

Supporting Information

Tuning d -orbital to Controlling Spin-Orbit Coupling in Terminated MXenes

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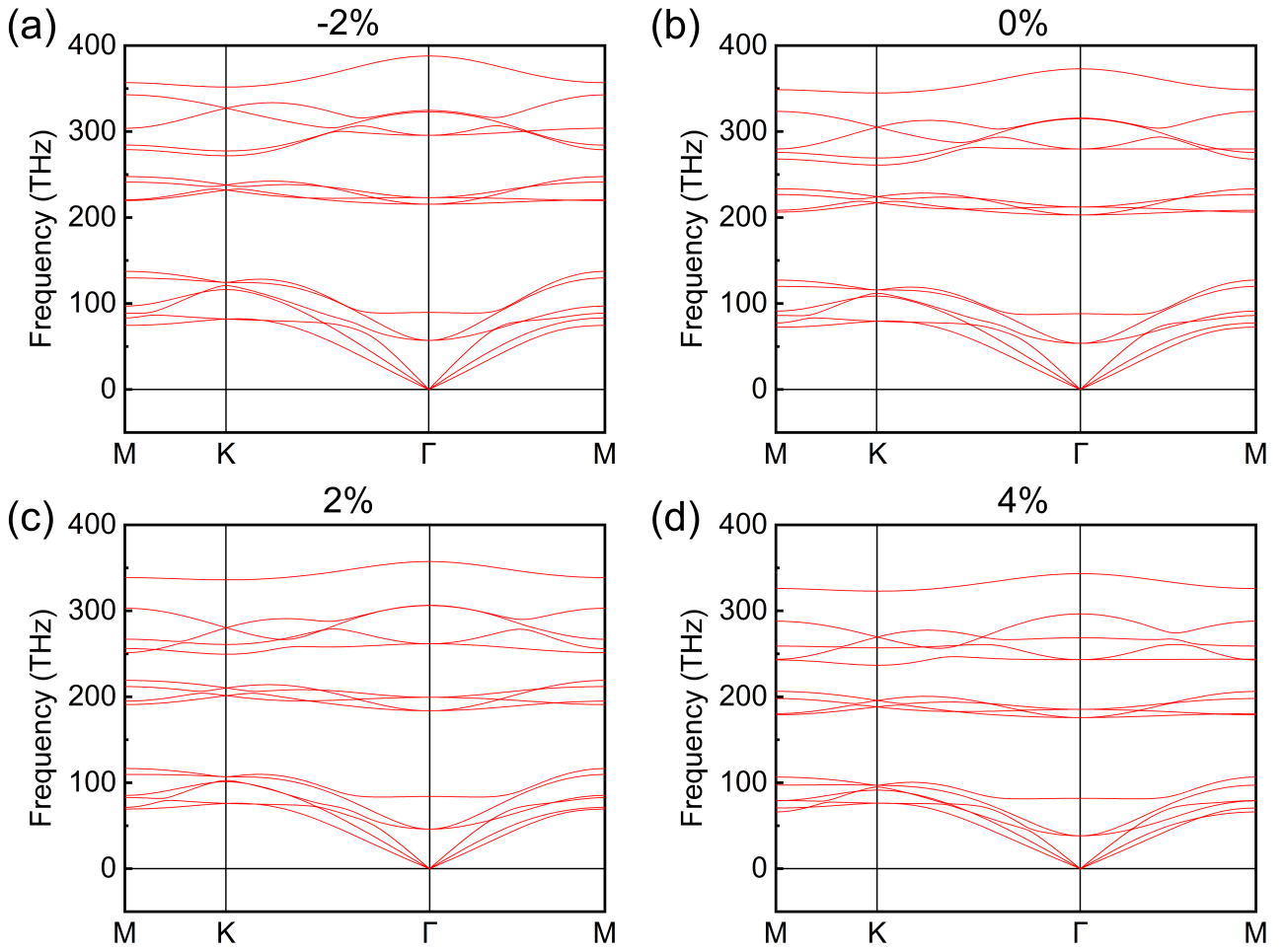


Figure S1: The phonon spectrum of W_2CO_2 under different hydrostatic strains (the compressing or elongating of the lattice from -2% to 4%).

