Supporting Information for

Two-dimensional CdS/SnS₂ heterostructure: A highly efficient direct Z-scheme

water splitting photocatalyst

Can Fu[a], Guangzhao Wang*[bc], Yuhong Huang[a], Ying Chen[ad], Hongkuan Yuan [a], Yee

Sin Ang[c] and Hong Chen*[a]

[a] School of Physics Science and Technology, Southwest University, Chongqing 400715,

China.

[b] Key Laboratory of Extraordinary Bond Engineering and Advanced Materials

Technology of Chongqing, School of Electronic Information Engineering, Yangtze

Normal University, Chongqing 408100, China.

[c] Science, Mathematics and Technology, Singapore University of Technology and

Design, Singapore 487372, Singpore.

[d] School of Mathematics and Physics, Anshun College, Guizhou 561000, China.

[*] Corresponding author.

E-mail address: wangyan6930@yznu.edu.cn(G. Wang) chenh@swu.edu.cn(H. Chen)

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

The free energy is calculated by the method proposed by Norskov et al. The calculation formula is as follows[1,2]:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S, \tag{1}$$

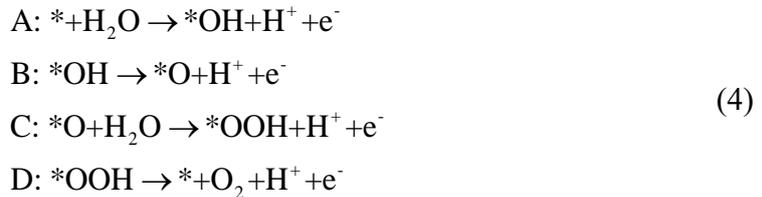where ΔE represents the change in total energy, ΔE_{ZPE} and ΔS are the difference of zero point energy and entropy between the products and reactants of the reactions. For reactions involving protons and electrons ($H^+ + e^-$), the free energy of a pair of protons and electrons is substituted by $\frac{1}{2}G_{H_2}$. ΔE can be calculated by VASP and T is the system temperature. And the zero point energy and entropy are calculated by the following formula:

$$E_{ZPE} = \frac{1}{2}\sum_{i=1}^{N_F} hv_i \tag{2}$$

$$TS = k_B T \sum_{i=1}^{N_F} \left[\frac{hv_i}{k_B T} \left(e^{\frac{hv_i}{k_B T}} - 1 \right)^{-1} - \ln\left(1 - e^{-\frac{hv_i}{k_B T}} \right) \right], \tag{3}$$

where N_F represents the vibrational degree of freedom, and v_i is the vibration frequency. When the surface of the catalyst is fixed, the vibrational degrees of freedom for free linear molecules and nonlinear molecules are 3N-5 and 3N-6, respectively. While the vibrational degrees of freedom of adsorbed molecules are 3N, and N is the number of atoms of free molecules or adsorbed molecules[3], and the zero point energy of the adsorption site can be ignored. The free energy of $O_2(g)$ is derived from $G_{O_2} = 2G_{H_2O} - 2G_{H_2} + 4.92$ eV. All the E_{ZPE} and TS results can be obtained from the reference and are shown in Table S2 and S3.

The oxygen evolution reaction (OER) involves a four-electron process, which is divided into the following four steps:
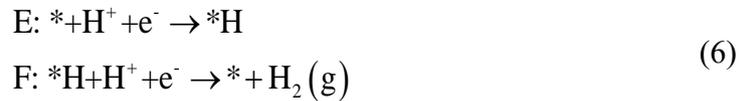
$$\begin{aligned}
&A: *+H_2O \rightarrow *OH+H^+ +e^- \\
&B: *OH \rightarrow *O+H^+ +e^- \\
&C: *O+H_2O \rightarrow *OOH+H^+ +e^- \\
&D: *OOH \rightarrow *+O_2 +H^+ +e^-
\end{aligned} \tag{4}$$

where * means adsorption site, *OH, *O, *OOH are adsorption intermediates. Therefore, the free energy of each step changes as：

$$\Delta G_A = G_{*OH} + \frac{1}{2}G_{H_2} - G_* - G_{H_2O} + \Delta G_{pH} - eU$$

$$\Delta G_B = G_{*O} + \frac{1}{2}G_{H_2} - G_{*OH} + \Delta G_{pH} - eU$$

$$\Delta G_C = G_{*OOH} + \frac{1}{2}G_{H_2} - G_{*O} - G_{H_2O} + \Delta G_{pH} - eU \tag{5}$$

$$\Delta G_D = G_* + \frac{1}{2}G_{H_2} + G_{O_2} - G_{*OOH} + \Delta G_{pH} - eU$$

