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Heterostructured Co₂P Nanocomposite Embedded in a N, P Co-Doped Carbon Layer as a High Performance Electrocatalyst for Overall Water Splitting

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Abstract: Hydrogen is the mainstream future energy source because of its high energy density and environmentally-friendly properties. In this study, Fe-Co₂P/NPC materials were prepared by the wet chemical synthesis method, in which Fe-Co₂P nanowires were wrapped by the N, P co-doped carbon layers (NPC) under aging and phosphorylation strategies. When Fe-Co₂P/NPC/NF was subjected to hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), the overpotential was only 73 mV and 217 mV to reach the current density of 10 mA cm⁻², respectively. When the cathode and anode were both Fe-Co₂P/NPC/NF, a current density of 10 mA cm⁻² was achieved with only 1.56 V. This work provides a new idea for the design and preparation of non-precious metal-based transition metal phosphide catalysts.

Keywords: transition metal phosphide; water splitting; hydrogen evolution; oxygen evolution; N, P co-doped carbon



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1. Introduction

There are growing concerns about rapid energy consumption, gradually increasing CO₂ emissions, and serious environmental issues reported by the International Energy Agency [1,2]. Therefore, it is necessary to develop emerging energy sources to address the significant threat associated with fossil fuel combustion [3]. Hydrogen produced by water splitting is a sustainable substitute for conventional fossil fuels owing to its high energy density by weight (up to 142 MJ⁻¹) and environmental friendliness [4–6]. Electrochemical water splitting involves the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) [7–10]. This is considered a promising pathway for hydrogen generation, which is also an important component of fuel cells and metal–air batteries and has attracted great interest in the past decades. The HER and OER require noble metals and their oxides; for example, Ru/Ir-based and Pt-based catalysts are used for the OER and HER, respectively [11]. These catalysts aim at reducing the overpotential and improving the energy conversion efficiency. However, these noble metal catalysts are expensive; hence, their commercial application in water splitting is limited. To overcome this shortcoming, there is an urgent need to design and develop high-performance electrocatalysts based on non-noble metals [12–15].

To date, transition metal phosphides (TMP) have been widely studied because of their abundant earth content and high electrocatalytic activity, especially Co-based phosphides, which have shown obvious advantages when employed in water electrolysis because of their low cost and good catalytic activity for the HER and OER [16]. Metal cation doping has been considered a promising strategy to boost the intrinsic catalytic activity of the active sites, as it may not only enhance electron transfer during electrocatalysis but also modify the electronic structure of the catalysts that further optimize the reaction

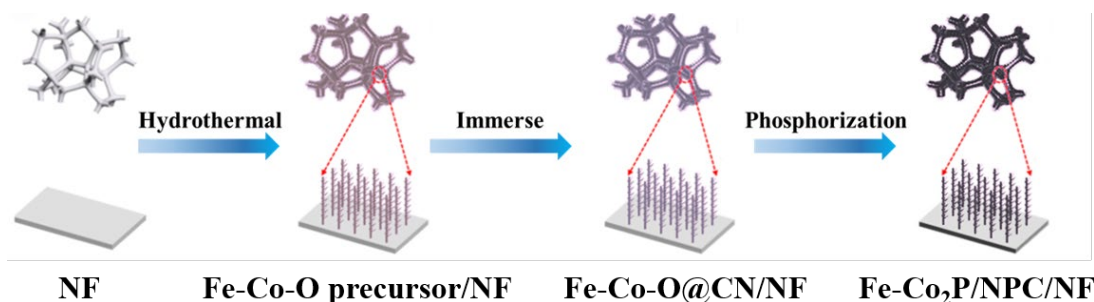
energy barrier for the HER or OER, for example, Ni, Mo, and Fe doping has been reported to be effective for improving the catalytic activity of TMPs [17,18]. Owing to their fast charge transfer and excellent reaction kinetics, TMP-based electrocatalysts have been considered the most possible alternatives to noble metal catalysts [19–22]. However, their electrocatalytic performance must be improved for water splitting. The HER and OER are also effectively catalyzed in the same electrolyte to minimize the thermodynamic barrier of the reaction system. In TMP catalysts, phosphorus and metal sites are used as proton receptors and hydride receptors, respectively, resulting in outstanding conductivity and robust active sites [23–25]. However, the adhesion and pathways of the generated gas bubbles (H_2 and O_2) are equally important factors in water splitting [26–28]. Therefore, directly constructing hierarchical nanomaterials with three-dimensional (3D) architecture may alleviate the above issues due to their unique structural advantages, and also can be beneficial for their surface area, mass, and charge transport. For instance, CoP [29], Cu_3P [30], FeP [31], MoP [32], and Ni_2P [33] are considered promising electrocatalysts because of their low cost, suitable energy band structure, and high electrochemical stability. Although significant progress has been made with TMPs, their clumsy conductivity limits their catalytic activity. In this regard, catalytic efficiency can be further improved by coupling TMP-based catalysts with carbon nanomaterials [34,35].

