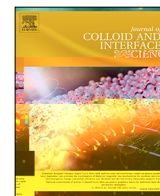




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Regular Article

Nanowire-structured FeP-CoP arrays as highly active and stable bifunctional electrocatalyst synergistically promoting high-current overall water splitting

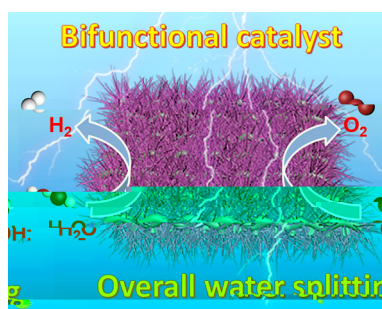

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HIGHLIGHTS

- Fe_{0.14}Co_{0.86}-P/CC is fabricated by hydrothermal plus phosphating treatment.
- The catalyst exhibits excellent HER/OER performance in alkaline solution.
- The bifunctional catalyst only needs 1.95/2.14 V to reach 500/1000 mA cm⁻².
- The synergy between FeP and CoP species dominates the excellent performance.

GRAPHICAL ABSTRACT



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ABSTRACT

The design and construction of highly efficient and durable non-noble metal bifunctional catalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) in alkaline media is essential for developing the hydrogen economy. To achieve this goal, we have developed a bifunctional nanowire-structured FeP-CoP array catalyst on carbon cloth with uniform distribution through in-situ hydrothermal growth and phosphating treatment. The unique nanowire array structure and the strong electronic interaction between FeP and CoP species have been confirmed. Electrochemical studies have found that the designed Fe_{0.14}Co_{0.86}-P/CC catalyst appears excellent HER (130 mV@10 mA cm⁻²)/OER (270 mV@10 mA cm⁻²) activity and stability. Moreover, the bifunctional Fe_{0.14}Co_{0.86}-P/CC^(+/-) catalyst is also used in simulated industrial water splitting system, where the pair catalyst requires about 1.95 and 2.14 V to reach 500 and 1000 mA cm⁻², even superior to the control RuO₂/Pt/C⁽⁻⁾ catalyst, showing good industrial application prospects. These excellent electrocatalytic properties are attributed to the synergy between FeP and CoP species as well as the unique microstructure, which can accelerate charge transfer, expose more active sites and enhance electrolyte diffusion and gas emissions.

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1. Introduction

Rapid development of society, the demand for energy supply and ecological environment quality is increasing [1]. However, energy supply is mainly dependent on fossil fuels, which not only have limited sources, but pollute the environment [2]. Therefore, it is urgent to find clean and renewable energy [3]. Currently, the

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clean renewable energy conversion and storage systems developed by the society include fuel cells [4], metal-air cells [5], and electrochemical water splitting devices [6], etc. Among these systems, electrochemical water splitting devices are the best choice for the clean production of H₂ and O₂ [7,8]. However, the price of H₂ from electrolysis is more than five times higher than that of dry methane reforming. The two main factors that limit commercial application of the water electrolysis are price of the electricity and system efficiency. The system efficiency is mainly governed by the catalyst stability, hydrogen evolution reaction (HER), and oxygen evolution reaction (OER) efficiencies under high current density (>200 mA cm⁻²) and low over potentials (less than 100 mV). Because the slow oxygen evolution reaction (OER) kinetics involves a four-electron step, it requires high overpotential and high activation energy to overcome the complex oxidation process. To overcome this limitation, Wang et al. reported a series of transition metals (Fe and Mn) co-doped three-dimensional Ni₃S₂/NF via hydrothermal and sulfuration treatments. The resulting OER catalyst showed a low overpotential of 216 mV@30 mA cm⁻² [9]. Meanwhile, high overpotential and poor stability of hydrogen evolution reaction (HER) is also another bottleneck to be addressed. Therefore, it is urgent to develop OER and HER catalysts with excellent performance [10,11]. Up to now, the best OER (IrO₂/RuO₂) [12,13] and HER (Pt) [14] catalysts are based on noble metals. However, the high cost and scarcity of these precious metals limit their industrial application. Therefore, it is urgent to design and construct non-noble metal electrocatalysts with high OER and HER performance [15,16]. So far, a series of transition metal-based (TMB) catalysts with a good electrocatalytic performance, such as oxides [17,18], hydroxides [19,20], carbides [21,22], borides [23,24], phosphides [25,26], sulfides [27], and selenides [28,29], etc.

Transition metal-based bifunctional catalysts with low HER and OER overpotentials are particularly interesting, due to the simplicity of cell design and the possible capital cost reduction. However, it has its own challenges to overcome because the HER and OER follow different mechanisms, whereas the HER kinetics determined by chemisorption OH⁻ and H* and subsequent desorption of water molecule in an alkaline solution [30]. The recombination of two adsorbed H* atoms is the rate determining step of HER [31]. Similarly, the OH⁻ dissociation and surface intermediate (OH*, OOH*, and H*) chemisorption. Therefore, the catalysts that could bind with both hydrogen and oxygen containing intermediates are favored for overall water splitting. However, the reaction kinetics of two-electrode system is limited by the slow four-electron transfer kinetics of the OER that makes it even harder to design bifunctional water splitting catalyst [32,33].

