Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Highly Active Bifunctional Oxygen Electrocatalysts Derived from Nickel- or Cobalt-Phytic Acid Xerogel for Zinc-Air Batteries

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Calculation of Electron Transfer Number (n) and % HO_2^- for Oxygen Reduction Reaction

On the basis of rotating disk electrode (RDE) measurements, the electron transfer numbers (n) per O_2 involved in ORR were calculated from the slopes of the Koutecky-Levich plots according to the following equations[1]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k} \qquad (1)$$

where j is the measured current density, j_k and j_l are the kinetic and diffusion-limiting current densities, ω is the rotating rate of electrode (rpm). B is determined from the slope of the Koutecky-Levich plots according to the Levich equation.

$$B = 0.2nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6} \qquad (2)$$

where n is electron transfer number per oxygen molecule, F is Faraday constant (96485 C mol^{-1}), C_{O2} is the bulk concentration of O_2 (1.2×10^{-6} mol cm^{-3}), ν is the kinetic viscosity of electrolyte (0.01 cm^2 S^{-1}). D_{O2} is the diffusion coefficient of O_2 in 0.1 M KOH and 0.1 M $HClO_4$ (1.9×10^{-5} cm^2 S^{-1}).

Hydrogen peroxide yields and the electron transfer number (n) were calculated by the following equations:

$$\%\left(HO_2^-\right) = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}} \qquad (3)$$

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}} \qquad (4)$$

Where I_d is disk current, I_r is ring current, the collection efficiency (N) was determined to be 0.40 by using 10 mM $K_3[Fe(CN)_6]$.

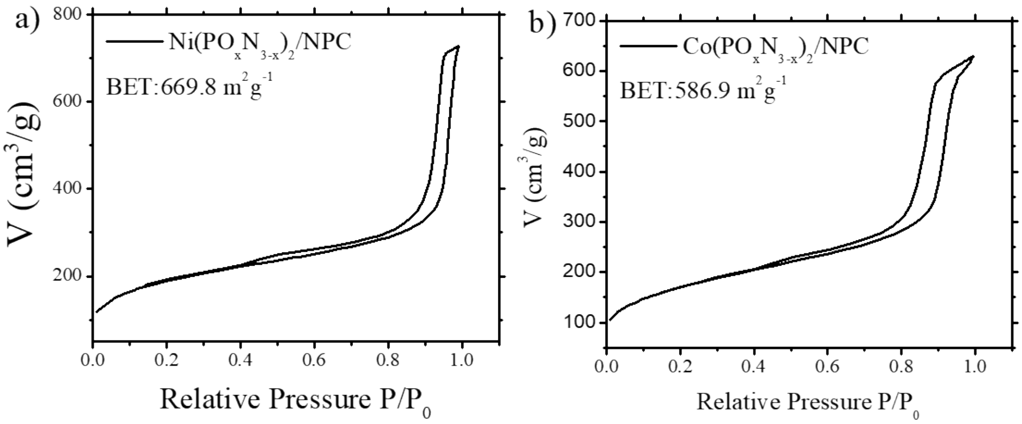

Figure S1. N_2 adsorption and desorption isotherms of Ni (PO_xN_{3-x}) $_2$/NPC a) and Co (PO_xN_{3-x}) $_2$/NPC b).

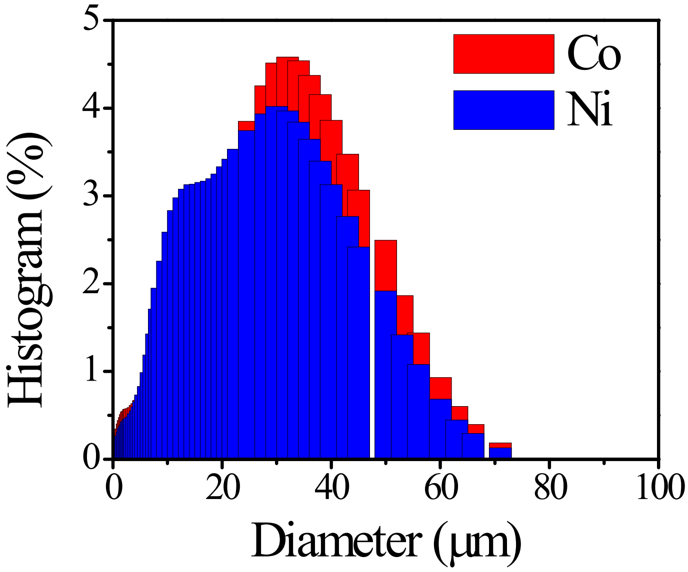

Figure S2. The pore size distribution of Ni $(PO_xN_{3-x})_2$/NPC a) and Co $(PO_xN_{3-x})_2$/NPC

