Supporting Information

Nitrogen-doped biomass carbon fibers with surface encapsulated Co nanoparticles for electrocatalytic overall water-splitting

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1. Experimental section

Chemicals. Platinum on carbon (Pt/C ,5% wt %, AR), ruthenium (IV) oxide (RuO_2, 99.9%, AR) was purchased from Shanghai Macklin Biochemical Co., LTD. 2,2' -Bipyridyl ($C_{10}H_8N_2$, 99%, AR), nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, 98%, AR), potassium hydroxide (KOH, 99%, AR), sodium chlorite ($NaClO_2$, 80% , AR) were purchased from Aladdin Chemical Reagents Co., LTD. Iron(II) chloride tetrhydrate ($FeCl_2{\cdot}4H_2O$, 98%, AR), cobalt(II) nitrate hexahydrate($Co(NO_3)_2{\cdot}6H_2O$, 98.5%, AR) were purchased from Sinopharm Chemical Reagent Co.,Ltd. Nafion (5 wt %, AR) were purchased from Alfa Aesar. Cotton fibre was purchased from a farm in Changji City, Xinjiang Province, China. Deionized (DI) water was employed as solvent.

Pretreatment of cotton. Add the cotton fibers to the $NaClO_2$ (1 wt%) solution and magnetically stir for 10 minutes. The resulting suspension was refluxed at 120 °C for 4 hours to remove the wax protective layer on the surface. After filtration, it was washed several times with distilled water and dried at 60 ℃ overnight to obtain treated cotton fibers.

Synthesis of the samples. Firstly, 6.7 mmol Co $(NO_3)_2{\cdot}6H_2O$ was dissolved in 10 ml absolute ethanol. Then, the above metal ion solution was slowly dropped into another 20ml of anhydrous ethanol solution containing 4mmol 2,2 '- bipyridine and stirred under ambient conditions for 10 min. After that, 0.9g $NaClO_2$ treated cotton was put into 20ml mixed solution until the cotton absorbed all the solutions and dried at 60 ℃. Then, the cotton was heated to 800 ℃ in a tubular furnace at a heating rate of 5 ℃ min^{-1} and kept in a high purity argon gas stream for 4 hours. After calcination, the sample was stirred with 1wt% HCl for 3 days, washed with ethanol and deionized water 3 times, and finally dried at 60°C overnight to obtain the target product Co/N-BCFs. For comparison, Fe/N-BCFs and Ni/N-BCFs are prepared by the same method, adding the same molar mass of $FeCl_2{\cdot}4H_2O$ and $NiCl_2{\cdot}6H_2O$ instead of Co $(NO_3)_2{\cdot}6H_2O$. BCFs samples were prepared from $NaClO_2$ treated cotton in a tubular furnace at 800 ℃ for 4 h under an argon atmosphere with a temperature ramp of 5 °C min^{-1}.

Preparation the working electrode. Typically, the ink was prepared by dispersing 5 mg of samples into 1ml mixture containing 960 μL ethanol and 40 μL Nafion (5 wt %) with an ultrasonic treatment for 30 min. Then, as-made ink of all the catalysts was dropped onto carbon paper (0.25×0.25 cm^{-2}) to afford a loading density of 2.4 mg cm^{-2}. After drying, the working electrodes were obtained. Electrochemical tests were carried out by using a VERSTAT-3 (Princeton Applied Research, America) electrochemical workstation with a conventional three-electrode system at room temperature, in which sample coated carbon paper electrode, the Hg/HgO electrode and platinum sheet served as the working, reference, and counter electrode, respectively. 1 M KOH solution was used as the electrolyte.

Materials characterization. X-ray diffraction (XRD) was recorded by a D/MAX-2500 diffractometer (Rigaku, Japan) with a Cu Kα radiation source from 10−80º. Scanning electron microscopy (SEM) images were analyzed by JSM-7800F. Transmission electron microscopy (TEM) images were conducted on JEM-2800 electron microscope with an accelerating voltage of 200 kV. In addition, the chemical state of the sample was studied by the X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha), All XPS spectra were corrected using the C 1s line at 284.6 eV. Curve fitting and background subtraction were accomplished. Raman spectra were recorded on a Thermo Fisher DXR instrument with an Ar laser source of 532 nm in a macroscopic configuration. The Brunauer-EmmettTeller (BET) specific surface area and average pore diameter distribution were recorded by using a Micromeritics TriStar II3020 instrument. The ICP measurement was performed on Shimadzu ICPE-9820.

