Single-Crystalline $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ Nanosheets with Dominant $\{011\bar{1}\bar{1}\}$ Facets: Efficient Electrocatalysts for Hydrogen Evolution Reaction at All pH Values

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Single-Crystalline $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ Nanosheets with Dominant $\{01\bar{1}\bar{1}\}$ Facets: Efficient Electrocatalysts for Hydrogen Evolution Reaction at All pH Values

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ABSTRACT:

Electrocatalytic hydrogen evolution reaction (HER) plays a critical role in developing hydrogen and fuel cell technologies. At present, only platinum (Pt) and its compounds are thought to be efficient electrocatalysts for HER, particularly at all-pH values. However, the scarcity and high cost of Pt-based catalysts have seriously hindered their practical application in HER. Here, we report a two-step method for synthesizing single-crystalline $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets with exposed $\{01\bar{1}\bar{1}\}$ facets on Ni foam. Compared with pristine Ni_2P , the $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets exhibit a dramatically improved HER activity (an overpotential of 81, 90, 103 mV at 10 mA cm^{-2} in acidic, neutral and alkaline media, respectively). Based on the density functional theory (DFT) calculations, it is observed that trace Fe-doping can lead to more charge accumulation around P active sites, which accordingly decreases the ΔG_{H^*} and $\Delta G_{\text{H}_2\text{O}}$ and promotes the catalytic activity.

Graphical Abstract:

Single-Crystalline $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ Nanosheets with Dominant $\{01\bar{1}\bar{1}\}$ Facets were synthesized through the phosphating of FeNi-LDH. The $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ Nanosheets exhibit remarkable electrocatalytic hydrogen evolution reaction (HER) activity at all pH values, which results from the more charge accumulation around P active sites and decreased ΔG_{H^*} and $\Delta G_{\text{H}_2\text{O}}$ after Fe-doping based on the density functional theory (DFT) calculations.

Keywords: $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$; Hydrogen evolution reaction; Electrocatalysis; All pH values; DFT calculations

1. Introduction

As one of the most promising substitutes for fossil fuels, hydrogen energy plays a vital role in our energy revolution due to its high energy density [1, 2]. Electrochemical water splitting is one of the most efficient methods for H_2 production, and the electrocatalysts for hydrogen evolution reaction (HER) is the key factor for achieving efficient water splitting. Presently, platinum (Pt) and its compounds are thought to be efficient electrocatalysts for HER, due to the splendid kinetics for actuating the HER and enhancing the negligible overpotentials [3-7]. However, the scarcity and high cost of Pt-based noble metal have seriously hindered their practical application in the field of catalysis.

Recently, in order to develop low-cost electrocatalysts with excellent performance for water splitting, various transition metals and their compounds have been widely investigated [8-12]. In particular, transition metal phosphides (TMPs) are viewed as ideal substitutes for precious Pt-group electrocatalysts because of their analogous mimics of the active sites in hydrogenases, such as Ni_2P , MoP_2 , and CoP [10, 13-15]. However, most reported single-metal phosphides only exhibited high activity in acidic or alkaline media, which have poor activity in neutral media. Compared with the acidic and alkaline media, the neutral media has the lowest

electric conductance ($G=1/R$). This could result in larger Ohmic loss and a slower kinetics in neutral media [16]. In addition, the corrosive attack on HER equipment is easier to take place in strong acidic or alkaline condition than in neutral solution, seriously limiting its practical application. Furthermore, the catalysts are more stable in neutral solution. Therefore, developing all-pH catalysts that have both excellent performance and stability, is significantly important and meaningful, but still a great challenge.

To address the issues of single-metal phosphides, numerous efforts have been devoted to doping heteroatom (e.g. Fe, Mo, and Mn) into a single-metal phosphide [17-19]. For instance, the overpotential of $\text{Co}_{1-x}\text{Fe}_x\text{P/CNT}$ was reduced to 105 mV in 1 M PBS compared with 150 mV of CoP/CNT [17]. However, the detailed mechanism for the doping-triggered HER improvement is still unclear. This hinders the further performance gains of the doped HER catalysts. Generally, the HER process involves three elementary reactions. The first step is Volmer reaction, in which an electron is transferred to a hydrogen proton attached on the catalyst to form H^* . In the second step, the attached H^* trends to couple with a new electron and another hydrogen proton to form H_2 molecules at a low H^* coverage. This process is named Heyrovsky reaction. If the H^* coverage is high, the recombination between the adjacent H^* atoms will be dominant and then generate H_2 . This is a typical Tafel route. The last step is desorption of H_2 molecules from the catalysts. The reaction mechanisms in different media differs from the initial Volmer reaction. In acidic media, the catalyst can capture hydrogen protons in solution. However, in alkaline and

