

Supplementary Information

Fluoride-incorporating cobalt-based electrocatalyst toward enhanced hydrogen evolution reaction

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Experimental section

Chemicals. 1-methylimidazole (99%), KF (99%) and potassium citrate tribasic monohydrate (99 %) were bought from Acros Organics. KOH and K₂SO₄ were bought from Duksan. KH₂PO₄ and K₂HPO₄ were purchased from Fluka. CoSO₄·7H₂O (99 %), platinum on carbon (40 wt. % Pt/C, Pt on an activated carbon support) and Nafion® perfluorinated resin solution (5 wt. % in lower aliphatic alcohols and water, contains 15-20% water) were bought from Sigma-Aldrich. All chemicals were used directly without further purification. Ultrapure water (18.2 MΩ) used in the experiments was supplied by a Millipore System (Direct-Q® 3).

Electrode Preparation. The electrodeposition was carried out with a standard three-electrode electrochemical cell containing glassy carbon disk (surface area: 0.0707 cm²), a graphite rod (L 100 mm, diam. 3 mm) and a saturated calomel electrode (SCE) as the working, auxiliary and reference electrodes, respectively. In order to the physical characterizations, electrodepositions on graphite plate electrodes as the working electrode were performed. The electrolyte solution of CoO-F/Co was prepared; CoSO₄·7H₂O (0.281 g, 1.0 mmol), 1-methylimidazole (0.478 mL, 6.0 mmol) and KF (5.810 g, 0.1 mol) were dissolved in 100 mL DI water. Similar to above the procedure, the preparation of CoO/Co electrolyte solution was change KF to potassium citrate tribasic monohydrate (16.21 g, 0.05 mol). The electrolyte solution of CoO-F_{0.5}/Co was prepared; CoSO₄·7H₂O (0.281 g, 1.0 mmol), 1-methylimidazole (0.478 mL, 6.0 mmol), potassium citrate tribasic monohydrate (8.105 g, 0.025 mol) and KF (2.905 g, 0.05 mol) were dissolved in 100 mL DI water. The CoO-F/Co and CoO/Co films were prepared though controlled potential electrolysis at -1.644 V vs SCE with violently stirring until the constant current (~380 mA cm⁻² for CoO-F/Co,

~340 mA cm⁻² for CoO/Co) for 12 h at 30 °C. After deposition, the films by careful rinse with water were directly used for electrochemistry tests. 40 wt.% Pt-C (20 mg) was dispersed in a 5 mL mixture solution containing 0.5 mL 5% Nafion solution and 4.5 mL methanol, followed by sonication for 30 min to obtain a homogeneous catalyst ink. The catalyst ink was loaded on the surfaces of the glassy carbon disk electrode to achieve 27.1 mg cm⁻².

Physical characterization. Powder X-ray diffraction (pXRD) data were obtained using a Bruker D8 X-ray Powder Diffractometer with a Cu K- α radiation source in the range $2\theta = 5-80^\circ$. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectra (EDX) were obtained with a JSM 7000F microscope (JEOL) equipped with an Oxford EDX system. The morphologies of samples were characterized on a transmission electron microscope (TEM, JEOL JEM-2100, Japan) by dropping sample solutions on Cu grids. X-ray photoelectron spectroscopy (XPS) spectra were collected on a ULVAC-PHI XPS spectrometer equipped with a monochromatized 1486.6 eV Al K α X-ray line source directed 45° with respect to the sample surface. The spectra were registered at a base pressure of $<5 \times 10^{-10}$ torr. Low-resolution survey scans were acquired with a 100 μ m spot size between the binding energies of 1-1100 eV. High-resolution scans with a resolution of 0.1 eV were collected between 280-292 (for C), 392-408 (for N), 525-540 (for O), 679-691 (for F) and 770-810 (for Co) eV.

X-ray Absorption Measurements. All X-ray absorption experiments were carried out at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. Co K-edge XAS was recorded at room temperature. For Co K-edge measurements, the experiments were performed in transmission mode at the BL-17C X-ray Wiggler beamline with a double crystal Si(111) monochromator. The spectra

were scanned from 7.509 to 8.305 KeV using a gas-ionization detector. A reference Co foil is always used simultaneously for the calibration of energy. The ion chambers used to measure the incident (I_0) and transmitted (I) intensities were filled with a mixture of N_2 and He gases and a mixture of N_2 and Ar gases, respectively.

