Synergistic electronic and morphological modulation on ternary $\text{Co}_{1-x}\text{V}_x\text{P}$ nanoneedle arrays for hydrogen evolution reaction with large current density

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ABSTRACT It is a great challenge to prepare non-noble metal electrocatalysts toward hydrogen evolution reaction (HER) with large current density. Synergistic electronic and morphological structures of the catalyst have been considered as an effective method to improve the catalytic performance, due to the enhanced intrinsic activity and enlarged accessible active sites. Herein, we present novel ternary $\text{Co}_{1-x}\text{V}_x\text{P}$ nanoneedle arrays with modulated electronic and morphological structures as an electrocatalyst for highly efficient HER in alkaline solution. The $\text{NF@Co}_{1-x}\text{V}_x\text{P}$ catalyst shows a remarkable catalytic ability with low overpotentials of 46 and 226 mV at current densities of 10 and 400 mA cm^{-2} , respectively, as well as a small Tafel slope and superior stability. Combining the experimental and computational study, the excellent catalytic performance was attributed to the improved physical and chemical properties (conductivity and surface activity), large active surface area, and fast reaction kinetics. Furthermore, the assembled Co–V based electrolyzer ($\text{NF@Co}_{1-x}\text{V}_x\text{P}-\text{HNNs}(+)|\text{NF@Co}_{1-x}\text{V}_x\text{P}(-)$) delivers small full-cell voltages of 1.58, 1.75, and 1.92 V at 10, 100, and 300 mA cm^{-2} , respectively. Our findings provide a systematic understanding on the V-incorporation strategy to promote highly efficient ternary electrocatalysts *via* synergistic control of morphology and electronic structures.

Keywords: modulated morphology and electronic structures, ternary $\text{Co}_{1-x}\text{V}_x\text{P}$, hydrogen evolution reaction, overall water splitting

INTRODUCTION

Hydrogen (H_2) has been considered as the ultimate clean and renewable energy carrier due to its ultra-high energy density and carbon-free emission [1–3]. Electrical-driven water splitting is an environmentally friendly and economic way to produce highly pure H_2 on large scale. However, the conversion efficiency from electricity to H_2 is still low due to the low-efficiency electrocatalysts used in the process, leading to high cost. It is necessary to achieve high-efficiency electrocatalysts that are critical components in electrocatalysis. Up to now, platinum-based materials have been investigated as the most effective catalysts for hydrogen evolution reaction (HER) in both acidic and alkaline environments. However, the rareness and high consumption restrict their wide applications in practice. Many efforts have been made over the past years to develop effective and low-cost non-noble electrocatalysts for HER [4,5]. To date, numerous non-noble electrocatalysts, such as metal oxides [6–9], sulfides [10–14], selenides [15–18], phosphides [19–22], nitrides [23,24] and carbides [25–27] have been extensively explored. However, most non-noble metal-based catalysts, especially oxides, are unstable in acidic solution [28]. Additionally, HER in alkaline solution suffers a much slow dynamic process due to the additional water dissociation step [28,29]. Therefore, it is more appealing but challenging to develop non-noble-based electrocatalysts

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for robust HER ability in alkaline media.

Transition metal phosphides, such as binary Co-based phosphides, have been investigated as electrocatalysts toward efficient HER in alkaline solution due to their high conductivity and active sites with hydrogenases, which have strong ability to attract protons [28,30,31]. Nevertheless, their performance is still insufficient compared with the benchmark platinum-based materials for commercial application. Ternary transition metal phosphides have been demonstrated to show improved electrocatalytic performance due to modulated electronic structure. For instance, ternary NiCo_2P_x and $\text{Ni}_{2(1-x)}\text{Mo}_{2x}\text{P}$ catalysts show high HER activities due to excellent intrinsic activities and fast kinetics on the catalyst surface [32,33]. Recently, V doping has been evidenced as an effective strategy to improve HER performance of Co phosphides through improved electronic structure [34,35]. However, the reported performance is limited on the large current, and the mechanism of V-doping is not well studied. Besides, the content of V doping is not enough to induce obvious morphology evolution to increase the active sites and accelerate mass transfer and gas evolution, resulting in inefficient catalytic performance [36].

