

Electronic Supplementary Information

EXPERIMENTAL SECTION

Materials: Carbon cloth (CC) was provided by Hongshan District, Wu-han Instrument Surgical Instruments business. Nitric acid (HNO₃), ammonium fluoride (NH₄F) and urea (CH₄N₂O) were purchased from Beijing Chemical Works. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) and sodium hypophosphite monohydrate (NaH₂PO₂·H₂O) were purchased from Chengdu Kelong Chemical Reagent Co. Ltd. (China). The water used throughout all experiments was purified through a Millipore system. All the reagents and chemicals were used as received without further purification. Before using, carbon cloths were first treated with 69% concentrated nitric acid at 120 °C for 2 h, and then ultrasonically washed with deionized water and absolute ethanol each for 10 min for several times, followed by drying at 60 °C for 2 h.

Preparation of Co(OH)F/CC: Co(OH)F/CC precursor was prepared as follows. Co(NO₃)₂·6H₂O (0.582 g), urea (0.61 g), and NH₄F (0.186 g) were dissolved in 40 mL distilled water. After gently stirring for 20 min, the clear solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and then a piece of pre-treated carbon cloth (2 cm × 4 cm) was immersed into the solution. The autoclave was sealed and maintained at 120 °C for 6 h in an electric oven. After the autoclave cooled down at room temperature, the resulting Co(OH)F/CC was taken out and washed with distilled water and ethanol several times, followed by drying at 60 °C for 2 h.

Preparation of CoP/CC: Co(OH)F/CC precursor and NaH₂PO₂·H₂O were put at two separate positions in a porcelain boat with NaH₂PO₂·H₂O at the upstream side of the furnace. The molar ratio for Co to P is 1:3. Subsequently, the sample was heated at 300 °C for 120 min in a static Ar atmosphere, and then naturally cooled to ambient temperature under Ar. After that, a black film was observed on carbon cloth.

Preparation of CoP@NiCo-LDH/CC and NiCo-LDH/CC: The electrodeposition of NiCo-LDH was carried out in a three-electrode configuration, by using as-prepared CoP/CC (4 cm² in area), Pt plate (4 cm² in area) and saturated calomel electrode (SCE) as the working, counter and reference electrode, respectively. The electrolyte was obtained by dissolving Co(NO₃)₂·6H₂O (0.15 M) and Ni(NO₃)₂·6H₂O (0.15 M) in 100 mL water. The electrodeposition potential was controlled at -1.0 V vs SCE for 200 s. After electrodeposition, the CoP@NiCo-LDH/CC electrode was rinsed consecutively with ultrapure water and dried in a vacuum oven at 40 °C for 24 h. The mass of the deposited NiCo-LDH was measured from the weight difference before and after electrodeposition by means of a micro-balance (Sartorius BT125D) with an accuracy of 0.01 mg. The mass loading of CoP@NiCo-LDH/CC is calculated to be 4.39 mg cm⁻³. For comparison, NiCo-LDH/CC was also synthesized in a similar way and CoP/CC was replaced by CC.

Preparation of RuO₂: RuO₂ was prepared according to a previous publication.¹ Briefly, 2.61 g of RuCl₃·3H₂O and 30 mL KOH (1.0 M) were added into 100 mL distilled water and stirred for 45 min at 100 °C. Then the above solution was centrifuged for 10 minutes and filtered. The precipitates were collected and washed with water several times. Finally, the product was dried at 80 °C overnight and then annealed at 350 °C in air atmosphere for 1 h.

Characterizations: X-ray diffraction (XRD) measurements were operated on a Paralytical/Empryan diffractometer with Cu K α radiation ($\lambda=1.5418$ Å). Scanning electron microscope (SEM) measurements were conducted on a XL30 ESEM FEG scanning electron microscope with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were recorded on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data of the samples was collected on an ESCALABMK II X-ray photoelectron spectrometer using Al as the excitation source.

