Electronic Supplementary Information

Experimental Section

Materials: All chemical reagents were purchased from commercial suppliers and were used as received without further purification. Cu foam (CF) was provided by Tianjin Kemiou Chemical Reagent Co., Ltd. Water used throughout all experiments was purified by a Millipore ultrapure water system. Seawater used in this work was collected from Weihai, Shandong, China. The collected seawater was first filtered by a 0.22 μm filter membrane to get rid of the pollutants. After adding KOH, the sample was centrifuged to remove the precipitate and used as the electrolyte. The major ions in seawater are: Cl^- (18980 ppm), Na^+ (10556 ppm), SO_4^{2-} (2649 ppm), Mg^{2+} (1262 ppm), Ca^{2+} (400 ppm), K^+ (380 ppm), HCO_3^- (140 ppm), Sr^{2+} (13 ppm), Br^- (65 ppm), BO_3^{3-} (26 ppm), F^- (1 ppm), SiO_3^{2-} (1 ppm), and I^- (<1 ppm).

Preparation of Cu_2O-CoO/CF: In brief, CF was washed with diluted HCl and water for several times to remove the surface impurities. Then a piece of clean CF was rapidly immersed into a 30 mL mixed solution (0.685 g ammonium persulfate and 3.0 g NaOH) at room temperature for 20 minutes to get $Cu(OH)_2$ nanowire arrays on CF ($Cu(OH)_2$/CF) (Fig. S1). The $Cu(OH)_2$/CF was transferred to a 50 mL glass beaker containing 0.075 M $CoSO_4 \cdot 7H_2O$ and 1.125 M urea. Subsequently, it was reacted at 85 °C for 4 hours. Finally, the resulting precursor (Fig. S2) was annealed at 350 °C in Ar for 2 h to obtain Cu_2O-CoO/CF.

Preparation of CoO/CF and Cu_2O/CF: $Co(NO_3)_2 \cdot 6H_2O$ (1.245 g), NH_4F (0.315 g) and urea (1.283 g) were dissolved in 40 mL water under vigorous stirring for 20 min. Then the solution was transferred into a Teflon-lined stainless autoclave and a piece of CF was immersed into the autoclave contained solution. The autoclave was sealed and maintained at 120 °C for 6 h in an electric oven. The resulting CF was annealed at 350 °C for 2 h under Ar atmosphere to obtain CoO/CF. To prepare Cu_2O/CF, the $Cu(OH)_2$/CF was heated at 350 °C for 2 h in a flow Ar atmosphere.

Characterizations: XRD data were acquired by a LabX XRD-6100 X-ray diffractometer with a Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm

(SHIMADZU, Japan). SEM measurements were carried out on a GeminiSEM 300 scanning electron microscope (ZEISS, Germany) at an accelerating voltage of 5 kV. TEM image was obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed using an ESCALABMK II X-ray photoelectron spectrometer with the exciting source of Mg. Cu and Co content in electrolyte was measured by inductively coupled plasma mass spectrometry (ICP-MS; Bruker Aurora M90 ICP-MS). Raman spectra were measured using a RENISHAW in Via Reflex spectrometer. UV-Vis spectra were obtained using a Hitachi U-3900H spectrophotometer.

Electrochemical measurements: The OER and HER measurements were performed with a CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai) in a conventional three electrode system. The electrolyte was 1.0 M KOH or 1.0 M KOH + seawater, using carbon rod as the counter electrode and Hg/HgO as the reference electrode. The overall water/seawater-splitting performance of the electrolyzers were tested in a two-electrode system, where OER electrodes are as the anode and HER electrodes as the cathode. All potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale: ($E_{RHE} = E_{Hg/HgO} + 0.059 \times pH + 0.098$ V). The catalytic activity of catalysts was determined by linear sweep voltammetry (LSV) curves with a scan rate of 5 mV/s. All polarization curves have been reported with *iR* compensation. The *iR*-compensated potential was obtained after the correction of solution resistance measured following the equation: $E_{corr} = E - iR$, where E is the original potential, R is the solution resistance, i is the corresponding current, and E_{corr} is the *iR*-compensated potential. The C_{dl} values for electrodes were calculated according to the CV curves at different scan rates (20-100 mV/s) in the double-layer region without Faradaic processes.

Determination of ClO^-: The yield of ClO^- in the electrolyte was measured based on the N,N-diethyl-1,4-phenylenediamine sulfate (DPD) colorimetric method using a UV-Vis spectrophotometer. Firstly, the 100 μL of electrolyte was successively mixed with 50 μL of H_2SO_4 (1.0 M), 50 μL of NaOH (2.0 M), and 4.8 mL of deionized water. Then, 250 μL of DPD reagent and 250 μL of PBS were added to the above

solution. After standing for two minutes, the color of the solution changed to transparent pink. The concentration of ClO^- was calculated by UV-vis spectroscopy for a certain wavelength of about 515 nm.

