

Supplementary information

One-Step Fabrication of Self-supported Co@CoTe₂ Electrocatalyst for Efficient and Durable Oxygen Evolution Reaction

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Experimental details:

Materials synthesis

All chemicals used are of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. Prior to hydrothermal reaction, the Co foam (110 PPI, 1 mm thick) was cleaned by ultrasonication in 1.0 M HCl for 5 min to remove the surface oxide layer, washed successively in water and acetone, and finally dried at 60 °C in vacuum for 30 min. In a typical hydrothermal experiment, 0.443 g sodium tellurite (Na_2TeO_3) was dissolved in 65 mL of deionized (DI) water to form a homogeneous solution by continuous magnetic stirring for 30 min. Subsequently, 5 ml hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) used as reducing agent was added into the above solution. The precursor reagents were stirred for another 30 minutes at room temperature until a homogeneous suspension was formed, and then the solution was loaded into a 100 mL Teflon-lined autoclave reactor where a piece of cleaned Co foam ($\sim 3.0 \times 4.0 \text{ cm}^2$) was placed against the wall. Subsequently, the autoclave reactor was sealed, heated to 200 °C or 240 °C (denoted as Co@CoTe₂-200 and Co@CoTe₂-240) and maintained 24 hours for reaction. Finally, the reactor was naturally cooled down to room temperature. After the hydrothermal processing, the color of Co foam turned to dark black from light grey, suggesting the formation of CoTe₂ nanoparticles on the foam surface. The resultant sample was then rinsed successively with DI water and ethanol, and dried in a N₂ flow.

Structural characterization

The morphology, microstructure, and chemical composition of Co@CoTe₂ electrodes were examined by field-emission scanning electron microscopy (FESEM, FEG Quanta

450) and transmission electron microscopy (TEM, JEOL JEM-2100 operating at 200 keV) equipped with energy-dispersive X-ray spectroscopy (EDX). The crystalline structure of samples was studied by X-ray diffractometry (XRD, PANalytical X'Pert PRO) using Cu K α radiation ($\lambda = 1.540598 \text{ \AA}$) and a PIXcel detector. The surface chemical states of Co@CoTe₂ were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi), and the C (1s) line (at 284.70 eV) corresponding to the surface adventitious carbon (C–C line bond) has been used as the reference binding energy.

Electrochemical measurements

The OER performance was evaluated by cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) in a three-electrode configuration in 1.0 M KOH (pH = 13.5) using a CS2350H electrochemical workstation (Wuhan Corrtest Instruments Corp., China). A platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The as-fabricated Co@CoTe₂ working electrode was directly used as the working electrode, and the active electrode area was kept to 1×1 cm². Cyclic voltammetric (CV) scans were recorded between 1.00 and 1.70 V vs. reversible hydrogen electrode (RHE) at the scan rates from 1 to 20 mV s⁻¹. The electrochemical double-layer capacitance (C_{dl}) of each sample was measured given that C_{dl} is positively proportional to the effective surface areas (ESA). C_{dl} can be extracted through CV scans at different rates (from 10 to 100 mV s⁻¹) in the non-faradaic potential window of -0.05-0.05 V vs. SCE. All current density values were normalized with respect to the

geometrical surface area of the working electrode. For comparison, the electrocatalytic performance of a bare Co foam was also measured. All CV curves presented in this work are iR -corrected (85%), and the correction was done according to the following equation:

$$E_c = E_m - iR_s \quad (S1)$$

where E_c is the iR -corrected potential, E_m experimentally measured potential, and R_s the equivalent series resistance extracted from the electrochemical impedance spectroscopy (EIS) measurements. Unless otherwise specified, all potentials are reported versus reversible hydrogen electrode (RHE) by converting the potentials measured vs. SCE according to the following formula:

$$E \text{ (RHE)} = E \text{ (SCE)} + 0.241 + 0.059 \text{ pH} \quad (S2)$$

The EIS measurements were performed in the frequency range of 10 mHz – 100 kHz under a constant potential of 1.60 V vs. RHE. The mass activity (MA, $A \text{ g}^{-1}$) value of sample was calculated from the loading mass (M , mg cm^{-2}) of each electrocatalyst and the measured current density (J , mA cm^{-2}) at different overpotentials, such as $\eta = 270$, 290, 310, 330 and 350 mV:

$$\text{MA} = J/M \quad (S3)$$

Supplementary figures:

