Supporting Information

Janus MoSSe/WSeTe heterostructure: A Direct Z-scheme

Photocatalyst for Hydrogen Evolution

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1. Band edge position of transition metal chalcogenides (TMD)

The direct Z-scheme photocatalyst usually consists of two connected semiconductor photocatalysts: one is oxidation photocatalyst and another is reduction photocatalyst. Meanwhile, the interlayer band gap should be much smaller than the intralayer band gap to obtain fast interlayer electron-hole (e-h) recombination. Thus, the band edge position of two semiconductors in direct Z-scheme photocatalyst is particularly important. Transition metal chalcogenides (TMD) have attracted widespread attention in heterostructures application due to their flexible band edge position in which moves up step by step with the increase of atomic number of element. Herein, the band edge position of typical TMD¹ and Janus TMD as candidate materials were shown in Fig. S1. Compared with typical TMD, it is believed that the heterostructure based on MoSSe and WSeTe monolayers exhibit a small interlayer band gap because of their large staggered band alignent, which is favorable for rapid interlayer e-h recombination. Meanwhile. the CBM of WSeTe monolayer is higher than all others, revealing its highest H₂ evolution capacity. In addition, MoSSe/WSeTe heterostructure possesses a small lattice mismatch (2.6%). Thus, the MoSSe and WSeTe monolayers are expected to be appropriate candidates to construct direct Z-scheme photocatalysts.



Fig. S1 Conduction band (CB) and valence band (VB) potentials of some common TMD (MX_2) and Janus TMD (MoSSe and WSeTe) versus vacuum level at pH=7 and pH=0. The data of typical TMD are all derived from Ref. 1 and that of Janus TMD (MoSSe and WSeTe) were calculated by ourselves. The band gap calculated from HSE06.

2. Geometric and electronic structures of monolayer MoSSe and WSeTe

To construct the theoretical model of Janus MoSSe/WSeTe heterostructure, the geometry optimizations of the monolayer MoSSe and WSeTe were performed. The optimized lattice parameters were a= b= 3.25 Å for monolayer MoSSe and a=b= 3.43 Å for monolayer WSeTe, as indicated in Fig. S2. These values are in good agreement with the experimental and theoretical values (a=b= 3.22 Å for MoSSe; a=b=3.41Å for WSeTe).^{2, 3} Band structures of MoSSe and WSSe obtained from PBE and HSE06 are also presented in Fig. S2. The calculated band structures indicate that both of them possess direct band-gaps at the K point. The gap values from HSE06 are 1.79 eV for WSeTe and 2.01 eV for MoSSe respectively, which agree well with previous works,^{3,4} indicating that MoSSe and WSeTe monolayers have a wide range of absorption of sunlight.



Fig. S2 Top and side views of (a) MoSSe and (b) WSeTe monolayers, where the unit cell is represented by the solid frame. The green, yellow, purple, grey and brown sphere represents Se, S, Mo, W and Te atom, respectively. Band structures of MoSSe monolayer from PBE (c) and HSE06 (d). Band structures of WSeTe monolayer from PBE (e) and HSE06 (f). The fermi level is set as dash line.

3. Stacking models of Janus MoSSe/WSeTe heterostructure

To get a comprehensive understanding, we consider six possible stacking patterns of Te-Se stacking and Te-S stacking labeled AA, AB, AC, AA', AB' and AC' in Fig. S3 and S4 respectively. After relaxation, the interlayer distance is in a range from 3.29 to 3.88 Å for Te-Se stacking and range from 3.17 to 3.78 Å for Te-S stacking. In order to assess the relative stability of the heterostructure, we calculate the binding energy (E_b) using the formula: $E_b=E_t-E_{MoSSe}-E_{WSeTe}$, where E_t is the total energy of the MoSSe/WSeTe heterostructure, and E_{MoSSe} and E_{WSeTe} are the total energies of the isolated MoSSe and WSeTe monolayer, respectively. According to this definition, a more negative binding energy among the six configurations is the AA' configuration for both Te-Se and Te-S stacking. Therefore, we only study the AA' stacking configuration as an example in the following calculations.



