Supplementary Information

Electronic Structure of Strongly Bound Sandwich MoS_2–WS_2 Heterobilayer

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Carrier Mobility:

The carrier mobility of 2D materials (μ_{2D}) is usually estimated from the deformation-potential theory, which can be expressed according to Equation (S1):

$$\mu_{2D} = \frac{e\hbar^3 C_{2D}}{k_B T m^* m_d (E_1^i)^2} \quad \text{(S1)}$$

Where e is the electron charge, $\hbar$ is the reduced Planck constant, C_{2D} is the in-plane elastic modulus in the transport direction, k_B is Boltzmann constant, T is the temperature at 300 K, m^* is

the effective mass of the carrier in the same direction, m_d is the average effective mass in the two directions as given by $m_d = \sqrt{m_a^* + m_b^*}$, and E_1^i is the deformation potential constant for both electrons and holes along the *a*- and *b*-directions. E_1^i is obtained by linearly fitting the VBM and CBM as functions of the applied strain. The *m** of electrons and holes are calculated according to Equation (S2):

$$m^* = \frac{\hbar^2}{\partial^2 E / \partial K^2} \tag{S2}$$

Here, *K* is the wave vector and *E* is the energy corresponding to the wave vector.

Absorption Coefficients:

The optical absorption coefficient (α(ω)) can be obtained from the frequency-dependent complex dielectric function (ε(ω)) according to Equation S3:

$$\alpha(\omega) = \sqrt{2}\frac{\omega}{C}\left(\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)\right)^{1/2} \tag{S3}$$

In this equation, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ represent the real and imaginary parts of the dielectric function, respectively. While, ω is the photon frequency.

Table S1: The difference in the energy eigenvalues (in eV) of the valence band (VB) and VB-1 (E_{VBM}-E_{VB-1}), and that of the conduction band (CB) and CB+1 (E_{CB+1}-E_{CB}) at the K and Γ points of the sandwich homobilayer (HoBL) under external E-field. Under zero E-field, numbers inside parentheses correspond to those of the pristine MoS_2 HoBL. The PBE exchange-correlation functional is employed.

Sandwich HoBL				
E-field (V/Å)	E_{VB}-E_{VB-1}		E_{CB+1}-E_{CB}	
	at K point	at Γ point	at K point	at Γ point
-0.50	0.59	0.72	0.08	0.20
-0.25	0.34	0.44	0.07	0.19
0.00	0.04 (0.09)	0.28 (0.67)	0.01 (0.00)	0.05 (0.00)
+0.25	0.34	0.44	0.07	0.19
+0.50	0.59	0.72	0.08	0.20

Table S2. The difference in the energy eigenvalues (in eV) of the valence band (VB) and VB-1 (E_{VB}-E_{VB-1}), and that of the conduction band (CB) and CB+1 (E_{CB+1}-E_{CB}) at the K and Γ points of the sandwich heterobilayer (HtBL) under external E-field. Under zero E-field, numbers inside parentheses correspond to those of the pristine WS_2–MoS_2 HtBL. The PBE exchange-correlation functional is employed.

Sandwich HtBL				
E-field (V/Å)	E_{VB}-E_{VB-1}		E_{CB+1}-E_{CB}	
	at K point	at Γ point	at K point	at Γ point
-0.50	0.67	0.85	0.13	0.20
-0.25	0.59	0.60	0.11	0.18
0.00	0.26 (0.23)	0.34 (0.70)	0.09 (0.11)	0.09 (0.00)
+0.25	0.08	0.33	0.02	0.10
+0.50	0.40	0.57	0.09	0.10

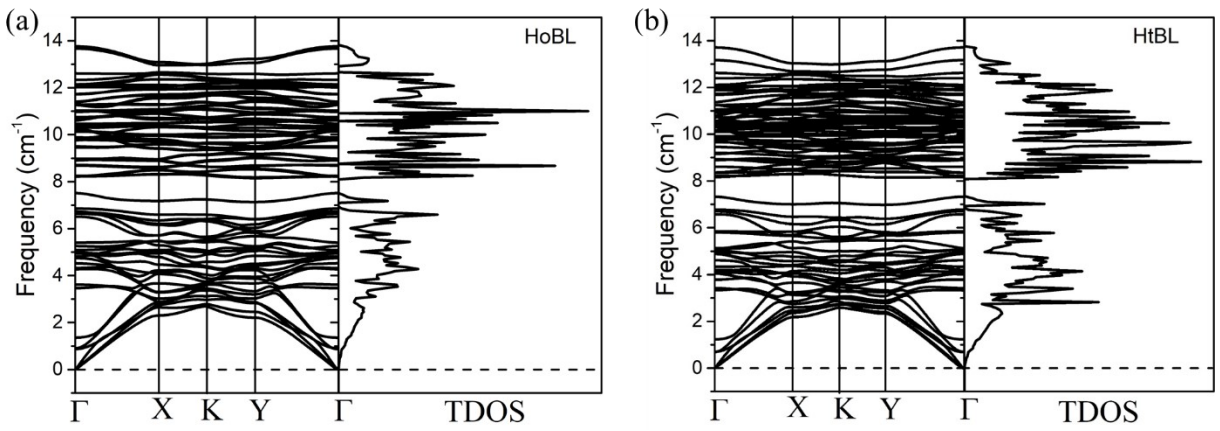

Fig. S1 (a)-(b) Phonon dispersion spectra and phonon density of states of the sandwich homobilayer (HoBL) and heterobilayer (HtBL).

