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Controllable transformation of sheet-like CoMo-hydro(oxide) and phosphide arrays on nickel foam as efficient catalysts for alkali water splitting and Zn–H₂O cell

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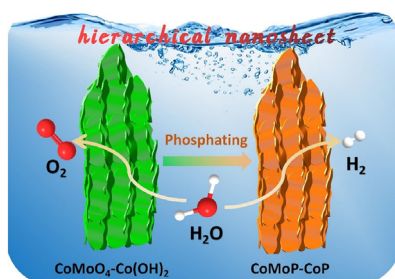
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HIGHLIGHTS

- CoMoO₄–Co(OH)₂ and CoMoP–CoP nanosheets on nickel foam are precisely fabricated by a controllable method.
- Both catalysts exhibited high electrocatalytic activity and stability for OER and HER, respectively.
- The two catalysts constructed overall water splitting system shows robust activity and stability.
- The unique structure and strong electronic interactions between the different components lead to excellent performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Design and synthesis of cost-effective electrocatalysts with remarkable activity and stability is highly desirable for renewable energy devices. Herein, we have successfully constructed sheet-like CoMoO₄–Co(OH)₂ and CoMoP–CoP arrays on nickel foam (NF) through chemical etching ZIF-67 arrays and phosphorization in sequence. Series CoMoO₄–Co(OH)₂/NF as anode and CoMoP–CoP/NF as cathode showed excellent electrocatalytic activity and stability in alkali water splitting, where the combined catalysts only need 1.67 V cell voltage

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CoMoO₄–Co(OH)₂ (P)
Synergistic effect
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to drive 10 mA cm⁻² and obtain robust high current stability at 500 mA cm⁻² for 110 h with almost no attenuation. In addition, using CoMoP–CoP/NF as the cathode of a Zn–H₂O cell can provide a power density of 11.5 mW cm⁻² and a stable 170 h for simultaneous H₂ and electricity generation. The excellent performance of the system is attributed to the unique sheet-like array morphology of combined catalysts providing large surface area and rich pore structure conducive to electrolyte diffusion and gas emission, as well as the synergies between the different components providing more catalytic active sites.

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Introduction

In view of the serious carbon dioxide pollution caused by the excessive consumption of traditional fossil fuels, considerable efforts have been devoted to find clean and sustainable energy sources [1]. Hydrogen is deemed as an ideal sustainable chemical energy carrier, owing to its high energy density [2]. Electrochemical water splitting is generally regarded as prospective technologies for industrial-scale hydrogen production. Currently, Pt/C and RuO₂ noble catalysts have been considered as pioneering electrocatalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) catalysts [3,4], but their expensiveness and scarcity limit the industrial applications [5], prompting us to investigate non-noble metal catalysts. However, non-precious metal catalysts still require higher overpotential compared to precious metal-based catalysts, which unfortunately impedes large-scale hydrogen generation. Therefore, the development of low-cost and efficient transition metal-based catalysts is necessary for hydrogen production.

The state-of-the-art transition metals OER catalysts reported in the literature are based on Ni active sites that raise a severe environmental concern (Table S1) [6]. Cobalt hydroxide as an alternative is a reasonable OER electrocatalyst, which can serve as an alternative to RuO₂ due to its low cost and less environmental impact. However, its insufficient active surface and high charge transfer resistance can't significantly improve sluggish OER kinetics [7,8]. Based on this, doping with other transition metal compounds is an effective strategy for improving catalytic performance through a synergistic effect. Chen et al. [9] reported a hybrid composite of CoO_x–CoMoO₄ nanorod, which shows excellent OER performance due to the electron transfer between two components. Wang et al. [10] exhibited the hierarchical heterostructure CoP₃–NiMoO₄ nanosheets for overall water splitting on Ni foam. The HER performance originates from electronegativity of P atoms to capture positively charged protons [11]. Meanwhile, to meet the industrial requirements, the catalyst still faces severe challenges to continuously, rapidly and stably generate O₂ and H₂ at high current density (≥ 500 mA cm⁻²) [12]. So the electrocatalysts required for overall water splitting still need to be further optimized through design strategies. The HER catalyst can serve as the cathode for Zn–H₂O cells that simultaneously generate electricity and hydrogen to reduce further the additional electricity required for overall water splitting [13]. While, the robust stability and mechanism of Zn–H₂O cell still need to be explored based on transition metal phosphides.

Herein, we reported a novel multifunctional CoMoO₄–Co(OH)₂/NF and CoMoP–CoP/NF combined catalysts that can be used for OER, HER, alkali water splitting and Zn–H₂O cell. The synthesis process of two hybrids is as follows, where the sheet-like ZIF-67 arrays were firstly synthesized on the surface of NF via dipping method. Then, the unstable ZIF-67 arrays in water were transformed into hierarchical CoMoO₄–Co(OH)₂ nanosheets by immersion etching method. Finally, it was further phosphated into CoMoP–CoP nanosheets. The microstructure, crystal structure, specific surface area, chemical state and composition of the CoMoO₄–Co(OH)₂/NF and CoMoP–CoP/NF hybrids have been systematically studied. Subsequently, we designed a system including “CoMoO₄–Co(OH)₂/NF had high OER activity, and CoMoP–CoP/NF showed better HER activity”, and then their combination was used as high current alkali water splitting. Besides, the CoMoP–CoP/NF was also adopted as the cathode of alkaline Zn–H₂O cell, which could release H₂ and generate electricity at the same time. Most importantly, the optimized catalysts showed low overpotential and good stability at high current density (500 mA cm⁻²), which is essential for industrial applications. In short, this work proposes a facile catalyst synthesis strategy that can be applied to both Zn–H₂O cell and alkali water splitting.