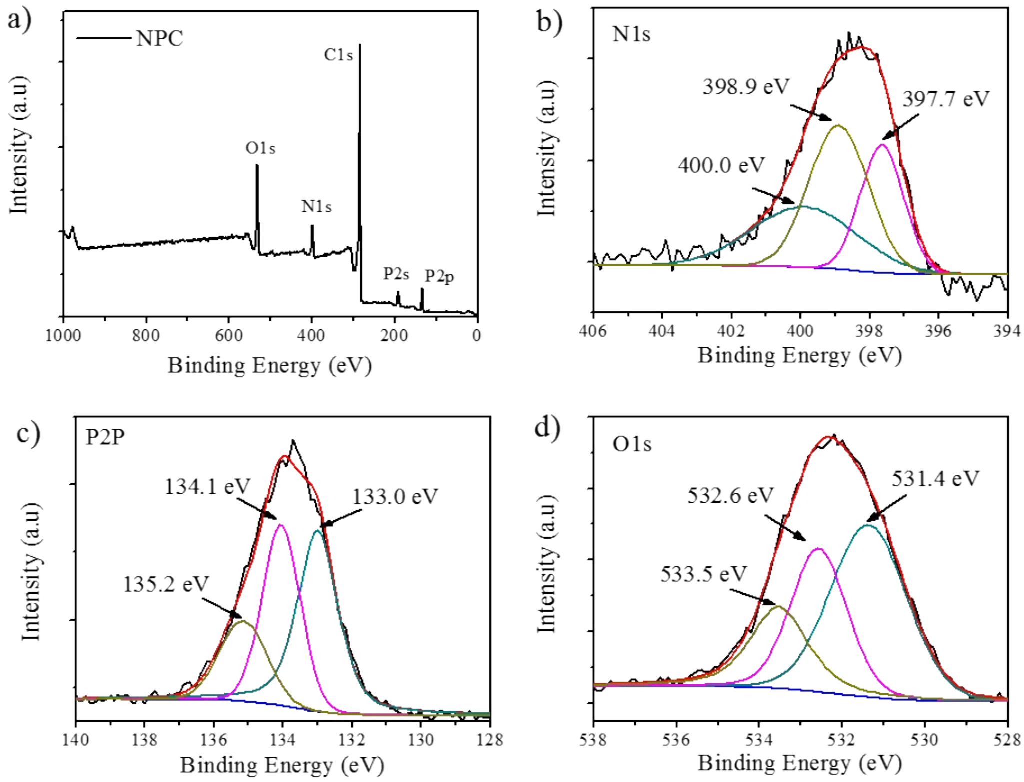

Figure S3. XPS survey spectrum of NPC a) and corresponding high resolution N 1s b), P 2p c) and O 1s d).

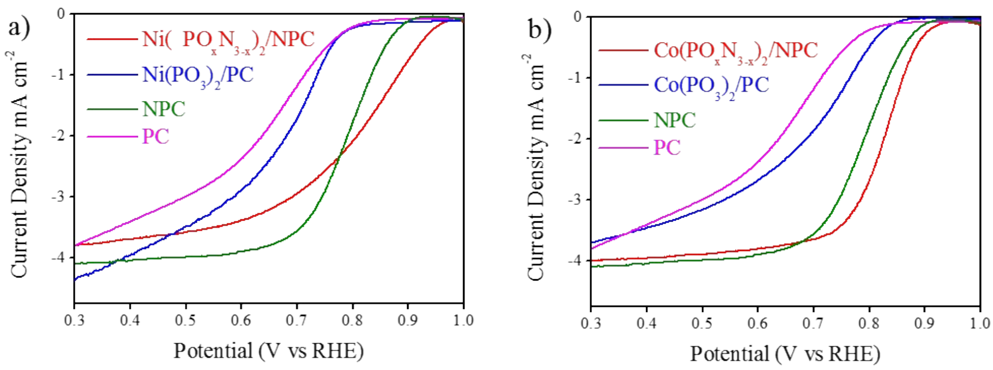

Figure S4. LSVs of catalysts before and after NH_3 treatment.

