Electronic Supplementary Information

Molten-salt-assisted preparation of porous carbon foams for efficient oxygen electrocatalysis

Jizhen Ma, Xinxin Shu, Song Chen, Qianwu Chen, An-Liang Wang, Jintao Zhang*

Key Laboratory for Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China.

*Corresponding author: E-mail: jtzhang@sdu.edu.cn (Jintao Zhang)

Experiments

1. Preparation of three-dimensional macro–microporous carbon foams

1.25 g of starch was dissolved in 10 mL of deionic (DI) water under stirring, and then 10 g of potassium chloride was added the above solution, subsequently. After adding 3 mmol $CoCl_2$, $NiCl_2$, respectively, the mixed solution kept overnight under stirring and freeze-dried to produce precursors. The precursors were thermally treated at 700, °C for 1 h in inert atmosphere. The obtained samples were washed with diluted acid and then vacuum-dried at 60 ∘C. The final product was obtained by further calcined at a temperature of 700, 800, and 900 ∘C in NH_3 atmosphere for 3 h and named as MCF-Co-700, MCF-Co-800, MCF-Co-900, MCF-Co1Ni2-800 MCF-Co2Ni1-800 with changing mole ratio, respectively.

2.2 Characterization

Scanning electron microscopy (SEM, JEOL JSM-6510LV, Japan) was performed to characterize the morphology of samples. X-ray photoelectron spectroscopic (XPS) measurements were tested on a VG Microtech ESCA 2000 (UK) using a monochromic Al X-ray source (97.9 W, 93.9 eV).   The microstructure of the sample was characterized by HRTEM with Tecnai G2 F30 S-TWIN. For the electrochemical measurements, the homogeneous catalyst ink was prepared by dispersing 5 mg of electrocatalysts into an aqueous solution containing 950 μL DI water and 50 μL of 5 wt% Nafion under sonication. The working electrode was prepared by dropping 8 μL of the catalyst ink onto a mirror polished glassy carbon electrode. The electrolyte is 0.1

M KOH aqueous solution. The air electrode was prepared by coating the catalyst ink on a piece of carbon paper (catalyst loading 0.5 mg cm^{-2}), which is coupled with a Zn plate for fabricating a Zn-air battery in 6 M KOH electrolyte..
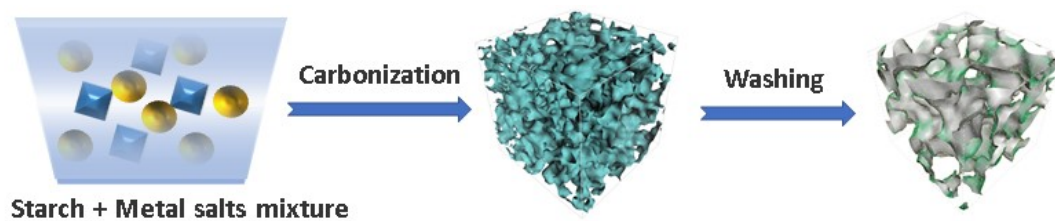
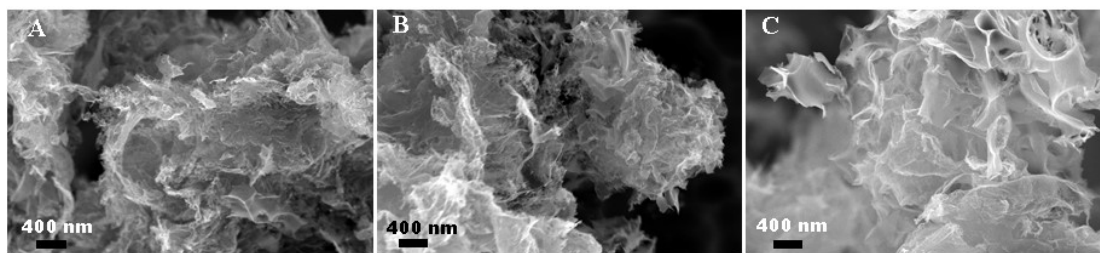**Fig. S1.** Scheme illustration for the preparation of porous carbon foams.

