Puffing quaternary $\text{Fe}_x\text{Co}_y\text{Ni}_{1-x-y}\text{P}$ nanoarray via kinetically controlled alkaline etching for robust overall water splitting

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ABSTRACT Designing and constructing bifunctional electrocatalysts with high efficiency, high stability and low cost for overall water splitting to produce clean hydrogen fuel is attractive but highly challenging. Here we constructed puffed quaternary $\text{Fe}_x\text{Co}_y\text{Ni}_{1-x-y}\text{P}$ nanoarrays as bifunctional electrodes for robust overall water splitting. The iron was used as the modulator to manipulate the electron density of NiCoP nanoarray, which could increase the positive charges of metal (Ni and Co) and P sites. The resultant electronic structure of $\text{Fe}_x\text{Co}_y\text{Ni}_{1-x-y}\text{P}$ was supposed to balance the adsorption and desorption of H and accelerate the oxygen evolution reaction (OER) kinetics. Moreover, the morphological structure of $\text{Fe}_x\text{Co}_y\text{Ni}_{1-x-y}\text{P}$ was modulated through the kinetically controlled alkaline etching by using the amphoteric features of initial FeCoNi hydroxide nanowires. The resultant puffed structure has rich porosity, cavity and defects, which benefit the exposure of more active sites and the transport of mass/charge. As a result, the cell integrated with the puffed quaternary $\text{Fe}_x\text{Co}_y\text{Ni}_{1-x-y}\text{P}$ nanoarrays as both the cathode and anode only requires the overpotentials of 25 and 230 mV for hydrogen evolution reaction (HER) and OER at the current density of 10 mA cm^{-2} in alkaline media and a cell voltage of 1.48 V to drive the overall water splitting. Moreover, the puffed $\text{Fe}_x\text{Co}_y\text{Ni}_{1-x-y}\text{P}$ demonstrates remarkable durability for continuous electrolysis even at a large current density of 240 mA cm^{-2} .

Keywords: puffed nanoarray, morphology control, alkaline etching, electrocatalysis, water splitting

INTRODUCTION

Propelled by the exigent demand for sustainable and green energy sources, the energy conversion technologies have drawn widespread attention of researchers. Electrochemical water splitting has been regarded as a promising and environmentally friendly pathway for energy supply, especially when it is driven by renewable solar, wind, and geothermal energy [1,2]. Searching cost-effective and high-performance alternatives to replace the state-of-the-art Pt and Ir/Ru is of great significance and urgency for more widespread applications of electrocatalytic water splitting devices. The designing strategies of electronic structure (or composition) and morphological structure especially deserve more attention for precious-metal-free electrocatalysts to enhance the intrinsic activity, increase the number of active sites, and promote the mass transfer/charge transport [3–7]. Among the precious-metal-free electrocatalysts, such as oxides, sulfides, carbides, and phosphides, transition-metal-based phosphides have recently emerged as promising new-generation electrode materials [8], due to the moderate electronegativity of phosphorus (P) as anion and the fact that the surface charge states of transition metals can be well mediated by P which has the special electronic structure of lone-pair electrons in 3p orbitals and vacant 3d orbitals [9]. In the view of mechanism, the state changes in alkaline hydrogen evolution reaction (HER) proceed from the incipient catalyst-water (hydroxylion),

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to the intermediate H-catalyst, and the eventual H₂-catalyst [1,8]. Taking cobalt phosphide (CoP) as an instance, the electronegative P atom acts as the center of proton acceptor to form P-H_{ads} on the surfaces of the electrocatalysts while the metal cation accepts water-(hydroxide) at the initial step [10]. Unfortunately, the interactions between P-H_{ads} bonds are usually too strong to desorb H_{ads} for the evolution of hydrogen molecules (H₂) [11]. At this very moment, the active surfaces of metal phosphides would be saturated with the coordinated H_{ads}, thereby resulting in a sluggish dynamics for water adsorption and dissociation in the alkaline HER process [11]. Therefore, the balance of hydrogen adsorption/desorption should be tuned in order to achieve a high HER performance. Very recently, one study found that introducing Ni into CoP to form binary phosphides (NiCoP) could further improve the HER activity due to the synergistic effect of bimetal atoms and a low overpotential (η) of ca. 80 mV was achieved at the current density of 10 mA cm⁻² [10]. However, most of the present studies of metal phosphides are mainly focused on improving the activity of HER [5,8,10–16]. As for oxygen evolution reaction (OER) at the anode side, the intrinsic multi proton-couple electron transfer process results in very sluggish reaction kinetics. Specifically, the breaking of O–H bond and the formation of attendant O–O bond have to conquer the high energy barrier [1]. The development of superior electrocatalyst with low-cost requires the coupling of the multiple proton and electron transfer steps. Besides, the engineering for the morphological structures, such as porosity, defect, cavity, and nanoarray of electrocatalysts can also serve as effective strategies to enhance the activity through increasing the exposure of active sites and providing unobstructed reaction pathways [3,17–19]. As for the electrocatalytic water splitting, the bi-functional electrocatalyst integrated cell always holds great convenience, high efficiency and low cost [1–4]. Therefore, the electronic and morphological structures of metal phosphide electrocatalysts are needed to address the present challenge for overall water splitting (both HER and OER) in the same electrolyte.