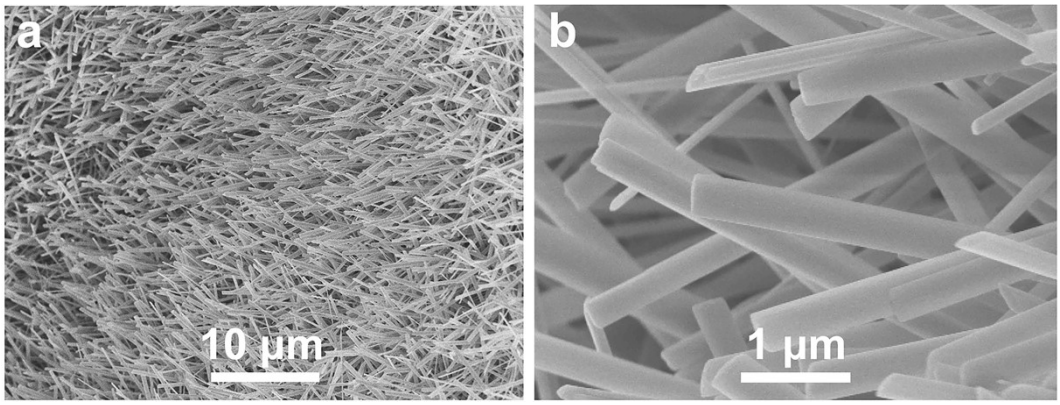

Fig. S1. SEM images of $Cu(OH)_2$ nanowire arrays.

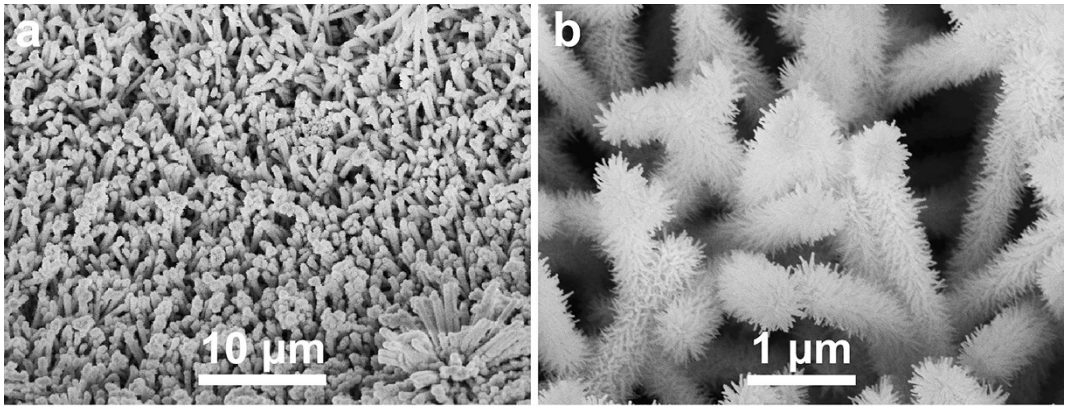

Fig. S2. SEM images of Cu_2O-CoO/CF precursor.

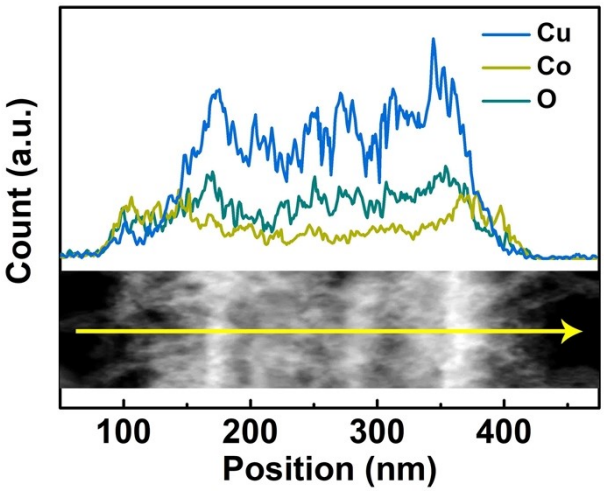

Fig. S3. EDS line-scan profiles of Cu_2O-CoO nanowire.

