Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for:

Active Edge Sites in $MoSe_2$ and WSe_2 Catalysts for the Hydrogen Evolution Reaction

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1 Determining the Stable Edge Configuration

Here we present the details for determining the stable configurations on the $(10\bar{1}0)$ Mo/W-edge and $(\bar{1}010)$ Se-edge. The edge free energy γ was determined as

$$\gamma = \frac{1}{2L}\left[G\left(MSe_2 + N_H H\right) - N_M E^{bulk}_{MSe_2} + \left(2N_M - N_{Se}\right)\mu_{Se} - N_H \mu_H\right] \quad (1)$$

with

$$\mu_{Se} = \mu_{H_2Se} - 2\left(\frac{1}{2}\mu_{H_2} - eU_{RHE}\right) \quad (2)$$

$$\mu_H = \frac{1}{2}\mu_{H_2} - eU_{RHE} \quad (3)$$

where $M =$ Mo or W and the computational hydrogen electrode (CHE) has been used.[S1]

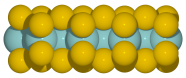
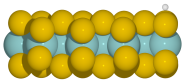
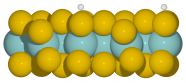
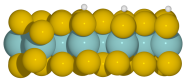
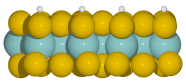
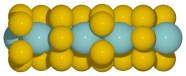
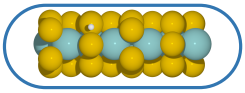
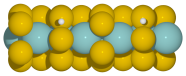
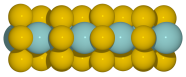
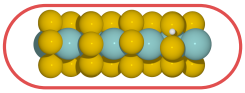
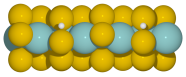
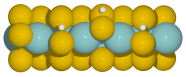
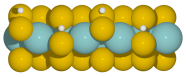
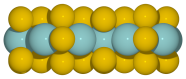
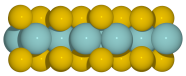
The configurations for each edge type for $MoSe_2$ and WSe_2 are shown below, along with the edge free energy γ plotted against the H_2Se pressure. Using the stable edge configuration at $U_{RHE} = 0$ V for a $P(H_2Se) = 10^{-5}$ to 10^{-8} bar, we determine the free energies for evolving H_2, adsorbing an additional H, and evolving H_2Se. The structure for which H_2 evolution is the most favorable reaction is chosen as the stable structure. To a first approximation, this is the structure that is likely stable against further Se desorption. Accurate kinetic barriers will be needed to determine the relevant structure with more certainty.

We did not consider structures with greater values of θ_H if it was clear that the edge configuration was unstable for the given θ_{Se} or if the ΔG_H was such that further hydrogen adsorption was not possible. In some cases it was clear after having studied several configurations that certain coverages of Se would not be stable, and we therefore neglected those structures.

1.1 $MoSe_2$ Mo-edge

The edge structures we considered are shown in Table S1. According to Fig. S1, the structures with $\theta_{Se} = 0.5$ ML and 0.75 ML and $\theta_H = 0.25$ ML are similarly stable under the assumed conditions (circled in Table S1, with the color corresponding to the plot in Fig. S1). Upon checking the possible reaction paths from these structures (Fig. S2 and Fig. S3), we confirm that these are the two possible edge structures for the Mo-edge of $MoSe_2$.

Table S1: Mo-edge Configurations Considered for $MoSe_2$

	θ_H (ML)				
θ_{Se} (ML)	0.0	0.25	0.5	0.75	1.0
1.0					
0.75					
0.5					
0.25					
0.0					