Experimental section

CoMoO₄–Co(OH)₂/NF and Co(OH)₂/NF

ZIF-67/NF was fabricated by our reported work (detailed in supporting information) [14]. Then, Na₂MoO₄ (300 mg) was dissolved in 20 mL deionized water, and heated up to 80 °C. After that, ZIF-67/NF was fixed in the Na₂MoO₄ solution, gently stirred for 1 h. The resulted light blue sample was washed with deionized water, and dried at 60 °C, which was nominated as CoMoO₄–Co(OH)₂/NF. As a comparison, ZIF-67/NF was set in the deionized water, and stirred for 12 h. The light blue sample was rinsed and dried in the same conditions, and was designated as Co(OH)₂/NF. Moreover, RuO₂/NF was assembled by the reported method [14], the loading of RuO₂ was set to 2.0 mg cm⁻² (detailed in supporting information).

CoMoP–CoP/NF and CoP/NF

CoMoO₄–Co(OH)₂/NF and Co(OH)₂/NF were converted into CoMoP–CoP/NF and CoP/NF by gas phosphatization according

to the following method: NaH_2PO_2 (0.7 g) was located at the intake side of the tube furnace, then $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ was located next to NaH_2PO_2 in direction of airflow. Then the temperature was rose from room temperature to 350°C at 5°C min^{-1} , and maintained for 3 h under Ar atmosphere. The resulted black sample was nominated as $\text{CoMoP-CoP}/\text{NF}$. As a comparison, CoP/NF was also prepared with $\text{Co(OH)}_2/\text{NF}$ by the same phosphatization. Furthermore, $\text{Pt}/\text{C}/\text{NF}$ was installed in the same method as RuO_2/NF , the loading of Pt/C were set to 1.0 mg cm^{-2} .

Electrochemical measurement

The electrocatalytic activity for OER and HER was estimated by the standard three-electrode mode of electrochemical workstation (Biologic VMP3) with 1.0 M KOH. The pH value of the 1.0 M KOH freshly prepared was 13.5 by pH meter and RHE voltage calibration in Fig. S1. The reference electrode and the counter electrode were saturated calomel electrode and carbon plate, respectively. The details were discussed in the supporting information (experimental section). For alkali water splitting, the performances were evaluated by two-electrode mode in 1.0 M KOH solution. The designed $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}^{(+)}$ and $\text{CoMoP-CoP}/\text{NF}^{(-)}$ catalyst acted as anode and cathode electrodes, respectively. Then, we continued to evaluate the catalysts in 30 wt% KOH solution that simulated industrial application conditions. We particularly explored the electrocatalytic activity and stability of the catalysts under high current density conditions. Aimed at alkaline Zn-H₂O cell, it was carried out in the mixture of 6.0 M KOH with 0.2 M Zn(AC)_2 . Zn plate and $\text{CoMoP-CoP}/\text{NF}$ were used as anode and cathode, respectively. The power density was calculated by the polarization curves, which performed by LSV method at 10 mV s^{-1} . The long-time durability was measured at 10 mA cm^{-2} using LAND testing system.

Results and discussion

In-situ conversion strategy and crystallinity analysis

The $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ and $\text{CoMoP-CoP}/\text{NF}$ were finely designed through ZIF-67 in-situ conversion and phosphating procedure in Fig. 1a. Sheet-like ZIF-67 is evenly self-assembled on the surface of NF by dipping process [14]. Fig. S2 shows the characteristic peaks of ZIF-67 crystal that match previously published ZIF-67 [15,16]. ZIFs crystal is synthesized via the coordination of metal ions and imidazolite ligands [17]. Previous reports demonstrate that ZIF-67 is unstable in water and etched into released Co^{2+} ions [18]. ZIF-67 could be transformed into light blue $\text{CoMoO}_4\text{-Co(OH)}_2$ via dipping in NaMoO_4 water solution (Fig. S3a), and the quantitative ratio between Co(OH)_2 and CoMoO_4 was calculated as 3.4:1 (Table S2). Then, $\text{CoMoO}_4\text{-Co(OH)}_2$ was converted into black CoMoP-CoP during phosphating. The loadings of $\text{CoMoO}_4\text{-Co(OH)}_2$ and CoMoP-CoP were respectively 6.9 and 7.3 mg cm^{-2} .

Fig. 1a and b illustrate the X-ray powder diffraction (XRD) patterns of $\text{CoMoO}_4\text{-Co(OH)}_2$ and CoMoP-CoP , together with Co(OH)_2 and CoP as comparative catalysts. The diffraction peaks at 11.5° , 23.2° , 34.5° and 59.8° can be indexed to the (003), (006), (102) and (110) planes of hexagonal Co(OH)_2 (JCPDS: 46-0605), respectively. The diffraction peaks at 23.3° , 27.5° , 32.9° , 36.8° and 48.8° can be corresponding to the (021), (-202), (-222), (400) and (-133) planes of monoclinic CoMoO_4 (JCPDS: 21-0868), respectively. This result explains that partial cobalt ions dissociated from ZIF-67 react with molybdate ions according to $\text{MoO}_4^{2-} + \text{Co}^{2+} = \text{CoMoO}_4\downarrow$, another part react with hydroxide ions to generate cobalt hydroxide according to the $2\text{OH}^- + \text{Co}^{2+} = \text{Co(OH)}_2\downarrow$, because the sodium molybdate solution is weak alkaline. XRD patterns of comparative

