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# **Supplementary Information**

#### Tuning the Catalytic Activity of Heterogeneous Two-dimensional Transition Metal Dichalcogenide for Hydrogen Evolution

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### **Computational details**

First-principles density functional (DFT) calculations were carried out as implemented in Vienna Ab-initio Simulation Package (VASP).<sup>1</sup> Interaction of core electrons was simulated by the Project Augmented Wave (PAW) method.<sup>2</sup> Exchange-correlation energy was employed with the functional by Generalized Gradient Approximation (GGA) in the form of Perdew– Burke–Ernzerhof (PBE). Effect of spin-polarization and van der Waals (vdW) interactions by method (DFT-D2) of Grimme <sup>3</sup> on total energy of our 2D-TMD models were considered in all the calculations. The Kohn-sham pseudo wavefunctions were expanded by plane waves with cut-off energy of 520 eV. Calculations were continued until the energy for ionic relaxation step was converged within 1x10<sup>-3</sup> eV. The criteria of electronic convergence for ground state energy is 1e<sup>-4</sup> eV. Vacuum space of approximately 10 Å was inserted to preclude interactions among images of a model system.

The gamma-point scheme was applied with 3x3x1 and 3x1x1 meshes to integrate Brillouin zones for terrace and ribbon-edge models of TMDs, respectively. Lattice constants calculated were consistent with experimental measurements within ~3%, as tabulated in Table S2. M- and C-edges were simulated with lengthy ribbon structures, while we utilized bulk TMD structure for the terrace.

Heterogeneous TMD structure was designed by identifying thermodynamically the most stable combination by DFT calculations as shown in Fig. S3-S6. For instance, the  $MoS_2/MoS_2$  TMD bilayer was stacked with *AB* stacking while *AA* stacking for the  $TiS_2/TiS_2$ . We tested the hydrogen adsorption energies of TMD catalysts by exposing to solvating water molecules and found slight differences from what calculated in vacuum condition. However, the effect was not crucial to change our conclusions on the catalytic properties of TMDs, as shown in Fig. S10 and 11.

Gibbs free energy of hydrogen adsorption ( $\Delta G_{H^*}$ ) was defined as equations S1and S2.

$$\Delta E_{ads(cat+sup)}^{H*} = E_{(cat+sup)}^{nH*} - E_{(cat+sup)}^{(n-1)H*} - \frac{1}{2}E(H_2)$$
(S1)

$$\Delta G_{H^*} = \Delta E_{ads(cat+sup)}^{H^*} + \Delta E_{ZPE} - T\Delta S$$
(S2)

where  $\Delta E_{ads(cat+sup)}^{H*}$  is a calculated adsorption energy of hydrogen, while  $E_{(cat+sup)}^{nH*}$  and  $E_{(cat+sup)}^{(n-1)H*}$  mean a calculated ground state energy of a heterogeneous bilayer TMD material with each *n* and *n*-1 adsorbed hydrogen atoms.  $E(H_2)$  is the ground state energy of hydrogen molecule. Asterisk (\*) implies adsorbed state of hydrogen atom.  $\Delta ZPE$ , T and S are zero-point energy correction, temperature and entropy. In our study,  $\Delta E_{ZPE} - T\Delta S$  were estimated as 0.29 eV at the 298 K and 1 bar.<sup>4-6</sup>

In this study, the concept of computational standard hydrogen electrode (SHE) was utilized in the calculations of Gibbs free energy of hydrogen evolution reaction to incorporate the activity of solvated proton (H<sup>+</sup>) in acidic environment. All the Gibbs free energies were computed at pH = 0. Therefore, we omitted the term  $k_BT \ln 10 \times pH$  ( $k_B$  is Boltzmann constant) in the equation of Gibbs free energy,<sup>7, 8</sup> but the full formalism can be used for other solutions such as neutral and alkaline with  $pH \neq 0$ .