Electrochemical measurements. All electrochemical properties were collected using a three-electrode electrochemical system at room temperature. The electrocatalytic HER, OER and full water splitting activity were characterized in 1M KOH with a scan rate of 5 mV s^{-1}, and the electropotential for water oxidation was evaluated at 10 mA cm^{-2} current density ($E_{j=10}$). Furthermore, the HER and OER potentials were converted to standard reversible hydrogen electrode (RHE) scale according to the equation: E (vs. RHE) = E (vs. Hg/HgO) + 0.059*pH + 0.098 V. The polarization curves of the HER and OER were iR-corrected. The Tafel slopes were calculated according to the Tafel equation: $\eta = b\log j + a$, where η is the overpotential, b is the Tafel slope, j is the current density and a is the Tafel intercept relative to the exchange current density j_0. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 10^5 to 0.01 Hz with AC amplitude of 10 mV. The double layer capacitance (C_{dl}) was determined by cyclic voltammetry curves measured by scan rates of 60, 70,80, 90 and 100 mV s^{-1}. Notably, the generated H_2 and O_2 gases during overall water splitting were quantitatively collected by the water drainage method.

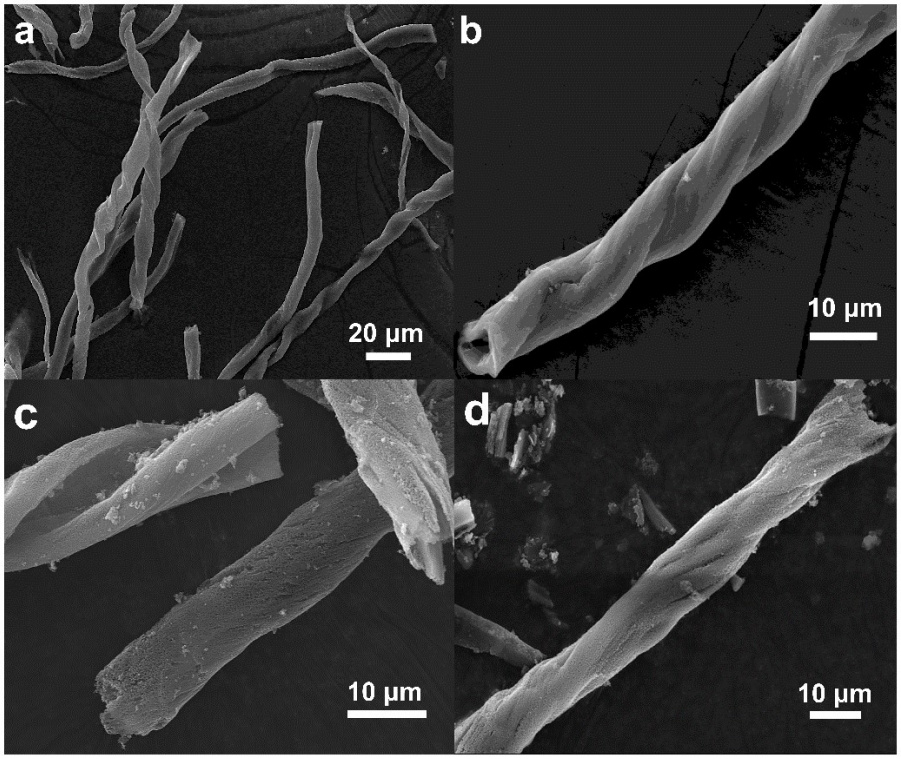

Fig. S1. SEM images of (a, b) BCFs and (c, d) Co/N-BCFs.