In this study, a novel hybrid nanostructure of Co_2P nanowire arrays was designed using an improved wet chemical synthesis strategy. The nanostructure was uniformly wrapped in ultrathin N, P-doped carbon layers (donated as NPC). As a result, a monolithic water decomposition electrocatalyst (Fe- Co_2P /NPC/NF) with excellent structure and performance was obtained on an NF substrate by in situ growth technology. Owing to the electronic structure of Co_2P , the prepared water decomposition catalyst provides more active sites. Moreover, the high stability of the ultrathin N, P-doped carbon layers can effectively safeguard the catalyst from degradation and agglomeration in an alkaline electrolyte. Detailed studies showed that Fe- Co_2P /NPC/NF exhibited extraordinary electrocatalytic performance in the HER (overpotential of 73 mV at 10 mA cm^{-2}) and OER (overpotential of 217 mV at 10 mA cm^{-2}). More importantly, the cell assembled by Fe- Co_2P /NPC/NF consumes as low as 1.56 and 1.68 V (at 10 and 100 mA cm^{-2} , respectively) of electrolysis water at 100 mA cm^{-2} for 20 h, and some of its performance is even better than those of the cells containing commercial Pt/C and RuO_2 catalysts.

2. Results and Discussion

Scheme 1 illustrates the fabrication process of the Fe- Co_2P /NPC/NF catalyst. Please consider referring to the supporting information for more information on the preparation process. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) was used to analyze the topography and microstructure of the Fe- Co_2P /NPC/NF catalysts, as shown in Figure 1A,B. Fe-doped Co_2P nanowires encapsulated with a N, P co-doped carbon protective layer were uniformly grown on the surface of the NF, resulting in a multihole and loose surface on the Fe- Co_2P /NPC/NF catalyst. Compared to the original NF and obtained precursor catalysts, this unique heterostructure with a hierarchical structure offers basic internal units and a large surface area that can contact the ion and facilitate the electrocatalytic reaction of water splitting. Furthermore, the surface of the NF was completely wrapped with the Fe-Co-O precursor nanoarray (Figure S1) and exhibited morphological evolution of the hybrid structure in the reaction stages. As shown in Figure 1C,D, the TEM images confirm that the Fe- Co_2P /NPC nanowires had a width of approximately 100 nm. Moreover, a carbon layer of the N, P co-doped protective shell was wrapped tightly to the surface. Several bicontinuous and open pores on the surface further confirm that the resulting N, P co-doped shell grew uniformly on the nanoarray and provided more electroactive sites for water splitting. The co-doped carbon thin layer with a thickness of $\sim 5\text{ nm}$ also prevented the oxidation and aggregation of the Fe- Co_2P NWs. As shown in Figure 1E, the high-resolution TEM (HRTEM) image indicates that the lattice spacings of 0.283 nm and 0.245 nm correspond to the (120) lattice plane for the Co_2P

substrate material and the (200) lattice plane for the Fe_2P crystallized material, respectively. More heterointerfaces and disordered structures derived from the lattice mismatch of Co_2P and Fe_2P crystallized nanoparticles could result in rich defects and active sites. As shown in Figure 1F, the selected area electron diffraction (SAED) pattern of the $\text{Fe-Co}_2\text{P}/\text{NPC}$ catalyst revealed diffraction rings corresponding to the (120), (031), and (320) planes of Co_2P and the (200) plane of Fe_2P . Furthermore, energy-dispersive X-ray spectrometry mapping (EDS) showed a homogeneous distribution of Fe, Co, N, P, and C in $\text{Fe-Co}_2\text{P}/\text{NPC}$ (Figure 1G).



Scheme 1. Schematic illustration of the preparation process of $\text{Fe-Co}_2\text{P}/\text{NPC}/\text{NF}$.

