Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Electronic Reconfiguration of Co_2P Induced by Cu Doping for Enhancing Oxygen Reduction Reaction Activity in Zinc–Air Batteries

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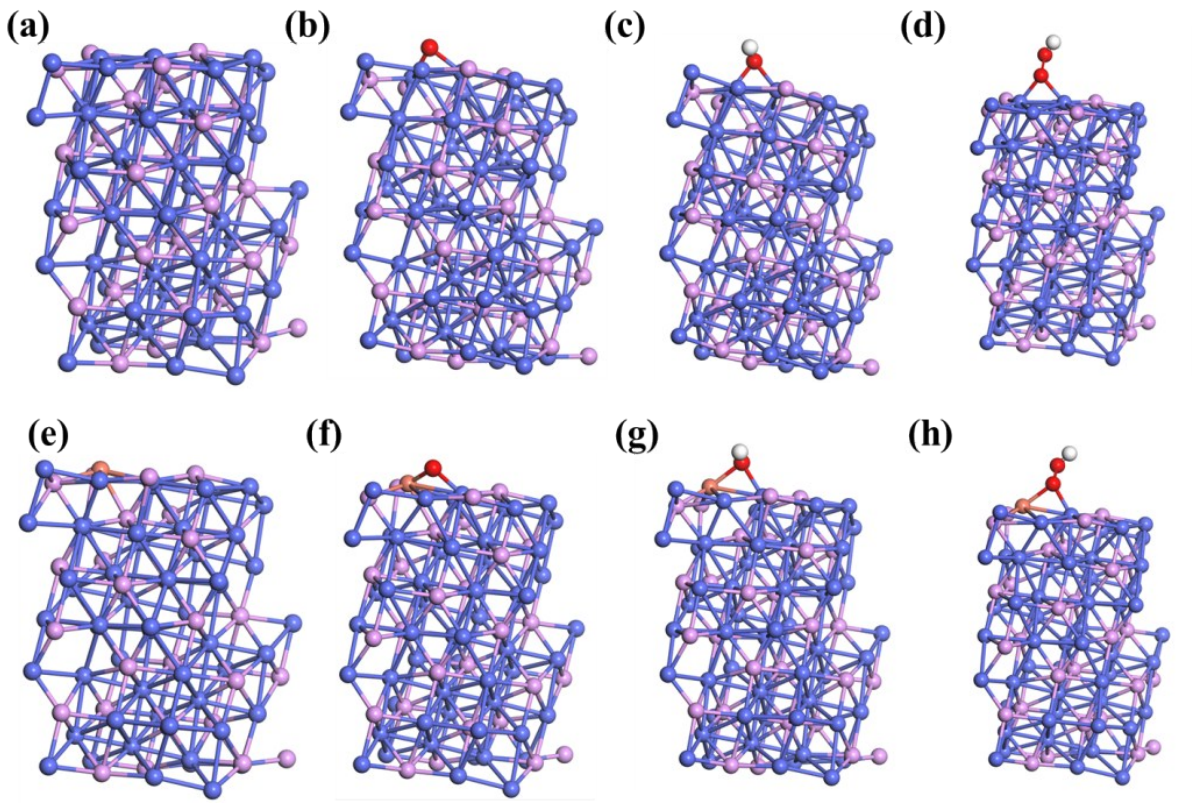

Fig. S1. Side views of atomic configurations for ORR intermediate states: a-d) Co_2P, e-h) Cu-Co_2P. (blue: Co, pink: P, red: O, white: H, brown: Cu).

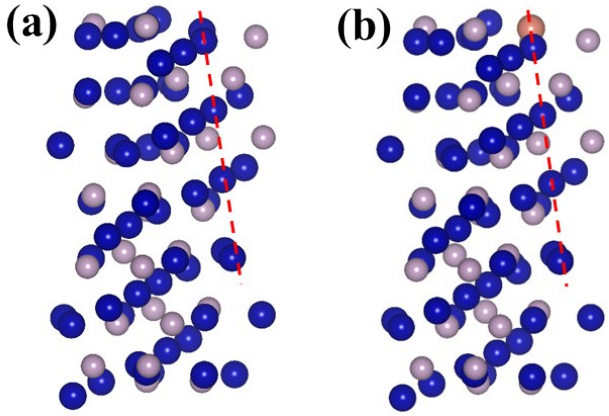

Fig. S2. Structure of (a) Co_2P and (b) Cu-Co_2P . The inset cross section denotes the plane used to calculate the difference charge density in Fig. **1c,d.**

