Supplementary Information (SI) for New Journal of Chemistry.

ZIF-67 Derived CoNiP-N-C as an Efficient Catalyst for Water Splitting

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1. Experimental

1.1. Chemical Substances

All chemical reagents were of analytical grade (AR) and used without further purification unless otherwise noted. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, ≥99.0%), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, ≥99.0%), 2-Methylimidazole ($C_4H_6N_2$, ≥99.0%), trisodium citrate dehydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, ≥99.0%), urea ($CO(NH_2)_2$, ≥99.5%), and anhydrous methanol (CH_3OH, ≥99.5%) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Macklin). Phytic acid was used as a 50 wt% aqueous solution (PA, Macklin). Ultrapure water (18.25 MΩ·cm) was used throughout the entire experiment.

1.2. Preparation of ZIF-67

First, $Co(NO_3)_2 \cdot 6H_2O$ (1.0 g) was dissolved in 30 mL of anhydrous methanol to form solution A, and 2-methylimidazole (1.5 g) was dissolved in 30 mL of anhydrous methanol to form solution B. Then, solution A and solution B were mixed and stirred at room temperature for 24 h. The products were collected by centrifugation, and washed with anhydrous methanol several times. The obtained purple powder ZIF-67 was dried in a vacuum oven at 60 °C for 12 h.

1.3. Preparation of CoNi-PA

First, $Co(NO_3)_2 \cdot 6H_2O$ (0.5 g, 1.718 mmol) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.5 g, 1.719 mmol) (with Co/Ni ratio of 0.5/0.5) were weighed and dispersed into 40 mL of anhydrous methanol and stirred at 60 °C for 30 min, and then 1 mL of 50% PA was added dropwise to the above mixture and stirring was continued at 60 °C for 6 h. After cooling down to room temperature, the precursors were washed with anhydrous methanol for a few times and dried in a vacuum oven at 60 °C for 12 h. The precursor of other Co/Ni ratios (0.25/0.75 and 0.75/0.25) were synthesized via the similar method as mentioned above except that the amounts of $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were changed.

1.4. Preparation of CoNiP-N-C

ZIF-67 (60 mg) and CoNi-PA (60 mg) obtained from the above steps were mixed and ground, annealed at 800 °C for 2 h under Ar atmosphere with a temperature increase rate of 5 °C·min^{-1}, and then cooled down to room temperature. The CoNiP-N-C with Co/Ni ratio was 0.5/0.5 was named as CoNiP-N-C. The CoNiP-N-C with other ratios (0.25/0.75 and 0.75/0.25) were named as$Co_{0.25}Ni_{0.75}P$-N-C and $Co_{0.75}Ni_{0.25}P$-N-C, respectively.

1.5. Preparation of CoNiP

CoNi-PA obtained in the above steps was ground and annealed at 800 °C for 2 h under Ar atmosphere. Then, the CoNiP was obtained.

1.6. Instruments and Equipment

The surface morphology and structure of the catalyst were studied using Gemini300 scanning electron microscope at a voltage of 10.0 kV. At the same time, in order to explore the internal structural characteristics, we used a transmission electron microscope for image acquisition. Use Rigaku Smart Lab to collect XRD patterns for analyzing crystal structure. Record 2θ Spectral information within the range of 20° to 80°. Using ESCALAB 250 electron spectrometer (American Thermo Fisher Scientific) and Al K α 150 W is used as an X-ray excitation source to record X-ray photoelectron spectroscopy (XPS). Perform elemental analysis on the catalyst using JEOLJSM-6700F EDS spectroscopy analysis. Finally, all electrochemical measurements were taken at the Shanghai Chenhua Electrochemical Workstation (CHI 760D). Using a conventional three electrode system: a glassy carbon electrode modified with a catalyst as the working electrode, Ag/AgCl as the reference electrode, and platinum as the counter electrode. Among them, the diameter of the glassy carbon electrode is 3 mm.

