Supporting Information

Popcorn-like Co_3O_4 Nanoparticles Confined in Three-Dimensional Hierarchical N-doped carbon nanotubes Networks as Highly Efficient Trifunctional Electrocatalyst for Zinc-Air Batteries and Water Splitting Device

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1. Computational Simulation Process

Density functional theory (DFT) calculations were performed via the Vienna Ab-initio Simulation Package (VASP). The cut-off energy for the plane-wave basis was 520 eV. K-point mesh of 2×2×1 was applied to all structures. The geometry optimizations were performed until convergence criterion for the total energy and force were reduced below 10-5 eV and 0.01 eV $Å^{-1}$. The vacuum layer of 15 Å was added along the normal direction to avoid spurious interactions between adjacent structures. Long-range Van Der Waals (VDW) interactions were treated based on the empirical correction scheme of Grimme (DFT+D3).

The binding energy of absorbates including H, OH, O and OOH on substrates can be defined as:

$$E_{ads} = E_{substrate+adsorbate} - (E_{substrate} + Eadsorbate) \quad (5)$$

In which E_{ads} was the absorbing energy between the catalyst and adsorbate; $E_{substrate+adsorbate}$ referred to the total energy of catalyst surface with the adsorbate, while $E_{substrate}$ and $E_{adsorbate}$ stand for the total energy of the catalyst surface and adsorbates.

In present work, the Gibbs free energy change (ΔG) of each elementary step was obtained by

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \quad (6)$$

Where the ΔE denotes the adsorption energy, ΔE_{ZPE} and ΔS are the changes of zero-point energy and entropy, and the temperature T is set to 300 K.

2. Supplementary Figures

Fig. S1 TEM images of NGC@Co/NCNTs/CNF. (a) a niblet-like branch tip of NGC@Co/NCNTs/CNF and (b) the corresponding HR-TEM image of the tip.

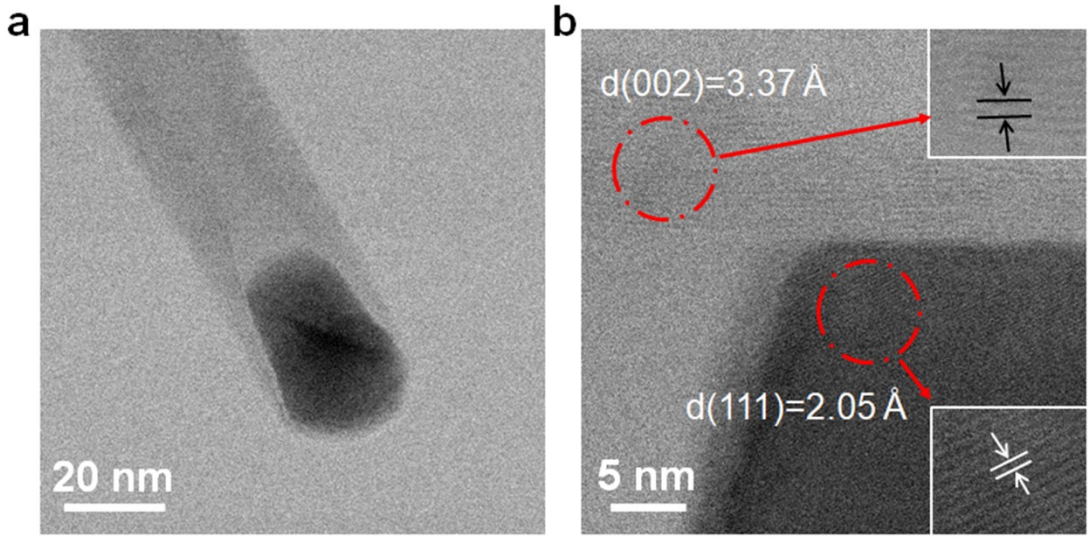


Fig. S2 SEM images of (a) ZIF-8/ZIF-67 NPs catalyst and (b) Co_3O_4 NPs electrocatalyst.

