Electronic supplementary information

2D Layered BP/Group-IV monochalcogenide Van der Waals Heterostructures for Photovoltaics: Electronic Structure, Band Alignment, and Carrier Dynamics

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1. Sampling tests in the Brillouin zone of different grids

All of our calculations were carried out with a mesh of 0.02/Å. We tested the total energy of pristine BP, group-IV monochalcogenides, and four vdW heterostructures, as well as the binding energy of vdW heterostructures with different meshes. Fig. S1 (a) and (b) show the total energy per unit cell of pristine BP, group-IV monochalcogenides, and four vdW heterostructures, respectively, and it can be seen that the energy error of total energy with the mesh of 0.02/Å is less than 1 *m*eV per unit cell compared with smaller meshes. Fig. S1 (c) shows the binding energy of four vdW heterostructures, and it can be seen that the energy error is less than 1 *m*eV/Å^2. Therefore, the accuracy of a mesh of 0.02/Å is sufficient.

2. Effect of horizontal sliding on the stability and electrical properties of vdW heterostructures

In order to explore the effect of the horizontal slide, we compared the binding energy and band gap of different sliding configurations using BP/SnSe as an example. Considering the symmetry and computational cost, we considered BP/SnSe heterostructures sliding horizontally along the armchair direction by 1, 2, 3, and 4 Å as well as along the zigzag direction by 1 and 2 Å. We labelled them as a_1, a_2, a_3, a_4, z_1, and z_2, respectively. As shown in Fig. S4, horizontal slides do give rise to configurations with different stabilities and band gaps as expected. For the BP/SnSe example, the original configuration and the a_3 horizontal slide configuration are the most stable configurations. Among all configurations considered, the maximum difference of binding energy is less than 1 *m*eV/A^2, with band gap differences up to 0.01 eV.

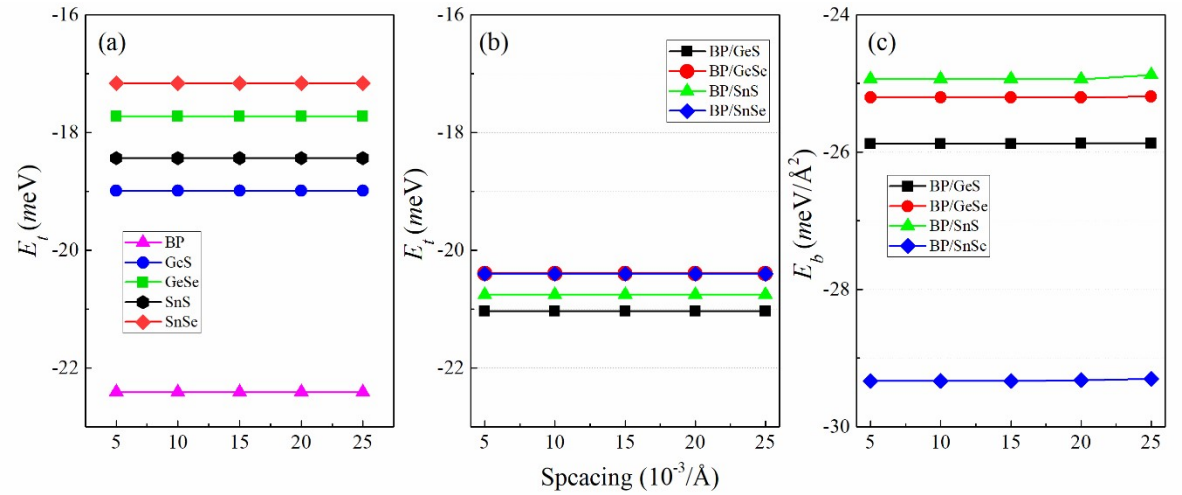

Fig. S1 The total energy per unit cell of (a) pristine BP, group-IV monochalcogenides and (b) four vdW heterostructures. (c) The binding energy of four vdW heterostructures with different meshes of 5, 10, 15, 20, and 25 $\times 10^{-3}$/Å.

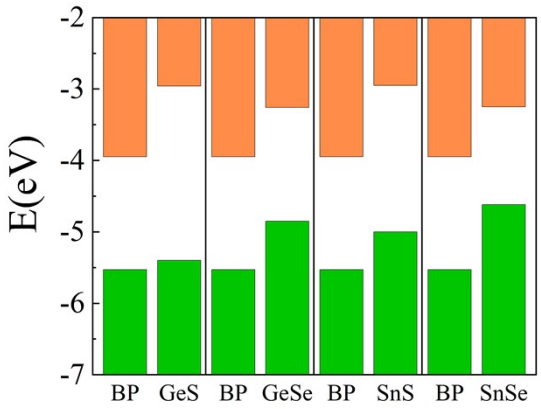

Fig. S2 Band alignments of BP/GeS, BP/GeSe, BP/SnS, and BP/SnSe at Anderson limit calculated with the HSE06 functional.