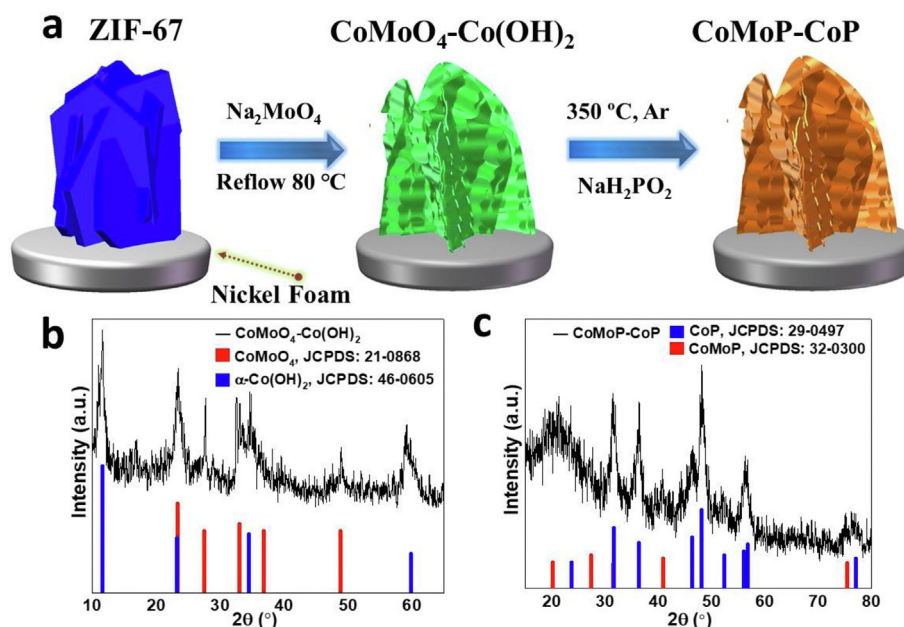


Fig. 1 – (a) The fabricating scheme of $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ and $\text{CoMoP-CoP}/\text{NF}$. XRD patterns of (b) $\text{CoMoO}_4\text{-Co(OH)}_2$ and (c) CoMoP-CoP .

Co(OH)_2 and CoP are the same as that of the corresponding substance in the $\text{CoMoO}_4\text{-Co(OH)}_2$ and CoMoP-CoP (Figs. S4a–b), implying that ZIF-67 in water is converted to Co(OH)_2 , and then convert into CoP after phosphating.

Microstructure analysis

The hierarchical and array structure of two catalysts was characterized by scanning electron microscopy (SEM). As shown in Fig. 2a, ZIF-67 is a smooth sheet with a thickness of ~ 154 nm. After ZIF-67 was transformed into $\text{CoMoO}_4\text{-Co(OH)}_2$, its smooth sheets convert into hierarchical sheets composed of many nanosheets (Fig. 2b). The CoMoP-CoP structure has little change during phosphating compared to $\text{CoMoO}_4\text{-Co(OH)}_2$ (Fig. 2c). Moreover, according to N_2 adsorption-desorption isotherm (Fig. 2d), they belong to typical type-III isotherm with the hysteresis loop. The specific surface area of CoMoP-CoP is $25.5 \text{ m}^2 \text{ g}^{-1}$, it is lower than $\text{CoMoO}_4\text{-Co(OH)}_2$ ($51.6 \text{ m}^2 \text{ g}^{-1}$). The average gap sizes between the interwoven nanosheets of $\text{CoMoO}_4\text{-Co(OH)}_2$ and CoMoP-CoP are 25.5 and 23.6 nm, respectively, demonstrating a typical mesoporous material, which is beneficial to enhance gas emission and ion diffusion rate [19].

The TEM images reveal that $\text{CoMoO}_4\text{-Co(OH)}_2$ is composed by nanosheets (Fig. 3a), its 0.767 nm lattice spacing matches the (003) crystal plane of $\alpha\text{-Co(OH)}_2$ (Fig. 3b). The SAED shows concentric diffraction rings consisting of discrete spots, which can be unambiguously assigned to the (110) plane of $\alpha\text{-Co(OH)}_2$ and (-222) plane of CoMoO_4 (Fig. 3c). The high-angle annular

dark field (HAADF) TEM elemental mappings in Fig. 3d demonstrate a uniform distribution of Co, Mo and O in $\text{CoMoO}_4\text{-Co(OH)}_2$ hybrid.

XPS analysis

The XPS survey spectra of $\text{CoMoO}_4\text{-Co(OH)}_2$ and CoMoP-CoP display the co-existence of Co, Mo, O, P and C elements (Fig. S5a). As a calibration standard, we deconvolute the high resolution C 1s region into C=C (284.0 eV), C–C (284.8 eV) and C–N/C–O (286.0 eV) (Fig. S5b) [20]. In Fig. 4a, the Co $2p_{3/2}$ spectrum of $\text{Co(OH)}_2\text{-CoMoO}_4$ displays two fitting peaks at 780.2 and 781.5 eV, belonging to Co^{2+} [2,21], the Co $2p_{3/2}$ region for CoMoP-CoP shows two fitting peaks at 778.3 and 781.2 eV, they respectively match the cobalt phosphide and partial oxide [22,23]. As shown in Fig. 4b, the Mo 3d spectrum of CoMoO_4 respectively shows the spin orbit doublet Mo $3d_{5/2}$ (231.5 eV) and Mo $3d_{3/2}$ (234.7 eV) [24], the distance between the two peaks is 3.2 eV, this is the feature of the Mo^{6+} oxidation state [25]. The two peaks at 227.3 and 230.4 eV of Mo 3d are assigned to $\text{Mo}^{\delta+}$ species ($0 < \delta < 4$), other two doublets located at 234.9/231.8 eV and 233.1/230.0 eV are assigned to Mo^{6+} and Mo^{4+} , respectively, indicating the surface oxidation of CoMoP [26,27]. In the O 1s region of $\text{CoMoO}_4\text{-Co(OH)}_2$ (Fig. 4c), three binding energies of 530.0, 531.0 and 532.4 eV respectively correspond to the lattice oxygen, oxygen vacancies and absorbed oxygen species in the metal compounds [14,28]. According to Fig. 4d, in the P 2p region of CoMoP-CoP , the peak at 134.4 eV denotes the P–O binding energy because the phosphide surface is oxidized