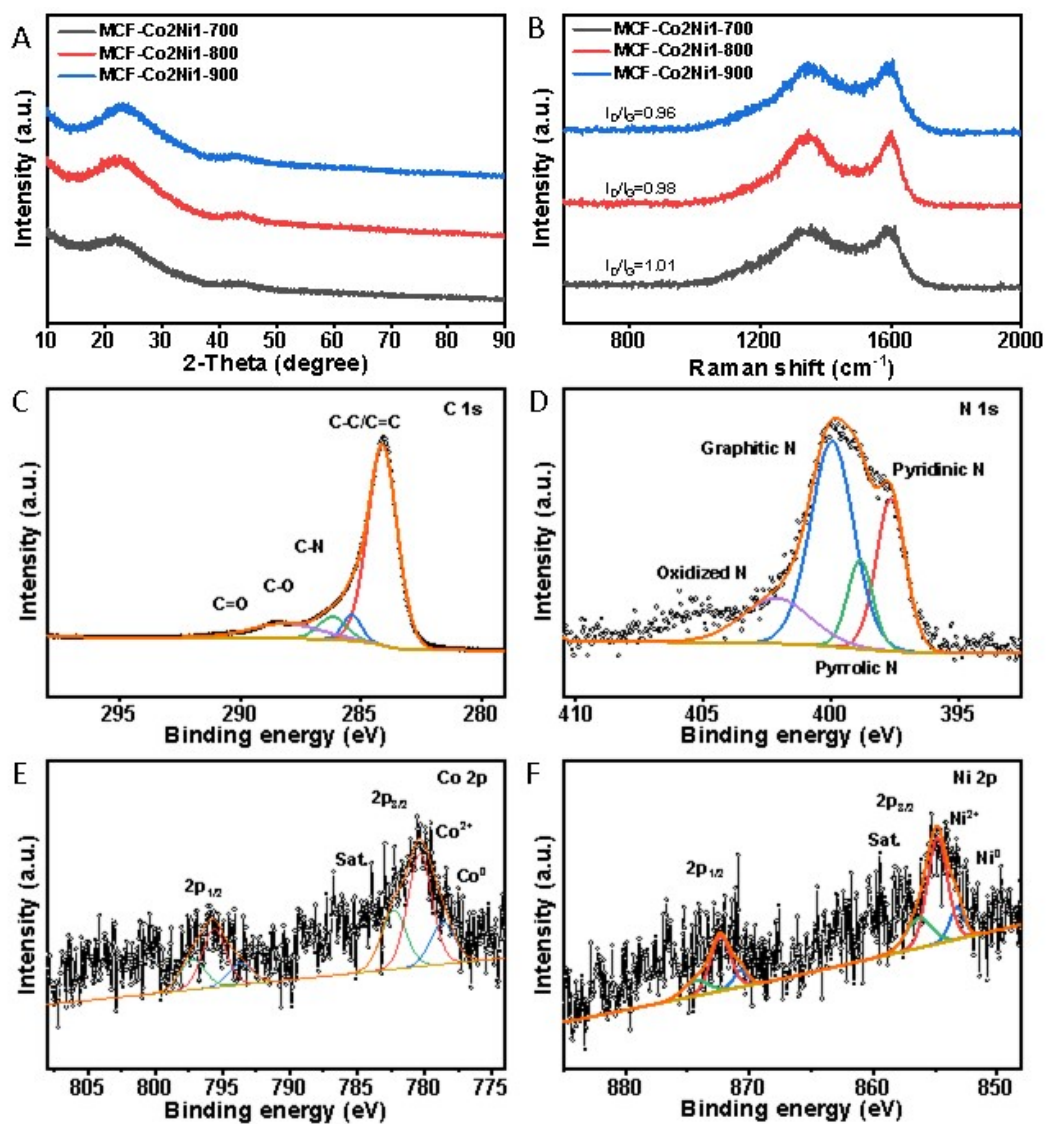**Fig. S2.** SEM images of the samples prepared at 700, 800, 900 °C.