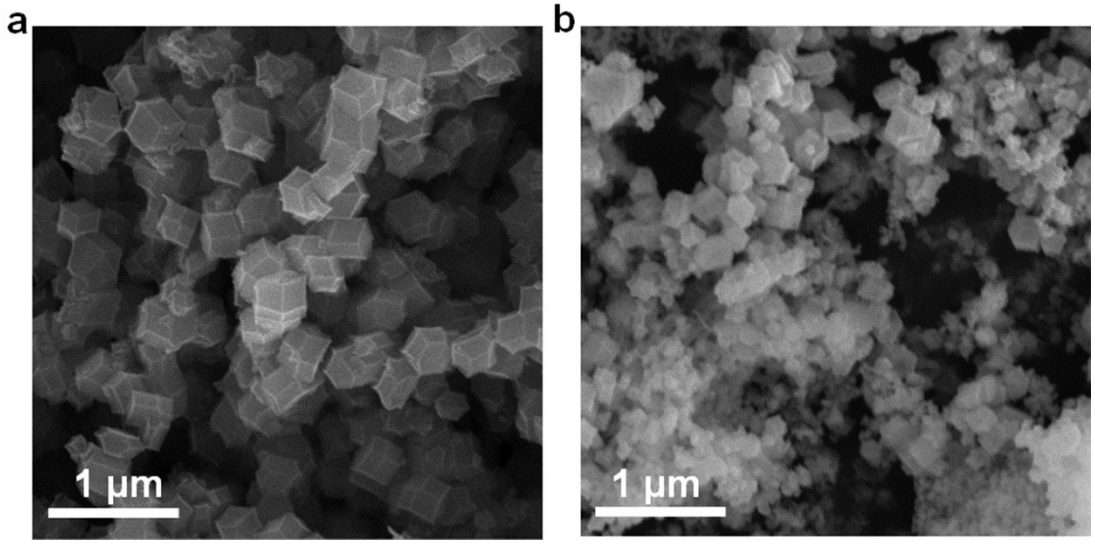


Fig. S3 XPS survey spectra of NAC@Co_3O_4/NCNTs/CNF.

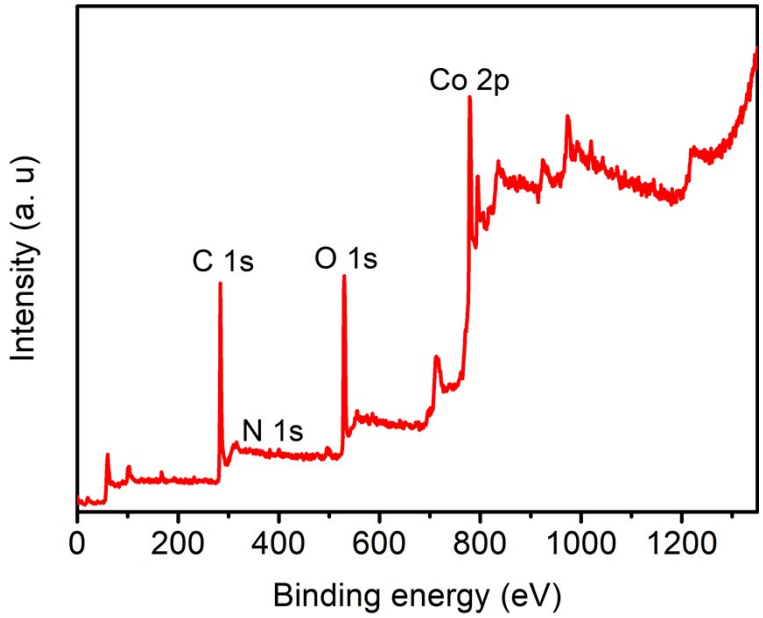


Fig. S4 Pore size distribution for Co_3O_4 NPs, NGC@Co/NCNTs/CNF and NAC@Co_3O_4/NCNTs/CNF electrocatalysts.

