Supporting Information

MoSSe/Hf(Zr)S_2 heterostructures used for efficient Z-scheme photocatalytic water-splitting

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Table S1 Free energy changes for all the reaction steps in the HER process of HfS_2/SMoSe HS under different conditions.

	ΔG_{H1} (eV)	ΔG_{H2} (eV)
$pH = 0$, $U = 0$ eV	1.87	-1.87
$pH = 7$, $U = 0$ eV	2.29	-1.46
$pH = 0$, $U = 0.95$ eV	0.92	-2.82
$pH = 7$, $U = 0.95$ eV	1.34	-2.41

Table S2 Free energy changes for all the reaction steps in the HER process of HfS_2/SeMoS HS under different conditions.

	ΔG_{H1} (eV)	ΔG_{H2} (eV)
$pH = 0$, $U = 0$ eV	1.58	-1.58
$pH = 7$, $U = 0$ eV	2.00	-1.17
$pH = 0$, $U = 0.28$ eV	1.30	-1.86
$pH = 7$, $U = 0.28$ eV	1.72	-1.45

Table S3 Free energy changes for all the reaction steps in the HER process of ZrS_2/SMoSe HS under different conditions.

	ΔG_{H1} (eV)	ΔG_{H2} (eV)
$pH = 0$, $U = 0$ eV	1.87	-1.87
$pH = 7$, $U = 0$ eV	2.28	-1.46
$pH = 0$, $U = 1.05$ eV	0.82	-2.92
$pH = 7$, $U = 1.05$ eV	1.23	-2.51

Table S4 Free energy changes for all the reaction steps in the HER process of ZrS_2/SeMoS HS under different conditions.

	ΔG_{H1} (eV)	ΔG_{H2} (eV)
$pH = 0$, $U = 0$ eV	1.55	-1.55
$pH = 7$, $U = 0$ eV	1.97	-1.14
$pH = 0$, $U = 0.25$ eV	1.30	-1.80
$pH = 7$, $U = 0.25$ eV	1.72	-1.39

Table S5 The free energy changes for all the reaction steps in the OER process of HfS_2/SMoSe HS under different conditions.

	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)
$pH = 0$, $U = 0$ eV	2.29	0.58	2.64	-0.59
$pH = 7$, $U = 0$ eV	1.88	0.17	2.23	-1.01
$pH = 0$, $U = 2.80$ eV	-0.50	-2.22	-0.16	-3.40
$pH = 7$, $U = 2.80$ eV	-0.92	-2.63	-0.57	-3.81

Table S6 The free energy changes for all the reaction steps in the OER process of HfS_2/SeMoS HS under different conditions.

	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)
$pH = 0$, $U = 0$ eV	2.28	0.62	2.62	-0.60
$pH = 7$, $U = 0$ eV	1.86	0.21	2.21	-1.01
$pH = 0$, $U = 2.71$ eV	-0.43	-2.09	-0.09	-3.31
$pH = 7$, $U = 2.71$ eV	-0.85	-2.50	-0.50	-3.72

Table S7 The free energy changes for all the reaction steps in the OER process of ZrS_2/SMoSe HS under different conditions.

	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)
$pH = 0$, $U = 0$ eV	2.13	0.61	2.65	-0.47
$pH = 7$, $U = 0$ eV	1.72	0.19	2.24	-0.88
$pH = 0$, $U = 2.67$ eV	-0.54	-2.07	-0.01	-3.14
$pH = 7$, $U = 2.67$ eV	-0.95	-2.48	-0.43	-3.55

Table S8 The free energy changes for all the reaction steps in the OER process of ZrS_2/SeMoS HS under different conditions.

	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)
$pH = 0$, $U = 0$ eV	2.12	0.64	2.65	-0.49
$pH = 7$, $U = 0$ eV	1.71	0.23	2.23	-0.90
$pH = 0$, $U = 2.73$ eV	-0.61	-2.09	-0.08	-3.22
$pH = 7$, $U = 2.73$ eV	-1.02	-2.50	-0.50	-3.63

Table S9 Free energy changes for all the reaction steps in the HER process of Se defected HfS_2/SMoSe HS under different conditions.

	ΔG_{H1} (eV)	ΔG_{H2} (eV)
$pH = 0$, $U = 0$ eV	0.01	-0.01
$pH = 7$, $U = 0$ eV	0.43	0.40
$pH = 0$, $U = 0.95$ eV	-0.94	-0.96
$pH = 7$, $U = 0.95$ eV	-0.52	-0.55

Table S10 Free energy changes for all the reaction steps in the HER process of S defected HfS_2/SeMoS HS under different conditions.

	ΔG_{H1} (eV)	ΔG_{H2} (eV)
$pH = 0$, $U = 0$ eV	-0.30	0.30
$pH = 7$, $U = 0$ eV	0.11	0.72
$pH = 0$, $U = 0.28$ eV	-0.58	0.02
$pH = 7$, $U = 0.28$ eV	-0.17	0.44

Table S11 Free energy changes for all the reaction steps in the HER process of Se defected ZrS_2/SMoSe HS under different conditions.

