Electronic Supporting Information

Bamboo-like nitrogen-doped porous carbon nanofibers encapsulated nickel-cobalt alloy nanoparticles composite material derived from the electrospun fiber of bimetal–organicframework as efficient bifunctional oxygen electrocatalysts

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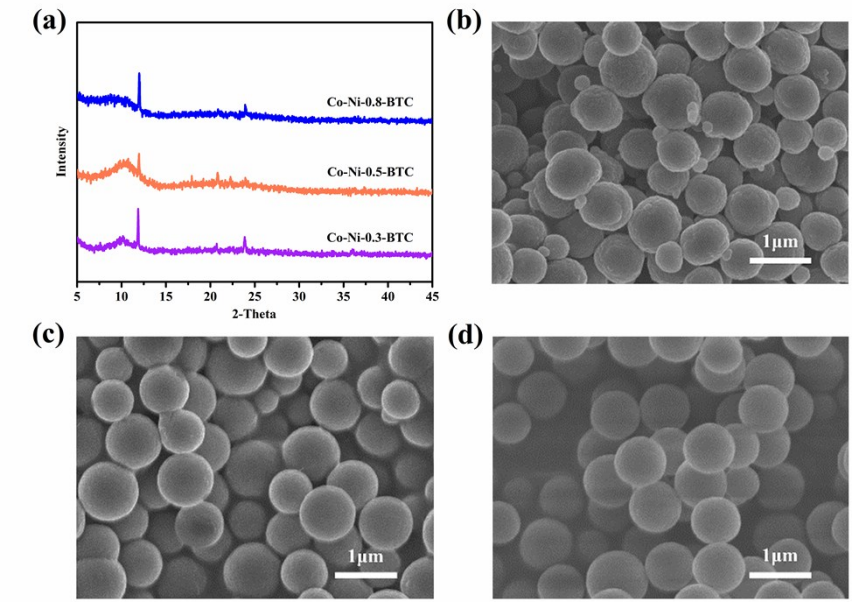

Fig. S1 (a) XRD patterns and SEM images of (b) Ni-Co-0.3-BTC, (c) Ni-Co-0.5-BTC and (d) Ni-Co-0.8-BTC.

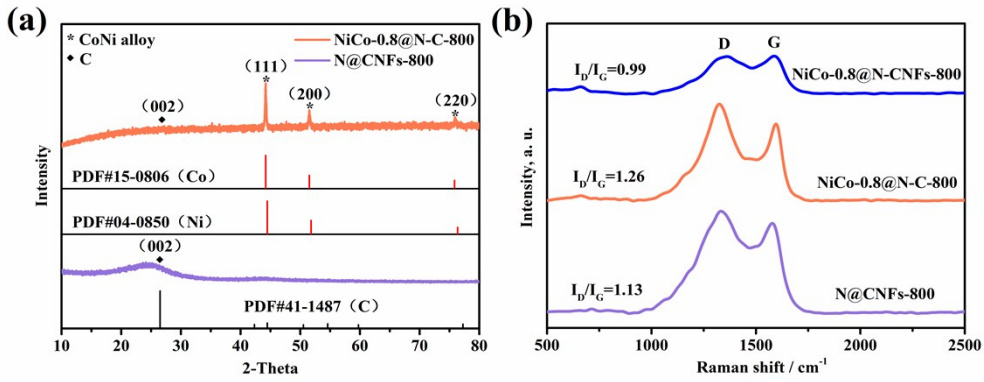

Fig. S2 (a) XRD patterns of NiCo-0.8@N-C-800 and N@CNFs-800 and (b) Raman spectra of NiCo-0.8@N-CNFs-800, N@CNFs-800 and NiCo-0.8@N-C-800.

