3D ordered mesoporous cobalt ferrite phosphides for overall water splitting

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ABSTRACT Developing low-cost and earth-abundant electrocatalysts with high performance for electrochemical water splitting is a challenging issue. Herein, we report a facile and effective way to fabricate three-dimension (3D) ordered mesoporous $\text{Co}_{1-x}\text{Fe}_x\text{P}$ ($x=0, 0.25, 0.5, 0.75$) electrocatalyst. Benefiting from 3D ordered mesoporous pore channels and composition optimization, the $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ exhibits excellent electrocatalytic activities with low overpotentials of 270 and 209 mV at 10 mA cm^{-2} for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), respectively, in the alkaline electrolyte along with a durable electrochemical stability. In addition, as both the cathode and anode, the $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ also exhibits superior electrolysis water splitting performance with only an applied voltage of 1.63 V to attain a current density of 10 mA cm^{-2} without obvious decay for 18 h, indicating that the $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ is an efficient electrocatalyst for overall water splitting.

Keywords: cobalt ferrite phosphides, 3D ordered mesoporous structure, highly efficient electrocatalysts, water splitting

INTRODUCTION

Electrochemical water splitting is generally accepted as an effective way for producing hydrogen and oxygen *via* the anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER) [1–5]. Traditionally, $\text{IrO}_2/\text{RuO}_2$ and Pt/C have been recognized as the most state-of-the-art electrocatalysts for the OER and HER, respectively. However, the natural scarcity and high price of these noble metal-based materials greatly hinder their scale-up practical implementations [6,7]. Therefore, extensive studies have been performed to construct economical and earth-abundant catalysts as alternative candidates toward high-efficiency water electrolysis. Transition metal (Co, Ni, Fe, Mn) oxides [8], sulfides [9–11], phosphides [12,13], selenides [14,15], and perovskites

[16] have been exploited as electrocatalysts for water electrolysis and impressive progress has been achieved. Particularly, transition metal phosphides attract more attention attributed to their low cost, natural abundance, and superior catalytic performance [17–21]. Compared with mono-metal phosphides, bi-metal phosphides have been proved to show richer faradaic redox and higher electrical conductivity and stability owing to their electronic structure optimization and synergistic effect [22–24]. Thus, it is extremely worthwhile but challenging to further develop efficient bi-metal phosphides catalysts for overall water splitting.

In addition, structural and morphological engineering of electrocatalysts is a vital route to improve the catalytic activity for overall water splitting. Compared with zero dimensional (0D), 1D, and 2D nanocatalysts toward overall water splitting, 3D nanostructures generally possess large specific surface areas, which can be advantageous as the electrocatalysts through exposing abundant active sites [25–28]. Recently, Cheng *et al.* [29] developed Ni-Fe (hydr)oxide@NiCu electrocatalysts with 3D hierarchical nanoarchitectures with superior activity, owing to the large surface and synergistic effects from the unique structure. Fan *et al.* [30] assembled 3D core-shell NiFeCr metal/metal hydroxide on the Cu nanorods, and yielded a current density of 10 mA cm^{-2} with a lower overpotential of 200 mV on the OER electrode, demonstrating that nanostructure regulation and electronic structure modulation could improve the catalytic kinetics effectively. Zhou *et al.* [31] reported a Ni/Ni₂P inverse opal bifunctional electrode, which showed robust catalytic performance and long-term stability attributed to the 3D microporous structure. Transition metal phosphides with mesoporous structure show more structure advantages in overall water splitting due to their large surface area and high porosity [32]. In addition, interconnected channels

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of mesoporous structure have been regarded as an effective way to improve the charge transfer and mass transfer [33–35]. Therefore, constructing well-ordered mesoporous 3D nanostructures with interconnected channels is an effective way to further enhance the catalytic activity of bi-metal phosphides for overall water splitting.