	ΔG_{H1} (eV)	ΔG_{H2} (eV)
$pH = 0$, $U = 0$ eV	-0.01	0.01
$pH = 7$, $U = 0$ eV	0.40	0.43
$pH = 0$, $U = 1.05$ eV	-1.06	-1.04
$pH = 7$, $U = 1.05$ eV	-0.65	-0.62

Table S12 Free energy changes for all the reaction steps in the HER process of S defected ZrS_2/SeMoS HS under different conditions.

	ΔG_{H1} (eV)	ΔG_{H2} (eV)
$pH = 0$, $U = 0$ eV	-0.40	0.40
$pH = 7$, $U = 0$ eV	0.01	0.82
$pH = 0$, $U = 1.05$ eV	-0.65	0.15
$pH = 7$, $U = 1.05$ eV	-0.24	0.57

Table S13 Values used for the entropy and zero-point energy (ZPE) corrections in determining the free energy of reactants, products, and intermediate species adsorbed on catalysts.

system	$T\times S$ (eV)	ZPE (eV)
HfS_2/SMoSe@H	0.02	0.15
HfS_2/SMoSe@O	0.08	0.07
HfS_2/SMoSe@OH	0.12	0.35
HfS_2/SMoSe@OOH	0.18	0.42
HfS_2/SeMoS@H	0.02	0.18
HfS_2/SeMoS@O	0.08	0.06
HfS_2/SeMoS@OH	0.10	0.34
HfS_2/SeMoS@OOH	0.20	0.44
ZrS_2/SMoSe@H	0.02	0.15
ZrS_2/SMoSe@O	0.09	0.06
ZrS_2/SMoSe@OH	0.09	0.34
ZrS_2/SMoSe@OOH	0.16	0.43
ZrS_2/SeMoS@H	0.02	0.19
ZrS_2/SeMoS@O	0.09	0.06
ZrS_2/SeMoS@OH	0.12	0.35
ZrS_2/SeMoS@OOH	0.11	0.42
Defective HfS_2/SMoSe@H	0.01	0.16
Defective HfS_2/SeMoS@H	0.01	0.16
Defective ZrS_2/SMoSe@H	0.01	0.16
Defective ZrS_2/SeMoS@H	0.01	0.16

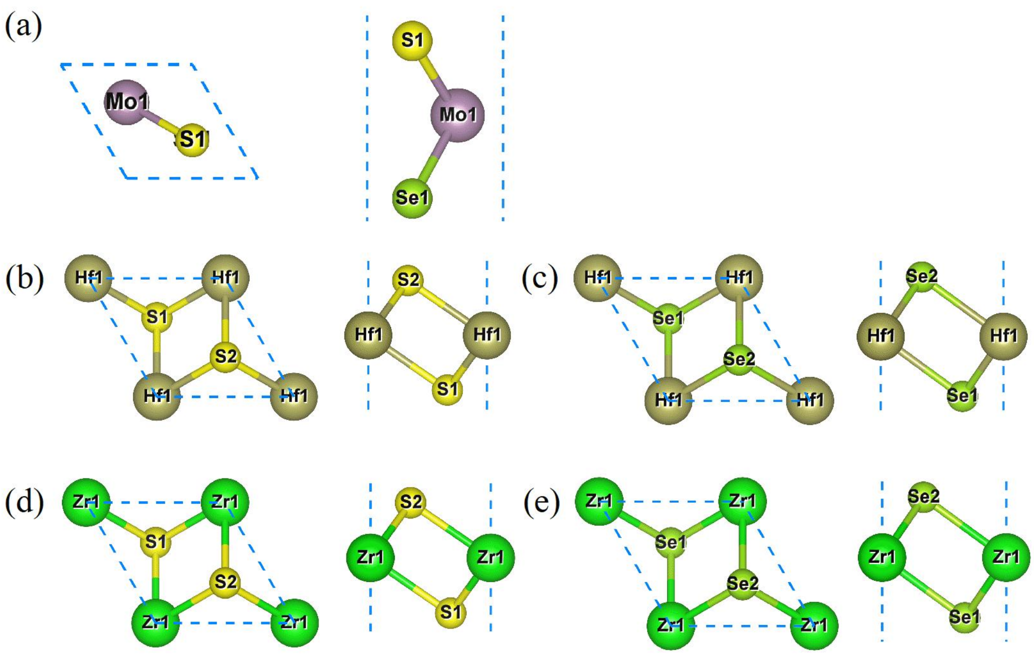

Fig. S1 Top and side views of the unit cells of (a) MoSSe, (b) HfS_2, (c) $HfSe_2$, (d) ZrS_2, and (e) $ZrSe_2$ SLs.

