Supporting Information for

N&S co-doped carbon nanofiber network embedded with ultrafine NiCo nanoalloy for efficient oxygen electrocatalysis and Zn-air battery

Chaojun Liu, [a] *Zhuang Wang,*[a] *Xin Zong,* [a] *Yingmin Jin,* [a] *Dong Li,* [a] *Yueping Xiong**[a] *and Gang Wu**[b]

[a.] Department MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, P.R. China.

[b.]Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA.

Corresponding authors: ypxiong@hit.edu.cn (Y. Xiong) and gangwu@buffalo.edu (G. Wu)

Figure S1-S33
Table S1-S5

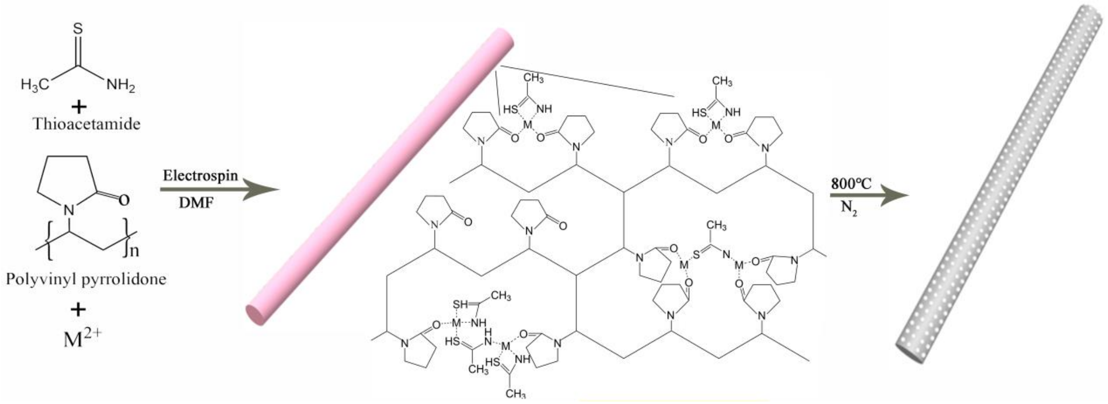

Figure S1 Schematic illustration of the formation of NSCFs/Ni-Co-$NiCo_2O$.

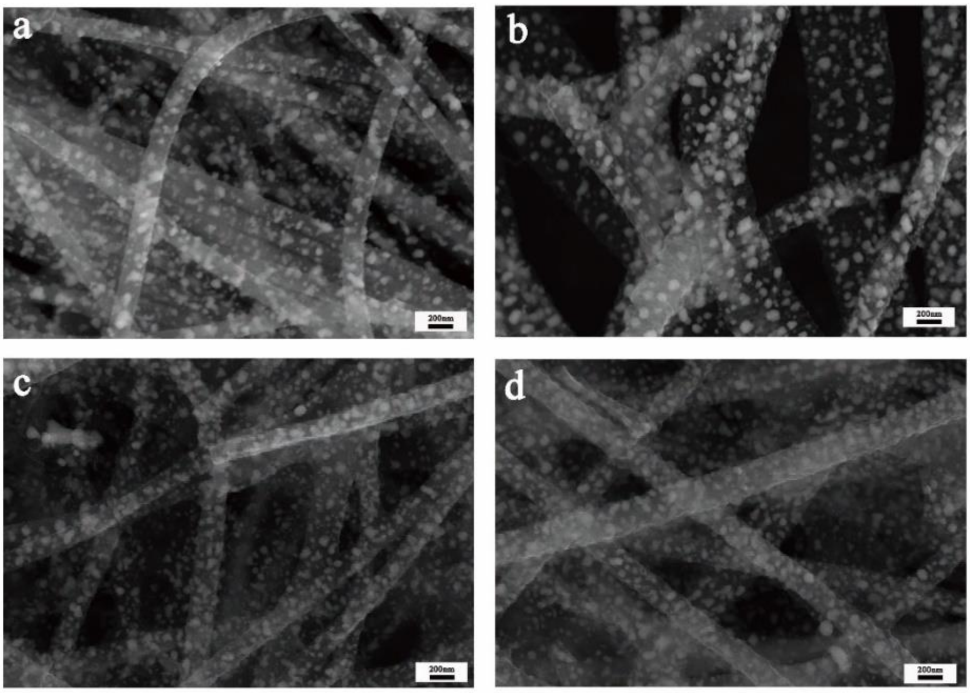

Figure S2 SEM image of a) CFs/Ni-Co-Ni_2CoO, b) CFs/Ni-Co-NiCoO, c) CFs/Ni-Co-$NiCo_2O$, d) CFs/Ni-Co-$NiCo_3O$.

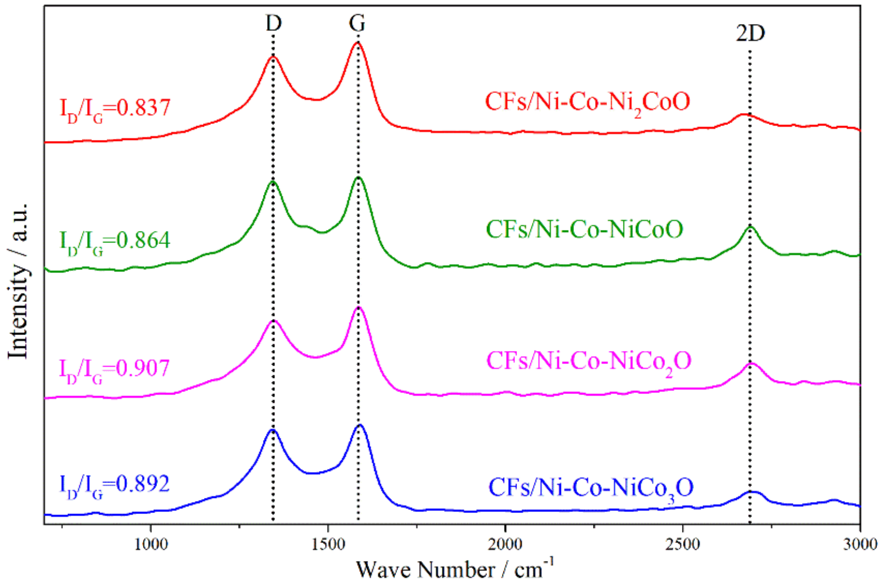

Figure S3 Raman spectra of CFs/Ni-Co-Ni$_2$CoO, CFs/Ni-Co-NiCoO, CFs/Ni-Co-NiCo$_2$O, and CFs/Ni-Co-NiCo$_3$O.

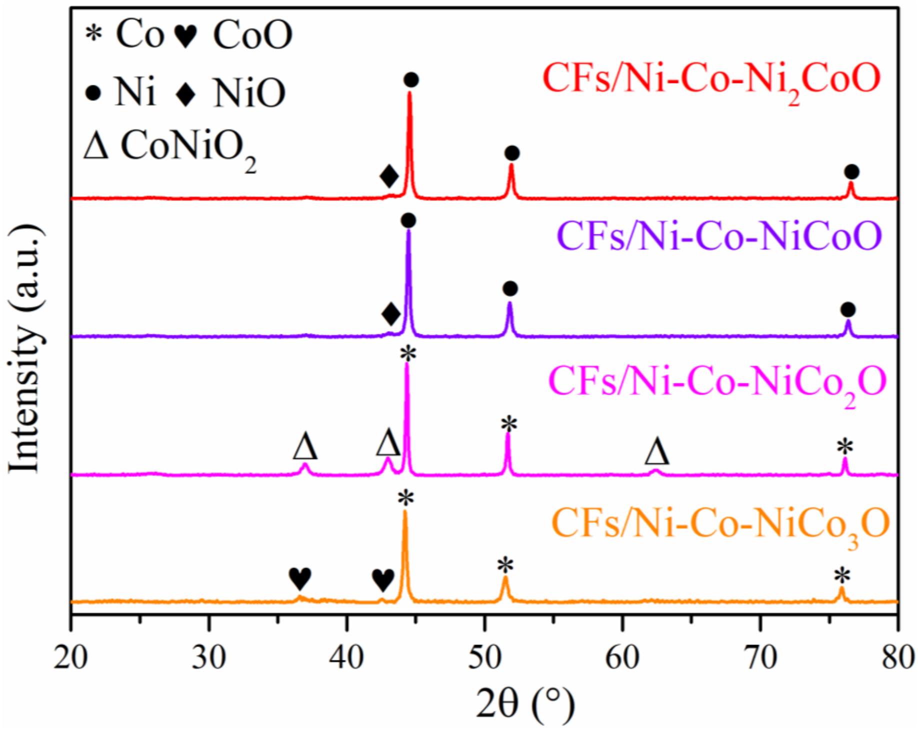

Figure S4 XRD analyses of CFs/Ni-Co-Ni$_2$CoO, CFs/Ni-Co-NiCoO, CFs/Ni-Co-NiCo$_2$O, and CFs/Ni-Co-NiCo$_3$O.

