Electronic Supplementary Material (ESI) for Nanoscale.

Band Alignments and Heterostructures of Monolayer Transition Metal Trichalcogenides: MX_3 (M = Zr, Hf; X = S, Se) and Dichalcogenides: MX_2 (M = Tc, Re; S, Se) for Solar applications

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1. Lattice constants of VIIB-VIA TMDs MX_2 (M = Tc, Re; X = S, Se) and IVB-VIA TMTs MX_3 (M = Zr, Hf; X = S, Se)

Table S1 Calculated and experimental equilibrium parameters of VIIB-VIA TMDs: Lattice constants (***a*** (Å), ***b*** (Å), ***c*** (Å), ***α*** (deg), ***β*** (deg), ***γ*** (deg)) and atomic volume V_o(Å^3).

	functional	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	Vo (Å^3)
	vdW-DF	6.44	6.54	6.83	63.46	103.40	118.90	225.48
	vdW-D3	6.378	6.484	6.650	62.97	103.55	118.78	214.65
TcS_2	vdW-TS/HI	6.373	6.468	6.365	61.28	104.11	118.92	201.35
	[a]Expt.	6.371	6.464	6.654	62.94	103.61	119.00	213.39
	vdW-DF	6.712	6.832	7.240	64.07	103.25	118.90	261.33
	vdW-D3	6.64	6.76	7.00	63.70	103.47	118.76	246.64
$TcSe_2$	vdW-TS/HI	6.622	6.732	6.696	62.43	104.09	118.89	231.62
	Expt.							
	vdW-DF	6.435	6.538	13.113	91.55	104.89	118.90	459.30
	vdW-D3	6.381	6.486	12.801	91.70	105.13	118.83	440.46
ReS_2	vdW-TS/HI	6.364	6.464	12.818	91.64	105.12	118.67	438.30
	[a]Expt.	6.352	6.446	12.779	91.51	105.17	118.97	434.49
	vdW-DF	6.697	6.821	6.931	91.91	104.76	118.86	263.56
	vdW-D3	6.610	6.742	6.680	91.87	105.01	118.70	247.83
$ReSe_2$	vdW-TS/HI	6.603	6.728	6.742	91.92	104.90	118.79	249.26
	[a]Expt.	6.597	6.710	6.721	91.84	104.90	118.91	247.34

a Ref. [1]

Table S2 Calculated and experimental equilibrium parameters of IVB-VIA TMTs:

Lattice constants (***a*** (Å), ***b*** (Å), ***c*** (Å), ***β*** (deg)) and atomic volume V_o (Å^3).

	functional	a (Å)	b (Å)	c (Å)	β (deg)	Vo (Å^3)
ZrS_3	vdW-DF	5.207	3.663	9.165	97.036	173.496
	vdW-D3	5.110	3.638	9.065	96.936	167.29
	vdW-TS/HI	5.123	3.628	9.287	96.595	171.167
	[a]Exp.	5.124	3.624	8.980	97.280	165.437
$ZrSe_3$	vdW-DF	5.521	3.792	9.675	97.494	200.809
	vdW-D3	5.383	3.760	9.534	97.244	191.438
	vdW-TS/HI	5.382	3.744	9.740	96.972	194.824
	[a]Exp.	5.411	3.749	9.444	97.480	189.936
HfS_3	vdW-DF	5.157	3.623	9.134	97.380	169.272
	vdW-D3	5.065	3.595	9.011	97.336	162.766
	vdW-TS/HI	5.072	3.589	9.235	96.561	166.894
	[a]Exp.	5.092	3.595	8.967	97.380	162.806
$HfSe_3$	vdW-DF	5.466	3.760	9.575	83.846	195.659
	vdW-D3	5.348	3.729	9.463	83.682	187.540
	vdW-TS/HI	5.355	3.716	9.654	84.829	191.334
	[a]Exp.	5.388	3.722	9.428	97.780	187.310

a Ref. [2]