Fig. S3 XRD patterns (A), Raman spectra (B), and XPS spectra of MCF-Co2Ni1-800
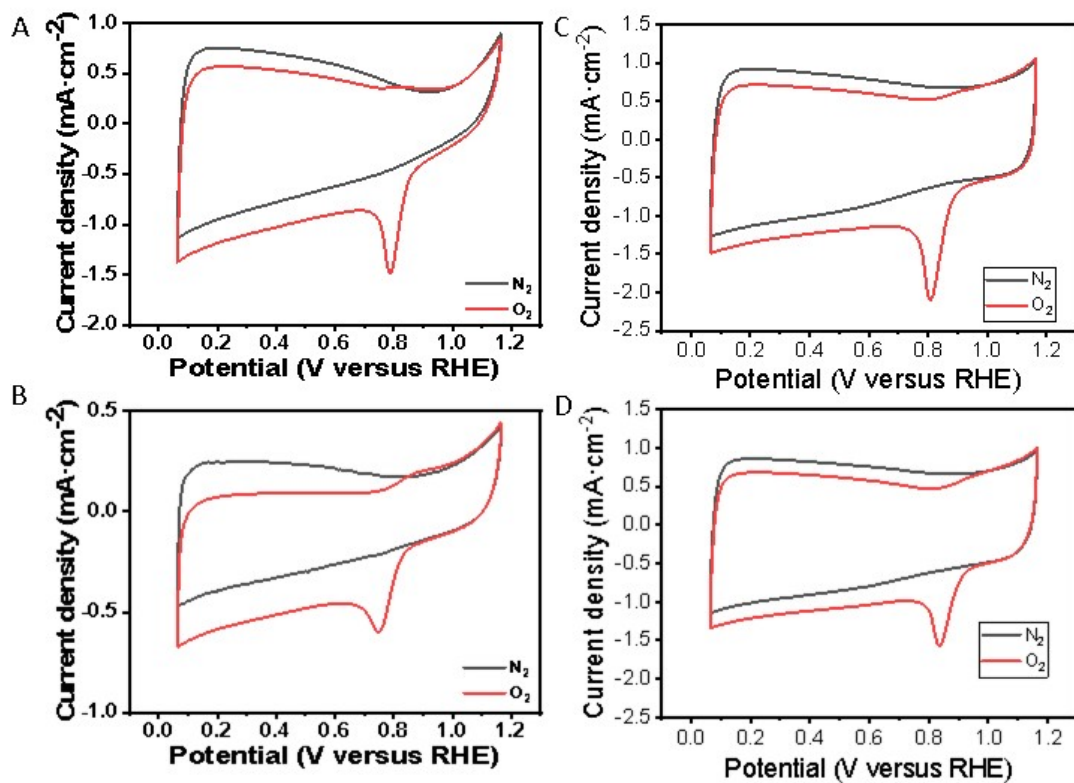
for C1s (C), N1s (D), Co2p (E) and Ni2p (F).