neutral media, the hydrogen protons are formed by breaking the H-O-H bond of H₂O. According to previous studies [20, 21], the Gibbs free energy of adsorption of hydrogen (ΔG_{H^*}) of a single-metal sulfide and phosphide such as MoS₂ and CoP could be significantly reduced after Fe-doping. This means that H^{*} are much easier to be captured by active sites, thus enhancing the HER performance. However, the calculated ΔG_{H^*} is only suitable for HER in acidic media since the abundant H⁺ in acidic solution can easily transform to H^{*} by getting electrons [22]. In alkaline electrolyte, HER needs an initial water dissociation step to produce H^{*}. So it is not enough to fully explain the reaction mechanism of HER in alkaline by calculating ΔG_{H^*} . The previous studies merely explained the mechanism from thermodynamic viewpoint. The electronic structure turning caused by the Fe-doping was completely ignored. Actually, the charge density difference calculations can directly reveal the change of charge transfer before and after doping [21], and the effect of dopant on the active sites can be disclosed by the changes of charge accumulation and depletion region [23].

Herein, we report the synthesis of single-crystalline (Fe_xNi_{1-x})₂P nanosheets with a preferentially exposed {01 $\bar{1}\bar{1}$ } facet through a two-step strategy (*in-situ* growth of Fe_xNi_{1-x}-LDH followed by a phosphidation process). Benefiting from the doping of trace Fe, the as-prepared (Fe_{0.048}Ni_{0.952})₂P nanosheets exhibit a high performance towards HER. For instance, it only requires an overpotential of 90 mV, 81 mV, and 103 mV to approach 10 mA cm⁻² in neutral media (1 M PBS), acidic media (0.5 M H₂SO₄), and alkaline media (1 M KOH), respectively. They also have excellent

stability in all-pH media, maintaining 95.2 % for 20 h in neutral media, 77.6 % for 10 h in acidic media, and 97.2% for 20 h in alkaline media. Based on DFT calculations of Fe-doping effect on active P sites, ΔG_{H^*} of $(Fe_{0.048}Ni_{0.952})_2P$ is much closer to zero (0.17 eV) than that of $(Fe_{0.077}Ni_{0.923})_2P$, $(Fe_{0.035}Ni_{0.965})_2P$, $(Fe_{0.028}Ni_{0.972})_2P$, and Ni_2P under acidic conditions. The calculated water dissociation energy (ΔG_{H_2O}) indicates that $(Fe_{0.048}Ni_{0.952})_2P$ shows the lowest ΔG_{H_2O} (0.03 eV) in alkaline media. Furthermore, DFT calculations reveal that the Fe-doping can lead to obvious charge accumulation around P active sites. This is beneficial to optimize the activity of the P active sites. Besides, the charge density difference around H atom indicates that the doped Fe can promote the electron transfer from P atom to H atom, which is favorable for generation of H_2 .

2. Experimental section

2.1 Sample preparation

Experimental materials were used without any additional purification: Ni foam was purchased from CeTech Co., Ltd. $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $CO(NH_2)_2$, $NaH_2PO_2 \cdot H_2O$ were purchased from Sinopharm Chemical Reagent. NH_4F was purchased from Aladdin Reagent. Argon gases were supplied in cylinders by Heli factory with 99.999% purity. Nafion[®] perfluorinated resin solution containing 5% Nafion[®] was purchased from Sigma-Aldrich. Ultra-pure water with resistivity $> 18 \text{ M}\Omega \cdot \text{cm}^{-1}$ was used.

Preparation of $(Fe_xNi_{1-x})_2P$ nanosheets. First, a piece of Ni foam ($55 \times 10 \times 1 \text{ mm}^3$) was thorough cleaned with acetone, absolute ethanol, and deionized

water in an ultrasound bath, respectively. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0 mmol, 0.3 mmol, 0.5 mmol, 0.6 mmol, 1 mmol), NH_4F (16 mmol), and $\text{CO}(\text{NH}_2)_2$ (40 mmol) were added to 80 mL distilled water with continuously stirring for 60 min. The obtained solution and the Ni foam were put into a 100 mL autoclave reactor and maintained at 140 °C for 12 hours in a drying oven. After washed with deionized water and absolute ethanol, and dried at 60 °C for 6 h, the FeNi-LDH was obtained. Then, the synthesized FeNi-LDH and 2 g $\text{NaH}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$ were put into two separate porcelain boats, respectively. The porcelain boat containing $\text{NaH}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$ was placed at the upstream side in the tubular furnace and the heating rate was 2 °C min⁻¹. After heating to 450 °C and maintaining for 3 h in the Ar, the final $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets were collected by washing with 0.1 mol/L HCl and absolute ethanol for 10 min and drying at 60 °C for 60 min.

