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# Engineering the electronic structure towards enhanced performances of CO<sub>2</sub> adsorption and conversion of a Ti-doped MoS<sub>2</sub> monolayer: a DFT study

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The active site of MoS<sub>2</sub>, predominantly located at the crystalline edge, limits selectivity for the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). Single-Atom Catalysts (SACs), have emerged as a promising avenue to enhance the catalytic performance of MoS<sub>2</sub>, owing to their high catalytic selectivity on the basal plane and tunable activity in various chemical reactions. In this regard, transition metals from the 8B and 1B groups (Cr, Cu, Sc, Ti, V, and Ni) were investigated as dopants on the basal plane for the first time, employing first-principles calculations based on a 4 × 4 × 1 supercell of the MoS<sub>2</sub> monolayer. The Ti/MoS<sub>2</sub> catalyst was identified as the most stable among the SACs, attributed to its optimal formation energy. Various Ti-doped models were analyzed, encompassing energy band structure, density of states, charge differential density, Bader charge, and Gibbs free energy. Our findings indicate that Ti induces diminished electron binding, thereby weakening C=O with lower energy, consequently enhancing the availability of surface sites and facilitating catalytic reactions. In our investigation of possible reaction pathways, the preferred CO<sub>2</sub>RR pathway was identified as the reverse water gas conversion (RWGS), with the rate-limiting step being CO<sub>2</sub> hydrogenation into carboxyl (\*COOH). The Ti modification model on the MoS<sub>2</sub> basal surface demonstrated exceptional catalytic performance, reducing the rate-limiting step to 0.177 eV, which is 17 times lower than that of pure MoS<sub>2</sub>. These calculational results provide valuable theoretical insights for designing highly efficient SACs on MoS<sub>2</sub>-based functional materials.

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## 1 Introduction

The escalating emission of greenhouse gases (GHGs) has led to significant detrimental effects on Earth's climate systems, driving urgent demand for efficient CO<sub>2</sub> capture and conversion technologies.<sup>1</sup> This urgency has catalyzed the development of advanced carbon capture and utilization (CCU) technologies, among which the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) stands out for its dual capacity to mitigate emissions and generate value-added carbon-based products (*e.g.*, CH<sub>4</sub>, CH<sub>3</sub>OH).<sup>2</sup> Central to CO<sub>2</sub>RR efficiency is the intricate interplay between CO<sub>2</sub> adsorption energetics and intermediate desorption kinetics on catalyst surfaces—a dynamic process governed by the modulation of electronic structure and atomic-scale site specificity.<sup>3–5</sup>

Two-dimensional (2D) transition metal dichalcogenides (TMDs), particularly molybdenum disulfide (MoS<sub>2</sub>), have

emerged as versatile platforms for CO<sub>2</sub>RR due to their tunable band structures (1.2–1.9 eV), layer-dependent conductivity, and propensity for defect engineering.<sup>6–9</sup> Unlike graphene's homogeneous π-electron system, the anisotropic d-orbital configuration of MoS<sub>2</sub> enables selective activation of CO<sub>2</sub>'s degenerate molecular orbitals.<sup>10</sup> However, intrinsic limitations persist: the basal plane exhibits weak CO<sub>2</sub> physisorption (*E*<sub>ads</sub> < 0.3 eV), while catalytically active edge sites constitute <5% surface coverage in conventional synthesis.<sup>11,12</sup>

To overcome the limitations of pristine MoS<sub>2</sub> in CO<sub>2</sub> reduction, chemical doping has emerged as an effective strategy to reconfigure its electronic structure and unlock new catalytic functionalities. Noble metals (*e.g.*, Au, Pt, Pd, Ag) reduce the bandgap and facilitate charge transfer, while transition metals (TMs) such as Cu, Fe, and Ni introduce localized electronic states near the Fermi level, enabling direct interaction with CO<sub>2</sub>'s antibonding orbitals and modulating the d-band center.<sup>13–15</sup> These dopants not only enhance CO<sub>2</sub> chemisorption but also reshape intermediate binding energies. For instance, Cu doping increases CO<sub>2</sub> adsorption by up to 200%, attributed to synergistic surface area expansion and charge redistribution.<sup>16</sup> Fe dopants, *via* Fe 3d–C 2p orbital

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hybridization, weaken the C=O bond, achieving  $\Delta E_{\text{ads}} \approx -1.2$  eV.<sup>17</sup> Furthermore, Ni-doped MoS<sub>2</sub> demonstrates altered spin polarization and charge transfer dynamics that influence catalytic selectivity.<sup>18</sup> *In situ* spectroscopic studies reveal that even minor shifts in charge density ( $\Delta\rho < 0.1$  e<sup>-</sup> Å<sup>-3</sup>) at active sites can lead to over 50% changes in product selectivity, highlighting the catalytic sensitivity to local electronic environments.<sup>19</sup> In addition, a recent systematic investigation demonstrated that substitutional doping at both Mo and S sites strongly modulates the work function of MoS<sub>2</sub>, with Ti and Nb identified as the most effective dopants for enhancing electronic responsiveness.<sup>20</sup>

Despite these advances, balancing CO<sub>2</sub> adsorption with controlled CO desorption remains a persistent challenge that limits catalyst performance and product selectivity. While reduced energy barriers for CO<sub>2</sub> activation are often desirable, excessively facile \*CO desorption can hinder further reduction steps, resulting in accumulation of CO as a by-product. Lv *et al.*<sup>21</sup> showed that doped MoS<sub>2</sub> structures with enhanced surface charge densities lower reaction barriers, yet compromise \*CO retention required for deeper reduction. Similarly, vertical Nb-doping reported by Abbasi *et al.* promotes CO desorption but restricts C–C coupling pathways.<sup>22</sup> Conversely, strategies aimed at increasing \*CO desorption barriers—such as transition metal doping designed by Li *et al.*—successfully suppress CO evolution, enabling longer cascade reactions.<sup>23</sup> These findings underscore the importance of fine-tuning \*CO binding energies to balance catalytic activity and selectivity. However, most existing studies focus on isolated descriptors (*e.g.*, adsorption energy or conversion), without a holistic view of how dopant characteristics simultaneously influence both CO<sub>2</sub> capture and conversion steps.

To address this critical gap, we employ first-principles density functional theory (DFT) to systematically evaluate a set of transition metal dopants (Cr, Cu, Sc, Ti, V, Ni) in MoS<sub>2</sub>, targeting dual-functionality in CO<sub>2</sub> reduction. Among these, Ti emerges as the most promising candidate, offering the lowest formation energy and a favorable electronic environment for CO<sub>2</sub> activation. We conduct a comprehensive comparison of three distinct Ti doping configurations—sulfur substitution, molybdenum substitution, and interlayer intercalation<sup>24,25</sup>—revealing clear structure–function relationships among dopant positioning, Bader charge transfer, and activation barriers. Furthermore, our detailed reaction pathway analysis elucidates the CO<sub>2</sub>-to-CO conversion mechanism on Ti/MoS<sub>2</sub>, identifying rate-limiting steps and quantifying \*CO desorption energetics. Our study offers a unified design framework that links dopant physicochemical properties with catalytic performance, providing critical insights for the development of next-generation MoS<sub>2</sub>-based CO<sub>2</sub>RR catalysts with optimized capture–conversion synergy.

## 2 Computational approach

In order to ensure the simulation was sufficiently large that an adsorbed gas molecule was not affected by nearby gas molecules, a periodic (4 × 4 × 1) supercell of the MoS<sub>2</sub> monolayer

was modelled. The MoS<sub>2</sub> monolayer was composed of 16 Mo and 32 S atoms.<sup>26</sup> It should be noted that to avoid interlayer interactions, a vacuum layer of 15 Å was constructed in the direction from the interface to the isolated slab boundary condition.

