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1 Interfacing Epitaxial Dinickel Phosphide to Nickel

2 Thiophosphate for Boosting Electrocatalytic Water Splitting

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ABSTRACT Heterostructures with abundant phase boundaries are compelling for surface-mediated electrochemical applications. However, rational design of such bifunctional electrocatalysts for efficient hydrogen and oxygen evolution reactions (HER and OER) is still challenging. Here, due to the well-matched lattice parameters, we easily achieved the epitaxy of two-dimensional ternary nickel thiophosphate (NiPS₃) nanosheets with in-grown dinickel phosphide (Ni₂P) through an *in situ* growth strategy. Density functional theory calculations reveal that the NiPS₃/Ni₂P heterojunction significantly decreases the kinetic barrier for hydrogen adsorption and accelerates electron transfer due to the built-in electric field at the epitaxial interfaces. The significantly improved electrocatalytic performance is shown to be closely related to the epitaxial interfacial area rather than the amount of secondary phase. Notably, the resultant NiPS₃/Ni₂P heterostructures enable an overall water splitting electrolyser to achieve 50 mA cm⁻² at a lower bias of 1.65 V than the pristine NiPS₃ alone (2.02 V) and even the benchmark Pt/C//IrO₂ electrocatalysts (1.69 V).

KEYWORDS: epitaxial interfaces, nickel thiophosphate, hydrogen evolution, water splitting, heterostructures

1 Electrocatalytic overall water splitting is widely deemed as an appealing technology to
2 address increasing energy demand by employing renewable electricity to convert water
3 into value-added hydrogen and oxygen products.¹⁻⁶ However, the high energy barriers of
4 hydrogen and oxygen evolution reactions (HER and OER) require the use of efficient
5 bifunctional electrocatalysts to reduce energy consumption.^{5, 7-14} Despite the commercial
6 availability of noble metal based electrocatalysts for HER (Pt) or OER (Ir/RuO_x),
7 developing low-cost alternatives with earth-abundant elements is imperative for future
8 scale-up industrial viability.^{12, 13, 15-20}

9 Interfacial engineering of the electrocatalysts has been emerging as one of the most
10 effective methods to improve intrinsic activity since electrocatalytic reaction takes place
11 at the electrochemical interfaces of solid electrodes, aqueous electrolyte, and gaseous
12 products.²¹⁻²³ Particularly, one promising strategy is to judiciously grow epitaxial
13 interfaces with two different components and thereby optimize surface electronic
14 environment and energetics of intermediates and adsorbents, leading to the rapid mass
15 diffusion and electron transfer during the electrocatalysis.²⁴⁻²⁷ This points to the
16 importance of constructing epitaxial interfaces on conventional electrocatalysts for
17 improving intrinsic activity in addition to search new ones. Taking the two-dimensional
18 (2D) ternary nickel thiophosphate (NiPS₃) nanosheet as a representative example, it has
19 been demonstrated to be an appreciable precursor for electrocatalytic water oxidation due
20 to the high OER activity in alkaline medium, good stability, and cost-effective
21 composition.²⁸⁻³¹ Nevertheless, both theoretical and experimental studies have indicated
22 that pristine NiPS₃ is not an ideal candidate for electrocatalytic HER because of
23 extremely high kinetic energy barriers (ΔG_{H^*}) for hydrogen binding.^{30, 32, 33} Bearing this

1 in mind, tuning the local atomic coordination on (110) facets by epitaxial growth could be
2 able to optimize its ΔG_{H^*} and enhance HER performance since hydrogen atoms are
3 preferentially stabilized on sulfur and **phosphorus atoms** at the edge sites of NiPS₃.^{30, 34}
4 Toward this end, we took the view that an epitaxial growth of dinickel phosphide (Ni₂P)
5 on the specific (001) facets of NiPS₃ could be practicable because of their well-matched
6 lattice parameters (see discussion below). Our density functional theory (DFT)
7 calculations on the influence of (001) epitaxial interfacing between NiPS₃ and Ni₂P on
8 the energetics of hydrogen absorption on NiPS₃ (110) indicates significantly lowered
9 energy barriers for hydrogen binding and enhanced electron transfer kinetics due to an in-
10 situ formed built-in electric field at the atomic interface.

11 Encouraged by this, we here report the design of NiPS₃/Ni₂P heterostructures with
12 abundant epitaxial interfaces to improve the intrinsic activities of NiPS₃ for both
13 electrocatalytic HER and OER. Experimentally, we achieved *in situ* epitaxial growth of
14 Ni₂P nanodomains on 2D NiPS₃ nanosheets exposed with (001) facets by an easy thermal
15 treatment under H₂/Ar atmosphere. This process, mediated by preferential hydrogen
16 adsorption on sulfur atoms,³⁰ enables the tunable desulfuration and interface growth at
17 nanoscale. To our delight, benefiting from decreased energy barriers and strong electronic
18 interactions at epitaxial interfaces, the resultant NiPS₃/Ni₂P heterostructures exhibit a
19 significant improvement in electrocatalytic activities for both HER and OER compared to
20 NiPS₃ nanosheets alone. A prototypical water electrolyzer based on NiPS₃/Ni₂P
21 heterostructures requires a lower voltage (1.65 V) than that assembled with Pt/C//IrO₂
22 (1.69 V), and NiPS₃ (2.02 V) to reach a durable current density of 50 mA cm⁻².