Electrochemical measurements: Electrochemical measurements were performed on a DH 7000 electrochemical workstation (Jingjiang Donghua Technology Co., Ltd.) in a standard three-electrode setup using a freshly prepared CoP@NiCo-LDH/CC as the working electrode without any physical or chemical activation process, a platinum wire and an Hg/HgO were used as the counter electrode and the reference electrode, respectively. The temperature of solution was kept at 25 °C for all the measurements via the adjustment of air condition and heating support, which ensured the variation of diffusion coefficient below 1%. All potentials reported in this work were calibrated to RHE unless especially illustrated, using the following equation (1):

$$E(\text{RHE}) = E(\text{Hg/HgO}) + (0.0977 + 0.0591 \text{ pH}) \text{ V} \quad (1)$$

Turnover frequency (TOF) calculations: For TOF calculations, the surface concentration of active sites associated with the redox Co species should be first calculated, and the linear relationship between the oxidation peak current and scan rate is extracted from the electrochemical cyclic voltammetry scans. The slope of the line can be calculated based on the following equation (2):

$$\text{Slope} = n^2 F^2 A \Gamma_0 / 4RT \quad (2)$$

Where n is the number of electrons transferred; F is Faraday's constant; A is the surface area of the electrode; Γ_0 is the surface concentration of active sites (mol cm⁻²), and R and T are the ideal gas constant and the absolute

temperature, respectively.²TOF values can be finally calculated from the formula (3):

$$\text{TOF} = JA/4Fm \quad (3)$$

Where J is the current density at a certain overpotential, A is the area of the electrode, 4 indicates the mole of electrons consumed for evolving one mole of O_2 from water, F is Faraday's constant and m is the number of moles of active sites.³

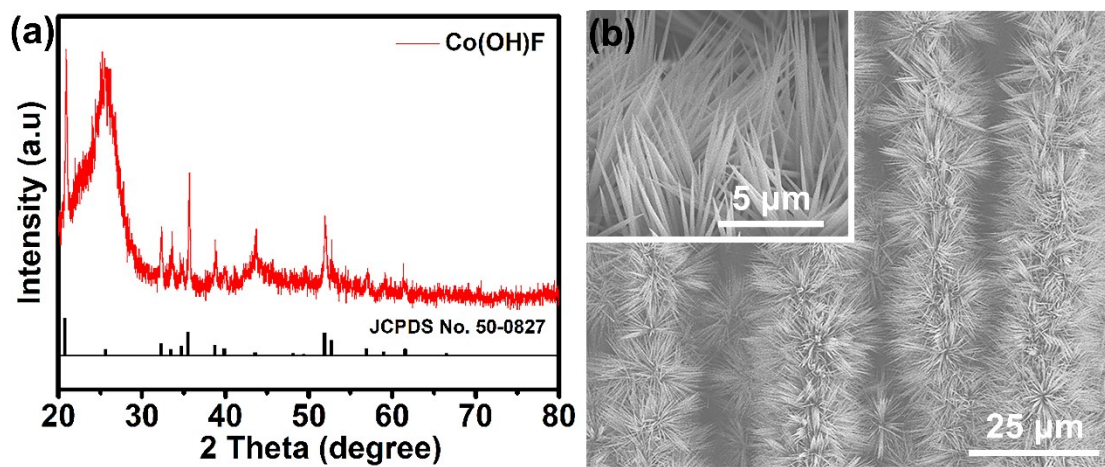


Fig. S1. XRD pattern and SEM images for Co(OH)F/CC.

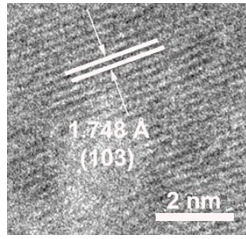


Fig. S2. HRTEM image for CoP NW.