We conducted all calculations using CASTEP on the DFT theory plane-wave pseudopotential method for exploring the electronic and structural properties.<sup>27</sup> Electronic interaction energies were computed employing the generalized gradient approximation (GGA) functional and the Perdew–Burke–Ernzerhof (PBE) functional.<sup>28</sup> Here, the cutoff energy was set to be 500 eV, and the *k*-point grids used were 6 × 6 × 1.<sup>29</sup> We set the convergence criteria for the optimization of energy, remaining stress, and force to be 0.01 meV per atom, 0.05 GPa, and 0.01 eV Å<sup>-1</sup>, respectively.<sup>30</sup> The long-range dispersion correction (DFT-D2) method, proposed by Grimme, was selected to modify the effects of the van der Waals interactions in all the constructed models.<sup>31,32</sup> The total energy was converged to <10 meV. All calculations were performed using the same relaxation criteria.

The validity of the calculation can be established by comparing the formation energy of the M-doping model. The formation energy ( $E_f$ ) served as a metric to evaluate the feasibility of dopant integration and the stability of the doped system within the lattice, as outlined in eqn (1):<sup>33</sup>

$$E_f = \left( E_{\text{doped}} - \sum n_{\text{doped}} \mu_{\text{doped}} \right) - \left( E_{\text{pure}} - \sum n_{\text{superseded}} \mu_{\text{superseded}} \right) \quad (1)$$

where  $E_{\text{doped}}$  and  $E_{\text{pure}}$  are the total energy of doped and pure MoS<sub>2</sub> models, respectively.  $n_{\text{doped}}$  and  $n_{\text{superseded}}$  represent the number of doped and superseded elements.  $\mu_{\text{doped}}$  and  $\mu_{\text{superseded}}$  refer to the chemical potential of doped and superseded elements. For metal elements,  $\mu_{\text{Mo}}$ ,  $\mu_{\text{Cr}}$ ,  $\mu_{\text{Cu}}$ ,  $\mu_{\text{Sc}}$ ,  $\mu_{\text{Ti}}$ ,  $\mu_{\text{V}}$ , and  $\mu_{\text{Ni}}$  were defined as the total energy of metal divided by the number of atoms in bulk. For non-metallic elements,  $\mu_{\text{S}}$  was obtained by putting the most stable element in a 10 Å × 10 Å × 10 Å cube box, respectively.

In terms of adsorption energy, the greater the absolute value of adsorption energy on the surface, the better the adsorption performance of CO<sub>2</sub>. The formula is as follows:

$$E_{\text{ads}} = E_{\text{gas+surface}} - E_{\text{gas}} - E_{\text{surface}} \quad (2)$$

where  $E_{\text{gas+surface}}$  and  $E_{\text{gas}}$  are the calculated energies of the model after adsorption of the CO<sub>2</sub> on the surface and the free CO<sub>2</sub> molecule, respectively.

## 3 Results and discussion

### 3.1 Properties of Ti-doped MoS<sub>2</sub> monolayer

To identify suitable dopants for MoS<sub>2</sub> in CO<sub>2</sub> hydrogenation, we focused on 3d transition metals (Cr, Cu, Sc, Ti, V, and Ni) due to their propensity to modulate the electronic structure of the host catalyst. The practical feasibility of doping hinges critically on the thermodynamic stability of the doped structure. Therefore, we first computed the formation energy ( $E_f$ ) for each candidate,



Table 1 Formation energy of M1/MoS<sub>2</sub>

Dopant	Formation energy (eV)	Dopant	Formation energy (eV)
Cr	-3.45	Ti	-3.93
Cu	-0.29	V	-3.88
Sc	-2.54	Ni	-2.27

as presented in Table 1. Among them, Ti doping exhibits the most negative formation energy, indicating its most stable incorporation into the MoS<sub>2</sub> lattice.

Although V and Cr also show reasonably low formation energies, the difference from Ti remains sufficient to suggest that Ti is the most thermodynamically favorable dopant under comparable conditions. For this reason—and to allow a focused mechanistic analysis—we selected Ti as the representative dopant for detailed electronic, adsorption, and reaction-pathway investigations. This computational selection aligns with and provides a theoretical foundation for experimental observations of Ti's enhanced catalytic performance.<sup>34–36</sup> The comparative study of other dopants with similar stability (e.g., V, Cr) is considered an interesting direction for future work. Fig. 1(a) depicts the relaxed structure of MoS<sub>2</sub> obtained in this study, while Fig. 1(b–d) illustrates the Ti-doped and decorated structures. Overall, the influence of doping and decorating on the MoS<sub>2</sub> structure was observed to be minimal. Doping agents remain centered between neighboring atoms, and the positions of Mo and S atoms within the structure exhibit minor changes. The calculated Mo–S bond length and Mo–Mo distance in pristine MoS<sub>2</sub> were determined to be 2.400 Å and 3.167 Å, respectively, and were consistent with theoretical data (2.420 Å and 3.190 Å).<sup>37,38</sup> Additionally, the angle of the S–Mo–S bonds in the optimized pure MoS<sub>2</sub> was calculated to be 82.548°, showing reasonable agreement with theoretical and experimental data.<sup>39–41</sup> In this regard, the calculation method and parameters used for modeling MoS<sub>2</sub> were appropriate. Table 2 reveals that the  $E_f$  values for all Ti-doped MoS<sub>2</sub> surfaces are negative, indicating an exothermic process. We considered all potential sites on the basal plane. In this context, 1Ti-MoS<sub>2</sub> denotes MoS<sub>2</sub> with a Ti atom substituting for a Mo atom, 2Ti-MoS<sub>2</sub> represents MoS<sub>2</sub> with a Ti atom replacing an S atom, and

Table 2 Structure formation energy and atomic details of different doping sites. ( $\Delta_{\text{Ti-X}}$  represent the distance between the Ti atom and its nearest neighbor atom;  $\theta_{\text{O=C=O}}$  is the angle between the Ti atom and its two nearest neighbors)

Structure	$E_f$ , eV	$\Delta_{\text{Ti-X}}$ , Å	$\theta_{\text{X=Ti=X}}$ , °
MoS <sub>2</sub>	*	*	*
1Ti-MoS <sub>2</sub>	-9.15	2.415	83.718
2Ti-MoS <sub>2</sub>	-3.93	2.611	73.609
3Ti-MoS <sub>2</sub>	-3.81	2.319	89.510

3Ti-MoS<sub>2</sub> signifies MoS<sub>2</sub> with a single Ti atom modifying the surface. Among them, given the comparable ionic radii of Ti<sup>4+</sup> and Mo<sup>6+</sup>, the incorporation of Ti dopant into the lattice induced subtle deviations in the lattice parameters; nevertheless, the observed alterations were deemed negligible in magnitude. In contrast, 2Ti-MoS<sub>2</sub> and 3Ti-MoS<sub>2</sub> are challenging to synthesize compared to 1Ti-MoS<sub>2</sub>, owing to differences in ionic radius and doping site. However, overall, they still provide indications of thermodynamic stability.

It is important to clarify the purpose of studying these less-favorable configurations: they are not presented as the most readily synthesizable structures, but as critical models to elucidate the structure–property relationship. The comparative analysis of 1Ti, 2Ti, and 3Ti-MoS<sub>2</sub> allows us to isolate the effect of Ti coordination environment—from fully coordinated lattice substitution to under-coordinated surface sites—on the electronic structure and catalytic activity.