2.2 Characterization

The crystalline structure was characterized by X-ray diffraction (XRD, DX2700, China) with 2 θ range from 5 to 90°. The morphology was observed with field emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and HAADF-STEM with energy-dispersive X-ray spectrometry (EDS) images were obtained using a FEI Tecnai F20 electron microscope. The surface elemental compositions and valence states of $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ were investigated by X-ray photoelectron spectroscopy (XPS) using an ESCALab250 electron spectrometer (Thermo Scientific Corporation) with monochromatic 150 W Al

K α radiation. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on Optima 8000.

2.3 Electrochemical Measurements

All the electrochemical experiments data were collected by a CHI 750E electrochemistry workstation in a standard three-electrode system. The (Fe_xNi_{1-x})₂P nanosheets (1 cm×1 cm) were directly used as the working electrode (the loading of (Fe_xNi_{1-x})₂P nanosheets was approximately 1.0 mg). An Ag/AgCl electrode with 1 M KOH filling solution was used as the reference electrode. A graphite rod was used as the counter electrode in order to prevent the interference of platinum foil as the counter electrode. For comparison, 3 mg of 20 wt% Pt/C, 30 μ L of Nafion (5 wt%), 300 μ L of deionized water, and 300 μ L of ethanol were mixed to form a homogeneous ink. Then, 105 μ L of as-prepared ink was dropped onto the Ni foam (1 cm $\times$ 1 cm) twice as a contrast working electrode (loading: 1.0 mg cm⁻²). 1 M PBS, 1 M KOH and 0.5 M H₂SO₄ solution were used as electrolytes. The scan rate of linear scan voltammetry (LSV) were 5 mV s⁻¹. All potentials measured in this study were converted to reversible hydrogen electrode (RHE) according to the formulas:

$$E(\text{RHE}) = E\left(\frac{\text{Ag}}{\text{AgCl}}\right) + 0.197 \text{ V} + 0.059 \times \text{pH} - iR$$

All the presented curves are the steady-state ones after several cycles. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 0.01 to 10000 Hz. The double-layer capacitance (C_{dl}) was tested by CV at various scan rates (20, 40, 60, 80, 100, and 120 mV s⁻¹).

2.4 Computational methods

DFT calculations were performed by Vienna *ab initio* simulation package (VASP) [24, 25]. The ion–electron interactions were described by the projector plane wave (PAW) approach. Electron exchange–correlations were represented by the functional of Perdew, Burke and Ernzerhof (PBE) of generalized gradient approximation (GGA) [26]. The condition of optimization calculations was shown in supporting information.

From HRTEM, $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets $\{01\bar{1}\bar{1}\}$ was chosen as the model to calculate. A 2×2 supercell was built and the model thickness was 10 Å. And vacuum space was set to be 15 Å. Therefore, the model was composed of 42 P atoms and 84 Ni atoms. Then 2 Ni atoms, 3 Ni atoms, 4 Ni atoms, 6 Ni atoms were replaced by Fe atoms. We chose the same active site to compare the catalytic activity of Fe doping [27].

3. Results and discussion

As displayed in Scheme 1, a series of $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets grown on Ni foam were fabricated *via* a two-step method. Firstly, FeNi-layered double hydroxides (FeNi-LDH) with different Ni/Fe atomic ratio were grown on Ni foam by a general hydrothermal method with the reactants of NH_4F and urea in a weak acid environment ($\text{pH} = 6.5$). With the increase of doping amount of iron, the color of FeNi-LDH on the Ni foam gradually turned from green to yellow. Secondly, the as-prepared FeNi-LDH was converted to $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ by heating at 450 °C for 3 h in the presence of $\text{NaH}_2\text{PO}_2\cdot 2\text{H}_2\text{O}$ as P source with the protection of flowing Ar. The XRD patterns of FeNi-LDH nanosheets and $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets on Ni foam were shown in Fig. 1a and 1b, respectively. We scratched FeNi-LDH powders from Ni foam for

measurement, since the peaks of FeNi-LDH are blocked by the strong peaks of Ni foam (Fig. S1). As shown in Fig. 1a, four diffraction peaks of FeNi-LDH are observed, which are assigned to the (003), (006), (012), and (015) planes [28], respectively. As shown in Fig. 1b, the XRD patterns of the $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ are matched well with that of Ni_2P (JCPDS no. 65-3544) [29]. To determine the exact amount of Fe doping in $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets, the ICP-AES analysis was carried out. As shown in Table S1, the four samples exhibit the atomic ratio of Fe/Ni are 1/12, 1/20, 1/28, 1/35, corresponding to $(\text{Fe}_{0.077}\text{Ni}_{0.923})_2\text{P}$, $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$, $(\text{Fe}_{0.035}\text{Ni}_{0.965})_2\text{P}$, $(\text{Fe}_{0.028}\text{Ni}_{0.972})_2\text{P}$, respectively.