Electrochemical measurements. All electrochemical experiments were performed with a CH Instrument 621b potentiostat. Fundamental electrochemical testing was carried out, consisting of samples as the working electrode, a graphite rod (L 100 mm, diam. 3 mm) auxiliary electrode and a saturated calomel electrode (SCE) reference electrode. All potentials reported in this paper were converted from vs SCE to vs reversible hydrogen electrode (RHE). $RHE = SCE + 0.244 + 0.059 \times pH$. In all experiments, the iR compensation was performed by CHI model 621b software. The linear sweep voltammetry (LSV) curves were obtained in 1.0 M $KOH_{(aq)}$ at a scan rate of 2 mV/s. Tafel slopes were calculated using the Polarization curves by plotting overpotential against $\log(\text{current density})$. Controlled potential electrolysis (CPE) experiments were conducted in 1.0 M $KOH_{(aq)}$ stirred constantly. The auxiliary electrode in CPE cell was separated from the solution of the working electrode by a medium-porosity sintered-glass frit. The electrochemically active surface area (ECSA) was evaluated in terms of double-layer capacitance. Cyclic voltammogram (CV) scans were conducted in static solution by sweeping the potential from the more positive to negative potential and back at 8 different scan rates: 2, 4, 8, 12, 16, 20, 40 and 80 $mV s^{-1}$. The capacitance was determined from the tenth cyclic voltammetry curve of each scan rate. The electrochemical double-layer capacitance, C_{DL} , as given by $i_c = \nu C_{DL}$ (i_c : current density from CV, ν : scan rate). The specific capacitance for a flat surface is generally found to be in the range of 20-60 $mF cm^{-2}$. We used a value of 40 $mF cm^{-2}$ in the following calculations of the electrochemical active surface area.

The electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 0.1 Hz to 100 kHz with an amplitude of 5 mV at an overpotential of 190 mV. The curve fitting was performed by Zview2 software.

ICP-MS experiment. ICP-MS was performed on a Agilent 7500ce. Dry sample was dissolved in concentrated HNO₃.

Determinations of Faradaic Efficiency and TOF. Quantification of the produced H₂ gas was performed by gas chromatography (Chromatec-Crystal 9000) equipped with a micropacked column (ShinCarbon ST #19808, Restek) and thermal conductivity detector (TCD). Helium was used as the carrier gas. Calibration curves were built by the injection of the known amounts of pure H₂. The amounts of H₂ dissolved in the solution were corrected by the Henry's law ($K_H = 7.8 \times 10^{-4}$ mol/atm·L for H₂).

Faradaic efficiency (%) = [Volume (H₂ gas of GC detection)/24.5]×100%/[Charge (CPE)/2/96485]

TON = [Charge (CPE)/2/96485]×[Faradaic efficiency (%)]/[number of catalyst (mol)]
The number of catalyst was determined from ICP analysis.

TOF = [TON]/[time of CPE] (s⁻¹)

Author Contributions. T.-W. C. conceived and supervised the research. T.-W. C. guided and designed the entire experiment. T.-W. C. performed most of the experiments and data analysis. W.-L. L., C.-Y. T., Z.-Q. Y. and T.-W. L. participated in various aspects of the experiments and discussion. I.-J. H. and J.-F. L. performed the XRD and XAS experiments. T.-W. C. wrote the paper. All authors discussed the results and commented on the manuscript.

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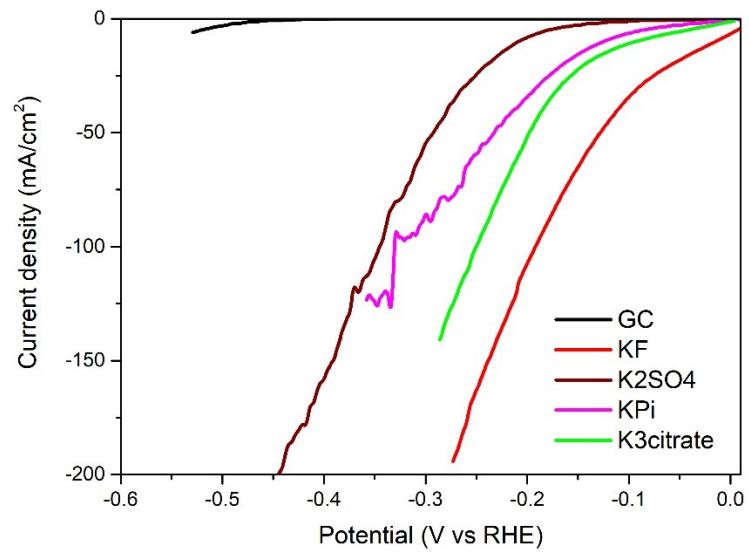


Figure S1. LSV curves of Co based catalysts depositing from various electrolytes.

