Supplementary information

Modulating the electronic structure of cobalt sites by zinc to promote the oxygen evolution electrocatalysis

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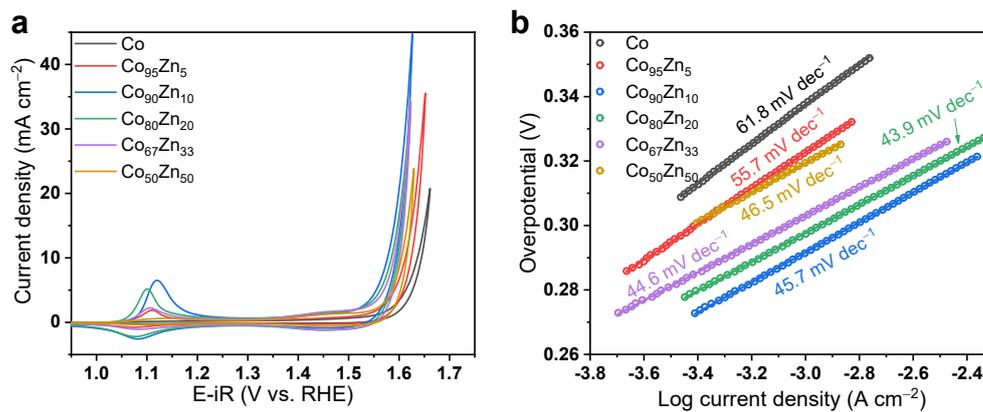E-mail: chz@ruc.edu.cn.

Results and discussion

