

Supplementary Information

The surface reconstruction induced enhancement of the oxygen evolution reaction on α -SnWO₄ (010) based on a density functional theory study

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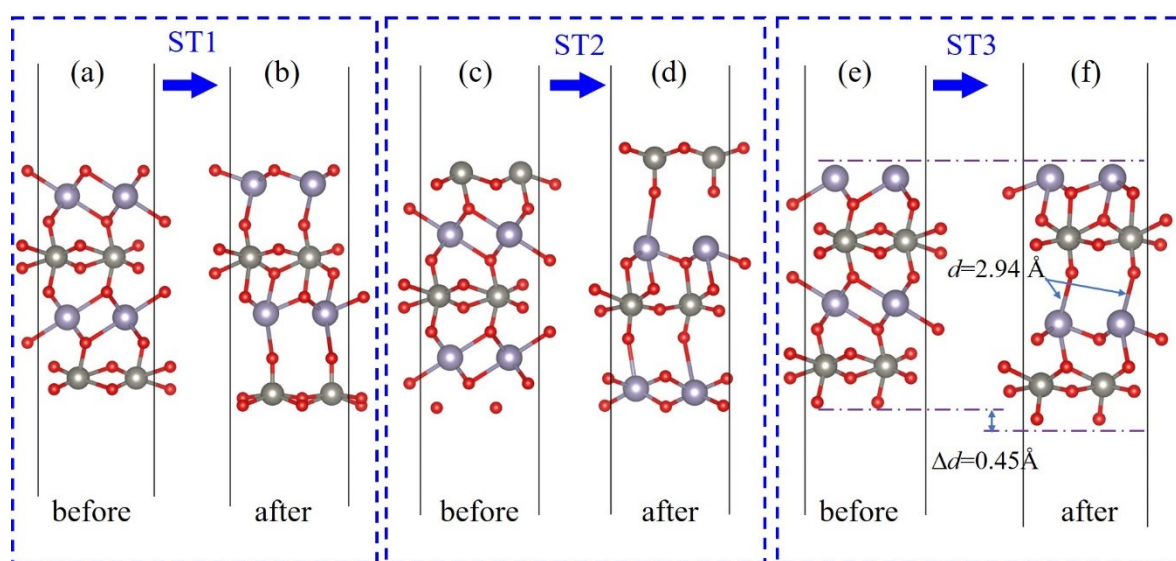


Fig. S1. Side view of three possible stoichiometric structures of α -SnWO₄ (010): (a) ST1, (c) ST2, and (e) ST3 are the structures before optimization, and (b), (d), and (f) are after optimization, respectively. The red, gray and light blue balls represent O, W, and Sn atoms.