Here we constructed the puffed quaternary Fe_xCo_yNi_{1-x-y}P nanoarray *via* kinetically controlled alkaline etching for robust overall water splitting. The iron was used as the modulator to manipulate the electron densities of NiCoP nanoarray in order to balance the adsorption and desorption of H. Besides, the effects of iron incorporation on OER were also investigated. The puffed structure with rich porosity, cavity and defects possesses optimized morphological features as electro-

catalyst. The puffed quaternary Fe_xCo_yNi_{1-x-y}P nanoarray demonstrates robust catalytic dual-functionality and durability for HER and OER towards overall water splitting.

EXPERIMENTAL SECTION

Synthesis of Co-Ni and Fe-Co-Ni hydroxide nanowire arrays (CoNi-NWAs and FeCoNi-NWAs)

In a typical procedure, 436 mg of Co(NO₃)₂·6H₂O, 450 mg of (NH₂)₂CO, and 222 mg of NH₄F were dissolved into 40 mL of deionized water and packaged into a 50-mL teflon-lined autoclave with steel shell. A piece of Ni foam (1 cm×3 cm) was cleaned ultrasonically with ethanol and 3 mol L⁻¹ HCl aqueous solution in sequence, and then immersed into the above-mentioned aqueous solution and treated at 120°C for 10 h in the autoclave. Then the CoNi-NWAs were obtained and washed several times with deionized water and dried in the air. The FeCoNi-NWAs were prepared *via* the same procedure with the addition of 122 mg Fe(NO₃)₃·9H₂O as Fe source.

Synthesis of puffed quaternary Fe_xCo_yNi_{1-x-y}P nanoarrays (FeCoNiP-PNAs)

With the above FeCoNi-NWAs as precursor, a hydrothermal process was utilized to achieve the intermediate puffed quaternary Fe_xCo_yNi_{1-x-y} hydroxide nanoarrays (FeCoNi-PNAs). In a typical procedure, the FeCoNi-NWAs were transformed into a 50-mL teflon-lined stainless-steel autoclave containing 30 mL of 0.1 mol L⁻¹ KOH (0.01, 0.02 and 0.05 mol L⁻¹ KOH) aqueous solution. Subsequently, the autoclave was kept at 120°C for 5 h. Then FeCoNi-PNAs were obtained and calcined at 400°C for 2 h followed by a phosphorization procedure at 400°C for 30 min with a heating rate of 5°C/min under a flowing Ar atmosphere with NaH₂PO₂·H₂O at the upstream side (the weight ratio of the sample to NaH₂PO₂·H₂O was 1:20). After naturally cooling down to room temperature, the achieved black samples (FeCoNiP-PNAs) were obtained. The phosphorization process for preparing CoNiP-PNAs and FeCoNiP-PNAs is same.

Material characterizations

X-ray diffraction (XRD) patterns of the samples were measured on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation (λ =1.5418 Å). Scanning electron microscopy (SEM) images were acquired with a Hitachi Regulus-8100 Field Emission Scanning Electron Microscope. Transmission electron microscopy (TEM) graphs were observed by using a Hitachi H-7700 TEM operating

at 100 kV. High-resolution TEM (HRTEM) test was performed on an FEI Tecnai G2 F20 STwin microscope at 200 kV. X-ray photoelectron spectroscopy (XPS) signals were collected by a Thermo Fisher ESCALAB 250Xi spectrometer applying monochromatic Al K α X-ray sources (1486.6 eV) at 2.0 kV and 20 mA.

