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Anion-Defect Engineering of Mo₂CO₂ MXenes for Site-Selective Hydrogen Binding in Hydrogen Evolution

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Abstract

MXenes are a novel family of 2D materials that have garnered significant interest in electrocatalytic applications due to their high conductivity, stability, and surface versatility. The present study explores the electrocatalytic properties of molybdenum-based MXenes (Mo₂CO₂) modified with sulfur (S), phosphorus (P), and oxygen vacancies (V_O) to optimise catalytic performance and promote hydrogen evolution reaction (HER) activity. Using first-principles calculations, we investigated the electronic structures and hydrogen adsorption behavior of these modified MXenes and benchmarked them against MoS₂ and MoP₃. Our findings reveal that the surface's S weakens H binding and activates neighboring HER-active sites, achieving near-total thermoneutrality ($\Delta G_{H^*} = +0.03$ eV). In contrast, P draws electron density from Mo and exerts a proton-attracting effect, thereby favouring H binding to P and enhancing HER activity. This study highlights the role of anion engineering in tailoring the electrocatalytic properties of MXenes for sustainable energy applications.

Key words: MXenes, Hydrogen Evolution Reaction, Anion-Defect Engineering, DFT

Introduction

Producing hydrogen from water and using it as an energy vector requires operating at an industrial scale and efficiently driving the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Catalysts are crucial for driving and enhancing the performance of these electrochemical reactions powered by renewable energy sources. Two-dimensional (2D) functional materials, such as molybdenum-based catalysts,¹⁻³ have garnered considerable attention in the field due to their excellent conductivity, high catalytic activity, and abundant active sites per area.⁴

MXenes, a new family of 2D transition metal carbides, nitrides, and carbonitrides ($M_{n+1}X_nT_2$; $M \in$ groups III to VI, and X is $\{C/N\}$ with $n=1-3$), are renowned for their tunable surface chemistry through functionalisation and defect engineering. These materials have recently emerged as promising materials with a variety of electrochemical applications, including supercapacitors,⁵ Li-ion battery electrodes,⁶ and electrocatalysts for the hydrogen^{7,8} and oxygen^{9,10} evolution reactions, and oxygen reduction reactions.¹¹ Owing to their high surface area, tunable electronic properties, and facile synthesis, MXenes with tailored compositions have demonstrated exceptional catalytic activity and stability.¹²

Pristine MXene surfaces are terminated with functional groups such as hydroxyl (-OH), oxygen (-O), and fluorine (-F) to compensate for the unsaturated surface charges. These terminations can be functionalised with diverse elemental compositions and stoichiometry, allowing the MXene's electronic structure to be tuned.^{13,14} Earlier studies suggest that surface oxygen vacancies (V_O) in MXenes play a crucial role in facilitating the formation of catalytic interfaces with noble (e.g., Pt, Au) and non-noble transition metal catalysts (e.g., Fe) and enhancing reaction kinetics by reducing overpotentials in HER,¹¹ CO₂RR,¹⁵ and eNRRt^{16,17} Heteroatoms such as sulfur (S) and phosphorus (P) can substitute anions in the surface terminations and modify the surface binding energies and electronic states of the 2D structures. In batteries, sulfur-doped MXene structures can effectively homogenise the distribution of electric fields, alleviate volume changes, and extend the lifespan of zinc-ion¹⁸ and sodium-ion batteries.¹⁹ Lin *et al.*'s recent experimental study demonstrated that N, S co-doping of MXenes formed a bridging structure to anchor Ir single atoms, enabling good dispersion of Ir metal.²⁰ This doped metal-MXene shows remarkable catalytic activity towards HER in both

acidic and alkaline electrolytes. Phosphate-doped MXenes (e.g., $\text{Ti}_3\text{C}_2\text{T}_x$) also exhibit enhanced supercapacitance.^{21, 22} Qu *et al.* proposed the phosphorised Mo_2CT_x MXenes as an earth-abundant HER electrocatalyst that offers a dramatic decrease in overpotential (more than 100 mV at 10 mA cm^{-2}) and significantly improves electrocatalytic performance.²³

Among mid-to-late metal MXenes, molybdenum carbide (Mo_2C) and its derivatives, such as Mo_2CO_2 , exhibit high conductivity, stability, and surface versatility.¹³ Extensive studies suggest that Mo-based compounds present high electrocatalytic activity and stability across a wide pH range, including strongly acidic, alkaline, and neutral solutions.^{3, 24} Besides, molybdenum disulfide (MoS_2) and molybdenum phosphide (Mo_3P) are prominent candidates for HER electrocatalysis due to their 2D layered structure and exposed active sites.^{1, 2, 25, 26, 27} In addition, MoS_2 -based catalysts have demonstrated remarkable stability and efficiency under HER conditions, further solidifying their potential in practical applications. Its robustness against corrosion and degradation ensures prolonged catalytic performance, a crucial property for its swift implementation. According to Kondori *et al.*, $\text{Mo}_3\text{P}(110)$ exhibits excellent HER activity and shows promise as an oxygen reduction (ORR) and evolution reaction (OER) catalyst.²⁸ Therefore, Mo-based materials are considered promising candidates for replacing expensive Pt-based catalysts in industry.

