Supplementary Materials

Self-supported Al-doped cobalt phosphide nanosheets grown on three-dimensional Ni foam for highly efficient water reduction and oxidation

Xianwei Lv,[a] Zhongpan Hu,[a] Jintao Ren,[a] Yuping Liu,[a,*] Zheng Wang,[b] and Zhongyong Yuan[a,*]

[a] *Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, School of Materials Science and Engineering, Nankai University, Tianjin 300071, China. E-mail: zyyuan@nankai.edu.cn*

[b] *State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China*

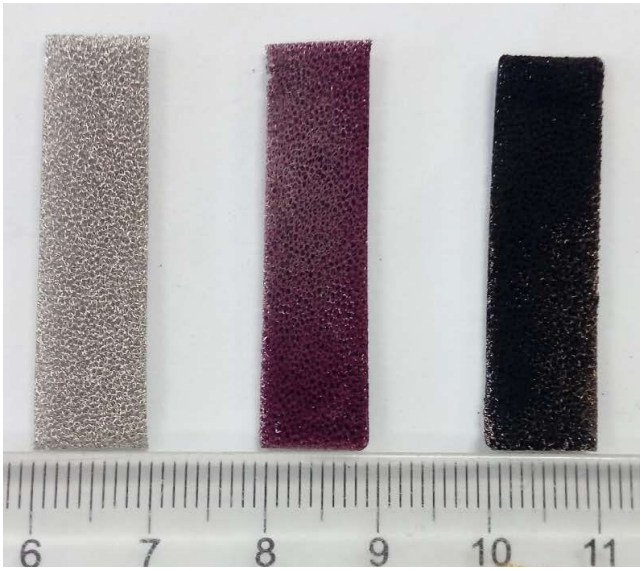

Fig. S1 Digital photographs of pristine Ni foam, CoAl-LDH/NF and Al-CoP/NF (from left to right).

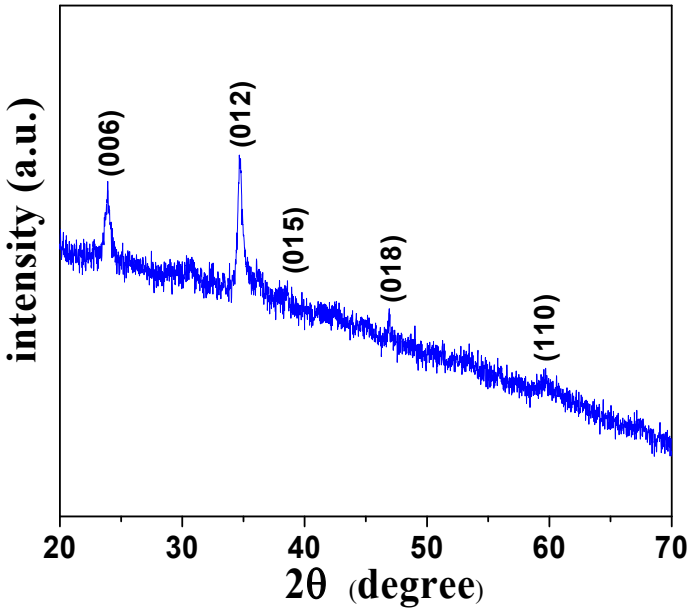

Fig. S2 Wide-angle XRD pattern of CoAl-LDH scratched down from Ni foam.