Fig. S3 Top and side views of high symmetry stacking model of AA (a), AB (b), AC (c), AA' (d), AB' (e) and AC' (f) for Te-Se stacking and the interlayer distances are labeled.



Fig. S4 Top and side views of high symmetry stacking model of AA (a), AB (b), AC (c), AA' (d), AB' (e) and AC' (f) for Te-S stacking and the interlayer distances are labeled.

4. The thermal stability of Janus MoSSe/WSeTe heterostructure

The stability of 2D heterostructure is crucial for experimental fabrication and practical applications. To study its room-temperature thermal stability, ab initio molecular dynamics (AIMD) simulations have been performed at 300 K for $3 \times 3 \times 1$ supercell. As indicated by the AIMD snapshots illustrated in Fig. S5, the planar 2H phase stacking networks are well maintained and only a slight dislocation within 4 ps, demonstrating the MoSSe/WSeTe heterostructure is stable at room temperature. The thermal stability of MoSSe/WSeTe heterostructure is further confirmed by the time-dependent evolution of total energies, which are oscillating within a very narrow range. All the atoms in the cell are vibrating around their equilibrium positions during the AIMD simulations, and no phase transition or bonds broken occurs at 300 K. These results further demonstrate that the studied systems are stable even at room temperature.



Fig. S5 Evolution of total energy and snapshots of Te-Se (a) and Te-S (b) from AIMD simulations at 0 and 4 ps.

5. Geometric and electronic structures of Janus MoSSe/WSeTe heterostructure

with interface chalcogen vacancy

To consider the effect of chalcogen vacancy position on e-h recombination rate of Te-Se stacking, we calculated the band structure of Te-Se stacking with interface chalcogen vacancies. In addition, the charge density difference of Te-Se stacking with surface and interface chalcogen vacancies are also calculated.



Fig. S6 Geometric structure (a) and band structure (b) of Te-Se-defect stacking with interface chalcogen vacancies. The blue and red balls represent the electron orbitals of MoSSe and WSeTe, respectively. The dashed line represents the Fermi level.



Fig. S7 Charge density difference of Te-Se-defect stacking with (a) surface chalcogen vacancies and (b) interface chalcogen vacancies. The single arrow represents the direction of a built-in electric field. The cyan and yellow areas represent electron depletion and accumulation, respectively. The red dotted circles represent the chalcogen vacancies.

6. Intermediate adsorption energies, zero point energies, entropies and free

energies

To realize the water splitting, the catalytic activity of the heterostructure should be checked. Here we performed the free energy calculations in Table S1. The free energies (ΔG) of intermediate in hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) were calculated using: $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$ (1)

Where ΔE is the intermediate adsorption energy (H*, OH*, O* and OOH*) calculated from DFT, ΔE_{ZPE} is the difference in zero point energy, T ΔS is the change in entropy.

Table S1 Adsorption energy (ΔE), zero point energy difference (ΔE_{ZPE}), entropy difference (T ΔS) and free energy (ΔG) of HER and OER in MoSSe/WSeTe heterostructure with Te-Se-defect stacking.

Reaction	Intermediate	Adsorption energy (ΔE) /eV	Zero point energy (ΔE_{ZPE}) /eV	Entropy (T Δ S) /eV	Free energy (ΔG) /eV
HER	H*	-0.40	0.02	-0.20	-0.18
OER	OH*	-1.16	0.03	-0.41	-0.72
	O*	-1.59	-0.21	-0.22	-1.58
	OOH*	1.45	-0.34	-0.53	1.64



Fig. S8 HER free energy change of H* in MoSSe/WSeTe heterostructure with Te-Se-defect stacking.

References

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