Phosphorus-doped MoS₂ with sulfur vacancy defects for enhanced electrochemical water splitting

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ABSTRACT MoS₂ is a promising electrocatalyst because of its natural abundance and outstanding electrochemical stability. However, the poor conductivity and low activity limit its catalytic performance; furthermore, MoS₂ is unable to satisfy the requirements of most industrial applications. In this study, to obtain a P-doped MoS₂ catalyst with S vacancy defects, P is inserted into the MoS₂ matrix *via* a solid phase ion exchange at room temperature. The optimal P-doping amount is 11.4 wt%, and the resultant catalyst delivers excellent electrocatalytic properties for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) with the corresponding overpotentials of 93 and 316 mV at 10 mA cm⁻² in an alkaline solution; these values surpass the overpotentials of most previously reported MoS₂-based materials. Theoretical calculations and results demonstrate that the synergistic effect of the doped P, which forms active centers in the basal plane of MoS₂, and S vacancy defects caused by P doping intensifies the intrinsic electronic conductivity and electrocatalytic activity of the catalyst. Density functional theory calculations demonstrate that P optimizes the free energy of the MoS₂ matrix for hydrogen adsorption, thereby considerably increasing the intrinsic activity of the doped catalyst for the HER compared with that observed from pristine MoS₂. The enhanced catalytic activity of P-doped MoS₂ for the OER is attributed to the ability of the doped P which facilitates the adsorption of hydroxyl and hydroperoxy intermediates and reduces the reaction energy barrier. This study provides a new environmentally friendly and convenient solid-phase ion exchange method to improve the electrocatalytic capability of two-dimensional transition-metal dichalcogenides in large-scale applications.

Keywords: molybdenum disulfide, phosphorus doping, sulfur vacancy defects, overall water splitting, electron redistribution, density functional theory calculations

INTRODUCTION

The continued depletion of fossil fuels (e.g., oil and coal) and exacerbation of environmental pollution and greenhouse effect have highlighted the requirement to identify solutions to the current energy crisis [1–3]. Researchers accelerated the search for novel energy sources to simultaneously alleviate the energy crisis and realize economic development and environmental protection [4–6]. Hydrogen energy is generally considered an advanced green energy source that could potentially replace traditional fossil fuels because of its high efficiency, environmental friendliness, and renewability [7]. Electricity-driven water splitting is extensively recognized as an efficient, simple, and inexpensive approach to generate large amounts of pure hydrogen energy [8,9]. Electrocatalysts can reduce the kinetic overpotential required for the oxygen (OER) and hydrogen (HER) evolution reactions and ultimately improve the efficiency of water decomposition; therefore, these materials are recognized as the most important components of electricity-driven water-splitting technology [10,11]. Although RuO₂ and Pt/C are acknowledged to be the most effective electrocatalysts for the OER and HER, respectively, the commercial applications of these compounds are severely limited by their scarcity and high cost [12–14]. Hence, for electrocatalysis, the development of a highly active, naturally abundant, and cost-effective electrocatalyst without noble metal-based compounds is an important subject.

MoS₂, a representative two-dimensional (2D) transitional metal dichalcogenide (TMD), has received considerable attention because of its abundant resources, high electrochemical stability, and low cost [15]. Because the theoretical free energy of MoS₂ for hydrogen adsorption during the electrocatalytic process is similar to that of Pt, the former is an ideal candidate for HER catalyst [16–19]. Excellent OER performance over MoS₂ is indispensable to achieve efficient overall water splitting. However, because of the low activity and conductivity of the catalyst, the OER over MoS₂ is rarely considered. In theory, the edge of the valence band of MoS₂ is more positive than the oxidation

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potential of water; thus, the compound should exhibit OER activity [20]. Exploration of a suitable method to strengthen the catalytic activity of MoS₂ for the HER and OER could encourage the development of overall water splitting. Heteroatom doping is known as a suitable strategy to ameliorate the electrochemical properties of MoS₂ [21–23]; several efforts have been reported to modulate the electronic structure of MoS₂ and modify the electronic density of Mo to reduce the hydrogen-adsorption free energy for high HER performance [24,25]. Compared with those of pristine MoS₂ [26,27], the electronic conductivity and HER catalytic activity of the MoS₂ matrix are effectively strengthened by the introduction of P atoms.