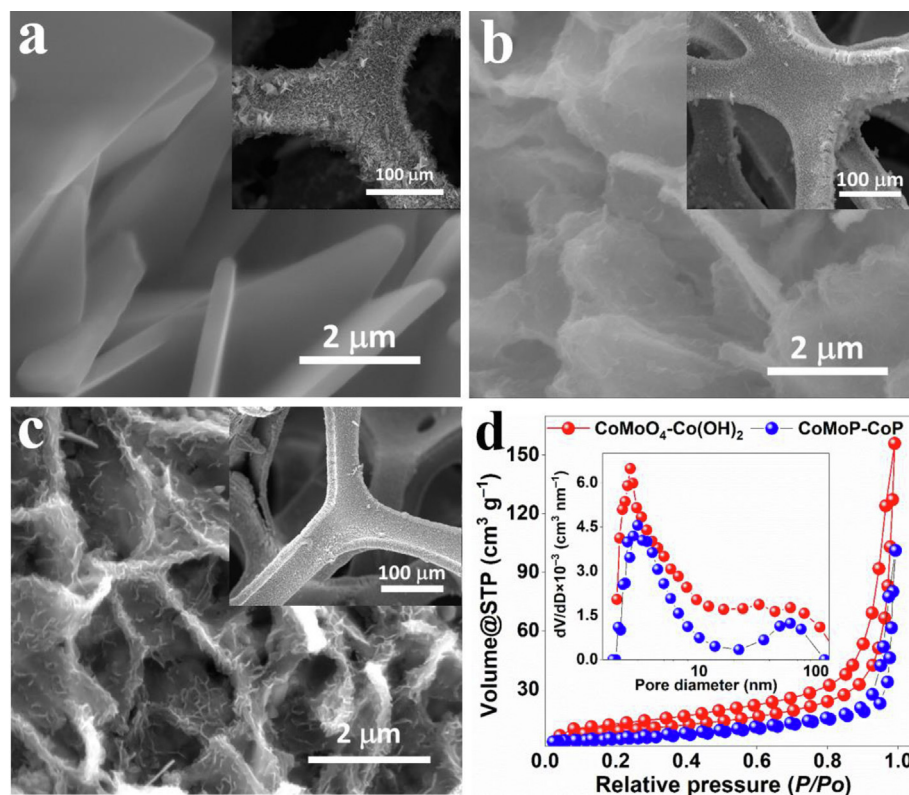


Fig. 2 – SEM images of (a) ZIF-67/NF, (b) $\text{CoMoO}_4\text{-Co(OH)}_2$ /NF and (c) CoMoP-CoP /NF with different magnifications. (d) Nitrogen adsorption-desorption isotherms of $\text{CoMoO}_4\text{-Co(OH)}_2$ and CoMoP-CoP .

