

Electronic structure modulation of Fe-Ni₂P@CoP heterojunction for efficient industrial water electrolysis toward hydrogen production

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ABSTRACT: Using anion exchange membrane water electrolysis (AEMWE) technology to produce hydrogen is one of the effective pathways for future energy development. Designing efficient and stable anode oxygen evolution reaction (OER) catalysts is crucial for improving hydrogen production efficiency. In this study, Fe-doped Ni₂P material was designed using a MOF as a precursor, and then combined with CoP nanowire arrays to form Fe-Ni₂P@CoP heterojunction composite. Different from previous reports, this work features precise Fe doping (~3.6 at%), a unique 0D/1D morphology, and systematic AEMWE evaluation at 1.0 A cm⁻². It is found that doping and interface engineering induce charge transfer between Fe atoms and the heterojunction interfaces, optimizing the overall electronic structure and enhancing the adsorption of reaction intermediates at the active sites, thereby improving electrocatalytic performance. The Fe-Ni₂P@CoP catalyst demonstrates highly efficient OER activity and requires only 276 mV overpotential to achieve a current density of 100 mA cm⁻², maintaining stability for 100 hours. Subsequently, it is assembled with Pt/C into an AEM electrolyzer, achieving a cell voltage of only 1.77 V at a high current density of 1.0 A cm⁻² relevant to industrial applications, demonstrating promising potential for industrial hydrogen production under specific AEMWE operating conditions.

KEYWORDS: Anion exchange membrane water electrolysis, Oxygen evolution reaction, Interface engineering, Doping.

Graphical abstract

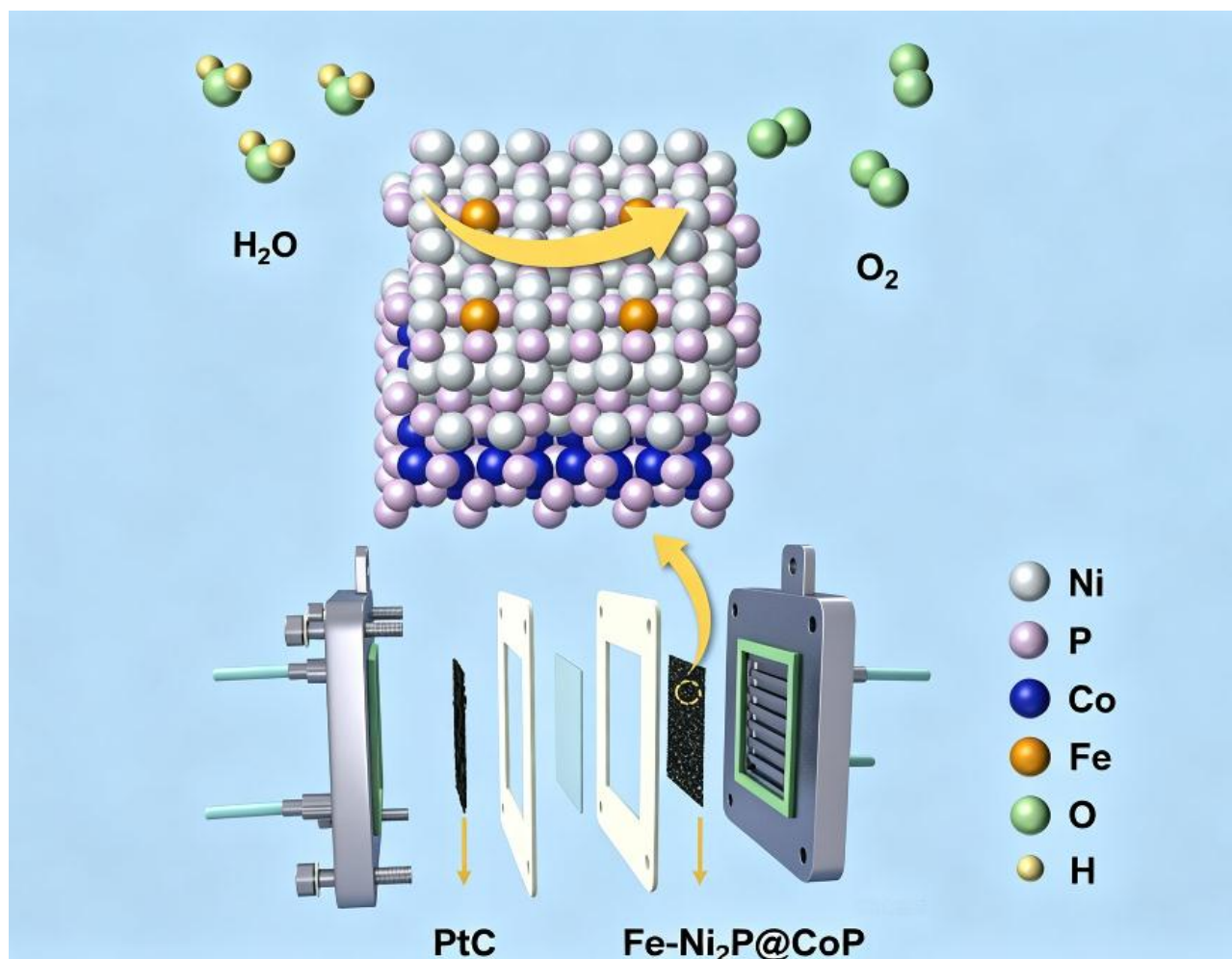
Synthesized via a MOF-templated phosphorization strategy, integrates doping and interfacial engineering to boost industrial AEMWE performance. Fe incorporation induces charge redistribution, optimizing the d-band center to -1.28 eV, balancing *OOH adsorption/desorption, and lowering the OH→O energy barrier. The catalyst achieves a low overpotential of 276 mV at 100 mA cm⁻² and delivers 1.77 V at 1.0 A cm⁻² in AEMWE, highlighting its promise for high-current-density green hydrogen production.

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1. Introduction

Among various new energy sources, hydrogen is regarded as a core future energy carrier due to its high energy density, environmental friendliness, and renewability^[1-4]. Anion exchange membrane water electrolysis (AEMWE) is a green and efficient technology for hydrogen production^[5-8]. However, the anodic oxygen evolution reaction (OER) involves complex multi-electron and proton-coupled transfer steps, and its kinetics are relatively sluggish^[9-12]. Therefore, developing highly active and stable OER catalysts remains a key challenge^[13-15].

Transition metal phosphides (TMPs) exhibit excellent catalytic potential in water electrolysis owing to their metal-like conductivity and fast charge transfer capability^[16, 17]. Their unique electronic structure allows phosphorus to provide appropriate bonding strength with reaction intermediates, avoiding overly strong adsorption of intermediates on

the metal surface and alleviating slow desorption, thereby maintaining high catalytic activity^[18-20]. Moreover, TMPs undergo surface reconstruction under anodic conditions, forming a catalytically active (oxy) hydroxide layer while retaining most of the conductive phosphide phase^[17, 21-23]. However, excessive reconstruction increases charge transfer resistance, limiting practical application, and thus modification strategies are needed to address the above challenges.