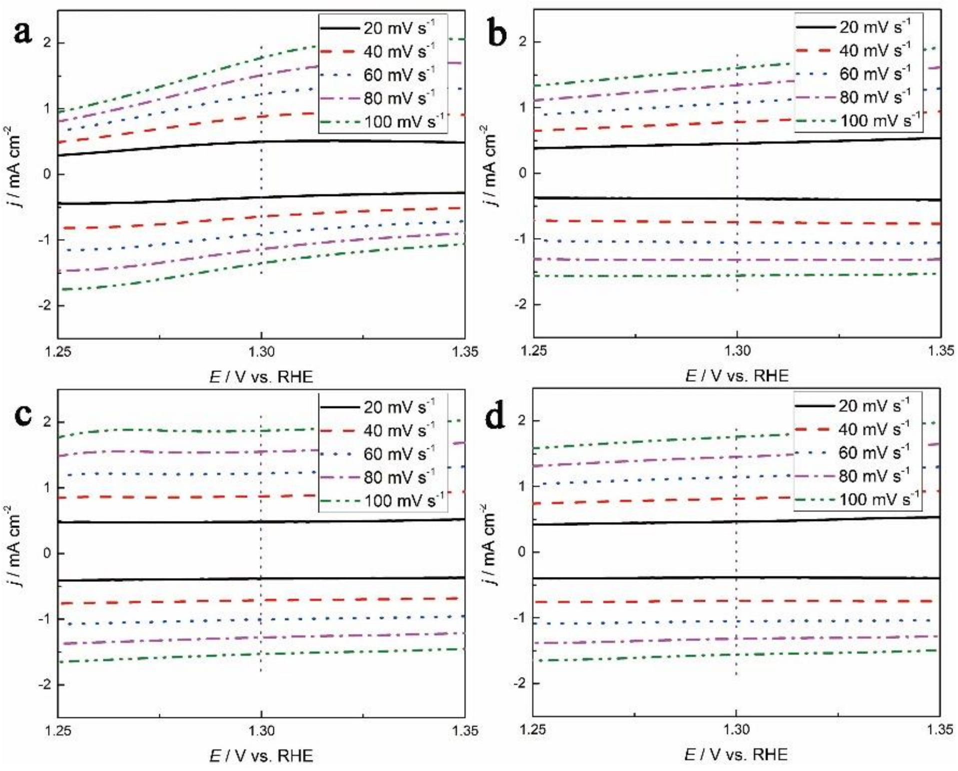

Figure S5 CV curves of the a) CFs/Ni-Co-Ni_2CoO, b) CFs/Ni-Co-NiCoO, c) CFs/Ni-Co-$NiCo_2O$, d) CFs/Ni-Co-$NiCo_3O$ catalysts obtained in 1.0 M KOH with different scan rates between a potential range of 1.25-1.35 V *vs*. RHE.

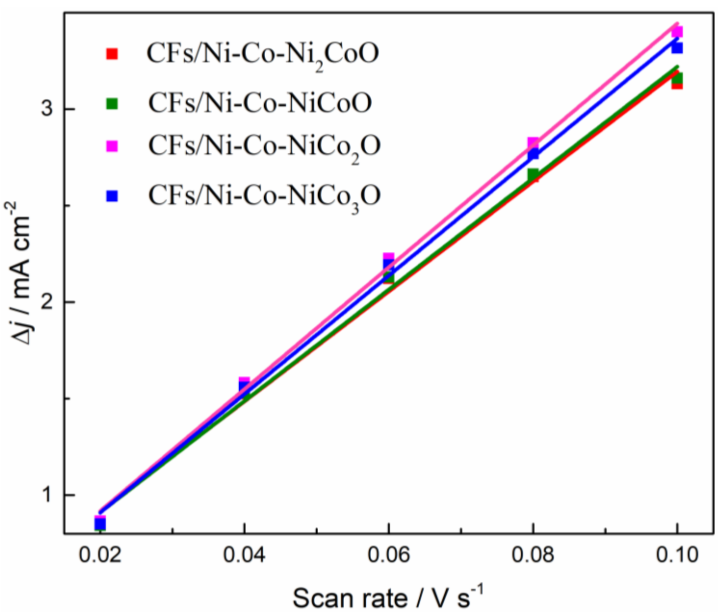

Figure S6 The corresponding C_{dl} values at 1.3 V *vs*. RHE of CFs/Ni-Co-Ni_2CoO, CFs/Ni-Co-NiCoO, CFs/Ni-Co-$NiCo_2O$, and CFs/Ni-Co-$NiCo_3O$.

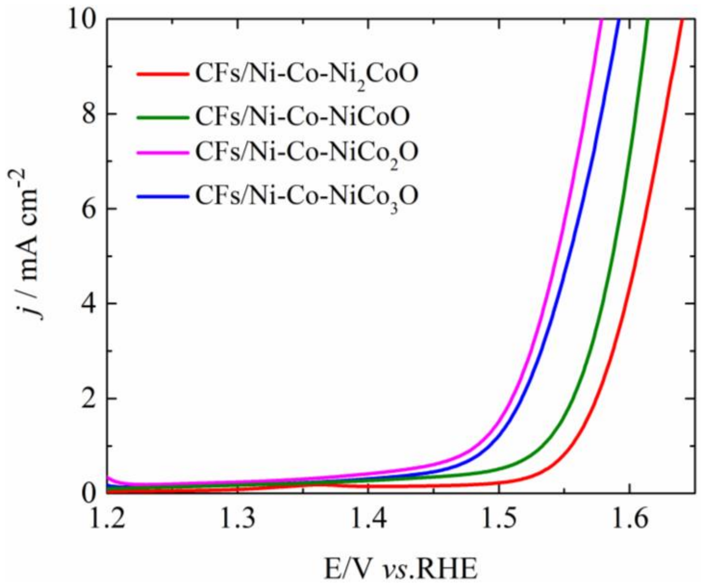

Figure S7 OER polarization curves of CFs/Ni-Co-Ni_2CoO, CFs/Ni-Co-NiCoO, CFs/Ni-Co-$NiCo_2O$, and CFs/Ni-Co-$NiCo_3O$.

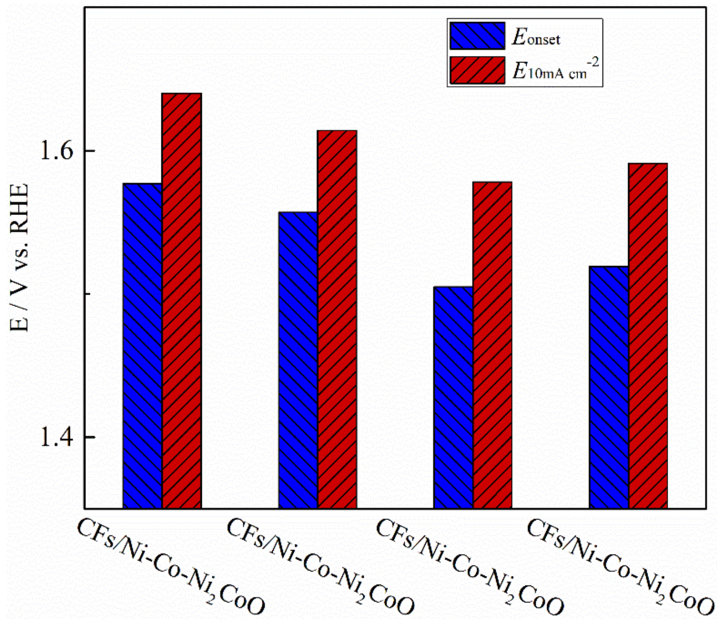

Figure S8 E_{onset} and E_{10} values of CFs/Ni-Co-Ni_2CoO, CFs/Ni-Co-NiCoO, CFs/Ni-Co-$NiCo_2O$, and CFs/Ni-Co-$NiCo_3O$.

OER catalytic activity measurement was performed in a standard three-electrode system. The OER catalytic activities of different nitrate ratio samples were measured in 1.0 M KOH by LSVs (Figure S7 and Figure S8). As expected, the CFs/Ni-Co-$NiCo_2O$ sample shows the lowest E_{onset} and E_{10}, which indicates the excellent OER catalytic performance.

