Multi-touch cobalt phosphide-tungsten phosphide heterojunctions anchored on reduced graphene oxide boosting wide pH hydrogen evolution

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ABSTRACT Multi-interface engineering is deemed as an effective strategy to boost catalytic activity *via* electronic structure modulation. However, it is still a big challenge due to the phase-separation tendency. Herein, we designed CoP-WP heterojunctions with multi-touch interfaces using Co₈W₁₈, a definite structure polyoxometalate-based polynuclear cobalt molecular cluster, as a precursor. The CoP-WP heterojunctions anchored on reduced graphene oxide (CoP-WP/rGO) were obtained by growing Co₈W₁₈ on GO followed by phosphorization. The intrinsic {Co-O-W} coordination modes in Co₈W₁₈ are conducive to the formation of the multiple interfaces between CoP and WP. The abundant intimate interfaces in CoP-WP heterojunctions promote the electron transfer from WP to CoP, thus regulating the interfacial electronic structure and optimizing the hydrogen adsorption free energy (ΔG_{H^+}), as verified by X-ray photoelectron spectroscopy analysis and theoretical calculations. Furthermore, the integration of rGO provides CoP-WP/rGO with a large surface area and high conductivity, aiding mass transport and charge transfer. CoP-WP/rGO exhibits remarkable hydrogen evolution reaction (HER) activity with low overpotentials of 96, 130, and 138 mV at 10 mA cm⁻² in alkaline, acidic and neutral media, respectively, and has long-term durability. Our discovery provides an opportunity to design heterojunction materials with multi-coupled interfaces at low-cost and efficient HER catalysts.

Keywords: heterojunction, modulating electronic structure, electrocatalytic hydrogen evolution, metal phosphides, polyoxometalates

INTRODUCTION

The excessive consumption of fossil fuels inevitably causes serious environmental problems. H₂, a clean energy carrier with the characteristic of high energy density, holds a bright promise to realize the green development of the whole society. Electrocatalytic hydrogen evolution reaction (HER) *via* water splitting is an environment-friendly and high-efficient strategy to produce high-purity hydrogen, driven by low-voltage electricity from photovoltaic power [1–3]. Currently, not more than 4% hydrogen is produced by electrolysis, partly because the sluggish

kinetics of HER requires efficient catalysts to catalyze [4]. Now, the most efficient HER electrocatalysts are still platinum-based materials. The prohibitive cost and scarcity of Pt are a strong driving force to search for cost-effective alternatives. Moreover, the HER process varies with pH values. Generally, the active performance in alkaline and neutral conditions could not reach that in acid electrolyte [5,6]. Therefore, the development of non-noble-metal materials that can be operated with high performance irrespective of pH value is pursued.

To optimize the catalytic activity, two focus points are increasing the number of active sites and improving the intrinsic catalytic activity [7,8]. In this regard, constructing heterostructure interfaces is an effective strategy for realizing the simultaneous modulations of the aforementioned aspects [9–11]. Heterojunctions constructed by early (W, Mo, V, etc.) and late transition metals (TM = Co, Ni, Fe, etc.) show an unusual catalytic activity due to interfacial electron redistribution based on the “d electron complementary effect” [12–14]. For instance, Ni₃N-VN/NF interstitial compound heterojunction exhibits an elevated HER performance due to the heterointerfaces for easy adsorption/activation of the intermediates [15]. On the other hand, tungsten/molybdenum-based phosphides with analogous Pt electronic structure, relatively high conductivity, and mechanical strength are emerging catalysts, where high electronegative P serves as a “proton trap” and Mo/W works as a “hydride acceptor” during the catalytic process [16]. However, single-metal phosphides (such as WP and MoP) often have low activity due to the strong electron-donating characteristic of Mo/W. Integrating foreign metals has been widely explored to modulate electronic structures and accelerate the hydrogen evolution kinetics [17,18]. For example, Lan’s group [19] prepared a CoP/MoP@NC/CC heterojunction with excellent catalytic activity (η_{10} = 94 mV), owing to the synergistic effect of CoP and MoP. In the case of W, it is challenging to construct analogous heterojunctions due to the phase-separation tendency [20]. Conventional strategies to build the Co-W-based heterojunctions can be summarized as follows: one is based on CoWO₄ precursor [21]; the second is the stepwise introduction of Co and W sources [22]; the third one selects CoW-based metal-organic framework as a precursor [23]. However, these strategies only produce limited heterointerfaces that are coupled loosely. Therefore, it is hard to realize a Co-W-based heterostructure

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with a high degree of integration and rich interfaces in one step.

Polyoxometalates (POMs) with nano sizes, high negative charges, adjustable composition, and oxygen-rich surface capable of strong coordination, have been widely utilized as transferable building blocks to target functional materials [24–26]. POMs containing TM (TM = Co, Ni, Fe, etc.) provide the flexibility to fabricate multi-interfacial hybrid nanomaterials since there exist abundant intramolecular interfaces due to the inherent {TM-O-W/Mo} coordination modes [26,27]. Considering the ratio of TM to W/Mo atoms could be controlled beforehand at a molecular level, we speculate that the precise ratio control may be achieved in the electrocatalysts. In this context, a POM-based polynuclear cobalt cluster $K_8Na_8[(A-\alpha-SiW_9O_{34})_2Co_8(OH)_6(H_2O)_2(CO_3)_3]\cdot 52H_2O$ (aliased as Co_8W_{18} , Fig. S1) captures our attention [28,29]. The assembly-immobilization strategy is preferred, considering it is useful that small-sized Mo/W-based catalysts on reduced graphene oxide (rGO) were synthesized by this method [30–32]. Herein, a unique CoP-WP heterostructure anchored on rGO (denoted as CoP-WP/rGO) was created through hydrothermal reaction and subsequently controlled phosphorization using Co_8W_{18} precursor. The ratio of Co to W atoms in CoP-WP/rGO is inherited from Co_8W_{18} . As expected, great interfaces are formed in CoP-WP/rGO, where the interfacial electron redistribution occurs, optimizing the hydrogen adsorption energy. As a result, CoP-WP/rGO can effectively drive the HER over a wide pH range. The required overpotentials to reach 10 mA cm^{-2} are 96, 130, and 138 mV in 1 mol L^{-1} KOH, 0.5 mol L^{-1} H_2SO_4 , and 1 mol L^{-1} phosphate buffer saline (PBS), respectively, outperforming the corresponding single-component samples. The excellent activity benefits from the synergistic effect of heterostructure between CoP and WP, and the enhanced electronic conductivity originated from the incorporation with rGO. This work seeks to construct heterojunctions with firm contact interfaces for targeting renewable energy electrocatalysis.

