Supplementary Materials

Well-defined CoP/Ni_2P nanohybrids encapsulated in the nitrogen-doped carbon matrix as advanced multifunctional electrocatalysts for efficient overall water splitting and zinc-air batteries

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Physicochemical characterization

The morphologies of catalysts were determined by scanning electron microscopy (SEM, JEOL JSF-7500 L) operated at 5 kV. Transmission electron microscopy (TEM) tests were recorded on a JEOL JEM-2800 (200 kV) electron microscopy. Powder X-ray diffraction (XRD) data of the as-obtained products were recorded on a Bruker D8 Focus diffractometer with Cu-*K*α radiation. X-ray photoelectron spectroscopy (XPS) measurements were recorded on Thermo Scientific ESCALAB 250Xi spectrometer used Al *K*α X-rays (1486.6 eV) as the excitation source.

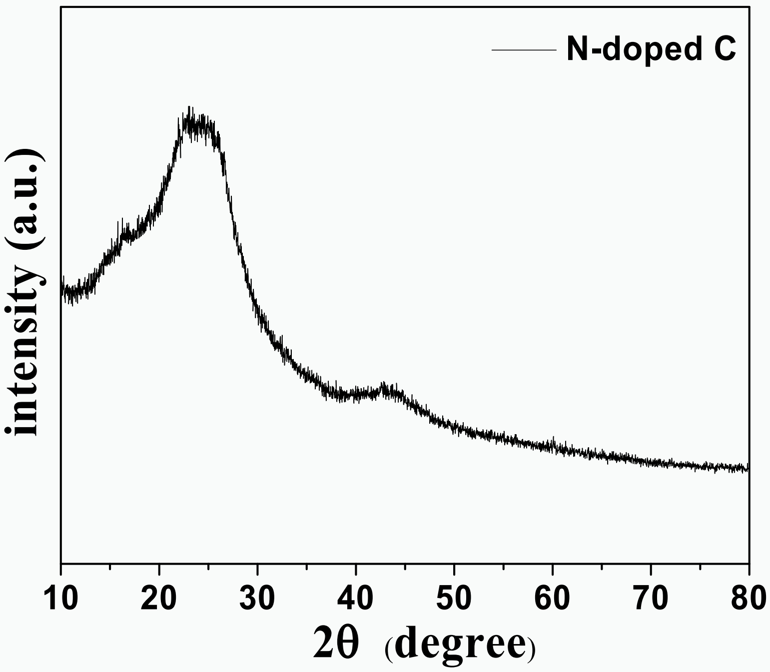

Fig. S1 XRD pattern for N-doped carbon.

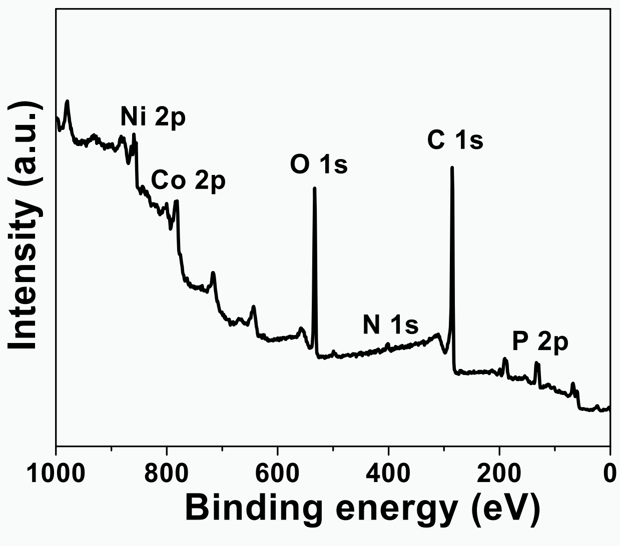

Fig. S2 XPS survey spectrum of CoP/Ni_2P@NC.