RESULTS AND DISCUSSION

As well known, a good lattice matching and elemental similarity are prerequisites for growing epitaxial structure. The monoclinic NiPS_3 crystallizes in ABC-stacking layers composed of $\text{P}_2\text{S}_6^{4-}$ bipyramids and Ni^{2+} ions with a honeycomb arrangement (**Figure 1a**).³⁵ The nickel phosphides has a close elemental composition to NiPS_3 . After a finely screening of nickel phosphides with compositions from metal-rich Ni_4P to phosphorus-rich NiP_{15} , we found that NiPS_3 and Ni_2P have an excellent lattice matching in terms of their crystal structures. The as-extracted rhombic unit from (001) facets of NiPS_3 shows lattice constants of $a = b = 5.85 \text{ \AA}$ (**Figure 1a**). These values are very close to the parameters of the rhombic unit derived from the (001) facets of hexagonal Ni_2P ($a = b = 5.81 \text{ \AA}$), demonstrating the feasibility that Ni_2P could be epitaxially grown on NiPS_3 along [001] direction with a small interfacial strain (-0.69%). With this in mind, we constructed the $\text{NiPS}_3/\text{Ni}_2\text{P}$ heterojunction for further structural optimization (**Figure 1a**). Interestingly, one of the dangling sulfur at the edge sites of NiPS_3 (110) is saturated with three nickel atoms from Ni_2P (110), resulting in the nickel hollow sites at the edge of the $\text{NiPS}_3/\text{Ni}_2\text{P}$ heterojunction. Such epitaxial in-growth heterojunction is very favorable for reinforcing electronic interaction between NiPS_3 and Ni_2P . Besides, the variation of atomic coordination on the NiPS_3 (110) would affect the hydrogen binding energy barrier. To verify above assumption, we performed DFT calculations to shed light on how the interfacing NiPS_3 with epitaxial Ni_2P affects the hydrogen adsorption behavior of NiPS_3 by calculating the ΔG_{H^*} . As known, a lower absolute values of ΔG_{H^*} ($|\Delta G_{\text{H}^*}|$) indicates a preferable hydrogen adsorption strength higher for HER. Our previous work indicated

1 that NiPS₃ showed poor HER activity due to the high $|\Delta G_{H^*}|$ (0.399 eV) at the (110)
2 edge.³¹ Furthermore, others verified that the Ni hollow sites on Ni₂P showed too negative
3 $|\Delta G_{H^*}|$ with strong hydrogen adsorption, while Ni₂P was demonstrated to show good HER
4 performance due to a weak ‘ligand effect’ produced by the Ni-P bond.³⁶ In the case of
5 NiPS₃/Ni₂P heterojunction here, new Ni hollow sites were produced by the relatively
6 strong Ni-S bond at the (110) edge of the NiPS₃/Ni₂P interface after a structural
7 relaxation. Since Ni-S bonds provide stronger ‘ligand effect’ than the Ni-P bond in Ni₂P,
8 these Ni hollow sites bonded with S are expected to have better HER performance than
9 Ni₂P. Benefiting from this, such NiPS₃/Ni₂P heterojunction indeed shows a much smaller
10 $|\Delta G_{H^*}|$ ($\Delta G_{H^*} = -0.122$ and 0.030 eV for the first and second H atoms, respectively) than
11 that of the pristine Ni₂P (110) ($\Delta G_{H^*} = 0.376$ eV) and NiPS₃ edge ($\Delta G_{H^*} = 0.399$ eV).
12 This energy barrier is also far lower than that for H^{*} absorption on (001) facets of Ni₂P
13 with a value of -0.158 eV (**Figure 1b**). Such a greatly decreased energy barrier for HER
14 at the NiPS₃/Ni₂P heterojunction **indicates** the strong electronic interaction between
15 NiPS₃ and Ni₂P at the interface. To further illustrate this, the charge density difference
16 was calculated to disclose the charge redistribution near the epitaxial in-growth interface
17 of NiPS₃/Ni₂P. As shown in **Figure 1c**, an obvious different charge density can be clearly
18 observed between NiPS₃ and Ni₂P at the interface because of the electron transfer from
19 metallic Ni₂P to NiPS₃, leading to the formation of a built-in electric field for further
20 facilitating the electron transfer near the interface. The electron loss of the nickel at the
21 interface also significantly weakens H^{*} affinity and improves HER activity, in agreement
22 with the relative strong ‘ligand effect’ of the Ni-S bond at the interface. **This result is also**
23 **further verified by the analysis of the density of state (DOS) plots for the near surface**

1 atoms of Ni, P and S that stem from the NiPS₃ and Ni₂P interactions (see **Figure S1**).
2 Collectively, these DFT results confirm our above hypothesis that the epitaxial in-growth
3 interface of NiPS₃/Ni₂P indeed shows the lowest absolute value of ΔG_{H^*} (nearly zero) for
4 hydrogen evolution.