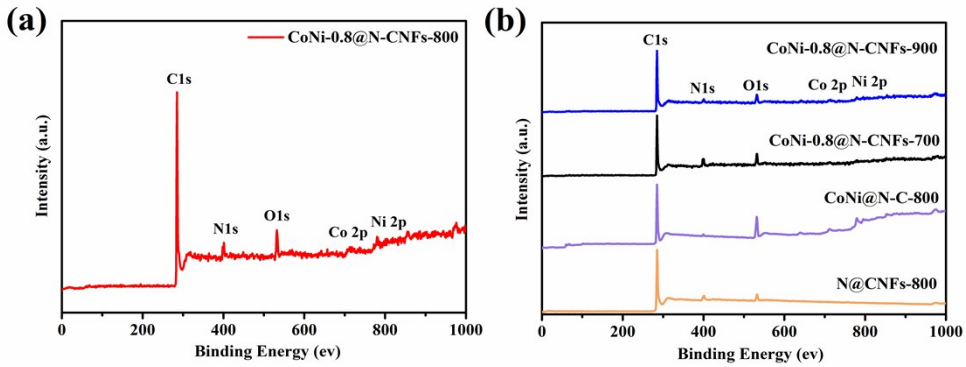

Fig. S3 Surface full spectrum of (a) NiCo-0.8@N-CNFs-800 (b) NiCo-0.8@N-CNFs-900, NiCo-0.8@N-CNFs-700, NiCo-0.8@N-C-800 and
N@CNFs-800.

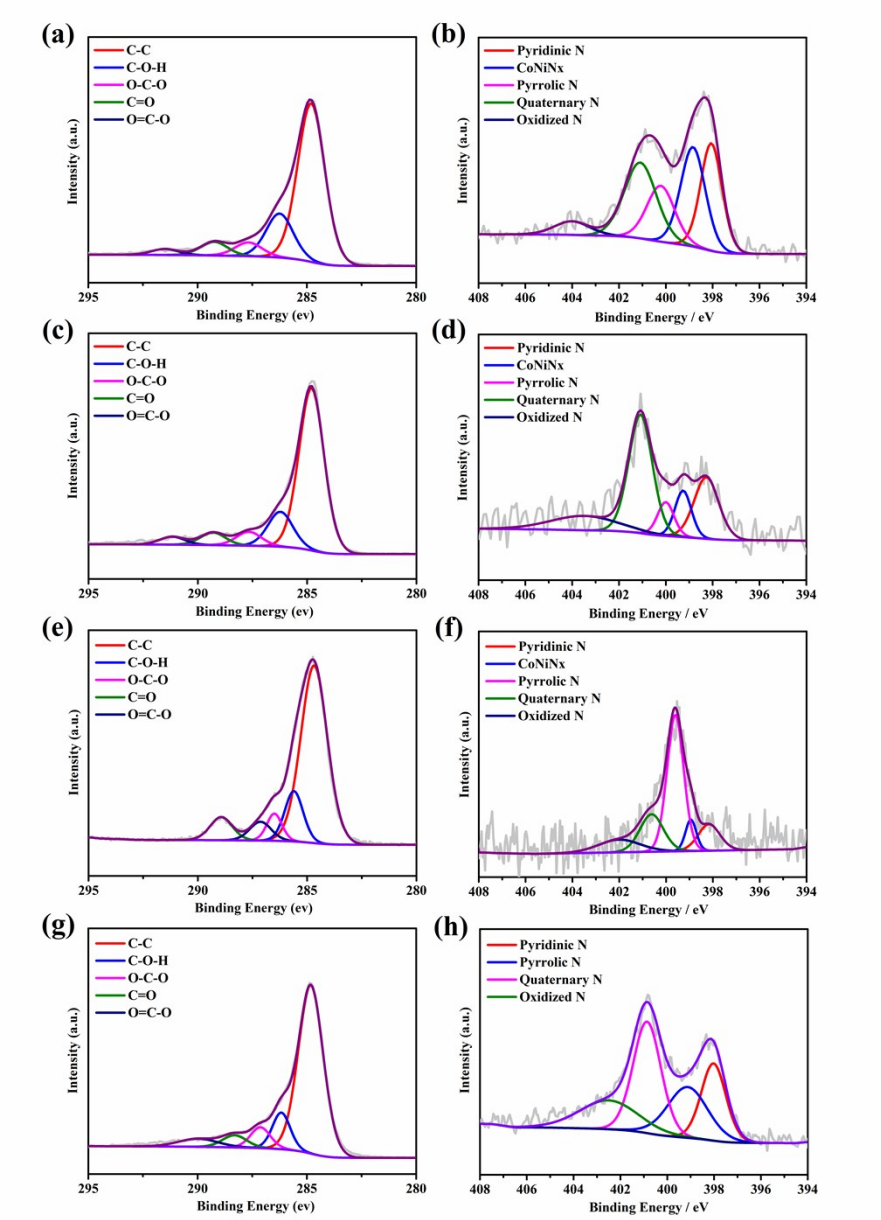

Fig. S4 (a) C 1s spectra and (b) N 1s spectra of NiCo-0.8@N-CNFs-700, (c) C 1s spectra and (d) N 1s spectra of NiCo-0.8@N-CNFs-900, (e) C 1s spectra and (f) N 1s spectra of NiCo-0.8@N-C-800; (g) C 1s spectra and (h) N 1s spectra of N@CNFs-800.

