Supplemental Information for:

Achieving Non-Degenerate Sliding Ferroelectricity via Band-Edge Pinning: A General Design Principle for Controllable Photocatalysis and Photovoltaics

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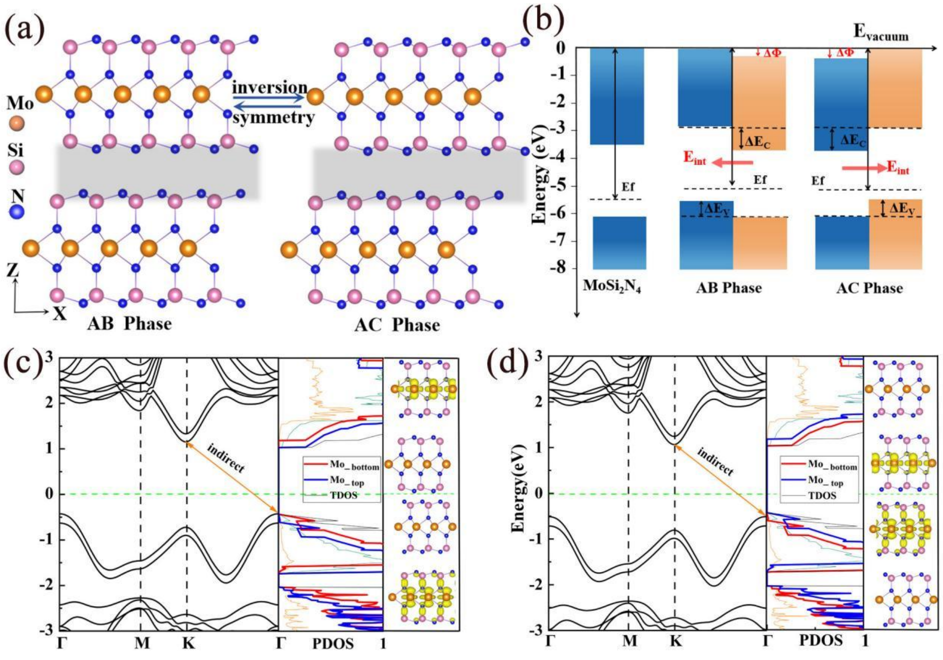

Fig. S1 . (a) Atomic structure diagrams between initial (AB) and final (AC) phases of $MoSi_2N_4$ homo-bilayer sliding ferroelectrics, with the red diamond in each panel indicating the unit cell. (b) Band alignment diagrams between monolayer $MoSi_2N_4$ and it based AB and AC homo-bilayers. (c-d) Band structures (left panel), partial density of states (PDOS,middle panel), and partial charge densities (right panel) at CBM and VBM between AB and AC stacked $MoSi_2N_4$ bilayers.

Table. S1. Binding energies (E_b) of the $MoSi_2N_4/WSi_2N_4$ hetero-bilayers under different stackings.

Stacking	AA	AB	AC	AA’	AB’	AC’
E_b (eV)	-0.3064	-0.3685	-0.3557	-0.3372	-0.3505	-0.3555