5 Guided by above DFT results, we sought to construct such 2D NiPS₃/Ni₂P
6 heterostructures with abundant epitaxial interfaces. After an *in situ* desulfuration under
7 H₂/Ar atmosphere, Ni₂P nanodomains could be epitaxially grown within 2D NiPS₃
8 nanosheets. Typically, the 2D NiPS₃ nanosheets exposed with (001) facet were firstly
9 prepared by a modified scalable solid-state method based on our previous reports.^{34, 37}

10 The pristine NiPS₃ nanosheets show smooth surface and single-crystalline structure with
11 an average lateral size and thickness of about 500 and 30 nm, respectively (see **Figures**
12 **S2-S3**). Subsequently, by an optimization of desulfurization temperature and duration
13 under H₂/Ar atmosphere, we obtained the 2D NiPS₃/Ni₂P heterostructures, as indicated
14 by color change from carmine to black (insets in **Figure 2a**). Unless otherwise specified,
15 the resultant NiPS₃/Ni₂P heterostructures obtained at 450 °C for 3 h were mainly
16 discussed due to their best electrocatalytic performance (see **Figure S4**). The as-
17 developed epitaxial in-growth strategy is clean, simple, and practicable for scalable
18 preparation without complicated post-treatments.

19 We first verified the formation of the best-performing NiPS₃/Ni₂P heterostructures by
20 employing powder X-ray diffraction (XRD). As depicted in **Figure 2a**, those typical
21 diffraction peaks of both NiPS₃ and Ni₂P can be clearly observed in the XRD pattern. A
22 much higher diffraction intensity of (00l) planes, similar to that of origin NiPS₃
23 nanosheets suggests a retained preferred orientation along <001> direction in the

1 NiPS₃/Ni₂P heterostructures. This also indicates that Ni₂P probably forms on NiPS₃ (001)
2 through an epitaxial growth because of the smallest strain and formation energy. Rietveld
3 refinement verifies the coexistence of NiPS₃ and Ni₂P without other detectable impurity,
4 as reflected by the small reliability factors (**Figure 2a**). A quantitative phase analysis
5 using the Rietveld method reveals that the weight ratio of NiPS₃ and Ni₂P is about 0.79:
6 0.21, in agreement with the measurement by X-ray photoelectron spectroscopy (XPS).
7 Quantitative analysis from the survey XPS spectra reveals the decreased molar ratio of
8 sulfur to nickel from ~2.98 in NiPS₃ to ~1.85 in the NiPS₃/Ni₂P heterostructure (see
9 **Figure S5**). A normalization with the relative molecular weights shows that the weight
10 ratio of NiPS₃ and Ni₂P is close to 4: 1. Analysis of the high-resolution XPS spectrum of
11 Ni 2p signal for NiPS₃ and NiPS₃/Ni₂P heterostructure indicates that nickel is mainly at
12 +2 valence state (**Figure 2a**). The higher binding energy (~1.0 eV) of Ni 2p in the
13 NiPS₃/Ni₂P heterostructure is indicative of the electron accumulation in epitaxial
14 interfaces (**Figure 2b**). Besides, the intensity of the Ni 2p binding energy of an identical
15 peak in the NiPS₃/Ni₂P heterostructure is much lower than that in NiPS₃, suggesting a
16 higher electron density of the Ni at the interface. This result is also in agreement with the
17 above bader charge and DOS analysis by DFT calculations (**Figure 1d and Figure S1**).
18 Further, the appearance of two bands at 852.7 and 870.6 eV in the Ni 2p spectrum of the
19 NiPS₃/Ni₂P heterostructure aligns well with the spin-orbit doublets of Ni 2p_{3/2} and Ni
20 2p_{1/2} of Ni₂P, respectively. The lower binding energy (~0.5 eV) of Ni 2p of NiPS₃/Ni₂P
21 heterostructure than that in normal Ni₂P suggests the down-shifting of electron center
22 after an epitaxial growth on NiPS₃. Besides, the narrow-scan S 2p spectrum compared in
23 **Figure 2c** could be assigned to two peaks at 161.8 (S 2p_{3/2}) and 163.0 eV (S 2p_{1/2}),

1 which are the characteristic of S^{2-} species. The relatively lower intensity of S 2p in
2 $NiPS_3/Ni_2P$ heterostructure than that in pristine $NiPS_3$ also suggests the decreased sulfur
3 content in the $NiPS_3/Ni_2P$ heterostructures.

