Supplementary information (SI) for

Electrostatic gating dependent multiple band alignments in ferroelectric VS_2/Ga_2O_3 van der Waals heterostructures

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Table S1 Optimized lattice constant (a=b), interlayer distance (d), the energy difference (ΔE) with the lowest energy states under different polarizations, binding energy (E_b) of 2D VS_2/Ga_2O_3 heterostructures without vdW correction.

Structure	Stacking	a=b(Å)	d_{min}(Å)	ΔE (meV)	E_b(meV/Å^2)
VS_2/Ga_2O_3	U_1	3.125	3.826	4.7	-3.547
	U_2	3.125	3.432	0	-4.174
	U_3	3.125	3.475	0.4	-4.138
	D_1	3.123	3.688	0	-1.421
	D_2	3.132	3.791	0.3	-1.365
	D_3	3.125	4.042	1.7	-1.182

To explore the effect of DFT-D2 vdW method on 2D VS_2/Ga_2O_3 heterostructures, the structural properties without vdW correction were also calculated. The parameters of optimized lattice constants (a), the interlayer distance (d), the energy difference compared with the lowest energy states in different polarized direction (ΔE) and the binding energy (E_b) without vdW correction are listed in **Table S1**. Compared with the results using DFT-D2 method, there is an evident increasement in the interlayer distance,

even reaching up to 4 Å for VS_2/ P↑ Ga_2O_3 heterostructure in D_3 stacking. In addition, the energy difference ΔE under different polarizations is not obvious and the binding energy E_b is too small, implying there is nearly no vdW interlayer interactions in 2D VS_2/Ga_2O_3 heterostructures, which doesn't agree with the fact.

In addition, the DFT-D3 method was also adopted to calculate the 2D VS_2/Ga_2O_3 heterostructures. The parameters of optimized lattice constants (a), the interlayer distance (d), the energy difference compared with the lowest energy states in different polarized direction (ΔE) and the binding energy (E_b) using DFT-D3 method are listed in **Table S2**. Compared with the results using DFT-D2 method, there are only minor changes in the lattice constants and interlayer distance. Notably, U_3 stacking possesses the most stable structure in the VS_2/ P↑ Ga_2O_3 structure, while D_2 stacking has 0.6 meV lower energy than the D_1 stacking (the most stable one using DFT-D2 method) and becomes the most stable one in the VS_2/P↓ Ga_2O_3 structure.

Table S2 Optimized lattice constant (a=b), interlayer distance (d), the energy difference (ΔE) with the lowest energy states under different polarizations, binding energy (E_b) of 2D VS_2/Ga_2O_3 heterostructures using the DFT-D3 method.

Structure	Stacking	a=b(Å)	d_{min}(Å)	ΔE (meV)	E_b(meV/Å^2)
VS_2/Ga_2O_3	U_1	3.111	3.171	61.9	-124.3
	U_2	3.112	2.857	10.4	-130.3
	U_3	3.113	2.758	0	-131.4
	D_1	3.113	2.911	0.6	-127.2
	D_2	3.113	2.859	0	-127.2
	D_3	3.111	3.28	53.8	-121.3

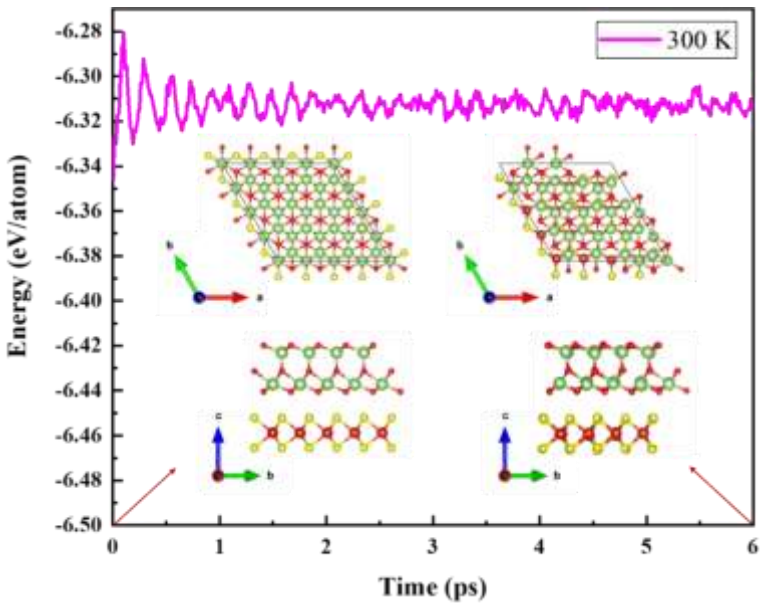

Fig. S1 Total potential energy fluctuation as a function of the AIMD simulation, and the initial and final structures of VS_2/Ga_2O_3 vdW heterostructures at 300 K.