In this study, we present novel ternary $\text{Co}_{1-x}\text{V}_x\text{P}$ nanoneedle arrays with tunable morphology and electronic structure, as an effective electrocatalyst for HER under

large current evidenced by the experimental results and theoretical calculations. The as-prepared $\text{NF@Co}_{1-x}\text{V}_x\text{P}$ catalyst exhibits low overpotentials at high current densities, small Tafel slope and long-term stability which are ascribed to (1) the modulated electronic structure and improved intrinsic HER activity in ternary $\text{Co}_{1-x}\text{V}_x\text{P}$, (2) the enlarged active surface area originating from the $\text{Co}_{1-x}\text{V}_x\text{P}$ nanoneedles with reduced sizes and numerous porous structures, and (3) the robust structure on nickel foam (NF) that favors fast kinetics. Our theoretical calculations confirm that the improved conductivity and optimal free energies for water activation and hydrogen adsorption are achieved by the incorporation of V into CoP, leading to fast kinetics toward HER. Furthermore, the $\text{NF@Co}_{1-x}\text{V}_x\text{-HNNs}(+)|\text{NF@Co}_{1-x}\text{V}_x\text{P}(-)$ electrolyzer delivers small voltages to drive high current densities and shows excellent stability.

EXPERIMENTAL SECTION

Preparation of $\text{NF@Co}_{1-x}\text{V}_x\text{-HNN}$ precursor

The $\text{Co}_{1-x}\text{V}_x$ hydroxide nanoneedle arrays on NF ($\text{NF@Co}_{1-x}\text{V}_x\text{-HNNs}$) were prepared by a one-step hydrothermal method as reported in literature (Fig. 1a) [37]. In a typical process, 0.218 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.0393 g of VCl_3 , 0.6 g of $\text{CO}(\text{NH}_2)_2$ and 0.16 g of NH_4F were added into 30 mL of distilled water successively to form a

Figure 1 (a) Schematic illustration of the synthesis of $\text{NF@Co}_{1-x}\text{V}_x\text{P}$. SEM images of (b) Co-HNNs precursor, (c) $\text{Co}_{1-x}\text{V}_x\text{-HNNs}$ precursor, (d) CoP, and (e) $\text{Co}_{1-x}\text{V}_x\text{P}$ at different magnifications. (f) SEM image and the corresponding elemental mapping of Ni, Co, V, P and O for $\text{NF@Co}_{1-x}\text{V}_x\text{P}$.

clear solution under continuous stirring for 10 min. Then, a piece of acid-treated NF (2 cm×4 cm) and the above solution were transferred to a 50-mL stainless-steel Teflon-lined autoclave and heat-treated at 120°C for 12 h. After that, the as-obtained NF@Co_{1-x}V_x-HNN precursor was collected and rinsed with distilled water and ethanol, and then dried at 60°C under vacuum for 24 h. The Co_{1-x}V_x hydroxide nanoneedle arrays on NF (NF@Co-HNNs) were prepared in a similar procedure without VCl₃.

Synthesis of NF@Co_{1-x}V_xP

The NF@Co_{1-x}V_xP nanoneedle arrays were prepared by annealing the NF@Co_{1-x}V_x-HNN precursor with NaH₂PO₂ at 350°C under a flow of Ar gas (80 sccm) for 2 h (Fig. 1a). The NF@Co_{1-x}V_xP nanoneedle arrays with different Co/V molar ratios, denoted as 8:1, 4:1, 3:1, and 2:1, were prepared by precisely controlling the corresponding Co/V molar ratios in the solution during the hydrothermal process. The NF@CoP and NF@Ni₂P were also prepared by treating the NF@Co-HNNs and pure NF in the same procedure, respectively.

Material characterization

The morphology characterizations and elemental distribution of the as-prepared samples were performed on a scanning electron microscope (SEM, TESCAN) with energy dispersive X-ray spectroscopy (EDX). Nitrogen adsorption/desorption experiments were conducted at 77 K with a BELSORP-max analyzer. Before the measurement, all the samples were degassed in vacuum at 120°C for 12 h. The crystal structures of the as-prepared samples were determined by a powder X-ray diffractometer (XRD) with Cu K α ($\lambda=0.15406$ nm) radiation (Bruke D8 Advance). The microstructures of Co_{1-x}V_xP nanoneedles were investigated with a high-resolution transmission electron microscope (HRTEM, FEI Tecnai F30). The chemical composition and valence states of the NF@CoP and NF@Co_{1-x}V_xP samples were collected with X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Scientific).