EXPERIMENTAL SECTION

Synthesis of CoP-WP/rGO

The fresh GO dispersion (20 mL , 4 mg mL^{-1}) reacted with 20 mL of 4 mg mL^{-1} polyethyleneimine (PEI) aqueous solution, under stirring for 24 h. After centrifugal separation, the obtained PEI-GO was dispersed in deionized water to form 40 mL 2 mg mL^{-1} PEI-GO solution. Next, Co_8W_{18} (120 mg) in CH_3COONa solution (30 mL , 0.5 mol L^{-1}) was added dropwise into the PEI-GO solution under vigorous stirring. After 24 h, the mixture was transferred into a 100-mL Teflon-lined autoclave, followed by heating at 160°C for 18 h. During the hydrothermal treatment, the GO was partially reduced to rGO. After cooling down to room temperature, the as-prepared precipitate (Co_8W_{18}/rGO) was centrifuged and washed with deionized water and ethanol several times, then dried at 60°C overnight. After that, the Co_8W_{18}/rGO powder was first calcined from ambient temperature to 320°C and then maintained for 6 h. Subsequently, the as-obtained sample (100 mg) and NaH_2PO_2 (1 g) were put into two single porcelain boats, respectively. The porcelain boat loaded with NaH_2PO_2 was placed at the upstream side of the quartz tube at a distance of about 5 cm from the other one. Then, the quartz tube was calcinated at 800°C for 3 h with a ramping rate of 5°C min^{-1} in an inert N_2 atmosphere. After natural cooling, the targeted sample (CoP-WP/rGO) was

obtained.

A series of control samples were synthesized by either changing the phosphating temperature or tuning the concentration of the starting reactant Co_8W_{18} to investigate the influence of calcination temperature and Co_8W_{18} amount on the catalytic activity. The CoP-WP/rGO-700 and CoP-WP/rGO-900 were obtained under the same conditions, except that the phosphating temperature was changed to 700 and 900°C , respectively. Similar to the above, when the reactant amount of Co_8W_{18} was 80 and 160 mg (the mass ratios of Co_8W_{18} and GO were 1 and 2), the final products calcinated at 800°C were designated as CoP-WP/rGO-1 and CoP-WP/rGO-2.

Synthesis of WP/rGO

The synthetic procedure is very similar to that for CoP-WP/rGO, except that $H_4[SiO_4(W_3O_9)_4]$ (SiW_{12}) was used in place of Co_8W_{18} .

Synthesis of CoP/rGO

The synthetic procedure is the same as that for CoP-WP/rGO, except that $CoSO_4\cdot 7H_2O$ was used instead of Co_8W_{18} .

Synthesis of CoP-WP nanoparticles (NPs)

The obtained Co_8W_{18} precursor was ground into powder and then calcined under the same condition for CoP-WP/rGO. Therefore, the as-obtained sample is denoted as CoP-WP NPs.

Characterizations

Powder X-ray diffraction (XRD) measurement was recorded on a Bruker D8 diffractometer using $Cu\ K\alpha$ ($\lambda = 1.5418\text{ \AA}$) radiation with an acceleration voltage of 40 kV . Fourier transformed infrared (FT-IR) spectroscopy was performed using a Perkin-Elmer Spectrum. Thermogravimetric (TG) analysis was obtained on an SDT Q600 instrument with constant air flow. The Raman spectrum was recorded on a Raman spectrometer (JY, Labram HR 800). A scanning electron microscopy (SEM) test was conducted on a Hitachi S-4800 instrument at an accelerating voltage of 5 kV . Transmission electron microscopy (TEM) was carried out on a JEM-2100 at 200 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) was measured on a VG ESCALAB MKII with $Mg\ K\alpha$ (1253.6 eV) achromatic X-ray radiation. The N_2 adsorption-desorption isotherms of the samples were conducted using a Micromeritics Tristar II. Scanning Kelvin Probe (SKP) measurement (SKP5050 system, Scotland) was performed in an ambient atmosphere using a gold electrode as the reference electrode.

Electrochemical measurements

The electrochemical measurement was carried out using a conventional three-electrode system at ambient temperature connected to a CHI 760E electrochemical workstation. The working electrode was prepared by mixing 2.5 mg of catalyst and 0.5 mg of carbon black dispersed in 1 mL of water/ethanol ($v/v = 1:1$). Then, $30\text{ }\mu\text{L}$ $5\text{ wt\%}$ Nafion solution was added to the mixture. The mixture was treated to obtain a dispersed slurry. The slurry was pasted on a piece of Ni foam current collector ($1.0\text{ cm} \times 1.0\text{ cm}$) for alkaline and neutral HER tests or carbon fiber paper (CFP, $1.0\text{ cm} \times 1.0\text{ cm}$) for acidic HER test and dried at 60°C overnight. A saturated calomel electrode was employed as the reference electrode in both acidic and neutral electrolytes, while a standard Hg/HgO electrode as the reference electrode

was selected under alkaline conditions. A graphite rod was used as the counter electrodes in all the electrochemical tests. After 20 cycles of cyclic voltammetry (CV) tests to stabilize the current, a linear sweep voltammogram (LSV) was conducted at a scan rate of 5 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) data were gathered in the frequency range of 0.01–100,000 Hz. CV was tested at varied scan rates in the non-Faradaic potential range to calculate the electrochemical double-layer capacitance (C_{dl}). The long-term stability was evaluated by implementing 2000 cycles CV at 100 mV s^{-1} scan rate in the selected potential ranges. Moreover, the chronoamperometry current density-time (i - t) curves were conducted under controlled potentials for 30 h. All the potentials reported here were calibrated to a reversible hydrogen electrode (RHE) using the corresponding Nernst equation as suggested by the previous literature [15]. A 90% iR compensation was employed in all the electrochemical measurements. The overall water splitting measurement was carried out in a standard two-electrode system using CoP-WP/rGO as the cathode and NiFe-layered double hydroxide/nickel foam (LDH/NF) as the anode in alkaline electrolyte.