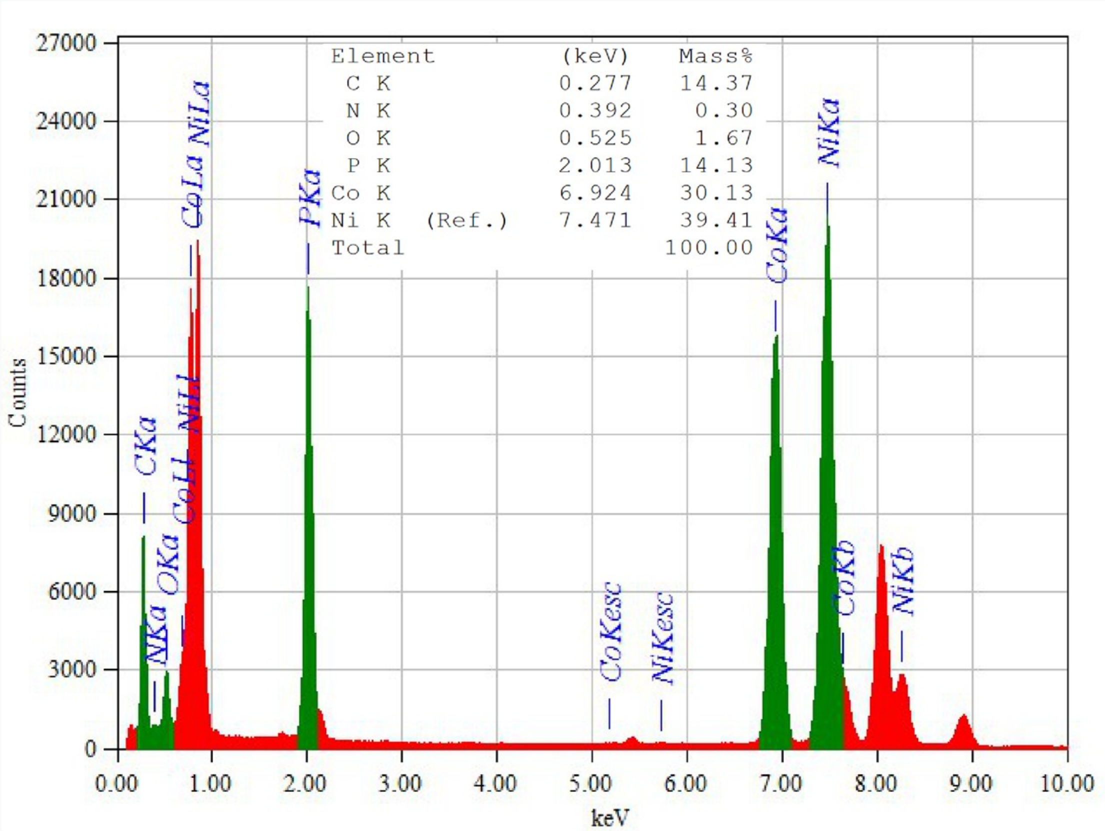

Fig. S3 EDX spectrum of the obtained CoP/Ni_2P@NC.

