Supporting Information for

Determination of optimum optoelectronic properties in vertically stacked

MoS$_2$/h-BN/WSe$_2$ van der Waals heterostructures

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Theoretical details:

Considering the difference between surface and core interior of a nanosystem, the lattice strain can be expressed as: $\langle\varepsilon\rangle=\sum_{i\leq n_s}\gamma_i\left(z_ic_i/z_b-1\right)$, where n_s is number of surface layer, z_i, z_b and $c_i=2/(1+\exp((12-z_i)/8z_i))$ are the effective coordination numbers (CNs) of specific ith atomic layer and that of the bulk, and the bond contraction coefficient, respectively.[1] $\gamma_i=\tau_0c_id_0/D$ is the surface-to-volume ratio (SVR), where d_0 is the bond length of Mo-S (W-Se) and B-N, D represents the thickness, and τ_0 is the dimensionality of TMD ($\tau_0=2$) and a thin plate ($\tau_0=1$).[1-3]

Furthermore, the cohesive energy of a nanosystem can be shown as:[3,4]

$E_{coh}(D)=\sum_{i\leq n_s}N_iz_iE_i+\left(N-\sum_{i\leq n_s}N_i\right)z_bE_b$, because the sum of single-bond energy (E_b) of an atom with all nearest neighbors can be approximated by its cohesive energy (E_{coh}), i.e, $E_{coh}=zE_b$, where z is the atomic CNs.[5] $E_i=c_i^{-m}E_b$ is the single-bond energy of Mo-S (W-Se) and B-N in the ith surface layer owing to the surface effect, m is the bond nature factor, and N_i (N) is the number of atoms in the ith surface layer (total atoms).[1] Therefore, we have

$$\Delta E_{coh}(D)\big/E_{coh}(\infty)=\sum_{i\leq n_s}\gamma_i\left(z_ic_i^{-m}\big/z_b-1\right)\qquad(\text{S1})$$

Physically, the width of bandgap (E_g) from the crystal potential is proportional to first Fourier coefficient of the entire crystal potential energy,[4,5] i.e., $E_g\propto\langle E_0\rangle=E_{coh}/N\langle z\rangle$, where $\langle z\rangle=\sum_{i\leq n_s}\gamma_i(z_i-z_b)+z_b$ is the average CNs. Consequently, we obtain the size-dependent bandgap from the above relationships

$$E_g(D)=\frac{z_b}{\langle z\rangle}\left[\sum_{i\leq n_s}\gamma_i\left(\frac{z_i}{z_b}c_i^{-m}-1\right)+1\right]E_g(\infty)\qquad(\text{S2})$$

where $E_g(\infty)$ denotes the bandgap energy of bulk.

In addition, in the light of size-dependent shifts of conduction band minimum (CBM) and valence band maximum (VBM) deduced by Brus[6] and Colvin,[7] $\Delta E_{\mathrm{CBM}}(D) = \hbar^2\pi^2/2m_e D^2$ and $\Delta E_{\mathrm{VBM}}(D) = \hbar^2\pi^2/2m_h D^2$, respectively, and combined with thermodynamic method,[8] the size-dependent shifts of CBM and VBM are

$$\begin{cases} \Delta E_{\mathrm{CBM}}(D) = \dfrac{z_b E_{coh}/\langle z \rangle E_{coh}(\infty) - 1}{m_e/m_h + 1} E_g(\infty) \\ \Delta E_{\mathrm{VBM}}(D) = \dfrac{z_b E_{coh}/\langle z \rangle E_{coh}(\infty) - 1}{m_h/m_e + 1} E_g(\infty) \end{cases} \tag{S3}$$

where m_e and m_h are the effective mass of electron and hole, and $\hbar$ is the reduced Planck constant. Meanwhile, the barrier height defined by the band offset at a heterointerface has an effect on the interlayer recombination and photocarrier collection, thus we need to analyze the conduction band offset (CBO) ΔE_c and valence band offset (VBO) ΔE_v at the heterointerface by work function and electron affinities, i.e.,