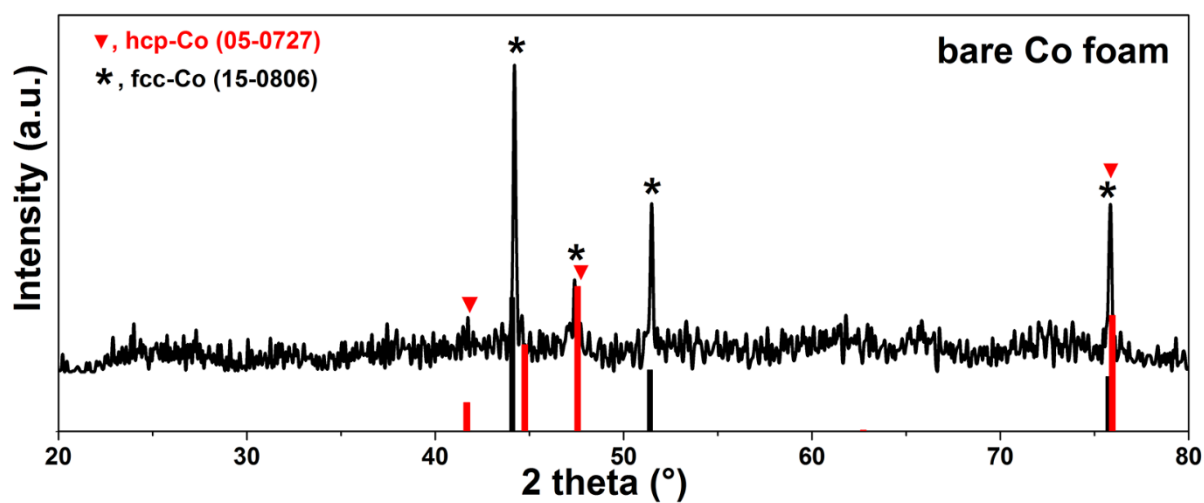


Fig. S1. XRD pattern of a bare Co foam. The standard powder diffraction pattern of metallic cobalt is given for reference.

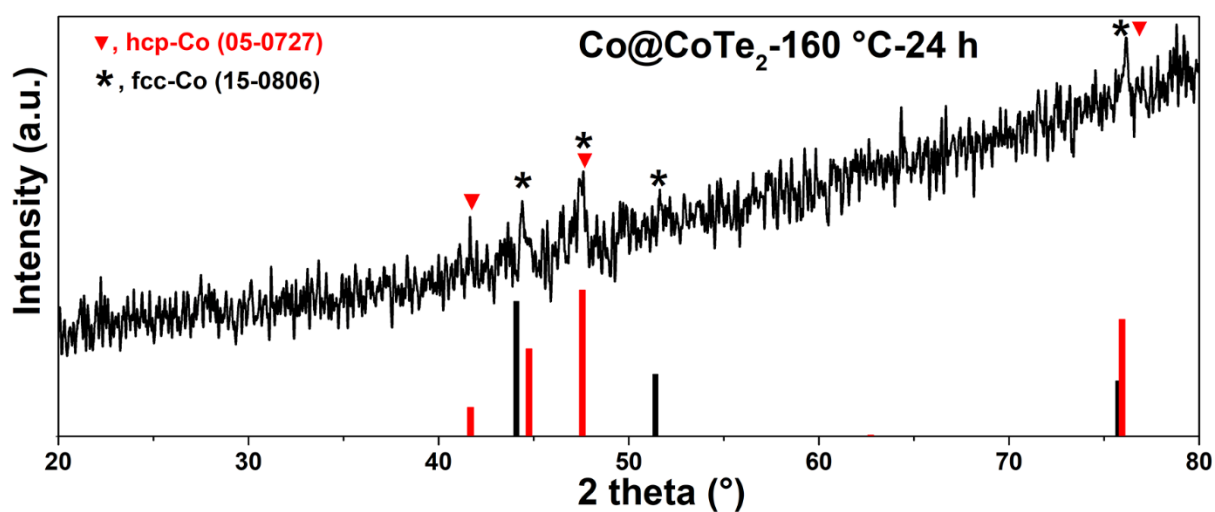


Fig. S2 XRD pattern of Co@CoTe₂ electrode obtained at 160 °C. The standard powder diffraction pattern of metallic cobalt is given for reference.