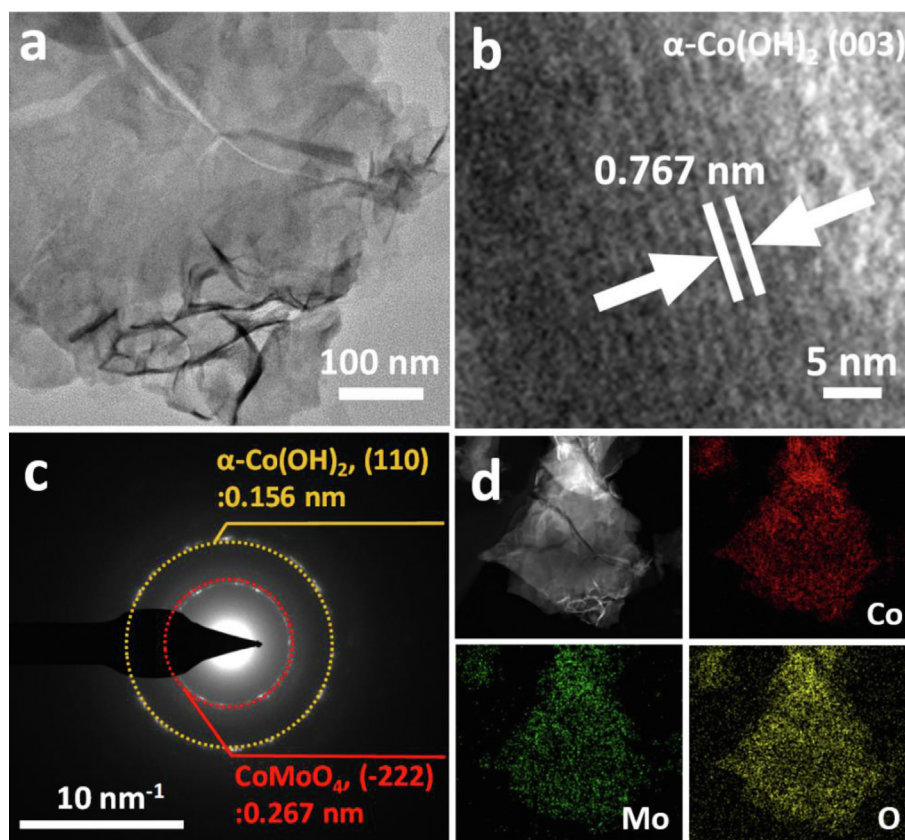


Fig. 3 – (a, b) TEM images of $\text{CoMoO}_4\text{-Co(OH)}_2$. (c) The corresponding selected area electron diffraction (SAED) images of $\text{CoMoO}_4\text{-Co(OH)}_2$. (d) Elemental mapping images of Co, Mo and O of $\text{CoMoO}_4\text{-Co(OH)}_2$.

[4], two fitting peaks at 130.0 (P $2p_{3/2}$) and 130.9 eV (P $2p_{1/2}$) are the binding energy of metal-P [29]. Notably, the Co $2p_{3/2}$ of $\text{CoMoO}_4\text{-Co(OH)}_2$ and CoMoP-CoP produces a negative shift of 0.42 and 0.24 eV relative to Co(OH)_2 and CoP , respectively (Figs. S6a-b), indicating the existence of strong electronic interactions between two components of two catalysts [30], which in turn facilitates charge transfer, thereby enhancing OER and HER performance [9,31].

OER and HER analysis

The OER performance of different catalysts are initially analyzed in alkaline media. According to Fig. 5a, the $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ presents a lower overpotential of 245.5 mV at 10 mA cm^{-2} , and outperforms those of RuO_2/NF (253.6 mV), $\text{CoMoP-CoP}/\text{NF}$ (317.8 mV), and $\text{Co(OH)}_2/\text{NF}$ (292.7 mV), respectively. Besides, the catalyst also exceeds most of the high-performance OER catalysts reported in the literature (Table S1) [9,10,32–45]. Since ZIF-67/NF cannot be converted to CoMoO_4/NF *in situ*, we reference the literature for array-type CoMoO_4 (JCPDS: 21-0868) catalysts supported on nickel foam or carbon cloth, and the overpotentials were between 302 and 350 mV in Table S3. Particularly, the performance advantage is more prominent at higher current densities. The results imply a observable synergistic effect between Co and Mo species, namely the octahedral coordinated Co^{2+} in the CoMoO_4 is easier to oxidize to Co^{3+} in CoOOH , this evidently reinforces the electrochemical activity [42]. The $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ has the

Tafel slope of 55.5 mV dec^{-1} , it is smaller than those of $\text{Co(OH)}_2/\text{NF}$ (71.9 mV dec^{-1}) and RuO_2/NF (59.6 mV dec^{-1}) (Fig. 5b). In Fig. 5c, compared to the literatures of similar catalysts, $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ processes the lower values of the Tafel slope and overpotential, which indicate better catalytic kinetics of OER [46]. Many studies have found that the ECSA grows with the increasing electrochemical double layer capacitance (C_{dl}) [47]. In Fig. 5d and Fig. S7, the C_{dl} of $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ is 374.2 mF cm^{-2} , higher than those of $\text{Co(OH)}_2/\text{NF}$ and RuO_2/NF , indicating its larger electrochemically active surface area [47]. The Nyquist plots are acquired by electrochemical impedance spectroscopy (EIS) [48]. As shown in Fig. S8a, the smaller semicircle diameter, the faster the charge transport rate of the electrode [49], $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ exhibits smaller semicircular diameter compared to $\text{Co(OH)}_2/\text{NF}$, implying that it has faster charge transfer ability. Furthermore, $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ can achieve a 0.01 s^{-1} turnover frequency (TOF) value at 313.3 mV overpotential (Fig. S9, Table S2), it is much lower than the 374.8 mV overpotential of $\text{Co(OH)}_2/\text{NF}$, revealing a better intrinsic activity of $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ [50].

The HER properties of different catalysts were evaluated via LSV in the three-electrode mode. The $\text{CoMoP-CoP}/\text{NF}$ shows a lower 123.9 mV overpotential at 10 mA cm^{-2} in 1.0 M KOH, in comparison with CoP/NF (219.3 mV) and $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ (237.1 mV) (Fig. S10a). According to Fig. S10b, $\text{CoMoP-CoP}/\text{NF}$ has the Tafel slope of 62.5 mV dec^{-1} , it is less than those of CoP/NF ($114.6 \text{ mV dec}^{-1}$) and $\text{CoMoO}_4\text{-Co(OH)}_2/\text{NF}$ ($196.9 \text{ mV dec}^{-1}$), this result reveals that the HER of