Fig. S4. The CV curves of MCF-Co-800 (A), MCF-Ni-800 (B), MCF-Co1Ni2-800 (C),

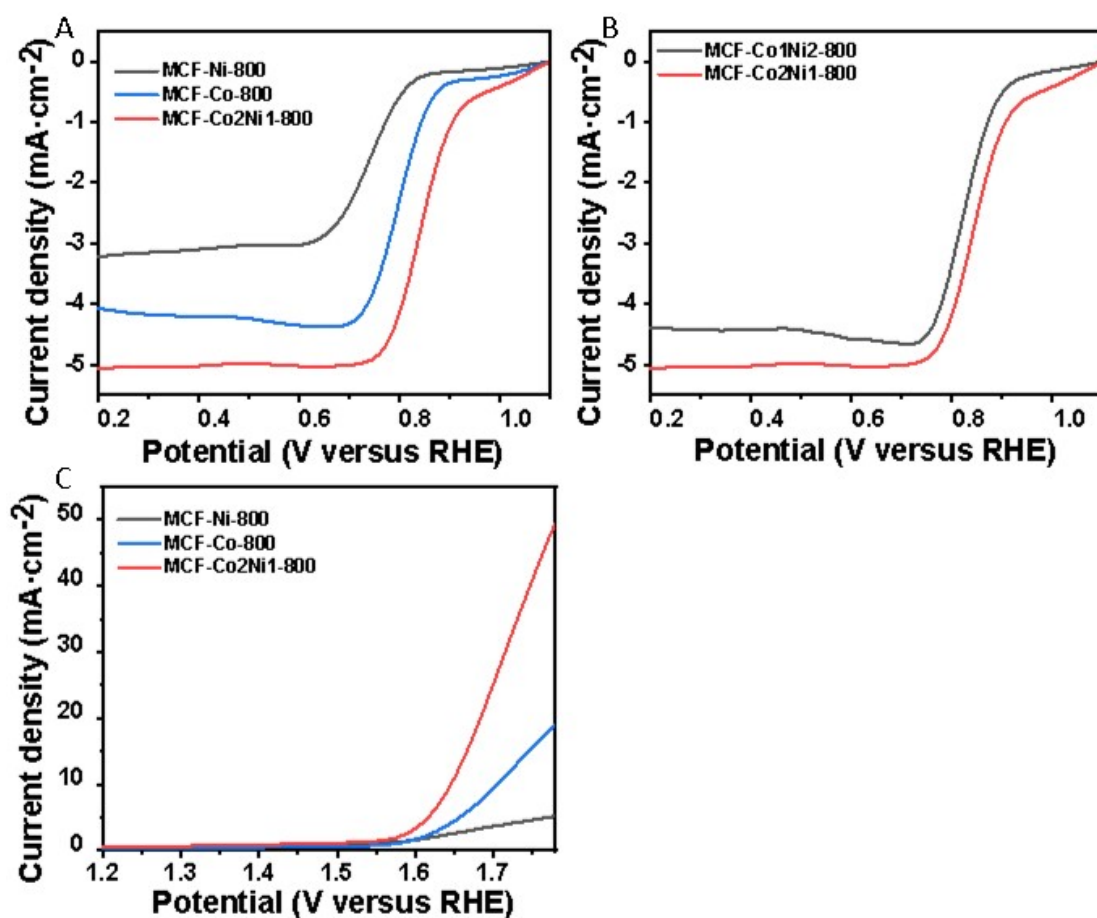MCF-Co2Ni1-800 (D) in nitrogen and oxygen-saturated electrolytes, respectively.

Fig. S5. (A) Polarization profile of oxygen reduction at a rotating speed of 1600 rpm and (B) Polarization profile of oxygen evolution reaction. (C) Polarization profile of oxygen reduction at MCF-Co1Ni2-800 and MCF-Co2Ni1-800.

