

Supporting Information

Improved water oxidation with metal oxide catalysts via regenerable and redox-inactive ZnO_xH_y overlayer

Swarnava Nandy ^{a,b,c,†}, Qianbao Wu ^{c,†}, S. David Tilley ^{b,*} and Chunhua Cui ^{a,c,*}

^aYangtze Delta Region Institute (Huzhou), University of Electronic Science and Technology of China, Huzhou, 313001, China

^bDepartment of Chemistry, University of Zurich, Zurich, CH-8057, Switzerland.

^cMolecular Electrochemistry Laboratory, Institute of Fundamental & Frontier Sciences, University of Electronic Science & Technology of China, Chengdu, 610054, China.

[†]Contributed equally to this work

Table of Contents

Experimental.....	2
Fabrication of $\text{MO}_2/\text{ZnO}_x\text{H}_y$ (M= Co, Fe, Ni) films	
Electrochemical measurements	
Physical characterization	
Supplementary Figures.....	4

Experimental:

Fabrication of $\text{MO}_2/\text{ZnO}_x\text{H}_y$ (M= Co, Fe, Ni) :

Cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from General reagent; Nickel (II) chloride hexahydrate $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was purchased from Kelong; Zinc(II) nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], was purchased from Adamas.

Bare FTO was exposed to UV light for 10 min before deposition. Each of the respective metal chloride precursors was dissolved into water to form a 0.2-1.0 M aqueous solution. 1 mL metal precursor solution was spin-coated each time onto FTO at 500 rpm for 10 seconds thrice followed by at 3000 rpm once for one minute.¹ After spin-coating, the films were left under a non-coherent UV lamp for 12 h to decompose chloride ligands. After UV treatment, the MO_2 films were annealed at a temperature with a range from 50-500 °C.

Electrochemical measurements:

All electrochemical experiments were performed at room temperature (at 298 K) with a Bio-Logic SP-200 electrochemical workstation in a standard three-electrode system using FTO (F-doped SnO_2) glass substrates as working electrode, a Pt wire as a counter electrode, and Ag/AgCl as a reference electrode. 1.0 M NaOH (pH 13.6 at 298 K) electrolyte solution was applied to measure OER performance of $\text{MO}_2/\text{ZnO}_x\text{H}_y$ (M= Co and Fe) films. Whereas, 1.0 M Fe-free NaOH was prepared according to a reported procedure utilized as an electrolyte to measure OER performance of $\text{NiO}_2/\text{ZnO}_x\text{H}_y$ films.² Polarization curves were obtained using cyclic voltammetry with a scan rate of 10 mV/s. The Tafel slope was drawn from polarization curves. All potentials reported in this manuscript were converted to a reversible hydrogen electrode (RHE) using $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + (0.197 + 0.059 \times \text{pH}) \text{ V}$. The overpotentials were obtained using $\eta = E_{\text{RHE}} - 1.23 \text{ V}$. Electrochemical impedance spectroscopy (EIS) was measured at potential 1.60 V vs RHE with a frequency scan range from 100 kHz to 1 mHz, and the amplitude of the sinusoidal wave was 10 mV.

Physical Characterizations:

The absorbance of the film was evaluated by QE Pro UV-visible spectrometer (Ocean Optics) equipped with an HL-2000 light source that connected via fiber-optic cables (200 μm fiber core diameter). The baseline was subtracted in each specific experiment. Atomic Co/Zn ratio and valence state of constituting elements of different $\text{CoO}_2/\text{ZnO}_x\text{H}_y$ films were confirmed by X-ray photoelectron spectroscopy on Escalab 250Xi and the binding energies were calibrated using the adventitious carbon by shifting the C1s peak to 284.8 eV. All XPS experiments were carried out by the Al K Alpha source gun and a constant spot size of 500 μm . The morphology of the catalyst films was examined by scanning electron microscope (SEM) and elemental mapping on FEI Inspect F50. The structure was further analyzed by high-resolution TEM (HRTEM). The elements mapping and the lattice planes are characterized by selected area electron diffraction (SAED) (FEI TECNAL G2 F30) field emission

transmission electron microscope. The mass content of Co and Zn in $\text{CoO}_z/\text{ZnO}_x\text{H}_y$ catalyst film were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (Optima 7000DV).

