Supplementary data for

Unraveling the Photocatalytic Potential of Transition Metal sulfides and selenides Monolayers for Overall Water Splitting and Photo-corrosion inhibition

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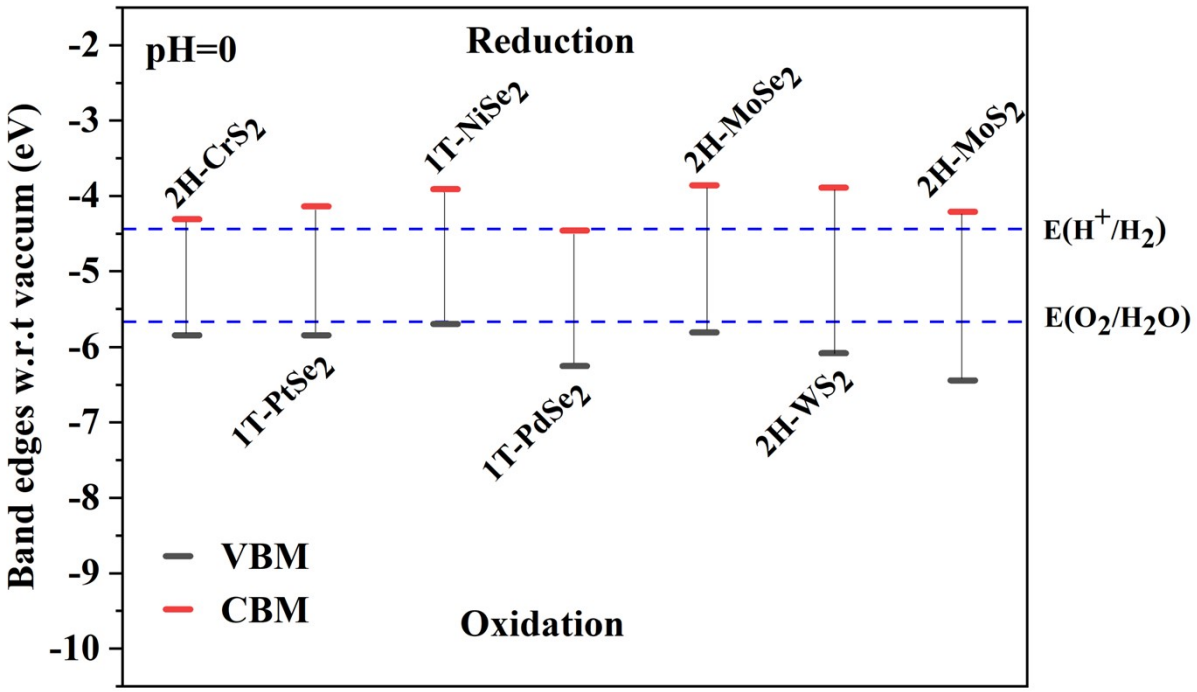

Figure S1. Thermodynamically stable monolayers with suitable CBM (red bars) and VBM (black bars) w.r.t vacuum level for overall water splitting (OWS). The blue dotted lines represent the standard potential for water reduction (-4.45 eV) and oxidation (-5.67 eV) at pH=0.

