

Supplementary Materials for: Design of a noble-metal-free direct Z-scheme photocatalyst for overall water splitting based on SnC/SnSSe van der Waals heterostructure

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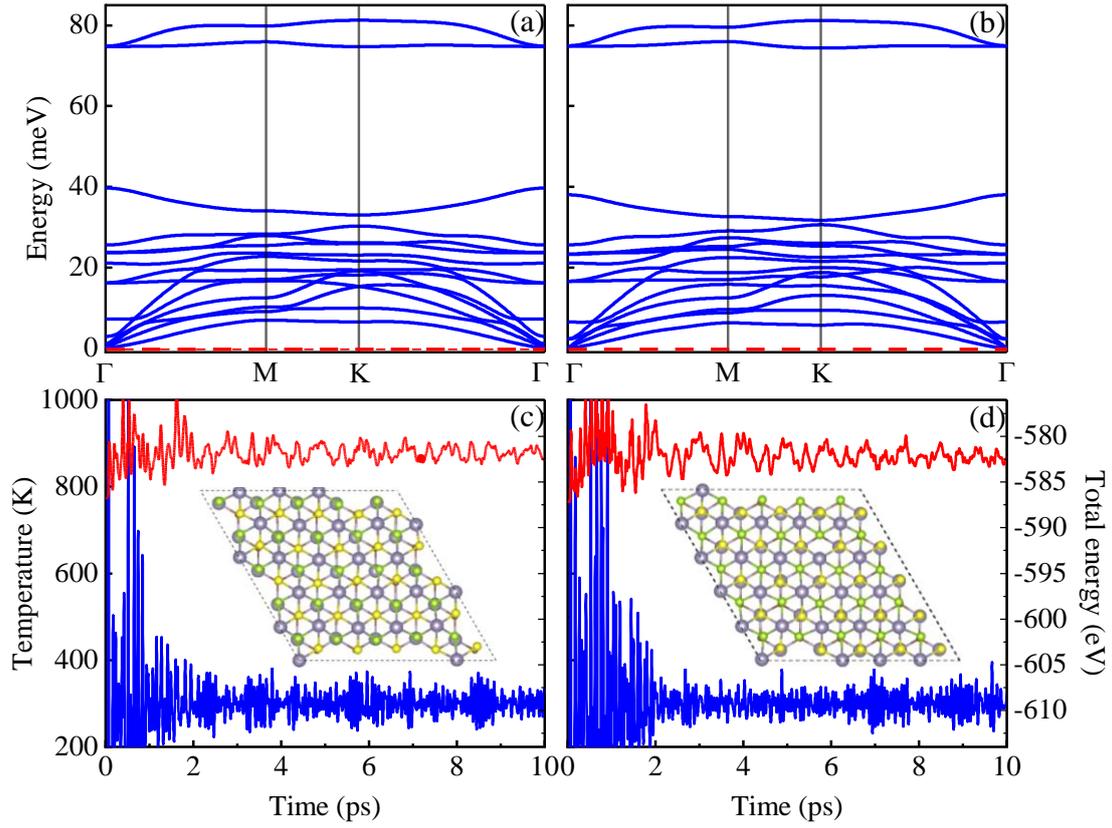


Fig. S1. Phonon dispersions of (a) SnC/SeSnS vdWH and (b) SnC/SSnSe vdWH, respectively. The total energy and temperature fluctuations as a function of time at 300 K for (c) SnC/SeSnS vdWH, (d) SnC/SSnSe vdWH, as well as the final snapshots after 10 ps simulation are displayed in the inset.