The HER process involves the reaction of two electrons and is divided into the following two steps：

$$\text{E: } *+H^+ +e^- \rightarrow *H$$
$$\text{F: } *H+H^+ +e^- \rightarrow *+H_2(g) \tag{6}$$

where *H stands for adsorption intermediates. The free energy change of the HER reaction can be calculated as:

$$\Delta G_E = G_{*H} - \frac{1}{2}G_{H_2} - G_* - \Delta G_{pH} - eU$$

$$\Delta G_F = G_* + \frac{1}{2}G_{H_2} - G_{*H} - \Delta G_{pH} - eU \tag{7}$$

where ΔG_{pH} represents the effect of pH on the change of free energy, and $\Delta G_{pH} = -2.303 k_B T \times pH$, in which k_B is Boltzmann's constant. 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 standard hydrogen electrode (SHE). Here, T is set to 298.15 K, and pH is set to 0.

Table S1. The computed formation energy (E_f), lattice constant (a), the bandgap (E_g) of five different layers.

System	E_f (meV/Å^2)	a (Å)	E_g(eV)
CdS	--	4.26	2.68
SnS$_2$	--	3.70	2.37
CdS/ SnS$_2$ (i)	-15.96	7.39	0.72
CdS/ SnS$_2$ (ii)	-16.83	7.39	1.31
CdS/ SnS$_2$ (iii)	-15.94	7.39	0.84

Table S2. Values used for the entropy and zero-point energy (ZPE) corrections in determining the free energy of reactants, products, and intermediate species adsorbed on CSHS. The following data is reserved for two significant digits.

System	$T \times S$ (eV)	ZPE (eV)
*H	0.013	0.23
*OH	0.086	0.35
*O	0.053	0.076
*OOH	0.20	0.43
H_2	0.40	0.28
H_2O(0.035bar)	0.67	0.57

Table S3. Values used for the entropy and zero-point energy (ZPE) corrections in determining the free energy of reactants, products, and intermediate species adsorbed on CSHS with S-vacancy. The following data is reserved for two significant digits.

System	$T \times S$ (eV)	ZPE (eV)
*H	0.015	0.23
*OH	0.083	0.36
*O	0.043	0.068
*OOH	0.18	0.43
H_2	0.40	0.28
H_2O(0.035bar)	0.67	0.57

Table S4. The free energy changes for all the reaction steps in OER process of CSHS with S-vacancy defect at different potential.

	ΔG_A (eV)	ΔG_B (eV)	ΔG_C (eV)	ΔG_D (eV)
U= 0 V	-0.60	0.10	2.62	2.79
U=1.23 V	-1.83	-1.13	1.39	1.56
U=3.02 V	-3.62	-2.92	-0.4	-0.23
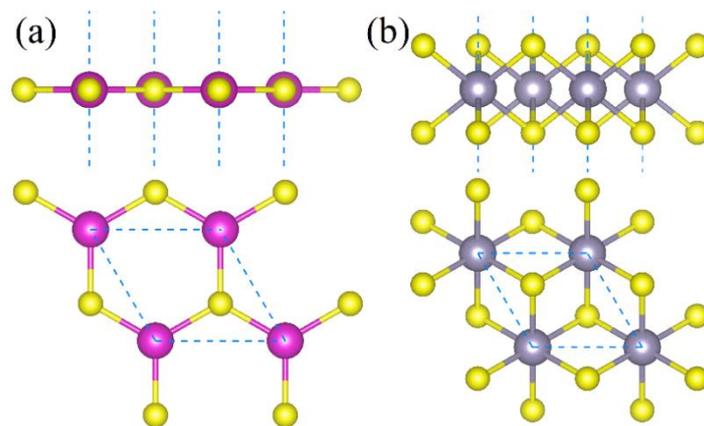
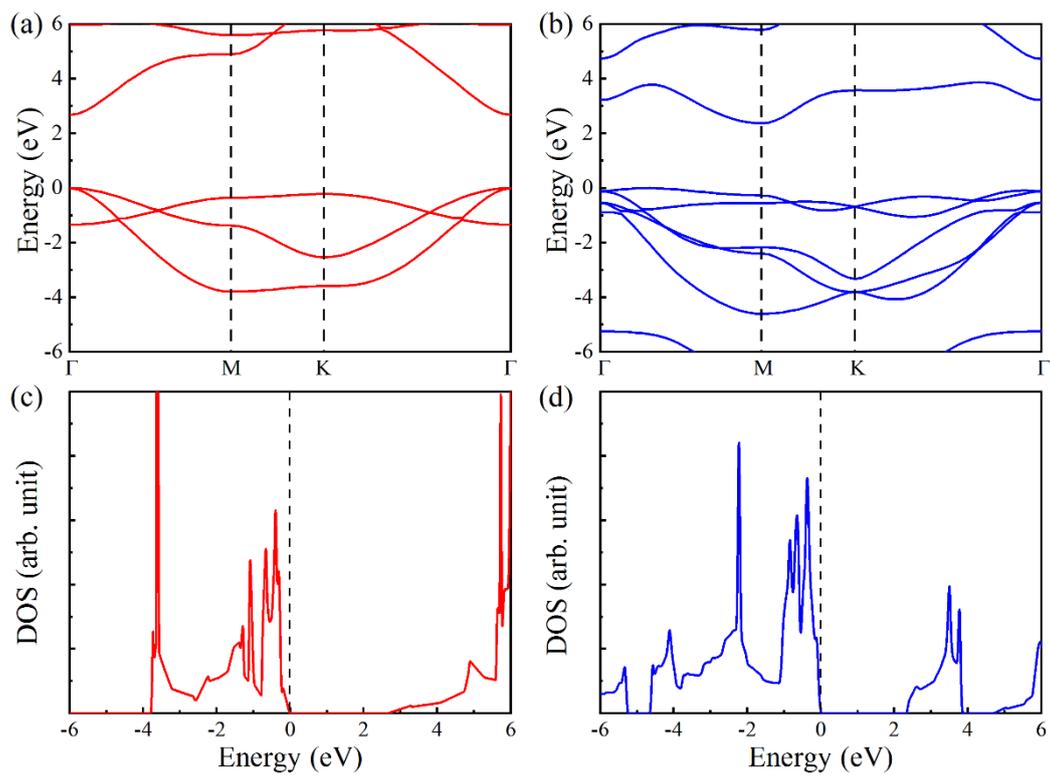**Fig. S1** Top and side views of the optimized geometries of (a) CdS and (b) SnS$_2$ primitive cell.