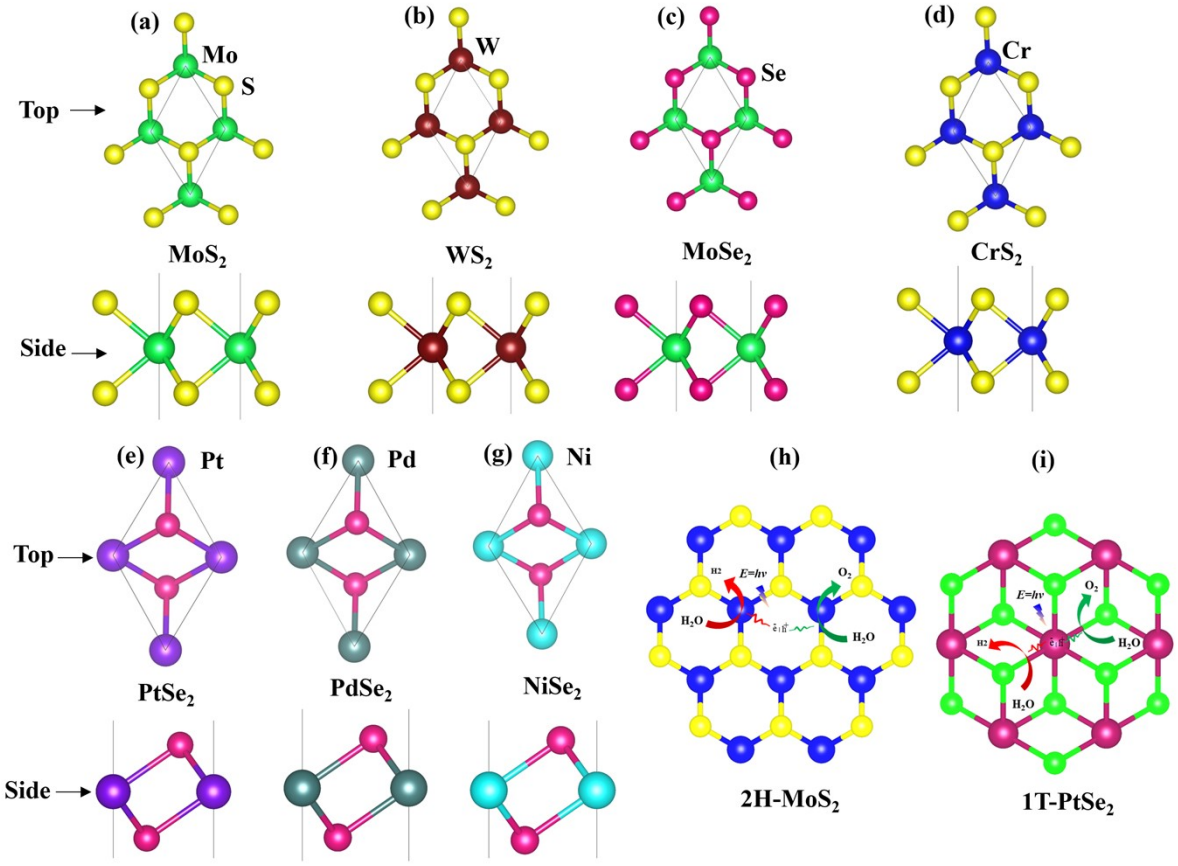

Figure S2. Promising TMSS monolayers with suitable band edge positions for OWS (a-d) Top and side view of MoS_2, WS_2, $MoSe_2$ and CrS_2 monolayers in 2H phase (e-g) Top and side view of 1T phase $PtSe_2$, $PdSe_2$ and $NiSe_2$ monolayers (h-i) Schematic illustration of OWS reactions on 2H-MoS_2 and 1T-$PtSe_2$ monolayers without incorporating any co-catalyst.

