

Prismatic rod-like structure CoP for efficient hydrogen evolution reaction

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Abstract

The development of efficient and stable non-precious metal electrocatalysts for the hydrogen evolution reaction (HER) is critical for sustainable hydrogen production through water electrolysis. Herein, we report the metal organic framework (MOF) -derived CoP prismatic structure electrode (CoP/NF) that exposes abundant active sites while facilitating electron transfer and mass transport. The CoP/NF electrode exhibited excellent HER catalytic activity, achieving a low overpotential of 125 mV at a current density of 10 mA cm^{-2} and a Tafel slope of 62.8 mV dec^{-1} . Furthermore, the CoP/NF electrode demonstrated remarkable stability, with negligible degradation in LSV current density, polarization behavior, or morphological integrity after 12 hours of chronoamperometric testing and 1000 cycles of cyclic voltammetry (CV). These results confirm that the CoP/NF self-supporting electrode possesses outstanding HER catalytic activity and long-term durability. The superior HER performance is attributed to the synergistic effects of phosphorus-induced electronic modulation of the active sites, the conductive carbon matrix ensuring efficient charge transfer, and the prismatic rod-like structure exposing rich and highly active sites. This work provides a rational strategy for designing high-performance, MOF-derived electrocatalysts through simultaneous optimization of electronic structure and nanoarchitecture.

1. Introduction

The continuous consumption of fossil fuels has led to energy crisis and environmental degradation, promoting the continuous development of green, clean and renewable energy. Hydrogen energy, characterized by its high energy density, zero carbon emissions, and environmental sustainability, has emerged as a promising clean energy carrier and a viable alternative to conventional fossil fuels. Electrolysis of water for hydrogen production is a green and efficient hydrogen production method that uses electricity to decompose water molecules into hydrogen and oxygen, and is considered one of the most promising sustainable hydrogen production technologies.^[1–3] Efficient and highly stable catalysts are required in the process of electrolyzing water for hydrogen production to reduce the overpotential of hydrogen evolution reaction (HER), accelerate the reaction kinetics, and achieve large-scale production of hydrogen gas.^[4, 5] At present, precious metal Pt based catalysts are the most efficient hydrogen evolution catalysts, but their widespread commercialization is hindered by prohibitive costs and scarcity.^[6, 7] Consequently, the development of cost-effective, high-performance non-precious metal HER catalysts holds significant scientific and industrial importance^[8].

Transition metal phosphides (TMPs) as non-precious HER catalysts has gained considerable attention due to their unique electronic properties and cost-effectiveness.^[9–11] Among various TMPs, cobalt phosphide (CoP) has emerged as a particularly promising candidate owing to its unique electronic configuration.^[12] The phosphorus atoms not only modulate the d-band center of cobalt but also serve as proton-acceptor sites, thereby synergistically enhancing the HER activity through optimized hydrogen adsorption/desorption energetics.^[13, 14] This electronic synergy, coupled with the material's inherent metallic conductivity, endows CoP with remarkable HER performance. Zhao et al. synthesized atomically

dispersed CoP₄ on ultra-thin carbon nanosheets using a thermal exfoliation strategy.^[15] The atomically dispersed CoP₄ electrocatalyst has excellent performance for the HER reaction, with an overpotential of only 52 mV at a current density of 10 mA cm⁻². This highlights the extraordinary intrinsic catalytic activity of CoP materials for HER. Nevertheless, despite these promising characteristics, CoP catalysts still face substantial challenges that hinder their practical implementation, including inefficient charge/mass transport, limited active site exposure due to particle aggregation, and structural instability during prolonged operation.

To address these challenges, researchers have developed innovative synthetic strategies, including nanostructuring, heteroatom doping, and hybrid composite formation.^[16–20] Metal-organic frameworks (MOFs) have revolutionized the design of CoP catalysts due to their unique structural features.^[21–23] As crystalline porous materials, MOFs offer unparalleled advantages as sacrificial templates, including the inherent porosity facilitates mass transport, and the carbonizable organic components can form conductive networks during pyrolysis.^[24] The CoP/carbon interface has been proven to effectively regulate the electronic properties of the surface and enhance its charge transfer, thereby reducing the adsorption and activation energy of intermediates.^[25, 26] However, most reported CoP-based materials are in powder form and require binders for electrode fabrication, which hinders charge transfer, blocks active sites, and suppresses gas diffusion.^[27] The electrode obtained by in-situ conversion of MOF precursor on conductive substrate (such as foam nickel (NF)) has enhanced electrical contact and mechanical stability, which can effectively overcome these shortcomings.