1.7. Electrocatalytic Activity Test Method

The working electrode was prepared as follows: first, the catalyst dispersion was prepared by dispersing 5 mg of catalyst in 1 mL of anhydrous ethanol, then adding 10 μL of Nafion solution, and continuously sonicating for 1 h to obtain the catalyst dispersion. Take 10 μL of the catalyst dispersion and apply it onto the polished surface of the glassy carbon (GC) electrode, and then the working electrode was dried (the loaded amount of catalyst was calculated to be 0.14 mg·cm^{-2}).Prior to drop-casting, the carbon cloth (CC, CeTech, 1 cm × 1.5 cm × 0.41 cm) was pretreated by sequential ultrasonication in acetone, deionized water, and ethanol for 30 min each to remove surface impurities, followed by drying at 60 °C. Subsequently, 100 μL of the catalyst ink was carefully dropped onto the pretreated CC surface using a micropipette, covering an area of 1 cm^2. Finally, the electrode was dried at 60 °C in a vacuum oven for 12 h to evaporate the solvent. The final mass loading of the catalyst on the carbon cloth was calculated to be approximately 0.5 mg cm^{-2}.

Electrochemical testing of catalyst performance in a 1 M KOH environment at room temperature (25 ± 2 °C) and ambient humidity (~ 40 - 60% RH). For the HER test, we first cycled the obtained working electrode 20 times in the potential range of 0 ~ -0.6 V (vs. RHE) at a scan rate of 100 mV·s^{-1} to activate and stabilize the catalyst. Then, the polarization curves were tested by linear scanning voltammetry (LSV) in the same voltage range at a scan rate of 5 mV·s^{-1} in O_2 prostrated 1 M KOH medium. double layer capacitance (C_{dl}) was measured using cyclic voltammetry (CV) in the voltage range of 0.0 ~ 0.1 V (vs. RHE) with different sweep rates (10, 20, 40, 60, 80 and 100 $mV \cdot s^{-1}$). Similarly, to test the stability of the catalysts, 1000 consecutive cyclic scans were performed in the voltage range of 0.2 ~ -0.6 V (vs. RHE) at a sweep rate of 100 $mV \cdot s^{-1}$, and the LSV polarization curves were recorded again at a sweep rate of 5 $mV \cdot s^{-1}$ after the cycle. In addition to this, we also tested the material for a long time with timed currents at -0.20 V.

For the OER test, similarly, the obtained working electrode was first cycled 20 times in the potential range of 1.2 ~ 1.8 V (vs. RHE) at a scan rate of 100 $mV \cdot s^{-1}$ to activate and stabilize the catalyst. Then, Electrochemical ac impedance (EIS) measurements were performed on the catalyst in the frequency range of 100 kHz ~ 0.1 mHz with an amplitude of 7 mV. To test the stability of the catalyst, 1000 consecutive cyclic scans were performed at a sweep rate of 100 $mV \cdot s^{-1}$ in the voltage range of 1.0 V ~ 1.8 V (vs. RHE), and the cyclic followed by another recording of LSV polarization curves at a sweep rate of 5 $mV \cdot s^{-1}$. In addition to this, we also performed a long time timed current test on the material at a voltage of 1.59 V.

2. Structure Characterization of ZIF-67, CoNiP and CoNiP-N-C

2.1. High-resolution XPS Total Spectra of CoNiP-N-C

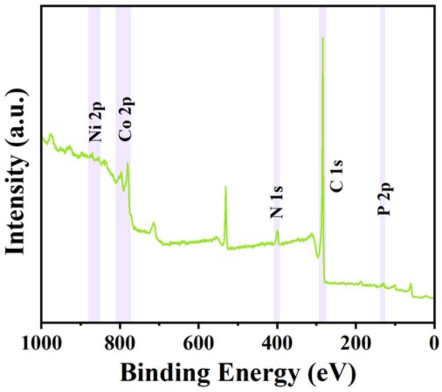

Fig. S1. High-resolution XPS total spectra of CoNiP-N-C.

