Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supplementary Materials

Versatile van der Waals Heterostructures of γ-GeSe with h-BN/Graphene/MoS_2

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Lattice mismatches and strains

The lattice mismatches (η) were calculated through

$$\eta = \left|\frac{a_0 \times n - a_v}{a_v}\right|$$

where a_0 and a_v represent the lattice constant of the freestanding monolayers and the vdWHs, respectively, n represents the scaling factor from monolayer unit cells to heterojunction supercells.

Furthermore, the strains (ε) induced by lattice mismatches can be calculated as

$$\varepsilon = \frac{a_v - a_0 \times n}{a_0 \times n}$$

The calculated lattice constants, lattice mismatches and strains are shown in the Table S1.

Table S1. The calculated lattice constants and lattice mismatches of γ-GeSe/BN, γ-GeSe/graphene, and γ-GeSe/MoS_2 vdWHs, and the strains of constituent layers in vdWHs relative to their freestanding monolayers where negative (positive) values represent compressive (tensile) strain.

	γ-GeSe	BN	γ-GeSe	Graphene	γ-GeSe	MoS_2
a_0 (Å)	3.76	2.51	3.76	2.47	3.76	3.15
a_v (Å)	7.53		7.42		6.39	
η (%)	0.13%	0	1.35%	0.13%	1.92%	1.41%
ε (%)	+0.13%	0	−1.33%	+0.13%	−1.88%	+1.43%

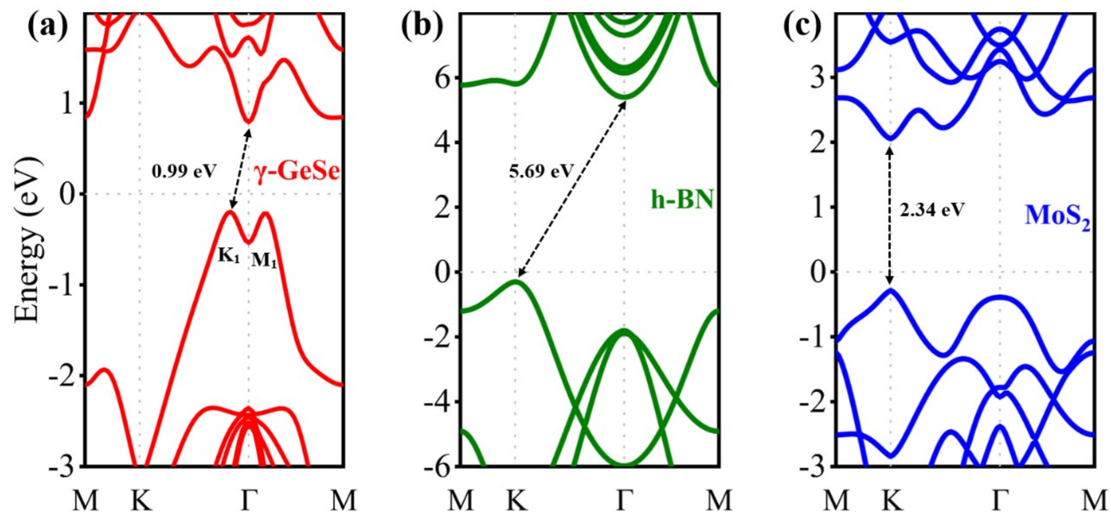

Fig. S1 The band structures of γ-GeSe (a), h-BN (b), and 2H-MoS_2 (c) monolayers by HSE06 functionals. The Fermi level is aligned to 0 eV.