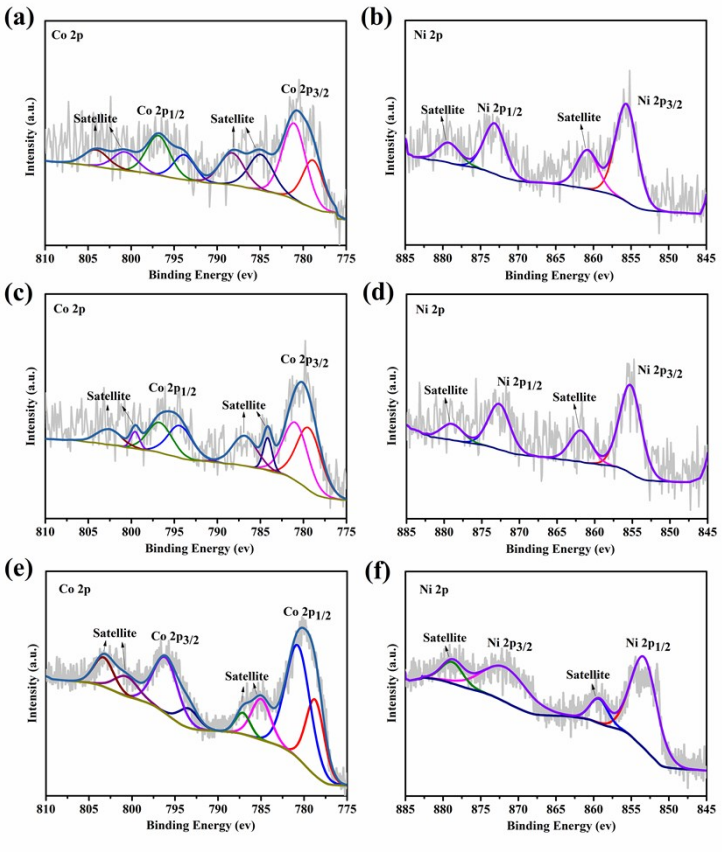

Fig. S5 (a) Co 2p spectra and (b) Ni 2p spectra of NiCo-0.8@N-CNFs-700; (c) Co 2p spectra and (d) Ni 2p spectra of NiCo-0.8@N-CNFs-900; (e) Co 2p spectra and (f) Ni 2p spectra of NiCo-0.8@N-C-800.

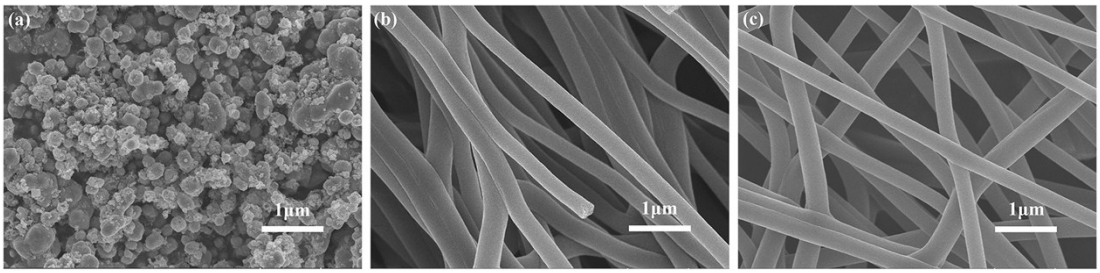

Fig. S6 SEM images of (a) NiCo-0.8@N-C-800, (b) Pure PAN fibers and (c) N@CNFs-800.