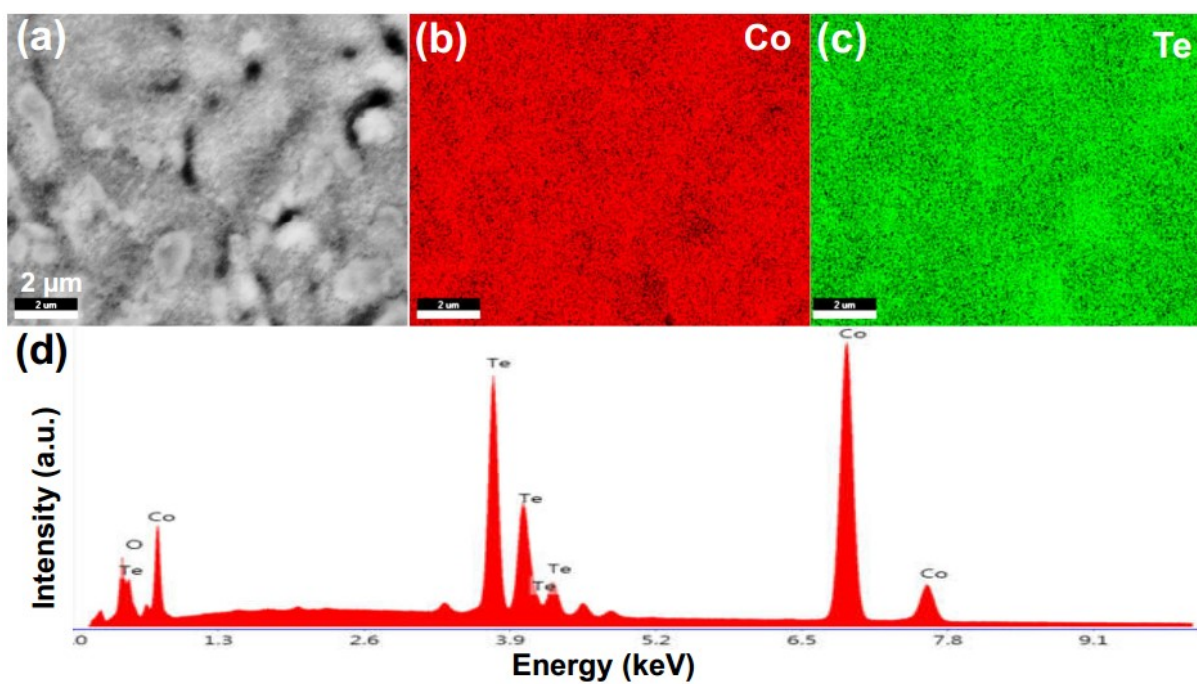


Fig. S3. SEM-EDX results of Co@CoTe₂-240 electrode.