RESULTS AND DISCUSSION

Morphology and structure characterization

The hybrid nanocatalyst CoP-WP/rGO was fabricated *via* several steps, as shown in Scheme 1. The hydrothermal method combined the as-synthesized POM Co_8W_{18} and GO based on our previously reported assembly-immobilization strategy [30–32], forming the nanocomposite precursor Co_8W_{18} /rGO. Afterward, the as-synthesized Co_8W_{18} /rGO was *in-situ* transformed to CoP-WP/rGO by air calcination and then phosphorized under an inert N_2 atmosphere at 800°C for 3 h. The POM-based polynuclear cobalt cluster Co_8W_{18} was selected as the precursor *via* deliberate design and consideration based on the following points. i. Co_8W_{18} contains two metal atoms, Co and W. They are in a determined ratio and are joined together in tight contact due to the {Co-O-W} coordination modes, guaranteeing efficient *in-situ* generation of CoP-WP interwoven heterostructure in a precise ratio. ii. The integrity of POM structure in an aqueous solution is key, to some extent. The POM structure is subject to

the pH value, which sometimes decomposes into fragments or ions [33]. At this point, Co_8W_{18} is stable in an aqueous solution of about 9.0 pH [29], ensuring its structural integrity during the assembly process with PEI-GO and supporting the proportion control reliability. iii. Co_8W_{18} species with high negative charges up to 16 can easily combine with PEI-GO with positive surface charges, enhancing the inhibition of agglomeration and coalescence. The GO served as a support and carbon source to realize the good dispersion and deoxygenation of Co_8W_{18} and enhance the conductivity of the corresponding materials. The PEI acted as a coupling agent to trap POM on GO, aside from nitrogen source for *in-situ* generation of N-doped carbon. The structure and composition of Co_8W_{18} were investigated by XRD, FT-IR, and TG analysis (Figs S2, S3, and S4). Also, the IR test was used to identify the successful formation of Co_8W_{18} /rGO. As shown in Fig. S3, the characteristic peaks of the Co_8W_{18} polyanion are 1488, 1383, 985, 936, 887, 860, 803, 680, and 523 cm^{-1} , which are in line with the literature [28,29]. They are retained in the as-synthesized Co_8W_{18} /rGO assembly. The characteristic absorption peak at 3428 cm^{-1} can be attributed to the vibration of O–H ($\nu_{as}(\text{O–H})$). The new peaks at 1646, 1550, and 1162 cm^{-1} associated with $\nu_{as}(\text{C=O})$, $\nu_{as}(\text{C=C})$, and $\nu_{as}(\text{C–O–N})$, respectively, are observed, which can be ascribed to PEI-GO, suggesting the formation of Co_8W_{18} /rGO. After pyrolysis of Co_8W_{18} /rGO at 800°C , CoP-WP/rGO was obtained. As shown in Fig. S3, the characteristic peaks of the Co_8W_{18} polyanion disappear, implying that Co_8W_{18} was somewhat converted to CoP-WP/rGO. According to the above results, CoP-WP/rGO contains many hydrophilic groups (hydroxyl and carboxylic groups), which are beneficial to the adsorption of reactant molecules and electrolyte penetration, promoting the surface reaction kinetics [34,35].

WP/rGO and CoP-WP NPs samples were also prepared for comparison. XRD was further performed to confirm the structures of the as-obtained catalysts. The XRD patterns (Fig. 1a and Fig. S5) of CoP-WP/rGO, WP/rGO, and CoP-WP NPs display intense and dominant diffraction peaks at 21.1° , 28.7° , 31.1° , 43.3° , 44.7° , 46.6° , and 56.8° , which match well with the (101), (002), (011), (112), (211), (103), and (020) lattice planes of the orthorhombic WP (JCPDS No. 65-1484), respectively. In contrast, some other peaks are observed in the XRD patterns of

Scheme 1 Schematic illustration of the preparation of CoP-WP/rGO.

Figure 1 (a) XRD patterns of CoP-WP/rGO, WP/rGO and CoP/rGO, (b) EDS spectrum and the relative content in atomic percent in CoP-WP/rGO, (c) TEM image, (d) HRTEM image, (e) the IFFTs of the corresponding areas in (d), (f) scanning TEM image, and the corresponding elemental mapping images of C, N, P, W and Co elements in CoP-WP/rGO.

CoP-WP/rGO, CoP/rGO, and CoP-WP NPs. The residual ones located at 31.6° , 35.3° , 45.1° , 48.1° , and 56.0° can be well-indexed to (011), (200), (210), (211), and (020) orthorhombic CoP (JCPDS No. 65-1474) reflections. A broad peak at about 26.2° in CoP/rGO can be assigned to the (002) facet of graphitic carbon because Co species has a highly catalytic ability for graphitization. Comparing the XRD patterns (Fig. 1a), we can conclude that both WP and CoP phases exist in CoP-WP/rGO, suggesting the CoP-WP heterostructure formation. Besides, the peaks in the XRD pattern for CoP-WP/rGO appear wider than those for CoP-WP NPs, illustrating that immobilizing CoP-WP on the rGO layer strongly restricted the overgrowth of CoP-WP NPs. Raman spectroscopy was carried out to investigate the structural information of carbon materials. At around 1348 and 1583 cm^{-1} , two distinct peaks are assigned to the D and G bands (Fig. S6). The intensity ratio of D and G bands (I_D/I_G) reflects the disorder degree of graphite materials [32]. CoP-WP/rGO displays a higher I_D/I_G value than $\text{Co}_8\text{W}_{18}/\text{rGO}$, illustrating that the phosphating process brings a particular increase of disorder degree, caused by the fact that nitrogen and phosphorus were

inserted into the carbon framework during the high-temperature pyrolysis. In carbon materials, heteroatom doping (N and P, etc.) can tune the electron donor-acceptor behavior or spin density, regulating the hydrogen/hydroxyl adsorption energy, which is responsible for the elevated catalytic activity [23,36]. Moreover, the interaction between CoP-WP and rGO intensifies after phosphorization, conducive to charge transfer during the electrochemical reaction.