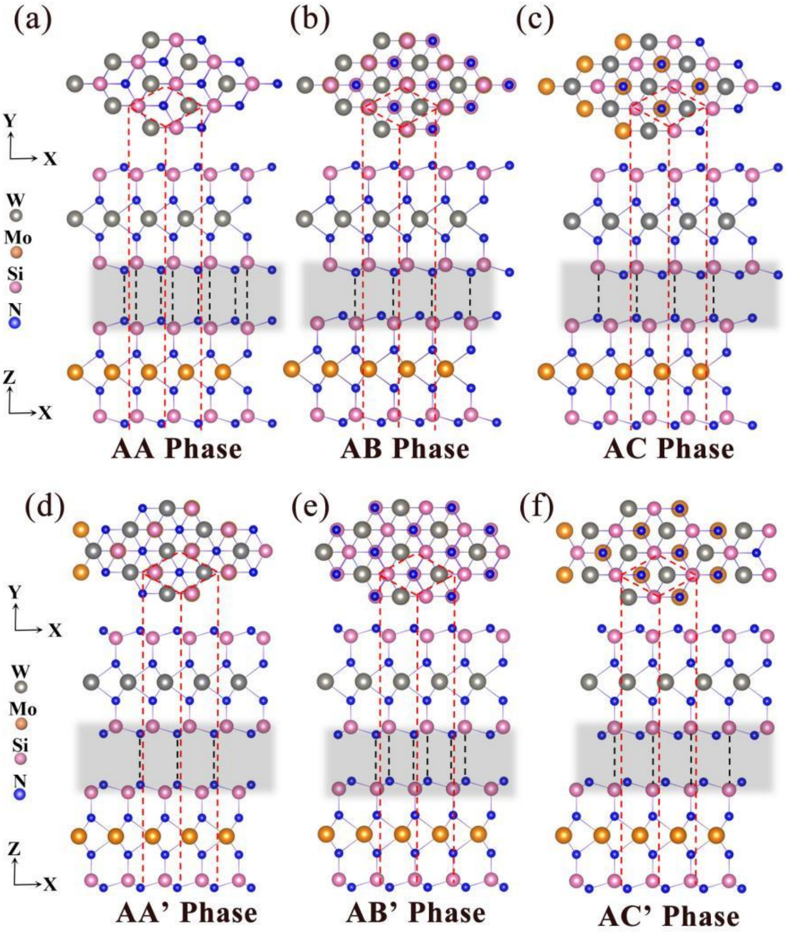

Fig. S2. (a-f) Top and side views of $MoSi_2N_4/WSi_2N_4$ hetero-bilayer under different stacking phases. In each panel, the unit cell is outlined by the red diamond.

Table. S2 . Total energies of all absorbed species between AB and AC phases, including the absorption sites at Si atom, N atom, the bond, and the vacancy sites.

Stacking		**Si (eV)**	**N**	**bond**	**vacancy**
AB	**H***	**-519.75**	-519.17	-518.70	-519.41
	OH*	-528.08	**-528.11**	-528.01	-528.01
	O*	-521.49	-520.68	-521.37	**-521.89**
	OOH*	-532.03	-531.20	**-532.09**	-531.31
AC	**H***	**-519.73**	-519.19	-518.61	-519.40
	OH*	-528.10	-528.01	**-528.12**	-527.98
	O*	**-521.68**	-520.13	-518.32	-520.87
	OOH*	-532.05	-531.12	-531.31	**-532.09**

Solar-to-hydrogen (STH) efficiency

The calculation method for solar-to-hydrogen (STH) efficiency is defined as follows:

$$\eta_{STH} = \eta_{abs} \times \eta_{cu} \tag{1}$$

Where η_{abs} and η_{cu} are the efficiency of light absorption and carrier utilization, respectively, in which η_{abs} is evaluated via:

$$\eta_{abs} = \frac{\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)}{\int_{0}^{\infty} P(\hbar\omega)d(\hbar\omega)} \tag{2}$$

where P(ħω) is the solar flux at AM1.5 photon energy ħω and E_g is the band gap of the material.The $\eta_{cu}$is estimated by:

$$\eta_{cu} = \frac{\Delta G \int_{E}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)}{\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)} \tag{3}$$

where ΔG is the potential difference 1.23 eV for water splitting reaction, and E denotes the actual photon energy used for water splitting, which can be defined as:

$$E = \begin{cases} E_g, (\chi_{H_2} \geq 0.2, \chi_{O_2} \geq 0.6) \\ E_g + 0.2 - \chi_{H_2}, (\chi_{H_2} < 0.2, \chi_{O_2} \geq 0.6) \\ E_g + 0.6 - \chi_{O_2}, (\chi_{H_2} \geq 0.2, \chi_{O_2} < 0.6) \\ E_g + 0.8 - \chi_{H_2} - \chi_{O_2}, (\chi_{H_2} < 0.2, \chi_{O_2} < 0.6) \end{cases} \tag{4}$$

where $\chi(H2)$ and $\chi(O2)$ represent the overpotentials for HER and OER, respectively. To account for the energy losses during charge carrier transport across material interfaces, these overpotentials are assumed to be 0.2 eV for HER and 0.6 eV for OER.