Electrochemical testing

The obtained NF@Co_{1-x}V_xP samples with an area of 1×1 cm² were directly evaluated as working electrodes to characterize the catalytic performance for HER in 1.0 mol L⁻¹ KOH. The electrochemical tests were carried out on an electrochemical workstation (Biological VMP3) in a three-electrode system with an Hg/HgO (1.0 mol L⁻¹ KOH) electrode and a carbon rod as the reference and

counter electrodes, respectively. The linear sweep voltammetry (LSV) curves were recorded with a voltage range from 0.05 to -0.4 V at a scan rate of 2 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was carried out under various overpotentials from 100 to 180 mV in the frequency range from 0.1 Hz to 100 kHz with an amplitude of 10 mV. The electrochemical surface areas (ECSA) were measured using cyclic voltammetry (CV) technique with a potential range between 0.10 and 0.20 V. The long-term stability test was evaluated using a chronoamperometric method for 24 h under a constant current density. All potentials were referenced to the reversible hydrogen electrode (RHE). All the electrochemical measurements were recorded with the *iR* compensation at ambient temperature.

Computational details

The density-functional-theory (DFT) calculations were performed based on Vienna *ab initio* simulation package (VASP) [38]. The generalized gradient approximation with the Perdew-Burke-Eznerhof generalized gradient approximation (GGA-PBE) was used in this study [39]. The model of CoP was cleaved from the (211) surface of bulk orthorhombic CoP, because the peak value of (221) surface in the XRD pattern of CoP is the highest. The model was composed of 16 Co and 16 P atoms. A vacuum of 15 Å was used to eliminate the interaction between the neighboring cells. In the Co_{1-x}V_xP model, Co atoms were substituted by V atoms according to the V/Co atomic ratio (Co:V:P=3:1:4) in the experiments. A 5×5×1 grid for *k*-point sampling for geometry optimization was applied using the Monkhorst and Pack scheme. DFT-D3 method was used to evaluate the van der Waals (vdW) interaction [40]. A cut-off energy of 450 eV was consistently used. The total energy was converged to 10⁻⁴ eV per atom and the convergence threshold of force was 0.02 eV Å⁻¹ in our calculations. The transition states were calculated by the climbing image nudged elastic band (CLNEB) method [41].

RESULTS AND DISCUSSION

The as-prepared NF@Co_{1-x}V_x-HNNs and NF@Co_{1-x}V_xP nanoneedle arrays are brown and black, respectively (Fig. 1a and Fig. S1). The SEM image indicates that the obtained Co-HNNs are nanoneedles with a length of more than 2 μm and a diameter ranging from 60–100 nm (Fig. 1b). After the incorporation of vanadium, the as-obtained CoV-HNNs precursor (Fig. 1c) exhibits the same morphology but with shorter length (less than 1 μm) and smaller diameter ranging from 20–50 nm,

because the existence of vanadium hinders the nanoneedle growth due to the competitive interaction between the V^{3+} and Co^{2+} with OH^- derived from urea during the formation of CoV hydroxide. Further, more nucleation sites result in the formation of dense $Co_{1-x}V_x$ -HNNs with shorter length and smaller diameter. The BET results from N_2 adsorption-desorption isotherms (Fig. S2 and Table S1) confirm the enlarged specific surface areas of $NF@Co_{1-x}V_x$ -NNS along with increasing V contents. After the mild phosphidation at $350^\circ C$, both the as-obtained CoP and $Co_{1-x}V_xP$ (Fig. 1d, e) keep the morphology of nanoneedle well. The $Co_{1-x}V_xP$ nanoneedles are getting shorter and denser as the V content increases (Fig. S3). The EDX elemental mapping images confirm the existence and uniform distribution of Ni, Co, V, P, and O in the $NF@Co_{1-x}V_xP$ electrode (Fig. 1f), but no V element in the $NF@CoP$ electrode (Fig. S4). The extra Ni element is derived from the NF and the O element can be ascribed to the surface oxidation that is unavoidable in the hydrothermal process. The XRD patterns of $NF@CoP$ and $NF@Co_{1-x}V_xP$ (Figs S5, S6) show the co-existence of CoP and Ni_2P phases, which are consistent with the standard patterns of CoP (PDF No. 29-0497) [19] and Ni_2P (PDF No. 03-0953, the Ni_2P phase is induced by the phosphidation of the NF substrate during the phosphating process (Fig. S7)) [33], respectively. The intensities of the diffraction peaks of the $NF@Co_{1-x}V_xP$ are much lower than those of $NF@CoP$, implying the weak crystallization of the CoP phase in $NF@Co_{1-x}V_xP$, which agrees well with the reduced sizes of $Co_{1-x}V_xP$ as the content of V increases (Fig. S6). The EDS results (Fig. S8 and Table S2) show that the atomic ratios of P to Co in $NF@CoP$ and $NF@Co_{1-x}V_xP$ are over 1, which are larger than the