To unveil the electronic structure changes in doped MoS<sub>2</sub> on the basal plane, DFT calculations were conducted for pure MoS<sub>2</sub> and three distinct doping systems at various sites. Fig. 2 shows the band structure and partial density of states (PDOS) of all the models. The results indicate that the band gap of pure MoS<sub>2</sub> is 1.735 eV, consistent and reliable compared to previous calculations.<sup>42</sup>

Additionally, Fig. 2(b) illustrates that the Mo 4d and S 3p states constitute the conduction and valence bands of pure MoS<sub>2</sub>, respectively. In the case of 1Ti-MoS<sub>2</sub>, the Ti 3d state exhibits a slight peak change in the band gap, as depicted in Fig. 2(c and d). Despite Ti replacing Mo, the system undergoes insignificant changes due to the similar atomic radius and the

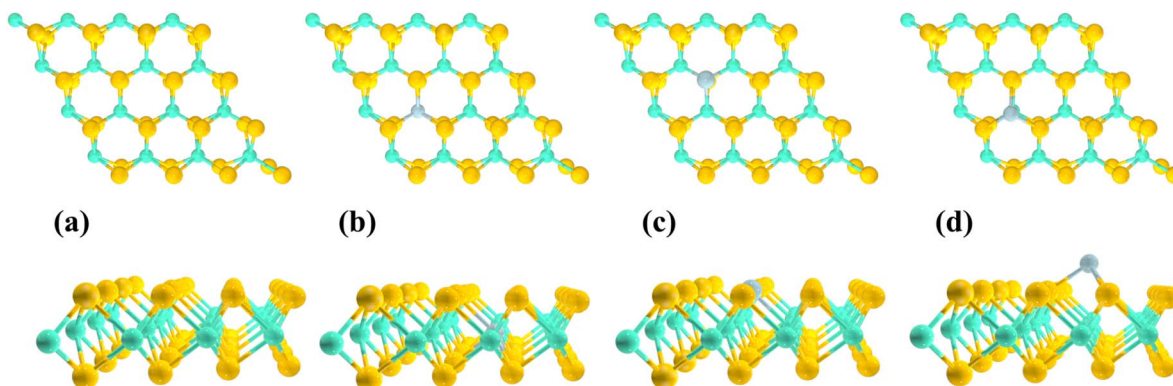


Fig. 1 (a) The top and side views of the optimized pure MoS<sub>2</sub> monolayer, (b and c) the MoS<sub>2</sub> monolayer doped with one Ti atom, and (d) the MoS<sub>2</sub> monolayer decorated with one Ti atom. Here, the light green, yellow, and gray circles represent Mo, S, and Ti atoms, respectively.



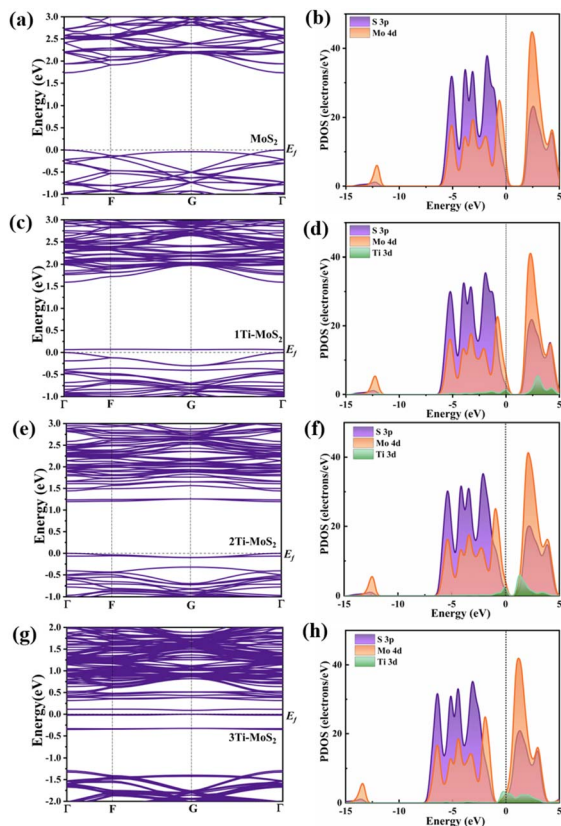


Fig. 2 Band structure and PDOS of (a and b)  $\text{MoS}_2$ ; (c and d)  $1\text{Ti-MoS}_2$ ; (e and f)  $2\text{Ti-MoS}_2$ ; (g and h)  $3\text{Ti-MoS}_2$ . The dash lines are Fermi level. The energy is referenced to the Fermi level ( $E_F$ ), which is indicated by the dashed line at 0 eV.

same number of valence electrons. The Mo 4d state and Ti 3d state exhibit a consistent trend above the Fermi level and effectively overlap with the S 3p state, demonstrating a stable bonding effect. In comparison to  $1\text{Ti-MoS}_2$ , the Ti state effect in  $2\text{Ti-MoS}_2$  is more pronounced. Due to the substitution at the S-site, Ti introduces additional electrons in the model, represented as the donor level.

As depicted in Fig. 2(e), noticeable isolated energy levels appear. Fig. 2(f) corresponds to the contribution of the Ti 3d state, where influences the bottom of the conduction band, concurrently reducing the overall band gap to 1.196 eV, a value similar to the other theoretically calculated one.<sup>43</sup> In contrast to the empty band in  $1\text{Ti-MoS}_2$ , these filled electrons can more effectively facilitate electron participation in surface  $\text{CO}_2$  adsorption and catalytic conversion. Among these, the peak coincidence between Ti 3d and the other two states in PDOS is reduced, suggesting that alternative sites in  $2\text{Ti-MoS}_2$  may weaken the bonding ability with surrounding atoms, potentially leading to lattice distortion in the model. Besides, from Fig. 2(g and h), Ti doping on the surface significantly influences the energy band, introducing multiple impurity levels within the band gap. This facilitates easier electron transition to surface reactions. The PDOS diagram also illustrates that doping causes a leftward shift in the overall band edge, with Ti 3d states comprising the majority of the impurity levels.<sup>24</sup> In contrast to

the previous calculation model, the Ti 3d state in PDOS and its binding ability with the surrounding S atoms is not as strong as in  $1\text{Ti-MoS}_2$ .

Combining the band structure and PDOS analysis, it can be concluded that the introduction of impurity energy levels into the model through Ti doping facilitates the migration of carriers and improves catalytic activity. Moreover, with the different doping sites, the electron density differences and Bader charge were calculated to explore the influence of doping on charge transfer and interaction. The difference in electron density between pure  $\text{MoS}_2$ ,  $1\text{Ti-MoS}_2$ ,  $2\text{Ti-MoS}_2$  and  $3\text{Ti-MoS}_2$  is represented in Fig. 3. From Fig. 3(a), it can be clearly seen that Mo and S gain and lose electrons in the model. In line with the electronic structure results in Fig. 2(c and d), there is no noticeable change in the gain and loss of electrons after Ti substitutes for Mo atoms, and the electrons remain relatively stable. Similarly, in the  $2\text{Ti-MoS}_2$  model, the relatively large atomic radius of Ti and the additional electron contribution result in a slightly distorted optimized model, leading to the appearance of impurity levels. The substitution of Ti at the S site introduces extra electrons on the surface, enhancing their involvement in reactions. This phenomenon is likely to be advantageous for  $\text{CO}_2$  adsorption and subsequent catalytic conversion reactions.