Supplementary Figures:

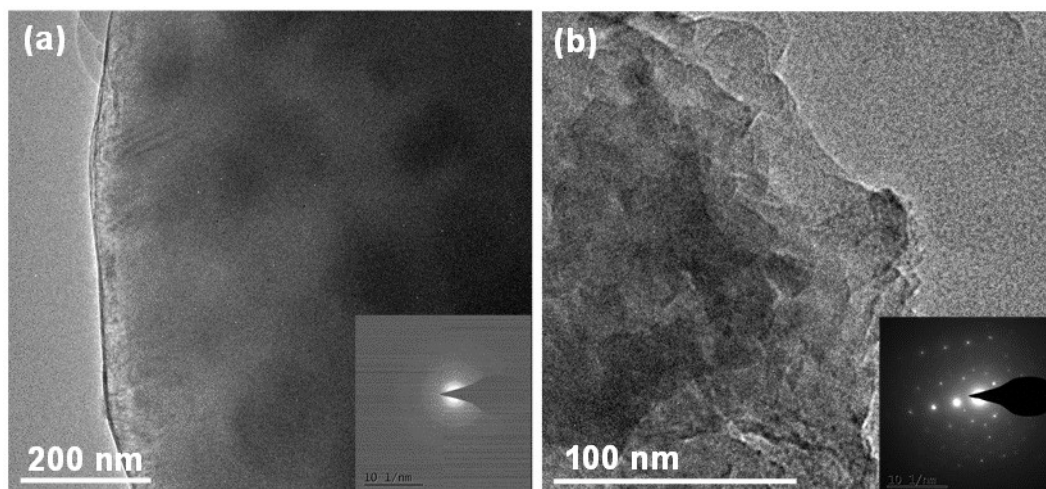


Figure S1. TEM and SAED patterns of CoO₂ films annealed at (a) 150 °C, (b) 500 °C prepared from aqueous 1.0 M CoCl₂·6H₂O precursor solution.

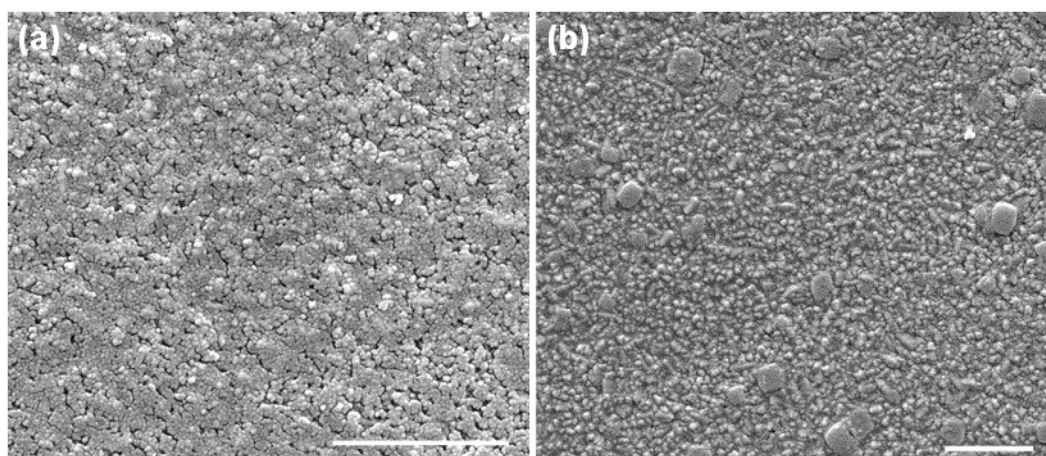


Figure S2. SEM images of CoO₂ films annealed at (a) 150 and (b) 500 °C, respectively, prepared from aqueous 1.0 M CoCl₂·6H₂O precursor solution. Scale bar represents 1.0 μm.