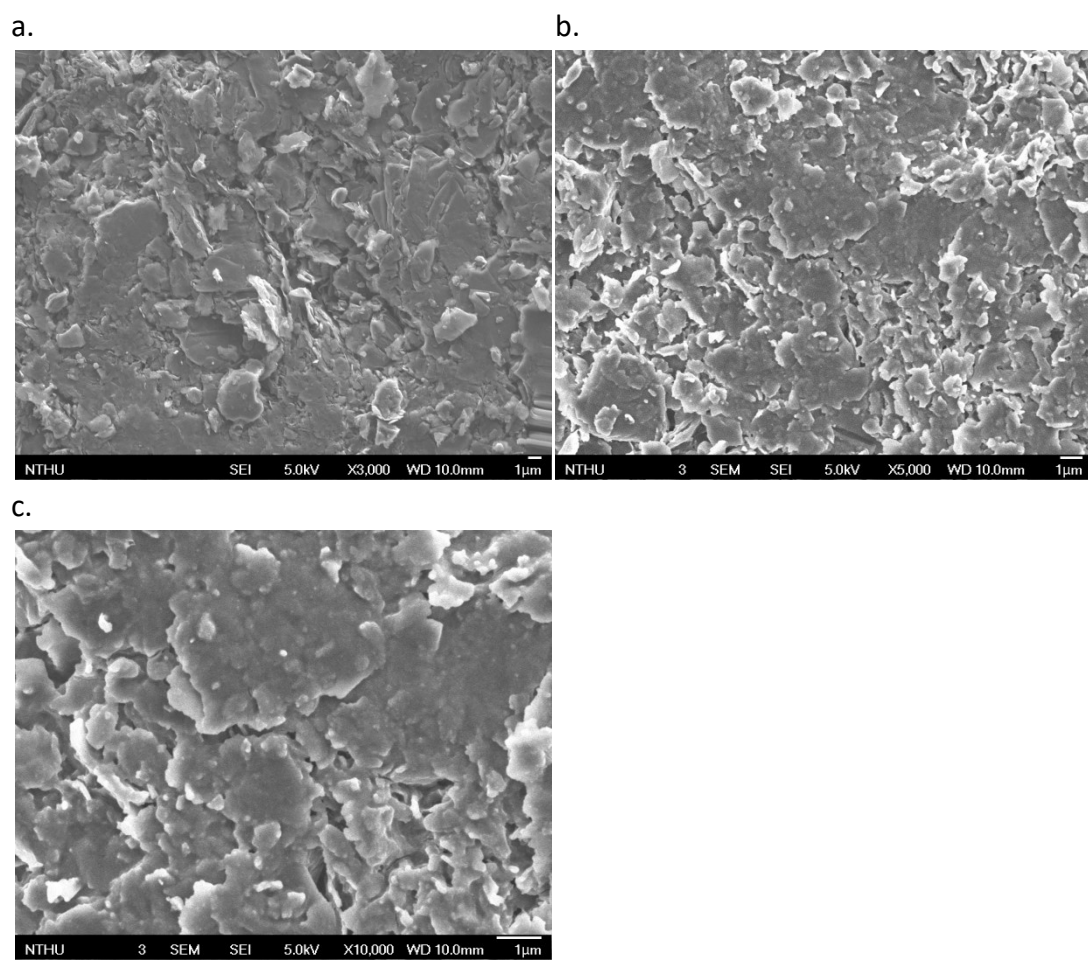


Figure S2. SEM images of (a) fresh graphite and (b, c) CoO/Co.

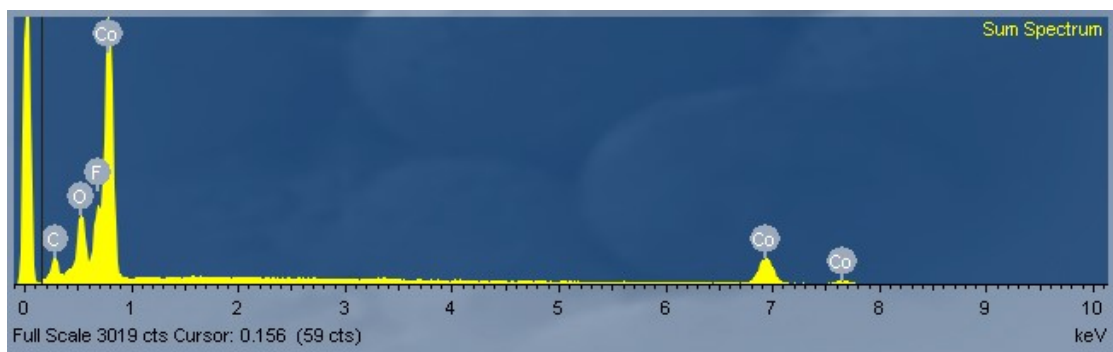


Figure S3. EDX spectrum of CoO-F/Co.

