## Supporting information

### **Double Built-in Electric Fields and Surface Reconstruction**

## Endow Ag/CoNiV-LDH/CoO with Superior Water Splitting Activity

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#### **1.** Electrode preparation and electrochemical measurement

All the electrochemical measurements were conducted on a CHI 660E electrochemical analyzer (Chenhua, Shanghai) in 1 mol/L KOH electrolyte. To obtain the working electrode, 5 mg of the catalyst and 20  $\mu$ L of Nafion was dispersed in 1 mL of water/ethanol (V/V = 1:1) to form the slurry. The slurry was pasted onto a piece of clean nickel foam (NF)  $(1 \times 1 \text{ cm}^2)$  and dried in a vacuum oven. For comparison, 20% Pt/C and RuO<sub>2</sub> were loaded on NF by drop casting. A graphite rod was performed as the counter electrode, and a Hg/HgO electrode was used as the reference electrode. All potentials reported in this study were calibrated to reversible hydrogen electrode (RHE) by the following equation:  $E_{RHE} = E_{Hg/HgO} + 0.05914 \times pH + 0.098$  V. The overpotential ( $\eta$ ) was calculated by  $\eta = E_{RHE} - 1.23$  V. The polarization curves were measured by linear sweep voltammetry (LSV) at a rate of 5 mV s<sup>-1</sup> with potential range from  $1.0 \text{ V} \sim 2.0 \text{ V}$ (vs. RHE). The Tafel plots were figured out by the Tafel equation:  $\eta$  $= a + b \lg j$ , where  $\eta$  is overpotential, j is the current density, and b is the Tafel slope. Cyclic voltammetry (CV) curves were collected in non-faradaic region (-0.3  $\sim$  -0.2 V and 1.06  $\sim$  1.166 V vs. RHE) with scan rates (v) of 20 mV s<sup>-1</sup> ~ 100 mV s<sup>-1</sup> in 1.0 mol/L KOH. The double-layer capacitance (C<sub>dl</sub>) values were figured out by the

equation:  $i_c = C_{dl} \times v$ , where  $i_c$  is the charging current obtained by measuring the CV curves at different sweep speeds (v) in the nonfaradaic region.  $C_{dl}$  was calculated by linear fitting of  $i_c$  according to:  $C_{dl} = d (\Delta j_{(0 \ V \ vs. \ RHE)}) / 2dv$ . The electrochemical impedance spectroscopy (EIS) tests were carried out with the frequency ranging from 0.01 to 100 kHz under open circuit potential (OCP) conditions. All the electrochemical tests were conducted with 95% iR compensation.

## 2. Computational details

### 2.1 Calculation method of ECSA:

A potential range where no apparent Faradaic process happened was determined firstly using the static CV. The charging current  $i_c$ was measured from the CVs at different scan rates. The relation between  $i_c$ , the scan rate (v) and the double layer capacitance (C<sub>dl</sub>) was given in eq S1. Therefore, the C<sub>dl</sub> is then calculated according to: C<sub>dl</sub> =d ( $\Delta j_{(0 \text{ V vs. RHE})}$ ) / 2dv.

$$i_c = v C_{dl} \qquad (S1)$$

For the estimation of ECSA, a specific capacitance ( $C_S$ ) value  $C_S$ = 0.040 mFcm<sup>-2</sup> in 1.0 mol/L KOH<sup>1</sup>. And S was the actual area used to measure the working electrode.

$$ECSA = C_{dl} / C_S \times S$$
 (S2)

2.2 Calculation method of work function:

The work functions  $(\Phi)$  can be calculated via following equation:

$$\Phi = h\nu - (E_{cutoff} - E_f) \qquad (S3)$$

where  $\Phi$  reflects the work function, hv reflects the photon energy (eV),  $E_{cutoff}$  reflects the binding energy of the secondary cutoff edge (eV), and  $E_f$  reflects the binding energy of Fermi level (eV). In this work, the photon energy (hv) of 21.22 eV (He<sub>1</sub>) was employed during the UPS analysis. In addition, the binding energy of Fermi level is well known to be 0 eV.

#### 3. 3. Characterizations

Transmission electron microscopy (TEM) was performed on a HITACHI HT7700 at 120 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and highresolution TEM (HRTEM) was recorded on a FEI TecnaiG2F2 FEI Talos F200X S/TEM with a field-emission gun at 200 kV. Scanning electron microscopy (SEM) was conducted on a Hitachi S-4700 instrument operated at 15 kV under high vacuum. X-ray diffractometers (XRD) was carried out by Bruker D8 ADVANCE with Cu K $\alpha$  radiation. The atomic composition was determined by Energy-dispersive X-ray spectroscopy (EDS) on Hitachi S-4700 instrument (15 kV). The chemical states of the samples were illustrated by X-ray photoelectron spectroscopy (XPS) and valence band spectra (VBS) performed on a VG scientific ESCA Lab 220 XL electron spectrometer using 300 W Al K $\alpha$  radiation. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed with an unfiltered He (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV. Raman spectra were recorded on a LabRAM Soleil Raman Microscope with a 532 nm laser.



# 4. 5. Supporting figures and tables

Fig.S1 SEM images of (a-c) CoO, (d-f) Co-MOF/CoO, (g-i)

CoNiV-LDH/CoO and (j-l) Ag/CoNiV-LDH/CoO.



Fig.S2 XRD patterns of main samples.



Fig.S3 Mott-Schottky curves of (a) CoO and (b) CoNiV-LDH.



Fig.S4 UPS survey spectra of CoO and CoNiV-LDH.



Fig.S5 HER performance of Ag/CoNiV-LDH/CoO. (a) LSV

curves, (b) Tafel slopes and (c)  $C_{dl}$  values.



Fig.S6 CV curves for (a-d) OER and (e-h) HER at scan rates of

 $20\ mV\ s^{\text{-1}} \sim 100\ mV\ s^{\text{-1}}.$ 



Fig.S7  $C_{dl}$  values vs. scan rates at non-faradaic regions for OER.



Fig.S8 EDS results of main samples.



Fig.S9 (a-c) OER and (d-e) HER performance of Ag/CoNiV-

## LDH/CoO-5/10/15 min.



Fig.S10 Self-activation of Ag/CoNiV-LDH/CoO in OER.



Fig.S11 HRTEM image of Ag/CoNiV-LDH/CoO after OER.



Fig.S12 XPS survey patterns of main samples.

# 5. Reference

H. Wu, Z. Wang, Z. Li, Y. Ma, F. Ding, F. Li, H. Bian, Q. Zhai,
Y. Ren, Y. Shi, Y. Yang, Y. Deng, S. Tang and X. Meng, *Adv. Energy Mater.*, 2023, 13.