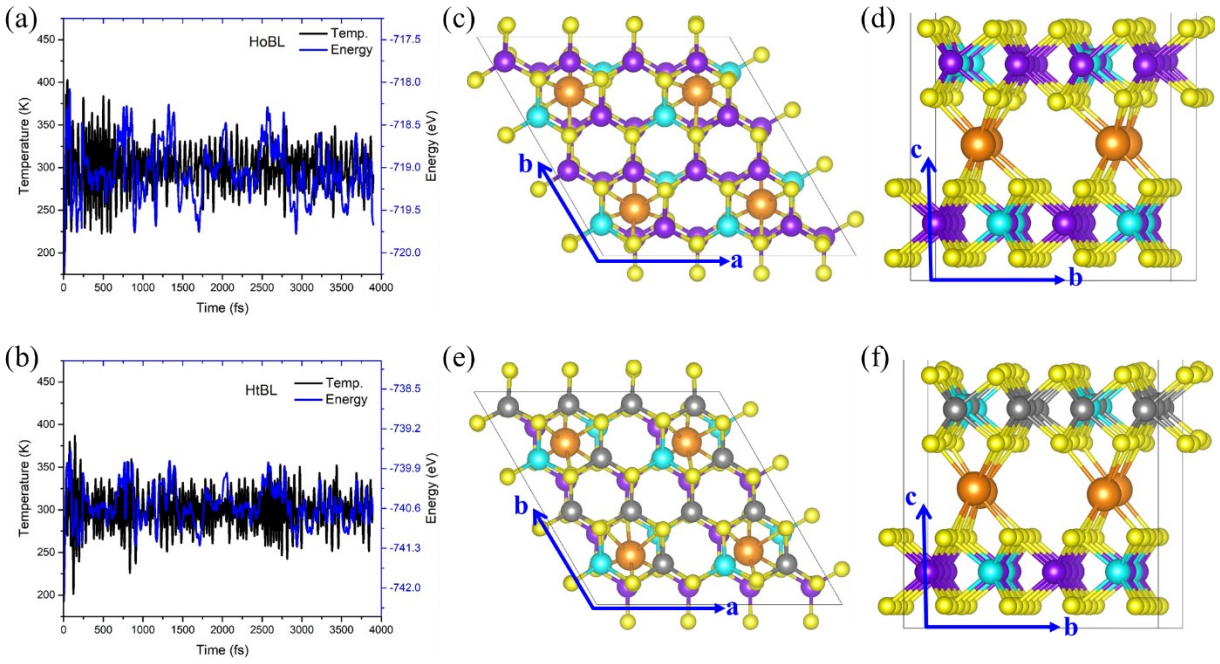

Fig. S2 (a)-(b) The time evolutions of temperature (K) and corresponding total energy (eV) in the sandwich homobilayer (HoBL) and heterobilayer (HtBL) during the AIMD simulation at 300 K. (c)-(d) Top and side views of the chemical structure of the sandwich HoBL at the end of the AIMD simulation. (e)-(f) Top and side views of the chemical structure of the sandwich HtBL at the end of the AIMD simulation. Orange, cyan, purple, grey, and yellow colors represent Ca, Nb, Mo, W, and S atoms, respectively.