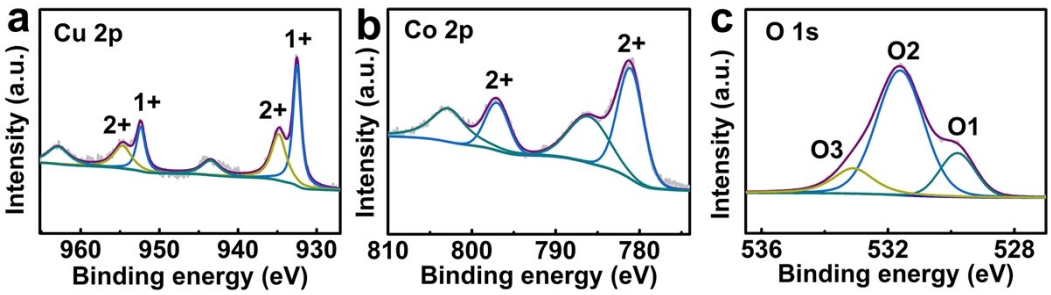

Fig. S4. XPS spectra of Cu 2p, Co 2p, and O 1s for Cu_2O-CoO/CF.

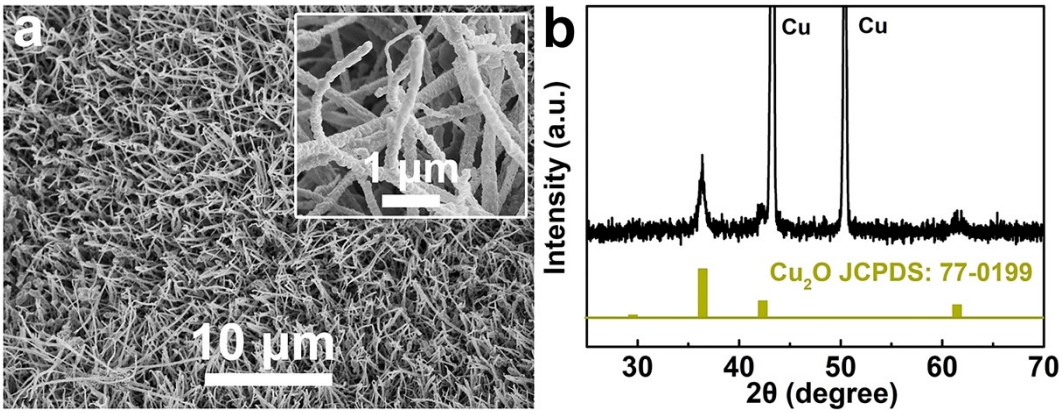

Fig. S5. SEM images and XRD pattern of Cu_2O/CF.

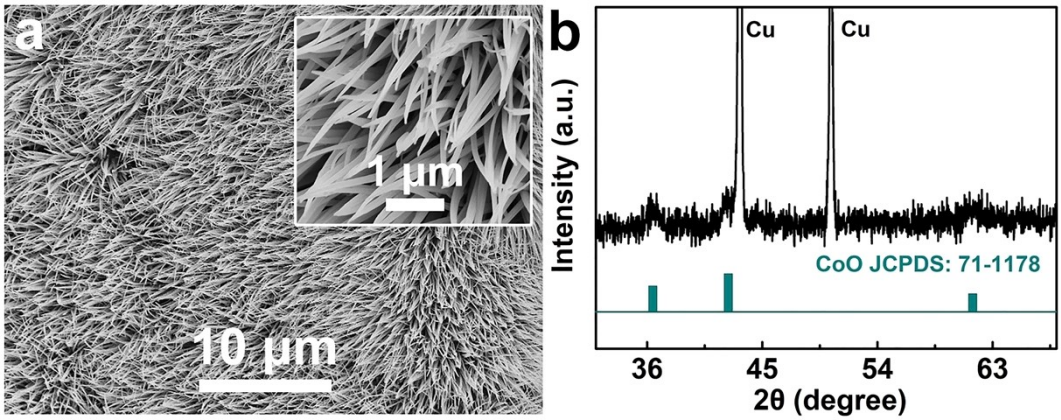

Fig. S6. SEM images and XRD pattern of CoO/CF.

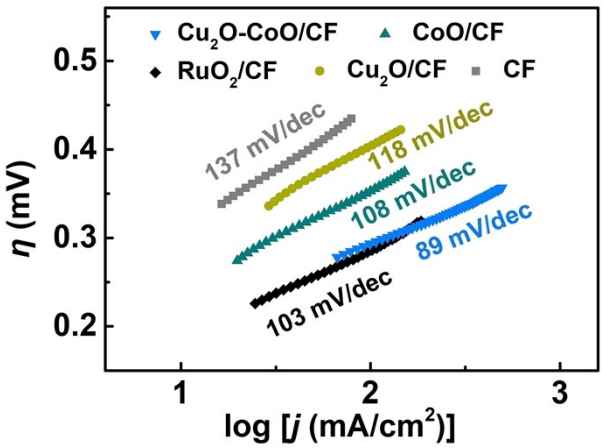

Fig. S7. Tafel plots of Cu_2O-CoO/CF, Cu_2O/CF, CoO/CF, RuO_2/CF, and CF.