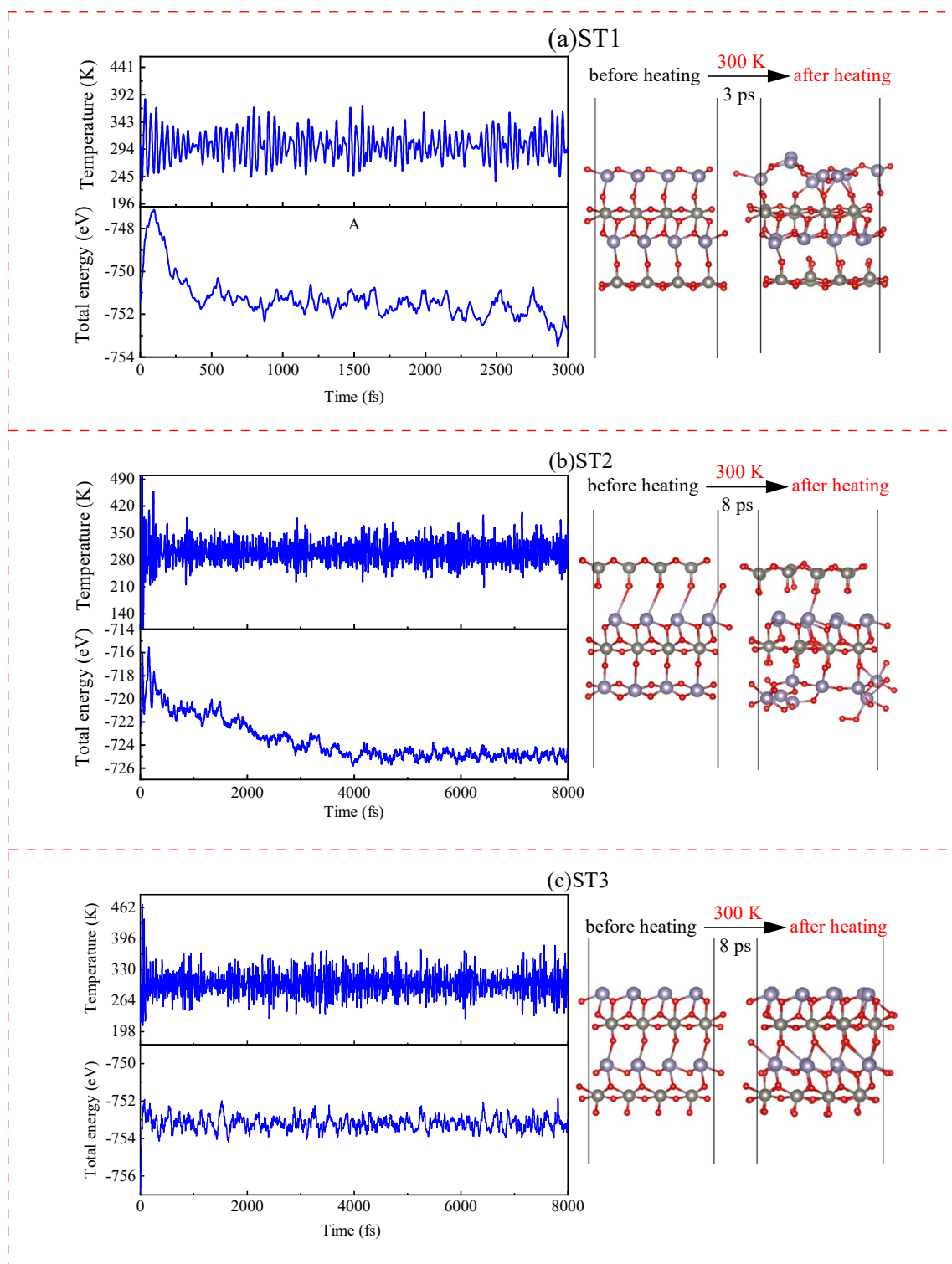


Fig. S2. Variations of temperature and energy plotted as a function of time for AIMD simulations of (a) ST1 (b)ST2, and (c)ST3 terminations under 300 K for 8 ps with a time step of 1fs. The right parts show the termination structures at 0 ps and 8 ps.