Interface engineering can enhance catalytic activity by modulating the electronic structure or forming a built-in electric field^[24, 25], as demonstrated in systems such as CoP@WP₂/NF^[26], Ni₂P@FeP@Co₂P^[27], and FeP@NiCoP/Mo₄P₃^[28]. The CoP@WP₂/NF heterojunction forms a crystalline-amorphous core-shell nanowire array, where the amorphous WP₂ shell provides abundant active sites and interfacial charge coupling accelerates reaction kinetics^[26]. The Ni₂P@FeP@Co₂P multi-component heterostructure

builds an asymmetric built-in electric field via work function differences, driving charge transfer among the three phases to balance electron distribution and optimize intermediate adsorption for both HER and OER^[27]. The FeP@NiCoP/Mo₄P₃ system uses Mo₄P₃ quantum dots as "electron islands" on NiCoP nanosheets, where quantum confinement induces interfacial charge polarization, forming a built-in electric field that modulates the d-band center of active sites^[28]. In addition, elemental doping can alter catalytic activity: the electronegativity difference between dopant and host atoms induces charge redistribution, thereby tuning the d-band center position of active sites and optimizing the Gibbs free energy of adsorption for reaction intermediates^[29-32]. Su *et al.* introduced Ce into NiCoP, inducing lattice distortion for enhanced stability and promoting firm carbon-layer bonding to prevent detachment^[33]. The carbon layer serves dual functions: facilitating electron transport and protecting the phosphide from oxidation during prolonged operation^[33]. The carbon layer serves dual functions: facilitating electron transport and protecting the phosphide from oxidation during prolonged operation^[33]. Therefore, combining interface engineering with elemental doping provides a potential strategy for designing TMP catalysts for application in AEMWE.

Recent reviews have covered electrocatalytic H₂O₂ synthesis^[34] and Ti-based hydrogen storage materials^[35]. Based on this, the Fe-Ni₂P@CoP composite catalyst material was designed, in which Fe-Ni₂P nanoparticles are loaded onto a heterophase CoP nanowire array, achieving excellent OER catalytic activity: a current density of 100 mA cm⁻² is reached with an overpotential of only 276 mV. This material can also be applied in an AEM electrolyzer, delivering a high current density of 1.0 A cm⁻² at a voltage of 1.77 V. The novelty of this work lies in the MOF-derived PBA-mediated synthesis with controllable hetero-interface density, the systematic optimization of Fe doping (~3.6 at%), and the demonstration of industrial-level AEMWE performance. Density functional theory (DFT) calculations indicate that the synergistic effect of interface engineering and elemental doping optimizes the electronic structure (d-band center of Ni active sites), ensures a balance between adsorption and desorption of OER intermediates (OH*, O*, and OOH*), and lowers the energy barrier of the rate-determining step (*OH → *O) during the OER process. This research not only provides novel strategies for the modulation of TMP catalysts, but also establishes a theoretical foundation for designing highly efficient water-splitting phosphide materials.

2. Experimental section

2.1. Materials

Nickel (II) chloride hexahydrate (NiCl₂ 6H₂O, analytical reagent grade), trisodium citrate dihydrate (C₆H₅Na₃O₇ 2H₂O, analytical reagent grade), and urea (CO(NH₂)₂, ≥98%) were purchased from Aladdin. Cobalt (II) nitrate hexahydrate (Co(NO₃)₂ 6H₂O, ≥99.0%) and potassium ferricyanide (K₃[Fe(CN)₆], analytical reagent grade) were purchased from MACKLIN. Sodium hypophosphite monohydrate (NaH₂PO₂ H₂O, analytical reagent grade) was purchased from Xiya Reagent. Ammonium chloride (NH₄Cl, analytical reagent grade) was purchased from Tianjin Guangfu Technology Development Co., Ltd. Commercial Pt/C (platinum on carbon) catalyst (40 wt%) was purchased from Johnson Matthey. Ruthenium (IV) oxide (RuO₂, analytical reagent grade) was purchased from Bide Pharmatech Co., Ltd. Nickel foam (NF) was purchased from Beijing Aian Science Co., Ltd., and conductive carbon paper was purchased from Beijing Jingke Instrument Science Co., Ltd.

2.2. Synthesis of Co precursor

First, nickel foam (NF, 2 × 3 cm²) was ultrasonicated in 1 M HCl, deionized water, and ethanol for 10 minutes to remove surface impurities and grease. Then, 2 mmol of Co(NO₃)₂ 6H₂O, 10 mmol of CO(NH₂)₂, and 4 mmol of NH₄Cl were dissolved in 35 mL of deionized water. After stirring uniformly, the solution was transferred into a 50 mL autoclave containing the NF and heated at 120 °C for 8 hours. Finally, the product was taken out, washed and dried.

2.3. Synthesis of PBA@Co pre

Prussian blue analogue (PBA) was synthesized on the Co precursor (Co pre). 1.2 mmol of C₆H₅Na₃O₇ 2H₂O and 0.8 mmol of NiCl₂ 6H₂O were dissolved in 20 mL of deionized water as solution A. Another 0.5 mmol of K₃[Fe(CN)₆] was dissolved in 20 mL of deionized water as solution B. Solution A was stirred, and solution B was slowly added to solution A, followed by further stirring for 5 minutes. Subsequently, the NF loaded with Co pre was immersed into the mixed solution and kept at 60 °C for 4 h, 8 h, 12 h, 16 h, 20 h and 24 h, respectively. The synthesized samples were washed and dried for later use.

2.4. Synthesis of Fe-Ni₂P@CoP

A mass of 1.0 g of NaH₂PO₂ · H₂O was weighed and placed in a porcelain boat, and the PBA@Co precursor was placed in another porcelain boat. Both boats were placed in a tube furnace, with NaH₂PO₂ · H₂O close to the gas inlet and the sample close to the gas outlet. Under an argon atmosphere, the temperature was maintained at 350 °C for 2 hours. After natural cooling, the sample was taken out, washed repeatedly with deionized water and ethanol, and dried for later use.

2.5. Synthesis of CoP and Fe-Ni₂P

Synthesis of CoP: 1.0 g of NaH₂PO₂ · H₂O was weighed and placed in a porcelain boat, while another porcelain boat was loaded with the pre-loaded NF. The two boats were placed in a tube furnace, with NaH₂PO₂ · H₂O positioned close to the gas inlet and the sample close to the gas outlet. Under an argon atmosphere, the temperature was maintained at 350 °C for 2 hours. After natural cooling, the sample was taken out, washed repeatedly with deionized water and ethanol, and dried for subsequent use.

Synthesis of Fe-Ni₂P: PBA was first directly synthesized on NF via an immersion method, and then phosphorized using the same procedure as described above with the only difference being that the NF pre-loaded with the Co precursor was replaced by the NF loaded with PBA.

2.6. Synthesis of RuO₂ and Pt/C electrodes

A mass of 5 mg of RuO₂ was dispersed in a mixture containing 800 µL of isopropanol, 180 µL of deionized water, and 20 µL of FAA-3-SOLUT-10 ionomer solution (10.0 wt%). The mixture was then sonicated for 20 min to obtain a homogeneous suspension. Subsequently, the suspension was transferred to a spray gun and sprayed onto a clean NF surface (1 × 4 cm²). The sample was dried in a vacuum oven. The RuO₂ loading is approximately 1.25 mg cm⁻². The procedure for the Pt/C electrode is similar to that of the RuO₂ electrode, except that the suspension is sprayed onto a carbon paper surface. The Pt/C loading is also approximately 1.25 mg cm⁻².

2.7. Material characterization

The phase composition and crystal structure of the samples were analyzed by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5406 Å). Data were collected in the 2θ

range of 20 ° to 80 ° at a scanning rate of 5 ° min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha+ XPS system equipped with a monochromatic Al Kα X-ray source (1486.6 eV). The binding energies were calibrated relative to the adventitious C 1s peak at 284.8 eV. Survey and high-resolution spectra were acquired with a pass energy of 100 eV and 50 eV, respectively. Data analysis and peak fitting were conducted using the Avantage software. The morphology and microstructure of the catalysts were investigated by scanning electron microscopy (SEM) on a FEI Quanta 200F field-emission microscope operating at an accelerating voltage of 15 kV. Further microstructural analysis, including high-resolution imaging and elemental mapping, was performed by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and high-angle annular dark-field scanning TEM (HAADF-STEM) coupled with energy-dispersive X-ray spectroscopy (EDS). These analyses were conducted on a FEI Tecnai G2 F20 S-TWIN microscope operating at 200 kV. The samples for TEM were prepared by ultrasonically dispersing the powder in ethanol and drop-casting the suspension onto a copper grid coated with a lacey carbon film.