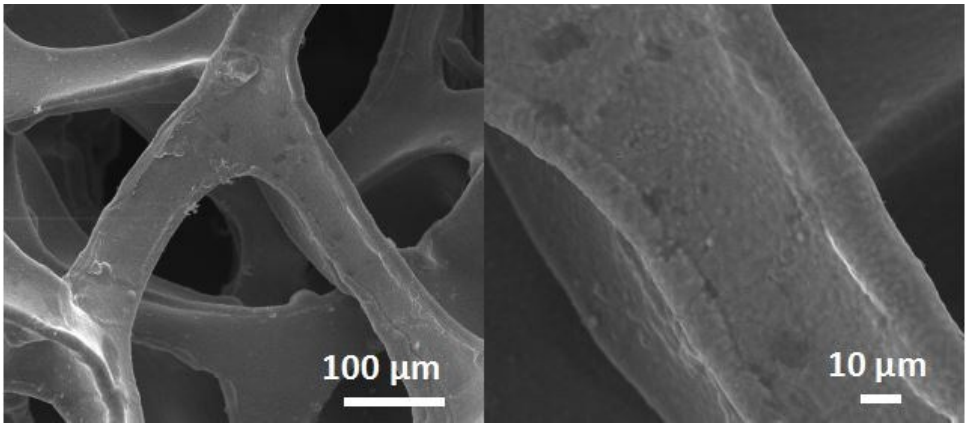

Fig. S3 SEM image of pristine Ni foam.

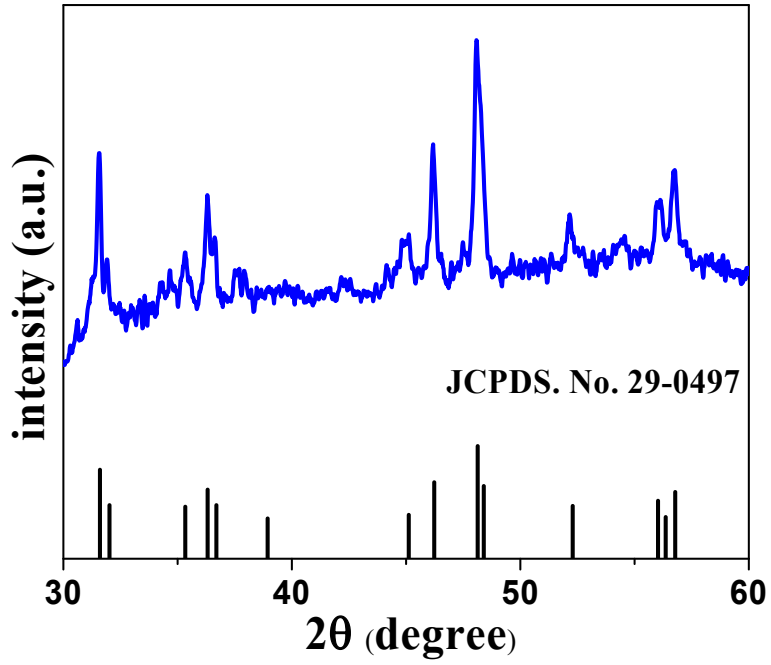

Fig. S4 XRD pattern of Al-CoP/NF after long-term HER durability test.

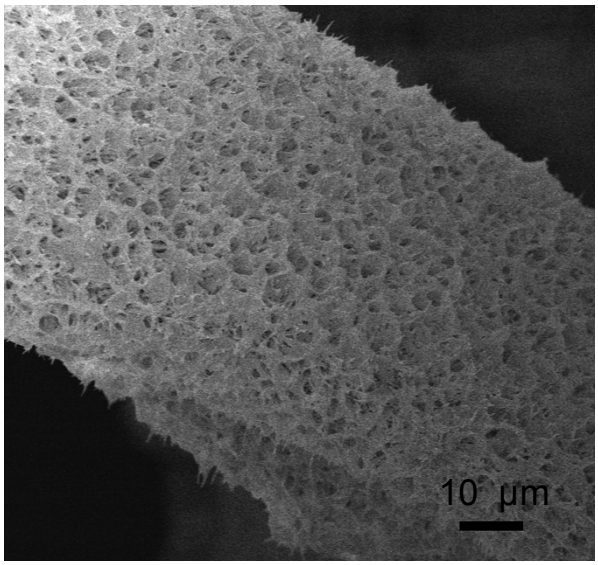

Fig. S5 SEM image of Al-CoP/NF after long-term HER durability test.