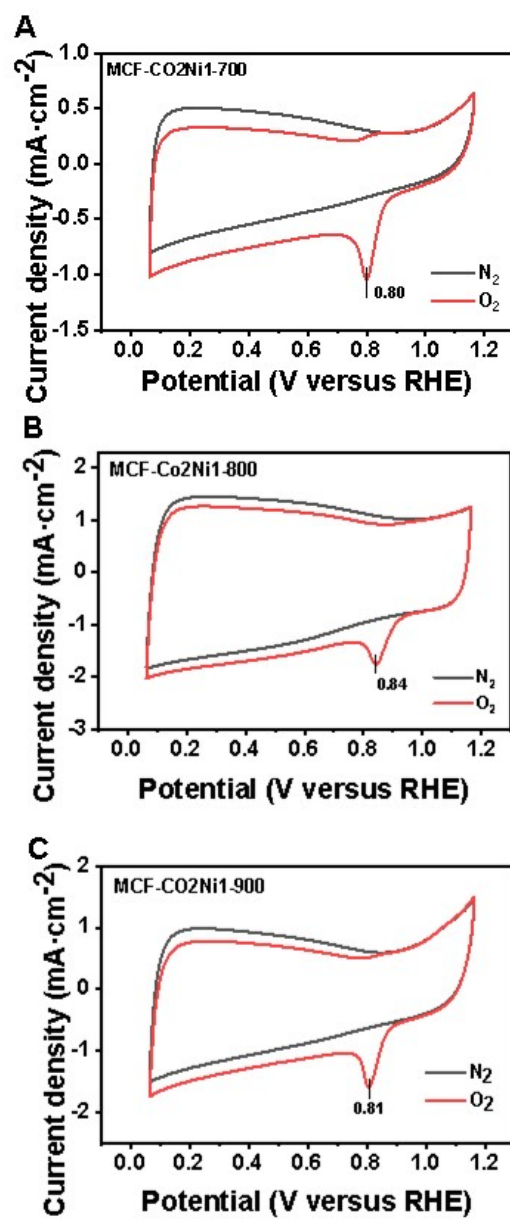**Fig. S6.** The CV curves for oxygen reduction reaction at the MCF-Co2Ni1-700 (A), MCF-Co2Ni1-800 (B), MCF-Co2Ni1-900 (C) electrodes in nitrogen and oxygen-saturated electrolytes, respectively.
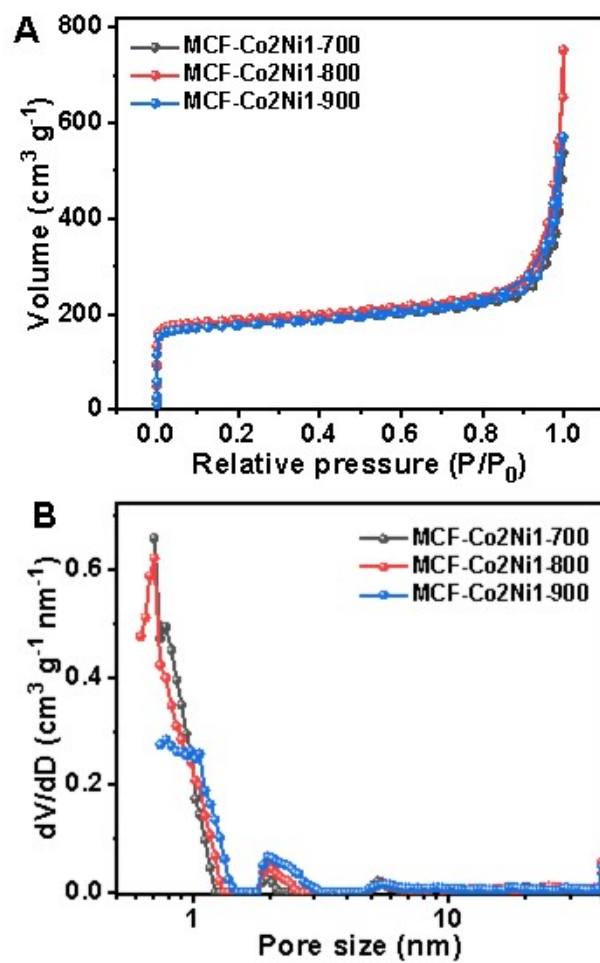
Fig. S7. The nitrogen adsorption-desorption isotherms (A) and the corresponding pore size distribution curves (B).
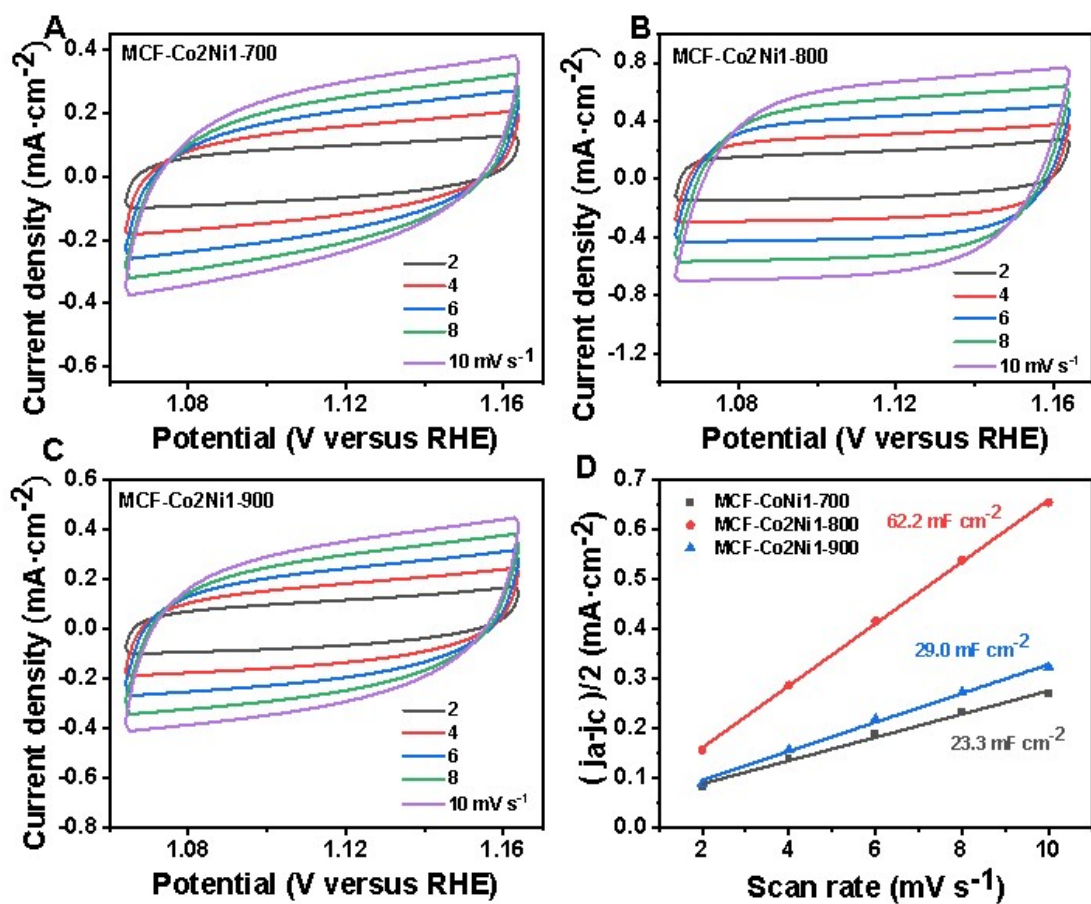
Fig. S8. The CV curves at the changing scan rates (A-C) and the fitting curves (D).

