Electronic Supplementary Information (ESI)

Pentagonal PdX_2 (X = S, Se) nanosheets with X vacancies as high-performance electrocatalysts for the hydrogen evolution reaction

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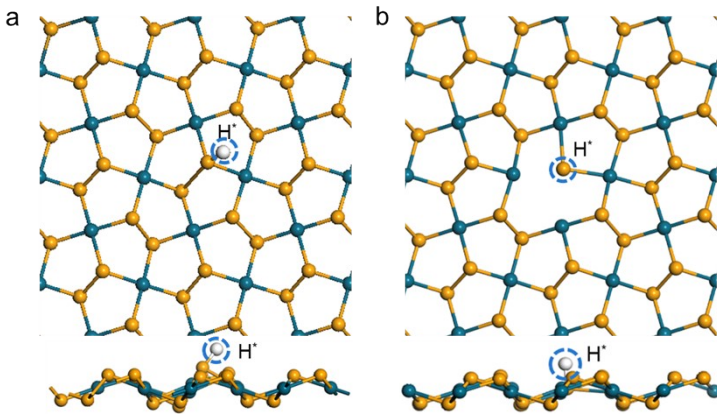

Fig. S1 Views of the structures of (a) pristine and (b) defective SL $PdSe_2$ with absorbed H*.

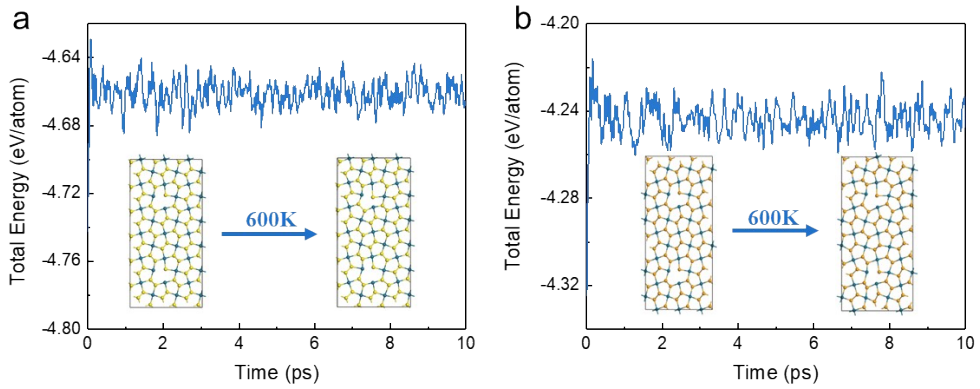

Fig. S2 Total energy during AIMD simulations for 3 × 3 SL (a) PdS_2 and (b) $PdSe_2$ supercells with one S and Se vacancy. Insets show the snapshots of initial and final atomic configurations of AIMD simulations.

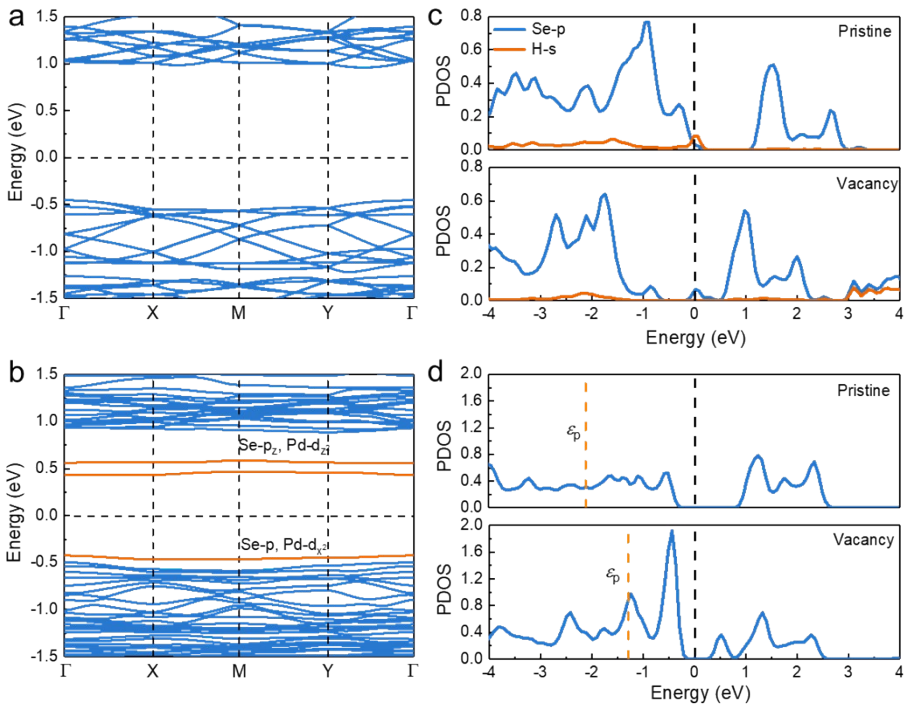

Fig. S3 Band structures of (a) pristine and (b) defective $PdSe_2$ with 2.78% V_{Se}. Three defect states in the gap are highlighted in orange. (c) The p-orbital PDOS of H* on the pristine and defective SL $PdSe_2$. (d) The p-orbital PDOS of the active Se sites of pristine and defective SL $PdSe_2$. The orange dashed lines represent the position of p-band center ε_p.