In the  $3\text{Ti-MoS}_2$  model, the charge density difference reveals substantial electron accumulation around the Ti sites, indicating that Ti introduces additional surface-active electrons capable of strengthening  $\text{CO}_2$  adsorption and facilitating its subsequent activation. Meanwhile, the structural deformation after Ti incorporation remains minimal, allowing the reaction to occur on a geometrically stable surface. Combined with the reduced band gap and enhanced charge redistribution observed in the  $2\text{Ti-MoS}_2$  and  $3\text{Ti-MoS}_2$  models, these features collectively

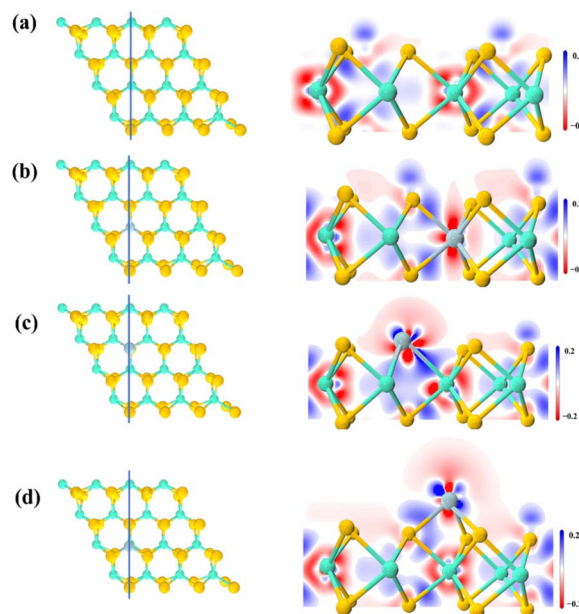


Fig. 3 The line in the figure represents the location of the slice of the electron density difference plot. Electron density difference: (a)  $\text{MoS}_2$ ; (b)  $1\text{Ti-MoS}_2$ ; (c)  $2\text{Ti-MoS}_2$ ; (d)  $3\text{Ti-MoS}_2$ . The isovalue is set to  $0.2 \text{ e}^- \text{ \AA}^{-3}$ .



contribute to more efficient catalytic behavior. Notably, these trends are consistent with the recent systematic doping study,<sup>20</sup> which also identified Ti as one of the most effective dopants for tuning the electronic structure and reactivity of MoS<sub>2</sub>.

In this regard, we meticulously calculated the Bader net atomic charge of each atom in all structures in order to determine an atom's charge state quantitatively by comparing its calculated charge with its own valence charge. Table 3 outlines the range of variation in Bader charge for different doping configurations. Within pure MoS<sub>2</sub>, the S atom exhibits an acquired electron state, while the Mo atom experiences electron loss. In 1Ti-MoS<sub>2</sub>, some S atoms gain additional electrons, indicating a relative equilibrium between Ti doping and surrounding S electrons at the Mo site. Contrastingly, in 2Ti-MoS<sub>2</sub>, the Ti contribution to the electron decreases compared to 1Ti-MoS<sub>2</sub>, resulting in an increase in electron donation from Mo. This phenomenon correlates with the observed change in Ti 3d states depicted in Fig. 2(f), where the overlap between Ti 3d and other energy levels near the Fermi level diminishes, thereby weakening electron transfer. In 3Ti-MoS<sub>2</sub>, the Ti atom loses 0.96e of electrons. However, unlike 1Ti-MoS<sub>2</sub>, electron gains and losses predominantly occur at the surface rather than achieving charge equilibrium with surrounding S atoms. Consequently, Mo atoms, which originally lost electrons, now gain electrons within the system. This phenomenon likely activates the surface active region, thereby facilitating the adsorption and conversion of gas molecules.

Besides, the bonding between different atoms inside MoS<sub>2</sub> before and after doping was investigated using Mulliken bond population calculations.<sup>44</sup> These calculations further quantify the extent of electron sharing between two atoms, providing deeper insights into the bonding characteristics.<sup>45</sup> It should be noted, however, that negative values for Mulliken bond populations are possible, indicating that the bond type is ionic and relatively easy to break if the absolute value is low.<sup>46</sup> Although Mulliken bond populations do not have a precise threshold value for distinguishing between ionic and covalent bonds, a bond with a Mulliken bond population greater than 0.1 is typically considered covalent, according to the literature.<sup>47–49</sup> Fig. 4 shows the calculated Mulliken bond populations for all models. Through calculations, it is observed that Mo and S exhibit distinct covalent bond characteristics. Similarly, in 1Ti-MoS<sub>2</sub> and 3Ti-MoS<sub>2</sub>, Ti and S also form covalent bonds. However, the covalent bond characteristics in 2Ti-MoS<sub>2</sub> are significantly weakened. This result aligns with the lower overlap of Ti and Mo orbitals in the PDOS.

### 3.2 CO<sub>2</sub> adsorption on the Ti-doped MoS<sub>2</sub> monolayer

In order to analyze the optimal adsorption site of CO<sub>2</sub> on the surface, the geometric structure of the CO<sub>2</sub> was first optimized

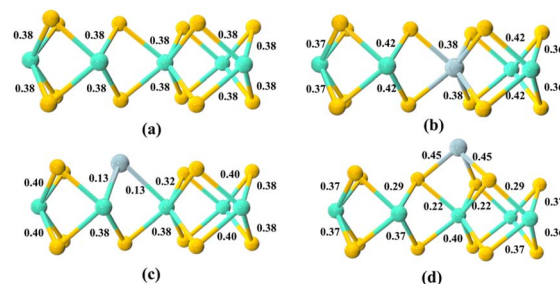


Fig. 4 The Mulliken bond populations for the: (a) MoS<sub>2</sub>; (b) 1Ti-MoS<sub>2</sub>; (c) 2Ti-MoS<sub>2</sub>; (d) 3Ti-MoS<sub>2</sub>.

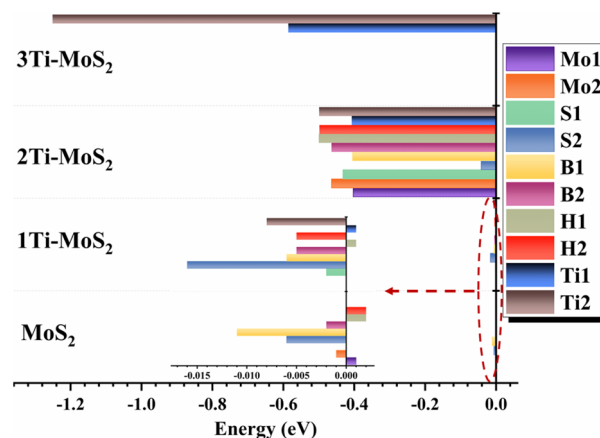


Fig. 5 The optimized energy of CO<sub>2</sub> adsorption on different site.

to its most stable configuration. The calculated C=O bond length was 1.172 Å, and the O=C=O bond angle was found to be 180°, which is in good agreement with the experimental data and previously derived theoretical values.<sup>50</sup>

Then the adsorption energy of CO<sub>2</sub> at different sites on the surface after optimization was calculated. The molecular height is defined as the minimum distance from any atom in the CO<sub>2</sub> molecule from any atom in the MoS<sub>2</sub>. Four potential locations for CO<sub>2</sub> adsorption on the MoS<sub>2</sub> surface were identified: above a Mo atom (Mo site), above an S atom (S site), above a Ti atom (Ti site), above the center of a hexagon composed of three Mo atoms and three S atoms (Hollow site), and above a Mo-S bond (Bridge site). With a view to establish which of these are the most stable configuration for the CO<sub>2</sub> adsorption, two adsorption orientations (horizontal-1 and vertical-2) of the CO<sub>2</sub> molecule were also considered. Fig. 5 illustrates the CO<sub>2</sub> adsorption energy for all potential adsorption sites. Certain adsorption sites, not depicted in the figure, result from CO<sub>2</sub> relocating to

Table 3 The calculated Bader charge for all models

Atom type	Bader net atomic charge			
	MoS <sub>2</sub>	1Ti-MoS <sub>2</sub>	2Ti-MoS <sub>2</sub>	3Ti-MoS <sub>2</sub>
S	(−0.30) – (−0.35)	(−0.23) – (−0.54)	(−0.45) – (−0.68)	(−0.03) – (−1.00)
Mo	(0.65) – (0.66)	(0.51) – (1.10)	(0.75) – (1.12)	(−0.84) – (1.05)
Ti	*	1.00	0.62	0.96



other best adsorption sites during calculations. For simplicity, we only present the optimal adsorption sites.