The solid phase ion exchange method was used to fabricate a P-doped MoS₂ catalyst with S vacancy defects. Compared with conventional methods, such as electrospinning [28], thermal annealing [29], and hydrothermal technique [30], solid-phase ion exchange does not involve solvents, and the preparation process is shorter, more environmentally friendly, and safer. Accordingly, its large-scale production complies with the principle of sustainable development. As shown in Scheme 1, the optimized catalyst was prepared *via* a two-step procedure at room temperature. MoS₂ and black phosphorus (BP) powder were ball-milled with grinding balls to achieve a high-energy non-equilibrium state and intensify the diffusion of atoms. During grinding, S atoms in the MoS₂ lattice left their equilibrium position because of the high energy of the reaction system, thereby forming S defects. Some of the available vacancies were then filled with P atoms to obtain P-doped MoS₂ with S vacancy defects. Both experimental and theoretical results demonstrate that the synergistic effects between P active sites and S vacancy defects could simultaneously intensify the electrical conductivity and optimize the adsorption free energy for hydrogen-/oxygen-containing intermediates, thereby improving the performance of the resultant electrocatalyst. The catalyst demonstrated excellent HER (Table S1) and OER performance.

Moreover, for overall water splitting, in a two-electrode system with P-doped MoS₂ as the cathode and anode electrodes, a cell voltage of only 1.59 V was required to achieve a current density of 10 mA cm⁻² (Table S2).

RESULTS AND DISCUSSION

As shown in Fig. 1a, the phase compositions of BP, pristine MoS₂, ball-milled MoS₂ (BM-MoS₂), and P-doped MoS₂ were confirmed by X-ray diffraction (XRD). Without P doping, all the observed Bragg peaks of pristine MoS₂ and BM-MoS₂ correspond to the hexagonal phase of 2H-MoS₂ (JCPDS Card No. 37-1492). The XRD pattern of the as-obtained P-doped MoS₂ was similar to that of undoped MoS₂, and no new diffraction peak was observed. The high intensity of the (002) diffraction peak indicated the layered structure of P-doped MoS₂. The comparison of the positions of the (002) diffraction angles of different samples demonstrate that the diffraction angle of P-doped MoS₂ is slightly shifted toward a smaller angle (Fig. 1a, inset). As per Bragg's law, the interlayer distance of P-doped MoS₂ increases from 0.613 (pristine MoS₂) to 0.629 nm. This increase in interlayer distance may be attributed to the larger atomic radius of P compared with that of S. The introduction of P atoms in the MoS₂ matrix results in lattice expansion, which increases the interlayer spacing. We observed that the diffraction peak intensity of BM-MoS₂ is significantly weaker than that of pristine MoS₂. Compared with the intensities of the diffraction peaks of BM-MoS₂, those of P-doped MoS₂ were reduced further, thereby indicating that the latter not only exhibits higher structural disorder but also features vacancy defects [21].

Fig. 1b shows the Raman spectra of pristine MoS₂, BM-MoS₂, and P-doped MoS₂. The pristine MoS₂ and BM-MoS₂ display two strong peaks at 372 and 399 cm⁻¹, which correspond to the in-plane E_{2g}¹ and out-of-plane A_{1g} vibration modes. Moreover, weak peaks in the range of 200–600 cm⁻¹ were observed. After P doping, the two characteristic Raman peaks of the catalyst

Scheme 1 Schematic of the solid phase ion exchange system to prepare P-doped MoS₂.