The morphology and structure of $(\text{Fe}_x\text{Ni}_{1-x})\text{-LDH}$ nanosheets and $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets were characterized by SEM and TEM. As shown in Fig. 1c and Fig. S2a-c, the $(\text{Fe}_x\text{Ni}_{1-x})\text{-LDH}$ samples display typical 2D nanosheet morphology. These nanosheets with average size of $\sim 2\ \mu\text{m}$ are anchored on Ni foam substrate vertically, and the introduction of iron does not affect the growth of the nanosheet. After phosphating at high temperature, the $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ samples completely inherit the nanosheet morphology from $(\text{Fe}_x\text{Ni}_{1-x})\text{-LDH}$ expect for the increased surface roughness (Fig. 1d-1g). Moreover, for pure Ni_2P sample, although the $\text{Ni}(\text{OH})_2$ precursor is composed of 2D nanosheets (Fig. S2d), an obvious nanoparticle aggregation is observed (Fig. 1h).

TEM and HRTEM images of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheet are shown in Fig. 2. This sample shows the best HER performance in following electrochemical test. The nanosheet structure of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ can be further verified by TEM in Fig. 2a. The

2D morphology is beneficial to HER because it has a short electron transfer pathway and abundant active sites [30, 31]. Fig. 2b shows the HRTEM image of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheet. Two sets of lattice fringes with same spacing of 0.220 nm are observed, which are corresponding to $\{11\bar{2}1\}$ and $\{\bar{1}2\bar{1}1\}$ planes of hexagonal $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$. The angel between the two sets of planes is 48.1° . We also collected the Fast Fourier Transform (FFT) pattern (inset in Fig. 2b) to determine the crystalline property of the $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheet. The FFT image can be indexed as single crystalline form with a preferential $\{01\bar{1}\bar{1}\}$ orientation. Fig. 2c shows the selected area electron diffraction (SAED) pattern of the $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheet, and the diffraction spots confirm its single-crystalline characteristic. Apparently, it indicates that the zone axis of hexagonal $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ is $[01\bar{1}\bar{3}]$. Elemental mapping by EDS was used to analyze the composition of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheets. As shown in Fig. 2d, Ni, Fe and P are homogeneously distributed over the nanosheet. The TEM and HRTEM images of other $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets were also detected. As shown in Fig. S3, all the samples have exposed $\{01\bar{1}\bar{1}\}$ facets.

XPS was used to determine the valence states of Fe, Ni, and P in the $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheets. Ni 2p, Fe 2p, and P 2p XPS spectra are displayed in Fig. 3. The corresponding XPS survey spectrum is shown in Fig. 3a. The signals of O and C are attributed to surface oxidation or surface adsorption when exposed to air [32, 33]. As shown in Fig. 3b, the high-resolution XPS spectrum of Ni 2p can be split into six peaks. The two peaks at 874.7 and 870.2 eV are attributed to Ni 2p_{1/2} [34]. The other three peaks at 862.3, 856.9, and 853.1 eV should be assigned to Ni 2p_{3/2} [29].

The additional peak at 880.4 eV corresponds to the shakeup (marked as the “Sat”) [35]. In the Fe 2p region (Fig. 3c), the two peaks at 712.8 and 707.3 eV are characteristic signals of Fe 2p_{3/2} [36-38]. The P 2p spectrum (Fig. 3d) can be split into three peaks at 134.1, 129.9, and 128.9 eV. The peak at 134.1 eV is ascribed to surface oxidation [39], while the peaks at 128.9 and 129.9 eV belong to metal phosphides [40]. The XPS spectra of other (Fe_xNi_{1-x})₂P samples are displayed in Figure S4-S7. The results are in agreement with that of the (Fe_{0.048}Ni_{0.952})₂P nanosheets.

The electrocatalytic HER activity of the (Fe_xNi_{1-x})₂P nanosheets were tested at all pH values, respectively. Fig. 4a shows the LSV curves of (Fe_xNi_{1-x})₂P nanosheets and commercial 20 wt% Pt/C on Ni foam in 1 M PBS (neutral electrolyte). All reaction currents presented were corrected against the effect of ohmic resistance. (Fe_{0.048}Ni_{0.952})₂P exhibited superior HER performance to that of (Fe_{0.077}Ni_{0.923})₂P, (Fe_{0.035}Ni_{0.965})₂P, (Fe_{0.028}Ni_{0.972})₂P, and Ni₂P. The overpotential for (Fe_{0.048}Ni_{0.952})₂P to achieve 10 mA cm⁻² is only 90 mV, lower than that of (Fe_{0.077}Ni_{0.923})₂P (127 mV), (Fe_{0.035}Ni_{0.965})₂P (106 mV), (Fe_{0.028}Ni_{0.972})₂P (211 mV), Ni₂P (293 mV), and most recent reported non-noble metal HER electrocatalysts in neutral electrolytes (Table S2). The results indicate that Fe-doping is quite beneficial for the improvement of HER performance of Ni₂P and the most appropriate Fe/Ni atomic ratio is 1/20. To further understand the influence of Fe doping on HER activities., Tafel plots are recorded with the linear regions fitted to the Tafel equation, $\eta = a + b \times \log(j)$, where η is the overpotential, j is the current density, and b is the Tafel slope (Fig. 4b). The Tafel slope is associated with HER kinetics