$$\begin{cases} \Delta E_c = \chi_i - \chi_2 \\ \Delta E_v = \Delta E_g - \Delta E_c \end{cases} \tag{S4}$$

where χ_i is the electron affinity of MoS_2 and WSe_2, χ_2 is the electron affinity of h-BN, $\chi = \chi^B - \Delta E_{\mathrm{CBM}}(D)$, ΔE_g is the bandgap difference between h-BN and MoS_2 (WSe_2), and the electron affinity in the bulk is $\chi^B = \chi^{\mathrm{monolayer}} + \Delta E_{\mathrm{CBM}}(\mathrm{monolayer})$.

Figure S1a shows the size-dependent cohesive energy of MoS_2 (WSe_2) and h-BN. Clearly, the change trend of cohesive energy of h-BN is smaller than that of MoS_2 (WSe_2). It should be related to the structure of the material, h-BN is a planar hexagonal structure semiconductor, the change of energy in multilayer h-BN is mainly provided by vdW force, and the relaxation of chemical bonds in the plane is

small, but the intralayer chemical bonds of the sandwich-structure TMDs has a large relaxation after stacking multilayer TMDs.
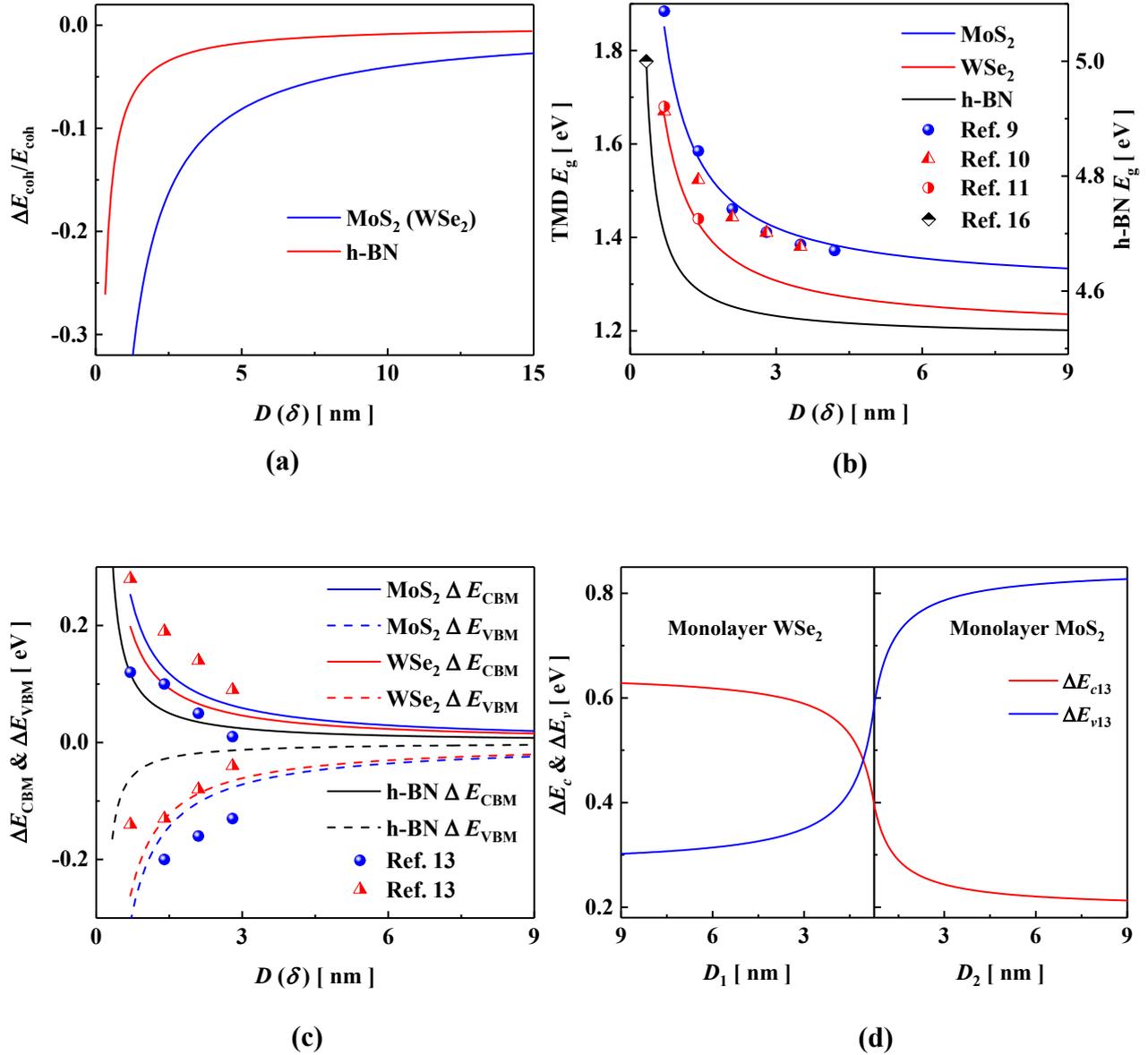
Figure S1. (a) Dependence of a relative change of cohesive energy on thickness. (b) Size-dependent bandgap, (c) band shift of MoS_2, WSe_2 and h-BN. (d) MoS_2 thickness-dependent CBO and VBO between MoS_2 and monolayer WSe_2 (Left), and WSe_2 thickness-dependent CBO and VBO between monolayer MoS_2 and WSe_2 (Right).