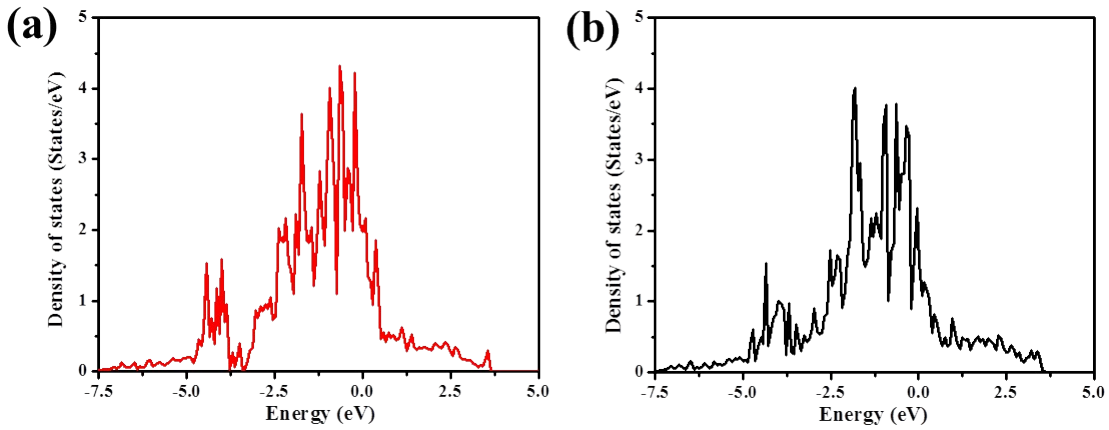

Fig. S3. Density of states of a) Co_2P and b) Cu-Co_2P.

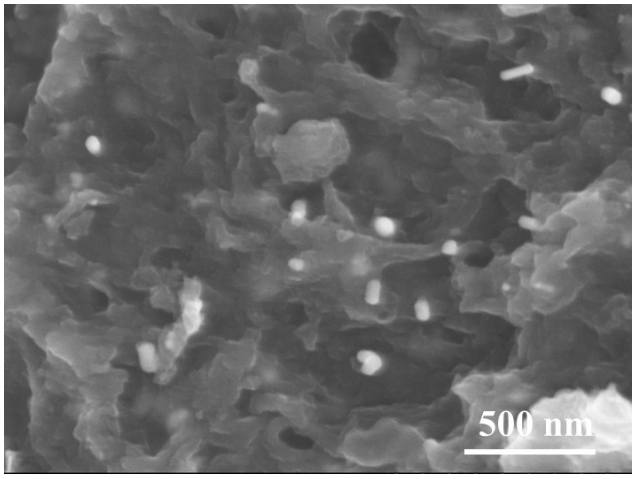

Fig. S4. SEM image of 7.1%Cu-Co_2P@NPC-aqueous. Polymerization occurred by adding aniline into the aqueous directly instead of interface polymerization.

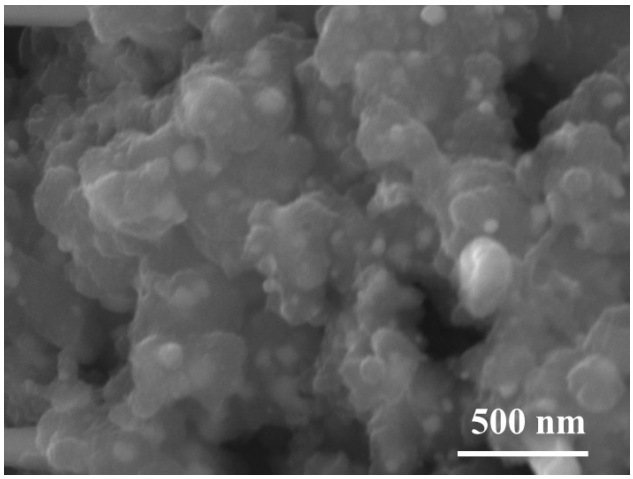

Fig. S5. SEM image of 7.1%Cu-Co_2P@NPC. Polymerization occurred without adding GO into the aqueous.