Electrochemical measurements

All HER/OER performances were tested on a CHI electrochemical workstation (Shanghai Chenhua Co., China) by using a three-electrode configuration in H₂/O₂-saturated 1 mol L⁻¹ KOH. The electrocatalyst (1 cm $\times$ 3 cm), a saturated calomel electrode (SCE) for HER test (Ag/AgCl electrode and saturated KCl-AgCl solution for OER test), and a graphite rod were used as the working, reference, and counter electrodes, respectively. The potentials for HER tests were converted to a reversible hydrogen electrode (RHE): $E(\text{RHE}) = E(\text{SCE}) + 0.244 + 0.059\text{pH}$. As for OER, the potentials were calculated with $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.198 + 0.059\text{pH}$. Besides, overall water splitting was measured in a typical two-electrode system by utilizing the as-prepared electrodes as cathode and anode simultaneously. All the data in this paper are without *iR* compensation. Linear sweep voltammetry (LSV) was recorded at a scan rate of 5 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) measurements were performed with the frequency range from 0.1 to 100,000 Hz at an overpotential of 0.1 V for HER and 0.35 V for OER. The stability measurements (*i-t*) were recorded for single HER and OER at a constant applied potential for 24 h or at varied potential for 40 h for overall water splitting. The electrochemical active surface area (ECSA) was roughly calculated according to the Equation: $\text{ECSA}(\text{cm}^2) = C_{\text{dl}}/40 \mu\text{F cm}^{-2}$ (C_{dl} : double-layer capacitance).

RESULTS AND DISCUSSION

Synthesis and characterization of FeCoNiP-PNAs

As shown in Fig. 1a, the FeCoNiP-PNAs on nickel foam were fabricated *via* an accessible two-step hydrothermal treatment and further phosphorization process. In the first step, the FeCoNi-NWAs were prepared based on the synthesis of CoNi-NWAs through introducing iron precursor. The field emission SEM and TEM images of FeCoNi-NWAs are shown in Fig. 1b. Fig. S1 (CoNi-NWAs in Fig. S2) reveals that the FeCoNi-NWAs consist entirely of uniform nanowires grown on the nickel foam substrates. TEM analysis of FeCoNi-NWAs (Fig. 1b, inset) indicates that the incipient nanowire possesses an intact outer surface and solid interior. The length of FeCoNi-

NWAs is ca. 4 μm and the average diameter is approximately 160 nm. The energy-dispersive X-ray (EDX) elemental mapping (Fig. S1) of the sample indicates the uniform distribution of the Fe, Co, Ni, and O. The XRD pattern (Fig. S3) can be indexed to the peaks of cobalt-nickel carbonate hydroxide (JCPDS No. 33-0429) and iron-nickel carbonate hydroxide (JCPDS No. 26-1286). The above results demonstrate the successful preparation of trimetallic FeCoNi NWAs. After that, a kinetically controlled alkaline etching strategy was applied to construct the puffed FeCoNi-PNAs with the FeCoNi-NWAs as the precursor and template. For the amphoteric nature of FeCoNi-NWAs, the pristine nanowires can coordinate with an excess amount of hydroxyl ions (OH⁻) to form soluble $[\text{Metal}(\text{OH})_4]^{2-}$ and $[\text{Metal}(\text{OH})_6]^{2-}$, which will gradually dissolve in the alkaline solution. And then, the soluble species will undergo thermodynamically favourable oxidation, forming insoluble boundary layer of high-valence metal species on the surface of nanowires [20]. The alkaline and acid etchings have been developed for achieving defects, pore, and cavity in nanomaterials by using different chemical properties of the compositions to regulate the morphological and electronic structures. The XRD pattern of FeCoNi-PNAs (Fig. S4) matches well with the peaks of FeCoNi-NWAs, implying the alkaline etching has almost no effect on the crystalline phase. A close observation of all XRD signals of FeCoNi-PNAs reveals a red shift in comparison with that of FeCoNi-NWAs, suggesting a decreased crystal lattice parameter. Considering the fact that Fe³⁺, Ni²⁺, and Co²⁺ have the diameters of approximately 129, 138 and 149 pm, the phenomenon implies the Co²⁺ with the biggest ionic diameter should be the main dissociation substance during the alkaline etching procedure [10,11,17,21]. The reason should be attributed to the different coordination abilities of Fe, Ni, and Co with OH⁻, which can be explained by the relationship of $K_{\text{sp}}(\text{Co}(\text{OH})_2) > K_{\text{sp}}(\text{Ni}(\text{OH})_2) > K_{\text{sp}}(\text{Fe}(\text{OH})_3)$ [20]. The loss of metal cations from the pristine FeCoNi NWAs may result in the formation of numerous defects in the FeCoNi-PNAs, thereby leading to more exposed active sites and promoted electrocatalytic performance [22]. The comparison of XPS results (Fig. S5) between FeCoNi-NWAs and FeCoNi-PNAs suggests there is no high valent metal species after etching. The SEM image of FeCoNi-PNAs demonstrates the well-preserved characteristics of nanoarrays (Fig. 1c). Close observation indicates that the kinetically controlled alkaline etching process endows the nanoarrays with the features of highly rough and porous outer surface, which is very similar with the features of