2.2 SEM Image and Elemental Mapping Images of ZIF-67

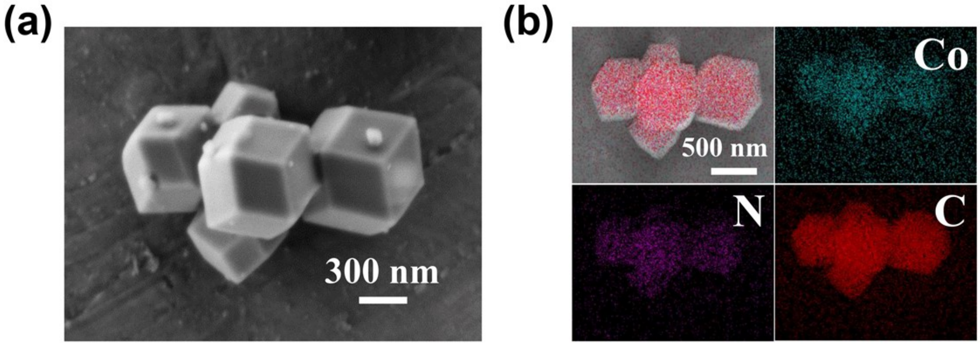

Fig. S2. (a) SEM image, (b) elemental mapping images of ZIF-67.

2.3. SEM Image and Elemental Mapping Images of CoNiP

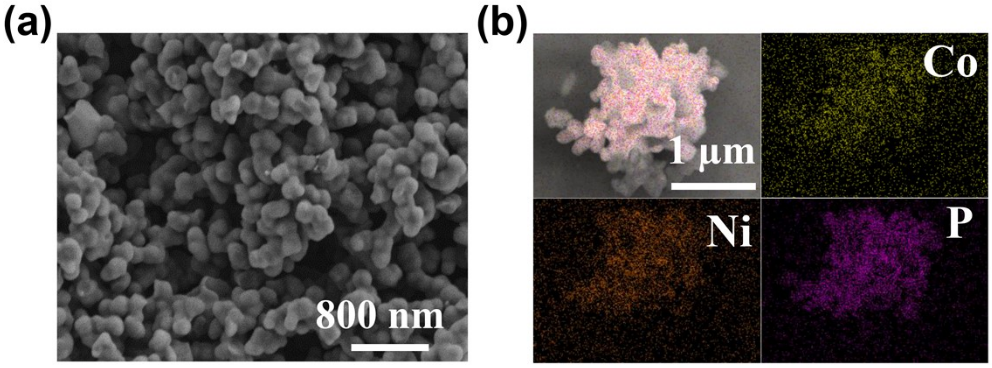

Fig. S3. (a) SEM image, (b) elemental mapping images of CoNiP.