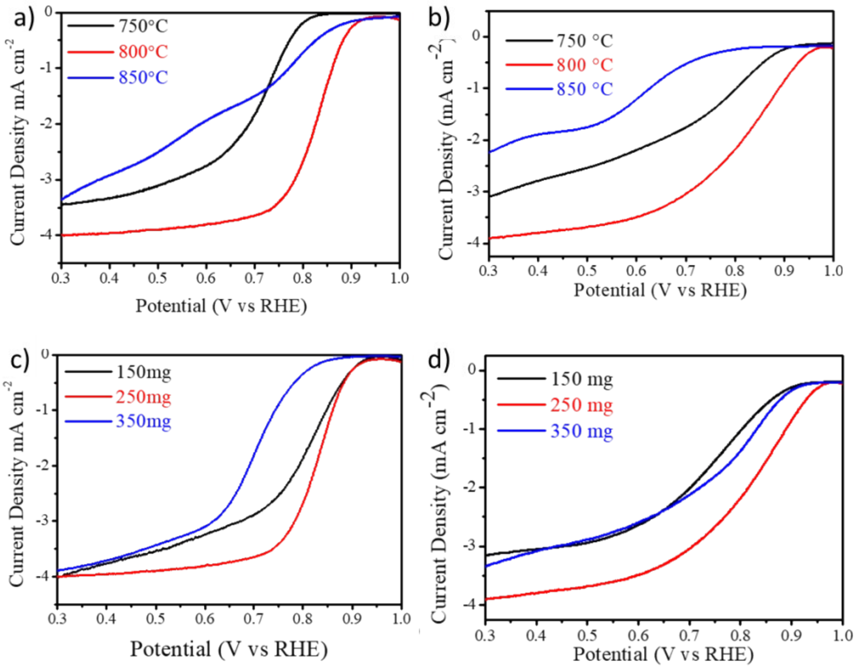

Figure S5. LSVs of Ni $(PO_xN_{3-x})_2$/NPC and Co $(PO_xN_{3-x})_2$/NPC with different pyrolysis treatment and metal contents.

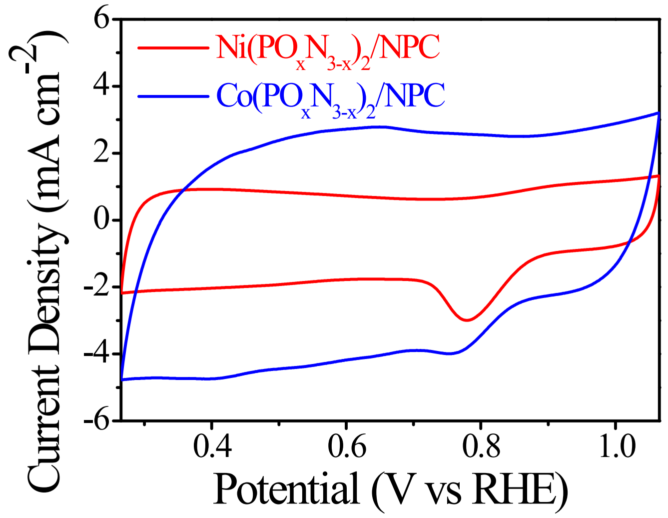

Figure S6. The cyclic voltammetry curves of Ni $(PO_xN_{3-x})_2$/NPC and Co $(PO_xN_{3-x})_2$/NPC for ORR at scanning rate of 5 mV/s in a 0.1 M KOH solution.