of catalysts [41, 42]. $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ exhibits a Tafel slope of 82.7 mV dec^{-1} , smaller than that of $(\text{Fe}_{0.077}\text{Ni}_{0.923})_2\text{P}$ ($110.1 \text{ mV dec}^{-1}$), $(\text{Fe}_{0.035}\text{Ni}_{0.965})_2\text{P}$ (95.2 mV dec^{-1}), $(\text{Fe}_{0.028}\text{Ni}_{0.972})_2\text{P}$ ($185.3 \text{ mV dec}^{-1}$), and Ni_2P ($226.7 \text{ mV dec}^{-1}$). This confirms that $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ is easier to occur HER *via* Volmer-Heyrovsky pathway.

To further study the intrinsic activity of the catalyst, the C_{dl} was measured by cyclic voltammetry (CV), which was performed in a certain potential current window without the faradic processes [43]. The larger C_{dl} value means more surface active sites exposed. As shown in Fig. S8, the C_{dl} of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ is 27.8 mF cm^{-2} , much higher than that of $(\text{Fe}_{0.077}\text{Ni}_{0.923})_2\text{P}$ (15.16 mF cm^{-2}), $(\text{Fe}_{0.035}\text{Ni}_{0.965})_2\text{P}$ (15.17 mF cm^{-2}), $(\text{Fe}_{0.028}\text{Ni}_{0.972})_2\text{P}$ (9.1 mF cm^{-2}), and pure Ni_2P (4 mF cm^{-2}). Apparently, the number of electrochemically active sites for water reduction can be efficiently increased with introduction of trace Fe. Furthermore, the electrochemical impedance spectroscopy (EIS) of the catalysts was measured and the charge-transfer resistance (R_{ct}) was obtained from the diameter of the semicircles under the high frequency region (Fig. 4c). Compared with other catalysts, $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ displays much lower R_{ct} , indicating that Fe-doping can efficiently enhance electron transfer rate and Faradic process [44]. The long-term stability is another critical parameter to evaluate the performance of a catalyst. Chronoamperometry test (i-t curves) was used for measuring the stability. As shown in Fig. 4d, the LSV of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ after 1000 sweeps shows an ignorable current loss. Moreover, the current density decrease is only ~5% at a high current density of

100 mA cm⁻² after 20 h, which is superior to most reported electrocatalysts [19, 44]. The XRD and SEM of the (Fe_{0.048}Ni_{0.952})₂P after the stability test of 20 h are shown in Fig. S11. Apparently, there are no obvious crystalline changes observed from the XRD pattern (Fig. S11a). The SEM image shows that its initial 2D nanosheet morphology is also maintained (Fig. S11b).

Significantly, the (Fe_xNi_{1-x})₂P samples also show outstanding HER performance in alkaline and acidic electrolytes. Fig. 5a shows the polarization curves of (Fe_{0.077}Ni_{0.923})₂P, (Fe_{0.048}Ni_{0.952})₂P, (Fe_{0.035}Ni_{0.965})₂P, (Fe_{0.028}Ni_{0.972})₂P, Ni₂P, and commercial 20 wt% Pt/C on Ni foam in alkaline media. It can be clearly observed that (Fe_{0.048}Ni_{0.952})₂P has the best activity with a much lower overpotential (103 mV) to reach a current density of 10 mA cm⁻² than that of (Fe_{0.077}Ni_{0.923})₂P (146 mV), (Fe_{0.035}Ni_{0.965})₂P (117 mV), (Fe_{0.028}Ni_{0.972})₂P (166 mV), and Ni₂P (190 mV). It also outperforms most of the other modified Ni₂P catalysts reported previously (Table S3). Fig. 5b shows the corresponding Tafel plots. (Fe_{0.048}Ni_{0.952})₂P shows the smaller Tafel slope (76.6 mV dec⁻¹) compared with that of (Fe_{0.077}Ni_{0.923})₂P (98.3 mV dec⁻¹), (Fe_{0.035}Ni_{0.965})₂P (88.1 mV dec⁻¹), (Fe_{0.028}Ni_{0.972})₂P (117.3 mV dec⁻¹), and Ni₂P (112.1 mV dec⁻¹), indicating the faster HER rate. The C_{dl} was also measured by CV (Fig. S9). In accordance with that measured in neutral media, (Fe_{0.048}Ni_{0.952})₂P shows the largest C_{dl} of 13.0 mF cm⁻² among all the samples. In addition, Fig. 5c shows the excellent long-term durability according the negligible loss of current, and as shown in Fig. 5d, little current decay (~3%) is observed after 20 h of chronoamperometric test in 1 M

KOH. Also, obvious crystalline and morphology change are not detected from XRD pattern and SEM image of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ before and after the durability test (Fig. S12). This superior stability at high current density in 1 M KOH is rare in previous reports [45, 46], which can be attributed to the stable combination of the well-crystallized structure of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ and 3D construction of Ni foam. This is of great significance for future applications in practice.