The single transition metal phosphides in particular are often regarded as HER catalyst because the phosphorus and the metal atom cooperatively moderate the catalyst and hydrogen intermediate interaction thereof facilitate the hydrogen generation process [34]. Besides, the metal phosphates not only facilitate the metal atom oxidation by acting as proton acceptors, but induce distorted local metal geometry enhancing OER. Consequently, the bimetallic phosphide systems raised a lot of attention in the community [35]. For example, Yu et al. reported a bimetallic (Ni-Fe)P with optimized Ni/Fe ratio and high level of porosity that showed a low over potential both in HER and OER [36]. Tan et al. reported the nanoporous bimetallic (Co_{1-x}Fe_x)₂P phosphides with controllable Co/Fe ratio and tunable porosity. The catalysts are prepared by electrochemical etching. The optimized catalyst exhibited versatile performance and low overpotential towards both HER and OER in an alkaline solution. Although they claim better performance than noble metal catalysts, the results were compared at a low current density [37].

Herein, we designed Fe-Co bimetallic phosphide nanowires on carbon cloth, which can directly undergo overall water splitting reaction. The bifunctional 3D catalyst arrays were prepared using a simple solvothermal approach followed by phosphatization with NaH₂PO₂. Because of the hierarchical nanostructures and synergistic effect between the FeP and CoP species, the optimized Fe_{0.14}Co_{0.86}-P/CC catalyst revealed comparable HER (130 mV@10 mA cm⁻²)/OER (270 mV@10 mA cm⁻²) activity and stability to the noble metal catalysts. Most importantly, the Fe_{0.14}Co_{0.86}-P/CC outperformed noble metal catalyst at industrial relevant high current density (>500 mA cm⁻²) two-electrode system with low cell voltages (1.97 V@500 mA cm⁻², 2.14 V@1000 mA cm⁻², and 2.31 V@1500 mA cm⁻²) and reasonable stability.

2. Experimental section

2.1. Synthesis of Fe_xCo_y-species on carbon cloth

All the chemicals used here are of analytical grade and used directly without further purification. The carbon cloth (CC, 1.5 cm × 4 cm) was ultrasonically cleaned with 1.0 M HCl, deionized water and ethanol for 10 min, and then repeated 3 times to remove impurities on the surface before further processing. The experimental details are the following: 0.7 mmol Fe(NO₃)₃·9H₂O, 4.2 mmol Co(NO₃)₂·6H₂O, 8.0 mmol CO(NH₂)₂ and 3.2 mmol NH₄F were dissolved in 70 mL ultra-pure water and 5 mL ethanol, and then stirred for 30 min to get a clear solution. The mixture was then transferred to a Teflon lined autoclave (100 mL) with a clean CC, heated to 140 °C at a heating rate of 5 °C min⁻¹, and then kept for 10 h. After cooling to room temperature, the modified CC material was rinsed with ultra-pure water, ethanol for several times, and then dried in an oven at 60 °C for 2 h. According to the Fe/Co ratio (x/y), the resulting composite is named Fe_xCo_y-species/CC. A series of composite materials with different Fe/Co ratios were synthesized with the total amount of Fe³⁺ and Co²⁺ being 4.9 mmol, in which the molar ratios of Fe/Co were 1/0, 1/4, 1/8, and 0/1, respectively.

2.2. Synthesis of Fe_xCo_y-P/CC by vapor phase phosphidation

The phosphating process is carried out in a tube furnace, where 1.0 g of NaH₂PO₂ is used as phosphorus source and placed in an upstream porcelain boat along with the precursor in another porcelain boat downstream. The furnace was heated to 350 °C with a heating rate of 5 °C min⁻¹ in N₂ atmosphere (20 sccm), and kept at 350 °C for 2 h. After phosphating treatment, the sample was cooled to ambient temperature in a flowing N₂ gas. After that, a series of samples were prepared using the similar method as discussed above, which were named as FeP/CC, Fe_{0.20}Co_{0.80}-P/CC, Fe_{0.11}Co_{0.89}-P/CC and CoP/CC, respectively.

For comparison, we also prepared RuO₂ and commercial Pt/C modified CC, of which 5.0 mg RuO₂ powder or commercial Pt/C (Johnson-Matthey) were dispersed in 480 μL deionized water, 480 μL absolute ethanol and 20 μL 5% Nafion to form a mixture solution. After sonication for 30 min, 200 μL of the slurry was pipetted onto a CC (1 cm × 1 cm) and dried at room temperature for later use.

2.3. Electrochemical measurements

An electrochemical workstation with a standard three-electrode system (Bio-Logic VMP3) was used to test the electrochemical performance of the designed catalyst in 1.0 M KOH electrolyte. Among them, the synthesized composite material, carbon rod, and saturated calomel electrode (SCE) are used as working,

counter, and reference electrodes, respectively. In the electrochemical test, we first used cyclic voltammetry (CV) for 3 ~ 5 consecutive tests to stabilize the performance of the catalyst with a scan rate of 10 mV s^{-1} . Second, the linear sweep voltammetry (LSV) was used to explore the catalytic performance of the catalyst for OER and HER at a sweep rate of 2 mV s^{-1} . Third, the electrochemical impedance spectroscopy (EIS) was tested near the onset potential in the frequency range of 200 kHz to 10 mHz. Finally, the stability of the catalyst was explored separately by chronopotentiometry. All those tests have been conducted *in situ* compensation and the potentials have been calibrated to standard hydrogen electrode (RHE). The calibration is obtained by using two clean Pt foils as working and counter electrodes in H_2 -saturated 1.0 M KOH with a scan rate of 5 mV s^{-1} , the correction equation is $E(\text{RHE}) = E(\text{SCE}) + 1.040 \text{ V}$ (Fig. S1).

