Supplementary Material

Bimetal-MOF nanosheets as efficient bifunctional electrocatalysts for oxygen evolution and nitrogen reduction reaction

Weixin Li[a,b‡], Wei Fang[b‡], Chen Wu [b,c], Khang Ngoc Dinh [b], Hao Ren[b], Lei Zhao[a], Chuntai Liu[d], Qingyu Yan*[b]

[a]The State Key Laboratory of Refractories and Metallurgy, School of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China

[b]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

[c]State Key Laboratory of Power Metallurgy, Central South University, Changsha 410083, China

[d]The Key Laboratory of Material Processing and Mold of Ministry of Education, Zhengzhou University, Zhengzhou, Henan 450001, China

Figures:

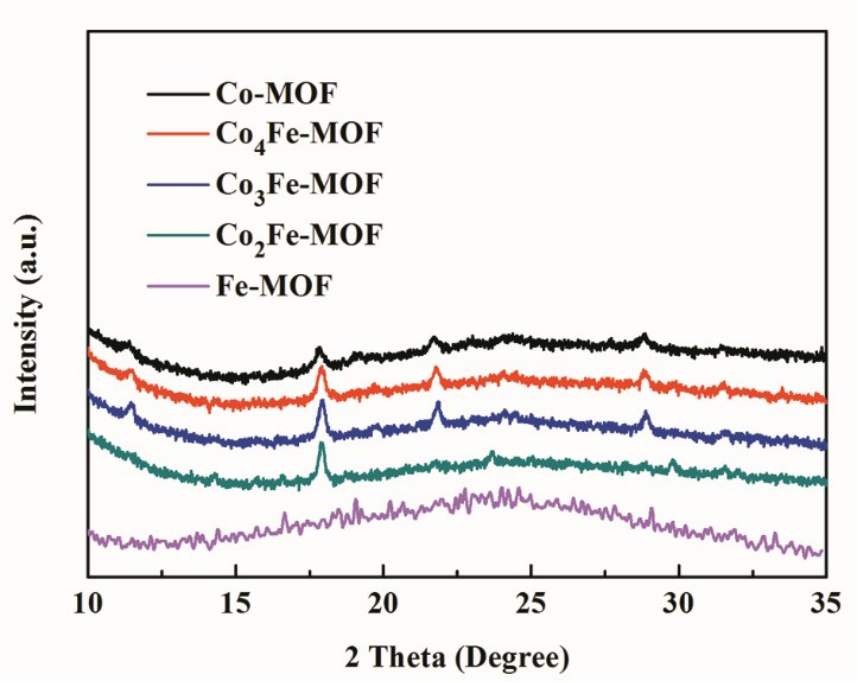

Fig. S1. XRD patterns of Co-MOF, Co_4Fe-MOF, Co_3Fe-MOF, Co_2Fe-MOF and Fe-MOF.