4 Further examinations of morphology and microstructures were imaged by scanning and
5 transmission electron microscopy (SEM and TEM). As shown in **Figure 3a**, the
6 $NiPS_3/Ni_2P$ heterostructures inherit the 2D flake structure with a thickness about 28 nm
7 from the pristine $NiPS_3$. However, the high-magnification SEM image shows that, unlike
8 the $NiPS_3$ nanosheets with smooth surface (see **Figure S3**), the $NiPS_3/Ni_2P$ nanosheets
9 show rough surface with many randomly distributed concave nanodomains (inset in
10 **Figure 3a**). In addition, the magnified TEM image further reveals the discontinuous
11 interior structure of the $NiPS_3/Ni_2P$ nanosheets with concave-convex nanostructures
12 (**Figure 3b**), as circled by the dash line (**Figure 3c**). This is obviously different from the
13 single crystalline structure of the pristine $NiPS_3$ nanosheet (see **Figure S3**), indicating
14 that the nucleation and growth of Ni_2P nanodomains from partial desulfurization of $NiPS_3$
15 nanosheets result in the formation of discrete nanostructures with abundant epitaxial
16 interfaces. Furthermore, the high-resolution TEM (HRTEM) image clearly reveals the
17 internal structural discontinuity with numerous randomly-distributed $NiPS_3/Ni_2P$
18 interfaces at nanoscale, as denoted by yellow dash line (**Figures 3c-3d** and **Figure S6**).
19 Typically, the labeled distances of 0.25, 0.30, and 0.34 nm are ascribed to the lattice
20 spacing of (200), (110), and (001) facets of hexagonal Ni_2P , respectively. Other lattice
21 fringes of 0.29, 0.33, and 0.51 nm are assigned to the (-210) , (130) , and (020) facets of
22 monoclinic $NiPS_3$, respectively. All these facets are perpendicular to the [001] direction,
23 suggesting the dominantly exposed with (001) facets. Further, the filtered HRTEM

images by color clearly indicates the nanoscale interface of NiPS₃ and Ni₂P (**Figure 3e**). The HRTEM observations also verify the epitaxial interfacing of Ni₂P with NiPS₃ along (001) facets due to the smallest interfacial strain. The indexed selected area electron diffraction pattern firmly reveals the coexistence of Ni₂P and NiPS₃ in the 2D NiPS₃/Ni₂P heterostructures (see **Figure S7**). The dark-field scanning transmission electron microscope (STEM) image also shows the structural complexity of the 2D NiPS₃/Ni₂P nanosheet with many irregularly distributed discrete nanodomains (**Figure 3f**). The energy-dispersive X-ray spectroscopy (EDS) mapping obtained under STEM mode reveals the uniform distribution of Ni, P, and S throughout the whole NiPS₃/Ni₂P nanosheet (**Figures 3g-3i**), indicating a tight attachment of two components at nanosized region due to the confinement of epitaxial interfaces. Taken together, these characterizations verify the epitaxial interfaces of NiPS₃/Ni₂P heterostructure at nanoscale. Such epitaxial interfaces are favorable for improving structural stability of the heterostructures and inducing strong electronic interaction during electrocatalytic process.

The electrocatalytic activities of the NiPS₃/Ni₂P heterostructures are investigated for both HER and OER in an alkaline medium (1.0 MKOH) since alkaline electrocatalysis is more attractive for practical applications. The polytetrafluoroethylene container was used for electrochemical measurement to avoid the Fe-contamination (see experimental details).^{38,}

³⁹ To better reveal the intrinsic activities of various electrocatalysts, we first optimized the loading mass of electrocatalysts coated on the glass carbon electrode because it is related to the electrocatalytic performance.⁴⁰ As shown in **Figure 4a**, the overpotential for HER of various electrocatalysts gradually decreased with the increase of loading mass. However, the HER performance was nearly unchanged when the loading mass was more

1 than 0.56 mg cm^{-2} . As such, this loading mass on glass carbon electrode is used for
2 evaluating the HER and OER performances of various electrocatalysts. The
3 electrocatalytic current density was normalized by both geometric and electrochemical
4 surface areas. The electrocatalytic results obtained by a normalization of geometric area
5 are firstly discussed. As shown in **Figure 4b**, the linear sweep voltammogram (LSV)
6 profiles for HER reveal a much lower onset potential of the $\text{NiPS}_3/\text{Ni}_2\text{P}$ heterocatalyst
7 ($\sim 20 \text{ mV}$) than that of NiPS_3 ($\sim 230 \text{ mV}$) and Ni_2P ($\sim 96 \text{ mV}$). To reach a cathodic current
8 density of -10 mA cm^{-2} , a much lower overpotential is required for the $\text{NiPS}_3/\text{Ni}_2\text{P}$
9 heterocatalyst (85 mV) than NiPS_3 (350 mV) and Ni_2P (218 mV). A linear fitting by
10 Tafel equation of the LSV curves in **Figure 4c** shows a much smaller slope of the
11 $\text{NiPS}_3/\text{Ni}_2\text{P}$ heterocatalyst (82 mV Dec^{-1}) compared to that of pristine NiPS_3 (128 mV
12 Dec^{-1}) and Ni_2P (116 mV Dec^{-1}). Generally, the turnover frequency (TOF) that refers to
13 the amount of transferred electron for every active site per second should be determined
14 for better comparing the intrinsic HER activity of various electrocatalysts.³⁵ However, it is
15 hard to exactly determine the number of active sites in our complex heterostructures, and
16 therefore the TOF is not provided here.