However, there is still limited understanding of how the anionic surface environment and defects in MXenes affect the HER activity. Specifically, the presence of anions such as sulfur (S), phosphorus (P), and oxygen vacancies (VO) can significantly alter the electronic properties of catalytically active sites. These modifications can influence hydrogen adsorption and desorption, thereby affecting the overall efficiency and stability of the HER. Understanding the precise role of these anion defects is crucial for optimising the catalytic performance and designing effective Mo-based electrocatalysts. In-depth studies of the interactions among anions, defects, and Mo metal atoms are essential to elucidate their impact on catalytic behaviour and to guide the development of next-generation electrocatalysts.

In this study, we used atomistic simulations based on density functional theory (DFT) to explore the effects of S and P doping and the presence of oxygen vacancies on the electronic structures and electrocatalytic properties of Mo-based MXenes. A

comparative study with MoS₂ and Mo₃P was also conducted to understand the role of Mo's local anion environment on HER activity. The insights gained contribute to the rational design of efficient non-precious-metal electrocatalysts for sustainable energy conversion technologies.

Computational Methods

First-principles calculations were carried out using the plane-wave VASP package.²⁹ The exchange-correlation functional employed was the Perdew-Burke-Ernzerhof (PBE) generalised gradient approximation (GGA).³⁰ The electronic wave functions were described using the projector-augmented wave (PAW)³¹ method with a plane-wave cutoff energy set to 500 eV. The valence electron configurations considered in this work are Mo 4d⁵6s¹, Pt 5d⁹6s¹, C 2s²2p², O 2s²2p⁴, S 3s²3p⁴, P 3s²3p³, and H 1s¹. The ionic and electronic convergence criteria during structural relaxation were set to 0.01 eV/Å and 1×10⁻⁵ eV, respectively. The DFT-D3 dispersion correction of Grimme *et al.* was implemented to account for long-range interactions.³²

The pristine MXene structures were modelled by removing the interlayer metal from the corresponding MAX phases and inserting a 20 Å vacuum layer along the z-direction. All calculations for the hexagonal unit cells of the 2D MXene structures were performed on a 12×12×1 Γ -centred k-point grid. Details for the MoS₂ and Mo₃P models are given in the Supporting Information. In addition, solvation effects for hydrogen adsorption on the MXene structures were incorporated using the VASPsol implicit solvation model with the dielectric constant of water ($\epsilon = 78.3$) to simulate the aqueous electrochemical environment.

The slabs' work functions were determined by comparing the differences between each substrate's vacuum level and Fermi level. Bader charge^{33, 34} and Crystal Orbital Hamilton Populations (COHP)³⁵ analyses were carried out to understand the hydrogen adsorption behaviour on the substrates. The formation energies of sulfur (S) and phosphorus (P) defects on the substrate surface containing O-vacancies were calculated as follows (Eq 1):

$$E_{\text{def}} = (E_{\text{sub}} + 1/2E_{\text{O}_2}) - (E_{\text{MX}} + E_{\text{S/P}}), \quad (1)$$

where E_{sub} is the total energy of the S/P-doped Vo-Mo₂CO_{2-x} substrate, E_{MX} is the energy of the Mo₂CO₂ model, and $E_{\text{S/P}}$ is the energy of an S/P atom in H₂S and H₃P

molecules derived by subtracting the corresponding number of ground state energies of H₂. The $1/2E_{O_2}$ term in Eq 1 accounts for the energy of a single O atom derived from the ground state energy of molecular oxygen.

To evaluate the thermal stability of defective MXene structures under realistic conditions, ab initio molecular dynamics (AIMD) simulations were performed in the NVT ensemble with the Nosé-Hoover thermostat. The simulations ran for 4.0 ps with a time step of 1.0 fs.

For hydrogen adsorption studies on MXene surfaces, a 2x2x1 supercell was employed. The H coverage investigated spans from 1/4 ML to 1 ML. The Gibbs free energy change for hydrogen adsorption (ΔG_{H^*}), a crucial HER activity descriptor,^{13, 18} was calculated as follows (Eq 2):

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S, \quad (2)$$

where ΔE_{H^*} is the adsorption energy of a hydrogen atom, ΔZPE is the zero-point energy correction obtained from vibrational frequency calculations of the adsorbed hydrogen species. $T\Delta S$ represents the entropy contribution, where ΔS is half the standard entropy of H₂ gas at 298 K obtained from standard thermodynamic databases. A ΔG_{H^*} value close to 0 eV indicates a thermoneutral reaction and, thus, better catalytic performance for the HER.