Figure 1 (a) Schematic representation for the synthetic process of FeCoNiP-PNAs. SEM images of FeCoNi-NWAs (b), FeCoNi-PNAs (c), and FeCoNiP-PNAs (d and e). TEM image (f), EDX line scanning (g), HRTEM image (h), EDX mapping (i), and XRD pattern (j) of FeCoNiP-PNAs.

puffed structures (inset). The effects of the concentration of hydroxyl ions on the nanostructures of nanoarrays were investigated. The SEM results (Figs S6 and S7) demonstrate that the higher concentration of alkaline solution can achieve uniform puffed nanoarrays, verifying a kinetically controlled alkaline etching process could obtain uniform puffed FeCoNi nanoarrays [20]. Finally, the P substituted the anion species in FeCoNi-PNAs through a simple phosphorization process, leading to the formation of puffed quaternary FeCoNiP-PNAs. As shown in Fig. 1d, the high-magnification SEM image of FeCoNiP-PNAs indicates the highly rough and porous outer surface and some of visible openings at the top of the nanoarrays, which remains the structural features of the FeCoNi-PNAs. The low-magnification SEM image (Fig. 1e) suggests the high degree of uniformity for the FeCoNiP-PNAs. Moreover, the TEM image of FeCoNiP-PNAs (Fig. 1f) verifies the rough and porous features throughout the single unit in the nanoarray. The EDX line scanning (Fig. 1g) and some of the visible top openings of

nanoarrays (Fig. 1d) demonstrate the presence of a cavity possibly along the *c*-axis of the single unit. The results imply the presence of the puffed structure in the FeCoNiP-PNAs. The diameter of the single unit is around 200 nm, and the wall thickness ranges from approximately 50 to 80 nm. Moreover, the incorporation of other ions normally can result in the changes of the interplanar distance. However, the three Fe-Co-Ni elements differ in the ion diameters, which makes it difficult to analyze the possible changes of the interplanar distance. As shown in Fig. 1h, the HRTEM image of FeCoNiP-PNAs indicates an interplanar distance of approximately 0.21 nm. As a result, we roughly attributed to the (111) plane of nickel phosphide [12]. The numerous lattice defects derived from the alkaline etching step are clearly observed, which may provide delocalized electrons and high active surface for electrocatalytic reaction. The EDX elemental mapping spectra (Fig. 1i) elucidate a uniform distribution of the elementary composition (Fe, Co, Ni, and P) throughout FeCoNiP-PNAs. However, as exhibited in Fig. S8, the

SEM and HRTEM images of FeCoNiP-NWAs indicate the smooth surface and the consecutive lattice fringes of the nanowires, respectively. The XRD pattern of FeCoNiP-PNAs is shown in Fig. 1j, which is assigned to the peaks of Ni₂P (JCPDS No.65-9706), CoP (JCPDS No.65-1474), and FeP (JCPDS No.65-2595). The XRD pattern of FeCoNiP-NWAs is the same with that of FeCoNiP-PNAs (Fig. S9). The nanowire arrays are also well remained in the CoNiP-NWAs, as shown in the SEM image (Fig. S2). By contrast, the porous and defective structure of FeCoNiP-PNAs implies more active sites and larger surface area for the improvement of electrocatalytic activity. By averaging three pieces of samples, the mass loading of catalyst is about 14 mg (1×3 cm²) during electrochemical characterizations. In addition, according to the very recent study, an intriguing possibility of superaerophobicity can also be expected in the puffed FeCoNiP nanoarrays for efficient transfer/charge transport through easily displacing as-formed gas bubbles from the surface of the electrode [16,19]. Therefore, the FeCoNiP-PNAs with engineered composition and structure were elaborately prepared.