The two-electrode industrial simulation test was conducted in a 30 wt% KOH solution with a scan rate of 10 mV s^{-1} . At the same time, a long-term stability test of the two-electrode bifunctional catalyst was also carried out at approximately 25°C .

3. Results and discussion

Fig. 1a is a schematic diagram of the synthesis of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ by a two-step method. In the first step, a certain amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, urea, and NH_4F are dissolved in H_2O -ethanol in an autoclave. As the temperature rises, urea will gradually decompose to create an alkaline environment, and the Fe and Co precursors therein can grow *in-situ* on CC surface in the presence of NH_4F . Next, the PH_3 produced by the pyrolysis of NaH_2PO_2 is used to phosphatize the precursor material in a tube furnace, thereby preparing $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ composite materials. The mass of CC ($1 \times 1 \text{ cm}^2$) loaded with catalysts and fresh CC were 14.5 mg and 13.4 mg, respectively. From this, we can conclude that the catalyst loading is 1.1 mg cm^{-2} . The ICP-AES test shows that the mass fractions of Fe and Co are 5.28% and 33.08% respectively, and the molar ratio is 1/6.15 in the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ composite (Table S1), which is consistent with the theoretical value.

To further study the crystal structure change of the catalytic material, we performed XRD analysis. Fig. 1b shows that the XRD patterns of the $\text{Fe}_{0.14}\text{Co}_{0.86}$ -species prepared on the CC surface are mainly consistent with Co_3O_4 (JCPDS: 43–1003) [38], and

FeOOH (JCPDS: 34–1266) [39], along with a small amount of CoFe_2O_4 (JCPDS: 22–1086). After phosphatization, the pure Fe species on the CC surface is subsequently converted to FeP (JCPDS: 39–0809) [40], and the pure Co species is phosphated to CoP (JCPDS: 29–0497) (Fig. S2) [41]. Notably, the $\text{Fe}_{0.14}\text{Co}_{0.86}$ -species after phosphatization completely inherited in the crystal structure of FeP and CoP simultaneously in a hybrid structure (Fig. 1c). The specific surface area and porosity of the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P}$ composite (Scrape off the CC surface) are measured using a N_2 adsorption-desorption isotherm test at 77 K. The results show that the Brunauer–Emmett–Teller (BET) surface area of the material is about $27.8 \text{ m}^2 \text{ g}^{-1}$, and the average pore size is *ca.* 18.1 nm through BJH method (Fig. S3). The larger BET surface area and porous characteristics increase the exposure of active sites, rapid electrolyte diffusion, and gas emission, thereby improving electrochemical activity.

The morphology and microstructure of the optimized catalyst were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. S4, the surface of pristine CC is smooth initially and become the interwoven nanowire array-like structure after *in-situ* hydrothermal growth of $\text{Fe}_{0.14}\text{Co}_{0.86}$ -species (Fig. S5). The nanowire array-like structure of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P}$ was preserved even after phosphatization (Fig. 2a). TEM was further used to explore the detailed morphology of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P}$ nanowires in nanoscale. As shown in Fig. 2b, the width of the nanowire is approximately 150 nm, and there are some particulate materials on the surface, which make the nanowire have a concave-convex structure, thereby exposing more reaction sites. The high-resolution TEM image shows two types of well-defined lattice fringes (Fig. 2c), one with a lattice spacing of 0.29 nm corresponds to the (020) crystal plane of orthorhombic FeP , and the other with lattice spacings of 0.19 nm and 0.24 nm attribute to the (202) and (102) crystal planes of orthorhombic CoP , respectively [42,43]. The selection electron diffraction (SAED) image shows a series of diffraction rings with dense bright spots (Fig. 2d) that represent the (020) and (230) crystal planes of FeP , and the (201) and (202) crystal planes of CoP . Furthermore, HAADF-STEM and the corresponding element mappings show that the elements of Fe, Co, and P are uniformly dispersed throughout the nanowire structure of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P}$ (Fig. 2e).