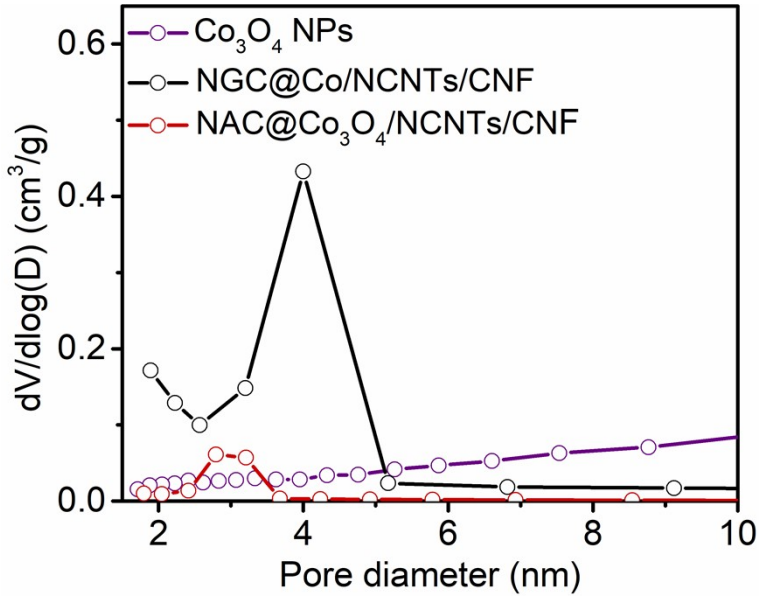


Fig. S5 Rotating ring-disk electrode (RRDE) voltammograms for NAC@Co_3O_4/NCNTs/CNF in O_2-saturated 0.1 M KOH at 1600 rpm.

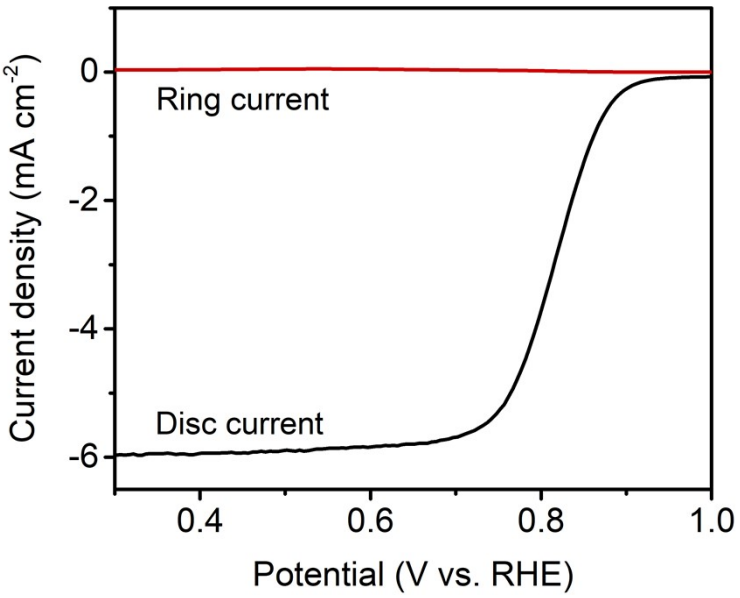


Fig. S6 Current-time (i-t) chronoamperometric responses of NGC@Co/NCNTs/CNF and Pt/C at 0.4 V for 30 h in O_2 saturated 0.1 M KOH solution at 1600 rpm.