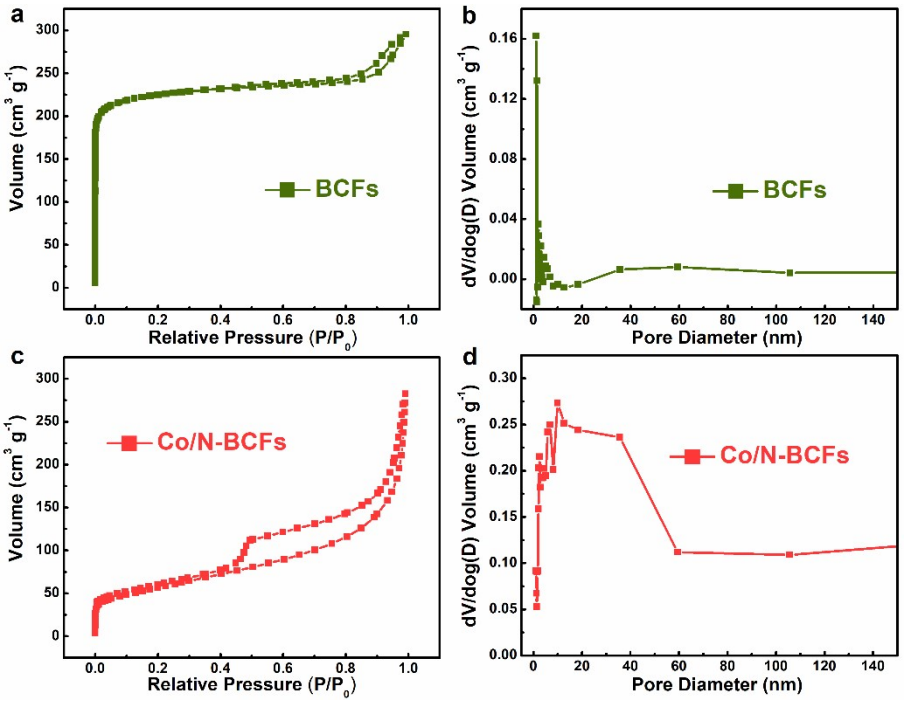

Fig. S2. (a, c) N_2 sorption isotherms and (b, d) pore size distributions of BCFs and Co/N-BCFs.

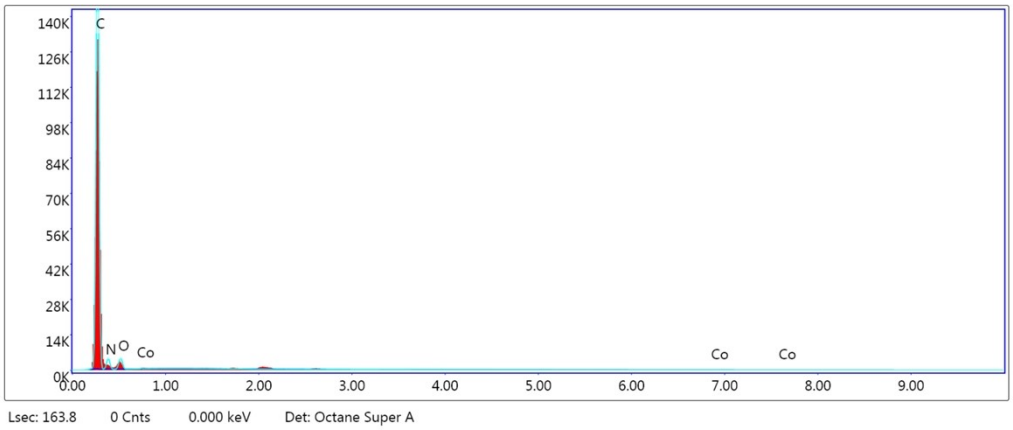

Fig. S3. SEM-EDS spectrum of Co/N-BCFs.

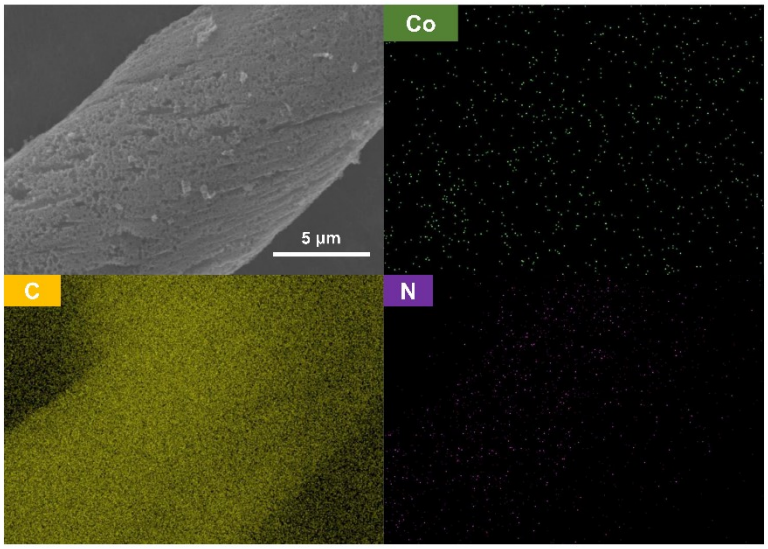

Fig. S4. SEM and corresponding elemental mapping images of Co/N-BCFs.

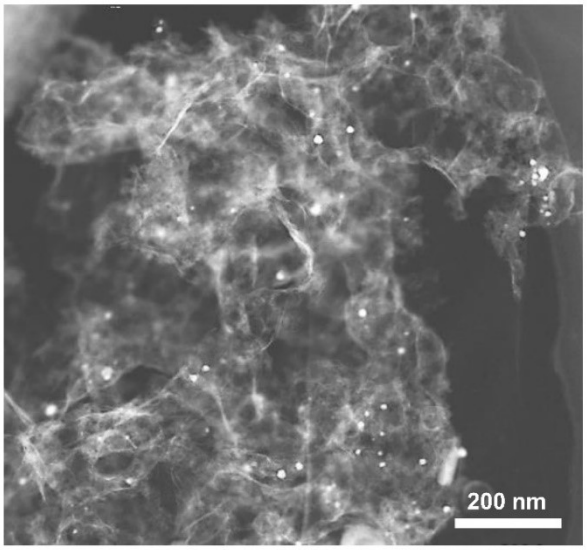

Fig. S5. HAADF-TEM image of Co/N-BCFs.