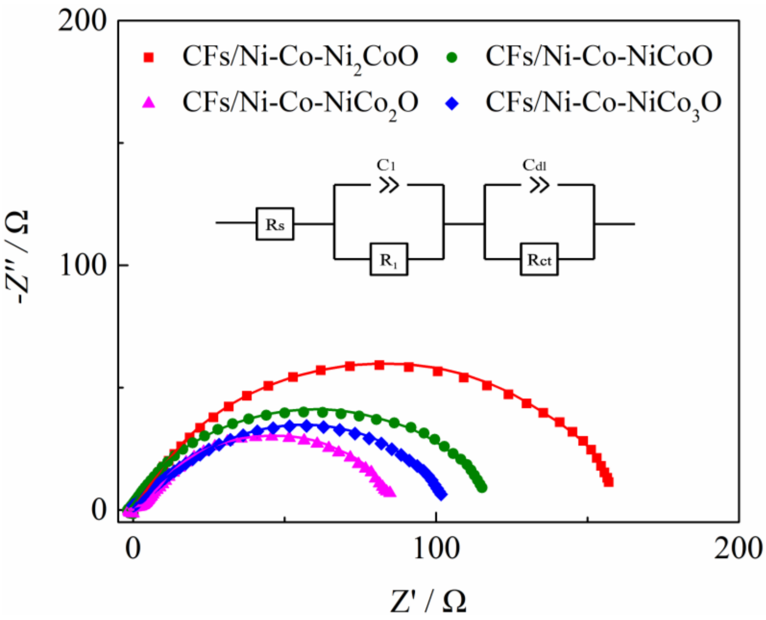

Figure S9 The Nyquist plots of different molar ratios examined at 1.5V *vs.* RHE for OER.

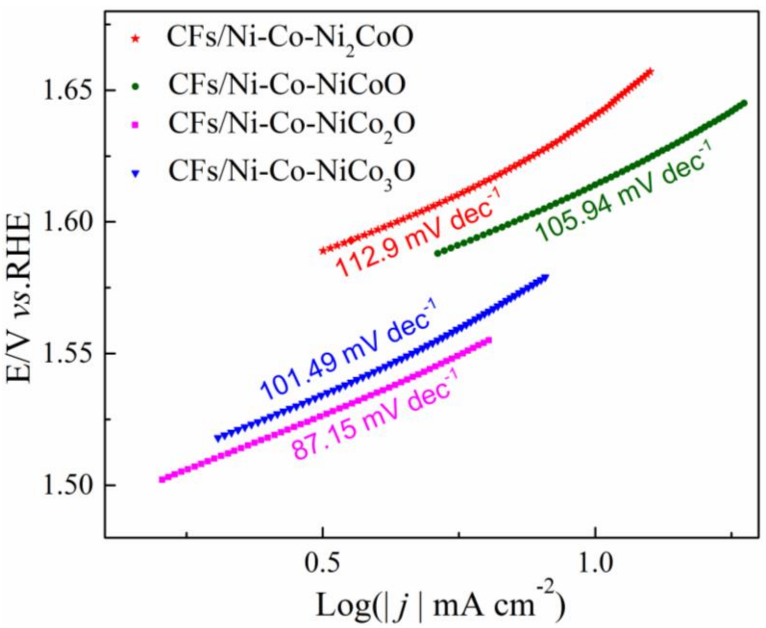

Figure S10 The corresponding Tafel plots of CFs/Ni-Co-Ni_2CoO, CFs/Ni-Co-NiCoO, CFs/Ni-Co-$NiCo_2O$, and CFs/Ni-Co-$NiCo_3O$.

Figure S9 and Figure S10 show the Nyquist plots and Tafel plots of different samples. All EIS data can be fitted perfected by using the Equivalent electrical circuit (EEC) shown the inset figure of Figure S9. The lowest Rct value (89 Ω) and the smallest Tafel slope (87.15 mV dec-1) all correspond to a more favorable OER kinetics of CFs/Ni-Co-$NiCo_2O$.

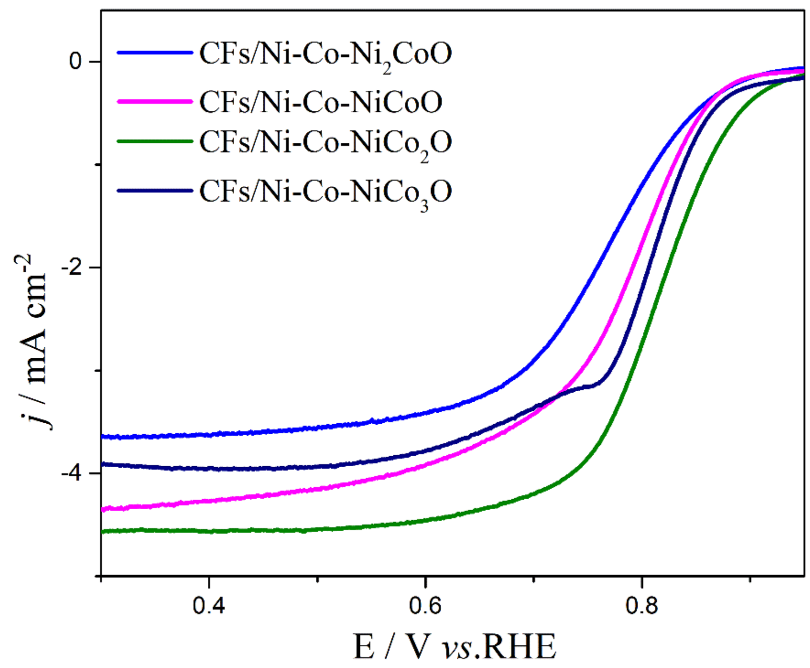

Figure S11 The ORR polarization curves of CFs/Ni-Co-Ni_2CoO, CFs/Ni-Co-NiCoO, CFs/Ni-Co-$NiCo_2O$, and CFs/Ni-Co-$NiCo_3O$.

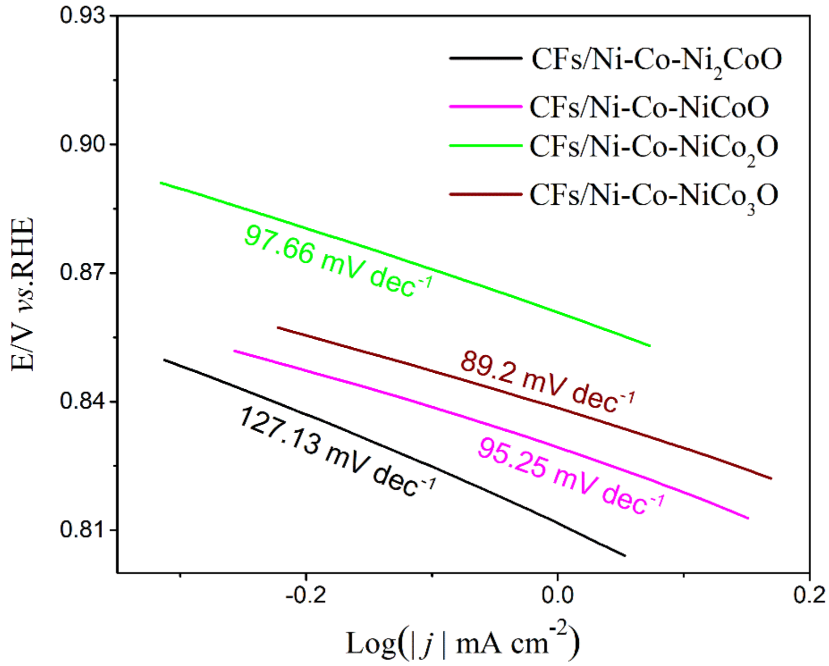

Figure S12 The ORR Tafel plots of CFs/Ni-Co-Ni_2CoO, CFs/Ni-Co-NiCoO, CFs/Ni-Co-$NiCo_2O$, and CFs/Ni-Co-$NiCo_3O$.

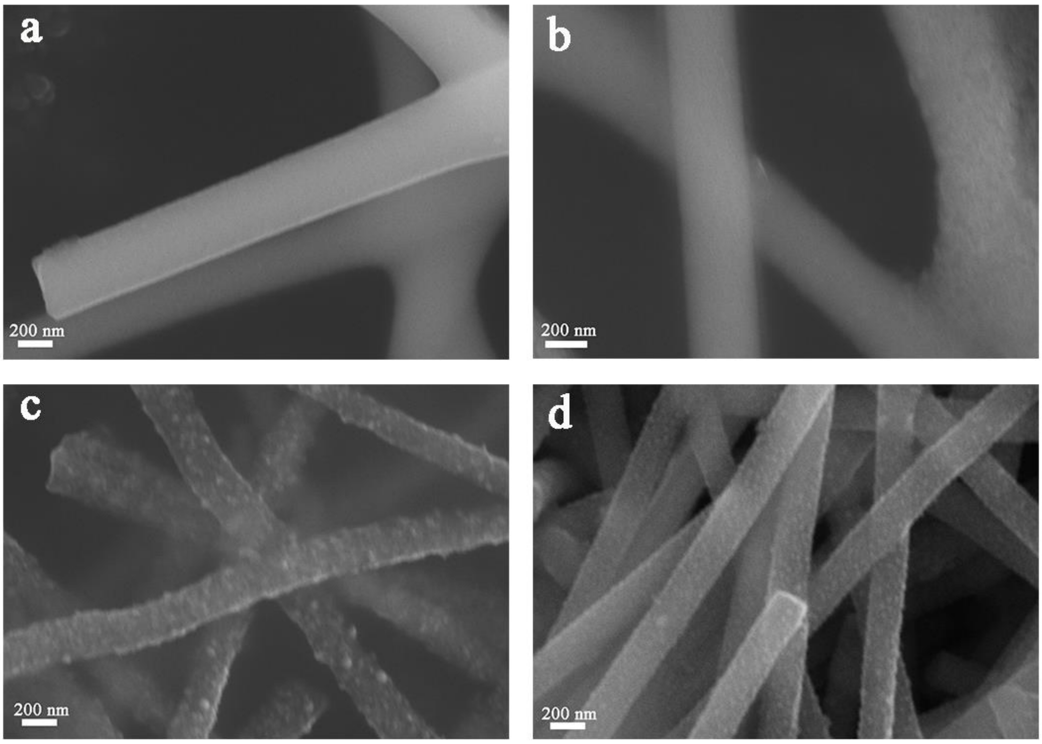

Figure S13 The SEM images of a) CFs, b) NSCFs, c) NSCFs/Ni-NiO, and d) NSCFs/Co-CoO.

