

Supporting Information

Acid-etched Layered Double Hydroxides with Rich Defects for Enhancing the Oxygen Evolution Reaction

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Experimental Section.

Synthesis of the CoFe LDHs. The CoFe LDHs were synthesized by a hydrothermal method.¹ 9.3 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 6.5 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 40 mL of distilled water. 3.1 g of NaOH and 3.4 g of Na_2CO_3 were dissolved in another 40 mL of distilled water. The salt and basic solutions were simultaneously mixed and added into a 250 mL beaker under vigorous stirring. The resulting slurry was then transferred into a teflon-lined stainless steel autoclave and heated at 80 °C for 48 h. After cooling down to room temperature, the CoFe LDHs were collected by centrifugation, washed thoroughly with DI water and ethanol, and then dried at 60 °C under vacuum oven.

Synthesis of the E-CoFe LDHs: the HNO_3 etching of the CoFe LDHs. An aqueous solution containing 200 mg CoFe LDHs was stirred thoroughly, and then 1.0 mL, 2.0 mL and 2.0 mL 1 M HNO_3 was added to the CoFe LDHs suspension, respectively. Then the mixture was stirred at room temperature for 30 min. The resulting products were filtered and washed with DI water and ethanol and dried under a vacuum at 60 °C for 24 h.

Electrode Preparation. Four milligram of catalyst powder was dispersed in 500 μL of ethanol, 450 μL of water, and 50 μL of 5 wt% Nafion solution by sonication for at least 30 min to form a homogeneous ink. Then, 10 μL of the catalyst ink (containing 0.04 mg of catalyst) was loaded onto a glassy carbon, thus with a constant catalyst areal loading amount of 0.204 mg cm^{-2} . The glassy carbon electrode was polished to a mirror finish and thoroughly cleaned before use. Finally, the as-prepared catalyst film was dried at room temperature.

Electrochemical Characterization. All of the electrochemical measurements were performed with a CHI 760D electrochemical workstation. OER was performed in a three-electrode configuration. For electrochemical measures of OER, the catalyst dropped on a glassy carbon electrode was used as the working electrode, saturate calomel electrode (SCE) was used as the reference electrode in 1 M KOH electrolyte, and platinum gauze was used as the counter electrode. The scan rate for linear sweep voltammetry (LSV) was kept at 5 mV/s to minimize the capacitive current. In addition, the LSV polarization curves for OER was measured in saturating the solution with O_2 . The scan rate for linear sweep voltammetry (LSV) was kept at 5 mV/s respectively. Before recording the catalytic activity, catalysts were activated by a chronopotentiometry scan with constant current density until reaching a stable state (see nature communications, 2016, 7. doi:10.1038/ncomms12324). All the polarization curves in this work were corrected by eliminating iR drop with respect to the ohmic resistance of the solution. Calibration of SCE reference electrodes was done by measuring the reversible hydrogen electrode (RHE) potential using a Pt electrode under a H_2 atmosphere. Span life measurements were performed to evaluate the long-term stability. The impedance spectra of OER was measured in the three-electrode system under 1.50 V versus RHE over the frequency range from 1 MHz to 0.1 Hz in 1 M KOH.

Characterization. The morphology of all electrocatalysts was investigated by scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, FEI Tecnai G20). The crystal structures of the samples were characterized using powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer, $\text{Cu K}\alpha 1$). The synchrotron EXAFS and XANES of Co and Fe K-edge were carried out at BL17C at National Synchrotron Radiation Research Center, Taiwan. The Infrared spectrum tests were performed at the Fourier transformation infrared spectrometer (FT-IR, Bruker TENSOR II).

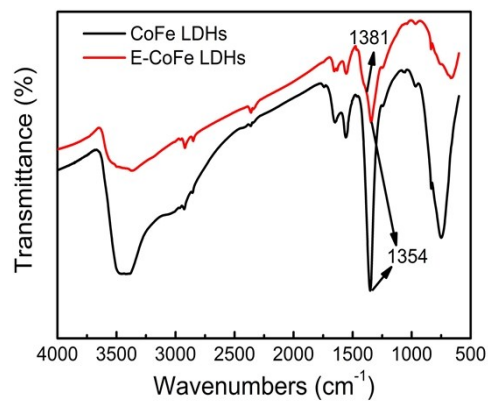


Figure S1. Fourier transformation infrared spectra of the CoFe LDHs and E-CoFe LDHs