The XPS tests were further conducted to investigate the oxidation state and surface composition of the CoNiP-NWAs, FeCoNiP-NWAs, and FeCoNiP-PNAs. As shown in Fig. 2a, the XPS spectrum demonstrates that FeCoNiP-PNAs consists of Fe, Co, Ni, and P elements. The elemental composition of Fe, Co, Ni and P in FeCoNiP-NWAs and FeCoNiP-PNAs are close to 1:2:1:6.3 and 1:1.7:1:7.5 of mole ratios, respectively. The decrease in the Co composition along with the increase in the P composition suggests the occurrence of Co cation loss and high specific surface area for FeCoNiP-PNAs after the alkaline etching process, consistent with the XRD, SEM and TEM observations. The distinct P signal in the XPS spectrum of FeCoNiP-PNAs (Fig. 2b) indicates the successful anion substitution. The high binding energy peak at 134.4 eV is attributed to the surface phosphate (PO₄³⁻) species arising from the partial oxidation of P when the sample was exposed to air [23]. While the two peaks at 129.2 and 130.2 eV in the P 2p spectrum indexed to the binding energy of P 2p_{1/2} and P 2p_{3/2} correspond to the bonding formation between P and metal cations. The peak at 129.2 eV indicates the partially negatively charged P atom (P^{δ-}) [10]. As for the spectrum in the Fe 2p region, two spin-orbit doublets (at 711.5 and 721.2 eV, and at 715.1 and 726.0 eV) are observed (Fig. 2c), which are assigned to Fe²⁺ and Fe³⁺, respectively [24]. The signal characteristic attributed to the weak bonding of Fe–P, implying that the Fe element should mainly exist in the

form of a quaternary Fe_xCo_yNi_{1-x-y}P rather than a single phase [12,17,25]. As for Ni 2p_{3/2} spectra (Fig. 2d), the FeCoNiP-PNAs show three peaks at 853.9, 857.3, and 862.6 eV [26,27]. The binding energy of the first peak at 853.9 eV can be well consistent with the signal of Ni–P [5,6]. This peak is higher than that of metallic Ni (852.6 eV), implying the presence of partially charged Ni species (Ni^{δ+}) [11,28]. The binding energy at 857.3 eV with the shakeup satellite peak at 862.6 eV can be assigned to Ni–PO_x species arising from unavoidably superficial oxidation. Similarly, compared with the XPS signal of metallic Co at 778.2 eV, the peak at 779.3 eV in the Co 2p_{3/2} spectra of FeCoNiP-PNAs is related to partially charged Co species (Co^{δ+}) in Co–P (Fig. 2e) [29–31]. Compared with FeCoNiP-NWAs, the weak Co XPS peak (Fig. 2i) in FeCoNiP-PNAs implies the Co element was mainly etched among the three metals, according well with the aforementioned observations. As illustrated in Fig. 2f, the energy levels of 3d orbitals of Fe, Co, Ni, and the 3p orbital of P illustrate that the available energy level and open-shell of Fe 3d orbital can effectively modulate the electron densities of the active sites in the pristine CoNiP-NWAs. Note that compared with the initial CoNiP-NWAs (Fig. S10), a positive shift of ~0.4 eV (0.8 and 0.7 eV) is observed for the binding energy of P (Ni and Co) in FeCoNiP-PNAs, which are exhibited in Fig. 2g–i, respectively. The positive shift of P (Co and Ni) spectrum implies more positively charged P (Co and Ni) atom in FeCoNiP-PNAs in comparison with CoNiP-NWAs [7,17].

Performance evaluation of electrocatalytic water splitting

The HER and OER performances of the samples were evaluated in an alkaline solution with a standard three-electrode system. The SCE was utilized as the reference electrode for HER test (Ag/AgCl electrode for OER test), and a graphite rod was used as the counter electrode. The electrocatalysis was conducted in an H₂/O₂-saturated 1 mol L⁻¹ KOH solution for HER and OER tests, respectively. At the beginning of the tests, the cyclic voltammetry (CV) measurement was performed to activate and stabilize the electrodes. The LSV curves were carried out to analyze the polarization ability of the prepared electrodes (all the data presented in this manuscript were without *iR* compensation). The electrocatalytic activities of the bare nickel foam, the commercial Pt/C (for HER) and RuO₂ (for OER), FeCoNi-NWAs, CoNiP-NWAs, FeCoNiP-NWAs, and FeCoNiP-PNAs were tested. As shown in Fig. 3a, the bare nickel foam as a reference requires a large overpotential of about 300 mV to achieve

Figure 2 XPS spectra of FeCoNiP-PNAs: (a) XPS full survey spectrum, high-resolution spectra of (b) P 2p, (c) Fe 2p, (d) Ni 2p_{3/2}, and (e) Co 2p_{3/2}. (f) Scheme of the orbital splitting of Fe, Co, Ni and P. (g) P 2p, (h) Ni 2p_{3/2}, and (i) Co 2p_{3/2} spectra of (1) CoNiP-NWAs, (2) FeCoNiP-NWAs, and (3) FeCoNiP-PNAs.