Analyzing changes in adsorption energy at different sites reveals that pure MoS<sub>2</sub> exhibits the maximum adsorption energy of  $-0.011$  eV for horizontal placed CO<sub>2</sub> at the bridge site. Meanwhile, MoS<sub>2</sub> and 1Ti-MoS<sub>2</sub>, lacking effective Ti sites on the surface, exhibit minimal changes in adsorption energy. In some cases, the CO<sub>2</sub> adsorption energy at certain sites is positive, significantly impeding the adsorption process and hindering the catalytic conversion of CO<sub>2</sub>. Furthermore, the adsorption energy of 2Ti-MoS<sub>2</sub> and 3Ti-MoS<sub>2</sub> increases at multiple sites, with vertically placed CO<sub>2</sub> displaying higher adsorption energy, indicating that the activation of oxygen atoms may be the key to CO<sub>2</sub> adsorption.

Fig. 6 depicts the optimal structure of the four models with the best adsorption energy. In Fig. 6(a), the relaxed structure of a CO<sub>2</sub> molecule adsorbed on pristine MoS<sub>2</sub> is shown. The calculated distance between CO<sub>2</sub> and MoS<sub>2</sub> is  $3.544$  Å. The length of the C=O bond in the adsorbed CO<sub>2</sub> measures  $1.172$  Å, similar to the C=O bond length in free CO<sub>2</sub>, indicating that MoS<sub>2</sub> does not significantly affect the adsorbed CO<sub>2</sub>.

This suggests a weak interaction between the CO<sub>2</sub> and MoS<sub>2</sub>. Fig. 6(b–d) clearly shows a gradual decrease in the physical adsorption distance of CO<sub>2</sub>, with the minimum adsorption distance between 3Ti-MoS<sub>2</sub> and CO<sub>2</sub> measuring  $1.878$  Å. This aligns with our predictions in Fig. 2 and 3, showing that 2Ti-MoS<sub>2</sub> and 3Ti-MoS<sub>2</sub> exhibit stronger adsorption capacity due to the additional electron cloud.

By further calculating adsorption energy, total charge, and the absolute values of the change in bond length/angle, we identified the adsorption changes of CO<sub>2</sub> on the surface, as presented in Table 4. Table 4 reveals that the  $E_{\text{ads}}$  value for CO<sub>2</sub> on pristine MoS<sub>2</sub> is  $0.04$  eV, consistent with the theoretically calculated value,<sup>12</sup> further indicating the limited CO<sub>2</sub> adsorption capacity of MoS<sub>2</sub>. Additionally, the adsorption energy of 3Ti-MoS<sub>2</sub> is as high as  $-1.251$  eV, suggesting a potential strong chemisorption reaction on the surface. The bond length of CO<sub>2</sub> in MoS<sub>2</sub> and 1Ti-MoS<sub>2</sub> remains unchanged, indicating ineffective activation of the surface C=O in the system. The absolute

Table 4 Characteristics of the most stable configurations of CO<sub>2</sub> adsorbed on MoS<sub>2</sub>. ( $\Delta d_{1\text{C-O}}$  and  $\Delta d_{2\text{C-O}}$  represent the absolute values of the change in the length of the C=O bond in CO<sub>2</sub>, respectively.  $\theta_{\text{O=C=O}}$  is the O=C=O bond angle.  $\Delta\theta_{\text{O=C=O}}$  is the absolute value of the change in the O=C=O angle from when the molecule is free)

Structure	$E_{\text{ads}}$ , eV	$\Delta d_{1\text{C-O}}$ , Å	$\Delta d_{2\text{C-O}}$ , Å	$\theta_{\text{O=C=O}}$ , °	$\Delta\theta_{\text{O=C=O}}$ , °
MoS <sub>2</sub>	$-0.011$	0	0	179.971	0.029
1Ti-MoS <sub>2</sub>	$-0.016$	0	0	179.535	0.465
2Ti-MoS <sub>2</sub>	$-0.500$	0.013	0.013	176.228	3.772
3Ti-MoS <sub>2</sub>	$-1.251$	0.029	0.199	130.230	49.770

values of the change in the length of the C=O bond in CO<sub>2</sub> for 2Ti-MoS<sub>2</sub> exhibit a change of  $0.013$  Å, while the change for 3Ti-MoS<sub>2</sub> is twice that amount. Besides, similar conclusions are observed in the change of bond angle. The extra electrons and surplus active sites provided by Ti on the surface lead to significant distortion of C=O in 3Ti-MoS<sub>2</sub> ( $\Delta\theta_{\text{O=C=O}}=49.770^\circ$ ), enhancing surface catalytic performance. Considering the changes in C=O bond length and bond angle, both 2Ti-MoS<sub>2</sub> and 3Ti-MoS<sub>2</sub> demonstrate remarkable catalytic performance, with the activation performance of 3Ti-MoS<sub>2</sub> on CO<sub>2</sub> being more than 2 times higher than that of 2Ti-MoS<sub>2</sub>.

In order to further investigate the electron effect of different doped configuration on CO<sub>2</sub> adsorption, we also calculate the energy band and density state of all models. As shown in Fig. 7, comparing the structure of unadsorbed CO<sub>2</sub> model, it is found that the energy band and PDOS of pure MoS<sub>2</sub>/CO<sub>2</sub> and 1Ti-MoS<sub>2</sub>/CO<sub>2</sub> do not change significantly. The PDOS before and after CO<sub>2</sub> adsorption largely overlap, particularly in the region near the Fermi level. Consequently, the interaction between CO<sub>2</sub> and 1Ti-MoS<sub>2</sub> resembles the interaction between CO<sub>2</sub> and the pristine MoS<sub>2</sub>.

Thus, we can infer that the interaction between CO<sub>2</sub> molecules and 1Ti-MoS<sub>2</sub> monolayers is weak, consistent with the calculated adsorption energy. The bandgaps of 2Ti-MoS<sub>2</sub>/CO<sub>2</sub> and 3Ti-MoS<sub>2</sub>/CO<sub>2</sub> undergo slight variations within a certain range after CO<sub>2</sub> adsorption, but the electronic transition types remain essentially unchanged.

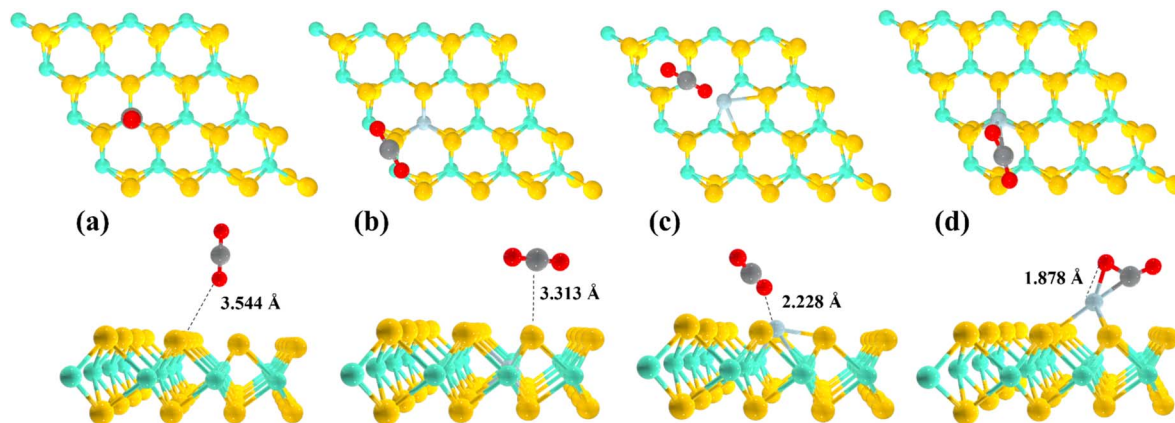


Fig. 6 The optimized structure of CO<sub>2</sub> adsorption on pristine MoS<sub>2</sub> (a), 1Ti-MoS<sub>2</sub> (b), 2Ti-MoS<sub>2</sub> (c), 3Ti-MoS<sub>2</sub> (d). The figure shows both plan (above) and side (below) views. The red and black ball in this paper represents O and C atoms, respectively. Dash line is the minimum distance from any atom in the CO<sub>2</sub> molecule from any atom in the MoS<sub>2</sub>.