Figure 1 (a) XRD patterns, (b) Raman spectra and (c) XPS of P-doped MoS₂, BM-MoS₂, and pristine MoS₂. High-resolution XPS of (d) Mo 3d, (e) S 2p, and (f) P 2p of pristine MoS₂, BM-MoS₂, and P-doped MoS₂.

shifted to 381 and 406 cm⁻¹. The decrease in peak difference of P-doped MoS₂ (i.e., 25 cm⁻¹) compared with that of the undoped samples (i.e., 27 cm⁻¹) indicates a reduction in the number of layers of the former, which facilitates the contact between active sites in the catalyst and the electrolyte, thereby enhancing catalytic activity [21]. Compared with other samples, the intensity of the E_{1g} peak in P-doped MoS₂ is weaker, thus confirming the presence of vacancy defects in the crystal structure.

X-ray photoelectron spectroscopy (XPS) was performed to determine the detailed valence states and chemical compositions of the as-synthesized catalyst. Fig. 1c shows the XPS spectra of pristine MoS₂ and BM-MoS₂ indicating the presence of Mo, S, C, and O. In addition to these elements, P was identified in the XPS spectrum of P-doped MoS₂. The presence of O in the samples may be attributed to the adsorbed O₂ or CO₂ and partial oxidation in air. The C 1s peak recorded at ~284.6 eV could be assigned to the carbon in the apparatus, and this peak was used for calibration. In the high-resolution XPS spectra of MoS₂ and BM-MoS₂, the characteristic peaks of Mo 3d_{3/2} and Mo 3d_{5/2} (Fig. 1d) and S 2p_{3/2} and S 2p_{1/2} (Fig. 1e) are at 232.3, 229.1, 161.9, and 163 eV, respectively. These results agree with the previous values reported for 2H-MoS₂ [31]. The binding energies for S 2p and Mo 3d in P-doped MoS₂ are higher than those recorded for pristine MoS₂ [32,33]. Because three 3p orbitals of P are occupied by only three electrons (i.e., the orbitals are in a half-filled state), the resulting atomic energy is extremely low. When P loses an electron, it must absorb a large amount of energy. By comparison, the S atom has four electrons in its 3p orbitals. When three electrons occupy the 3p orbitals, the fourth electron must be paired with one of the remaining three electrons; however, because electrons repel each other, the atomic energy of the element increases. Therefore, compared with P atoms, S atoms require much less energy to lose an electron. When non-metallic P atoms are introduced to MoS₂, certain

electrons transfer from Mo and S to P (S atoms lose an electron more easily than P atoms), thus resulting in the positive shift of peaks in S 2p and Mo 3d. In the P 2p spectrum shown in Fig. 1f, the peaks of P 2p_{3/2} at 129.7 and P 2p_{1/2} at 130.5 eV correspond to a P–Mo bond [34], thus confirming that P was successfully incorporated in the crystal lattice of MoS₂. Peaks at 133.8 eV could be attributed to P–O resulting from surface oxidation. The XPS results demonstrate that P doping can effectively adjust the electronic structure of the catalyst and accelerate the electron transfer rate, which is conducive to improving the catalytic performance.

The surface morphology and microstructure of pristine MoS₂, BM-MoS₂, and P-doped MoS₂ were characterized using scanning electron microscopy (SEM). In Fig. S1, pristine MoS₂ aggregates and is tightly stacked in layers, thus resulting in poor exposure of its active sites. Fig. S2 and Fig. 2a, b show P-doped MoS₂ and BM-MoS₂ similarly stacked by well-defined thin layers. Ball milling could effectively prevent material aggregation and reduce the size of the layers, thereby increasing the contact area between the catalysts and electrolytes. Energy-dispersive X-ray spectroscopy (EDX, Fig. S3) and SEM elemental analyses (Fig. S4) demonstrate the uniform elemental distribution over P-doped MoS₂. The transmission electron microscopy (TEM) result of P-doped MoS₂ shown in Fig. 2c confirms the multilayered structure of the catalyst. The high-resolution TEM image shown in Fig. 2d shows a clear lattice structure with a certain degree of disorder and abundant vacancy defects, thus resulting in an incomplete (002) lattice (interplanar spacing, 0.631 nm) that could provide a large number of unsaturated S atoms as active sites. We then observed that the lattice fringes are partially curled, which could expose active sites. Large clusters or nanoparticles do not appear in TEM images, thus eliminating the possibility that MoP are formed on the surface of the catalyst, consistent with the XRD results. The TEM-EDX result shown in

