

Supplementary material

Experimental:

All the reagents in this work are analytical grade without additional purification. Nickel foam, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) are purchased from Sinopharm Chemical Reagent Co. Ltd.

Synthesis of $\text{Ni}(\text{OH})_2/\text{NF}$

At room temperature, nickel hydroxide nanosheets were fabricated on nickel foam by etching growth method. Firstly, nickel foam ($2 \times 1 \text{ cm}^2$, NF) was sonicated in acetone, ethanol and deionized water for 15 min, respectively. The cleaned nickel foam was immersed in hydrochloric acid for 1.5 hours to etch the surface, and then immersed in deionized water for 24 hours to grow nickel hydroxide nanosheets on the surface. After natural drying in air, $\text{Ni}(\text{OH})_2/\text{NF}$ was obtained.

Synthesis of $\text{Ni}_2\text{P}/\text{NF}$

To obtain $\text{Ni}_2\text{P}/\text{NF}$, NaH_2PO_2 was placed upstream of the tube as phosphorus source. Then, the fabricated $\text{Ni}(\text{OH})_2/\text{NF}$ precursor was placed in the center of the tube and phosphated at 300°C for 1 hour under the mixed gases of $\text{Ar}-\text{H}_2$ (5% H_2). After cooling down, the obtained product was denoted as $\text{Ni}_2\text{P}/\text{NF}$.

Synthesis of CoNiP/NF

$\text{Ni}(\text{OH})_2/\text{NF}$ was soaked in 0.15 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for 1 hour to exchange Ni cations with Co cations at room temperature. Upon completion of ion exchange, the $\text{Co}_x\text{Ni}_{1-x}(\text{OH})/\text{NF}$ precursor was taken out from the solution. The obtained $\text{Co}_x\text{Ni}_{1-x}(\text{OH})/\text{NF}$ precursor was performed the phosphating process as described above for fabricating $\text{Ni}_2\text{P}/\text{NF}$. After cooling down, the obtained product was denoted $\text{CoNiP}/\text{NF}-0.15\text{M}$. In order to ascertain the optimum concentration of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution, other $\text{CoNiP}/\text{NF}-\text{X}$ ($\text{X} = 0.1, 0.2$) samples were prepared in a similar way by only adjusting the concentrations of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 M, 0.2 M), denoted as $\text{CoNiP}/\text{NF}-0.1\text{M}$, $\text{CoNiP}/\text{NF}-0.2\text{M}$, respectively.

Physical and Chemical Characterization:

The crystal structures of as-fabricated samples were characterized by X-ray polycrystalline diffraction (XRD, UltimaV). The morphologies were examined by field emission scanning electron microscope (SEM, ZEISS sigma500) and field emission transmission electron microscope (TEM, JEOL JEM-2100F). The energy-dispersive spectroscopy analysis was performed by BRUKER XFlash 6130. X-ray photoelectron spectroscopy (XPS) analysis was investigated by Thermo SCIENTIFIC ESCALAB 250Xi.

Electrochemical Measurements:

The electrochemical characterization of all samples was tested by CHI660E electrochemical workstation (Shang-hai Chenhua Instruments, Shanghai, China). Electrochemical measurement was carried out by standard three-electrode configuration, in which platinum sheet, Ag/AgCl electrodes and as-fabricated samples was used as counter electrode, reference electrode and working electrode, respectively. 3 M potassium hydroxide aqueous solution was used as electrolyte. All applied potentials are calibrated to the reversible hydrogen electrode (RHE) using the following equation: $E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.197 + 0.0591 \times \text{pH}$, where the pH of the KOH electrolyte. The overpotential (η) of HER is recorded as calculated value, and the overpotential of OER is calculated as $\eta(\text{V}) = E_{\text{RHE}} - 1.23 \text{ V}$. The linear sweep voltammetry (LSV) curve was recorded at a scanning rate of $5 \text{ mV} \cdot \text{s}^{-1}$. The electrochemical impedance spectroscopies (EIS) were investigated in electrochemical workstation of Autolab PGSTAT 302N (Metrohm AG, Herisau, Switzerland).