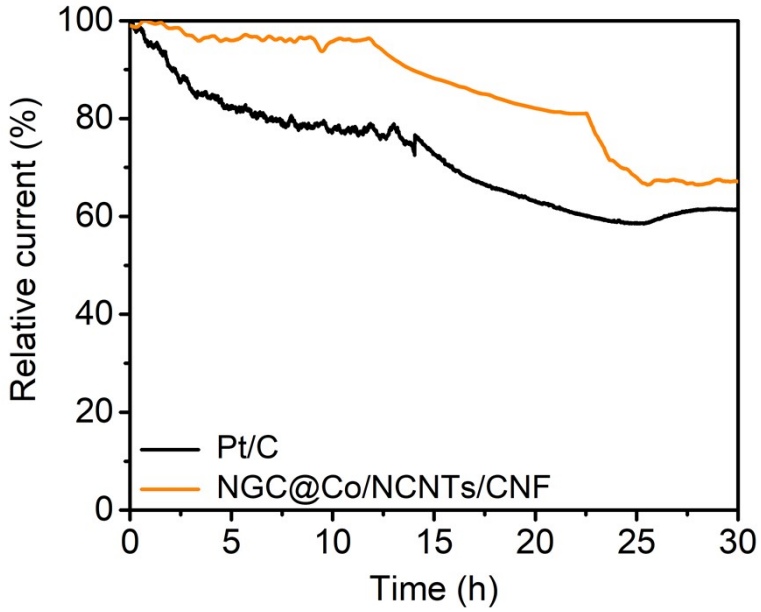


Fig. S7 (a-c) CVs measured in 1 M KOH at scan rates from 20 to 80 mV s^{-1} for Co_3O_4 NPs, NGC@Co/NCNTs/CNF and NAC@Co_3O_4/NCNTs/CNF electrocatalysts.

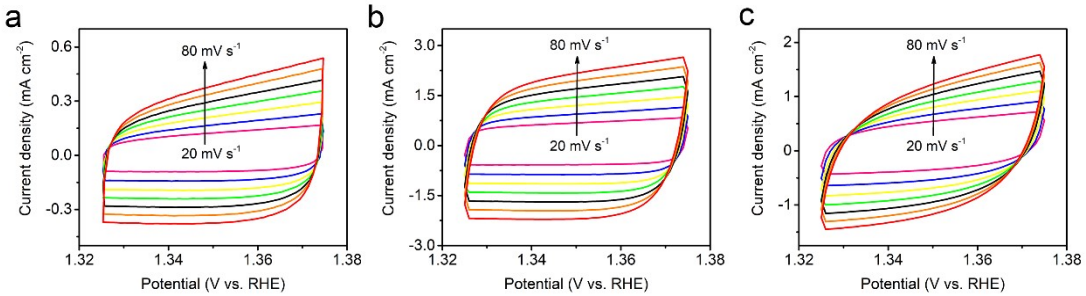


Fig. S8 (a-d) CVs measured in 1 M KOH at scan rates from 20 to 80 mV s^{-1} for Co_3O_4 NPs, NGC@Co/NCNTs/CNF, NAC@Co_3O_4/NCNTs/CNF and Pt/C electrocatalysts, respectively.