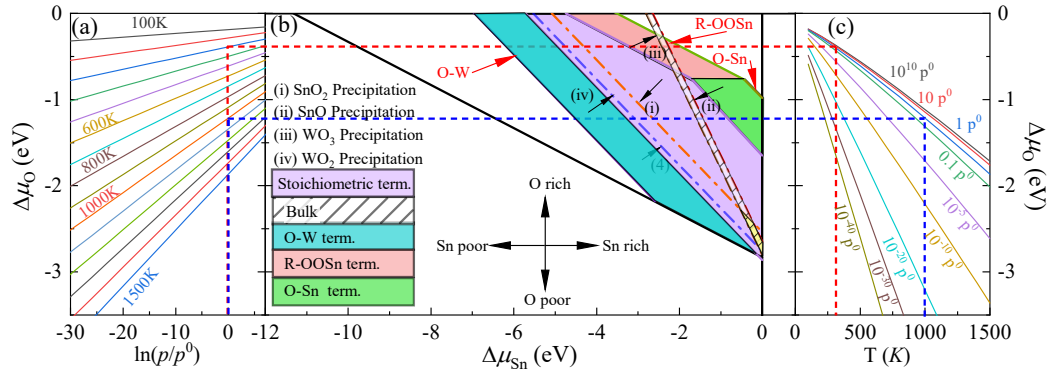


Fig. S3. (a) The $\Delta\mu_{\text{O}}$ as a function of oxygen gas pressure at various temperatures according to Equation (20), (b) the phase diagrams for $\alpha\text{-SnWO}_4$ (010) surface with different terminations (including O-Sn term., M-Sn term., R-OOW term., O-W term., W-O term., R-OOSn term., and ST3 term.) as functions of chemical potential variations for Sn and oxygen atoms, (c) the $\Delta\mu_{\text{O}}$ as a function of temperature at various oxygen gas pressures. All total energies are obtained using the PBE method.

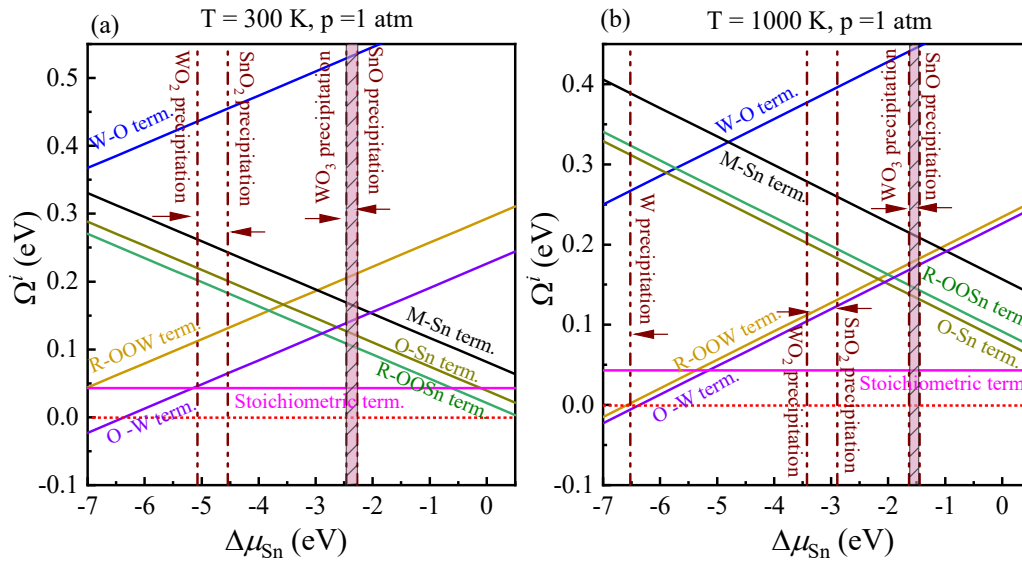


Fig. S4. Surface Gibbs free energies as a function of $\Delta\mu_{\text{Sn}}$ at a certain temperature and pressure for $\alpha\text{-SnWO}_4$ (010) surface using the PBE method (a) at $T = 300\text{K}$ and (b) $T = 1000\text{K}$.

