Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information (ESI)

Bimetallic NiCo/CNF Encapsulated in N-doped Carbon Shell as Electrocatalyst for Zn-Air Battery and Water Splitting

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Materials used in this work

All of the chemical regents were of analytical grade and directly used as received without further purification. Cobalt (II) acetate tetrahydrate ($Co(CH_3COO)_2.4H_2O$, > 99.5%) and potassium hydroxide (KOH) were supplied by Guangdong chemicals. Nickel acetate tetrahydrate ($Ni(CH_3COO)_2.4H_2O$, > 99 %), urea (H_2NCONH_2, > 99.0 %) and ethanol (C_2H_5OH, >99.7 %) were supplied by Tianjin Fuchen. Platinum on carbon (Pt/C, 20 wt.%) was provided by Johnson Matthey fuel cells. Nafion ionomer solution (5 %) was obtained from Dupont. Carbon nanofibers (CNF) was supplied by Aladdin Co. Ltd. Trizma base and dopamine hydrochloride were bought from Sigma–Aldrich. Argon (Ar), nitrogen (N_2) and oxygen (O_2) (99.99 %) gases were provided by Xi'an Taida Chemical Reagent Co. Ltd. Ultra–pure distilled water (18.25 MΩ.cm $^{-1}$) was used to prepare all electrolyte solutions.