The morphology and microstructure of CoP-WP/rGO were investigated by SEM and TEM. As displayed in Fig. S7, CoP-WP heterostructure NPs with high uniformity are anchored and well-dispersed on the thin graphene layer. The SEM images of CoP-WP NPs and CoP-WP/rGO illustrate that rGO plays a crucial role in inhibiting the excessive aggregation of CoP-WP NPs, closely agreeing with the XRD results. The graphene layer shows no stacking due to the “space separator” role of CoP-WP NPs. X-ray energy-dispersive spectroscopy (EDS) analysis shows that the atomic ratio of W:Co:P:N:C is approximately 0.53:0.25:0.76:2.61:89.15 (Fig. 1b). The atomic ratio of W and Co measured at 2.12:1, is in good agreement with the ratio (2.25:1)

in the Co_8W_{18} cluster. The atomic ratio of W and Co in CoP-WP/rGO is inherited from Co_8W_{18} POM, achieving accurate control. Fig. 1c and Fig. S8 show that CoP-WP NPs with different sizes are evenly distributed on the thin graphene layer. The size of the Co_8W_{18} precursor is about 2 nm. $[\text{WO}_6]$ and $[\text{CoO}_6]$ octahedrons are connected by $\{\text{Co-O-W}\}$ linkages, which favor the construction of rich interfaces. After calcination, only a slight aggregation of the neighboring particles exists due to the anchoring function of PEI. High-resolution TEM (HRTEM) images (Fig. 1d) show the lattice fringes with an interplanar distance of 0.196, 0.209, and 0.311 nm, which correspond to the (112) lattice plane of CoP, (112) and (002) planes of WP, respectively. The detailed inverse fast Fourier transform (IFFT) spectra (Fig. 1e) further confirm the corresponding lattice distances of CoP and WP in the selected areas. More HRTEM images (Fig. S9) prove clear interfaces between CoP and WP in close contact. It should be noted that abundant interfaces are observed, which indicates the formation of multi-touch CoP-WP heterojunctions, enabling more accessible active sites. The uniform distribution of W, Co, P, N, and C elements in CoP-WP/rGO is verified by X-ray EDS elemental mapping graphs (Fig. 1f), demonstrating the successful fabrication of CoP-WP/rGO, in which CoP and WP are firmly held together. The abundant multi-touch interfaces are considered as active sites in favor of HER. The nitrogen adsorption/desorption isotherm measurement was carried out to investigate the specific surface areas using the Brunauer-Emmett-Teller (BET) method. N_2 adsorption/desorption isotherms (Fig. S10) of CoP-WP/rGO present typical type-IV isotherms with H3-type hysteresis loop, signifying the presence of mesoporous structure. The BET surface area is determined to be $112.1 \text{ m}^2 \text{ g}^{-1}$ for CoP-WP/rGO, which is much larger than 79.2 and $4.3 \text{ m}^2 \text{ g}^{-1}$ for rGO and CoP-WP NPs. The far higher value of CoP-WP/rGO than that of CoP-WP NPs verifies the significant effect of rGO again. In addition, CoP-WP/rGO shows a higher BET surface area than rGO due to the “space separator” role of CoP-WP NPs in pre-

venting rGO from stacking. The higher surface area is expected to expose more active sites. In the meantime, the porous structure is conducive to electrolyte penetration and charge transfer. The two points render CoP-WP/rGO superior thermodynamics and kinetics in the electrochemical process.

To gain further insight into the surface composition and valence states as well as the electron effect between WP and CoP, XPS was implemented. The survey spectra in Fig. 2a demonstrate the presence of W, P, N, C, and O elements in CoP-WP/rGO and WP/rGO. The appearance of the O 1s signal is caused by the inevitable surface oxidation of the materials when exposed to air [37]. For CoP-WP/rGO, a new peak assigned to Co 2p emerges, meaning the successful incorporation of Co. As shown in Fig. 2b, the W 4f spectrum can be deconvoluted into two pairs of peaks. The sharp peaks at 32.0 and 34.1 eV are characteristics of W $4f_{7/2}$ and $4f_{5/2}$, which can be assigned to the W-P bonds [38]. In addition, the other two peaks located at 36.1 and 38.2 eV are associated with the W(VI) species due to the ineluctable surface oxidation [39]. Fig. 2c shows the high-resolution spectrum of Co 2p. The Co $2p_{3/2}$ spectrum can be deconvoluted into three main peaks. The binding energy of 778.5 eV is ascribed to the Co-P, which agrees with the reported $\text{Co}^{\delta+}$ signal from CoP in the literature [40]. The peak at 782.3 eV implies the Co oxidation due to surface oxidation, accompanied by a shake-up satellite peak located at 786.8 eV [41]. The presence of W-P and Co-P verifies the successful phosphorization of the W and Co elements. In the case of P 2p (Fig. 2d), the binding energies at 129.7 and 130.6 eV are derived from P $2p_{3/2}$ and P $2p_{1/2}$, respectively, corresponding to metal-phosphide (M-P) bonds [42]. The binding energy at 132.7 eV belonging to P-C implies the presence of strong chemical interactions between rGO layer and CoP-WP [43]. The peak at 134.1 eV (P-O) stems from the superficial PO_4^{3-} [42]. The high-resolution N 1s spectrum (Fig. 2e) reveals the existence of metal-nitrogen bond (M-N, 397.6 eV), pyridinic N (398.8 eV), pyrrolic N (399.6 eV), and graphitic N (401.0 eV) [42,44]. As Fig. 2f

