Interface engineering of tungsten carbide/phosphide heterostructures anchored on N,P-codoped carbon for high-efficiency hydrogen evolution reaction

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ABSTRACT The development of inexpensive and efficient Pt-free electrocatalysts for the hydrogen evolution reaction (HER) is greatly crucial for water electrolysis. Tungsten carbide (WC) exhibiting a Pt-like electronic structure represents an attractive alternative, although its overall performance is limited by the strong W–H bond that impedes hydrogen desorption. Here, we employed an *in-situ* interface engineering strategy to construct high-performance and cost effective electrocatalysts comprising WC/tungsten phosphide (WP) heterostructures that were anchored on N,P-codoped carbon (WC/WP@NPC) *via* a one-step pyrolysis of a melamine polyphosphate/WO₃ hybrid in an inert atmosphere. Owing to the crystal structure compatibility and electron-rich property of WP, it optimizes the electronic structure and hydrogen adsorption configuration of WC, thus significantly weakening the W–H bond with a thermoneutral Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) of -0.05 eV. Additionally, NPC ensures fast electron transport and structural stability of the WC/WP@NPC ternary architecture. These synergistically lead to outstanding HER performances of the catalyst in acidic and alkaline media. Our finding offers a new strategy for designing Pt-alternative electrocatalysts with outstanding electrochemical performances for high-efficiency water splitting and other applications.

Keywords: WC, WP, heterostructure, interface engineering, hydrogen evolution reaction

INTRODUCTION

Hydrogen, a sustainable and environmentally benign energy carrier, is being extensively investigated as a promising fossil-fuel alternative [1,2]. Water splitting employing earth-abundant water resources and renewable electrical energy is among the simplest and most ecofriendly approaches for producing hydrogen [3,4]. However, electrolyzers strongly require noble-metal electrocatalysts, which are scarce and expensive, to drive

water splitting because of the sluggish electrode kinetics [5]. For example, Pt-based electrocatalysts are required to achieve a high-efficiency hydrogen evolution reaction (HER), which is the cathodic half-reaction in water splitting [6]. Thus, it is imperative to develop cost-effective HER catalysts with high activity to substitute the traditional Pt-based ones [7–9]. Thus far, transition-metal-based compounds (Fe, Co, Ni, Mo, W, etc.) have been identified as promising electrocatalysts for HER. Among them, W-based materials are highly desirable for practical application because of their inexpensiveness and attractive electrocatalytic activities [10].

Further, tungsten carbide (WC) has emerged as a noble metal alternative because of its Pt-like electronic structure and catalytic behaviors in hydrogenolysis [11–14]. Unfortunately, WC does not behave like Pt in HER because of its potent affinity to the hydrogen intermediate, which is disadvantageous to hydrogen desorption [14]. Thus, the tuning of the electronic structure of WC *via* doping [15,16], hybridization [17–20], or heterostructuring [21–24] is an effective approach for weakening the W–H bond to facilitate HER. Specifically, heterostructuring *via* employing other transition metal compounds generates hetero-interfaces that can redistribute electrons, which would synergistically enhance the electrocatalytic activity of WC [25]. Consequently, WC-based heterostructures, including W₂C/WC [21,23,26,27], Mo₂C/WC [24], W₂N/WC [6,28], a-WO_x/WC [22], and WS₂/W₃C [29], have been reported. However, these materials cannot adequately tune the electronic structure of WC because of the mismatches in their physicochemical properties. Fortunately, tungsten phosphide (WP) with high conductivity holds similar building blocks with WC. Fig. 1a, b, as well as Table S1, reveal that WC and WP consist of W trigonal prism units that are selectively occupied by C or P atoms at the interstitial positions [30]; the prism of WP is slightly distorted compared with that of WC. Additionally, the electron-rich nature of WP is expected to effectively tune the electronic structure of WC. Therefore, it would be interesting to investigate the catalytic properties of the WC/WP heterostructure to

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Figure 1 Crystal structures of (a) tungsten carbide (WC; JCPDS No. 619096) and (b) tungsten phosphide (WP; JCPDS No. 42056). (c) XRD patterns of WO_3 and WC/WP@NPC. High-resolution (d) W 4f, (e) C 1s, and (f) P 2p XPS spectra of WC/WP@NPC.

determine how their synergistic effects promote HER performance. To the best of our knowledge, the synthesis of nanostructured WC/WP heterostructure electrocatalysts has not been reported yet.