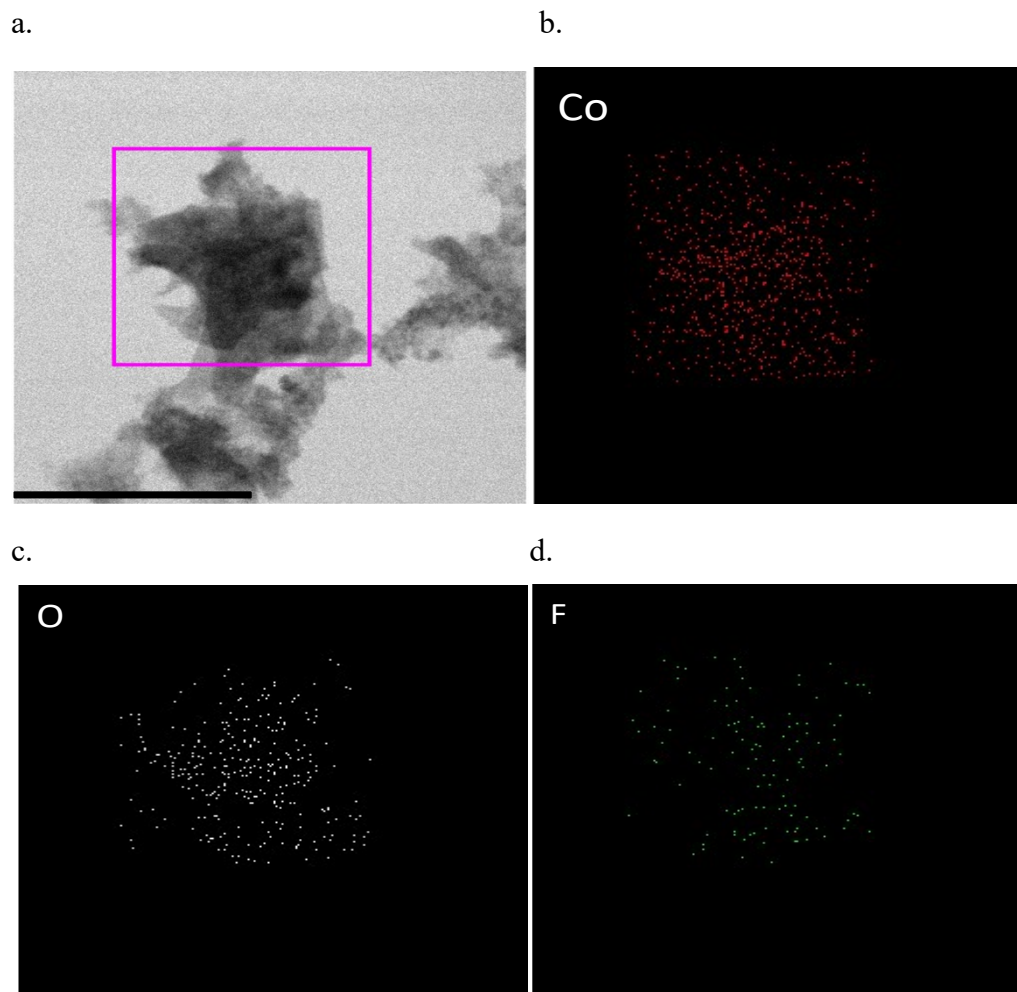


Figure S4. Elemental mapping images of CoO-F/Co (scale bar: 70 nm).

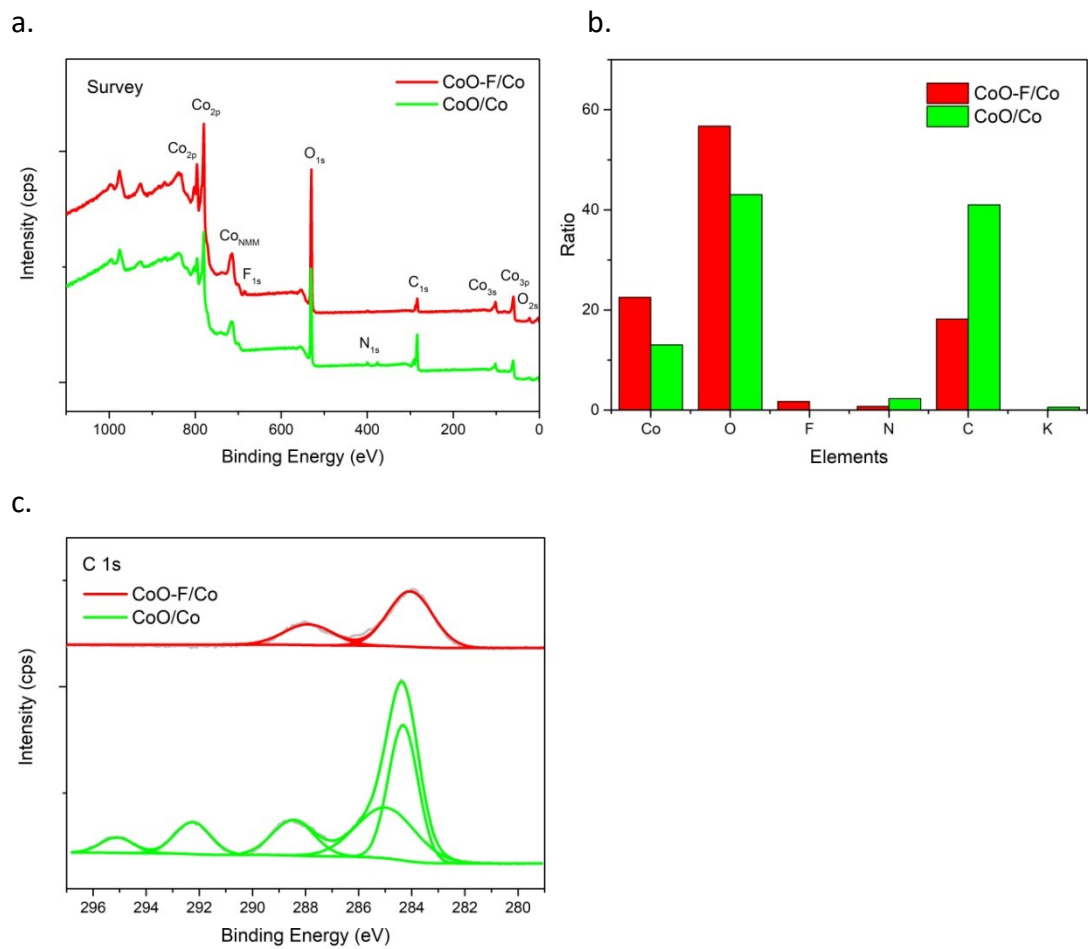


Figure S5. XPS spectra of CoO-F/Co (red) and CoO/Co (green). (a) Survey, (b) elemental compositions and (c) C 1s.