2.8. Electrochemical performance tests

Electrochemical tests were conducted utilizing the CorrTest CS310MA electrochemical workstation. The prepared catalyst acted as the working electrode, while the graphite rod and Ag/AgCl (saturated KCl solution) electrode served as the counter electrode and reference electrode, respectively. Linear scanning voltammetry (LSV) was employed to test the polarization curves at a scan rate of 5 mV s⁻¹. Unless stated otherwise, all potentials were based on the reversible hydrogen electrode, and all polarization curves were corrected for the 90% iR compensation within the cell. The Tafel slope was determined by fitting the corresponding LSV: $\eta = a + b \log j$ (where η and j represent potential and current density, respectively; a and b are constants, with b being the Tafel slope)^[36, 37]. Electrochemical impedance spectroscopy (EIS) was conducted across a frequency spectrum of 100 kHz to 0.1 Hz. To determine the effective surface area of the electrode, non-Faraday zone range cyclic voltammetry (CV) cycles were conducted at various scan rates including 20, 40, 60, 80, 100, and 120 mV s⁻¹. The durability evaluation of the as-prepared electrocatalysts was conducted by galvanostatic measurements for 100 h.

An anion-exchange membrane (AEM) water

electrolyzer was constructed using the prepared catalysts as anode and Pt/C (pasted on carbon paper) as cathode. The tests were carried out using the membrane electrode assembly (MEA), where the cathode and anode catalysts as separated by an anion-exchange membrane ($2 \times 2 \text{ cm}^2$, PiperION-A40-HCO₃, Versogen), and the working electrodes were 1 cm^2 . Electrolysis performance and stability were evaluated with the CorrTest CS310MA electrochemical workstation and CorrTest CS2020B power booster. An alkaline electrolyte (1 M KOH) was continuously circulated using a peristaltic pump to both the anode and cathode sides. The electrolyte temperature was maintained at around 60 °C using a heating plate. For comparison, a standard anion exchange membrane (AEM) water electrolysis cell was constructed using RuO₂ (pasted on nickel foam) as the anode and PtC (pasted on carbon cloth) as the cathode.

2.9. Density functional theory (DFT) calculation

All DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) developed at the University of Vienna. The interaction between the ion core and the valence electron is treated using the augmented plane wave pseudopotential method based on the plane wave basis set. Under the generalized gradient approximation, the PBE (Perdew-Burke-Ernzerhof) function is selected as the exchange-correlation function. In all calculations, the kinetic energy cutoff for the plane waves is set at 400 eV. During the structural relaxation process, the convergence tolerances for energy and force on each atom are set to less than 10^{-5} eV and $0.05 \text{ eV } \text{\AA}^{-1}$, respectively. The Monkhorst-Pack method was utilized with $3 \times 3 \times 1$ k-point samplings for the structural optimization and surface calculations of the Fe-Ni₂P@CoP heterostructures. All structural models were derived from experimental XRD and HRTEM data and established and output using Material Studio and Vesta software. The CoP (002) and Fe-Ni₂P (300) surfaces were constructed and selected these surfaces to construct heterojunctions for computational simulation. All surfaces were set to a vacuum layer thickness of 15 Å. In this work, the free energy of all species was calculated by the formula: $\Delta G = \Delta E_{\text{DFT}} + \Delta ZPE - T\Delta S$, where ΔE_{DFT} , ΔZPE and ΔS were the changes in DFT total energy, zero-point energy, and entropic contributions, respectively. T was temperature and set to be 298.15 K. All DFT calculations in this work are based on the pristine pre-catalyst surface model. They are intended only to reveal the initial electronic structure modulation trend induced by Fe doping and

heterojunction construction prior to surface reconstruction, and are not intended to represent the real catalytic surface under alkaline OER conditions. The reconstructed (oxy)hydroxide active phase is not simulated here.

3. Results and discussion

3.1. Synthesis and characterizations

The synthesis route of Fe-Ni₂P@CoP is illustrated in **Fig. 1a**. First, a Co precursor is synthesized on nickel foam (NF) via a hydrothermal method. Subsequently, the precursor is immersed in a specific solution to grow on Fe-Ni Prussian blue analogue (PBA) on its surface. Finally, the resulting product is phosphorized in a tube furnace to obtain the target Fe-Ni₂P@CoP heterojunction. To investigate the growth behavior and microstructure of the Fe-Ni₂P@CoP heterostructure, the sample and its precursors are characterized by scanning electron microscopy (SEM). As shown in **Fig. S1d**, the CoP backbone exhibits a nanowire array morphology. This in-situ grown nanowire array not only ensures intimate contact with the NF substrate for efficient electron transport, but also provides abundant anchoring sites for the loading of other components owing to its interconnected network ^[11, 38]. **Fig. S1a** reveals that Fe-Ni₂P displays an ill-defined nanocube structure, resembling the morphology of the PBA precursor. **Figs. S1b** and **S1c** present the precursors of Fe-Ni₂P@CoP. The Co precursor (Co pre, before phosphorization) shows a relatively smooth nanowire array (**Fig. S1b**), whereas the PBA-modified Co precursor (PBA@Co pre) gives particulate decoration on the nanowire backbones, indicating the initial formation of a heterointerface. Through this synthetic strategy, heterogeneous assembly of nanoparticles onto the nanowire array is successfully achieved, constructing a unique 0D/1D hierarchical structure.

By adjusting the growth time, the evolution of Fe-Ni₂P nanoparticles on the surface of CoP nanowires could be observed. At the early stages of reaction (4 h and 8 h, **Fig. S1e** and **S1f**), only tiny Fe-Ni₂P nuclei are sparsely scattered on the CoP nanowire surface, with the nanowire backbone remaining clearly visible. At 4 h (**Fig. S1e**), the nanoparticles are barely observable with diameters of only about 2-5 nm. At 8 h (**Fig. S1f**), the particles grow to approximately 5-12 nm with a sparse distribution. At 12 h (**Fig. 1b**), the nanoparticles reach an average size of about 15-30 nm with a significantly increased loading density, achieving an optimal loading amount of Fe-Ni₂P accompanied by an