In this work, we prepared 3D ordered mesoporous $\text{Co}_{1-x}\text{Fe}_x\text{P}$ with uniformly interconnected channels and introduced different proportion of iron to obtain electrocatalysts with high performance for overall water splitting through structural and compositional engineering. The optimized 3D ordered mesoporous $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ electrocatalyst exhibited remarkable catalytic activity for both OER and HER in alkaline electrolyte and obtained the overpotentials of 270 mV (OER) and 209 mV (HER) at a current density of 10 mA cm^{-2} . The 3D ordered mesoporous $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ as the catalyst for overall water splitting achieved a current density of 10 mA cm^{-2} at a voltage of 1.63 V. This work provides a new avenue for the design and development of highly efficient 3D ordered mesoporous bi-metal phosphides electrocatalysts for overall water splitting.

EXPERIMENTAL SECTION

Preparation of 3D mesoporous $\text{Co}_{1-x}\text{Fe}_x\text{P}$

3D mesoporous $\text{Co}_{1-x}\text{Fe}_x\text{P}$ was prepared *via* a facile nanocasting method. KIT-6 was synthesized as previously reported [36]. Briefly, 3 g P123 was dissolved in 108 mL deionized water to form a homogeneous solution. 5 mL HCl was added and stirred vigorously until P123 was completely dissolved. Then 3 g *n*-butanol was added to the solution and kept in a 35°C oil bath. After 1 h stirring, 6.45 g tetraethyl orthosilicate (TEOS) was added into the solution and stirred for 24 h. Hydrothermal treatment (100°C) was applied for 24 h. After hydrothermal process, the product was precipitated and collected by filtration. The solid product was put into a crucible and calcinated at 550°C for 6 h.

KIT-6-100 (0.5 g) was immersed into 4 mL ethanol solution containing 0.8 mol L^{-1} metal precursor ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Aladdin) and $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%, Aladdin) mixed with different ratios). The mixture was stirred and heated at 50°C overnight until the solvent was completely evaporated. Afterwards, the dry powder was calcinated at 200°C for 6 h. The obtained powder was annealed at 500°C for 5 h after the repeated impregnation process. Then, the resulting product was mixed with $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (weight ratio: 1:10) and calcinated at

325°C for 2 h under Ar atmosphere. The final product was obtained after etching by 5% HF solution for 12 h and washing with deionized water for three times. The schematic of preparation process was illustrated in Fig. 1a.

Characterization

Transmission electron microscopy (TEM) was conducted on a JEOL JEM-1400. High resolution TEM (HRTEM) images were obtained using a FEI Tecnai G2 F30 at 300 kV. X-ray diffraction (XRD) patterns were recorded using a PANalytical X' Pert powder with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The specific surface areas and pore diameter distributions of the catalysts were investigated at 77 K in N_2 on a Beishide 3H-2000PS1 Gas Sorption and Porosimetry system by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. X-ray photoelectron spectroscopic (XPS) measurements were conducted on a Perkin-Elmer PHI 5000C ESCA using twin anode $\text{Mg K}\alpha$ (1253.6 eV) radiation.

Electrochemical measurements

Electrocatalytic properties were tested on a workstation (CHI 760E). 5 mg as-prepared materials or commercial RuO_2 or Pt/C were dispersed in a mixture of 750 μL distilled water, 250 μL isopropanol and 20 μL Nafion solution (5 wt%, Alfa Aesar). After sonication for 30 min, 5 μL of catalyst ink was dropped on the surface of the

Figure 1 (a) Schematic illustration of the preparation process of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$; (b) and (c) TEM images with different magnification; (d) HRTEM image for $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$.

glass carbon electrode (GCE) and dried at room temperature. The polished GCE (surface area: 0.07 cm^2), Pt wire (a graphite rod) and saturated Ag/AgCl were applied as the working electrode, counter electrode and reference electrode, respectively. The loading amount of catalysts was 0.35 mg cm^{-2} . Every electrode was first activated by cyclic voltammetry (CV) until the stable performance exhibited. The calibration of the potentials was based on $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059\text{ pH}$, $\text{pH} = 13.7$, and linear sweep voltammetry (LSV) with a scan rate of 5 mV s^{-1} was used to get the polarization curves without iR compensation. Electrochemical impedance spectroscopy (EIS) was obtained at $1.5\text{ V vs. reversible hydrogen electrode (RHE)}$ for the OER in the frequency region of $0.01\text{--}100\text{ kHz}$ with the amplitude of 5 mV . The electrochemical active surface areas (ECSAs) were determined at different scan rates of $2, 4, 6, 8$, and 10 mV s^{-1} (potential region: $1.2\text{--}1.3\text{ V vs. RHE}$). Amperometric $i\text{--}t$ curves (durability measurements) were conducted at 10 and 40 mA cm^{-2} for OER, 10 mA cm^{-2} for HER and overall water splitting. CV was used for cycling test at 100 mV s^{-1} for 1000 cycles. The electrochemical activity of overall water splitting setup applied with $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ as both anode and cathode, was performed through LSV with a scanning rate of 5 mV s^{-1} . The loading amount of catalysts for overall water splitting was 1 mg cm^{-2} .

