Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Electronic properties of Janus MXY/graphene (M = Mo, W; X ≠ Y = S, Se) van der Waals structures: A first-principles study

Shiqiang Yu, Wei Wei,* Fengping Li, Baibiao Huang, and Ying Dai*

School of Physics, State Key Laboratory of Crystal Materials, Shandong University,

Jinan 250100, China

E-mail: weiw@sdu.edu.cn, daiy60@sdu.edu.cn

Table S1: Total energy (in eV) calculated with different vacuum space. E_T (eV): total energy.

	Structures	E_T
Monolayers	MoSSe (20 Å)	-83.57
	MoSSe (80 Å)	-83.43
Bilayers	SeMoS/SeMoS(AA′) (20 Å)	-172.96
	SeMoS/SeMoS(AA′) (80 Å)	-172.96
	MoSSe/graphene(C-S) (20 Å)	-216.56
	MoSSe/graphene(C-S) (80 Å)	-216.54
Trilayers	SeMoS/graphene/SeMoS(AA′) (20 Å)	-303.38
	SeMoS/graphene/SeMoS(AA′) (80 Å)	-303.36
	SeMoS/graphene/SMoSe(AA′) (20 Å)	-303.28
	SeMoS/graphene/SMoSe(AA′) (80 Å)	-303.26

Table S2: Total energy (in eV) calculated by DFT–D2, DFT–D3, optP88. C–S, C–Se, C–S and C–Se denote the type of interface.

	MoSSe/graphene		WSSe/graphene	
	C–S	C–Se	C–S	C–Se
DFT-^{D_2}	-216.54	-216.64	-225.12	-225.16
DFT-^{D_3}	-215.89	-215.93	-223.18	-223.21
optB88	-171.32	-171.31	-178.74	-178.73

Table S3: Orbital contribution percentage (%) at Γ_V, K_V and K_C for MoSSe and WSSe monolayer. The serial numbers ①, ②, ③ represent the S, Mo and Se of the MoSSe monolayer， and ④, ⑤, ⑥ represent the S, W and Se of the WSSe monolayer.

		MoSSe	WSSe
Γ_V	p_z	① 13.6%	④ 12.4%
		② 1.60%	⑤ 2.00%
	d_{z^2}	③ 58.1%	⑥ 58.0%
K_V	p_x	① 2.40%	④ 2.80%
		② 3.60%	⑤ 4.00%
	p_y	① 2.40%	④ 2.80%
		② 3.60%	⑤ 4.00%
	d_{xy}	③ 35.2%	⑥ 32.8%
	$d_{x^2-y^2}$	③ 35.2%	⑥ 32.8%
K_C	p_x	① 1.60%	④ 0.80%
		② 1.60%	⑤ 1.20%
	p_y	① 1.60%	④ 0.80%
		② 1.60%	⑤ 1.20%
	d_{z^2}	③ 77.6%	⑥ 75.5%

Table S4: Parameters for MXY/graphene vdW bilayers. a (Å): lattice constants; d (Å): interlayer distance between interfacial chalcogen atoms; $\Delta\varphi$ (eV): work function change. C–S, C–Se, C–S and C–Se denote the type of interface.

	MoSSe/graphene		WSSe/graphene	
	C–S	C–Se	C–S	C–Se
a	6.520	6.519	6.521	6.519
d	3.342	3.412	3.303	3.368
$\Delta\varphi$	0.474	1.014	0.417	1.002

Table S5: Parameters for SeMS/graphene/SeMS vdW trilayers with Se/S interface. a (Å): lattice constants; d_1 (Å): interlayer distance between S atomic layer and graphene; d_2 (Å): interlayer distance between graphene and Se atomic layer; $\Delta\varphi$ (eV): work function change.

	SeMoS/graphene/SeMoS					SeWS/graphene/SeWS				
	AA	AA′	AB	A′B	AB′	AA	AA′	AB	A′B	AB′
a	6.514	6.513	6.513	6.512	6.513	6.513	6.514	6.514	6.514	6.514
d_1	3.332	3.341	3.351	3.343	3.332	3.278	3.279	3.278	3.281	3.287
d_2	3.393	3.372	3.387	3.390	3.391	3.334	3.331	3.338	3.341	3.334
$\Delta\varphi$	1.273	1.307	1.533	1.588	1.542	1.328	1.427	1.431	1.440	1.486

Table S6: Parameters for SeMS/graphene/SMSe vdW trilayers with S/S interface. a (Å): lattice constants; d_1 (Å): interlayer distance between S atomic layer and graphene; d_2 (Å): interlayer distance between graphene and S atomic layer; $\Delta\varphi$ (eV): work function change.