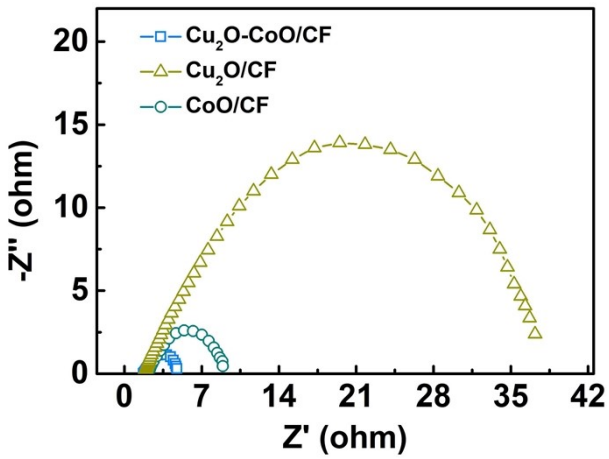

Fig. S8. Nyquist plots of Cu_2O-CoO/CF, Cu_2O/CF, and CoO/CF. The electrical resistances of Cu_2O-CoO/CF, CoO/CF, and Cu_2O/CF are 2.65 Ω, 5.66 Ω, and 25.67 Ω, respectively.

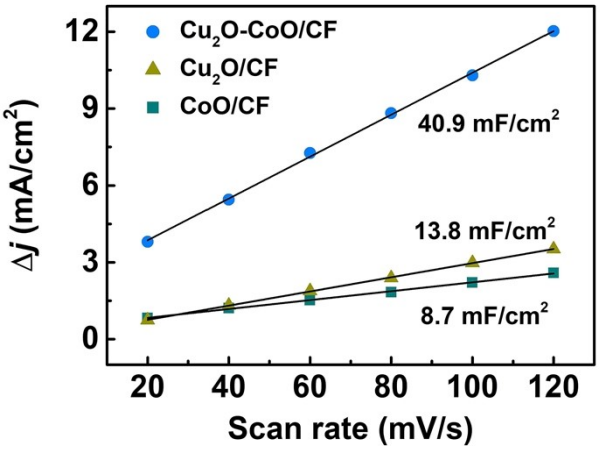

Fig. S9. Calculated electrochemical C_{dl} for Cu_2O-CoO/CF, Cu_2O/CF, and CoO/CF.

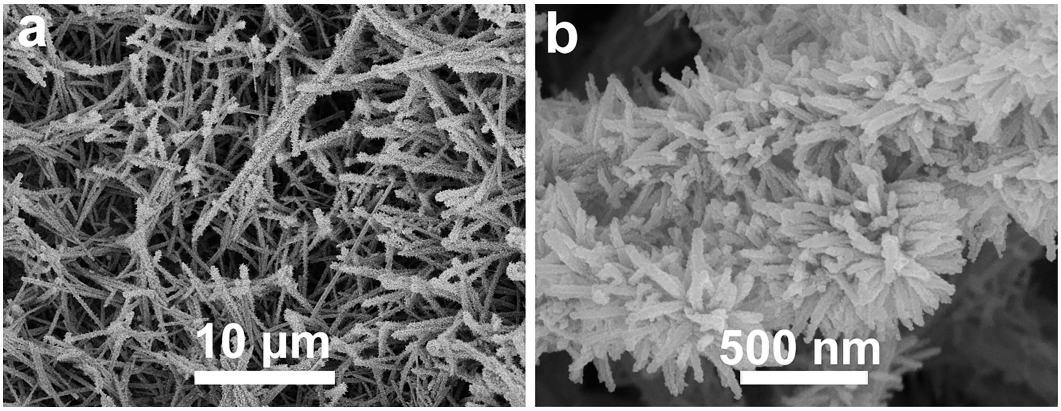

Fig. S10. SEM images of post-OER Cu_2O-CoO/CF tested in alkaline seawater.

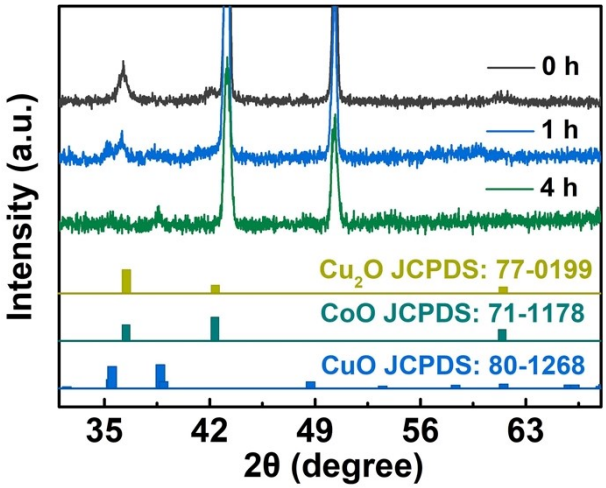

Fig. S11. XRD pattern of Cu_2O-CoO/CF at different OER electrolysis times in alkaline seawater.