3. Electrochemical Characterization

3.1. CV Curves of $Co_{0.25}Ni_{0.75}$P-N-C, CoNiP-N-C, $Co_{0.75}Ni_{0.25}$P-N-C and CoNiP

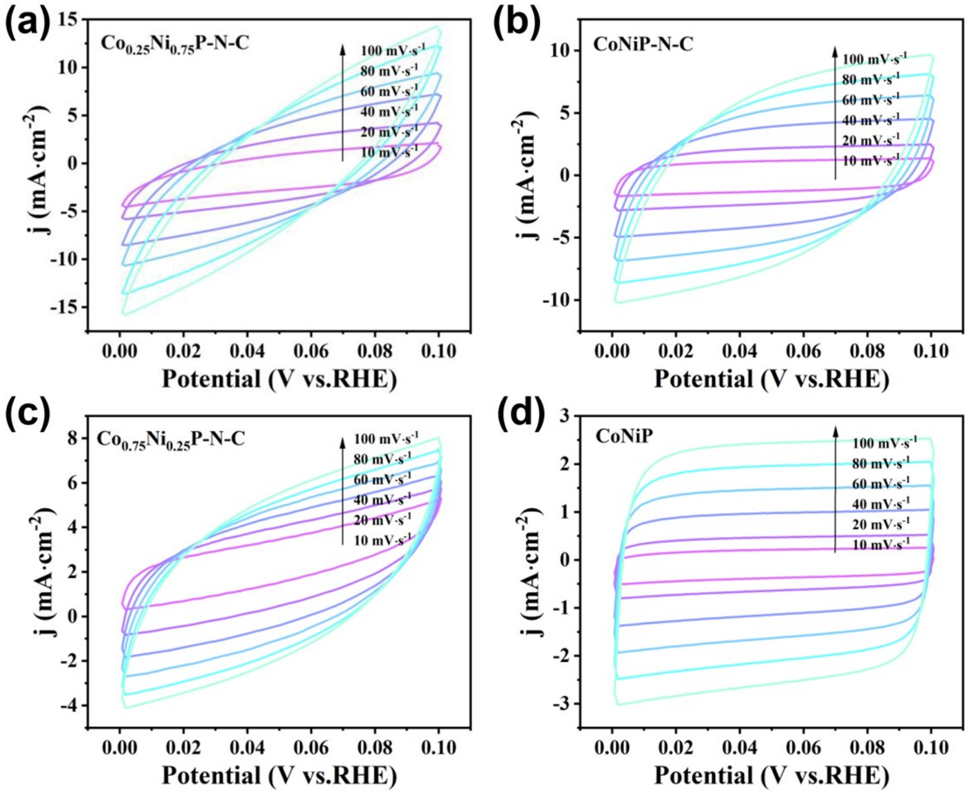

Fig. S4. HER performance of $Co_{0.25}Ni_{0.75}$P-N-C, CoNiP-N-C, $Co_{0.75}Ni_{0.25}$P-N-C and CoNiP in 1 M KOH: CV curves of (a) $Co_{0.25}Ni_{0.75}$P-N-C, (b) CoNiP-N-C, (c) $Co_{0.75}Ni_{0.25}$P-N-C, Co-N-C and (d) CoNiP.

3.2. HER Performance in 1 M KOH: Stability Tests of CoNiP-N-C

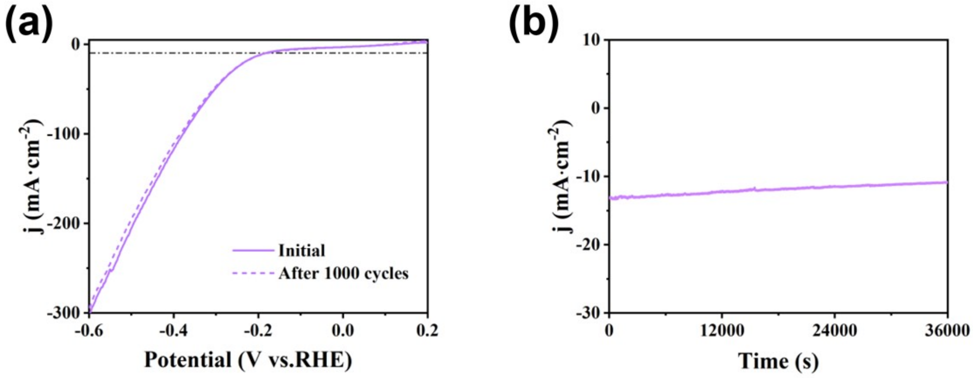

Fig. S5. HER performance in 1 M KOH: stability tests of CoNiP-N-C. (a) LSV curves of the CoNiP-N-C before and after the 1000 cycles. (d) Chronoamperometry of the CoNiP-N-C at -0.20 V (vs. RHE) for 36000 s.

3.3. Fitted Circuit Diagram of Electrocatalytic Reaction Process

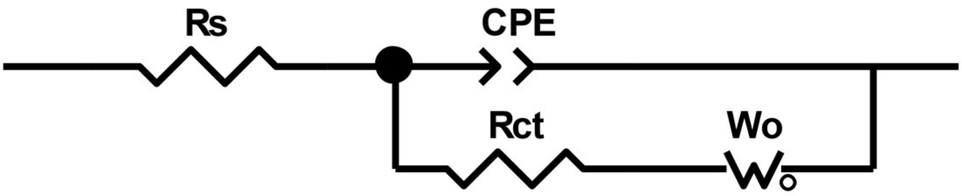

Fig. S6. Fitted circuit diagram of electrocatalytic reaction process.

3.4. Circuit Fitting Parameters of Co$_{0.25}$Ni$_{0.75}$P-N-C, CoNiP-N-C, Co$_{0.75}$Ni$_{0.25}$P-N-C and CoNiP

Table S1. Fitting parameters of equivalent circuits for various catalytic materials.