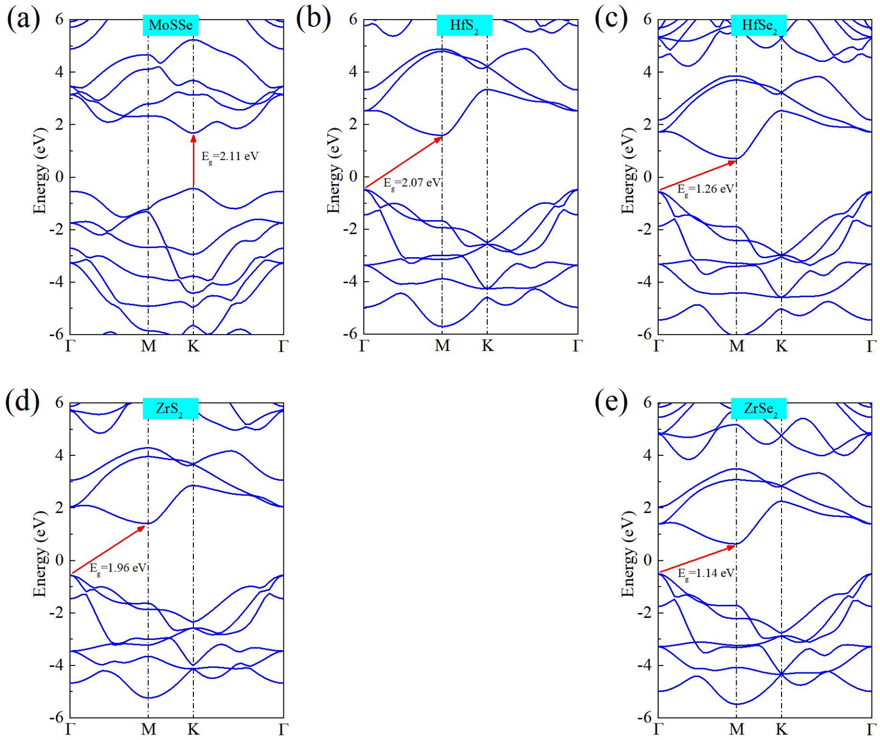

Fig. S2 Band structures of (a) MoSSe, (b) HfS_2, (c) $HfSe_2$, (d) ZrS_2, and (e) $ZrSe_2$ SLs.

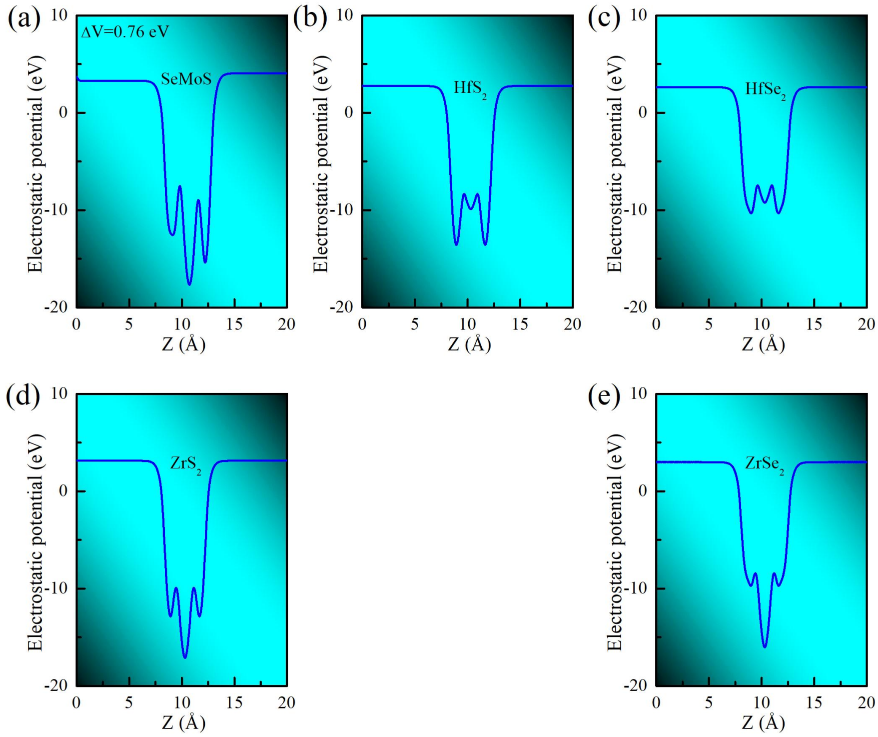

Fig. S3 Plane-averaged electrostatic potentials of (a) MoSSe, (b) HfS_2, (c) $HfSe_2$, (d) ZrS_2, and (e) $ZrSe_2$ SLs.