Figure 2 (a) XPS wide scan spectra of CoP-WP/rGO and WP/rGO, the high-resolution spectra of (b) W 4f, (c) Co 2p, (d) P 2p, (e) N 1s, and (f) C 1s in CoP-WP/rGO.

illustrates, a dominant peak of C–C/C=C species (284.6 eV) and three relatively weak peaks of C–N/C–P (285.4 eV), C–O (286.6 eV), and C=O (289.0 eV) suggest graphite-like sp^2 bonded carbon accompanied by the successful doping of heteroatoms (N, P, O) into rGO layer [42,45]. The high portion of sp^2 -carbon accounts for the enhanced electron conductivity. Meanwhile, heteroatoms doping could be conducive to optimizing hydrogen/hydroxyl adsorption energy [23,42]. The above analysis is suggestive of the successful fabrication of CoP-WP/rGO. In comparison with the high-resolution W 4f spectrum of WP/rGO sample (Fig. S11a), the W 4f_{7/2} (32.0 eV) and 4f_{5/2} (34.1 eV) peaks assigned to W–P of CoP-WP/rGO shift 0.4 eV toward higher binding energies. As shown in Fig. S11b, no peak exists in the Co 2p zone of the WP/rGO sample. The significant positive shift indicates electron redistribution between WP and CoP at the interfaces, in which CoP works as the electron-attracting unit and draws the electrons from WP in CoP-WP/rGO. The strong electronic interaction between CoP and WP in close contact can modulate the electronic structure of Co and W, improving the intrinsic electrochemical activity of catalysts [46].

Electrochemical performance

It is vital to exploit pH-universal HER electrocatalysts with excellent catalytic activity for various renewable technologies in the future. Even though Pt is regarded as the benchmark HER electrocatalyst, performing effectively in acidic electrolyte, the HER activity in alkaline and neutral media drops 2–3 orders of magnitude because of the extra energy required for water dissociation [47]. Therefore, to meet the application requirements in different fields, developing pH-universal efficient hydrogen-evolving electrocatalysts is imperative.

The HER performance of CoP-WP/rGO was evaluated in 1.0 mol L^{−1} KOH using a standard three-electrode setup with Hg/HgO electrode as the reference electrode and graphite rod as the counter electrode. Meanwhile, Pt/C, CoP/rGO, WP/rGO, and CoP-WP NPs were used as the control samples. Fig. 3a shows the typical LSV curves of CoP-WP NPs, WP/rGO, CoP/rGO, CoP-WP/rGO, and Pt/C at a scan rate of 5 mV s^{−1}. The commercial Pt/C catalyst displays the anticipative outstanding catalytic activity. As observed, in comparison with CoP/rGO, WP/rGO, and CoP-WP NPs, CoP-WP/rGO gives the best HER catalytic activity, suggesting the heterostructure of CoP and WP, and the rGO integration in boosting the HER catalysis. To drive a current density of 10 mA cm^{−2}, CoP-WP/rGO requires a small overpotential (η_{10}) of 96 mV, much lower than 123, 157, and 208 mV for CoP/rGO, WP/rGO, and CoP-WP NPs, respectively. In consistent with the tendency of overpotentials at 10 mA cm^{−2}, the overpotentials of CoP-WP/rGO at 50, 100, and 200 mA cm^{−2} are also far below those of CoP/rGO, WP/rGO, and CoP-WP NPs at the same current densities (Fig. 3b). The CoP-WP/rGO demonstrates superior activity compared with the ever-reported WP-based HER catalysts (Table S1) [48–51], surpassing TM-doped WP electrocatalysts such as Co-WP (η_{10} = 119 mV) and Mo-WP (η_{10} = 175 mV) [48]. In one sense, the above phenomenon implies that constructing a heterostructure improves the catalytic activity more effectively than doping Co in WP. The HER performance of the CoP-WP/rGO is also one of the best among the previously reported W-based and CoP-based catalysts (Tables S1 and S2) [48–55].

Tafel slopes were calculated (Fig. 3c) to elucidate the catalytic kinetic mechanism. The Tafel slopes are 125, 94, 74, 62, and 36 mV dec^{−1} for CoP-WP NPs, WP/rGO, CoP/rGO, CoP-WP/rGO, and Pt/C, respectively.

Figure 3 HER performance of the samples in 1 mol L^{−1} KOH electrolyte. (a) Linear sweep polarization curves at a scan rate of 5 mV s^{−1}, (b) comparison of overpotentials at current densities of 10, 50, 100, and 200 mA cm^{−2} of various electrocatalysts, (c) the corresponding Tafel plots of the electrocatalysts in (a), (d) estimation of C_{dl} by plotting the current density variation ($\Delta j = (j_a - j_c)/2$), (e) Nyquist plots of different electrodes with a frequency range from 0.01 Hz to 100 kHz, (f) polarization curves for CoP-WP/rGO before and after 2000 cycles of CV test. Inset: the current-time ($I-t$) curve of CoP-WP/rGO under a static overpotential for 30 h.

rGO, and Pt/C, respectively. The Tafel slope of CoP-WP/rGO is smaller than the three counterparts, implying the HER kinetics on the CoP-WP/rGO catalyst is faster. The Tafel slope illustrates a Volmer-Heyrovsky reaction pathway on CoP-WP/rGO, signifying the electrochemical desorption is the rate-determining step [56]. The decreased Tafel slope after combining with rGO highlights the effective facilitation of the hydrogen evolution kinetics. To further explore the intrinsic property of the CoP-WP/rGO, the exchange current density (j_0) was probed by extrapolating the Tafel plot. As shown in Fig. S12, the j_0 of CoP-WP/rGO is 0.342 mA cm^{-2} , which is much larger than those of CoP/rGO (0.215 mA cm^{-2}), WP/rGO (0.157 mA cm^{-2}), and CoP-WP NPs catalysts (0.135 mA cm^{-2}), indicating the superior H_2 evolution activity of the CoP-WP/rGO.

