

Electronic Supplementary Information(ESI)

Sn(OH)_x-assisted synthesis of mesoporous Mn-porphyrinic frameworks and their carbon derivatives for electrocatalysis

Xiaoying Zhang, Luyao Liu, Yu Qiao, Jiaxin Liu, Aiguo Kong, and Yongkui Shan**

*School of Chemistry and Molecular Engineering, East China Normal University,
Shanghai, 200241, China*

E-mail: agkong@chem.ecnu.edu.cn

CONTENTS

Figure S1. Calibration to reversible hydrogen electrode(RHE) for ORR in 0.1 M KOH (A) and 0.1 M HClO₄(B)

Figure S2. TEM images of Mn-COFs (A and B) and Mn-COFs*(C).

Figure S3. (A) N₂-sorption isotherm curves of Mn-COFs and Mn-COFs*. (B) Raman spectra of S-N-C-800 and Mn-S-N-C-800. (C) N₂-sorption isotherm curves of Mn-S-N-C-800 and Mn-S-N-C-800*. (D) XPS survey spectrum of Mn-S-N-C-800.

Figure S4. (A) LSV curves of Mn-S-N-C-800 with Pt wire and graphite rod as counter electrode in 0.1 M O₂-saturated KOH, respectively. (B) CV curves before and after 5,000 cycles with graphite rod as counter electrode. (C) LSV curves of Mn-S-N-C-800 with different loading. (D) LSV curves of Mn-S-N-C-800 and commercial Pt/C with different loading.

Figure S5 LSV curves of Mn-S-N-C-800 and Mn-S-N-C-800 after poisoning with 0.1 M and 0.2 M NaF in 0.1 M HClO₄.

Figure S6. TEM images of Mn-S-N-C-700 (A) and Mn-S-N-C-900 (B).

Figure S7. The deconvoluted N 1s (A), Mn 2p (B), C1s (C) and S2p (D) XPS spectra of Mn-S-N-C-700, -800 and -900.

Table S1. The ORR performance of Mn-S-N-C-800 in 0.1 M KOH solution, in contrast to the previously reported Mn-based ORR catalysts.

Table S2. The surface species analyses of Mn-S-N-C-700,-800 and -900 by XPS (at.%).

FigureS1. Calibration to reversible hydrogen electrode (RHE) for ORR in 0.1 M KOH (A) and 0.1M KClO₄ (B).

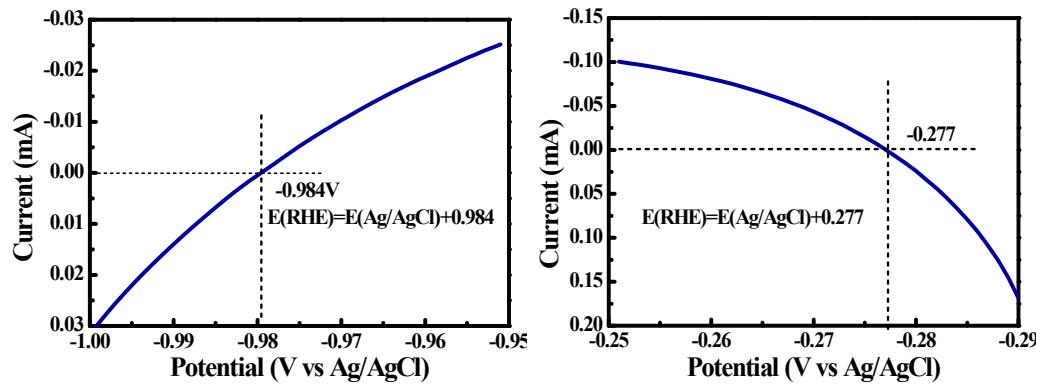


Figure S2. TEM images of Mn-COFs (A and B) and Mn-COFs*(C).