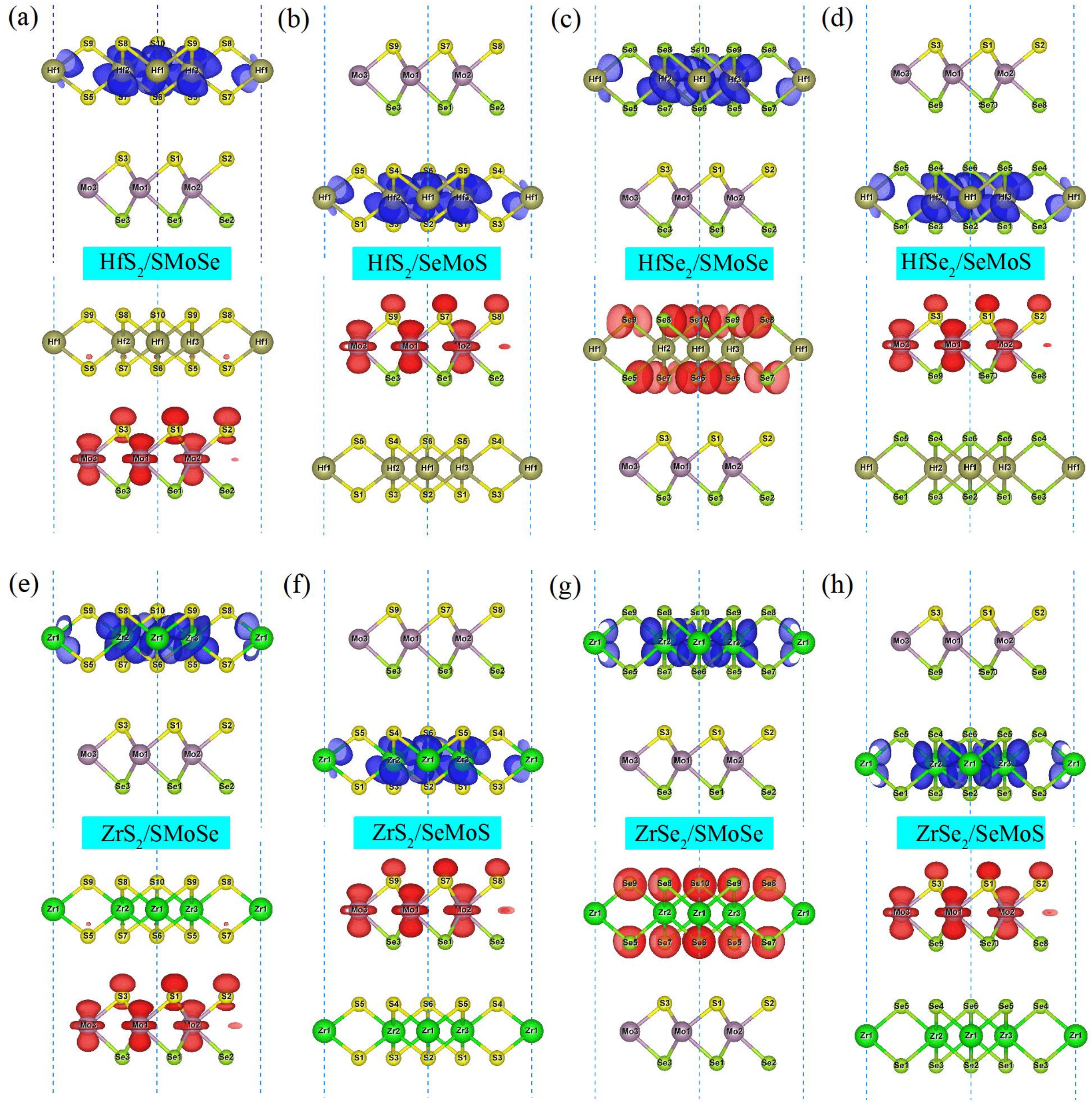

Fig. S4 The band-decomposed charge densities of the CBM and VBM for (a) HfS_2/SMoSe, (b) HfS_2/SeMoS, (c) $HfSe_2$/SMoSe, (d) $HfSe_2$/SeMoS, (e) ZrS_2/SMoSe, (f) ZrS_2/SeMoS, (g) $ZrSe_2$/SMoSe, and (h) $ZrSe_2$/SeMoS HSs. The blue and red regions represent the CBM and VBM, respectively.