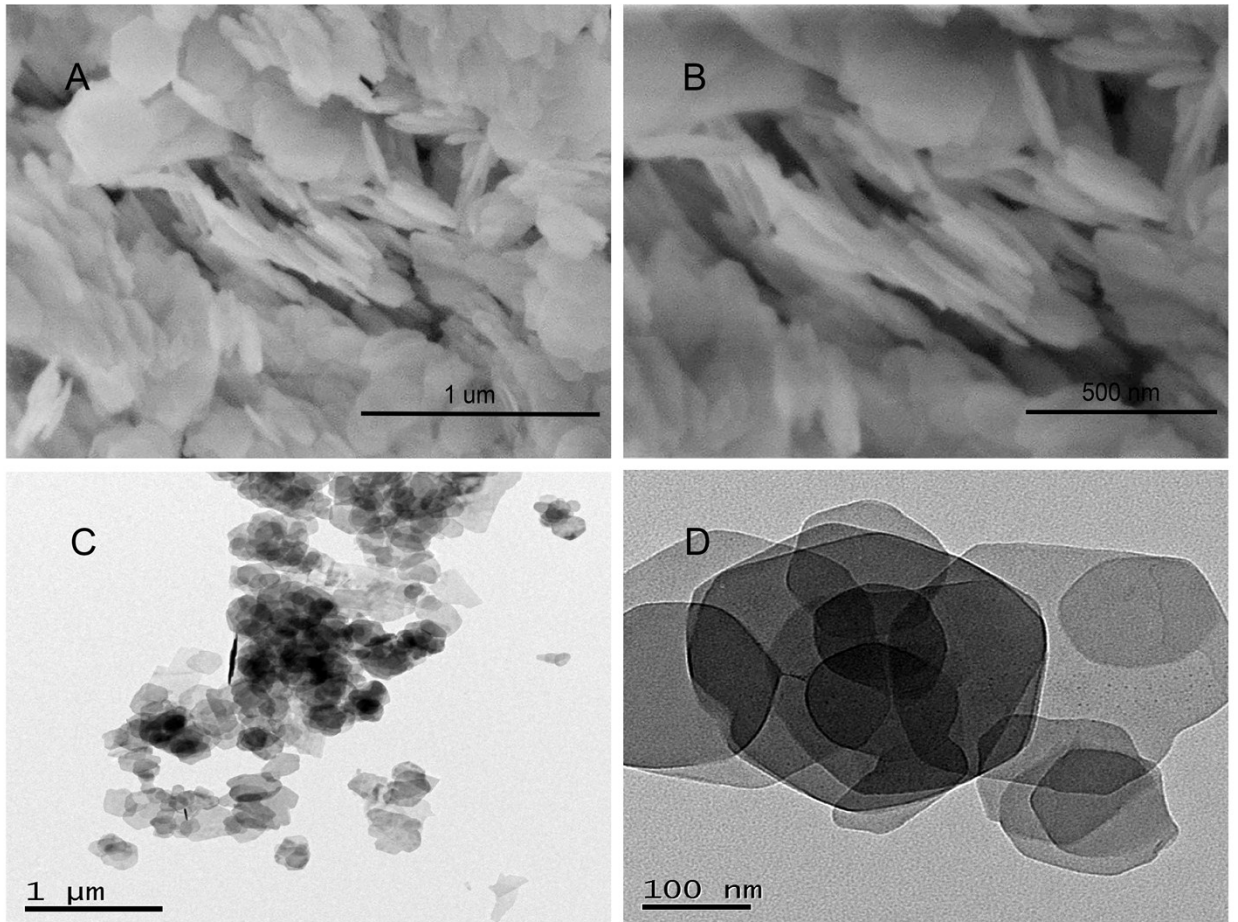


Figure S2. The SEM (A and B) and TEM (C and D) images of the CoFe LDHs.