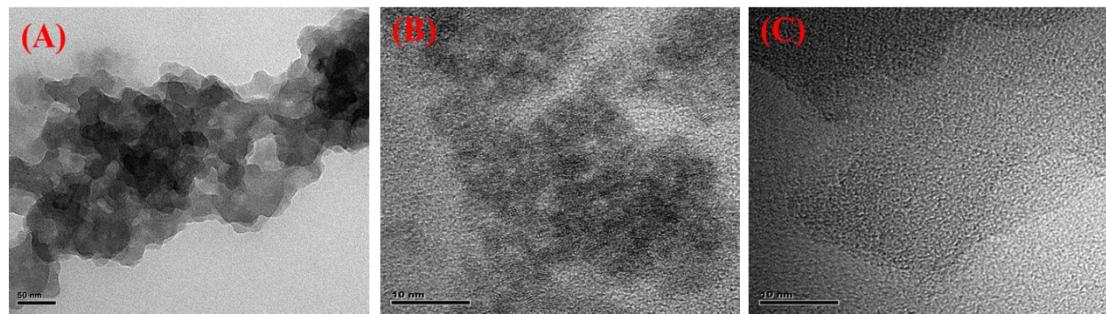


Figure S3. (A) N₂-sorption isotherm curves of Mn-COFs and Mn-COFs*. (B) Raman spectra of S-N-C-800 and Mn-S-N-C-800. (C) N₂-sorption isotherm curves of Mn-S-N-C-800 and Mn-S-N-C-800*. (D) XPS survey spectrum of Mn-S-N-C-800.

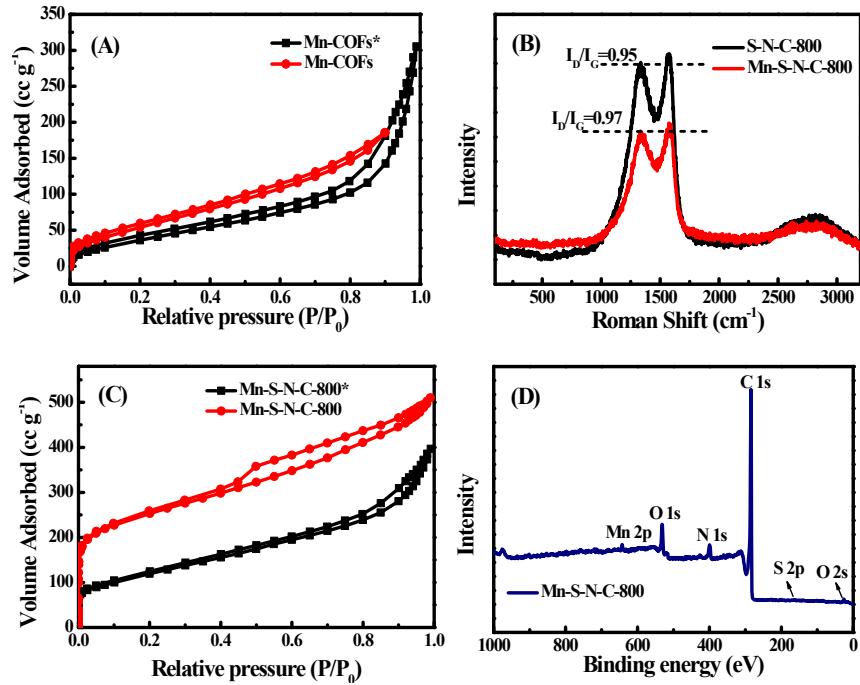


Figure S4. (A) LSV curves of Mn-S-N-C-800 with Pt wire and graphite rod as counter electrode in 0.1 M O₂-saturated KOH, respectively. (B) CV curves before and after 5,000 cycles with graphite rod as counter electrode. (C) LSV curves of Mn-S-N-C-800 with different loading. (D) LSV curves of Mn-S-N-C-800 and commercial Pt/C with different loading.