Herein, we report a simple yet very efficient interface engineering strategy for constructing WC/WP heterostructures anchored on N,P-codoped carbon (WC/WP@NPC) *via* a one-step pyrolysis process with cost-effective melamine polyphosphate (MPP) and commercial WO_3 functioned as the C/N/P and W sources, respectively. Further, theoretical simulations indicated that WP effectively optimized the hydrogen adsorption configuration of WC, resulting in a favorable Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) of -0.05 eV, which was more thermoneutral than that of pure WC (-0.81 eV). In addition, the three-dimensional (3D) NPC matrix, which functioned as a scaffold, ensured fast electron transport and robust structural stability. With these merits, WC/WP@NPC displayed extraordinary HER activity, including a low overpotential of 165 mV to reach 10 mA cm^{-2} and a small Tafel slope of 57 mV dec^{-1} . Moreover, the large-scale production, as well as extensive application of WC/WP@NPC could be achieved because of the simplicity and cost effectiveness of the methodology. This work paves the interface engineering approach for the rational design of high-performance electrocatalysts toward industrial-scale water splitting.

EXPERIMENTAL SECTION

Synthesis of WC/WP@NPC

Both MPP and NPC were prepared following the method in our previous study [31]. To synthesize the WC/WP@NPC electrocatalysts, WO_3 (Sigma-Aldrich) and MPP powders with mass

ratios of 2.5%, 5.0%, and 10.0% were carefully mixed and annealed for 2 h in an Ar-protected tube furnace at 900°C with a ramping rate of $10^\circ\text{C min}^{-1}$ and Ar flow rate of 100 sccm (standard cubic centimeter per minute). After cooling naturally to room temperature, the WC/WP@NPC catalysts were obtained without any posttreatment.

Characterizations

Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analyses were performed on a ZEISS focused ion beam-scanning electron microscope. The Raman spectra were recorded on a WITEC CRM200 Raman system with a 532 nm laser. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100 transmission electron microscope at a working voltage of 200 kV. The powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-7000 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi X-ray photoelectron spectrometer employing an Al K α X-ray source (1486.6 eV, 15 kV).

Electrochemical measurements

The electrochemical measurements were conducted employing a typical three-electrode system with $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ (pH 0.3) or $1 \text{ mol L}^{-1} \text{ KOH}$ (pH 14) solution as the electrolyte. The saturated calomel electrode (SCE) equipped with a salt bridge, a graphite plate, and glassy carbon electrode (GCE, $\Phi = 4.0 \text{ mm}$) were served as the reference, counter, and working electrodes, respectively. All the potentials reported herein were converted into the reversible hydrogen electrode (RHE) scale ($E_{\text{RHE}} = E_{\text{SCE}} + 0.242 + 0.059\text{pH}$). The catalyst was loaded onto GCE (mass loading was about 0.5 mg cm^{-2}) employing Nafion (5wt.%, Sig-

ma-Aldrich) as the binder. All the electrochemical data were *iR*-corrected.

Theoretical calculations

The theoretical calculations were conducted within the density functional theory (DFT) framework employing the Vienna *ab initio* simulation package [32,33]. The generalized gradient approximation was selected for the exchange-correlation potential [34,35]. The van der Waals interaction was investigated *via* Grimme's dispersion-corrected DFT (DFT-D3) [36]. The cutoff energy of the plane wave and energy criterion were set to 400 and 5×10^{-6} eV in the iterative solution of the Kohn–Sham equation. The $p(3 \times 3)$ WC (100) and $p(1 \times 1)$ WP (211) surfaces were employed as the structural models of WC and WP, respectively. A vacuum thickness of 25 Å was employed to avoid the interactions between the slabs. A *k*-point grid of $3 \times 3 \times 1$ was selected. The WC (100)–WP (211) cluster was constructed as the structural model of the WC/WP heterostructure. All the structures were optimized until the forces on the atoms were <0.05 eV/Å.