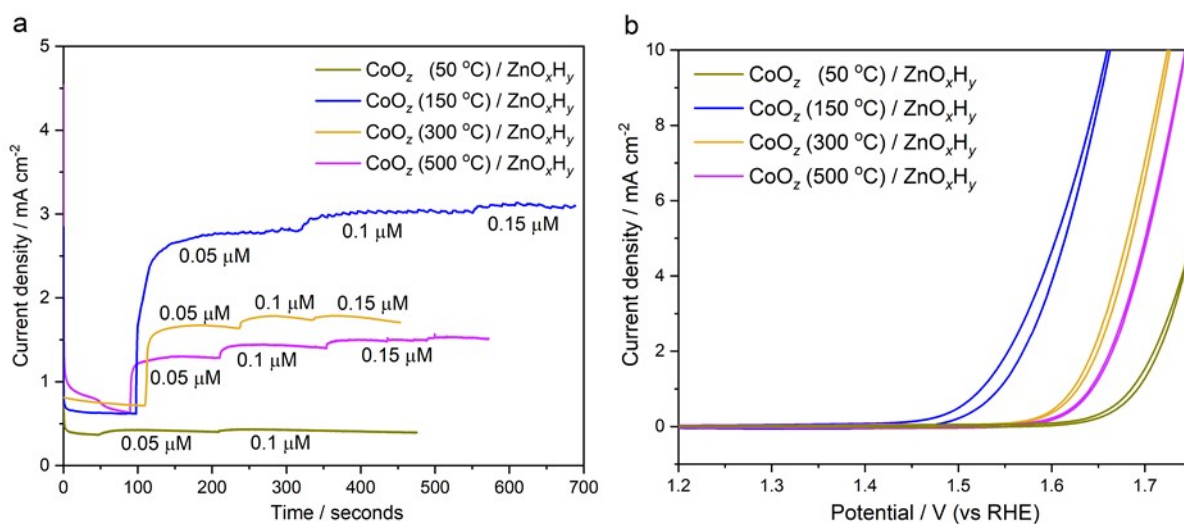


Figure S3. (a) CA with stepwise addition of Zn-anion solution measured at 1.6 V vs RHE and (b) CV curves of CoO₂/ZnO_xH_y films where CoO₂ films onto FTO substrates were annealed at different temperatures. CoO₂ films were prepared from an aqueous 1.0 M CoCl₂·6H₂O precursor solution.