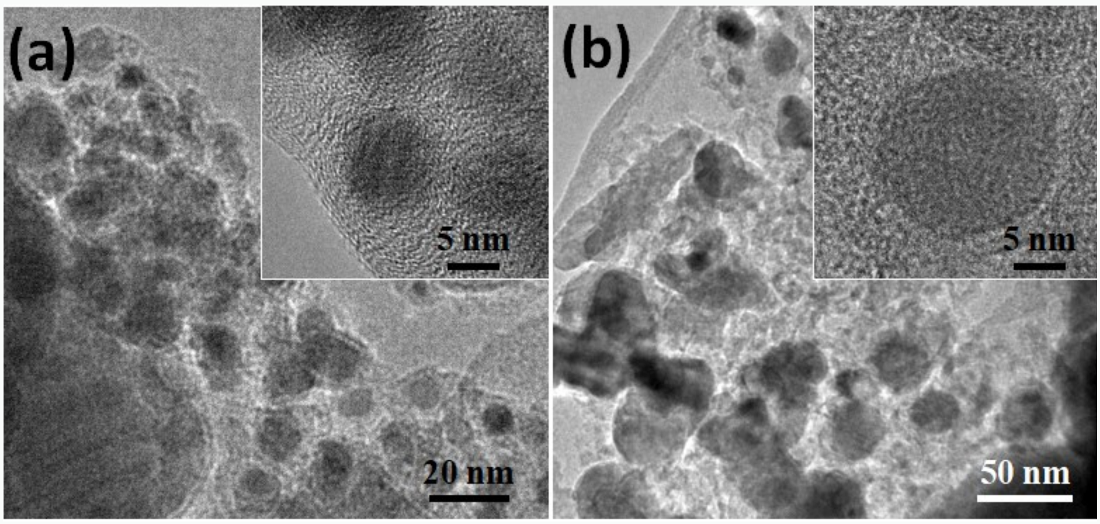

Fig. S4 TEM images of (a) CoP@NC and (b) Ni_2P@NC.

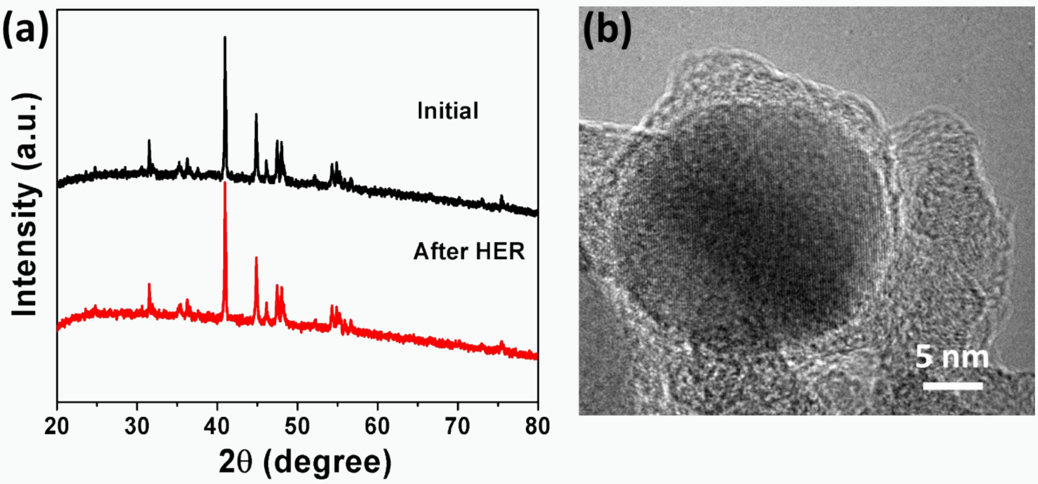

Fig. S5 (a) XRD patterns of CoP/Ni_2P@NC before and after long-term HER durability test in 0.5 M H_2SO_4. (b) HRTEM image of CoP/Ni_2P@NC after long-term HER durability test in 0.5 M H_2SO_4.