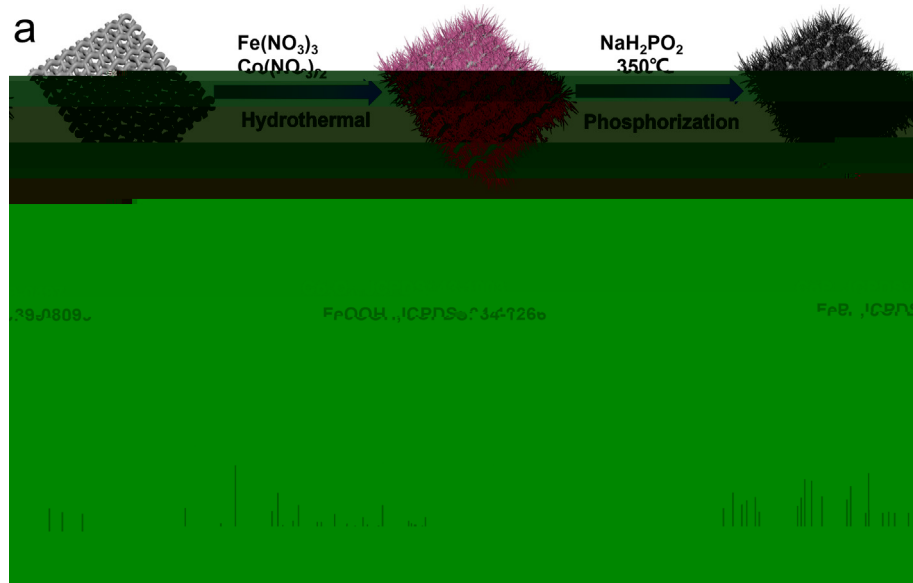


Fig. 1. (a) Schematic diagram of the formation of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst. (b) X-ray diffraction (XRD) patterns of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{/CC}$. (c) X-ray diffraction (XRD) patterns of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$.

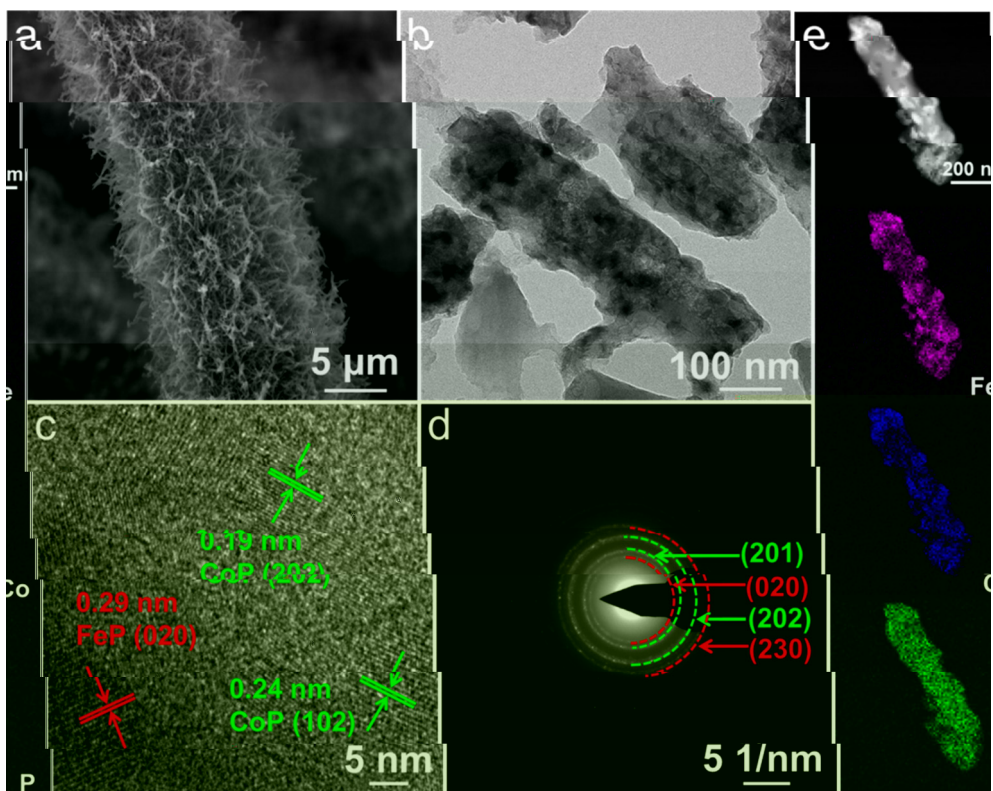
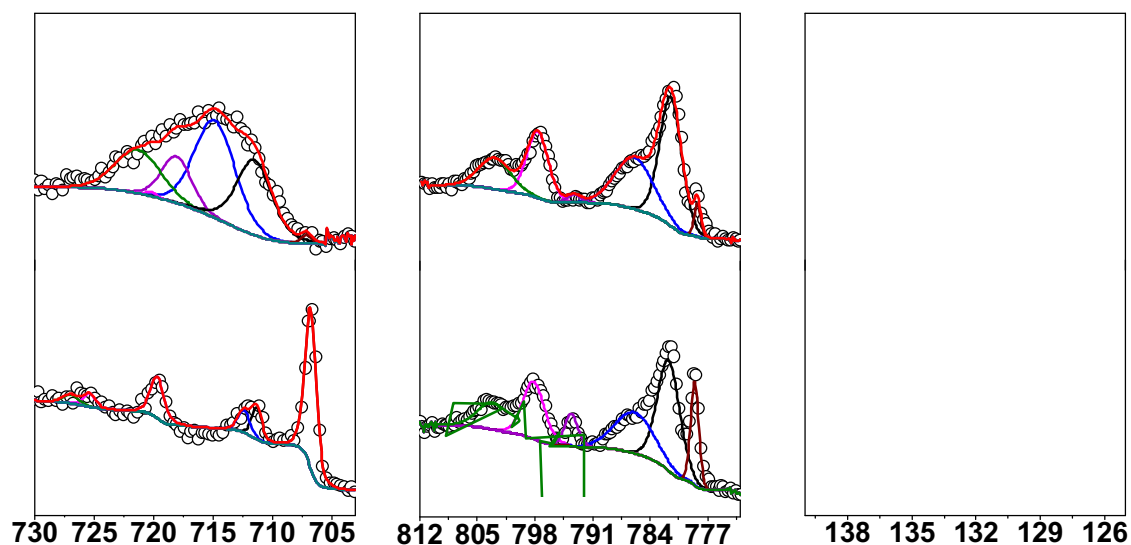


Fig. 2. SEM images of (a) $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$, (b) TEM image and (c) high-resolution TEM image of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$. (d) SAED images of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$. (e) HAADF TEM image and elemental mappings of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$.