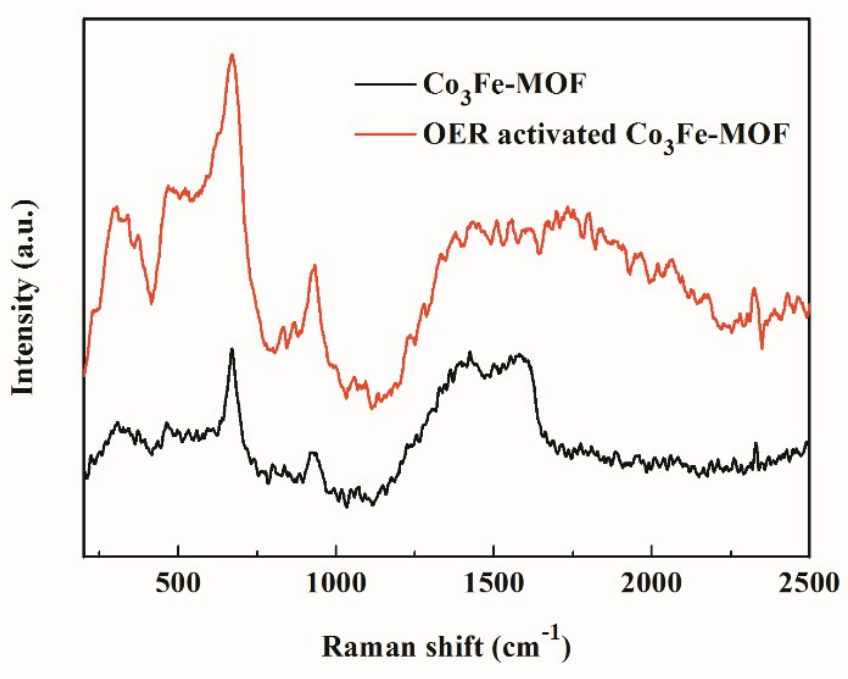

Fig. S2. Raman spectra of Co_3Fe-MOF and OER-activated Co_3Fe-MOF.

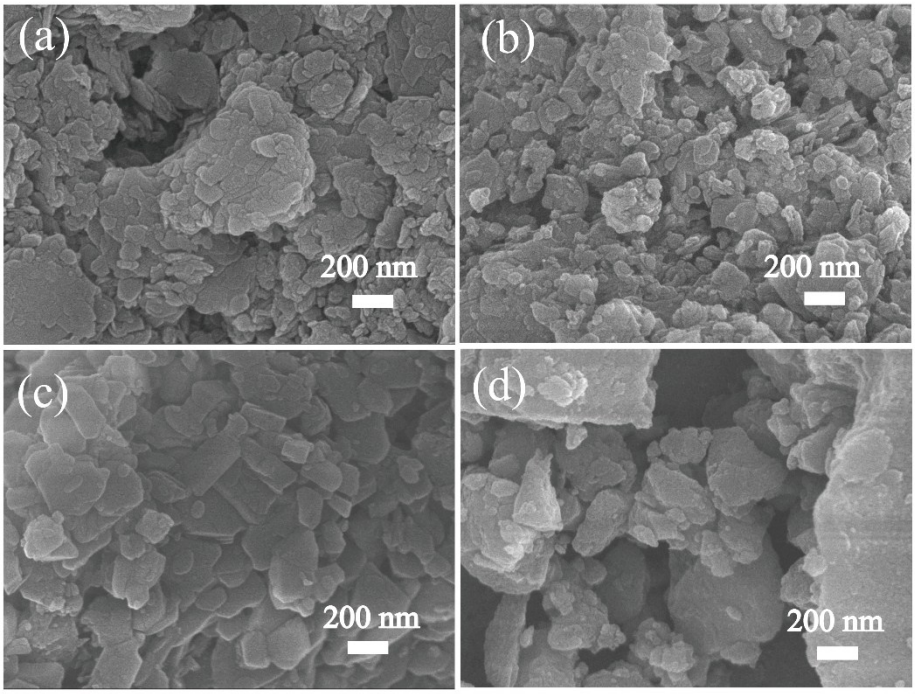

Fig. S3. SEM images of (a) Co-MOF, (b) Co_4Fe-MOF, (c) Co_2Fe-MOF and (d) Fe-MOF.