2. Crystal structures of VIIB-VIA TMDs MX_2 (M = Tc, Re; X = S, Se) and IVB-VIA TMTs MX_3 (M = Zr, Hf; X = S, Se)

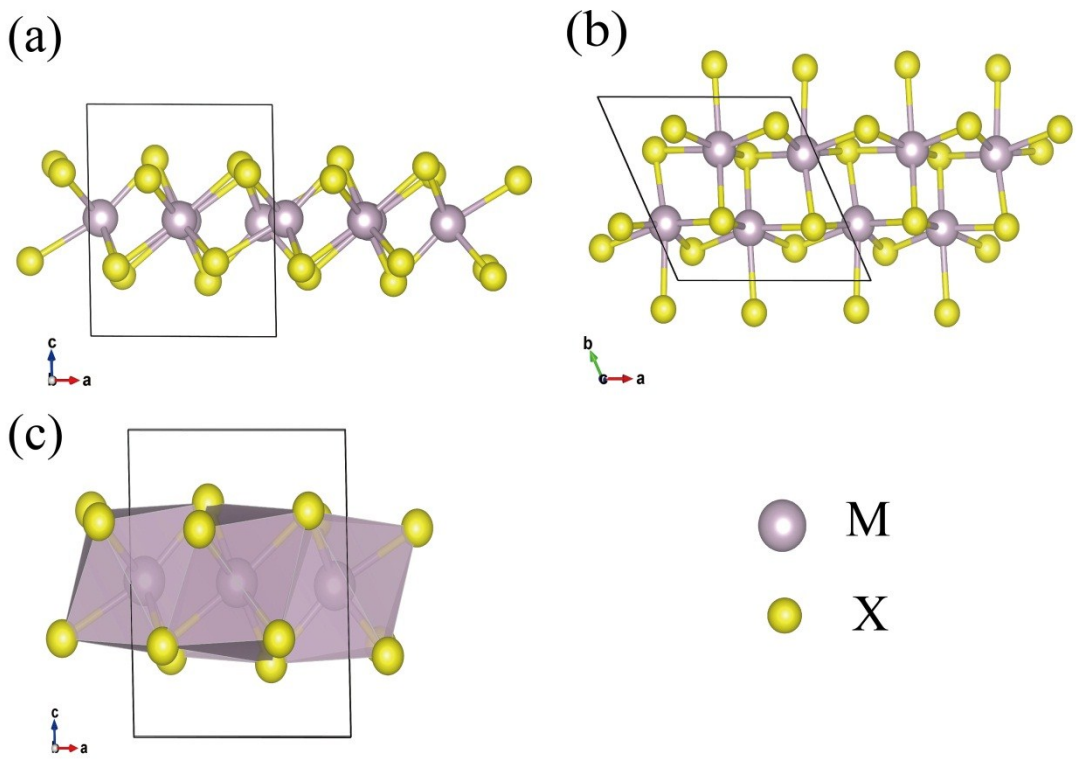

Fig.S1 (a) Side view of MX_2; (b) Top view of MX_2; (c) The unit cell of MX_2 structure and the yellow represent chalcogen atoms and purple represent transition metal atoms.

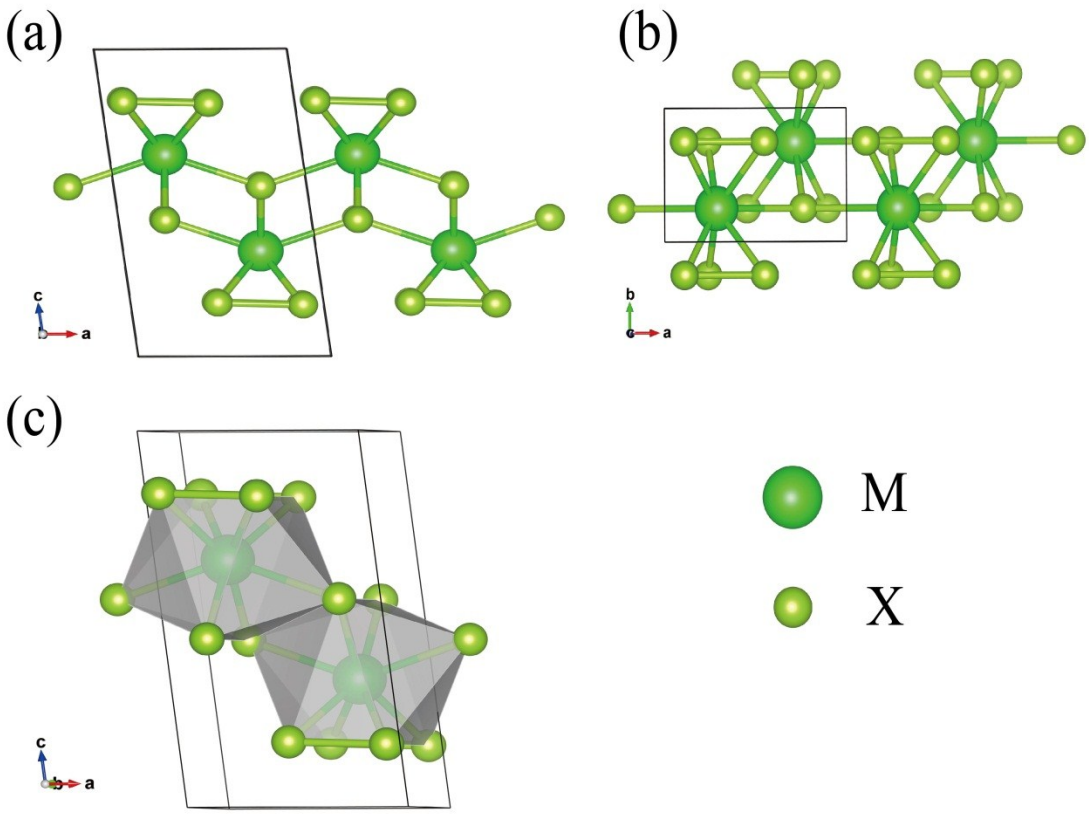

Fig.S2 (a) Side view of MX_3; (b) Top view of MX_3; (c) The unit cell of MX_3 structure

and the viridity represent transition metal atoms and green represent chalcogen atoms.

3. Parameters for the calculation of heterostructures

The vacuum gaps of ZrS_3/HfS_3 and TcS_2/ReS_2 heterostructures are 2.55 Å and 1.79 Å, respectively. For atomic relaxation, we used Γ-centered 10×12×2 and 9×9×2 grids, respectively. The structural optimization was carried out until the residual forces fell below 0.01 eV/Å. The electronic convergence tolerance was set to 10^{-4} eV. Besides, an energy cutoff of 400 eV was chosen for the calculation.

REFERENCES:

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