Fig. S1. (a) Cyclic voltammograms and (b) Tafel plots of Co_xZn_{1-x}-oxa on an Au substrate.
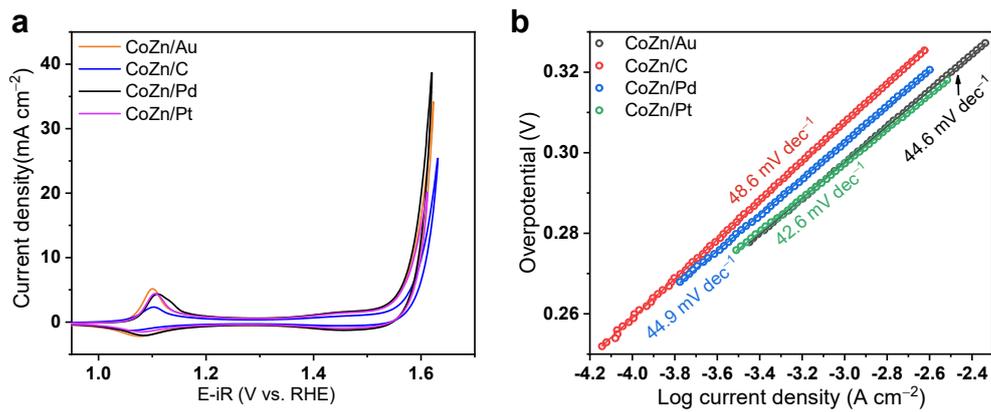
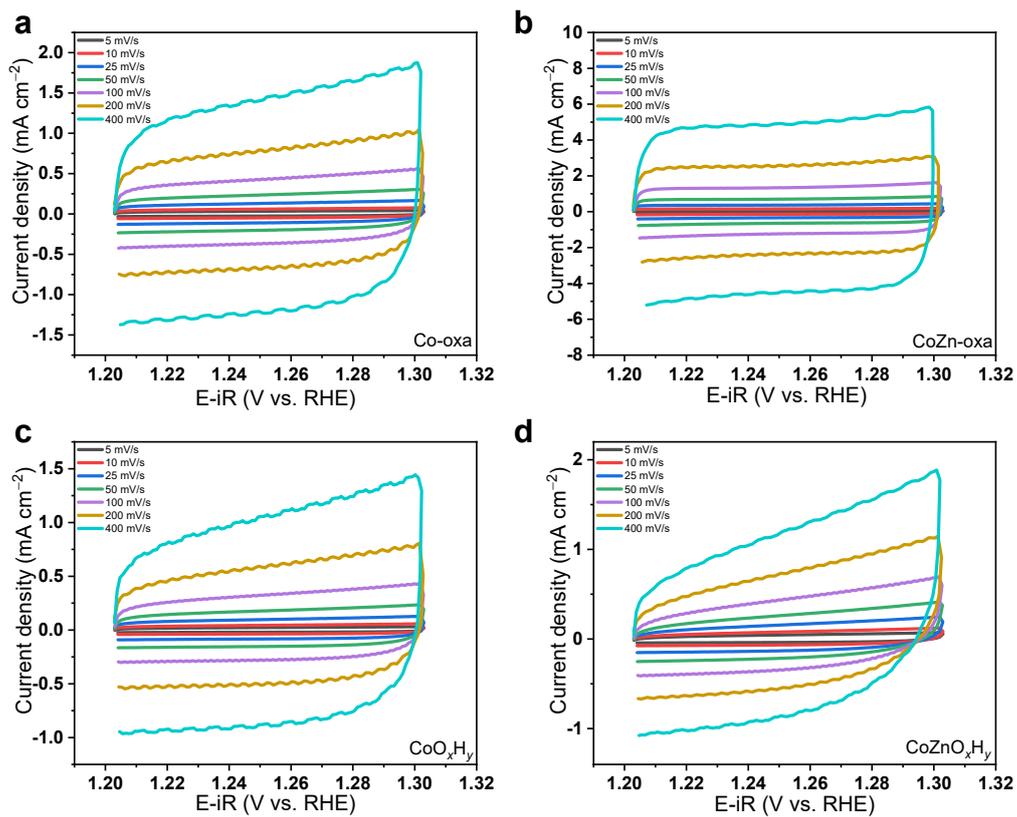**Fig. S2.** (a) Cyclic voltammograms and (b) Tafel plots of Co_xZn_{1-x}-oxa on different substrates.