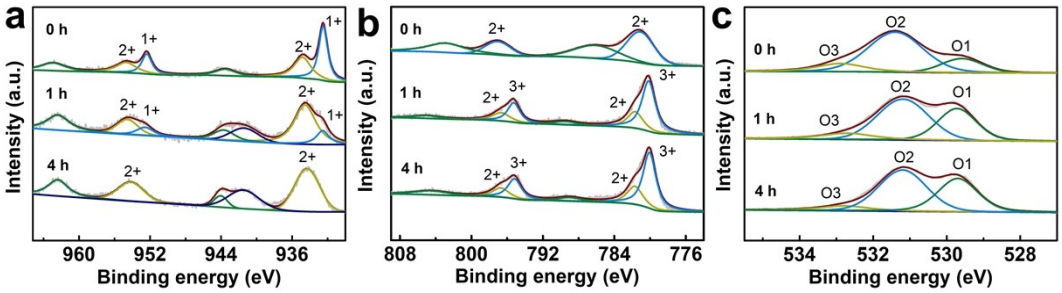

Fig. S12. XPS spectra of (a) Cu 2p, (b) Co 2p, and (c) O 1s for Cu_2O-CoO/CF at different OER electrolysis times in alkaline seawater.

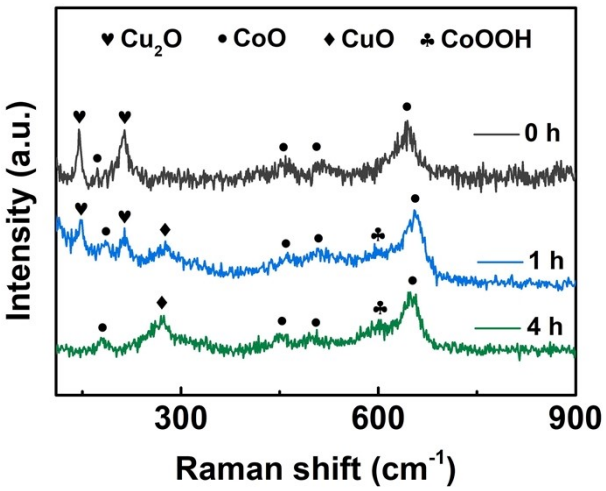

Fig. S13. Raman spectra of Cu_2O-CoO/CF at different OER electrolysis times in alkaline seawater.

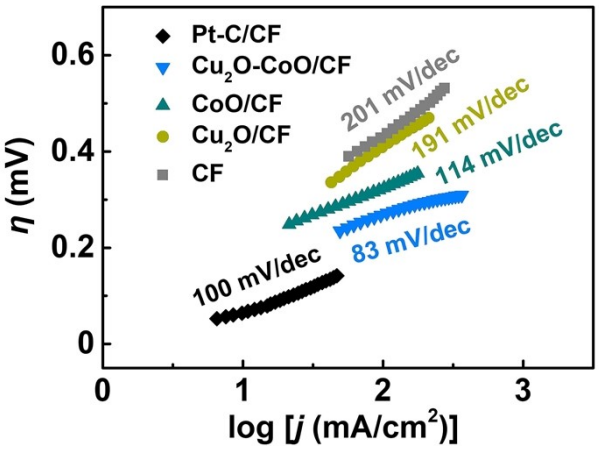

Fig. S14. Tafel plots of Cu_2O-CoO/CF, Cu_2O/CF, CoO/CF, Pt-C/CF, and CF.

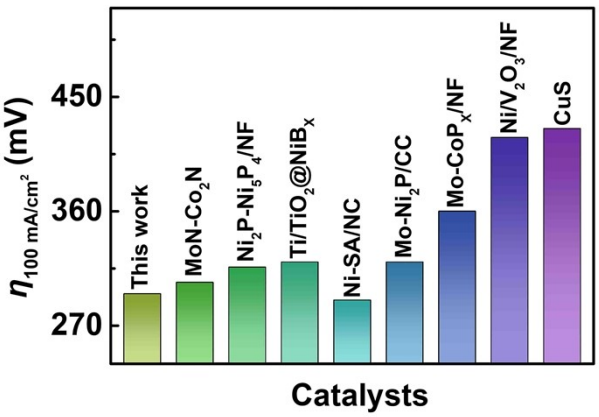

Fig. S15. Comparison of the η required at 100 mA/cm^2 for Cu_2O-CoO/CF with those of other seawater electrocatalysts.