The adhesion energy of the heterogeneous bilayer TMD was calculated by equations S3-S5.

$$E_{adh(cat+sup)}^{H*} = E_{(cat+sup)}^{nH*} - E_{(cat)}^{nH*} - E_{(sup)}$$
(S3)

$$E_{adh(cat+sup)} = E_{(cat+sup)} - E_{(cat)} - E_{(sup)}$$
(S4)

$$\Delta E_{adh} = E_{adh(cat+sup)}^{H^*} - E_{adh(cat+sup)}$$
(S5)

where  $E_{(cat+sup)}$ ,  $E_{(cat)}$  and  $E_{(sup)}$  are the ground state energies of a whole bilayer with overlaying and supporting TMD, overlaying TMD only and supporting TMD only, respectively. The difference of adhesion energy ( $\Delta E_{adh}$ ) defined in eqn (S5) as normalized by numbers of metal atoms in catalytic TMD.  $E_{adh(cat+sup)}^{H*}$  and  $E_{adh(cat+sup)}^{*}$  mean the adhesion energies of hydrogen adsorbed and pristine 2D-TMD materials, respectively.

## Correlation between adhesion energy difference and hydrogen adsorption

If one hydrogen atom is adsorbed in unit cell (0.25 ML in this study),

$$\Delta E_{adh(cat+sup)} = E_{(cat+sup)}^{H^*} - E_{(cat+sup)} - E_{(cat)}^{H^*} + E_{(cat)}$$
(S6)

$$\Delta E_{ads(cat+sup)}^{H^*} = E_{(cat+sup)}^{H^*} - E_{(cat+sup)} - \frac{1}{2}E(H_2)$$
(S7)

Hence, hydrogen adsorption energy is indicated as following terms.

$$\Delta E_{ads(cat+sup)}^{H^*} = \Delta E_{adh(cat+sup)} + E_{(cat)}^{H^*} - E_{(cat)} - \frac{1}{2}E(H_2)$$
(S8)

Equation S8 can be simplified using the definition of adsorption energy as eqn S9

$$\Delta E_{ads(cat+sup)}^{H*} = \Delta E_{adh(cat+sup)} + E_{ads(cat)}^{H*}$$
(S9)

Thus, in a heterogeneous TMD, hydrogen adsorption energy consists of hydrogen adsorption energy in the overlaying TMD and the adhesion energy differences.



**Fig. S1** Top and side views of a monolayer TMD with *T*-structure in (a) and in (b) *H*-structure activated at C-edges and in (c) *H*-structure activated at M-edges.

In Fig. S1, *H*-structure has different adsorption sites depending of the termination of 2D-TMD: M- and C- edges. A single layered *T*-structure is symmetrically in up and down sides of the surfaces; however, in a supported TMD (a bilayer) the symmetry is broken into heterogeneous structure. Hence, the edges of the *T*-structure are also different M- and C-edges.



Fig. S2 Possible hydrogen adsorption sites in *T*-structure materials

As shown in Fig.S2, hydrogen adsorption energies were calculated in five symmetrically different sites of *T*-type TMD to identify an active site. Our results indicated that the site 1 is thermodynamically the most preferred for hydrogen adsorption, followed by site 2 (Table S1).

**Table S1** Hydrogen adsorption energy on active sites shown in Fig. S2. The energies are relative values with respect to that at the site 1.

Adsorption site	TiS <sub>2</sub>	$ZrS_2$	$HfS_2$	TiSe <sub>2</sub>	ZrSe <sub>2</sub>	HfSe <sub>2</sub>
1	0.00	0.00	0.00	0.00	0.00	0.00
2	0.17	0.12	0.10	0.09	0.09	0.07
3	0.60	0.61	0.55	0.53	0.58	0.54
4	0.82	0.75	0.67	0.87	0.92	0.90
5	0.82	0.44	0.41	0.46	0.47	0.45

		Lattice constant							
Materials	Structure	Cal.	Exp.	CalExp. (%)	Ref.				
TiS <sub>2</sub>	1 <i>T</i>	3.424	3.400	0.69	9				
$ZrS_2$	1 <i>T</i>	3.666	3.661	0.13	10				
$HfS_2$	1 <i>T</i>	3.648	3.631	0.48	10				
VS <sub>2</sub>	2H	3.197	3.221	-0.75	11				
$NbS_2$	2H	3.379	3.330	1.46	12				
TaS <sub>2</sub>	2H	3.379	3.310	2.09	13				
$MoS_2$	2H	3.219	3.160	1.87	14				
$WS_2$	2H	3.213	3.153	1.92	14				
TiSe <sub>2</sub>	1 <i>T</i>	3.561	3.540	0.58	11				
ZrSe <sub>2</sub>	1 <i>T</i>	3.772	3.773	-0.03	10				
HfSe <sub>2</sub>	1 <i>T</i>	3.749	3.746	0.08	10				
VSe <sub>2</sub>	2H	3.355	3.359	-0.10	11				
$NbSe_2$	2H	3.493	3.445	1.40	15				
TaSe <sub>2</sub>	2H	3.504	3.436	1.98	16				
$MoSe_2$	2H	3.340	3.320	0.61	14				
WSe <sub>2</sub>	2H	3.393	3.286	3.26	14				

**Table S2** Lattice constants for single-layer TMD materials. Calculated (Cal.) and experimentally measured (Exp.) <sup>9-16</sup> values were compared.