Figure 2 (a, b) SEM, (c) TEM, and (d) high-resolution TEM images of P-doped MoS₂. (e) TEM elemental mapping of P-doped MoS₂. (f) Electron paramagnetic resonance measurements of pristine MoS₂, BM-MoS₂, and P-doped MoS₂ for S vacancy detection.

Fig. S5 and the corresponding elemental mapping of P-doped MoS₂ in Fig. 2e reflect the presence of Mo (in red), S (in green), and P (in yellow). The images confirm the even distribution of P along the MoS₂ sheets.

Electron paramagnetic resonance measurements were adopted to confirm the existence of S vacancy defects in the P-doped sample. As shown in Fig. 2f, compared with pristine MoS₂, which reveals weak signals, BM-MoS₂ and P-doped MoS₂ demonstrate resonance peaks at the *g* value of 2.01, which could be attributed to S vacancies. The relative peak intensity of P-doped MoS₂ is stronger than that of BM-MoS₂, which indicates the increased formation of S vacancy defects after P doping, in accordance with the XRD, Raman, and TEM results [35].

The catalytic potential of a material could be described by its specific surface area, which is an important evaluation parameter of its practical applications. Thus, to measure the surface area of the samples, N₂ adsorption-desorption isotherms were employed. As shown in Fig. S6, P-doped MoS₂ has a specific surface area of 4.98 m² g⁻¹, which is higher than that of pristine MoS₂ (1.59 m² g⁻¹). A large specific surface area is conducive to the contact between the exposed active sites of a material and the electrolyte, thereby accelerating the catalytic process [36].

The electrocatalytic OER and HER performance of P-doped MoS₂ with various BP/MoS₂ molar ratios (i.e., 1:1, 1:2, and 1:3) was evaluated using a three-electrode system in an alkaline medium at a scan rate of 5 mV s⁻¹ with 90% *iR* compensation. Fig. S7 shows that among the samples obtained, the one with a BP/MoS₂ molar ratio of 1:2 possesses the best OER and HER performance. As shown in Table S3, the inductively coupled plasma mass spectrometry test results show that the P contents of the three samples are 6.8, 11.4, and 17.6 wt%, respectively. As the P content of the doped samples increased, the catalytic performance of the resultant sample improved. When the molar ratio of BP/MoS₂ was 1:2 (P content = 11.4 wt%, Fig. S7), the sample obtained exhibited the highest catalytic activity. When the P content increased to 17.6 wt%, the electrocatalytic property of the resultant material decreased. As shown in Fig. S8, the

sample with 17.6 wt% P (i.e., MoS₂/Mo₈P₅) presented two new peaks at ~32° and 35°, which could be attributed to Mo₈P₅ (JCPDS Card No. 71-2263). This result shows that introduction of excess P atoms could generate new products, which results in a decline in the electrocatalytic activity of the target catalyst. Thus, the subsequent electrochemical tests were performed under the optimal BP/MoS₂ molar ratio (P content, 11.4 wt%).

The characteristics of BM-MoS₂, pristine MoS₂, BP, red phosphorous (RP), and RuO₂ were examined for comparison with those of P-doped MoS₂. The required overpotential of P-doped MoS₂ (316 mV) during linear sweep voltammetry (LSV) in 1.0 mol L⁻¹ KOH solution (Fig. 3a) was extremely similar to that of RuO₂ (310 mV) at 10 mA cm⁻². This overpotential is not as high as those of BM-MoS₂ (530 mV), pristine MoS₂ (620 mV), BP (380 mV), and RP (690 mV) under similar conditions. Importantly, P-doped MoS₂ demonstrated remarkable OER performance, even surpassing that of RuO₂, under high current densities.