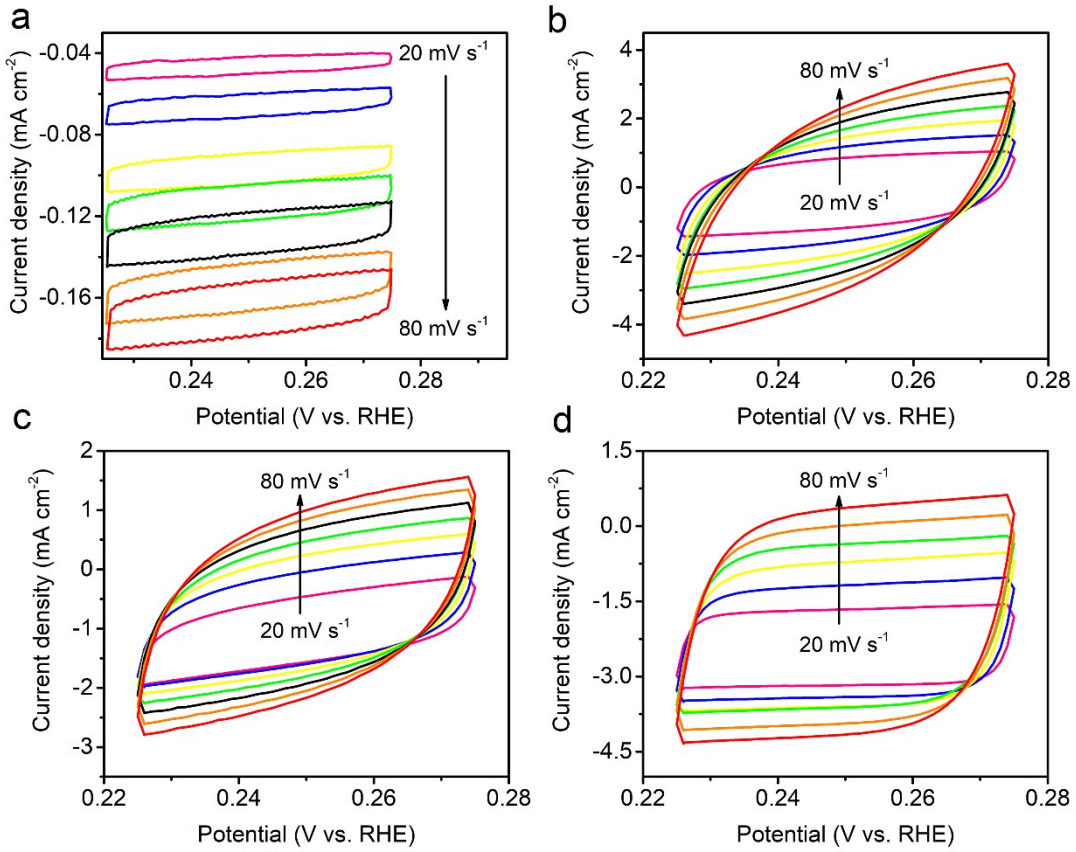


Fig. S9 Atomic configurations of NAC@Co_3O_4/NCNTs/CNF for HER.

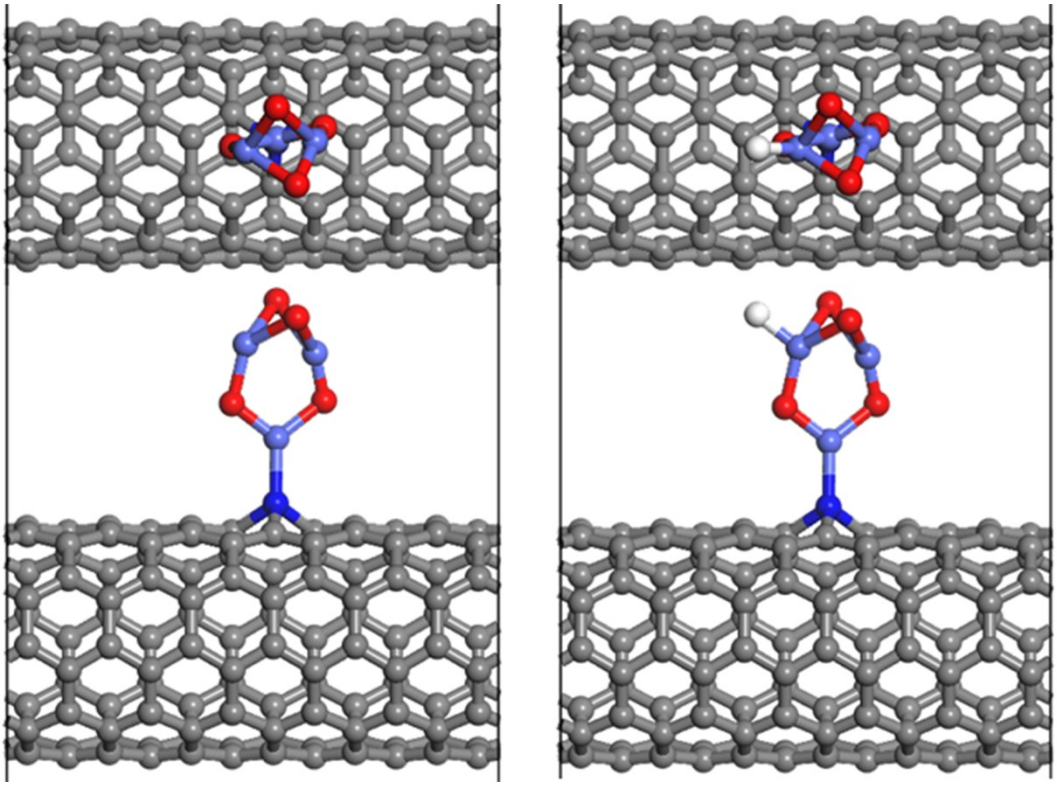


Fig. S10 Atomic configurations of NGC@Co/NCNTs/CNF for OER/ORR with different adsorption states toward intermediates.