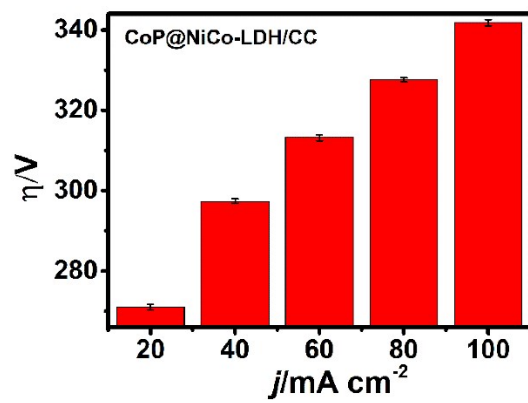


Fig. S3. Overpotential values needed for achieving fixed geometric catalytic current densities for five CoP@NiCo-LDH/CC electrodes.

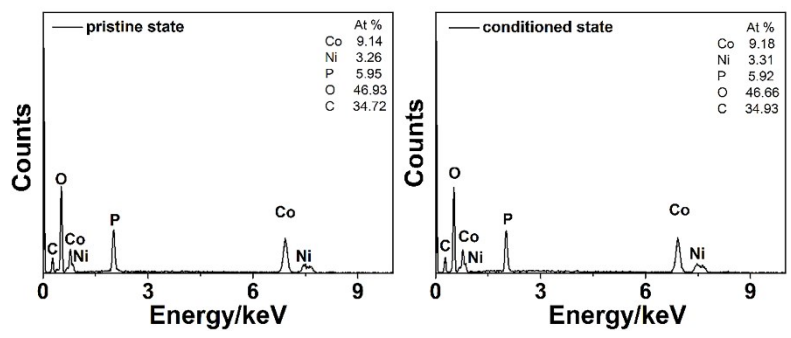


Fig. S4. EDX spectra and the corresponding atomic contents for CoP@NiCo-LDH/CC in the pristine state and the conditioned state.

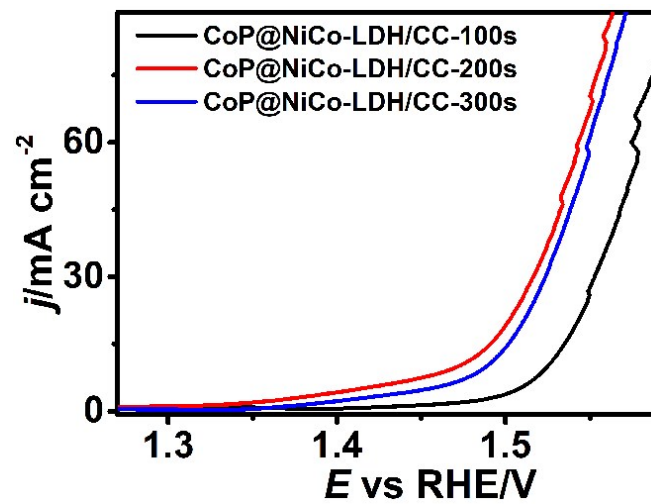


Fig. S5. LSV curves for CoP@NiCo-LDH/CC under varied electrodeposition times in 1.0 M KOH.

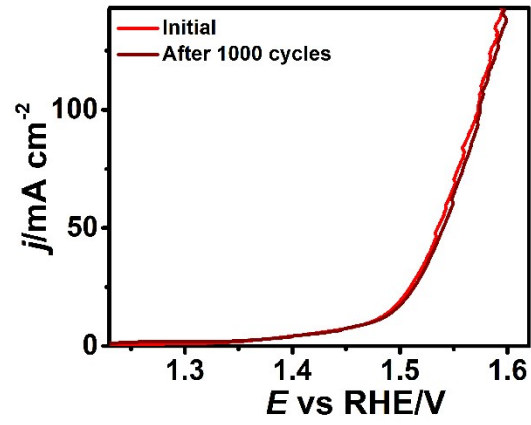


Fig. S6. LSV curves for CoP@NiCo-LDH/CC before and after 1000 CV cycles.