stoichiometric value in CoP, suggesting the extra P belonging to the Ni_2P on the surface NF, consistent with the XRD data.

TEM images further reveal that both CoP and $Co_{1-x}V_xP$ nanoneedles are highly porous. The pores in CoP nanoneedles (Fig. 2a, b) range from several to tens of nanometers. However, $Co_{1-x}V_xP$ with extremely rough surface shows a uniform pore size of ~ 5 nm (Fig. 2c, d), which may provide more exposed active sites for catalytic reaction. HRTEM image (Fig. 2e) reveals apparent lattice fringes with an inter-planar spacing of 0.25 nm in $Co_{1-x}V_xP$, which is assigned to the (111) plane of CoP phase, indicating the successful incorporation of V in $Co_{1-x}V_xP$, matching well with the above XRD results. Furthermore, the selected area electron diffraction (SAED) pattern (Fig. 2f) verifies the polycrystalline structure of $Co_{1-x}V_xP$. These results imply the successful preparation of the ternary $Co_{1-x}V_xP$ with enlarged surface areas and controllable porous structure through the V-incorporation, which can induce rich accessible reaction sites for HER.

XPS measurements were performed to investigate the surface composition and chemical states of the $NF@CoP$ and $NF@Co_{1-x}V_xP$ electrodes. The XPS survey spectra (Fig. 3a) confirm the presence of the Ni, Co, V, and P elements in $NF@Co_{1-x}V_xP$, while only the Ni, Co and P elements in $NF@CoP$. The comparative high-resolution Co 2p and P 2p spectra (Fig. 3b, c) show that the surface oxidation is inevitable, when they are exposed to air, leading to the presence of the Co-O and P-O bonds in CoP and $Co_{1-x}V_xP$. For the $NF@CoP$ electrode, the Co $2p_{3/2}$ (~ 778.3 eV) and $2p_{1/2}$ peaks (793.4 eV) indicate the existence of metallic Co in CoP [42,43], while the

Figure 2 (a, b) TEM images of CoP at different magnifications. (c, d, e) TEM images of $Co_{1-x}V_xP$ at different magnifications. (f) The SEAD of $Co_{1-x}V_xP$.

Figure 3 (a) XPS survey, and high-resolution XPS spectra of (b) Co 2p, (c) P 2p of the NF@CoP and NF@Co_{1-x}V_xP electrodes, and (d) V 2p of the Co_{1-x}V_x-HNN precursor and NF@Co_{1-x}V_xP electrode.

peaks at ~ 781.4 , ~ 783.2 , ~ 797.7 and ~ 799.7 eV are ascribed to Co–O bond [37,42]. The strong shakeup satellites (identified as “Sat.”) at ~ 787.0 and ~ 804.0 eV imply the massive Co²⁺ in Co–O bonds. The P 2p spectra (Fig. 3c) show that the characteristic peaks centered at 129.2 and 130.2 eV match well with P 2p_{3/2} and P 2p_{1/2} in CoP. In addition, a broad peak at 134.2 eV corresponding to the P–O bond is ascribed to the oxidation. Clearly, the Co 2p and P 2p spectra in Co_{1-x}V_xP shift toward lower binding energies (BEs) in comparison with those in CoP, indicating an increase of electron density as induced by the V-incorporation [34]. Furthermore, we compare the V 2p spectra of the Co_{1-x}V_x-HNNs precursor and NF@Co_{1-x}V_xP electrode (Fig. 3d). For NF@Co_{1-x}V_x-HNNs, the V 2p signal can be fitted as V³⁺ (located at 515.7 and 523.3 eV), V⁴⁺ (located at 516.8 and 524.3 eV) and V⁵⁺ (located at 517.8 and 525.4 eV), respectively, indicating the mixture of V³⁺, V⁴⁺ and V⁵⁺ in the precursor [37]. After phosphation, two new peaks appear at the lower binding energy of 514.5 and 521.9 eV, which are ascribed to the formation of V–P bond in the NF@Co_{1-x}V_xP electrode [33,44]. These results reveal the strong electronic modulation of CoP by V incorporating. Besides,