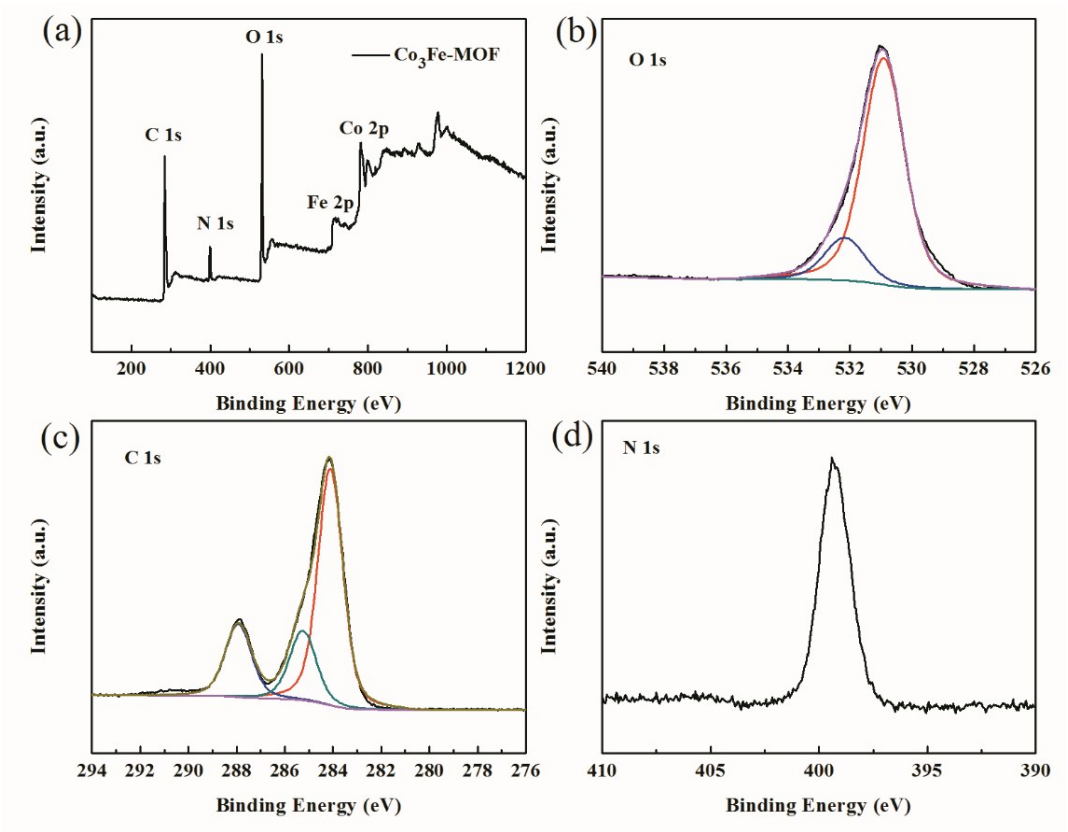

Fig. S4. (a) XPS survey spectra, (b) O 1s, (c) C 1s and (d) N 1s of Co_3Fe-MOF.