Besides, upon comparing the PDOS of different models in Fig. 7, it is evident that as the Ti doping site approaches the surface, the overall PDOS energy gradually shifts to the left. This characteristic is consistent with the unadsorbed structure.

Moreover, detailed comparisons of the changes in CO<sub>2</sub> 1s state, CO<sub>2</sub> 2p state, and Ti 3d state are depicted in Fig. 8. It is more evident from Fig. 8(a) that the orbitals of CO<sub>2</sub> and Ti do not significantly overlap, and the doping of Ti at the Mo site also does not affect the adsorption effect of CO<sub>2</sub>. In Fig. 8(b), partial energy overlap is observed in the region above the 2–3 eV, and a faint overlap near –6 eV. These overlaps in state density confirm the increased adsorption energy of CO<sub>2</sub> on 2Ti-MoS<sub>2</sub>. Simultaneously, Fig. 8(c) reveals a substantial decrease in the overall density of states compared to the previous model. This reduction in the electron state density of CO<sub>2</sub> suggests that the original C=O electron binding is influenced by Ti-doping. The diminished electron binding can weaken the double bond energy with lower energy, thereby increasing the availability of surface sites and facilitating the catalytic reaction. Furthermore, the overlapping range of the Ti 3d state and CO<sub>2</sub> electronic state near the Fermi level increases. This undoubtedly enhances the binding performance of Ti and CO<sub>2</sub>, aligning with the calculated maximum adsorption energy.

In view of the above results, we also used electron differential charge density and Bader charge calculation to verify the charge

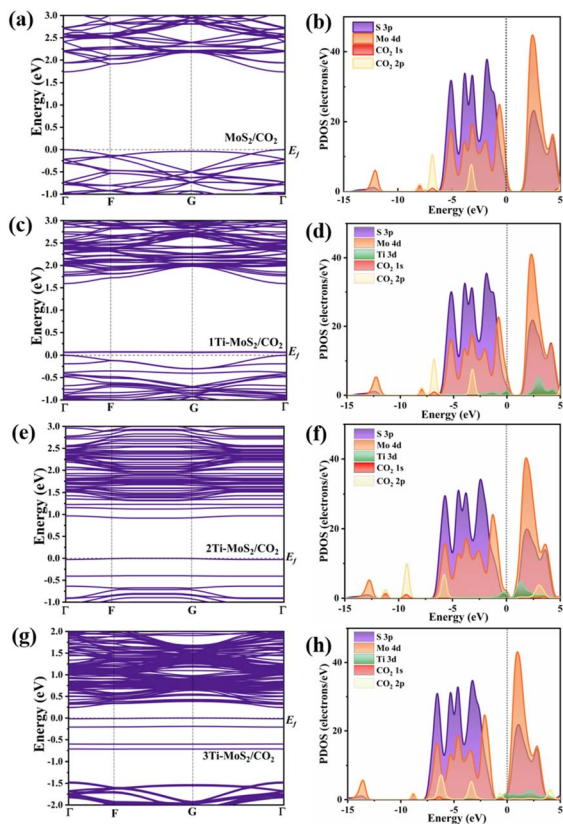


Fig. 7 Band structure and PDOS of (a and b) MoS<sub>2</sub>/CO<sub>2</sub>; (c and d) 1Ti-MoS<sub>2</sub>/CO<sub>2</sub>; (e and f) 2Ti-MoS<sub>2</sub>/CO<sub>2</sub>; (g and h) 3Ti-MoS<sub>2</sub>/CO<sub>2</sub>. The energy is referenced to the Fermi level ( $E_f$ ), which is indicated by the dashed line at 0 eV.

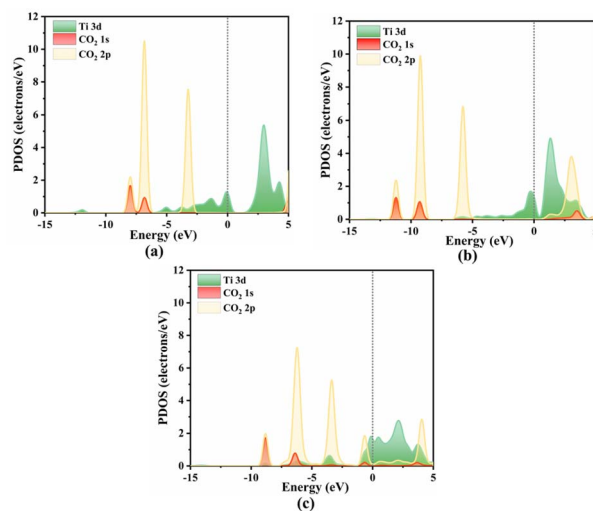


Fig. 8 The PDOS curves of (a) 1Ti-MoS<sub>2</sub>; (b) 2Ti-MoS<sub>2</sub>; (c) 3Ti-MoS<sub>2</sub>. The dash lines are Fermi level. The energy is referenced to the Fermi level ( $E_f$ ), which is indicated by the dashed line at 0 eV.

transfer between CO<sub>2</sub> and the catalyst, as shown in Fig. 9 and Table 5. Table 5 specifically presents the Bader net atomic charge of CO<sub>2</sub> and its closest atom. Where  $S_{\text{near}}$  represents the S atom closest to CO<sub>2</sub>. Consistent with the previously calculated total charge results, the Bader net atomic charge sum of C and O in the remaining structures, except for the 3Ti-MoS<sub>2</sub> structure, remained relatively stable. This is also evident in Fig. 9, where

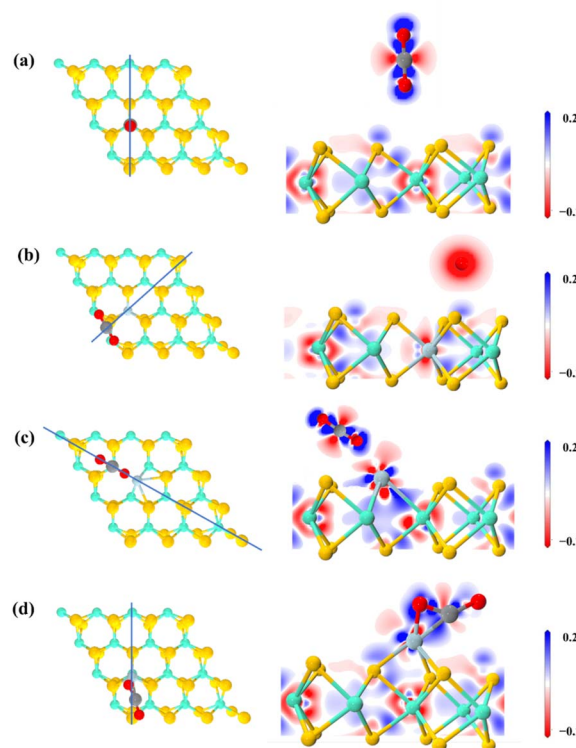


Fig. 9 The line in the figure represents the location of the slice of the electron density difference plot. (a) MoS<sub>2</sub>/CO<sub>2</sub>; (b) 1Ti-MoS<sub>2</sub>/CO<sub>2</sub>; (c) 2Ti-MoS<sub>2</sub>/CO<sub>2</sub>; (d) 3Ti-MoS<sub>2</sub>/CO<sub>2</sub>. The isovalue is set to 0.2 e Å<sup>-3</sup>.