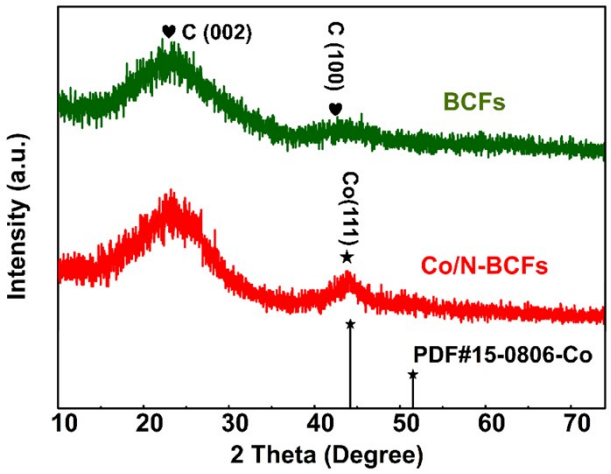

Fig. S6. XRD spectra of BCFs and Co/N-BCFs.

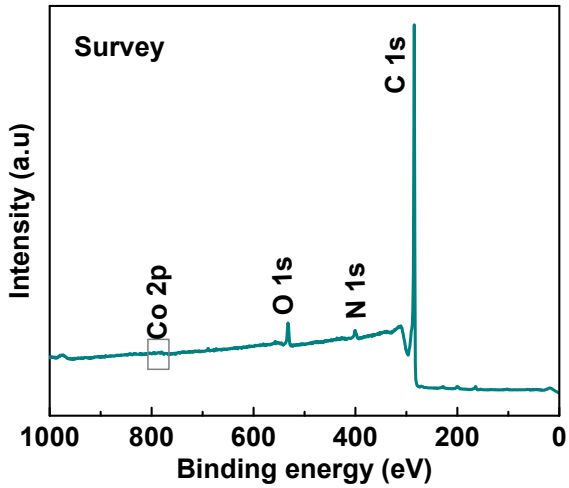

Fig. S7. Survey XPS of Co/N-BCFs.

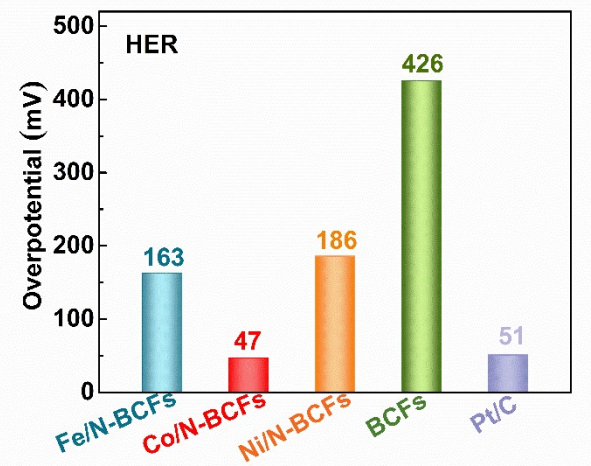

Fig. S8. HER corresponding overpotentials at 10 mA cm^{-2} for Co/N-BCFs, Fe/N-BCFs, Ni/N-BCFs, BCFs and Pt/C.

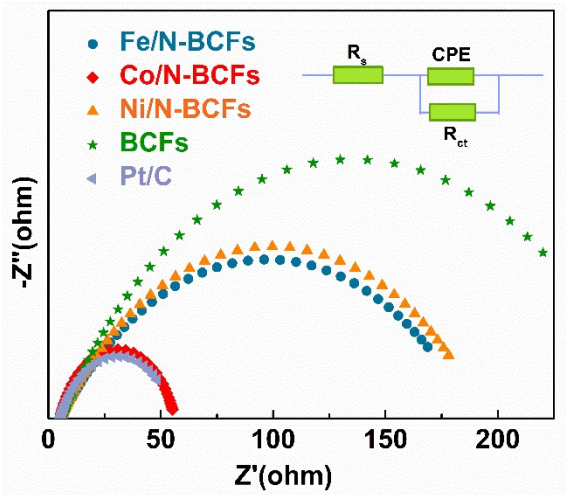

Fig. S9. Nyquist plots of Co/N-BCFs, Fe/N-BCFs, Ni/N-BCFs, BCFs and Pt/C with the fitting curves for HER.