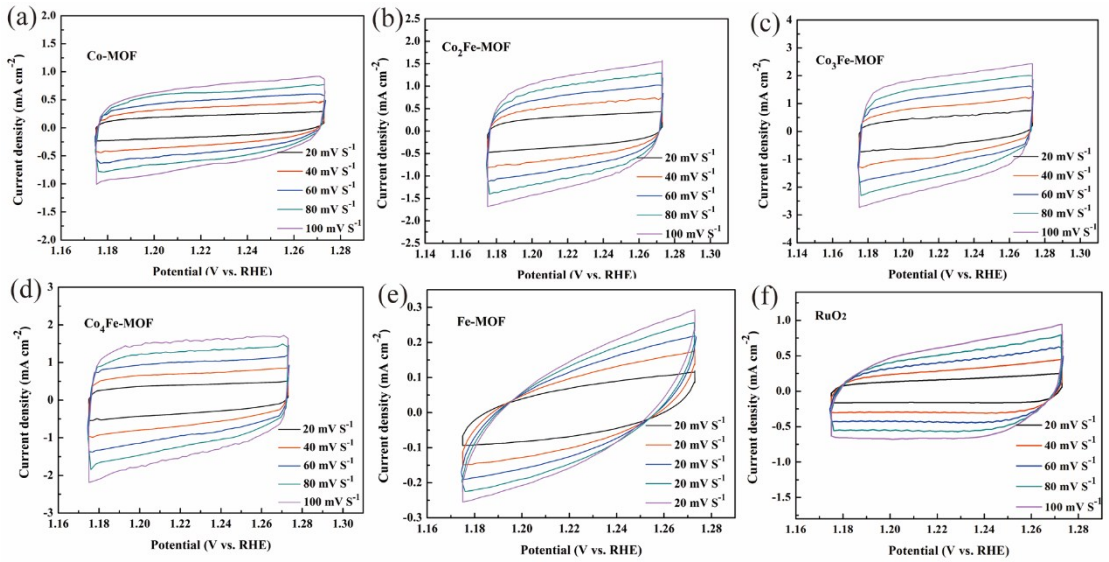

Fig. S5. CV plot of (a) Co-MOF, (b) Co_2Fe-MOF, (c) Co_3Fe-MOF, (d) Co_4Fe-MOF, (e) Fe-MOF and (f) RuO_2 at different scan rates.

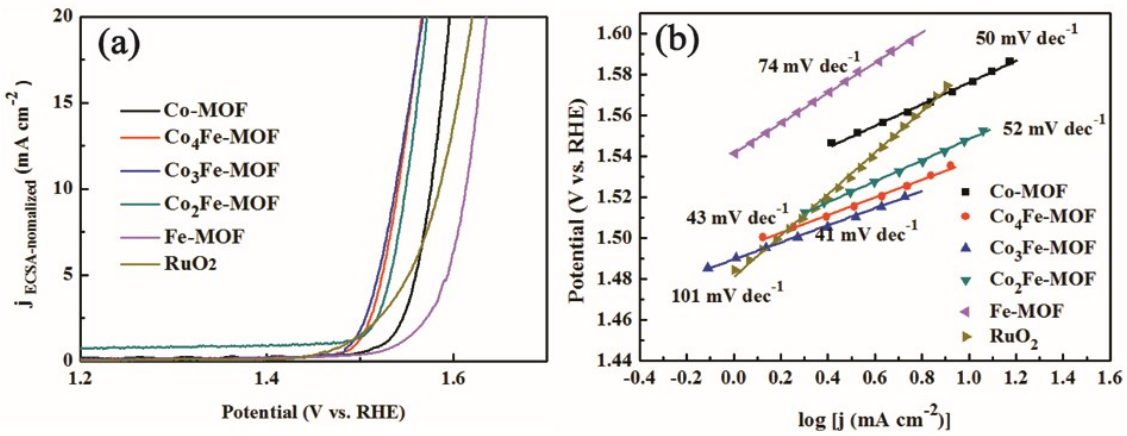

Fig. S6. (a) LSV curves of of different working electrodes normalized by ECSA ($j_{ECSA\text{-}normalized}$) and (b) Tafel plots which also normalized by ECSA ($j_{ECSA\text{-}normalized}$) of different working electrodes.