The enhanced HER electrocatalytic activity of CoP-WP/rGO is related to the electrochemically active surface area, which is linearly proportional to the double-layer capacitance (C_{dl}). Therefore, CV tests were performed in a non-Faradic potential region of 0.10 to 0.20 V *versus* RHE at different scan rates (Fig. S13). The C_{dl} was estimated by plotting the current density variation at 0.15 V *versus* the scan rate. As displayed in Fig. 3d, the CoP-WP/rGO has a high C_{dl} value of 124.3 mF cm^{-2} , higher than CoP/rGO (89.6 mF cm^{-2}) and WP/rGO (66.3 mF cm^{-2}). It is worth mentioning that the C_{dl} of CoP-WP/rGO is nearly 38 times as large as that of CoP-WP NPs (3.3 mF cm^{-2}), which is closely in agreement with the BET surface area results. The high C_{dl} value of CoP-WP/rGO indicates CoP-WP/rGO can offer abundant catalytic active sites, giving rise to the best HER performance. The EIS test was performed to explore the HER reaction kinetics. Fig. 3e shows the Nyquist plots of the different electrodes. The CoP-WP/rGO Nyquist plot shows the smallest semicircle among all tested materials, which means CoP-WP/rGO has the lowest charge transfer resistance (R_{ct}) at the electrode/electrolyte interface. The lowest R_{ct} value suggests the fastest charge transfer on the CoP-WP/rGO catalyst during the HER. The charge transfer ability enhancement of CoP-WP/rGO can be ascribed to incorporating high conductive rGO substrate. The durability of CoP-WP/rGO was investigated by the long-term CV cycles and chronoamperometric response test in 1.0 mol L^{-1} KOH. As shown in Fig. 3f, after 2000 CV cycles, the polarization curve almost overlaps with the original curve, suggesting excellent stability. The time-dependent current density curve exhibits almost constant current density after 30 h (inset in Fig. 3f), further illustrating the superior durability. After the durability test, no apparent changes emerge in the XRD pattern and XPS spectra (Figs S14 and S15). The crystal structure and chemical state are held, implying exceptional electrochemistry stability of CoP-WP/rGO.

A series of contrast samples were fabricated by changing the phosphating temperature and mass ratio of Co_8W_{18} and GO to explore their influences on the HER activity (Table S3). Compared with CoP-WP/rGO-700 and CoP-WP/rGO-900, the CoP-WP/rGO catalyst (calcinated at 800°C) exhibits the best HER activity with the smallest η_{10} and Tafel slope (Fig. S16), demonstrating the appropriate phosphating temperature is an essential factor in HER activity. The primary reason is that phosphating temperature can affect the degree of crystallinity and the sizes of particles. As shown in Fig. S17, the peak intensity increases, and the peak width gradually narrows along with increasing phosphating temperature. Too high phosphating temperature results in an electrical conductivity decrease, ver-

ified by the EIS test (Fig. S18). In further exploration, the HER performance of the relevant CoP-WP/rGO catalyst is also influenced by the mass ratio of Co_8W_{18} and GO. As displayed in Fig. S19, the peak at about 26.2° assigned to the (002) facet of graphitic carbon becomes weak and disappears as the loading amount of Co_8W_{18} increases. Meanwhile, the intensities of other peaks, especially the one located at 31.6° , are enhanced gradually with the rise of the loading content. When the mass ratio of Co_8W_{18} and GO is 1.5, CoP-WP/rGO catalyst shows the most excellent HER performance, given the lowest η_{10} and smallest Tafel slope (Fig. S20). The EIS test shows that the loading content has an impact on the electrical conductivity (Fig. S21). The above results illustrate that the catalytic activity toward HER is closely correlated with suitable phosphating temperature and loading mass.

Developing acidic media HER electrocatalysts is also a significant and valuable subject since the acidic environment is conducive to HER. Therefore, the HER activity of the CoP-WP/rGO sample was also investigated in 0.5 mol L^{-1} H_2SO_4 electrolyte. As shown in Fig. 4a, commercial Pt/C possesses outstanding activity with low overpotentials, aligning closely with the literature [56]. Apart from Pt/C, the CoP-WP/rGO represents the smallest η_{10} of 130 mV, while CoP/rGO, WP/rGO, and CoP-WP NPs need 159, 194, and 239 mV to reach a current density of 10 mA cm^{-2} , respectively (Fig. 4b). The Tafel slopes (Fig. 4c) of Pt/C, CoP-WP/rGO, CoP/rGO, WP/rGO, and CoP-WP NPs are 37, 54, 62, 78, and 124 mV dec^{-1} , respectively. The Tafel slope of CoP-WP/rGO is close to that of commercial Pt/C, indicating that CoP-WP/rGO undergoes a Volmer-Heyrovsky mechanism during the HER process. j_0 is another critical metric to evaluate the inherent HER electrocatalytic activity. CoP-WP/rGO has the largest j_0 of 0.0383 A cm^{-2} , which is higher than those of CoP/rGO ($0.0319 \text{ mA cm}^{-2}$), WP/rGO ($0.0207 \text{ mA cm}^{-2}$), and CoP-WP NPs ($0.0175 \text{ mA cm}^{-2}$), as shown in Fig. S22. The C_{dl} was calculated to explore the effective active surface area during the electrocatalytic process. The CV curves (Fig. S23) of different samples were tested at different rates from 10 to 50 mV s^{-1} . The C_{dl} of CoP-WP/rGO (Fig. 4d) is 109.1 mF cm^{-2} , which is far larger than that of CoP/rGO (76.9 mF cm^{-2}), WP/rGO (62.4 mF cm^{-2}), and about two orders of magnitudes higher than that of CoP-WP NPs (1.7 mF cm^{-2}). CoP-WP/rGO has the highest C_{dl} value, signifying the exposure of abundant active sites. As displayed in Fig. 4e, the Nyquist plot shows the smallest semicircle for CoP-WP/rGO, indicating that it holds a much smaller R_{ct} , in contrast to the CoP/rGO, WP/rGO, and CoP-WP NPs. The smallest R_{ct} endows CoP-WP/rGO with efficient electron transport and catalytic kinetics, giving rise to high activity and low Tafel slope. After 2000 cycles of the CV test, no apparent change can be observed (Fig. 4f), which shows the high stability of CoP-WP/rGO in corrosive acidic electrolyte. Besides, CoP-WP/rGO exhibits excellent stability with negligible degradation over 30 h operation (Fig. 4f inset). The CoP-WP/rGO electrocatalyst possesses exceptional HER activity with a low overpotential, a small Tafel slope, a high exchange current density, and excellent stability in acidic electrolyte.