RESULTS AND DISCUSSION

Fig. S1 schematically shows the synthesis of WC/WP@NPC. Generally, commercial WO_3 powder (diameter = 93.4 nm, Fig. S2) and MPP with a mass ratio of 5.0% were thoroughly ground before they were transferred to the tube furnace. The mixture was annealed to 900°C for 2 h in an Ar atmosphere, after which WC/WP@NPC was obtained without any post-treatment. The decomposition of MPP during annealing released a large amount of P-containing gases, thus triggering the conversion of WO_3 into WPO_{3-x} ($0 < x < 3$) [31,37]. Subsequently, the interface reaction between WPO_{3-x} and the MPP-derived porous carbon proceeded *via* carbothermal reduction, which facilitated the formation of the WC/WP heterostructures anchored on the NPC matrix. Fig. 1c shows that the XRD peaks of the WO_3 precursor corresponded well to the monoclinic-type structure (JCPDS No. 71-2141). Interestingly, these peaks disappeared in WC/WP@NPC, and several new diffraction peaks appeared. The peaks at 31.5°, 35.7°, 48.3°, 64.1°, 73.2°, and 77.1° were indexed to WC (JCPDS No. 65-8828) [38], while those at 21.0°, 28.7°, 31.0°, 43.2°, 44.6°, 46.5°, 56.7°, 68.8°, and 76.2° were indexed to WP (JCPDS No. 29-1364) [39], indicating the conversion of WO_3 into WC/WP heterostructures. The Raman spectra were obtained to further probe the structure of the samples. Fig. S3 shows that the Raman peaks, which corresponded to the stretching (ν) and bending (δ) vibrations of the O–W–O and W–O bonds, were detected in the spectrum of WO_3 [40]. However, after the annealing treatment with MPP, only two broad peaks were observed at 1348 and 1595 cm^{-1} , and they were sequentially assigned to the D and G bands of the carbonaceous materials [31]. These results once again confirmed the formation of WC/WP@NPC.

The XPS measurements were conducted to analyze the constituents of WC/WP@NPC. The survey XPS spectrum revealed the presence of W, C, P, N, and O elements (Fig. S4). The high-resolution W 4f spectrum exhibited six fitting peaks, where the two dominant peaks at 32.0 and 34.2 eV were assigned to W–C [41,42], and the pair of small peaks at 32.9 and 35.2 eV were assigned to W–P (Fig. 1d) [43]. Further, the other two peaks at 38.8 and 36.8 eV corresponded to the W^{6+} -based material, which was probably generated *via* superficial oxidation [44]. The high-

resolution C 1s spectrum (Fig. 1e) could be deconvoluted into three peaks that corresponded to C–N (286.2 eV), C–C (284.7 eV), and C–W (283.0 eV) [31,45]. The P 2p spectrum exhibited four fitting peaks (Fig. 1f): the two peaks at 134.5 and 133.6 eV were assignable to the P–O (the phosphate groups) and P–C bonds in NPC [46], while the other two at lower binding energies of 130.7 and 129.8 eV corresponded to the P 2p_{1/2} and P 2p_{3/2} bands of P–W [44], respectively. The N 1s spectrum (Fig. S5a) exhibited two peaks, which were attributable to the graphitic (401.7 eV) and pyridinic (398.8 eV) N of NPC [46]. The O 1s band exhibited four peaks (Fig. S5b), which were assignable to O–P (533.4 eV), O–C (531.9 eV), O–W (531.1 eV), and O–H (530.3 eV). Compared with NPC (Fig. S6), the P 2p and N 1s spectra of WC/WP@NPC shifted to higher binding energies, indicating the transfer of electrons from NPC to the WC/WP heterostructure, which favored HER [47].