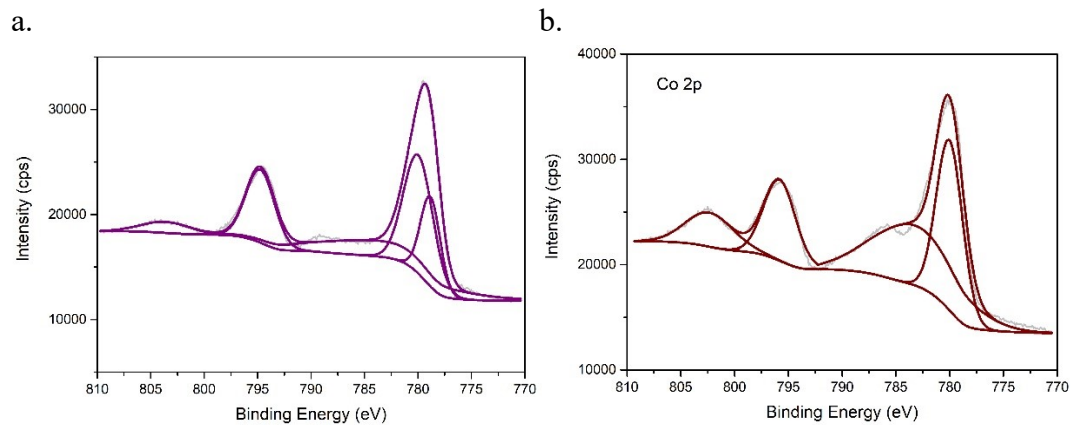


Figure S6. Co 2p XPS spectra of commercial (a) Co_3O_4 (purple) and (b) CoO (brown).

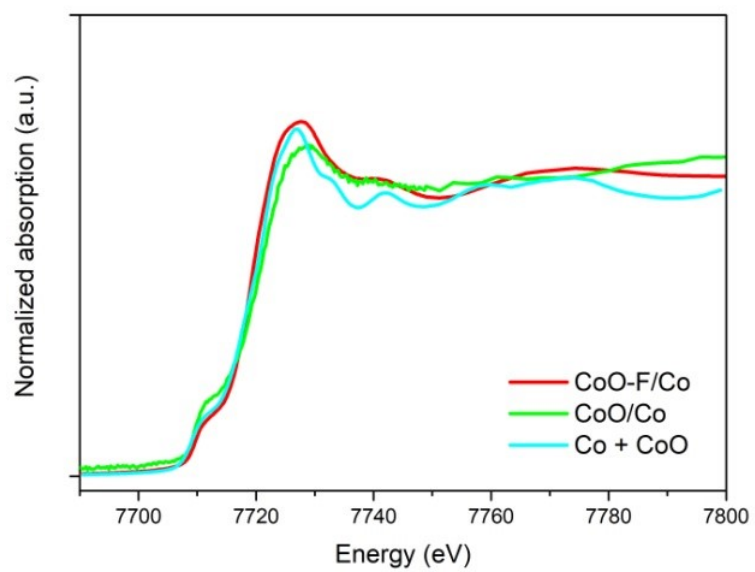


Figure S7. Co K-edge XANES spectra of CoO-F/Co, CoO/Co and the mixture of Co foil and CoO.

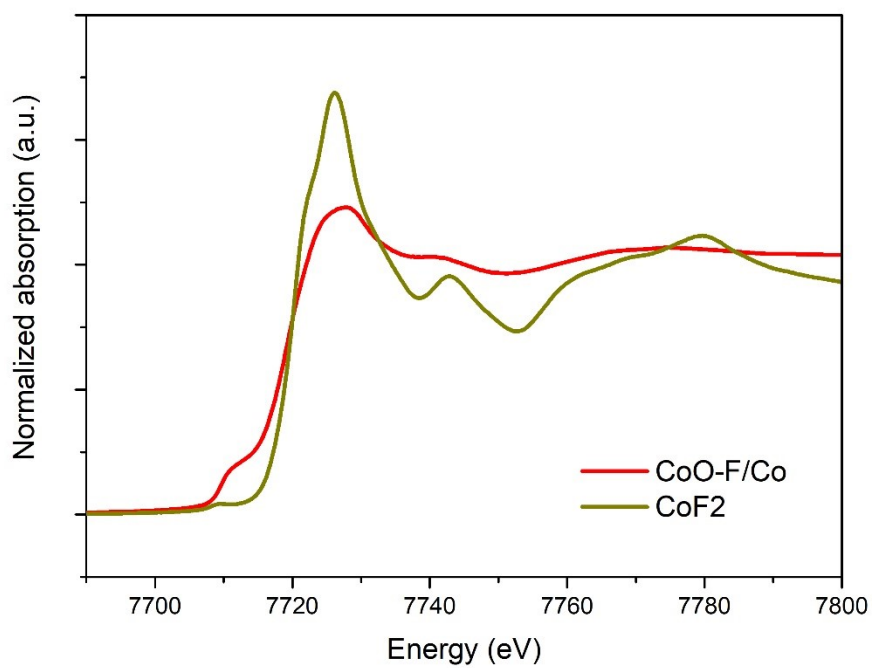


Figure S8. Co K-edge XANES spectra of CoO-F/Co and CoF₂.

