Supporting Information
Janus monolayer SnPAs: a stable two-dimensional direct band gap semiconductor for overall photocatalytic water-splitting in a wide pH range

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A. Gibbs Free Energy

Photocatalytic water-splitting contains two half-reactions, the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), where the two half-reactions can be obtained based on the theory developed by Nørskov et al [1]. The Gibbs free energy change (ΔG) can be calculated by the following equation [2–4]:

$$\Delta G = \Delta E + \Delta E_{\mathrm{ZPE}} - T\Delta S, \tag{S1}$$

where ΔE, ΔE_{ZPE}, and ΔS represent the differences in total energy, zero-point energy, and entropy of the slab with and without adsorbed intermediates. The system temperature T is set to be 298.15 K.

For the redox reactions of water-splitting, the reaction of HER can be decomposed into two steps:

$$* + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{H^*}, \tag{S2}$$

$$\mathrm{H^*} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{H_2}, \tag{S3}$$

For OER, the half-reaction is divided into four steps:

$$* + \mathrm{H_2O} \rightarrow \mathrm{OH^*} + \mathrm{e^-} + \mathrm{H^+}, \tag{S4}$$

$$\mathrm{OH^*} \rightarrow \mathrm{O^*} + \mathrm{e^-} + \mathrm{H^+}, \tag{S5}$$

$$\mathrm{O^*} + \mathrm{H_2O} \rightarrow \mathrm{OOH^*} + \mathrm{e^-} + \mathrm{H^+}, \tag{S6}$$

$$\mathrm{OOH^*} \rightarrow \mathrm{O_2} + \mathrm{e^-} + \mathrm{H^+}, \tag{S7}$$

where $*$ is the active site on photocatalysts, $\mathrm{O^*}$, $\mathrm{OH^*}$, $\mathrm{OOH^*}$, and $\mathrm{H^*}$ represent the adsorbed intermediates.

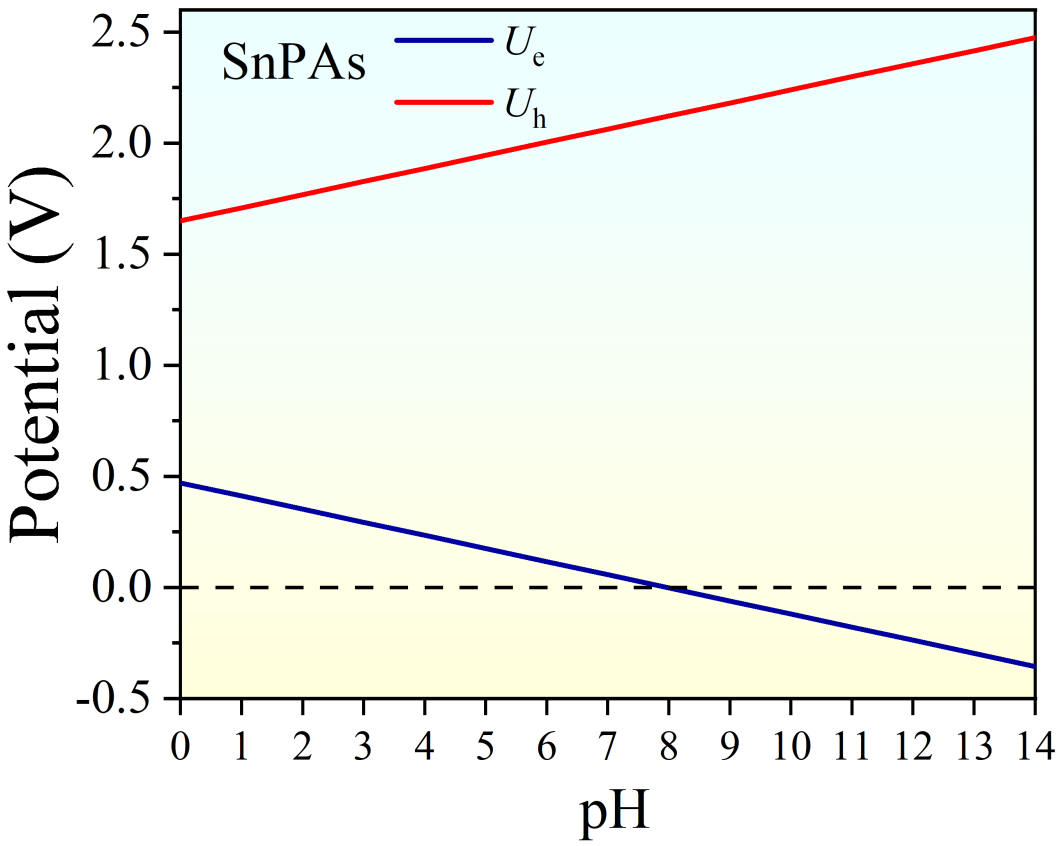

Fig. S1: The driving force for the photoreduction U_{e} and photooxidation U_{h} of the Janus SnPAs monolayer.