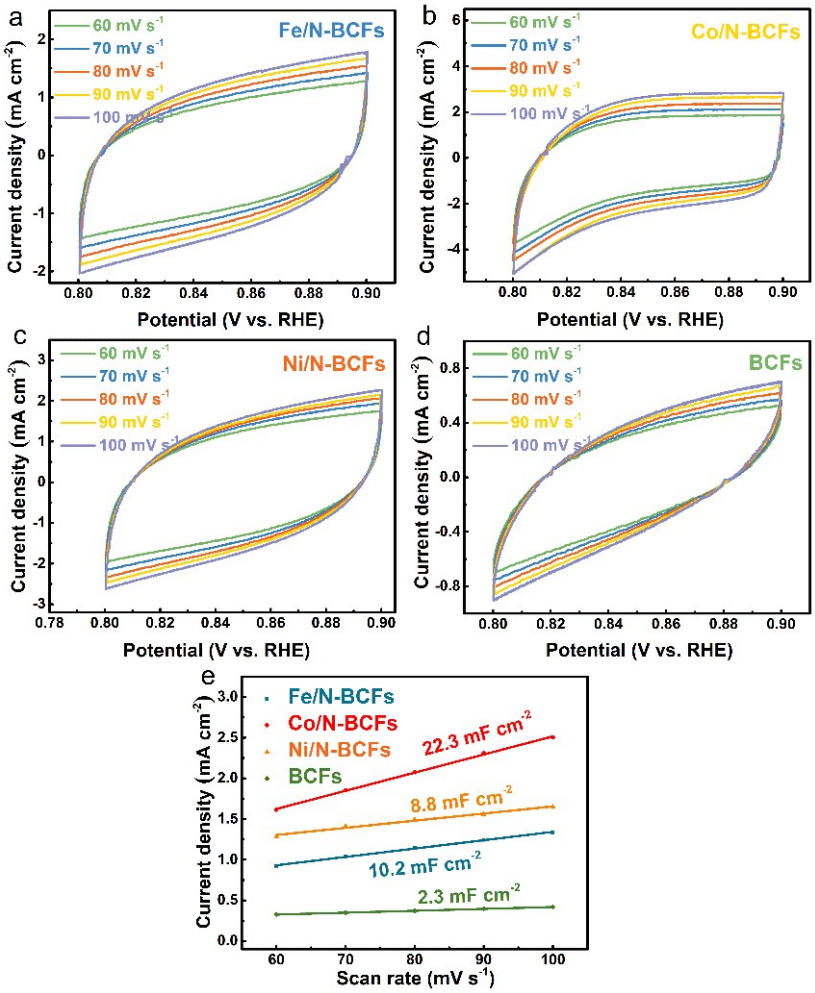

Fig. S10. Cyclic voltammograms of (a) Co/N-BCFs, (b)Fe/N-BCFs, (c) Ni/N-BCFs, and (d) BCFs in the region of 0.8 - 0.9 V (vs. RHE) at different scan rates, (e) Double-layer capacitance (C_{dl}) of Co/N-BCFs, Fe/N-BCFs, Ni/N-BCFs and BCFs.

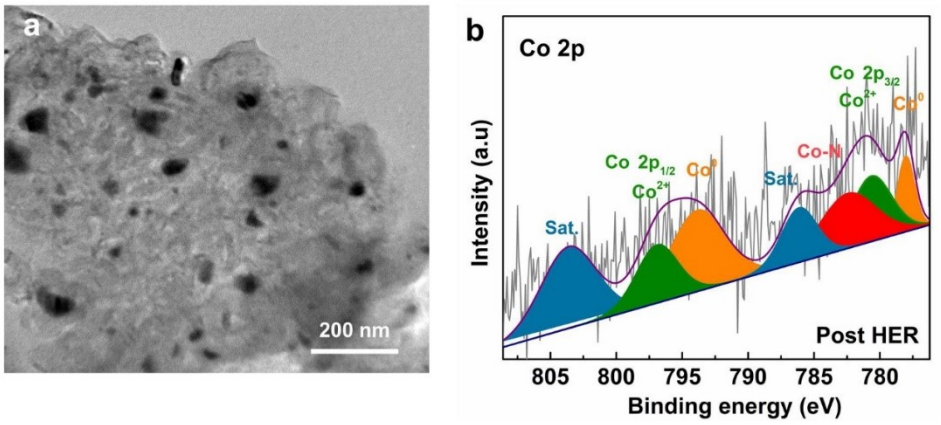

Fig. S11. (a) TEM image of Co/N-BCFs and (b) High-resolution XPS spectrum of Co 2p after HER electrolysis.