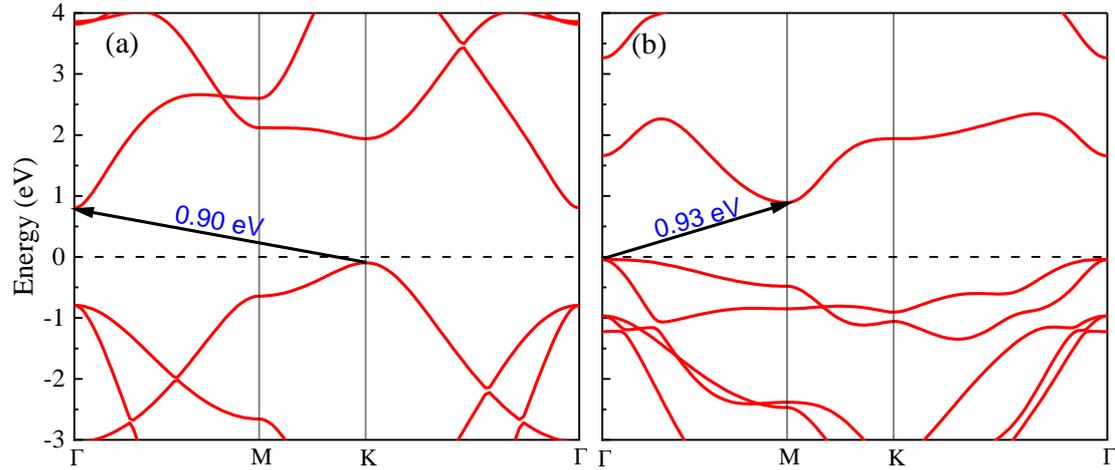


Fig. S2. DFT calculated electronic band structures at the PBE level for (a) SnC and (b) SnSSe monolayers, respectively.

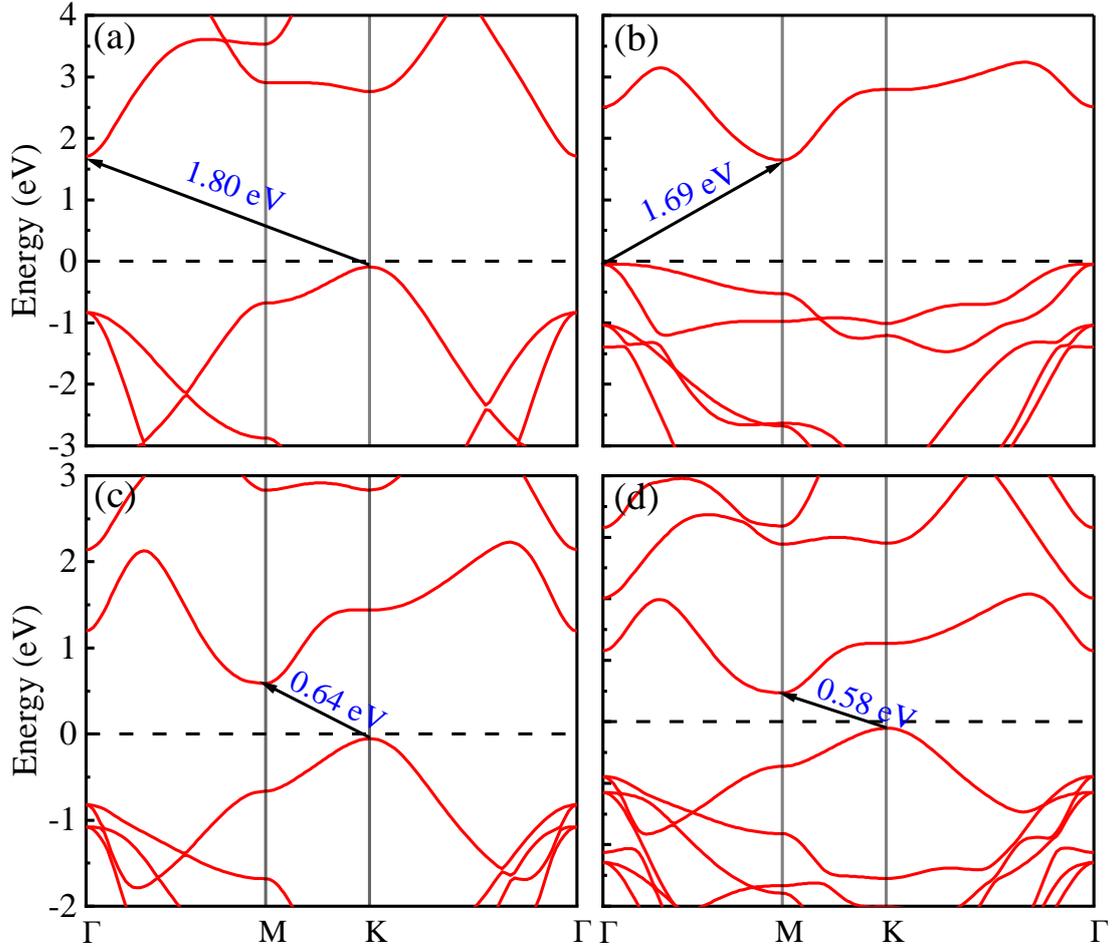


Fig. S3. DFT calculated electronic band structures for monolayered (a) SnC and (b) SnSSe, and for (c) SnC/SeSnS and (d) SnC/SSnSe vdWHs, respectively, based on the HSE06 functional. The Fermi level is set to zero and represented by the black dashed line.

