Electronic Supplementary Information

Anion-dependent topochemical conversion of CoAl-LDH microplates to hierarchical superstructures of CoOOH nanoplates with controllable orientation

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1. Experimental Section

1.1 Chemicals and materials

Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99.8%) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Urea ($CO(NH_2)_2$, 98%) and NaOH (NaOH, 98%) were purchased from Aladdin (Shanghai, China). Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, ≥98%), thioacetamide (CH_3CSNH_2, ≥99%), and Nafion perfluorinated resin solution were purchased from Sigma-Aldrich (Beijing, China). Ethanol (C_2H_5OH, 99.7%) was purchased from J&K Chemical (Shanghai, China). All chemicals and materials were used without further purification. The deionized (DI) water was purified using a Milli-Q3 system (Millipore, France).

1.2 Synthesis of CoAl-LDH microplates and related composite

According to a previous procedure,[1, 2] pristine CoAl-CO_3^{2-}-LDH microplates were prepared by the coprecipitation method. In a typical experiment, 0.26 g of

$Co(NO_3)_2·6H_2O$, 0.034 g of $Al(NO_3)_3·9H_2O$ (Co:Al = 10:1) and 0.27 g of urea powder were mixed with 100 mL DI water in a beaker and ultrasonicated for 5 min to obtain a homogeneous solution. 30 mL of the above solution was transferred to a 40 mL glass bottle, heated to 97 °C, and maintained at this temperature for 3 h before being naturally cooled to room temperature. The pink precipitate, i.e. CoAl-CO_3^{2-}-LDH, was collected and washed three times with ethanol.

15 mL ethanol solution containing 10 mg of the abovementioned pink product and 20 mg of as-purchased thioacetamide powder were mixed in a 20 mL Teflon-lined stainless steel autoclave. The autoclave was placed in a preheated oven at 120 °C and heated for 6.5 h. After that, it was cooled to room temperature, and the dark solution was centrifugated and washed with DI water for several times to obtain CoAl-SO_4^{2-}-LDH microplates.

1.3 Preparation of CoOOH hierarchical superstructures

5 mg of as-prepared CoAl-CO_3^{2-}-LDH powder was mixed with 15 mL of NaOH aqueous solution (1 M) in a 20 mL glass bottle. The bottle was then placed in a preheated water bath at 30 °C and the solution was stirred for 12 h. Finally, the black powder was immediately centrifugated and washed with DI water for several times to obtain CoOOH-lateral hierarchical superstructures. The preparation method for CoOOH-vertical hierarchical superstructures is similar to that for CoOOH-lateral hierarchical superstructure, except that the concentration of NaOH aqueous solution was 0.75 M and the stirring time was 8 h.

1.4 Characterizations

X-ray diffraction (XRD, SmartLab Rigaku) was performed with Cu Kα radiation (λ = 1.54 Å) as the X-ray source. Fourier transform infra-red (FTIR, Thermo IS5) measurements were performed to analyze the interlayer anions. Scanning electron microscopy (SEM, JSM-7800F) was used for the morphology analysis. To gain the crystal structure information, transmission electron microscopy (TEM, JEM 2100Plus, Japan), high-resolution transmission electron microscopy (HRTEM, JEM 2100F, Japan), and energy-dispersive X-ray (EDX) spectroscopy analysis were performed.

1.5 Electrochemical measurements

A catalyst dispersion was prepared by mixing 2.5 mg of the active material, namely CoOOH-lateral or CoOOH-vertical in a solution containing 10 μL of Nafion (5 wt %) aqueous solution, 400 μL DI water and 100 μL absolute ethanol, followed by ultrasonication for 30 min. 10 or 3 μL of the catalyst dispersion was drop-deposited on the surface of a carbon working electrode (with a diameter of 5 mm) of a screen-printed electrode (SPE) (Neopro, Shandong, China), or a glassy carbon (GC) electrode (with a diameter of 3 mm), respectively, and then dried naturally at room temperature.