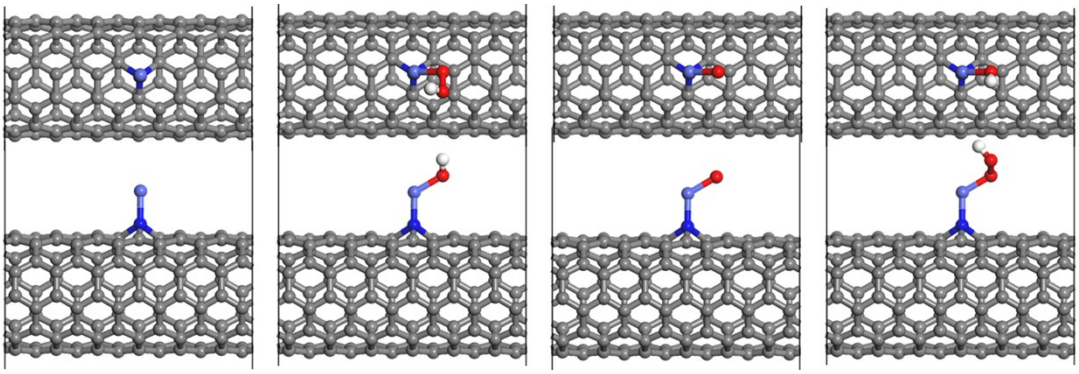
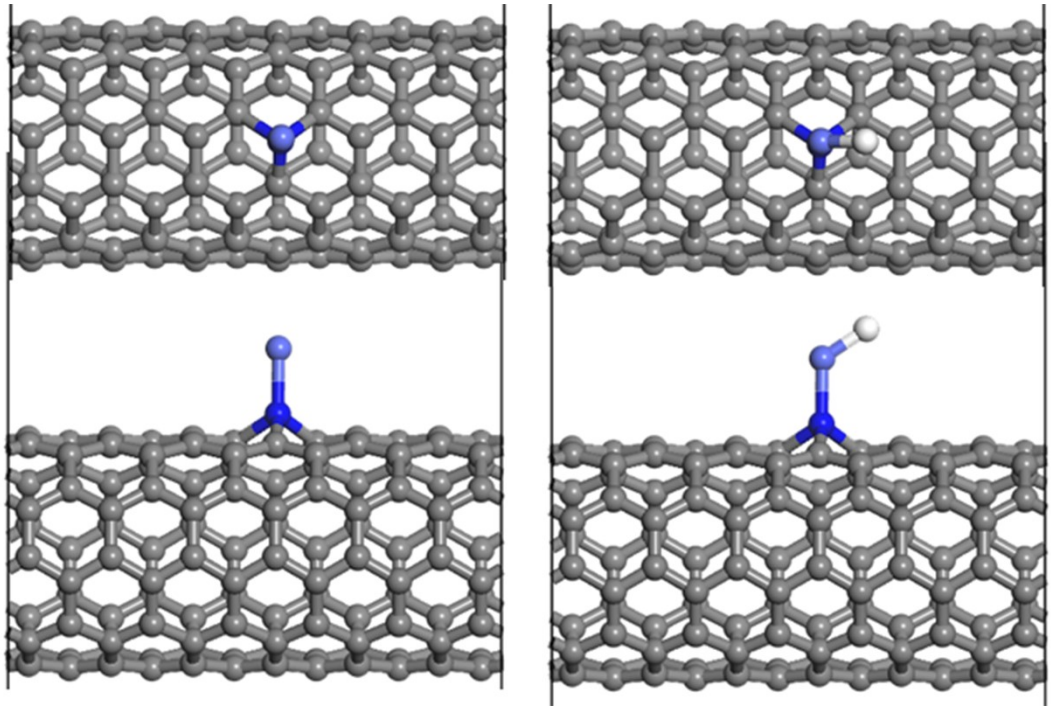


Fig. S11 Atomic configurations of NGC@Co/NCNTs/CNF for HER.



3. Supplementary Table

Table S1 BET surface area, total pore volume, micropore volume and adsorption average pore width of Co_3O_4 NPs, NGC@Co/NCNTs/CNF and NAC@Co_3O_4/NCNTs/CNF.