The Tafel slope (89 mV dec⁻¹, Fig. 3b) derived from the LSV curve of P-doped MoS₂ was extremely low, thus confirming the superior OER kinetic properties of the catalyst. Indeed, the Tafel slope of this sample is smaller than those of RuO₂ (196 mV dec⁻¹), BM-MoS₂ (332 mV dec⁻¹), pristine MoS₂ (457 mV dec⁻¹), BP (185 mV dec⁻¹), and RP (363 mV dec⁻¹). The durability of a catalyst is an important criterion for its potential commercial applications. The LSV curves shown in Fig. 3c nearly overlap, thus demonstrating the long-term stability of P-doped MoS₂ in the OER. The enhanced durability of P-doped MoS₂ is supported by the data presented in the inset of Fig. 3c (Fig. S9). After 24-h testing in an alkaline medium, only a small increase in potential was reported. As shown in Fig. S10, the characteristic peaks of P-doped MoS₂ obtained after continuous OER stability testing completely correspond to those of the pristine sample without new phases. These results indicate that the basic structure of the doped sample is not damaged by testing, which indicates the doped material may be used long-term to catalyze the OER. The SEM images in Fig. S11

Figure 3 (a) OER polarization curves of RuO₂, P-doped MoS₂, BM-MoS₂, pristine MoS₂, BP, and RP in 1.0 mol L⁻¹ KOH solution. (b) Tafel plots of P-doped MoS₂, BM-MoS₂, pristine MoS₂, BP, RP, and Pt/C. (c) OER durability measurements of P-doped MoS₂ and the corresponding polarization curves before and after 3000 cyclic voltammetry (CV) cycles. (d) Polarization curves of Pt/C, P-doped MoS₂, BM-MoS₂, pristine MoS₂, BP, and RP for the HER in 1.0 mol L⁻¹ KOH. (e) Tafel plots of Pt/C, P-doped MoS₂, BM-MoS₂, pristine MoS₂, BP, and RP. (f) HER durability measurements of P-doped MoS₂ and the corresponding polarization curves before and after 3000 CV cycles.

demonstrate that the morphology of the doped sample did not change significantly after continuous OER stability testing.

The HER activity of P-doped MoS₂ was examined and compared with that obtained on other materials in an alkaline medium. The LSV curves in Fig. 3d show that P-doped MoS₂ exhibits good HER catalytic activity with an overpotential of as low as 93 mV to achieve a current density of 10 mA cm⁻². This overpotential is slightly inferior to that of commercial Pt/C (39 mV at 10 mA cm⁻²) but superior to those of BM-MoS₂, undoped MoS₂, BP, and RP (245, 260, 320, and 467 mV, respectively, at 10 mA cm⁻²). Fig. 3e shows the Tafel slopes of the investigated materials; this slope is an inherent parameter for assessing HER reaction kinetics. P-doped MoS₂ yielded a Tafel slope of 81 mV dec⁻¹, which is smaller than those obtained for pristine MoS₂, BP, and RP (116, 123, and 107 mV dec⁻¹, respectively). The LSV curves of P-doped MoS₂ were plotted over 3000 cycles to explore the stability of the catalyst. No variation compared with the original data was reported (Fig. 3f). Furthermore, only a small increase in overpotential was recorded at 10 mA cm⁻² after 24 h (Fig. 3f, inset). The XRD patterns in Fig. S12 show that the basic structure of P-doped MoS₂ remains nearly unchanged after electrochemical stability testing. As shown by the SEM, TEM, and high-angle annular dark field-EDX elemental mapping images in Fig. S13, the lamellar stacking morphology and elemental composition of the P-doped MoS₂ catalyst also hardly changed after long-term testing in an alkaline solution for the HER. The abovementioned characterization results demonstrate that P-doped MoS₂ presents outstanding stability in the HER.