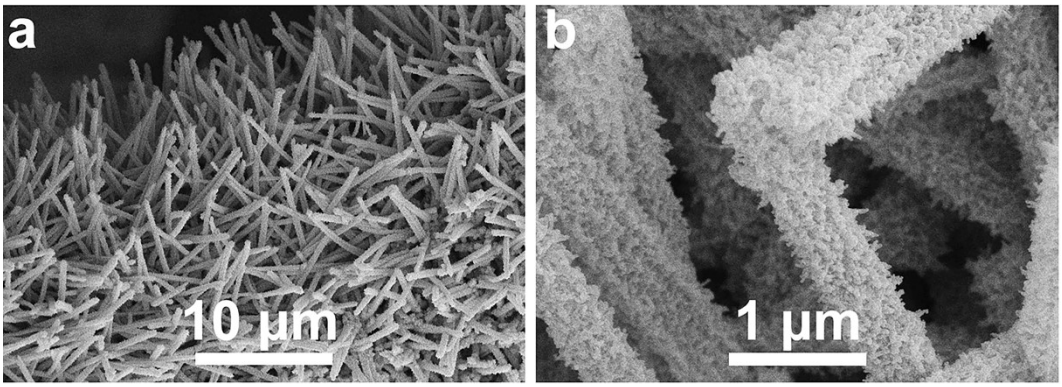

Fig. S16. SEM images of post-HER Cu_2O-CoO/CF tested in alkaline seawater.

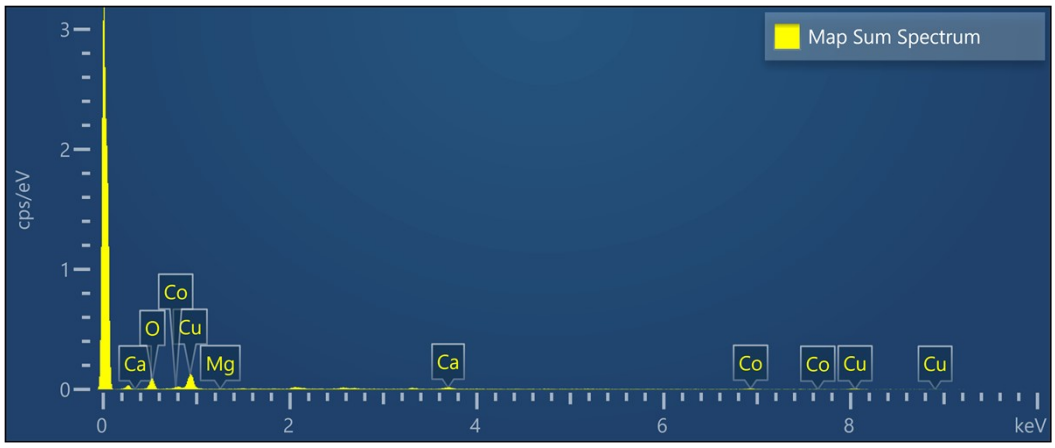

Fig. S17. EDS spectrum of post-HER Cu_2O-CoO/CF tested in alkaline seawater.

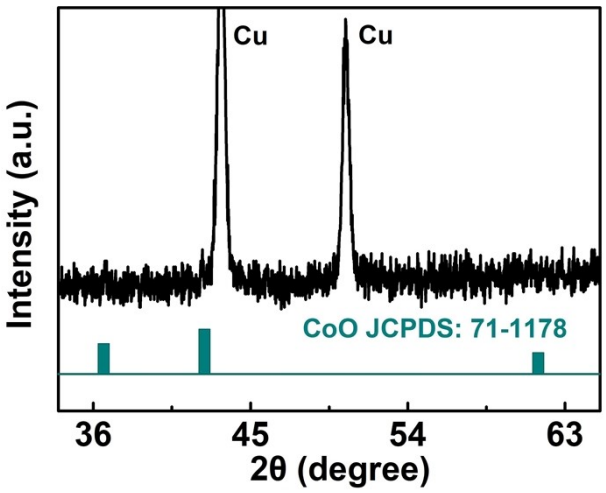

Fig. S18. XRD pattern of post-HER Cu_2O-CoO/CF tested in alkaline seawater.