	SeMoS/graphene/SMoSe					SeWS/graphene/SWSe				
	AA	AA′	AB	A′B	AB′	AA	AA′	AB	A′B	AB′
a	6.514	6.514	6.514	6.514	6.514	6.515	6.515	6.514	6.514	6.514
d_1	3.318	3.319	3.330	3.336	3.321	3.268	3.269	3.270	3.278	3.252

d_2	3.353	3.352	3.343	3.350	3.343	3.277	3.273	3.279	3.277	3.285
$\Delta\varphi$	0	0	0	0	0	0	0	0	0	0

Table S7: Rashba spin splitting values for MXY monolayers. ^{K_R}(Å^{-1}): momentum variation; ^{E_R}(MeV): Rashba energy; $^{\alpha_R}$(eV·Å): Rashba parameter. M and K indicate the Γ-M and Γ-K directions in the Brillouin zone, respectively.

	Monolayers	
	MoSSe	WSSe
E_R^M	1.46	3.88
E_R^K	1.48	3.90
K_R^M	0.0067	0.0089
K_R^K	0.0068	0.0086
α_R^M	0.436	0.872
α_R^K	0.435	0.907

Table S8: Rashba spin splitting values for MXY bilayers. ^{K_R}(Å^{-1}): momentum variation; ^{E_R}(MeV): Rashba energy; $^{\alpha_R}$(eV·Å): Rashba parameter. M and K indicate the Γ-M and Γ-K directions in the Brillouin zone, respectively.

	SeMoS/SeMoS					SeWS/SeWS				
	AA	AA′	AB	A′B	AB′	AA	AA′	AB	A′B	AB′
E_R^M	0.12	0	0	0.16	0	0.56	0	0	0.44	0
E_R^K	0.11	0	0	0.16	0	0.51	0	0	0.45	0
K_R^M	0.0015	0	0	0.0015	0	0.0030	0	0	0.0030	0

K_R^K	0.0017	0	0	0.0017	0	0.0026	0	0	0.0025	0
α_R^M	0.160	-	-	0.213	-	0.373	-	-	0.293	-
α_R^K	0.129	-	-	0.188	-	0.392	-	-	0.360	-

Table S9: Rashba spin splitting values for MXY/graphene heterobilayers. K_R (Å^{-1}): momentum variation; E_R (MeV): Rashba energy; α_R (eV·Å): Rashba parameter. M and K indicate the Γ-M and Γ-K directions in the Brillouin zone, respectively.

	MoSSe/graphene		WSSe/graphene	
	C-S	C-Se	C-S	C-Se
E_R^M	0.94	0.83	2.49	2.30
E_R^K	0.92	0.81	2.44	2.25
K_R^M	0.0044	0.0044	0.0059	0.0059
K_R^K	0.0051	0.0051	0.0051	0.0051
α_R^M	0.427	0.377	0.844	0.780
α_R^K	0.361	0.318	0.957	0.882

Table S10: Rashba spin splitting values for MXY/graphene/MXY heterotrilayers. K_R (Å^{-1}): momentum variation; E_R (MeV): Rashba energy; α_R (eV·Å): Rashba parameter. M and K indicate the Γ-M and Γ-K directions in the Brillouin zone, respectively.