Catalysts	BET surface area ($m^2\ g^{-1}$)	total pore volume ($cm^3\ g^{-1}$)	Adsorption average pore width (nm)	Reference
Co_3O_4 NPs	44	0.19	17.36	This work
NGC@Co/NCNTs/CNF	261	0.19	2.95	This work
NAC@Co_3O_4/NCNTs/CNF	309	0.23	2.96	This work
Co_3O_4@NC	35.22	-	-	Chem. Eng. J. 2021, 424, 130400
Co_3O_4@NCs	303.9	-	4.9	Nano Energy 2020, 77, 105200
Co-NC	249.9	-	-	Chem. Eng. J. 2021, 419, 129619
ZrO2 NT/Co_3O_4	33.28	-	-	Appl. Catal. B-Environ. 2021, 283, 119653
$Co_3O_{3.87}F_{0.13}$	70.4	0.134	3.43	Appl. Catal. B-Environ. 2021, 281, 119535
CoPNC@NFP	247	-	5	Chem. Eng. J. In Press
Ru/Co_3O_4 NWs	49.86	-	-	Nano Energy 2021, 85, 105940
Co3O/NCNTs/3D	361.5	-	11.1	Chem. Eng. J. 2020, 381, 122681
Co_2P/CoP NAs	20.25	-	-	Nano-Micro Lett. 2020, 12, 154
Co-N_4/NC	257.91	-	-	Nano-Micro Lett. 2021, 13, 60
FeCo/Se-CNT	23.51	-	-	Nano Lett. 2021, 21, 5, 2255
$PtCo_2$/Zn_6Co	600	-	3	ACS Nano 2020, 14, 13069
Co_3O_4/Co-Fe oxide DSNBs	43.3	-	-	Adv. Mater. 2018, 30, 1801211
Co_3O_4C-NA	251	-	-	J. Am. Chem. Soc. 2014, 136, 13925
CoO@Co_3O_4/NSG-750	70	0.22	-	ACS. Appl. Mater. Inter. 2018, 10, 7180
Co_3O_4-NWs	57	-	4.31	ChemElectroChem 2018, 5, 2181
Co_3O_4 NW	22	-	3.4	Adv. Energy Mater. 2014, 4, 1301389

Table S2 Performance of important non-precious metal based electrocatalysts for ORR, OER, HER in alkaline environment. η is the over potentials to deliver a –10 mA cm^{-2} current density for OER, HER. All of the catalytic electrodes for OER, HER in 1 M KOH, and 0.1M KOH for ORR without special instructions.

Catalysts	ORR		OER		HER		Reference
	Diffusion-limiting current density (mA cm^{-2})	Tafel slope (mV dec^{-1})	η (mV)	Tafel slope (mV dec^{-1})	η (mV)	Tafel slope (mV dec^{-1})	
NAC@Co_3O_4/NCNTs/CNF	-5.6	67	368	56	76	173	This work
NGC@Co/NCNTs/CNF	-5.7	111	390	82	193	209	This work
Co_3O_4 NPs	-1.9	-	410	76	380	245	This work
Pt/C	-5.7	112	-	-	40	106	This work
RuO_2	-	-	320	73	-	-	This work
NCN-1000-5	-6.43	86	410[a]	142[a]	90[b]	43[b]	Energy Environ. Sci. 2019, 12, 322
Co/CNFs	-5.7	-	320	79	190[a]	66[a]	Adv. Mater. 2019, 31, 1808043
NOGB-800	-5.5		400	90.5	220	98	Adv. Energy Mater. 2019, 1803867
CoSA + Co_9S_8/HCNT	-6.3	30	330[a]	21[a]	250	101	Small 2020, 1906735
Fe_3C-Co/NC	-5.5	-	340	-	238	-	Adv. Funct. Mater. 2019, 29, 1901949
W_2N/WC	-5.0	58.73	320	122.8	148.5	47.4	Adv. Mater. 2020, 32, 1905679
Co/CNFs	-5.8		320	79	190	66	Adv. Mater. 2019, 31, 1808043
FeCo/Co_2P@NPCF	-5.0	62	330[a]	61[a]	260	120	Adv. Energy Mater. 2020, 1903854
C_{60}-SWCNT	-1.75	-	460[a]	46.7[a]	400[a]	120.8[a]	J. Am. Chem. Soc. 2019, 141, 11658
Cu-14-Co_3Se_4/GC	-4.0	56	280[a]	111[a]	166	168	ACS Catal. 2019, 9, 10761
N,P-HCNF-8	-5.1	47	320[a]	248[a]	550[a]	161[a]	Nano Energy 2019, 64, 103879
$TiO_2C@CN_{x,950}$	-5.0	-	270[a]	69[a]	255[a]	60[a]	Appl. Catal. B-