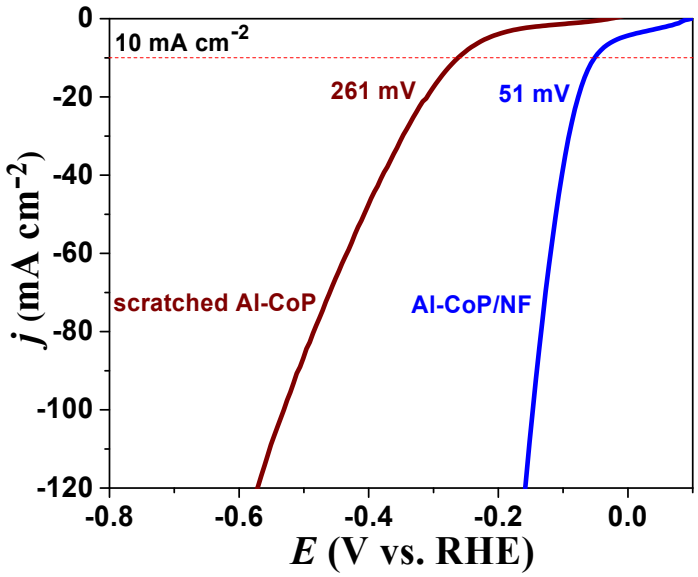

Fig. S6 Comparison of HER polarization curves of Al-CoP/NF and scratched Al-CoP on Ni foam at a scan rate of 2 mV s^{-1} in 0.5 M H_2SO_4.

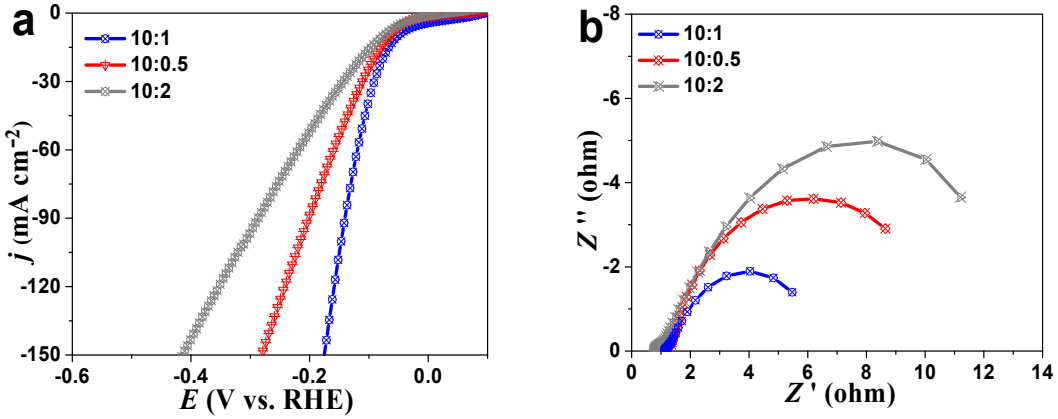

Fig. S7 (a) Polarization curves for HER of Al-CoP/NF with different ratios of Co : Al = 10 : 0.5, 10 : 1 and 10 : 2 (scan rate: 2 mV s^{-1}). (b) The Nyquist plots of Al-CoP/NF with different ratios of Co : Al = 10 : 0.5, 10 : 1 and 10 : 2. All experiments were carried out in 0.5M H_2SO_4.