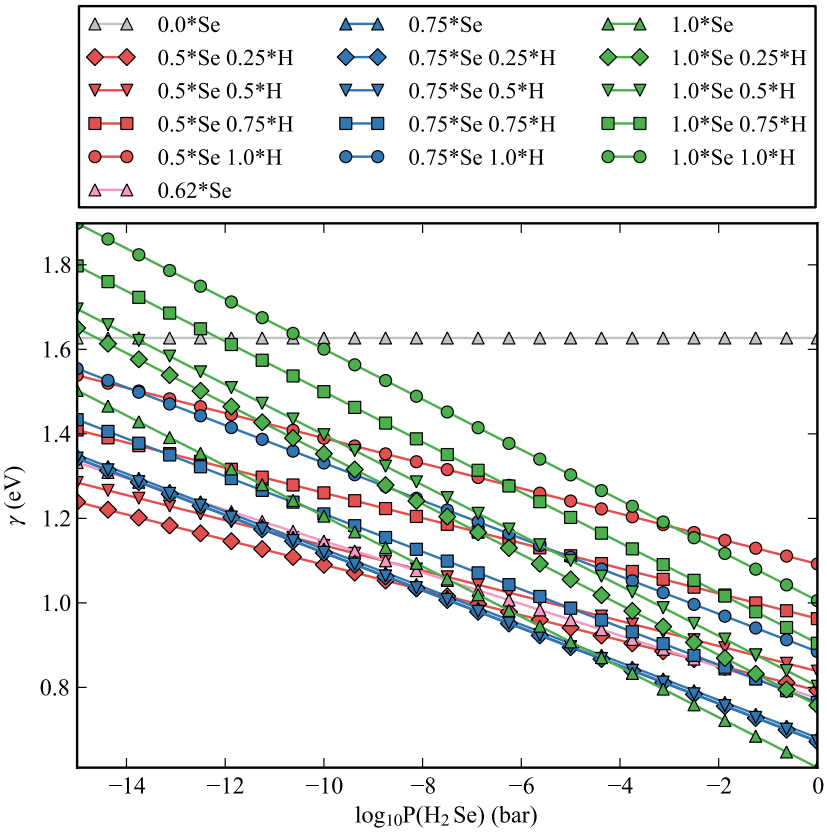


Figure S1: Plot of γ vs. $\log_{10}P(H_2Se)$ for the Mo-edge of $MoSe_2$.

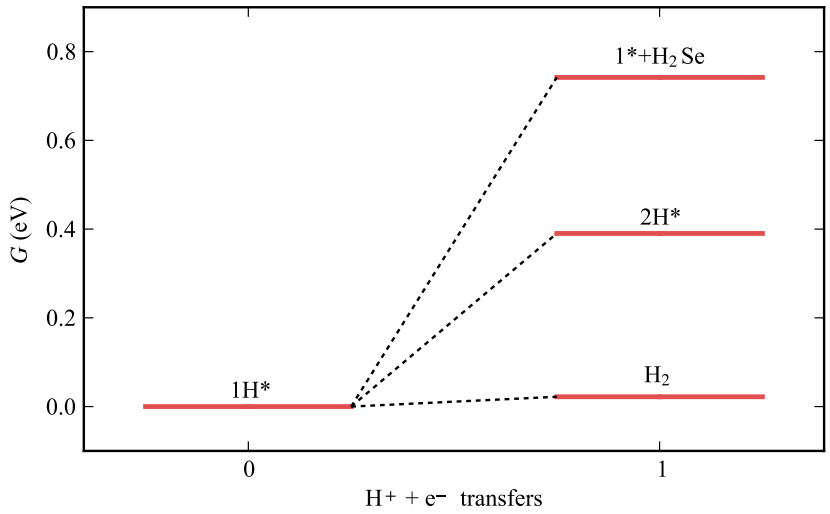


Figure S2: Free energy diagram for H_2 evolution, H adsorption, and H_2Se evolution on the Mo-edge of $MoSe_2$ with $\theta_{Se} = 0.5$ ML and $\theta_H = 0.25$ ML. Here, H* denotes an adsorbed hydrogen, and * denotes a selenide vacancy.