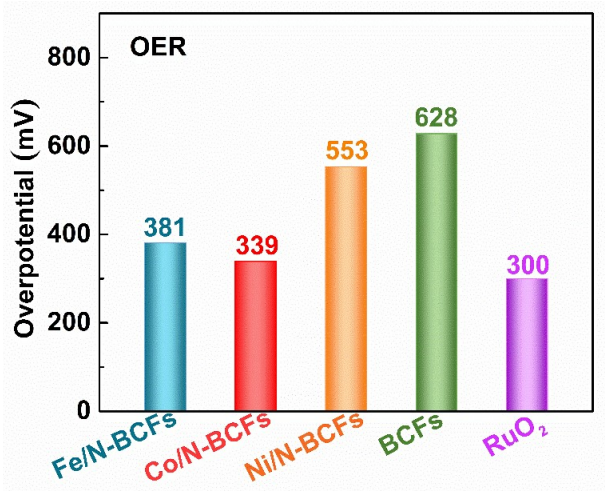

Fig. S12. OER corresponding overpotentials at 10 mA cm^{-2} for Co/N-BCFs, Fe/N-BCFs, Ni/N-BCFs, BCFs and RuO_2.

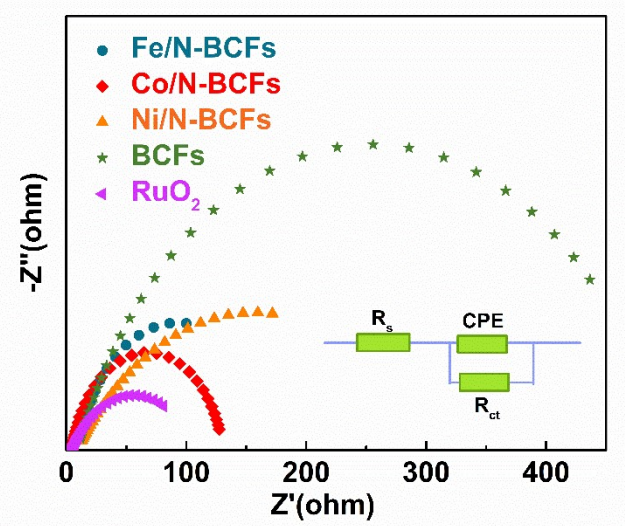

Fig. S13. Nyquist plots of Co/N-BCFs, Fe/N-BCFs, Ni/N-BCFs, BCFs and Pt/C with the fitting curves for OER.

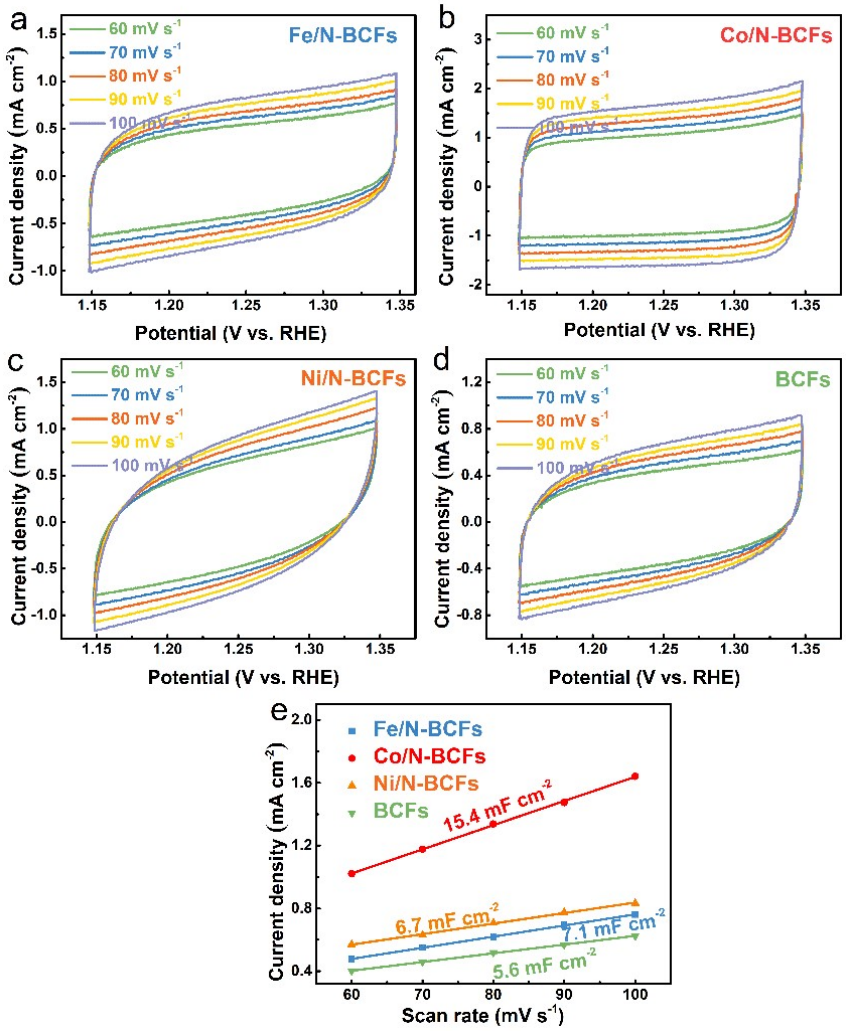

Fig. S14. Cyclic voltammograms of (a) Co/N-BCFs, (b)Fe/N-BCFs, (c) Ni/N-BCFs, and (d) BCFs in the region of 1.15 – 1.35 V (vs. RHE) at different scan rates, (e) Double-layer capacitance (C_{dl}) of Co/N-BCFs, Fe/N-BCFs, Ni/N-BCFs and BCFs.