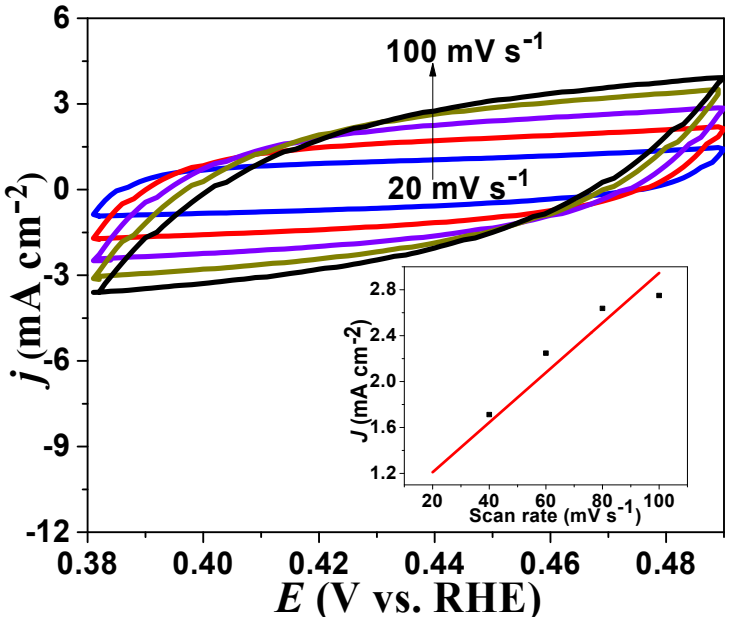

Fig. S8 Cyclic voltammograms of CoP/NF measured at different scan rates from 20 to 100 mV s^{-1}. Inset: The plots of the current density at 0.44 V (vs. RHE) against the scan rate.

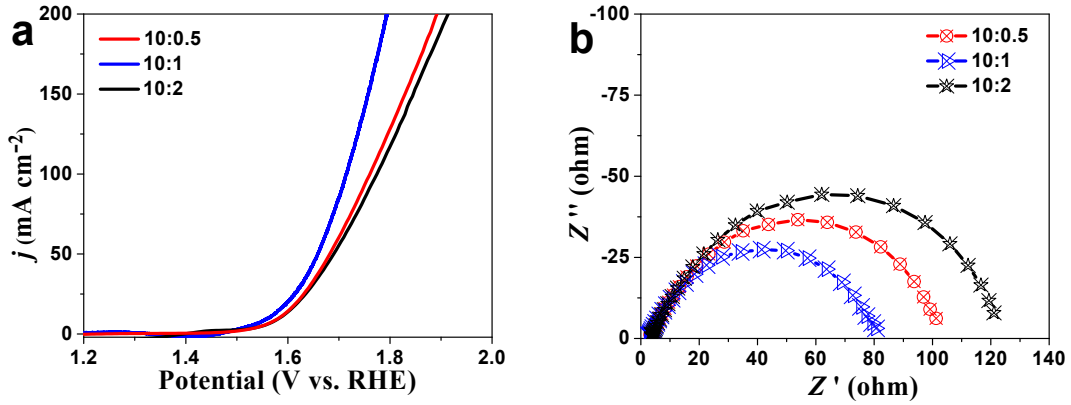

Fig. S9 (a) Polarization curves for OER (scan rate: 2 mV s^{-1}) and (b) the Nyquist plots of Al-CoP/NF with Co / Al ratios of 10 : 0.5, 10 : 1 and 10 : 2. All experiments were carried out in 1.0 M KOH.

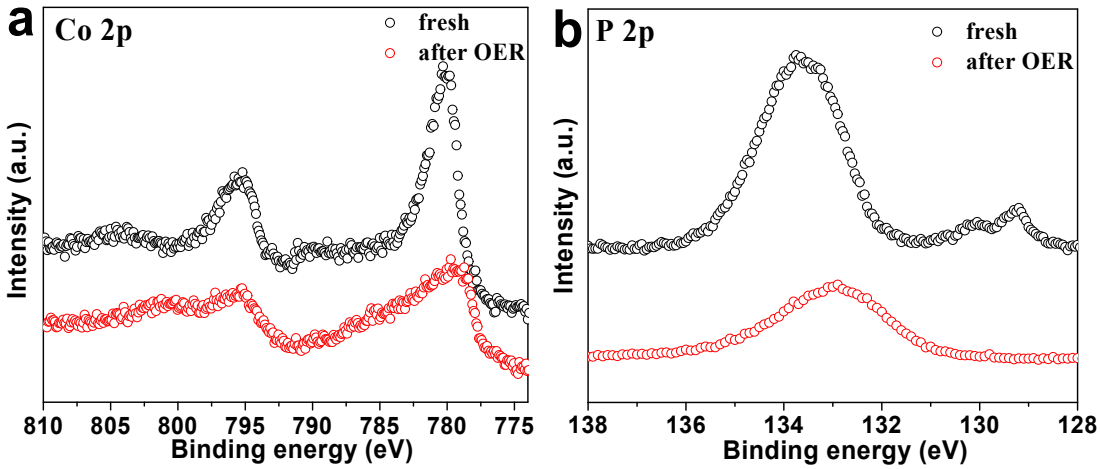

Fig. S10 XPS spectra of Al-CoP in (a) Co 2p and (b) P 2p regions before and after OER.