Fig. 2a shows the SEM image of WC/WP@NPC exhibiting a moss-like morphology. The high-magnification SEM image (Fig. 2b) reveals that the nanoparticles were uniformly anchored on NPC. Furthermore, the average diameter of the particles was ~68.9 nm (Fig. S7), which was smaller than that of the WO_3 precursor (93.4 nm). Notably, the morphology of WC/WP@NPC completely differed from that of NPC (Fig. S8), reflecting the interface reaction between WPO_{3-x} and NPC. The EDS mapping observations (Fig. 2c) indicate that the W, C, P, N, and O elements were uniformly distributed in the sample. The TEM image (Fig. 2d) further reveals the dispersion of the nanoparticles on NPC. High-resolution TEM of a randomly selected particle was performed to elucidate the structure of the

Figure 2 (a, b) SEM images of WC/WP@NPC at different magnifications. (c) EDS mapping, (d) TEM, and (e) high-resolution TEM images of WC/WP@NPC. The inset of Fig. 2e is the fast Fourier-transform pattern of the WC/WP heterostructures, as acquired from the dash line area. (f) Schematic of WC/WP@NPC.

catalyst. Fig. 2e shows clear lattice fringes with spacings of 0.25 and 0.20 nm, corresponding to the (100) and (211) planes of WC and WP, respectively [15]. Moreover, the existence of the WC/WP heterointerfaces was confirmed. Concurrently, the interface of the WC and WP phases was selected for the fast Fourier transform analysis (inset of Fig. 2e), which revealed two pairs of bright diffraction points that stemmed from the WC (100) and WP (211) phases. These results indicate the synthesis of the WC/WP heterostructures *via* interface engineering. Fig. 2f schematically shows the extensive dispersion of the heterostructures on the NPC matrix, forming a 3D interconnected network, which could favor HER.

Considering that the mass ratio of WO_3 to MPP could affect the interface reactions, their effects on the properties of the eventual products were evaluated. Fig. S9a shows that when a smaller dosage of WO_3 (mass ratio of WO_3 to MPP = 2.5%) was utilized, the resulting composite exhibited fewer nanoparticles compared with the original WC/WP@NPC (mass ratio = 5.0%, Fig. 1a, b and Fig. S9b). Upon increasing the mass ratio to 10.0%, large aggregated nanoparticles with a small amount of NPC were detected in the sample (Fig. S9c). The average diameter of the nanoparticles increased to 133.0 nm (Fig. S10), which was almost two-fold larger than the average diameter of the nanoparticles that were synthesized at a mass ratio of 5.0% (68.9 nm). These results indicate that an optimum mass ratio (5.0%) could produce a moderate amount of NPC and prevent the aggregation of the WC/WP nanoparticles. The XRD patterns (Fig. S11) confirmed that the materials that were synthesized at mass ratios of 2.5% and 10.0% comprised crystalline WC and WP, as those obtained in the materials synthesized in a mass ratio of 5.0%. The Raman spectra indicated that the peak intensities of the D

and G bands of carbon rapidly decreased with an increase in the mass ratio from 2.5% to 10.0% (Fig. S12), and this was attributed to the reduced yield of NPC in the samples, as observed in the SEM images (Fig. S9). This phenomenon is due to the consumption of carbon during the carbothermal reduction process, which further confirms the syntheses of the WC/WP heterostructures *via* interface engineering.

The electrocatalytic behaviors of WC/WP@NPC toward HER were examined in 0.5 mol L⁻¹ H_2SO_4 electrolyte with a standard three-electrode system at a scan rate of 2 mV s⁻¹. The corresponding samples were denoted as WC/WP@NPC(_x) (*x* represents the mass ratio of WO_3 to MPP). For further comparison, the benchmark Pt/C (20wt.%, Johnson Matthey) and NPC were also investigated under the same condition. Expectedly, the Pt/C catalyst required an overpotential of 13 mV to reach the current density of 10 mA cm⁻² (η_{10}), while NPC exhibited negligible electrocatalytic activity (Fig. 3a). Notably, the WC/WP@NPC catalysts exhibited high activity toward HER, where WC/WP@NPC(_{5.0}) exhibited the most prominent activity with a small η_{10} of 165 mV, which was lower than those of WC/WP@NPC(_{2.5}) (η_{10} = 180 mV) and WC/WP@NPC(_{10.0}) (η_{10} = 172 mV). The Tafel curves were derived from the corresponding polarization curves and further fitted by the Tafel equation: $\eta = a + b \log(j)$ [48], where η is the overpotential, j is the current density, a is a constant, and b is the Tafel slope. Fig. 3b shows that Pt/C exhibited a small Tafel slope of 30 mV dec⁻¹, which correlated well with the reported data [15]. The obtained Tafel slopes of WC/WP@NPC(_{2.5}), WC/WP@NPC(_{5.0}), and WC/WP@NPC(_{10.0}) were 69, 57, and 60 mV dec⁻¹, respectively. This result indicates that HER on WC/WP@NPC proceeded *via* the Volmer–Heyrovsky mechanism in which the electrochemical desorption