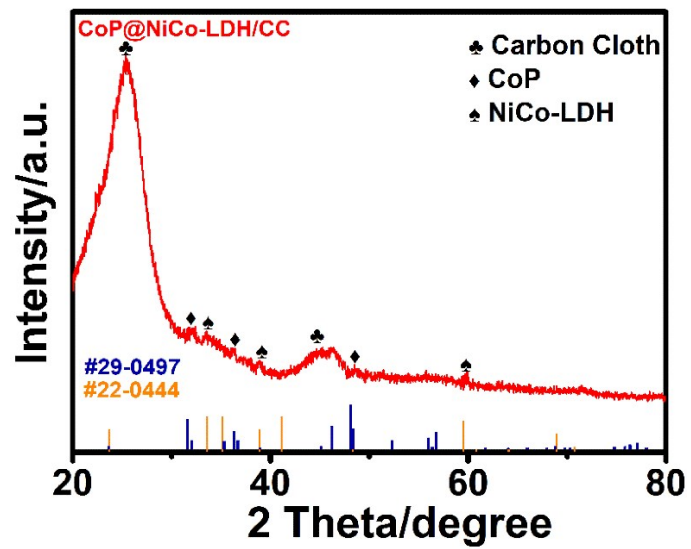


Fig. S7. XRD pattern for CoP@NiCo-LDH/CC after long-term durability test.

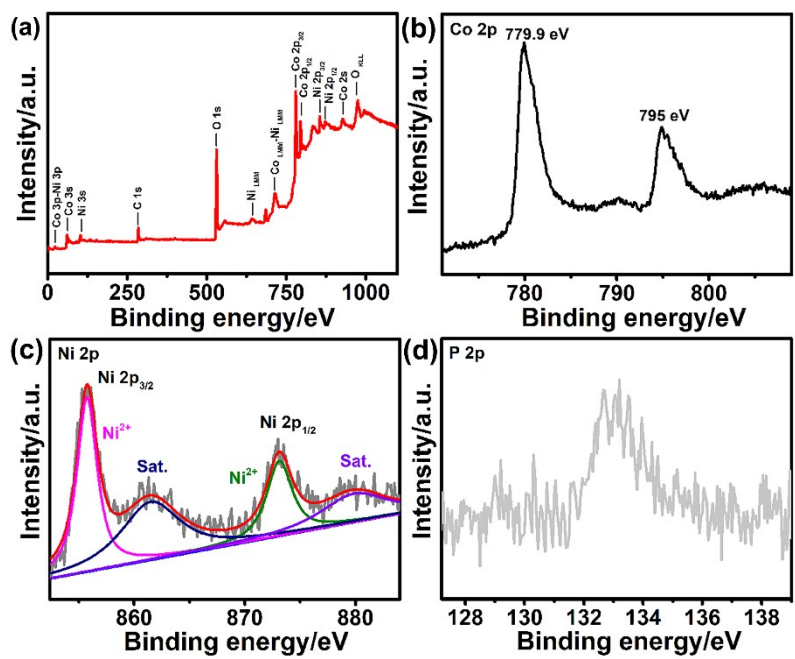


Fig. S8. (a) XPS survey spectrum for CoP@NiCo-LDH after long-term durability test. XPS spectra for CoP@NiCo-LDH after long-term durability test in the (b) Co 2p, (c) Ni 2p, and (d) P 2p regions.