the signal of Ni–P bond is also found in the XPS spectra of the NF@CoP and NF@Co_{1-x}V_x-HNNs electrodes (Fig. S9), which agrees well with the XRD and EDS analyses.

NF@Co_{1-x}V_xP, NF@CoP, NF@Ni₂P, NF@Pt/C, and pure NF were directly evaluated as working electrodes in 1 mol L⁻¹ KOH solution under a three-electrode configuration with Hg/HgO (1 mol L⁻¹ KOH) as the reference electrode and a carbon plate as the counter electrode. The NF@Co_{1-x}V_xP catalyst shows a small overpotential of 46 and 115 mV at the benchmark current densities of 10 and 100 mA cm⁻², respectively, which are superior to NF@CoP (96 and 172 mV), NF@Ni₂P (141 and 257 mV), and pure NF (160 and 294 mV) (Fig. 4a). Although inferior to NF@Pt/C (16 and 90 mV) at the same current densities, its performance is much better than those of most of the reported metal phosphides [1,19,32–34,45–50], metal selenides [15,51–53], metal nitrides [54–57] and heterogeneous structure catalysts [58–61] in alkaline solution (Table. S3). Importantly, the NF@Co_{1-x}V_xP electrode is better than NF@Pt/C at high current densities (> 190 mA cm⁻²). For example, it delivers the current densities of 200 and 400 mA cm⁻² at the overpotentials of

Figure 4 (a) Polarization curves of the NF@Co_{1-x}V_xP, NF@CoP, NF@Ni₂P, NF@Pt/C, and pure NF electrodes in 1.0 mol L⁻¹ KOH. (b) The corresponding Tafel plots. (c) Comparison of NF@Co_{1-x}V_xP, NF@CoP, NF@Ni₂P, and pure NF at various double-layer charging currents at 0.15 V (vs. RHE) with various potential scan rates. (d) Comparison of j_{specific} and R_i for NF@Co_{1-x}V_xP, NF@CoP, and NF@Ni₂P in 1.0 mol L⁻¹ KOH. (e) The EIS of NF@Co_{1-x}V_xP, NF@CoP, NF@Ni₂P, and pure NF at the HER overpotential of 120 mV. (f) Voltage-time chronoamperometric curves of NF@Co_{1-x}V_xP, NF@CoP, NF@Ni₂P, and pure NF in 1.0 mol L⁻¹ KOH at the current densities of 10, 20 and 24 mA cm⁻² during 6-h interval.

158 and 226 mV, respectively, while the overpotentials are 161 and 279 mV for NF@Pt/C to reach the same current densities (Fig. 4a). The excellent performance of NF@Co_{1-x}V_xP at large current density indicates its commercial applications.

A small Tafel slope is always indicative of fast reaction kinetics for HER. The NF@Co_{1-x}V_xP electrode shows a Tafel slope of 58 mV dec⁻¹, which is close to that of the NF@Pt/C (38 mV dec⁻¹) and smaller than those of NF@CoP (76 mV dec⁻¹), NF@Ni₂P (104 mV dec⁻¹), and

pure NF (103 mV dec⁻¹), suggesting its favorable reaction kinetics (Fig. 4b). Since the overall HER activity of a catalyst is determined by its intrinsic activity and the number of active sites, the ECSAs of the prepared electrodes were evaluated *via* CV to characterize their corresponding electro-catalytically active surface areas. The calculated ECSA value of the NF@Co_{1-x}V_xP electrode is 233.5 mF cm⁻², which is much higher than those of NF@CoP (53.3 mF cm⁻²), NF@Ni₂P (44.6 mF cm⁻²), and pure NF (1.74 mF cm⁻²) (Fig. 4c and Fig. S10), indicating