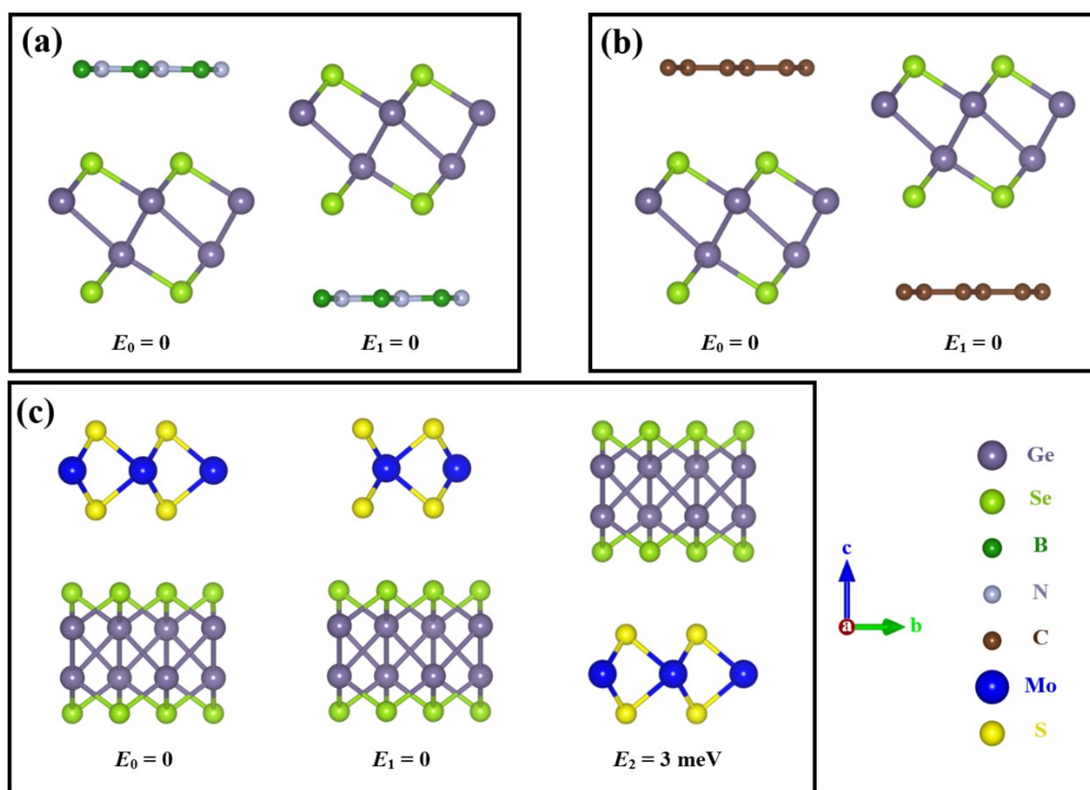

Fig. S2 Total energies of γ-GeSe/BN (a), γ-GeSe/graphene (b), and γ-GeSe/MoS_2 (c) vdWHs with different stacking order. The energy of γ-GeSe/X vdWH (E_0) discussed in this work is set to 0 for reference.