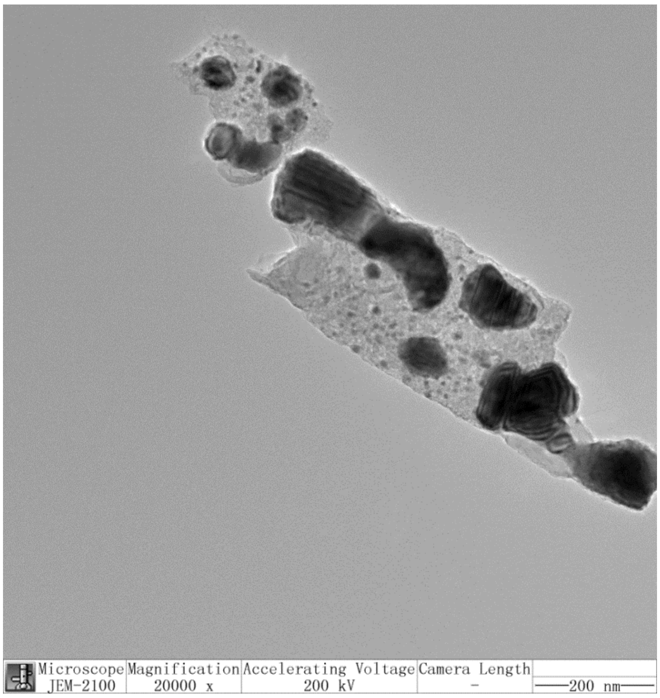

Figure S14 TEM image of CFs/Ni-Co-$NiCo_2O$.

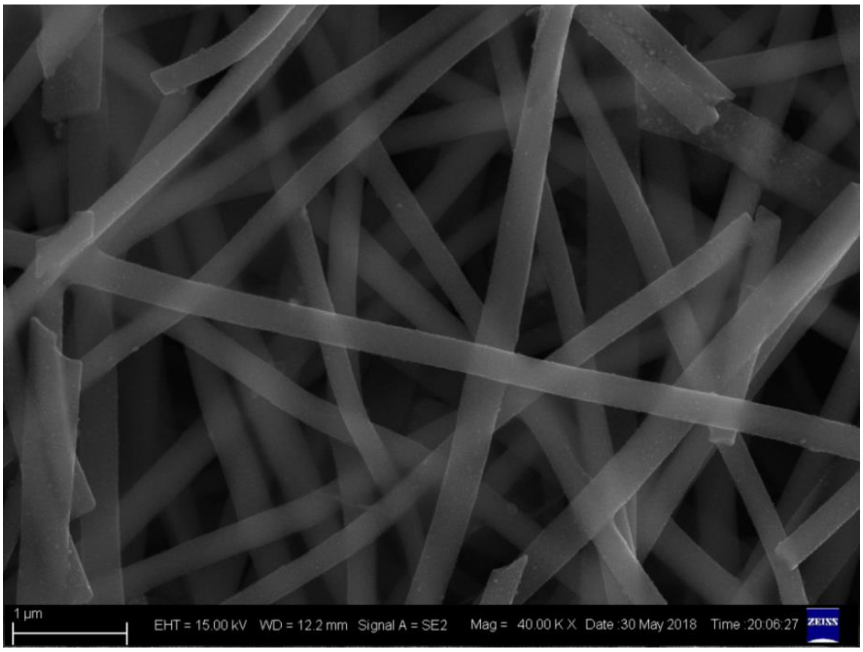

Figure S15 SEM image of NSCFs/Ni-Co-$NiCo_2O$.

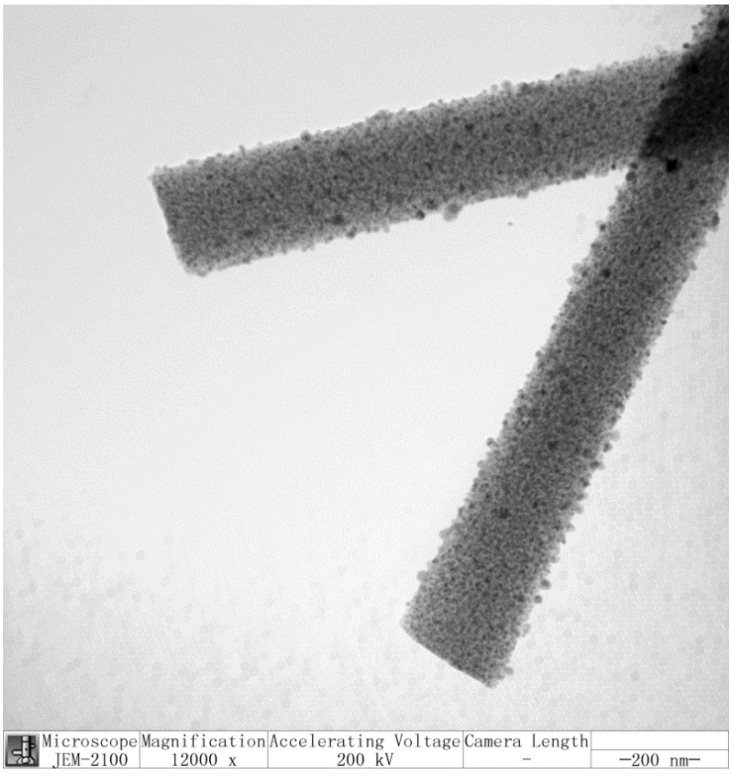

Figure S16 TEM image of NSCFs/Ni-Co-$NiCo_2O$.

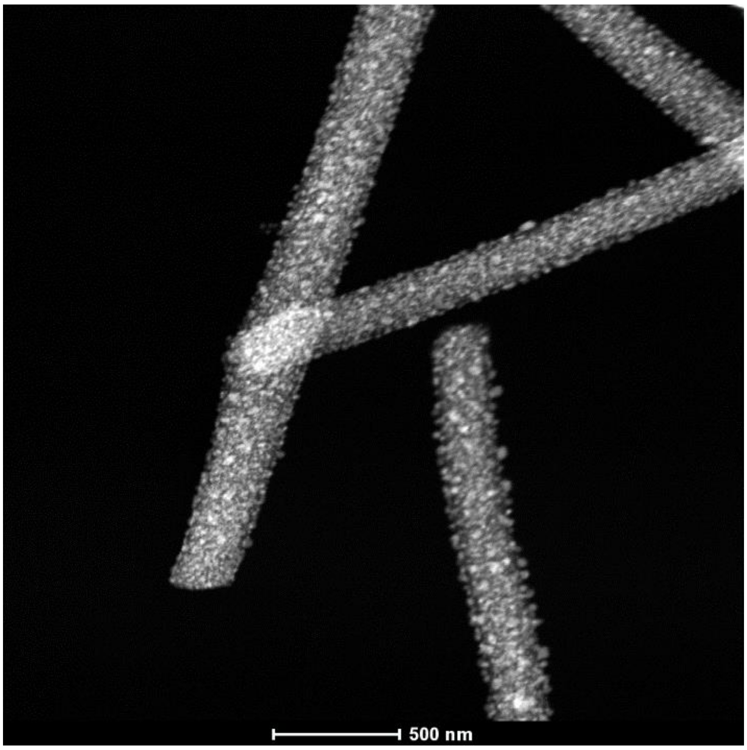

Figure S17 HAADF-STEM image of NSCFs/Ni-Co-$NiCo_2O$.