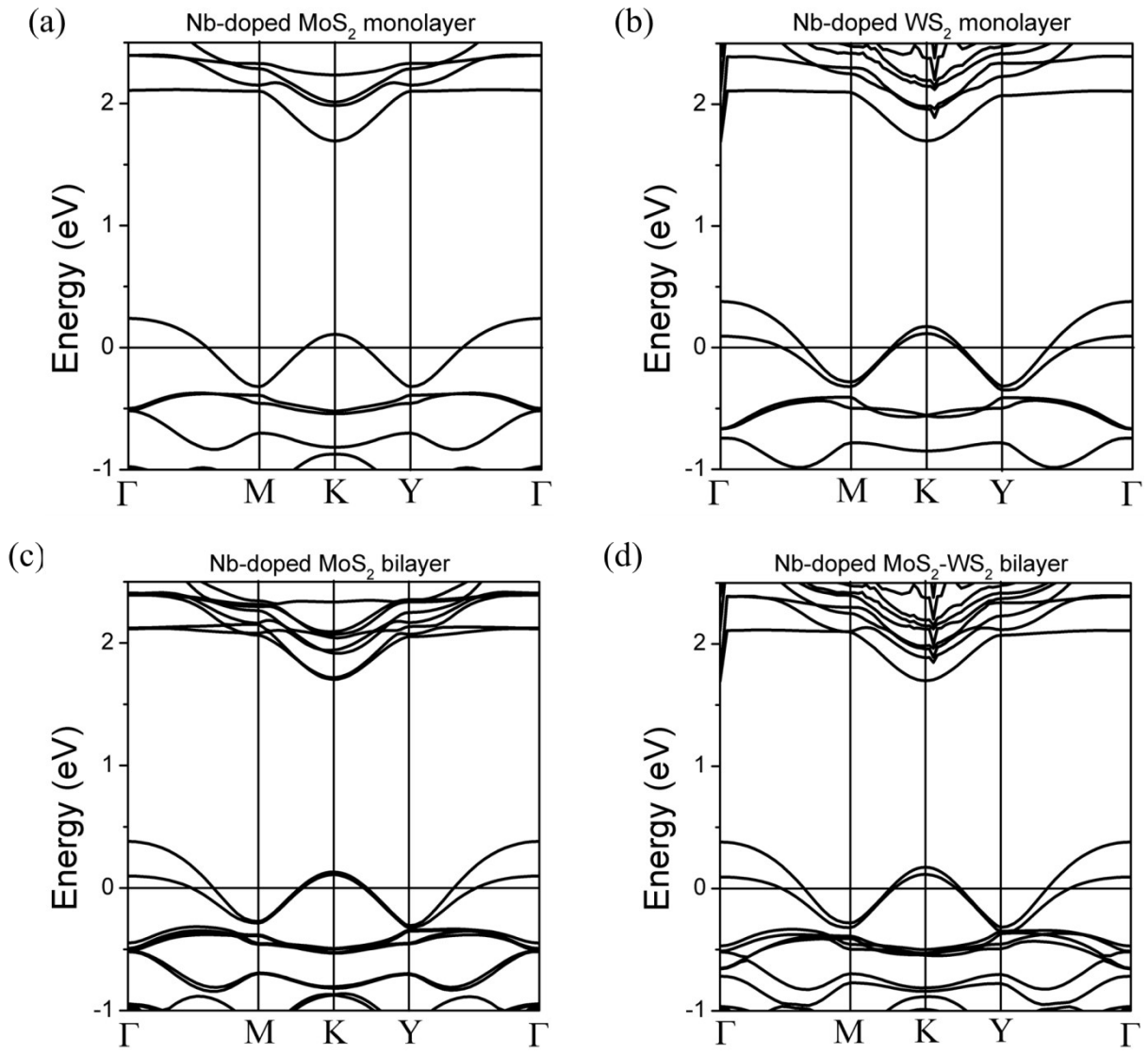

Fig. S3 (a)-(d) The electronic band structures of the Nb-doped MoS_2 monolayer, Nb-doped WS_2 monolayer, Nb-doped MoS_2 homobilayer, and Nb-doped WS_2–MoS_2 heterobilayer using the PBE method.

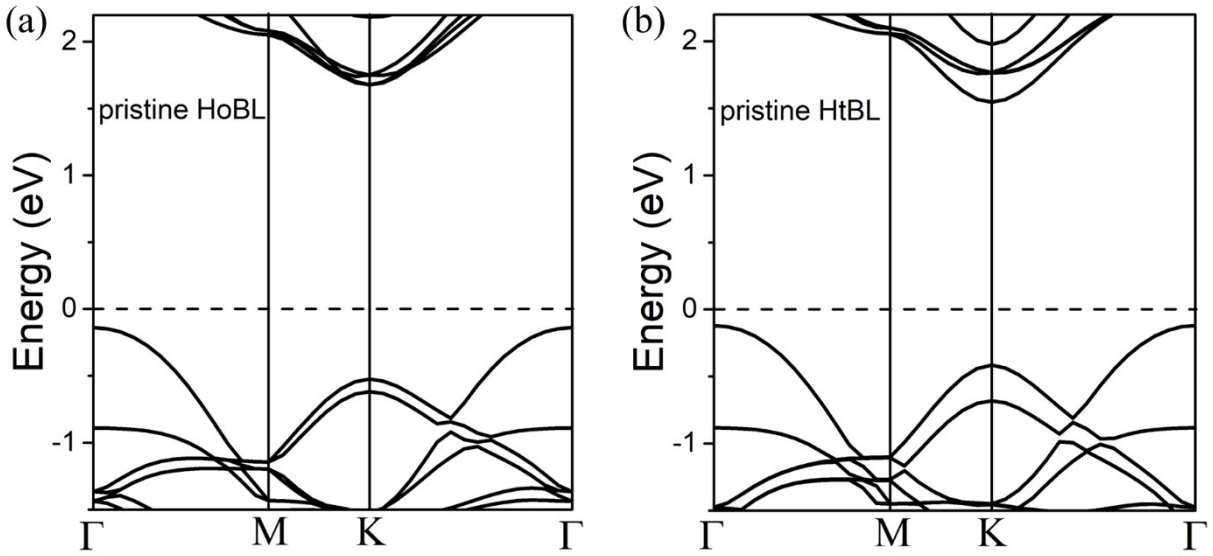

Fig. S4 (a)-(b) The electronic band structures of the pristine MoS_2 homobilayer (HoBL) and WS_2–MoS_2 heterobilayer (HtBL). using the HSE06 method.