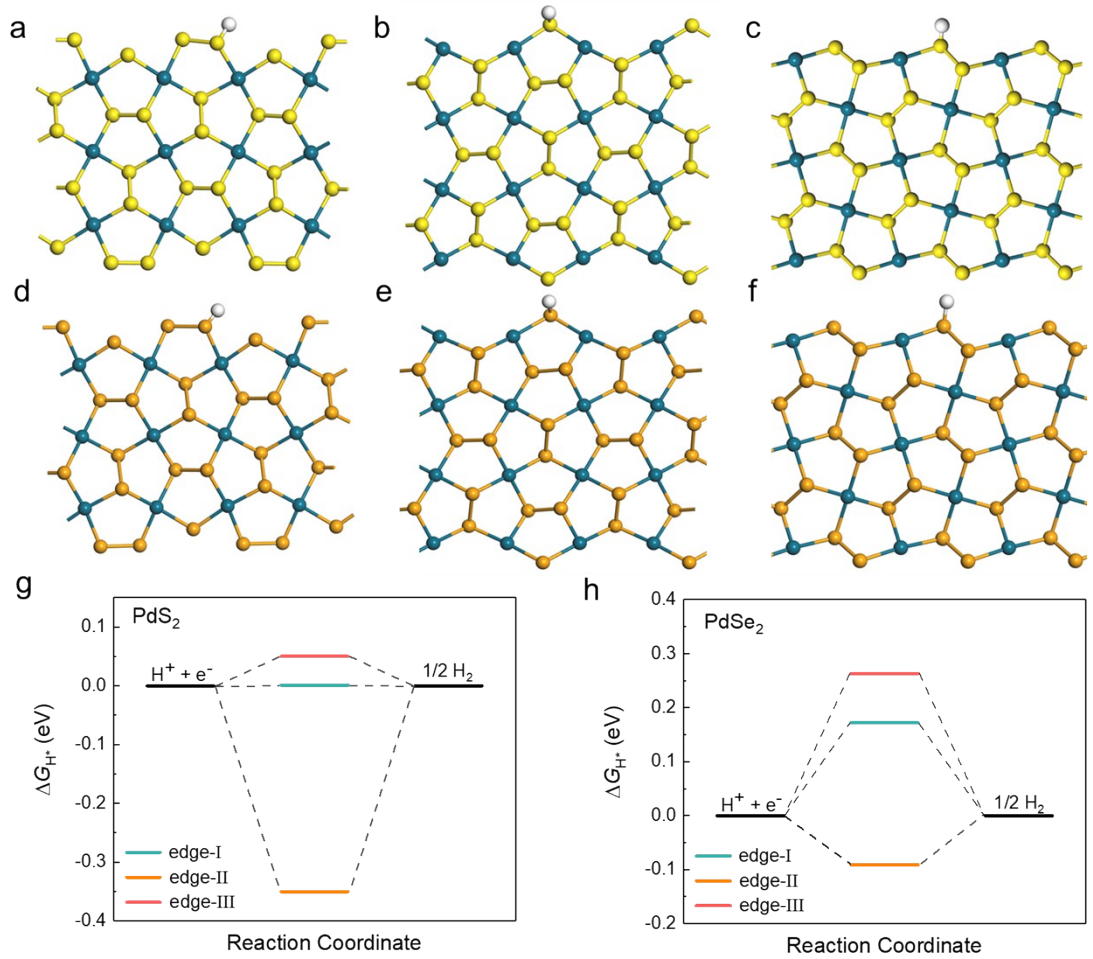

Fig. S4 Structural models of hydrogen adsorption at three kinds of edge sites in (a-c) PdS_2 and (d-f) $PdSe_2$. Hydrogen adsorption free energy of (g) PdS_2 and (h) $PdSe_2$ with different edges.

Table S1 Calculated hydrogen adsorption energy ΔE_H (eV) and Gibbs free energy ΔG_{H^*} (eV) of the Pd or X site of SL PdX_2.

Adsorption sites	ΔE_H (eV)	ΔG_{H^*} (eV)
Pd (PdS_2)	1.55	1.84
S (PdS_2)	1.02	1.31
Pd ($PdSe_2$)	1.28	1.54
Se ($PdSe_2$)	1.08	1.34