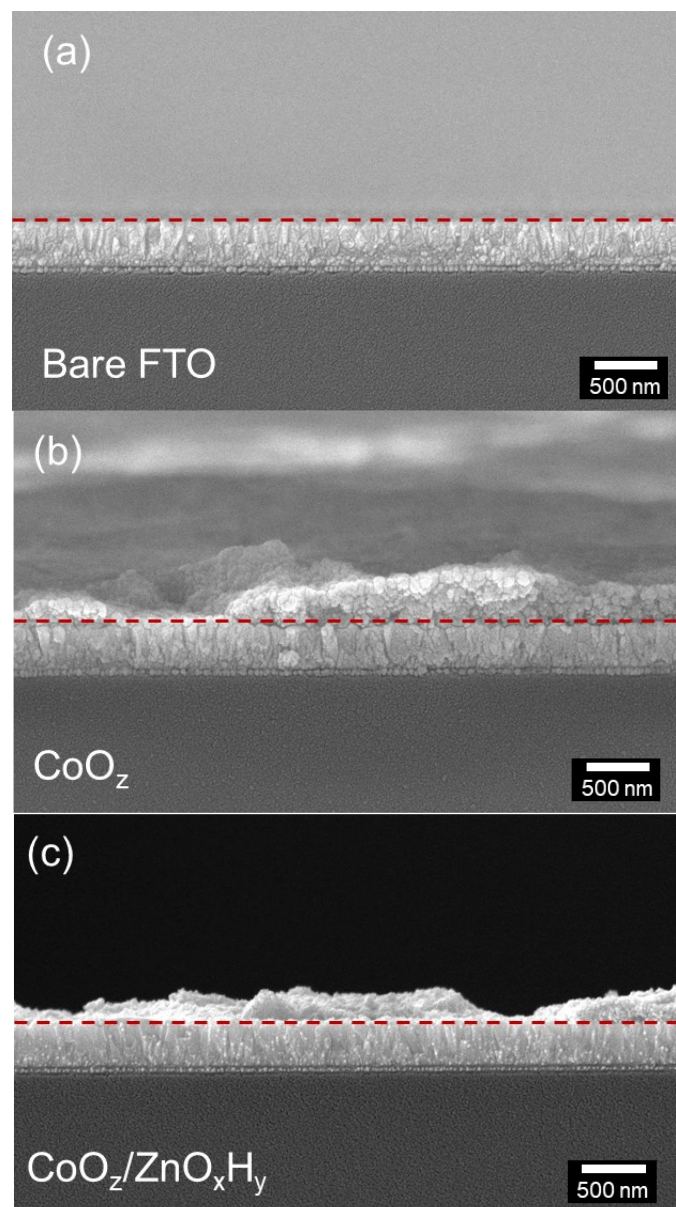


Figure S4. Cross-sectional SEM images of bare FTO, CoO_z , and $\text{CoO}_z/\text{ZnO}_y\text{H}_z$ films.

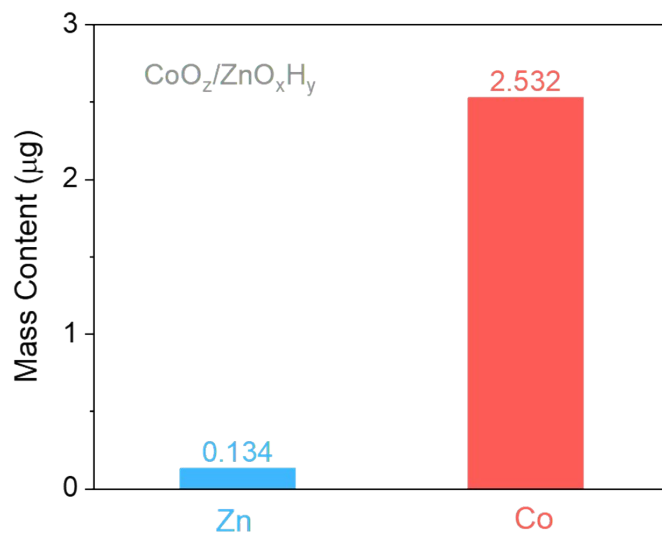


Figure S5. The Co and Zn content in CoO_z/ZnO_xH_y film was analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (Optima 7000DV). The as-prepared CoO_z/ZnO_xH_y catalyst film was put into HNO₃ for 24 hours to ensure complete dissolution which was further diluted to perform the analysis.

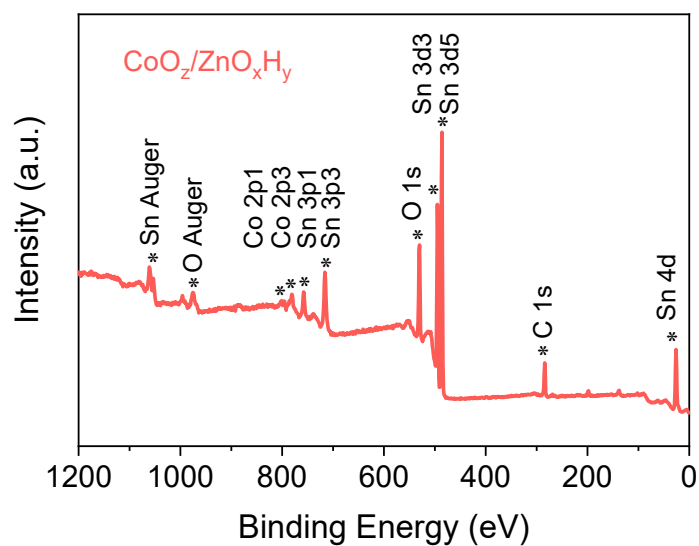


Figure S6. The XPS spectra of CoO_z/ZnO_yH_z films.