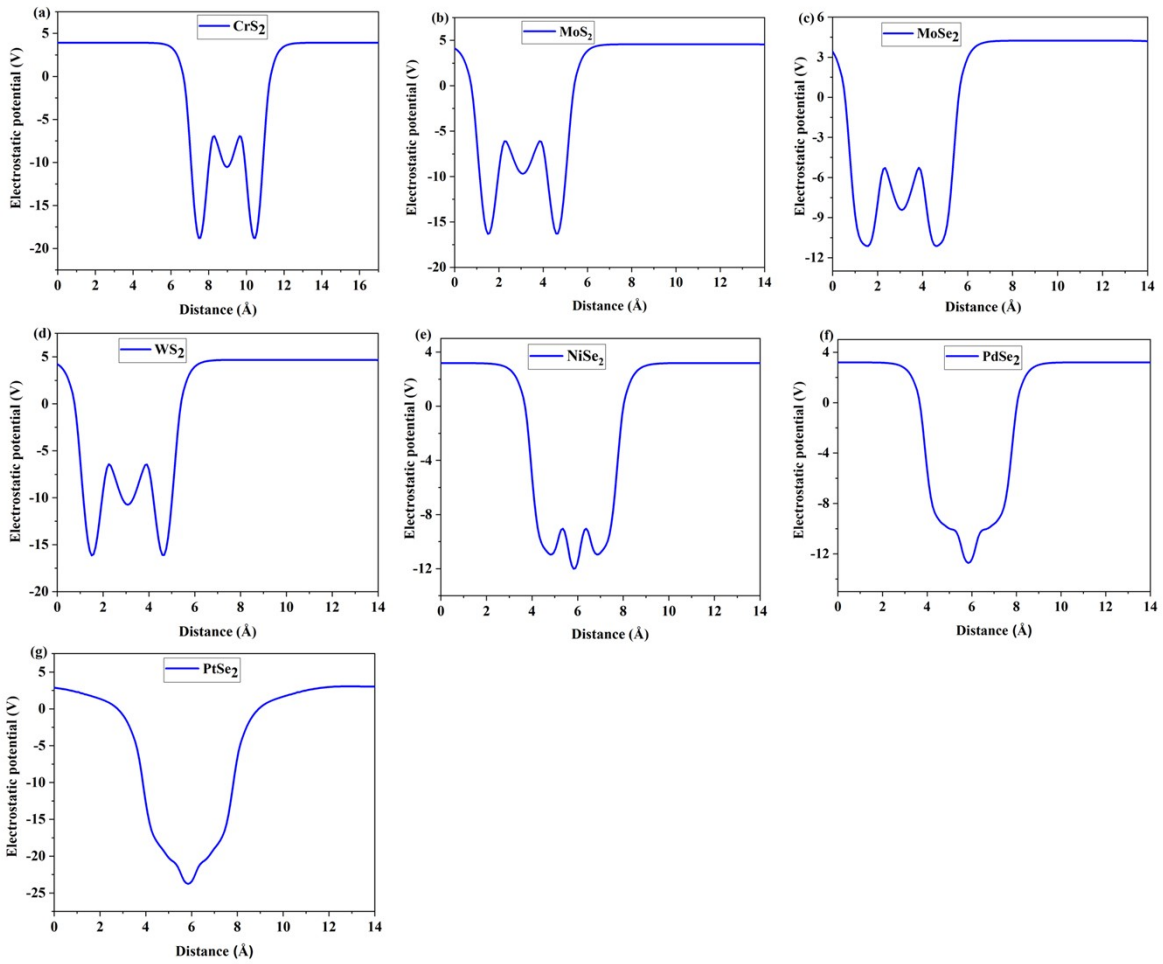

Figure S3. The G_0W_0 based calculated electrostatic potentials for (a-d) CrS_2, MoS_2, $MoSe_2$, and WS_2 monolayers in 2H phase (e-g) $NiSe_2$, $PdSe_2$ and $PtSe_2$ monolayers in 1T phase for extracting the conduction band edge (CBM) and valence band edge (VBM) w.r.t the vacuum level.

Table S1 The G_0W_0 calculated CBM, VBM and vacuum level (φ_{vac}) of the CrS_2, MoS_2, $MoSe_2$, WS_2, $NiSe_2$, $PdSe_2$ and $PtSe_2$ monolayers are given below.

property	CrS_2	MoS_2	$MoSe_2$	WS_2	$NiSe_2$	$PdSe_2$	$PtSe_2$
CBM (eV)	-3.44	-3.09	-3.06	-3.26	-4.14	-3.84	-3.65
VBM (eV)	-5.80	-5.75	-5.07	-5.76	-4.92	-5.20	-5.84
φ_{vac}	3.91	4.58	4.24	4.68	3.192	3.19	3.32

Table S2. The proposed mechanism for calculating the thermodynamic oxidation and reduction potentials of TMSS monolayers.