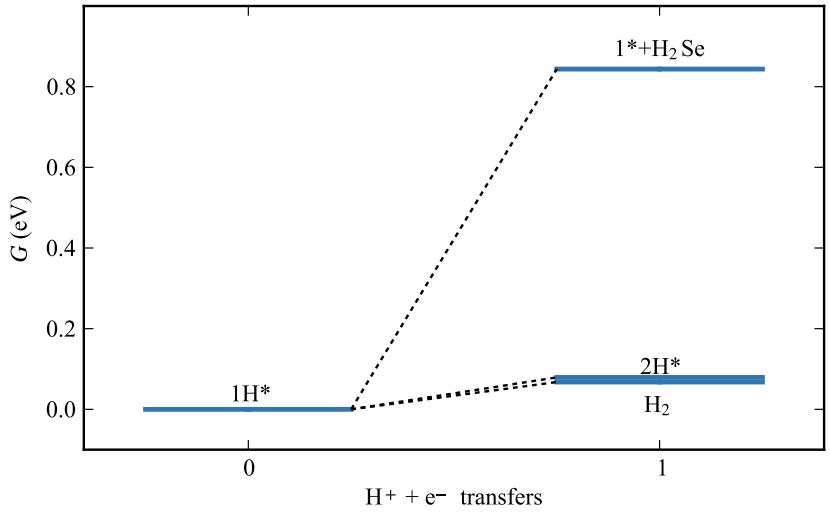
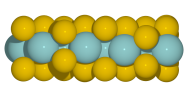
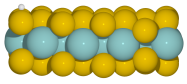
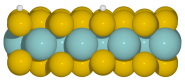
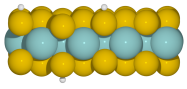
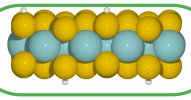
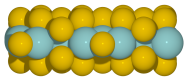
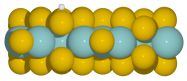
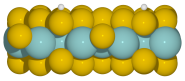
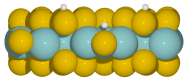
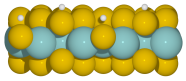
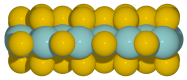
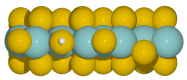
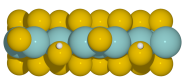
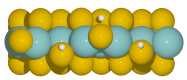
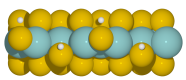
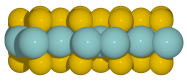
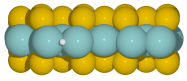
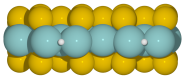
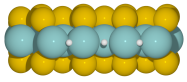
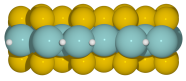


Figure S3: Free energy diagram for H_2 evolution, H adsorption, and H_2Se evolution on the Mo-edge of $MoSe_2$ with $\theta_{Se} = 0.75$ ML and $\theta_H = 0.25$ ML. Here, H* denotes an adsorbed hydrogen, and * denotes a selenide vacancy.

1.2 $MoSe_2$ Se-edge

The stable Se-edge structure for $MoSe_2$ is clearly determined from Fig. S4 to be $\theta_{Se} = 1.0$ ML and $\theta_H = 1.0$ ML (circled in Table S2). Checking the possible pathways for this structure (Fig. S5), we confirm that this is the correct structure for HER conditions. Based on the Fig. S8, it was clear that θ_{Se} between 0.0 ML and 0.5 ML would be unstable so they were not considered.