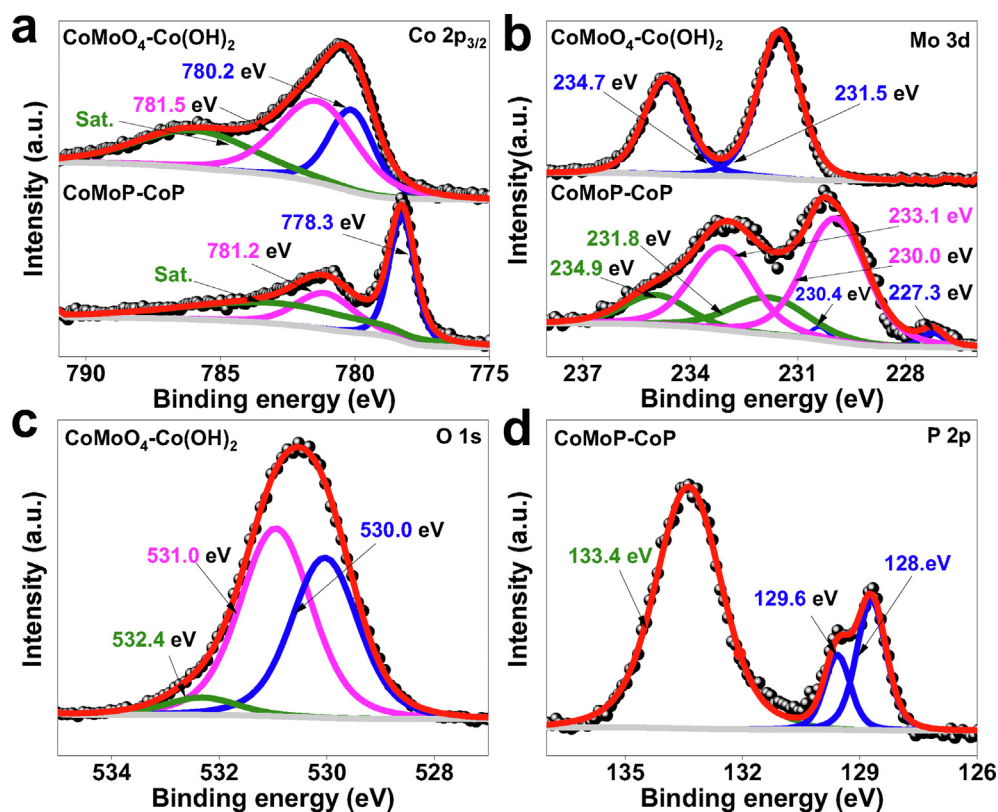


Fig. 4 – The XPS of (a) Co 2p_{3/2}, (b) Mo 3d for CoMoP–CoP and CoMoO₄–Co(OH)₂, (c) O 1s for CoMoO₄–Co(OH)₂, (d) P 2p for CoMoP–CoP.

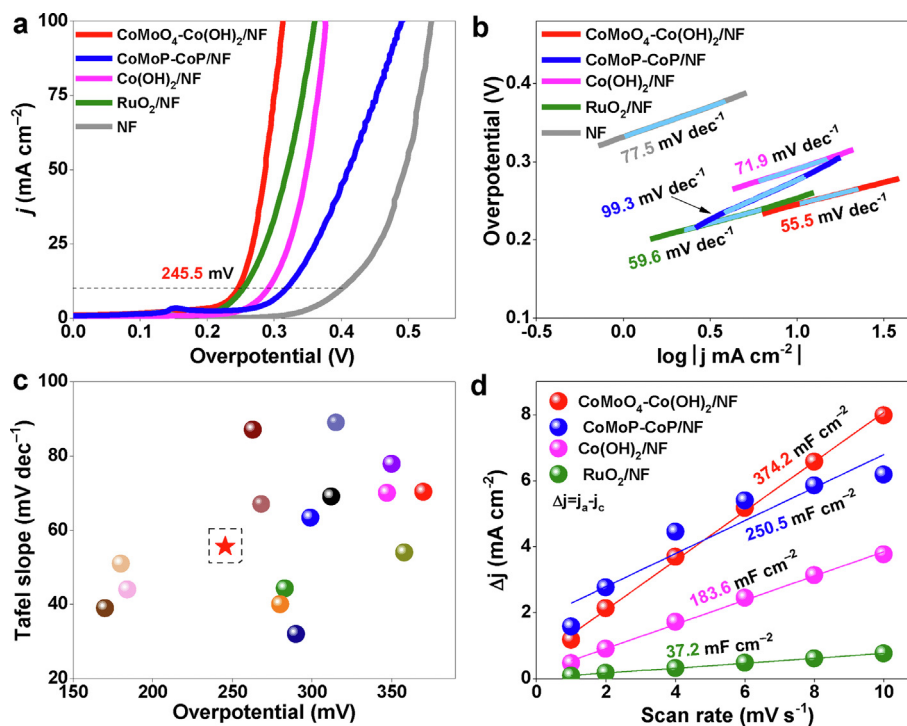


Fig. 5 – (a) Polarization curves of NF, RuO₂/NF, Co(OH)₂/NF, CoMoP–CoP/NF and CoMoO₄–Co(OH)₂/NF. (b) Tafel slope of corresponding OER. (c) Comparison of OER performance between CoMoO₄–Co(OH)₂/NF and similar published catalysts (Table S1). (d) C_{dl} diagram summarized by the CV curves of different voltage scan rates.

CoMoP–CoP/NF may follow by Volmer-Heyrovsky pathway [51], which suggests that electrochemical desorption is the rate determining step [52]. As we expected, the optimized CoMoO₄–Co(OH)₂/NF was designed as an OER catalyst, which showed a relatively low HER activity reflecting as high overpotential and Tafel slope. CoMoP–CoP/NF exhibits smaller semicircular diameters than that of CoP/NF, showing it has faster charge transfer ability (Fig. S8b). For CoMoO₄–Co(OH)₂/NF and CoMoP–CoP/NF catalyst, average relative deviations of voltage are below or equal to 2.0% at 10 mA cm⁻² during 48 h (Figs. S10c–d). Although two catalysts are partially agglomerated after the 48 h stability test, they still showed a complete hierarchical array structure (Fig. S11), demonstrating that they have excellent stability due to the stable and interconnected array structure. Subsequently, the XPS technique was used to probe the changes in the surface chemical states after catalytic stability. The new peak detected at 779.4 eV corresponds to Co³⁺ of the CoOOH, which is the surface-active species generated during OER (Fig. S12a) [53,54], while the Mo signal of CoMoO₄ remains unchanged (Fig. S12b). On the other hand, the CoMoP–CoP/NF still retains the original elemental composition and the chemical states due to the electron-rich reduction environment during the HER in Figs. S12c–e [13,55].