System	Reaction equation	ΔZPE-TΔS ($P_{(gas, atm)}$, 10^{-2}-10^{-4})	ΔE	Potential	Type
CrS_2	CrS_2+2H_2O-> CrO_2+2H_2+2S	-0.35, -0.46, -0.59	4.02	0.92, 0.89, 0.86	oxidation
	CrS_2+2H_2-> Cr + $2H_2S$	-0.17, -0.17, -0.17	1.42	0.31, 0.31, 0.13	reduction
MoS_2	MoS_2+2H_2O-> MoO_2+2H_2+2S	-0.36, -0.46, -0.58	4.38	1.0, 0.98, 0.95	oxidation
	MoS_2+2H_2-> Mo + $2H_2Se$	-0.18, -0.18, -0.81	2.05	0.47, 0.47,0.47	reduction
$MoSe_2$	$MoSe_2+2H_2O$-> MoO_2+2H_2+2Se	-0.35, -0.47, -0.59	2.69	0.58, 0.56, 0.53	oxidation
	$MoSe_2+2H_2$-> Mo + $2H_2Se$	-0.17, -0.17, -0.17	2.37	0.55, 0.55, 0.55	reduction
WS_2	WS_2+2H_2O-> WO_2+2H_2+2S	-0.36, -0.46, -0.58	4.08	0.93, 0.87, 0.87	oxidation
	WS_2+2H_2-> W + $2H_2S$	-0.18, -0.18, -0.18	1.87	0.42, 0.42, 0.42	reduction
$NiSe_2$	$NiSe_2+2H_2O$-> NiO_2+2H_2+2Se	-0.31, -0.43, -0.55	4.79	1.12, 1.09, 1.06	oxidation
	$NiSe_2+2H_2$-> Ni + $2H_2Se$	-0.17, -0.17, -0.17	1.37	0.30, 0.30, 0.30	reduction
$PdSe_2$	$PdSe_2+2H_2O$-> PdO_2+2H_2+2Se	-0.33, -0.45, -0.57	6.69	1.59, 1.56, 1.53	oxidation
	$PdSe_2+2H_2$-> Pd + $2H_2Se$	-0.17, -0.17, -0.17	1.08	0.23, 0.23, 0.23	reduction
$PtSe_2$	$PtSe_2+2H_2O$-> PtO_2+2H_2+2Se	-0.33, -0.45, -0.57	5.83	1.38, 1.35, 1.32	oxidation
	$PtSe_2+2H_2$-> Pt + $2H_2Se$	-0.17, -0.17, -0.17	1.55	0.35, 0.35, 0.35	reduction

The Gibbs free energy change of reactants and products involved in the proposed mechanism of thermodynamic oxidation and reduction potentials are calculated according to the following equations.

$$\Delta G1 = G(CrO_2)+2G(H_2)+2G(S)-G(CrS_2)-2G(H_2O) \quad (1)$$

$$\Delta G2 = G(Cr)+2G(H_2S)-G(CrS_2)-2G(H_2) \quad (2)$$

$$\Delta G3 = G(MoO_2)+2G(H_2)+2G(S)-G(MoS_2)-2G(H_2O) \quad (3)$$

$$\Delta G4 = G(Mo)+2G(H_2S)-G(MoS_2)-2G(H_2) \quad (4)$$

$$\Delta G5 = G(MoO_2)+2G(H_2)+2G(Se)-G(MoSe_2)\ 2G(H_2O) \quad (5)$$

$\Delta G6 = G(Mo)+2G(H_2Se)-G(MoSe_2)-2G(H_2)$ (6)

$\Delta G7 = G(WO_2)+2G(H_2)+2G(S)-G(WS_2)-2G(H_2O)$ (7)

$\Delta G8 = G(W)+2G(H_2S)-G(WS_2)-2G(H_2)$ (8)

$\Delta G9 = G(NiO_2)+2G(H_2)+2G(Se)-G(NiSe_2)-2G(H_2O)$ (9)

$\Delta G10 = G(Ni)+2G(H_2Se)-G(NiSe_2)-2G(H_2)$ (10)

$\Delta G11 = G(PdO_2)+2G(H_2)+2G(Se)-G(PdSe_2)-2G(H_2O)$ (11)

$\Delta G12 = G(Pd)+2G(H_2Se)-G(PdSe_2)-2G(H_2)$ (12)

$\Delta G13 = G(PtO_2)+2G(H_2)+2G(Se)-G(PtSe_2)-2G(H_2O)$ (13)

$\Delta G14 = G(Pt)+2G(H_2Se)-G(PtSe_2)-2G(H_2)$ (14)

During the free energy calculations in equations (1-14), when reactants and products have different phases (crystal, solution or gas), the phase with the lowest Gibbs free energy under 300 K and 1 bar is considered. Where for the solids the considered temperature is 300K in all energy corrections. All structures for reactants and products are considered in bulk form. The reaction conditions for the calculations of free energies of reactants and products involved in the reduction and oxidation potentials are shown below.