Linear sweep voltammetry measurements were conducted on an electrochemical station (Autolab 302N) coupled with a SPE (including a carbon working electrode and a carbon counter electrode) and a 3 M Ag/AgCl reference electrode. The measurements were conducted in 0.1 M KOH at a scan rate of 20 mV s^{-1} in a saturated N_2 environment. All measurements were referenced to a reversible hydrogen electrode (RHE) scale based on the Nernst equation below.[3, 4]

$$V_{\mathrm{RHE}}\ (\mathrm{V}) = V_{\mathrm{Ag/AgCl}}\ (\mathrm{V}) + 0.0591 \times \mathrm{pH} + V^{\theta}_{\mathrm{Ag/AgCl}}$$

where V_{RHE} is the applied potential *vs.* RHE; $V_{\mathrm{Ag/AgCl}}$ is the applied potential *vs.* Ag/AgCl reference electrode, pH is the pH of the electrolyte, and $V^{\theta}_{\mathrm{Ag/AgCl}}$ is the standard potential of the Ag/AgCl reference electrode.

Electrochemical impedance spectroscopy (EIS) measurements were conducted on the SPE as well in 0.1 M KOH at a potential of 0.35 V by applying an AC voltage with an amplitude of 10 mV over a frequency range of 10 to 100 kHz.

The electrical double-layer capacitance (C_{dl}) of the catalyst deposited on a rotating GC electrode was measured from the double-layer charging curves using cyclic voltammetry (CV) in a small potential range of 1.45-1.49 V (*vs*. RHE) without apparent faradaic processes occurring. The rotating speed was set at 1000 rpm. The plot of the different current density at 1.47 V against the scan rate (20-100 mV s^{-1}) was linearly fitted, and its slope is the C_{dl} of the tested catalyst.

2. Supplementary Figures

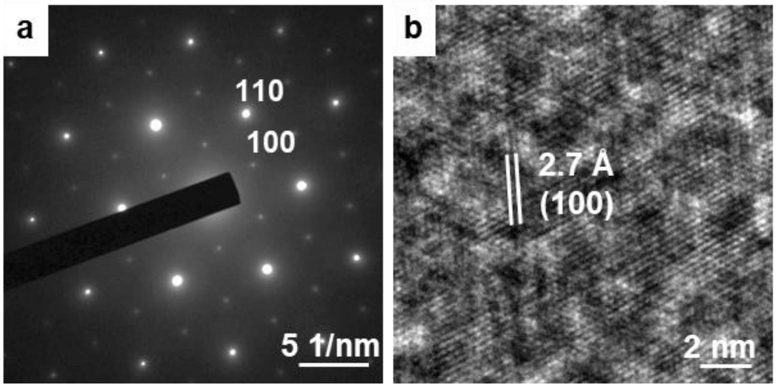

Fig. S1 (a) SAED pattern and (b) HRTEM image of a typical CoAl-CO_3^{2-}-LDH microplate, revealing lattice spacing of ~0.27 nm, assignable to the (100) planes of $Co_6Al_2(OH)_{16}CO_3$ (JCPDS 00-051-0054, space group *R-3m*).

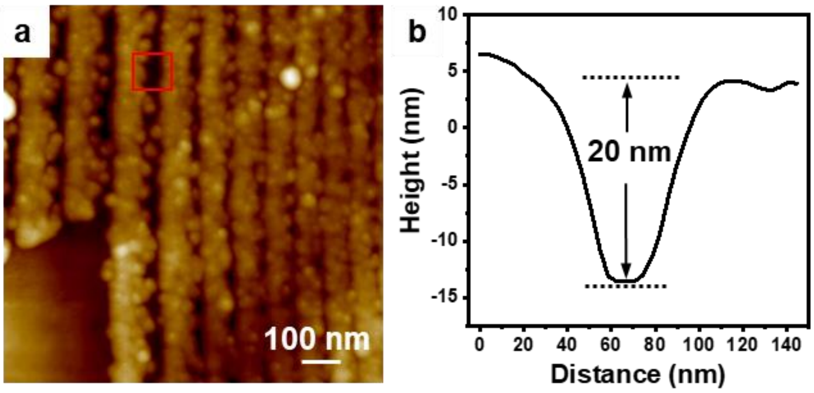

Fig. S2 (a) AFM image revealing the surface strips of a CoAl-SO_4^{2-}-LDH microplate, and (b) the height analysis of the area highlighted in the red rectangle in (a).