Catalysts	Rs (Ω)	CPE-T ($\Omega^{-1}\cdot cm^{-2}\cdot s^{-n}$)	CPE-P	Rct (Ω)	Wo-R ($\Omega\cdot s^{-1/2}$)	Wo-T (s)	Wo-P
Co$_{0.25}$Ni$_{0.75}$P-N-C	105.5	4.1667E-6	0.86499	67.37	0.4325	1.0362E-7	0.23895
CoNiP-N-C	105.3	4.7191E-6	0.85869	35.99	6.896	2.9663E-5	0.23492
Co$_{0.75}$Ni$_{0.25}$P-N-C	106.2	3.0438E-6	0.88944	168.2	426.7	0.17755	0.51619
CoNiP	95.3	3.0466E-6	0.904	150.8	0.72674	5.6991E-7	0.25305

3.5. OER Performance in 1 M KOH: StabilityTests of CoNiP-N-C

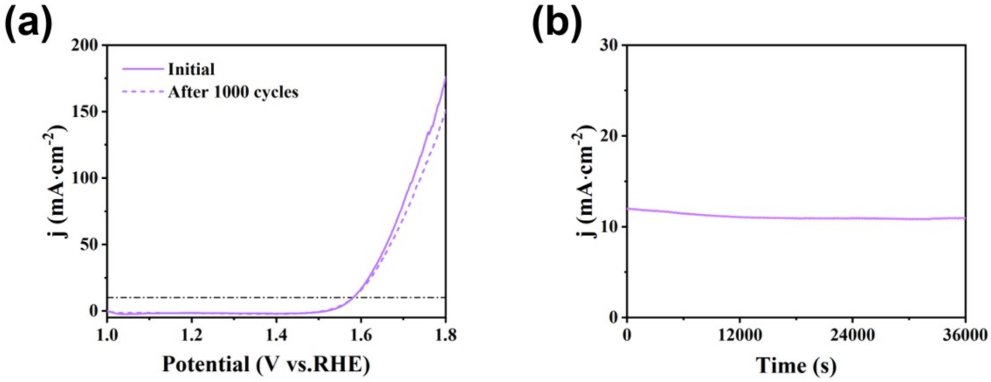

Fig. S7. OER performance in 1 M KOH: stability tests of CoNiP-N-C. (a) LSV curves of the CoNiP-N-C before and after the 1000 cycles. (d) Chronoamperometry of the CoNiP-N-C at 1.59 V (vs. RHE) for 36000 s.

3.6. Reported Bifunctional Catalysts for Water Splitting

Table S2. Reported bifunctional catalysts for water splitting.

Bifunctional Catalyst	**Electrolyte**	**HER Overpotentials at 10 mA·cm^{-2} (mV)**	**OER Overpotentials at 10 mA·cm^{-2} (mV)**	**Cell Voltage at 10 mA·cm^{-2} (V)**
CoNiP-N-C	1.0 M KOH	170	350	1.69
Fe_3O_4-CoP_x/TiN	1.0 M KOH	177	331	1.75[1]
Co/CeO_2/Co_2P/CoP@NC	1.0 M KOH	195	307	1.76[2]
CoMoP NFs	1.0 M KOH	126	362 **(at 50 mA·cm^{-2})**	1.75[3]
$CoMoO_4$/NF	1.0 M KOH	289	292	1.86[4]

4. Reference

1. B. Guo, J. Sun, X. Hu, Y. Wang, Y. Sun, R. Hu, L. Yu, H. Zhao and J. Zhu, *ACS Appl. Nano Mater.*, 2019, **2**, 40-47.

2. X.-Z. Song, Q.-F. Su, S.-J. Li, G.-C. Liu, N. Zhang, W.-Y. Zhu, Z.-H. Wang and Z. Tan, *Int. J. Hydrogen Energy*, 2020, **45**, 30559-30570.

3. X. Chang, J. Yan, X. Ding, Y. Jia, S. Li and M. Zhang, *Nanomaterials*, 2022, **12**, 3886.

4. Y. Lu, Z. Li, Y. Xu, L. Tang, S. Xu, D. Li, J. Zhu and D. Jiang, *Chem. Eng. J.*, 2021, **411**, 128433.