X-ray photoelectron spectroscopy (XPS) is used to explore the composition and chemical state of the composite. As shown in Fig. S6a, the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ material is composed of C, Fe, Co and P elements. The high-resolution XPS of C 1s was identified as C=C (284.0 eV), C-C (284.8 eV), C-O (286.0 eV) and C=O (288.0 eV) (Fig. S6b) [44], and was used as a calibration standard for other elements. As shown in Fig. 3a, the Fe $2p_{3/2}$ region of $\text{Fe}_{0.14}\text{-Co}_{0.86}\text{-P/CC}$ is fitted with three peaks of FeP (707.2 eV), Fe-O

(711.4 eV) and one satellite peak (715.0 eV) [45,46]. Compared with FeP/CC, the binding energy of the Fe-P of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ is positively shifted by 0.35 eV. Moreover, the Co $2p$ region of $\text{Fe}_{0.14}\text{-Co}_{0.86}\text{-P/CC}$ contains a pair of Co $2p_{3/2}$ and Co $2p_{1/2}$, where the Co $2p_{3/2}$ is fitted with three peaks of CoP (778.3 eV), CoO (781.6 eV) and a satellite (786.1 eV), respectively (Fig. 3b) [47]. As compare to CoP/CC, the Co-P binding energy of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ presented a negatively shifted of 0.31 eV. These phenomena indicate that



there is a strong electronic interaction between FeP and CoP species in the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ composite [48]. Besides, the P 2p fitting of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ is shown in Fig. 3c, in which the high-resolution P 2p mainly was de-convoluted into two distinctive peaks as P $2p_{3/2}$ (129.1 eV) and P $2p_{1/2}$ (130.0 eV) for metal phosphates as well as an additional peaks for P–O bonds (133.6 eV) [40,49]. Moreover, we also compared the XPS before and after the stability test of the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst. The results show that part of the FeP and CoP species on the surface are oxidized to metal (oxy)hydroxide during the OER process (Figs. S6c-e) [35,50].

In order to evaluate the electrochemical performance of all catalysts, we first used LSV polarization curves to explore the changes in OER activity in 1.0 M KOH solution. The Fig. S7 shows the effect of different Fe/Co ratios on OER performance of $\text{Fe}_x\text{Co}_y\text{-P/CC}$. The $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ revealed the best OER performance. If not specifically stated, the hybrid catalyst discussed below is $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$. Furthermore, we employed the LSV polarization curve to explore the electrochemical performance of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$, along with FeP/CC, CoP/CC and $\text{RuO}_2\text{/CC}$ with a scan rate of 2 mV s^{-1} . Fig. 4a shows that $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst only needs 270 mV to reach 10 mA cm^{-2} , which is far lower than that of FeP/CC (456 mV), CoP/CC (334 mV), and close to $\text{RuO}_2\text{/CC}$ (252 mV). It is worth noting that at a higher current density ($>35\text{ mA cm}^{-2}$), the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst begins to outperform $\text{RuO}_2\text{/CC}$, showing a good industrial application prospect, which requires a stable performance at high current density at low overpotential. The superior electrocatalytic performance can be attributed to the synergy between the CoP and FeP components, which is also widely reported in the literature [51–53]. Previous DFT calculations also show that the Co-Fe-P hybrid composite can increase the density of states near the Fermi level [52], thereby increasing the inherent electrocatalytic activity.

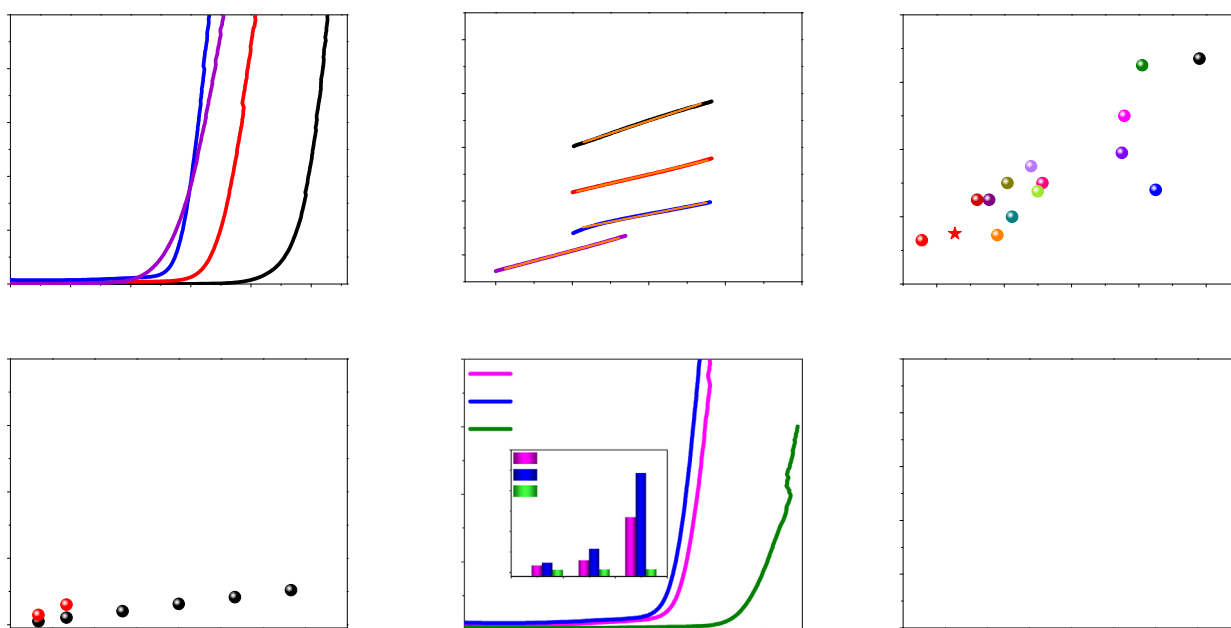
To study the OER kinetics of different catalysts, the Tafel plots derived from the corresponding LSV curves were evaluated in Fig. 4b. The Tafel slope of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst is 45.4 mV