RESULTS AND DISCUSSION

KIT-6 was first prepared according to the previous report and used as a hard template for subsequent synthesis (Fig. S1a). In view of the highly interconnectivity microstructure of mesoporous channels on the KIT-6, a perfectly replicated nanocast material can be shaped [37–40]. Therefore, in order to obtain 3D ordered mesoporous cobalt ferrite phosphides, the immersion, calcination, phosphatization and etching processes were performed (Fig. 1a). By changing the ratio of precursors, cobalt ferrite phosphides with different compositions were obtained. Inductively coupled plasma optical emission spectrometry (ICP-OES) was further applied to analyze the compositions of products, and finally determined to be $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$, $\text{Co}_{0.5}\text{Fe}_{0.5}\text{P}$, and $\text{Co}_{0.25}\text{Fe}_{0.75}\text{P}$ (Table S1). It can be clearly seen that slit-like pores are well distributed among the entire $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$, as shown in Fig. 1b, c. All of these mesopores are well-ordered, revealing the faithful replication of the cubic structured KIT-6-100 template. Furthermore, the morphology and structure of different phosphides are not affected by the compositions of $\text{Co}_{1-x}\text{Fe}_x\text{P}$ (Fig. S1b–d). HRTEM image further confirms its porous and the selected area electron diffraction

(SAED) pattern of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ clearly shows a well-resolved lattice fringe of 0.247 nm (Fig. 1d), ascribed to the (111) crystal plane of CoP [41].

The XRD patterns of $\text{Co}_{1-x}\text{Fe}_x\text{P}$ with different Co/Fe ratios are shown in Fig. 2a. The XRD patterns of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ and $\text{Co}_{0.5}\text{Fe}_{0.5}\text{P}$ exhibit diffraction peaks at 31.6° , 36.3° , 46.2° , 48.1° and 56.7° , corresponding to the (011), (111), (112), (211) and (301) planes of CoP (PDF No. 29-0497). Further increasing the Fe composition, the diffraction peaks of $\text{Co}_{0.25}\text{Fe}_{0.75}\text{P}$ appear at 40.2° , 44.1° , 47.3° , 52.9° and 54.1° which can be assigned to the (111), (201), (210), (002), and (300) crystal planes of Fe_2P (PDF No. 27-1171). These results reveal that the $\text{Co}_{1-x}\text{Fe}_x\text{P}$ with $x \leq 0.5$ features the crystal structure of CoP.

To investigate the specific surface area and the pore size distribution of the $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$, N_2 adsorption-desorption measurement was performed at 77 K (Fig. 2b). The curve of the $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ shows IV-type sorption isotherms, with hysteresis loops characteristic of mesoporous materials, consistent with the results of the TEM measurement. The specific surface area and pore volume of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ are $148\text{ m}^2\text{ g}^{-1}$ and $0.56\text{ cm}^3\text{ g}^{-1}$, respectively. Moreover, the pore size distribution (inset of Fig. 2b) of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ reveals a bimodal pore size distribution centered around 4 and 12 nm . The unique 3D ordered mesoporous structure with high surface area and conjunct bimodal pores is expected to afford a larger electroactive surface area for efficient HER and OER, while providing sufficient channels for rapid mass transport [42].