In this study, one-dimensional (1D) prismatic Co-MOF precursors were in-situ grown on nickel foam (NF) substrates via a solvothermal reaction. Subsequent low-temperature oxidation and phosphidation treatments transformed these precursors into 1D prismatic rod-like structure CoP self-supported electrodes (CoP/NF). The morphology and characteristics of self-supported electrode were systematically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). And those characterization confirms the successful phase transformation and reveals the electronic structure modulation induced by phosphorus incorporation. The electrocatalytic performance of the CoP/NF electrode toward the hydrogen evolution reaction (HER) was evaluated in a 1 mol L⁻¹ KOH electrolyte. The optimized CoP/NF electrode achieved a low overpotential of 125 mV at 10 mA cm⁻² with a Tafel slope of 68.2 mV dec⁻¹. The values significantly outperform those of the precursor Co-MOF/NF (312 mV, 171.9 mV dec⁻¹) and Co₃O₄/NF (240 mV, 89.1 mV dec⁻¹). Remarkably, the electrode exhibited outstanding long-term stability, maintaining its original polarization behavior, current density, and morphological integrity after 1000 cycles and a 12-hour chronoamperometric test, confirming its excellent durability for practical applications. This is benefiting from the unique prismatic rod-like structure and the synergistic effects between the MOF-derived CoP and conductive carbon matrix, the CoP/NF electrode demonstrated matrix excellent HER catalytic performance. This work not only

presents a high-performance HER electrode but also provides insights into the rational design of MOF-derived electrocatalysts through simultaneous control of composition and nanoarchitecture.

2. Experimental

2.1 Materials

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2,5-dihydroxyterephthalic acid, sodium hypophosphite, potassium hydroxide (KOH), methanol, ethanol, N, N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2 Preparation

Surface nickel oxide layer of NF was removed by ultrasonic treatment in 3 mol L^{-1} HCl solution for 30 minutes. A precursor solution was prepared by dissolving $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.25 g) and 2,5-dihydroxyterephthalic acid (60 mg) in a mixed solvent system comprising DMF (20 mL), ethanol (1.2 mL), and H_2O (1.2 mL). The cleaned NF substrate was then immersed in the precursor solution and subjected to solvothermal treatment at 120°C for 12 h in a sealed autoclave. After cooling to room temperature, the resulting Co-MOF/NF composite was thoroughly rinsed with ethanol and dried at 60°C overnight. The as-prepared Co-MOF/NF was calcined at 350°C for 2 hours in an air, yielding $\text{Co}_3\text{O}_4/\text{NF}$. Subsequent phosphorization was performed by placing the $\text{Co}_3\text{O}_4/\text{NF}$ sample and sodium hypophosphite at the center and upstream positions of a tube furnace, respectively. The conversion to CoP/NF was achieved through thermal treatment at 350°C for 2 h under argon atmosphere. Then, $\text{Co}_3\text{O}_4/\text{NF}$ with a mass ratio of 1:10 and sodium hypophosphite were placed in the middle and upper air inlet of a tube furnace. Phosphating reaction was carried out at 350°C for 2 hours under argon atmosphere, and the sample was named CoP/NF. The schematic illustration of the entire preparation process is shown in Fig. 1.

2.3 Characterization and electrochemical measurements

The microstructure and elemental distribution of the sample were observed using a scanning electron microscope (SEM, Phenpm pure+ type, FLYNA, Netherlands). the functional groups, chemical bonds, and structural characteristics of the material were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Fisher Scientific, USA) and Raman spectroscopy (Raman, DXR, Thermo Fisher Scientific, USA). The crystal structure and chemical valence states of surface elements of the samples were tested using X-ray diffraction (XRD, D2 PHASER type, Bruker, Germany) and X-ray photoelectron spectroscopy (XPS, AXIS type, Shimadzu, Japan). Electrochemical testing was conducted using an electrochemical workstation (CHI 660E model, Shanghai Chenhua Instrument).

The HER performance was evaluated using a standard three-electrode configuration in 1 mol L^{-1} KOH electrolyte. The counter electrode was a graphite rod, the reference electrode was Hg/HgO, a self-supporting electrode served as the working electrode. Linear sweep voltammetry (LSV) measurements

were performed at a scan rate of 5 mV s^{-1} after electrode activation through 20 cyclic voltammetry (CV) cycles. The LSV test data was processed with IR compensation and the electrode potential was converted to reversible hydrogen electrode (RHE) according to the equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098$. The overpotential $\eta = 1.23 \text{ V} - E_{\text{RHE}}$. Electrochemical impedance spectroscopy (EIS) testing was conducted within the frequency range of 0.01 Hz to 100 kHz. The long-term stability of the catalyst was assessed through chronoamperometric testing at a fixed potential corresponding to a current density of 10 mA cm^{-2} for 12 h. Using cyclic voltammetry, 1000 cyclic stability tests were conducted in the potential range of $-0.05 \sim 0.05 \text{ V}$ vs. RHE at a scan rate of 0.1 V s^{-1} . The polarization curves before and after the tests were compared to determine the cyclic stability performance.

3. Results and discussion

3.1 Phase analysis

X-ray diffraction (XRD) analysis was systematically conducted to investigate the phase evolution during material transformation. As shown in Fig. 2a, the XRD pattern of as-synthesized Co-MOF/NF exhibited characteristic diffraction peaks at 7.1° , 11.7° , and 18.3° , which match well with the standard spectrum of Co-MOF, demonstrating the successful synthesis of Co-MOF.^[28] The diffraction peaks at 31.2° , 36.9° , and 59.3° of the samples obtained after Co-MOF/NF oxidation are attributed to the (220), (311), and (511) crystal planes of Co_3O_4 (JCPDS No. 74-2120), indicating that Co-MOF generated Co_3O_4 after calcination (Fig. 2b). After phosphorization reaction, the emergence of distinct diffraction peaks at 31.6° , 36.3° , 48.1° , and 56.8° are consistent with the characteristic peaks of CoP (JCPDS No. 29-0497), corresponding to the (011), (111), (211), and (301) crystal planes (Fig. 2c), indicating the conversion of Co_3O_4 to CoP.^[14]