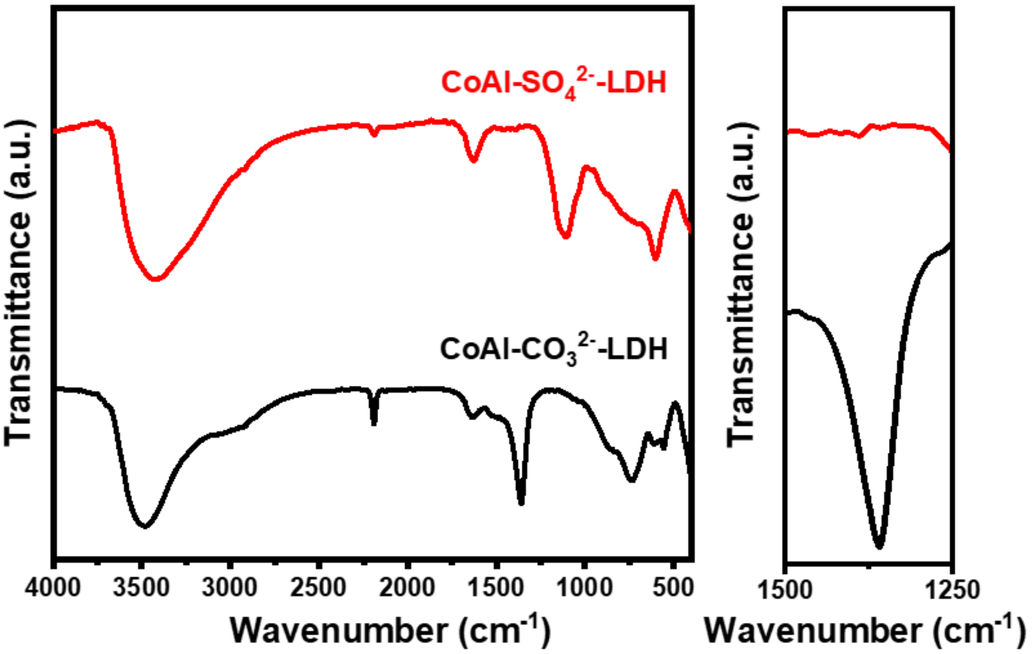

Fig. S3 FTIR spectra with magnified region between 1500 and 1250 cm^{-1} of CoAl-CO$_3^{2-}$-LDH and CoAl-SO$_4^{2-}$-LDH microplates.

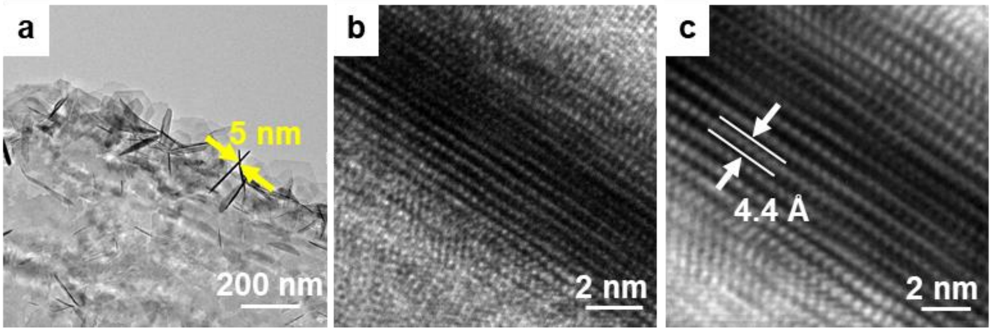

Fig. S4 (a) Zoom-in TEM image, (b) HRTEM image and (c) the corresponding inverse-FFT HRTEM of a vertically oriented CoOOH nanoplate located at the edge area of a typical CoOOH-lateral hierarchical superstructure.

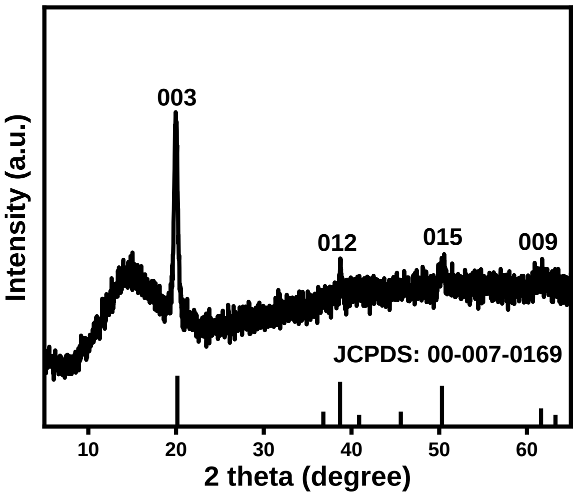

Fig. S5 XRD pattern of CoOOH-vertical hierarchical superstructure.