**Table S3** Relative thermodynamic stability between *T*- and *H*-structures for various 2D-TMD materials. The positive (negative) energy means T(H)-structure is more stable structure.

$MS_2$	$E_{2H}$ - $E_{1T}$	MSe <sub>2</sub>	$E_{2H}-E_{1T}$
TiS <sub>2</sub>	0.417	TiSe <sub>2</sub>	0.364
$ZrS_2$	0.521	ZrSe <sub>2</sub>	0.411
$HfS_2$	0.674	HfSe <sub>2</sub>	0.523
$VS_2$	-0.048	VSe <sub>2</sub>	-0.031
$NbS_2$	-0.092	NbSe <sub>2</sub>	-0.076
TaS <sub>2</sub>	-0.032	TaSe <sub>2</sub>	-0.037
$MoS_2$	-0.812	MoSe <sub>2</sub>	-0.690
WS <sub>2</sub>	-0.860	$WSe_2$	-0.758

Relative thermodynamic stability between *T*- and *H*-structures for various 2D-TMD materials were estimated. Herein, positive (negative) value means the T(H)- structure is a stable form. For example, (Ti, Zr, Hf)/(S, Se) are stable as *T*-structures, while the others are in *H*-structures.

**Table S4** Adhesion energy of heterogeneous 2D-TMD materials at terrace sites without hydrogen adsorption

		TiS <sub>2</sub>	ZrS <sub>2</sub>	HfS <sub>2</sub>	VS <sub>2</sub>	NbS <sub>2</sub>	TaS₂	MoS <sub>2</sub>	WS <sub>2</sub>	TiSe <sub>2</sub>	ZrSe <sub>2</sub>	HfSe₂	VSe <sub>2</sub>	NbSe <sub>2</sub>	TaSe₂	MoSe <sub>2</sub>	WSe <sub>2</sub>
	TiS₂	-0.14	-0.10	-0.16	0.04	-0.19	-0.22	0.05	0.00	-0.11	-0.04	-0.15	-0.15	-0.27	-0.35	-0.10	-0.17
	ZrS <sub>2</sub>	-0.10	-0.41	-0.48	0.49	-0.06	-0.07	0.51	0.46	-0.27	-0.51	-0.61	-0.01	-0.35	-0.46	0.06	-0.06
S	HfS₂	-0.16	-0.48	-0.57	0.40	-0.14	-0.20	0.43	0.32	-0.35	-0.58	-0.72	-0.10	-0.46	-0.58	-0.04	-0.18
ສ	VS <sub>2</sub>	0.03	0.49	0.40	-0.13	-0.06	-0.07	-0.05	-0.09	0.28	0.71	0.59	-0.02	0.11	0.06	0.08	0.03
	NbS <sub>2</sub>	-0.19	-0.06	-0.13	-0.06	-0.24	-0.28	-0.02	-0.08	-0.13	0.07	-0.06	-0.19	-0.28	-0.34	-0.14	-0.23
Ψ	TaS₂	-0.22	-0.07	-0.20	-0.07	-0.28	-0.35	-0.08	-0.14	-0.17	0.01	-0.13	-0.25	-0.35	-0.42	-0.23	-0.30
ສ	MoS <sub>2</sub>	0.05	0.51	0.43	-0.05	-0.02	-0.08	0.02	-0.02	0.31	0.81	0.69	0.01	0.14	0.09	0.13	0.07
L	WS <sub>2</sub>	0.00	0.46	0.33	-0.09	-0.08	-0.14	-0.02	-0.09	0.23	0.69	0.56	-0.04	0.05	-0.02	0.04	-0.02
Ļ	TiSe <sub>2</sub>	-0.12	-0.27	-0.36	0.28	-0.13	-0.17	0.31	0.23	-0.19	-0.28	-0.40	-0.03	-0.31	-0.39	0.05	-0.07
Ы	ZrSe <sub>2</sub>	-0.07	-0.51	-0.59	0.70	0.07	0.02	0.82	0.69	-0.28	-0.65	-0.76	0.12	-0.31	-0.40	0.27	0.10
ă	HfSe <sub>2</sub>	-0.19	-0.61	-0.72	0.58	-0.06	-0.13	0.69	0.56	-0.40	-0.76	-0.89	0.00	-0.48	-0.57	0.11	-0.05
9	VSe <sub>2</sub>	-0.15	-0.01	-0.10	-0.02	-0.19	-0.25	0.01	-0.05	-0.03	0.13	0.00	-0.12	-0.19	-0.26	-0.07	-0.14
2	NbSe <sub>2</sub>	-0.27	-0.35	-0.46	0.11	-0.28	-0.34	0.13	0.05	-0.31	-0.31	-0.48	-0.19	-0.44	-0.52	-0.14	-0.24
0)	TaSe <sub>2</sub>	-0.35	-0.46	-0.58	0.07	-0.34	-0.42	0.09	-0.02	-0.39	-0.40	-0.57	-0.26	-0.52	-0.62	-0.21	-0.34
	MoSe <sub>2</sub>	-0.10	0.06	-0.04	0.08	-0.14	-0.23	0.13	0.04	0.04	0.27	0.10	-0.07	-0.13	-0.21	0.01	-0.07
	WSe <sub>2</sub>	-0.17	-0.06	-0.18	0.03	-0.22	-0.31	0.07	-0.02	-0.07	0.10	-0.06	-0.13	-0.24	-0.34	-0.07	-0.17