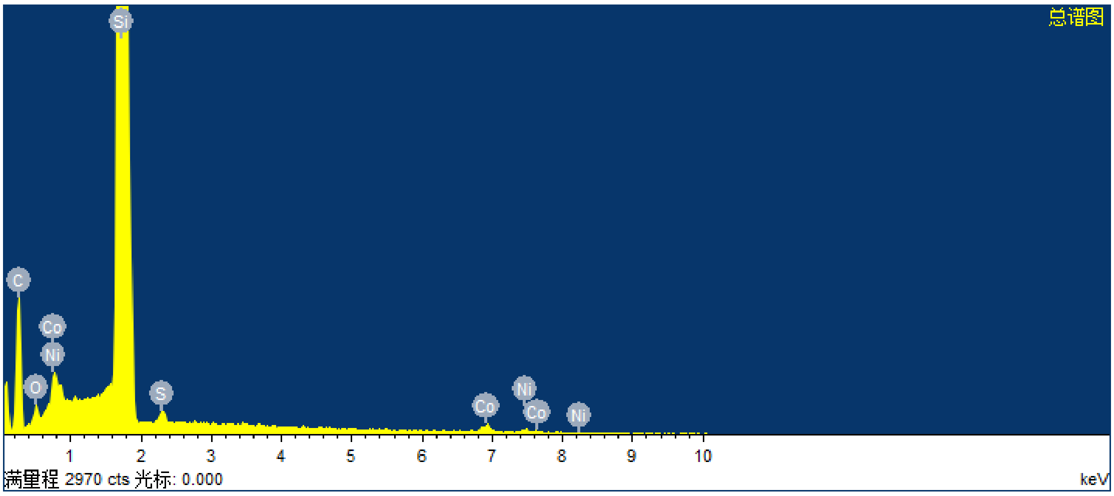

Figure S18 EDS pattern for NSCFs/Ni-Co-$NiCo_2O$ catalyst.

Table S1 Element mass percentages for NSCFs/Ni-Co-$NiCo_2O$ measured by EDX.

Element	Mass percentages
Ni	1.47 %
Co	3.37 %
S	0.94 %
O	3.28 %
C	90.94 %

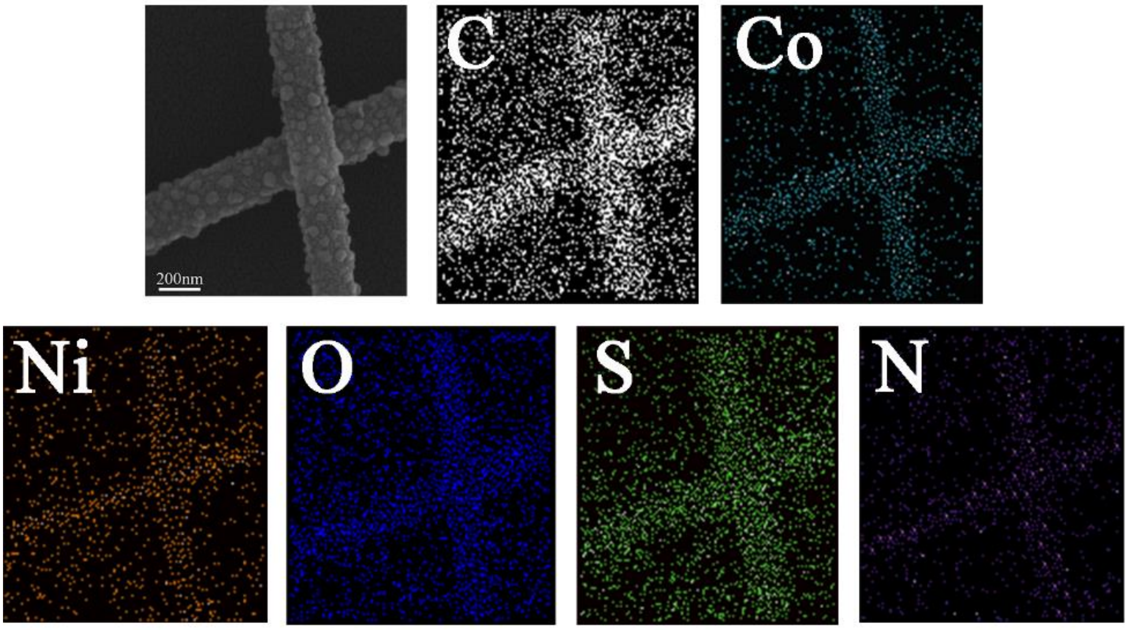

Figure S19 Elemental mapping of NSCFs/Ni-Co-$NiCo_2O$.

Table S2 Element mass percentages for NSCFs/Ni-Co-$NiCo_2O$ measured by ICP.

Element	Mass percentages
Ni	11.78 %
Co	23.28 %

Table S3 Element mass percentages for NSCFs/Ni-Co-$NiCo_2O$ measured by XPS.

Element	Mass percentages
Ni	3.12 %
Co	4.84 %
N	2.22 %
S	2.17 %
O	11.43 %
C	76.22 %

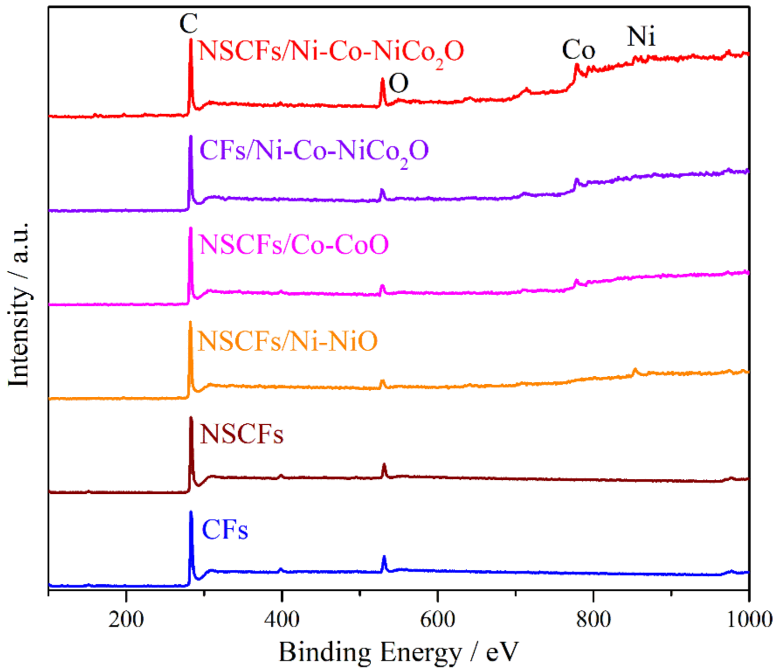

Figure S20 XPS survey spectra of CFs, NSCFs, NSCFs/Ni-NiO, NSCFs/Co-CoO, CFs/Ni-Co-NiCo$_2$O, NSCFs/Ni-Co-NiCo$_2$O.

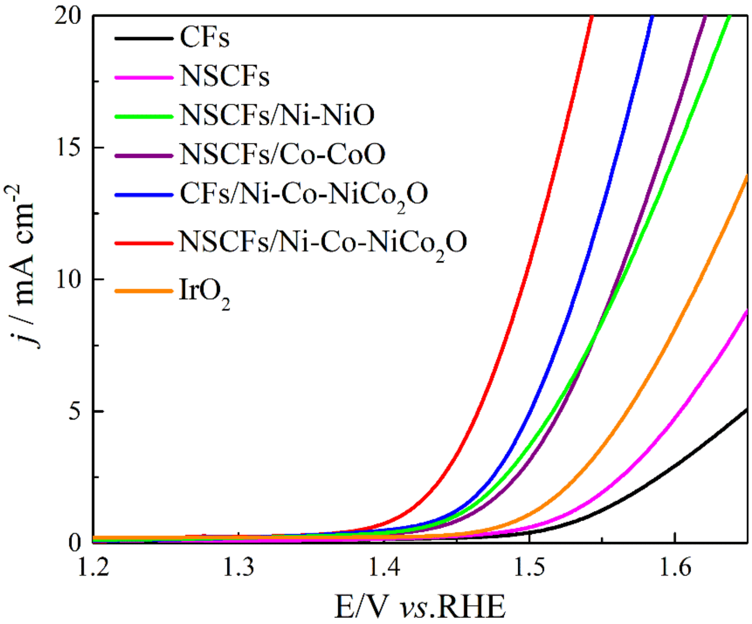

Figure S21 OER polarization curves of CFs, NSCFs, NSCFs/Ni-NiO, NSCFs/Co-CoO, CFs/Ni-Co-NiCo$_2$O, NSCFs/Ni-Co-NiCo$_2$O, and IrO$_2$.

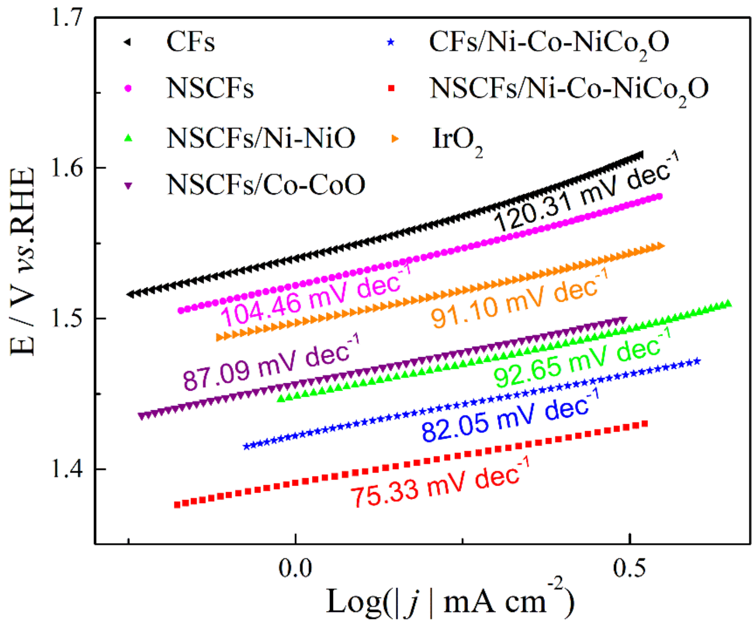

Figure S22 The corresponding Tafel plots of CFs, NSCFs, NSCFs/Ni-NiO, NSCFs/Co-CoO, $CFs/Ni\text{-}Co\text{-}NiCo_2O$, $NSCFs/Ni\text{-}Co\text{-}NiCo_2O$, and IrO_2.