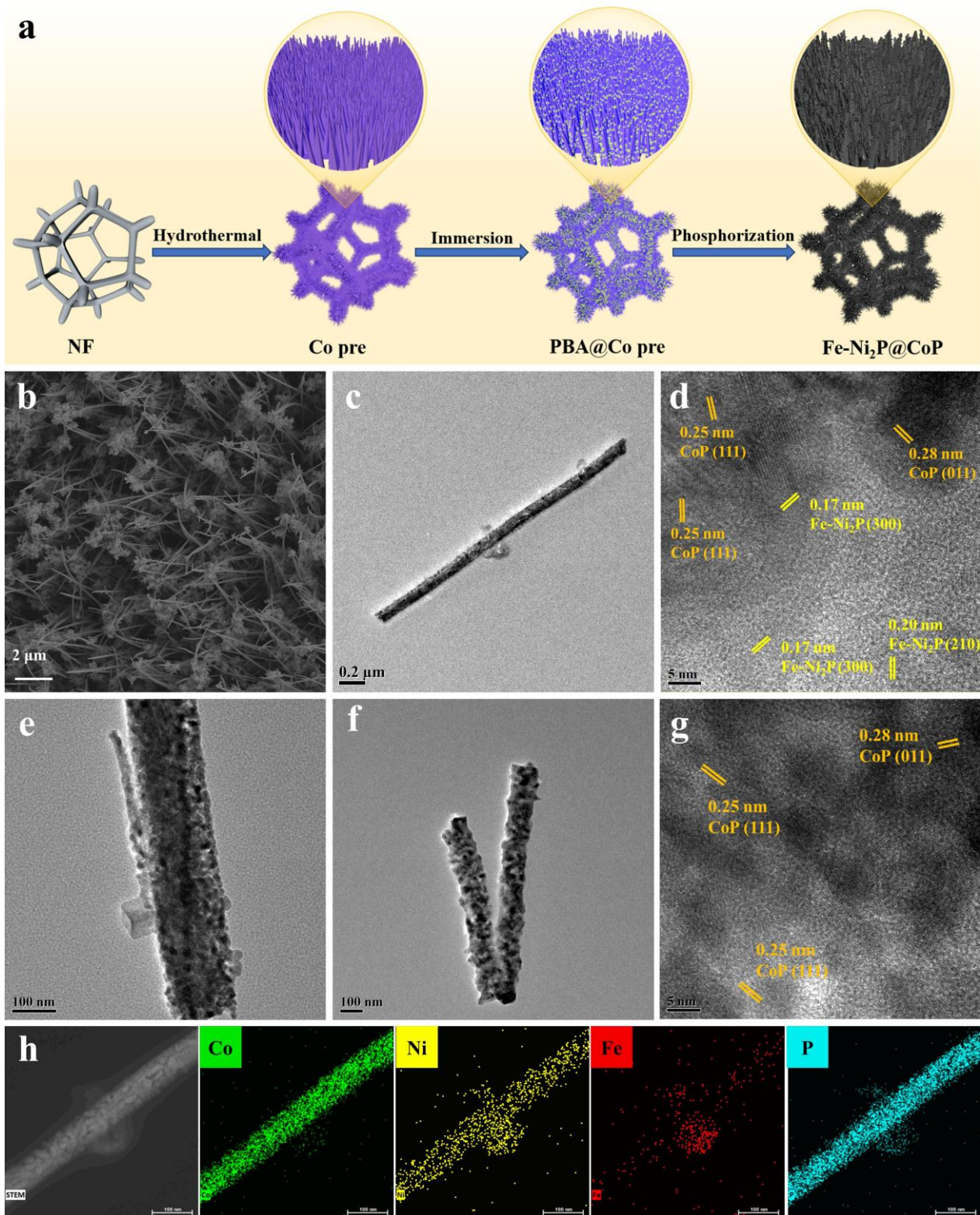


Fig.1. a) Schematic diagram of the synthesis of Fe-Ni₂P@CoP; b) SEM image; c, e) TEM images; d) HR-TEM image of Fe-Ni₂P@CoP sample; f) TEM image of CoP (after phosphorization); g) HR-TEM image of CoP; h) HAADF-STEM image and EDS mapping result of Fe-Ni₂P@CoP sample.

appropriate degree of heterojunction formation and a large active surface area. When the reaction time is extended to 16 h and 20 h (**Fig. S1g and S1h**), excessive Fe-Ni₂P undergoes severe aggregation and overgrowth between the nanowires, with nanoparticle sizes reaching approximately 30-50 nm and 40-60 nm, respectively, and the initially well-defined 0D/1D hierarchical structure gradually becomes blurred. At a reaction time of 24 h (**Fig. S1i**), the Fe-Ni₂P particle layer, with sizes approaching 60-80 nm, has almost completely covered the underlying CoP nanowire array. Such excessive overgrowth reduces the active surface area, hinders electrolyte diffusion to the internal active sites, and impedes bubble release, thereby negatively affecting the catalytic performance, which is confirmed by later OER performance tests. Moreover, it can be found that at the edge of the nickel foam (NF), the morphology is not a simple nanowire array (**Fig. S2**); rather, the nanowires assemble into spherical structures. This is likely because the edge region, being unconfined on both sides, allows for more divergent growth during nucleation and growth. Such a morphology is more favorable for increasing the active surface area and exposing active sites.

In the TEM images of Fe-Ni₂P@CoP (**Fig. 1c and e**), it can be observed that single CoP nanowire is decorated with Fe-Ni₂P nanocubes, and the two components are in intimate contact, which is consistent with the SEM images. In the high-resolution TEM (HR-TEM) image of Fe-Ni₂P@CoP (**Fig. 1d**), lattice fringes corresponding to the (111) and (011) planes of CoP (PDF #29-0497) are visible. In addition, lattice fringes of 0.17 nm and 0.20 nm are observed, which correspond to the (300) and (210) planes of Ni₂P (PDF #74-1385). No iron-related lattice fringes are detected, and no separate Fe phase is observed. Combined with the XRD peak shifts (discussed below) and the Ni 2p chemical shifts in XPS, this confirms that Fe is incorporated into the Ni₂P lattice with a low doping content, without forming a new phase. A close contact between the nanoparticles and the nanowire is evident, and a heterojunction interface exists between them, confirming the successful synthesis of the Fe-Ni₂P@CoP heterojunction catalyst. The CoP sample (after phosphorization) is also characterized by TEM (**Fig. 1f**), showing a nanowire morphology consistent with the SEM observations, with no growth of other materials on its surface. Notably, compared with the relatively smooth Co precursor nanowires (**Fig. S1b**), the CoP nanowires exhibit a slightly roughened surface, which is attributed to the phosphorization process. Meanwhile, **Fig. 1g** presents that CoP has lattice fringes corresponding to those of CoP

(PDF #29-0497). Furthermore, energy-dispersive X-ray spectroscopy (EDS) reveals that Fe, Ni, Co and P are uniformly distributed. Co is almost exclusively distributed on the nanowires, while Fe is predominantly distributed on the nanoparticles, further confirming the successful synthesis of the Fe-Ni₂P@CoP sample.

To further investigate the crystal structure, the phase structures of Fe-Ni₂P@CoP and its precursors at various stages are characterized by X-ray diffraction (XRD). Since all samples are grown in-situ on nickel foam (NF) substrates, strong diffraction peaks corresponding to Ni (PDF #04-0850) appear at $2\theta = 44.5^\circ$, 51.8° and 76.4° in all patterns. As shown in **Fig. 2a**, the diffraction peaks of the Fe-Ni₂P@CoP sample at 31.6° , 36.3° and 48.1° are assigned to the (011), (111) and (211) planes of CoP (PDF #29-0497), while characteristic peaks corresponding to the (111), (210) and (300) planes of Ni₂P (PDF #74-1385) are also observed. No diffraction peaks related to Fe are detected due to its low content, which is consistent with the TEM results, collectively confirming the successful synthesis of the Fe-doped Ni₂P@CoP catalyst on NF. Notably, the XRD pattern of Fe-Ni₂P@CoP also contains some peaks belonging to K₂FeNi(CN)₆ (PDF #20-0915), indicating partial residue of the PBA precursor, which may be associated with the heterointerface. The precursors before phosphorization are also characterized by XRD (**Fig. 2b**). For Co pre and PBA@Co pre, the diffraction peaks at $2\theta = 9.9^\circ$, 17.5° , 26.8° and 33.8° correspond to the (100), (020), (220) and (221) planes of Co(CO₃)_{0.5}(OH) (PDF #48-0083). Meanwhile, the diffraction peaks of PBA@Co pre at $2\theta = 17.6^\circ$, 24.9° , 35.8° and 57.9° are assigned to the (200), (220), (400) and (620) planes of K₂FeNi(CN)₆ (PDF #20-0915). This transformation process not only confirms the effectiveness of the phosphorization strategy but also demonstrates that the material undergoes compositional reconstruction while preserving its original morphology, laying a structural foundation for enhanced electrochemical performance. Furthermore, two reference samples, Fe-Ni₂P and CoP, are also characterized by XRD (**Fig. S4a**), further verifying the rationality of the synthesis method and the successful preparation of the samples.