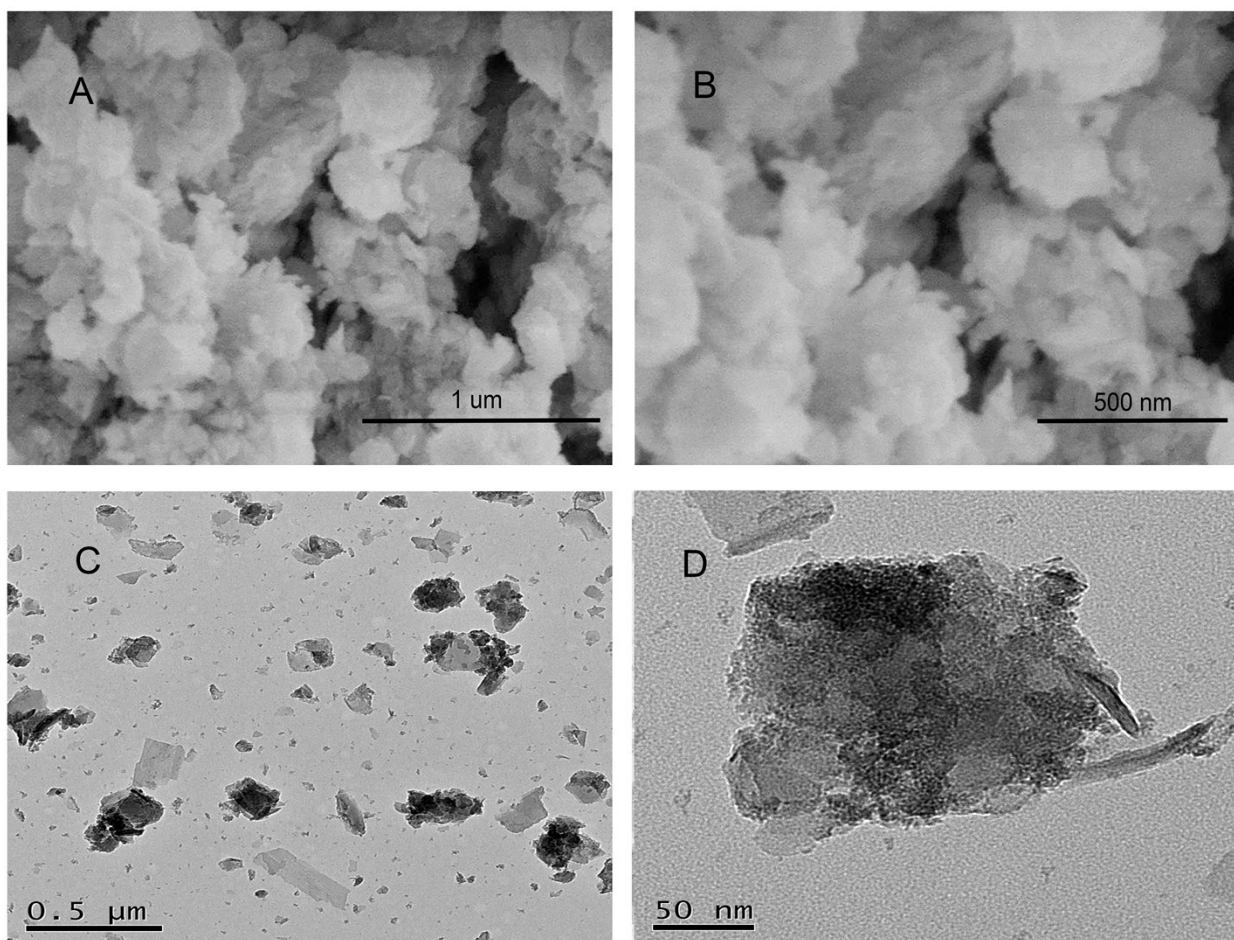


Figure S3. The SEM (A and B) and TEM (C and D) images of the E-CoFe LDHs.