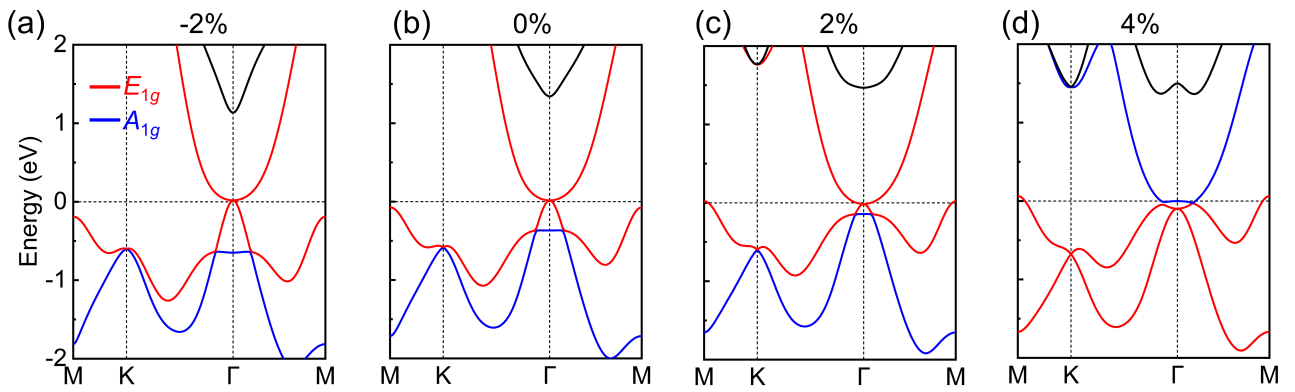


Figure S2: Without SOC effect, the electronic band structures of W_2CO_2 under different hydrostatic strains by using the PBE functionals.

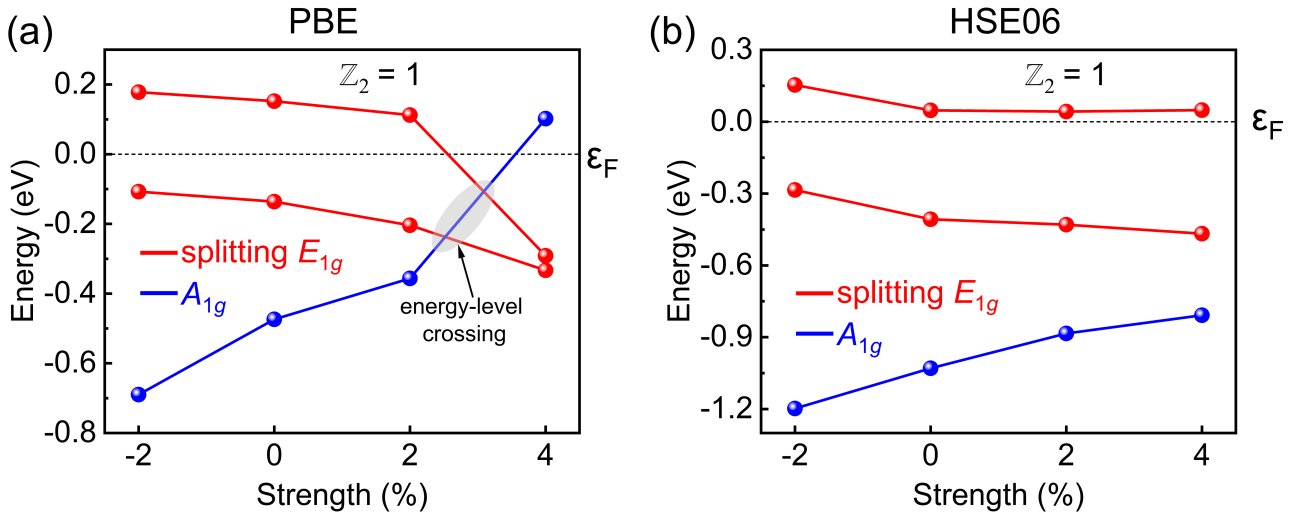


Figure S3: By using the PBE (a) and HSE06 (b) calculation, the shift of energy levels E_{1g} and A_{1g} of W_2CO_2 at the Γ -point under different hydrostatic strains.