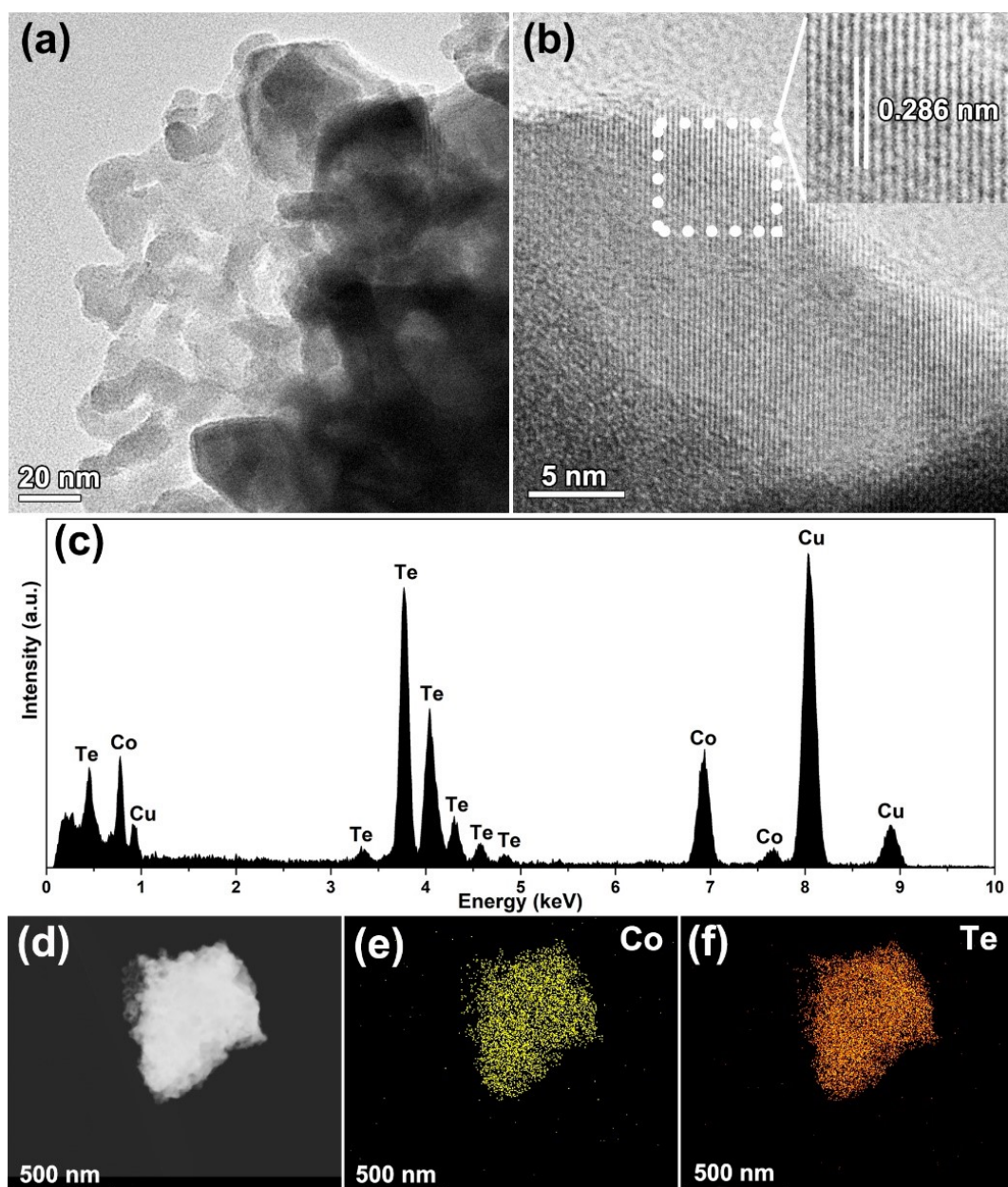


Fig. S4. TEM (a) and high-resolution TEM (b) images, EDX spectrum (c), HAADF-STEM image (d) and elemental maps (e-f) of Co@CoTe₂-200 electrode. The inset in (b) is a zoomed view of the lattice fringe.

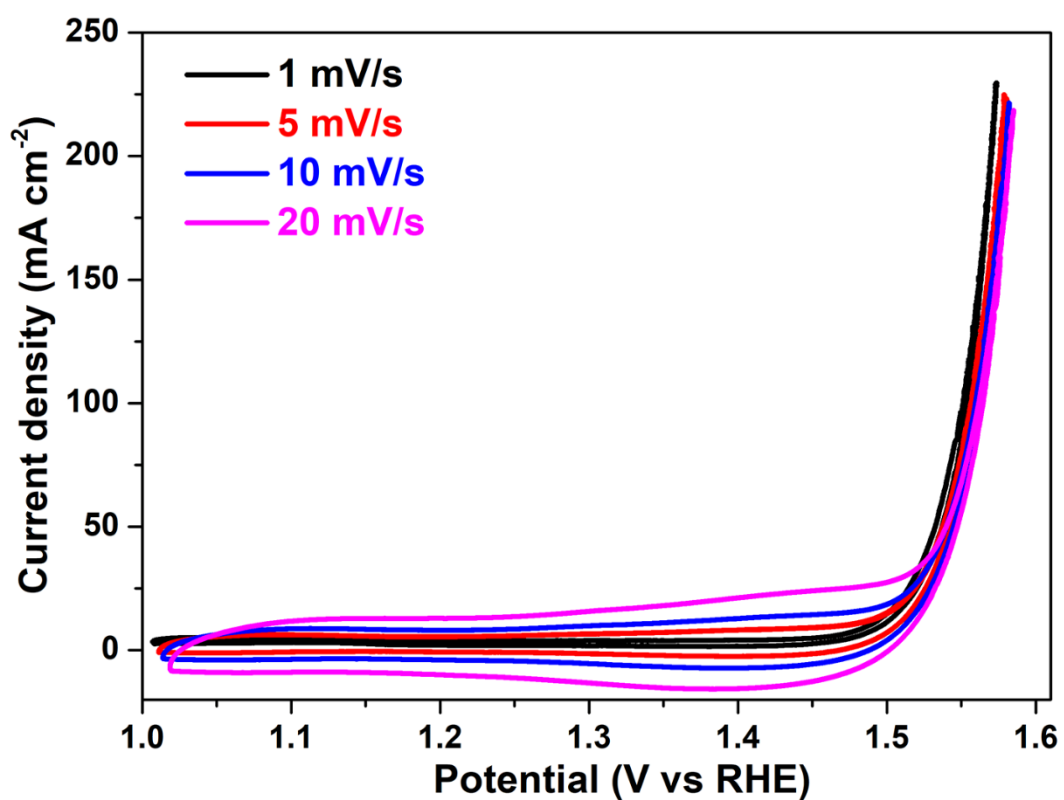


Fig. S5. CV scans of the Co@CoTe₂-240 electrode for OER with different sweep speeds, including of 1, 5, 10 and 20 mV/s.

