Supporting Information

Tunable Band Structures of Heterostructured Bilayers with Transition Metal Dichalcogenide and MXene Monolayer

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Effect of spin-orbit coupling (SOC)

As shown in Figure S1, due to the SOC effect, the valence band maximum (VBM) or conduction band minimum (CBM) could split into two energy levels with an energy difference of ΔSOC. Therefore, the VBM/CBM value computed through the method including SOC is higher/lower than VBM/CBM through the method ignoring SOC by ΔSOC/2. To investigate the effect of SOC on TMD-Sc_2CF_2 bilayers, we computed the band structures including SOC effect for MoS_2, WS_2, $MoSe_2$, WSe_2 and Sc_2CF_2 monolayers with the hybrid functional of Heyd-Scuseria-Ernzerhof (HSE) within the Vienna ab initio package (VASP).[1,2] The ion−electron interaction is described with the projector augmented wave (PAW) method.[3] A 400 eV cutoff was used for the plane-wave basis set. 6 × 6 × 1 k-points were used for sampling the Brillouin zone. All these computations were performed in supercells with a vacuum space lager than 10 Å above and below the layered materials. The ΔSOCs at VBM and CBM for all the monolayers are displayed in Table S1. In Sc_2CF_2 the SOC effect is nearly zero. Though the CBMs of TMD-Sc_2CF_2 bilayers are located at TMD monolayers, the SOC affects the CBMs scarcely because the values of $\Delta SOC_{VBM}/2$ are so small in the range of 0.005~0.013 eV. The VBMs for TMD-Sc_2CF_2 bilayers are located at Sc_2CF_2 monolayer. In Figure 6, it could be seen that the VBM at Sc_2CF_2 is higher than the VBM at TMDs by at least 0.45 eV (WSe_2-Sc_2CF_2 bilayer) which is larger than $\Delta SOC_{VBM}/2$ of VBM at TMDs (0.084~0.258 eV). Therefore, even if the SOC effect is included, the VBM at TMD monolayers would not exceed the VBM at Sc_2CF_2 and it means that the SOC effect does not impact the VBM of TMD-Sc_2CF_2

bilayers. We could safely neglect the SOC effect in our CASTEP computations and reach the same reliable conclusions.

Table S1. ΔSOC (eV) for TMD and Sc_2CF_2 monolayers.

TMD	MoS_2	WS_2	$MoSe_2$	WSe_2	Sc_2CF_2
ΔSOC_{CBM}	0.009	0.019	0.029	0.026	0
$\Delta SOC_{CBM}/2$	0.005	0.008	0.015	0.013	0
ΔSOC_{VBM}	0.167	0.473	0.212	0.516	0
$\Delta SOC_{VBM}/2$	0.084	0.237	0.106	0.258	0

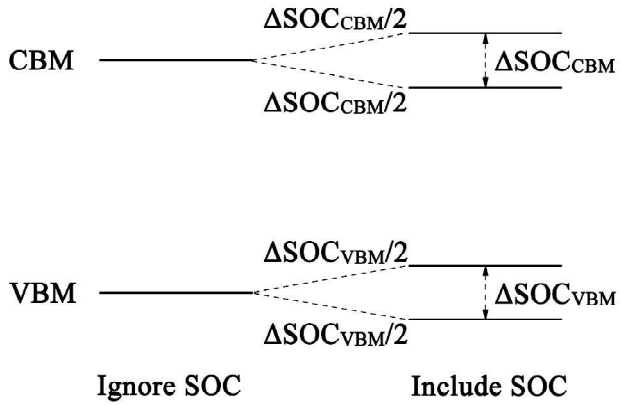

Figure S1. The diagrammatic sketch of the effect of SOC on band gap.