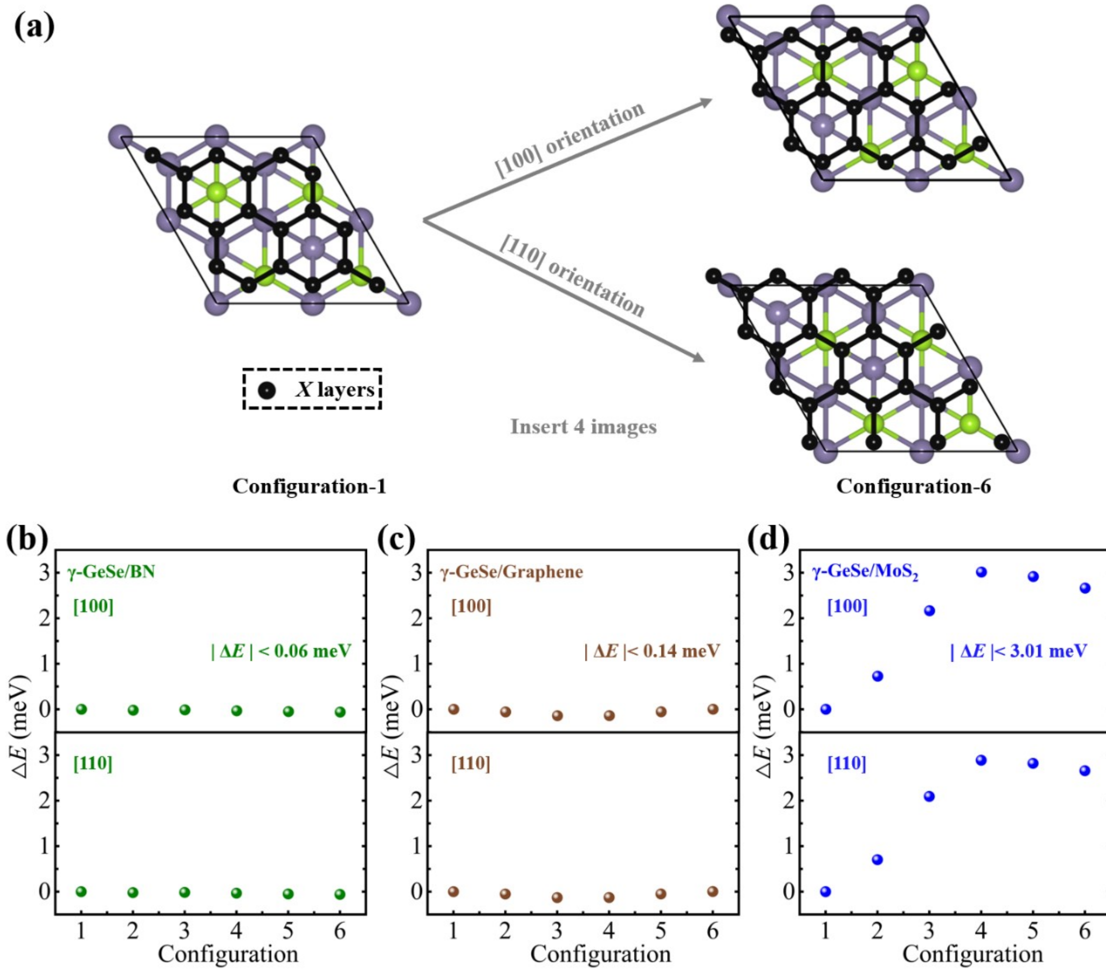

Fig. S3 Schematic of the structures (a) obtained by linearly shifting half the unit-cell parameters along the [100] and [110] orientation, and the relative energies of the six structures of γ-GeSe/BN (b), γ-GeSe/graphene (c), and γ-GeSe/MoS_2 vdWHs (d). The total energy of configuration-1 is set to 0 as a reference.