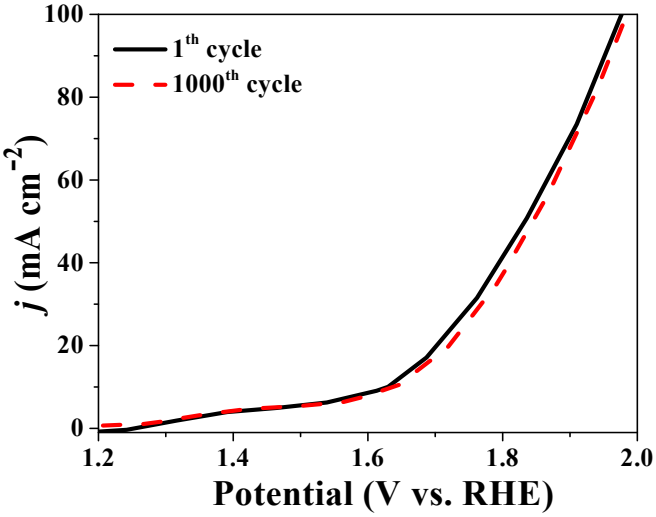

Fig. S11 Polarization curves of Al-CoP/NF ‖ Al-CoP/NF in a two-electrode setup for full water splitting before and after 1000 CV cycles with scan rate: 100 mV s^{-1}.

Table S1. Comparison of HER performance of some recently reported Co-based phosphide electrocatalysts in 0.5 M H_2SO_4.

Catalyst	Substrate	Electrolyte	$E_{\eta=10}$ (mV) vs. RHE	Tafel slop (mV·dec^{-1})	Reference
Al-CoP/NF	Ni foam	0.5M H_2SO_4	51	68	This work
CoNiP@NF	Ni foam	0.5M H_2SO_4	60	39	1
$Fe_{0.5}Co_{0.5}P$/CC	Carbon cloth	0.5M H_2SO_4	37	30	2
CoP/CC	Carbon cloth	0.5M H_2SO_4	92	58	3
CoP/CC	Carbon cloth	0.5M H_2SO_4	67	51	4
CoP NBAs/Ti	Ti mesh	0.5M H_2SO_4	203	40	5
CoP/Ti	Ti mesh	0.5M H_2SO_4	85 ($E_{\eta=20}$)	50	6
np-CoP NWs/Ti	Ti mesh	0.5M H_2SO_4	95 ($E_{\eta=20}$)	65	7
Co_2P/Ti	Ti mesh	0.5M H_2SO_4	95	45	8
u-CoP/Ti	Ti mesh	0.5M H_2SO_4	45	49.3	9
Mn-CoP/Ti	Ti mesh	0.5M H_2SO_4	49	55	10
Co-P film	Copper foil	0.5M H_2SO_4	94	42	11
CoP/Hb	Hastelloy belt	0.5M H_2SO_4	78	68	12
CoP/CNT	Carbon Nanotube	0.5M H_2SO_4	122	54	13
CoS|P/CNT	Carbon Nanotube	0.5M H_2SO_4	48	55	14
CoP	CoP film	0.5M H_2SO_4	85	50	15

Table S2. Comparison of HER performance of some recently reported Co-based phosphide electrocatalysts in 1.0 M KOH.

Catalyst	Substrate	Electrolyte	$E_{\eta=10}$ (mV) vs. RHE	Tafel slop (mV·dec^{-1})	Reference
Al-CoP/NF	Ni foam	1.0 M KOH	66	94	This work
CoNiP@NF	Ni foam	1.0 M KOH	155	115	1
CoP/CC	Carbon cloth	1.0 M KOH	90	68	3
CoP/Hb	Hastelloy belt	1.0 M KOH	52	88	12
CoP-MNA/NF	Ni foam	1.0 M KOH	54	51	16
Ni@Co-Ni-P	Ni foam	1.0 M KOH	52	65.1	17
CoP/TM	Ti mesh	1.0 M KOH	72	65	18
Fe-CoP/Ti	Ti mesh	1.0 M KOH	78	75	19
Co_2P/Co-foil	Co foil	1.0 M KOH	157	59	20

Table S3. Comparison of HER performance of some recently reported Co-based phosphide electrocatalysts in neutral media.