3.2 Morphology analysis

The morphology characterization of Co-MOF/NF is shown in Fig. 3a-c. The surface of foam nickel is loaded with Co-MOF composed of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2,5-dihydroxyterephthalic acid. Prismatic Co-MOF nanorods grow on foam nickel, with sharp edges and rough surfaces. This structure features rich active sites and excellent structural stability. Additionally, it forms a complete conductive pathway, accelerates electron transfer, reduces electrochemical impedance, and accelerates the reaction kinetics process. Figures 3d-f confirm that after heat treatment, the Co-MOF framework did not collapse and retained its prismatic nanorod morphology. During the heat treatment stage, the pyrolysis and removal of organic ligands from the Co-MOF not only generated abundant pores within the rod-like prisms and caused an overall diameter shrinkage, but also led to the *in situ* conversion of Co metal sites into Co_3O_4 embedded in the carbon skeleton. SEM images of CoP/NF (Figures S1 and 4a-c) reveal that the phosphorized product still preserved the original prismatic rod-like structure. In contrast to the pyrolyzed precursor with formed pores, the subsequent phosphorization filled and covered the original pores, resulting in a rough surface texture. EDS elemental mapping (Figs. 4d-g) on a single prism showed a homogeneous

dispersion of Co, P, C and O, with an atomic percentage of carbon reaching 22.64% (Table S1). These results indicate that CoP/NF, derived from the Co-MOF/NF precursor, can maintain the intact 1D prismatic rod-like structure skeleton while introducing a conductive carbon substrate. The continuous conductive carbon network synergistically accelerates charge transfer and enhances electrochemical cycling stability, whereas the CoP active phase provides abundant active sites for the HER. The synergistic interplay between the two components thus significantly optimizes the HER catalytic performance.

3.3 Infrared and Raman analysis

Figure 5a shows the Fourier transform infrared (FTIR) of prismatic rod-like structure CoP. The absorption peaks at 3416, 2356 and 1630 cm^{-1} are attributed to the stretching and bending vibration peaks of O-H.^[29] In the lower wavenumber region, two distinct absorption peaks at 1090 cm^{-1} and 566 cm^{-1} are assigned to the stretching vibration peaks of P = O and P-O, confirming the successful phosphorous.^[30] Raman spectroscopic analysis reveals the presence of carbon species within the CoP, as evidenced by the characteristic D-band at 1387 cm^{-1} and G-band at 1588 cm^{-1} (Fig. 5b). The D peak corresponds to the stretching vibration of C-C and C = C bonds, reflecting the defective or disordered graphite structure. The G peak corresponds to the stretching vibration of sp² hybridized carbon atoms, reflecting the number of graphite layers and lattice integrity. This spectrum indicates that the carbon matrix is preserved during the phase transition process, in agreement with the EDS findings, which originates from the carbonization of organic ligands during the thermal treatment process.

3.4 XPS analysis

X-ray photoelectron spectroscopy (XPS) analysis was employed to investigate the chemical composition and surface valence states of MOF-derived prismatic rod-like CoP. The full spectrum of CoP/NF exhibits characteristic peaks corresponding to Co 2p, P 2p, C 1s, and O 1s, confirming the coexistence of these four elements in the CoP/NF (Figure S2). The presence of carbon species originates from the decomposition of organic ligands during thermal treatment, forming a conductive carbon matrix. Figure 5c shows the high-resolution spectrum of Co 2p, which can be fitted as 2p_{3/2}, 2p_{1/2}, and two satellite peaks. The two peaks at 778.9 and 782.5 eV belong to Co 2p_{3/2}, the peaks at 793.9 and 798.7 eV correspond to Co 2p_{1/2}, and the two peaks at 786.4 and 802.9 eV belong to satellite peaks.^[31] This result indicates that Co mainly exists in the +2/+3 valence state in the material. In the P 2p spectrum (Fig. 5d), the peaks located at 139.6 eV and 130.8 eV are attributed to P 2p_{3/2} and P 2p_{1/2}, while the peak at 134.6 eV is due to oxygen-containing phosphorus species adsorbed on the sample surface or oxidized by air, namely the P-O chemical bond.^[32, 33] This is consistent with the test results of FTIR. Figure 5e shows the high-resolution spectrum of C 1s, where the C 1s peak is divided into peaks located at 284.8, 286.3, and 289.1 eV, corresponding to C-C, C-O, and C = O bonds, respectively. For the high-resolution spectra of O 1s (Fig. 5f), the characteristic peaks located at 531.6 eV, 532.4 eV, and 534.5 eV are attributed to M-O, C = O, and C-O bonds, respectively.^[32] These XPS results collectively verify the

successful conversion of Co-MOF to CoP while maintaining a carbon matrix, with minor surface oxidation products that are typical for transition metal phosphides exposed to ambient conditions.