17 Notably, it is found that the trend of experimental HER activities of different $\text{NiPS}_3/\text{Ni}_2\text{P}$
18 heterostructures agree with the roughly **estimated** area of epitaxial interfaces (see
19 calculation details in supporting information). As shown in **Figure 4d**, as the amount of
20 Ni_2P increases gradually, the interfacial area of $\text{NiPS}_3/\text{Ni}_2\text{P}$ increases first and reach its
21 maximum at $\sim 21\%$, after which it starts to decrease. Accordingly, the HER activity, as
22 indicated by the overpotential, decreases first and also reach its minimum at $\sim 21\%$, after
23 which it starts to increase. This indicates that the epitaxial interfacial area is important for

the improved HER performance rather than the Ni₂P amount in the samples. Although the HER performance is not as good as that of the commercial Pt/C electrocatalyst (52 mV and 56 mV Dec⁻¹), the noble metal-free NiPS₃/Ni₂P heterostructures are more attractive with a durable HER activity. A higher current retention over 86% was obtained in the NiPS₃/Ni₂P than Pt/C electrocatalyst (78%) after holding at their starting potential to reach 10 mA cm⁻² for 12 h (see Figures S8-S9). Indicatively, two phases of NiPS₃ and Ni₂P with the ~4:1 ratio could be retained, as reflected by the XRD refinement (see Figures S10). Further, the SEM and TEM observations reveal that the NiPS₃/Ni₂P heterostructures still showed nanoplate morphology with rough surface and numerous discrete scratches (Figures 5a-5b). The HRTEM images also verify the similar structural discontinuity with epitaxial interfaces (Figure 5c). Besides, STEM image and the corresponding EDS mapping reveal the retained uniform distribution of S, P, and Ni elements in the 2D NiPS₃/Ni₂P heterostructure after HER process (Figures 5d-5g). These results demonstrate that the NiPS₃/Ni₂P heterostructures show good structural stability with retained epitaxial interfaces and chemical compositions during long-term HER process.

Furthermore, the 2D NiPS₃/Ni₂P heterostructures also exhibited high OER activity after *in-situ* activation in 1.0 MKOH during OER process. As shown in Figure 6a, the LSV curves of the NiPS₃/Ni₂P, Ni₂P, and NiPS₃-derived electrocatalysts show a broad anodic peak centered at ~1.41 V. This peak is attributed to the redox Ni²⁺/Ni³⁺ reaction,⁴¹ indicating that the surface of these electrocatalysts were oxidized to nickel oxides and/or hydroxides after *in-situ* activation, as verified by the XPS measurement of NiPS₃/Ni₂P after OER (see Figure S11). As a matter of fact, similar transformation of nickel carbides,

1 sulfides and phosphides or thiophosphates to nickel hydroxides and/or oxyhydroxides
2 during the OER process has been widely studied in many previous reports.⁴²⁻⁴⁴ It needs to
3 be mentioned that the voltage for reaching an **anodic** current density of 20 mA cm⁻² was
4 explored to compare the OER activity to exclude the current density contribution from
5 the redox peak. The NiPS₃ and Ni₂P-derived electrocatalysts and IrO₂ requires 1.60, 1.70,
6 and 1.57 V (overpotential: 370, 470, and 340 mV) to deliver 20 mA cm⁻² (**Figure 6a**),
7 respectively. The NiPS₃/Ni₂P-derived electrocatalyst needs a much lower potential of
8 1.49 V to deliver the same current density (overpotential: 260 mV). Besides, the
9 NiPS₃/Ni₂P-derived electrocatalyst also shows faster OER kinetics with a smaller Tafel
10 slope of 78 mV Dec⁻¹ (**Figure 6b**) than the pristine NiPS₃ (108 mV Dec⁻¹) and Ni₂P-
11 derived electrocatalysts (342 mV Dec⁻¹). **We understand that the *in-situ* formed**
12 **oxide/oxyhydroxide layers, as a result of the surface reconstruction, would be the real**
13 **active species for OER,⁴⁵ the NiPS₃/Ni₂P heterostructures are better precursors as OER**
14 **electrocatalyst than NiPS₃ and Ni₂P counterparts. This assumption is also reflected by the**
15 **decreased OER activity of the NiPS₃/Ni₂P heterostructures when the CV scan was**
16 **conducted in the region of 0.80~1.35 V vs. RHE (see **Figure S12**). It may be attributed to**
17 **the better synergistic electronic interactions and structural benefits from the precursor of**
18 **NiPS₃/Ni₂P heterostructure. More mechanistic studies with *in-situ* characterization**
19 **techniques would be carried out in the future to reveal the real active species that make**
20 **these the NiPS₃/Ni₂P-derived OER catalysts show high activity. Although the benchmark**
21 **IrO₂ show a smaller Tafel slope (58 mV Dec⁻¹), the NiPS₃/Ni₂P-derived electrocatalysts**
22 **show a much more stable OER activity with a current retention over 76% after 12 h at 20**
23 **mA cm⁻² (see **Figure S13**). We understand that the surface of the NiPS₃/Ni₂P**