Entity	Temperature (K)	Pressure (atm)	Phase
H_2O	300	0.035	liquid
H_2	300	10^{-2}-10^{-4}	gas
H_2S	300	10^{-2}-10^{-4}	gas
O_2	300	0.21	gas
CO_2	300	0.00039	gas
CH_2O_2	300	10^{-2}-10^{-4}	liquid

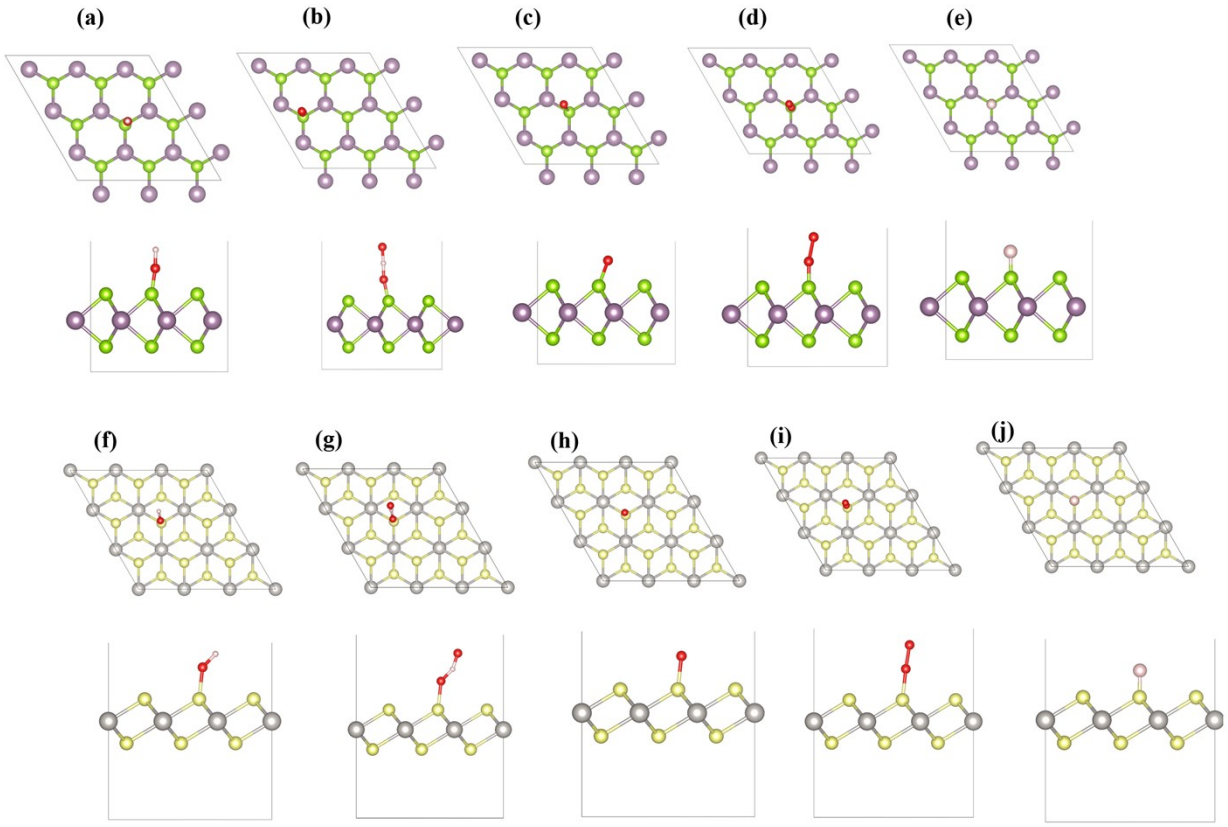

Figure S4. The top and side views of the optimized structures of stable adsorption sites of OH^*, O^*, O-H-O*, $O_2{}^*$ and H^* intermediates on the surface of 3×3×1 supercell (a-e) 2H-MoS_2 monolayer (f-j) 1T-$PtSe_2$ monolayer.