Catalyst	Substrate	Electrolyte	$E_{\eta=10}$ (mV) vs. RHE	Tafel slop (mV·dec^{-1})	Reference
Al-CoP/NF	Ni foam	1.0 M PBS	83	89	This work
CoNiP@NF	Ni foam	1.0 M KPi	120	103	1
CoP/CC	Carbon cloth	1.0 M PBS	162	93	3
np-CoP NWs/Ti	Ti mesh	1.0 M PBS	178	125	7
Mn-CoP/Ti	Ti mesh	1.0 M PBS	86	82	10
CoP/Hb	Hastelloy belt	1.0 M PBS	121	106	12

Table S4. Comparison of OER performance of some recently reported non-noble-metal catalysts in 1.0 M KOH.

Catalyst	Substrate	Electrolyte	$E_{\eta=10}$ (mV) vs. RHE	Tafel slop ($mV \cdot dec^{-1}$)	Reference
Al-CoP/NF	Ni foam	1M KOH	330	69	This work
Co-P film	Copper foil	1M KOH	345	47	11
CoP-MNA/NF	Ni foam	1M KOH	290	65	16
NiCoP/NF	Ni foam	1M KOH	280	87	21
CoO_X@CN	GCE	1M KOH	260	N.A.	22
NiOOH/Ni_5P_4	Ni foil	1M KOH	290	N.A.	23
CoP/TM	Ti mesh	1M KOH	310	87	18
Ni_3Se_2/CF	Cu foam	1M KOH	340 ($E_{\eta=50}$)	80	24
Ni_3N/Ni-foam	Ni foam	1M KOH	~ 399	65	25

Table S5. The overall water splitting activities of Al-CoP/NF and the previously reported bifunctional non-noble metal catalysts in 1.0 M KOH.

Catalyst	Substrate	Electrolyte	$E_{\eta=10}$ (V) vs. RHE	Reference
Al-CoP/NF	Ni foam	1M KOH	1.63	This work
Co-P film	Copper foil	1M KOH	1.65	11
CoP-MNA/NF	Ni foam	1M KOH	1.62	16
NiCoP/NF	Ni foam	1M KOH	1.58	21
CoO_X@CN	GCE	1M KOH	1.55 ($E_{\eta=20}$)	22
Ni_5P_4 Films	Ni foil	1M KOH	~ 1.7	23
CoP/TM	Ti mesh	1M KOH	1.64	18
Ni_3Se_2/CF	Cu foam	1M KOH	1.65	24
Ni_3S_2/Ni foam	Ni foam	1M KOH	~ 1.7	26
NiP/NF	Ni foam	1M KOH	1.63	27
$NiCo_2S_4$ NA/CC	Carbon cloth	1M KOH	1.68	28
$NiWO_4$/TM	Ti mesh	1M KOH	1.65 ($E_{\eta=20}$)	29