3.5 HER Performance Analysis

In order to systematically evaluate the electrochemical performance of composite materials, comparative tests were conducted on Co-MOF/NF, Co₃O₄/NF, CoP/NF, and commercial Pt/C catalysts. Linear scanning voltammetry (LSV) tests were conducted in 1 mol L⁻¹ KOH electrolyte using a standard three-electrode system. As anticipated, the commercial Pt/C benchmark catalyst demonstrates the most outstanding HER catalytic activity, which is consistent with its characteristics as a reference catalyst. Notably, the CoP/NF electrode exhibits remarkable catalytic performance with a substantially lower overpotential (125 mV) compared to both Co₃O₄/NF (240 mV) and pristine Co-MOF/NF (312 mV) at equivalent current density (Fig. 6a, b). This enhanced catalytic efficiency can be attributed to the phosphidation-induced electronic structure modification. The phosphating treatment facilitates surface charge redistribution within the carbon matrix, increasing material electronegativity and promoting more effective OH⁻ adsorption, thereby significantly accelerating the HER process.^[34] The Tafel slope is an important parameter for evaluating the dynamic performance of HER. Figure 6c shows the Tafel slope curves of four samples. The CoP/NF electrode exhibit a Tafel slope of 62.8 mV dec⁻¹, approaching the performance of Pt/C (41.3 mV dec⁻¹) and substantially outperforming both Co₃O₄/NF (89.1 mV dec⁻¹) and Co-MOF/NF (171.9 mV dec⁻¹). The significantly reduced Tafel slope of CoP/NF confirms enhanced charge transfer efficiency and improved catalytic activity compared to its precursor materials.

The electrochemically active surface area (ECSA), as a key parameter for evaluating catalyst performance, is positively correlated with the double-layer capacitance (C_{dl}) of the material. The ECSA (Figure S3) was quantitatively assessed through CV measurements in the non-Faradaic potential region at varying scan rates (5–50 mV s⁻¹). As illustrated in Fig. 7a, the C_{dl} values, determined from the linear slope of the current density (Δj) versus scan rate plot, reveal significant differences among the catalysts. The C_{dl} of Co-MOF/NF, Co₃O₄/NF, and CoP/NF are 10.83, 14.21 and 27.79 mF cm⁻², respectively. The remarkably higher C_{dl} value of CoP/NF demonstrates its substantially larger ECSA compared to the precursor materials. The CoP/NF has a large electrochemical active area, which can expose more catalytic active sites and can fully contact with the electrolyte, effectively enhancing the electrochemical reaction activity. This result is consistent with the excellent HER activity exhibited by CoP/NF in the aforementioned LSV test, further confirming the important influence of material structure design on catalytic performance. These comprehensive results demonstrate that the MOF-derived CoP/NF with well-preserved nanorod array architecture successfully integrates favorable electronic properties with advantageous morphological characteristics.

In order to explore the charge transport characteristics of Co-MOF/NF, Co₃O₄/NF, and CoP/NF, electrochemical impedance spectroscopy (EIS) technology was adopted to characterize them. As shown in the Nyquist diagram in Fig. 7b, the spectra exhibit typical features consisting of a semicircular arc in

the high-frequency region, corresponding to charge transfer resistance (R_{ct}), and a linear Warburg region in the low-frequency range, representing mass transport processes.^[30] Compared to Co-MOF/NF and Co_3O_4 /NF, CoP/NF has the smallest semi-circular diameter in the high-frequency region, which means that its charge transfer resistance value is the smallest and the charge transfer rate is the fastest. This result clearly indicates that phosphating treatment effectively improves the electrical conductivity of the material and reduces the charge transfer resistance at the electrode/electrolyte interface. In the low-frequency region, the slope of CoP/NF is greater than that of other electrical materials, indicating the minimum ion diffusion resistance and excellent ion diffusion kinetics at the interface between the electrode and electrolyte. This may be attributed to the good conductivity of the porous carbon matrix and the prismatic rod-like structure, which facilitate the exposure of active sites, the adsorption and desorption of intermediates, and the rapid transport of electrolytes. These impedance results correlate well with the observed electrochemical performance, where CoP/NF exhibited the lowest overpotential, most favorable Tafel slope, and largest electrochemically active surface area. The combined EIS and catalytic data provide compelling evidence that the phosphidation-induced modifications to both electronic structure and morphological features collectively contribute to the enhanced HER activity of CoP/NF compared to its precursor materials.

The long-term operational stability of electrocatalysts represents a critical performance metric for practical hydrogen evolution applications. To evaluate the stability of the CoP/NF electrode, the durability and cycling stability tests were performed through both chronoamperometry and cyclic voltammetry. Firstly, a 12-hour current-time stability test was conducted at the potential corresponding to the current density of 10 mA cm^{-2} (Fig. 7c). The current density can be maintained around 10 mA cm^{-2} within 12 hours without significant changes, indicating that the CoP/NF electrode has good durability. Furthermore, cycling stability testing through 1000 continuous CV cycles yielded equally promising results. As shown in Fig. 7d, the post-cycling polarization curve exhibits negligible right-shifting. The exceptional stability of the CoP/NF electrode stems from its unique structural and compositional advantages. The robust prismatic rod-like CoP ensures mechanical stability during prolonged operation, while the surrounding conductive carbon matrix serves as both an electron transport pathway and protective layer, effectively preventing dissolution of active components.^[35, 36] Furthermore, the inherent chemical stability of the cobalt phosphide phase under alkaline conditions resists oxidative degradation, maintaining catalytic integrity. This synergistic combination of structural durability and chemical stability makes the CoP/NF electrode a highly promising candidate for practical hydrogen production applications.