In addition, the cohesive energy decreases with decreasing thickness of TMD (h-BN), this trend is mainly related to the CN imperfection and the SVR that decrease with increasing thickness. As the size decreases, the surface effect of bond-order loss and the less-CNs will induce the bond spontaneous shrinkage, resulting in system relaxation into a new self-equilibrium state. Therefore, the bandgap of MoS_2, WSe_2 and h-BN shows a significant redshift with increasing thickness (Fig.S1b). Our results agree reasonably well with the experimental observations and DFT calculations.[9-11] Moreover, it has been reported that the binding energy of interlayer excitons decreases with increasing of h-BN thickness or vacuum between MoS_2 and WSe_2 while the binding energy of intralayer excitons remains constant in MoS_2/h-BN/WSe_2.[12]

Figure S1c shows the size-dependent band-edge shifts of MoS_2, WSe_2 and h-BN. Clearly, as the thickness decreases, the shifts of CBM and VBM increase, that is, the conduction band energy increases and the valence band energy decreases. The trend is related to the cohesive energy of system and can be attributed to the repulsion between cation d orbital and anion p orbital for TMDs.[13] Meanwhile, we obtain band offsets at MoS_2-WSe_2 interface (Fig.S1d). Evidently, the CBO between MoS_2 and WSe_2 in monolayer WSe_2 (MoS_2) increases with increasing (decreasing) thickness of MoS_2 (WSe_2), whereas the VBO in monolayer WSe_2 (MoS_2) decreases as the thickness of MoS_2 (WSe_2) increases (decreases). Physically, the conduction band energy decreases and the valence band energy increases as the thickness increases,[13] thus this trend of CBO and VBO is exhibited in the MoS_2/$WSe_2$with type II band alignment. In addition, due to the difference of electron affinity and bandgap, and the distinct CBO and VBO at the interface, it supplies a viable approach that the band alignment can be modulated by the thickness.

Figure S2 shows the band alignment of the vertical stacked MoS_2/h-BN/WSe_2 vdW heterostructure under different thicknesses. Obviously, regardless of the thickness of TMDs and h-BN, MoS_2 and WSe_2can form type II band alignment, which facilitate the separation of photogenerated carriers to reduce intralayer radiation recombination, and h-BN forms type I band alignment with MoS_2 and WSe_2.