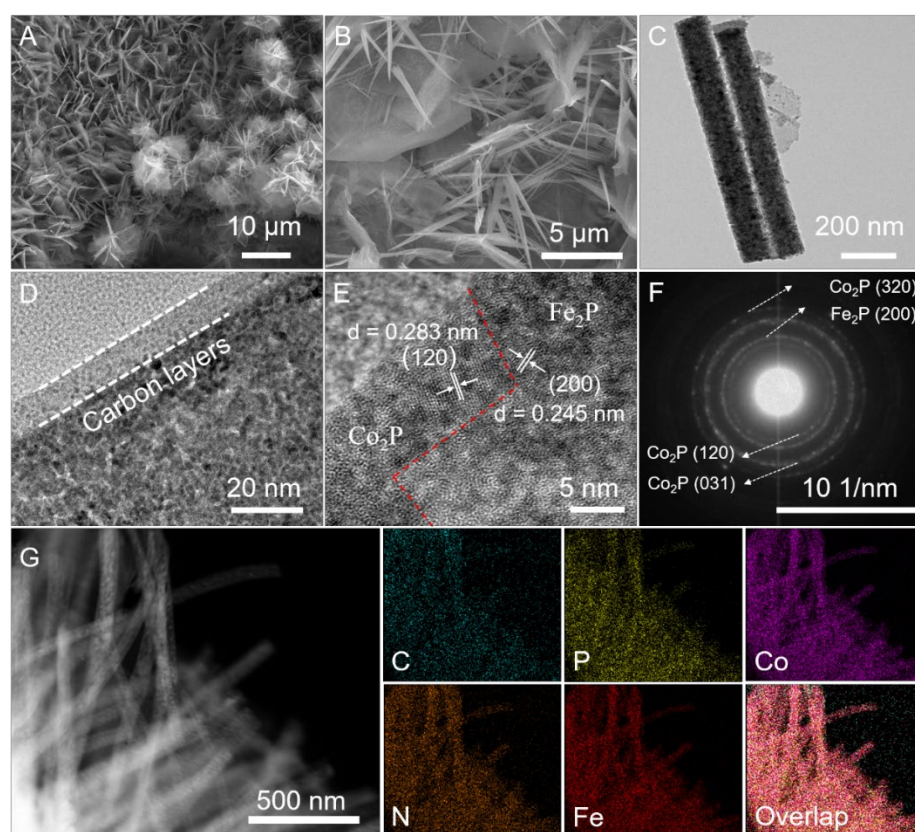


Figure 1. (A,B) SEM images, (C,D) TEM images, (E) HRTEM image, (F) SAED patterns, and (G) HAADF-STEM image and EDS mapping of the $\text{Fe-Co}_2\text{P}/\text{NPC}/\text{NF}$ catalyst.

The crystal phases of the $\text{Fe-Co}_2\text{P}/\text{NPC}/\text{NF}$ catalyst were investigated by X-ray diffraction (XRD). As shown in Figure 2B, the characteristic peaks at 42.5° , 43.3° , 44.1° , 50.4° , 52.0° , and 56.2° correspond to the (220), (211), (130), (310), (002), and (320) crystal planes of Co_2P (PDF#32-0306), respectively. In addition, three characteristic peaks at 40.3° , 47.2° , and 54.6° confirm that the (111), (210), and (211) crystal planes of Fe_2P (JCPDS#83-2337) were also formed in the $\text{Fe-Co}_2\text{P}/\text{NPC}/\text{NF}$ catalyst (Figure 2A shows the precursor of Fe-doped CoO_2). It is important to investigate the composition and surface chemical state because

water-splitting reactions mainly occur on the surface of the obtained catalysts. The elements Fe, Co, and P were probed in the X-ray photoelectron spectroscopy (XPS) survey spectrum (Figure 2C), which is consistent with the EDS results mentioned above. Two characteristic peaks at 129.8 eV and 130.9 eV in Figure 2D are ascribed to P 2p_{1/2} and P 2p_{3/2} and correspond to the existing metal phosphates. The weak peak at 134.3 eV corresponds to phosphate or phosphite (P-O) owing to the exposed air environment [36–39]. As shown in Figure 2E, the binding energies at 778.7 eV of Co 2p_{1/2} and 793.6 eV of Co 2p_{3/2} correspond to Co³⁺ or Co⁴⁺, respectively. The Co 2p_{1/2} and Co 2p_{3/2} peaks of the precursor are located at 780.7 eV and 796.5 eV, respectively. The Co 2p_{1/2} and Co 2p_{3/2} peaks shifted negatively by approximately 2 eV for the electrocatalyst, which is mainly attributed to the reduction of Ni in the electrocatalyst [40–42]. In the XPS patterns of Fe 2p, two peaks at 711.0 eV and 723.6 eV correspond to Fe 2p_{3/2} and Fe 2p_{1/2} (Figure 2F), indicating the presence of Fe²⁺/Fe³⁺ in the Fe-Co-O precursor/NF and the Fe-Co₂P/NPC/NF electrocatalyst, respectively. The characteristic peaks of the Fe satellite are located at 715.2 eV and 729.5 eV. The significantly stronger Fe²⁺ XPS peaks in the Fe-Co₂P/NPC/NF electrocatalyst with decreasing Fe³⁺ XPS peaks confirm the reduction of Fe in the electrocatalyst. Furthermore, the peak at 707.8 eV corresponds to Fe-P, which proves that the doping strategy using Fe was successful and the Fe-Co₂P/NPC/NF electrocatalyst possesses a more defective interface for rich active sites, which results in excellent electrocatalytic performance [43,44]. For the high-resolution N 1s XPS spectra (Figure S10), three peaks at 398.3 eV, 400.1 eV and 401.5 eV correspond to the pyridinic N, pyrrolic N and graphitic N, respectively, which also confirm the successful formation of N-doped carbon [30,45].