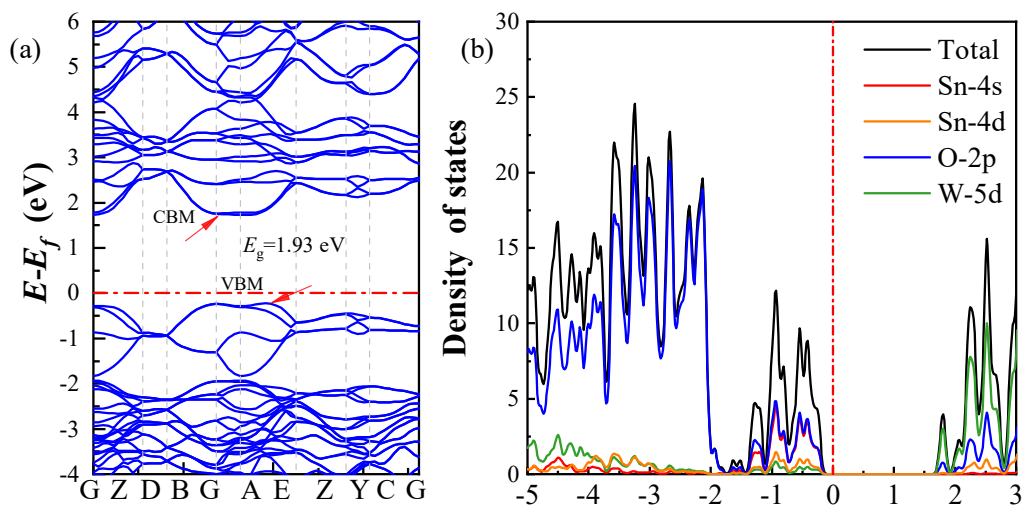
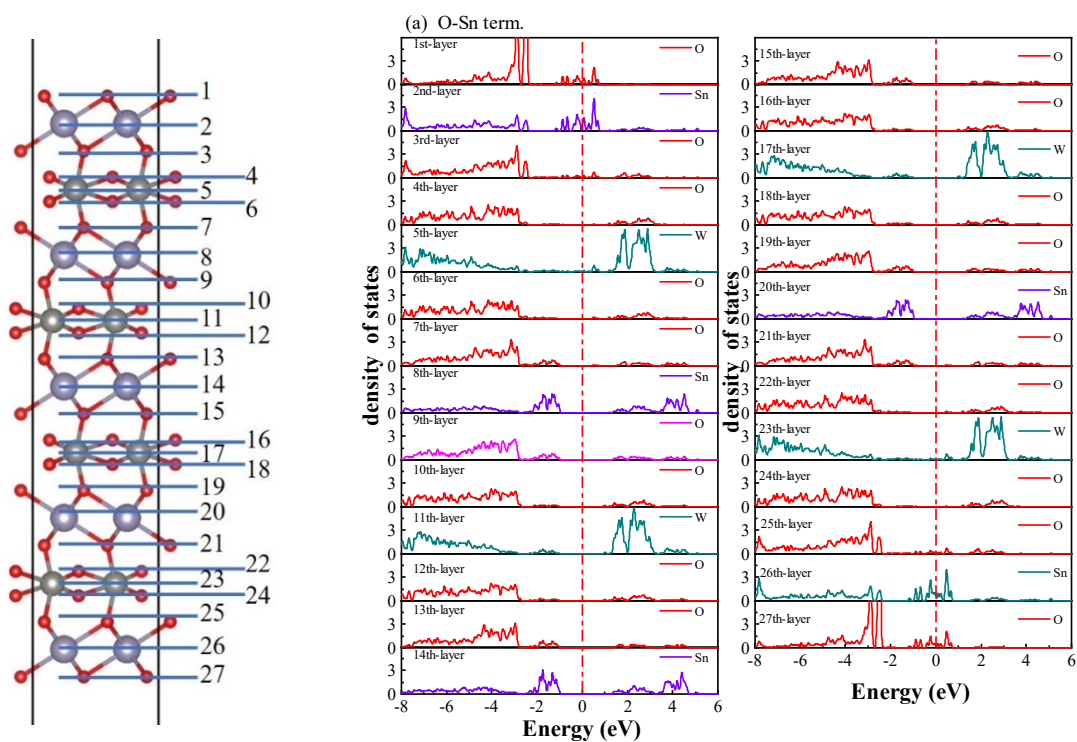
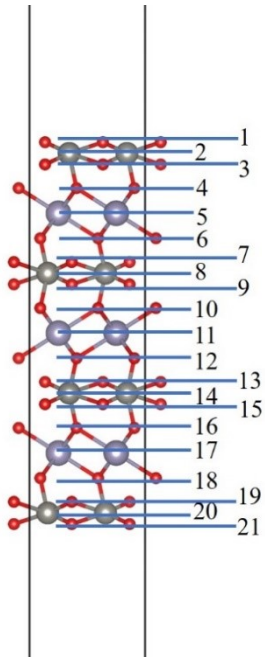
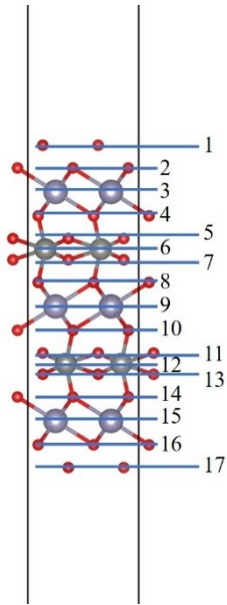
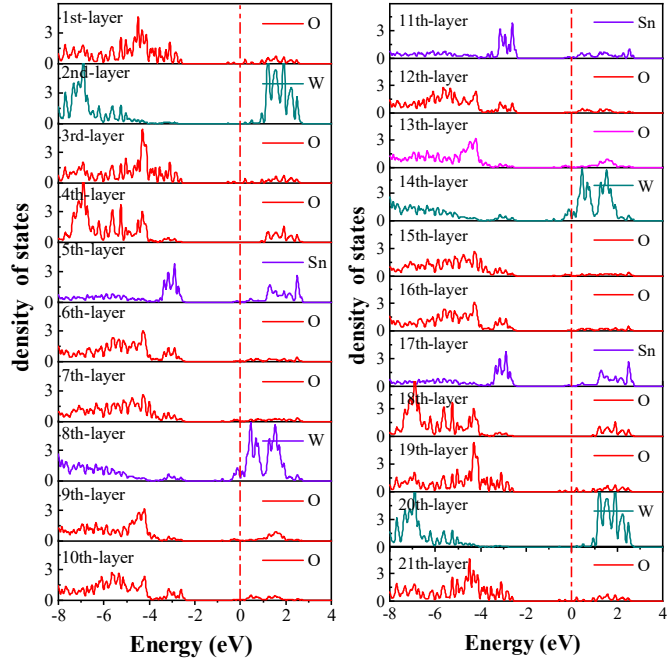