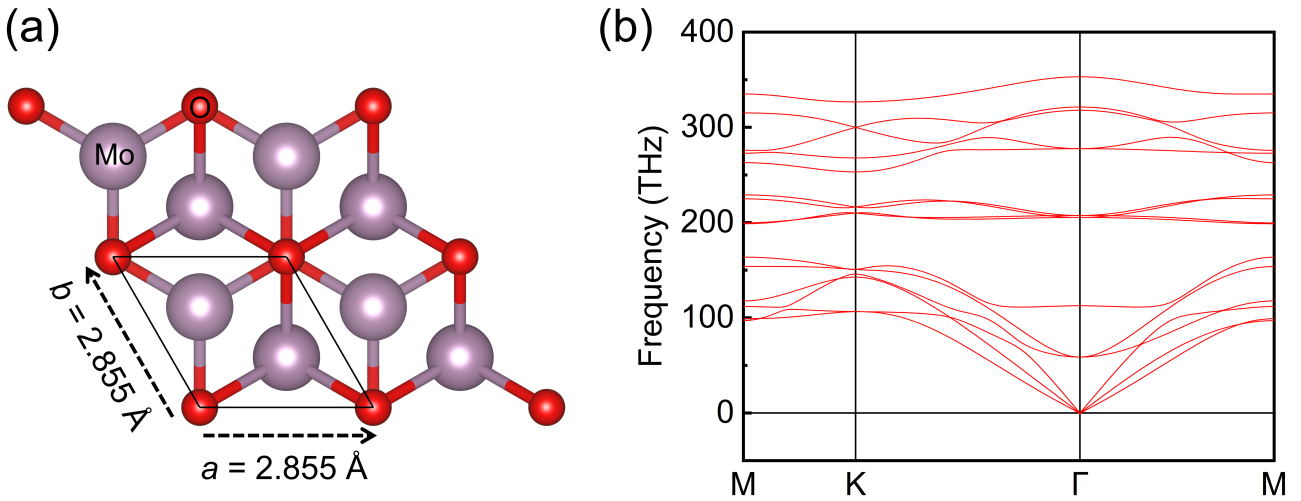


Figure S4: (a) By using the HSE06 functional, top view of the crystal structure of Mo_2CO_2 monolayer with lattice vectors a and b . (b) The phonon spectrum of the Mo_2CO_2 monolayer.

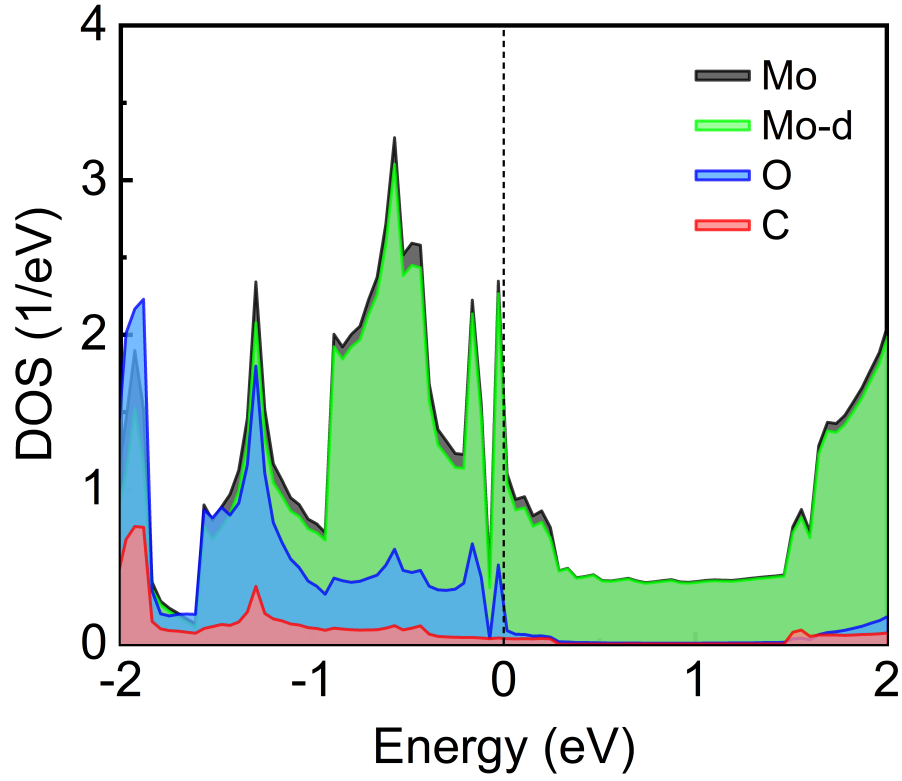


Figure S5: The projected partial densities of states (PDOS) of atoms orbitals with SOC by using the PBE functionals for Mo_2CO_2 monolayer.