	SeMoS/graphene/SeMoS					SeWS/graphene/SeWS				
	AA	AA′	AB	A′B	AB′	AA	AA′	AB	A′B	AB′
E_R^M	0.70	0.77	0.75	0.78	0.76	2.11	2.08	2.10	2.08	2.14
E_R^K	0.75	0.75	0.73	0.75	0.74	2.10	2.07	2.09	2.06	2.12
K_R^M	0.0044	0.0044	0.0044	0.0044	0.0044	0.0059	0.0059	0.0059	0.0059	0.0059
K_R^K	0.0034	0.0034	0.0034	0.0034	0.0034	0.0051	0.0051	0.0051	0.0051	0.0051
α_R^M	0.318	0.350	0.341	0.355	0.345	0.715	0.705	0.712	0.705	0.725
α_R^K	0.441	0.441	0.429	0.441	0.435	0.824	0.812	0.820	0.808	0.831
	SeMoS/graphene/SMoSe					SeWS/graphene/SWSe				
	AA	AA′	AB	A′B	AB′	AA	AA′	AB	A′B	AB′
E_R^M	0	0	0	0	0	0	0	0	0	0
E_R^K	0	0	0	0	0	0	0	0	0	0
K_R^M	0	0	0	0	0	0	0	0	0	0
K_R^K	0	0	0	0	0	0	0	0	0	0
α_R^M	-	-	-	-	-	-	-	-	-	-