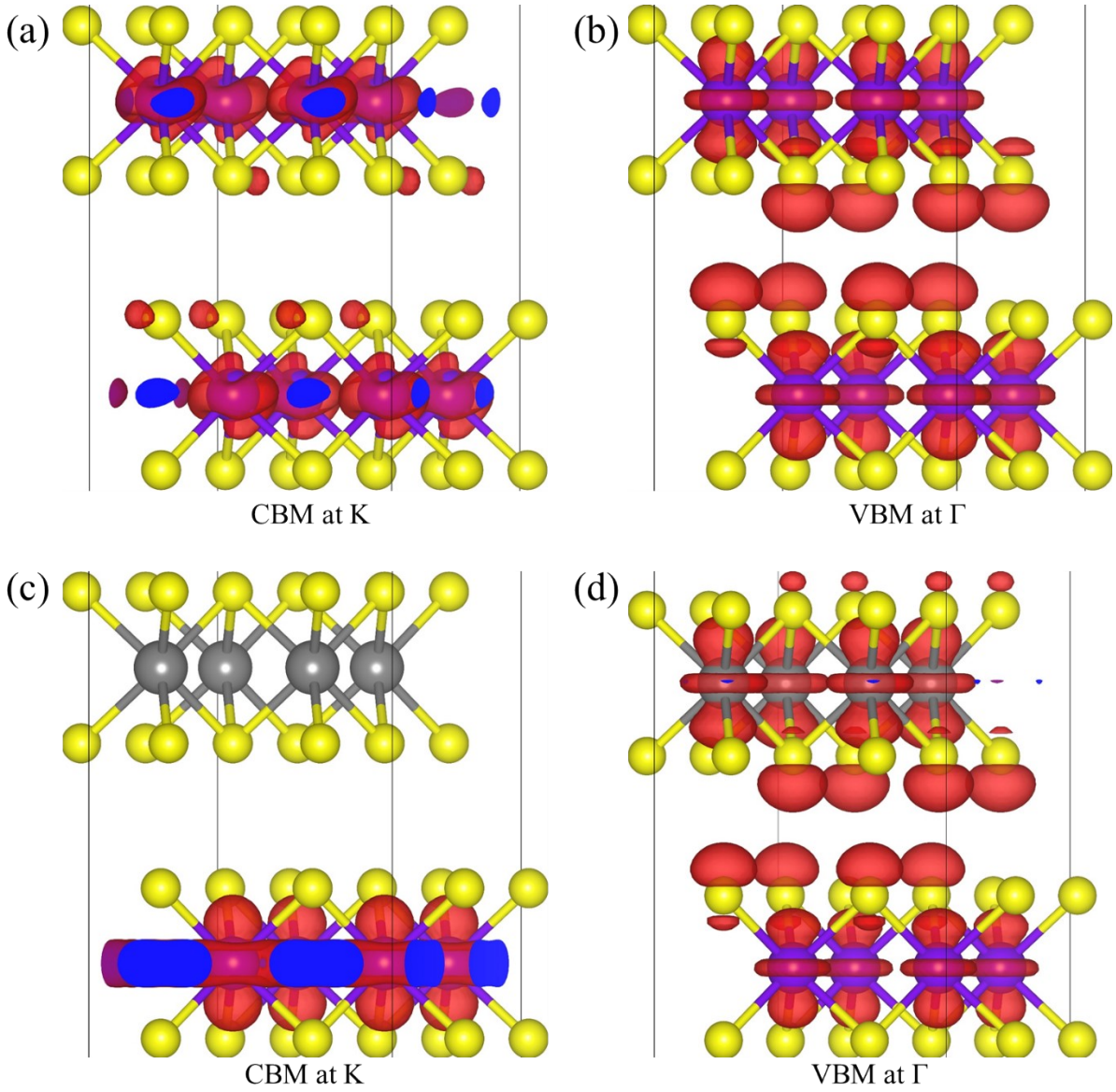

Fig. S5 The decomposed charge densities of the pristine (a)-(b) MoS_2 homobilayer (HoBL) and (c)-(d) WS_2–MoS_2 heterobilayer (HtBL). at the CBM(K) and VBM(Γ). The isosurface value is set to 1.8×10^{-3} eÅ^3. Purple, grey, and yellow colors represent Mo, W, and S atoms, respectively.

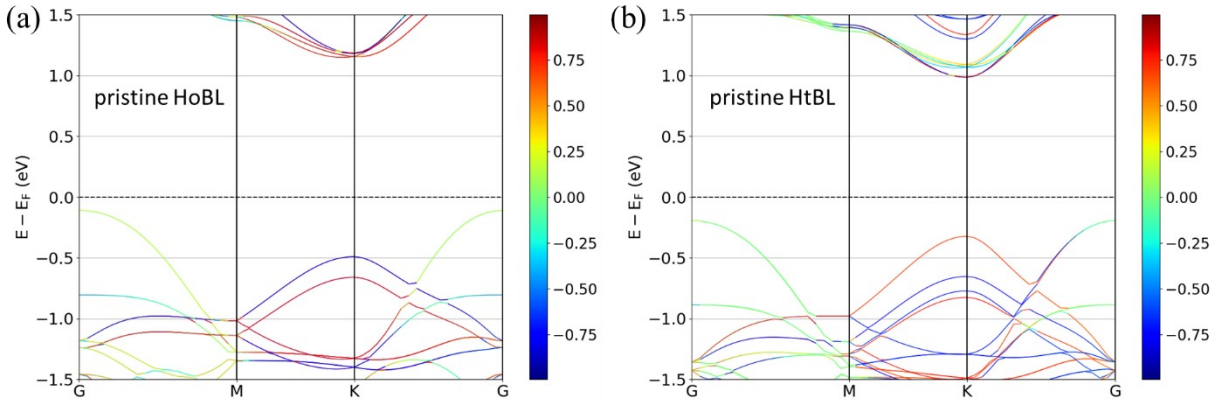

Fig. S6 (a)-(b) The electronic band structures of the pristine MoS_2 homobilayer (HoBL) and WS_2–MoS_2 heterobilayer (HtBL) with Spin-Orbit Coupling (SOC) using the PBE method, respectively.

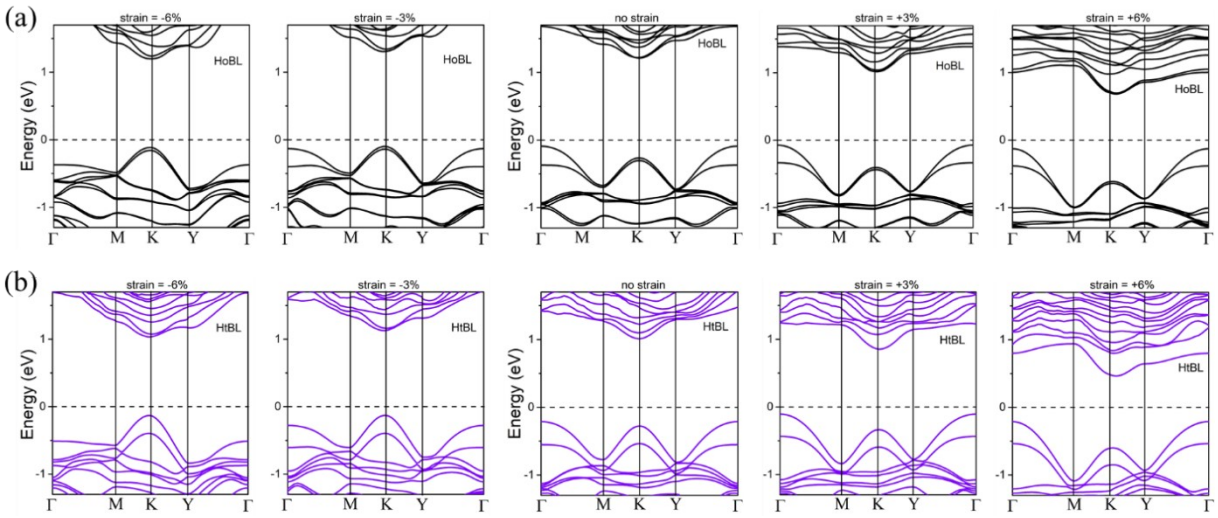

Fig. S7 (a)-(b) The electronic band structures of the sandwich homobilayer (HoBL) and heterobilayer (HtBL) under strain along the *a* direction from -6% to 6% using the PBE method.