After identifying the crystal phases of the samples, X-ray photoelectron spectroscopy (XPS) is employed to analyze the surface elemental valence states and electronic states of the Fe-Ni₂P@CoP heterostructure. The survey spectrum (**Fig. S4b**) confirms the presence of Co, Ni, Fe, P, and O in the system. In the high-resolution Ni 2p spectrum (**Fig. 2c**), Fe-Ni₂P@CoP exhibits complex valence state distributions: the peaks at 856.5 eV and 874.1 eV

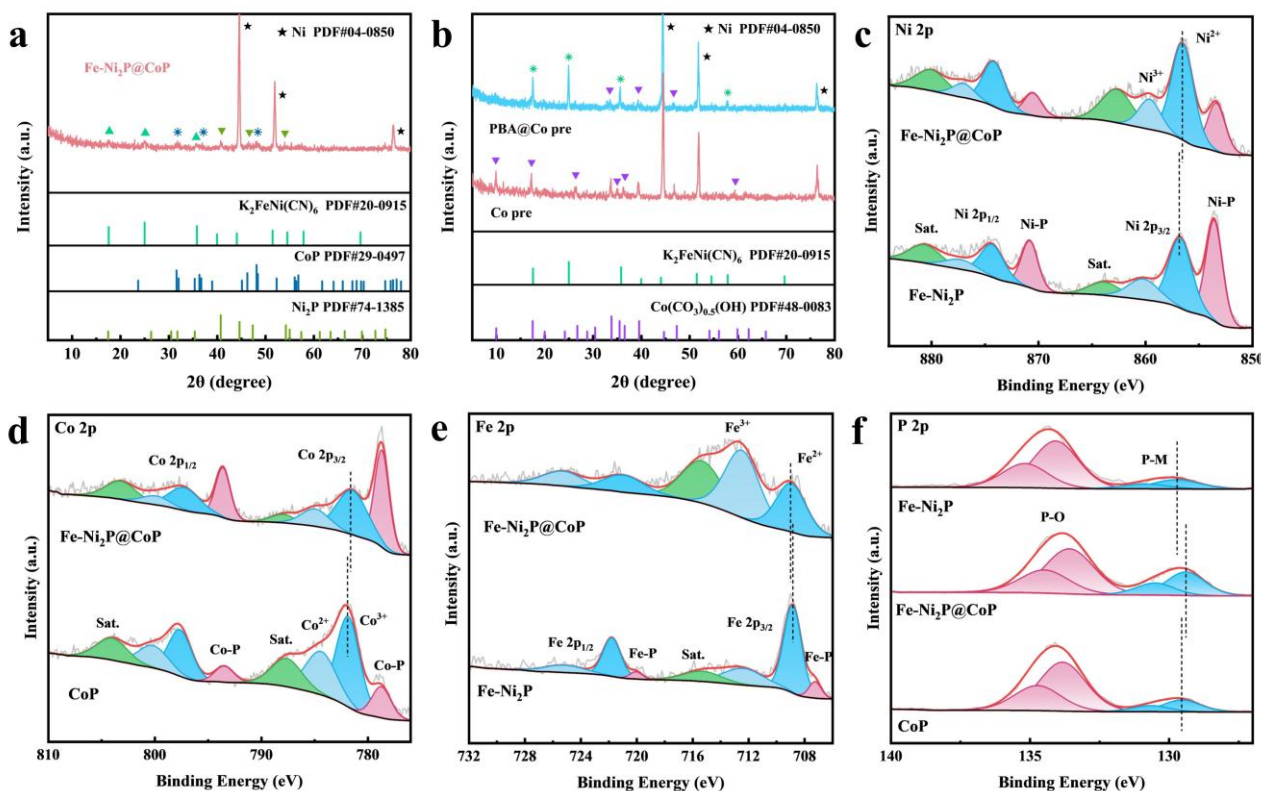


Fig.2. XRD patterns of a) Fe-Ni₂P@CoP and b) its precursor; High-resolution XPS spectra of c) Ni 2p, d) Co 2p, e) Fe 2p, and f) P 2p for different samples.

correspond to the Ni²⁺ 2p_{3/2} and Ni²⁺ 2p_{1/2} orbitals, while those at 859.6 eV and 876.7 eV correspond to the Ni³⁺ 2p_{3/2} and Ni³⁺ 2p_{1/2} orbitals [39, 40]. Additionally, peaks corresponding to Ni-P bonds are also observed, indicating the formation of phosphides. In the Co 2p XPS spectrum (Fig. 2d), Fe-Ni₂P@CoP shows characteristic peaks of the Co³⁺ (781.5 eV/797.3 eV) and Co²⁺ (784.9 eV/799.9 eV) 2p_{3/2} and 2p_{1/2} orbitals, as well as peaks assigned to Co-P bonds [41, 42]. In Fig. 2e, Fe-Ni₂P@CoP illustrates characteristic peaks corresponding to Fe²⁺ and Fe³⁺ in their 2p_{3/2} and 2p_{1/2} orbitals [4, 43]. In the high-resolution P 2p spectrum, in addition to the characteristic peaks of P-M bonds, peaks corresponding to P-O are also presented, which mainly originate from surface oxidation of the material upon exposure to air [44, 45].

In addition to the XPS fine-spectrum analysis of the Fe-Ni₂P@CoP sample, comparisons with the single components are also conducted to investigate the charge transfer behavior. Compared with the Ni 2p peak in Fe-Ni₂P (856.7 eV), the corresponding peak in Fe-Ni₂P@CoP exhibits a negative shift of 0.2 eV, indicating electron gain. Compared with the Co 2p peak

in CoP (781.8 eV), the corresponding peak in Fe-Ni₂P@CoP shifts by 0.3 eV toward lower binding energy, also indicating electron gain. However, the Fe 2p peak in Fe-Ni₂P@CoP shifts by 0.2 eV toward higher binding energy relative to that in Fe-Ni₂P, suggesting electron loss. Collectively, these results demonstrate that after the formation of the heterojunction between Fe-Ni₂P and CoP, charge redistribution occurs at the heterointerface, with electrons transferring from Fe atoms to Co and Ni atoms. This modulation of the electronic structure can tune the adsorption strength of surface active sites toward water and reaction intermediates, optimize the adsorption energies, and thereby enhance the intrinsic catalytic activity [46].

3.2 Electrochemical performance of OER

The electrochemical (OER) performance of the synthesized Fe-Ni₂P@CoP catalysts was evaluated via LSV in a standard three-electrode system. First, LSV measurements are performed on Fe-Ni₂P@CoP samples with different immersion times (4 h, 8 h, 12 h,

16 h, 20 h, and 24 h, **Fig. S5**). The sample with an immersion time of 12 h demonstrates the best OER catalytic activity, with the lowest overpotential (276 mV at 100 mA cm^{-2}), while the 16 h, 20 h, and 24 h samples show progressively degraded performance (**Fig. S5**), consistent with the morphological evolution observed by SEM. Combined with the SEM analysis, this phenomenon may be attributed to the fact that, compared with shorter immersion times (4 h and 8 h), the 12 h immersion process leads to a higher amount of Fe-Ni₂P growth and more effective modulation of the electronic structure. Prolonged immersion (16 h, 20 h and 24 h) would result in complete coverage of the underlying CoP, causing the disappearance of the nanowire array morphology, which reduces the exposed active surface area and thus the number of active sites. An immersion time of 12 h avoids these issues and illustrates best electrocatalytic performance.