Table 5 The calculated Bader charge for all models

Atom type	Bader net atomic charge			
	MoS <sub>2</sub>	1Ti-MoS <sub>2</sub>	2Ti-MoS <sub>2</sub>	3Ti-MoS <sub>2</sub>
S <sub>near</sub>	-0.50	-0.38	—	—
Ti	—	1.02	0.79	1.12
C	1.45	1.89	1.82	0.69
O <sub>1</sub>	-0.71	-0.96	-0.92	-0.67
O <sub>2</sub>	-0.78	-0.96	-0.94	-0.90

only the CO<sub>2</sub> molecules in 2Ti-MoS<sub>2</sub> exhibit a slight change in adsorption among the first three catalysts. This, coupled with the electron density difference, substantiates the fact that its adsorption energy was heightened, leading to improved catalytic performance.

Despite Ti losing 1.02e, the gain and loss of these electrons remain stably coordinated with the surrounding S, considering its doping site is at the Mo site. As mentioned earlier, the optimal adsorption configuration of 2Ti-MoS<sub>2</sub> involves the vertical adsorption of Ti and O<sub>2</sub>. Table 5 reveals that Ti loses 0.79e electrons, while O<sub>2</sub> gains a slightly larger number of electrons. This enhances the adsorption energy and involves a small amount of charge transfer. Furthermore, the Bader net atomic charge calculation for 3Ti-MoS<sub>2</sub> revealed that Ti lost more electrons, and C transferred fewer electrons to O. These findings confirm that Ti doping at this site significantly activates C=O, reducing energy in the adsorption process. In alignment with Fig. 9(d), an electron cloud structure formed between Ti and CO<sub>2</sub>.

In addition, Mulliken bond populations of the adsorption model are also calculated, as shown in the Fig. 10. According to the calculation results, C=O presents a typical covalent double bond, and the calculated result is the same as the charge transfer observed in the MoS<sub>2</sub> and 1Ti-MoS<sub>2</sub> models, indicating that the bond type does not change. In the 2Ti-MoS<sub>2</sub> model, Ti and Mo tend to form ionic bonds, whereas in the 3Ti-MoS<sub>2</sub> model, both C and O atoms form covalent bonds with surface Ti atoms. These findings align well with the charge analysis results and suggest that Ti incorporation significantly enhances surface reactivity toward CO<sub>2</sub> adsorption. Such dopant-induced electronic reconstruction effectively activates the otherwise inert basal plane of MoS<sub>2</sub>, providing a general strategy for designing 2D catalysts with tunable intrinsic activity beyond conventional edge or defect engineering.

### 3.3 The reaction mechanism of CO<sub>2</sub>RR

Considering the importance of CO in CO<sub>2</sub>RR over MoS<sub>2</sub>, as observed in other experimental results,<sup>25</sup> we conducted further studies on the hydrogenation of intermediates \*COOH and \*CO to elucidate the underlying mechanisms. In order to comprehend the reaction mechanisms for the reduction of CO<sub>2</sub>RR over MoS<sub>2</sub> and Ti/MoS<sub>2</sub>, Fig. 9 illustrates the potential reaction pathways of CO<sub>2</sub>RR based on previous DFT calculations.<sup>22</sup> Additionally, for the optimal reaction pathway, the following steps take place:

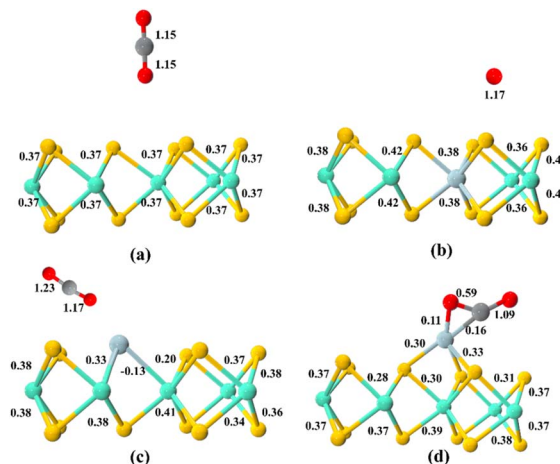
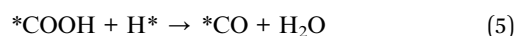
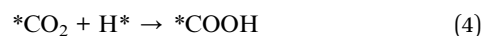


Fig. 10 The Mulliken bond populations for the: (a) MoS<sub>2</sub>/CO<sub>2</sub>; (b) 1Ti-MoS<sub>2</sub>/CO<sub>2</sub>; (c) 2Ti-MoS<sub>2</sub>/CO<sub>2</sub>; (d) 3Ti-MoS<sub>2</sub>/CO<sub>2</sub>.



Reaction step I involves the adsorption of CO<sub>2</sub>, activating the CO<sub>2</sub> molecule. Step II encompasses the hydrogenation process of \*CO<sub>2</sub>, and the proposed reaction step III involves the hydrogenation of carboxyl (\*COOH), leading to the reaction CO<sub>2</sub> → CO. As depicted in Fig. 9, the chemisorption of CO<sub>2</sub> on the surface lays the groundwork for subsequent reactions. Particularly evident in Fig. 11(b), the transition of CO<sub>2</sub> from the surface to the chemisorbed state reveals that the free energy barrier is lowest for 3Ti-MoS<sub>2</sub>. This finding suggests that 3Ti-MoS<sub>2</sub> facilitates further adsorption reactions. Following CO<sub>2</sub> chemisorption, \*CO<sub>2</sub> can undergo hydrogenation to form \*COOH. However, the hydrogenation of \*CO<sub>2</sub> to \*COOH on pristine MoS<sub>2</sub> is found to be kinetically unfavorable, attributed to the high barrier energy of 3.046 eV, as shown in Fig. 11(b).

Our analysis of the energy profiles indicates that the \*CO<sub>2</sub> → \*COOH hydrogenation step represents the rate-determining step (RDS) for pristine MoS<sub>2</sub>, 1Ti-MoS<sub>2</sub>, and 2Ti-MoS<sub>2</sub> due to its high activation barrier. In contrast, the most active 3Ti-MoS<sub>2</sub> exhibits a markedly reduced barrier of only 0.177 eV for this step, effectively eliminating this kinetic limitation. As a result, the CO desorption step becomes the new RDS, with a relative barrier of 1.017 eV. This shift of the RDS clearly reflects a fundamental change in catalytic behavior induced by surface-exposed Ti dopants, highlighting the superior CO<sub>2</sub>-to-CO conversion capability of 3Ti-MoS<sub>2</sub>.

The introduction of the Ti coordination site on the basal plane significantly reduces the Gibbs free energy of the \*COOH intermediate. It can be obviously found that Ti can effectively reduce the energy of the determination step under three different doping modes.