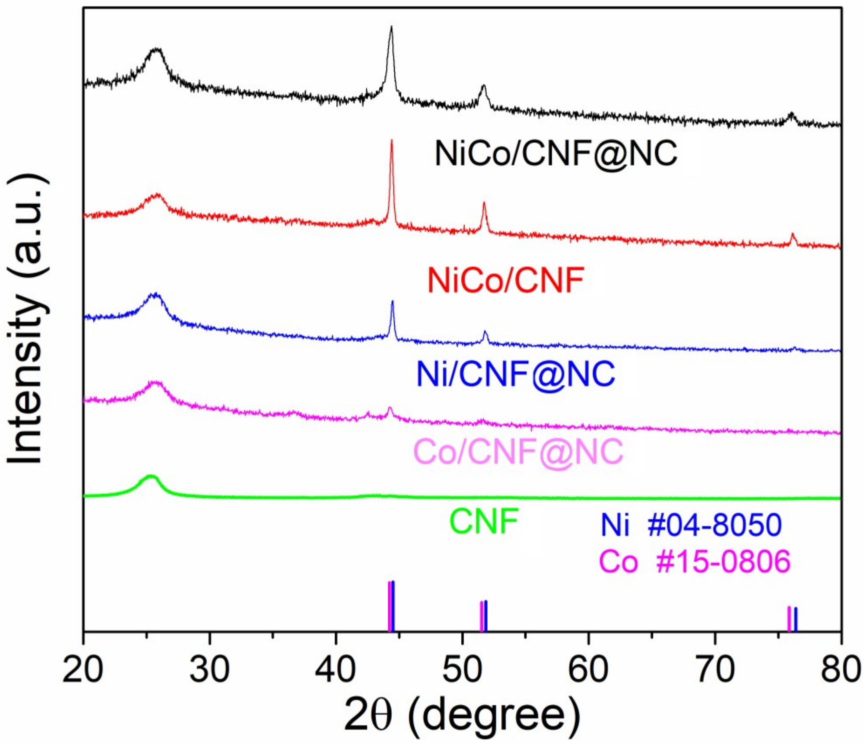

Figure S1. XRD patterns of NiCo/CNF@NC, NiCo/CNF, Ni/CNF@NC, Co/CNF@NC and CNF

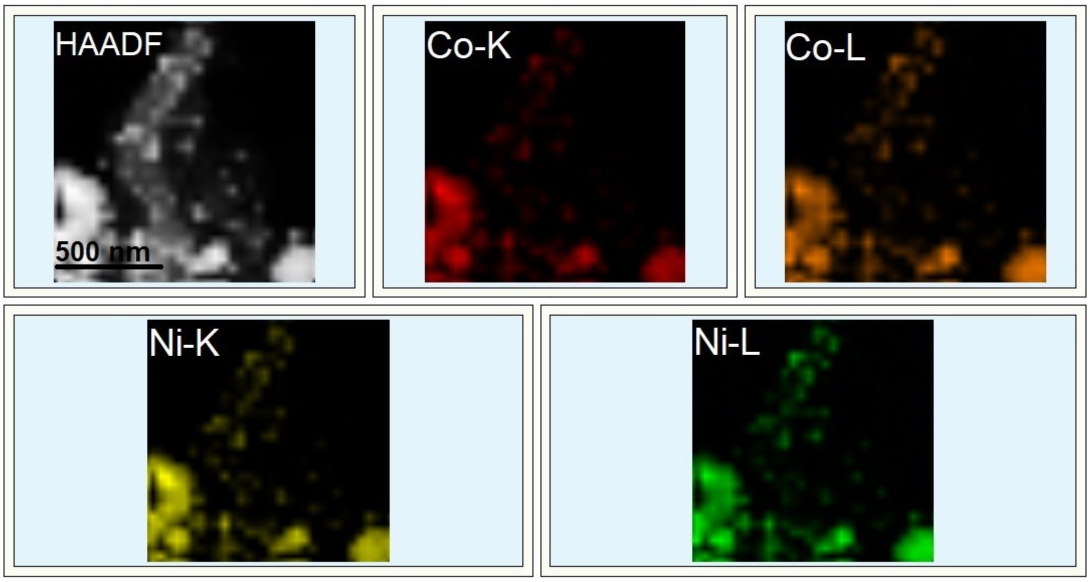

Figure S2. The typical high-angle annular dark-field scanning TEM (HAADF-STEM) image and the corresponding EDS mapping of NiCo/CNF@NC showing the distribution of Co and Ni elements.

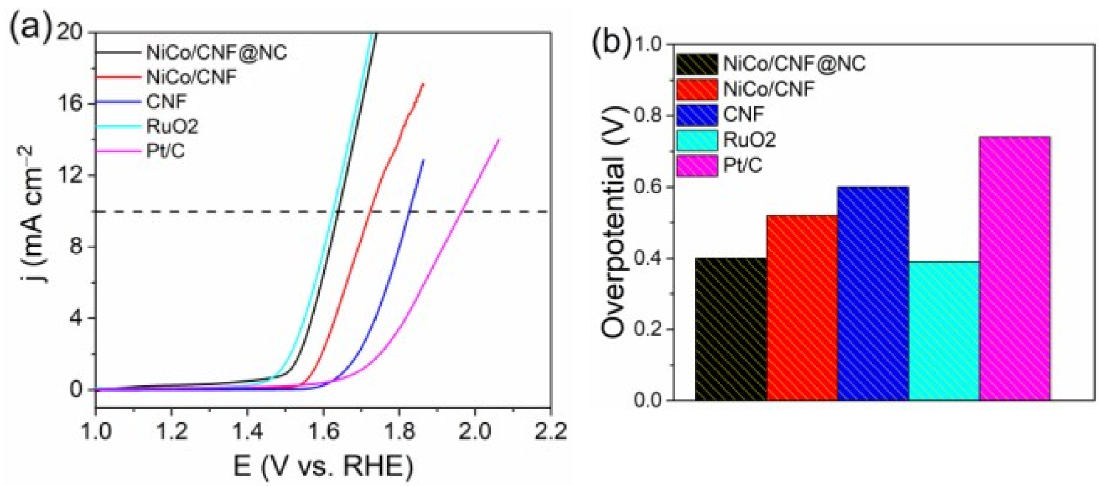

Figure S3 a) OER polarization curves for NiCo/CNF@NC, NiCo/CNF, CNF, RuO_2, and Pt/C catalysts in O_2 saturated 0.1 M KOH solution. (b) overpotentials derived from OER polarization curves at 10 mA cm^{-2}.