Fig. S5. The (a)Band structures, (b)TDOS and PDOS of bulk α -SnWO₄ are obtained from HSE06 calculations. The Fermi level is set to zero and indicated by the red dotted-dashed line.

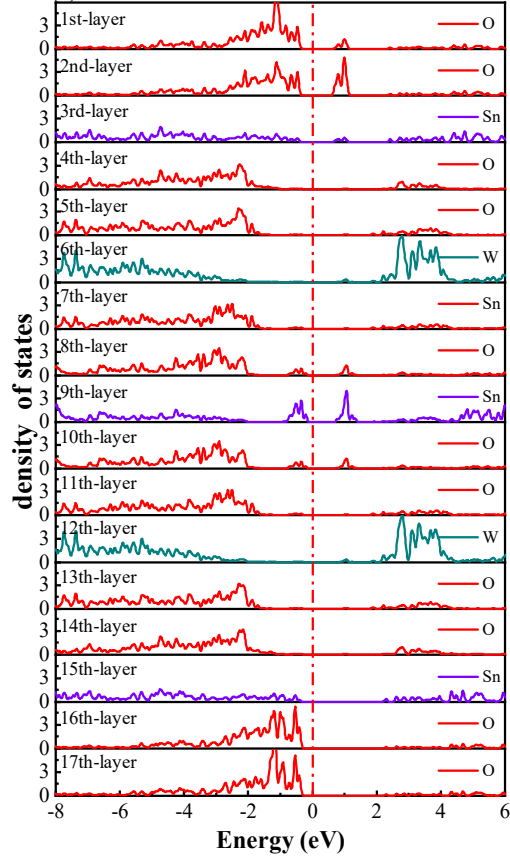




(b) O-W term.