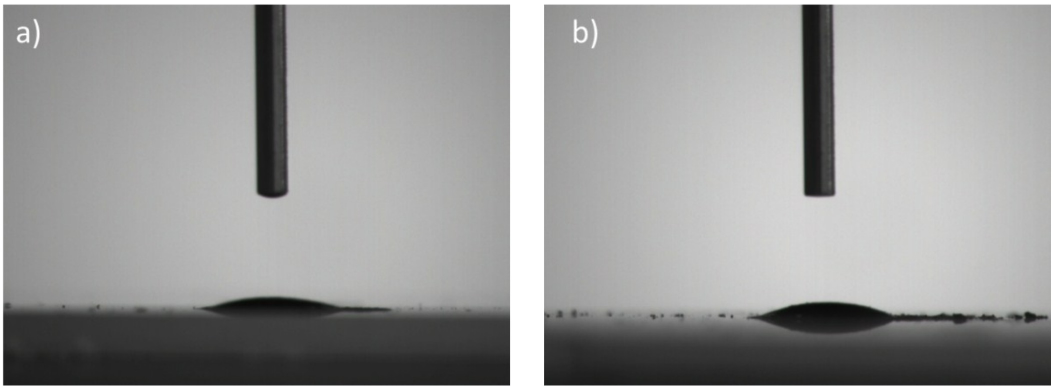

Figure S7. Snapshots for Ni $(PO_xN_{3-x})_2$/NPC a) and Co $(PO_xN_{3-x})_2$/NPC b).

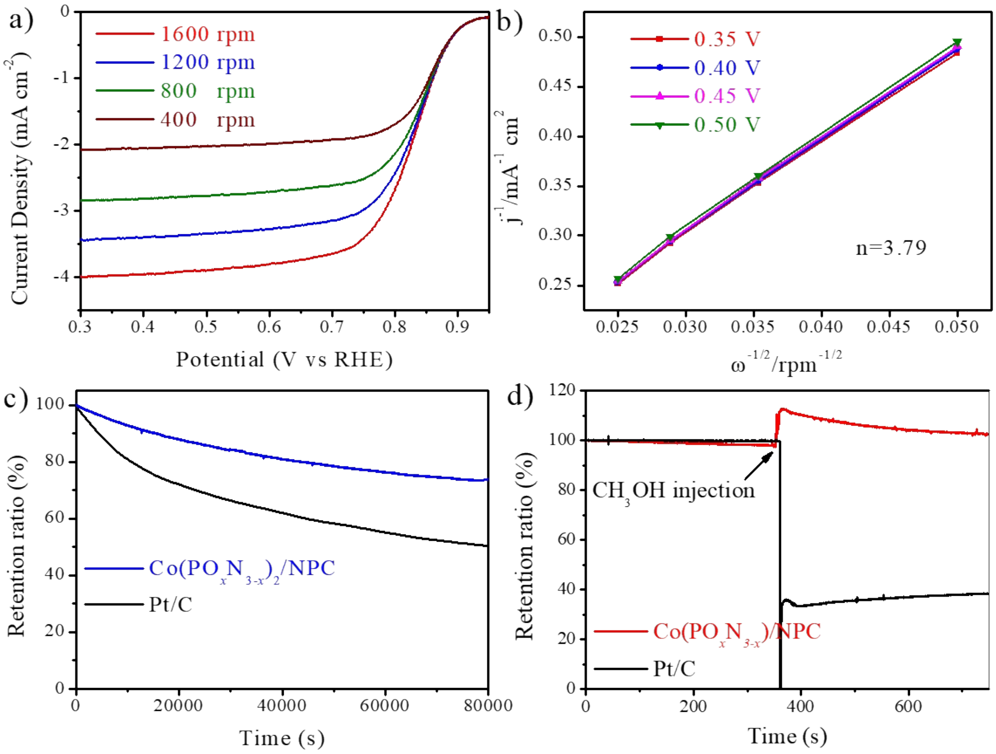

Figure S8. ORR activity in 0.1 M KOH electrolyte solution: a) LSVs of Ni $(PO_xN_{3\text{-}x})_2$/NPC at rotating speeds of 400, 800, 1200, 1600 rpm. b) K-L plots at different potentials. c) Chronoamperometric curves of Co $(PO_xN_{3\text{-}x})_2$/NPC and Pt/C at 0.6 V versus RHE in O_2-saturated 0.1 M KOH electrolyte. d) The stability test for Co $(PO_xN_{3\text{-}x})_2$/NPC and Pt/C with the adding of 8.5mL of Methanol into 70 mL of 0.1 M KOH.