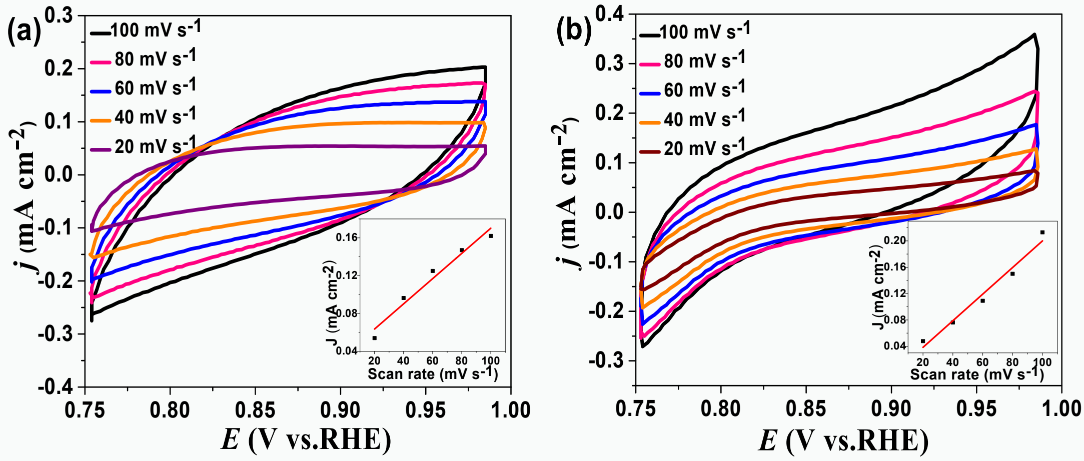

Fig. S6 Cyclic voltammograms of CoP@NC (a) and Ni_2P@NC (b) measured at different scan rates from 20 to 100 mV s^{-1}. Inset in (a, b): Plots of the current density at 0.90 V versus the scan rate.

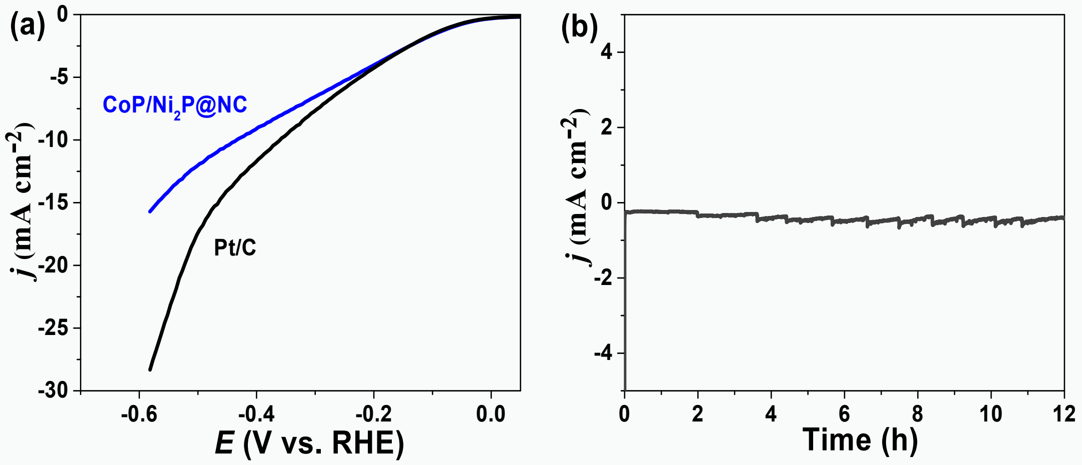

Fig. S7 (a) Polarization curves for Pt/C and CoP/Ni_2P@NC for HER with a scan rate of 2 mV s^{-1}. (b) Chronoamperometry curve of CoP/Ni_2P@NC at a fixed overpotential of -700 mV for 12 h.

Table S1. Comparison of HER performance of some recently reported bimetallic CoNi-based materials in 0.5 M H_2SO_4.

Catalyst	Electrolyte	$E_{\eta=10}$ (mV) VS. RHE	Tafel slop ($mV \cdot dec^{-1}$)	Reference
CoP/Ni_2P@NC	0.5 M H_2SO4	91	62	This work.
CoNiP@NF	0.1M H_2SO4	60	39	1
CoNi@NC	0.5M H_2SO4	142	104	2
CoP/CC	0.5M H_2SO_4	92	58	3
CoP NBAs/Ti	0.5M H_2SO_4	203	40	4
Co_2P/Ti	0.5M H_2SO_4	95	45	5
CoP/CNT	0.5M H_2SO_4	122	54	6
Ni_2P@C	0.5M H_2SO_4	186	64	7

Table S2. Comparison of HER performance of some recently reported bimetallic CoNi-based materials in 1.0 M KOH.