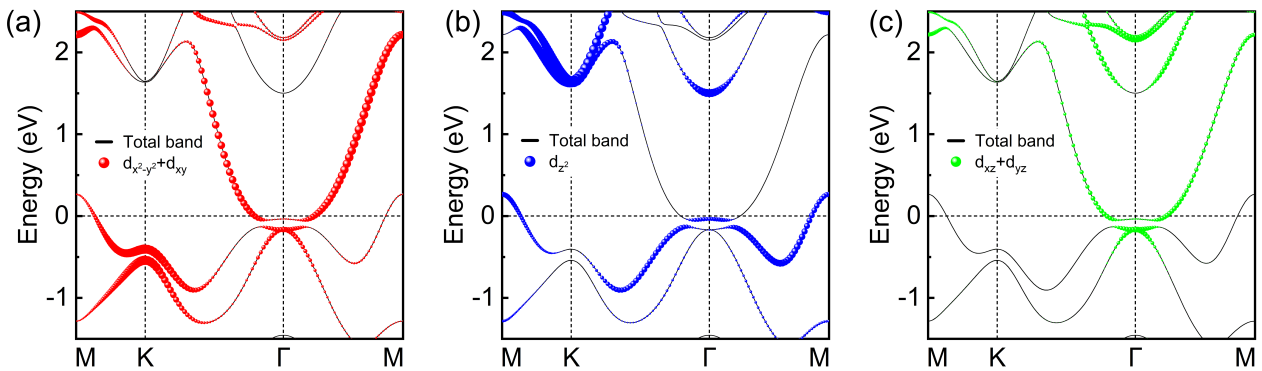


Figure S6: The wave functions with SOC are projected onto the different components of the d -orbitals of Mo atoms by using the PBE functionals for Mo_2CO_2 monolayer.

Table S1: Calculated the bandgaps (E_{bulk}) of the W_2CO_2 . The relative results are also listed for comparison.

W_2CO_2	E_{bulk} (eV)	
Present results	PBE	0.192
	HSE06	0.421
Reference results	PBE	0.194
	HSE06	0.472

The derivation of the electron correlation effect influence to the effective SOC in $d_{xy} + d_{x^2-y^2}$ orbitals:

I. Original SOC effects

Without the spin-orbit coupling (SOC) effect, the orbital angular momentum of the orbital doublet is quenched without SOC. Turning on the SOC, the presence of SOC splits the orbital degeneracy and slightly unquenches the orbital angular momentum, leading to orbital polarization. The SOC Hamiltonian reads

$$\hat{H}_{SOC} = \sum_{m,m',\sigma,\sigma'} \lambda \langle m, \sigma | \mathbf{L} \cdot \mathbf{S} | m', \sigma' \rangle \hat{C}_{m\sigma}^\dagger \hat{C}_{m'\sigma'} \quad (1)$$

where \mathbf{L} and \mathbf{S} denote the angular momentum and spin operators, respectively, while $\hat{C}_{m\sigma}^\dagger$ and $\hat{C}_{m\sigma}$ represent the creation and annihilation operators for an electron state with orbital m and spin σ . The parameter λ signifies the SOC strength. As we concentrate on the d -systems with strong exchange interaction, we can only consider the spin-preserved term $\mathbf{L} \cdot \mathbf{S} \approx L_z S_z$.

Import the doublet, $d_{xy} + d_{x^2-y^2}$ orbitals, to Eq. (1), the SOC Hamiltonian matrix under the basis of $\{|2, 2, \uparrow\rangle, |2, -2, \uparrow\rangle, |2, 2, \downarrow\rangle, |2, -2, \downarrow\rangle\}$ obtained

$$\tilde{H}_{SOC} = \lambda \hbar^2 \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & -1 & \\ & & & 1 \end{pmatrix}. \quad (2)$$

To express this Hamiltonian with creation and annihilation operators, we assign each basis state a pair of these operators, and the SOC Hamiltonian in terms of these new operators can be written as

$\hat{H}_{SOC} = \lambda\hbar^2 (\hat{n}_{1,\uparrow} - \hat{n}_{-1,\uparrow} - \hat{n}_{1,\downarrow} + \hat{n}_{-1,\downarrow})$ with $\hat{n}_{m\sigma} = \hat{C}_{m\sigma}^\dagger \hat{C}_{m\sigma}$ the occupation operator.