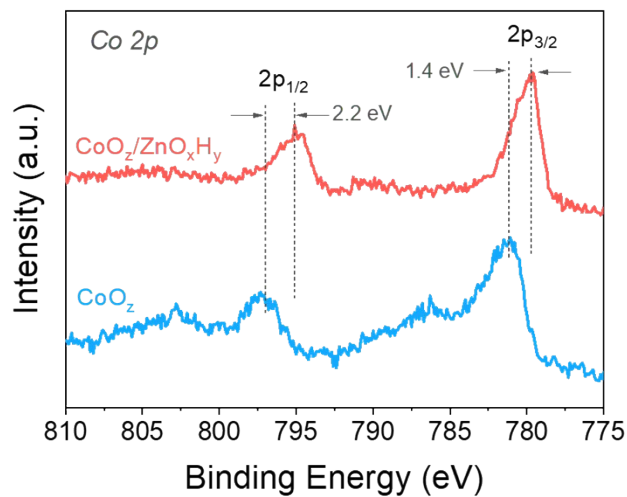


Figure S7. Co 2p XPS spectra of bare CoO_z and $\text{CoO}_z/\text{ZnO}_x\text{H}_y$.

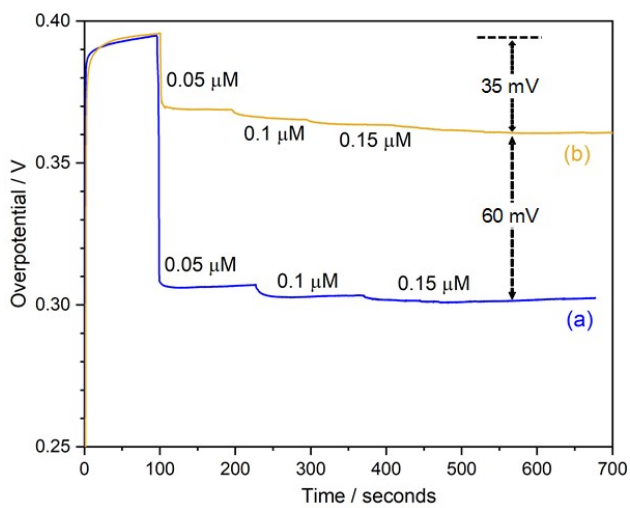


Figure S8. Chronopotentiometric (CP) curves of CoO_z films annealed at (a) 150 °C, and (b) 300 °C, respectively, with stepwise addition of $[\text{Zn}(\text{OH})_4]^{2-}$ solution operating at 1.0 mA/cm^2 .

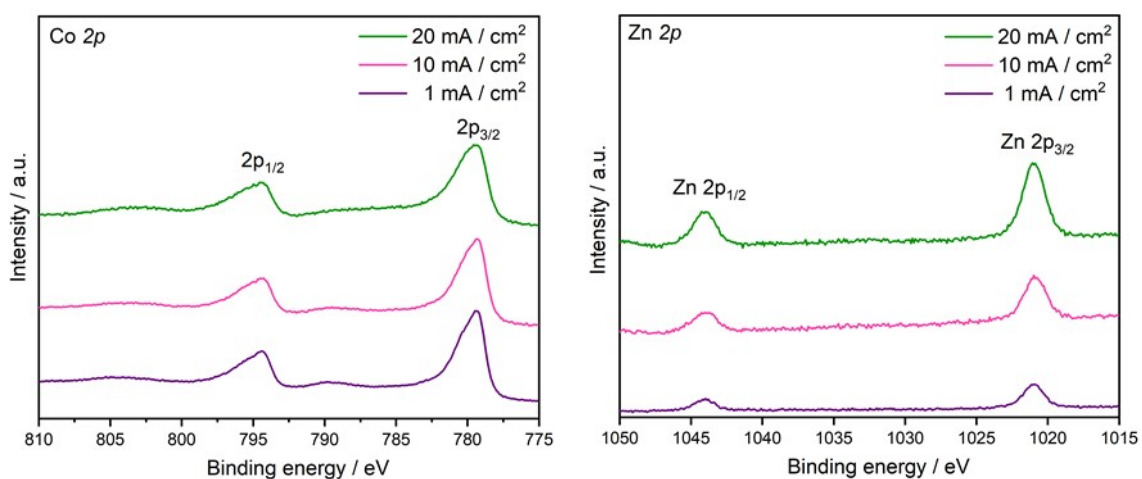


Figure S9. XPS spectra of $\text{CoO}_2/\text{ZnO}_x\text{H}_y$ films while using different current densities to deposit ZnO_xH_y onto CoO_2 surface.