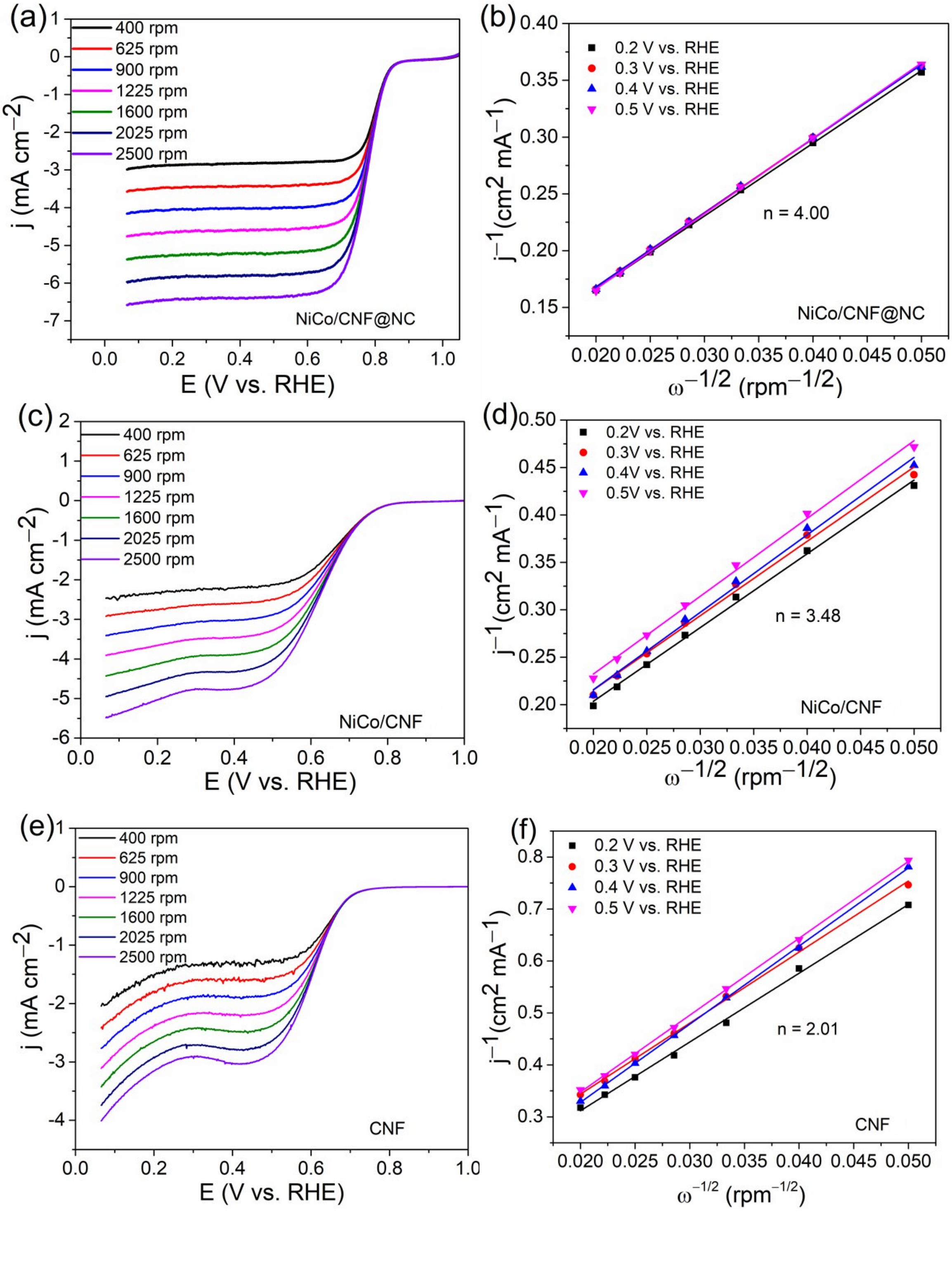

Figure S4. LSV curves of (a) NiCo/CNF@NC (c) NiCo/CNF, (e) CNF catalysts at different scanning rates and (b, d, f) the corresponding Koutecky–Levich (K–L) plots, respectively.