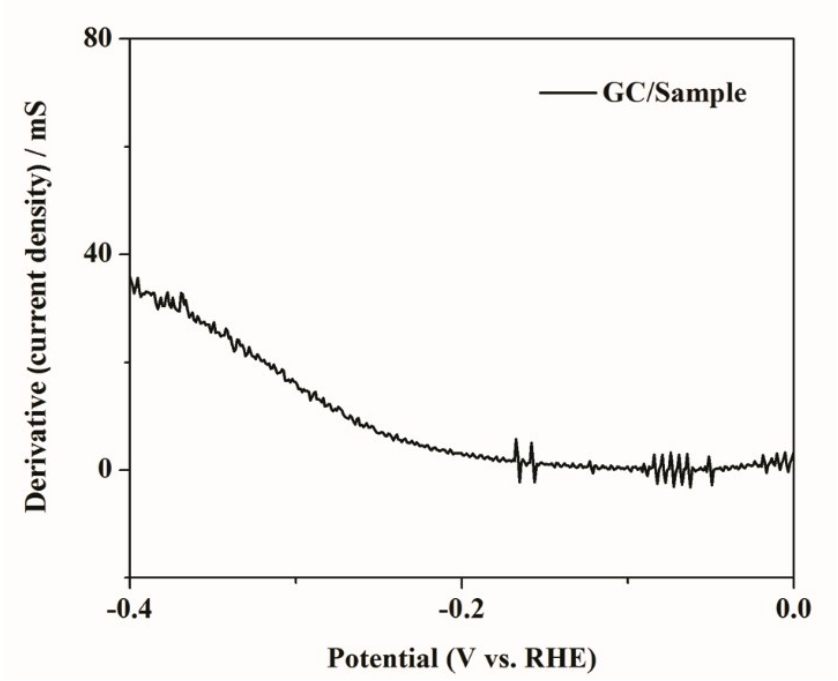

Fig. S7. Derivation of LSV of GC/sample (Co_3Fe-MOF).

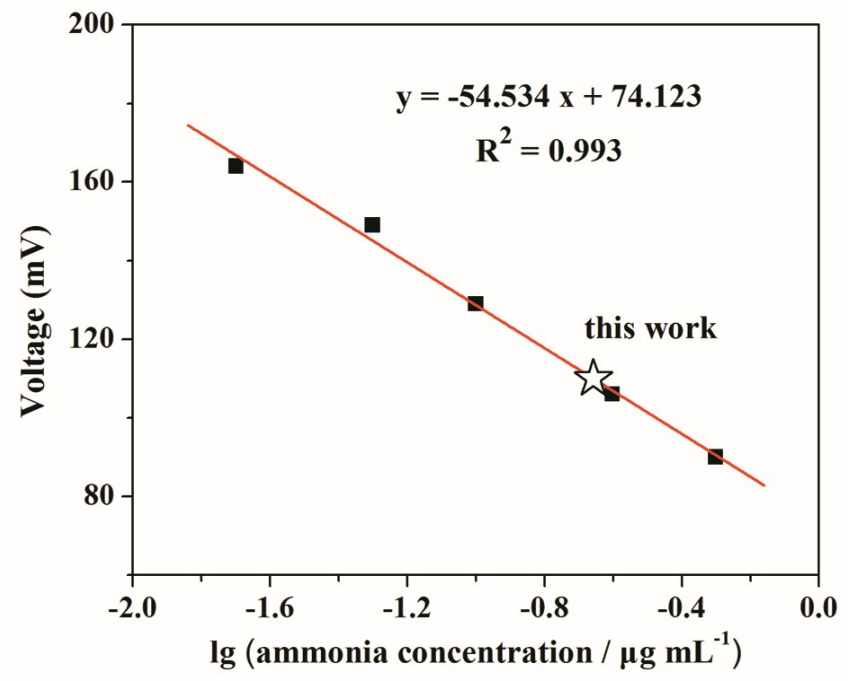

Fig. S8. Calibration of Calibration of standard NH_4^+ solution detected by the ammonia ion selective electrode.