Furthermore, the intrinsic built-in electric field within the interlayer actively promotes electron-hole separation during photocatalytic water splitting. Consequently, this contribution must be included in the total energy calculation. The corrected STH efficiency for a 2D material with an intrinsic E_{int} is calculated

$$\eta'_{STH} = \eta_{STH} \times \frac{\int_0^\infty P(h\omega)d(h\omega)}{\int_0^\infty P(h\omega)d(h\omega) + \Delta\Phi \int_{E_g}^\infty \frac{P(h\omega)}{h\omega}d(h\omega)} \tag{5}$$

where $\Delta\Phi$ is the vacuum level difference on the vdWH $MoSi_2N_4/WSi_2N_4$.

Calculation details of Gibbs free energy

The Gibbs free energy change (ΔG) for the Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) under non-irradiated, pH=0 conditions is given by the equation provided below.

$$\Delta G = \Delta E + \Delta E_{zpe} - T\Delta S \tag{6}$$

Here, ΔE denotes the total energy difference between the adsorbed and desorbed states, while ΔE_{ZPE} represents the corresponding zero-point energy correction. The term $T\Delta S$ accounts for the entropic contribution.

For the redox reactions of water-splitting, the reaction of HER can be divided into two steps:

$$* + H^+ + e^- \rightarrow H^* \tag{7}$$

$$H^* + H^+ + e^- \rightarrow * + H_2 \tag{8}$$

and for OER, the half-reaction is decomposed into four steps:

$$* + H_2O \rightarrow OH^* + e^- + H^+ \tag{9}$$

$$OH^* \rightarrow O^* + e^- + H^+ \tag{10}$$

$$H_2O + O^* \rightarrow OOH^* + e^- + H^+ \tag{11}$$

$$OOH^* \rightarrow * + O_2 + e^- + H^+ \tag{12}$$

where * means the adsorbed materials, O*, OH*, OOH* and H* represent the adsorbed intermediates. The free energy of both hydrogen production and oxidation reactions is influenced by pH and an applied external potential bias:

$$\Delta G_a = G_{H*} - \frac{1}{2}G_{H2} - G_* + \Delta G_U + \Delta G_{PH} \tag{13}$$

$$\Delta G_b = G_* + \frac{1}{2}G_{H2} - G_{H*} + \Delta G_U + \Delta G_{PH} \tag{14}$$

$$\Delta G_C = G_{OH*} + \frac{1}{2}G_{H2} - G_* - \Delta G_{H2O} + \Delta G_U - \Delta G_{PH} \tag{15}$$

$$\Delta G_d = G_{O*} + \frac{1}{2}G_{H2} - G_{OH*} + \Delta G_U - \Delta G_{PH} \tag{16}$$

$$\Delta G_e = G_{ooH*} + \frac{1}{2}G_{H2} - G_{o*} - G_{H2O} + \Delta G_U - \Delta G_{PH} \tag{17}$$

$$\Delta G_f = G_* + \frac{1}{2}G_{H2} + G_{O2} - \Delta G_{OOH*} + \Delta G_U - \Delta G_{PH} \tag{18}$$

Where ΔG_{PH} ($\Delta G_{PH} = 0.0591 \times pH$) represents the free energy contribution under varying pH conditions. Meanwhile, ΔG_U ($\Delta G_U = -eU$), signifies the influence of an additional potential bias on electrons and holes within the electrode. U is the electrode potential measured versus the Standard Hydrogen Electrode (SHE).