the large active surface area and abundant active catalytic sites originated from the incorporation of V, which agrees well with the SEM and TEM results. Furthermore, the roughness factor (R_f) and specific current density (j_{specific}) of various electrodes were calculated to reveal the intrinsic activities. NF@Co_{1-x}V_xP has the highest R_f and j_{specific} values in comparison with NF@CoP and NF@Ni₂P (Fig. 4d and Table. S4), indicating that the excellent activity of NF@Co_{1-x}V_xP for alkaline HER can be ascribed to the increased active sites and high intrinsic activity. The electrochemical tests of NF@Co_{1-x}V_xP with different Co/V ratios were performed to optimize the V content on the HER performance of NF@Co_{1-x}V_xP. Fig. S11a shows that the NF@Co_{1-x}V_xP catalyst with a Co/V ratio of 3:1 owns small overpotentials of 46 and 226 mV at the benchmark current density of 10, and large current density of 400 mA cm⁻², respectively, which are superior to the other samples. The NF@Co_{1-x}V_xP electrode with a Co/V ratio of 3:1 shows a Tafel slope of 58 mV dec⁻¹, smaller than those of the NF@Co_{1-x}V_xP electrodes with different Co/V ratios of 8:1 (70 mV dec⁻¹), 4:1 (73 mV dec⁻¹), and 2:1 (72 mV dec⁻¹), implying faster reaction kinetics (Fig. S11b). The calculated ECSA value of 3:1 electrode is 233.5 mF cm⁻², much higher than those of 8:1 (92.94 mF cm⁻²), 4:1 (149.6 mF cm⁻²), and 2:1 (118.35 mF cm⁻²) (Figs S11c, S12), which agrees well with their HER activities, indicating the enlarged active sites by V incorporation in Co_{1-x}V_xP. Furthermore, the NF@Co_{1-x}V_xP with a Co/V ratio of 3:1 has the highest R_f and j_{specific} values (Fig. S11d and Table S5), indicating that the excellent activity of NF@Co_{1-x}V_xP for alkaline HER can be ascribed to the improved active sites and high intrinsic activity. These results show that the NF@Co_{1-x}V_xP with a Co/V ratio of 3:1 has the smallest overpotential, lowest Tafel slope, largest ECSA, highest j_{specific} and highest R_f among the considered catalysts (Figs S11, S12 and Table. S5), confirming that the optimized electrocatalytic activity of our ternary Co_{1-x}V_xP catalysts is attributed to the enlarged active sites and improved intrinsic catalytic ability through the V-incorporation.

The value of EIS is an important parameter to characterize the kinetics at the electrode/electrolyte interface during the HER process. Especially, the charge transfer resistance (R_{ct}) is represented by the diameter of the semicircle in the low frequency zone, which is related to the electrocatalytic kinetics. In general, a low value of R_{ct} corresponds to a fast reaction rate, while a low value of R_s means a high conductivity of a catalyst. For the NF@Co_{1-x}V_xP catalyst, a small R_{ct} value of only 0.75 Ω is

recorded at the overpotential of 100 mV (Fig. S13). As the overpotential increases to 180 mV, the R_{ct} value decreases to 0.19 Ω , implying the fast electron transfer at the electrolyte interface of NF@Co_{1-x}V_xP. The NF@Co_{1-x}V_xP catalyst has the smallest R_{ct} among all the electrodes (Fig. 4e), suggesting the most favorable HER kinetics. Additionally, the EIS of NF@Co_{1-x}V_xP with Co/V ratios of 3:1 owns the smallest R_s among all the NF@Co_{1-x}V_xP electrodes (Fig. S14), implying the improved conductivity in the ternary Co_{1-x}V_xP. To explore the long-term stability of NF@Co_{1-x}V_xP, we compared the stability of the samples at the current densities of 10, 20, and 24 mA cm⁻² during 6-h interval (Fig. 4f), respectively. Remarkably, NF@Co_{1-x}V_xP at the four stages has even overpotentials about 46, 79, 87 and 48 mV at 10, 20, 24 and 10 mA cm⁻², respectively. A negligible voltage fluctuation in each interval can be observed, indicating the highly stable catalytic performance for HER in alkaline solution. For comparison, the other electrodes deliver much larger overpotentials and voltage fluctuation (35 mV for NF@CoP, 26 mV for NF@Ni₂P and 95 mV for pure NF) at 10 mA cm⁻² in 24 h stability tests (Fig. 4f). Furthermore, no obvious decay of the cathodic currents in the polarization testing after 24 h further demonstrates the prominent durability of NF@Co_{1-x}V_xP (Fig. S15). The structure and morphology of NF@Co_{1-x}V_xP after long-term test were further characterized by SEM and TEM (Fig. S16a-d). The nanoneedle arrays and porous nanostructures of NF@Co_{1-x}V_xP maintain well after 24-h testing, confirming that the excellent stability of the Co_{1-x}V_xP is closely associated with its robust structure.