Table S1 The lattice parameters of SnC and SnSSe monolayers, and their vdWHs, as well as the lattice mismatch for each monolayer.

	a (Å)	ϵ (%)		a (Å)	ϵ (%)
SnC/SeSnS	3.668		SnC/SSnSe	3.674	
SnC	3.601	1.86	SnC	3.601	2.03
SeSnS	3.760	-2.45	SSnSe	3.760	-2.29

We examine the mechanical stability by calculating elastic constants. Since the SnC/SnSSe vdWHs are elastically isotropic according to their hexagonal symmetry, where $C_{11}=C_{22}$ and only three elastic constants are independent: C_{11} , C_{12} , and C_{66} . As seen in Table S2, the elastic constants meet the Born criteria for mechanical stability $C_{11}C_{22}-C_{12}^2>0$, $C_{66}>0$,¹ indicating that they are mechanically stable.

We also calculated the modulus (Y) and Poisson's ratio (γ) based on the following formula:

$$Y = (C_{11}C_{22} - C_{12}^2) / C_{22}, \quad \gamma = C_{12} / C_{22} \quad (\text{S1})$$

For SnC/SeSnS vdWH, $C_{11} = 142.5$ N/m, $C_{12} = 41.1$ N/m, and $C_{66} = 52.3$ N/m, and for SnC/SSnSe vdWH, $C_{11} = 137.8$ N/m, $C_{12} = 37.3$ N/m, and $C_{66} = 50.4$ N/m. For comparison, the elastic constants of the graphene, MoS₂, SnC, and SnSSe monolayers are also calculated, which are in line with previous results.²⁻⁴ For example, for the SnC monolayer, $Y=93.1$ N/m and $\gamma=0.39$, which agree with a previous theoretical study ($Y=98$ N/m and $\gamma=0.41$).² For the SnSSe monolayer, $Y=58$ N/m and $\gamma=0.24$, which are consistent with a previous theoretical study ($Y=57.5$ N/m and $\gamma=0.28$).³ For graphene, $Y=338.9$ N/m and $\gamma=0.19$ coincide with previous results ($Y=335$ N/m and $\gamma=0.16$).² For MoS₂, $Y=123.2$ N/m and $\gamma=0.26$ are identical with previous results ($Y=128$ N/m).⁴ Furthermore, the elastic constants of the SnC/SnSSe vdWHs are greater compared to those of the SnC and SnSSe monolayers, suggesting that they hold stronger in-plane bonding than pristine monolayers. The SnC/SnSSe vdWHs possess higher theoretical mechanical stability than that of the SnC and SnSSe monolayers.

Table S2 Calculated results for the elastic constants C_{ij} , Young's modulus Y in N/m, Poisson's ratio γ .

	C_{11} (N/m)	C_{12} (N/m)	C_{66} (N/m)	Y (N/m)	γ
graphene	351.96	65.91	141.54	338.92	0.19
MoS ₂	132.66	31.89	50.67	123.18	0.26
SnC	109.95	42.57	33.75	93.07	0.39
SnSSe	61.08	14.22	23.4	58.03	0.24
SnC/SeSnS	142.5	41.07	52.28	129.32	0.28
SnC/SSnSe	137.82	37.29	50.4	126.68	0.26

Thermodynamics of HER and OER on the SnC/SeSnS vdWH

To further clarify the thermodynamics of water redox reactions on the SnC/SeSnS vdWH, we calculate the Gibbs free energy change of HER and OER at pH=0, with and without the effect of light irradiation.^{5,6} The hydrogen electrode model developed by Nørskov *et al.* is adopted to calculate the Gibbs free energy, as follows:⁷⁻¹⁰

$$\Delta G = \Delta E + \Delta E_{zpe} - T\Delta S + \Delta G_U + \Delta G_{pH} \quad (\text{S2})$$

where ΔE represents the DFT computed total energy difference, and ΔE_{zpe} and $T\Delta S$ are the zero-

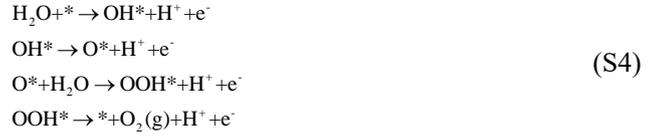
point energy difference and the entropy, respectively. ΔG_U ($\Delta G_U = -eU$) denotes the extra potential bias provided by an electron in the electrode, where U is the electrode potential relative to the standard hydrogen electrode (SHE). ΔG_{pH} represents the contribution of Gibbs free energy at different pH concentrations. Here, the pH is set to 0.