Catalytic materials

Table S4 shows adhesion energies of 256 different computational designed structures with combinations with 2D-TMD materials. Negative value means the structure spontaneously form. For example, bilayer heterogeneous structures of  $MoS_2/ZrSe_2$ ,  $MoS_2/HfSe_2$  and  $HfSe_2/MoS_2$  are thermodynamically unstable.



**Fig. S3** Stacking configuration of a *H*/*H* type TMD.



**Fig. S4** Stacking configuration of a *T*/T type TMD.



**Fig. S5** Stacking configuration of a *H*/*T* type TMD.

	TiS₂	ZrS₂	HfS₂	VS <sub>2</sub>	NbS <sub>2</sub>	TaS₂	MoS <sub>2</sub>	WS <sub>2</sub>	TiSe₂	ZrSe <sub>2</sub>	HfSe <sub>2</sub>	VSe <sub>2</sub>	NbSe <sub>2</sub>	TaSe <sub>2</sub>	MoSe <sub>2</sub>	WSe <sub>2</sub>
TiS <sub>2</sub>	AA	AA	AA	AA	AB'	AA'	AA	AB'	AA	AA	AA	AA	AB'	AA	AA	AB'
ZrS <sub>2</sub>		AA	AA	AA'	AA	AA'	AA	AA'	AA	AA	AA	AB'	AB	AA	AA	AB'
HfS <sub>2</sub>			AA	AB'	AA	AA	AA	AA	AA	AA	AA	AA	AB	AA	AA	AB'
VS <sub>2</sub>				AB					AB'	AA	AA					
NbS <sub>2</sub>					AB				AA	AA	AA					
TaS₂						AB			AB'	AA	AA					
MoS <sub>2</sub>							AB		AA	AB'	AA					
WS <sub>2</sub>									AA	AA	AA					
TiSe <sub>2</sub>									AA	AA	AA	AA	AA	AA	AA	AB'
ZrSe <sub>2</sub>	<i>T/</i>	7 stac	king							AA	AA	AA	AB'	AB'	AB'	AA
HfSe <sub>2</sub>											AA	AB'	AB'	AA	AA	AB'
VSe <sub>2</sub>	<u>H</u> /	H stal	king													
NbSe <sub>2</sub>													AB			
TaSe₂	T/	H stac	kina													
MoSe <sub>2</sub>			3												AB	
WSe <sub>2</sub>																AB

Fig. S6 The most stable stacking structures in the heterogeneous 2D-TMD materials.