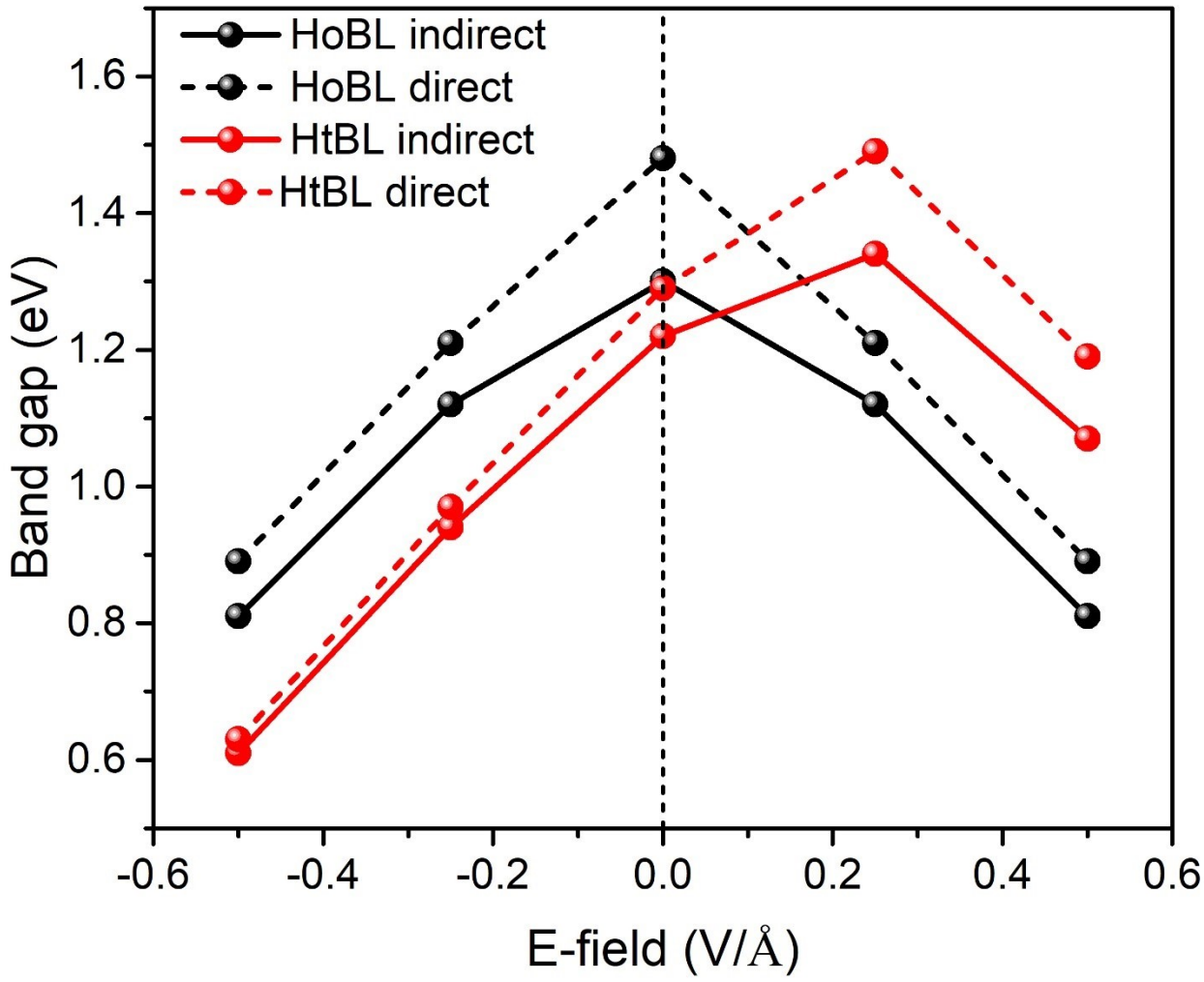

Fig. S8 The band gap of the sandwich homobilayer (HoBL) and heterobilayer (HtBL) as a function of external E-field along the vertical directions using the PBE method. Solid and dashed lines represent the *indirect* and *direct* band gaps, respectively.

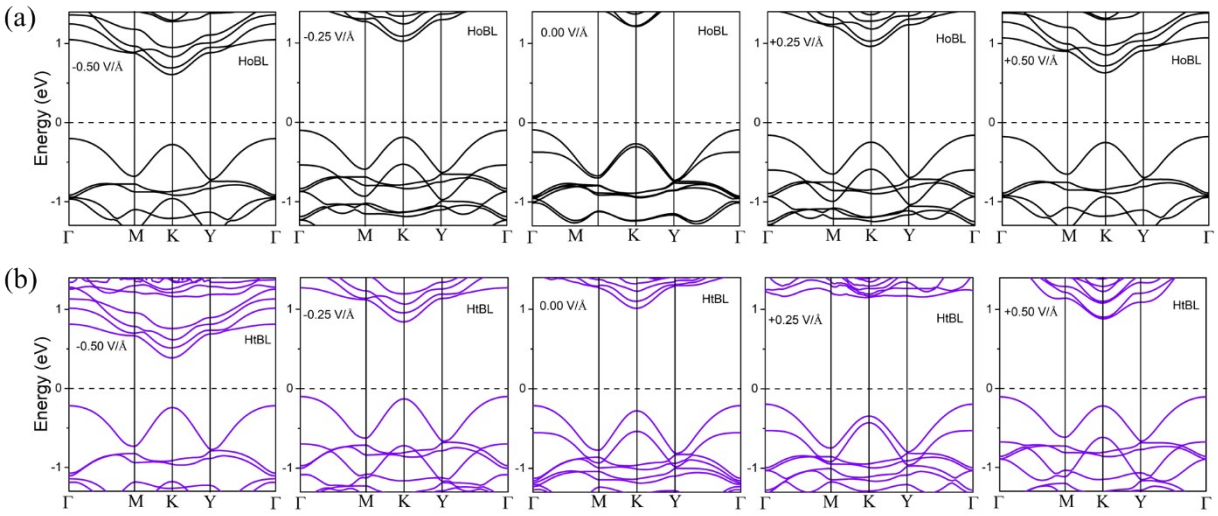

Fig. S9 (a)-(b) The electronic band structures of the sandwich homobilayer (HoBL) and heterobilayer (HtBL) under external E-field from -0.5 V/Å to 0.5 V/Å using the PBE method.