The HER half-reaction can be decomposed into a two-electron step, and the reaction equation can be written as:



where $*$ denotes the surface site and H^* represents the adsorbed H atoms.

Meanwhile, the OER half-reaction involves a four-electron reaction pathway, which can be written as:



where $*$ represents the surface site, and OH^* , O^* , and OOH^* denote the adsorbed intermediates.

The free energy diagrams are shown in Fig. S4. Clearly, for SnC/SeSnS vdWH, it is found that the Gibbs free energy of HER is 0.99 eV without light irradiation. Under light irradiation condition, the photogenerated electrons can provide an external potential ($U_e=0.45$ V) to facilitate the HER activity. The U_e is defined as the energy difference between the hydrogen reduction potential and the CBM. Therefore, the free energy barrier can be further reduced to be 0.53 eV under illumination. It is worth noting that this value is lower than that of other 2D photocatalysts, such as BiGaP₆¹¹ and this can be easily conquered by loading co-catalysts, e.g. Pt in the experiment.¹²

It is clear that when the SnC/SeSnS vdWH is in the dark environment ($U=0$ V), the Gibbs free energy of the first three steps for the OER gradually increases, except for the final step. Under the light irradiation condition, the photogenerated holes can provide an external potential ($U_h=2.21$ V), which is defined as the energy difference between the hydrogen reaction potential and the VBM, and the Gibbs free energy for OER are downhill, except for the O^* reacts with another H_2O molecule to generate the OOH^* species. Correspondingly, the limiting potential of 3.48 eV is required to oxidize O^* species into OOH^* species in the dark environment and this value decreases to 1.27 eV at light irradiation, suggesting that SnC/SeSnS vdWH could be a possible structure for OER under illumination.

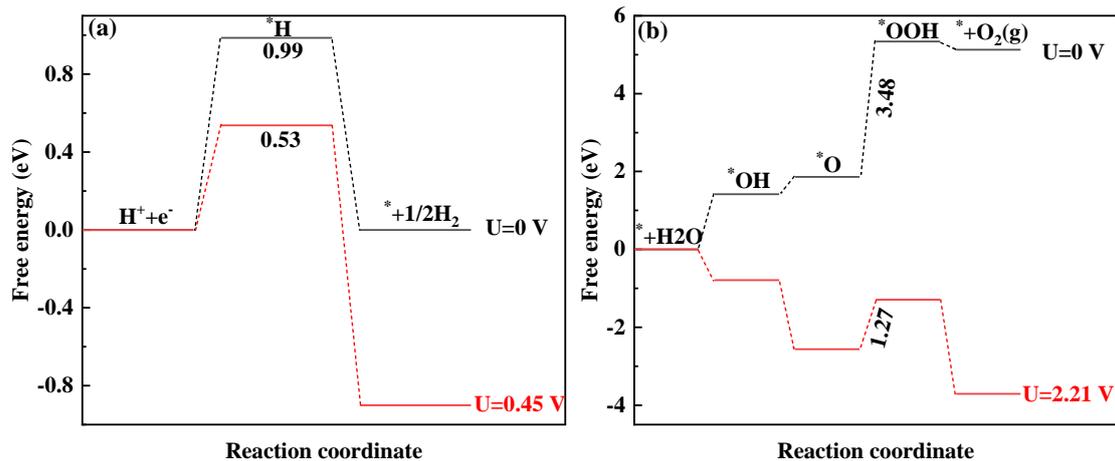


Fig. S4. Free energy diagrams of (a) HER and (b) OER under dark environment and light irradiation condition of SnC/SeSnS vdWH at pH=0, respectively.