4. Conclusion

The CoP self-supporting electrode (CoP/NF) was successfully fabricated through in situ growth of Co-MOF on nickel foam followed by sequential oxidation and phosphidation treatments. Electrochemical evaluation in 1 mol L^{-1} KOH electrolyte revealed outstanding hydrogen evolution activity, with the catalyst achieving a low overpotential of 125 mV at 10 mA cm^{-2} and exhibiting a Tafel slope of 62.8 mV

dec^{-1} . Remarkably, the electrode demonstrated excellent operational stability, maintaining its catalytic performance after both prolonged chronoamperometric testing (12 h) and cycling stability testing (1000 cycles). The exceptional hydrogen evolution performance of the CoP/NF electrode stems from a synergistic combination of electronic and structural factors. The MOF-derived CoP provide abundant active sites with optimized electronic structure. The P atoms induce the surface charge polarization of the surrounding material, attract more OH^- to participate in the reaction, and enhance the catalytic performance of HER. Moreover, the prismatic rod-like structure CoP and carbon matrix maximize the electrochemical active surface area, expose more active sites, promote effective mass transfer of reactants and products, and thus promotes HER.

Declarations

Declaration of competing 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 paper.

Author Contribution

Fan Yang wrote the main manuscript, Fan Yang and Pengyu Zhan prepared figures. All authors reviewed the manuscript.

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Figures

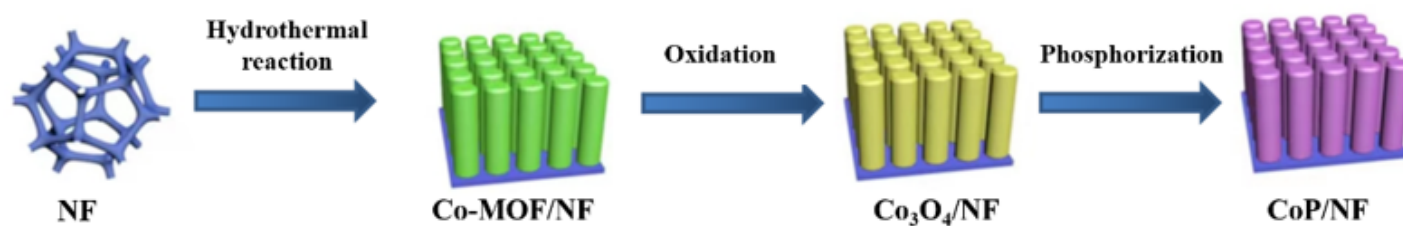


Figure 1

Preparation process of CoP/NF self-supporting electrode.

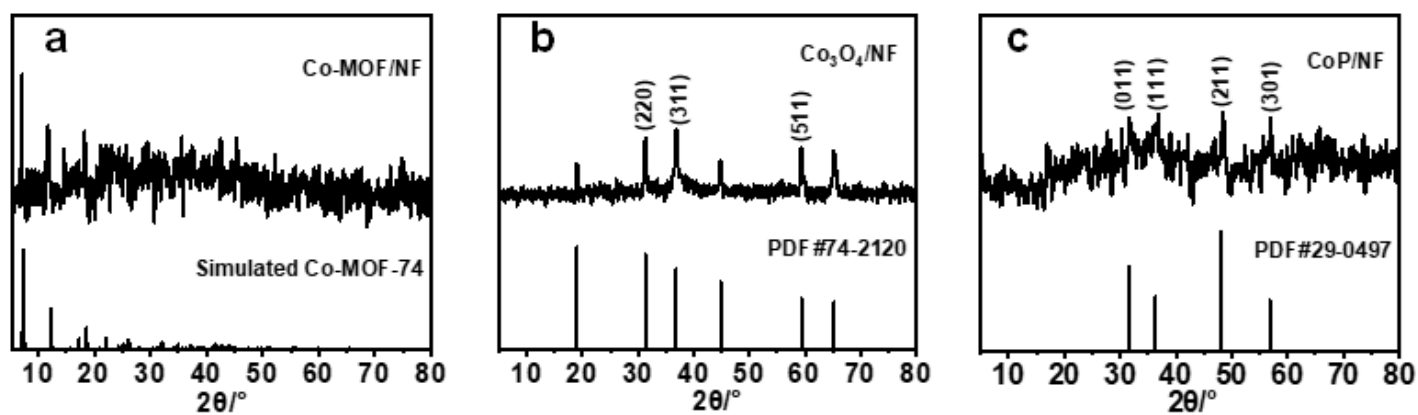


Figure 2

XRD spectra of (a) Co-MOF/NF and (b) $\text{Co}_3\text{O}_4/\text{NF}$ (c) CoP/NF.