Compared with alkaline and neutral electrolytes, water reduction is easier to occur in acidic electrolytes as there are abundant protons in the electrolyte. The $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ samples also exhibit much better HER performance in 0.5 M H_2SO_4 . For instance, the polarization curve of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ exhibits overpotential of 81 mV at 10 mA cm^{-2} , which is superior to that in 1 M PBS (90 mV), 1 M KOH (103 mV) and other catalysts (Table S4). As shown in Fig. 6b, the Tafel slope of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ is only 41.6 mV dec^{-1} , which is smaller than that of other samples. This value is also smaller than that in 1 M PBS (82.7 mV dec^{-1}) and 1 M KOH (76.6 mV dec^{-1}). The results indicate that $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ shows the faster kinetics and the rate-determining step of HER is Heyrovsky reaction in 0.5 M H_2SO_4 . Furthermore, in acid electrolyte, C_{dl} value of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ is higher compared with those of other $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ (Fig. S10). Interestingly, after 1000 continuous CV cycles in H_2SO_4 , the LSV of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ shifts significantly along the direction to high voltage (Fig. 6c), and a relatively large current decay (~23%) is observed (Fig. 6d). This should be ascribed to the strong corrosion of Ni foam by acidic electrolyte, which has

been reported previously [18, 41, 47]. After the long-term test, the XRD and SEM of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ were collected in the same way as those in neutral and alkaline media (Fig. S13a and Fig. S13b). The weakened XRD pattern of Ni_2P after cycling may be caused by the corrosion of Ni foam, but the morphology of nanosheets is still maintained. We compared the previous works about Fe-Co-P and Mo-Ni-P system with our work. As shown in Table S5, our samples exhibit best HER performance in neutral electrolyte and comparable performance in acidic and alkaline electrolyte.

Apparently, the Fe-doped Ni_2P samples display highly enhanced HER activity at all-pH values. To reveal the influence of Fe-doping on the HER activity, we carried out the DFT calculation to illustrate the changes in reaction energy and electronic structure before and after Fe-doping. Firstly, we designed five models to represent our samples with different Ni/Fe ratios. As shown in Fig. S14, $\text{Ni}_{84}\text{P}_{42}$, $\text{Fe}_2\text{Ni}_{82}\text{P}_{42}$, $\text{Fe}_3\text{Ni}_{81}\text{P}_{42}$, $\text{Fe}_4\text{Ni}_{80}\text{P}_{42}$, and $\text{Fe}_6\text{Ni}_{78}\text{P}_{42}$ represent Ni_2P , $(\text{Fe}_{0.028}\text{Ni}_{0.972})_2\text{P}$, $(\text{Fe}_{0.035}\text{Ni}_{0.965})_2\text{P}$, $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$, and $(\text{Fe}_{0.077}\text{Ni}_{0.923})_2\text{P}$, respectively. We also calculated $\text{Fe}_8\text{Ni}_{76}\text{P}_{42}$ to better explain the role of doped Fe. Most of the previous calculations focused on metals as catalytic sites, and the theoretical values were very close to or even exceed that of Pt. However, there is still a big gap between the actual experimental performance and Pt. For TMPs catalysts, recently, P catalytic sites were believed to be the active centers for HER [48, 49]. So in this work, we calculated ΔG_{H^*} and $\Delta G_{\text{H}_2\text{O}}$ on P site to explain the HER mechanism in acidic and alkaline electrolytes.

It is well accepted that ΔG_{H^*} is a vital factor to estimate the activity of catalysts