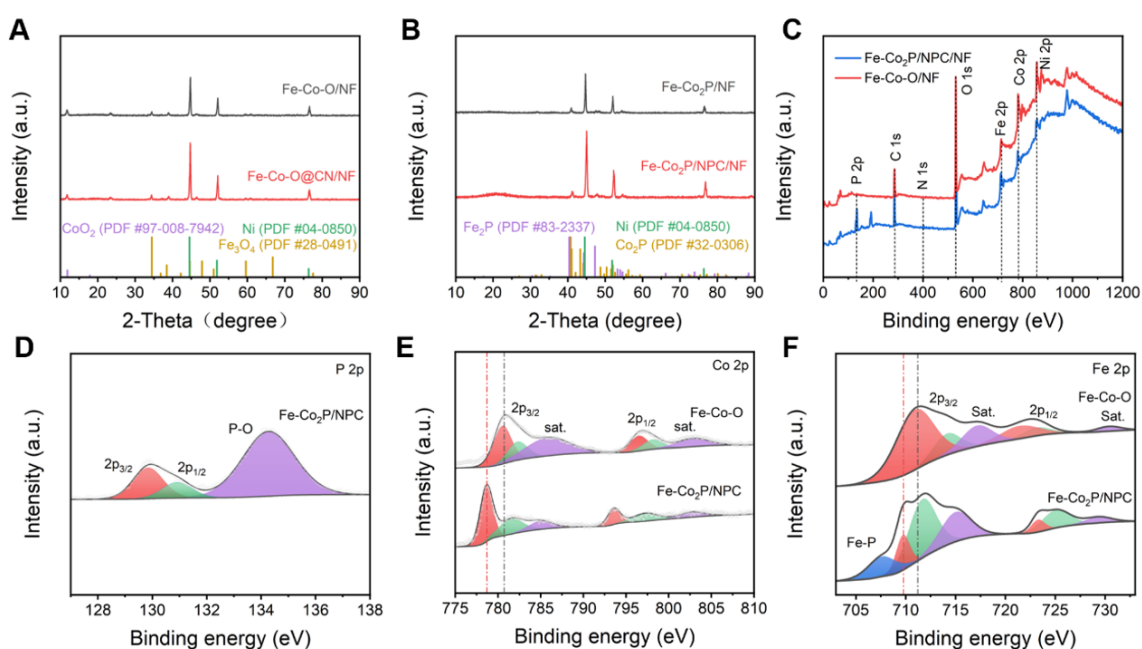


Figure 2. (A,B) XRD patterns of Fe-Co-O/NF, Fe-Co-O@CN/NF, Fe-Co₂P/NF, and Fe-Co₂P/NPC/NF. XPS results of Fe-Co-O and Fe-Co₂P/NPC: (C) full spectra, (D) P 2p, (E) Co 2p, and (F) Fe 2p.

The HER activity of the Fe-Co₂P/NPC catalysts was measured in a three-electrode system using 1 M KOH solution as the electrolyte under 5 mV s^{−1}. For comparison, the control samples included Fe-Co-O/NF, Fe-Co-O@CN/NF, Fe-Co₂P/NF, and Pt/C. Figure 3A shows the polarization curves of the catalysts with 90% iR compensation. It can be seen that Fe-Co₂P/NPC achieved outstanding HER activity, with overpotentials of 73 mV and 185 mV at the current densities of 10 and 100 mA cm^{−2}. The HER activity of Fe-Co₂P/NPC was superior to NF (325 mV at 10 mA cm^{−2}, Figure S9), Fe-Co-O/NF (223 mV and 340 mV), Fe-Co-O@CN/NF (232 mV and 347 mV), and Fe-Co₂P/NF (84 mV and 182 mV), suggesting the synergy between Co₂P and Fe₂P. In addition, from the polarization curves

of Fe-Co₂P/NPC/NF (Figure 3B), a Tafel slope of 92.7 mV dec^{−1} of Fe-Co₂P/NPC/NF was calculated, which is smaller than those of Fe-Co-O@CN/NF (108.76 mV dec^{−1}) and Fe-Co-O/NF (106.11 mV dec^{−1}), and close to that of 20% Pt/C (46.5 mV dec^{−1}). Under alkaline conditions, the Tafel slope of the Fe-Co₂P/NPC/NF catalyst suggests that the HER follows the Volmer–Heyrovsky mechanism [30]. Fe-Co₂P/NPC/NF exhibited better mass transfer capability than previously published Co-based HER catalysts because of its lower overpotential and smaller Tafel slope (Table S1). Meanwhile, the lowest charge transfer resistance (R_{ct}) of Fe-Co₂P/NPC/NF (Figure 3D) was observed among all the samples, indicating good conductivity and remarkable charge transfer capability. In addition, we evaluated the electrochemically active surface area (ECSA) of the catalysts using the double-layer capacitance (C_{dl}). The C_{dl} increases from 4.92 mF cm^{−2} for Fe-Co-O/NF to 5.34 mF cm^{−2} for Fe-Co-O@CN/NF, 98.47 mF cm^{−2} for Fe-Co₂P/NF, and reaches a higher value of 110.83 mF cm^{−2} for Fe-Co₂P/NPC/NF (Figure S3). This indicates that the N, P-doped carbon layer can adjust the ECSA and produce the most abundant active sites. Stability is an essential criterion for the commercialization of electrocatalysts. Fe-Co₂P/NPC/NF maintained a stable horizontal line over 20 h in the chronoamperometry (j-t) measurements at 100 mA cm^{−2} (Figure 3E) and showed a negligible shift after 5000 cycles (Figure 3F). This observation indicates that the synergistic effect plays a key role in the HER reaction and results in outstanding retention of catalytic activity. In addition, the SEM results in Figure S4 demonstrates that the microscopic morphology and structure of Fe-Co₂P/NPC/NF were well retained in the durability tests. As shown in Figure S5, the binding energy of Co 2p is about the positive shift of 2.03 eV, which indicates that the Co atom is further oxidized; the binding energy of Fe 2p is about 0.77 eV, which also indicates that the Fe atom is further oxidized; and the metal-phosphorus bond in P 2p does not disappear before and after the reaction, which also proves that Fe-Co₂P/NPC/NF catalyst has excellent stability in HER reaction. The excellent catalytic activity and stability of the Fe-Co₂P/NPC/NF electrode significantly contributed to its excellent HER performance under alkaline conditions.