Table S1. Atomic Co/Zn ratio of $\text{CoO}_2/\text{ZnO}_x\text{H}_y$ films while using different current densities to deposit ZnO_xH_y layer onto CoO_2 surface.

Current density (mA cm^{-2})	Surface Co/Zn ratio
1.0	21.24
10.0	12.29
20.0	10.69

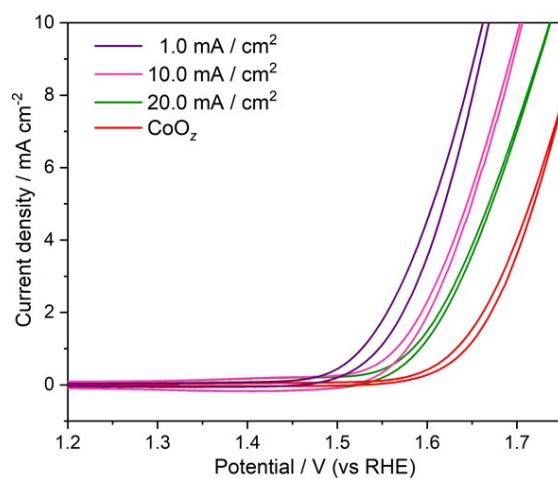


Figure S10. CV curves of CoO₂/ZnO_xH_y films while using different current densities to deposit ZnO_xH_y layer onto CoO₂ surface.

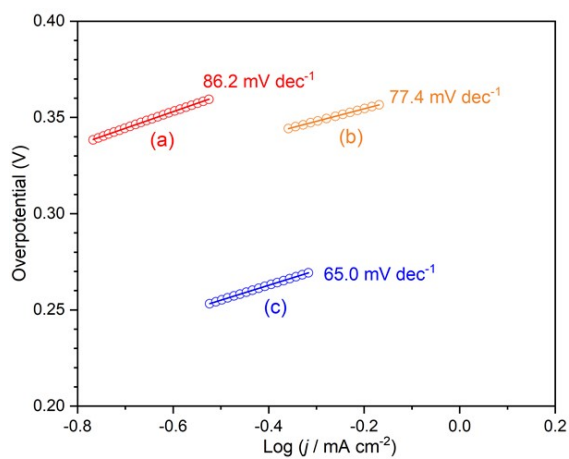


Figure S11. Tafel slopes of (a) CoO₂, (b) CoZnO_xH_y, and (c) CoO₂/ZnO_xH_y films.

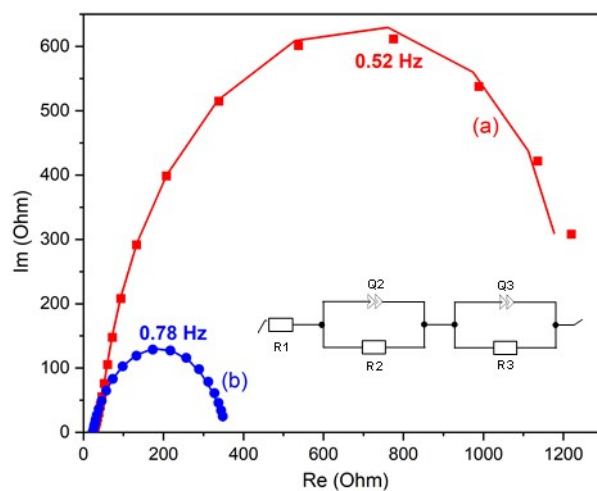


Figure S12. Charge transfer of (a) CoO₂, and (b) CoO₂/ZnO_xH_y films. Inset shows the electrical equivalent circuit.

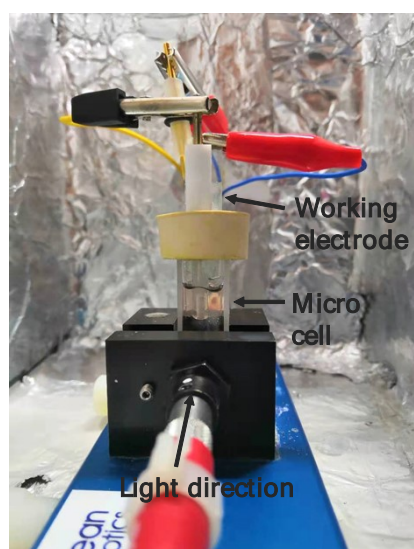


Figure S13. Photograph of home-made cell for in-situ spectroelectrochemical UV-vis setup.