Table S2: Se-edge Configurations Considered for $MoSe_2$

θ_{Se} (ML)	θ_H (ML) 0.0	0.25	0.5	0.75	1.0
1.0					
0.75					
0.5					
0.0					

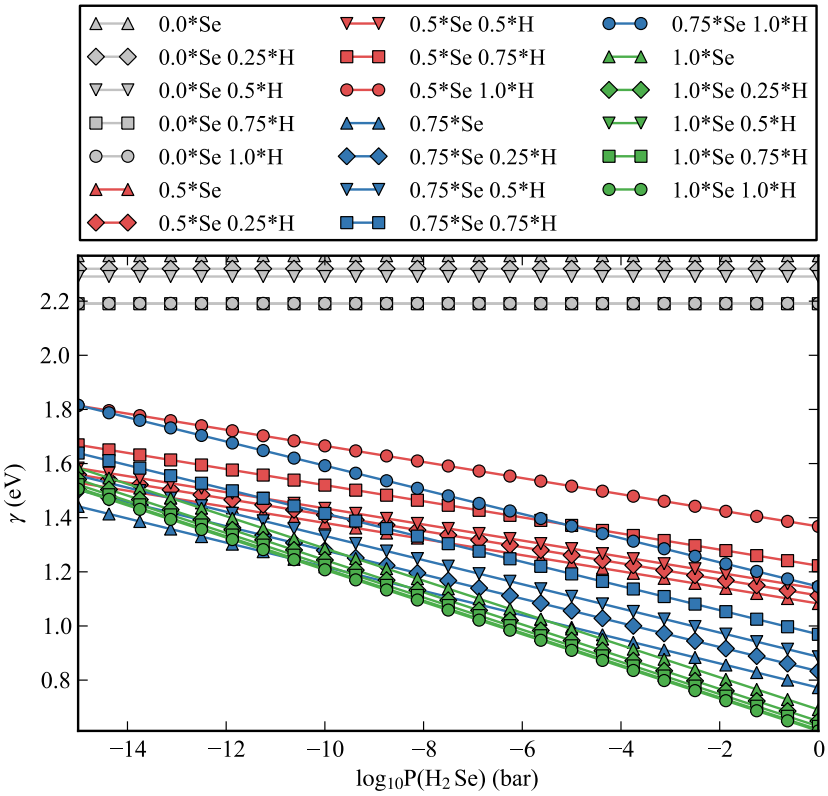


Figure S4: Plot of γ vs. $\log_{10}P(H_2Se)$ for the Se-edge of $MoSe_2$.

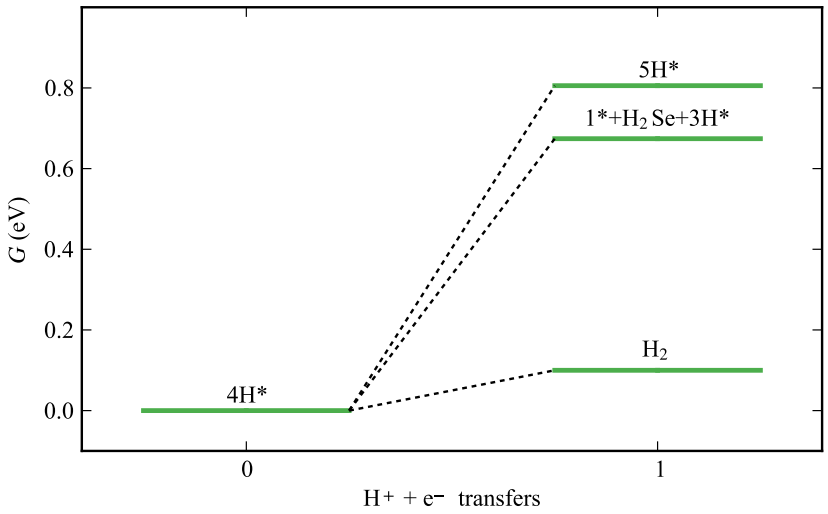
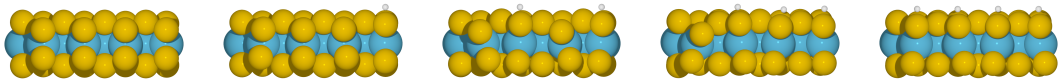
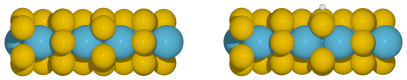
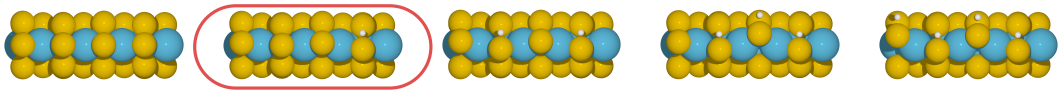
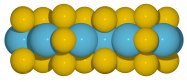
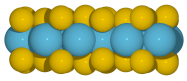


Figure S5: Free energy diagram for H_2 evolution, H adsorption, and H_2Se evolution on the Se-edge of $MoSe_2$ with $\theta_{Se} = 1.0$ ML and $\theta_H = 1.0$ ML. Here, H* denotes an adsorbed hydrogen, and * denotes a selenide vacancy.

1.3 WSe_2 W-edge

For the W-edge on WSe_2, we found the stable edge configuration to be $\theta_{Se} = 0.5$ ML and $\theta_H = 0.25$ ML (cirlced in Table S3).