Results and discussion

1. Surface Anion Defects in Mo-based MXenes surfaces

To determine the most stable configuration of Mo₂CO₂, we considered four O-termination configurations based on the pristine Mo₂C MXene structure, as illustrated in **Figure S1**. Based on their relative stabilities, a symmetric hcp O-terminated (BB) Mo₂CO₂ is the most favourable configuration (**Table S1**). To understand the influence of surface anion defects, we construct MXene structure models with oxygen vacancies and S/P surface defects, as shown in **Figure 1**.

Based on the three defective models, the defect formation energies are summarised in **Table S2**. The formation energy of an O-vacancy in the hcp-O terminated Mo₂CO₂ is estimated to be +3.86 eV (**Table S2**) when removing 1/8 of the surface O. Bader

charge analysis reveals that forming the oxygen vacancy reduces the charge state of surrounding Mo atoms from +1.62 to +1.11 e (Table S4). Incorporating an S or P atom into the O-vacancy (S-Mo₂CO_{2-x} and P-Mo₂CO_{2-x}) could stabilise the structure compared to the oxygen-deficient Vo-Mo₂CO_{2-x}; however, it is still less stable than the fully hcp O-terminated Mo₂CO₂. The S and P defect formation energies are +1.66 eV (relative to S in H₂S) and +3.38 eV (relative to P in H₃P). The heteroatoms on the O-vacancies occupy the hcp sites of Mo. The Mo-S and Mo-P bond lengths are 2.39 and 2.45 Å, respectively, close to those in MoS₂ and Mo₃P (Table S4). The charge density differences in Figure 1 are for S-Mo₂CO_{2-x} and P-Mo₂CO_{2-x} and suggest significant charge redistribution due to the dopant, particularly between the Mo and P heteroatoms.

AIMD simulations have been carried out to assess the thermal stability of the three defective MXene models at room temperature. As shown in Figure S2, the total energies of V_O-Mo₂CO_{2-x}, S-Mo₂CO_{2-x}, and P-Mo₂CO_{2-x} systems exhibit only minor fluctuations around their equilibrium values throughout the simulation time. S-Mo₂CO_{2-x} exhibits slightly larger fluctuations than P-Mo₂CO_{2-x} at the beginning; however, the energy stabilises after ~1500 fs, consistent with a thermally equilibrated system. Therefore, no abrupt energy changes or structural instabilities were observed, indicating that all three defective models maintain robust structural integrity at room temperature.

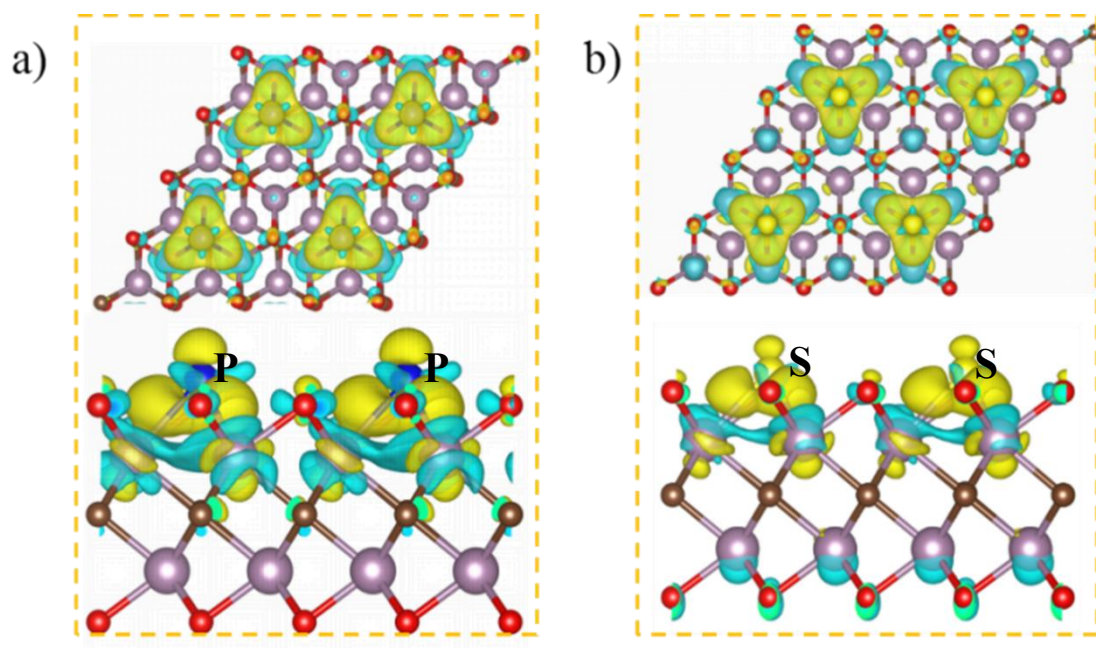


Figure 1. Charge density differences for P and S at the oxygen vacancy (Vo) site on the