Monolayer/Monolayer/Monolayer

Energy Level

$\chi = 2.0\,eV$
$\chi = 4.2\,eV$
$\chi = 3.8\,eV$
E_c
$\Delta E_{c23} = 1.8\,eV$
E_c
E_c
$\Delta E_{c12} = 2.2\,eV$
$E_g = 1.66\,eV$
$E_g = 5.0\,eV$
$E_g = 1.85\,eV$
E_v
$\Delta E_{v12} = 0.95\,eV$
$\Delta E_{v23} = 1.54\,eV$
E_v
E_v

MoS_2 h-BN WSe_2

(a)

Monolayer/11 layers/Monolayer

Energy Level

$\chi = 2.29\,eV$
$\chi = 4.2\,eV$
$\chi = 3.8\,eV$
E_c
$\Delta E_{c23} = 1.51\,eV$
E_c
E_c
$\Delta E_{c12} = 1.91\,eV$
$E_g = 1.66\,eV$
$E_g = 4.55\,eV$
$E_g = 1.85\,eV$
E_v
$\Delta E_{v12} = 0.79\,eV$
$\Delta E_{v23} = 1.38\,eV$
E_v
E_v

MoS_2 h-BN WSe_2

(b)

Monolayer/Bulk/Monolayer

Energy Level

$\chi = 2.31\,eV$
$\chi = 4.2\,eV$
$\chi = 3.8\,eV$
E_c
$\Delta E_{c23} = 1.49\,eV$
E_c
E_c
$\Delta E_{c12} = 1.89\,eV$
$E_g = 1.66\,eV$
$E_g = 4.52\,eV$
$E_g = 1.85\,eV$
E_v
$\Delta E_{v12} = 0.78\,eV$
$\Delta E_{v23} = 1.37\,eV$
E_v
E_v

MoS_2 h-BN WSe_2

(c)

Bulk/11 layers/Bulk

Energy Level

$\chi = 2.29\,eV$
$\chi = 4.45\,eV$
$\chi = 4.0\,eV$
E_c
$\Delta E_{c23} = 1.71\,eV$
E_c
E_c
$\Delta E_{c12} = 2.16\,eV$
$E_g = 1.20\,eV$
$E_g = 4.55\,eV$
$E_g = 1.29\,eV$
$\Delta E_{v12} = 1.10\,eV$
E_v
$\Delta E_{v23} = 1.64\,eV$
E_v
E_v

MoS_2 h-BN WSe_2

(d)

Figure S2. Band alignment of MoS_2/h-BN/WSe_2 with different configurations, (a) monolayer/monolayer/monolayer, (b) monolayer/11-layers/monolayer, (c) monolayer/bulk/monolayer, (d) bulk/11-layers/bulk, (e)monolayer/11-layers/bulk, and (f) bulk/11-layers/monolayer, respectively.

Besides, the VBO (ΔE_v) at h-BN/MoS_2 interface is small (< 0.78 eV), and the CBO (ΔE_c) at h-BN/MoS_2 interface is larger (> 1.89 eV). It is expected that the intercalated h-BN has less influence on the hole current and can suppress the transfer of electrons from n-type MoS_2 to p-type WSe_2 to reduce the interlayer recombination. This special type band alignment makes the h-BN have the characteristics of electron-blocking/hole-transporting and can improve the photoelectric conversion, which has been verified in some experiments.[14-17] Otherwise, the band alignment at different thicknesses reveals that the electron affinity and ionization energy of MoS_2, WSe_2 and h-BN are different, which supplies the theoretical support for the design of optoelectronic devices.