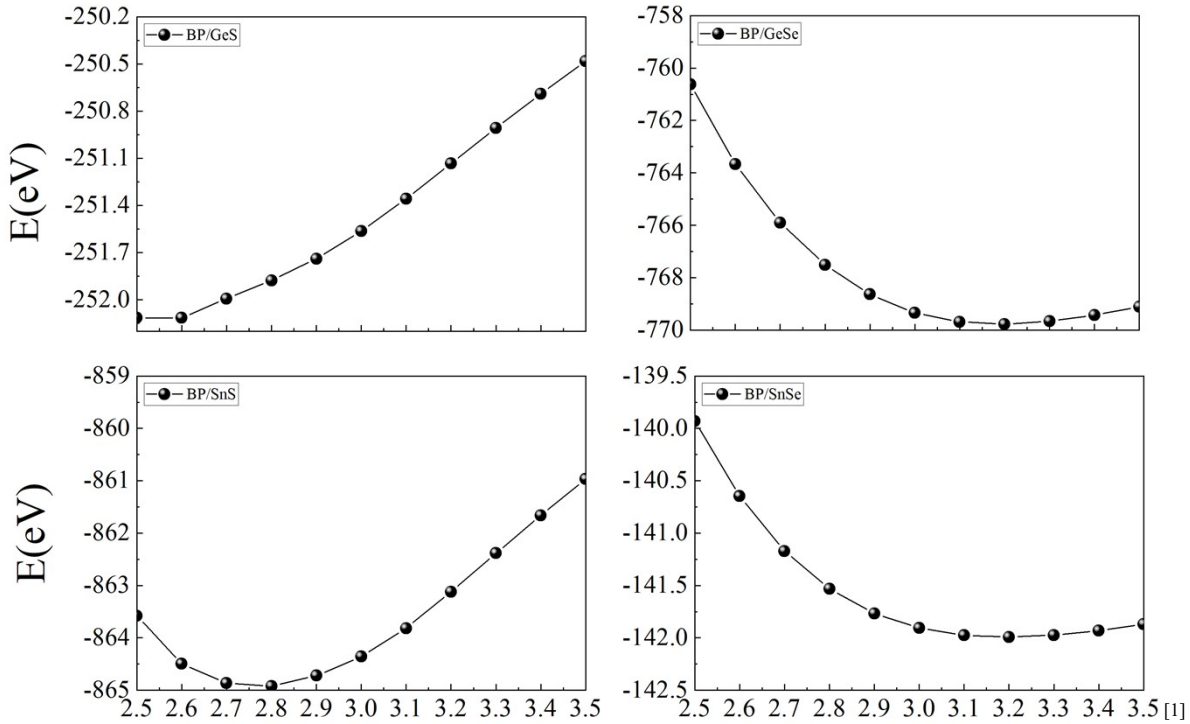

Fig. S3 The total energy of heterostructures with interlayer distance from 2.5 to 3.5 Å with a spacing of 0.1 Å.

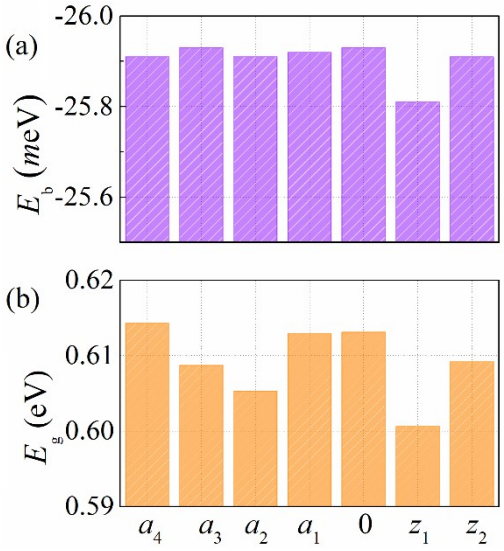

Fig. S4 Binding energy and bandgap of BP/SnSe heterostructure when sliding horizontally along the armchair direction by 1, 2, 3, and 4 Å (a_1, a_2, a_3, and a_4) as well as along the zigzag direction by 1 and 2 Å (z_1 and z_2).