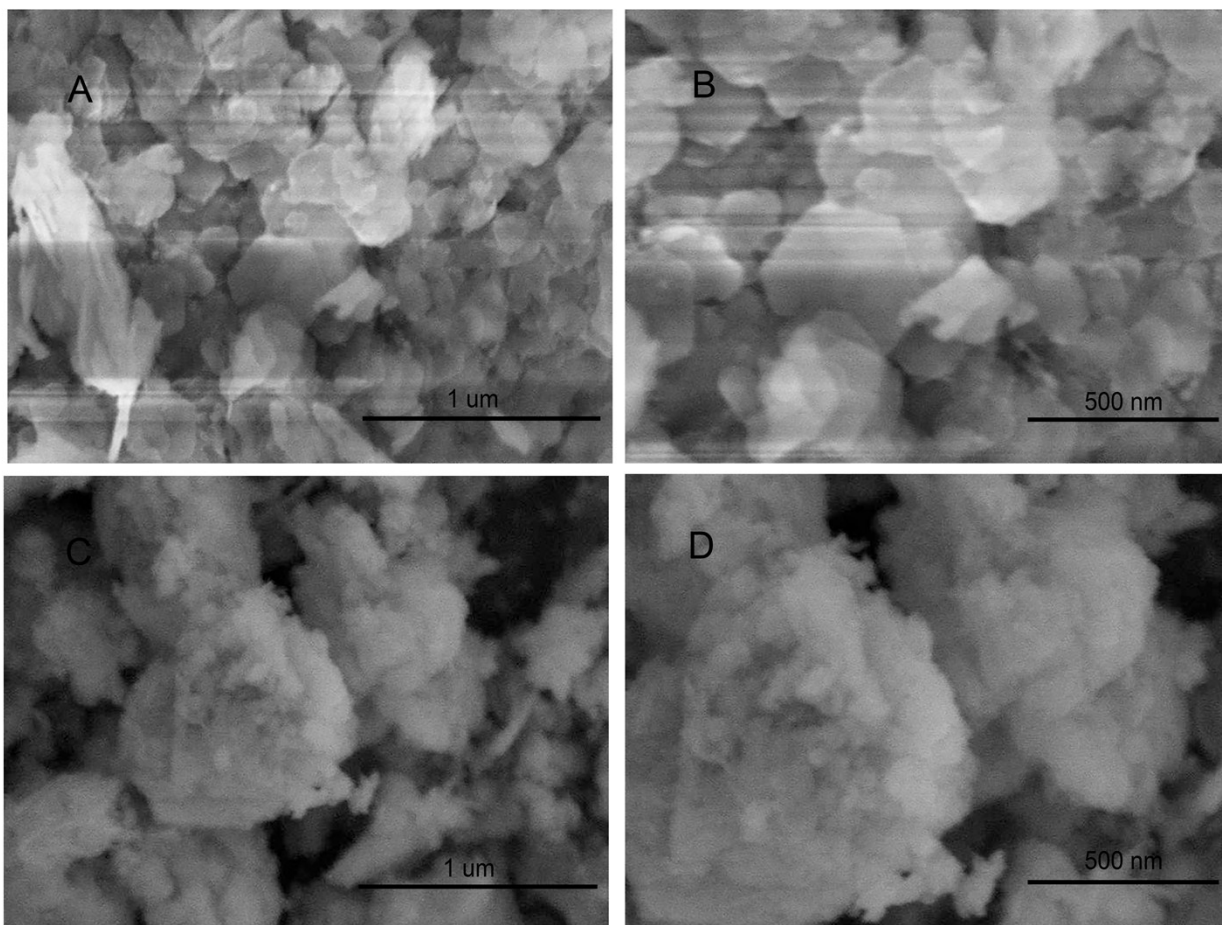


Figure S4. A) and B) the SEM images of the CoFe LDHs after acid treatment (1.0 mL). C) and D) the SEM images of the CoFe LDHs after acid treatment (3.0 mL).