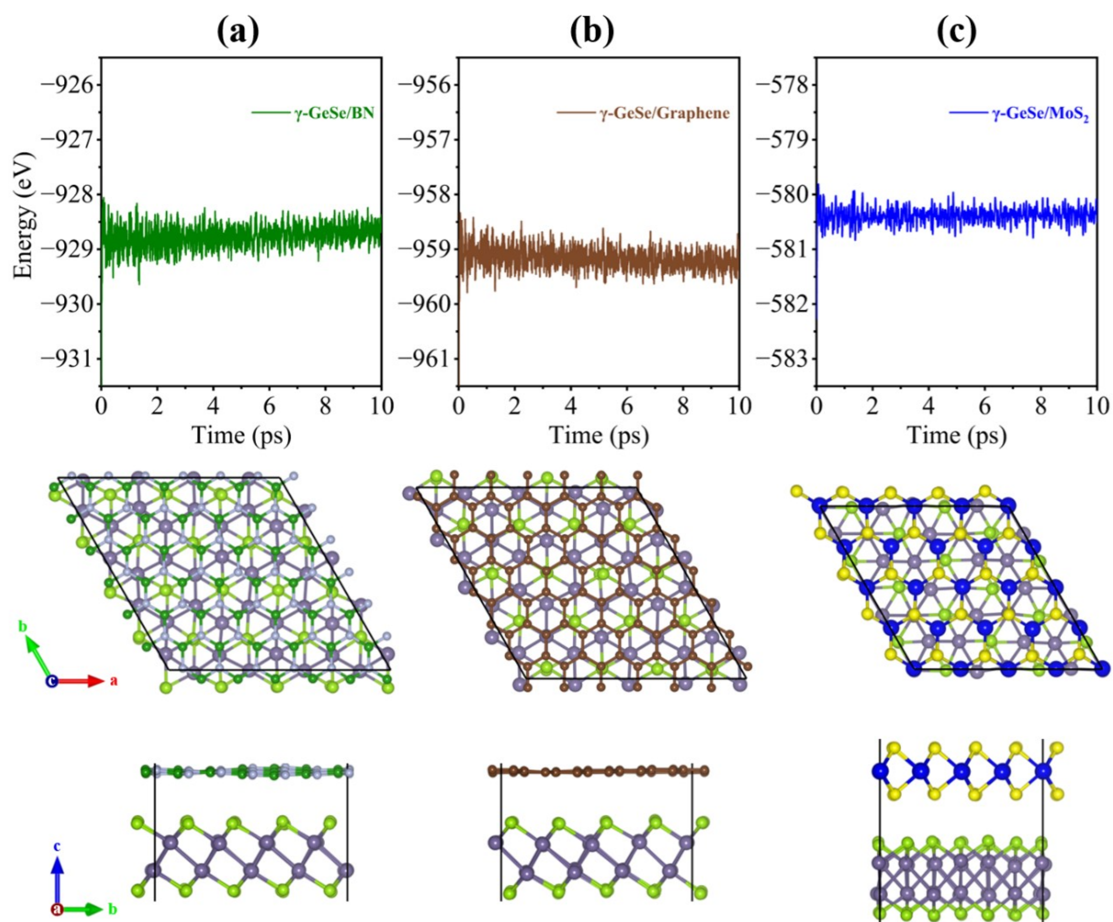

Fig. S4 Total energy evolution and 10 ps snapshots of γ-GeSe/BN (a), γ-GeSe/graphene (b), and γ-GeSe/MoS_2 (c) vdWHs from ab initio molecular dynamics calculations (AIMD).