α_R^K	-	-	-	-	-	-	-	-	-	-

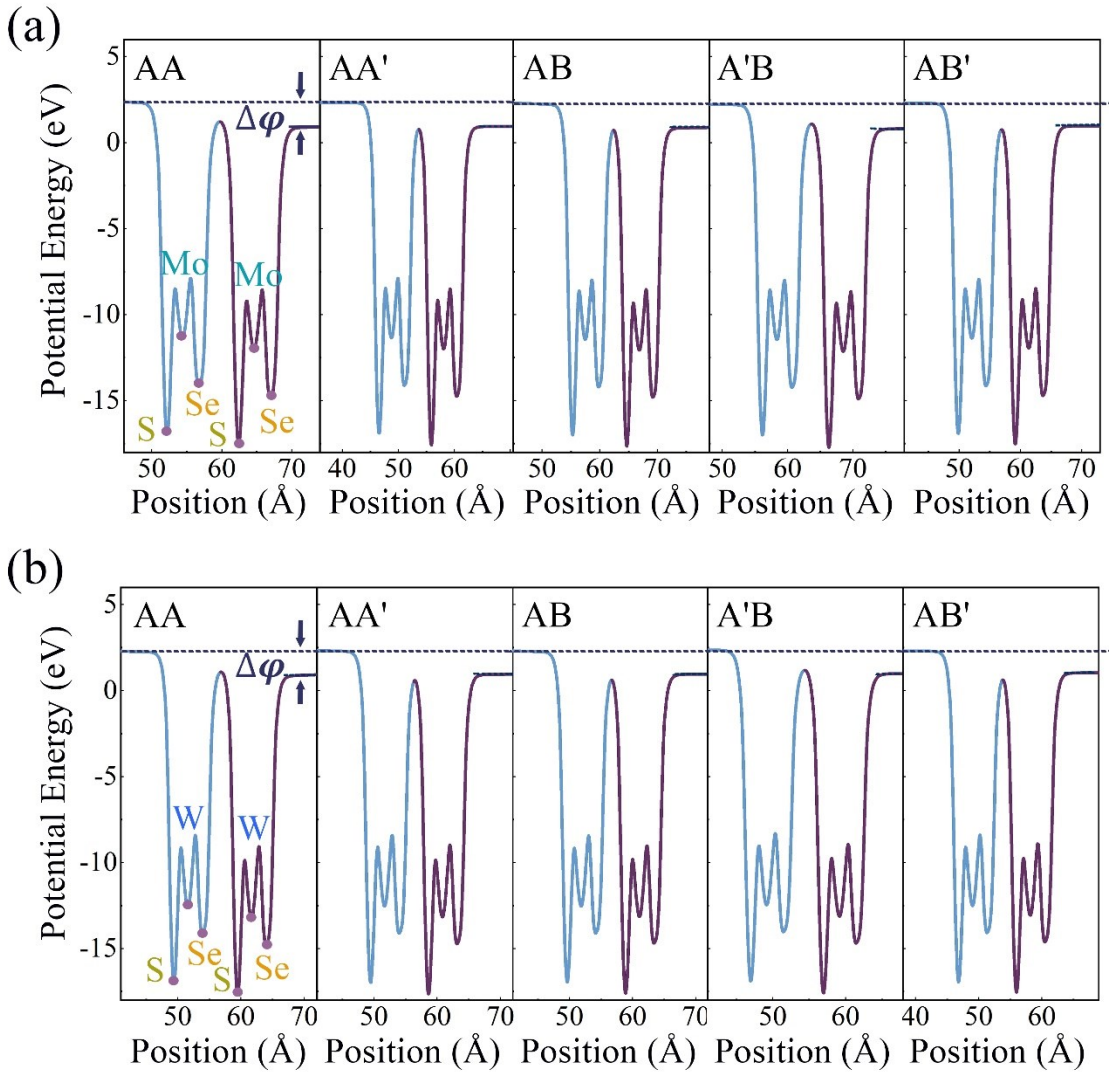

Fig. S1: Planar averaged electrostatic potential energy and work function change of (a) MoSSe and (b) WSSe vdW bilayers with five stacking styles. The corresponding colors of upper and bottom layers are claret and blue, respectively.

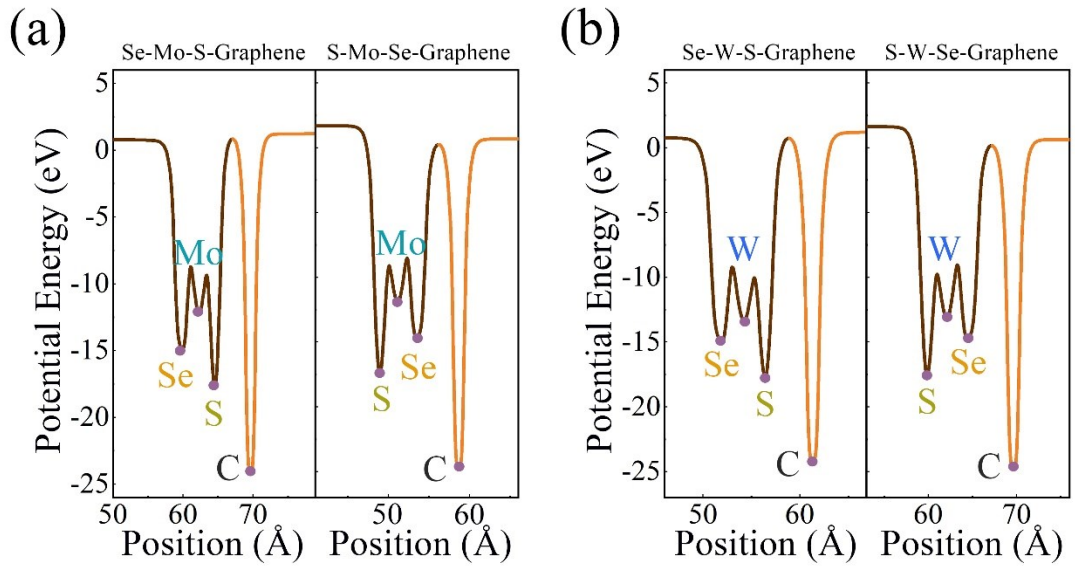

Fig. S2: Planar averaged electrostatic potential energy and work function change for two types of (a) MoSSe/graphene and (b) WSSe/graphene vdW heterostructures with different interfaces.