The elemental composition and surface chemistry of the as-synthesized $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ samples were studied by XPS. The full scan XPS spectrum of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ in Fig. 2c shows the coexistence of Co, Fe, P, C and O, wherein C and O originate from the superficial oxidation and contamination of the samples. In the high-resolution Co 2p spectra (Fig. 2d), 781.9 and 798.0 eV are related to the oxide state binding energy of Co $2p_{3/2}$ and Co $2p_{1/2}$, while 778.9 and 793.9 eV are assigned to Co–P in $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ and 786.5 and 802.7 eV are corresponded with the satellite peak [43]. Similarly, the high-resolution Fe 2p spectra (Fig. 2e) of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ has two intense peaks at 706.5 and 719.4 eV , corresponding to Fe–P [44]. The peaks located at 711.2 , 713.9 , 725.1 and 730.4 eV are assigned to the oxide state binding energy of Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively [45,46]. In the XPS spectrum of P 2p (Fig. 2f), the binding energies of 128.6 and 129.5 eV are ascribed to P $2p_{3/2}$ and P $2p_{1/2}$, respectively, which reveals that the Co, Fe and P have strong electron interaction with each other. And the peak in P 2p spectra at 133 eV is

Figure 2 (a) XRD patterns of $\text{Co}_{0.25}\text{Fe}_{0.75}\text{P}$, $\text{Co}_{0.5}\text{Fe}_{0.5}\text{P}$, $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ and CoP , (b) N_2 adsorption-desorption isotherms of the mesoporous $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$, and the inset is the corresponding pore size distributions, (c) XPS survey spectra of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$, XPS spectra of Co 2p (d), Fe 2p (e) and P 2p (f).

ascribed to oxidized P species [47–49].

The electrocatalytic activities of the as-synthesized catalysts for OER were tested in 1.0 mol L^{-1} KOH electrolyte using a three-electrode configuration. Fig. 3a exhibits the LSV polarization curves of CoP , $\text{Co}_{0.25}\text{Fe}_{0.75}\text{P}$, $\text{Co}_{0.5}\text{Fe}_{0.5}\text{P}$, $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ and commercial RuO_2 with a scan rate of 5 mV s^{-1} and without iR compensation. Obviously, $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ exhibits the best OER performance among all the catalysts (Fig. 3b). Especially, to afford a current density of 10 mA cm^{-2} , it only needs a small overpotential of 270 mV (RuO_2 : 277 mV). It was reported that Fe may have the positive role for OER since the doping of Fe may exert a partial-charge transfer activation effect on Co and improve the conductivity [50]. In addition, larger overpotentials of 319 mV are required to achieve the same current density for CoP , which further demonstrates that the synergetic effect of Co and Fe in the catalyst. Furthermore, the overpotential of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ at a current density of 40 mA cm^{-2} is 316 mV, which is remarkably smaller than that of CoP (370 mV), $\text{Co}_{0.25}\text{Fe}_{0.75}\text{P}$ (398 mV), $\text{Co}_{0.5}\text{Fe}_{0.5}\text{P}$ (347 mV)

and RuO_2 (470 mV), respectively (Fig. 3b). The corresponding Tafel slopes of $\text{Co}_{1-x}\text{Fe}_x\text{P}$ samples with different Co/Fe ratios given in Fig. 3c reveal that the $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ possesses the smallest Tafel value of 48.2 mV dec^{-1} . The extremely low Tafel slope reveals that the $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ has a better reaction kinetics and faster charge transfer during the OER than other samples. Note that the overpotential of the as-prepared $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ catalyst is much smaller than most of the state-of-the-art reported phosphide-based OER catalysts (Table S2).

Low charge-transfer resistance and abundant accessible active sites are indispensable for superior electrocatalytic performance. The electrochemical double layer capacitances (C_{dl}) and the resistance of different mesoporous cobalt ferrite phosphates were further investigated by CV under different scan rates (Fig. S2). The C_{dl} calculated from CVs of $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ is 47.2 mF cm^{-2} , higher than the other phosphates catalysts, indicating that $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ can exposure more catalytic active sites due to a large contact between the catalysts and electrolyte, which is beneficial to enhancing the catalytic activity for OER [51].