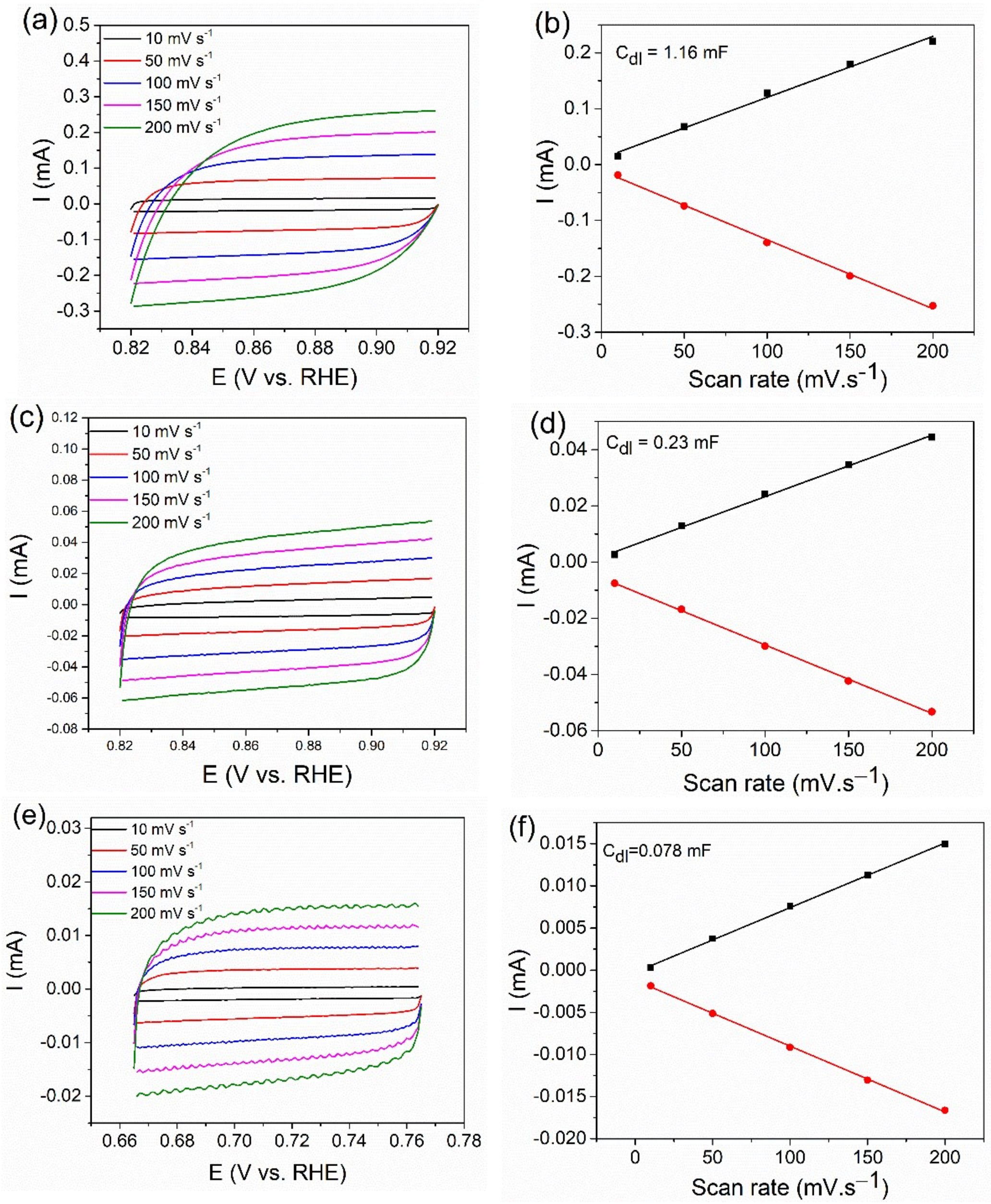

Figure S5. CV in N_2 saturated 0.1 M KOH within non-Faradaic regions (a, c and e) and the corresponding current vs. scan rates respectively (b, d and f) for NiCo/CNF@NC, NiCo/CNF and CNF catalysts, respectively.

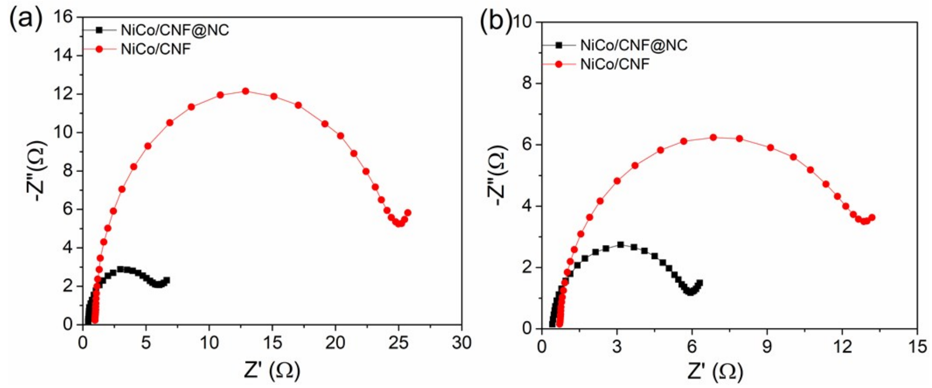

Figure S6 Nyquist plots of NiCo/CNF@NC and NiCo/CNF (a)At OER overpotential of 0.35 V (b) At HER overpotential of 0.22 V.