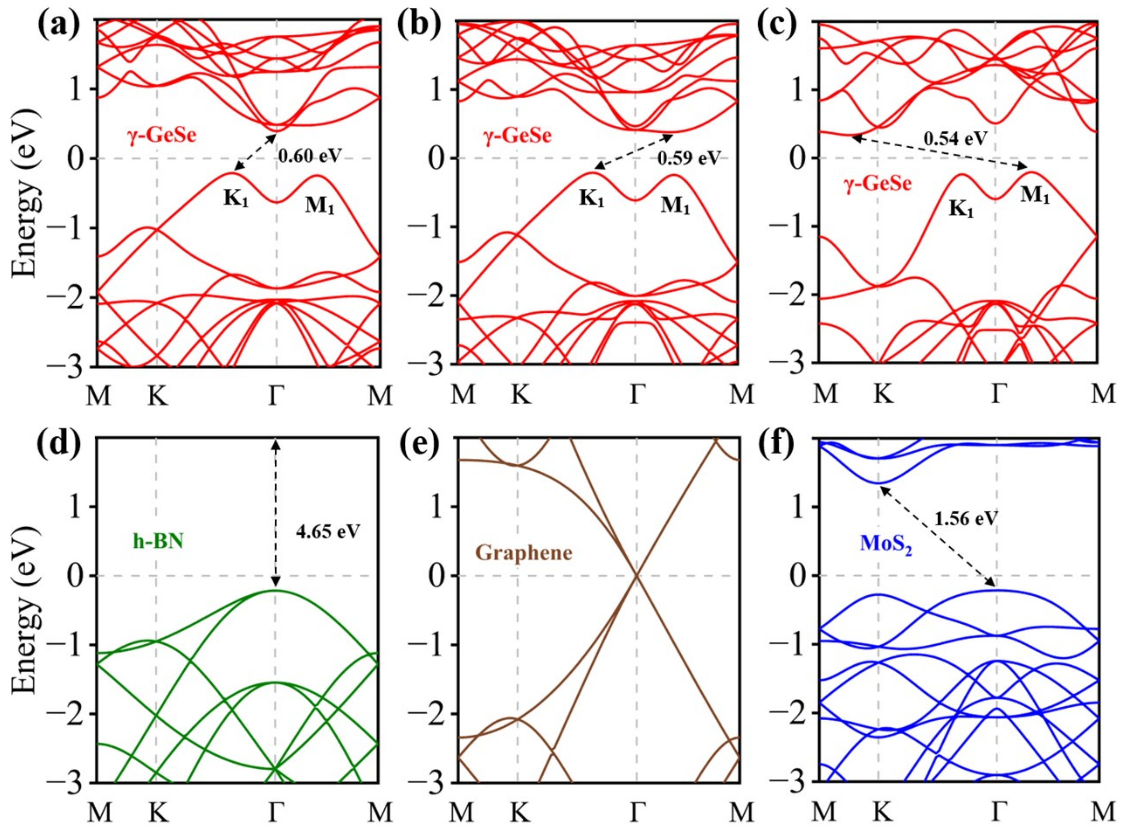

Fig. S5 Band structures of (a) γ-GeSe and (d) h-BN monolayer supercell under the strain equivalent to that in the γ-GeSe/BN vdWH, band structures of (b) γ-GeSe and (e) graphene monolayer supercell under the strain equivalent to that in the γ-GeSe/graphene vdWH, and (c) γ-GeSe and (f) MoS_2 monolayer supercell under the strain equivalent to that in γ-GeSe/MoS_2 vdWH.

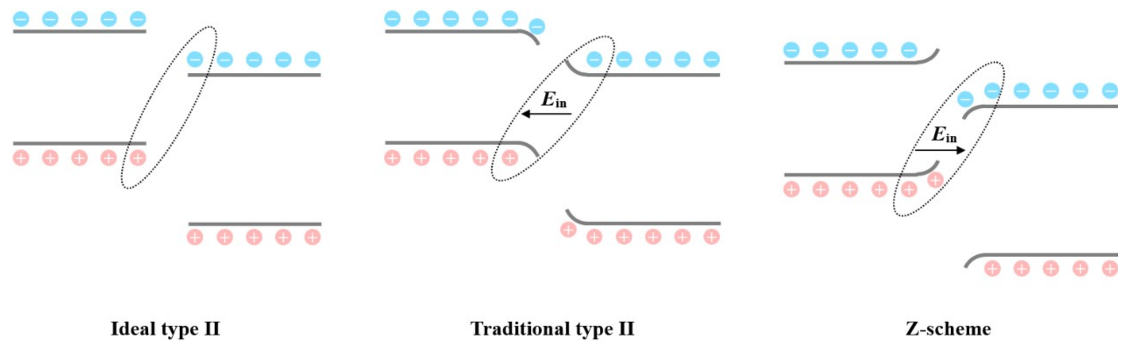

Fig. S6 Band alignment interface of ideal type II, traditional type I, and Z-scheme.