Subsequently, the Fe-Ni₂P@CoP sample with immersion time of 12 h is selected for comparison with other catalysts. As shown in **Fig. 3a** and **b**, Fe-Ni₂P@CoP achieves a current density of 100 mA cm^{-2} at an overpotential of only 276 mV, outperforming Fe-Ni₂P (312 mV), CoP (347 mV) and pure NF (628 mV). It also illustrates excellent catalytic activity at high current densities ($\eta_{500} = 349 \text{ mV}$). The reaction kinetics are also investigated using Tafel plots (**Fig. 3c**). The Tafel slope of Fe-Ni₂P@CoP is only 42.2 mV dec^{-1} , which is significantly lower than those of Fe-Ni₂P, CoP and pure NF, indicating faster electron transfer kinetics after heterojunction formation [47, 48]. This result is further confirmed by electrochemical impedance spectroscopy (EIS, **Fig. 3e**). The semicircle diameter exhibited by the Fe-Ni₂P@CoP electrode is comparable to that of Fe-Ni₂P and smaller than those of CoP and pure NF, implying that it inherits the low charge

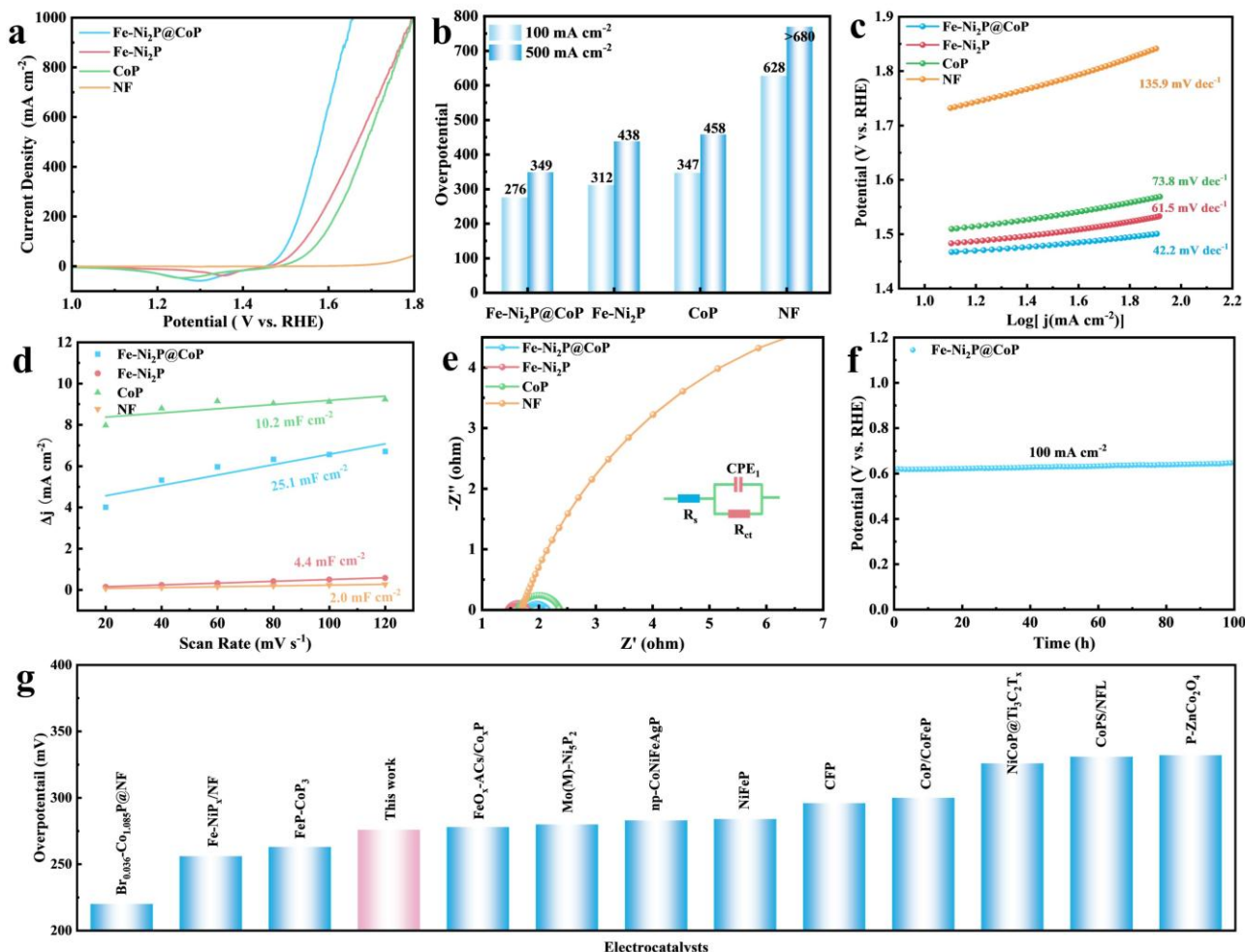


Fig.3. a) LSV curves, b) overpotentials, c) Tafel slopes, d) C_{dl} , and e) EIS spectra of different phosphide samples; f) chronopotentiometric curve of Fe-Ni₂P@CoP over 100 hours; g) comparison of overpotentials between Fe-Ni₂P@CoP and reported catalysts (Table S1).

transfer resistance (R_{ct}) of Fe-Ni₂P^[49, 50]. In addition, CV measurements are performed on different samples at various scan rates (**Fig. S6**), and the double-layer capacitance (C_{dl}) is calculated to evaluate the relative electrochemical active surface area (ECSA) of the electrodes (**Fig. 3d**). Fe-Ni₂P@CoP exhibits the highest C_{dl} value (25.1 mF cm⁻²), indicating that it possesses a larger active surface area and can expose more catalytic active sites^[7, 51].

For practical applications, excellent catalytic activity must be accompanied by long-term stability. To evaluate the stability, the Fe-Ni₂P@CoP catalyst is tested at a constant current density of 100 mA cm⁻² for 100 h (**Fig. 3f**). During this period, the voltage of the electrode does not change significantly, demonstrating outstanding stability. After the OER stability test, the sample is characterized by SEM (**Fig. S7a**). The nanowire array appears slightly roughened, but the overall morphology shows no significant change, indicating excellent structural integrity. Furthermore, the XRD pattern of the sample after the stability test (**Fig. S8**) exhibits no new peaks, and the original peaks show no noticeable shift, confirming that the crystal phase remains unchanged. These results further demonstrate the excellent stability of the Fe-Ni₂P@CoP material. Finally, Fe-Ni₂P@CoP is compared with previously reported OER catalysts (**Fig. 3g** and **Table S1**), showing that its OER catalytic activity is currently at an above-average level.

To verify surface reconstruction, Raman spectroscopy was performed on the post-OER Fe-Ni₂P@CoP electrode (**Fig. S9**). The peaks at 501, 552, 590, and 653 cm⁻¹ are assigned to CoOOH (E_g), NiOOH (Ni-O), high-valent Co(IV) species and CoOOH (A_{1g}), respectively, confirming the reconstruction of the phosphide surface into NiOOH/CoOOH active phases under alkaline OER conditions^[52-54].

3.3 Electrocatalytic OER mechanism investigation

Under alkaline OER conditions, the true active phase is the reconstructed (oxy)hydroxide, as confirmed by our post-OER Raman results (**Fig. S9**). Therefore, the DFT results should be understood as the intrinsic electronic origin of the enhanced activity of the pre-catalyst, rather than a direct simulation of the catalytic cycle on the reconstructed surface. Density functional theory (DFT) calculations are further performed to investigate the electronic structure modulation of the Fe-Ni₂P@CoP catalyst and the mechanism underlying its enhanced OER performance. First, the corresponding structural models are constructed based

on XRD and TEM results, along with models of the adsorbed structures during the OER process (**Fig. S10**). Charge density difference calculations are then carried out (**Fig. 4a**). The clearly defined electron accumulation (yellow) and depletion (cyan) regions indicate that charge transfer occurs at the heterointerface after heterojunction formation, corroborating the XPS results. Such charge redistribution modifies the electronic structure of the material surface, thereby enhancing the catalytic activity. It should be noted that our DFT calculations are based on the pre-catalyst surface model, aiming to reveal the modulation mechanism of doping and interface engineering on the intrinsic electronic structure, which is fundamental to understanding the enhanced catalytic activity^[55].