10 mA cm⁻². The pristine FeCoNi-NWAs exhibit inferior HER activity with an overpotential of 205 mV to drive 10 mA cm⁻². The phosphide CoNiP-NWAs and FeCoNiP-NWAs show greatly enhanced HER activity with a low overpotential of 65 and 36 mV, respectively, to achieve 10 mA cm⁻². Remarkably, the FeCoNiP-PNAs electrocatalyst only needs 25 mV to obtain the current density of 10 mA cm⁻², which is close to 24 mV of the commercial Pt/C catalyst at 10 mA cm⁻². As for the high current density of 50 mA cm⁻², the FeCoNiP-PNAs only require a small overpotential of ca. 105 mV, superior to ca. 150 and 200 mV of FeCoNiP-NWAs and CoNiP-NWAs, respectively. The Tafel slope is generally used to analyze the catalytic reaction kinetics for the HER process. As shown in Fig. 3b, the FeCoNiP-PNAs show a Tafel slope of ca. 40 mV dec⁻¹, which is similar to 30 mV dec⁻¹ of commercial Pt/C but smaller than 52 mV dec⁻¹ of FeCoNiP-NWAs and 92 mV dec⁻¹ of

CoNiP-NWAs. According to the proposed HER mechanism [32], the small Tafel slope of FeCoNiP-PNAs suggests the more rapid HER catalytic rate and the better inherent HER catalytic activity. The EIS was further carried out to analyze the HER kinetics of the catalysts. As shown in Fig. S11, the small semicircles of the samples at the high frequency indicate a low level of charge transfer resistance due to the highly conductive nickel foam substrate. In addition, the ECSA was roughly assessed *via* measuring C_{dl} in the regions of non-Faradaic processes. A linear correlation between current densities and the scan rates is shown in Fig. 3c and Fig. S12. The FeCoNiP-PNAs show the largest slope value of 24 mF cm⁻² with a calculated ECSA value of 600 cm² among the tested samples, suggesting the increased density of electrocatalytic active sites compared with FeCoNiP-NWAs and CoNiP-NWAs. To evaluate the durability of FeCoNiP-PNAs for HER, a long-time chron-

Figure 3 (a) HER LSV curves without *iR* compensation in 1 mol L⁻¹ KOH electrolyte. (b) Tafel plots. (c) *C_{dl}* measurements. (d) Chronoamperometric measurements (*i-t*) recorded on FeCoNiP-PNAs.

opotentiometry measurement was carried out at ca. 15 mA cm⁻² ($\eta=50$ mV) for 24 h. As shown in Fig. 3d, no obvious degradation can be observed, suggesting the good stability of the nanoarrays in FeCoNiP-PNAs. The improved HER activity in metal phosphide should be attributed to the special electronic structure of lone-pair electrons in 3p orbitals and vacant 3d orbitals in phosphorus, which can mediate the local charge density and the surface charge state of the transition-metal electrocatalysts, leading to a satisfying performance [17]. Specifically, as for the alkaline HER mechanism, the state changes proceed from the incipient catalyst-water (hydroxylion), to the intermediate H-catalyst, and the eventual H₂-catalyst. The partially positively charged metal cations can accept the initial water-(hydroxide), while the P atoms acts as the center of proton acceptor to form P-H_{ads} on the surfaces of the electrocatalysts [9,10,12]. Unfortunately, the interactions between P-H_{ads} bonds are usually too strong to desorb H_{ads} for the evolution of hydrogen molecules (H₂) [11]. Then the active surfaces of metal phosphides would be saturated with the coordinated H_{ads}, thereby resulting in a sluggish dynamics for water adsorption and dissociation in alkaline HER process [8]. The positive shift of P spectrum implies more

positively charged P atom in FeCoNiP-PNAs in comparison with CoNiP-NWAs, which will weaken the bonds of P-H_{ads} [10]. As for the metal sites, the increased positive charge of Co and Ni in FeCoNiP-PNAs will contribute to the adsorption of H₂O molecules and the cleavage of H-O [11]. The aforementioned analyses suggest that the iron can act as a good modulator to manipulate the electron densities of catalytic sites in CoNiP toward high intrinsic activity for HER.