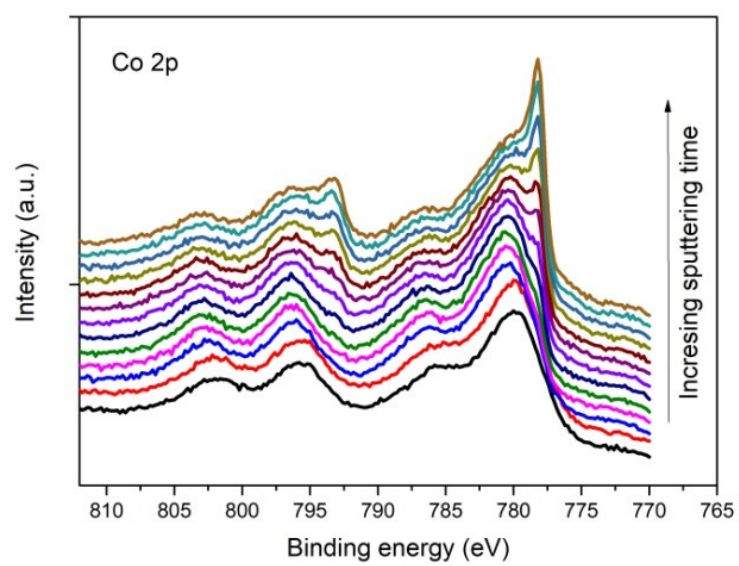


Figure S9. XPS depth profile of CoO-F/Co. Subsequent scans were taken after additional 30s Ar sputters.

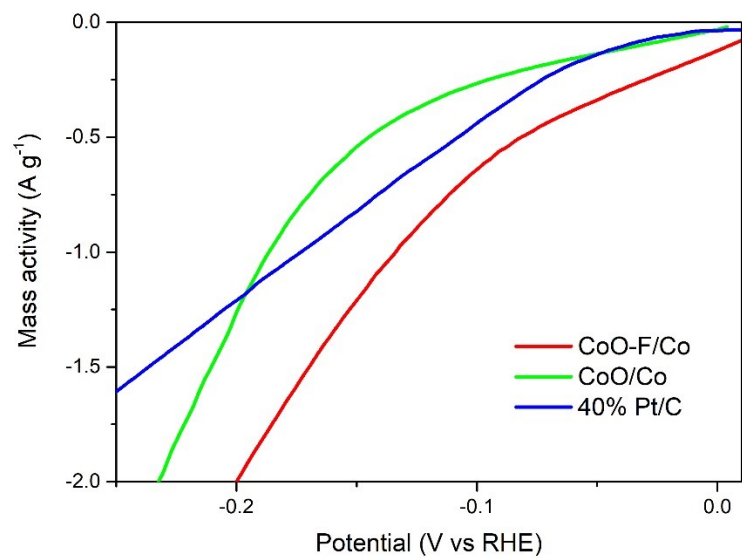
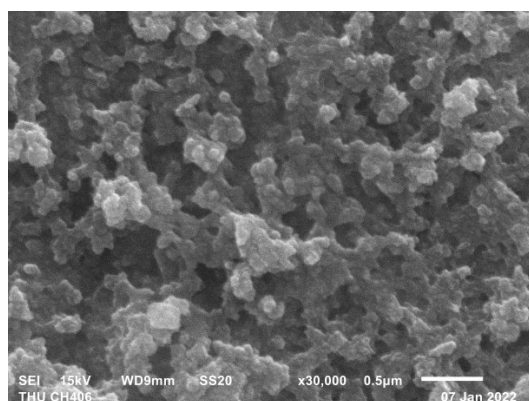


Figure S10. Mass activity of CoO-F/Co, CoO/Co and 40% Pt/C.

(a)



(b)

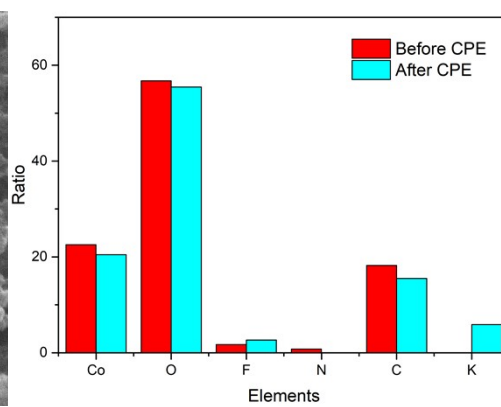


Figure S11. (a) SEM image and (b) elemental compositions of XPS spectra after CPE.