Figure S3a clearly shows that the PCE increases with increasing thickness of MoS_2 (D_1) and WSe_2 (D_2) and almost reaches maximum of 14% at ~15 nm without h-

BN. It can be attributed to the optical absorption and bandgap, resulting in a lower threshold value of photo-generating carriers.
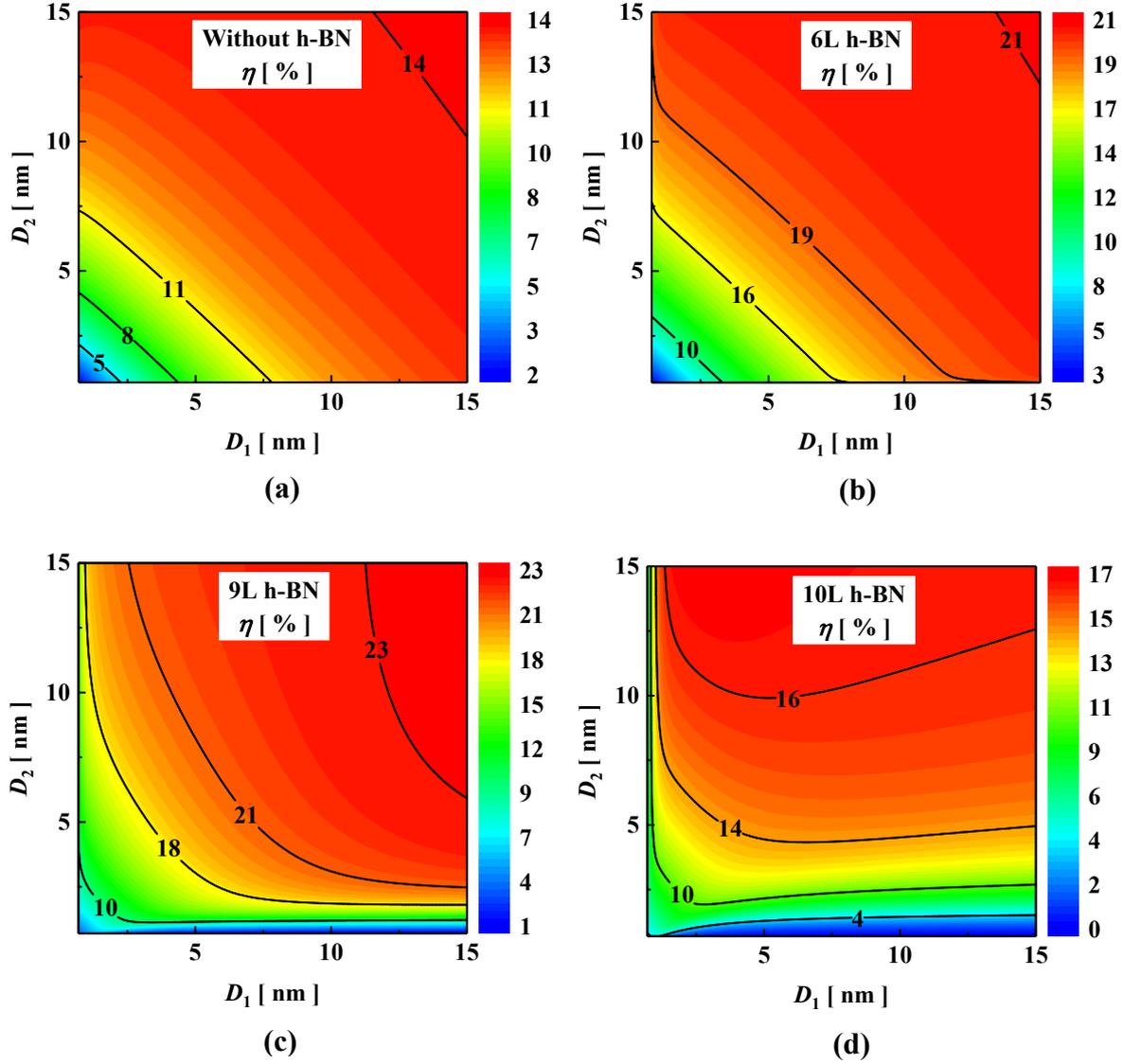
Figure S3. Size-dependent PCE diagram of MoS_2/h-BN/WSe_2 under different intercalated layers, (a) 0L, (b) 6-layers, (c) 9-layers, (d) 10-layers.