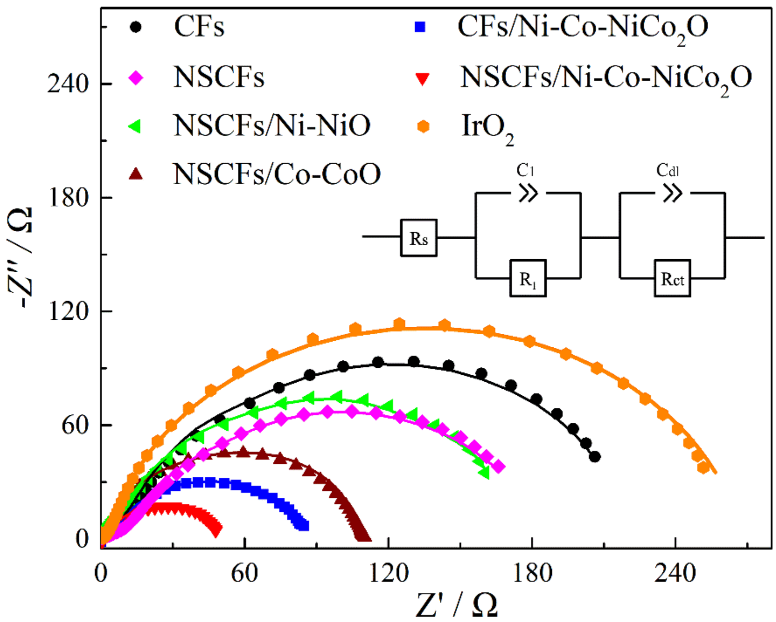

Figure S23 The Nyquist plots of CFs, NSCFs, NSCFs/Ni-NiO, NSCFs/Co-CoO, CFs/Ni-Co-$NiCo_2O$, $NSCFs/Ni\text{-}Co\text{-}NiCo_2O$, and IrO_2 at 1.5V vs. RHE for OER.

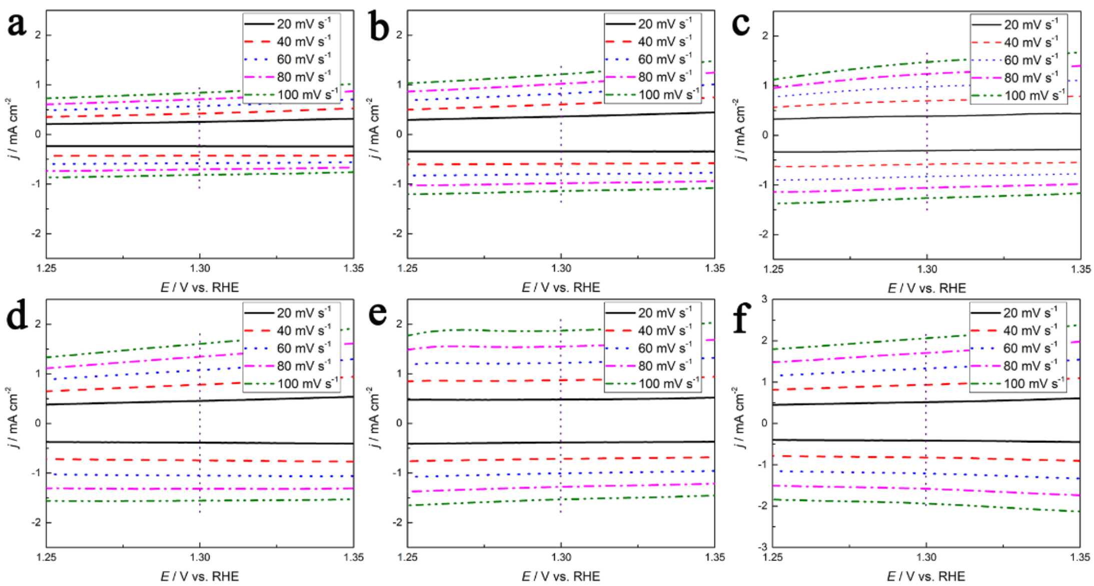

Figure S24 CV curves of the a) CFs, b) NSCFs, c) NSCFs/Ni-NiO, d) NSCFs/Co-CoO, e) CFs/Ni-Co-$NiCo_2O$, f) NSCFs/Ni-Co-$NiCo_2O$ catalysts obtained in 1.0 M KOH with different scan rates between a potential range of 1.25-1.35 V *vs*. RHE.

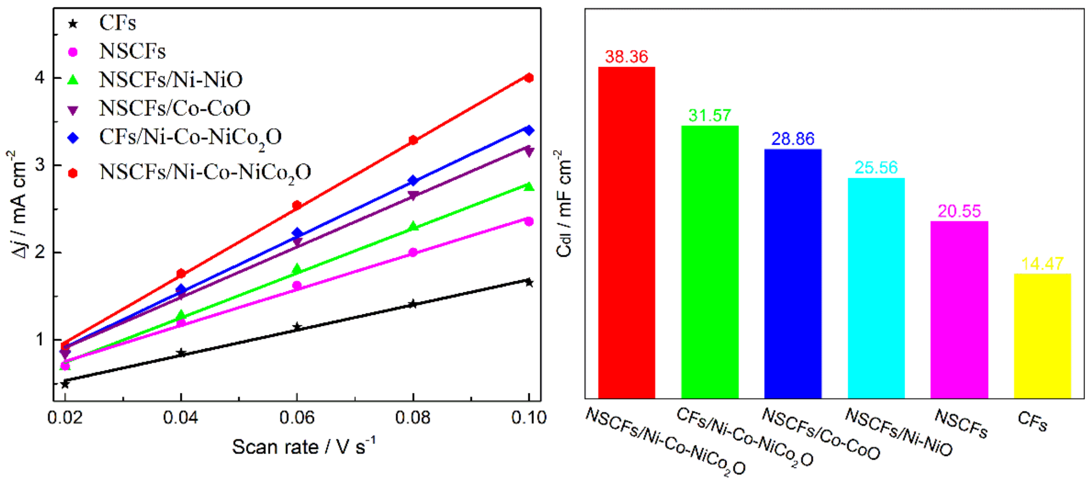

Figure S25 The corresponding C_{dl} values at 1.3 V *vs*. RHE of CFs, NSCFs, NSCFs/Ni-NiO, NSCFs/Co-CoO, CFs/Ni-Co-$NiCo_2O$, NSCFs/Ni-Co-$NiCo_2O$ catalysts.

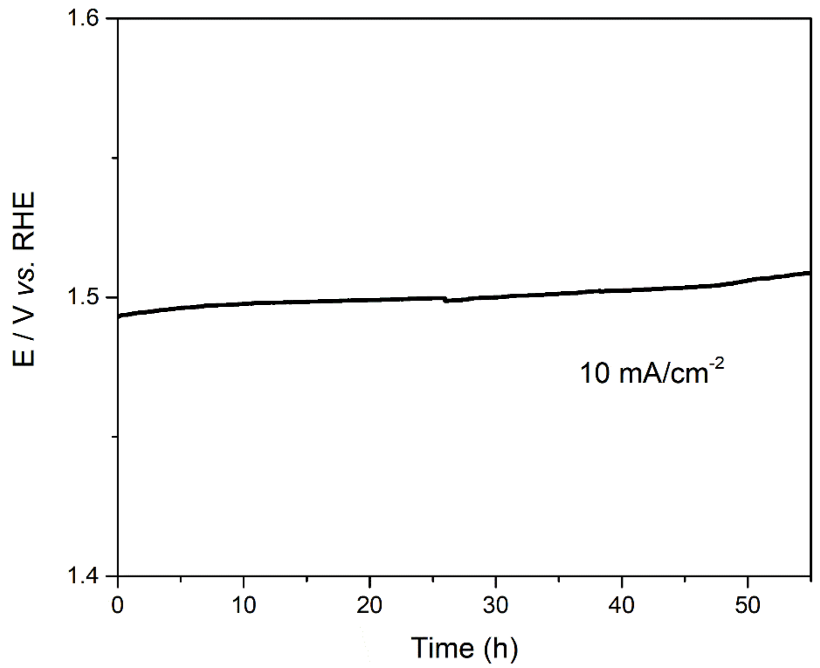

Figure S26 The prolonged chronopotentiometric response of NSCFs/Ni-Co-$NiCo_2O$.