Table S3: W-edge Configurations Considered for WSe_2

	θ_H (ML)				
θ_{Se} (ML)	0.0	0.25	0.5	0.75	1.0
1.0					
0.75					
0.5					
0.25					
0.0					

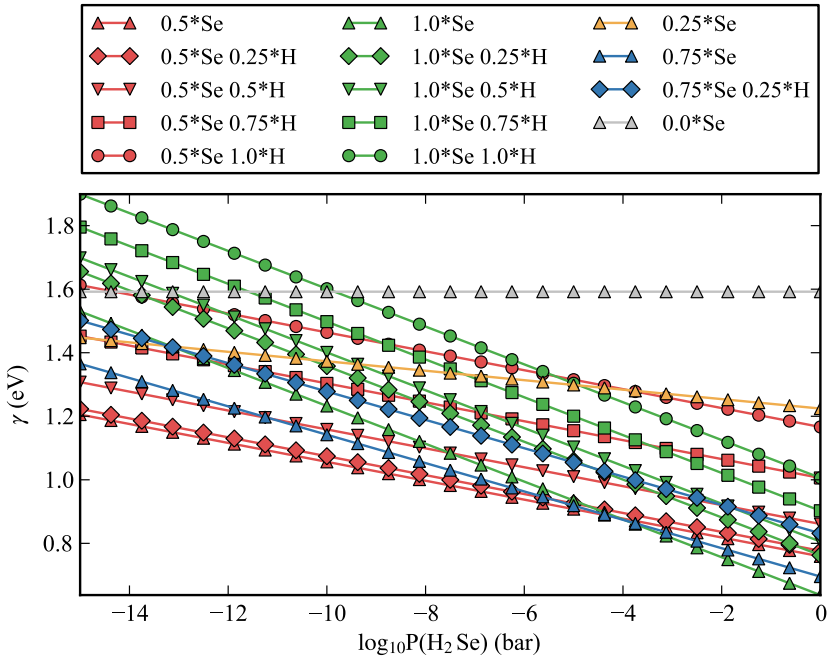


Figure S6: Plot of γ vs. $\log_{10}$P(H_2Se) for the W-edge of WSe_2.

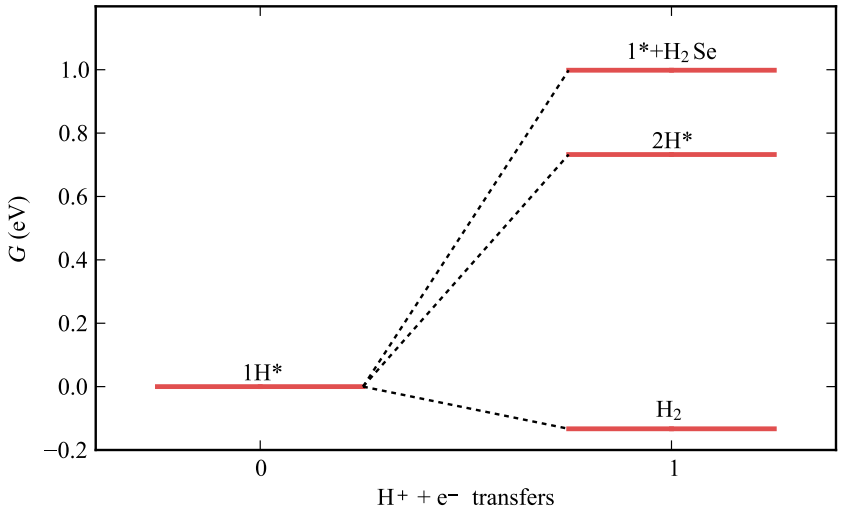
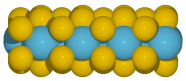
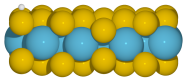
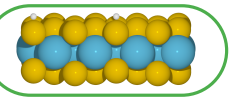
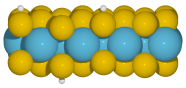
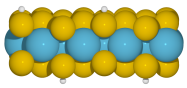
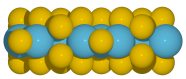
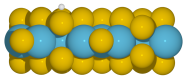
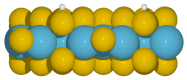
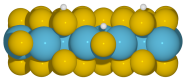
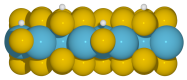
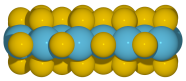
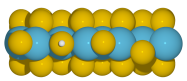
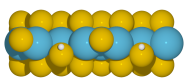
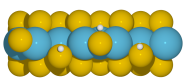
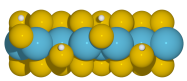
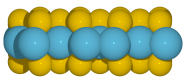
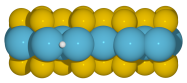
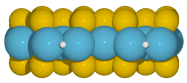
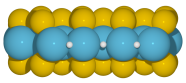
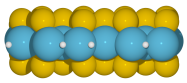