Alkali water splitting and Zn–H₂O cell

Based on alkali water splitting, two-electrode mode of CoMoO₄–Co(OH)₂/NF⁽⁺⁾ and CoMoP–CoP/NF⁽⁻⁾ was constructed. The total voltage required for CoMoO₄–Co(OH)₂/NF⁽⁺⁾ || CoMoP–CoP/NF⁽⁻⁾ is 1.67 V at 10 mA cm⁻² in 1.0 M KOH (Fig. S13a), it is better than most reported similar catalysts (Fig. S13b). Note that the oxidation peaks between 1.05 and 1.35 V are the contribution of the Co²⁺ to Co³⁺ conversion on the catalyst surface [56]. Aimed at industrial applications, alkali water splitting is mostly carried out under 30 wt% KOH solution and high current density (≥ 500 mA cm⁻²) [57]. The voltage of CoMoO₄–Co(OH)₂/NF⁽⁺⁾ || CoMoP–CoP/NF⁽⁻⁾ is 1.81 V at 500 mA cm⁻² (Fig. 6a), it is close to noble metal catalysts of RuO₂⁽⁺⁾ || NiS_x–MoO₂⁽⁻⁾ and RuO₂⁽⁺⁾ || Pt/C⁽⁻⁾ under similar reaction conditions as we previously reported [58]. In addition, we conducted stability tests at 10 and 500 mA cm⁻², respectively. Even at 500 mA cm⁻² for 110 h of continuous operation, the

average relative deviation of the voltage was still less than 1.7% (Fig. 6b).

The CoMoP–CoP/NF and commercial zinc plate are used as the cathode and anode of the Zn–H₂O cell, respectively, which can simultaneously produce hydrogen and electricity (Fig. 7a). The power density of the cell is 11.5 mW cm⁻² in the mixture of 6.0 M KOH and 0.2 M Zn(AC)₂ (Fig. 7b), which is higher than CoP/NF (10.1 mW cm⁻²) and most of the reported results in Table S4. In order to observe hydrogen generation on the cathode surface, we assemble a two-electrode system, and many hydrogen bubbles are generated on the surface of CoMoP–CoP/NF (Fig. 7c). As shown in Fig. 7d, an LED light can be lit by two Zn–H₂O cell with a total voltage of 1.66 V (Fig. S14a) which can drive the alkali water splitting (Fig. S15). In Fig. 7e and Figs. S14b–c, zinc is transformed into hexagonal ZnO (JCPDS: 36-1451) and orthorhombic Zn(OH)₂ (JCPDS: 38-0385) during each 36-h discharge, which are dissolved in the electrolyte and covered on the catalyst to stop the Zn–H₂O cell. Then we replace the electrolyte, zinc plate, and clean CoMoP–CoP/NF with 0.5 M H₂SO₄, the cell is resurrected. So its Zn–H₂O cell exhibits strong discharge stabilization for more than 170 h by five resurrection operations according to chronopotentiometry curves, indicating that the CoMoP–CoP/NF electrode shows potential reusable value due to its acid resistance. The average relative deviation of its discharge voltage is only 4.9%, showing remarkable discharge stability.

Based on the above discussion, the excellent catalytic activities of CoMoO₄–Co(OH)₂/NF and CoMoP–CoP/NF are attributed to the following aspects: (I) Both catalysts show the hierarchical nanosheet structure with high specific surface area, exposing more active sites. Moreover, the array structures benefit gas diffusion and electrolyte transport during electrocatalysis. (II) Both self-supporting catalysts exhibit low charge transfer resistance, enabling lower required potential during electrocatalysis. (III) There are strong electronic interactions between the respective different components of the two catalysts by XPS analysis, this feature promotes the charge transfer and synergistically improves the HER and OER performance. (IV) After electrocatalytic stability, CoMoP–CoP still retains the original chemical structure for HER, while the CoOOH is formed on the surface of CoMoO₄–Co(OH)₂ as active site for OER [54].

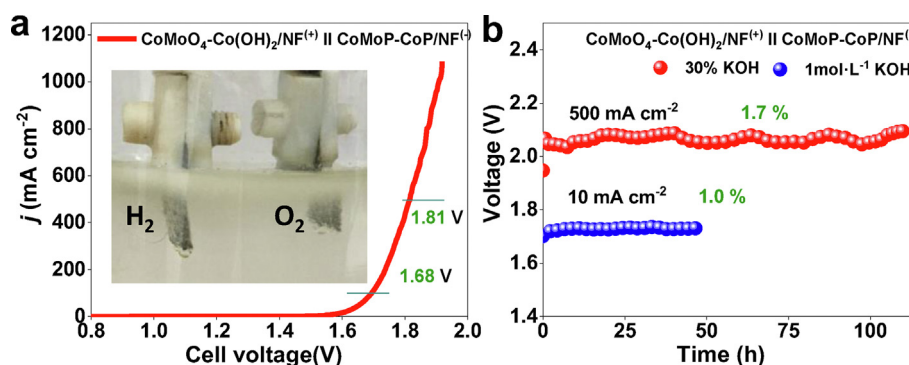


Fig. 6 – (a) The polarization curve of CoMoO₄–Co(OH)₂/NF⁽⁺⁾ || CoMoP–CoP/NF⁽⁻⁾ in 30 wt% KOH. (b) Durability tests of CoMoO₄–Co(OH)₂/NF⁽⁺⁾ || CoMoP–CoP/NF⁽⁻⁾ (30 wt% and 1.0 M KOH).