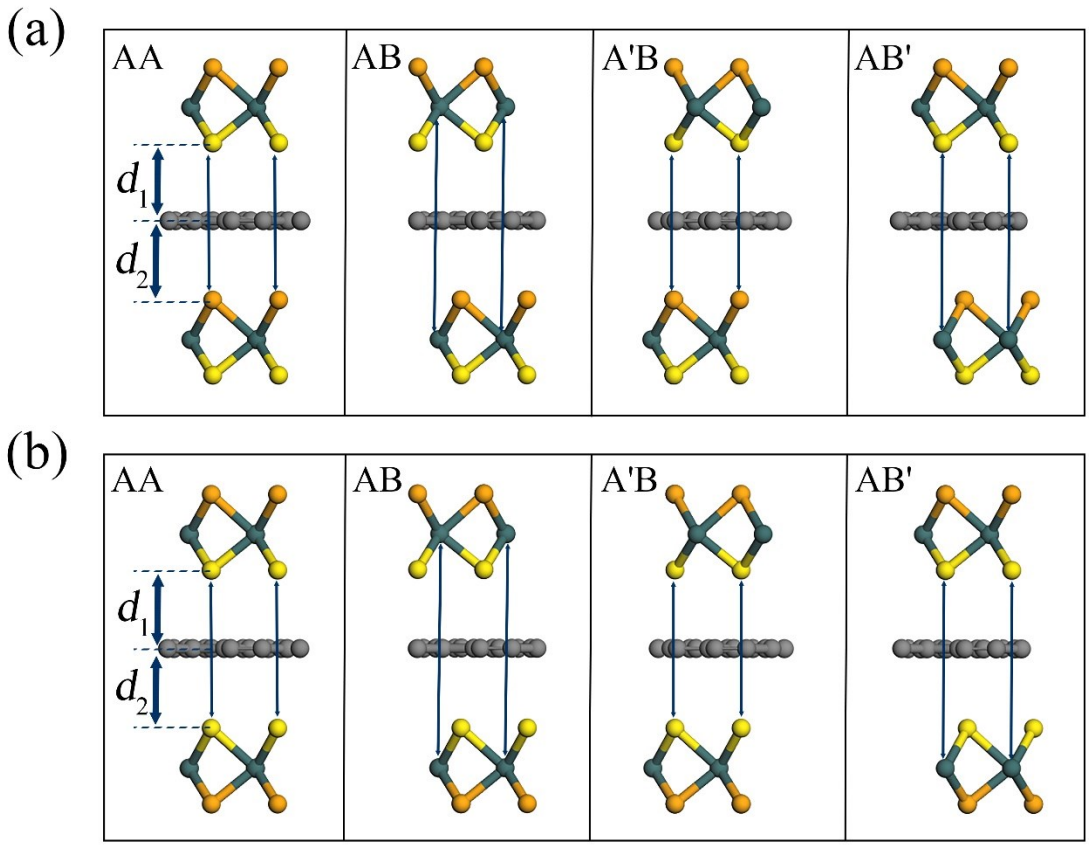

Fig. S3: Side views of atomic structures of four stacking styles for MSSe/graphene vdW trilayers, with (a) S/Se interface and (b) S/S interface. M, S, Se and C atoms are denoted by teal, orange, yellow and gray spheres, respectively.