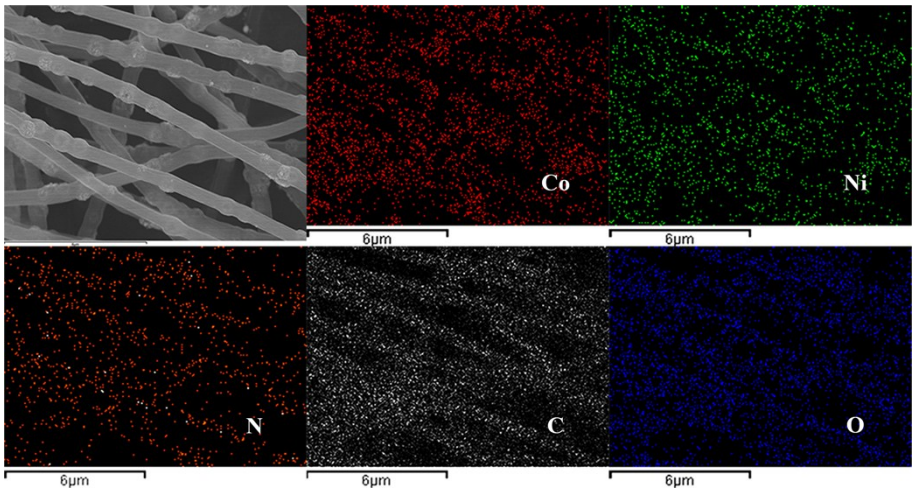

Fig. S7 Elemental mapping of NiCo-0.8@N-CNFs-800 electrocatalyst.

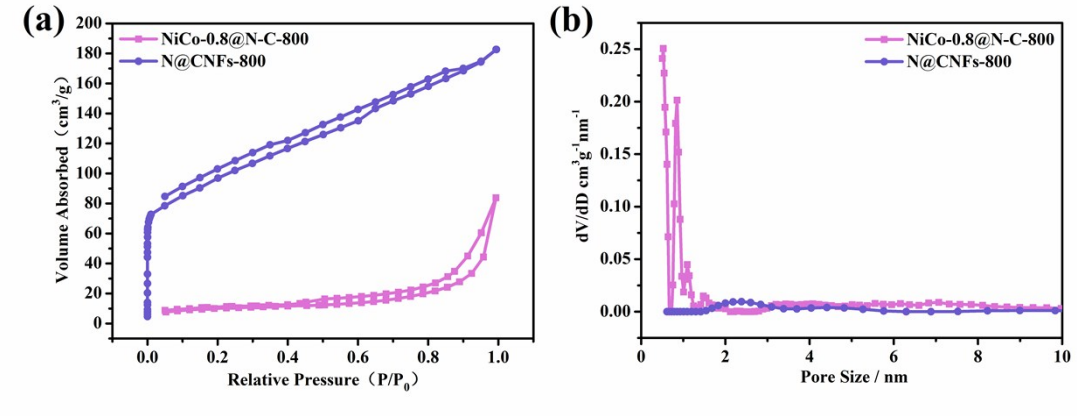

Fig. S8 (a) N_2 adsorption-desorption isotherms and (b) Pore diameter distribution determined by BJH method of NiCo-0.8@N-CNFs-800 and N@CNFs-800.

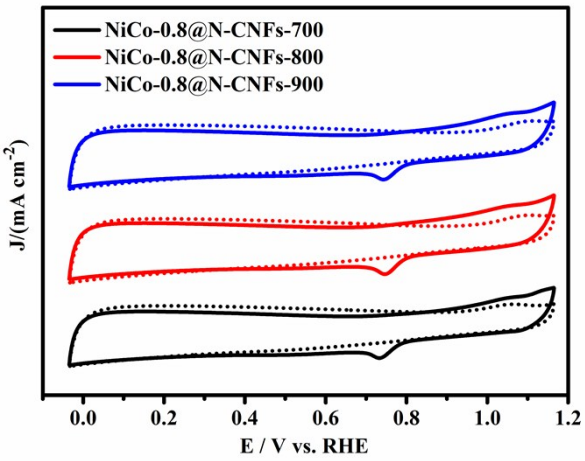

Fig. S9 CV curves of as-prepared NiCo-0.8@N-CNFs-Ts samples for ORR in N_2 and O_2 saturated KOH solution.