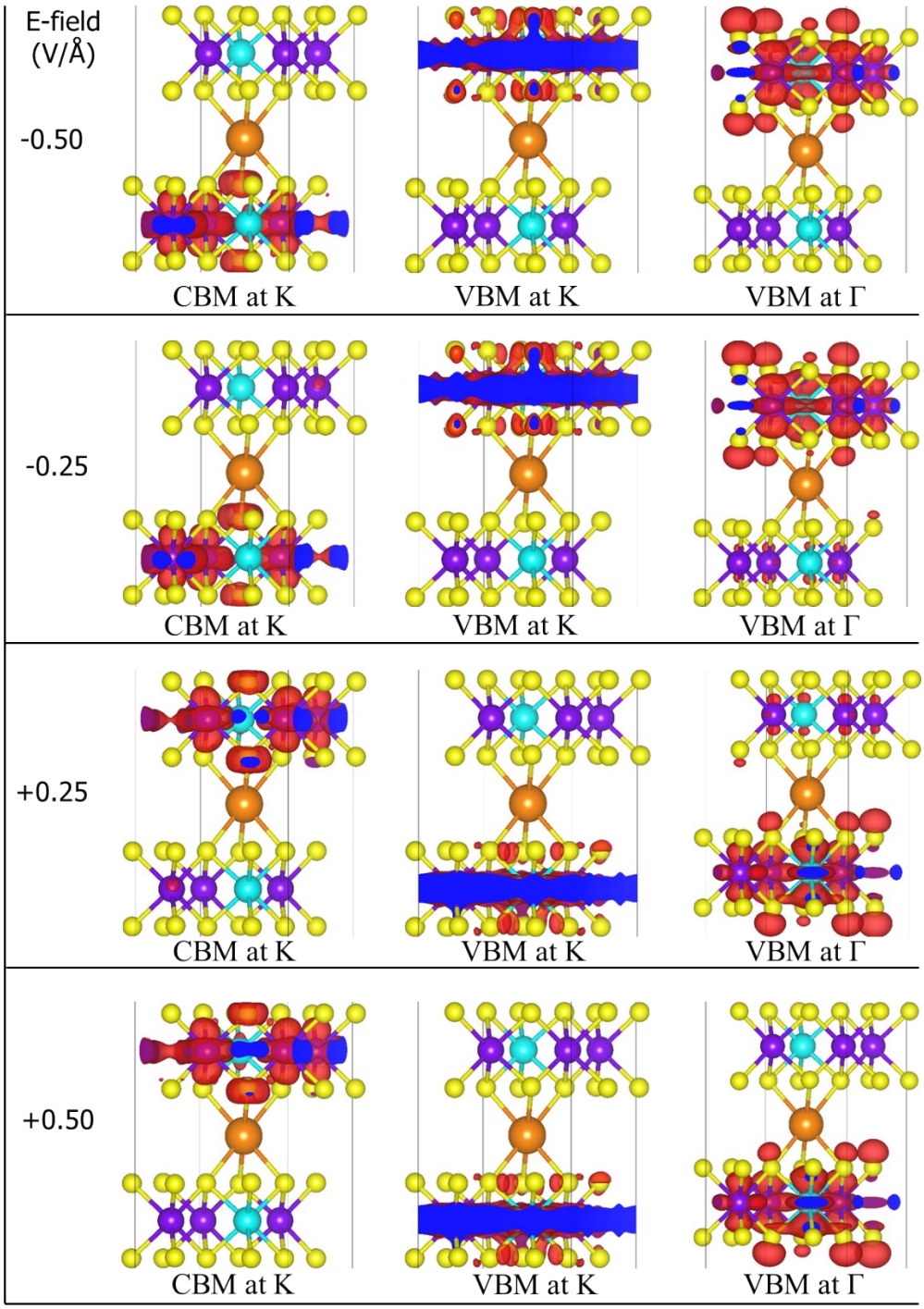

Fig. S10 The decomposed charge densities of the sandwich homobilayer (HoBL) under external E-field at the CBM(K), VBM(K), and VBM(Γ). The isosurface value is set to 2.3 × 10^{-3} eÅ^3. Orange, cyan, purple, and yellow colors represent Ca, Nb, Mo, and S atoms, respectively.