For HER, ΔG under the effect of electrolyte pH is given by the following equation:

$$\Delta G_{\mathrm{H}^*} = G_{\mathrm{H}^*} - \frac{1}{2}G_{\mathrm{H_2}} - G^* + 0.059 \times \mathrm{pH} - eU. \tag{S8}$$

For OER, ΔG under the effect of electrolyte pH is given by the following equations:

$$\Delta G_1 = G_{\mathrm{OH}^*} + \frac{1}{2}G_{\mathrm{H_2}} - G_{\mathrm{H_2O}} - G^* - 0.059 \times \mathrm{pH} - eU, \tag{S9}$$

$$\Delta G_2 = G_{\mathrm{O}^*} + \frac{1}{2}G_{\mathrm{H_2}} - G_{\mathrm{OH}^*} - 0.059 \times \mathrm{pH} - eU, \tag{S10}$$

$$\Delta G_3 = G_{\mathrm{OOH}^*} + \frac{1}{2}G_{\mathrm{H_2}} - G_{\mathrm{H_2O}} - G_{\mathrm{O}^*} - 0.059 \times \mathrm{pH} - eU, \tag{S11}$$

$$\Delta G_4 = G_{\mathrm{O_2}} + G^* + \frac{1}{2}G_{\mathrm{H_2}} - G_{\mathrm{OOH}^*} - 0.059 \times \mathrm{pH} - eU, \tag{S12}$$

where $0.059 \times$ pH is the free energy contribution under the effect of pH, eU denotes the influence of extra potential bias provided by the electrons or holes in the electrode, and U is the electrode potential relative to the standard hydrogen electrode (SHE).

B. Thermal Stability

To assess thermal stability, we conducted AIMD simulations on the SnPAs monolayer at 300 K for a duration of 20 ps, utilizing a 120-atom supercell with a time step of 2 fs, as shown in Fig. S2.