Table S1. EXAFS fitting results of MCF-Co$_2$Ni$_1$-800 and Ni foil, S$_0^2$ = 0.7.

Sample	Shell	CN	R(Å)	σ^2	ΔE$_0$	R factor
Ni foil	Ni-Ni	12	2.48	0.006	0.68±0.03	0.002
MCF-Co$_2$Ni$_1$-800	Ni-N	3.9	2.08±0.01	0.005	1.66±1.07	0.008
	Ni-Ni	2.3	3.07±0.03	0.01		

Table S2. EXAFS fitting results of MCF-Co$_2$Ni$_1$-800 and Ni foil, S$_0^2$ = 0.7.

Sample	Shell	CN	R(Å)	σ^2	ΔE$_0$	R factor
Co foil	Co-Co	12	2.49	0.008	-6.49±0.71	0.005
MCF-Co2Ni1-800	Co-N	1.7	1.46±0.01	0.001	-7.9±3.5	0.016
	Co-N	2.8	1.72±0.01	0.005		
	Co-Co	1.1	2.25±0.01	0.004		

Table S3. Comparison of Zn-air batteries performance of this work with other art-of-state non-noble metal catalysts.

Catalysts	Open circuit potential (V)	Peak power density (mW cm^{-2})	Cycling stability	Ref.
MCF-Co2Ni1-800	1.48	208	485 h @ 5 mA cm^{-2}	This work
FeCo-SAs	1.48	203	550 h @10 mA cm^{-2}	[1]
Fe$_2$NiO$_4$/FeNiS$_2$ MTs	1.47	144.2	1000 h @2 mA cm^{-2}	[2]
FeCo/Se-CNT	1.54	173.4	70 h @5 mA cm^{-2}	[3]
MnSs@NGA	1.52	115.0	N/A	[4]
CoFe–N–C DAC	1.49	142	200 h @5 mA cm^{-2}	[5]
Co$_3$O$_4$/Co@NCs	1.50	123.5	600 h @10 mA cm^{-2}	[6]
CoS$_{1-\delta}$/SnS$_{2-\delta}$	1.54	249	168 h @20 mA cm^{-2}	[7]
RuFe–N–C	1.52	139.9	200 h @ 5 mA cm^{-2}	[8]
PCACoCN-1	1.47	130	170 h @ 10 mA cm^{-2}	[9]
VC-MOF-Fe	1.49	113	26 h	[10]
Co@NPCP/NB-CNF-2-800	1.48	143.8	110 h @10 mA cm^{-2}	[11]
0.05CoOx@PNC	1.49	157.1	110 h@10 mA cm^{-2}	[12]
MnO/Co/PGC	1.52	172	350 cycles	[13]
Fe-2-WNPC-NCNTs	1.43	101.3	66 h @ 2 mA cm^{-2}	[14]
Co@hNCTs-800	1.45	149	50 h @ 5 mA cm^{-2}	[15]
NC@Co-HPNC	NA	165	230 h @ 5 mA cm^{-2}	[16]