1 heterostructures could be reconstructed during OER process, but the epitaxial interfaces
2 could be retained after 12 h testing due to the protection of thin layer of
3 oxide/oxyhydroxides (see **Figure S11 and S14-S15**). It is noted that both the HER and
4 OER activities of the NiPS₃/Ni₂P heterocatalyst are highly competent with other recently
5 reported Ni based electrocatalysts operated in same conditions (see **Tables S1 and S2**).⁴⁶

6 Recent reports have indicated that the enhanced electrocatalytic activity could be ascribed
7 to the enlarged electrochemical surface area (ECSA).^{40, 47-49} To exclude this, we further
8 estimated the ECSA of NiPS₃/Ni₂P, NiPS₃, and Ni₂P electrocatalysts by the following
9 equation:

10
$$ECSA = C_{dl} / C_s$$

11 where C_{dl} refers to the double layer capacitance determined by CV profiles at different
12 scan rates (see **Figure S16**), and C_s is the assumed specific capacitance ($\sim 60 \mu F cm^{-2}$).⁵⁰⁻

13 ⁵² As shown in **Figure 6c**, linear fitting of the cyclic voltamogram curves at different scan
14 rates reveals a close C_{dl} value of the NiPS₃/Ni₂P ($10.9 mF cm^{-2}$), NiPS₃ ($9.3 mF cm^{-2}$),
15 and Ni₂P electrocatalysts ($6.5 mF cm^{-2}$). After normalization by the ECSA, the current
16 densities of LSV profiles for both HER and OER the NiPS₃/Ni₂P heterostructures are still
17 much higher than that of NiPS₃ and Ni₂P electrocatalysts. For example, the NiPS₃/Ni₂P
18 heterostructures realized an ESCA current density of $0.1 mA cm^{-2}$ for HER with the
19 overpotential of 102 mV (**Figure 6d**). In contrast, the NiPS₃ and Ni₂P electrocatalysts
20 need much higher overpotentials of 368 and 265 mV to deliver the same current density,
21 respectively. In the case of OER, the overpotentials at a current density of $0.15 mA cm^{-2}$
22 for the NiPS₃/Ni₂P, NiPS₃ and Ni₂P-derived electrocatalysts were 275, 373, and 471 mV
23 (**Figure 6e**), respectively, indicating that NiPS₃/Ni₂P heterostructure are better OER

precursor electrocatalyst. As for the benchmark catalysts (*e.g.* Pt/C), the estimated ESCA is an order of magnitude higher than our NiPS₃/Ni₂P heterocatalysts due to the underestimated ESCA contribution from carbon support. Thus, we did not compare the normalized current density with the benchmark ones. Based on above results, we conclude that such greatly improved electrocatalytic activities should originate from the epitaxial interfaces not the larger ESCA of the 2D NiPS₃/Ni₂P heterostructures. On one hand, the in-growth epitaxial interfaces enable the NiPS₃/Ni₂P heterostructures to stabilize hydrogen absorption with a much lower energy barrier, as indicated by above DFT calculations. This together with hydrogenase-like Ni₂P nanodomains significantly enhances the intrinsic HER activity.^{22, 53, 54} On the other hand, as indicated by the bader charge and DOS analysis (**Figure S1**), the accelerated charge transfer at the epitaxial interfaces enabled by the built-in electric field improves the electrocatalytic dynamic for both HER and OER.⁵⁵ This is further verified in term of electrochemical impedance spectroscopy (EIS) measurement that reveals a much smaller radius of Nyquist plot for the NiPS₃/Ni₂P electrocatalyst when applying a same bias (see **Figure S17**), assuring the smaller charge transfer resistance. Besides, the metallic Ni₂P nanodomains are helpful for improving electrocatalytic performance by increasing electrical conductivity.

Encouraged by the exceptional electrocatalytic activities for both HER and OER of the NiPS₃/Ni₂P heterostructures, a symmetric electrolyzer was constructed using the heterocatalyst as both anode and cathode for overall water splitting. As shown in **Figure 6f**, the electrolyzer based on NiPS₃/Ni₂P heterocatalyst demonstrates much better thermodynamic and kinetic merits as compared to that based on pristine NiPS₃ electrocatalysts. To reach a current density of 50 mA cm⁻², the water splitting electrolyzer

1 with NiPS₃/Ni₂P heterostructure requires applied voltages of 1.57 V *versus* higher
2 potentials of 2.02 and 2.05 V for the cell based on NiPS₃ and Ni₂P electrocatalysts,
3 respectively. The overall water splitting performance of the NiPS₃/Ni₂P-catalyzed cell is
4 also superior to that of the electrolyzers assembled by coupling Pt/C and IrO₂
5 electrocatalysts (50 mA cm⁻² at 1.69 V), and is also among that of the best cells based on
6 other recently reported electrocatalysts (see **Table S3**). Besides, such 2D NiPS₃/Ni₂P
7 heterstructures-assembled electrolyzer can retain 10 mA cm⁻² over 10 h of continuous
8 operation with a current retention over 86% (see **Figure S18**), which is much better than
9 that of the cell with Pt/C and IrO₂ (see **Figure S19**). **Although the electrochemical**
10 **performance of NiPS₃/Ni₂P electrocatalysts need to be further improved, such impressive**
11 **water splitting performance enables the as-designed NiPS₃/Ni₂P heterostructures to be**
12 **promising electrocatalysts for renewable energy technologies.**