Mo₂CO₂ structure. Yellow spheres represent V_O defects and S/P atoms substitution sites, cyan spheres represent Mo atoms, and red spheres represent the surface oxygen atoms. The yellow and cyan electron density isosurfaces ($\pm 0.005 \text{ e } \text{\AA}^{-3}$) represent gain and loss, respectively.

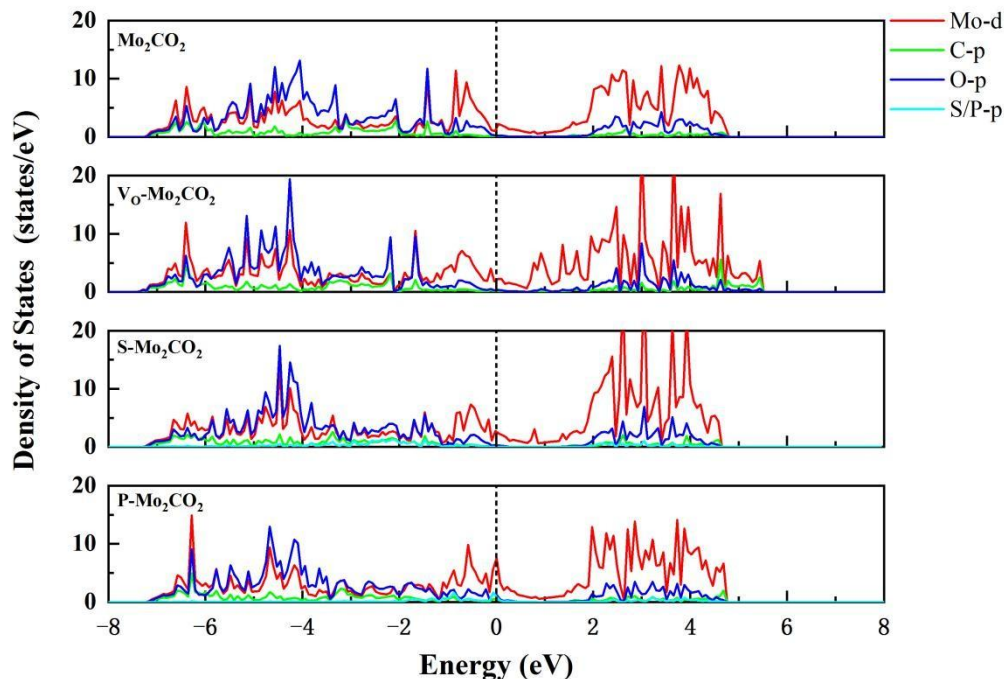


Figure 2. Projected density of states for Mo₂CO₂, V_O-Mo₂CO_{2-x}, and S- and P-doped Mo₂CO_{2-x} structures.

Figure 2 compares the projected density of states (PDOS) for the investigated Mo-based MXenes. It can be seen that all these Mo-based MXenes are metallic. The pristine Mo₂CO₂ (*i.e.* O-terminated) exhibits a substantially higher work function ($\Phi = 7.37 \text{ eV}$) and a more negative Fermi energy ($E_F = -4.29 \text{ eV}$) than the original Mo₂C ($\Phi = 4.96 \text{ eV}$). Introducing oxygen vacancies (Mo₂CO_{1.75}) reduces the work function marginally to 7.29 eV, whereas S dopants have minimal impact on the work function and the Fermi energy. P doping raises the Fermi energy to -3.86 eV and increases the density of states (DOS) at E_F , thereby improving electrical conductivity.

We also constructed the surfaces of MoS₂ and Mo₃P, enabling comparison of the HER catalytic activity of Mo-based compounds under different anionic environments. MoS₂ is a 2D material, whereas Mo₃P is not, for which several low-energy surfaces were optimised and represented in **Figure S3**. **Table S3** presents the surface energies

of different low-index Mo₃P surfaces, in which the (110) surface of Mo₃P shows the lowest surface energy, chosen for further HER studies. The results of the geometric and electronic calculations of MoS₂ and Mo₃P are summarised in **Table S4**.