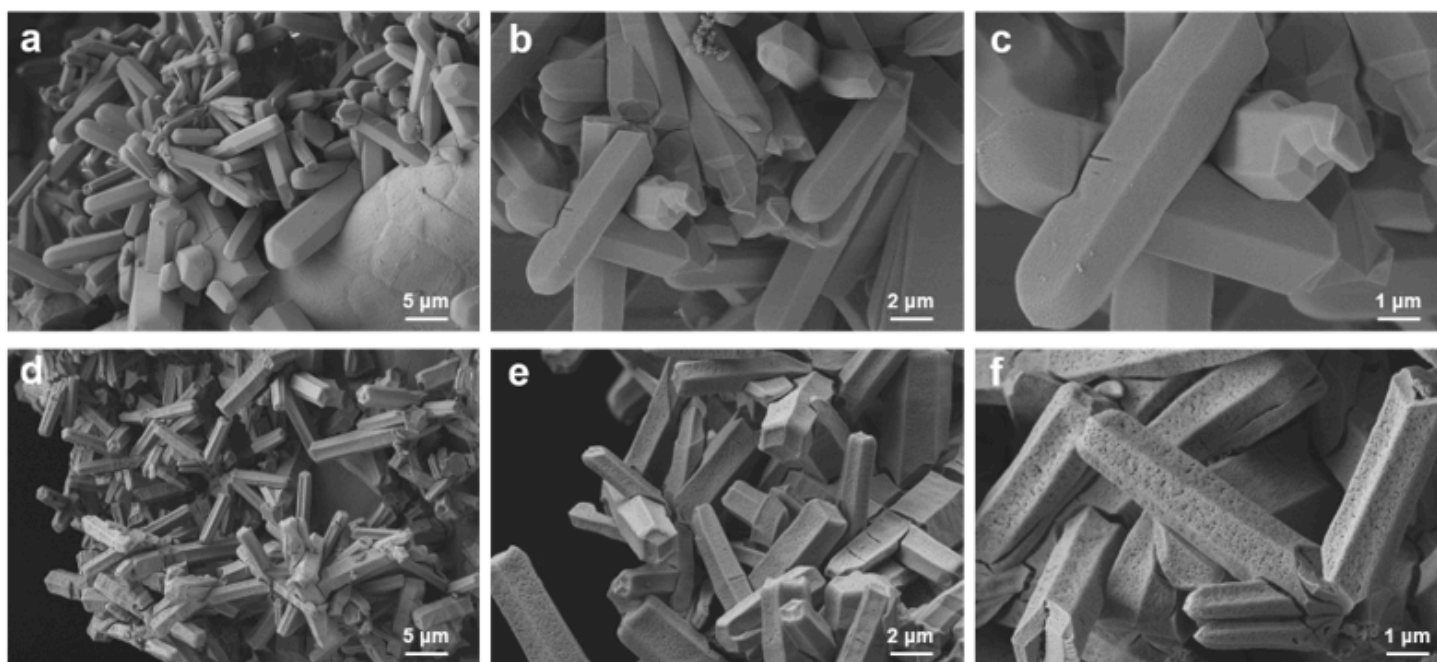


Figure 3

(a-c) SEM images of CoP/NF (d-g) elemental mapping.

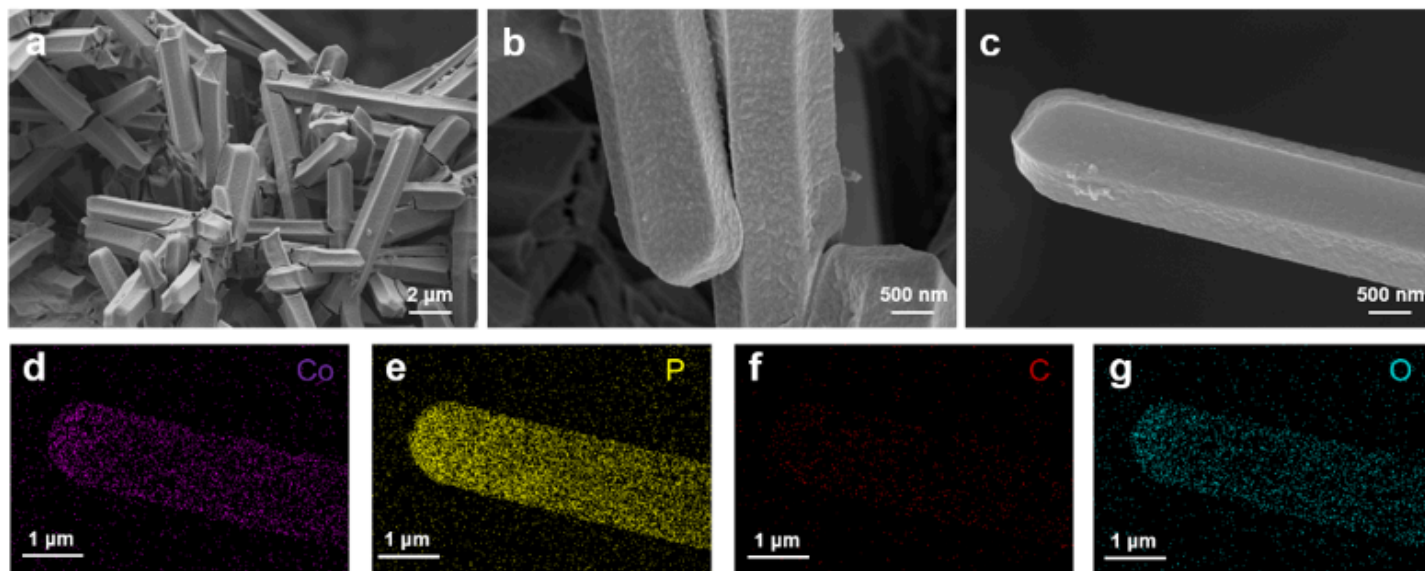


Figure 4

(a-c) SEM images of CoP/NF (d-g) elemental mapping.