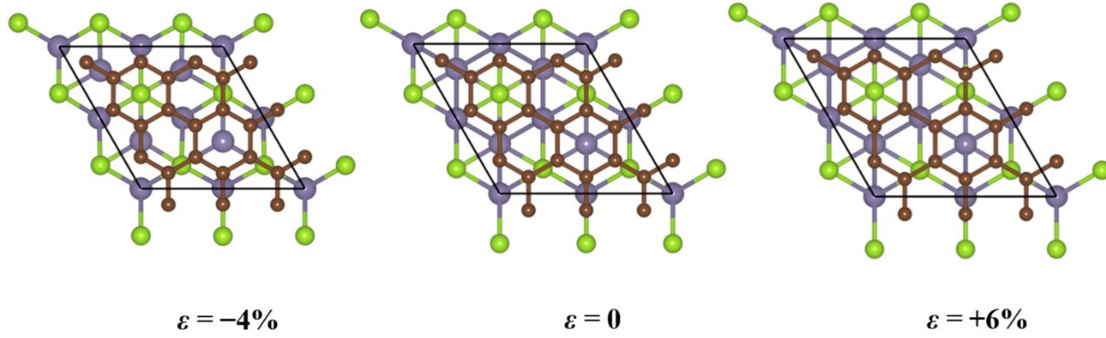

Fig. S7 Top view of the optimized heterostructures of γ-GeSe/graphene under different strains.

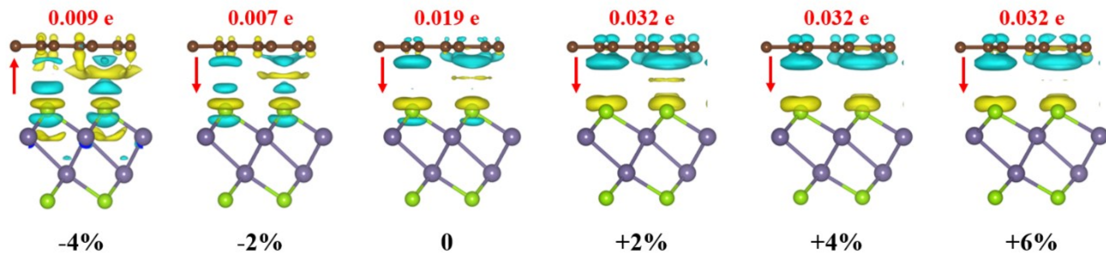

Fig. S8 Front view of the DCD isosurface for γ-GeSe/graphene vdWH under different strains with the isovalue of 10^{-4} e/Å^3. The red arrows and numerical values indicate the direction and amount of charge transfer, respectively.

Discussion on the 2L-GeSe/X vdWHs

The electronic properties of gamma-GeSe are very sensitive to the number of layers, and the band gaps of 1L, 2L and 4L of γ-GeSe are 0.60, 0.34, and 0.04 eV, respectively. Herein, we conducted some calculations regarding the heterostructures of 2L γ-GeSe with the *X* layers. As shown in Table S2, the lattice constants and lattice mismatches of the fully relaxed 2L-GeSe/*X* vdWHs are slightly different from those of 1L-GeSe/*X*

vdWHs. The band structures in Fig. S9 show that the features in the band structures of 2L-GeSe and *X* layers are preserved, and the valence and conduction bands also show a strong hybridization between 2L-GeSe and *X* layers, which are in line with the trend in 1L-GeSe/*X* vdWHs. However, band alignments (Fig. S10) of 2L-GeSe/*X* vdWHs are different from that in 1L-GeSe/*X* vdWHs due to the bandgaps change (i.e., change in the relative positions of the valence and conduction bands) in the 2L-GeSe as well as the strain effect. In 2L-GeSe/BN vdWH, the position of the CBM of GeSe relative to BN remains unchanged (2.56 to 2.58 eV), while the VBM of GeSe is moved up, leaving a ΔE_V to 1.65 eV. Similarly, in 2L-GeSe/Graphene vdWH, the Fermi level is located within the valence band of 2L-GeSe due to the upward shift of the VBM of GeSe, forming a metal-semiconductor ohmic contact. In 2L-GeSe/MoS_2 vdWH, the strain caused by the lattice mismatch makes the bandgap (1.42 eV) of MoS_2 smaller than that in 1L-GeSe/MoS_2 vdWH (1.56 eV). The change in the bandgaps of 2L-GeSe and MoS_2 is manifested as an up-shift of the VBM of GeSe and a down-shift of the CBM of MoS_2 in the 2L-GeSe/MoS_2 vdWH, finally forming a type-III band alignment. Therefore, the trend of interlayer interaction in 2L-GeSe/*X* vdWHs are basically consistent with that of 1L-GeSe/*X* vdWHs except for the bandgap and strain effects.