It is no wonder that HER electrocatalysts working in neutral or near-neutral electrolytes are of more practical significance given their potential application in seawater electrolysis and microbial electrolysis cell. In this regard, the HER performances in 1.0 mol L^{-1} PBS electrolyte were further evaluated. As seen in Fig. 5a, except Pt/C, CoP-WP/rGO performs very well in the

Figure 4 HER performance of the samples in 0.5 mol L⁻¹ H₂SO₄ electrolyte. (a) Linear sweep polarization curves at a scan rate of 5 mV s⁻¹, (b) the corresponding Tafel plots of the electrocatalysts in (a), (c) overpotentials at 10 mA cm⁻² of the electrocatalysts, (d) plots showing extraction of the double-layer capacitance (C_{dl}), (e) Nyquist plots of different electrodes with a frequency range from 0.01 Hz to 100 kHz, (f) polarization curves of CoP-WP/rGO before and after 2000 cycles of CV test. Inset: the I-t curve of CoP-WP/rGO for 30 h.

Figure 5 HER performance of the samples in 1.0 mol L⁻¹ PBS electrolyte. (a) Linear sweep polarization curves at a scan rate of 5 mV s⁻¹, (b) the corresponding Tafel plots of the electrocatalysts in (a), (c) C_{dl} values of different electrodes, (d) polarization curves for CoP-WP/rGO before and after 2000 cycles of CV test. Inset: the I-t curve of CoP-WP/rGO under a static overpotential for 30 h.

neutral HER, with about 138 mV to deliver 10 mA cm⁻² current density, which is much lower than that of CoP/rGO (254 mV), WP/rGO (249 mV), and CoP-WP NPs (392 mV). This confirms the vital function of heterojunction and hybridization with rGO. The Tafel slope (80 mV dec⁻¹) for CoP-WP/rGO is also lower than 143 mV dec⁻¹ for CoP/rGO, 135 mV dec⁻¹ for WP/rGO, and 198 mV dec⁻¹ for CoP-WP NPs (Fig. 5b). In this case, the exchange current densities of the above samples (Fig. S24) follow the same trend, j_0 (CoP-WP/rGO, 0.387 mA cm⁻²) > j_0 (WP/rGO, 0.199 mA cm⁻²) > j_0 (CoP/rGO, 0.189 mA cm⁻²) > j_0 (CoP-WP NPs, 0.154 mA cm⁻²). The lowest Tafel slope and the largest j_0 indicate CoP-WP/rGO is equipped with the most efficient kinetics toward HER. In addition, EIS was tested to gain further insight into electrode kinetics. As shown in Fig. S25, CoP-WP/rGO possesses the smallest semicircle, suggesting the lowest charge transfer resistance and the fastest charge transfer. The charge transfer capacity of CoP-WP/rGO is far beyond that of CoP-WP NPs, mainly due to its high conductivity inherited from rGO, apart from the electronic interaction between CoP, WP, and rGO. Then, C_{dl} was used as the indicator to compare the electrochemical active surface areas. The C_{dl} of CoP-WP/rGO is evaluated as 51.9 mF cm⁻² (Fig. 5c and Fig. S26). The C_{dl} values of CoP/rGO, WP/rGO, and CoP-WP NPs are lower, i.e., 48.6, 49.3, and 1.8 mF cm⁻², respectively. The highest C_{dl} indicates CoP-WP/rGO holds the most exposed active sites. Catalytic durability is also an essential factor for applications. As observed in Fig. 5d, the polarization curve presents negligible degradation after successive 2000 cycles of CV test. The CoP-WP/rGO maintains the initial catalytic activity after continuous 30 h in 1.0 mol L⁻¹ PBS electrolyte.

Taking the characteristic structure and composition of CoP-WP/rGO as well as the performance differences between CoP-WP/rGO and the contrast samples into account, the excellent electrocatalytic activity of CoP-WP/rGO toward HER is stemmed from the following points. (1) The synergistic effect among CoP, WP, and rGO could modulate the electron density states to facilitate the adsorption and desorption of the active intermediates, thus boosting hydrogen evolution. (2) The introduction of rGO as carbon support could improve the electrical conductivity of the as-obtained material and offer a large specific surface area, which is essential to promote the HER. (3) The confinement effect of the rGO support could prevent the migration of the NPs, conducive to the uniform distribution of the two metal-phosphide NPs, leading to enhanced stability.