Reference

[1]   Z. Li, X. Zhong, L. Gao, J. Hu, W. Peng, X. Wang, G. Zhou, B. Xu, *ACS Nano* **2024**, *18*, 13006-13018.

[2]   X. Li, D. C. Nguyen, K. Dong, S. Prabhakaran, D. T. Tran, D. H. Kim, N. H. Kim, J. H. Le, *Chem. Eng. J.* **2024**, *489*, 151210.

[3]   H. Zhang, M. Zhao, H. Liu, S. Shi, Z. Wang, B. Zhang, L. Song, J. Shang, Y. Yang, C. Ma, L. Zheng, Y. Han, W. Huang, *Nano Lett.* **2021**, *21*, 2255.

[4]   H. Zhao, R. Jiang, Y. Zhang, B. Xie, J. Fu, X. Yuan, W. Yang, Y. Wu, R. Zhang, *J. Mater. Chem. A* **2021**, *9*, 5848.

[5]   X. Zhou, J. Gao, Y. Hu, Z. Jin, K. Hu, K. M. Reddy, Q. Yuan, X. Lin, H.-J. Qiu, *Nano Letters* **2022**, *22*, 3392-3399.

[6]   N.-F. Yu, C. Wu, W. Huang, Y.-H. Chen, D.-Q. Ruan, K.-L. Bao, H. Chen, Y. Zhang, Y. Zhu, Q.-H. Huang, W.-H. Lai, Y.-X. Wang, H.-G. Liao, S.-G. Sun, Y.-P. Wu, J. Wang, *Nano Energy* **2020**, *77*,105200.

[7]   N. K. Wagh, D.-H. Kim, C. H. Lee, S.-H. Kim, H.-D. Um, J. S.-I. Kwon, S. S. Shinde, S. U. Lee, J.-H. Lee, *Nanoscale Horizons* **2023**, *8*, 921-934.

[8]   X. Zhou, S. Chu, Z. Jin, K. Hu, P. Liu, H.-J. Qiu, X. Lin, *ACS Mater. Letters* **2023**, *5*, 1656-1664.

[9]   J.H. Park, C.H. Lee, J.-M. Ju, J.-H. Lee, D. Yim, C. Choi, P.V. Braun, S.U. Lee, J.-H. Kim, *Appl.Catal.B Environ.* **2020**, *270*, 118869.

[10]   C. Hu, H. Jin, B. Liu, L. Liang, Z. Wang, D. Chen, D. He, S. Mu, *Nano Energy* **2021**, *82*, 105714.

[11]   C. Gu, J. Li, J.-P. Liu, H. Wang, Y. Peng, C.-S. Liu, *Appl.Catal.B Environ.* **2021**, *286*, 119888.

[12]   Y. Tan, W. Zhu, Z. Zhang, W. Wu, R. Chen, S. Mu, H. Lv, N. Cheng, *Nano Energy* **2021**, *83*, 105813.

[13]   X.F. Lu, Y. Chen, S. Wang, S. Gao, X.W.D. Lou, *Adv Mater* **2019**, *31*, e1902339.

[14]   Z. Liu, Y. Zhu, K. Xiao, Y. Xu, Y. Peng, J. Liu, X. Chen, *ACS Appl. Mater. Interfaces* **2021**, *13*, 24710.

[15]   Q. Zhou, Z. Zhang, J. Cai, B. Liu, Y. Zhang, X. Gong, X. Sui, A. Yu, L. Zhao, Z. Wang, Z. Chen, *Nano Energy* **2020**, *71*, 104592.

[16]   Z. Chi, Y. Feng, Y. Ma, D. Kong, H. Yin, S. Li, L. Li, Z. Guo, L. Wang, *Chem. Commun.* **2021**, 57, 11248-11251.