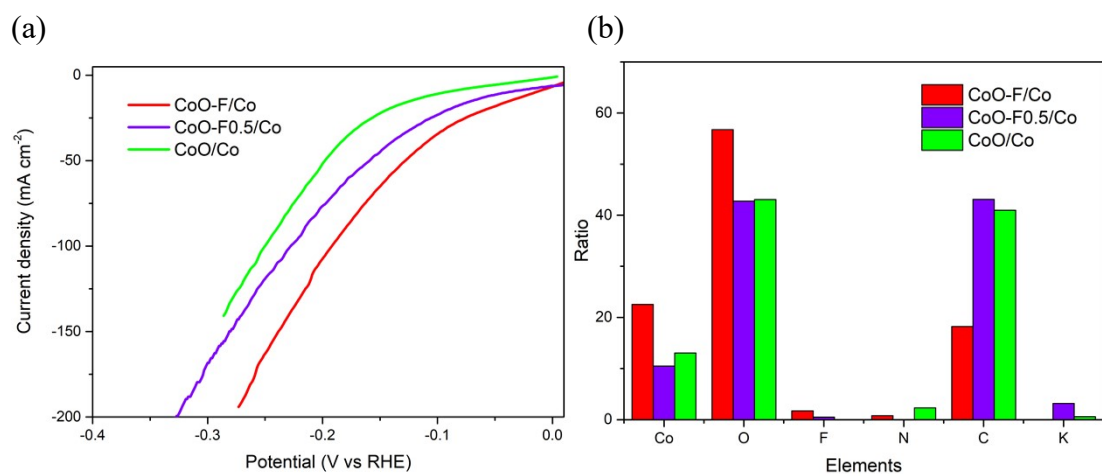


Figure S12. (a) LSV curves and (b) elemental compositions of XPS spectra of CoO-F/Co, CoO-F_{0.5}/Co and CoO/Co in 1.0 M KOH(aq).

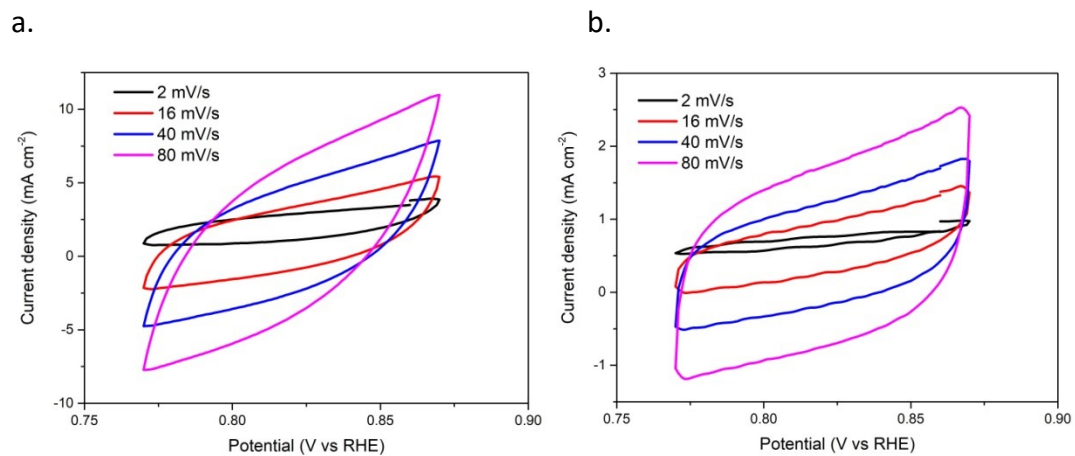


Figure S13. CV curves of (a) CoO-F/Co and (b) CoO/Co in 1.0 M KOH(aq) at different scan rates of 2, 16, 40 and 80 mV s⁻¹.

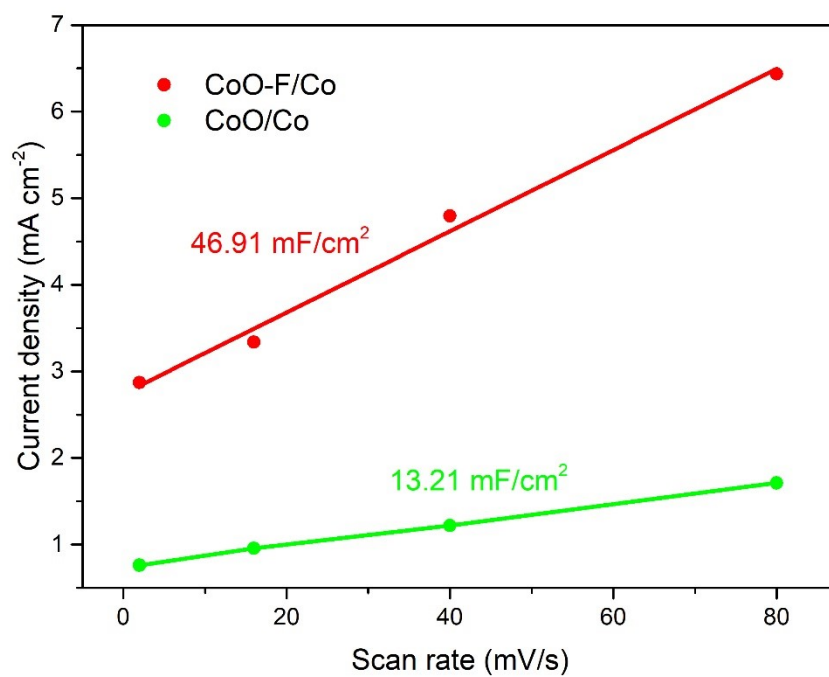


Figure S14. Linear fitting of the capacitive currents versus CV scan rates for CoO-F/Co and CoO/Co.