Figure 3 (a) Polarization curves and (b) the corresponding Tafel plots of the samples. (c) η_{10} of WC/WP@NPC(_{5.0}) compared with those of recently reported WC-based catalysts. (d) Nyquist plots of the WC/WP@NPC electrodes. (e) Polarization curves of WC/WP@NPC(_{5.0}) before and after 5000 CV cycles. (f) Chronopotentiometric curve of WC/WP@NPC(_{5.0}).

reaction is the rate-determining step [21]. The lower η_{10} and Tafel slope of WC/WP@NPC_(5,0) compared with those of the others reflected its superior catalytic activity [49], mainly because of the optimized WO₃/MPP ratio to produce sufficient NPC and prevent the aggregation of WC/WP nanoparticles. The electrocatalytic performances of WC/WP@NPC_(5,0) regarding η_{10} and the Tafel slope were comparable or even superior to those of most recently reported WC-based HER catalysts (Fig. 3c and Table S2).

To further elucidate the electrode behaviors, electrochemical impedance spectroscopy was performed at an HER overpotential of 200 mV in a frequency range of 0.1–100 kHz employing an alternating current potential amplitude of 5 mV. The Nyquist plots (Fig. 3d) revealed that WC/WP@NPC_(10,0) exhibited two large arcs, indicating its high resistance toward HER. The arc in the high-frequency region corresponded to the electronic resistance of the catalyst inner-layer/interface, while the arc in the low-frequency region corresponded to the charge-transfer resistance on the electrolyte–catalyst interface [50]. The increases in the electronic conductivity and charge-transfer efficiency of the electrode induce the merging of the two arcs. Thus, WC/WP@NPC_(2,5) and WC/WP@NPC_(5,0) exhibited smaller resistance compared with WC/WP@NPC_(10,0), and only one arc was observed. WC/WP@NPC_(5,0) exhibited the lowest impedance, which corresponds to superior electrode kinetics for HER. Additionally, NPC also provided paths for bubble release and electrolyte diffusion, thus benefiting mass transport. Notably, despite the negligible HER electrocatalytic activity of NPC, it could still contribute to the excellent electrocatalytic activity of WC/WP@NPC_(5,0). For example, the codoped N and P atoms promoted proton adsorption, while the conducting 3D network facilitated electron transport, both ensuring fast electrode kinetics [51–53]. To evaluate the long-term stability of WC/WP@NPC_(5,0), cyclic voltammetry (CV) tests were performed in a potential range of –0.25 to 0.1 V at a scan rate of 100 mV s^{–1}. The polarization curves before and after 5000 cycles did not exhibit any significant difference (Fig. 3e), indicating the excellent electrochemical stability of the electrocatalyst. Moreover, no sharp increase was observed in the potential after 24 h of chronopotentiometric test at a constant current density (20 mA cm^{–2}) (Fig. 3f), further verifying the excellent durability of WC/WP@NPC_(5,0) toward HER.

In addition to the remarkable HER performance in an acidic medium, the electrocatalytic behaviors of WC/WP@NPC_(5,0) were also evaluated in a basic medium (1.0 mol L^{–1} KOH solution). Fig. S13 shows that the η_{10} and Tafel slope of WC/WP@NPC_(5,0) in the basic medium were almost equal to those in the acidic one, indicating its superior HER activities in both media. Although this WC/WP@NPC_(5,0) exhibited a slightly higher Tafel slope (58 mV dec^{–1}) compared with Pt/C (38 mV dec^{–1}), the value was among the most active alkaline WC-based electrocatalysts for HER (Table S3). Such impressive HER performances might render WC/WP@NPC_(5,0) a promising electrocatalyst for practical application under wide pH conditions.