Table S2. The calculated lattice constants, lattice mismatches and strains of 2L-γ-GeSe/*X* vdWHs.

	2L γ-GeSe	BN	2L γ-GeSe	Graphene	2L γ-GeSe	MoS_2
a_0 (Å)	3.77	2.51	3.77	2.47	3.77	3.15

a_v (Å)	7.53		7.44		6.43	
η (%)	0.13%	0	1.34%	0.40%	1.55%	2.02%
ε (%)	-0.13%	0	−1.33%	+0.40%	−1.53%	+2.06 %

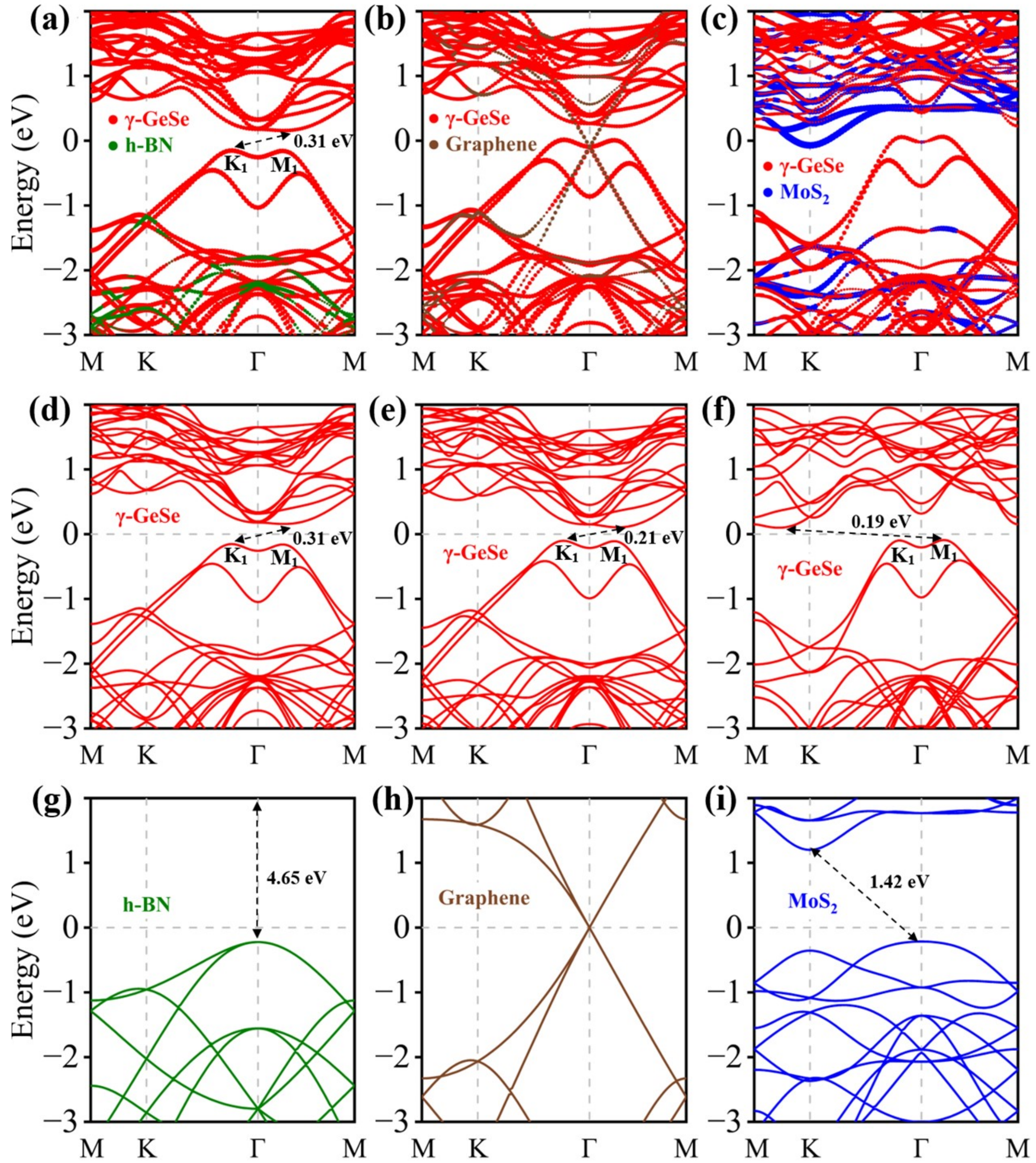

Fig. S9 Band structures of 2L-γ-GeSe/BN vdWH (a), and 2L-γ-GeSe (d) and h-BN (g) monolayer under the strain equivalent to that in the 2L-γ-GeSe/BN vdWH; band

