Supporting Information for

Spontaneous full photocatalytic water splitting on 2D $MoSe_2/SnSe_2$ and $WSe_2/SnSe_2$ vdW heterostructures

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13 pages, 2 text, 2 table, 6 figures

CONTENTS

Text S1. The strategy of free energy calculation for OER and HER

To compute the free energy change (ΔG) in the hydrogen reduction and water oxidation reactions, we adopted the method developed by Nørskov *et al*, according to which the ΔG of an electrochemical reaction is computed as[1-4]:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

where ΔE is the DFT computed reaction (electronic) energy, ΔE_{ZPE} and ΔS are the zero-point energy difference and the entropy difference between the adsorbed state and the gas phase, respectively, and T is the system temperature (298 K, in our work). For each system, its E_{zpe} for each adsorbate and free molecules can be calculated by summing vibrational frequencies over all normal modes ν ($E_{\mathrm{zpe}} = 1/2\Sigma\hbar\nu$), while the zero-point energy of adsorption sites is negligible. The entropies of the free molecules (O_2, H_2, H_2O) were taken from taken from the standard tables in Physical Chemistry[5]. For those reactions involving the release of protons and electrons, the free energy of one pair of proton and electron ($H^+ + e^-$) was taken as $1/2G_{\mathrm{H2}}$. The free energy of O_2(g) was derived as $G_{O2} = 2G_{H2O} - 2G_{H2} + 4.92$ eV since O_2 in triplet ground state is notoriously poorly described by DFT calculations. All the E_{ZPE} and S results can be obtained from the reference[6] and are shown in Table S1.

In the aqueous solution, the OER process generally involves four-electron oxidation steps, which can be written as:

$$H_2O + * \rightarrow OH* + H^+ + e^-$$

$$OH* \rightarrow O* + H^+ + e^-$$

$$O* + H_2O \rightarrow OOH* + H^+ + e^-$$

$$OOH^* \rightarrow * + O_2(g) + H^+ + e^-$$

Where * denotes the adsorption site, OH*, O* and OOH* denote the adsorbed intermediates.

Meanwhile, the HER process with two-electron pathways, including a fast ptoton/electron transfer step and a fast hydrogen release step, can be written as:

$$* + H^+ + e^- \rightarrow H^*$$

$$H^* + H^+ + e^- \rightarrow * + H_2(g)$$

Then, the free energy change for OER electrochemical steps can be expressed as:

$$\Delta G_1 = G_{OH^*} + 1/2G_{H_2} - G_{H_2O} - G^* - 0.059 \times pH - eU$$

$$\Delta G_2 = G_{O^*} + 1/2G_{H_2} - G_{OH^*} - 0.059 \times pH - eU$$

$$\Delta G_3 = G_{OOH^*} + 1/2G_{H_2} - G_{H_2O} - G_{O^*} - 0.059 \times pH - eU$$

$$\Delta G_4 = 2G_{H_2O} + G^* - 3/2G_{H_2} - G_{OOH^*} + 4.92 - 0.059 \times pH - eU$$

The free energy change for HER electrochemical step can be expressed as:

$$\Delta G_{H^*} = G_{H^*} - 1/2G_{H_2} - G^* + 0.059 \times pH - eU$$

where $0.059 \times pH$ represents the free energy contribution due to the variations in H concentration, eU represents the effect of a potential bias on all states involving one electron or hole in the electrode by shifting the energy, and U is the electrode potential relative to the normal hydrogen electrode (NHE).

Table S1. Values used for the entropy and zero-point energy corrections in determining the free energy of reactants, products, and intermediate species adsorbed on catalysts[6]. For the adsorbates, the ZPE values are averaged over all single atom catalyst systems since they have rather close value.

Species	**T×S (eV) (298K)**	**ZPE (eV)**
H^*	0	0.17
O^*	0	0.07
OH^*	0	0.33
OOH^*	0	0.43
$H_2(g)$	0.41	0.27
$H_2O(g)$	0.58	0.57

Text S2. Computational method of absorption coefficient.

