. Am. Chem. Soc.* **2015**, *137*, 1436–1439.