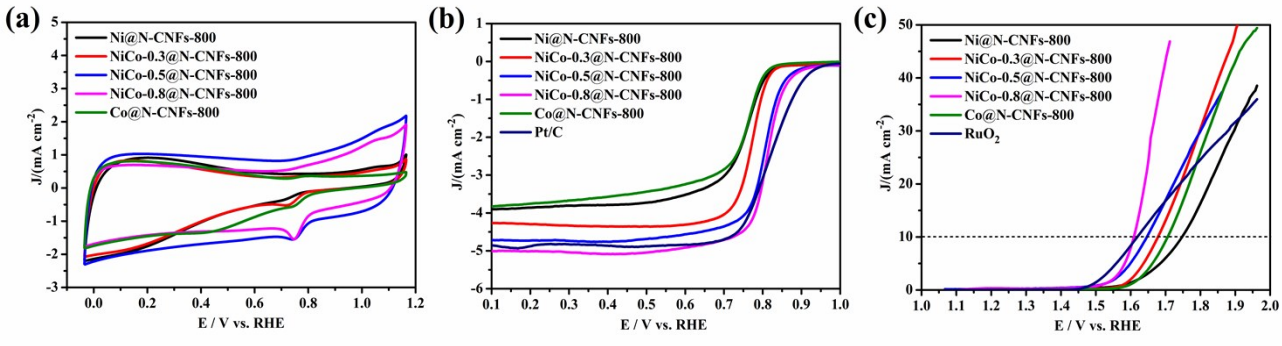

Fig. S10 (a) CV curves at a scan rate of 50 mV s^{-1} in O_2-saturated 0.1 M KOH solution; (b, c) LSV curves for ORR and OER at a rotation speed of 1600 rpm with a scan rate of 5 mV s^{-1} in 0.1 M O_2-saturated KOH electrolyte of as-prepared NiCo-X@N-CNFs-800 samples by adding different Co/Ni mole ratio of Ni-Co-X-BTC (X = 0, 0.3, 0.5, 0.8, 1).

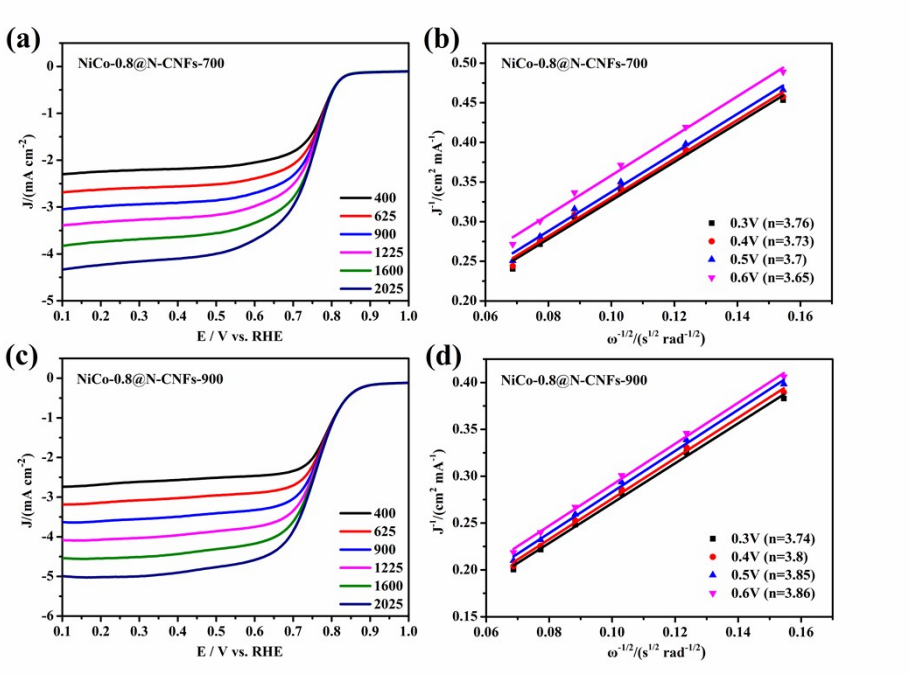

Fig. S11 (a, b) LSV curves and corresponding K-L curves of NiCo-0.8@N-CNFs-700 and (c, d) NiCo-0.8@N-CNFs-900 at different rotation speeds (400-2025rpm) with a scan rate of 5 mV s^{-1} in 0.1 M O_2-saturated KOH.