MoS₂ has a higher work function (5.32 eV) and a higher Fermi level than pristine Mo₂C, while the Mo₃P (110) surface has a significantly lower work function (4.13 eV) than Mo₂C. For MoS₂, the upward shift in the Fermi energy aligns with its reduced-dimensional conductivity, as evidenced by a diminished DOS near E_F. In contrast, Mo₃P(110) exhibits metallic behaviour, with a pronounced density of states at the E_F (**Figure S4**).²⁸ Both the work function and density of states (DOS) at the Fermi level (E_F) are critical electronic descriptors for HER activity. The modulation of Φ directly correlates with the interfacial electron-transfer efficiency. Lower work function values tend to reduce the energy barrier for proton adsorption. High DOS occupancy near E_F enhances electrical conductivity by providing abundant delocalised electrons for charge transfer during Volmer steps. Therefore, the electronic structures of P-Mo₂CO_{2-x} and Mo₃P suggest that phosphatised Mo structures facilitate electron transfer, thereby substantially improving electrical conductivity and catalysing redox reaction kinetics.

2. HER Catalytic Properties of Mo-based compounds

The HER catalytic mechanism involves the desorption from the surfaces. Hence, starting from the dissociative adsorption of H₂, a smooth HER energy profile requires the adsorption energy (ΔG_{H^*}) to be close to zero. A positive ΔG_{H^*} value indicates an unfavourable interaction between the hydrogen and the catalyst, hindering adsorption and favouring desorption. Conversely, a ΔG_{H^*} value that is too negative indicates an excessively strong interaction between the adsorbed hydrogen and the catalyst surface, hindering hydrogen desorption. Typically, a $|\Delta G_{H^*}|$ value below +0.20 eV indicates a promising HER catalyst.³⁶ The calculated HER reaction pathways on the Mo-based compound are summarised in **Figure 3**. The related H adsorption sites and configurations are illustrated in **Figure S5**.

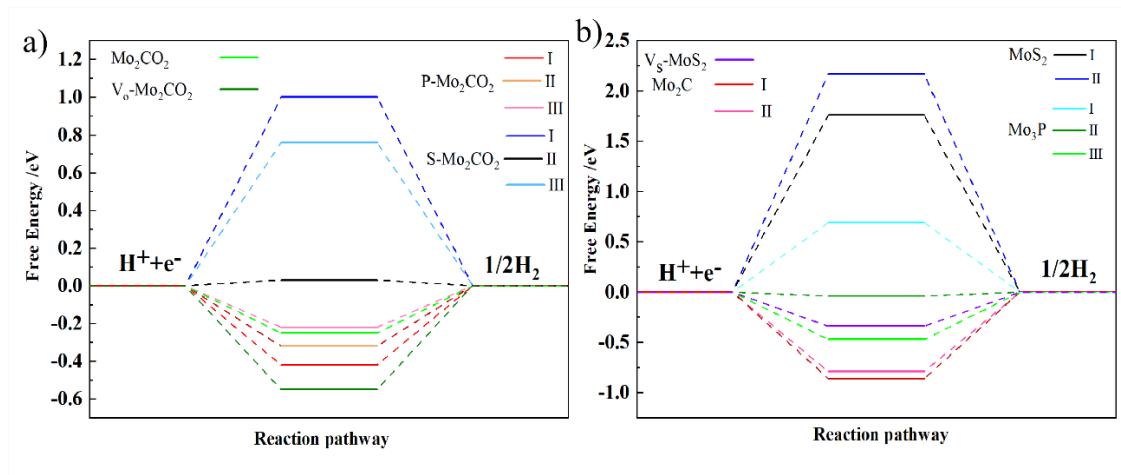


Figure 3. HER energy profiles on Mo₂CO₂, V₀-Mo₂CO_{2-x}, S- and P-Mo₂CO_{2-x} (a) and Mo₂C, MoS₂, V_s-MoS₂ and Mo₃P substrates with the different adsorption sites (b).

The only exothermic site for H adsorption on Mo₂CO₂ is site II (O_{sur}), with a ΔG_{H^*} of -0.25 eV. The presence of an oxygen vacancy (V_O-Mo₂CO_{2-x}) makes the H binding to the surface's unsaturated Mo stronger (ΔG_{H^*} of -0.55 eV). The S-doped surface shows positive ΔG_{H^*} values of +1.00 eV and +0.76 eV at sites I and III, respectively, promoting deprotonation; however, at neighbouring oxygens (site II), the ΔG_{H^*} of +0.03 eV is close to ideal. The P-doping enhances H adsorption (ΔG_{H^*} of -0.42 eV), with hydrogen preferentially adsorbing on the P top site (site I). The bridging site between P and Mo (site III) shows slightly weaker H adsorption than pristine Mo₂CO₂ (site II), with ΔG_{H^*} values of -0.22 eV (site III) and -0.32 eV (site II), respectively. **Figure 3a** displays the HER energy profiles for Mo₂CO_{2-x}, S- and P-Mo₂CO_{2-x} at pH = 0. These active sites have been tested and verified by VASPsol calculations (**Figure S7**), which yielded nearly identical results, and the relative order of H binding energies remains unchanged.