under acidic condition [50], and the ΔG_{H^*} values on P site under acidic condition are shown in Fig. 7a. In addition, the different stages of H_3O^+ transformed to H_2 on P site of $Fe_4Ni_{80}P_{42}$ are displayed in (i)-(iii) of Fig. 7a. The ΔG_{H^*} value on P site of $Fe_4Ni_{80}P_{42}$ (0.17 eV) is much lower than those of $Fe_8Ni_{76}P_{42}$ (0.58 eV), $Fe_6Ni_{78}P_{42}$ (0.45 eV), $Fe_3Ni_{81}P_{42}$ (0.36 eV), $Fe_2Ni_{82}P_{42}$ (0.54 eV), and $Ni_{84}P_{42}$ (0.62 eV). This indicates $Fe_4Ni_{80}P_{42}$ has a lower reaction barrier than other samples [51], which is the reason why the appropriate doped Fe atoms can effectively enhance the HER performance in acidic media. In addition, calculations were also carried out on P site under alkaline condition. The (i)-(iv) in Fig. 7b represent the different stages of H_2O transformed to H_2 on P site. The reaction pathway of alkaline HER is consisted of prior water dissociation to form H^* and OH^- and hydrogen generation [52]. The ΔG_{H_2O} on P site is only 0.03 eV for $Fe_4Ni_{80}P_{42}$, much lower than those of other samples (1.18 eV for $Ni_{84}P_{42}$, 0.50 eV for $Fe_2Ni_{82}P_{42}$, 0.47 eV for $Fe_3Ni_{81}P_{42}$, 0.44 eV for $Fe_6Ni_{78}P_{42}$, and 0.63 eV for $Fe_8Ni_{76}P_{42}$). The ΔG_{H^*} values on P site for different models exhibit the similar trend with the situation of ΔG_{H_2O} on P site, and $Fe_4Ni_{80}P_{42}$ also displays the lowest ΔG_{H^*} of 0.17 eV. The calculation results indicate that the doped Fe atoms can effectively stimulates cleavage of H-OH bonds. Additionally, $Fe_6Ni_{78}P_{42}$ and $Fe_8Ni_{76}P_{42}$ show greater ΔG_{H_2O} and ΔG_{H^*} on P site than those of $Fe_4Ni_{80}P_{42}$, meaning that excessive doping of Fe atoms plays a negative effect on HER.

To further analyze the electronic structures before and after Fe-doping, charge density difference calculations of H adsorbed on the same adsorption sites (P site) of $Ni_{84}P_{42}$ (Fig. 8a) and $Fe_4Ni_{80}P_{42}$ (Fig. 8b) have been performed. Charge accumulation

(yellow color) around H atom and charge depletion (cyan color) around P atom mean that the charge transfers from P atom to H atom. However, the charge accumulation region around H atom of $\text{Ni}_{84}\text{P}_{42}$ (Fig. 8c) is smaller than that of $\text{Fe}_4\text{Ni}_{80}\text{P}_{42}$ (Fig. 8d), and the corresponding charge depletion region around P atom of $\text{Ni}_{84}\text{P}_{42}$ (Fig. 8e) is slightly smaller than that of $\text{Fe}_4\text{Ni}_{80}\text{P}_{42}$ (Fig. 8f). These results indicate more charge transfer takes place between H atom and P atom after Fe-doping, which was further confirmed by the interfacial charge transfer according to Bader charge calculations, the Bader charge change of $\text{Ni}_{84}\text{P}_{42}$ is 0.296 e smaller than the Bader charge change of $\text{Fe}_4\text{Ni}_{80}\text{P}_{42}$ (0.344 e), and thus can further reduce the ΔG_{H^*} of P site. As shown in Fig. S15, the enhanced charge accumulation around the P site caused by Fe-doping makes the active sites more active toward HER [51]. This may be the reason why the $\Delta G_{\text{H}_2\text{O}}$ can be significantly reduced after Fe-doping. Clearly, the proper Fe-doping is crucial to tune the electronic structure and boost the HER kinetics of $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$.

4. Conclusions

In summary, $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets were successfully fabricated by phosphorization of FeNi-LDH. Compared with pure Ni_2P , these Fe-doped 2D nanosheets exhibit significantly enhanced HER performance at all-pH values. In particular, $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ exhibits the most active HER performance and best stability in neutral and alkaline electrolytes. DFT calculations reveal that the doped Fe atoms can trigger more charge accumulation around P active site and enhance electron transfer between P atom and H atom. This can make the P sites more active and reduce the kinetic energy barrier. A more thermoneutral ΔG_{H^*} and a

significantly reduced $\Delta G_{\text{H}_2\text{O}}$ after Fe-doping may be associated with the change of electronic structure. Besides, to fully understand the HER performance at different pH values, we calculated the ΔG_{H^*} and $\Delta G_{\text{H}_2\text{O}}$ to meet the acid and alkaline electrolytes, respectively. This work provided a reliable way to improve HER performance by doping another metal into a single crystal structure.

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Supporting Information

Supporting Information contains this information is available free of charge *via* the Internet at <http://XXX>

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Figures

Scheme 1. The synthesis process of $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets on Ni foam.

Fig. 1. (a) The XRD patterns of the scratched $\text{Fe}_x\text{Ni}_{1-x}$ -LDH powders from Ni foam. (b) The XRD patterns of the $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ nanosheets on Ni foam. (c) The SEM image of the $\text{Fe}_{0.048}\text{Ni}_{0.952}$ -LDH nanosheets on Ni foam. (d) The SEM image of the $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheets on Ni foam. (e-h) The SEM images of the $(\text{Fe}_{0.077}\text{Ni}_{0.923})_2\text{P}$, $(\text{Fe}_{0.035}\text{Ni}_{0.965})_2\text{P}$, $(\text{Fe}_{0.028}\text{Ni}_{0.972})_2\text{P}$, and Ni_2P nanosheets on Ni foam.