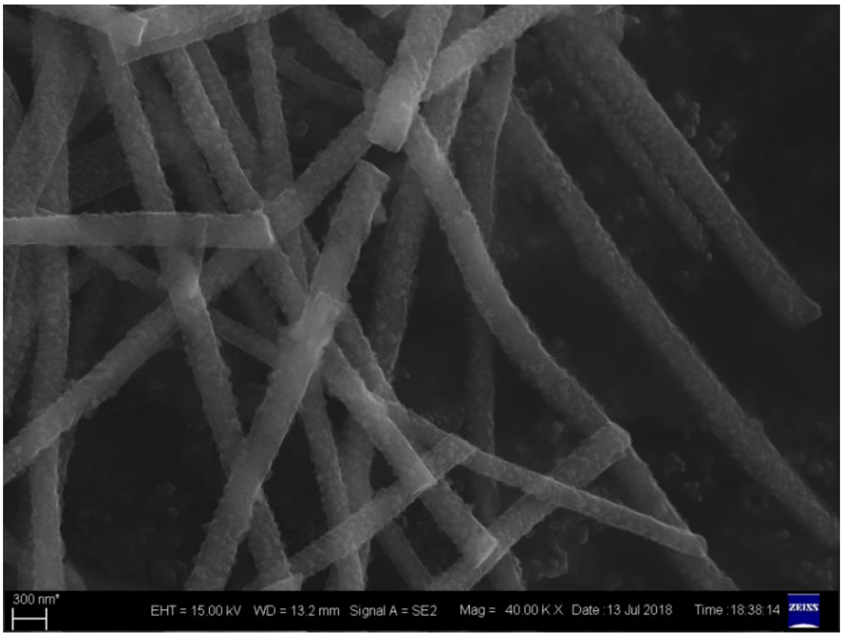

Figure S27 SEM image of the $NiCo_2$-N_3-S_3-C after chronopotentiometry measurement.

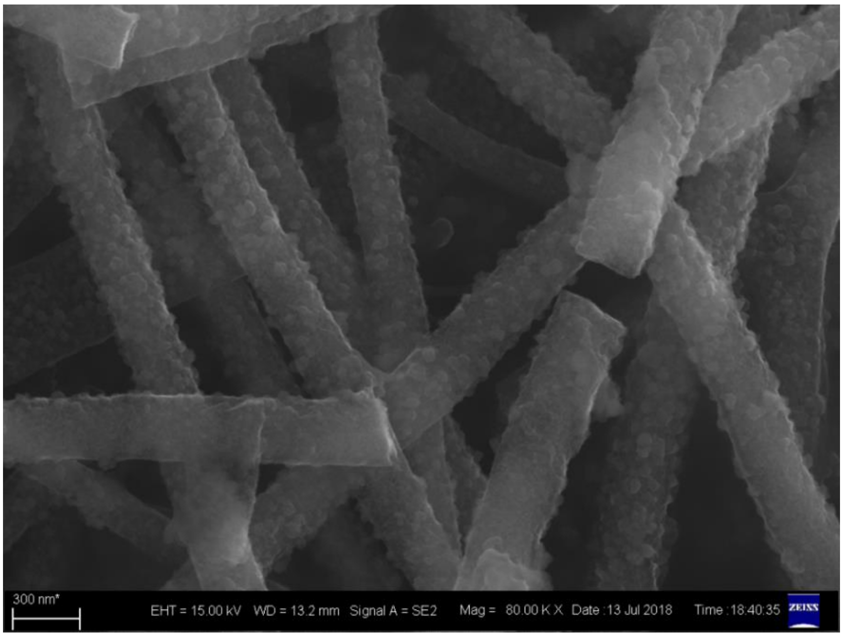

Figure S28 SEM image of the $NiCo_2$-N_3-S_3-C after chronopotentiometry measurement.

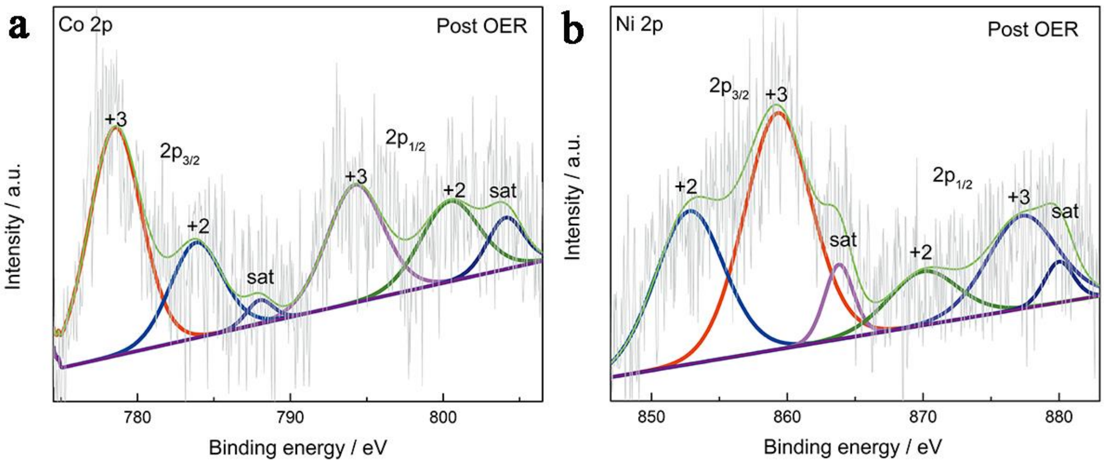

Figure S29 a) High resolution XPS spectra of Co 2p for NSCFs/Ni-Co-$NiCo_2O$ after OER. b) High resolution XPS spectra of Ni 2p for NSCFs/Ni-Co-$NiCo_2O$ after OER.

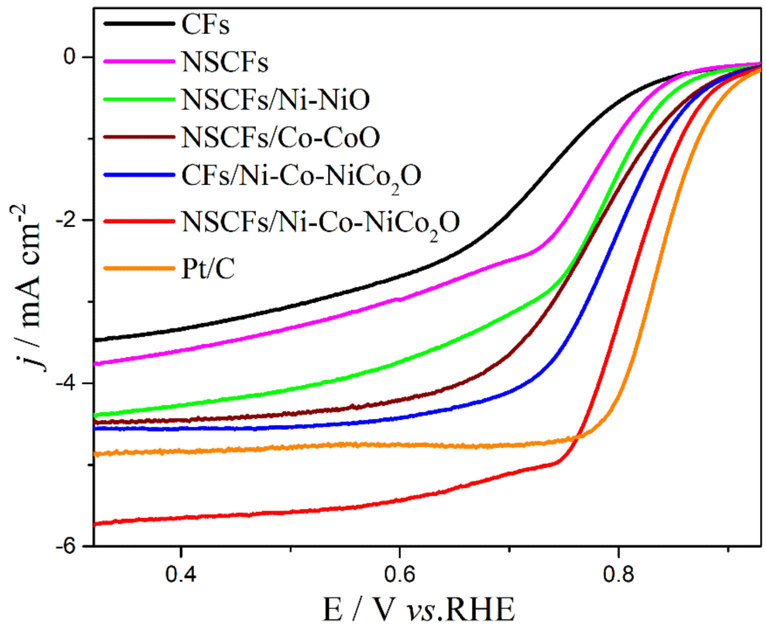

Figure S30 ORR polarization curves of CFs, NSCFs, NSCFs/Ni-NiO, NSCFs/Co-CoO, CFs/Ni-Co-$NiCo_2O$, NSCFs/Ni-Co-$NiCo_2O$, and Pt/C.

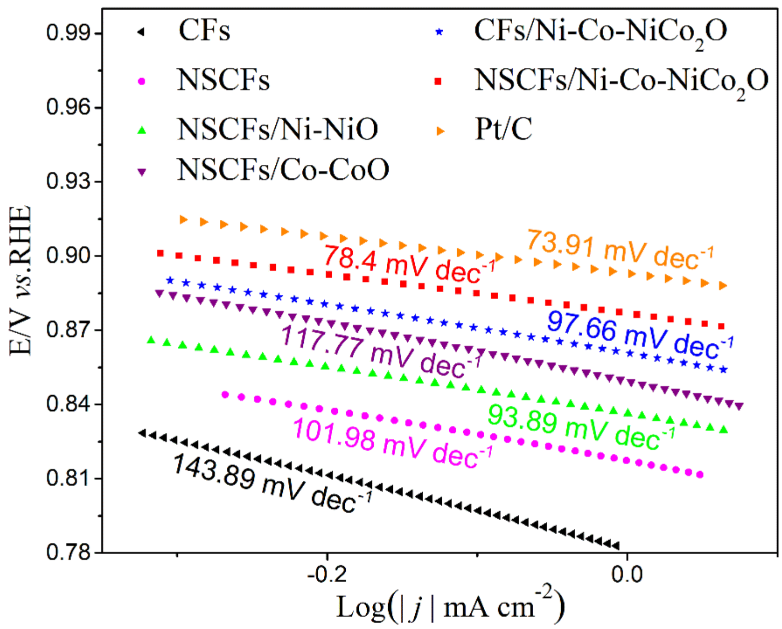

Figure S31 The corresponding Tafel plots of CFs, NSCFs, NSCFs/Ni-NiO, NSCFs/Co-CoO, CFs/Ni-Co-$NiCo_2O$, NSCFs/Ni-Co-$NiCo_2O$, and Pt/C.