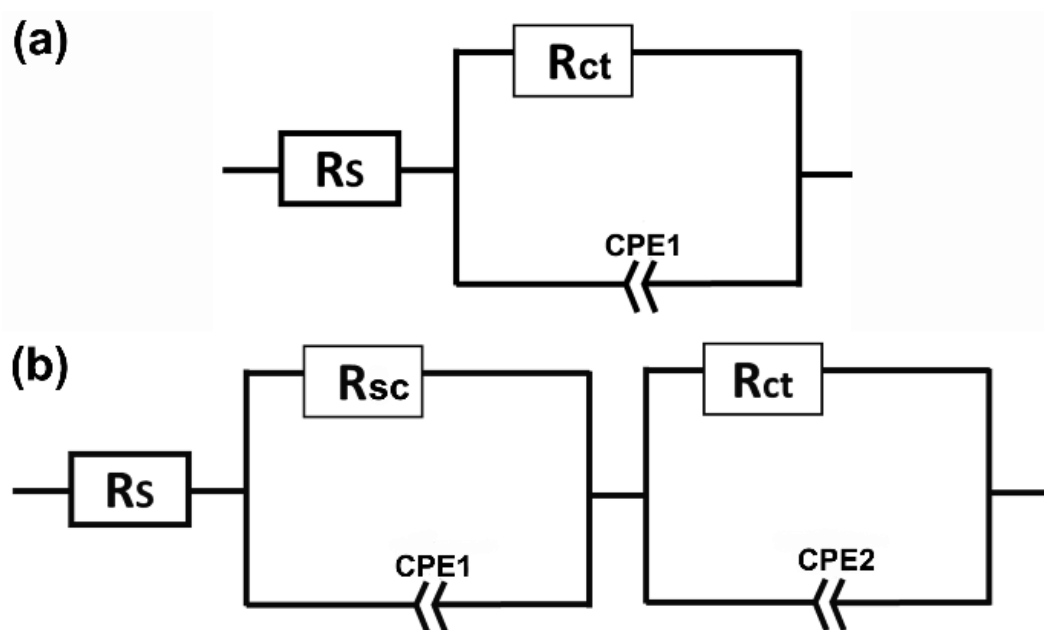


Fig. S6. Equivalent circuit models of bare Co foam (a) and Co@CoTe₂ electrodes (b) used for EIS fitting.

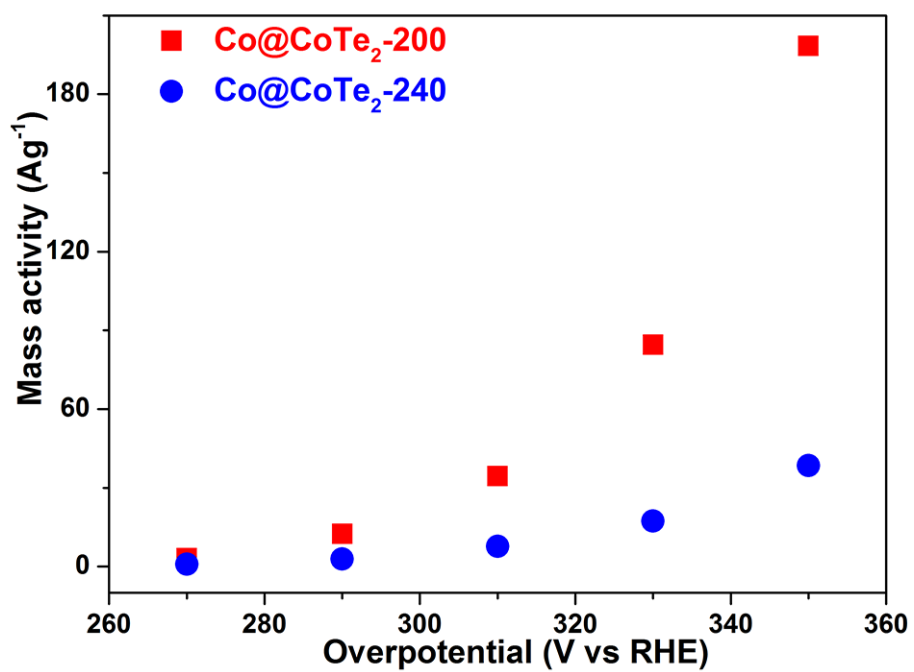


Fig. S7. Mass activity as a function of the overpotential for Co@CoTe₂ electrodes.