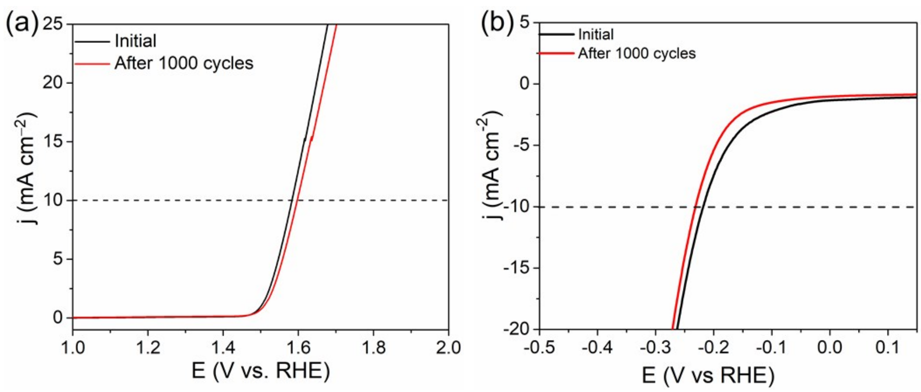

Figure S7 LSV of NiCo/CNF@NC catalyst before and after ADT test (a) OER by cycling between 1.2 and 1.8 V vs. RHE at scan rate of 100 mV s^{-1}. (b) HER by cycling between -0.3 and 0.2 V vs. RHE at scan rate of 100 mV s^{-1}.

Table S1. Comparison of the electrochemical performances of the electrocatalysts in this work and other related literature. *E_{onset}*, ORR onset potential; *$E_{1/2}$*, the half–wave potential; *j,* diffusion limiting current density at 1600 rpm: *η_{OER}, OER* overpotential at 10 mA cm^{-2}; *ΔE* the potential gap between *OER* potential and *$E_{1/2}$*. All the potentials reported are *V vs. RHE.*

Catalysts	Loading mg/cm^2	*KOH Molarity*	*ORR*			*OER*	*ΔE (V)*	*Ref.*
			E_{onset}	*$E_{1/2}$*	*j (mA cm^{-2})*	*η_{OER}*		
NiCo/CNF@NC	0.26	0.1 M	1.00	0.78	-5.37	0.40	0.85	This work
NiCo/CNF	0.26	0.1 M	0.84	0.62	-4.43	0.52	1.13	This work
CNF	0.26	0.1 M	0.74	0.58	-3.43	0.60	1.25	This work
NiCo@NCNT-700	0.212	0.1 M	0.93	0.82	~-5.0	---	---	1
NiCo@NC-2	0.40	0.1 M	0.96	0.81	-6.54	0.53	0.95	2
NCNT/CoONiO-NiCo	0.21	1 M	0.97	0.83	~-4.4	0.27	0.67	3
NiCo@NCNTs	0.464	0.1 M	---	---	---	0.41	---	4
Ni_1Co_2	0.28	0.1 M	---	---	---	0.4	---	5
$NiCo_2O_4$/G	0.4	0.1 M	0.87	0.54	~-4.2	0.44	1.13	6
$NiCo_2O_4$	---	0.1 M	0.84	0.75	-5.13	0.49	0.97	7
1D $NiCo_2O_4$	0.9	0.1 M	1.03	0.78	~-6.0	0.39	0.84	8
Ni_xO_y/NC	0.21	0.1 M	---	0.71	---	0.41	0.93	9
Co-N/C 800	0.24	0.1 M	---	0.78	~-6.2	0.51	0.96	10
Pt/C	0.16	0.1 M	1.03	0.80	–5.40	0.74	1.17	This work