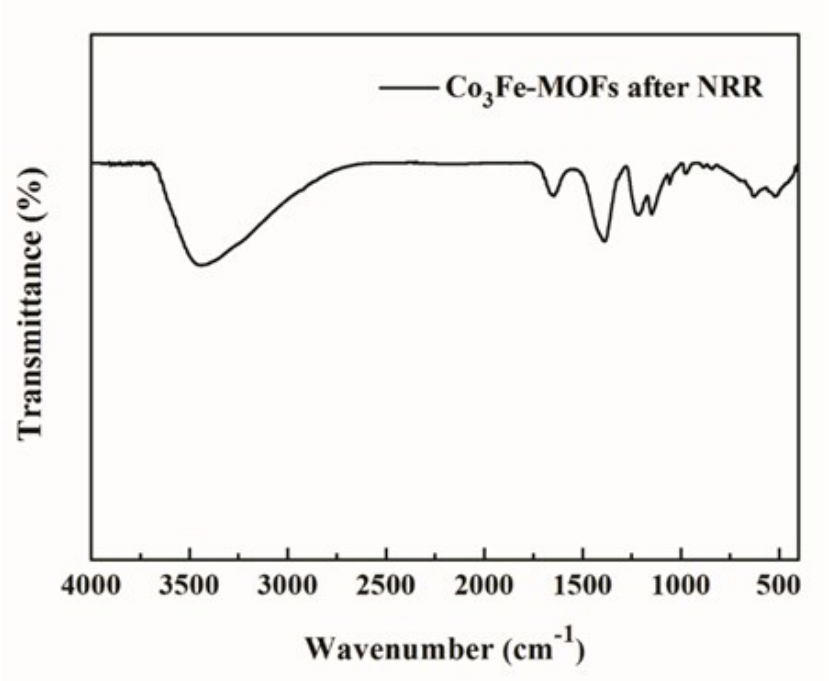

Fig. S9. FT-IR spectrum of Co_3Fe-MOF after NRR process.

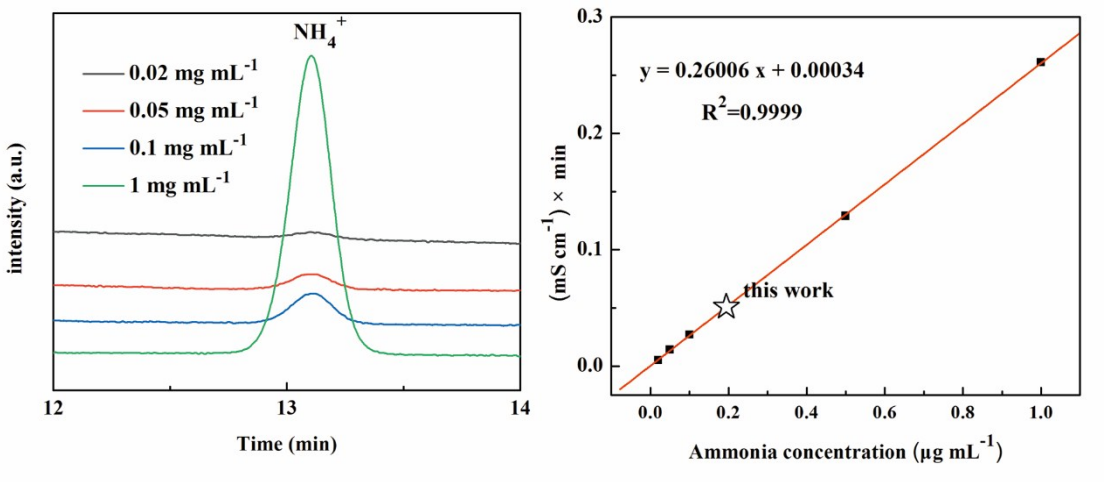

Fig. S10. The concentrations of produced ammonia solution quantified by ion chromatography (IC) method.

Tables:

Table S1. Atomic ratio of Co_4Fe-MOF, Co_3Fe-MOF and Co_2Fe-MOF obtained from SEM-EDS.

Element atomic%	Co	Fe	C	O	N
Co_4Fe-MOFs	9.00	2.26	43.09	32.80	12.86
Co_3Fe-MOFs	5.60	1.87	48.72	37.93	5.89
Co_2Fe-MOFs	4.06	1.95	47.86	39.78	6.36

Table S2. Comparison of OER activity of Co_3Fe-MOF and recently reported active catalysts in 1 M KOH solutions.

Sample	Overpotential (at 10 mA cm^{-2})	Substrate	iR correction	Reference
Co_3Fe-MOF	280	GC	no	This work
Fe–Co–P nanoboxes	269	carbon fiber paper	yes	1
NiSO-BDC	298	GC	yes	2
NiO/CN‐5:1	281	GC	yes	3
NiFe MOF/OM‐NFH	270	GC	no	4
CoNi1@C	335	GC	yes	5
hcp-NiFe@NC	226	carbon cloth	yes	6

Table S3. Comparison of NRR performances of several electrocatalytsts in 0.1 M KOH electrolyte at ambient conditions.