By comparison, MoS₂ and Mo₃P exhibit lower ΔG_{H^*} values (**Figure 3b**). MoS₂ exhibits large positive ΔG_{H^*} values at both sites I and II, indicating that adsorption of atomic hydrogen is unlikely. However, creating an S vacancy (V_S) on MoS₂ can significantly lower ΔG_{H^*} to -0.34 eV. For Mo₃P (110), the considered active sites were site I (P atom), site II (sub-layer Mo2 atom), and site III (outer-layer Mo1 atom), as shown in **Figure S5**. The positive ΔG_{H^*} of +0.69 eV required to form the H-P bond involves H pulling the P atom upward from the outer layer, resulting in consequent Mo-

P bond elongation. The bridging sites between two outer-layer Mo1 atoms are H's most stable adsorption sites ($\Delta G_{H^*} = -0.47$ eV), yet the adsorption sites located between the outer-layer Mo1 and sub-layer Mo2 exhibit near-neutral H absorption ($\Delta G_{H^*} = -0.04$ eV), suggesting that the presence of sub-layer Mo in Mo₃P could facilitate HER activity.

Given that extensive previous studies have shown that H coverage affects HER performance,³⁷ We further considered the impact of increasing H coverage on MXene surfaces. When a monolayer of H atoms (1 ML) covers the Mo₂CO₂ surface, ΔG_{H^*} rises slightly to +0.23 eV per hydrogen atom. For P-Mo₂CO_{2-x}, placing an H atom per surface Mo (1 ML) resulted in three H atoms around the P atom moving closer to form an H₃P structure, with a P-H bond length of 1.43 Å. Another H atom moved to the top site of the adjacent oxygen atom, as shown in **Figure 4**. The calculated ΔG_{H^*} also increased to +0.21 eV. When 1 ML of H was placed on S-doped Mo₂CO₂, H₂S ($d(\text{S-H}) = 1.35$ Å) was formed regardless of both O(S) and Mo binding sites.

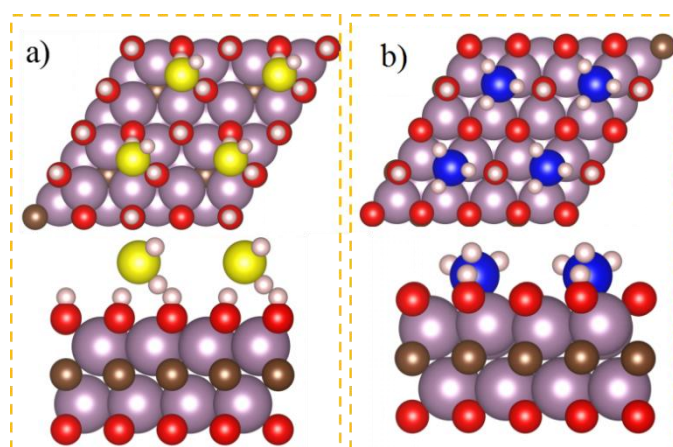


Figure 4. 1 ML coverage of H adsorption on the a) S and b) P-doped Mo₂CO_{2-x}. (Mo atoms in purple, C atoms in brown, O atoms in red, S atoms in yellow, P atoms in blue)

As H coverage increased over MoS₂, H atoms began to desorb as H₂. In the presence of S vacancies in Vs-MoS_{2-x}, a small ΔG_{H^*} value of +0.02 eV was observed when two H atoms dissociated at vacancy sites and formed bonds with exposed Mo (**Figure S8**). The exposed Mo at the S vacancy site further reduced ΔG_{H^*} , thereby enhancing HER activity. For Mo₃P(110), ΔG_{H^*} is calculated to be -0.29 eV (per atom) with an H coverage of 1 ML.

Regarding bare Mo₂C and V_O-Mo₂CO₂ (**Figure S8**), for Mo₂C, placing an additional H next to the hollow site (site II) on Mo shows strong H adsorption ($\Delta G_{H^*} = -0.78$ eV). When coverage increased, excess H atoms were shown to adsorb on the top sites of neighbouring Mo atoms ($\Delta G_{H^*} = -0.39$ eV). A similar weakening effect of hydrogen adsorption was observed on V_O-Mo₂CO_{2-x}, causing pairs of adjacent H atoms to evolve as H₂. At longer distances, Mo-H bonds were formed at hollow sites ($\Delta G_{H^*} = -0.07$ eV).