(c) R-OOSn term.



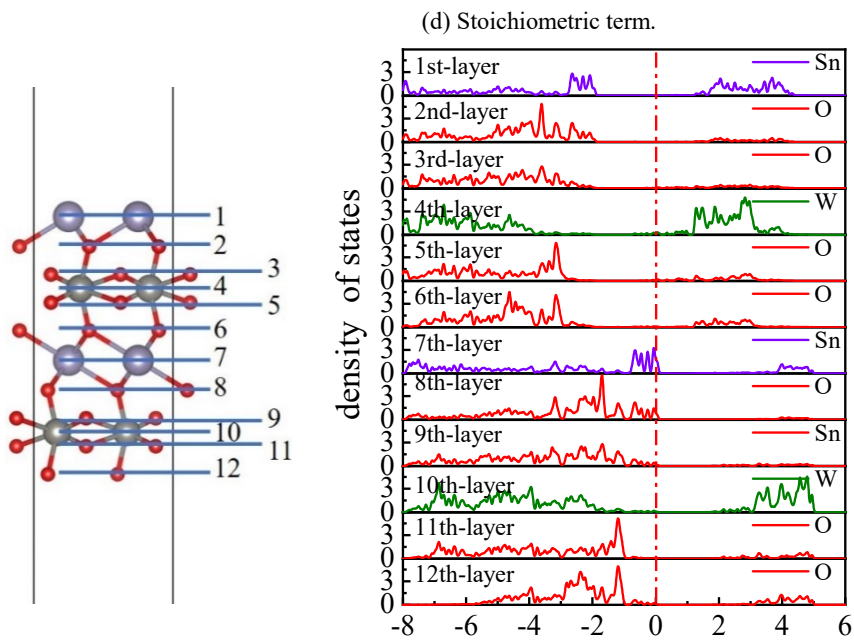
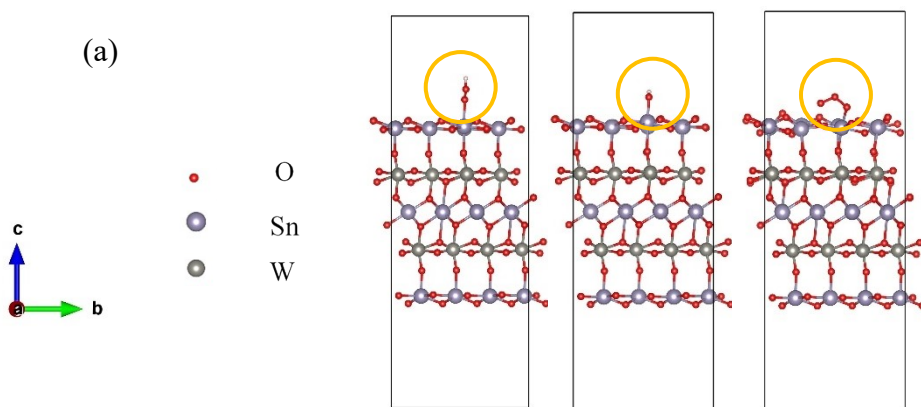


Fig. S6. The layer-resolved density of states of (a) O-Sn term., (b) O-W term. (c) R-OOSn term. and ST3 term., for SnWO_4 (010) surfaces, which are obtained from HSE06 calculations. The Fermi level is set to zero and indicated by a perpendicular red dot-dash line. The numbers represent the number of atomic layers for $\alpha\text{-SnWO}_4$ (010) surfaces