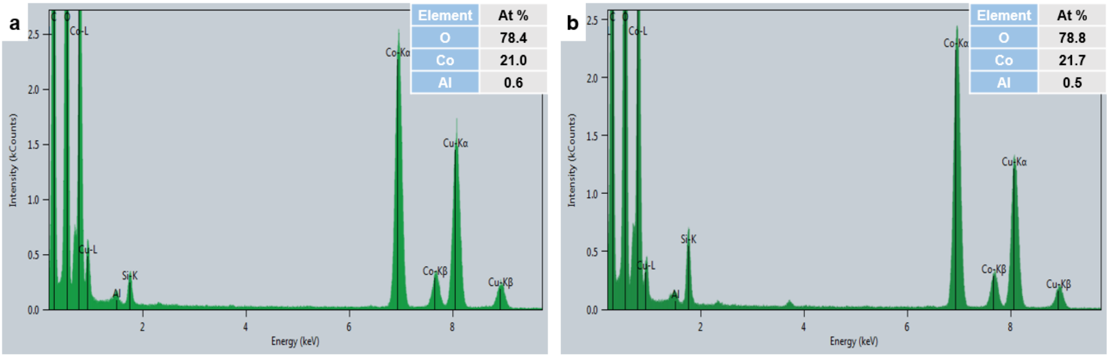

Fig. S6 EDX spectra of (a) CoOOH-lateral and (b) CoOOH-vertical hierarchical superstructures.

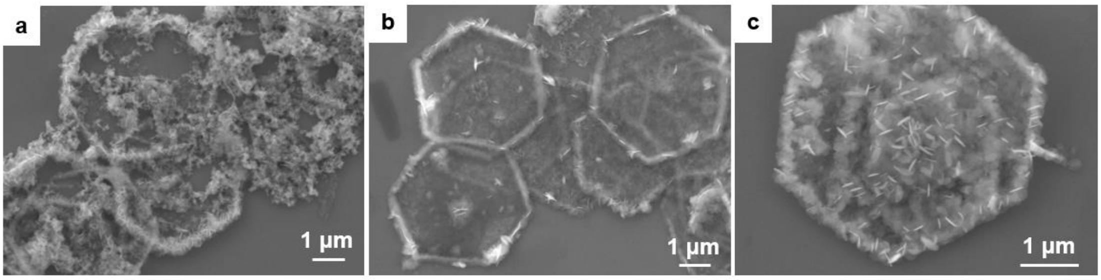

Fig. S7 SEM images of products obtained after etching (a) CoAl-SO_4^{2-}-LDH and (b) CoAl-CO_3^{2-}-LDH microplates in 1 M NaOH solution at 30 °C for 12 h.

(c) The product of etching CoAl-CO_3^{2-}-LDH microplates in 2.5 M NaOH solution at 30 °C for 12 h.

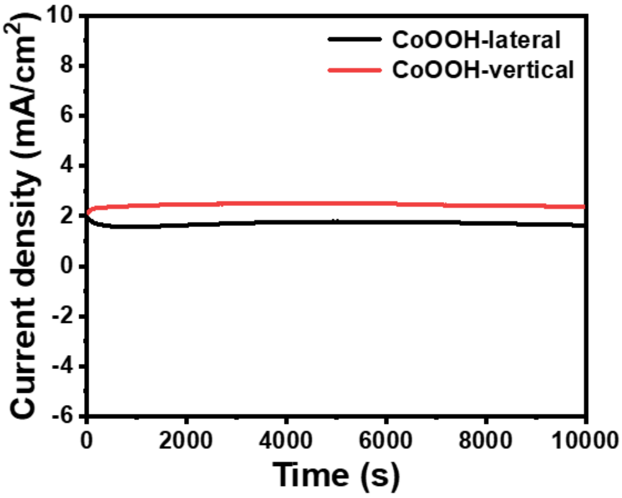

Fig. S8 Chronoamperometric test results of CoOOH-lateral and CoOOH-vertical hierarchical superstructures in 0.1 M KOH at 1.67 V *vs*. RHE.