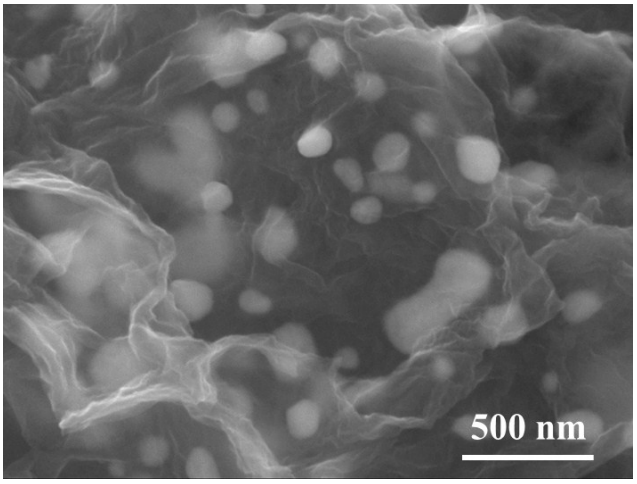

Fig. S6. SEM image of Cu-Co_2P@2D-PG. Sintered 7.1%Cu-Co_2P anchored on P doped rGO.

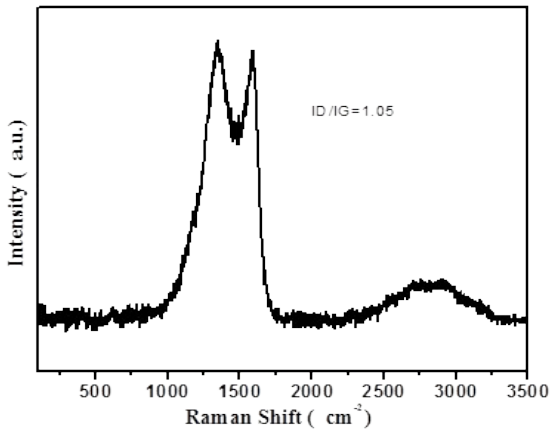

Fig. S7. Raman spectrum of 7.1%Cu-Co_2P@2D-NPC.

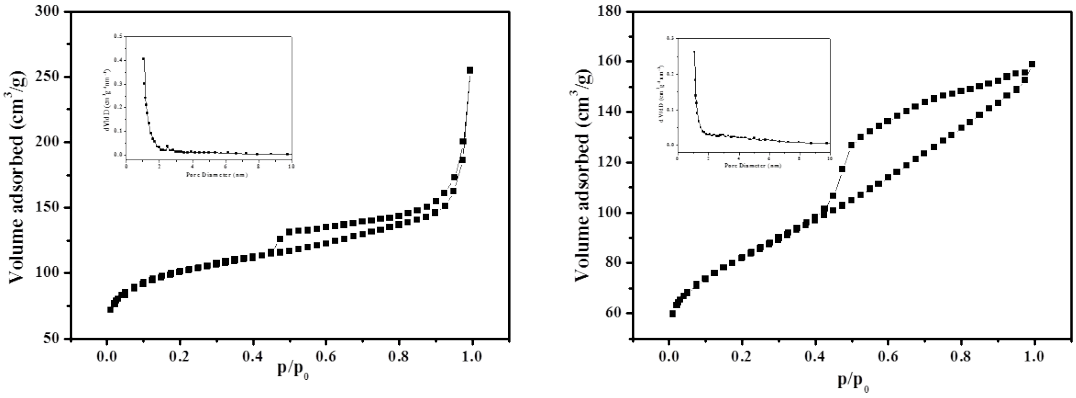

Fig. S8. BET specific surface area and pore size distribution (insert) of (a) 7.1% Cu-Co_2P @2D-NPC and (b) 7.1%Cu-Co_2P@NPC-aqueous.

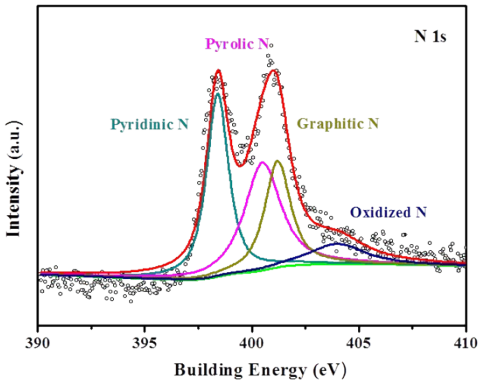

Fig. S9. High-resolution XPS spectrum of N 1s in the 7.1%Cu-Co_2P@2D-NPC.