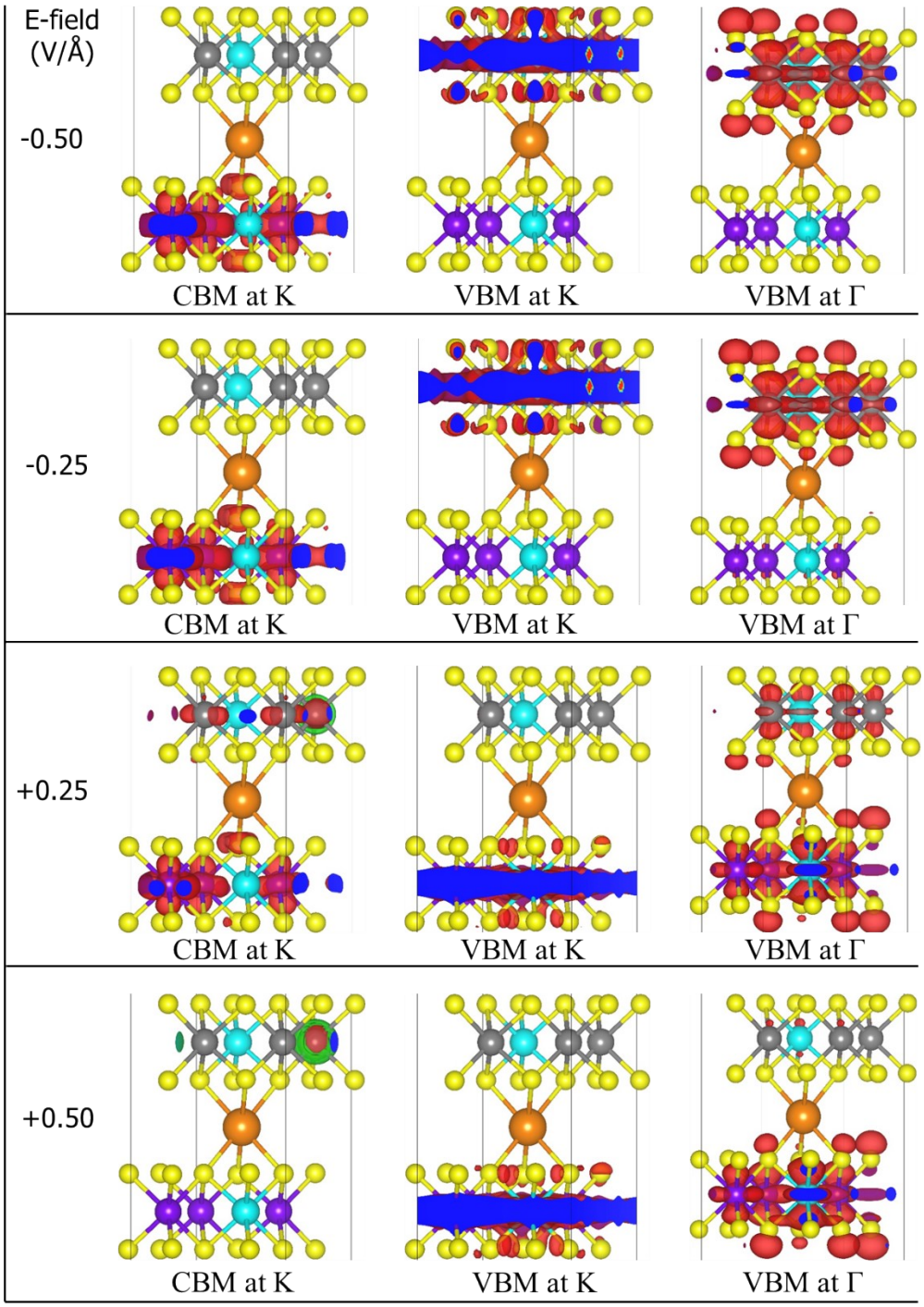

Fig. S11 The decomposed charge densities of the sandwich heterobilayer (HtBL) under external E-field at the CBM(K), VBM(K), and VBM(Γ). The isosurface value is set to 2.3 × 10^{-3} *e*Å^3. Orange, cyan, purple, grey, and yellow colors represent Ca, Nb, Mo, W, and S atoms, respectively.

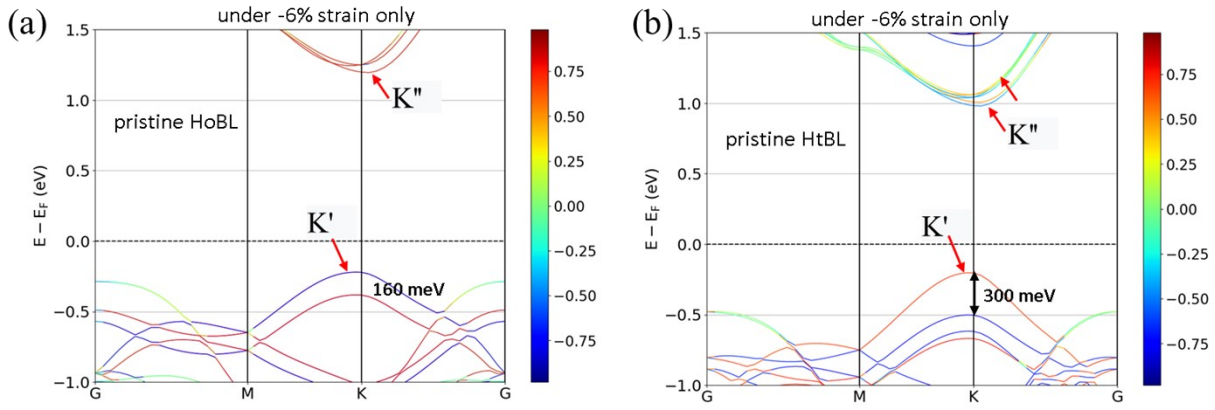

Fig. S12 The electronic band structures of the pristine MoS_2 homobilayer (HoBL) and WS_2–MoS_2 heterobilayer (HtBL) with Spin-Orbit Coupling (SOC) using the PBE method at 6% compressive strain. Arrows indicate band edge positions.