13 CONCLUSIONS

14 In summary, we have demonstrated that *in-situ* interfacing with epitaxial Ni₂P is an
15 effective strategy to drastically improve the electrocatalytic activity of NiPS₃ for overall
16 water splitting. The well-matched lattice parameters between NiPS₃ and Ni₂P are shown
17 to be the basis for constructing such epitaxial heterojunction. Experimentally, the 2D
18 NiPS₃/Ni₂P heterostructures were facilely obtained by a controllable desulfuration
19 strategy by thermal etching NiPS₃ nanosheets under H₂/Ar atmosphere. **Theoretically,**
20 **DFT calculations verified the lower energy barriers and favorable built-in electric field at**
21 **epitaxial interfaces for electrocatalytic reactions due to the reinforced electronic interaction,**
22 **in agreement with electrochemical testing results.** These findings highlight the

1 importance of rational designing heterostructures with in-grown epitaxial interfaces to
2 maximize electrocatalytic activities of 2D layered ternary thiophosphates for various
3 applications.

4 **EXPERIMENTAL METHODS**

5 **Preparation of NiPS₃ nanosheets**

6 The preparation of NiPS₃ nanosheets is based on our previous reports with slight
7 modification.^{34, 37} Typically, nickel hydroxide nanosheets were first prepared by a
8 hydrothermal treatment of 0.5 M Ni²⁺ in the presence of 1.0 M hexamethylenetetramine
9 at 100 °C for 8 h. After vacuum drying, the resultant nickel hydroxide nanosheets (100
10 mg) mixed well with stoichiometric red phosphorus and sulfur were sealed in a quartz
11 tube with oxyhydrogen flame. Subsequently, the quartz tube was transferred to a furnace
12 for further heating at 580 °C for one hour. After cooling to room temperature and
13 alternately washing with dimethyl formamide, chloroform, and ethanol, the 2D NiPS₃
14 nanosheets were finally obtained after vacuum drying.

15 **Safety note:** It must be taken care of opening the sealed quartz tubes inside fume hood
16 because of the possible internal pressure build-up in the glass ampoules.

17 **Preparation of 2D NiPS₃/Ni₂P heterostructures**

18 The *in situ* epitaxial growth of Ni₂P on 2D NiPS₃ nanosheets was facilely achieved by a
19 mild desulfuration of NiPS₃ nanosheets under H₂ (5 vol %)/Ar atmosphere. Specifically,
20 the above prepared NiPS₃ nanosheets (50 mg) were well spread on a silica boat. Then the
21 silica boat was transferred to a tube furnace. After totally removing the residue air at
22 room temperature, the 2D NiPS₃/Ni₂P heterostructures were obtained after thermal

1 treating under H₂/Ar atmosphere (100 mL min⁻¹). Notably, the mass ratio of NiPS₃ and
2 Ni₂P could be tuned by alternating the thermal treating temperature and duration.

3 **Theoretical calculations**

4 All the theoretical calculations were performed by spin-polarized DFT within the plane-
5 wave pseudopotential method using the Vienna *ab initio* simulation package.⁵⁶ The ion-
6 electron interactions were treated with the projector augmented wave (PAW)
7 pseudopotentials.⁵⁷ The generalized gradient approximation was explored to model the
8 electronic exchange-correlation energy using the revised Perdew-Burke-Ernzerhof
9 (RPBE) functional method.⁵⁸ An effective Hubbard parameter of 4.0 eV was added for
10 the Ni 3d states. The cut-off energy of 400.0 eV was choose for plane-wave expansion.
11 All structures were relaxed until the force component on each atom was less than 0.02
12 eV/Å using the conjugated gradient method. The convergence criteria of total energy (1
13 × 10⁻⁵ eV) was set in the self-consistent field method.

14 Bulk Ni₂P crystalizes a hexagonal structure and our optimized structural parameter ($a = b$
15 = 5.81, $c = 3.33$ Å), in agreement with experimental and other theoretical values.³⁶ The
16 simulated lattice parameters of antiferromagnetic NiPS₃ were $a = 5.85$, $b = 10.13$, $c =$
17 6.66 Å, and $\beta = 106.65^\circ$, which were also in consistent with previous reports.⁵⁹ The
18 NiPS₃ adopts a layered structure and the two-dimensional unit cell is hexagonal ($a = b =$
19 5.85 Å) for each single layer, which was well matched with the surface lattice constant of
20 Ni₂P (001). A slab model composed of Ni₂P (001) surface and NiPS₃ monolayer was
21 constructed to simulate the NiPS₃/Ni₂P heterojunction. The slap of NiPS₃/Ni₂P interface
22 was further sliced by the (110) plane to expose the active edge sites of the heterojunction.

1 The Gibbs free-energy (ΔG_{H^*}) is calculated as following description to evaluate the HER
2 performance of various catalysts.