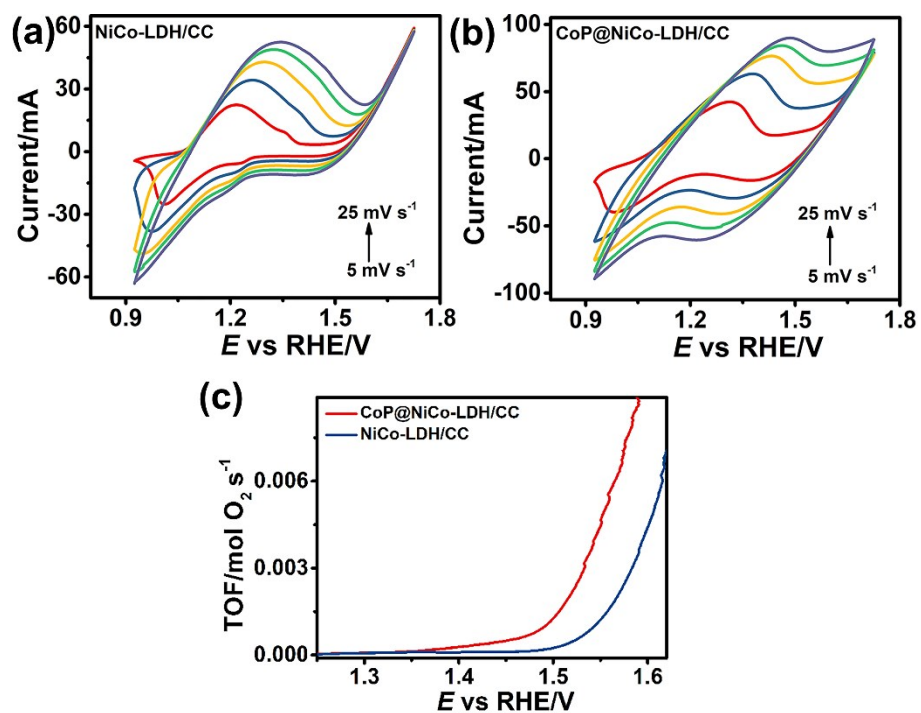


Fig. S9. CVs for (a) NiCo-LDH/CC and (b) CoP@NiCo-LDH/CC in the faradic capacitance current range at scan rates from 5 to 25 mV s^{-1} in 1.0 M KOH, (c) the polarization curves of NiCo-LDH/CC and CoP@NiCo-LDH/CC normalized by the active sites and expressed in terms of TOF.

Table S1. Comparison of water oxidation performance for CoP@NiCo-LDH/CC with other non-noble-metal OER catalysts under alkaline conditions.

Catalyst	j (mA cm ⁻²)	η (mV)	Electrolyte	Ref.
CoP@NiCo-LDH/CC	20	271	1.0 M KOH	This work
CoP/CC	20	358		
NiCo-LDH/CC	20	323		
NiCo-LDH/CFP	10	299	1.0 M NaOH	[4]
NiCo-NP	10	314	1.0 M KOH	[5]
NiCo-CH	10	343	1.0 M KOH	[6]
NiOOH-NiCr ₂ O ₄ /NF	20	271	1.0 M KOH	[7]
(Ni, Co) _{0.85} Se NSAs/NF	20	287	1.0 M KOH	[8]
Co ₉ S ₈ @NiCo-LDH/NF	30	278	1.0 M KOH	[9]
CoMoO ₄ /CC	10	290	1.0 M KOH	[10]
Co(OH) ₂ @Ni(OH) ₂ /CC	10	330	1.0 M KOH	[11]
P-CoMoS/CC	10	260	1.0 M KOH	[12]
CoP/CC	10	281	1.0 M KOH	[13]
NiCo hydroxide/CC	10	258	1.0 M KOH	[14]
Ni/MoN@NCNT/CC	10	252	1.0 M KOH	[15]
NiCu LDH/CC	10	290	1.0 M KOH	[16]
NiCoSe ₂ /CC	10	255.8	1.0 M KOH	[17]
NiMoP ₂ /CC	20	320	1.0 M KOH	[18]
CC@CoO@FeOOH-NWAs	10	255	1.0 M KOH	[19]
NiCo@NiCoO ₂ /C PMRAs	20	366	1.0 M KOH	[20]
CoMn-LDH/CNT	10	335	1.0 M KOH	[21]