Fig. S2 The band structures and density of states of CdS and SnS$_2$ primitive cell calculated by the HSE06 functional. The Fermi level set as 0 eV. The red line represents CdS and blue lines represents SnS$_2$.
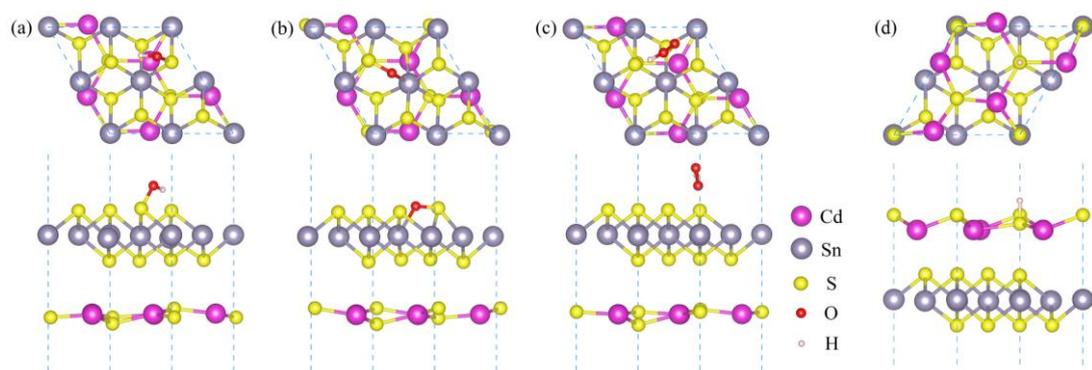
Fig. S3 Top and side views of optimized geometries of CSHS with (a) *OH, (b) *O, (c) *OOH, and (d) *H intermediates.
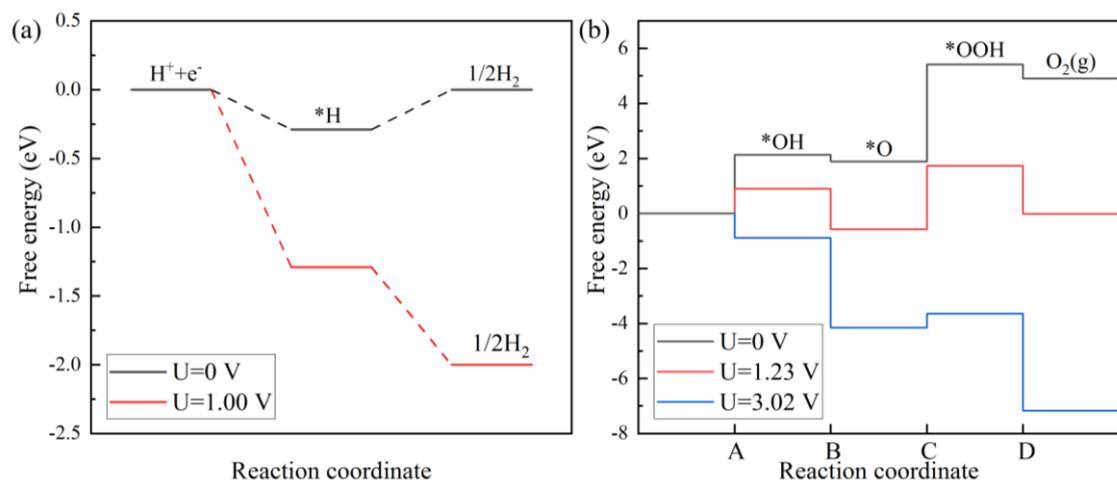
Fig. S4 The free energy changes of (a) HER and (b) OER steps in CSHS.
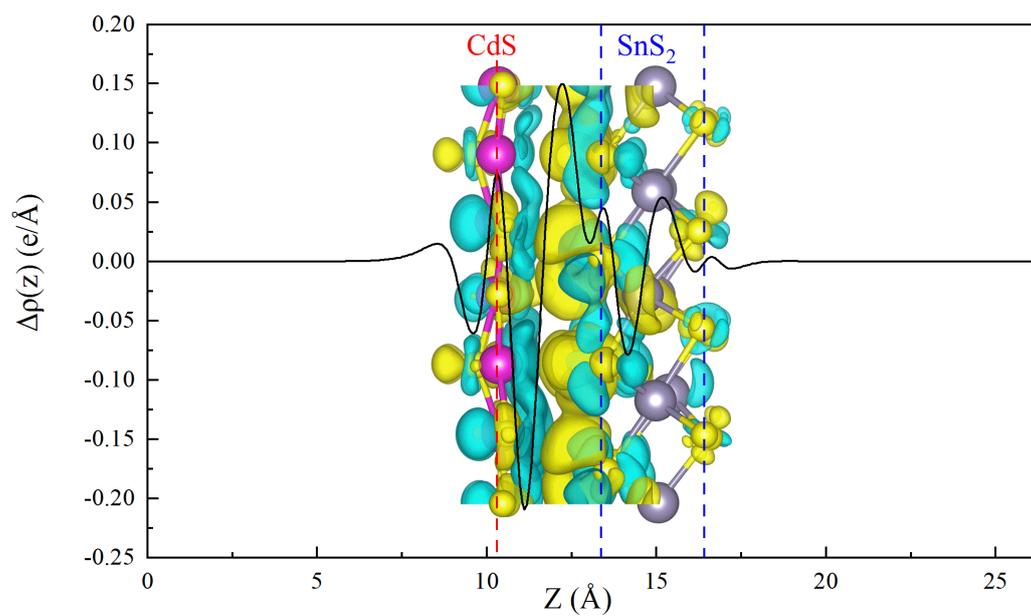
Fig. S5 The planar-averaged CDDs of CSHS with S-vacancy. The yellow and cyan areas indicate electron accumulation and depletion, respectively.
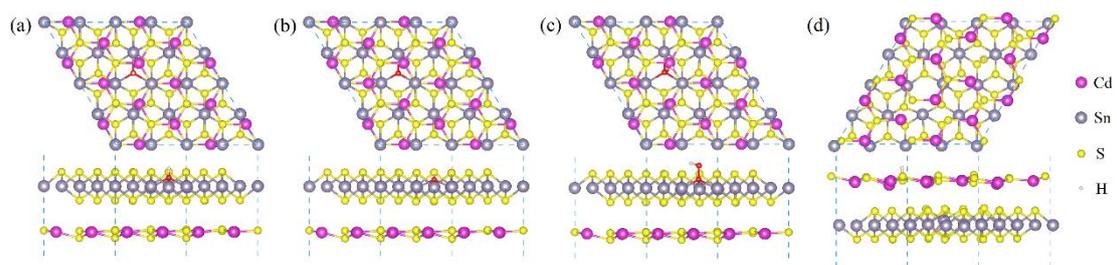
Fig. S6 Top and side views of optimized geometries of CSHS with S-vacancy about (a) *OH, (b) *O, (c) *OOH and (d) *H intermediates.

REFERENCES

[1] Norskov J K, Rossmeisl J, Logadottir A, et al. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. J. Phys. Chem. B, 2004, 108(46): 17886-17892.

[2] Skúlason E, Tripkovic V, Björketun M E, et al. Modeling the electrochemical hydrogen oxidation and evolution reactions on the basis of density functional theory calculations. J. Phys. Chem. C, 2010, 114(42): 18182-18197.

[3] Wang V, Xu N, Liu J C, et al. VASPKIT: a user-friendly interface facilitating high-throughput computing and analysis using VASP code. Comput. Phys. Commun., 2021, 267: 108033.