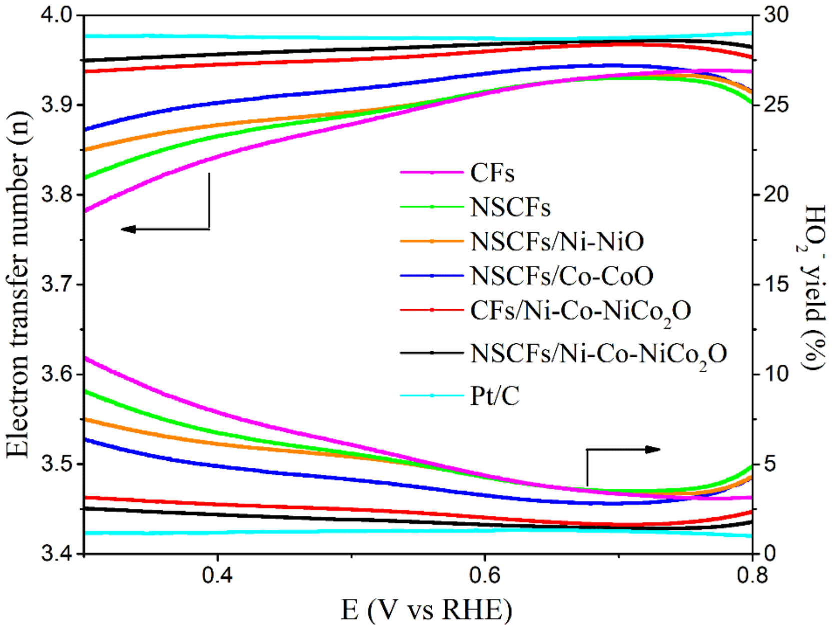

Figure S32 The electron transfer number (n) and HO_2^- yield ratio of CFs, NSCFs, NSCFs/Ni-NiO, NSCFs/Co-CoO, CFs/Ni-Co-$NiCo_2O$, NSCFs/Ni-Co-$NiCo_2O$, and Pt/C.

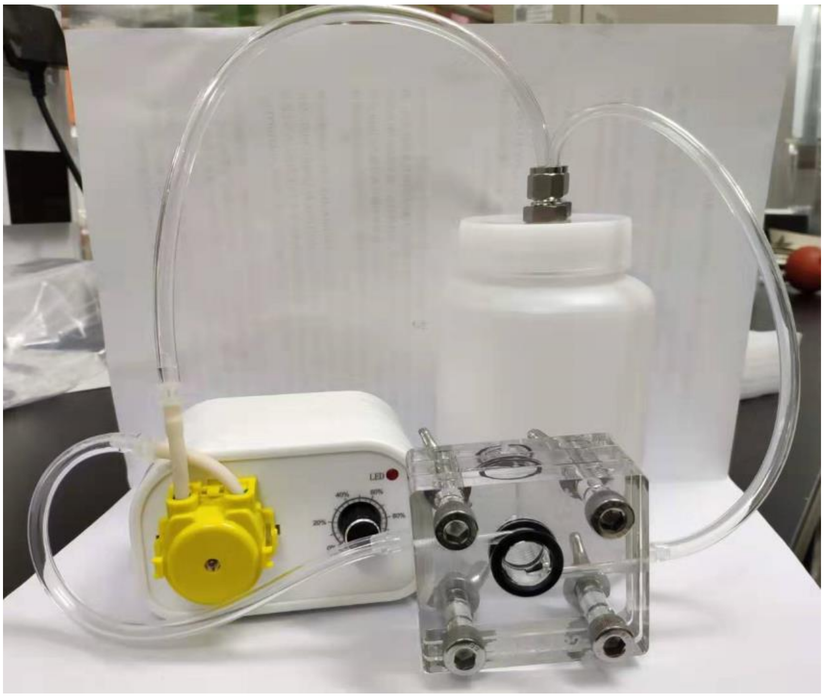

Figure S33 the photograph of the home-made Zn-air battery mold.

Table S4 Comparison of the OER and ORR performance of NSCFs/Ni-Co-$NiCo_2O$ with other reported electrocatalysts test under similar conditions.

Catalyst	OER&ORR performance				Ref.
	OER $E_{j=10}$ / V	ORR $E_{1/2}$ / V	ΔE / V	Electrolyte OER ORR	
NSCFs/Ni-Co-$NiCo_2O$	1.498	0.806	0.69	1.0 M	**This work**
NiCo/NLG-270	1.570	0.820	0.750	1.0 M 0.1 M	*Adv. Mater.* **2018**, 30, 1800005
Fe@C-NG/NCNTs	1.680	0.840	0.840	1.0 M 0.1 M	*J. Mater. Chem. A* **2018**, 6, 516-626
Meso/micro-FeCo-N_x-CN-30	1.670	0.886	0.784	1.0 M 0.1 M	*Angew. Chem. Int. Edit.* **2018**, 57, 1856-1862
CoFe/N-GCT	1.670	0.79	0.88	0.1 M	*Angew. Chem. Int. Edit.* **2018**, 57, 16166-16170
Fe/Co-N/S-Cs	1.515	0.832	0.683	0.1 M	*Appl. Catal. B Environ.* **2019**, 241, 95-103
FeCo/FeCoNi@NCNTs-HF	1.608	0.850	0.758	0.1 M	*Appl. Catal. B Environ.* **2019**, 254, 26-36
CoNi/BCF	1.600	0.800	0.800	0.1 M	*Appl. Catal. B Environ.* **2019**, 240, 193-200
In-CoO/CoP FNS	1.595	0.810	0.790	0.1 M	*Small.* **2019**, 15, 1904210
CoPi/NPGA	1.570	0.800	0.770	1.0 M 0.1 M	*ACS Sustain. Chem. Eng.* **2018**, 6, 9793-9803
CoS_2/SKJ	1.580	0.840	0.740	0.1 M	*ACS Nano* **2019**, 13, 7062-7072
$CoIn_2S_4$/S-rGO	1.600	0.820	0.780	0.1 M	*Adv. Energy Mater.* **2018**, 8, 1802263
$NiCo_2O_4$/Co,N-CNTs NCs	1.569	0.862	0.707	1.0 M	*ACS Sustain. Chem. Eng.* **2018**, 6, 10021-10029
$CuCo_2O_4$/N-CNTs	1.702	0.802	0.900	0.1 M	*Adv. Funct. Mater.* **2017**, 27 1701833
Co-POC	1.700	0.830	0.870	0.1 M	*Adv. Mater.* **2019**, 31, 1900592

Table S5 Comparison of the Zn-air batteries performance of NSCFs/Ni-Co-$NiCo_2O$ with other reported electrocatalysts test under similar conditions

Catalyst	Capability (mW cm^{-2})	Cyclability	Reference
NSCFs/Ni-Co-$NiCo_2O$	171.24	Lifetime of 380 h @ 10 mA cm^{-2}	**This work**
Co-POC	78.0	Lifetime of 25 h @ 2 mA cm^{-2}	*Adv. Mater.* **2019**, 31, 1900592
$CoIn_2S_4$/S-rGO	133	Lifetime of 50 h @ 10 mA cm^{-2}	*Adv. Energy Mater.* 2018, 8, 1802263.
NCO-250	166	Lifetime of 75 h @ 10 mA cm^{-2}	*ACS. Appl. Mater.* Interfaces **2019,** 11, 4915-4921.
FeCo@MNC	115	Lifetime of 24 h @ 20 mA cm^{-2}	*Appl. Catal. B: Environ.* **2019,** 244, 150-158.
CoNiFe-S MNs	140	Lifetime of 40 h @ 2 mA cm^{-2}	*Adv. Energy Mater.* **2018,** 8, 1801839.
CoS_2/SKJ	104	Lifetime of 330 h @ 25 mA cm^{-2}	*ACS Nano*. **2019**, 6, 7062-7072.
Co-N-CNTs	101	Lifetime of 15 h @ 2 mA cm^{-2}	*Adv. Funct. Mater.* **2018**, 28, 1705048
Co/Co_xM_y	125.2	Lifetime of 166 h @ 10 mA cm^{-2}	*Small*. 2019, 1901518.
C-MOF-C_2-900	105	Lifetime of 120 h @ 2 mA cm^{-2}	*Adv. Mater.* **2018,** 30, 1705431.