Catalyst	Electrolyte	$E_{\eta=10}$ (mV) VS. RHE	Tafel slop ($mV \cdot dec^{-1}$)	Reference
CoP/Ni_2P@NC	1.0 M KOH	143	62	This work.
CoNiP@NF	1.0 M KOH	155	115	1
NiCoP/NF	1.0 M KOH	32	37	8
$Co_{0.5}Ni_{0.5}P$/NC/NF	1.0 M KOH	90	70.9	9
Ni@Co-Ni-P	1.0 M KOH	52	65.1	10
$CoNi_2S_4$	1.0 M KOH	400 ($E_{\eta=32}$)	85	11
$CoNi_2Se_4$	1.0 M KOH	220	N.A.	12
FeCoNi	1.0 M KOH	149	77	13
Co_xNi_yP	1.0 M KOH	129	52	14

Table S3. Comparison of OER performance of some recently reported non-noble-metal catalysts in 1.0 M KOH.

Catalyst	Electrolyte	$E_{\eta=10}$ (mV) vs. RHE	Tafel slop (mV·dec^{-1})	Reference
CoP/Ni_2P@NC/NF	1.0 M KOH	330	68	This work
NiCoP/NF	1.0 M KOH	280	87	8
$CoNi_2Se_4$	1.0 M KOH	160	72	12
FeCoNi	1.0 M KOH	288	92	13
Co_xNi_yP	1.0 M KOH	245	61	14
Ni_3Se_2/CF	1.0 M KOH	340 ($E_{\eta=50}$)	80	15
CoNiP@LDH	1.0 M KOH	216	45	16
Co-P film	1.0 M KOH	345	47	17
Ni_3N/Ni-foam	1.0 M KOH	~ 399	65	18

Table S4. Comparison of ORR performance of some recently reported non-noble-metal catalysts in 0.1 M KOH.

Catalyst	Electrolyte	Half-cell potential (V vs. RHE)	Limiting current density (mA cm-2)	Reference
CoP/Ni_2P@NC/NF	0.1 M KOH	0.79	4.95	This work
CoO_x@NGCR	0.1 M KOH	0.80	4.90	19
Co/CoN_x/NCNT/C	0.1 M KOH	0.80	3.84	20
Co_9S_8/N, S-CNS	0.1 M KOH	0.80	4.50	21
Co-NC@CoP-NC	0.1 M KOH	0.78	3.74-4.15	22
Co/CoP-HNC	0.1 M KOH	0.83	N.A.	23
Co-Ni(1:1)@NC-900	0.1 M KOH	0.821	N.A.	24
NiO/CoN PINWs	0.1 M KOH	0.68	N.A.	25
$NiCo_2S_4$/N-CNT	0.1 M KOH	0.80	3.2	26
CoP@SNC	0.1 M KOH	0.79	N.A.	27
CoP NCs	0.1 M KOH	0.70	4.5	28
Co_2P@CoNPG-800	0.1 M KOH	0.80	6.68	29

Table S5. The overall water splitting activities of CoP/Ni_2P@NC/NF and the previously reported bifunctional non-noble metal catalysts in 1.0 M KOH.

Catalyst	Electrolyte	$E_{\eta=10}$ (V) vs. RHE	Reference
CoP/Ni_2P@NC/NF	1.0 M KOH	1.60	This work
NiCoP/NF	1.0 M KOH	1.58	8
$CoNi_2Se_4$	1.0 M KOH	1.61	12
FeCoNi	1.0 M KOH	1.687	13
Co_xNi_yP	1.0 M KOH	1.59	14
CoNiP@LDH	1.0 M KOH	1.44	16
$NiCo_2S_4$ NA/CC	1.0 M KOH	1.68	30
CoP-MNA/NF	1.0M KOH	1.62	31
Ni_5P_4 Films	1.0 M KOH	~ 1.7	32

Table S6. The comparisons of some recently reported Co/Ni-based cathodes for Zn-air battery in alkaline environment.