Fig. S3. Cyclic voltammograms of (a) Co-oxa, (b) CoZn-oxa, (c) CoO$_x$H$_y$, and (d) CoZnO$_x$H$_y$ with scanning rates varying from 5 to 400 mV s^{-1}.
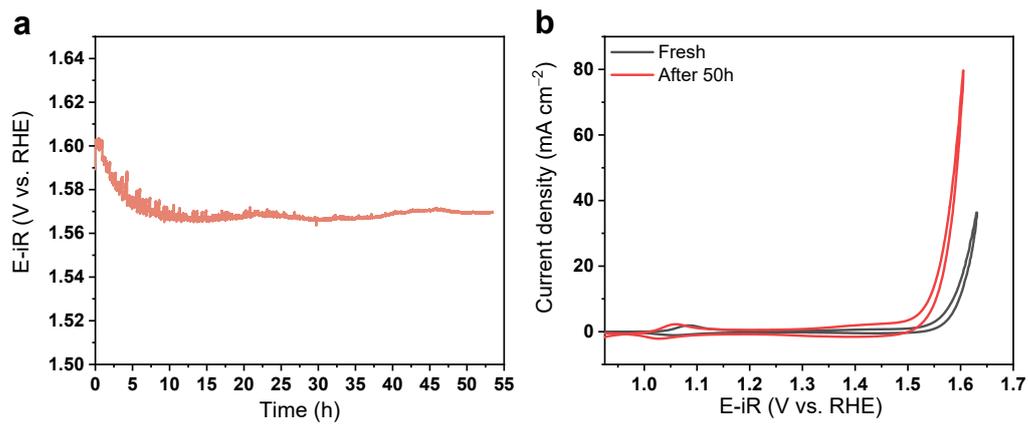
Fig. S4. (a) Chronopotentiometry curve of CoZn-oxa held at 10 mA cm^{-2} for 50 hours. (b) Cyclic voltammograms and (c) Tafel plots of CoZn-oxa recorded after 0 and 50 hours of stability testing.
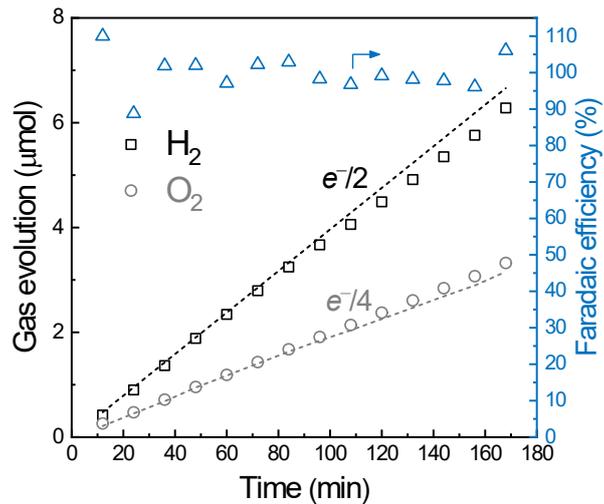
Fig. S5 Faradaic efficiency of CoZn-oxa. Evolved oxygen and hydrogen gases were continuously collected at 10 mA cm^{-2} by using a gas chromatography system (GC; Agilent Micro 490). Then the Faradaic efficiency of CoFe-SBH was calculated according to the total passed charge with time.
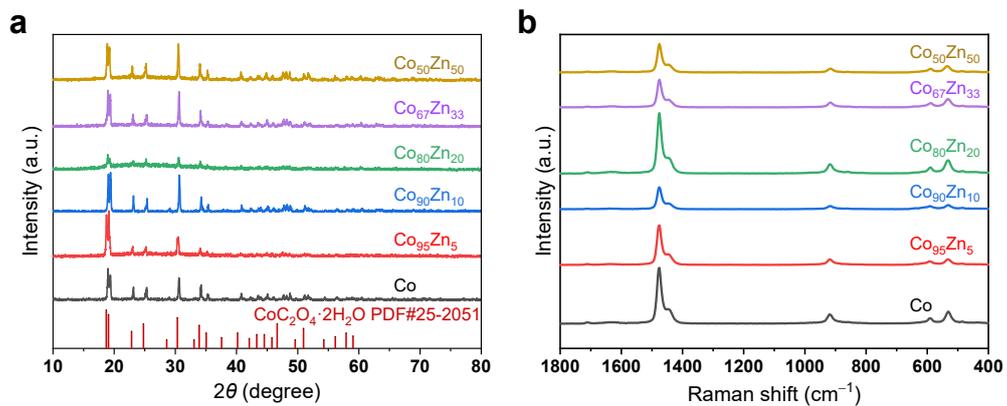
Fig. S6. (a) XRD patterns and (b) Raman spectra of Co_xZn_{1-x}-oxa catalysts.
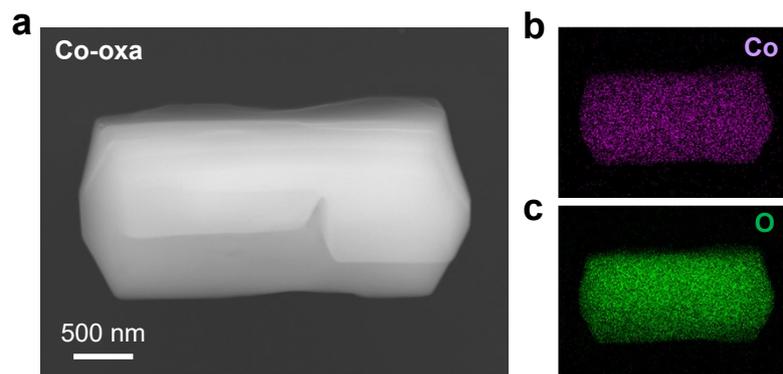