To calculate Gibbs free energy diagram for HER by 2D-TMDs we identified thermodynamically most stable stacking using DFT calculations. Four types of the stacks were considered as shown in Fig. S4-S6: *AA*, *AA'*, *AB* and *AB'* for *H/H*, *T/T* and *H/T*, respectively. Herein, *T/H* structure is symmetrically equivalent to *H/T* stacking for the structural stability since they are the same 2D bulk model as shown in Fig. S3~S5. *T/T* structure such as TiS<sub>2</sub>/TiS<sub>2</sub>, TiS<sub>2</sub>/ZrS<sub>2</sub> and HfS<sub>2</sub>/ZrS<sub>2</sub> have the configuration *AA* type, while *H/H* structures are stabilized as an *AB* type. On the other hand, *T/H* (*H/T*) structures present various stacking types such as *AA*, *AA'*, *AB*, *AB'*. Fig. 6S shows the most stable stacking structures of the heterogeneous TMDs.

	TiS <sub>2</sub>	ZrS <sub>2</sub>	HfS <sub>2</sub>	VS <sub>2</sub>	NbS <sub>2</sub>	TaS₂	MoS <sub>2</sub>	WS <sub>2</sub>	TiSe <sub>2</sub>	ZrSe <sub>2</sub>	HfSe <sub>2</sub>	VSe <sub>2</sub>	NbSe <sub>2</sub>	TaSe₂	MoSe <sub>2</sub>	WSe <sub>2</sub>
TiS <sub>2</sub>	5.97	5.97	5.89	6.17	6.26	6.17	6.22	5.94	6.14	6.09	5.99	6.15	6.33	6.11	6.30	6.12
ZrS₂		6.01	5.96	6.32	6.03	6.24	6.03	6.27	6.09	6.15	6.10	6.44	6.49	6.19	6.21	6.28
HfS₂			5.91	5.93	5.86	5.84	5.95	5.83	6.03	6.11	6.06	5.93	6.16	5.95	5.93	5.96
VS <sub>2</sub>				5.99	6.07	6.15	6.09	6.11	6.07	6.06	5.97	6.20	6.27	6.24	6.21	6.26
NbS <sub>2</sub>					6.25	6.26	6.18	6.17	6.10	6.10	6.00	6.50	6.41	6.39	6.39	6.32
TaS₂						6.09	6.14	6.10	6.23	6.06	5.98	6.26	6.35	6.22	6.18	6.23
MoS <sub>2</sub>							6.10	6.09	6.34	6.28	5.98	6.10	6.46	6.28	6.33	6.28
WS₂								6.01	6.08	6.06	5.95	6.13	6.40	6.19	6.23	6.16
TiSe <sub>2</sub>									6.15	6.23	6.25	6.29	6.48	6.33	6.37	6.30
ZrSe <sub>2</sub>										6.25	6.21	6.16	6.49	6.43	6.42	6.29
HfSe <sub>2</sub>											6.16	6.23	6.34	6.09	6.25	6.23
VSe <sub>2</sub>			$\sim$	T								6.37	6.55	6.34	6.29	6.44
NbSe <sub>2</sub>		<b>V</b> V	YY.	Inte	rlaver	distan	се						6.67	6.52	6.56	6.57
TaSe₂		AA	AA		nayer	alotan	00							6.50	6.42	6.28
MoSe <sub>2</sub>			$\mathbf{V}$	ι <u>τ</u>											6.41	6.37
WSe <sub>2</sub>																6.31

**Fig. S7** Interlayer distance of heterogeneous 2D-TMD materials. The interlayer distance is defined by the average distance between the metal layers.



Fig. S8 Charge density difference of monolayer NbS<sub>2</sub> with hydrogen atom on the terrace.



Fig. S9 Gibbs free energy of heterogeneous 2D-TMD materials at (a) M- and (b) C-edges.

M- and C-edge structures have a variety of hydrogen adsorption energies. In particular, they include stronger hydrogen adsorption than that of Pt(111), while the values of heterogeneous 2D-TMDs at terrace are located above Pt(111) surface regardless of their 256 combinations. It implies that M- and C- edges can be more broadly utilized in the other catalytic applications than that of terrace.



Fig. S10 Hydrogen adsorption model on monolayer TMD materials (a) with or (b) without explicit solvation.



Fig. S11 Correlations between Gibbs free energies with and without explicit solvation effect.

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