As is well known, the sluggish kinetics of anodic OER hinders the efficiency promotion of electrocatalysts in overall water splitting. The development of high-performance bifunctional electrocatalyst possesses great convenience and cost-efficiency in both the preparation and the assembly of two different electrodes in an electrolytic cell for water splitting. We also evaluated the performance of FeCoNiP-PNAs in the OER measurement. As shown in Fig. 4a, FeCoNiP-PNAs only require an overpotential of 230 mV to drive the current density of 10 mA cm⁻², which is smaller than 315 mV of the commercial RuO₂/C, 280 mV of FeCoNi-NWAs, 320 mV of CoNiP-NWAs, 250 mV of FeCoNiP-NWAs and 550 mV of nickel foam. The results indicate the superior HER and OER activities of FeCoNiP-PNAs do not originate from

Figure 4 (a) OER LSV curves without *iR* compensation in 1 mol L⁻¹ KOH electrolyte. (b) Tafel plots. (c) *C_{dl}* measurements. (d) Chronoamperometric measurements (*i-t*) recorded on FeCoNiP-PNAs.

the nickel foam support. An excellent polarization capability of FeCoNiP-PNAs in OER test was observed. A low Tafel slope of 66 mV dec⁻¹ (Fig. 4b) and the smallest semicircle (Fig. S11) of FeCoNiP-PNAs suggest faster catalytic reaction kinetics and smaller reaction resistance for electron transfer compared with FeCoNiP-NWAs and CoNiP-NWAs. Also, FeCoNiP-PNAs possess the maximum level of exposure of active catalytic sites for OER, due to the largest ECSA of ca. 1000 cm² estimated by the slope of *C_{dl}* (Fig. 4c) in the linear correlation between current densities and the scan rates (Fig. S12). In addition, The XRD result (Fig. S13) suggests the occurrence of newly formed metal oxide hydroxide (JCPDS No.40-1179) and metal_x(PO₄)_y(OH)_z (JCPDS No.45-1454) in FeCoNiP-PNAs after the OER test. The metal-P bond signals in XPS spectra (Fig. S14) of FeCoNiP-PNAs after OER test disappear. The results suggest the *in situ* surface transformation of metal phosphide into the corresponding active oxides/hydroxides. Simultaneously, the generated phosphate is reported to help form oxygen-evolving Co-P catalytic centers, which favours the promotion of OER activity [9]. Moreover, as shown in Fig. 4d, FeCoNiP-PNAs could maintain a stable 24 h chronoamperometry line at the current density of around

12 mA cm⁻² ($\eta=1.49$ V), suggesting good structural stability of FeCoNiP-PNAs in OER test. The overpotential difference between CoNiP-NWAs and FeCoNiP-NWAs suggests the incorporation of Fe can also act as a modulator and plays a positive role in OER activity enhancement, which should be possibly assigned to the synergetic effect of trimetal Fe, Co, and Ni [11]. The introduced Fe in the matrix of the CoOOH or NiOOH should exist in the form of defective FeO₆ structure, which is optimal to the adsorption of reaction intermediates, such as OH⁺ and OOH⁺ during alkaline OER procedure [7]. The presence of high-valence or increased oxidation-state metal species is also conducive to the OER process [13]. The Fe-containing OER catalyst in FeOOH sites was also reported to deliver a strong adsorbing affinity to OH⁺ intermediate. The residual P may decrease the valence of Fe through partly substituting O, thereby contributing to the adsorption energy of intermediates [33]. The aspects synergistically contribute to the performance improvement of FeCoNiP-PNAs in OER by accelerating proton and electron transfers. Considering the same crystalline phases of FeCoNiP-PNAs and FeCoNiP-NWAs (Fig. S9), the puffed geometrical structure of FeCoNiP-PNAs with porosity, cavity and lattice

defects derived from the kinetically controlled alkaline etching procedure can ensure adequate exposure and utilization of active sites in HER and OER [22]. Taken together, the simultaneous and elaborate manipulation of electronic and morphological structure in FeCoNiP-PNAs is responsible for the noticeable improvement in both HER and OER activities.

The above results demonstrate the superior bifunctional electrocatalytic performance of FeCoNiP-PNAs for HER and OER in the same alkaline electrolytes. Thus, an electrolyzer for overall water splitting was constructed in a two-electrode system by using FeCoNiP-PNAs as both anode and cathode. As shown in Fig. 5a, FeCoNiP-PNAs catalyst only needs a cell voltage of approximately 1.48 V to achieve a current density of 10 mA cm^{-2} , which is about 80 mV smaller than 1.56 V (at 10 mA cm^{-2}) of the electrolyzer assembled by Pt/C||RuO₂ catalysts. Additionally, the time-dependent current density curve (Fig. 5b) indicates the high durability of FeCoNiP-PNAs for the overall water splitting under different current densities. When the cell voltage is set to be 2.5 V, the FeCoNiP-PNAs deliver excellent steady operation even at such a high current density of about 240 mA cm^{-2} , which is rarely observed in other recently reported state-of-the-art bifunctional catalysts [34–36]. Note that the puffed structures are still well remained after the durability test