structures of 2L-γ-GeSe/graphene vdWH (b), and 2L-γ-GeSe (e) and graphene (h) monolayer under the strain equivalent to that in the 2L-γ-GeSe/graphene vdWH; band structures of 2L-γ-GeSe/MoS_2 vdWH (b), and 2L-γ-GeSe (f) and MoS_2 (i) monolayer under the strain equivalent to that in 2L-γ-GeSe/MoS_2 vdWH.

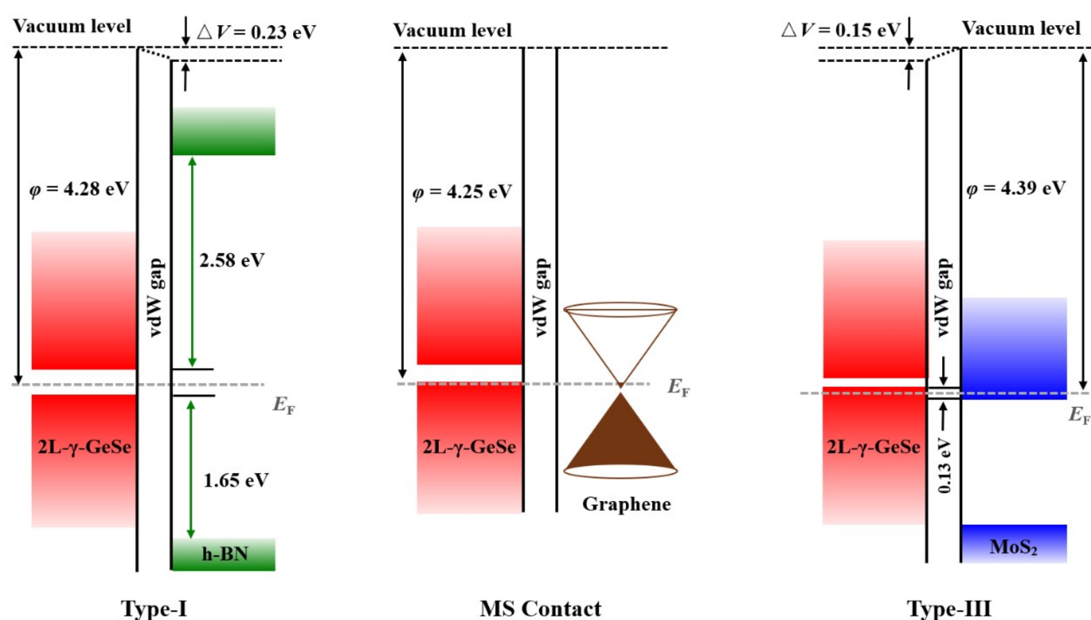

Fig. S10 The band alignment diagrams of 2L-γ-GeSe/BN, 2L-γ-GeSe/graphene and 2L-γ-GeSe/MoS_2 vdWHs.