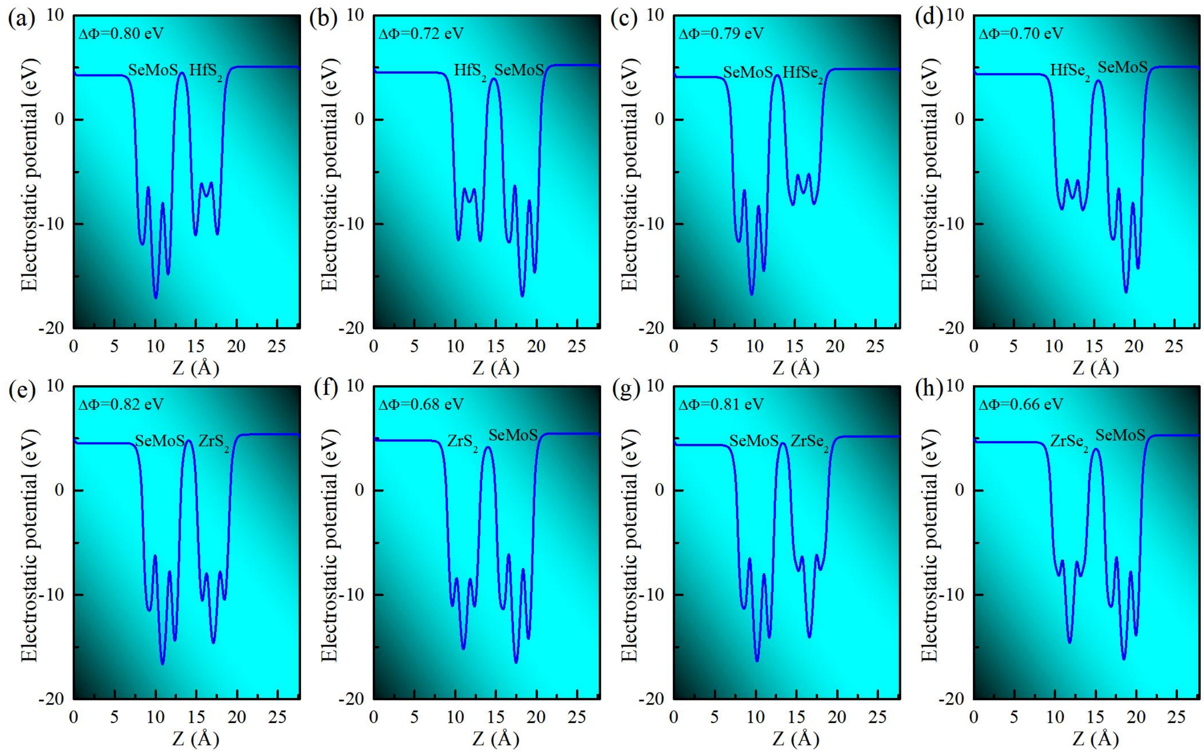

Fig. S5 Plane-averaged electrostatic potentials of (a) HfS_2/SMoSe, (b) HfS_2/SeMoS, (c) $HfSe_2$/SMoSe, (d) $HfSe_2$/SeMoS, (e) ZrS_2/SMoSe, (f) ZrS_2/SeMoS, (g) $ZrSe_2$/SMoSe, and (h) $ZrSe_2$/SeMoS HSs.

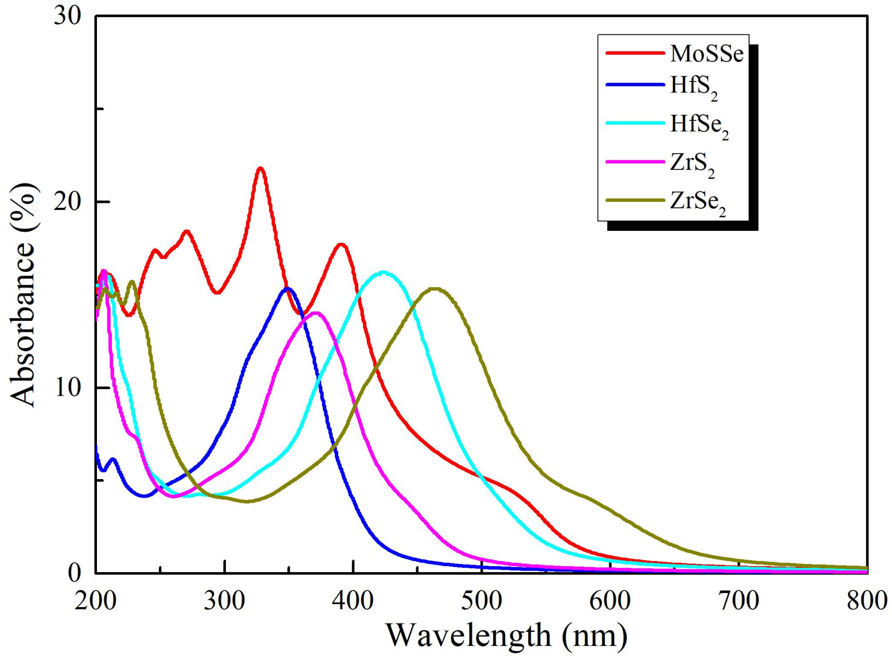

Fig. S6 The optical curves of MoSSe, HfS_2, $HfSe_2$, ZrS_2, and $ZrSe_2$ SLs.