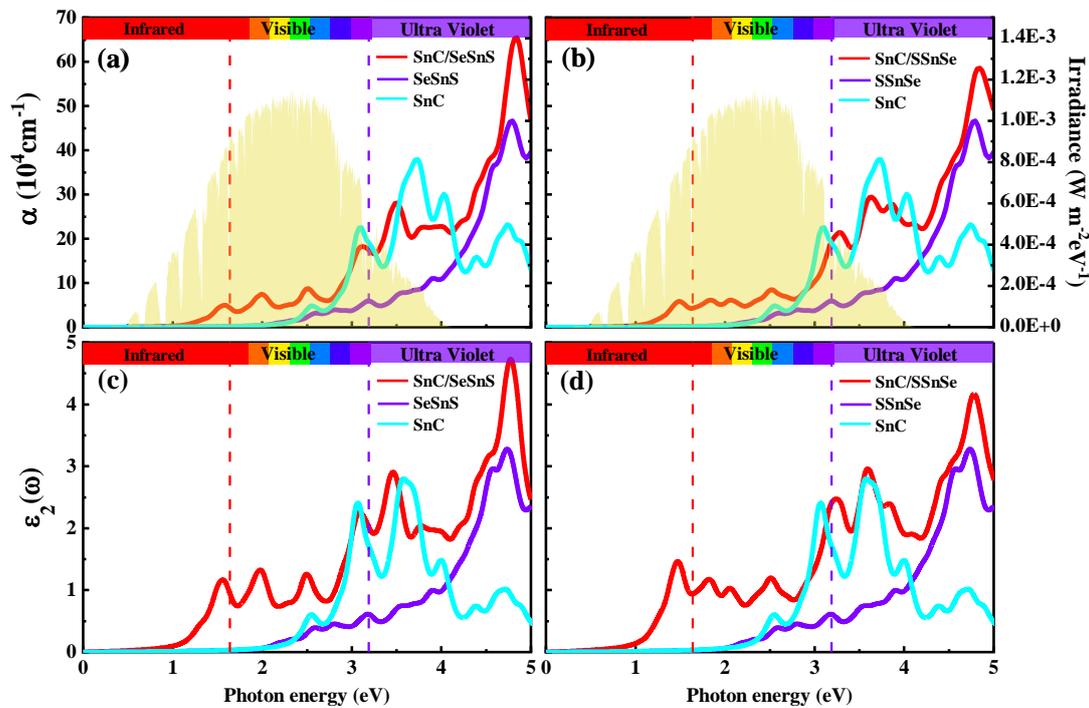


Fig. S5 Optical absorption coefficient α and the reference solar spectral irradiance at Air Mass 1.5 (yellow area) (upper panels) and imaginary part of frequency-dependent dielectric function $\epsilon_2(\omega)$ (lower panels) of isolated SnC (cyan), SnSSe (violet) monolayers and their vdWH (red) of SnC/SeSnS (left column) and SnC/SSnSe (right column), respectively, obtained at the HSE06 level.

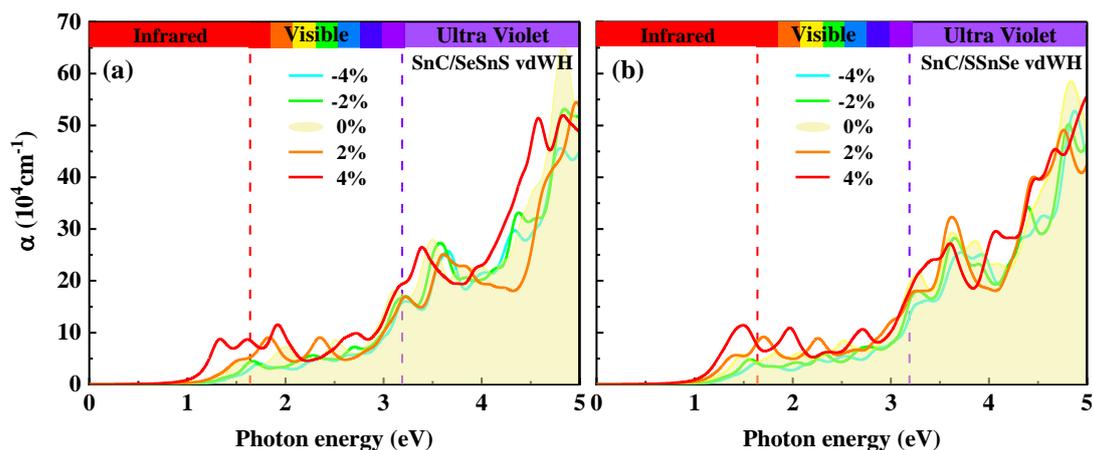


Fig. S6 Optical absorption coefficients of (a) SnC/SeSnS and (b) SnC/SSnSe vdWHs under four applied biaxial strains based on HSE06 level.

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