To investigate the optical absorption properties of the $MoSe_2$, WSe_2, $SnSe_2$ monolayers and $MoSe_2/SnSe_2$, $WSe_2/SnSe_2$ heterostructures, we calculated the absorption spectra by converting the complex dielectric function to the absorption coefficient α_{abs} according to the following expression[7]:

$$\alpha_{\mathrm{abs}} = \sqrt{2}\left(\sqrt{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)} - \varepsilon_1(\omega)\right)^{\frac{1}{2}}$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts, respectively, of the frequency-dependent complex dielectric function $\varepsilon(\omega)$. Because of the anisotropic optical absorption of the $MoSe_2$, WSe_2, $SnSe_2$ monolayers and $MoSe_2/SnSe_2$, $WSe_2/SnSe_2$ heterostructures, absorption coefficient was averaged over three different directions ($\alpha_{\mathrm{abs}}^{xx}$, $\alpha_{\mathrm{abs}}^{yy}$ and $\alpha_{\mathrm{abs}}^{zz}$).

Table S2. The computed formation energy E_f (meV/Å^2), lattice constant *a*, strain with respect to isolated $MoSe_2$/WSe_2 monolayer $\Delta = (a - a_0)/a_0$ (a_0 = 3.316/3.332 Å), total heights *h* of $MoSe_2$, $MoSe_2$ and $SnSe_2$ monolayers or interlayer distance *d* of the two heterostructures, the bandgap E_g of five different layers.

System	E_f(meV/Å^2)	a(Å)	Δ(%)	h/d (Å)	E_g(eV)
$MoSe_2$	--	3.316	--	3.333	1.89
WSe_2	--	3.332	--	3.333	1.92
$SnSe_2$	--	3.819	--	3.207	1.38
$MoSe_2$/ $SnSe_2$	-15.42	6.624	0.1	3.411	0.61
WSe_2/ $SnSe_2$	-18.80	6.640	0.4	3.356	0.41

The formation energy of $MoSe_2$/$SnSe_2$ or WSe_2/$SnSe_2$ heterostructure is defined as

$$E_f = (E_{tot} - E_{MoSe_2/WSe_2} - E_{SnSe_2})/S$$

where E_{tot}, E_{MoSe_2/WSe_2}, and E_{SnSe_2} represent the total energies of the $MoSe_2$ /$SnSe_2$ or WSe_2/$SnSe_2$ heterostructures, isolated $MoSe_2$ or WSe_2 monolayer, and isolated $SnSe_2$ monolayer, respectively. S is the transverse area of $MoSe_2$/$SnSe_2$ or WSe_2/$SnSe_2$ heterostructure. According to this definition, a stable heterostructure will have a negative formation energy.

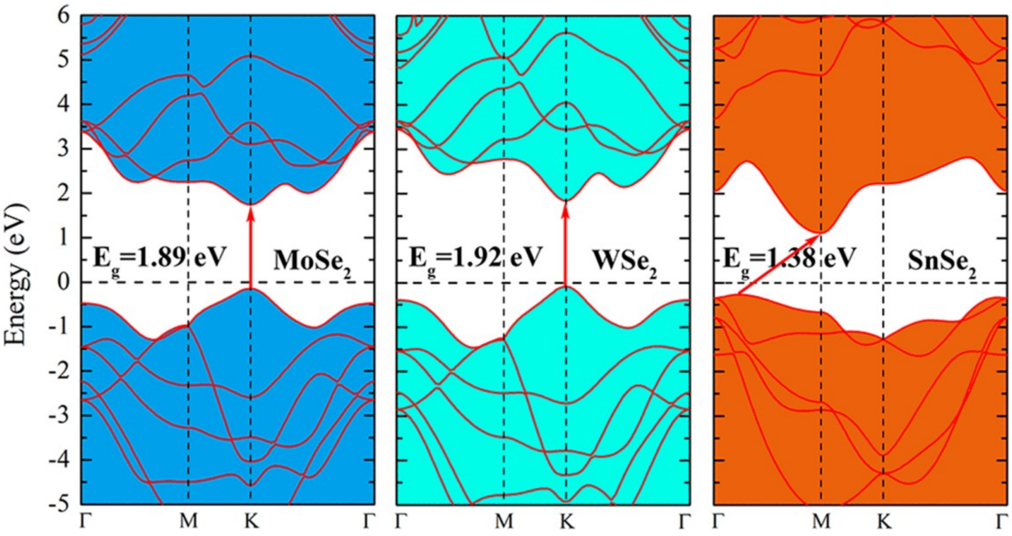

Figure S1. Band structures of the isolated $MoSe_2$, WSe_2 and $SnSe_2$ monolayers calculated with the HSE06 functional, respectively. The fermi levels are set to 0 eV.