In the regime of strong spin-splitting, electron states near the Fermi level are predominantly governed by a single spin channel, leading to a fully spin-polarized effective Hamiltonian near the Fermi level. Consequently, we simplify our analysis by neglecting the spin-down states and omitting the spin index from both the electron states and the creation/annihilation operators, i.e., $\hat{H}_{SOC} = \lambda\hbar^2 (\hat{n}_1 - \hat{n}_{-1})$. Notice that the matrix representation of the projected orbital momentum is also diagonal, under such circumstances, the SOC Hamiltonian in terms of orbital momentum operator can be written as $\hat{H}_{SOC} = \lambda\hbar\hat{L}_z$, where $\hat{L}_z = \sum_{m=l_z} \langle m | L_z | m \rangle \hat{n}_m$ is the operator of the angular momentum, \hat{n}_m is the occupation operator of doublet. The energy splitting of the degenerated $d_{xy} + d_{x^2-y^2}$ orbitals due to the SOC effect is

$$\Delta E_0 = 2\lambda\hbar^2. \quad (3)$$

II. Modified the effective SOC under the electron correlation effect

We further consider and import the electron correlation effect. As the case in W_2CO_2 with significant exchange interaction, the effective on-site correlation effect is captured by the Coulomb repulsion between states with parallel spin, described by $\hat{H}_c = U_{\text{eff}} \hat{n}_1 \hat{n}_{-1}$. In addition to the previously defined angular momentum operator $\hat{L}_z = \hbar(\hat{n}_1 - \hat{n}_{-1})$, the total occupation operator for the doublet as $\hat{n} = \hat{n}_1 + \hat{n}_{-1}$. Hence, the correlation Hamiltonian is reformulated as

$$\hat{H}_c = \frac{U_{\text{eff}}}{4} \left(\hat{n}^2 - \frac{\hat{L}_z^2}{\hbar^2} \right). \quad (4)$$

Using the Hartree-Fock approximation, we express \hat{A}^2 as $(\bar{A} + \delta\hat{A})^2 \approx 2\bar{A}\hat{A} - \bar{A}^2$, neglecting the term $(\delta\hat{A})^2$, where \bar{A} represents the expected value of \hat{A} . Consequently, the correlation Hamiltonian is approximated as

$$\hat{H}_c \approx U_{\text{eff}} \left[\frac{|\bar{L}_z|}{2\hbar^2} \hat{L}_z + \hat{\xi}(\bar{n}, \bar{L}_z) \right], \quad (5)$$

where $\hat{\xi}(\bar{n}, \bar{L}_z)$ is the energy shift and defined as $\frac{1}{2} \left[\bar{n} \left(\hat{n} - \frac{\bar{n}}{2} \right) + \frac{\bar{L}_z^2}{2\hbar^2} \right]$.

Recalling that the SOC Hamiltonian is expressed as $\hat{H}_{SOC} = \lambda\hbar\hat{L}_z$, the joint effect of SOC and correlation results in an effective Hamiltonian is reformulated as

$$\hat{H}_{SOC} + \hat{H}_c \approx \lambda_{\text{eff}}\hbar\hat{L}_z + U_{\text{eff}}\hat{\xi}(\bar{n}, \bar{L}_z), \quad (6)$$

which modifies the effective SOC effects, and produces an SOC parameter $\lambda_{\text{eff}} = 2\lambda + U_{\text{eff}} \frac{|\bar{L}_z|}{\hbar^3}$.

As a result, the energy splitting induced by the SOC effect is now enhanced, calculated as

$$\Delta E_{\text{eff}} = \Delta E_0 + U_{\text{eff}} \frac{|\bar{L}_z|}{\hbar} \quad (7)$$

where ΔE_0 is the original splitting energy from Eq. (3).

The modification $U_{\text{eff}} \frac{|\bar{L}_z|}{\hbar}$ originates from the SOC effect, because of the orbital polarization $|\bar{L}_z|$ originates from the SOC effect. The magnitude of modification $U_{\text{eff}} \frac{|\bar{L}_z|}{\hbar}$ can be iteratively enhanced by the correlation effect, because of the orbital polarization $|\bar{L}_z|$ be enhanced by correlation effect.