Figure 3 (a) LSV polarization curves, (b) overpotentials of current density of 10 and 40 mA cm⁻², (c) corresponding Tafel slopes and (d) the capacitive current of CoP, Co_{0.25}Fe_{0.75}P, Co_{0.5}Fe_{0.5}P, Co_{0.75}Fe_{0.25}P and RuO₂ for OER in 1 mol L⁻¹ KOH with a scan rate of 5 mV s⁻¹. (e) Nyquist plots of different mesoporous phosphides at 1.5 V vs. RHE. (f) OER stability of Co_{0.75}Fe_{0.25}P for 18 h under the overpotential of 270 and 320 mV.

In addition, as shown in Fig. 3e, the impedance of the catalysts increases following the sequence of Co_{0.75}Fe_{0.25}P, Co_{0.5}Fe_{0.5}P, CoP, Co_{0.25}Fe_{0.75}P, consistent with the results of OER activity. The lowest resistance of Co_{0.75}Fe_{0.25}P implies that the additional appropriate electronic structures caused by the introduction of the Fe and the abundant 3D ordered mesoporous pore channels accelerate the mass and charge transfer, while facilitating the escape of the generated gas, which results in more favorable electrocatalytic kinetics. Durability was further assessed to illustrate the excellent OER performance of Co_{0.75}Fe_{0.25}P (Fig. 3f). The overpotential of Co_{0.75}Fe_{0.25}P after 1000 cycles increases slightly, demonstrating the superior stability. On the other hand, overpotentials at 270 mV (10 mA cm⁻²) and 320 mV (40 mA cm⁻²) were also applied to carry out the stability test. The current density of Co_{0.75}Fe_{0.25}P at both 270 and 320 mV maintain high efficiency electrolysis for at least 18 h, further suggesting the excellent durability of mesoporous Co_{0.75}Fe_{0.25}P during the OER. To further understand the ex-

cellent OER activity source of the Co_{0.75}Fe_{0.25}P, XPS measurement was conducted to compare the chemical state with pure CoP (Fig. S3). The binding energy of Co 2p_{3/2} in Co_{0.75}Fe_{0.25}P (778.9 eV) is higher than that in CoP (778.6 eV), indicating that the incorporation of Fe causes a significant electronic structure modification and faster charge transfer, which is favorable to improve electronic behaviors and optimize reaction process for OER [52].

The HER performance of the as-synthesized Co_{1-x}Fe_xP with different Co/Fe ratios were also characterized under the same electrolyte conditions (1 mol L⁻¹ KOH). LSV curves reveal that Co_{0.75}Fe_{0.25}P has the lowest overpotential, and the HER activities are also following the same order as that of OER. To achieve a current density of 10 mA cm⁻², the Co_{0.75}Fe_{0.25}P requires an overpotential of 209 mV, lower than other catalysts, 278 mV for CoP, 319 mV for Co_{0.25}Fe_{0.75}P and 253 mV for Co_{0.5}Fe_{0.5}P, and higher than Pt/C (115 mV) at η_{10} (Fig. 4b). Meanwhile, the Tafel slope of the Co_{0.75}Fe_{0.25}P is 55.5 mV dec⁻¹, which is remarkably smaller than that of CoP (66.1 mV dec⁻¹),

Figure 4 (a) LSV polarization curves, (b) overpotentials of current density of 10 mA cm⁻², (c) corresponding Tafel slopes of CoP, Co_{0.25}Fe_{0.75}P, Co_{0.5}Fe_{0.5}P, Co_{0.75}Fe_{0.25}P and Pt/C for HER in 1 mol L⁻¹ KOH. (d) HER stability of Co_{0.75}Fe_{0.25}P for 18 h under the overpotential of 230 mV (15 mA cm⁻²).

Co_{0.25}Fe_{0.75}P (75.0 mV dec⁻¹), and Co_{0.5}Fe_{0.5}P (63.4 mV dec⁻¹), manifesting the superior rapid HER rates of Co_{0.75}Fe_{0.25}P (Fig. 4c). Additionally, the durability of the most active Co_{0.75}Fe_{0.25}P was evaluated by *i*-*t* measurement for 18 h (Fig. 4d). The current density vibrates at the initial stage, then presents an increment and finally maintains around -15 mA cm⁻² (overpotential: 230 mV) in the long-term electrocatalysis test, which suggests that the Co_{0.75}Fe_{0.25}P can also exhibit an excellent stability in the HER process.