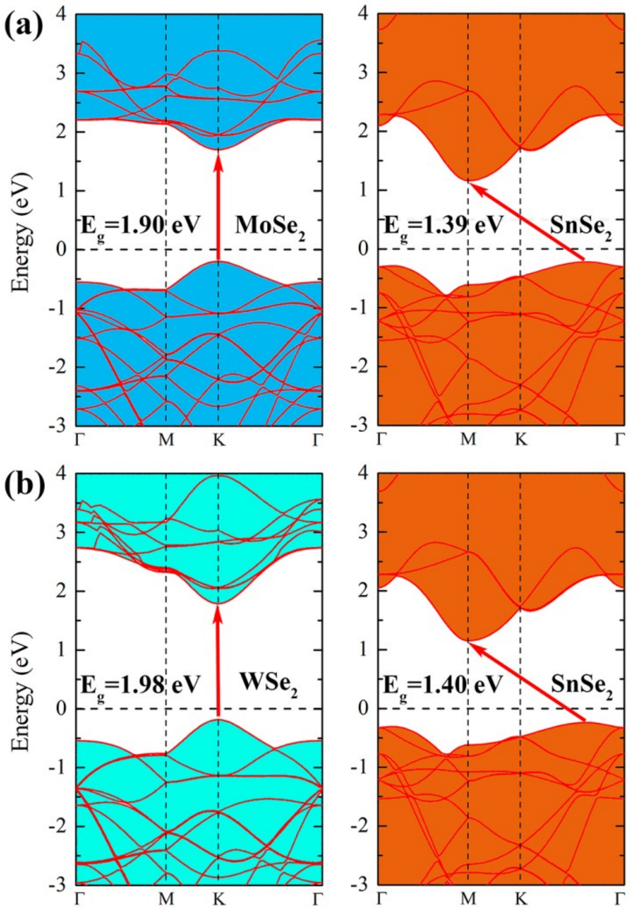

Figure S2. Band structures of (a) the distorted $MoSe_2$ and $SnSe_2$ monolayers in the $MoSe_2/SnSe_2$ heterostructure and (b) the distorted WSe_2 and $SnSe_2$ monolayers in the $WSe_2/SnSe_2$ heterostructure calculated with the HSE06 functional, respectively. The fermi levels are set to 0 eV.

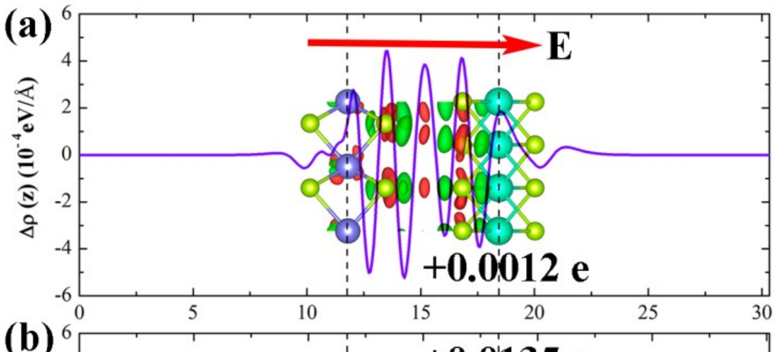

Figure S3. Plane-averaged electron density difference along the z direction for the (a) $MoSe_2/SnSe_2$ and (b) $WSe_2/SnSe_2$ heterostructures, respectively. The inset represents the 3D isosurface of the differential electron densities for the $MoSe_2/SnSe_2$ and $WSe_2/SnSe_2$ heterostructures, respectively. The red and green regions represent electron accumulation and depletion, respectively. The isovalue is $0.0002|e|/Å^3$.