Density functional theory calculations were further used to explore the heterojunction effect on the electronic structure of electrocatalyst and the corresponding HER performance. The theoretical calculation details are described in the Supplementary information. Fig. 6a shows the geometric models of CoP, WP, and CoP-WP heterojunction. Generally, the hydrogen adsorption Gibbs free energy (ΔG_{H^*}) is an indicator of HER activity. The closer the ΔG_{H^*} value is to zero for HER catalysts, the better the kinetics. For instance, the standard Pt shows a moderate ΔG_{H^*} about -0.09 eV [6]. Therefore, the H^{*} adsorption energies on CoP, WP, and CoP-WP heterojunction surfaces were calculated. As shown in Fig. 6b, the $|\Delta G_{H^*}|$ values of the pristine CoP and WP are 0.250 and 1.029 eV, respectively. Contrastively, CoP-WP heterojunction exhibits a small $|\Delta G_{H^*}|$ value of 0.177 eV, demonstrating a low energy barrier for H adsorption/desorption on CoP-WP heterojunction during the HER process. The lowest $|\Delta G_{H^*}|$ value of CoP-WP heterojunc-

tion indicates the heterointerfaces are conducive to optimizing H^{*} adsorption ability, causing the elevated HER activity. Additionally, Fig. 6c demonstrates the density of states (DOS) of CoP, WP, and CoP-WP heterojunction across the Fermi level, which indicates the metallic nature of the catalysts, facilitating rapid electron transfer for HER. Moreover, CoP-WP heterojunction holds higher DOS near the Fermi level than CoP and WP, implying that the charge carrier density of CoP-WP heterojunction increases. The relatively high conductivity of CoP-WP heterojunction greatly conduces to fast electron transport during the electrocatalytic process, which is consistent with the results from EIS tests. The electron density difference is introduced to investigate the electronic structure modulation by the heterointerfaces. The electron redistribution occurs at the interface, where the electrons transfer from WP to CoP, closely agreeing with the XPS results. It is beneficial to optimizing hydrogen adsorption free energy. The SKP test was implemented to estimate the work function (WF) values of the catalysts. As displayed in Fig. 6d and Fig. S27, the WF values of CoP-WP/rGO, WP/rGO, CoP/rGO, and CoP-WP NPs are 5.676, 5.751, 5.543, and 4.902 eV, respectively. The WF value of CoP-WP/rGO approaches that of Pt (5.680 eV) [42]. CoP-WP/rGO possesses exclusive ability to trap the electrons as Pt, perhaps accounting for the boosted HER catalytic activity. After comparing the WF values of the above samples side-by-side, it turns out that both the formation of the heterojunctions and the coupling with rGO substrate tailor the electronic structure of the CoP-WP/rGO, generating active sites for HER.

CoP-WP/rGO is coupled with NiFe-LDH/NF to explore its practicability for overall water splitting. NiFe-LDH/NF is chosen given its remarkable OER activity [57,58]. For comparison, Pt/C/NF and RuO₂/NF are assembled into a two-electrode electrolyzer. As shown in Fig. 6e, the CoP-WP/rGO/NF||NiFeLDH/NF electrolyzer shows remarkable activity for overall water splitting with a low cell voltage of 1.55 V to drive a current density of 10 mA cm⁻², which is very close to Pt/C/NF||RuO₂/NF electrolyzer. The CoP-WP/rGO/NF||NiFeLDH/NF at large current density displays higher catalytic performance (η_{20} = 1.60 V, η_{50} = 1.72 V) than Pt/C/NF||RuO₂/NF (η_{20} = 1.62 V, η_{50} = 1.77 V) and other previously reported catalysts (Table S4). The electrolyzer can be driven by a solar cell with 1.554 V (Fig. 6e, inset). In addition, the chronoamperometric curve (Fig. 6f) shows negligible degradation after continuous 30 h operation, indicating the long-term stability of CoP-WP/rGO/NF||NiFeLDH/NF. The excellent activity and durability endow it with practical application potential to convert low-voltage electricity into chemical energy.

CONCLUSIONS

In conclusion, we propose a powerful strategy to construct CoP-WP heterojunctions anchored on rGO (CoP-WP/rGO) with multi-coupled interfaces by utilizing a POM-based polynuclear cobalt molecular cluster (Co₈W₁₈) as a precursor. The precise ratio of CoP to WP can be achieved through inheriting the metal atom ratio from Co₈W₁₈. The CoP-WP/rGO improves HER performance with the low overpotentials and long durability in alkaline, acidic, and neutral electrolytes. The enhanced electrocatalytic performance can be ascribed to the abundant “multi-touch” CoP-WP heterointerfaces, where electron redistribution occurs, leading to the optimized free energy of adsorbed hydrogen (ΔG_{H^*}). This work offers a valuable reference for the

Figure 6 (a) Geometric models of CoP, WP, and CoP-WP heterojunction. (b) Free-energy diagram of $|\Delta G_H^*|$; (c) DOS of CoP, WP, and CoP-WP heterojunction system. (d) The WF drawings of CoP, WP, and CoP-WP heterojunction. (e) Polarization curves for CoP-WP/rGO/NF||NiFeLDH/NF and Pt/C/NF||RuO₂/NF in 1 mol L⁻¹ KOH. Inset: digital photograph of solar panel-assisted water splitting device. (f) *I-t* curve of CoP-WP/rGO/NF||NiFeLDH/NF for 30 h.

fabrication of multi-interface contacted heterostructure catalysts for electrocatalysis.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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具有多触点界面的CoP-WP/rGO异质结助力宽pH析氢

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摘要 界面工程是一种通过调整电子结构提高催化活性的有效手段。然而, 构建具有紧密接触界面的异质结仍然面临巨大的挑战。本研究工作中, 我们引入具有确定结构的多酸基多核钴分子团簇 Co_8W_{18} 作为前驱体, 构建了紧密接触的多重界面耦合的CoP-WP异质结。通过在氧化石墨烯上生长 Co_8W_{18} , 磷化处理后获得了锚定在还原氧化石墨烯上的CoP-WP异质结(CoP-WP/rGO)。 Co_8W_{18} 中固有的{Co-O-W}配位模式有利于形成紧密接触的界面。X射线光电子能谱分析和理论计算证实了CoP-WP异质结中丰富的紧密接触界面促进了电子从WP向CoP的转移, 从而调节了界面电子结构, 优化了氢吸附自由能(ΔG_{H^+})。与氧化石墨的复合使得CoP-WP/rGO具有大的表面积和高的电导性, 有利于物质传输和电荷转移。因此, CoP-WP/rGO在碱性、酸性和中性介质中皆表现出显著增强的HER活性, 在 10 mA cm^{-2} 下过电位分别为96、130和138 mV。这项工作为设计具有多触点界面的异质结材料用作低成本和高效HER电催化剂提供了一种新策略。