Computational Details:

Spin-polarized density functional theory (DFT) calculations were carried out using the Vienna ab initio simulation package (VASP). The plane-wave basis-set with an energy cutoff of 400 eV, the projector-augmented wave (PAW) potentials and the generalized gradient approximation (GGA) exchange–correlation functional parameterized by Perdew, Burke, and Ernzerhof (PBE) were employed. A vacuum region of 20 Å was added in the vertical direction to eliminate the interaction between neighboring slabs. The DFT optimized equilibrium lattice constants of CoNiP are $a = b = 5.834 \text{ Å}$, $c = 3.351 \text{ Å}$. For CoNiP (111), the periodically repeated triple-layer slab is modeled as an active surface to study the hydrogen evolution performance, with the two layers at the bottom fixed. The Brillouin zone is sampled with $5 \times 5 \times 1$ k-point grids. In the calculations of Gibbs free energy, the electron transfer and the pH effect are considered, and the effect of electric double layer is ignored. The adsorption free energies of hydrogen ($\Delta G_{\text{*H}}$) on a certain surface is calculated by $\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{U}} + \Delta G_{\text{pH}}$, where ΔE is DFT based adsorption energy, ΔE_{ZPE} and $T\Delta S$ are the corrections on zero-point energy and entropy, respectively.

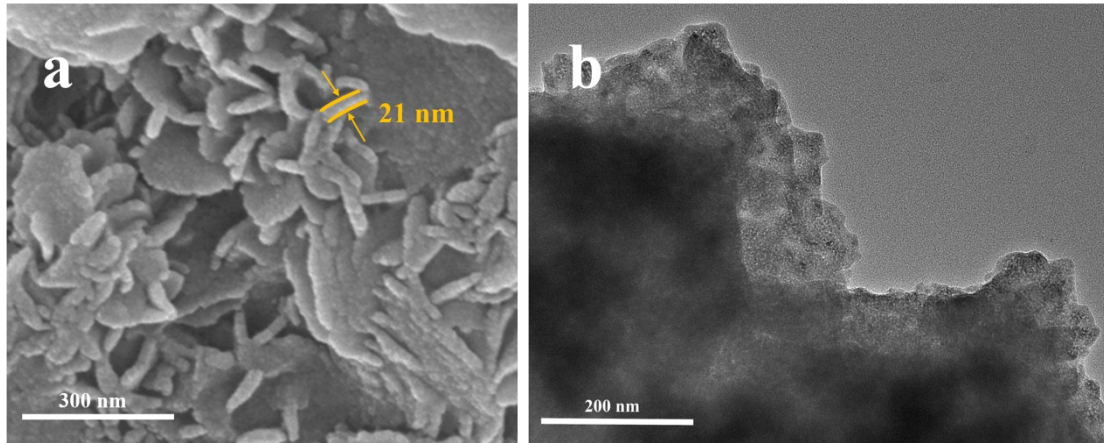


Figure S1. Thickness of CoNiP nanosheets

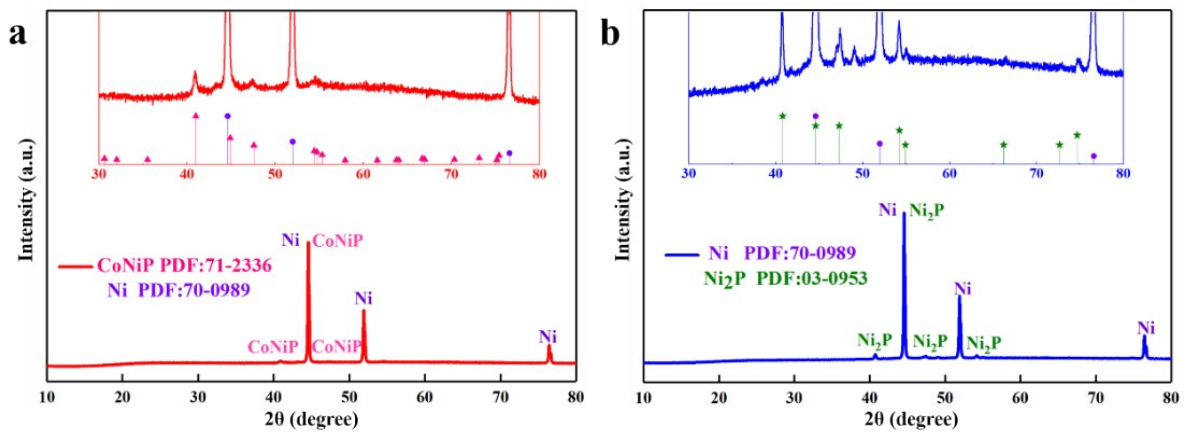


Figure S2. The XRD patterns of CoNiP-0.15M/NF (a) and Ni₂P/NF (b).