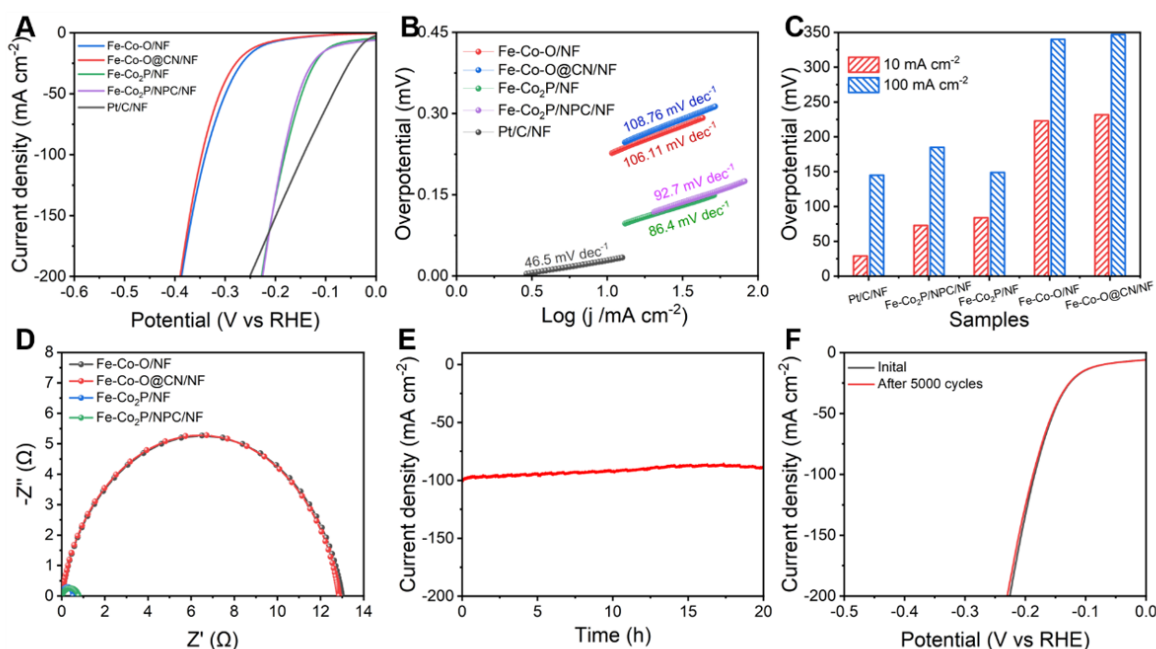


Figure 3. The HER performance of different catalysts: (A) polarization curves, (B) Tafel slope, (C) overpotentials, (D) EIS Nyquist plots, (E) chronoamperometry curve of Fe-Co₂P/NPC/NF recorded for 20 h at 100 mA cm^{−2}, and (F) polarization curves of Fe-Co₂P/NPC/NF before and after stability testing.

The OER activities of Fe-Co-O/NF, Fe-Co-O@CN/NF, Fe-Co₂P/NF, Fe-Co₂P/NPC/NF, and commercial RuO₂ were further evaluated because OER is another half-reaction of water splitting. As shown in Figure 4A,C, the polarization curves of Fe-Co₂P/NPC/NF exhibited excellent OER activity with overpotentials of 210 mV and 249 mV at 10 mA cm⁻² and 100 mA cm⁻², respectively. The overpotentials at 10 mA cm⁻² were 226, 226, and 217 mV for Fe-Co-O/NF, Fe-Co-O@CN/NF, Fe-Co₂P/NF, and commercial RuO₂, respectively, and the corresponding overpotentials at 100 mA cm⁻² were 267, 356, 262, and 340 mV, respectively (NF 428 mV at 10 mA cm⁻², Figure S9). The Fe-Co₂P/NPC/NF catalyst exhibited a lower Tafel slope (30.4 mV dec⁻¹) compared to the other catalysts, resulting in better OER kinetics (Figure 4B). Furthermore, Fe-Co₂P/NPC/NF had the lowest charge transfer resistance (R_{ct}) and highest C_{dl} value of all the samples, revealing its fast charge transfer behavior (Figure 3D and Figure S5). These results conclude that Fe-Co₂P/NPC/NF is a superior OER catalyst compared to other reported catalysts (Table S2). Moreover, the results indicate that the embedded N, P co-doped carbon layers exposed more catalytically active sites. In the stability test, Fe-Co₂P/NPC/NF exhibited insignificant current consumption after 20 h of operation at 100 mA cm⁻² (Figure 4E), and the polarization curves before and after 5000 cycles (Figure 4F) overlapped, displaying excellent OER stability. As shown in Figure S7, the SEM result after the durability tests revealed that Fe-Co₂P/NPC/NF was well preserved. As shown in Figure S8, the binding energy of Co 2p is about the positive shift of 1.9 eV, indicating that the Co atom is further oxidized in the OER process; the binding energy of Fe 2p is about the positive shift of 1.82 eV, which also indicates that the Fe atom is also further oxidized in the OER process, and the P 2p orbital metal-phosphorus bond does not disappear before and after the reaction, which also proves that the Fe-Co₂P/NPC/NF catalyst has excellent stability in the OER reaction.