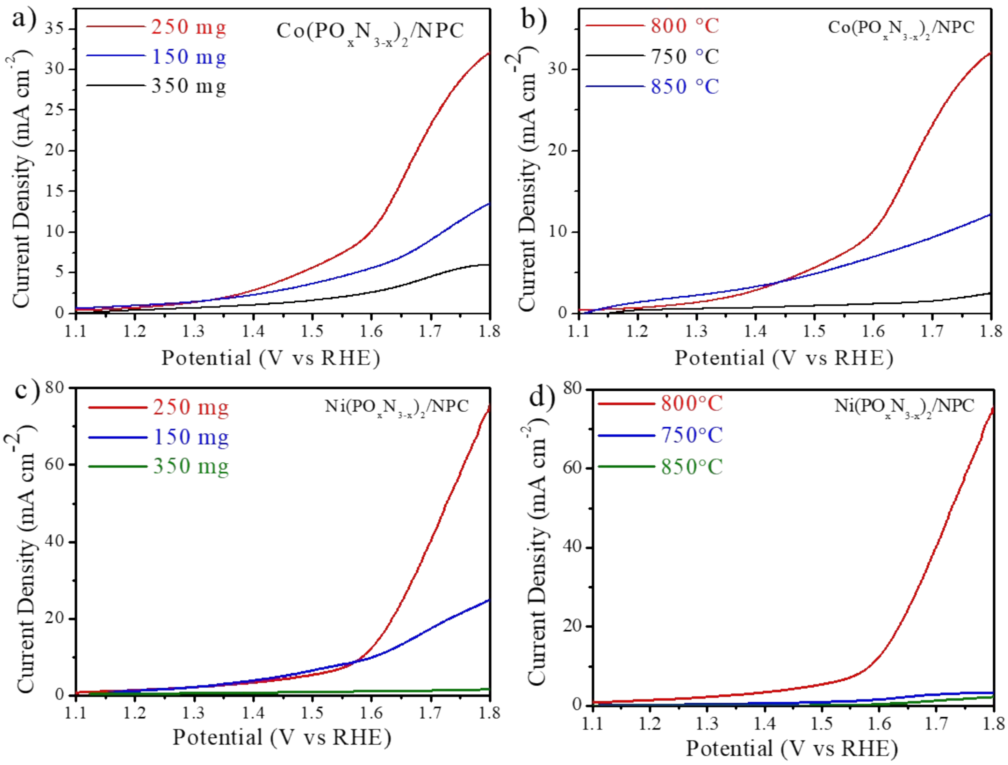

Figure S9. LSVs of Ni (PO$_x$N$_{3-x}$) $_2$/NPC and Co (PO$_x$N$_{3-x}$) $_2$/NPC with different pyrolysis treatment and metal contents for OER.

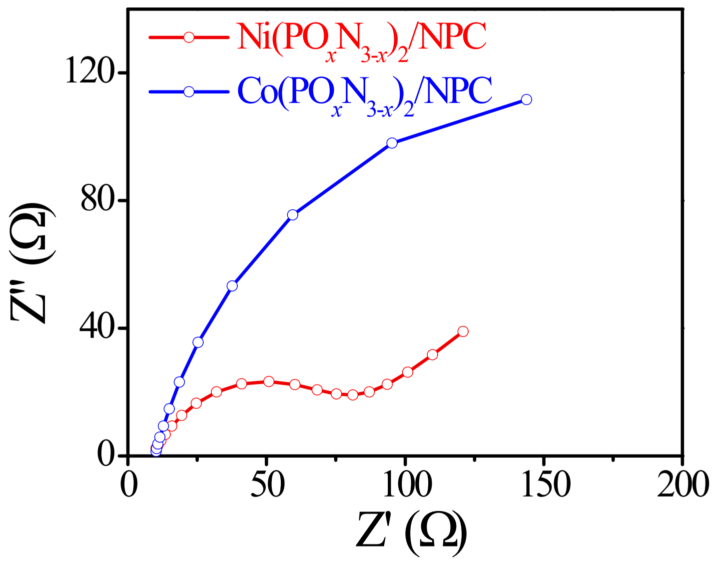

Figure S10. Nyquist plots of electrochemical impedance spectra (EIS) of Ni $(PO_xN_{3-x})_2$/NPC and Co $(PO_xN_{3-x})_2$/NPC in 1M KOH.