To elucidate the high HER activity of WC/WP@NPC, DFT calculations were conducted to investigate ΔG_{H^*} . Considering that the enhancement of the HER activity of WC by heteroatom-doped carbons has been studied [5,13,38], the calculations here only focused on the WC/WP heterostructure. Based on TEM analysis, the WC/WP heterostructure was prepared by com-

binning WC (100) and WP (211) surfaces (Fig. S14). For comparison, the WC (100) and WP (211) surfaces were employed as the structural models of WC (Fig. S15) and WP (Fig. S16), respectively. Fig. S17 shows that WC exhibited three probable hydrogen adsorption locations, namely the W top, W–W bridge, and hollow sites. However, after the structural optimization, the hydrogen that was adsorbed onto the top and hollow sites were rearranged into the bridge site (Fig. 4a and Fig. S18a), which is the most stable hydrogen adsorption configuration (denoted as WC_(B-H)). The calculated ΔG_{H^*} value of WC_(B-H) was –0.81 eV, which is consistent with the value (–0.84 eV) reported by Yu *et al.* [54]. Such a negative ΔG_{H^*} signified a large barrier for hydrogen desorption during HER owing to the strong W–H bond. Regarding WP, the optimized configuration involved the adsorption of hydrogen onto the P site (WP_(P-H)) (Fig. 4b and Fig. S18b). The corresponding ΔG_{H^*} value was calculated as –0.22 eV. Regarding the WC/WP heterostructure, the hydrogen adsorbed on the interfacial bridge site of WC (WC_(B-H)/WP) and the interfacial P site of WP (WC/WP_(P-H)) accounted for ΔG_{H^*} values of –0.63 and –0.31 eV, respectively (Fig. 4d, e, and Fig. S19). Compared with WC_(B-H) and WP_(P-H), the changes of ΔG_{H^*} in the heterostructure indicated a strong electronic interaction between the two components [29]. Surprisingly, the heterostructure stabilized the hydrogen adsorption on the W top site of WC (WC_(T-H)/WP; Fig. 4c and Fig. S19a). The more thermoneutral ΔG_{H^*} of WC_(T-H)/WP (–0.05 eV) than those of the others indicated the great weakening of the W–H bond. Therefore, the superb HER activity of WC/WP@NPC proceeded from the optimized hydrogen adsorption configuration, which promoted the hydrogen desorption kinetics during HER.

CONCLUSIONS

In summary, WC/WP@NPC electrocatalysts with WC/WP heterostructures anchored on NPC were developed *via* an

Figure 4 Optimized hydrogen adsorption models and the calculated ΔG_{H^*} of WC, WP, and the WC/WP heterostructure.

interface engineering strategy involving the solid-state transformation reactions between WO_3 and MPP. Owing to the structural compatibility and electron-rich feature of WP, it optimized the electronic structure and hydrogen adsorption configuration of WC, thus benefiting the HER process. Via the unique structure and synergistic effects of the ternary components, WC/WP@NPC exhibited enhanced HER kinetics and excellent electrochemical stability toward HER. Moreover, WC/WP@NPC also demonstrated prominent HER activity over a wide pH range. The inexpensive, scalable, and facile synthesis combined with the impressive HER performance might endow WC/WP@NPC with great potential for practical application. Notably, this work reveals a new methodology for rationally designing Pt-alternative electrocatalysts with particular heterostructures for HER and other applications.

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

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氮磷共掺杂碳负载WC/WP异质结的电催化析氢性能研究

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摘要 廉价、高效、稳定的非铂析氢催化剂是电解水制氢技术发展的关键。WC具有类似铂的电子结构,且价格低廉,是极具潜力的析氢催化剂。然而,反应中间体W-H的结合力强,不利于H解离,导致析氢性能不佳。针对这一难题,本工作利用与WC晶体结构兼容性好,且具有富电子特性的WP来调控其电子结构,通过一步原位固相界面反应成功制备了氮磷共掺杂碳负载WC/WP异质结(WC/WP@NPC)催化剂。密度泛函理论计算表明,该异质结设计有效减小了W-H键键强,使材料具有更适中的氢原子吸附自由能(−0.05 eV)。得益于WC/WP异质结与氮磷共掺杂碳之间的协同增效作用,WC/WP@NPC在酸性和碱性电解质中均表现出了优异的催化性能。本工作为高效非铂析氢催化剂的设计制备提供了新思路。