Theoretical calculation was employed to further understand the HER performance of our ternary Co_{1-x}V_xP catalyst. The atomic ratio of Co, V, and P in the Co_{1-x}V_xP is around 3:1:4, and the structure of Co_{1-x}V_xP is relaxed before calculating the physical and chemical properties (Fig. S17). The partial density of states (PDOSs) of CoP and Co_{1-x}V_xP (Fig. S18) show that the incorporation of V into CoP can greatly enhance the carrier density near the Fermi level, which is dominantly contributed by the V d electrons. This confirms the improved conductivity in ternary Co_{1-x}V_xP, which is consistent with the EIS analysis (Fig. S14) and the results of HER performance due to the improved electron transfer.

It is widely acknowledged that a two-step process occurs in a typical HER in alkaline media. The Volmer step includes the adsorption and activation of H₂O along with the cleavage of O-H bonds to form H atoms adsorbed on the surface of catalysts (H*). Then, in the Heyrovsky step, two protons are combined to H₂. Therefore, we further

calculated the free energies of the adsorption and activation of H_2O , the OH adsorption, and the H adsorption on the (211) surfaces of CoP and $\text{Co}_{1-x}\text{V}_x\text{P}$ to reveal the origin of the excellent HER activity of $\text{Co}_{1-x}\text{V}_x\text{P}$ (Fig. 5a). Our calculations (Fig. 5b) show that $\text{Co}_{1-x}\text{V}_x\text{P}$ has a much lower water adsorption energy ($\Delta E_{\text{H}_2\text{O}}$) than CoP, implying that water adsorption on $\text{Co}_{1-x}\text{V}_x\text{P}$ is more achievable than that on CoP. $\text{Co}_{1-x}\text{V}_x\text{P}$ delivers a smaller energy for the H_2O activation than CoP (Fig. 5c), indicating that the Volmer step of H_2O adsorption and activation is much easier on $\text{Co}_{1-x}\text{V}_x\text{P}$ than that on CoP. The calculated free energy diagram for H adsorption (ΔG_{H}) shows that $\text{Co}_{1-x}\text{V}_x\text{P}$ owns a low $|\Delta G_{\text{H}}|$ value of 0.26 eV, which is much lower than that of CoP (0.36 eV). The relatively low $|\Delta G_{\text{H}}|$ value leads to an optimized hydrogen adsorption and desorption capability, thus beneficial to the Heyrovsky step. Therefore, both the experimental and theoretical analyses support that the ternary $\text{Co}_{1-x}\text{V}_x\text{P}$ is highly efficient toward HER process in alkaline media.

The $\text{NF@Co}_{1-x}\text{V}_x\text{-HNNs}$ were investigated as high-performance OER electrocatalyst with a low overpotential and long-term stability [37]. Therefore, we combined our 3D ternary $\text{NF@Co}_{1-x}\text{V}_x\text{P}$ with $\text{NF@Co}_{1-x}\text{V}_x\text{-HNNs}$ to build an electrolyzer for overall water splitting in alkaline environment (Fig. 6a). We find that the $\text{NF@Co}_{1-x}\text{V}_x\text{-HNNs}(+)\|\text{NF@Co}_{1-x}\text{V}_x\text{P}(-)$ electrolyzer delivers the small voltages of 1.58, 1.75, 1.84, and 1.92 V at 10, 100,