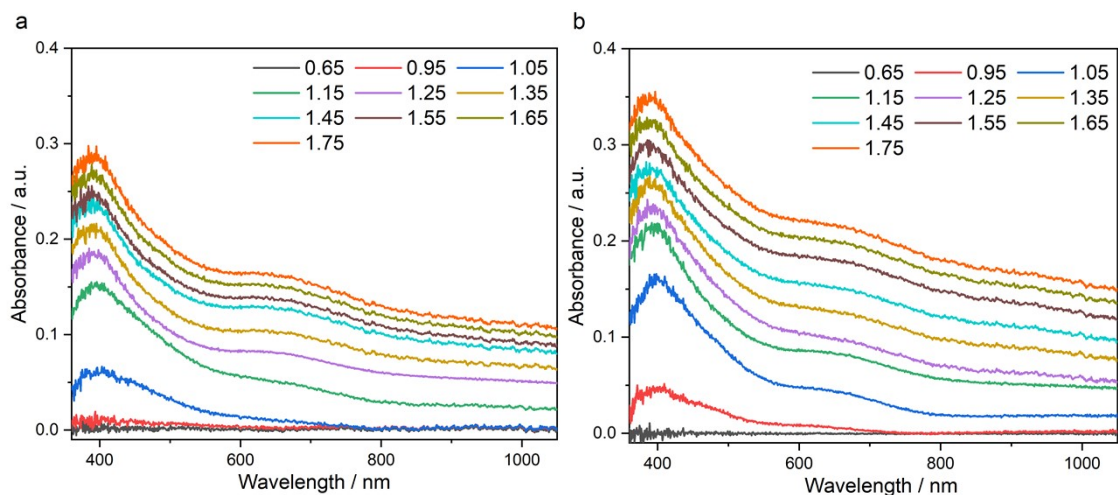


Figure S14. In-situ UV-vis absorbance of (A) CoO_2 , and (B) $\text{CoO}_2/\text{ZnO}_x\text{H}_y$ films at different potentials measured during OER.

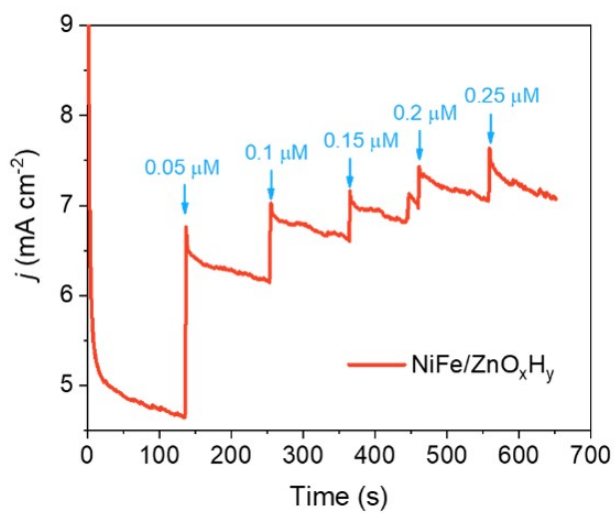


Figure S15. CA curve was recorded at 1.6 V vs RHE upon addition of Zn-anion on NiFeOOH catalyst. The NiFeOOH catalyst film was synthesized by hydrothermal method according to previously reported work.³