dec^{-1} , which is significantly lower than those of FeP/CC (74.5 mV dec^{-1}), CoP/CC (54.3 mV dec^{-1}), and $\text{RuO}_2\text{/CC}$ (61.1 mV dec^{-1}). These results indicate that $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst has the fastest reaction kinetics, thereof a favorable OER activity than other catalysts [54,55]. Moreover, it has outstanding OER activity than most recently reported metal phosphates with small Tafel slope and overpotential at 10 mA cm^{-2} in alkaline medium (Fig. 4c, Table S2).

As shown in Fig. 4d, the double layer capacitance (C_{dl}) value of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ is 230.0 mF cm^{-2} , which is much larger than those of FeP/CC (52.1 mF cm^{-2}), and CoP/CC (137.4 mF cm^{-2}). The C_{dl} was calculated from the cyclic voltammetry (CV) curves at various scan rates in a non-Faradaic potential region (Fig. S8) [56]. In general, the superior OER electrocatalytic activity relates with the large electrochemical active surface area (ECSA). The double layer capacitance (C_{dl}) is directly proportional to ECSA [17]. As shown in Fig. S9, the ECSA is calculated by $\text{ECSA} = C_{dl}/C_s$, where C_s is the average specific capacitance of 0.04 mF cm^{-2} [55]. The ECSA of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ is 5750 cm^2 , which is much higher than these of CoP/CC (3435 cm^2) and FeP/CC (1303 cm^2), implying higher OER active sites density in $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ [26].

The intrinsic catalytic activity per catalytic active site is estimated by the turnover frequency (TOF) value [57]. Fig. 4e shows the TOF curve at various overpotentials calculated using ICP metal contents from Table S1. As the overpotential increases, the TOF values of all catalysts increase monotonically. Among them, the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst shows the highest intrinsic catalytic activity once again confirmed the highest catalytic oxygen evolution conversion efficiency [18].

Electrochemical impedance spectroscopy (EIS) measurements were also performed to further understand the OER kinetics, and the corresponding results are shown in Fig. S10. The fitted charge transfer resistance (R_{ct}) obtained from the semicircle is used to evaluate the electrocatalytic kinetics at the catalyst/electrolyte interface, where a low value corresponds to a fast electron transfer and a superior OER kinetics [54]. The $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ presents the



smallest R_{ct} (2.07 Ω) among the as-prepared precatalysts, suggesting a superior electron transfer ability and much lowered energy barrier of OER. The ultralow R_{ct} of the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst is in good agreement with the small Tafel slope and the superior OER kinetics. The LSV curves of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ remain nearly unchanged after 2000 cycles (Fig. 4f), demonstrating remarkable stability. In addition, the stability test performed at a current density of 20 mA cm^{-2} (Fig. S11) for 24 h. No obvious decline in catalytic performance was observed. However, there is a significant change in catalyst morphology (Fig. S12).

The HER performance of all catalysts was also studied in 1.0 M KOH solution. As shown in Fig. 5a, the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst displayed the best HER catalytic activity among various catalysts except commercial Pt/C. The $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst can achieve a current density of 10 mA cm^{-2} at an overpotential (η_{10}) of 130 mV. In comparison, the overpotentials of FeP/CC and CoP/CC are as high as 185 mV and 163 mV. The $\text{Fe}_{0.20}\text{Co}_{0.80}\text{-P/CC}$ and $\text{Fe}_{0.11}\text{-Co}_{0.89}\text{-P/CC}$ also require higher overpotentials of 170 mV and 270 mV respectively at 10 mA cm^{-2} (Fig. S13). Note: Commercial Pt/C needs an overpotential of 49 mV to reach 10 mA cm^{-2} under the same condition. Tafel plots were then acquired to investigate the HER kinetics [18]. The Tafel slope of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ is 57.2 mV dec^{-1} , close to that of Pt/C (35.5 mV dec^{-1}), but significantly lower than those of all control catalysts (Fig. 5b) as expected. The results indicate that the electrochemical desorption of hydrogen of the Volmer-Heyrovsky reaction path is the rate-determining step ($\text{H}_2\text{O} + e^- = \text{H}_{\text{ads}} + \text{OH}^-$ and $\text{H}_{\text{ads}} + \text{H}_2\text{O} + e^- = \text{H}_2 + \text{OH}^-$) [18]. Fig. 5c is a comparison graph of the overpotential at -10 mA cm^{-2} and Tafel slope with the previously reported similar HER catalysts. It can be seen that the designed $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst is obviously superior to most of these catalysts (Table S3). In addition, long-term stability is another important criterion for evaluating the practical application of electrocatalysts. Along with multicycle LSV test (Fig. 5d), we also performed chronoamperom-

etry measurement to evaluate the catalyst durability. Fig. S14 showed that $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst maintained for up to 24 h at -10 mA cm^{-2} with only a decline of about 4.1%, some of which may be associated with surface chemical state change (Fig. S6) and structural agglomeration (Fig. S15).