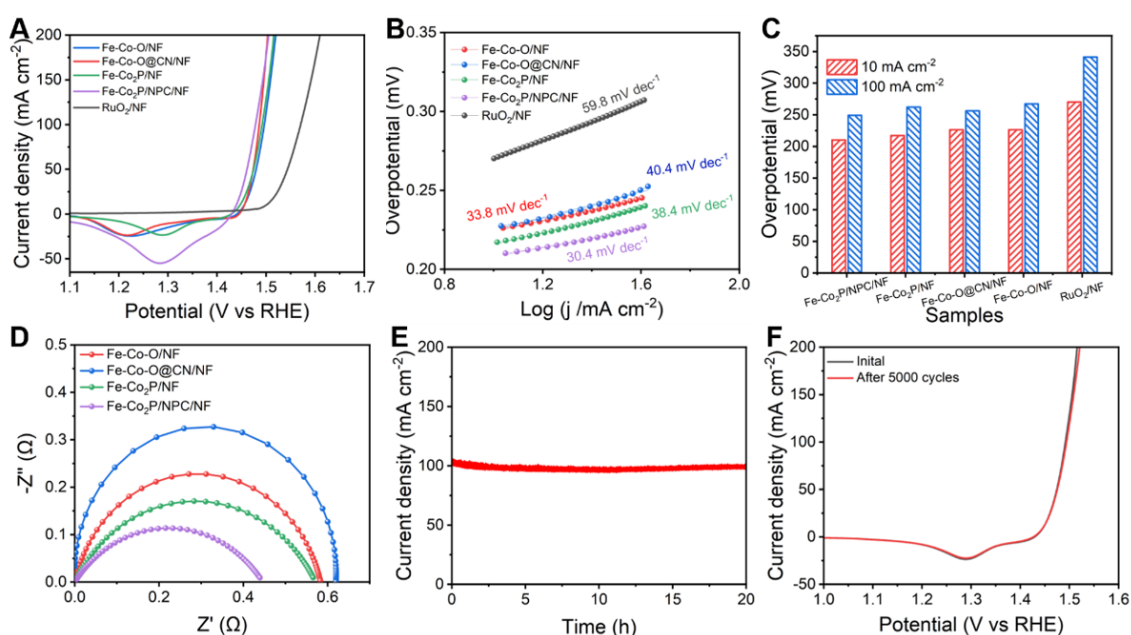


Figure 4. OER performances of different catalysts. (A) Polarization curves, (B) Tafel slope, (C) overpotentials, and (D) EIS Nyquist plots of different catalysts. (E) Chronoamperometry curve of Fe-Co₂P/NPC/NF. (F) Polarization curves of Fe-Co₂P/NPC/NF before and after stability testing.

Finally, Fe-Co₂P/NPC/NF was used as a bifunctional electrocatalyst for water splitting in a two-electrode system (Fe-Co₂P/NPC/NF // Fe-Co₂P/NPC/NF, Figure 5A). As shown in Figure 5B, the Fe-Co₂P/NPC/NF catalyst exhibited outstanding performance, which required cell voltages as low as 1.56 V, 1.68 V, and 1.74 V at 10, 100 and 200 mA cm⁻², respectively. The catalyst outperformed the benchmark Pt/C // RuO₂ electrode and previously published electrocatalysts (Table S3 and Figure 5C). The overall water-splitting

electrolyzer unit of Fe-Co₂P/NPC/NF//Fe-Co₂P/NPC/NF achieved prominent stability (Figure 5D).

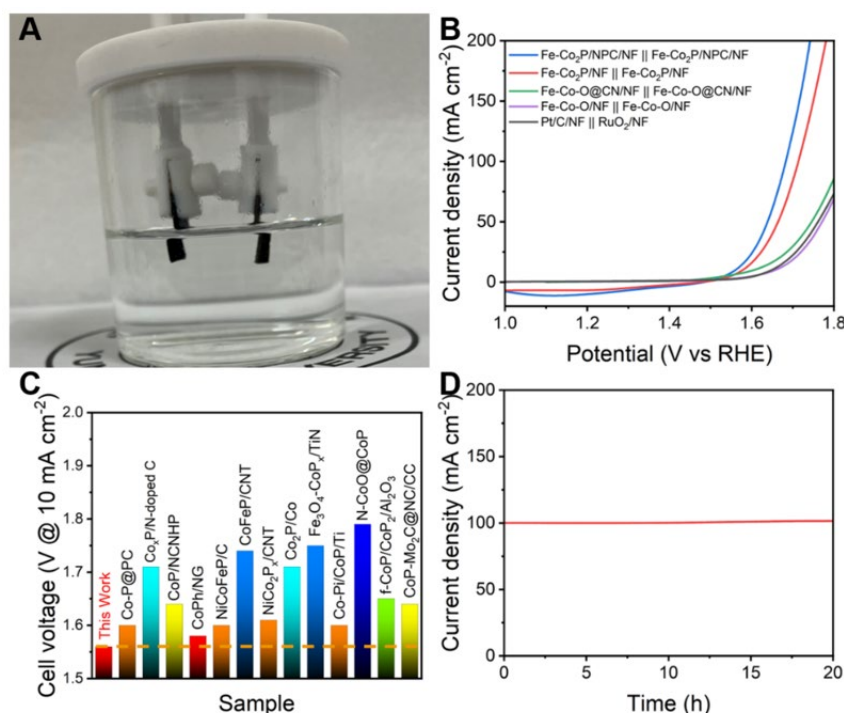


Figure 5. Performance of Fe-Co₂P/NPC/NF in water-splitting reaction. (A) Photograph of a Fe-Co₂P/NPC/NF electrolyzer unit. (B) Polarization curves in 1 M KOH with 90% iR correction. (C) Cell voltage of different catalysts. (D) Chronopotentiometry curve of Fe-Co₂P/NPC/NF.