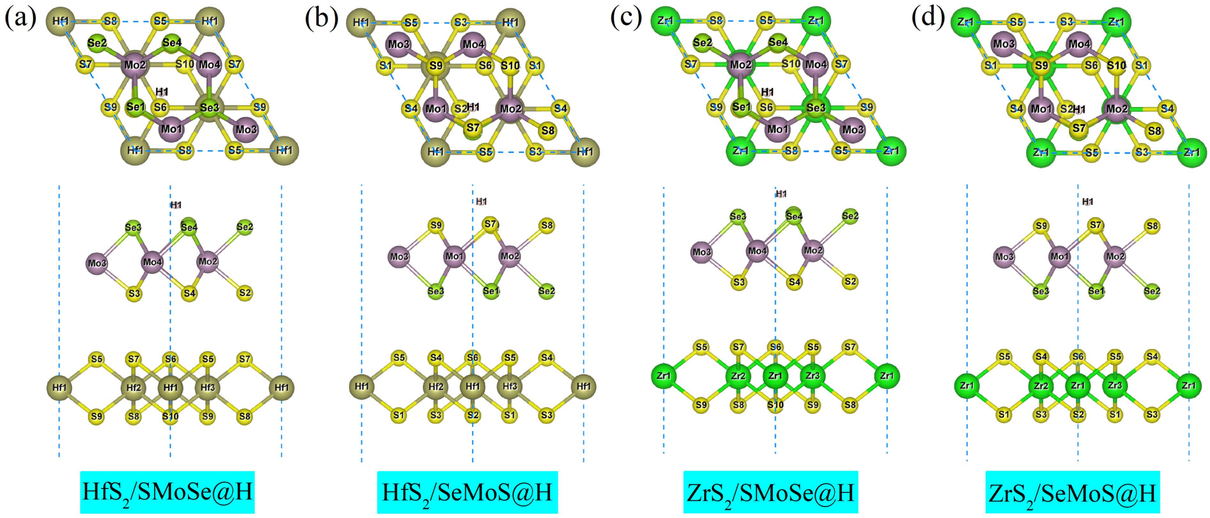

Fig. S7 Top and side views of optimized geometries of (a) HfS_2/SMoSe@H, (b) HfS_2/SeMoS@H, (c) ZrS_2/SMoSe@H, and (d) ZrS_2/SeMoS@H.

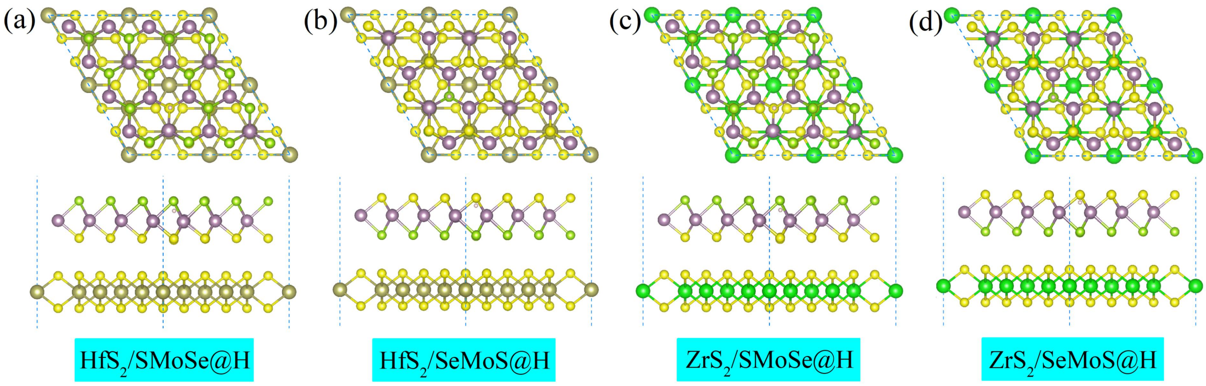

Fig. S8 Top and side views of optimized geometries of (a) HfS_2/SMoSe@H, (b) HfS_2/SeMoS@H, (c) ZrS_2/SMoSe@H, and (d) ZrS_2/SeMoS@H with one Se (or S) atom vacancy.