The density of states (DOS) analysis (**Fig. 4b**) shows that both Fe-Ni₂P@CoP and its reference samples exhibit continuous and non-zero DOS near the Fermi level, indicating that the heterojunction retains metallic-like conductive characteristics with low charge-transfer resistance. Furthermore, projected density of states (PDOS, **Fig. 4c**) is used to explore the correlation between electronic structure and performance enhancement. With the Fermi level set to 0 eV, the *d*-band center of Fe-Ni₂P is determined to be -1.73 eV, CoP: -1.23 eV and Fe-Ni₂P@CoP: -1.28 eV. The shift of the Ni *d*-band center from -1.73 eV (Fe-Ni₂P) to -1.28 eV (Fe-Ni₂P@CoP) originates from electron transfer from Fe to Ni (as evidenced by XPS), which moves the *d*-band center closer to the Fermi level and optimizes the adsorption strength of oxygen intermediates. The distance from the *d*-band center to the Fermi level reflects the strength of intermediate adsorption. Fe-Ni₂P@CoP lies between the two reference samples, following the Sabatier principle, which achieves a dynamic balance between the adsorption and desorption of reaction intermediates at the active sites^[56, 57]. This finding is corroborated by the experimental kinetic indicators, particularly the significantly reduced Tafel slope and charge-transfer resistance.

The Gibbs free energy of the OER process is calculated to analyze the experimentally observed excellent OER activity from a thermodynamic perspective (**Fig. 4d**). At zero potential, the rate-determining step (RDS) for both Fe-Ni₂P and Fe-Ni₂P@CoP is the second reaction step (*OH → *O). For Fe-Ni₂P, the binding energy of OH is relatively too strong due to its electronic structure, resulting in the highest energy barrier for this step. After heterojunction formation, the electronic reconstruction facilitates this step, lowering the energy barrier of the

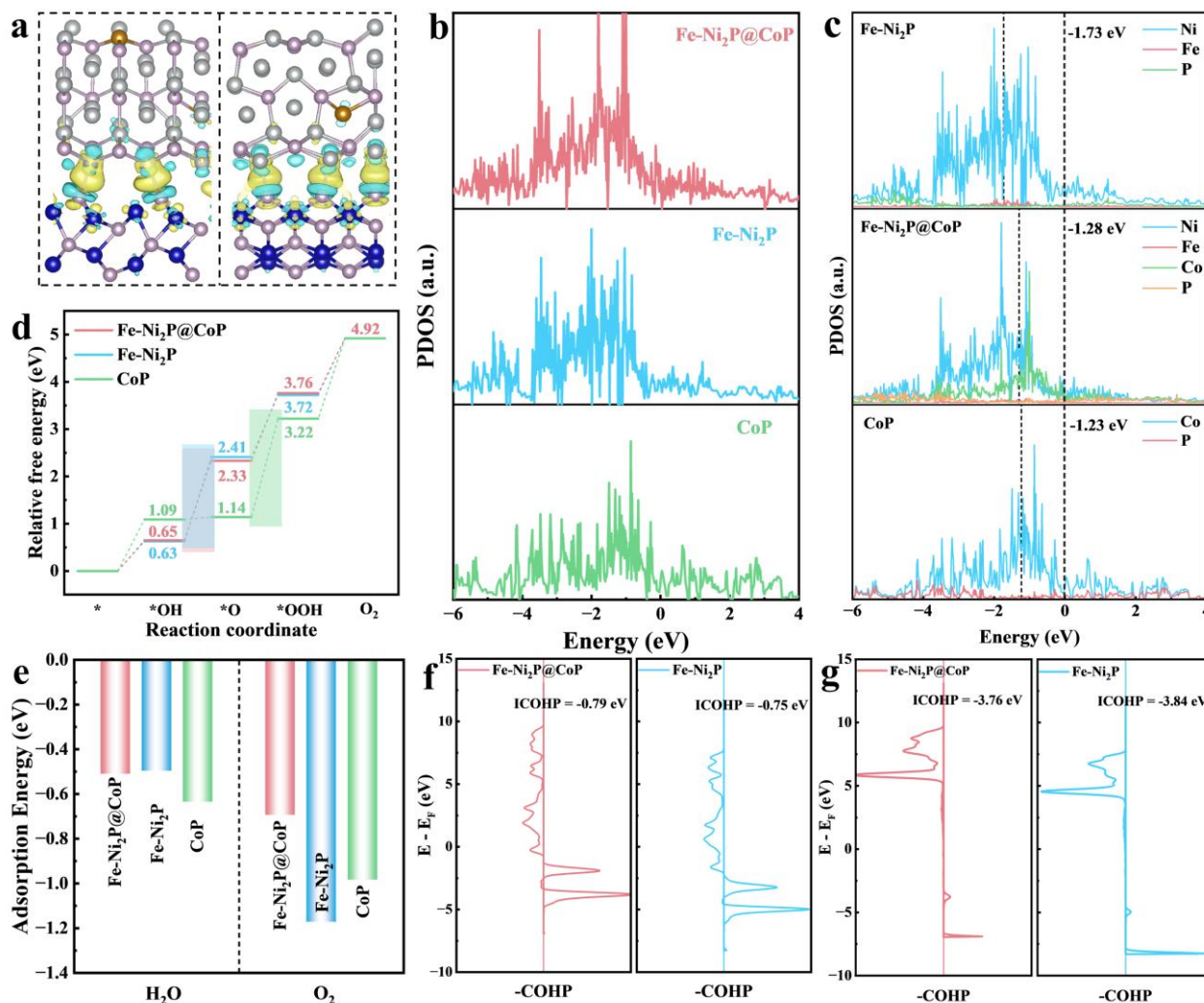


Fig.4. a) Charge density difference diagrams of Fe-Ni₂P@CoP (front view and side view); b) Density of states (DOS) diagrams; c) Projected density of states (PDOS); d) Calculated free energy diagrams of OER intermediates at U = 0. The diagram is based on the pristine pre-catalyst model and only reflects the electronic modulation by Fe doping and heterojunction construction, not the real catalytic behavior of the reconstructed (oxy)hydroxide phase; e) Adsorption energies of water and oxygen for different samples; f) Calculated COHP of Ni-O bond and g) O-H bond in Fe-Ni₂P@CoP and Fe-Ni₂P.

RDS to 1.68 eV and accelerating the evolution of intermediates. In contrast, the RDS for CoP is the third reaction step (*O → *OOH), which has a higher energy barrier and is less favorable. The balanced adsorption and desorption of reaction intermediates optimizes the RDS pathway and lowers the overall energy barriers, thereby achieving enhanced overall kinetic performance for the oxygen evolution reaction.

To further analyze the adsorption and desorption processes, the adsorption energies of water molecules and oxygen molecules are calculated (Fig. 4e). The results display that Fe-Ni₂P@CoP exhibits a water adsorption energy of -0.50 eV, which lies between

those of Fe-Ni₂P (-0.51 eV) and CoP (-0.63 eV), indicating that the heterojunction surface is hydrophilic, facilitating water adsorption and initial dissociation while ensuring the progression of subsequent reactions. The oxygen adsorption energy of Fe-Ni₂P@CoP is -0.69 eV, which is lower than those of Fe-Ni₂P (-1.17 eV) and CoP (-0.98 eV), suggesting that heterojunction formation favors oxygen release, prevents poisoning of active sites, and thus enables the catalytic cycle to proceed.