Current measurements of V_{oc} in the MoS_2/WSe_2 heterostructure solar cells is 0.2-0.3 V, and the PCEs are about 0.2% and 0.4%,[18-20] which is much lower than predicted, mainly due to the inferior V_{oc} of the system caused by surface contact,

impurity concentration and defects. Figure S3b, 3c and 3d depict the PCE under 6, 9 and 10 h-BN layers as a function of D_1 and D_2. Evidently, the PCE has a maximum of 23.24% under 9-layers h-BN, which is nearly twice that of without h-BN. And the PCE is reduced in the case of 10-layers h-BN, which can be attributed to the suppression of carrier collection. In addition, when the thickness of h-BN is >6-layers and the thickness of MoS_2 (WSe_2) is maintained at a certain value, the negative effect of intercalated h-BN on photoelectric conversion of multilayer/few-layer (few-layer/multilayer) MoS_2/WSe_2 is more obvious as the thickness of WSe_2 (MoS_2) increases. The physical origin is that the ΔE_{c13} (ΔE_{v13}) between MoS_2 and WSe_2 decreases as the thickness of WSe_2 (MoS_2) increases (Fig. S1d), which can weaken the photocarrier transport. Therefore, in order to enhance the photoelectric conversion of MoS_2/WSe_2 vdW heterostructure, it is a feasible method to introduce a dielectric layer at the heterointerface to reduce interlayer recombination.

Table S1. The parameters in our calculations are listed as: monolayer thickness D (δ), Mo-S (W-Se) and B-N bond length d_0, the effective mass of electron (m_e) and hole (m_h), electron affinity of single-layer material (χ), radiative lifetime of the excitons (τ_r), and surface recombination velocity (S_{00}). Note that the S_{00} is indirectly obtained by $S_{00} = \sqrt{D_L/\tau_L}$, where D_L and τ_L are the hot carrier diffusion coefficient and the carrier lifetime, respectively.

material	D (nm)	d_0 (nm)	m_e (m_0)	m_h (m_0)	χ (eV)	S_{00} (cm/s)	τ_r (ns)
MoS$_2$	0.65[3]	0.241[13]	0.46[21]	0.56[21]	4.2[3]	3.5×10^4[22]	1.16 [23]
WSe$_2$	0.65[3]	0.255[13]	0.34[21]	0.44[21]	3.4-4.0[3]	1.0×10^7[24]	4.0 [25]
h-BN	0.33[26]	0.250[27]	0.26[28]	0.50[28]	2.0-2.3[28]	—	—

Table S2. Calculated photoelectric parameters of MoS_2/h-BN/WSe_2 vdW heterostructures under different cases. The bandgap of monolayer h-BN is 5.0 eV, and $\xi/k_bT_c = 2.49 \text{nm}^{-1}$ is obtained by using the Eq. (5) from Ref. (16) under different h-BN thickness.

Monolayer TMDs	J_{sc} [mA/cm^2]	V_{oc} [V]	PCE [%]	FF [%]
MoS_2/WSe_2	3.56	0.58	1.70	82.4
MoS_2-h-BN(1L)-WSe_2	3.52	0.65	1.89	83.2
MoS_2-h-BN(7L)-WSe_2	3.25	1.01	2.78	84.7
MoS_2-h-BN(10L)-WSe_2	3.12	1.19	3.15	84.8
MoS_2-h-BN(11L)-WSe_2	3.04	1.25	3.23	85.0
MoS_2-h-BN(12L)-WSe_2	2.73	1.31	3.03	84.7
MoS_2-h-BN(13L)-WSe_2	1.50	1.36	1.72	84.3
MoS_2-h-BN(14L)-WSe_2	0.30	1.34	0.34	83.9
MoS_2-h-BN(15L)-WSe_2	0.04	1.28	0.04	78.1

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