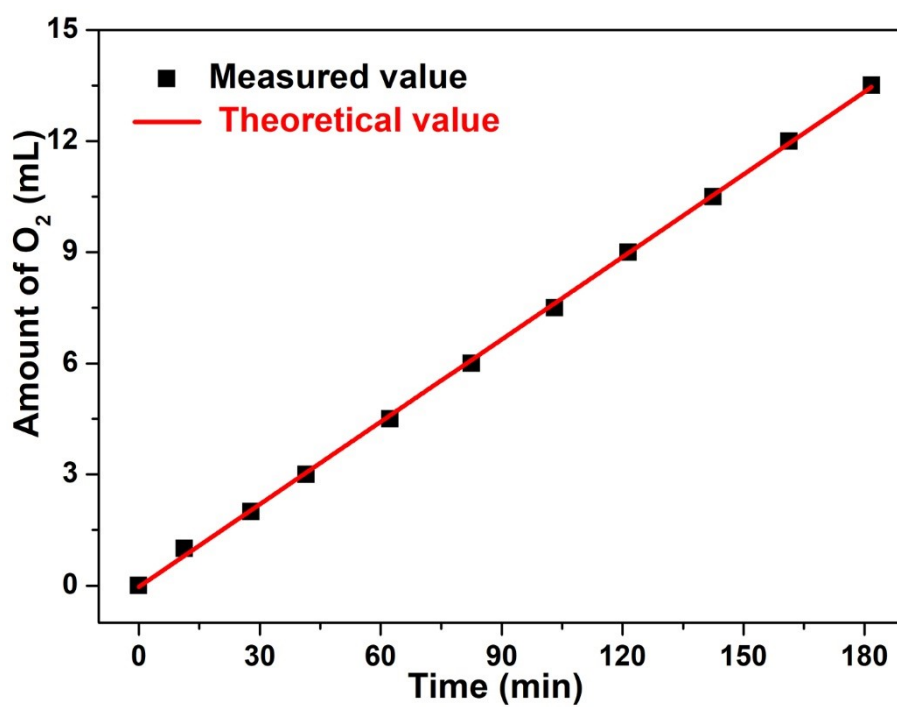


Fig. S8 The amount of gas theoretically calculated and experimentally measured vs. time for Co@CoTe₂-240 electrode over time recorded at 20 mA cm⁻² in 1 M KOH.

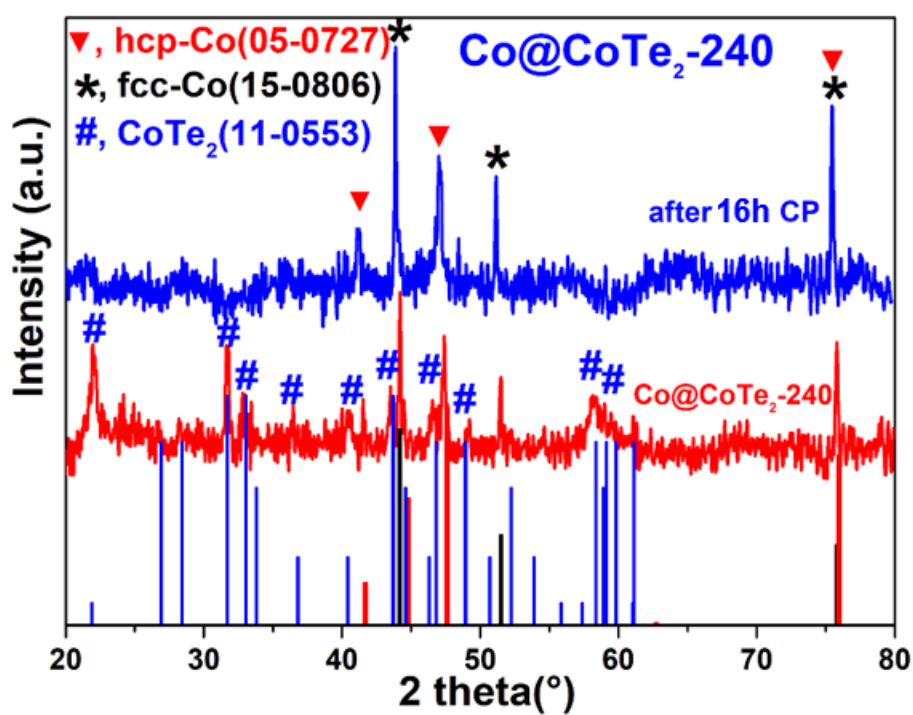


Fig. S9. XRD patterns of the Co@CoTe₂-240 electrode before and after the long-term stability test for 16 hours under OER conditions.