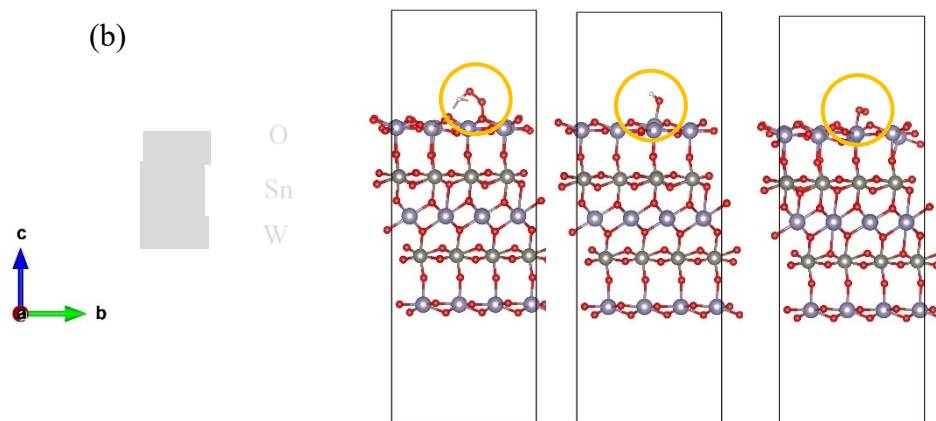


Fig. S7. The optimized structures for O*, OH*, and OOH* intermediates on the O-Sn termination of α -SnWO₄ (010) surfaces at different (a) and (b) sites.

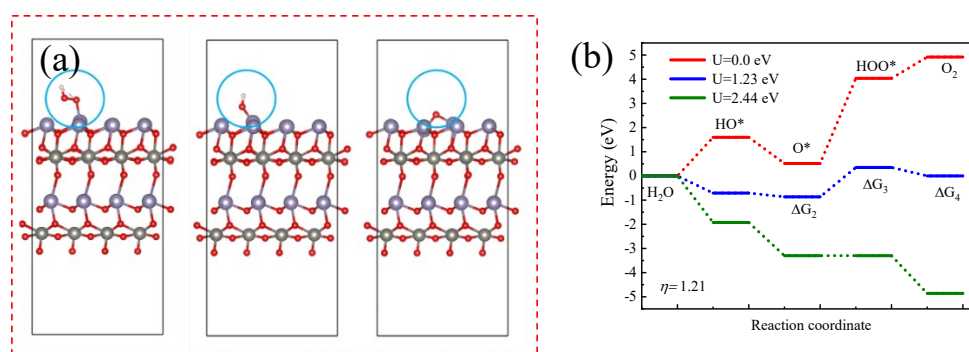
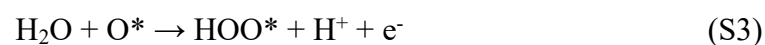
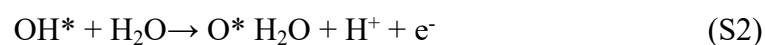
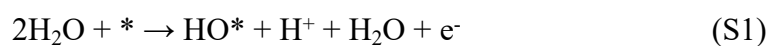


Fig. S8. The free energy profile for OER on the ST3 termination of α -SnWO₄(010) surface at different voltages. The optimized structures for O*, OH* and OOH* intermediates on the (b)ST3 termination of α -SnWO₄ (010) surfaces.

Note S1 Computational hydrogen electrode

For the OER reaction, four elementary steps are usually needed to proceed, as listed in equations (1) to (4), which involve adsorbed OH, O and OOH species on the surface (*):



The above mechanism is the most common one of the water-splitting on semiconductor surfaces. It involves the dehydrogenation of H₂O, followed by the dissociation of HO* to O*. Subsequently, O* reacts with another H₂O to generate HOO*, which then dehydrogenates to O₂.