Compared with the electronic structure of Ti/MoS<sub>2</sub> as discussed before, the Ti doping on MoS<sub>2</sub> changes the band gap and charge, which favors strong adsorption of CO<sub>2</sub>, resulting in



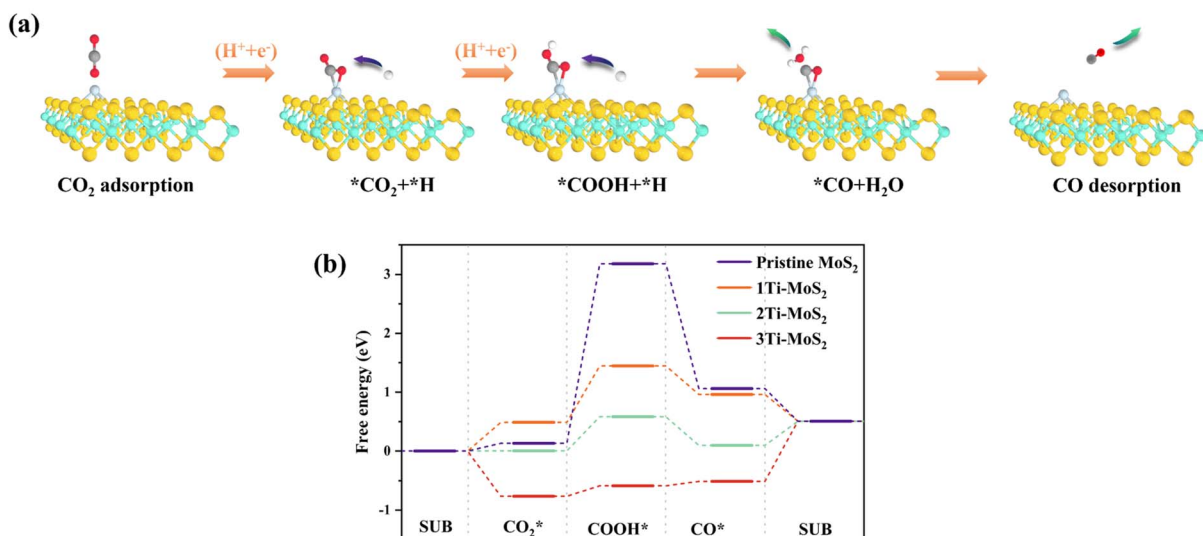


Fig. 11 The reaction mechanism for  $\text{CO}_2\text{RR}$  into  $\text{CO}$  on  $3\text{Ti-MoS}_2$ . (a) The structures of the reaction intermediates; (b) the energy profile for different catalytic.

superior catalytic  $\text{CO}_2\text{RR}$  performance toward  $\text{CO}$ . Notably,  $3\text{Ti-MoS}_2$  exhibits exceptional catalytic performance with its  $^*\text{CO}_2$  to  $^*\text{COOH}$  energy reduced to 0.177 eV, 17 times lower than that of pure  $\text{MoS}_2$ . Ultimately, the introduction of Ti enhances the desorption of  $\text{CO}$ , as evidenced by the calculated energy barrier for the  $\text{CO}$  desorption step on the surface. Both pure  $\text{MoS}_2$  and  $1\text{Ti-MoS}_2$  surfaces exhibit intensified  $\text{CO}$  desorption processes, whereas  $2\text{Ti-MoS}_2$  and  $3\text{Ti-MoS}_2$  demonstrate notable energy barriers for the reaction. Notably, the energy barrier for  $\text{CO}$  desorption on the  $3\text{Ti-MoS}_2$  surface is particularly significant, reaching 1.017 eV. This suggests that the presence of  $^*\text{CO}$  on this surface is conducive to further conversion processes. These theoretical trends are consistent with experimental observations<sup>20,21,51</sup> that  $\text{MoS}_2$ -based catalysts primarily yield  $\text{CO}$  as the dominant product in  $\text{CO}_2$  reduction reactions, where moderate  $\text{CO}$  binding and reduced  $\text{COOH}$  activation barriers favor  $\text{CO}$  evolution.

Based on the energy calculations described above, a comparison is made among the formation energy, adsorption energy, adsorption barrier, determination step, and desorption

barrier of various models, as illustrated in Fig. 12. It is worth noting that the formation energy of pure  $\text{MoS}_2$  is merely used as a reference value of 0 eV and holds no practical significance in this context.

Besides, the outstanding performance of the  $3\text{Ti-MoS}_2$  model pinpoints the surface-exposed Ti as the most potent active site design for  $\text{CO}_2\text{RR}$ , providing a valuable guiding principle for future catalyst development. The systematic theoretical analysis of the different doping sites offers valuable insight into future research on the TMD material, particularly in terms of assessing their overall  $\text{CO}_2\text{RR}$  performance. These results highlight a clear structure–property relationship between dopant configuration, charge redistribution, and catalytic activity, providing general design principles for developing efficient  $\text{MoS}_2$ -based single-atom catalysts that feature near-Fermi impurity levels and moderate charge transfer to optimize both adsorption and conversion steps.

Looking forward, the insights from this study offer clear pathways for experimental realization and application. The predicted thermodynamic stability of Ti in the  $\text{MoS}_2$  lattice guides its synthesis *via* controlled hydrothermal or chemical vapor deposition methods.<sup>52</sup> Furthermore, the exceptionally low reaction barrier and high selectivity predicted for  $\text{CO}$  production position  $\text{Ti/MoS}_2$  as a highly promising catalyst for  $\text{CO}_2$  electrolyzers, motivating future work on fabricating and testing gas diffusion electrodes for high-current-density  $\text{CO}_2$ -to- $\text{CO}$  conversion.

## 4 Conclusions

In conclusion, first principles quantum theory was employed to computationally screen  $\text{M1/MoS}_2$  ( $\text{M1} = \text{Cr, Cu, Sc, Ti, V, Ni}$ ) with the first series of transition metals.  $\text{Ti/MoS}_2$  exerted a significant impact on the energy band structure, inducing changes in the band gap and electronic transition energy

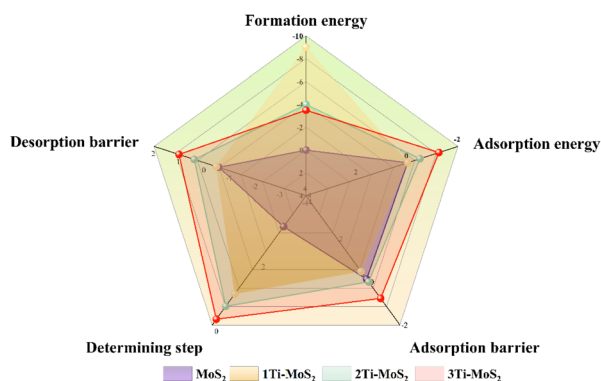


Fig. 12 Calculate each energy index diagram of the model.



through the introduction of impurity energy levels. Notably, the catalytic advantages of 3Ti-MoS<sub>2</sub> in CO<sub>2</sub> conversion were demonstrated through PDOS and electron density difference analysis. 3Ti-MoS<sub>2</sub> emerged as a potential material for CO<sub>2</sub> sensing due to its favorable adsorption and response characteristics. Furthermore, by calculating the reaction mechanism for CO<sub>2</sub>RR into CO, we observed exceptional catalytic performance in 3Ti-MoS<sub>2</sub>, with its \*CO<sub>2</sub> to \*COOH energy reduced to 0.177 eV, 17 times lower than that of pure MoS<sub>2</sub>. These results highlight a clear structure–property relationship between dopant configuration, charge redistribution, and catalytic activity. The insights obtained here provide general design principles for developing efficient MoS<sub>2</sub>-based single-atom catalysts, emphasizing dopants that introduce near-Fermi impurity levels and moderate charge transfer to optimize both adsorption and conversion steps.

## Author contributions

Junbo Wang: conceptualization, investigation, methodology, visualization, software, writing–original draft. Qiankai Zhang: formal analysis, methodology, visualization, software, writing–original draft. Qi Tang: investigation, visualization, software, writing–original draft. Yin Zhang: methodology, visualization. Jun Zhou: writing–review & editing, project administration, supervision. Yang Wang: writing–review & editing, project administration, supervision. Kai Wu: supervision.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting the findings of this study are available within the article. No additional data were generated or analyzed in the presented research.

Supplementary information (SI): the optimized crystal structure data (in .cif format) supporting the computational findings of this study. The data is organized into three composite files: (1) ‘All-Models\_Clean-Structures’ containing pristine and doped MoS<sub>2</sub> base models; (2) ‘All-Models\_with-CO<sub>2</sub>’ containing structures after CO<sub>2</sub> adsorption; and (3) ‘All-Models\_Step-Intermediates’ containing the key reaction intermediate structures for all models. See DOI: <https://doi.org/10.1039/d5ra08046k>.

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