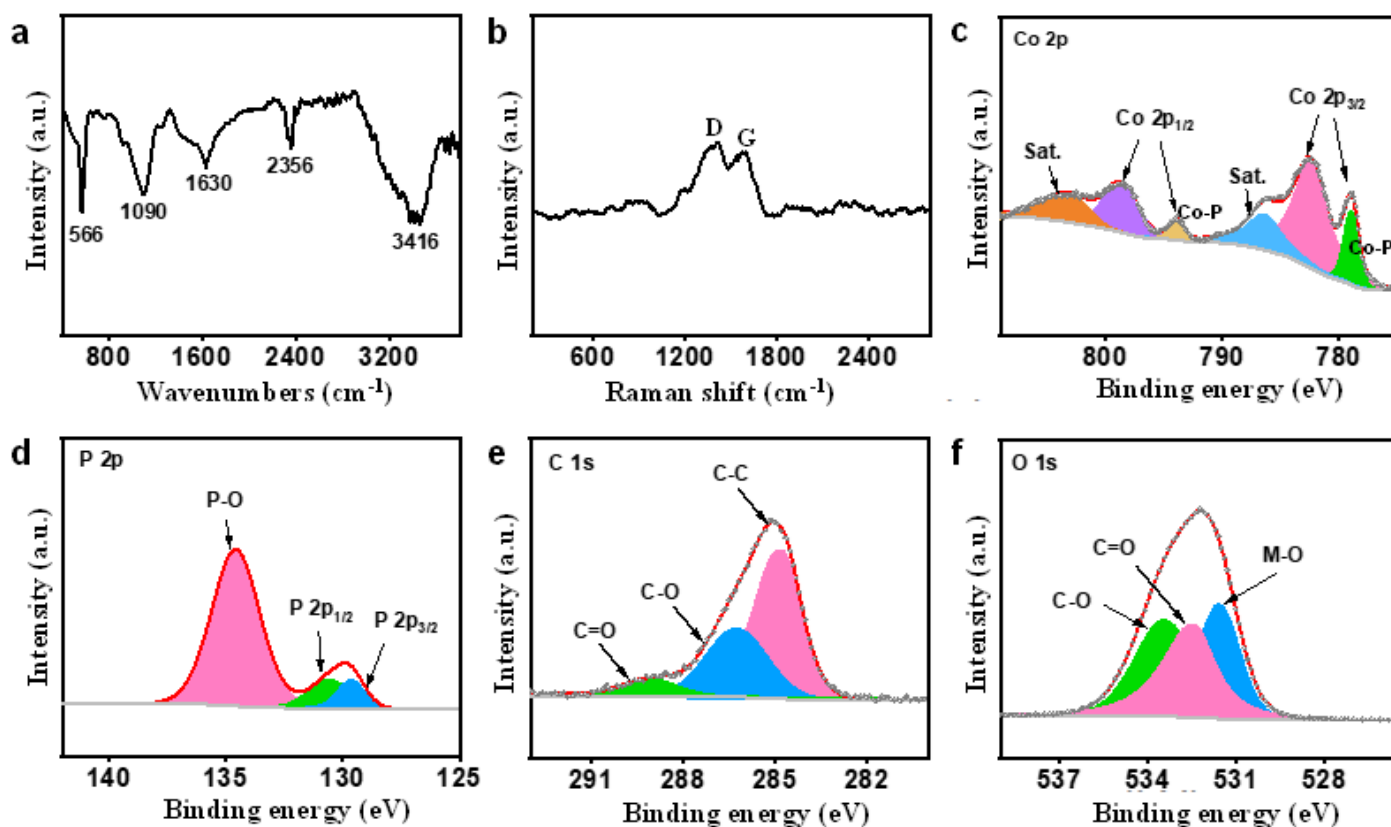


Figure 5

(a) Infrared and (b) Raman spectra of CoP/NF. XPS spectra of (c) Co 2p, (d) P 2p, (e) C 1s and (f) O 1s.