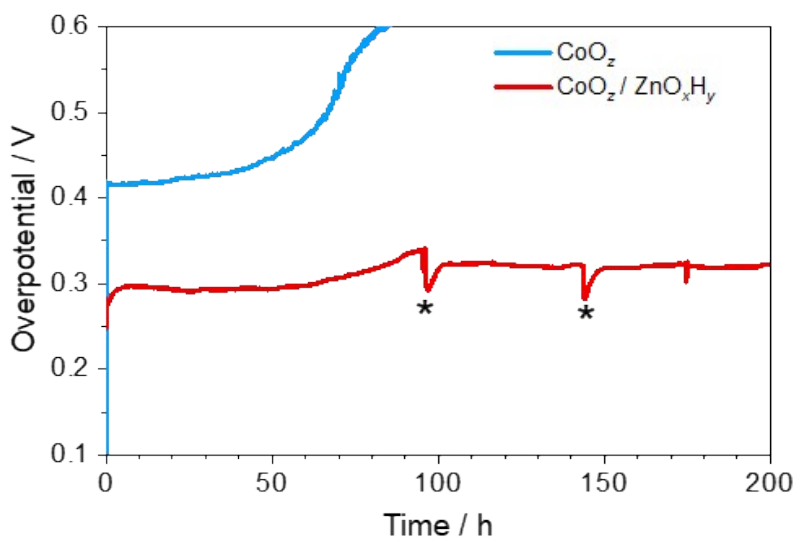


Figure S16. Long-term stability measurement of the bare CoO_2 and $\text{CoO}_2/\text{ZnO}_x\text{H}_y$ films operating at 1.0 mA/cm^2 . Asterisks (*) on the curve for the $\text{CoO}_2/\text{ZnO}_x\text{H}_y$ indicate an extra addition of $0.1 \mu\text{M} [\text{Zn}(\text{OH})_4]^{2-}$ into the electrolyte.

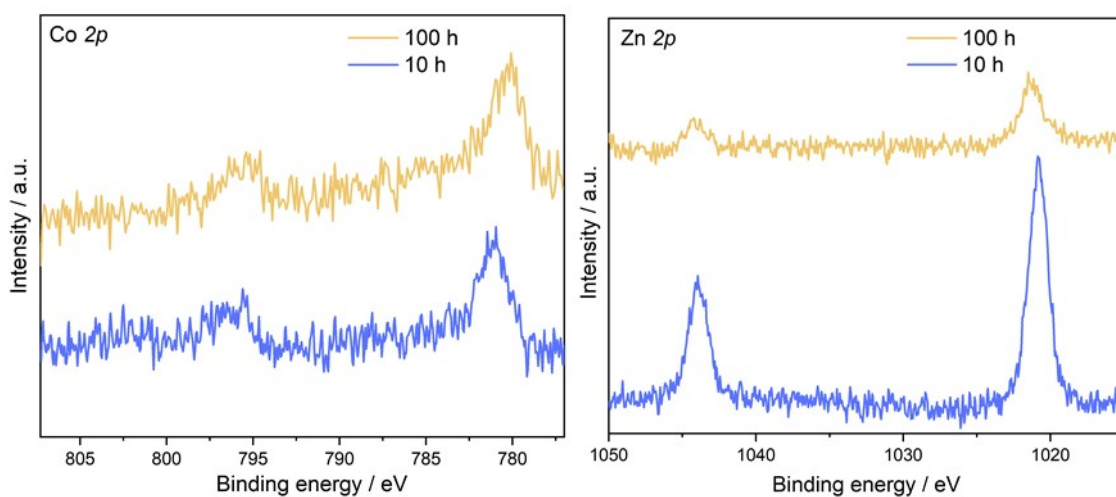


Figure S17. XPS spectra of $\text{CoO}_2/\text{ZnO}_x\text{H}_y$ films during stability experiment after 10 h and 100 h.

References

1. J. He, D. M. Weekes, W. Cheng, K. E. Dettelbach, A. Huang, T. Li and C. P. Berlinguette, Photodecomposition of Metal Nitrate and Chloride Compounds Yields Amorphous Metal Oxide Films. *J. Am. Chem. Soc.* 2017, **139**, 18174-18177.
2. L. Trotochaud, S. L. Young, J. K. Ranney and S. W. Boettcher, Nickel-iron oxyhydroxide oxygen-evolution electrocatalysts: the role of intentional and incidental iron incorporation. *J. Am. Chem. Soc.* 2014, **136**, 6744-6753.
3. Z. Lu, W. Xu, W. Zhu, Q. Yang, X. Lei, J. Liu, Y. Li, X. Sun and X. Duan, *Chem. Commun.*, 2014, **50**, 6479-6482.