Industrial application of electrocatalytic water splitting is limited by massive energy penalty from uphill reaction kinetics that requires much higher voltage (1.8 ~ 2.4 V) than 1.23 V to reach the current density of 200 ~ 400 mA cm^{-2} . Therefore, only less than 5% of H_2 is produced by electrolysis worldwide [36]. Therefore, our ultimate goal in this work is to achieve overall water splitting at a high current density and a lower voltage [17,18]. In this regard, a two electrode system of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ as both the cathode and anode for HER and OER in 30 wt% KOH electrolyte was constructed for overall water splitting (Fig. 6a), of which 30% KOH is a commonly used industrial H_2 production condition by water splitting. For comparison, $\text{RuO}_2^{(+)}||\text{Pt/C}^{(-)}$ was also examined under the same conditions. As shown in Fig. 6b, the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}^{(+/-)}$ could achieve the current density of 10 mA cm^{-2} at a cell voltage of 1.63 V, which is slightly higher than the benchmark $\text{RuO}_2^{(+)}||\text{Pt/C}^{(-)}$ (1.57 V). It is worth noting that when the current density exceeds 30 mA cm^{-2} , the overall water splitting performance of the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}^{(+/-)}$ begins to surpass that of $\text{RuO}_2^{(+)}||\text{Pt/C}^{(-)}$. In particular, when the cell voltages are 1.95, 2.14 and 2.31 V, the current densities can reach 500, 1000 and 1500 mA cm^{-2} , respectively, showing good catalytic performance at high current density. We found that the two-electrode overall water splitting reported in this work was obviously superior to most of the previously reported works (Fig. 6c and Table S4). In addition, we used chronopotentiometry to study the stability of the catalyst. The results show that the $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}^{(+/-)}$ electrodes can be maintained at 10 mA cm^{-2} for 48 h without any deterioration (Fig. 6d). The stability test at high current density was difficult due to the interference of large amounts of gas generated at both electrodes.

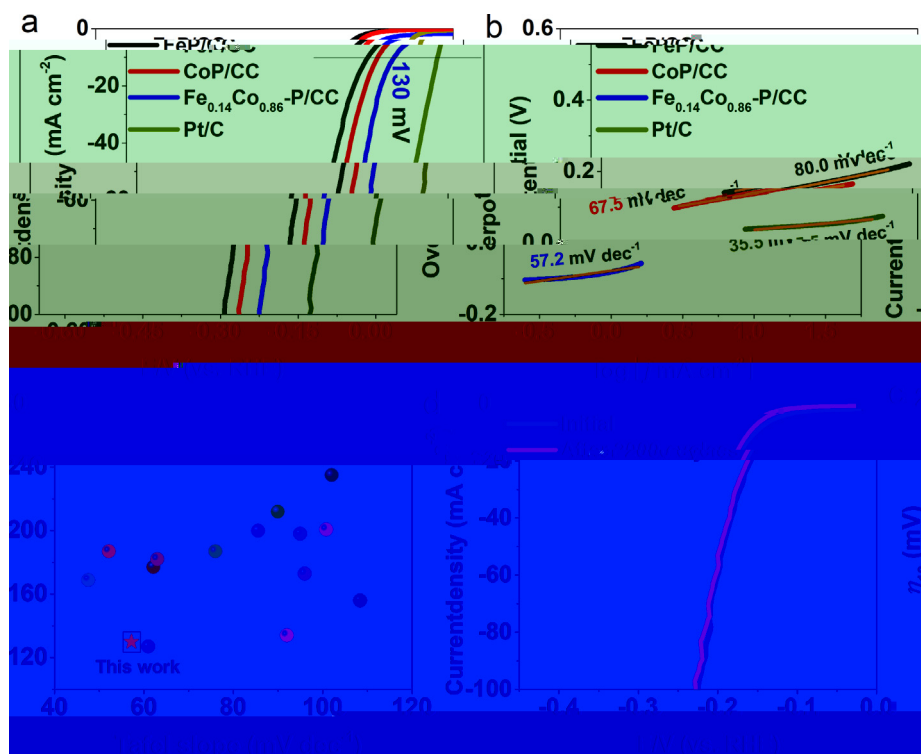


Fig. 5. (a) HER polarization curves of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ together with CoP/CC, FeP/CC, and Pt/C in 1.0 M KOH. (b) The corresponding Tafel slopes calculated from LSV curves in 1.0 M KOH. (c) Compare with the recently reported overpotential at -10 mA cm^{-2} and corresponding Tafel slope of different HER catalysts (Table S3). (d) Polarization curves of $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ before and after 2000 cycles.