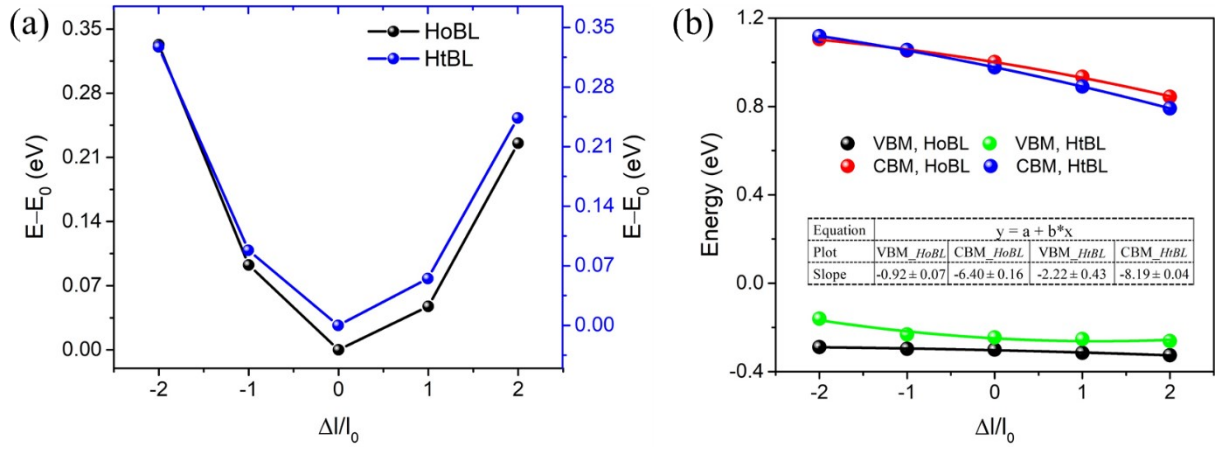

Fig. S13 (a) The total energy *vs*. strain in the sandwich homobilayer (HoBL) and heterobilayer (HtBL). (b) The energy shifts of the valence band maximum (VBM) and conduction band minimum (CBM) *vs*. strain.

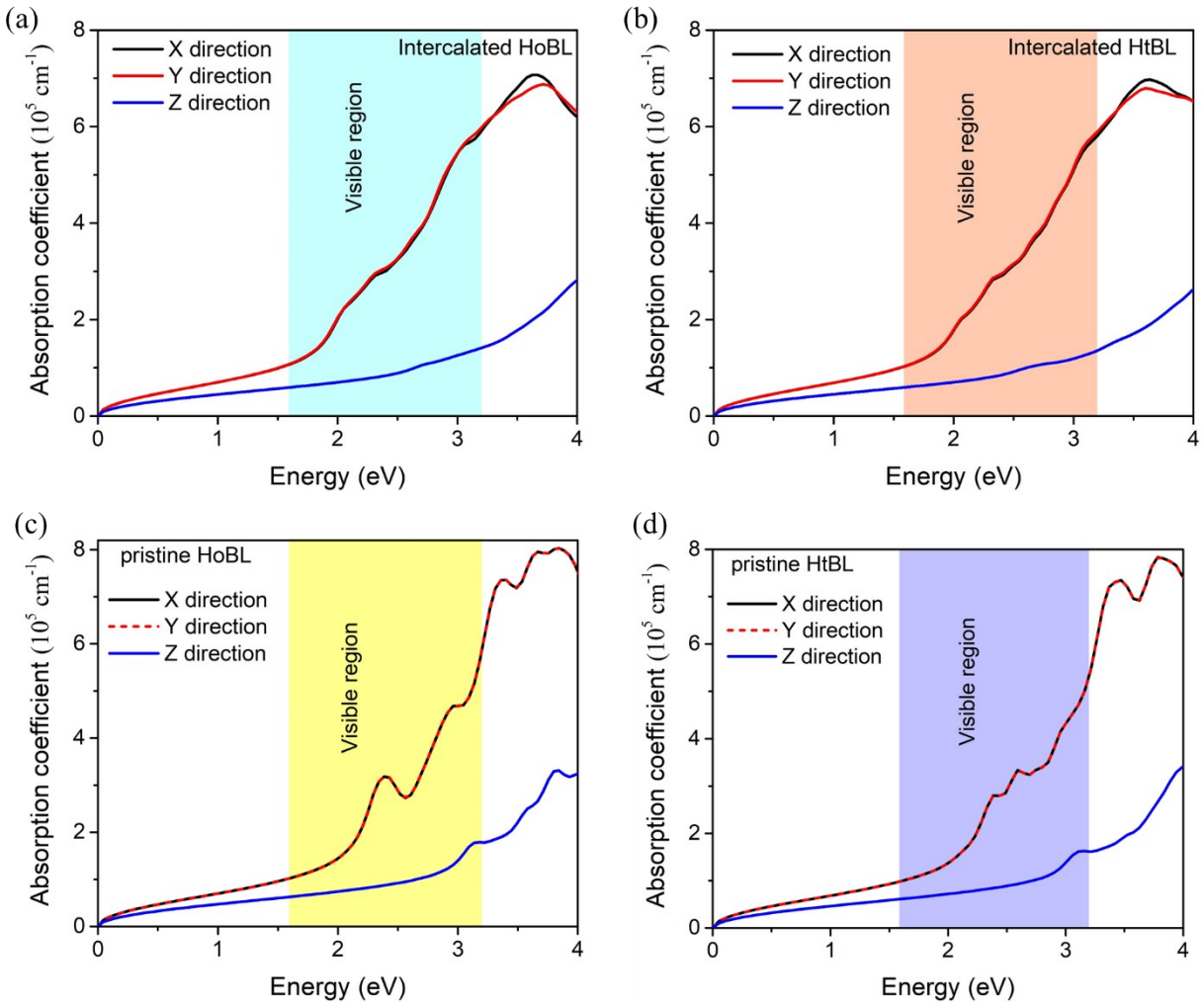

Fig. S14 Calculated absorption coefficients of the (a) sandwich homobilayer (HoBL) and (b) sandwich heterobilayer (HtBL), (c) pristine MoS_2 HoBL, and (d) pristine WS_2–MoS_2 HtBL for incident light polarized along the X, Y, and Z directions using the HSE06 method. The highlighted part represents the visible light region.