under high current densities (Fig. S15), suggesting the excellent structural stability of FeCoNiP-PNAs. Moreover, a solar power-assisted water-splitting device was applied to demonstrate the great promise of bifunctional FeCoNiP-PNAs electrocatalyst for large-scale and real-world water splitting electrolyzers. As exhibited in Fig. 5c, operated under natural solar light in an outdoor environment, the solar panel delivers a voltage of 1.50 V. The H₂ and O₂ gas bubbles are continuously generated from the surface of electrodes (Fig. 5d). In addition, compared with the recently reported bifunctional catalysts including metal sulphides, phosphides, nitrides, oxides, and perovskite (Fig. S16), FeCoNiP-PNAs possess clear superiority for overall water splitting in terms of the low cell voltage of 1.48 V at 10 mA cm^{-2} . These results not only suggest the excellent electrocatalytic activity and stability of the FeCoNiP-PNAs, but also demonstrate the great promise of FeCoNiP-PNAs to construct large-scale and real-world water splitting electrolyzers for energy supply *via* overall water splitting.

CONCLUSIONS

In summary, we successfully constructed the puffed quaternary Fe_xCo_yNi_{1-x-y}P nanoarrays as bifunctional electrodes for robust overall water splitting. The Fe was used as the modulator to manipulate the electron den-

Figure 5 (a) LSV curve of FeCoNiP-PNAs as HER and OER bifunctional electrocatalyst for overall water splitting in 1 mol L^{-1} KOH. (b) Time-dependent current density curve of FeCoNiP-PNAs in overall water splitting. (c) Demonstration of a solar-power-assisted water-splitting device with a voltage of 1.50 V. (d) Photograph of the electrode surface driven by the 1.50 V solar panel.

sities of NiCoP nanoarray, which can increase the positive charge of metal (Ni and Co) and P sites. The resultant electron densities in $\text{Fe}_x\text{Co}_y\text{Ni}_{1-x-y}\text{P}$ are supposed to optimize the adsorption and desorption of H through effectively adsorbing and dissociating of water molecules and weakening P–H_{ads} bonds. The Fe as the modulator also plays a positive role in OER activity enhancement possibly due to the synergetic effect of triple metals. Besides, the puffed structure with rich porosity, cavity and defects can ensure adequate exposure and utilization of active sites. The elaborate manipulation of both electronic and morphological structure in FeCoNiP-PNAs is responsible for the noticeable improvement in both HER and OER activities. Our research here can be expected to offer new perspectives in the design of high-efficiency non-noble bifunctional electrodes for energy conversion.

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Author contributions Wang H conceived the experiment, analyzed the data and wrote the paper. Liu HL and Wang J conducted the material characterizations and data analyses. Wang H and Zhang X conducted the material synthesis and electrochemical measurements. Hu S carried out the orbital splitting of elements. Wang X, Zhou W and Liu H provided suggestions to the final version of the manuscript. All authors contributed to the manuscript.

Conflict of interest The authors declare no conflict of interest.

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

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碱刻蚀法构建膨化Fe_xCo_yNi_{1-x-y}P四元阵列及其高效裂解水性能

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摘要 设计和构建低成本、高效、高稳定性双功能电催化剂用于全解水生产氢气燃料是非常吸引人的研究,同时也充满挑战。我们精心构建了膨化四元Fe_xCo_yNi_{1-x-y}P纳米阵列作为双功能电催化剂用于全解水。通过引入铁元素调节磷化镍钴的电子结构,可增加磷和金属的正电荷分布,从而可实现电催化析氢过程中对氢原子吸附脱附平衡,有利于水分子的吸附和解离。在电子调控的基础上,我们采用动力学控制碱刻蚀的方法优化催化剂的形貌结构,获得了膨化纳米阵列。膨化结构具有丰富的孔结构、空腔以及晶格缺陷,有利于更多活性位点的暴露和传质。膨化Fe_xCo_yNi_{1-x-y}P只需25和230 mV过电势即可分别实现产氢和产氧。利用膨化Fe_xCo_yNi_{1-x-y}P作为阳极和阴极搭建的电解池只需1.48 V即可实现全解水,并在较高电流中表现出优异的稳定性。我们期望协同优化电子和形貌结构促进电催化反应过程的研究思路对廉价高效稳定双功能电催化剂的研究有所启发。