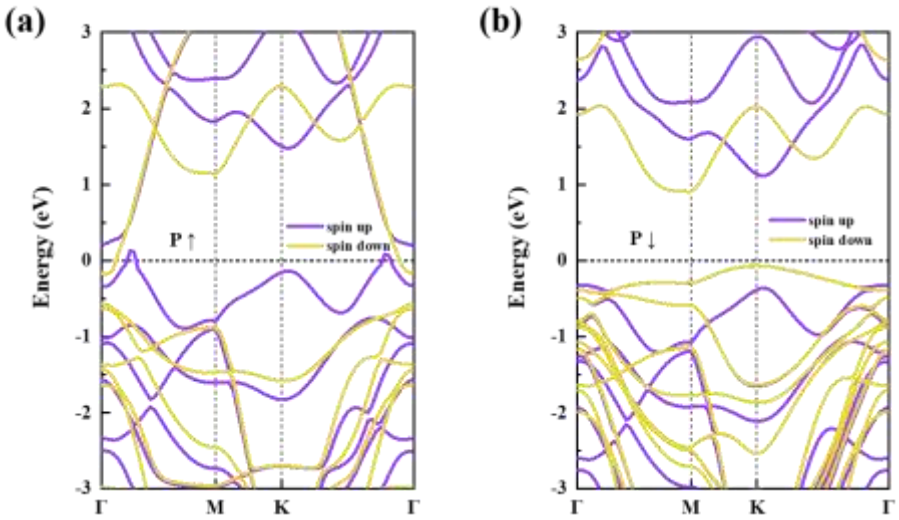

Fig. S2 Electronic band structures of VS_2/Ga_2O_3 with DFT-D3 correction for (a) P↑ structure and (b) P↓ structure.

The electronic properties in the most stable one (U_3 and D_2 stacking) under different polarizations using the DFT-D3 method were illustrated in **Fig. S2**. When the polarized direction of Ga_2O_3 monolayer is upward, the CBM and VBM all overlap the fermi energy, presenting metallic properties. However, when polarized direction is reversed, the CBM and VBM are located at the high-symmetric *M* and *K* point, respectively, exhibiting semiconducting properties. Obviously, there is also a band

structure reversion from metal to semiconductor due to the ferroelectric polarization reversal, which is consistent with DFT-D2 method.

Furthermore, due to the small energy difference between the D_1 and D_2 stacking, we calculated the electronic band structures of both the two stackings, depicted in **Fig. S3**. Obviously, these band structures all behave as semiconductors, whose CBM and VBM are located at the high-symmetric *M* and *K* point, respectively. Taking the optimized energy of VS_2/Ga_2O_3 heterostructures into consideration, the results with the DFT-D2 method own lower energy than those with the DFT-D3 method. Thus, the DFT-D2 vdW correction was adopted in our work.

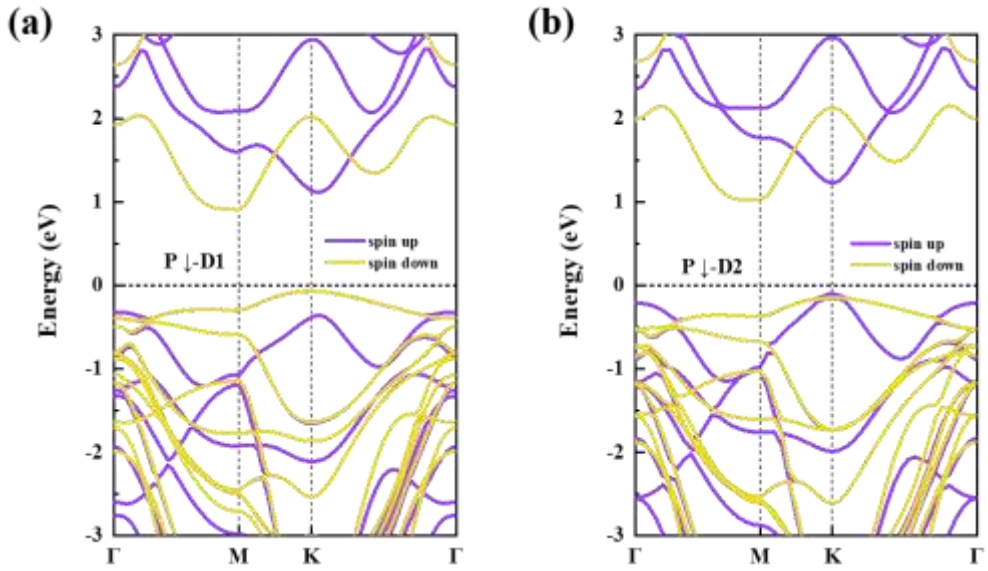

Fig. S3 Electronic band structures of VS_2/P↓ Ga_2O_3 structure with DFT-D3 correction in (a) D_1 stacking and (b) D_2 stacking.