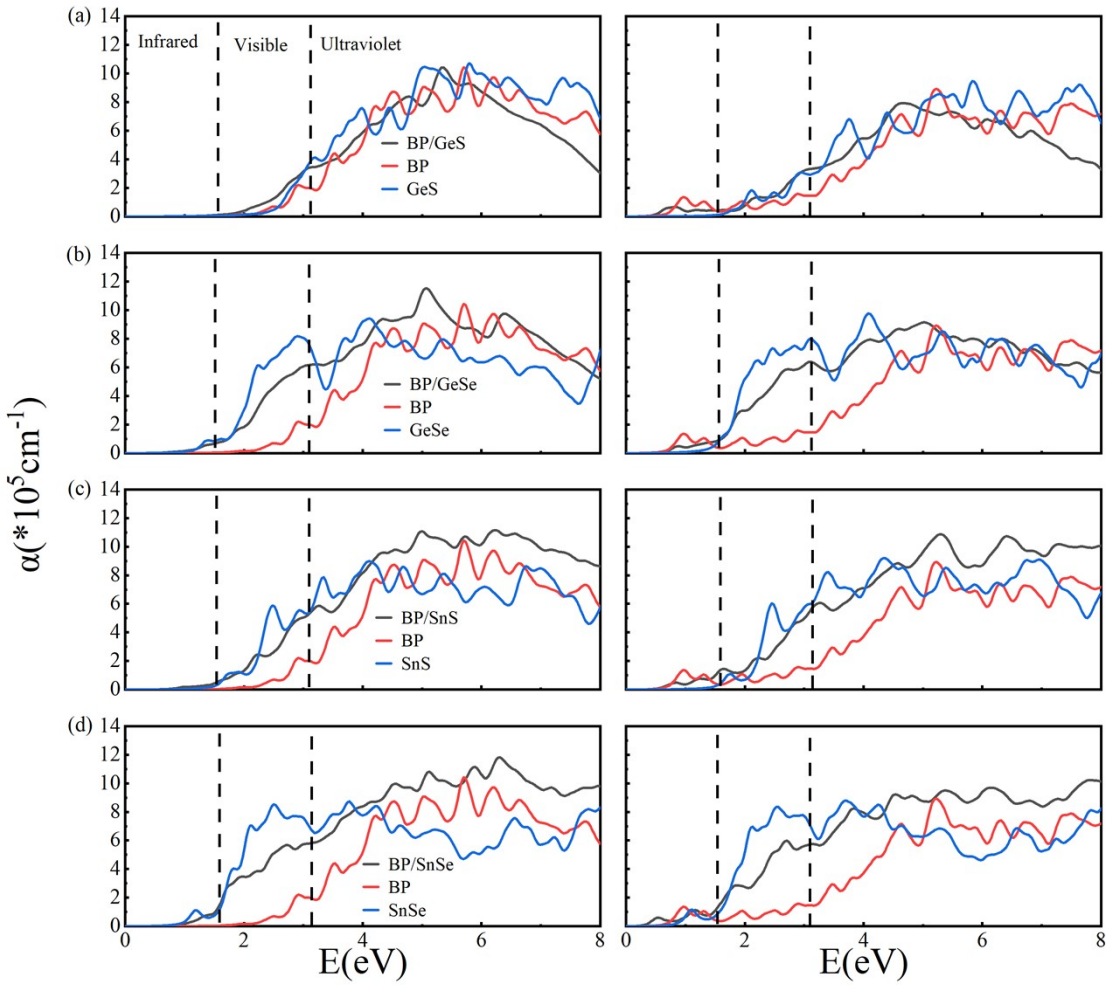

Fig. S5 The optical absorption spectra of (a) BP/GeS, (b) BP/GeSe, (c) BP/SnS, and (d) BP/SnSe vdW heterostructures along the zigzag direction (left) and the armchair direction (right) of BP calculated with the HSE06 functional.

Table S1 Atomic and electronic structure information for BP, GeS, GeSe, SnS, and SnSe: vasp and siesta lattice constants (a, b), band gap (E_g), electron affinity (χ), ionization energy (I) calculated by PBE and HSE06.

	VASP		Siesta		E_g(eV)		χ(eV)		I(eV)	
	a(Å)	b(Å)	a(Å)	b(Å)	PBE	HSE06	PBE	HSE06	PBE	HSE06
P	3.29	4.60	3.35	4.63	0.84	1.55	4.14	3.95	4.98	5.50
GeS	3.68	4.40	3.67	4.51	1.75	2.37	3.39	2.96	5.14	5.33
GeSe	3.99	4.25	3.99	4.36	1.11	1.64	3.40	3.26	4.51	4.90
SnS	4.07	4.30	4.11	4.33	1.44	2.03	3.15	2.95	4.59	4.98
SnSe	4.29	4.39	4.32	4.53	1.12	1.39	3.37	3.25	4.49	4.64