Fig. S7. (a) SEM image pristine Co-oxa. EDX elemental mapping: (b) Co and (c) O.
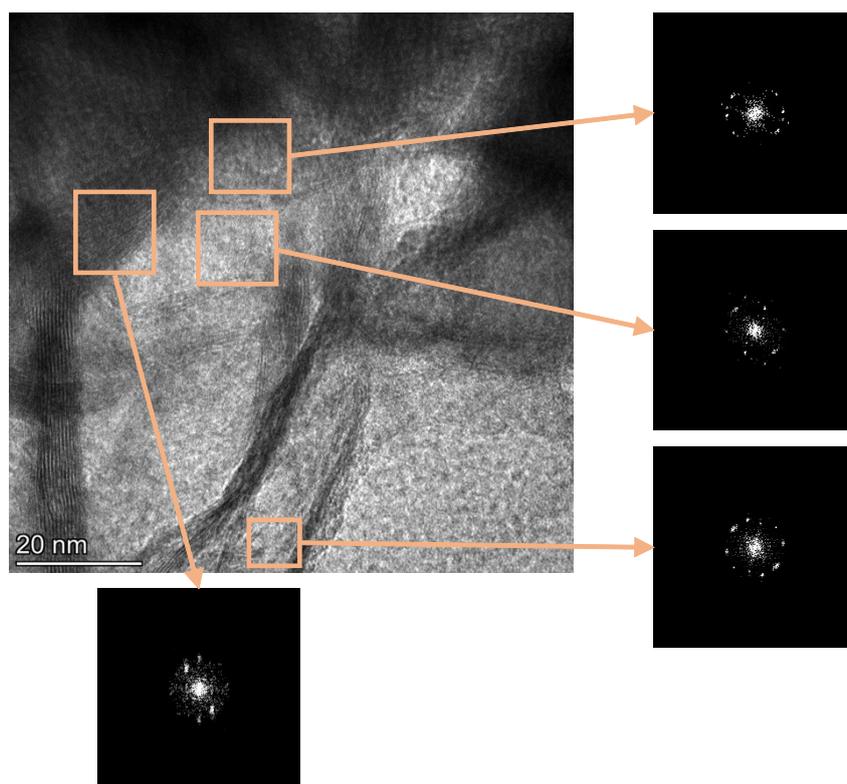
Fig. S8. High-resolution TEM image of CoZn-oxa with Fast Fourier Transform (FFT) patterns obtained from the selected area.
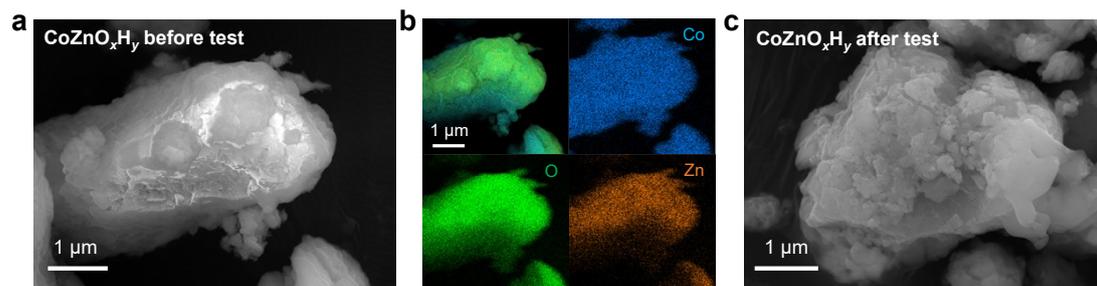
Fig. S9. SEM images of CoZnO$_x$H$_y$ (a) before and (b) after cyclic voltammetry tests. EDX elemental mapping corresponding to the area shown in panel (a).
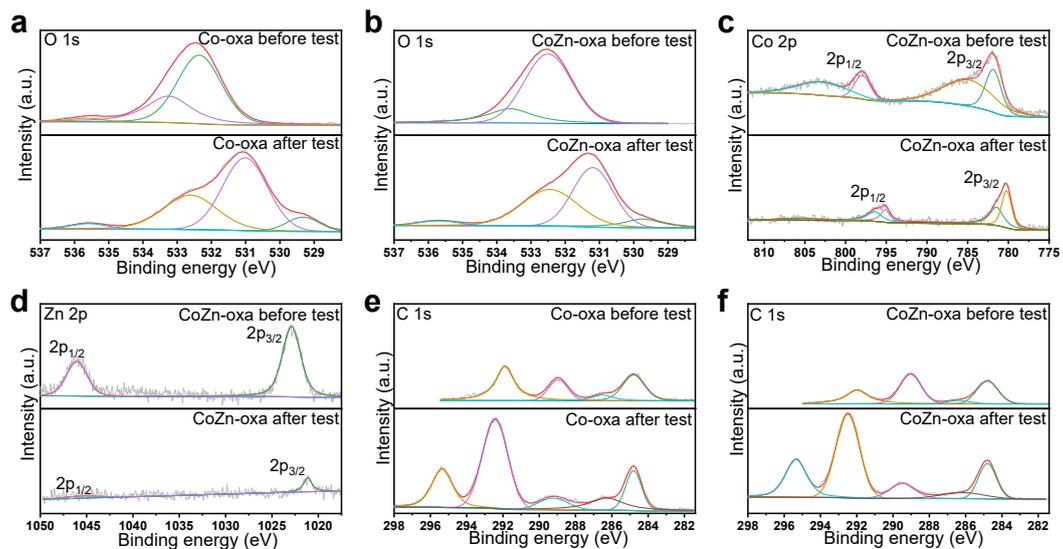
Fig. S10. XPS spectra of CoZn-oxa and Co-oxa before and after CV testing: O 1s spectra for (a) Co-oxa and (b) CoZn-oxa; (c) Co 2p spectra and (d) Zn 2p spectra of CoZn-oxa; C 1s spectra for (e) Co-oxa and (f) CoZn-oxa.
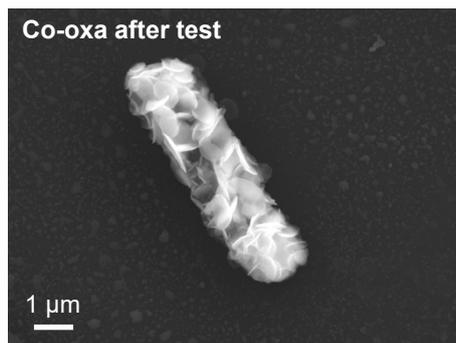
Fig. S11. SEM image of Co-oxa after cyclic voltammetry testing.

Table S1. Summary of OER performances (corresponding to Fig. 1a in the main text) and fitted equivalent circuit resistances obtained from the electrochemical impedance Nyquist plots (corresponding to Fig. 1c in the main text).

	η (mV) at 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	R_{CT} / Ω
CoZn-oxa	1.590±0.002	46.06±2.61	771
Co-oxa	1.622±0.002	56.44±1.03	2141
CoZnO$_x$H$_y$	1.618±0.003	53.66±0.77	3179
CoO$_x$H$_y$	1.615±0.003	60.08±0.74	1335

Table S2. Bond lengths, bond strengths, and σ- and π-bonding contributions to the planar Co–O_{pl} bond within the Co–μ_2–O–Co motif of CoOOH and the Zn–μ_2–O–Co motif of Zn: CoOOH. The bonding information were obtained from the pCOHP analysis of the corresponding Co–O_{pl} interactions shown in Figs. 5f and 5g of the main text.

Co–O_{pl}	Bond length	Bond strength	$\sigma_{d\text{-}p}$	$\pi_{d\text{-}p}$
CoOOH	1.93 Å	−2.16	77%	23%
Zn: CoOOH	1.99 Å	−1.63	58%	42%