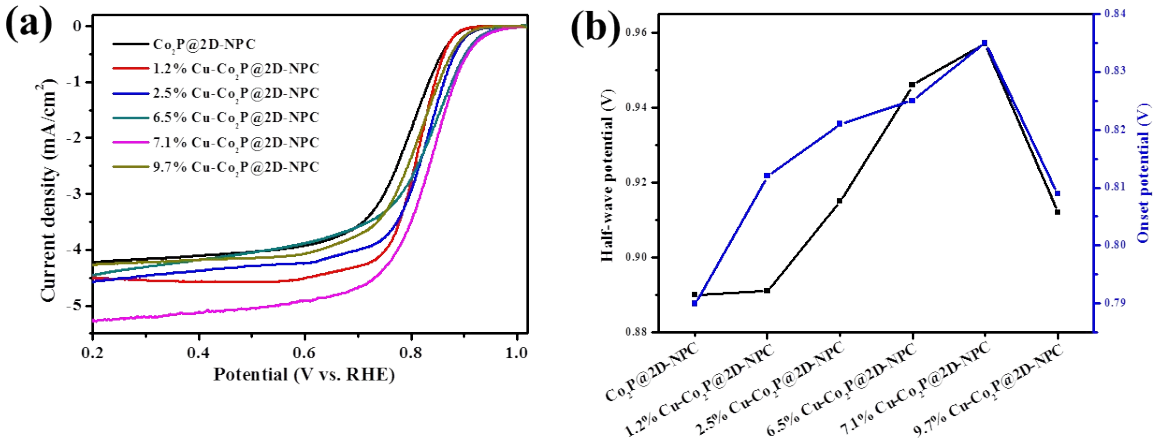

Fig. S10. The performance of Cu-Co_2P@2D-NPC with different Cu doping ratio. (a) LSV plot, (b) onset potential and half-wave potential.

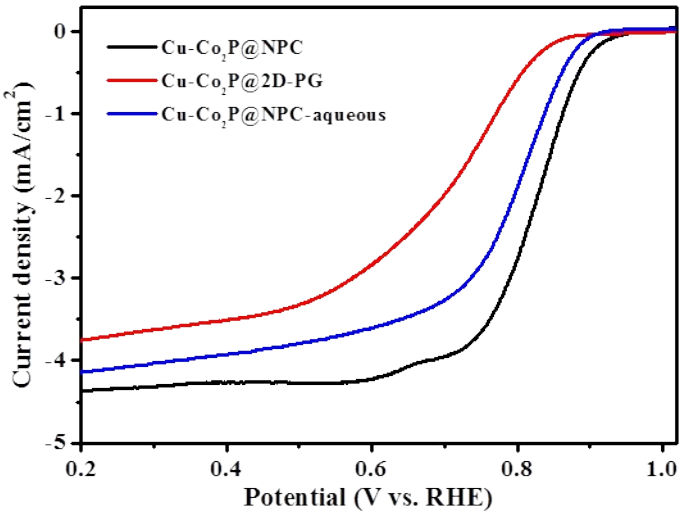

Fig. S11. The LSV plots of Cu-Co_2P@NPC-aqueous, Cu-Co_2P@NPC, and Cu-Co_2P@2D-PG.

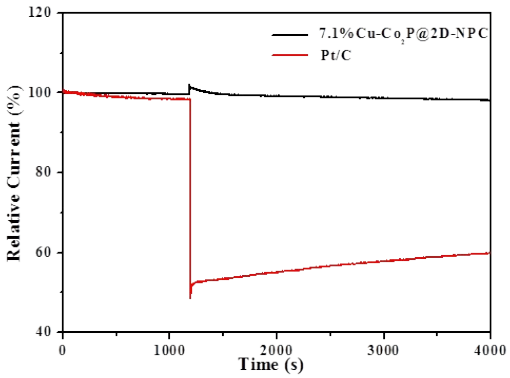

Fig. S12. Tolerance toward the methanol of the 7.1%Cu-Co_2P@2D-NPC and Pt/C. Methanol was added at 1200 s.