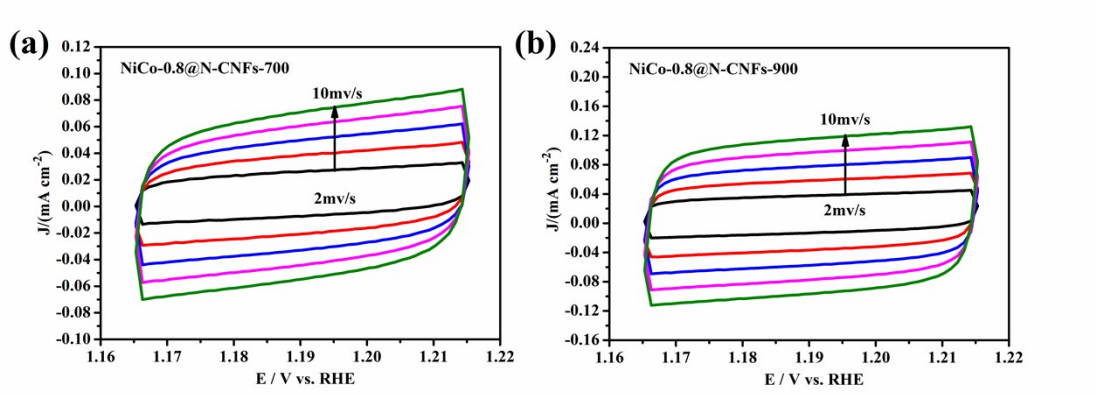

Fig. S12 CV curves of (a) NiCo-0.8@N-CNFs-700 and (b) NiCo-0.8@N-CNFs-900 scanned at 1.165-1.215 vs. RHE at scan rates from 2 to 10 mV s^{-1}.

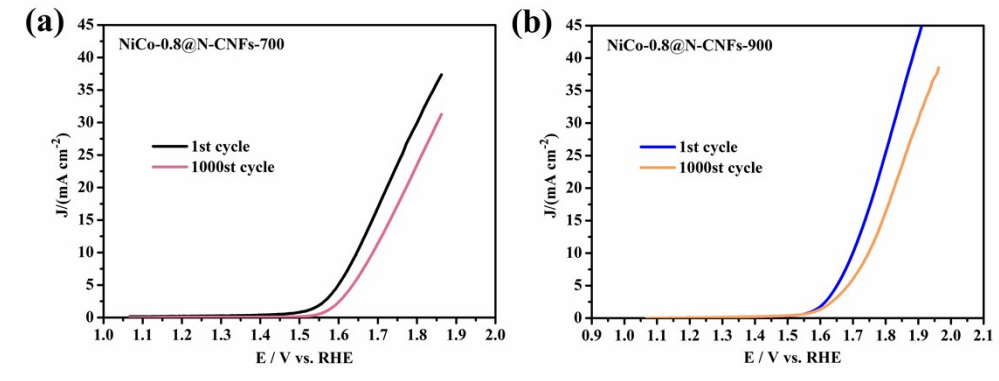

Fig. S13 LSV curves of (a) NiCo-0.8@N-CNFs-700 and (b) NiCo-0.8@N-CNFs-900 before and after 1000 cycles at a rotation speed of 1600 rpm with a scan rate of 5 mV s^{-1}.

Table S1. BET surface areas, I_D/I_G and N 1s components of different samples collected from XPS results.

Catalyst	$BET_{surface}$ (m^2 g^{-1})	I_D/I_G	Element content (wt%)		Relative content of the N species (%)				
			N	C	Pyridinic N	$NiCo-N_x$	Pyrrolic N	Graphitic N	Oxidized N
NiCo-0.8@N-CNFs-700	307.02	1.09	13.18	72.88	23.79	34.41	14.13	20.01	7.66
NiCo-0.8@N-CNFs-800	419.73	0.99	7.84	82.39	17.30	24.02	11.96	33.29	13.44
NiCo-0.8@N-CNFs-900	291.77	0.96	3.87	86.24	15.94	14.57	10.55	49.88	9.05
Ni-Co-0.8@N-C-800	33.91	1.26	2.25	77.43	9.51	14.05	53.16	11.16	12.13
N@CNFs-800	337.69	1.13	6.43	88.10	16.41	-	32.63	33.23	17.73

Table S2. Quantitative analysis of the Ni/Co ratio in NiCo-X@N-CNFs-800 samples by ICP-AES and theoretical value.

Samples	Molar ratio of Ni/Co	
	ICP-AES	Theoretical value
NiCo-0.3@N-CNFs-800	0.26	0.3
NiCo-0.5@N-CNFs-800	0.41	0.5
NiCo-0.8@N-CNFs-800	0.72	0.8

Table S3. ORR and OER catalytic performance of different electrocatalysts at 1600 rpm.