References

1. J. C. Cruz, V. Baglio, S. Siracusano, V. Antonucci, A. S. Aricò, R. Ornelas, L. Ortiz–Frade, G. Osorio–Monreal, S. M. Durón–Torres, and L. Arriaga, *Int. J. Electrochem. Sci.*, 2011, **6**, 6607-6619.
2. S. Pintado, S. Goberna–Ferron, E. C. Escudero–Adan, and J. R. Galan–Mascaros, *J. Am. Chem. Soc.*, 2013, **135**, 13270-13273.
3. M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, and H. Dai, *J. Am. Chem. Soc.*, 2013, **135**, 8452-8455.
4. Y. Liu, M. Zhang, D. Hu, R. Li, K. Hu, and K. Yan, *ACS Appl. Energy Mater.*, 2019, **2**, 1162-1168.
5. S. Sun, C. Lv, W. Hong, X. Zhou, F. Wu, and G. Chen, *ACS Appl. Energy Mater.*, 2019, **2**, 312-319.
6. S. Wang, T. Wang, X. Wang, Q. Deng, J. Yang, Y. Mao, and G. Wang, *International Journal of Hydrogen Energy*, 2020, **45**, 12629-12640.
7. J. Zhao, X. Ren, Q. Han, D. Fan, X. Sun, X. Kuang, Q. Wei, and D. Wu, *Chem. Commun.*, 2018, **54**, 4987-4990.
8. K. Xiao, L. Zhou, M. Shao, and M. Wei, *J. Mater. Chem. A*, 2018, **6**, 7585-7591.
9. J. Yan, L. Chen, and X. Liang, *Sci. Bull.*, 2019, **64**, 158-165.
10. J. Meng, J. Fu, X. Yang, M. Wei, S. Liang, H. Zang, H. Tan, Y. Wang, and Y. Li, *Inorg. Chem. Front.*, 2017, **4**, 1791-1797.
11. Y. Wang, Y. He, and M. Zhou, *Applied Surface Science*, 2019, **479**, 1270-1276.
12. C. Ray, S. Lee, K. V. Sankar, B. Jin, J. Lee, J. H. Park, and S. C. Jun, *ACS Appl. Mater. Interfaces*, 2017, **9**, 37739-37749.
13. P. Wang, F. Song, R. Amal, Y. H. Ng, and X. Hu, *ChemSusChem*, 2016, **9**, 472-477.
14. X. Wang, Y. Zheng, J. Yuan, J. Shen, J. Hud, A. Wang, L. Wu, and L. Niu, *Electrochimica Acta*, 2017, **225**, 503-513.
15. P. Wang, J. Qi, C. Li, X. Chen, T. Wang, and C. Liang, *ChemElectroChem*, 2020, **7**, 745-752.
16. Y. Zheng, J. Qiao, J. Yuan, J. Shen, A. Wang, P. Gong, X. Weng, and L. Niu, *Electrochimica Acta*, 2018, **282**, 735-742.
17. J. Yu, Y. Tian, F. Zhou, M. Zhang, R. Chen, Q. Liu, J. Liu, C. Xu, and J. Wang, *J. Mater. Chem. A*, 2018, **6**, 17353-17360.
18. X. Wang, H. Chen, Y. Xu, J. Liao, B. Chen, H. Rao, D. Kuang, and C. Su, *J. Mater. Chem. A*, 2017, **5**, 7191-7199.
19. Y. Wang, Y. Ni, B. Liu, S. Shang, S. Yang, M. Cao, and C. Hu, *Electrochimica Acta*, 2017, **257**, 356-363.
20. H. Xu, Z. Shi, Y. Tong, and G. Li, *Adv. Mater.*, 2018, **30**, 1705442.
21. Z. Liu, C. Yu, X. Han, J. Yang, C. Zhao, H. Huang, and J. Qiu, *ChemElectroChem*, 2016, **3**, 906-912.