3. Materials and Methods

3.1. Materials and Characterization Methods

The reagents and solvents used during the experimental execution of this work were used as received. Cobalt chloride hexahydrate (Co(NO₃)₂·6H₂O), Ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O), urea (CO(NH₂)₂), ammonium fluoride (NH₄F), potassium hydroxide (KOH), and 2-methylimidazole were (C₄H₆N₂) were purchased from Aladdin, Shanghai, China. Sodium hypophosphite (NaH₂PO₂·H₂O) and Pt/C (20 wt% Pt on Vulcan XC-72R), RuO₂ (ruthenium dioxide), and Nafion (5 wt%) were purchased from Alfa Aesar, Shanghai, China. All chemicals were used as received without further purification, and all solutions were prepared with ultrapure water (>18.25 MΩ·cm). Nickel foam (99.6%, 40 × 10 × 1.6 mm³) was purchased from Jinjia Metal, Kunshan, China.

The morphology of the products was investigated by scanning electron microscope (SEM, FEI Quanta, Nova Nano SEM 450, Hillsboro, OR, USA) at an acceleration voltage of 15 kV. Powder X-ray diffraction (XRD) pattern was recorded on a Rigaku TTRIII-18KW diffractometer (Tokyo, Japan) operated at 40 kV voltage and 30 mA current using Cu Kα radiation (λ = 1.5418 Å) in the range of 10–90°. X-ray photoelectron spectroscopy (XPS) test was performed on a Thermo Fisher (Hillsboro, OR, USA) K-Alpha+ equipped with monochromatic Al Kα radiation (150 W, 5 kV at 1486.6 eV). The surface charge was corrected by referencing the spectra to the C 1s peak for the C-C bond at a binding energy of 284.8 eV. The transmission electron microscope (TEM) analysis was performed on a J Tecnai G2F30S-TWIN (Hillsboro, OR, USA) operated at an accelerating voltage of 300 kV. The detailed information about apparatus and methods is found in the Supplementary Materials file.

3.2. Materials Preparation

Synthesis of Fe-Co-O precursor/NF: Fe(NO₃)₃·9H₂O (1 mmol), Co(NO₃)₂·6H₂O (3 mmol), urea (15 mmol) and NH₄F (8 mmol) were dissolved in 30 mL of ultrapure water under intense

stirring, and continuously stirred for 1 h. Subsequently, the appeal solution was transferred to a 50 mL stainless steel autoclave lining with Teflon, and the pretreated nickel foam (NF, 20 mm × 30 mm × 1.6 mm) was immersed in the solution. It was then placed in an autoclave oven at 120 °C for 6 h. When the temperature was cooled to room temperature, the obtained Fe-Co-O nanoarray precursor was washed with water and ethanol several times, and dried overnight at 60 °C in a vacuum dryer.

Synthesis of Fe-Co-O@CN/NF: The prepared Fe-Co-O nanoarray precursor was immersed in 2-methylimidazole aqueous solution (0.1 g/mL) for 6 h. Fe-Co-O@CN/NF was obtained by washing with anhydrous ethanol and ultrapure water was dried in a vacuum at 60 °C for 24 h.

Synthesis of Fe-Co₂P/NF: The synthesized Fe-Co-O/NF precursor samples and NaH₂PO₂ were placed in two porcelain boats, respectively, and NaH₂PO₂ (500 mg) was placed upstream of the tube furnace and Fe-Co-O/NF was placed downstream. The tube furnace was then heated to 350 °C at a heating rate of 2 °C min^{−1} and kept in a flowing Ar atmosphere for 2 h, then cooled naturally to room temperature.

Synthesis of Fe-Co₂P/NPC/NF: The synthesized Fe-Co-O@CN/NF precursor samples and NaH₂PO₂ were placed in two porcelain boats, respectively, and NaH₂PO₂ (500 mg) was placed upstream of the tube furnace and Fe-Co-O@CN/NF was placed downstream. The tube furnace was then heated to 350 °C at a heating rate of 2 °C min^{−1} and kept in a flowing Ar atmosphere for 2 h, then cooled naturally to room temperature.