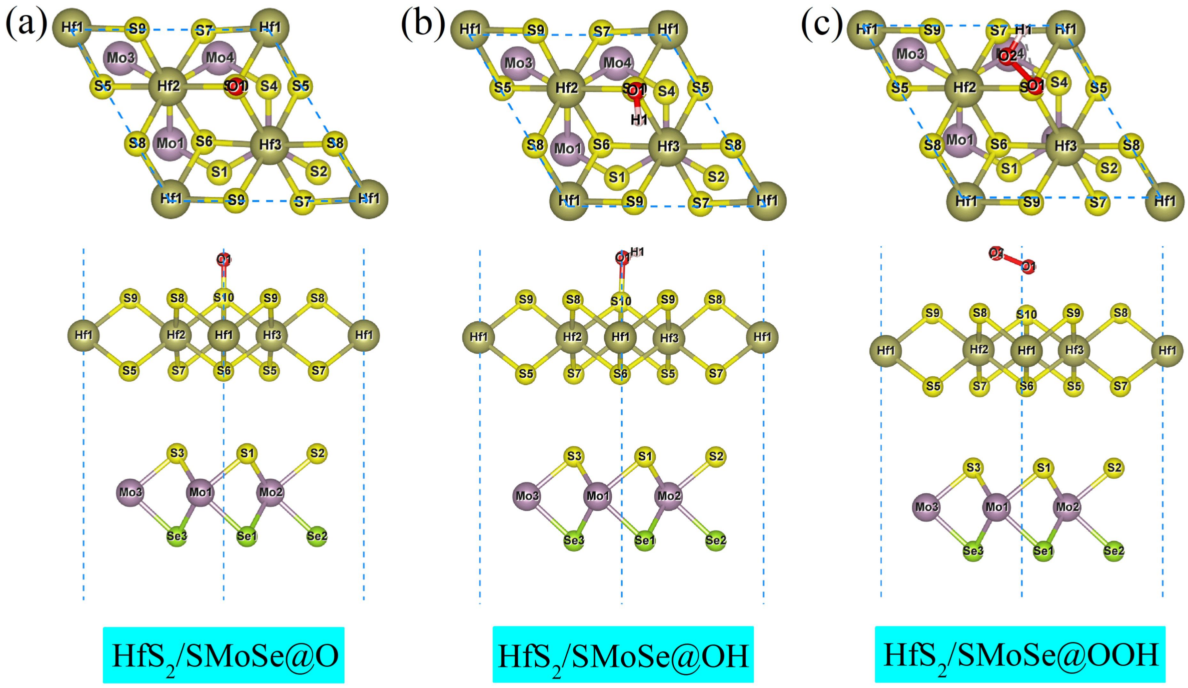

Fig. S9 Top and side views of optimized geometries of (a) HfS_2/SMoSe@O, (b) HfS_2/SMoSe@OH, and (c) HfS_2/SMoSe@OOH.

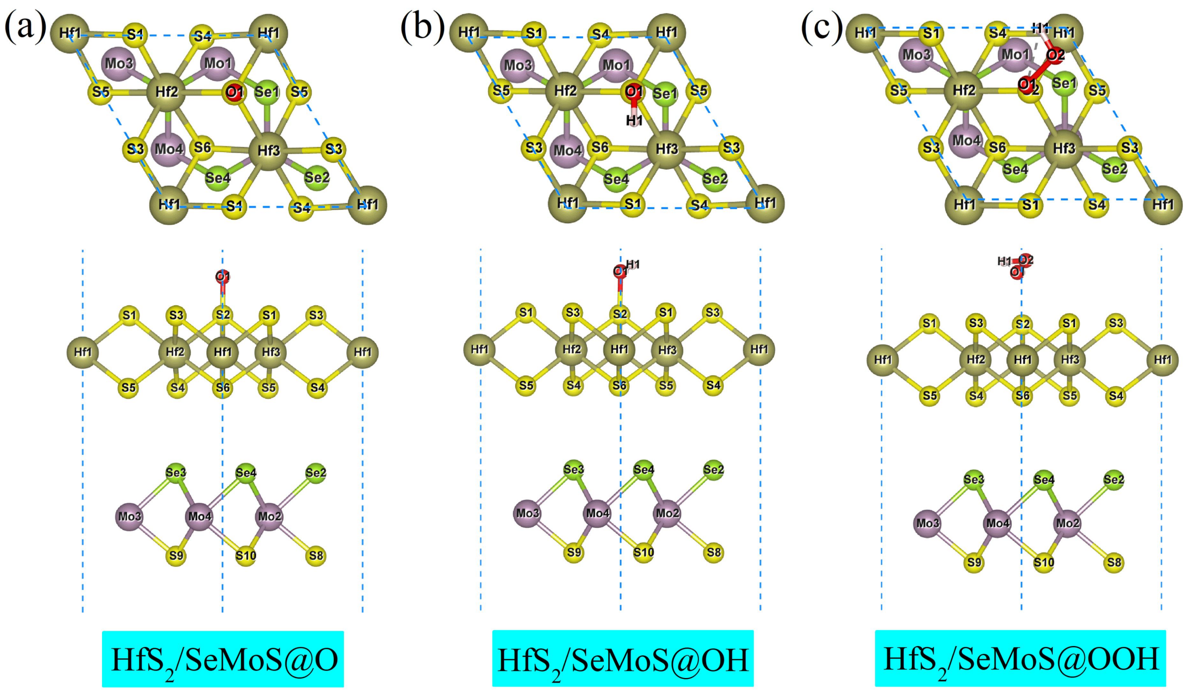

Fig. S10 Top and side views of optimized geometries of (a) HfS_2/SeMoS@O, (b) HfS_2/SeMoS@OH, and (c) HfS_2/SeMoS@OOH.