Electrochemical impedance spectroscopy measurements are often used to explore the electric charge transfer properties of various catalysts at the electrolyte/electrode interface. In Fig. 4a, the R_{ct} value of P-doped MoS₂ was 97 Ω, which is lower than

those of pristine MoS₂ (135 Ω) and BP (361 Ω). This result indicates that the electron transport rate of P-doped MoS₂ is higher than that of the latter samples. Previous studies demonstrate that the exchange current density of MoS₂ depends on its electron transfer rate [8]. Fig. 4b, c demonstrate that the exchange current density of P-doped MoS₂ is higher than that of pristine MoS₂; thus, the electron transfer rate of the former is higher than that of the latter. The enhanced conductivity of P-doped MoS₂ could be explained by the following mechanism. The outer shell electrons of Mo and S atoms of pristine MoS₂ are constrained by covalent bonding. In this case, extremely few electrons could become free carriers by thermal excitation at room temperature, which indicates pristine MoS₂ has poor conductivity. When P is doped in MoS₂, certain P atoms replace S atoms. Because P atoms have one less outermost shell electron than S atoms, equivalent holes are introduced and MoS₂ becomes a so-called P-type dopant. When a certain electric field is applied to P-doped MoS₂, the holes act as free carriers and directionally migrate under the electric field. Thus, P-doped MoS₂ has higher conductivity than pristine MoS₂. This mechanism based on the aforementioned characterization results demonstrates that P doping could lead to electron redistribution in the MoS₂ matrix, thereby accelerating the electron transfer rate and improving the conductivity of the resultant material.

Electrochemical surface areas (ECSAs) are usually positively correlated with catalytic activity and are linearly proportional to the electrochemical double-layer capacitance (C_{dl}) in most cases. CV measurements were conducted at scan rates of 30–150 mV (Fig. S14) to collect capacitance data to evaluate the C_{dl} of the samples, and the corresponding calculations are discussed in detail in Supplementary information. In Fig. 4d, the C_{dl} of P-doped MoS₂ (34.5 mF cm⁻²) significantly increases compared

Figure 4 (a) Nyquist plots of P-doped MoS₂, pristine MoS₂, and BP. Exchange current densities of P-doped MoS₂ and pristine MoS₂ at an overpotential of 0 V for the (b) OER and (c) HER. (d) C_{dl} , (e) ECSAs of P-doped MoS₂, BM-MoS₂, pristine MoS₂, BP, and RP. (f) Schematic of electrocatalytic water splitting in alkaline medium with the corresponding reactions and standard potentials (OWS, overall water splitting). (g) Water electrolysis polarization curves of P-doped MoS₂ graphite sheet || P-doped MoS₂ graphite sheet at a 5 mV s⁻¹ scan rate in 1.0 mol L⁻¹ KOH solution. (h) Chronoamperometry curve of P-doped MoS₂ graphite sheet || P-doped MoS₂ graphite sheet (10 mA cm⁻², 30 h).

with those of BM-MoS₂ (25.8 mF cm⁻²), pristine MoS₂ (14.5 mF cm⁻²), BP (19.7 mF cm⁻²), and RP (18.6 mF cm⁻²). Moreover, Fig. 4e shows that P-doped MoS₂ possesses an ECSA of 862.5 cm², which is considerably larger than those of BM-MoS₂ (645 cm²), pristine MoS₂ (362.5 cm²), BP (492.5 cm²), and RP (465 cm²). The aforementioned results suggest that the introduction of P to the S vacancy defects in P-doped MoS₂ generates new effective active centers, which are beneficial to the adsorption and dissociation of water molecules and promote close contact between the catalyst and electrolyte.