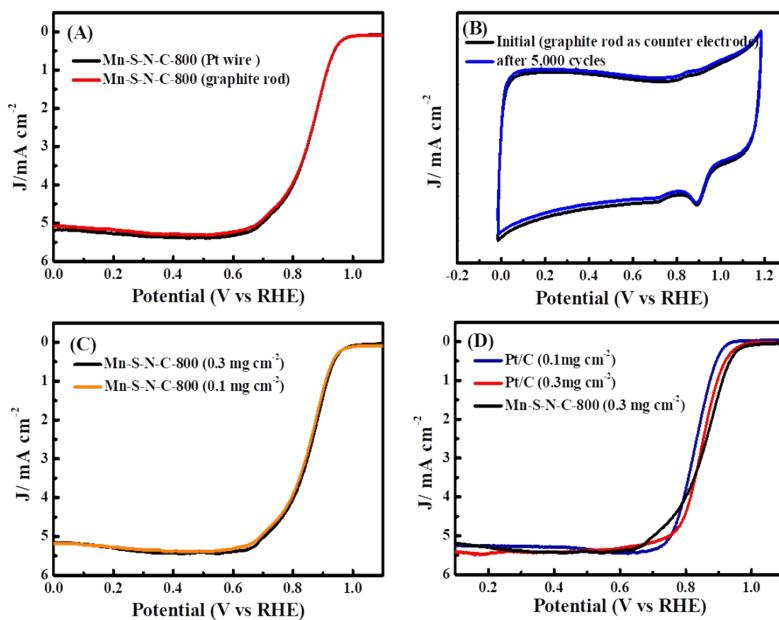


Figure S5. LSV curves of Mn-S-N-C-800 and Mn-S-N-C-800 after poisoning with 0.1 M and 0.2M NaF in 0.1 M HClO₄.

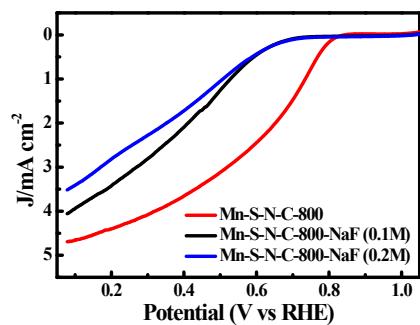


Figure S6. TEM images of Mn-S-N-C-700 (A) and Mn-S-N-C-900 (B).

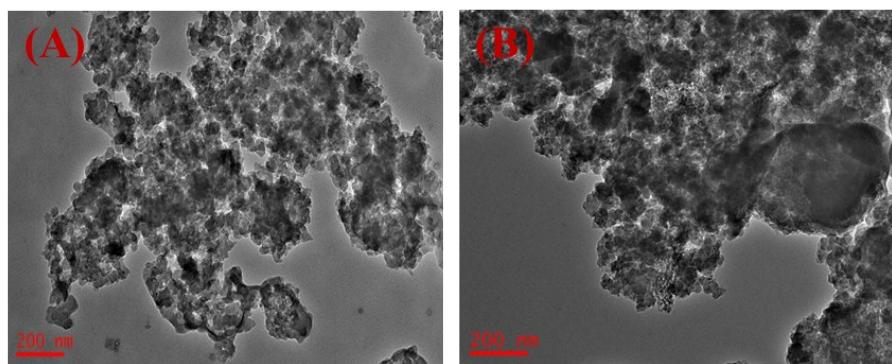


Figure S7. The deconvoluted N 1s (A), Mn 2p (B), C1s (C) and S2p (D) XPS spectra of Mn-S-N-C-700, -800 and -900.