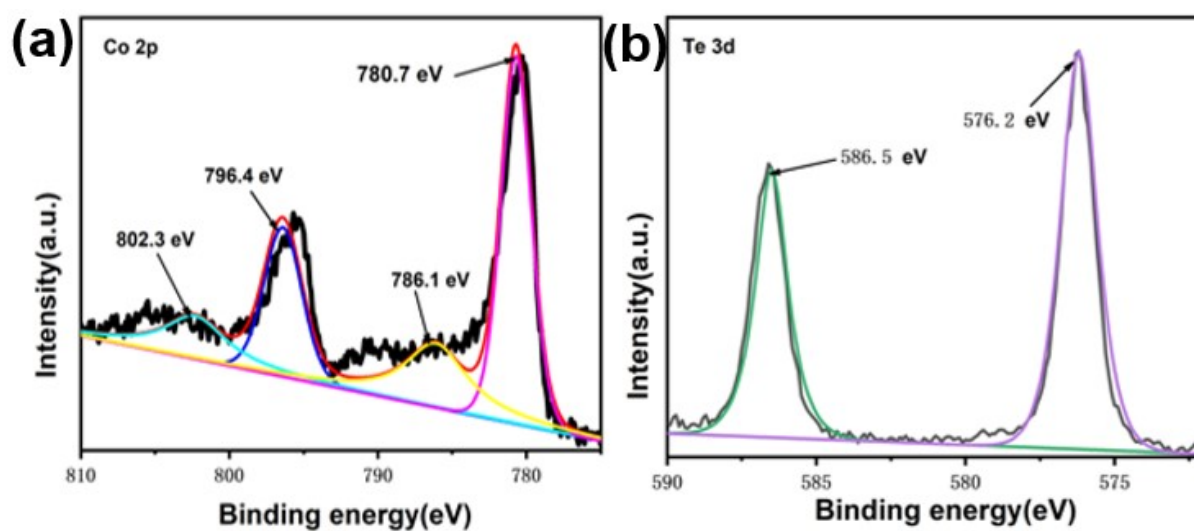


Fig. S10. High-resolution XPS spectra of Co 2p (a) and Te 3d (b) for Co@CoTe₂-240 electrode after the long-term stability test for 16 hours under OER conditions.

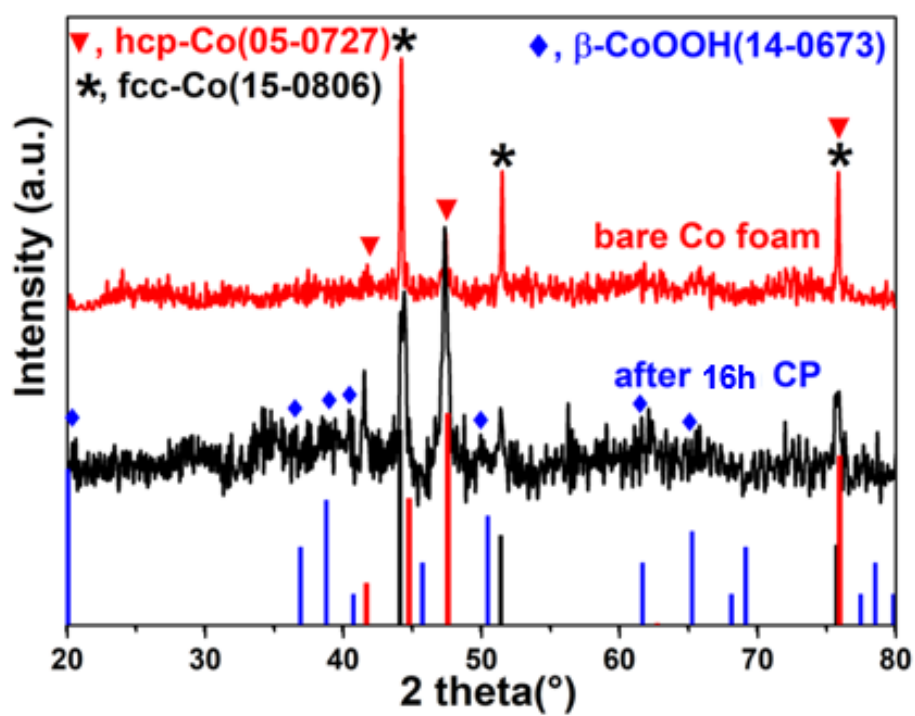


Fig. S11. XRD patterns of bare Co foam electrode before and after the long-term stability test for 16 hours under OER conditions.

Supplementary Tables:

Table S1. The OER activity of Co@CoTe₂ electrodes in comparison to that of other cobalt based chalcogenide OER catalysts recently reported in the literatures.

Catalysts	Electrolyte	Loadin g mass (mg cm ⁻²)	Tafel slope (mV dec ⁻¹)	J_{geo} (current density in mA cm ⁻² @overpotentia l in mV)	Reference
Co@CoTe ₂	1.0 M KOH	0.00	75.6	10@ η =360	This work
		1.01	40.8	10@ η =286 50@ η =318 100@ η =334	
		4.76	42.0	10@ η =284 50@ η =317 100@ η =335	
CoTe ₂ /CNT/GCE	1.0 M KOH		44.2	10@ η =290	<i>J. Phys. Chem. C</i> 2016, 120, 49, 28093-28099.
CoTe ₂ /GCE			85.1	10@ η =323	
CoTe ₂ /GCE	1.0 M KOH	0.28	58	10@ η =380	<i>ACS Catal.</i> 2016, 6, 7393-7397.
CoTe ₂ nanofleeces/GCE	0.1 M KOH	0.25	32	10@ η =357	<i>Angew. Chem.</i> <i>Int. Ed.</i> 2017, 56, 7769-7773.
CoTe nanofleeces /GCE			73	10@ η =365	
CoTe ₂ -MnTe ₂ /Ti	1.0 M KOH	1.96	118	50@ η =310	<i>Chem. Commun.</i> , 2018, 54, 10993- 10996.
CoTe ₂ @NCNTFs	1.0 M KOH	0.285	82.8	10@ η =330	<i>J. Mater. Chem.</i> <i>A</i> , 2018, 6, 3684- 3691.
CoTe ₂ @NC			94.9	10@ η =350	
CoTe ₂ NA/Ti	1.0 M KOH	1.45	67	50@ η =340	<i>ACS Sustainable</i> <i>Chem. Eng.</i> 2018, 6, 4481-4485.
CoTe ₂ @NF	1.0 M KOH	1.25	54	10@ η =340	<i>Electrochimica</i> <i>Acta</i> , 2019, 307, 451-458.
CoTe	1.0 M KOH	~	93.1	10@ η =445	<i>Electrochimica</i> <i>Acta</i> , 2019,
Fe-CoTe			45.0	10@ η =300	