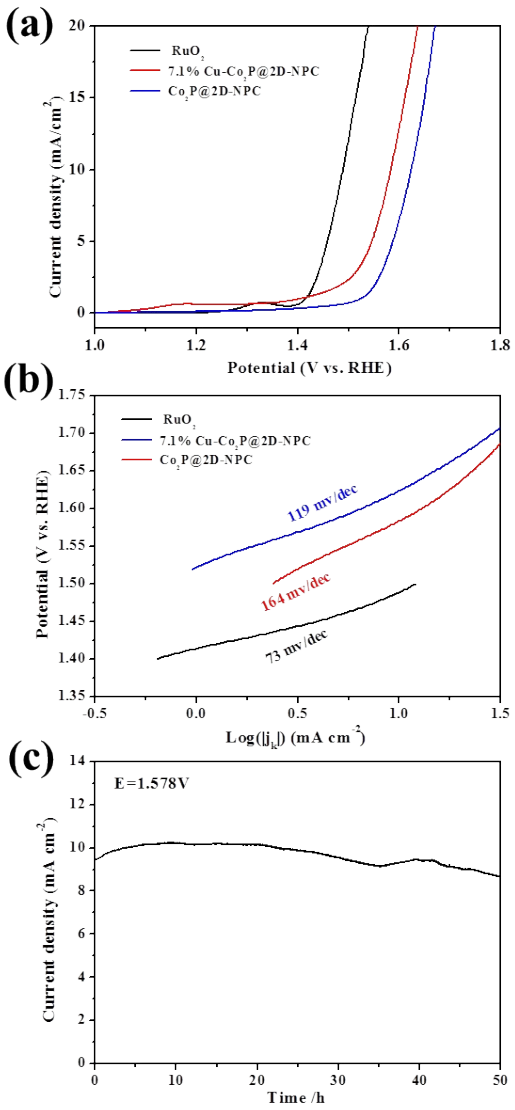

Fig. S13. (a) OER polarization curves, (b) Tafel plots determined from (a), (c) i-t curves of different catalysts in O_2-saturated 0.1 M KOH.

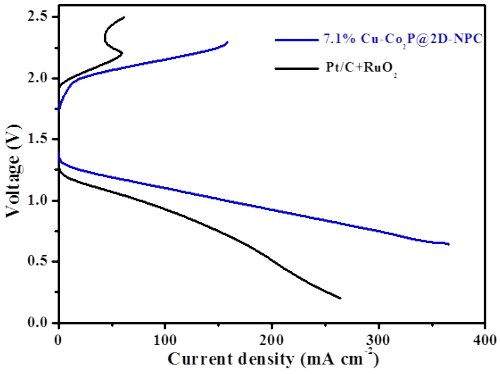

Fig. S14. Discharging and charging polarization curves of ZAB based on the 7.1% Cu-Co_2P@2D-NPC and Pt/C+RuO_2.

Table S1. The atom percentage of Cu in Cu-Co_2P@2D-NPC measured by ICP-OES

	1#	2#	3#	4#	5#
Feed（%）	1	3	6	7.5	10
ICP-OES（%）	1.2	2.5	6.5	7.1	9.7

Table S2. Comparison of some Co-based ORR electrocatalysts in 0.1 M KOH solution

Catalyst	Loading Mass (mg cm^{-2})	E_{onset} (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	J (mA cm^{-2})	reference
Co−N/CNFs	0.1	0.92	0.82	5.2	ACS Catal. 2017, 7, 6864−6871
Co_2P@CoNPG-900	2	0.90	0.81	6.68	Electrochimica Acta 231 (2017) 344–353
Co-CoO/N-rGO	0.21	0.88	0.78	5.6	Adv. Funct. Mater. 2015, 25, 5799
Cu_3P@NPPC-650	0.2		0.78	5.57	Adv. Mater. 2017, 1703711
Co/CoO_x-perovskite nanofibers	0.5	0.95	0.76	6.2	Nano Energy 2017, 32, 247
Co_3O_4/NCNT	3	0.9	0.81	5.3	Small, 2017, 13, 1700518
Co_2P/N-HCR-2	0.357	0.962	0.81	5.52	J. Mater. Chem. A, 2017, 5, 17563–17569
NCNT/CoO-NiO-NiCo	0.2	0.97	0.83	4.4	Angew. Chem. Int. Ed. 2015, 54, 9654 –9658
Co_2P	0.14		0.196 vs AgCl	4.7	ACS Nano 2015, 9, 8, 8108-8115
layer mesoporous Co_3O_4/N-rGO	0.128	0.90	0.79	5.34	Adv. Mater. 2018, 30, 1703657
CoNiFe-S MNs	0.7	0.93	0.78	5.8	Adv. Energy Mater. 2018, 1801839
Co/N-B-CSs	0.1	0.89	0.812	4.96	ACS Nano 2018, 12, 1894−1901
7.1%Cu-Co_2P@NPC	0.25	0.95	0.835	5.2	This work