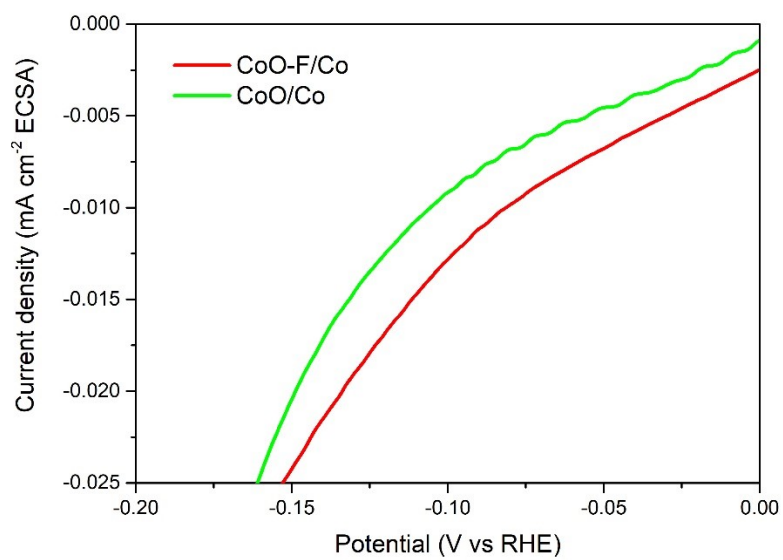


Figure S15. LSV curves from Fig. 3a normalized to the electrochemical active surface area (ECSA).

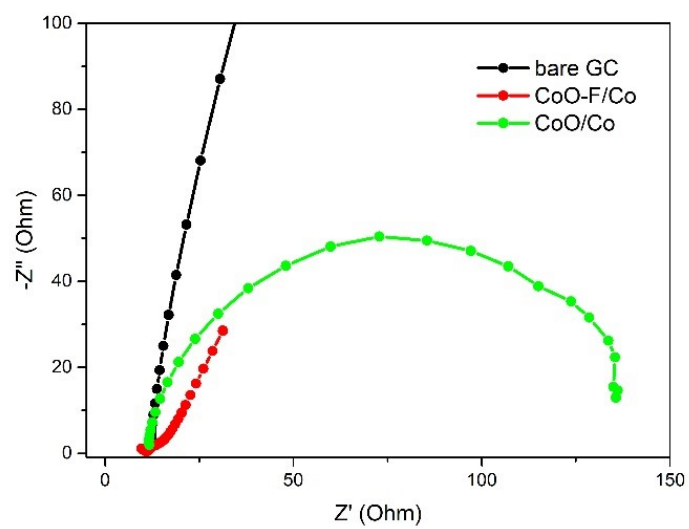


Figure S16. Nyquist plots of electrochemical impedance spectra of CoO-F/Co, CoO/Co and bare GC at $\eta = 190$ mV.

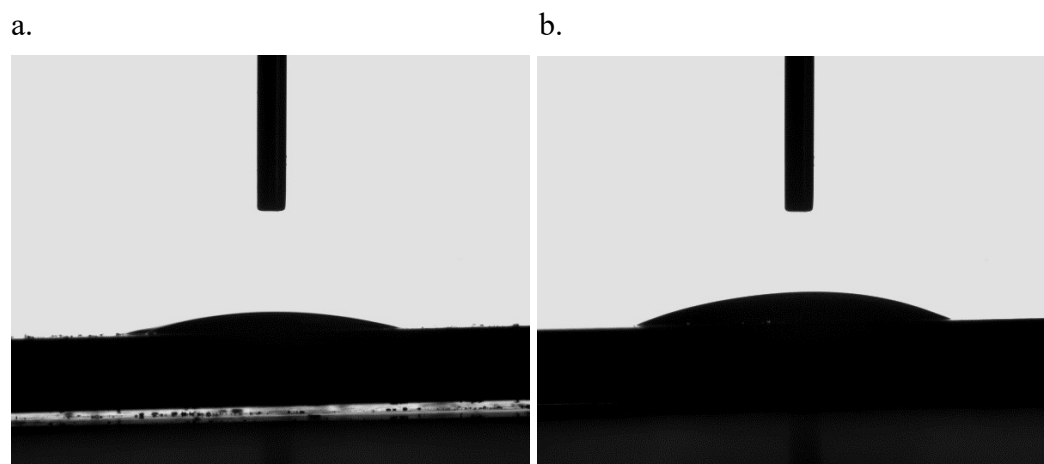


Figure S17. Static water contact-angle measurements of (a) CoO-F/Co and (b) CoO/Co.

Table S1. Compared the reported noble-metal HER catalysts.

	η_{10} (mV)	Tafel slope (mV/dec)	Ref.
CoO-F/Co	15	50.9	This work
Rh NP/C	7	19	33
RhCu NTs	8	33	34
Ru@CQDs	10	47	35
Ru-NC-700	12	14	36
RuCo ₂	13	29	37
Ir@CON	13.5	44	38
Ru/C-300	14	32.5	39
Ru@C ₂ N	17	38	40
Au-Rh	22	47	41
RuCo@NC	28	31	42
IrP ₂ @NC	28	50	43