Optical properties

Since the VBM and CBM for TMD-Sc_2CF_2 bilayers are located at Sc_2CF_2 and TMD monolayers respectively, it is necesary to consider the excitonic effect on optical properties.[4] Therefore, we calculated the imaginary part of the dielectric

constant (ε_2) for MoS_2-Sc_2CF_2 bilayer (black line), MoS_2 monolayer (red line) and Sc_2CF_2 monolayer (blue line) as an example. The optical properties computations were performed with plane-wave pseudopotentials implemented in CASTEP code.[5] The cutoff energy was set as 400 eV, and self-consistent field (SCF) computations were adopted with a convergence of 10^{-6} eV/atom. 7 × 7 × 1 k-points were used for sampling the Brillouin zone. The ε_2 calculated by CASTEP was defined in CASTEP tutorials (labeled as Eq. CASTEP 55) as following:

$$\varepsilon_2 = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{\mathrm{k},v,c}\left|\left\langle \Psi_{\mathrm{k}}^{c}\left|\mathrm{u}\cdot\mathrm{r}\right|\Psi_{\mathrm{k}}^{v}\right\rangle\right|^2 \delta\left(E_{\mathrm{k}}^{c}-E_{\mathrm{k}}^{v}-E\right)$$

where u is the vector defining the polarization of the incident electric field. ε_2 for electric vector perpendicular and parallel to c axis of MoS_2-Sc_2CF_2 bilayer, MoS_2 monolayer, and Sc_2CF_2 monolayer are in Figure S2. The ε_2 of MoS_2 in Figure S2 is similar to the results reported in a previous paper,[6] ensuring the reasonability of our results. It could be seen that the $\varepsilon_2^{MoS2\text{-}Sc2CF2}$ are not consistent to the 0.13 eV band gap and it means that interlayer transition is hard to happen.[4] The results seem more like the sum of two monolayers. Since the ε_2^{MoS2} is much larger than ε_2^{Sc2CF2} in the most region, the $\varepsilon_2^{MoS2\text{-}Sc2CF2}$ of the bilayer seem more like ε_2^{MoS2}. However, in the regions around 6 eV in Figure S2(a) and lower than 5 eV in Figure S2(b), the $\varepsilon_2^{MoS2\text{-}Sc2CF2}$ exhibits the sum of two layers. As mentioned above the excitions are confined in each monolayer.

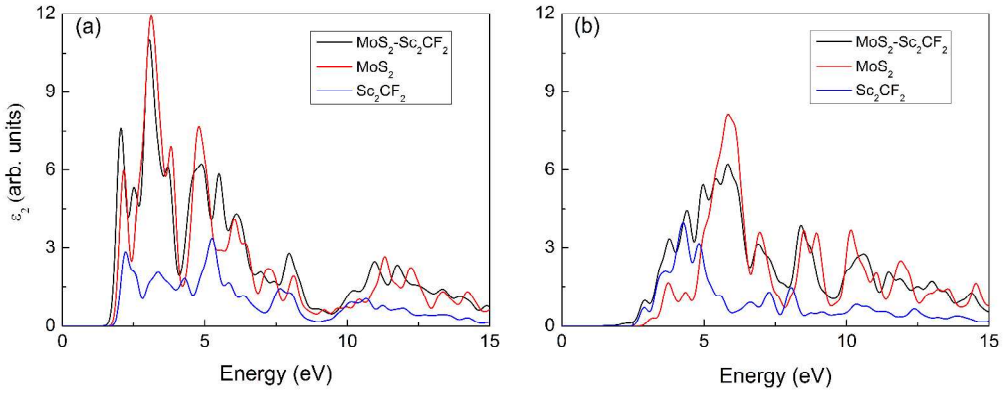

Figure S2. The imaginary part of the dielectric constant (ε_2) for electric vector (a) perpendicular and (b) parallel to c axis for MoS_2-Sc_2CF_2 bilayer (black line), MoS_2 monolayer (red line), and Sc_2CF_2 monolayer (blue line).

Reference

(1) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* **2003**, *118*, 8207-8215.

(2) Kresse, G.; Furthmullerr, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169-11186.

(3) Blöchl P. E. Projector augmented-wave method. *Phys. Rev. B* **1996**, *50*, 17953-17979.

(4) Komsa, H.; Krasheninnikov, A. V. Electronic structures and optical properties of realistic transition metal dichalcogenide heterostructures from first principles. *Phys. Rev. B* **2013**, *88*, 085318.

(5) Segall, M. D.; Lindan, P. J. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Payne, M. C. First-Principles Simulation: Ideas, Illustrations and the CASTEP Code. *J. Phys.: Condens. Matter.* **2002**, *14*, 2717-2744.

(6) Kumar, A.; Ahluwalia, P. K. A first principle Comparative study of electronic and optical properties of 1*H*-MoS_2 and 2*H*-MoS_2. *Mater. Chem. Phys.* **2012**, *135*, 755-761.