Electrocatalysts	ORR				OER			
	Eonset (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	Current density (mA cm^{-2})	Tafel slope (mV dec^{-1})	E at j=10mA cm^{-2} (V vs. RHE)	Tafel slope (kJ mol^{-1})	C_{dl} (mF cm^{-2})	R_{ct} (Ω)
NiCo-0.8@N-CNFs-700	0.825	0.760	3.82	78	1.645	132	5.76	45.02
NiCo-0.8@N-CNFs-800	0.913	0.820	5.01	72	1.61	89	12.86	14.1
NiCo-0.8@N-CNFs-900	0.875	0.770	4.54	105	1.70	118	10	30.04
NiCo-0.8@N-C 800	0.805	0.750	3.64	-	-	-	-	-
N@CNFs-800	0.705	0.605	2.84	-	-	-	-	-
Pt/C	0.935	0.825	4.86	91	-	-	-	-
RuO_2	0.645	-	3.28	-	1.62	65	-	-

TableS4. The bifunctional performance of various catalytic materials for ORR and OER at 1600 rpm.

Electrocatalysts	E_{ORR} half-wave potential ($E_{1/2}$) (V vs. RHE)	E_{OER} at j=10mA cm^{-2} (V vs. RHE)	$E=E_{OER}-E_{ORR}$ (Vvs. RHE)
NiCo-0.8@N-CNFs-700	0.760	1.645	0.885
NiCo-0.8@N-CNFs-800	0.820	1.61	0.79
NiCo-0.8@N-CNFs-900	0.770	1.70	0.93
NiCo-0.8@N-C-800	0.750	1.75	1
N@CNFs-800	0.605	-	-
Pt/C	0.825	-	-
RuO_2	-	1.62	-

TableS5. ORR/OER activities of previously reported bifunctional electrocatalysts in 0.1 M KOH solution at 1600rpm.

Catalyst	ORR		OER	Oxygen electrode activity	Reference
	Onset potential (V vs.RHE)	Half-wave potential (V vs.RHE)	E at j=10 mA cm^{-2} (V vs.RHE)	$\Delta E=E_{OER(j=10\ mA\ cm-2)}- E_{ORR(1/2)}$	
NiCo-0.8@N-CNF-700	0.825	0.760	1.645	0.885	This work
NiCo-0.8@N-CNF-800	0.913	0.820	1.61	0.79	This work
NiCo-0.8@N-CNF-900	0.875	0.770	1.70	0.93	This work
NiCoFe-LDH	0.8	0.63	1.57	0.94	Adv. Energy Mater. 2015, 5, 1500245
MOF(Fe/Co)-CNT	-	0.79	1.61	0.82	International journal of hydrogen 23 (2014) 16179
Ni_3Fe/N-C sheets	-	0.78	1.6	0.82	Adv. Energy Mater. 7 (2016) 1601172.
Co/N-CNTs	0.94	0.84	1.62	0.78	J. Mater. Chem. A 2016, 4, 1694 .
$Co_{0.5}Fe_{0.5}S$@N-M	0.913	0.808	1.64	0.832	ACS Appl. Mater. Interfaces 2015, 7, 1207.
Co_3O_4 NC/N-CNT	-	0.85	1.68	0.83	ChemSusChem 8 (2015) 3129.
Co_3O_4/NPGC	-	0.84	1.68	0.84	Angew. Chem. Int. Ed. 55 (2016) 4977.
Co_3O_4	0.75	0.62	1.64	1.02	J. Mater. Chem. A 2013, 1, 9992.
ZnCoNC-0.1	0.9	0.84	1.75	0.91	Nano Research 2018, 11(1): 163–173
CoNC	-	0.8	1.79	0.99	
FeCo-Co_4N/N-C	-	0.76	1.51	0.75	Adv. Mater. 2017, 29, 1704091
Co-N-GCI	-	0.857	1.656	0.799	ACS Sustainable Chem. Eng. 2016, 4, 4131-4136
Co-N-G	-	0.847	1.702	0.855	
NiO/CoN PINWs		0.68	1.53	0.85	ACS Nano 11 (2017) 2275.
NCNT/CoO-NiO-NiCo	0.97	0.83	1.5	0.67	Angew. Chem. Int. Ed. 2015,
CoP@SNC	0.87	0.79	1.58	0.79	Nanoscale, 2018, 10, 14613-14626.
CNF@Zn/CoNC	0.91	0.82	1.7	0.88	Small 2018, 14, 1704207.
CNF@ZnNC	0.87	0.78	1.78	1	

E(RHE)=E(Ag/AgCl)+0.965