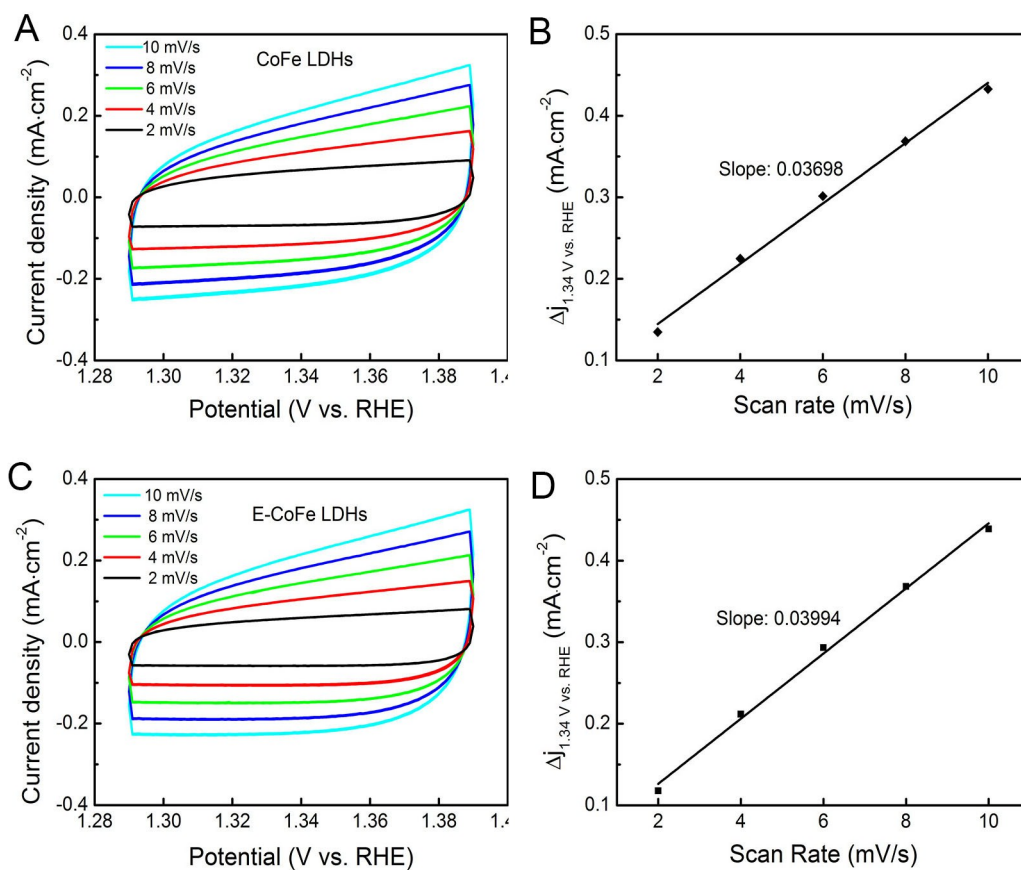


Figure S5. Cyclic voltammetry curves of A) CoFe LDHs and C) E-CoFe LDHs. The capacitive current measured at 1.34 V vs RHE was plotted as a function of scan rate B) CoFe LDHs and d) E-CoFe LDHs.

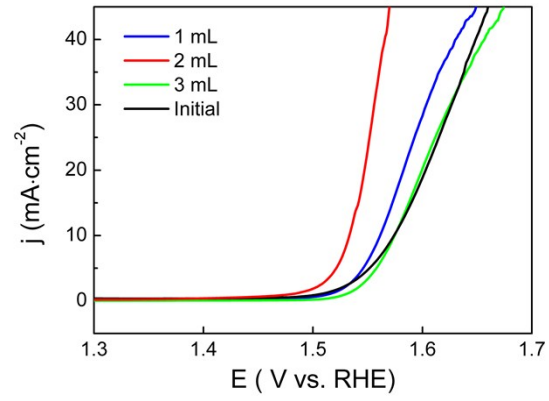


Figure S6 The polarization curves of acid etching CoFe LDHs for 0 mL, 1 mL, 2 mL and 3 mL.

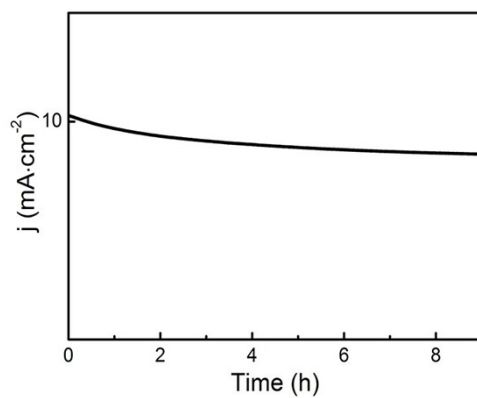


Figure S7. Time dependence of the current density under a constant overpotential of pristine CoFe LDHs.

Table S1. The Element quantification for E-CoFe LDHs by ICP

element	percentage (%)
Co	31.5
Fe	21.3

Table S2. Comparison of OER performance of the E-CoFe LDHs with recently reported catalyst

Electrocatalyst	Electrolyte solution	Current density (mA/cm ²)	Overpotential at the corresponding Current density (mV)	Tafel slope (mV/dec)	Reference
E-CoFe LDHs	1.0 M KOH	10	300	41	This work
Exfoliated CoNi LDHs/CP	1.0 M KOH	10	367	40	Ref. S2
Exfoliated NiCo LDHs	1.0 M KOH	10	330	41	Ref. S3
Exfoliated CoCo LDHs	1.0 M KOH	10	350	45	
Exfoliated NiFe LDHs	1.0 M KOH	10	300	40	
CoMnP	1.0 M KOH	10	330	61	Ref. S4
Amorphous NiCoO _x	1.0 M KOH	10	325	39	Ref. S5
CoN/NF	1.0 M KOH	10	290	70	Ref. S6
Ni-P	1.0 M KOH	10	300	64	Ref. S7
Co ₃ O ₄ /N-doped graphene	1.0 M KOH	10	310	67	Ref. S8
Co-B _i NS/graphene	1.0 M KOH	10	290	53	Ref. S9
Co-P/NC	1.0 M KOH	10	354	52	Ref. S10

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