3.3. HER and OER Electrochemical Performances

Electrochemical measurements are performed with a CHI 760E electrochemistry workstation (CH Instruments, Inc., Shanghai) in a standard three-electrode system using Fe-Co₂P/NPC as the working electrode, a graphite rod as the counter electrode and Hg/HgO electrode (in 1 M KOH) as the reference electrodes, respectively. All measured potentials were corrected according to the following equation: $E_{(RHE)} = E_{(Hg/HgO)} + 0.098 V + 0.059 \times pH$, and the current densities (*j*) were normalized by geometric surface area. To make a more reliable comparison, RuO₂ and Pt/C were loaded on NF with the same loading as that of Fe-Co₂P/NPC/NF. The polarization curves were 90% iR-corrected and recorded in 1.0 M KOH with a scan rate of 5 mV s^{−1}. Tafel slopes were calculated according to the equation $\eta = a + b \log(j)$, where η is the overpotential, *j* defines the current density, and *a* and *b* are the constants. Electrochemical impedance spectroscopy (EIS) was carried out from 100 kHz to 0.1 Hz at the given potential with an AC amplitude of 10 mV. Overall water splitting was conducted in a two-electrode system using the above solutions, with the polarization curve recorded at a scan rate of 5 mV s^{−1}. The active surface area of each catalyst was estimated from their electrochemical capacitances using the simple cyclic voltammetry (CV) method. The current was measured in a narrow potential window where no faradaic process was observed. CV was tested between 0.3 to 0.4 V vs. RHE (HER) or 1.01 to 1.11 V vs. RHE (OER) at five different scan rates (10, 20, 30, 40, and 50 mV s^{−1}), respectively. By plotting the difference in current density (*J*) between anodic and cathodic sweeps (ΔJ) at the fixed potential against the scan rate, the fitting slope is twice the double-layer capacitance (*C_{dl}*), which is linearly promotional to the ECSA. These values of *C_{dl}* permit comparison of relative surface activity of different electrodes, particularly in the same electrolyte.

4. Conclusions

A well-designed fabrication method for Fe-Co₂P nanowires coated with N, P-doped carbon layers was successfully developed, and TMPs were grown in situ on 3D Ni foam with a layered structure. The as-prepared Fe-Co₂P/NPC/NF catalyst exhibited excellent reaction kinetics and good long-term stability for both OER and HER. Moreover, as expected, the Fe-Co₂P/NPC/NF catalyst exhibited excellent performance in the HER (overpotential of 73 mV at 10 mA cm^{−2}) and OER (overpotential of 217 mV at 10 mA cm^{−2}), extraordinary electrocatalytic performance, and electrolytic water stability under continuous operation at 100 mA cm^{−2} for 20 h. Some performances of the Fe-Co₂P/NPC/NF catalyst were even

better than commercial Pt/C and RuO₂ catalysts. Notably, the electrolyzers assembled with the Fe-Co₂P/NPC/NF catalyst require cell voltages of only 1.56 and 1.68 V at 10 and 100 m Acm^{−2}, respectively, resulting in a huge improvement in efficient and low-cost design and synthesis.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12090957/s1>, Figure S1: SEM images of different catalysts. (A–C) Nickel foam. (D–F) Fe-Co-O precursor/NF; Figure S2: SEM images of different catalysts. (A–C) Fe-Co-O@CN/NF. (D–F) Fe-Co₂P/NPC/NF; Figure S3: Cyclic voltammograms (CV) curves of different catalysts between 0.3 to 0.4 V vs. RHE at five different scan rates (10, 20, 30, 40, and 50 mV s^{−1}) and electrochemical double layer capacitances (C_{dl}). (A) Fe-Co-O/NF. (B) Fe-Co-O@CN/NF. (C) Fe-Co₂P/NF. (D) Fe-Co₂P/NPC/NF. (E) The current density variation ($\Delta j = j_a - j_c$) at the potential of 0.35 V vs. RHE with varied scan rates fitted to estimate the electrochemical double layer capacitances (C_{dl}); Figure S4: (A) SEM patterns of Fe-Co₂P/NPC/NF before the HER stability test. (B) after the HER stability test; Figure S5: (A) XPS scanning full spectrum of Fe-Co₂P/NPC/NF before and after HER stability test. (B) P 2p, (C) Co 2p and (D) Fe 2p; Figure S6: Cyclic voltammograms (CV) curves of different catalysts between 1.01 to 1.11 V vs. RHE at five different scan rates (10, 20, 30, 40, and 50 mV s^{−1}) and electrochemical double layer capacitances (C_{dl}). (A) Fe-Co-O/NF. (B) Fe-Co-O@CN/NF. (C) Fe-Co₂P/NF. (D) Fe-Co₂P/NPC/NF. (E) The current density variation ($\Delta j = j_a - j_c$) at the potential of 1.06 V vs. RHE with varied scan rates fitted to estimate the electrochemical double layer capacitances (C_{dl}); Figure S7: (A) SEM patterns of Fe-Co₂P/NPC/NF before the OER stability test, (B) after the OER stability test; Figure S8: (A) XPS scanning full spectrum of Fe-Co₂P/NPC/NF before and after OER stability test. (B) P 2p, (C) Co 2p and (D) Fe 2p; Figure S9: polarization curves of NF. (A) HER. (B) OER; Figure S10: N 1s XPS result of Fe-Co₂P/NPC/NF; Figure S11: XRD patterns of Fe-Co-O@CN/NF; Table S1: HER performances of different electrocatalysts in alkaline media (1 M KOH); Table S2: OER performances of different electrocatalysts in alkaline media (1 M KOH); Table S3: Overall water splitting performances of different electrocatalysts in alkaline media (1 M KOH). References [46–59]. are cited in the Supplementary Materials.

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