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Co(Te _{0.72} Se _{0.28}) ₂	1.0 M KOH	1±0.1	69	10@η=315	<i>Nanoscale</i> , 2019, 11, 6108-6119.
Co(Te _{0.33} Se _{0.67}) ₂	1.0 M KOH		44	10@η=272	
CoTe NR/NF	1.0 M KOH	1.3	75	100@η=350	<i>Small Methods</i> . 2019, 3, 1900113.
NiTe NR/NF	1.0 M KOH		122	100@η=430	
Co _{0.13} Ni _{0.87} Se ₂ /Ti	1.0 M KOH	1.67	94	100@η=320	<i>Nanoscale</i> , 2016, 8, 3911-3915.
Porous CoSe ₂ NA/CC	1.0 M KOH	0.50	115	10@η=290	<i>ACS Appl. Mater. Interfaces</i> 2017, 9, 41, 35927-35935.
CoSe ₂ NA/CC			124	10@η=360	
CoSe ₂ UNM _{vac}	1.0 M KOH	0.28	46.3	10@η=284	<i>J. Mater. Chem. A</i> , 2019, 7, 2536-2540.
CoSe ₂ NS			97.7	10@η=343	
CoSe@NCNT/N CN	1.0 M KOH	0.357	75	10@η=310	<i>Electrochimica Acta</i> , 2020, 337, 135685.
CoSe ₂ @MoSe ₂	1.0 M KOH	0.6	84	10@η=309	<i>Nanoscale</i> , 2020, 12, 326-335.
Co ₉ S ₈ @NC	1.0 M KOH	0.22	-	10@η=320	<i>Dalton Trans.</i> , 2016, 45, 6352-6356.
Ni ₃ S ₂ @NC	1.0 M KOH		-	10@η=390	
Co ₉ S ₈ @NC	0.1 M KOH		124	10@η=370	
Ni ₃ S ₂ @NC	0.1 M KOH		196	10@η=470	
N-Co ₉ S ₈ /graphene	0.1 M KOH	0.2	82.7	10@η=409	<i>Energy Environ. Sci.</i> , 2016, 9, 1320-1326.
NA-Co ₉ S ₈ /graphene			83	10@η=441	
Co ₉ S ₈	1.0 M KOH	0.24	85.6	10@η=340	<i>J. Mater. Chem. A</i> , 2016, 4, 18314-18321.
Co ₉ S ₈ /CNS			50.7	10@η=294	
Co ₉ S ₈ /CNS/CNT			48.2	10@η=267	
Co@Co ₉ S ₈ -180	1.0 M KOH	1.09	55	10@η=350	<i>Chem. Eur. Journal</i> , 2017, 23: 8749-8755.
Co@Co ₉ S ₈ -220		9.73	52	10@η=360	
CoS ₂ hollow nanospheres/CP	1.0 M KOH	1.5	57	10@η=290 20@η=305	<i>Nanoscale</i> , 2018,10, 4816-4824.
Fe-CoS ₂ /CC	1.0 M KOH	~	128	10@η=302	<i>Chem. Commun.</i> , 2019, 55, 2469-2472.
CoS/CNT	1.0 M KOH	1.1	142	10@η=330	<i>Appl. Surf. Sci.</i> , 2019, 466, 830-836.

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Co ₈ FeS ₈ /CoS@C NT-500	1.0 M KOH	~	49	10@η=278	<i>J. Power Sour.</i> , 2020, 449, 227561.
Co ₈ FeS ₈ /CoS			83	10@η=292	

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Table S2. Fitting parameters for the Nyquist plots of the bare Co foam, Co@CoTe₂-200 and Co@CoTe₂-240 electrodes.

Samples	$R_s(\Omega)$	$R_{sc}(\Omega)$	$C_{sc} (F \text{ cm}^{-2} \text{ S}^{\text{m}^{-1}})$	$R_{ct} (\Omega)$	$C_h (F \text{ cm}^{-2} \text{ S}^{\text{m}^{-1}})$
Co foam	1.07	-	-	2.75	0.848
Co@CoTe ₂ -200	0.98	0.05	0.346	0.40	0.372
Co@CoTe ₂ -240	1.13	0.06	0.239	0.48	0.357