Fig. 2. (a) TEM image of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheets. (b) HRTEM image and the corresponding FFT pattern (inset b) of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheets. (c) SAED pattern of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheets. (d) EDS elemental mapping images (Ni, Fe, P) of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheets.

Fig. 3. XPS patterns of the $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheets on Ni foam. (a) XPS survey spectrum. High-resolution spectra of (b) Ni 2p, (c) Fe 2p, and (d) P 2p.

Fig. 4. (a) Polarization curves for $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ and Pt/C on Ni foam in 1 M PBS with a scan rate of 5 mV s^{-1} . (b) Tafel plots for $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ and Pt/C on Ni foam. (c) Nyquist plots of $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ on Ni foam. (d) Polarization curves recorded for the $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ before and after 1000 cycles of CV scans. (Inset: Time-dependent current density curve under static current density of 100 mA cm^{-2} for 20 h).

Fig. 5. (a) Polarization curves for $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ and Pt/C on Ni foam in 1 M KOH with a scan rate of 5 mV s^{-1} . (b) Tafel plots for $(\text{Fe}_x\text{Ni}_{1-x})_2\text{P}$ and Pt/C on Ni foam. (c) Polarization curves recorded for the $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ before and after 1000 cycles of CV scans. (d) Time-dependent current density curve of $(\text{Fe}_{0.048}\text{Ni}_{0.952})_2\text{P}$ nanosheets on Ni foam under static current density of 100 mA cm^{-2} for 20 hours (without iR correction).

Fig. 6. (a) Polarization curves for (Fe_xNi_{1-x})₂P and Pt/C on Ni foam in 0.5 M H₂SO₄ with a scan rate of 5 mV s⁻¹. (b) Tafel plots for (Fe_xNi_{1-x})₂P and Pt/C on Ni foam. (c) Polarization curves recorded for the (Fe_{0.048}Ni_{0.952})₂P before and after 1000 cycles of CV scans. (d) Time-dependent current density curve of (Fe_{0.048}Ni_{0.952})₂P nanosheets on Ni foam under static current density of 50 mA cm⁻² for 10 h (without iR correction).

Fig. 7. (a) Calculated hydrogen adsorption free energy on P site of acidic-HER on exposed $\{01\bar{1}\bar{1}\}$ facet of $\text{Fe}_8\text{Ni}_{76}\text{P}_{42}$, $\text{Fe}_6\text{Ni}_{78}\text{P}_{42}$, $\text{Fe}_4\text{Ni}_{80}\text{P}_{42}$, $\text{Fe}_3\text{Ni}_{81}\text{P}_{42}$, $\text{Fe}_2\text{Ni}_{82}\text{P}_{42}$, and $\text{Ni}_{84}\text{P}_{42}$, respectively. (i), (ii), and (iii) represent different stages of H_3O^+ generated to H_2 on $\text{Fe}_4\text{Ni}_{80}\text{P}_{42}$ under acidic condition. (b) Calculated water dissociation energy and hydrogen adsorption free energy on P site of alkaline-HER on exposed $\{01\bar{1}\bar{1}\}$ facet of $\text{Fe}_8\text{Ni}_{76}\text{P}_{42}$, $\text{Fe}_6\text{Ni}_{78}\text{P}_{42}$, $\text{Fe}_4\text{Ni}_{80}\text{P}_{42}$, $\text{Fe}_3\text{Ni}_{81}\text{P}_{42}$, $\text{Fe}_2\text{Ni}_{82}\text{P}_{42}$, and $\text{Ni}_{84}\text{P}_{42}$, respectively. (i), (ii), (iii), and (iv) represent different stages of H_2O generated to H_2 on $\text{Fe}_4\text{Ni}_{80}\text{P}_{42}$ under alkaline condition. The Ni, P, H, and O atoms are represented by blue, pink, white, and red spheres, respectively.

Fig. 8. (a, b) The images of charge density difference at $\text{Ni}_{84}\text{P}_{42}$ and $\text{Fe}_4\text{Ni}_{80}\text{P}_{42}$, respectively. The yellow color represents the charge accumulation and the cyan color represents the charge depletion in the space. (c, d) The enlarged image along the c axis of the adsorption sites in (a) and (b). (e, f) The enlarged image of the adsorption sites in (a) and (b). The Ni, P, Fe, H, and O atoms are represented by blue, pink, brown, white, and red spheres, respectively.

Highlights

- $(\text{Ni}_{0.048}\text{Fe}_{0.952})_2\text{P}$ with exposed $\{01\bar{1}\bar{1}\}$ facets for electrocatalytic HER at all pH values
- $(\text{Ni}_{0.048}\text{Fe}_{0.952})_2\text{P}$ shows the excellent stability in neutral and alkaline media
- DFT calculations for $(\text{Ni}_x\text{Fe}_{1-x})_2\text{P}$ in acidic and alkaline media, respectively
- The doped iron atoms can change the electronic structure around the P active sites