Electrochemical water splitting refers to the process that water is broken down into its molecular components, namely, hydrogen and oxygen, *via* the application of a direct current (DC) voltage between two submerged electrodes. The process comprises two spatially separated half-reactions: the HER occurs at the negatively polarized cathode, whereas the OER occurs at the positively polarized anode (Fig. 4f). P-doped MoS₂ was used as the cathode and anode electrodes in a two-electrode system to assess the potential large-scale applications of the bifunctional catalyst for water splitting. Fig. 4g shows that P-doped MoS₂ || P-doped MoS₂ only required a cell voltage of 1.59 V to achieve a current density of 10 mA cm⁻² in a basic solution, thereby indicating the high electrocatalytic activity of the system. As shown in Fig. 4h, a chronopotentiometry test was performed for 30 h at 10 mA cm⁻² to characterize the water-splitting capability of the doped catalyst. The results of this test demonstrate that the optimized catalyst with S vacancy defects is a potential candidate material for catalyzing alkaline water electrolysis.

Density functional theory (DFT) calculations were applied to identify the role of P doping in improving the electrocatalytic activity of P-doped MoS₂. The lowest formation energy was considered (Fig. S15), and the model of MoS₂ with one P atom replacing one S atom was compared with that of pristine MoS₂, as shown in Fig. 5a, b. The partial density of states (PDOS) of P-doped and pristine MoS₂ (Fig. 5c, d) were analyzed to demonstrate the electron redistribution in the catalysts after P doping.

P doping clearly moved the conduction band closer to the Fermi level; certain electronic states of P-doped MoS₂ even crossed the Fermi level, thereby indicating higher intrinsic electrical conductivity compared with that in pristine MoS₂. This result indicates that charge transfer could easily occur during the electrocatalytic process over P-doped MoS₂, which is in good agreement with previous experimental and electrochemical measurement results.

Because HER activity is affected by the adsorption/desorption energetics of H* on the catalyst, the hydrogen adsorption free energy (ΔG_{H^*}) was used to assess the HER activity of the catalysts [37,38]. After structural optimization, H* demonstrated preferential adsorption on S in pristine MoS₂ and on P in P-doped MoS₂ (Fig. 5e, inset). As shown in Fig. 5e and Table S4, compared with pristine MoS₂ (1.62 eV), P-doped MoS₂ possessed a lower ΔG_{H^*} value of -0.14 eV, which is close to the ideal ΔG_{H^*} value of 0 eV. This result reveals that P-doped MoS₂ may easily overcome the reaction barrier compared with pristine MoS₂, thus confirming that P-doping can effectively enhance the HER performance of the catalyst.

Because the OER involves four proton-coupled electron transfer (PCET) steps, this reaction is more challenging to be catalyzed compared to the HER. As shown in Scheme 2, the free energy diagrams for the OER under high pH conditions ($4OH^- \rightarrow 2H_2O + O_2 + 4e^-$) comprise four typical PCET steps. Fig. 5f shows the energy diagrams for the four PCET steps of pristine (blue line) and P-doped (red line) MoS₂. All of the reaction steps of an ideal catalyst must be as close to 1.23 eV as possible [39]. The energy diagram for the PCET steps of pristine MoS₂ does not display the ideal “staircase” graph. As shown in Table S5, the reaction steps with the highest energies are the first (1.97 eV) and third (1.85 eV) steps. Because the binding energy of hydroxyl (HO*) and hydroperoxy (HOO*) intermediates to the substrate is very low, a high overpotential η is generated (Fig. 5g). In this case, pristine MoS₂ is not an ideal catalyst for the OER. If the binding energy of these intermediates on MoS₂

Figure 5 Atomic structures of (a) pristine and (b) P-doped MoS₂. Partial and total DOS of (c) pristine and (d) P-doped MoS₂ (Fermi level = 0). Standard free-energy diagrams for the (e) HER and (f) OER of pristine and P-doped MoS₂. (g) Adsorption geometries of the reaction intermediates of the OER on pristine and P-doped MoS₂.