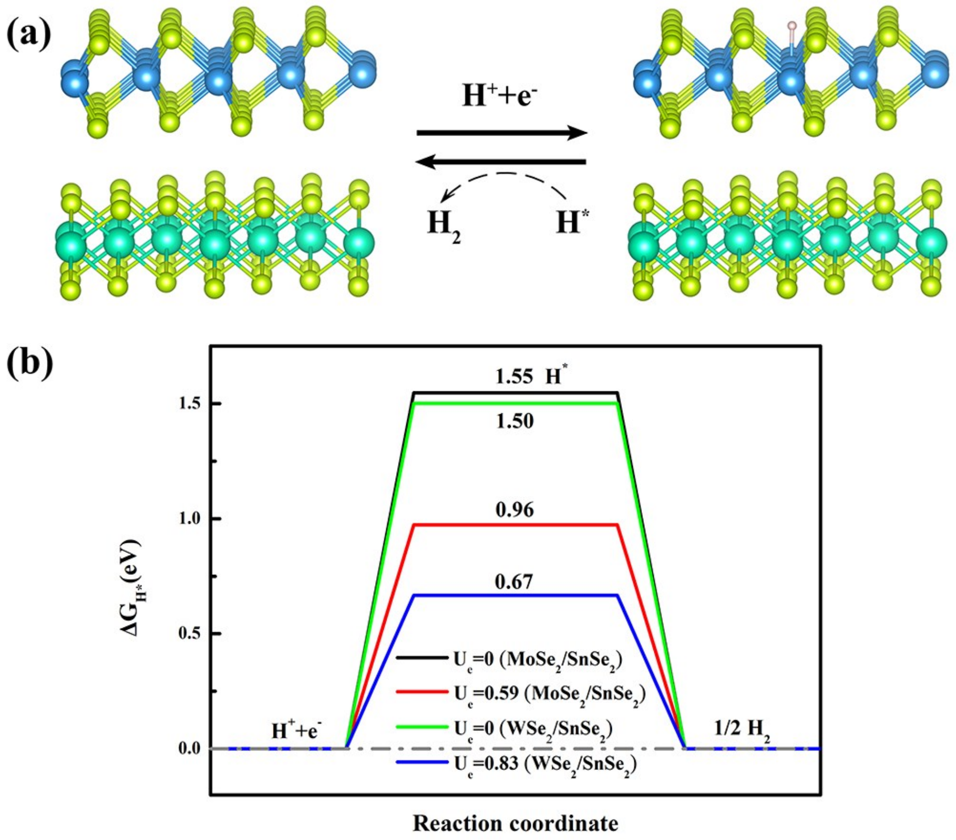

Figure S4. (a) Proposed photocatalytic pathways of hydrogen reduction half reactions with the most energetically favorable absorbed intermediates (H*) in the $MoSe_2/SnSe_2$ and $WSe_2/SnSe_2$ heterostructures. The white ball represents H atom. (b) Free energy diagrams for the 2e pathways of hydrogen reduction reactions in the $MoSe_2/SnSe_2$ and $WSe_2/SnSe_2$ heterostructures an pH=0.

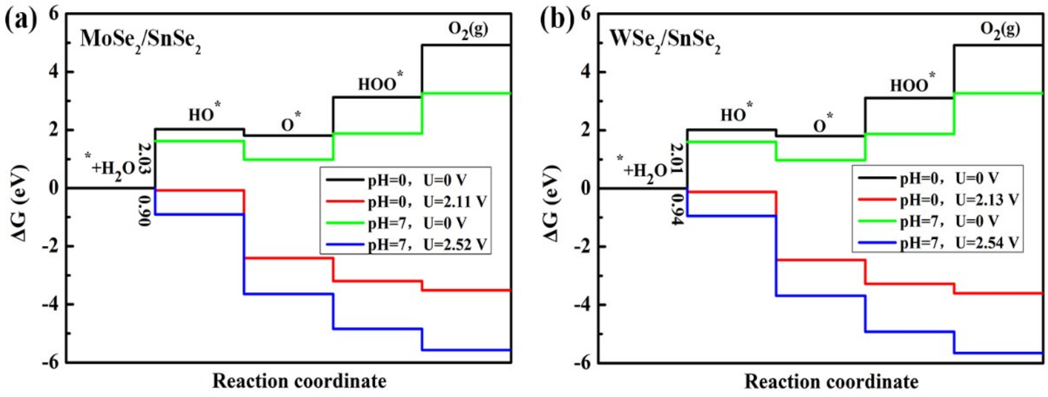

Figure S5. Free energy diagrams for the 4e pathways of water oxidation reactions in the (a) MoSe$_2$/SnSe$_2$ and (b) WSe$_2$/SnSe$_2$ heterostructures with no vacancy defect under different conditions. Compared with the case of heterostructures containing Se-vacancy defect, it is found that effect of Se-vacancy defect in the MoSe$_2$ (WSe$_2$) layer on the free energy diagram of OER occurring on the SnSe$_2$ is unnoticeable.

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