Catalyst	Potential (V vs. RHE)	Faradaic efficiency (%)	Yield rate	Ref.
Tetrahexahedral Au nanorods	-0.2	4.02	1.648 mg h^{-1} cm^{-2}	7
ZIF-derived carbon	-0.3	10.20	57.8 mg h^{-1} cm^{-2}	8
Amorphous $Pd_{0.2}Cu_{0.8}$ nanoclusters on rGO	-0.2	4.52	1.66 mg h^{-1} mg^{-1}	9

Single-atom-Fe-N-C	0	56.55	7.48 mg h^{-1} mg^{-1}	10
Single-atom-Mo/N-doped porous carbon	-0.3	14.6	34.0 mg h^{-1} mg^{-1}	11
Zr-doped TiO_2	-0.45	17.3	8.9 mg h^{-1} cm^{-2}	12
Co_3Fe-MOF	-0.2	25.64	8.79 mg h^{-1} mg^{-1}	This work

Reference:

[1] H. Zhang, W. Zhou, J. Dong, X.F. Lu, X. W. Lou, Energy Environ. Sci., 12 (2019) 3348-3355.

[2] J. Wang, H. C. Zeng, ACS Appl. Mater. Interfaces, 11 (2019) 23180-23191.

[3] C. Liao, B. Yang, N. Zhang, M. Liu, G. Chen, X. Jiang, G. Chen, J. Yang, X. Liu, T.-S. Chan, Y.-J. Lu, R. Ma, W. Zhou, Adv. Funct. Mater., 29 (2019) 1904020.

[4] X. Li, D.-D. Ma, C. Cao, R. Zou, Q. Xu, X.-T. Wu, Q.-L. Zhu, Small, 15 (2019): 1902218.

[5] X. Zhang, J. Luo, K. Wan, D. Plessers, B. Sels, J. Song, L. Chen, T. Zhang, P. Tang, J. R. Morante, J. Arbiol, J. Fransaer, J. Mater. Chem. A, 7 (2019) 1616-1628.

[6] C. Wang, H. Yang, Y. Zhang, Q. Wang, Angew. Chem. Int. Edit., 58 (2019) 6099-6103.

[7] D. Bao, Q. Zhang, F. L. Meng, H. X. Zhong, M. M. Shi, Y. Zhang, J. M. Yan, Q. Jiang, X. B. Zhang, Adv. Mater. 29 (2017) 1604799.

[8] S. Mukherjee, D. A. Cullen, S. Karakalos, K. X. Liu, H. Zhang, S. Zhao, H. Xu, K. L. More, G. F. Wang, G. Wu, Nano Energy, 48 (2018) 217.

[9] M. M. Shi, D. Bao, S. J. Li, B. R. Wulan, J. M. Yan, Q. Jiang, Adv. Energy Mater., 8 (2018) 1800124.

[10] M. F. Wang, S. S. Liu, T. Qian, J. Liu, J. Q. Zhou, H. Q. Ji, J. Xiong, J. Zhong, C. L. Yan, Nat. Commun., 10 (2019) 341.

[11] L. L. Han, X. J. Liu, J. P. Chen, R. Q. Lin, H. X. Liu, F. Lü, S. Bak, Z. X. Liang, S. Z. Zhao, E. Stavitski, J. Luo, R. R. Adzic, H. L. L. Xin, Angew. Chem. Int. Ed., 58 (2019) 2321.

[12] N. Cao, Z. Chen, K. T. Zang, J. Xu, J. Zhong, J. Luo, X. Xu, G. F. Zheng, Nat. Commun., 10 (2019) 2877.