The Gibbs free energy change for steps 1–4 can be expressed as

$$\Delta G_1 = \Delta G(\text{OH}_{ads}) - eU + \Delta G_{\text{H}^+}(\text{pH}) \quad (\text{S5})$$

$$\Delta G_2 = \Delta G(\text{O}_{ads}) - \Delta G(\text{OH}_{ads}) - eU + \Delta G_{\text{H}^+}(\text{pH}) \quad (\text{S6})$$

$$\Delta G_3 = \Delta G(\text{OOH}_{ads}) - \Delta G(\text{O}_{ads}) - eU + \Delta G_{\text{H}^+}(\text{pH}) \quad (\text{S7})$$

$$\Delta G_4 = 4.92 - \Delta G(\text{OOH}_{ads}) - eU + \Delta G_{\text{H}^+}(\text{pH}) \quad (\text{S8})$$

where U is the potential measured against normal hydrogen electrode (NHE) at standard conditions (T = 298.15 K, P = 1 bar, pH = 0). The free energy change of the protons relative to the above specified electrode at non-zero pH is represented by Nernst equation as $\Delta G_{\text{H}^+}(\text{pH}) = -k_{\text{B}}T \ln(10) \times \text{pH}$. The sum of ΔG_{1-4} is fixed to the negative of experimental Gibbs free energy of formation of two water molecules $-2 \Delta G_{\text{H}_2\text{O}}^{\text{exp}} = 4 \times 1.23 = 4.92$ eV to avoid calculating the O bond energy, which is difficult to determine accurately within GGA-DFT. The Gibbs free energies of eqs 5–8 depend on the adsorption energies of OH*, O*, and OOH*. To compute the free energy change (ΔG) of each elementary step of electrochemical urea synthesis, we adopted the computational hydrogen electrode model developed by Nørskov et al.¹ according to which the ΔG of an electrochemical reaction is defined as: $\Delta G_i = \Delta E_i + \Delta \text{ZPE}_i - T\Delta S_i$, where i means OH*, O* and OOH*. ZPE and S are the zero-point energy and entropy corrections, respectively. The energy differences ΔE_i calculated relative to H₂O and H₂ (at U = 0 and pH = 0) as

$$\Delta E_{\text{DFT}}(\text{OH}^*) = E_{\text{DFT}}(\text{OH}^*) - E(*) - [E_{\text{DFT}}(\text{H}_2\text{O}) - 1/2 * E_{\text{DFT}}(\text{H}_2)] \quad (\text{S9})$$

$$\Delta E_{\text{DFT}}(\text{O}^*) = E_{\text{DFT}}(\text{O}^*) - E(*) - [E_{\text{DFT}}(\text{H}_2\text{O}) - E_{\text{DFT}}(\text{H}_2)] \quad (\text{S10})$$

$$\Delta E_{\text{DFT}}(\text{OOH}^*) = E_{\text{DFT}}(\text{OOH}^*) - E(*) - [2 * E_{\text{DFT}}(\text{H}_2\text{O}) - 3/2 * E_{\text{DFT}}(\text{H}_2)] \quad (\text{S11})$$

The theoretical overpotential is then readily defined as:

$$\eta = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4] / e - 1.23 [\text{V}] \quad (\text{S12})$$

The entropies of gas-phase H_2 is obtained from the NIST database² with the standard condition, and the adsorbed species were only taken vibrational entropy (S_v) into account, as shown in the following formula:

$$S_v = \sum_i R \left\{ \frac{h\nu_i}{k_B T} \left[\exp\left(\frac{h\nu_i}{k_B T}\right) - 1 \right]^{-1} - \ln \left[1 - \exp\left(-\frac{h\nu_i}{k_B T}\right) \right] \right\} \quad (\text{S13})$$

Among which $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $T = 298.15 \text{ K}$, $h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$, $k_B = 1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$, i is the frequency number, ν_i is the vibrational frequency (unit is cm^{-1}).

1. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, *J. Phys. Chem. B*, 2004, **108**, 17886-17892.
2. R. D. J. III, *NIST Computational Chemistry Comparison and Benchmark Database*, 2022.