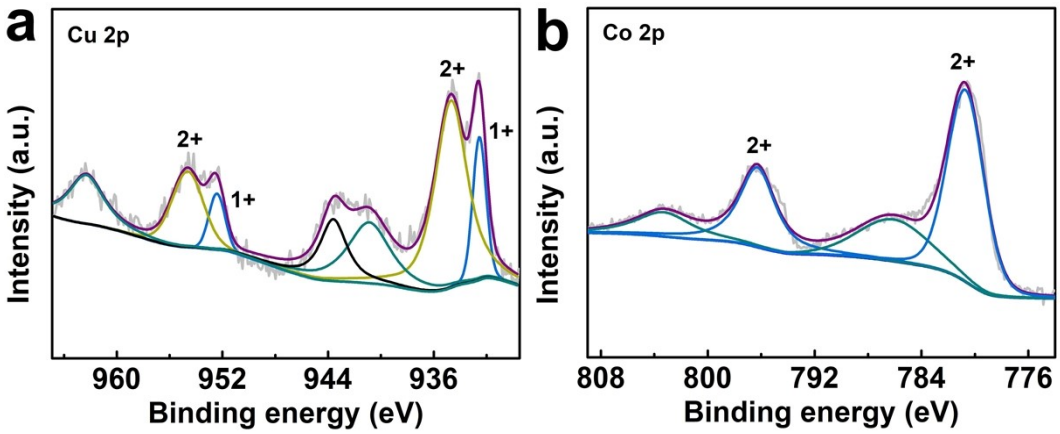

Fig. S19. XPS spectra of Cu 2p and Co 2p for Cu_2O-CoO/CF after stability test in alkaline seawater.

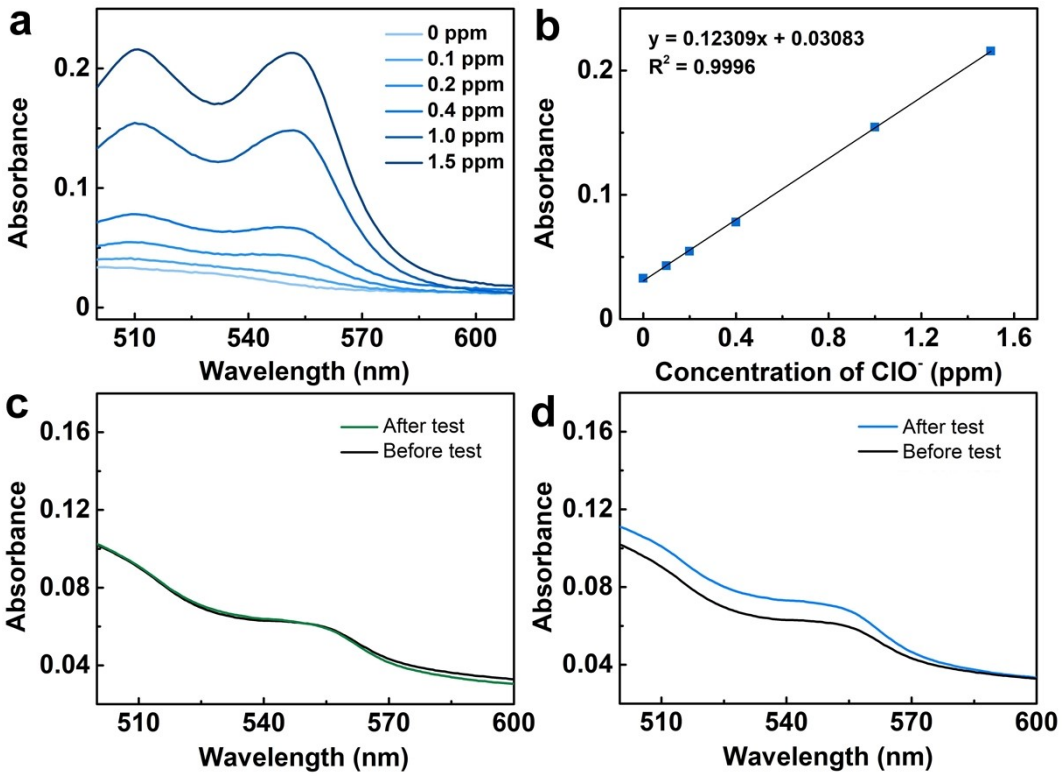

Fig. S20. (a) UV-Vis absorption spectra and (b) corresponding calibration curve used for calculation of ClO^- concentration. UV-Vis spectra of (c) catholyte and (d) anolyte for Cu_2O-CoO/CF before and after FE test in alkaline seawater. The volume of both cathode and anode electrolytes was 40 mL. As shown in Fig. S18c and S18d, no ClO^- was generated at the cathode, and only a small amount of ClO^- (0.032 mmol) was produced at the anode.

Table S1 Comparison of OER performances of Cu_2O-CoO/CF with other reported electrocatalysts in alkaline seawater.

