Supplementary Materials

Electronic structure and stability

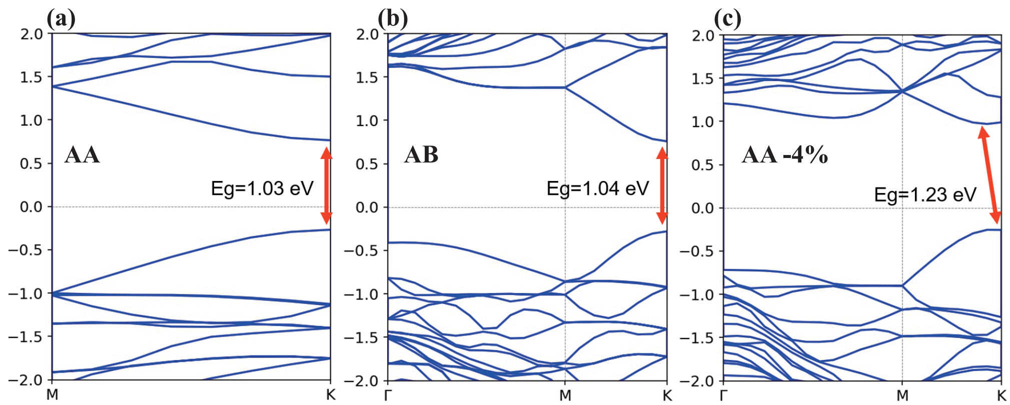

Figure S1: The band structures calculated by HSE06 hybrid functional for the (a) AA stacking, (b) AB stacking, and (c) AA stacking under -4% vertical strain, respectively.

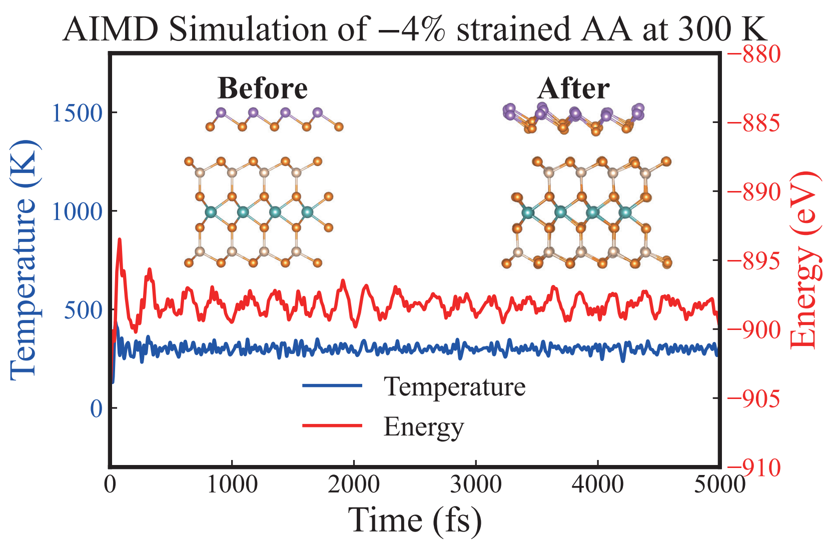

Figure S2: The *ab initio* molecular dynamics (AIMD) simulation of the AA stacking under -4% strain. The atomic structures before and after the simulation are also shown.

Bader charge analysis

To further explore the electronic properties of the heterostructure, the Bader population calculation is performed to quantify the charge transfer between the two sublayers. In the

AA stacking, each Mo and Si atom loses on average 0.78 e and 1.77 e, respectively, with the electrons predominantly transferred to the P atoms in the $MoSi_2P_4$ monolayer, particularly the outer P atoms ($\sim$1.08 e each). Within the AsP monolayer, charge redistribution occurs mainly from As to P atoms, consistent with the tendency of As to lose electrons and P to gain electrons.

For the AB stacking, the corresponding values are slightly different: each Mo and Si atom loses 0.77 e and 1.78 e, respectively, and the electrons are mainly transferred to the P atoms ($\sim$1.08 e each). The stacking configuration strongly affects the interlayer charge transfer. In the AB stacking, As atoms are positioned between two P atom layers-one from the AsP sublayer and the other from the $MoSi_2P_4$ sublayer-facilitating interlayer electron transfer. In contrast, the AA stacking makes such interlayer transfer less favorable. The Bader charge analysis reveals negligible interlayer transfer in the AA stacking (<0.01 e) and slightly larger transfer in AB stacking ($\sim$0.03 e), indicating relatively stronger interlayer hybridization in AB stacking. The interlayer charge transfer under various strain conditions is shown more specifically in Fig. S3.