Air catalyst used	Peak power density ($mW\ cm^{-2}$)	Cycling tests	Reference
CoP/Ni_2P@NC/NF	77	20 min/cycle for 100 cycles; 33.3 h	This work
NiO/CoN PINWs	79.6	10 min/cycle for 50 cycles; 8.3 h	25
CoP@SNC	N.A.	600 s/cycle for 180 cycles; 30 h	27
$NiO/Ni(OH)_2$	N.A.	70 min/cycle for 70 cycles; 82 h	33
NPMCs	55	N.A.	34
N-GRW	65	N.A.	35
MnO_2/Co_3O_4	33	7 min/cycle for 60 cycles; 7 h	36
Co@Co_3O_4@NC-900	~ 64	120 min/cycle for 100 cycles; 200 h	37
Co-Ni-S@NSPC	51.6	20 min/cycle for 180; 60 h	38
200-CNTs-Co/NC	83.1	N.A.	39
$ZnCo_2O_4$/N-CNT	82.3	20 min/cycle for 17 cycles; 5.67 h	40

References

1. A. Han, H. Chen, H. Zhang, Z. Sun and P. Du, *J. Mater. Chem. A*, 2016, **4**, 10195-10202.
2. J. Deng, P. Ren, D. Deng and X. Bao, *Angew. Chem. Int. Edit.,* 2015, **54**, 2100-2104.
3. X.-y. Yan, S. Devaramani, J. Chen, D.-l. Shan, D.-d. Qin, Q. Ma and X.-q. Lu, *New J. Chem.,* 2017, **41**, 2436-2442.
4. Z. Niu, J. Jiang and L. Ai, *Electrochem. Commun.,* 2015, **56**, 56-60.
5. J. F. Callejas, C. G. Read, E. J. Popczun, J. M. McEnaney and R. E. Schaak, *Chem. Mater.,* 2015, **27**, 3769-3774.
6. Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri and X. Sun, *Angew. Chem. Int. Edit.,* 2014, **53**, 6710-6714.
7. S. He, S. He, F. Gao, X. Bo, Q. Wang, X. Chen, J. Duan and C. Zhao, *Appl. Surf. Sci.,* 2018, **457**, 933-941.
8. H. Liang, A. N. Gandi, D. H. Anjum, X. Wang, U. Schwingenschlögl and H. N. Alshareef, *Nano Lett.,* 2016, **16**, 7718-7725.
9. C. Jiao, M. Hassan, X. Bo and M. Zhou, *J. Alloy. Compd.,* 2018, **764**, 88-95.
10. 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.
11. D. Wang, X. Zhang, Z. Du, Z. Mo, Y. Wu, Q. Yang, Y. Zhang and Z. Wu,*Int. J. Hydrogen Energ.,* 2017, **42**, 3043-3050.
12. B. GolrokháAmin, *Chem. Commun.* 2017, **53**, 5412-5415.
13. Y. Yang, Z. Lin, S. Gao, J. Su, Z. Lun, G. Xia, J. Chen, R. Zhang and Q. Chen, *ACS Catal.*, 2016, **7**, 469-479.
14. L. Yan, L. Cao, P. Dai, X. Gu, D. Liu, L. Li, Y. Wang and X. Zhao, *Adv. Funct. Mater*, 2017, **27**, 1703455.
15. J. Shi, J. Hu, Y. Luo, X. Sun and A. M. Asiri, *Catal. Sci. Technol.,* 2015, **5**, 4954-4958.
16. L. Zhou, S. Jiang, Y. Liu, M. Shao, M. Wei and X. Duan, *ACS Appl. Energy Mate.,* 2018, **1**, 623-631.
17. N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem. Int. Edit.,* 2015, **127**, 6349-6352.
18. M. Shalom, D. Ressnig, X. Yang, G. Clavel, T. P. Fellinger and M. Antonietti, *J. Mate. Chem. A*, 2015, **3**, 8171-8177.
19. C.-C. Weng, J.-T. Ren, Z.-P. Hu and Z.-Y. Yuan, *ACS Sustain. Chem. Eng.,* 2018, **6**, 15811-15821.
20. H. Zhong, Y. Luo, S. He, P. Tang, D. Li, N. Alonso-Vante and Y. Feng, *ACS Appl. Mater. Inter.,* 2017, **9**, 2541-2549.
21. C. Wu, Y. Zhang, D. Dong, H. Xie and J. Li, *Nanoscale*, 2017, **9**, 12432-12440.
22. X. Li, Q. Jiang, S. Dou, L. Deng, J. Huo and S. Wang, *J. Mater. Chem. A*, 2016, **4**, 15836-15840.
23. Y. Hao, Y. Xu, W. Liu and X. Sun, *Mater. Horiz.,* 2018, **5**, 108-115.
24. J. Long, R. Li and X. Gou, *Catal. Commun.,* 2017, **95**, 31-35.
25. J. Yin, Y. Li, F. Lv, Q. Fan, Y.-Q. Zhao, Q. Zhang, W. Wang, F. Cheng, P. Xi and S. Guo, *ACS Nano*, 2017, **11**, 2275-2283.
26. X. Han, X. Wu, C. Zhong, Y. Deng, N. Zhao and W. Hu, *Nano Energy*, 2017, **31**, 541-550.
27. T. Meng, Y.-N. Hao, L. Zheng and M. Cao, *Nanoscale*, 2018, **10**, 14613-14626.
28. H. Yang, Y. Zhang, F. Hu and Q. Wang, *Nano Lett.,* 2015, **15**, 7616-7620.
29. H. Jiang, C. Li, H. Shen, Y. Liu, W. Li and J. Li, *Electrochim. Acta*, 2017, **231**, 344-353.
30. D. Liu, Q. Lu, Y. Luo, X. Sun and A. M. Asiri, *Nanoscale*, 2015, **7**, 15122-15126.