Catalyst	Electrolyte	η (mV) @ j (100 mA/cm^2)	Refs.
Cu_2O-CoO/CF	**1 M KOH + Seawater**	**315**	**This work**
Ni_2P-Ni_5P_4/NF	1 M KOH + Seawater	345	*Adv. Funct. Mater.*, 2021, **31**, 2006484
NMN/NF	1 M KOH + Seawater	380	*Electrochim. Acta*, 2021, **390**, 138833
RuNi-Fe_2O_3/IF	1 M KOH + Seawater	320	*Chinese J. Catal.*, 2022, **43**, 2202
NiCoS/NF	1 M KOH + Seawater	360	*Appl. Catal. B*, 2021, **291**, 120071
Ti/TiO_2@NiB_X(PEE)	1 M KOH + Seawater	530	*Chem. Eng. J.*, 2022, **430**, 132881
NiMoN@NiFeN	1 M KOH + Seawater	307	*Nat. Commun.*, 2019, **10**, 5106
S-(Ni,Fe)OOH	1 M KOH + Seawater	300	*Energy Environ. Sci.*, 2020, **13**, 3439
NiFe/NiS_X	1 M KOH + Seawater	335	*Proc. Natl. Acad. Sci. USA*, 2019, **116**, 6624
Mo-CoP_X/NF	1 M KOH + Seawater	530	*Mater. Today Nano*, 2022, **18**, 100216
NiCo-DEA	1 M KOH + Seawater	670	*Electrochim. Acta*, 2017, **247**, 381
S-$NiMoO_4$@NiFe-LDH/NF	1 M KOH + Seawater	315	*J. Colloid Interface Sci.*, 2022, **613**, 349
MoN-Co_2N	1 M KOH + Seawater	357	*ACS Appl. Mater. Interfaces*, 2022, **14**, 41924
Ni(TCNQ)/GP	1 M KOH + Seawater	352	*Nano Res.*, 2022, **15**, 6084
NiPS/NF	1 M KOH + Seawater	344	*J. Energy Chem.*, 2022, **75**, 66

Table S2 Comparison of HER performances of Cu_2O-CoO/CF with other reported electrocatalysts in alkaline seawater.

Catalyst	Electrolyte	η (mV) @ j (100 mA/cm^2)	Refs.
Cu_2O-CoO/CF	**1 M KOH + Seawater**	**295**	**This work**
MoN-Co_2N	1 M KOH + Seawater	304	*ACS Appl. Mater. Interfaces*, 2022, **14**, 41924
Mo-CoP_X/NF	1 M KOH + Seawater	360	*Mater. Today Nano*, 2022, **18**, 100216
Ni_2P-Ni_5P_4/NF	1 M KOH + Seawater	316	*Adv. Funct. Mater.*, 2021, **31**, 2006484.
Ti/TiO_2@NiB_X(PEE)	1 M KOH + Seawater	320	*Chem. Eng. J.*, 2022, **430**, 132881
Ni-SA/NC	1 M KOH + Seawater	290	*Adv. Mater.*, 2021, **33**, 2003846
Mo-Ni_2P/CC	1 M KOH + Seawater	320	*New J. Chem.,* 2022, **46**, 20602
Ni/V_2O_3/NF	1 M KOH + Seawater	418	*Chem. Eng. J.*, 2022, **450**, 138079
CuS	1 M KOH + Seawater	425	*Int. J. Energy Res.*, 2022, **46**, 19723
1D-Cu@Co-CoO/Rh	1 M KOH + Seawater	320	*Small*, 2021, **17**, 2103826
NiFe LDH/FeOOH	1 M KOH + Seawater	350	*Inorg. Chem.*, 2021, **60**, 17371

Table S3 Comparison of overall seawater splitting performances of Cu_2O-CoO/CF with other reported bifunctional electrocatalysts in seawater.

Catalyst	Electrolyte	Voltage (V) @ *j* (100 mA/cm^2)	Refs.
Cu_2O-CoO/CF	**1 M KOH + Seawater**	**1.82**	**This work**
Mn-doped Ni_2P/Fe_2P	1 M KOH + 0.5 M NaCl	1.83	*Chem. Eng. J.*, 2022, DOI: 10.1016/j.cej.2022.140061
3%Er-MoO_2	1 M KOH + 0.5 M NaCl	2.0	*Appl. Surf. Sci.*, 2023, **615**, 156360
CoMnRu@CNT	1 M KOH + Seawater	2.15	*J. Colloid Inter. Sci.*, 2023, **646**, 844
Ru-CoO_x/NF	Seawater	1.86	*Small*, 2021, **17**, 2102777
GO@Fe@NiCo	1 M KOH + Seawater	1.82	*J. Mater. Chem. A*, 2020, **8**, 24501-24514
NMN/NF	1 M KOH + Seawater	1.82	*Electrochim. Acta*, 2021, **390**, 138833
1D-Cu@Co-CoO/Rh	1 M KOH + Seawater	1.9	*Small*, 2021, **17**, 2103826
Mo-CoP_X/NF	1 M KOH + Seawater	2.16	*Mater. Today Nano*, 2022, **18**, 100216

Table S4 Element analysis of electrolytes after the long-term overall water and seawater splitting tests.

Electrolyte	Element	Element concentration (ppm)	Weight loss wt%
1 M KOH	Co	1.50	2.96
	Cu	0.16	
1 M KOH + Seawater	Co	2.71	4.84
	Cu	0.27	