Table S3. Comparison of some recent aqueous rechargeable ZABs based on different catalysts

Catalyst	Loading mass (mg cm^{-2})	Specific capacity (mAh g^{-1})	OCV (V)	Power density (mW cm^{-2})	Stability	Ref.
Co–Nx–C	0.5	750 at 20.0 mA cm^{-2}	1.4	152	180 cycles for 60 h @ 2 mA cm^{-2}	Adv. Mater. 2017, 29, 1703185
CoN_4/NG	1	730	1.51	115	30 cycles for 100 h @10 mA cm^{-2}	Nano Energy 50 (2018) 691–698
Co_2P/CoN-in-NCNTs	0.5	649.6 at 20.0 mA cm^{-2}	1.35	194.6	95 h @ 5 mA cm^{-2}	Adv. Funct. Mater. 2018, 1805641
$Pb_2Ru_2O_{6.5}$	0.85	-		195	600s/cycle for 200 cycles 33h	Energy Environ. Sci., 2017, 10, 129
Co_4N/CNW/CC	1		1.4	-	408 cycles 136 h @ 10 mA cm^{-2}	J. Am. Chem. Soc.2016, 138, 10226
Ni–MnO/rGO		758 at 5 mA cm^{-2}	-	123	50 cycles @ 5 mA cm^{-2}	Adv. Mater. 2017, 1704609
Co-N,B-CSs	0.2	-	1.43	100.4	14 h@ 5 mA cm^{-2}	ACS Nano, 2018, 12, 1894–1901
$NiCo_2S_4$/N-CNT	1	554.6	1.49	147	150 cycles; 17 h	Nano Energy 2017, 31, 541
7.1%Cu-Co_2P@NPC	1	736.8 at 10 mA cm^{-2}	1.4	236.1	480 cycles for 160 h @ 10 mA cm^{-2}	This work

Table S4. Comparison of some recent flexible and rechargeable ZABs based on different catalysts and solid-state electrolytes

Catalyst	Loading mass (mg cm^{-2})	Cell structure	OCV (V)	Power density (mW cm^{-2})	Stability	Ref.
Co–Nx–C	1.5	Sandwich	1.44	29	18 cycles for 1 h @ 1 mA cm^{-2}	Adv. Mater. 2017, 29, 1703185
RuO_2-CNT sheet	-	Fiber	1.29	5.7 Wh L^{-1}	30 cycles for 30 h @ 1 A g^{-1}	Angew. Chem. Int. Ed. 2015, 54, 15390
Co_4N/Co-N-C	-	Cable	1.35	-	36 cycles for 12 h @ 1 mA cm^{-2}	J. Am. Chem. Soc. 2016, 138, 10226
N-doped porous carbon fiber	2	Sandwich	1.26	-	18 cycles for 6 h @ 2 mA cm^{-2}	Adv. Mater. 2016, 28, 3000
CoO_x on carbon paper	1	Sandwich	1.4	44.1	30 cycles for 10 h @ 1 mA cm^{-2}	Adv. Energy Mater. 2016, 6, 1600476
CoN4/NG	1	Sandwich	-	28	30 cycles for 6 h @ 1 mA cm-2	Nano Energy 50 (2018) 691–698
Co-N,B-CSs	0.5	Sandwich	1.345		stability for 22 h@ 2 mA cm^{-2}	ACS Nano, 2018, 12, 1894–1901
$CuCo_2O_4$/N-CNT	-	Sandwich	1.24	1.86 W g^{-1}	27 cycles for 9 h @ 0.5 A g-1	Adv. Funct. Mater. 2017, 27, 1701833
Co_3O_4 on carbon cloth	-	Sandwich	1.32	-	30 cycles for 10 h @	Adv. Energy Mater.

						2017, 7，1700779
Co_3O_4/NCNT	3.0	Sandwich	1.3	-	20 cycles for 20 h @ 2 mA cm^{-2}	Small, 2017, 13, 1700518
NiO/CoN nanowires on carbon cloth	-	Cable	1.34	-	50 cycles for 500 min @ 3 mA cm^{-2}	ACS Nano 2017, 11, 2275
7.1%Cu-Co_2P@NPC	**1**	**Sandwich**	**1.42**	**52.5**	**96 cycles for 32 h @ 2 mA cm^{-2}**	**This work**