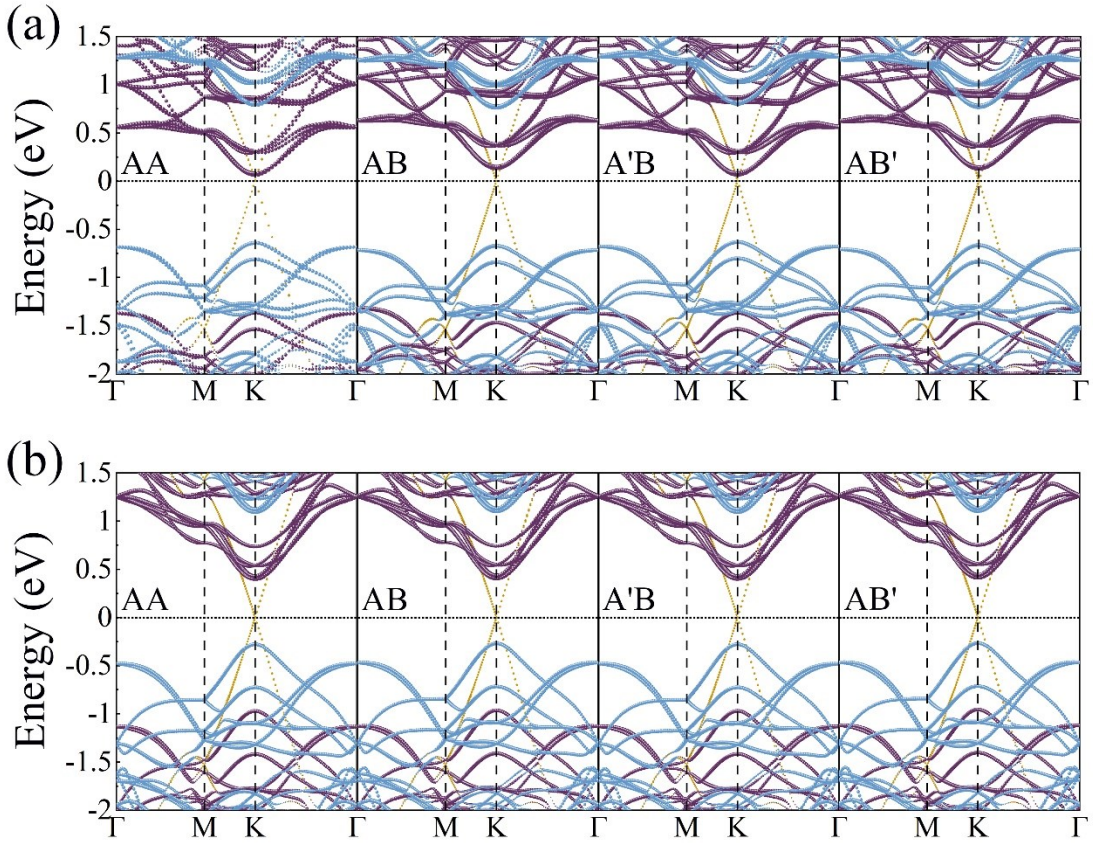

Fig. S4: Band structure for (a) MoSSe/graphene/MoSSe and (b) WSSe/graphene/WSSe vdW trilayers. MXY monolayers are stacked in AA' pattern, with S/Se interface. The corresponding colors of upper, bottom and graphene layer are claret, blue and orange, respectively.

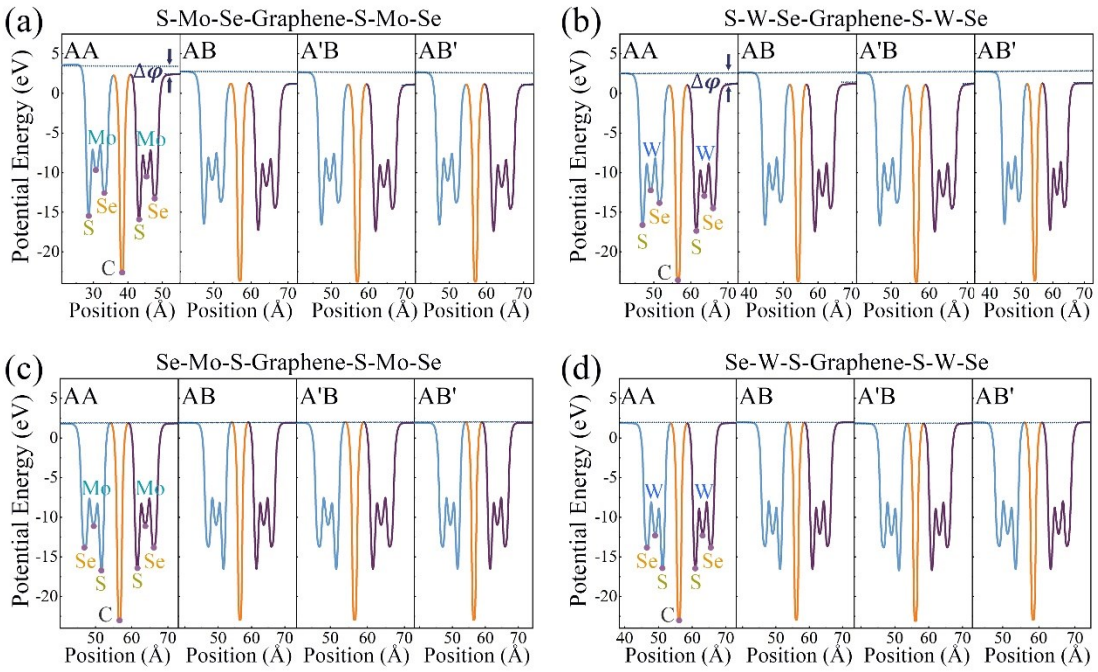

Fig. S5: Planar averaged electrostatic potential energy for (a) MoSSe/graphene/MoSSe, (b) WSSe/graphene/WSSe vdW trilayers with Se/S interface, and (c)–(d) with S/S interface. MXY monolayers are stacked in AA' pattern. The corresponding colors of upper, bottom and graphene layer are claret, blue and orange, respectively.