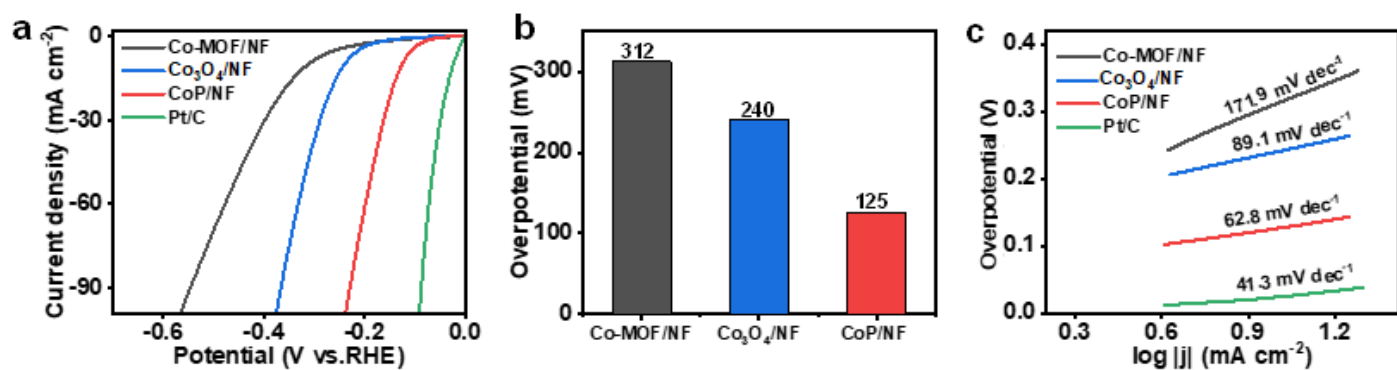


Figure 6

(a) LSV curves, (b) overpotential at a current density of 10 mA cm⁻² and (c) Tafel slope plot of Co-MOF/NF, Co₃O₄/NF, CoP/NF and Pt/C.

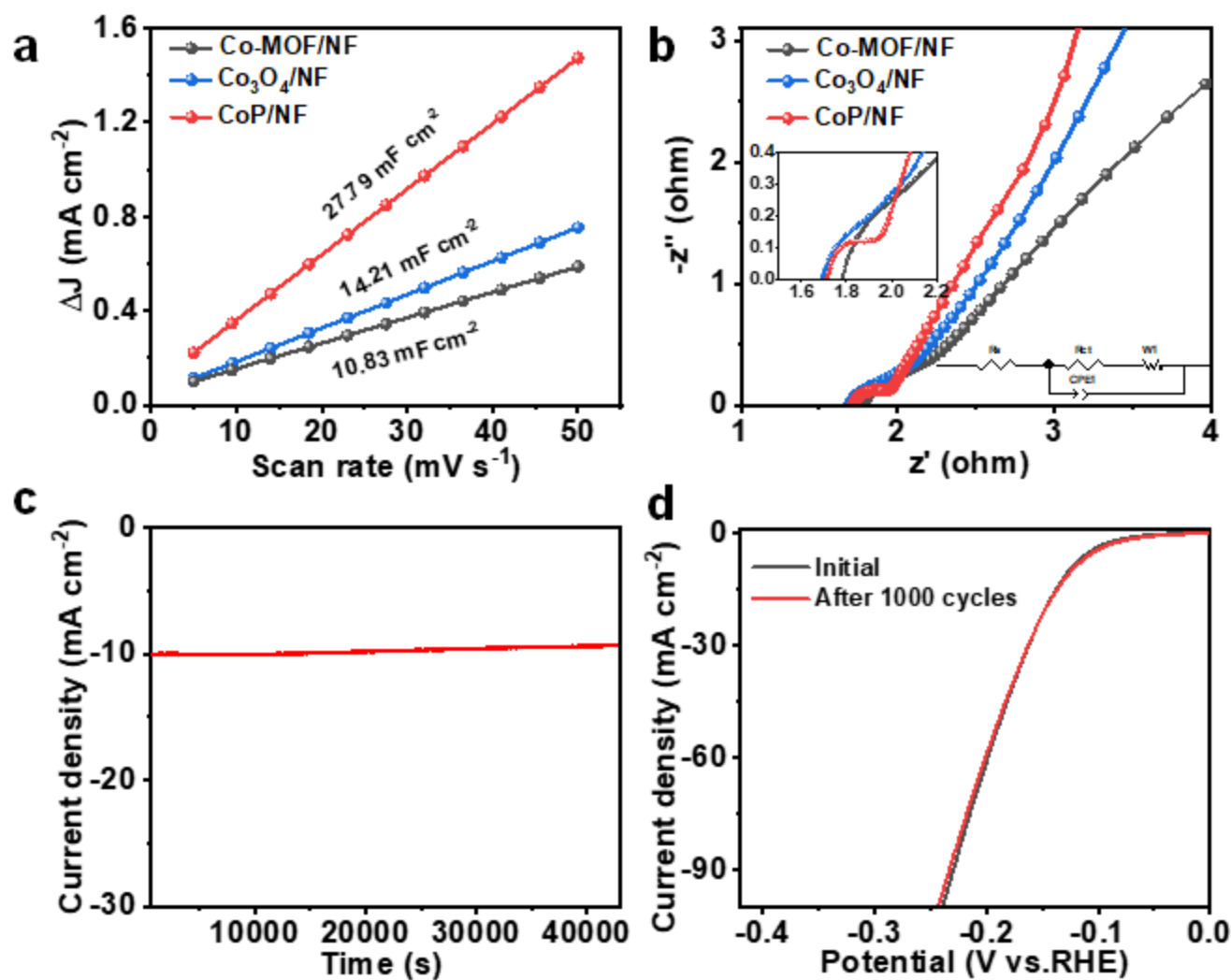


Figure 7

(a) The corresponding double-layer capacitance curves. (b) Electrochemical Impedance Spectroscopy of Co-MOF/NF, Co₃O₄/NF and CoP/NF. (c) The current-time stability test curve and (d) the LSV curve before and after 1000 cycles for CoP/NF.

Supplementary Files

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