200, and 300 mA cm^{-2} , respectively (Fig. 6b and Fig. S19), which is superior to those of the $\text{NF@Co-HNNs}(+)\|\text{NF@CoP}(-)$ electrolyzer and other reported electrocatalysts for overall water splitting in 1.0 mol L^{-1} KOH [44,62–66]. We further find that the voltage fluctuation in each current density of the $\text{NF@Co}_{1-x}\text{V}_x\text{-HNNs}(+)\|\text{NF@Co}_{1-x}\text{V}_x\text{P}(-)$ is very small, indicating the highly stable catalytic performance (Fig. 6c). In addition, negligible change can be observed in the LSV curves for the $\text{NF@Co}_{1-x}\text{V}_x\text{-HNNs}(+)\|\text{NF@Co}_{1-x}\text{V}_x\text{P}(-)$ electrolyzer before and after 20-h stability testing (Fig. 6a), which is superior to the $\text{NF@Co-HNNs}(+)\|\text{NF@CoP}(-)$ electrolyzer. These results suggest that the combination of our $\text{NF@Co}_{1-x}\text{V}_x\text{P}$ catalyst for HER and $\text{NF@Co}_{1-x}\text{V}_x\text{-HNNs}$ catalyst for OER is very promising for water electrolysis on large scale.

CONCLUSIONS

In summary, novel ternary $\text{Co}_{1-x}\text{V}_x\text{P}$ nanoneedle arrays are successfully fabricated on NF and intensively evaluated as electrocatalysts for HER in alkaline electrolyte. Our combined experimental and theoretical study reveals that $\text{NF@Co}_{1-x}\text{V}_x\text{P}$ has small overpotentials at both the benchmark current density (46 mV at 10 mA cm^{-2}) and large current density (226 mV at 400 mA cm^{-2}), as well as excellent long-term stability, which is attributed to the enhanced active surface areas, modulated electronic structures and fast kinetics toward HER. We further show

Figure 5 (a) Chemisorbed structural models for the calculated free energies of H_2O adsorption, OH adsorption, and H adsorption. Here TS represents a transition state of H_2O activation. Calculated adsorption free energy of H_2O ($\Delta E_{\text{H}_2\text{O}}$) (b), free energy diagram for H_2O activation (cleavage of O–H bonds of H_2O molecules) (c), and free energy diagram for H adsorption (ΔG_{H}) (d) on the (211) surfaces of CoP and $\text{Co}_{1-x}\text{V}_x\text{P}$.

Figure 6 (a) Schematic illustration of the electrolyzer using NF@Co_{1-x}V_xP and NF@Co_{1-x}V_x-HNNs as cathode and anode, respectively. (b) Polarization curves of the NF@Co_{1-x}V_x-HNNs(+)||NF@Co_{1-x}V_xP(-) and NF@Co-HNNs(+)||NF@CoP(-) electrolyzers recorded before and after 20-h stability tests. (c) Voltage-time chronoamperometric curves of the NF@Co_{1-x}V_x-HNNs(+)||NF@Co_{1-x}V_xP(-) and NF@Co-HNNs(+)||NF@CoP(-) electrolyzers in 1.0 mol L⁻¹ KOH at the current densities of 10, 20 and 24 mA cm⁻² during 5 h intervals without *iR* compensation.

that the assembled NF@Co_{1-x}V_x-HNNs(+)||NF@Co_{1-x}V_xP(-) electrolyzer needs small voltages of 1.58, and 1.92 V to deliver the current densities of 10, and 300 mA cm⁻², respectively. We believe that the strategy by the V-incorporation to construct ternary nanomaterials not only is an effective way to boost the overall water-splitting, but also promotes the exploration of novel catalysts/electrodes in other fields, such as nitrogen reduction reaction, supercapacitors, alkaline ion batteries, and so on.

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

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具有协同电子结构和形貌调控功能的三元Co_{1-x}V_xP纳米针阵列在大电流下的析氢性能研究

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摘要 制备具有大电流析氢性能的非贵金属电催化剂是一个巨大挑战。协同调控催化剂的电子结构和形貌能够增强其本征催化能力和增加活性位点,被认为是提高催化性能的有效方法。本文以具有协同电子结构和形貌调控功能的三元Co_{1-x}V_xP纳米针阵列作为碱性析氢的高效电催化剂。实验和理论计算结果表明,其优异的催化性能来源于物理化学性质的提高、活性表面积的增加及反应动力学的加速。此外,组装的(NF@Co_{1-x}V_x-HNNs(+))||NF@Co_{1-x}V_xP(-))电解池在1.58、1.75和1.92 V的电压下,能够分别得到10、100和300 mA cm⁻²的电流密度。