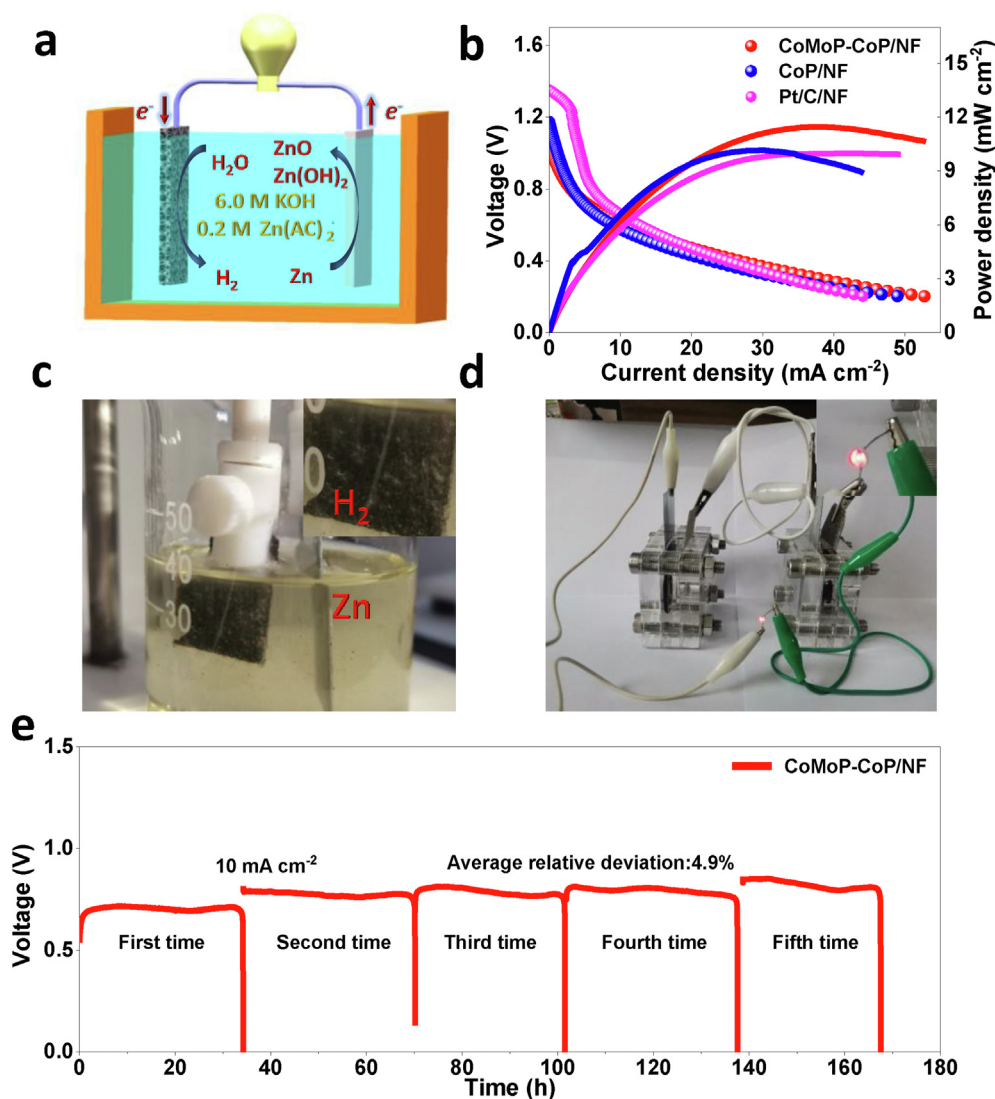


Fig. 7 – (a) Schematic diagram of the Zn–H₂O cell. (b) Polarization and power density curves about CoMoP–CoP/NF, CoP/NF and Pt/C. (c) Hydrogen bubbles produced on the cathode surface of CoMoP–CoP/NF. (d) Picture of one red LED light lit by two Zn–H₂O cell of CoMoP–CoP/NF. (e) Discharge curves of CoMoP–CoP/NF. The electrolyte in Fig. 7a–e is 6.0 M KOH and 0.2 M Zn(AC)₂.

Conclusions

In summary, the CoMoO₄–Co(OH)₂/NF and CoMoP–CoP/NF combined catalysts for water splitting and Zn–H₂O cell have successfully prepared via a two-step approach of *in-situ* conversion and phosphorization. The experimental results fully proved their multi-functional, robust and stable catalytic activities derived from the hierarchical structure, array-like sheets, fast charge transfer and synergistic effect. The combination of two catalysts could achieve highly stable water splitting at high current density used in industrial condition, and the resurrection of CoMoP–CoP/NF realized the repeated and stable operation of the same Zn–H₂O cell. We believe that the novel multifunctional non-noble metal-based catalysts has a bright future of realizing hydrogen production with lower energy consumption.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.ijhydene.2022.05.136.

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