							Environ. 2019, 248, 366
CoO_x-NeC/TiO_2C (22.7%)	-6.3	-	350	75	368[a]	134[a]	J. Power. Sources. 2019, 414, 333
15% PANI/ZIF-67	-4.6	-	330	41	425	123	Nano Energy 2018, 45, 127
NB-CN	-4.8	65	390[a]	-	175.3[b]	-	Nano Energy 2017, 42, 334
GO-PANi31-FP	-5.5	-	570[a]	136[a]	520[a]	-	Angew. Chem. Int. Ed. 2016, 55, 13296
Co_3O_4/NRGO_30	-3.0[c]	61[c]	410	76	-	-	ChemElectroChem. 2018, 5, 483
NC-Co_3O_4-90	-12.8[c]	-	358	-	-	-	Adv. Mater. 2017, 29, 1704117
Co/Co_3O_4@PGS,	-5.9	52.6	350[a]	76.1[a]	-	-	Adv. Energy Mater. 2018, 8, 1702900
MCO@NCNTs	-6.0	121	470[a]	106	-	-	ChemSusChem. 2018, 11, 1295
CoSAs@CNTs	-	99	410	85	-	-	ACS. Appl. Energy. Mater. 1, 3283
CNF@Zn/CoNC	-5.8	43.3	470[a]	124[a]	-	-	Small 2018. 14, 1704207
3D-CNTA	-4.2	-	360	89	185	135	Nano Energy 2017, 39, 626
Mo–N/C@MoS_2	-5	-	390[a]	72[a]	117	64.3	Adv. Funct. Mater. 2017, 27, 1702300
echo-MWCNTs	-	-	360	41	-	-	J. Am. Chem. Soc. 2015, 137, 2901
Co_3O_4/NSG-650	-6	63	460[a]	367[a]	-	-	ACS. Appl. Mater. Inter. 2018, 10, 7180
Co@Co_3O_4/NC-2	-4.2	-	435[a]	-	-	-	Appl. Surf. Sci. 2018, 427, 319
Co_3O_4/MnO_2-CNTs-350	-6.2	-	360[a]	-	-	-	Green Energy Environ. 2017, 2, 316
$NiMo_3S_4$	-	-	-	-	257	98	Angew. Chem. Int. Ed. 2016, 55, 15240
Co@NC-3/1	-4.7	-	340	85	-	-	Adv. Energy Mater. 2018, 8, 1702048
NGO/Ni_7S_6	-	-	380[a]	45[a]	370	145.5	Adv. Funct. Mater. 2017, 27, 1700451.

CoP/NCNHP	-	-	310	70	115	66	J. Am. Chem. Soc. 2018, 140, 2610
Ni_2P	-	-	290	-	-	-	Energy Environ. Sci. 2015, 8, 2347
PO-Ni/Ni-N-CNFs	-	-	420	113.10	262	97.42	Nano Energy 2018, 51, 286
APBCCF-H	-5.8	-	410	99	240	42	Nano Energy 2017, 32, 247
D-Co@CNG	-4.6	83	360	-	205	95	J. Mater. Chem. A. 2017, 5, 20882
CoFe LDH-F	-	-	270	47	255	95	ACS. Appl. Mater. Inter. 2016, 8, 34474
MNG-CoFe	-4	-	390	-	135	-	ACS. Appl. Energy. Mater. 2018, 1, 2440

[a]Represents 0.1M KOH solution.

[b]Represents 0.5 M H_2SO_4 solution.

[c]Represents 1M KOH solution.