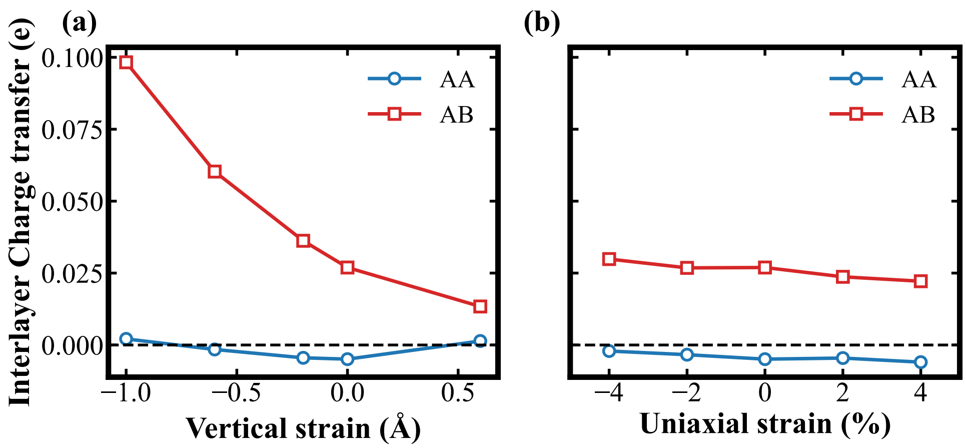

Figure S3: The calculated Bader charge transfer of the two stackings with respect to the (a) vertical strain and (b) uniaxial strain, respectively. The calculated AA and AB stackings are represented by circle and square, respectively.

Electrical Transport Properties

The carrier mobility is evaluated using the deformation potential (DP) theory originally proposed by Bardeen and Shockley. Since the effective masses of both electrons and holes along the x and y directions are nearly identical, the heterostructure can be reasonably approximated as isotropic. Accordingly, the carrier mobility is calculated using:

$$\mu = \frac{2e\hbar^3 C_{2D}}{3k_B T m^{*2} E_l^2} \tag{1}$$

where e is the elementary charge, $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, and T is the temperature. The m^* denotes the carrier effective mass along the

Table S1: Electrical transport properties of the AA stacking configuration. The effective masses $m^{(\nu)}$ are evaluated at the band edges (CBM for electrons and VBM for holes) and are expressed in units of the free electron mass m_0. The deformation potential constants $E_l^{(\nu)}$ are given in eV. The in-plane elastic moduli C_{2D} are in $J\,m^{-2}$. The carrier mobilities $\mu^{(\nu)}$ (in $cm^2\,V^{-1}\,s^{-1}$) are calculated using the isotropic Bardeen–Shockley deformation potential theory.

Direction	$m^{(e)}$	$m^{(h)}$	$E_l^{(e)}$	$E_l^{(h)}$	C_{2D}	$\mu^{(e)}$	$\mu^{(h)}$
x	0.381	0.343	-7.88	-4.45	276.84	436.95	1259.09
y	0.397	0.347	-7.84	-4.42	282.17	554.48	1708.20

transport direction, C_{2D} is the in-plane elastic modulus, and E_l is the deformation potential constant defined as:

$$E_l = \frac{\partial E_{\mathrm{edge}}}{\partial \varepsilon}, \tag{2}$$

where E_{edge} represents the conduction band minimum (CBM) for electrons or the valence band maximum (VBM) for holes, and ε is the applied uniaxial strain. It should be noted that the deformation potential (DP) theory considers only longitudinal acoustic phonon scattering within the effective mass approximation. Other scattering mechanisms, such as optical phonons, impurities, and defects, are not included. Therefore, the calculated mobilities represent the intrinsic, acoustic-phonon-limited transport at room temperature.

Power conversion efficiency

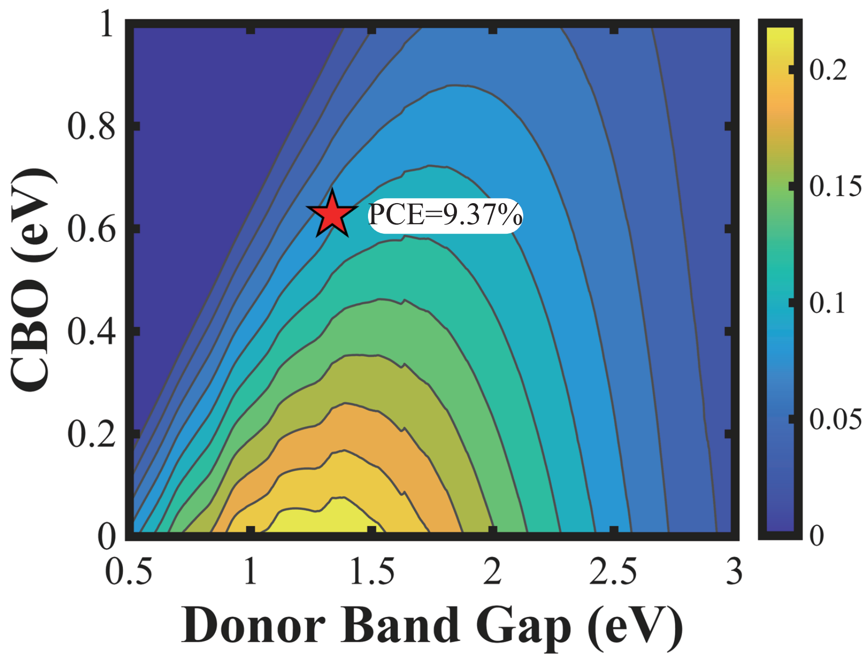

Figure S4: The calculated PCE of the unstrained AsP/$MoSi_2P_4$ heterostructure with AB stacking.