The strength of key chemical bonds is analyzed using Crystal Orbital Hamilton Population (COHP). An increase in the integrated area of the electronic states of

antibonding orbitals indicates that more electronic states occupy the antibonding orbitals, while an increase in the integrated area of bonding orbitals indicates greater occupation of bonding orbitals^[58, 59]. From these values, the integrated COHP (ICOHP) can be obtained, where a more negative ICOHP value corresponds to stronger bonding, and vice versa^[60]. In **Fig. 4f**, the bonding between metal and oxygen atoms in Fe-Ni₂P@CoP (ICOHP = -0.79 eV) is stronger than that in Fe-Ni₂P (ICOHP = -0.75 eV), indicating that the Ni-O bond in Fe-Ni₂P@CoP possesses a higher binding energy, which favors water adsorption. In **Fig. 4g**, the O-H bond in Fe-Ni₂P@CoP illustrates weaker binding energy, which facilitates bond cleavage and promotes oxygen release. These results are mutually consistent with the PDOS and adsorption energy calculations, further demonstrating that the modulation of the electronic structure achieves a balance between the adsorption and desorption of reaction intermediates.

3.4 Evaluation of AEMWE performance

The as-prepared Fe-Ni₂P@CoP catalyst displays excellent OER catalytic activity in three-electrode electrochemical tests. To evaluate its potential for

industrial applications, the Fe-Ni₂P@CoP is used as anode catalyst with Pt/C as the cathode to assemble anion-exchange membrane (AEM) electrolyzer (Fe-Ni₂P@CoP || Pt/C, **Fig. 5a**) using PiperION-A40-HCO₃ Versogen membrane, and its overall water splitting performance is evaluated at 60 °C (**Fig. S11**). As shown in **Fig. 5b**, the electrolyzer presents outstanding activity and a low overpotential. A cell voltage of only 1.77 V is required to achieve a high current density of 1.0 A cm⁻², and a voltage of 1.96 V is sufficient to reach an even higher current density of 2.0 A cm⁻². This performance is significantly superior to that of a reference electrolyzer assembled with commercial noble metal catalysts (RuO₂ || Pt/C) in our laboratory. Moreover, it is also at an advanced level compared with most recently reported catalyst systems (**Fig. 5d** and **Table 2**), fully demonstrating the high energy conversion efficiency of Fe-Ni₂P@CoP in practical working environments and its great potential to replace noble metals.

In addition to excellent catalytic activity, long-term operational stability is also critical for practical applications. The Fe-Ni₂P@CoP || Pt/C electrolyzer is subjected to a galvanostatic test at a high current density of 1.0 A cm⁻² for 100 h. As shown in **Fig. 5c**, the voltage of the electrolyzer does not exhibit a

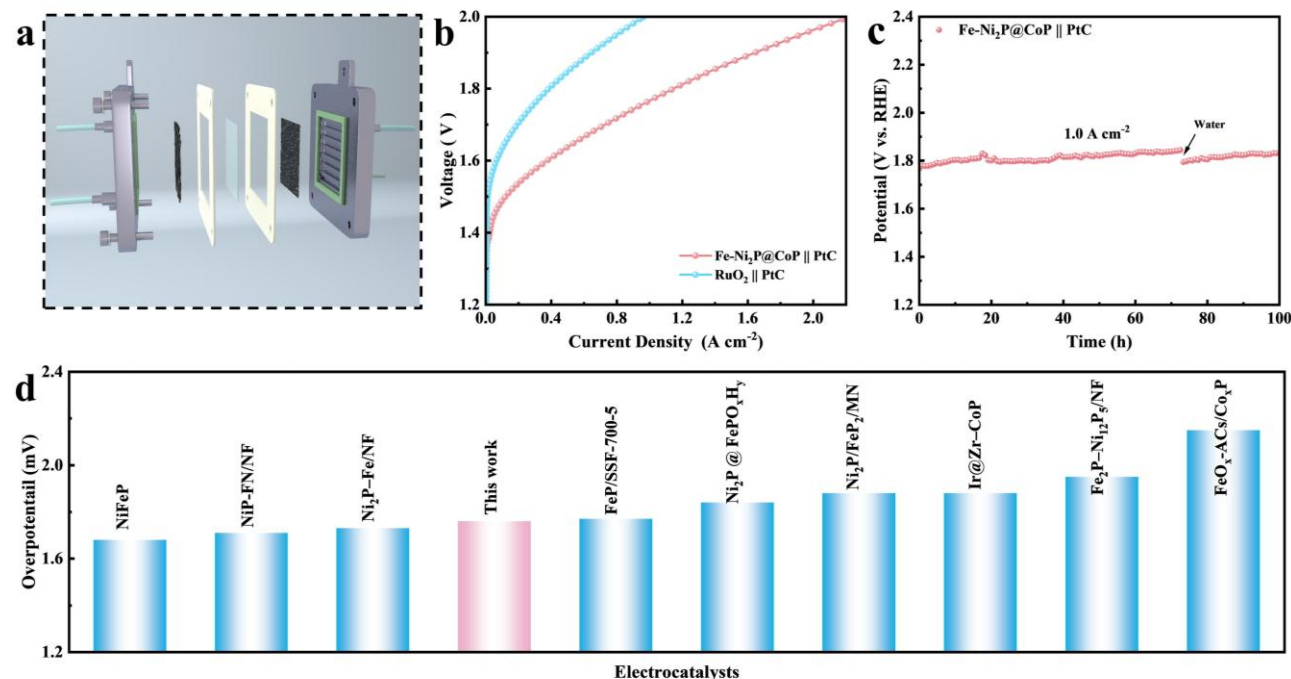


Fig.5. a) Schematic illustration of AEMWE electrolyzers; b) Polarization curves of AEMWEs using Fe-Ni₂P@CoP and RuO₂ as the anode in 1 M KOH at 60 °C; c) Chronopotentiometry of the electrolyzer at 1.0 A cm⁻²; d) Comparison of cell voltages with values reported in the literatures.

significant increasing trend during the 100 h stability test, demonstrating the outstanding stability of the Fe-Ni₂P@CoP || Pt/C electrolyzer. Furthermore, the electrode material after the stability test is analyzed for phase and morphology. The XRD pattern (**Fig. S8**) shows that Fe-Ni₂P@CoP retains its original characteristic diffraction peaks after the reaction, with no new peaks or peak shifts, indicating that the crystal structure of the catalyst remains intact without phase transformation. Meanwhile, the SEM image (**Fig. S7b**) reveals that the microstructure still maintains the nanowire array morphology, only becoming slightly rougher without obvious structural collapse, further confirming structural integrity. This excellent structural stability is the fundamental reason for the high durability of the sample in terms of macroscopic performance.

4. Conclusion

In summary, the Fe-Ni₂P@CoP heterojunction catalyst was successfully synthesized via a three step method. Characterization reveals that Fe-Ni₂P nanoparticles are uniformly loaded on the CoP nanowire array, and this microstructure provides a larger active surface area and more active sites. Electrochemical measurements show that the catalyst exhibits excellent OER catalytic activity (η_{100} = 276 mV). Moreover, when employed as the anode in an anion exchange membrane electrolyzer, it requires a cell voltage of only 1.77 V to achieve a high current density of 1.0 A cm⁻² suitable for industrial application. Structural modeling and DFT calculations display that Fe doping and heterojunction construction facilitate charge transfer, leading to modulated electronic structures, optimized adsorption of reaction intermediates on active sites, and reduced energy barriers, thereby enhancing catalytic activity. This work demonstrates the synergistic construction of a catalyst via doping and structural engineering and analyzes the underlying mechanism, providing a reference for the design and mechanistic understanding of advanced catalysts. Future work will focus on evaluating catalyst performance under simulated fluctuating conditions to further validate its industrial viability.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article. Lei Ge is an Editorial

Board Member of this journal and he was not involved in the editorial review or the decision to publish this article.

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