In summary, Mo-based MXenes exhibit significant potential as catalysts for the HER. S-doped Mo₂CO_{2-x} tends to deprotonate but also promotes its neighbouring O_{sur} as HER active sites. A similar deprotonation effect was observed for Vs-MoS₂, where unsaturated Mo was shown to play a crucial role in the moderate adsorption of H. P-doping leads to stronger H adsorption on the surface P in Mo₂CO_{2-x}. In contrast, for Mo₃P(110), the sublayer Mo provides HER-active sites. The formation of Mo-H bonds, with a ΔG_{H^*} of only -0.04 eV, suggests ideal HER catalytic activity.

To further investigate the hydrogen adsorption behaviour of Mo-based compounds, the bonding nature and charge transfer between the adsorbate and substrate were examined in detail. As shown in **Figure 5**, crystal orbital Hamilton population (COHP) analysis was conducted for H adsorption on S/P-doped Mo₂CO_{2-x}. It can be seen that all the H-O/S/P bonding pairs exhibit antibonding states above the Fermi energy, resulting in highly negative ICOHP values. In contrast, Mo-H bonding pairs show much higher ICOHP values and certain occupied antibonding states, suggesting weaker bonds. Bader charge analysis revealed a significant charge transfer from adsorbed H to the surface anions in P-doped Mo₂CO_{2-x}, compared with S-doped Mo₂CO_{2-x}. The oxidation states of the H atoms at neighbouring O sites (site I) of S/P defects were shown to be +0.31 and +0.41 e, respectively, with a typical O-H bond length of 0.91 Å, whereas H at the S/P defect top sites (site II), the H charge states are +0.11 and +0.21 e; For H located at the bridging sites of Mo and S/P (site III), the formation of Mo-H bonds suggests significant charge transfer from Mo to H (-0.41 vs. -0.59 e) and charge redistribution around the S/P defect (**Table S4**).

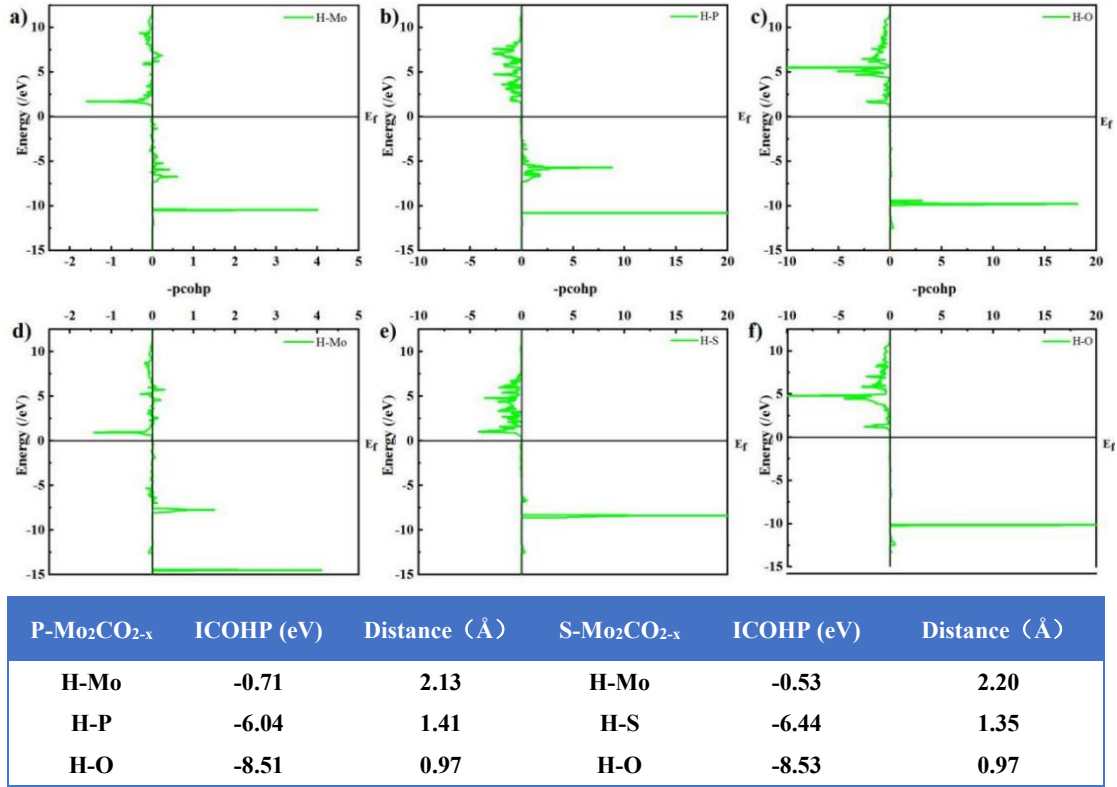


Figure 5. COHP analysis for H adsorption on MXene substrates: a) H-Mo bond, b) H-P bond and c) H-O bond on the P-Mo₂CO_{2-x}; d) H-Mo bond, e) H-S bond and f) H-O bond on the S-Mo₂CO_{2-x}. ICOHP values and bond lengths for H adsorption are listed in the above table.