Table S2. Comparison of HER and OER performance of NiCo/CNF@NC catalyst with reference catalyst prepared in this work and other related literatures. *η_{HER}* (*HER* overpotential) *η_{OER}* (*OER* overpotential). All the potential reported are *V vs. RHE.*

Catalysts	Loading mg/cm^2	*KOH Molarity*	*HER*		*OER*		*Ref.*
			Current density (mA cm^{-2})	*η_{HER}*	**Current density (mA cm^{-2})**	*η_{OER}*	
NiCo/CNF@NC	0.26	1 M	10	0.22	10	0.35	This work
NiCo/CNF	0.26	1 M	10	0.42	10	0.49	This work
Ni/CNF@NC	0.26	1 M	10	0.37	10	0.45	This work
Co/CNF@NC	0.26	1 M	10	0.36	10	0.39	This work
Ni–Co–Fe (NCF)-MOF	0.20	0.1 M	10	0.27	10	0.32	11
Ni-NiO/N-rGO	0.21	0.1 M	10	0.21	10	0.22	12
NGO/Ni_7S_6	0.21	0.1 M	10	0.38	10	0.38	13
$Ni_{0.33}Co_{0.67}S_2$	0.30	1 M	---	---	10	0.33	14
Nix$Co_{3-x}O_4$	3.0	1 M	---	---	10	0.37	15
CoO*x*@CN	0.12	1 M	10	0.232	10	0.26	16

Table S3. Comparison of NiCo/CNF@NC based Zn-air battery perfomances with the other related works in the reported literatureres. Where: OCP, open circuit potential.

Catalysts	*OCP (V)*	*Specific capacity mA h g^{-1}*	*Energy density Wh kg^{-1}*	*Cyclability*	*Ref.*
NiCo/CNFs@NC	1.46	764 @20 mA cm^{-2}	871 @20 mA cm^{-2}	1800 s/cycle (at 5 mA cm^{-2}) for 130 cylcles with negligble loss in voltage at the end.	This work
NCNT/CoONiO-NiCo	---	504 @20 mA cm^{-2}	615 @20 mA cm^{-2}	400 s/cycle (at 20 mA cm^{-2}) for 100 cylcles with negligble change of voltage at the end.	3
$NiCo_2S_4$/N-CNT	1.49	431.1 @10 mA cm^{-2}	554.6 @10 mA cm^{-2}	400 s/cycle (10 mA cm^{-2}) for 150 cycles.	17
Co_3O_4-NP/N-rGO	1.51	786 @5 mA cm^{-2}	997 @5 mA cm^{-2}	400 s/cycle (at 5 mA cm^{-2}) 1600 cycles no obvious voltage change.	18
$NiCo_2O_4$	1.45	580 @20 mA cm^{-2}	725@20 mA cm^{-2}	1200s/cycle (at 20 mA cm^{-2}) for 50 cycles with a small overpotential of 0.14 V.	8
NCO/N-rGO	---	712 @5 A g^{-2}	---	600s/cycle (10 at 5 A g^{-2}) for 50 cycles with only 0.07 V overpotential gap increase.	19
$NiCo_2O_4$-CNTs-400	1.38	670 @10 mA cm^{-2}	700 @10 mA cm^{-2}	600s/cycle (10 mA cm^{-2}) for 240 cycles.	20

Table S4. *Comparison of the water splitting performances of NiCo/CNF@NC catalyst and electrocatalysts based on other previously reported literatures.*

Catalysts	Loading mg/cm^2	*KOH Molarity*	*Support*	η*@10mA cm^{-2}*	*Ref.*
NiCo/CNF@NC	4.6	1 M	Ni foam	0.31	This work
Ni/NiP	11	1 M	Ni foam	0.38	21
$Ni_{0.9}Fe_{0.1}$/NC	2.0	1 M	Ni foam	0.35	22
Ni_5P_4	---	1 M	Ni foam	0.47	23
NiSe NWs	2.8	1 M	Ni foam	0.40	24
$NiCo_2S_4$@NiFe LDH/NF	---	1 M	Ni foam	0.37	25
$NiCo_2S_4$ NW	---	1 M	Ni foam	0.40	26
NiFe/$NiCo_2O_4$/NF	---	1 M	Ni foam	0.44	27
Pt-CoS_2/CC	~ 0.5	1 M	Carbon cloth	0.32	28

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