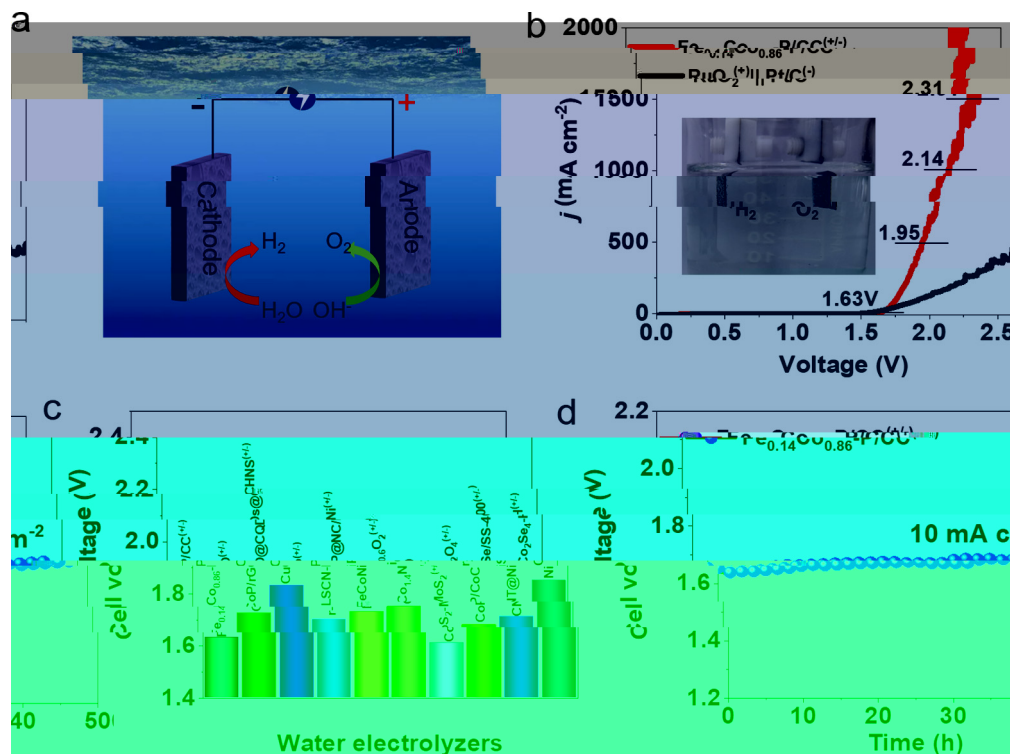


Fig. 6. (a) Schematic diagram of overall water splitting electrolytic cell using $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ as both cathode and anode. (b) LSV polarization curves of the bifunctional $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}^{(+/-)}$ and $\text{RuO}_2^{(2+)}|\text{Pt/C}^{(-)}$ for overall water splitting in 30 wt% KOH. (c) Comparing the cell voltage of the currently available electrolytic cell at 10 mA cm^{-2} in 1.0 M KOH. (d) Chronopotentiometric curve of the bifunctional $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}^{(+/-)}$ cell at a fixed current density of 10 mA cm^{-2} in 30 wt% KOH.

In general, the superior electrochemical activity and durability point toward the large-scale industrial applications for hydrogen production.

As discussed above, $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ has significant OER and HER activities due to the following aspects: (1) The nanowire array structure has a larger electrochemically active surface area, which enhances the exposure of more active sites and helps electrolyte transport and gas emission [58,59]. (2) The hybrid catalyst introduced with Fe component reduces the electron transfer resistance, thereby increasing the conductivity and charge transfer. (3) The strong electronic interaction between the Fe and Co components in the catalyst optimizes the binding energy between the active site and the intermediate in the electrochemical process, thereby significantly enhancing the electrocatalytic performance [60].

4. Conclusion

In summary, we have successfully synthesized $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ nanowire array bifunctional catalyst through simple hydrothermal reaction and subsequent phosphating treatment. XPS shows that there is a strong electronic interaction between FeP and CoP components, which is beneficial to the redistribution of charges in the composite, thereby regulating the binding energy between the active site and intermediate in the electrochemical process. Electrochemical studies have found that the designed $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}$ catalyst has excellent OER and HER electrocatalytic activity, small Tafel slope and good stability, which is consistent with the large electrochemical double-layer capacitance and TOF value of the catalyst. The simulated industrialized two-electrode overall water splitting study found that the bifunctional $\text{Fe}_{0.14}\text{Co}_{0.86}\text{-P/CC}^{(+/-)}$ catalyst requires smaller cell voltages to achieve high current densities ($> 200 \text{ mA cm}^{-2}$) combined with outstanding stability, which is apparently better than the representative $\text{RuO}_2^{(2+)}|\text{Pt/}$

$\text{C}^{(-)}$ catalyst under the same test conditions, showing a potential industrial prospect. These results indicate that this work can provide a valuable reference for the rational design of novel bifunctional ideal electrocatalysts for alkaline electrolyzers.

CRedit authorship contribution statement

Hongbo Yu: Writing - original draft. **Lu Luo Qi:** Investigation, Methodology. **Yan Hu:** Data curation. **Yuan Qu:** Conceptualization. **Puxuan Yan:** Data curation, Methodology. **Tayirjan Taylor Isimjan:** Writing - review & editing. **Xiulin Yang:** Supervision, Writing - review & editing.

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 <https://doi.org/10.1016/j.jcis.2021.05.074>.

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