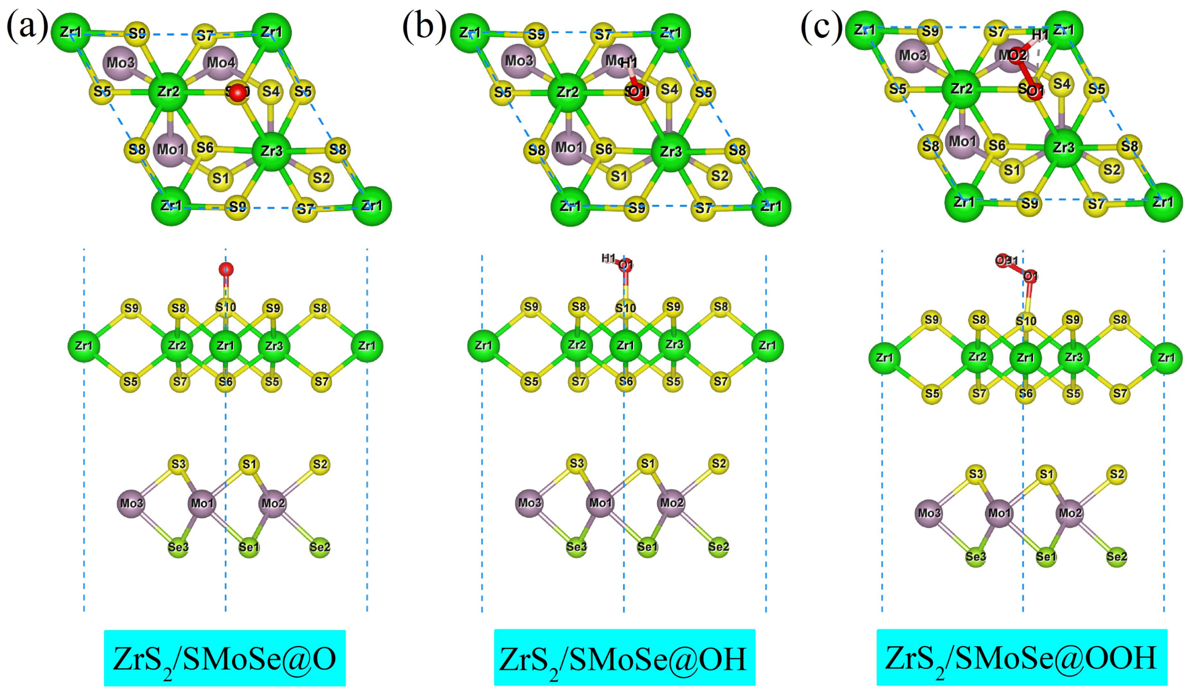

Fig. S11 Top and side views of optimized geometries of (a) ZrS_2/SMoSe@O, (b) ZrS_2/SMoSe@OH, and (c) ZrS_2/SMoSe@OOH.

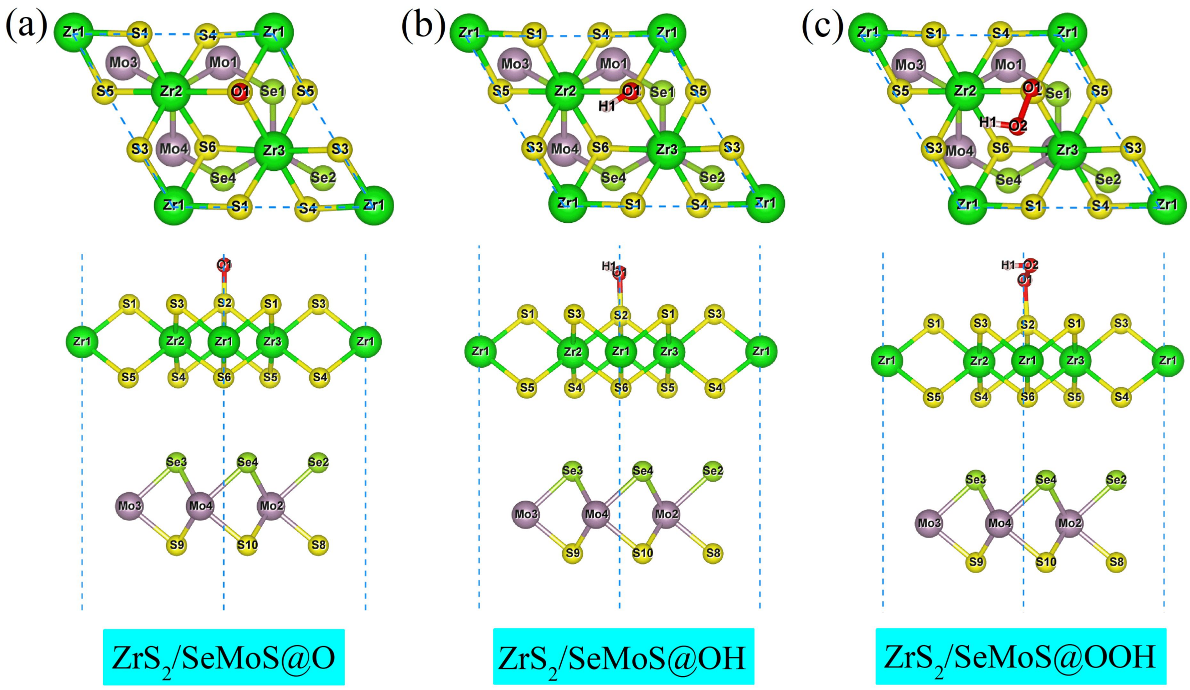

Fig. S12 Top and side views of optimized geometries of (a) ZrS_2/SeMoS@O, (b) ZrS_2/SeMoS@OH, and (c) ZrS_2/SeMoS@OOH.