3 Chemisorption energies of atomic hydrogen were calculated relative to H_2 (g) by:

4
$$\Delta E_{H^*} = E_{[\text{edge} + nH]} - E_{[\text{edge} + (n-1) H]} - \frac{1}{2} E_{[H_2]}$$

5 Where $E_{[\text{edge} + nH]}$ refers to the total DFT energy for the system with n hydrogen for a
6 hydrogen atoms adsorbed on the substrate, and $E_{[H_2]}$ is the DFT energy for one hydrogen
7 molecule in the gas state. The associated free energy of chemisorption was therefore
8 determined after correcting the values of E_{ZPE} (vibrational energy) and TS (entropy):

9
$$\Delta G_{H^*} = \Delta E + \Delta (E_{ZPE} - TS)$$

10 Where $\Delta E_{[H_2]}$ was calculated to be -6.978 eV, and $\Delta (E_{ZPE} - TS)$ was determined to be
11 0.24 eV.

12 ASSOCIATED CONTENTS

13 Supporting Information

14 The Supporting Information can be accessed free of charge on the ACS publications
15 websites at DOI:

16 Experimental details, instrumental characterization, and electrochemical measurements.
17 Figures S1-S19, and Tables S1-S3. The authors declare no competing financial interest.

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3 **Author Contributions**

4 Q. Liang and L. Zhong contributed equally to this work.

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Figure 1. (a) Schematic models to illustrate the lattice matching between NiPS_3 and Ni_2P . (b) The ΔG_{H^*} calculated at the equilibrium potential ($U = 0 \text{ V}$) for the $\text{NiPS}_3/\text{Ni}_2\text{P}$, Ni_2P (001), Ni_2P (110), and NiPS_3 (110), and the insets are the corresponding DFT-optimized configurations of H^* adsorption. (c) Distribution of charge density difference at the $\text{NiPS}_3/\text{Ni}_2\text{P}$ interface, where the red and green represent electron accumulation ($\Delta\rho = +0.01 \text{ e}\times\text{bohr}^{-3}$) and depletion ($\Delta\rho = -0.01 \text{ e}\times\text{bohr}^{-3}$), respectively. The Ni, S, P, and H atoms are marked in gray, yellow, purple, and blue, respectively.

Figure 2 (a) Rietveld refining XRD pattern of the NiPS₃/Ni₂P heterostructures. The reliability factors are $R_{wp} = 2.66\%$, $R_p = 2.0\%$, and $R_{exp} = 1.87\%$. The refined cell parameters for NiPS₃ are $a = 5.72 \text{ \AA}$, $b = 9.91 \text{ \AA}$, and $c = 6.50 \text{ \AA}$, and the refined cell parameters for Ni₂P are $a = b = 5.78 \text{ \AA}$, and $c = 3.31 \text{ \AA}$. The insets are the photo of pristine NiPS₃ (carmine) and NiPS₃/Ni₂P heterostructure (black) dispersed in water. (b) High-resolution Ni 2p and (c) S 2p XPS spectra of the NiPS₃/Ni₂P heterostructures and pristine NiPS₃ nanosheets.

Figure 3 (a) SEM, (b-d) TEM and HRTEM images, (e) the corresponding filtered HRTEM image by color, and (f) dark-field STEM image and (g-i) the corresponding EDS elemental mapping of the NiPS₃/Ni₂P heterostructures.

1
2 **Figure 4** (a) Optimization of the loading mass for evaluating the HER performance of various
3 electrocatalysts. The loading mass was calculated based on the concentration of the
4 catalyst ink after a normalization of geometric area of galss carbon electrode. (b) LSV
5 profiles and (c) Tafel plots for NiPS_3 Ni_2P , $\text{NiPS}_3/\text{Ni}_2\text{P}$, and Pt/C electrocatalysts for
6 HER. (d) The comparison of the HER overpotentials and the estimated interfacial area of
7 the $\text{NiPS}_3/\text{Ni}_2\text{P}$ with different ratio of Ni_2P .

Figure 5 (a) SEM, (b) TEM, (c) HRTEM, (d) STEM images, (e-g) EDS mapping of the $\text{NiPS}_3/\text{Ni}_2\text{P}$ heterojunction after a long-term HER testing.

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2 **Figure 6** (a) LSV profiles and (b) the corresponding Tafel plots for the NiPS_3 , Ni_2P ,
3 $\text{NiPS}_3/\text{Ni}_2\text{P}$, and IrO_2 for OER. (c) The determination of C_{dl} and (d, e) LSV curves for
4 HER and OER with current density normalized by ESCA (the contribution from
5 conductive carbon has been excluded). (f) Polarization curves of waer-splitting systems
6 based on $\text{Pt/C} // \text{IrO}_2$, NiPS_3 , Ni_2P , and $\text{NiPS}_3/\text{Ni}_2\text{P}$ electrocatalysts.

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1 Graphic Table of Contents

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3 Metallic Ni_2P nanodomains were *in-situ* interfaced with 2D NiPS_3 nanosheets for
4 boosting electrocatalytic overall water splitting.

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