31. Y. P. Zhu, Y. P. Liu, T. Z. Ren and Z. Y. Yuan, *Adv. Funct. Mater.*, 2015, **25**, 7337-7347.
32. M. Ledendecker, S. Krick Calderón, C. Papp, H. P. Steinrück, M. Antonietti and M. Shalom, *Angew. Chem. Int. Edit.*, 2015, **54**, 12361-12365.
33. D. U. Lee, J. Fu, M. G. Park, H. Liu, A. Ghorbani Kashkooli and Z. Chen, *Nano Lett.*, 2016, **16**, 1794-1802.
34. J. Zhang, Z. Zhao, Z. Xia and L. Dai, *Nat. Nanotechnol.*, 2015, **10**, 444.
35. H. B. Yang, J. Miao, S.-F. Hung, J. Chen, H. B. Tao, X. Wang, L. Zhang, R. Chen, J. Gao and H. M. Chen, *Sci. Adv.*, 2016, **2**, e1501122.
36. G. Du, X. Liu, Y. Zong, T. A. Hor, A. Yu and Z. Liu, *Nanoscale*, 2013, **5**, 4657-4661.
37. Z. Guo, F. Wang, Y. Xia, J. Li, A. G. Tamirat, Y. Liu, L. Wang, Y. Wang and Y. Xia, *J. Mater. Chem. A*, 2018, **6**, 1443-1453.
38. W. Fang, H. Hu, T. Jiang, G. Li and M. Wu, *Carbon*, 2019, **146**, 476-485.
39. S. Liu, I. S. Amiinu, X. Liu, J. Zhang, M. Bao, T. Meng and S. Mu, *Chem. Eng. J.*, 2018, **342**, 163-170.
40. Z. Q. Liu, H. Cheng, N. Li, T. Y. Ma and Y. Z. Su, *Adv, Mater.*, 2016, **28**, 3777-3784.