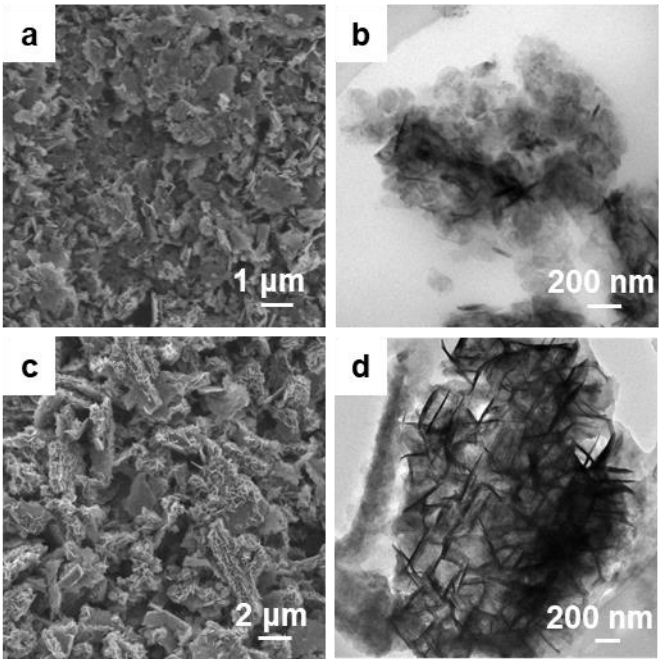

Fig. S9 (a) SEM image and (b) TEM image of CoOOH-lateral hierarchical superstructures after OER test. (c) SEM image and (d) TEM image of CoOOH-vertical hierarchical superstructures after OER test.

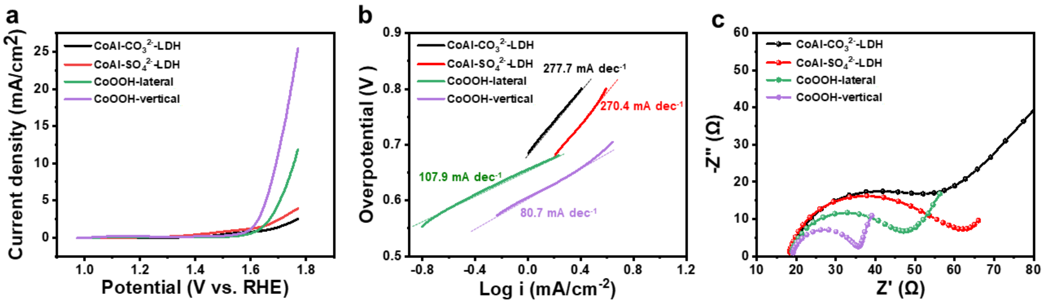

Fig. S10 (a) OER polarization curves and (b) the corresponding Tafel plots of various electrodes modified by CoAl-CO_3^{2-}-LDH, CoAl-SO_4^{2-}-LDH, CoOOH-lateral and CoOOH-vertical catalysts in 0.1 M KOH with a scan rate of 20 mV s^{-1}. (c) Nyquist plots of the various electrodes modified by CoAl-CO_3^{2-}-LDH, CoAl-SO_4^{2-}-LDH, CoOOH-lateral and CoOOH-vertical catalysts.

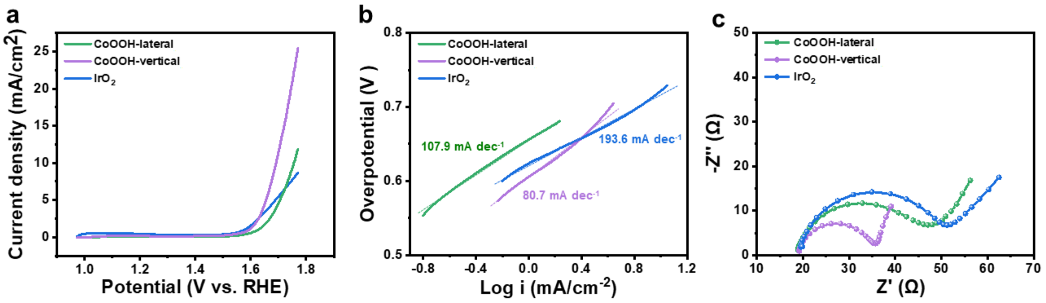

Fig. S11 (a) OER polarization curves and (b) the corresponding Tafel plots of various electrodes modified by CoOOH-lateral, CoOOH-vertical and IrO_2 catalysts in 0.1 M KOH with a scan rate of 20 mV s^{-1}. (c) Nyquist plots of the various electrodes modified by CoOOH-lateral, CoOOH-vertical and IrO_2 catalysts.

REFERENCES

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