Scheme 2 Four PCET steps of the OER in alkaline solution.

could be enhanced, the corresponding overpotential would be reduced, thereby improving the OER activity. When P is doped in the MoS₂ matrix, the reaction barrier is significantly reduced

during the steps of HO^{*} ($\Delta G = 1.65$ eV, $\eta = 0.42$ V) and HOO^{*} ($\Delta G = 1.79$ eV, $\eta = 0.56$ V). Moreover, as shown in Fig. S16, the d-band center (E_d) energy level of P-doped MoS₂ was calculated to be -0.76 eV, which is closer to the Fermi level compared with that of pristine MoS₂ ($E_d = -1.06$ eV). These results indicate that P doping facilitates the adsorption of oxygen intermediates. The calculation results show that P-doped MoS₂ has a stronger adsorption capacity for HO^{*} and HOO^{*} than pristine MoS₂, in accordance with the previous XPS results.

CONCLUSIONS

A new solid phase ion exchange method was employed to prepare P-doped MoS₂ with S vacancy defects. The proposed preparation process was convenient and time-saving, and no solvent or toxic substances were produced. The experimental electrochemical measurement and PDOS results demonstrate that P-doping could not only adjust the electronic structure of the MoS₂ matrix but also introduce S vacancy defects, thereby considerably enhancing the intrinsic electrical conductivity of the resultant material during the electrocatalytic process. As per the DFT calculations, the poor OER catalytic activity of pristine MoS₂ could be attributed to the weak binding of HO^{*} and HOO^{*} reaction intermediates to the substrate. We examined P-doping as a practical means to alter the binding energy of MoS₂

and reduce its overpotential for the OER. The DFT results demonstrate that the ΔG_{H^*} of P-doped MoS_2 is -0.14 eV, which is smaller than that of pristine MoS_2 (1.62 eV). Moreover, the ΔG for the OER on the doped catalyst is 1.79 eV, which is lower than that of the pristine material (1.97 eV). These values indicate that P doping could decrease the water dissociation energy barrier in an alkaline medium. The optimized P-doped MoS_2 catalyst with S vacancy defects exhibited excellent HER performance (an overpotential of 93 mV at 10 mA cm^{-2}) and OER catalytic activity (an overpotential of 316 mV at 10 mA cm^{-2}) in an alkaline medium. The prepared catalyst was used for overall water splitting and required a low cell voltage of only 1.59 V to achieve a current density of 10 mA cm^{-2} in a basic solution. The current work not only provides a comprehensive reference for the applications of TMD-based materials in the field of electrocatalysis, but also proposes a new method to obtain environmentally friendly catalysts.

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Author contributions Xue Hongyao and Li Z conceived the idea. Chen C and Wang C designed the experiments, collected and analyzed the data. Meng A assisted in the theoretical calculations, experiments and characterization. Xue Hongyan assisted in drawing the pictures. Xue Hongyao and Li Z co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

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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具有硫空位的磷掺杂二硫化钼用于增强电催化水分解

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摘要 由于其丰度高、电化学稳定性强, MoS₂被认为是一种极具前途的电催化剂。然而, 其导电性差和活性低, 因此催化性能受到限制。此外, MoS₂无法满足工业化大规模应用的要求。本工作中, 为了获得具有S空位缺陷的P掺杂MoS₂催化剂, 我们在室温下通过固相离子交换将P插入到MoS₂基体中。当P掺杂量为11.4 wt%时为最佳, 所制备的催化剂具有优异的电催化析氢(HER)和析氧(OER)性能。碱性条件下, 在10 mA cm⁻²电流密度下对应的过电位分别为93和316 mV, 这些数值超过了先前报道的大多数二硫化钼基材料的过电位。理论计算和实验结果都表明, MoS₂基面上形成的掺杂P活性中心及由P掺杂引起的S空位缺陷的协同作用增强了催化剂的本征电子电导率和电催化活性。密度泛函理论计算表明, 与原始的MoS₂相比, P优化了MoS₂氢吸附自由能, 从而显著提高了掺杂后催化剂对HER的固有活性。P掺杂MoS₂对OER的催化活性增强归因于掺杂P促进羟基和含氧中间体的吸附及反应能垒的降低。本研究提出了一种全新、环保、便捷的固相离子交换法来提高二维过渡金属硫化化合物在大规模应用中的电催化能力。