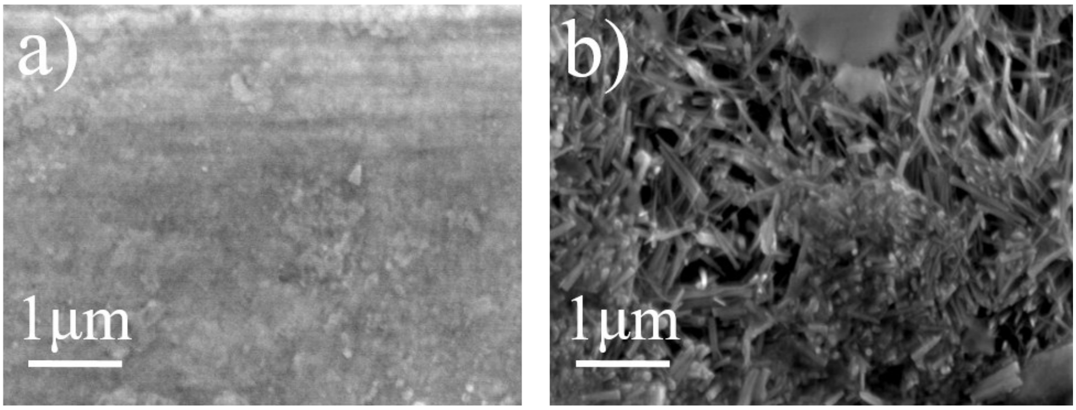

Figure S11. The SEM of Zn electrode. a) Before zinc air battery testing. b）After zinc air battery testing.

Table S1. Comparison of ORR performance of Ni $(PO_xN_{3-x})_2$/NPC and Co $(PO_xN_{3-x})_2$/NPC with recently reported catalysts in 0.1 M KOH solution

Catalysts	Catalyst Loading (mg cm^{-2})	$E_{1/2}$ (V vs. RHE)	Onset potentials (V vs. RHE)	Ref.
Ni $(PO_xN_{3-x})_2$/NPC	0.23	0.83	1.02	This work
S-GNS/$NiCo_2S_4$	0.42	0.88	/	[2]
Co/CoO_x	0.50	0.76	0.95	[3]
Co-N,B-CSs	0.10	0.83	0.89	[4]
Co-Nx/C NRA	/	0.877	/	[5]
Co@C-800	0.14	0.82	0.92	[6]
Co_3O_4/N-rGO	0.128	0.79	0.90	[7]
NC-Co_3O_4-90	1.2	0.87	0.91	[8]
NCNT/CoO-NiO-NiCo	0.21	0.83	1.0	[9]
NiFe-LDH/Co,N-CNF	0.12	0.79	0.893	[10]
Ni_3Fe/N-C sheets	0.13	/	0.90	[11]
CoP NCs	0.2	0.858	0.92	[12]
C-MOF-C2-900	0.2	0.817	/	[13]
CoS NWs@NSC-2	0.2113	0.84	0.93	[14]
NiO/CoN PINWs	0.2	0.68	0.89	[15]
CoOx NPs/BNG	/	0.805	0.95	[16]

Table S2. The performance of rechargeable zinc-air batteries of Ni $(PO_xN_{3-x})_2$/NPC, Co $(PO_xN_{3-x})_2$/NPC and other recently reported catalysts in 6 M KOH

Catalysts	**Catalyst loading (mg cm^{-2})**	**Specific capacity (mAh g^{-1})**	**Energy density (Wh Kg_{Zn}^{-1})**	**Ref.**
Ni $(PO_xN_{3-x})_2$/NPC	0.53	735@20	894@20	This work
Co $(PO_xN_{3-x})_2$/NPC	0.53	700@20	836@20	
Co-N*x*/C NRA	/	/	853@20	[5]
NGM-Co	0.50	750@20	840@20	[17]
CoO/N-CNT+NiFe LDH	1.00	~570@10	>700@10	[18]
NCNT/CoO-NiO-NiCo	0.53	545@20	615@20	[9]
Ni_3Fe/N-C sheets	/	528@10	634@10	[11]
C-MOF-C2-900	0.50	741@10	/	[13]
NiO/CoN PINWs	/	648@10	836@10	[15]
$ZnCo_2O_4$/N-CNT	2.00	428.47@10	595.57@10	[19]
CuS/NiS_2	2.00	775@5	695@25	[20]
N-GCNT/FeCo-3	2.00	872.2@100	1015.2@5	[21]

References

1 R. Zhou, Y. Zheng, M. Jaroniec and S.-Z. Qiao, *ACS Catal.*, 2016, **6**, 4720-4728.

2 W. Liu, J. Zhang, Z. Bai, G. Jiang, M. Li, K. Feng, L. Yang, Y. Ding, T. Yu, Z. Chen and A. Yu, *Adv. Funct. Mater.*, 2018, **28**, 1706675.