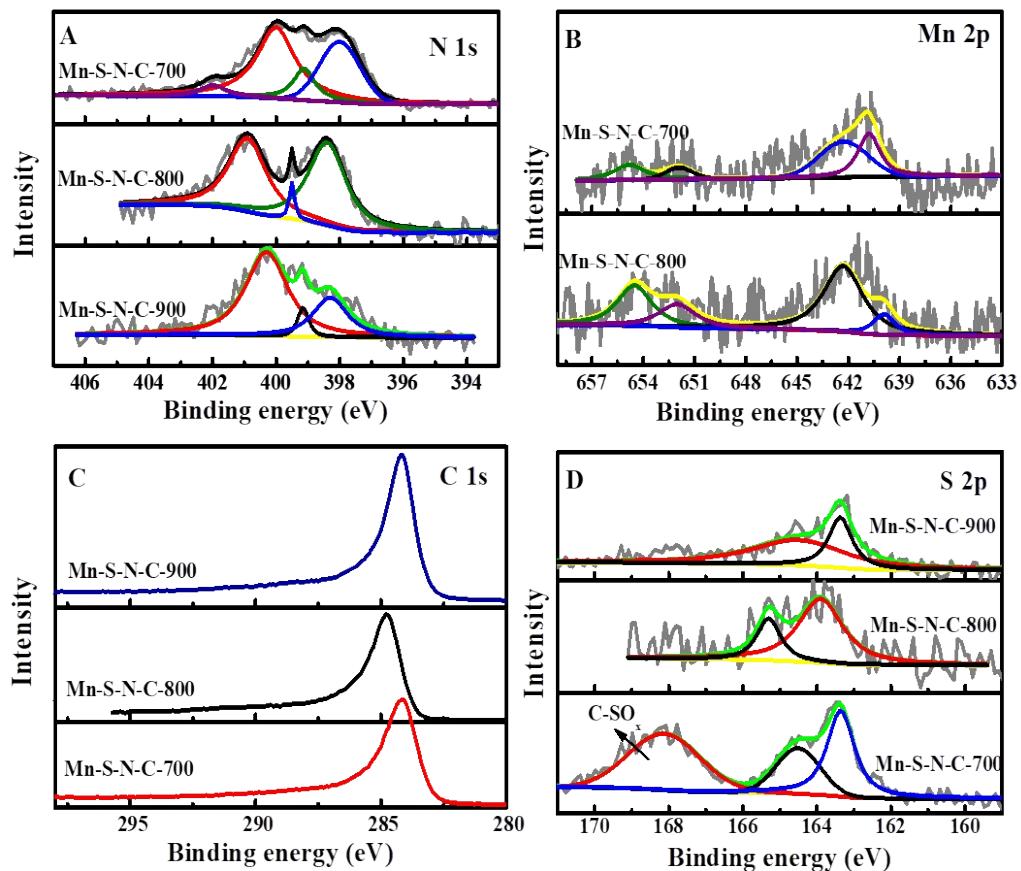


Table S1. The ORR performance of Mn-S-N-C-800 in 0.1 M KOH solution, in contrast to the previously reported Mn-based ORR catalysts.

Catalysts	loading	E _{onset} (V vs. RHE)	E _{1/2} (V vs.RHE)	Ref.
Mn-S-N-C-800	0.3 mg cm⁻²	0.98	0.86	This work
MnNPC-900	0.4 mg cm ⁻²	0.97	0.84	S1
Mn ₃ O ₄ QDs/N-p-MCNT	0.3 mg cm ⁻²	0.85	0.75	S2
Mn-N-C	0.8 mg cm ⁻²	0.92	0.78	S3
Mn/C-NO	0.3 mg cm ⁻²	1.0	0.86	S4
Mn _x O _y -NC	0.3 mg cm ⁻²	Not given	0.81	S5
D-AC@2Mn-4Co	0.3 mg cm ⁻²	0.88	0.80	S6
Mn ₃ O ₄ -CoO	0.3 mg cm ⁻²	0.86	0.75	S7
MnFe ₂ O ₄	0.6 mg cm ⁻²	Not given	0.81	S8

Table S2. The surface species analyses of Mn-S-N-C-700,-800 and -900 by XPS (at. %).

Samples	S	N	O	Mn	C
Mn-S-N-C-700	0.82	5.96	10.81	0.54	81.87
Mn-S-N-C-800	0.14	5.20	7.34	1.19	86.13
Mn-S-N-C-900	0.10	2.24	7.03	0.20	90.43

Reference

- S1. X. Zhu, R. Amal and X. Lu, *Small*, 2019, DOI: 10.1002/smll.201804524, e1804524.
- S2. Z. Huang, X. Qin, X. Gu, G. Li, Y. Mu, N. Wang, K. Ithisuphalap, H. Wang, Z. Guo, Z. Shi, G. Wu and M. Shao, *ACS Appl Mater Interfaces*, 2018, 10, 23900-23909.
- S3. K. Liu, Z. Qiao, S. Hwang, Z. Liu, H. Zhang, D. Su, H. Xu, G. Wu and G. Wang, *Appl. Catal. B*, 2019, 243, 195-203.
- S4. Y. Yang, K. Mao, S. Gao, H. Huang, G. Xia, Z. Lin, P. Jiang, C. Wang, H. Wang and Q. Chen, *Adv Mater*, 2018, 30, e1801732.
- S5. J. Masa, W. Xia, I. Sinev, A. Zhao, Z. Sun, S. Grutzke, P. Weide, M. Muhler and W. Schuhmann, *Angew Chem Int Ed Engl*, 2014, 53, 8508-8512.
- S6. X. Yan, Y. Jia, J. Chen, Z. Zhu and X. Yao, *Adv Mater*, 2016, 28, 8771-8778.
- S7. J. Xiao, L. Wan, X. Wang, Q. Kuang, S. Dong, F. Xiao and S. Wang, *Journal of Materials Chemistry A*, 2014, 2, 3794-3800.
- S8. H. Zhu, S. Zhang, Y. X. Huang, L. Wu and S. Sun, *Nano Lett*, 2013, 13, 2947-2951.