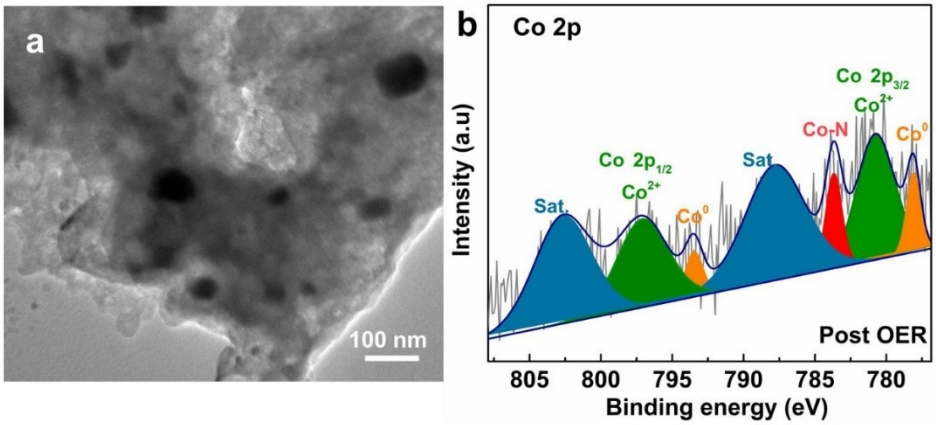

Fig. S15. (a) TEM image of Co/N-BCFs and (b) High-resolution XPS spectrum of Co 2p after OER electrolysis.

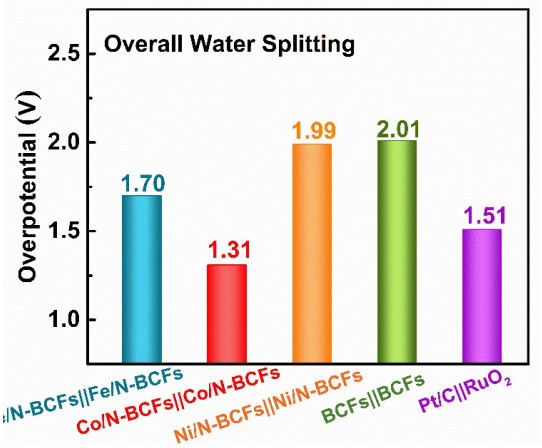

Fig. S16. The overpotentials at 10 mA cm^{-2} for Co/N-BCFs|| Co/N-BCFs, Fe/N-BCFs|| Fe/N-BCFs, Ni/N-BCFs|| Ni/N-BCFs, BCFs|| BCFs and Pt/C||RuO_2 in overall water splitting.

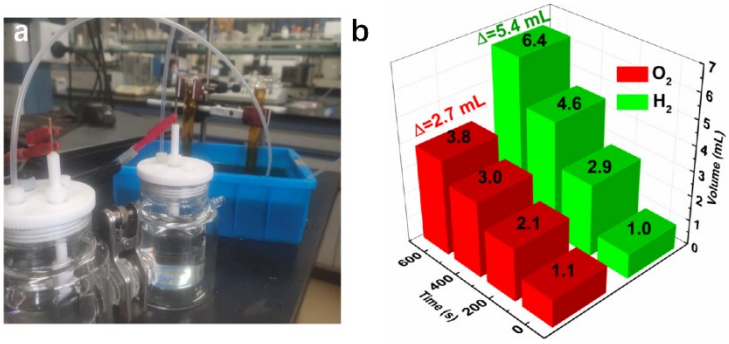

Fig. S17. (a) Faradic efficiency measurement device based on water splitting; (b) The variations of amount of H_2 and O_2 with time.

Table S1. Comparison of HER performance of Co/N-BCFs and metal-nitrogen doped carbon-based catalysts in literatures.