3 B. Hua, M. Li, Y.-F. Sun, Y.-Q. Zhang, N. Yan, J. Chen, T. Thundat, J. Li and J.-L. Luo, *Nano Energy*, 2017, **32**, 247-254.

4 Y. Guo, P. Yuan, J. Zhang, Y. Hu, I. S. Amiinu, X. Wang, J. Zhou, H. Xia, Z. Song, Q. Xu and S. Mu, *ACS Nano*, 2018, **12**, 1894-1901.

5 I. S. Amiinu, X. Liu, Z. Pu, W. Li, Q. Li, J. Zhang, H. Tang, H. Zhang and S. Mu, *Adv. Funct. Mater.*, 2018, **28**, 1704638.

6 B. Chen, G. Ma, Y. Zhu and Y. Xia, *Sci. Rep.*, 2017, **7**, 5266.

7 Y. Li, C. Zhong, J. Liu, X. Zeng, S. Qu, X. Han, Y. Deng, W. Hu and J. Lu, *Adv. Mater.*, 2018, **30**, 1703657.

8 C. Guan, A. Sumboja, H. Wu, W. Ren, X. Liu, H. Zhang, Z. Liu, C. Cheng, S. J. Pennycook and J. Wang, *Adv. Mater.*, 2017, **29**, 1704117.

9 X. Liu, M. Park, M. G. Kim, S. Gupta, G. Wu and J. Cho, *Angew. Chem. Int. Ed. Engl.*, 2015, **54**, 9654-9658.

10 Q. Wang, L. Shang, R. Shi, X. Zhang, Y. Zhao, G. I. N. Waterhouse, L.-Z. Wu, C.-H. Tung and T. Zhang, *Adv. Energy Mater.*, 2017, **7**, 1700467.

11 G. Fu, Z. Cui, Y. Chen, Y. Li, Y. Tang and J. B. Goodenough, *Adv. Energy Mater.*, 2017, **7**, 1601172.

12 H. Li, Q. Li, P. Wen, T. B. Williams, S. Adhikari, C. Dun, C. Lu, D. Itanze, L. Jiang, D. L. Carroll, G. L. Donati, P. M. Lundin, Y. Qiu and S. M. Geyer, *Adv. Mater.*, 2018, **30**, 1705796.

13 M. Zhang, Q. Dai, H. Zheng, M. Chen and L. Dai, *Adv. Mater.*, 2018, **30**, 1705431.

14 C. Han, Q. Li, D. Wang, Q. Lu, Z. Xing and X. Yang, *Small*, 2018, **14**, 1703642.

15 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.

16 Y. Tong, P. Chen, T. Zhou, K. Xu, W. Chu, C. Wu and Y. Xie, *Angew. Chem. Int. Ed. Engl.*, 2017, **56**, 7121-7125.

17 C. Tang, B. Wang, H. F. Wang and Q. Zhang, *Adv. Mater.*, 2017, **29**, 1703185.

18 Y. Li, M. Gong, Y. Liang, J. Feng, J. E. Kim, H. Wang, G. Hong, B. Zhang and H. Dai, *Nat. Commun.*, 2013, **4**, 1805.

19 Z. Q. Liu, H. Cheng, N. Li, T. Y. Ma and Y. Z. Su, *Adv. Mater.*, 2016, **28**, 3777-3784.

20 L. An, Y. Li, M. Luo, J. Yin, Y.-Q. Zhao, C. Xu, F. Cheng, Y. Yang, P. Xi and S. Guo, *Adv. Funct. Mater.*, 2017, **27**, 1703779.

21 C.-Y. Su, H. Cheng, W. Li, Z.-Q. Liu, N. Li, Z. Hou, F.-Q. Bai, H.-X. Zhang and T.-Y. Ma, *Adv. Energy*

Mater., 2017, **7**, 1602420.