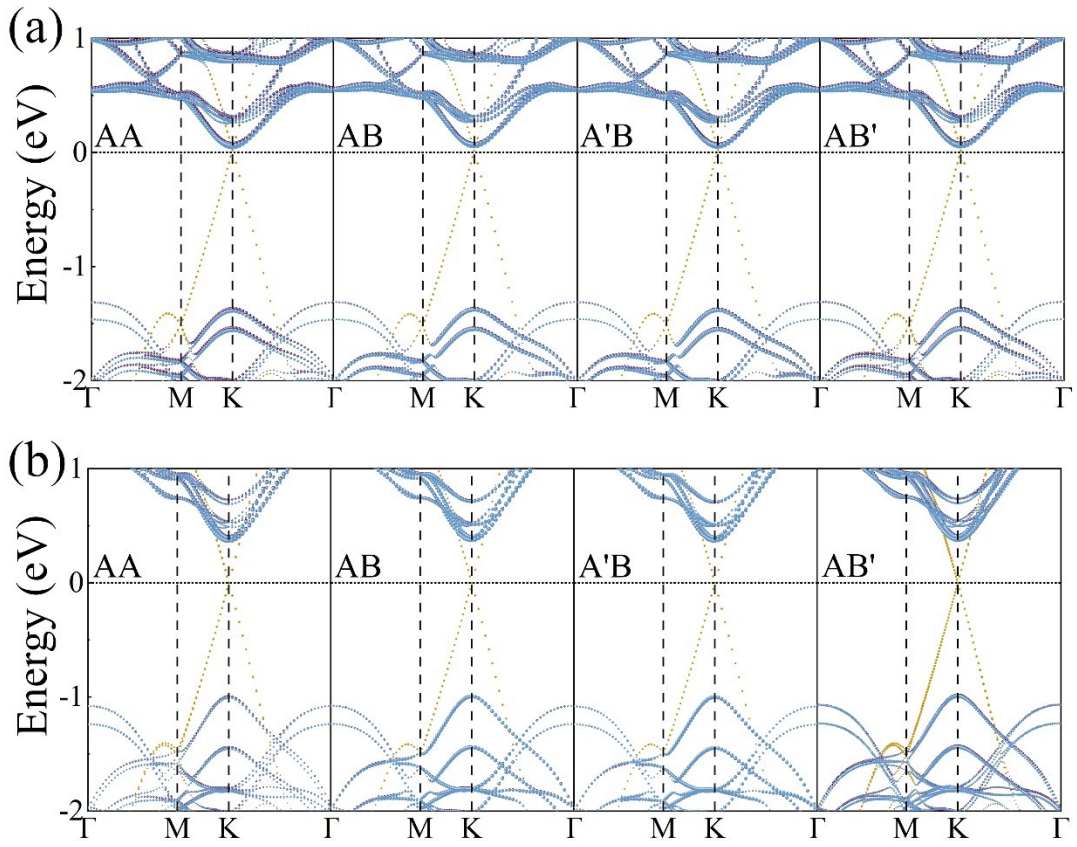

Fig. S6: Band structure for (a) MoSSe/graphene/MoSSe and (b) WSSe/graphene/WSSe vdW trilayers. MXY monolayers are stacked in AA' pattern, with S/S interface. The corresponding colors of upper, bottom and graphene layer are claret, blue and orange, respectively.

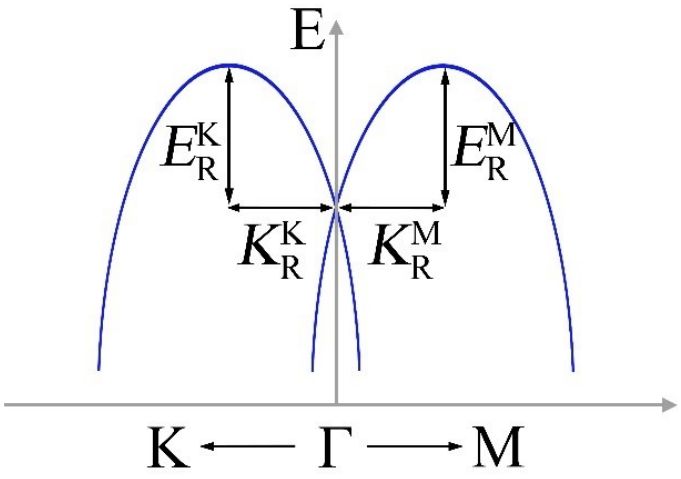

Fig. S7: Schematic of Rashba spin splitting.