Electrocatalysts	Electrolytes	E_{j10} (mV vs. RHE)	References
Co/N-BCFs	**1.0M KOH**	**47**	**This work**
$CoFe_2O_4$/SWNTs	1.0M KOH	263	ACS Appl. Energy Mater. 2019, 2, 1026−1032
Co@Co_3O_4-NC	1.0M KOH	221	J. Mater. Chem. A, 2017,5, 9533-9536
Co_3Fe_7@NCNTFs	1.0M KOH	197	Chem. Asian J,2020.7, 1728-1735
Co−SCN/RGO	1.0M KOH	150	ACS Sustainable Chem. Eng, 2019, 7, 15373-15384
C@Mo_2C/Co	1.0M KOH	146	Int J. Hydrogen Energ, 45 (2020) 22629-22637
Co-CeO_2@CNF	1.0M KOH	92	Materials 2020, 13, 856
CoN-400/CC	1.0M KOH	97	Electrochimica Acta, 273 (2018) 229-238
N, Co-CNTs	1.0M KOH	151	Appl. Catal. B-Environ, 2021, 283, 119643
Fe-Ni_3C-2%	1.0M KOH	292	Angew. Chem. Int. Ed. 2017, 56, 12566–12570
Co_6W_6C@NC	1.0M KOH	59	Small, 2020, 16, 1907556

Table S2. Comparison of OER performance of Co/N-BCFs samples and metal-nitrogen doped carbon-based catalysts in literatures.

Electrocatalysts	Electrolytes	E_{j10} (mV vs. RHE)	References
Co/N-BCFs	**1.0M KOH**	**339**	**This work**
$CoFe_2O_4$/SWNTs	1.0M KOH	310	ACS Appl. Energy Mater. 2019, 2, 1026−1032
N, Co-CNTs	1.0M KOH	308	Appl. Catal. B-Environ, 2021, 283, 119643
Fe-Ni_3C-2%	1.0M KOH	275	Angew. Chem. Int. Ed. 2017, 56, 12566–12570
$CoMoN_x$-500 NSAs/NF	1.0M KOH	231	Adv. Sci. 2020, 7, 1901833
Co_6W_6C@NC	1.0M KOH	286	Small, 2020, 16, 1907556
Co_9S_8/NC	0.1M KOH	400	RSC Adv., 7 (2017) 19181-19188.
RuNi-NCNFs	1.0M KOH	290	ACS Sustainable Chem. Eng., 6 (2018) 1527-1531.
Co−N−C	0.1M KOH	250	ACS Appl. Mater. Interfaces, 2019, 11, 39809−39819
Co/β Mo_2C@NCNTs	1.0M KOH	356	Angew. Chem. Int. Ed.,2019, 58, 4923-
Co/CNFs	1.0M KOH	320	Energy Environ. Sci. 2016, 9 (2), 478

Table S3 Comparison of water splitting performances of Co/N-BCFs samples and metal-nitrogen doped carbon-based catalysts in literatures.

Electrocatalysts	Electrolyte	E_{j10} (V)	References
Co/N-BCFs	**1.0M KOH**	**1.31**	**This work**
$CoFe_2O_4$/SWNTs	1.0M KOH	1.72	ACS Appl. Energy Mater. 2019, 2, 1026−1032
Co@Co_3O_4-NC	1.0M KOH	1.75	J. Mater. Chem. A, 2017,5, 9533-9536
Co_3Fe_7@NCNTFs	1.0M KOH	1.64	Chem. Asian J,2020.7, 1728-1735
Co−SCN/RGO	1.0M KOH	1.63	ACS Sustainable Chem. Eng. 2019, 7, 15373-15384
C@Mo_2C/Co	1.0M KOH	1.67	Int J. Hydrogen Energ, 45 (2020) 22629-22637
CoN-400/CC	1 M KOH	1.58	Electrochimica Acta, 273 (2018) 229-238
N, Co-CNTs	1.0M KOH	1.69	Appl. Catal. B-Environ, 2021, 283, 119643
Fe-Ni_3C-2%	1.0M KOH	1.56	Angew. Chem. Int. Ed. 2015, 54, 6251–6254
Co_6W_6C@NC	1.0M KOH	1.59	Small, 2020, 16, 1907556
$CoMoN_x$-500 NSAs/NF	1.0M KOH	1.55	Chem. Eng. J, 2021, 411, 128433

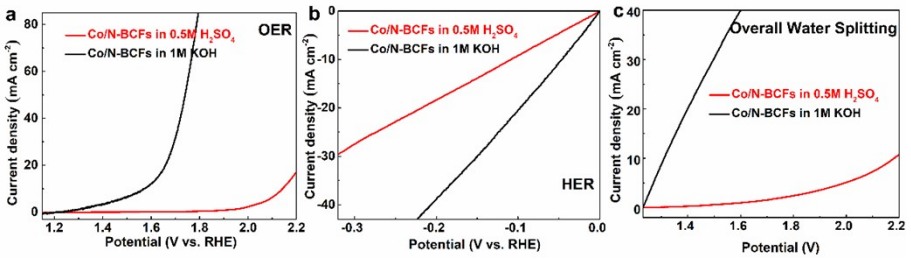

Fig. S18 (a) OER polarization curves, (b) HER polarization curves and (c) Polarization curves for overall water-splitting of Co/N-BCFs in acidic medium.