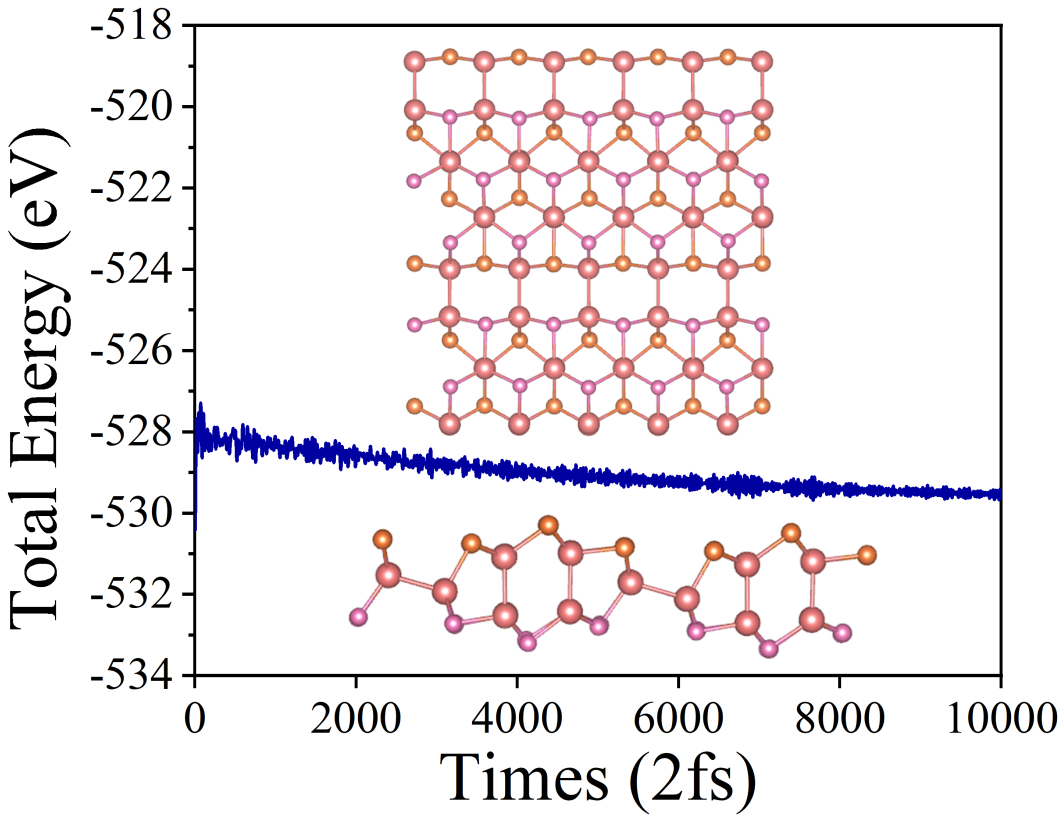

Fig. S2: Total energy of the SnPAs monolayer in AIMD simulations at 300 K over 20 ps. The top view and side view of the SnPAs monolayer supercell at 20 ps are inserted.

C. vdW Correction

To account for long-range van der Waals (vdW) interactions in the Janus SnPAs monolayer, the vdW correction proposed by Grimme (DFT-D3) with the PBE functional was employed [5]. The corresponding band structure results are presented in Fig. S3 of the Supporting Information. The inclusion of vdW correction has only a negligible effect on both the band structure and the band gap, as can be seen by comparing Fig. S3 and Fig. 4(a) of the main text.

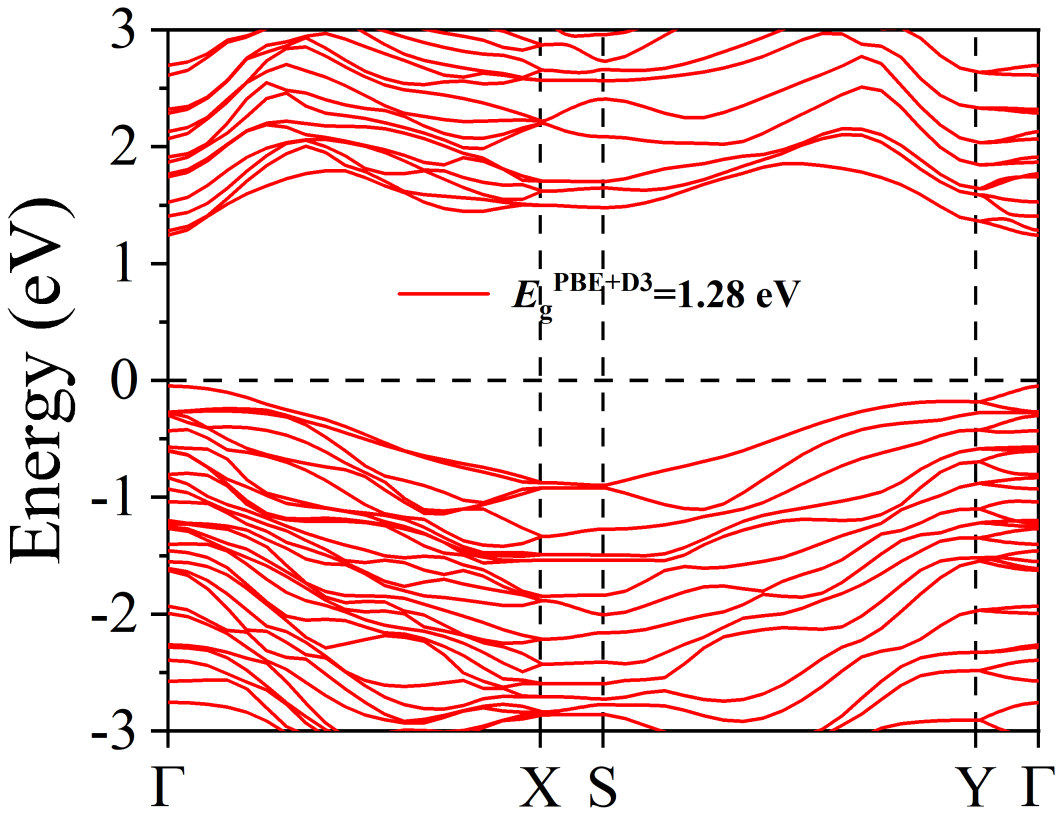

Fig. S3: The band structure calculated using the PBE method with the DFT-D3 van der Waals correction.

References

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