Figure S7 compares COHP for the H-Mo(P) bonding pairs at the Mo₃P(110) and V_s-MoS₂ surface. On Mo₃P(110), the H-Mo bond formed with the sub-layer Mo2 (site II in **Figure S5**) shows a significant antibonding occupation below the Fermi energy, indicating the instability of the bond ($\Delta G_{H^*} = -0.04$ eV). Bonds formed between H and outer layer Mo1 are stronger than those those formed with sub-layer Mo, namely, the lower ICOHP value is in accordance with the increase in H adsorption energy. The H-Mo bonding states scatter in a range of -2.5 to -7.5 eV respect the Fermi energy. For H-P bonding pairs, the COHP plot exhibits two peaks of strong bonding states at -6 eV and -12 eV, similar to P-doped MXenes. Exposed Mo in V_s-MoS_{2-x} was shown to form moderately strong Mo-H bonds. Bader charge analysis suggests stronger charge transfers from H adsorbates to the exposed Mo atoms of V_s-MoS_{2-x} and Mo₃P compared to the S/P doped MXenes.

The features of Mo-H bonds formed on various Mo-based substrates are summarised in **Table S4**. In the presence of V_O/S/P defects in Mo-based MXenes, the Mo charge states (around +1.10 e) are significantly reduced compared to those in

Mo₂CO₂ (+1.62 e). In contrast, the bonds in Mo₂C, MoS₂ and Mo₃P proved to be more covalent than those formed by Mo in oxygen-terminating MXenes; an observation that can be rationalised by the difference in electronegativity between the anions (i.e., O > S > C > P). High levels of charge transfer were observed between exposed Mo atoms and adsorbed H atoms on Mo₂C, V_s-MoS_{2-x} and Mo₃P(110) surfaces with lower work functions (**Table S2**). Surface sulfurising was shown to inhibit electron transfer from Mo to H and induce a deprotonation effect. In contrast, surface P tended to attract adsorbed H atoms on Mo, causing an elongation of the H-Mo bond. This suggests that exposing the Mo sublayer and the presence of surface P are pivotal to enhancing the HER activity of Mo-based catalysts.

Conclusions

In this work, we investigated the electrocatalytic properties of Mo-based MXenes and their P/S doped structures and compared them with MoS₂ and Mo₃P. We conducted a comprehensive analysis of how S/P doping and vacancy effects influence HER catalytic activity, incorporating both kinetic and electronic structure studies. The key findings of our work are summarised as follows:

- V_O-Mo₂CO_{2-x} and V_S-MoS_{2-x} exhibit active Mo sites in the presence of surface O/S vacancies, leading to considerable HER activity.
- Owing to the deprotonating effect of surface S, sulfurised Mo₂CO_{2-x} weakens hydrogen binding on neighbouring O atoms at defect sites, leading to an almost thermoneutral ΔG_{H^*} of +0.03 eV. In contrast, S vacancies in V_S-MoS_{2-x} serve to enhance H adsorption on exposed Mo atoms.
- Increasing H coverage on the S/P-doped MXenes leads to the formation of H₂S and H₃P as S and P atoms are extracted from the substrate.
- P-doped Mo₂CO_{2-x} promoted H binding to P atoms rather than to surface O atoms. Surface P in Mo₃P(110) was shown to attract charges from neighbouring sub-layer Mo atoms, resulting in moderate Mo-H bonding and superior HER activity.

In summary, S/P-doped Mo₂CO_{2-x}, V_S-MoS_{2-x} and Mo₃P show great potential as non-PGM catalysts for HER. The combination of theoretical calculations and defect engineering offers insights into designing efficient Mo-based electrocatalysts for

sustainable hydrogen production.

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Author contributions

X. X and A. R. conceived the idea. Y. L. and Y. Z. carried out the DFT calculations under X.X.'s supervision. M. Q., A. R., Y. F., and C. X. contributed to the results and discussion sections. X.X. and Y. L. drafted the manuscript, which was then revised by M. Q. and A. R. All authors contributed to the final manuscript.

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