References

1. A. Han, H. Chen, H. Zhang, Z. Sun and P. Du, *J. Mater. Chem. A*, 2016, **4**, 10195-10202.
2. C. Tang, L. Gan, R. Zhang, W. Lu, X. Jiang, A. M. Asiri, X. Sun, J. Wang and L. Chen, *Nano Lett.*, 2016, **16**, 6617-6621.
3. X. Y. Yan, S. Devaramani, J. Chen, D. I. Shan, D. D. Qin, Q. Ma and X. Q. Lu, *New J. Chem.*, 2017, **41**, 2436-2442.
4. J. Tian, Q. Liu, A. M. Asiri and X. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 7587-7590.
5. Z. Niu, J. Jiang and L. Ai, *Electrochem. Commun.*, 2015, **56**, 56-60.
6. E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis and R. E. Schaak, *Angew. Chem. Int. Ed.*, 2014, **53**, 5427-5430.
7. S. Gu, H. Du, A. M. Asiri, X. Sun and C. M. Li, *Phys. Chem. Chem. Phys.*, 2014, **16**, 16909-16913.
8. J. F. Callejas, C. G. Read, E. J. Popczun, J. M. McEnaney and R. E. Schaak, *Chem. Mater.*, 2015, **27**, 3769-3774.
9. D. Zhou, L. He, W. Zhu, X. Hou, K. Wang, G. Du, C. Zheng, X. Sun and A. M. Asiri, *J. Mater. Chem. A*, 2016, **4**, 10114-10117.
10. T. Liu, X. Ma, D. Liu, S. Hao, G. Du, Y. Ma, A. M. Asiri, X. Sun and L. Chen, *ACS Catal.*, 2016, **7**, 98-102.
11. N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem.*, 2015, **127**, 6349-6352.
12. J. Huang, Y. Li, Y. Xia, J. Zhu, Q. Yi, H. Wang, J. Xiong, Y. Sun and G. Zou, *Nano Res.*, 2017, **10**, 1010-1020.
13. Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri and X. Sun, *Angew. Chem. Int. Ed.*, 2014, **53**, 6710-6714.
14. W. Liu, E. Hu, H. Jiang, Y. Xiang, Z. Weng, M. Li, Q. Fan, X. Yu, E. I. Altman and H. Wang, *Nat. Commun.*, 2016, **7**, 10771.
15. F. H. Saadi, A. I. Carim, E. Verlage, J. C. Hemminger, N. S. Lewis and M. P. Soriaga, *J. Phys. Chem. C*, 2014, **118**, 29294-29300.
16. Y. P. Zhu, Y. P. Liu, T. Z. Ren and Z. Y. Yuan, *Adv. Funct. Mater.*, 2015, **25**, 7337-7347.
17. W. Li, X. Gao, X. Wang, D. Xiong, P. P. Huang, W. G. Song, X. Bao and L. Liu, *J. Power Sources*, 2016, **330**, 156-166.
18. L. Yang, H. Qi, C. Zhang and X. Sun, *Nanotechnology*, 2016, **27**, 23LT01.
19. C. Tang, R. Zhang, W. Lu, L. He, X. Jiang, A. M. Asiri and X. Sun, *Adv. Mater.*, 2017, **29**, 1602441.
20. C. Z. Yuan, S. L. Zhong, Y. F. Jiang, Z. K. Yang, Z. W. Zhao, S. J. Zhao, N. Jiang and A. W. Xu, *J. Mater. Chem. A*, 2017, **5**, 10561-10566.
21. H. Liang, A. N. Gandi, D. H. Anjum, X. Wang, U. Schwingenschlögl and H. N. Alshareef, *Nano Lett.*, 2016, **16**, 7718-7725.
22. H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 2688-2694.
23. M. Ledendecker, S. Krick Calderón, C. Papp, H. P. Steinrück, M. Antonietti and M. Shalom, *Angew. Chem. Int. Ed.* , 2015, **54**, 12361-12365.
24. J. Shi, J. Hu, Y. Luo, X. Sun and A. M. Asiri, *Catal. Sci. Technol.*, 2015, **5**, 4954-4958.
25. M. Shalom, D. Ressnig, X. Yang, G. Clavel, T. P. Fellinger and M. Antonietti, *J. Mater. Chem. A*, 2015, **3**, 8171-8177.
26. L. L. Feng, G. Yu, Y. Wu, G.-D. Li, H. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, *J. Am. Chem. Soc.*, 2015, **137**, 14023-14026.

27. J. Ren, Z. Hu, C. Chen, Y. Liu and Z. Yuan, *J. Energy Chem.*, 2017, **26**, 1196-1202.
28. D. Liu, Q. Lu, Y. Luo, X. Sun and A. M. Asiri, *Nanoscale*, 2015, **7**, 15122-15126.
29. Y. Ji, L. Yang, X. Ren, G. Cui, X. Xiong, and X. Sun, *ACS Sustain. Chem. Eng.*, 2018, **6**, 9555-9559.