Inspired by the outstanding catalytic activity and durability of the Co_{0.75}Fe_{0.25}P for both OER and HER, the water electrolysis activity of the Co_{0.75}Fe_{0.25}P was further evaluated by using two-electrode configurations in 1 mol L⁻¹ KOH electrolyte. As revealed in Fig. 5a, Co_{0.75}-Fe_{0.25}P||Co_{0.75}Fe_{0.25}P electrolyzer only needs a low cell voltage of 1.63 V to achieve 10 mA cm⁻², slightly higher than that of RuO₂||Pt/C (1.59 V@10 mA cm⁻²). It is no doubt that such relative low potential represents the best level among the state-of-art catalysts previously reported (Table S3). The durability of electrode was evaluated by *i*-*t* test in 1 mol L⁻¹ KOH for 18 h, many bubbles can be observed on the surface of anode and cathode during the test. As displayed in Fig. 5b, the current density does not fluctuate significantly at 10 mA cm⁻² for at least 18 h,

Figure 5 (a) Polarization curves of Co_{0.75}Fe_{0.25}P||Co_{0.75}Fe_{0.25}P and RuO₂||Pt/C two electrode system in 1 mol L⁻¹ KOH for overall water splitting. (b) *i*-*t* curves of Co_{0.75}Fe_{0.25}P||Co_{0.75}Fe_{0.25}P at the current density of 10 mA cm⁻² in 1 mol L⁻¹ KOH.

indicating that the Co_{0.75}Fe_{0.25}P electrode has an exceptional long-term stability. After the durability test, TEM measurements were applied to characterize the Co_{0.75}-Fe_{0.25}P electrode. As shown in Fig. S4a and S4b, the 3D ordered mesoporous structure of Co_{0.75}Fe_{0.25}P are maintained after the longtime stability test.

CONCLUSION

In summary, 3D ordered mesoporous Co_{1-x}Fe_xP electrocatalyst has been successfully developed by a simple route

through structural and compositional control. The optimized $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ shows excellent electrocatalytic OER and HER activities with low overpotentials of 270 and 209 mV at 10 mA cm^{-2} and Tafel slopes of 48.2 and 55.5 mV dec^{-1} in alkaline media, respectively, along with a durable electrochemical stability. Moreover, no matter used as the cathode or anode, the $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ also presented exceptional water electrolysis performance with an applied voltage of 1.63 V, yielding a current density of 10 mA cm^{-2} with outstanding stability for 18 h. This work offers a new tactic for the design and development of energy-efficient, stable, and 3D ordered mesoporous bi-metal phosphides electrocatalysts for overall water splitting.

Received 12 July 2019; accepted 27 August 2019;
published online 17 September 2019

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Acknowledgements This work was supported by the National Natural Science Foundation of China (51571072 and 51871078) and Heilongjiang Science Foundation (E2018028).

Author contributions Huang Y, Yang W and Yu Y designed the research. Huang Y fabricated the materials, analyzed the results, and wrote the manuscript with support from Li M and Hao S. Yu Y and Yang W supervised the project and revised the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of this paper.

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三维有序介孔钴铁磷化物在全解水中的应用

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摘要 构筑低成本、资源丰富、高效的电化学全解水催化剂是目前一个极具挑战的课题. 本文报道了一种简便高效地制备三维有序介孔 $\text{Co}_{1-x}\text{Fe}_x\text{P}$ ($x=0, 0.25, 0.5, 0.75$)电催化剂的方法. 得益于三维有序介孔孔道和成分的优化, $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ 催化剂在碱性电解质中表现出优异的电催化活性, 在电流密度为 10 mA cm^{-2} 下, 析氧和析氢的过电位分别是270和209 mV, 同时该催化剂也表现出良好的电化学稳定性. 利用 $\text{Co}_{0.75}\text{Fe}_{0.25}\text{P}$ 催化剂作为电解水制氢的阴极和阳极, 只需要施加1.63 V的电压即可获得 10 mA cm^{-2} 的电流密度, 并且在18 h稳定性测试后电流密度没有出现衰减, 证明其在全解水应用中具有优异的催化活性.