Figure S7: Free energy diagram for H_2 evolution, H adsorption, and H_2Se evolution on the W-edge of WSe_2 with $\theta_{Se} = 0.5$ ML and $\theta_H = 0.25$ ML. Here, H* denotes an adsorbed hydrogen, and * denotes a selenide vacancy.

1.4 WSe_2 Se-edge

For the Se-edge of WSe_2, the stable edge configuration was found to be $\theta_{Se} = 1.0$ ML and $\theta_H = 0.5$ ML. Based on the plot of γ as a function of H_2Se pressure (Fig. S8), it is clear that θ_{Se} between 0.0 ML and 0.5 ML would be unstable so they are not considered.

Table S4: Se-edge Configurations Considered for WSe_2

	θ_H (ML)				
θ_{Se} (ML)	0.0	0.25	0.5	0.75	1.0
1.0					
0.75					
0.5					
0.0					

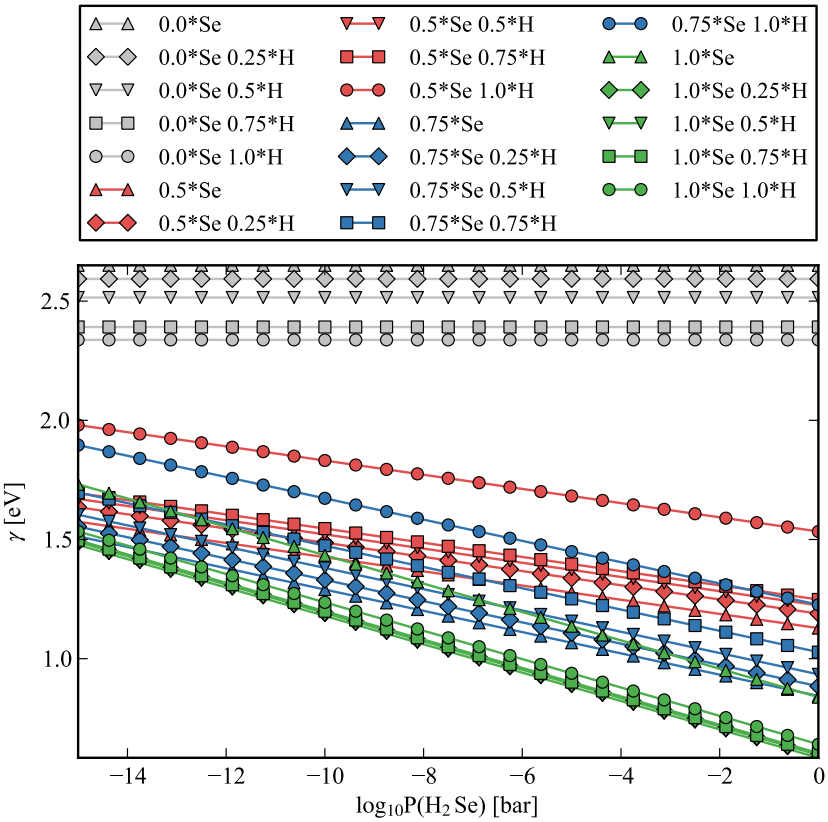


Figure S8: Plot of γ vs. $\log_{10}P(H_2Se)$ for the Se-edge of WSe_2.

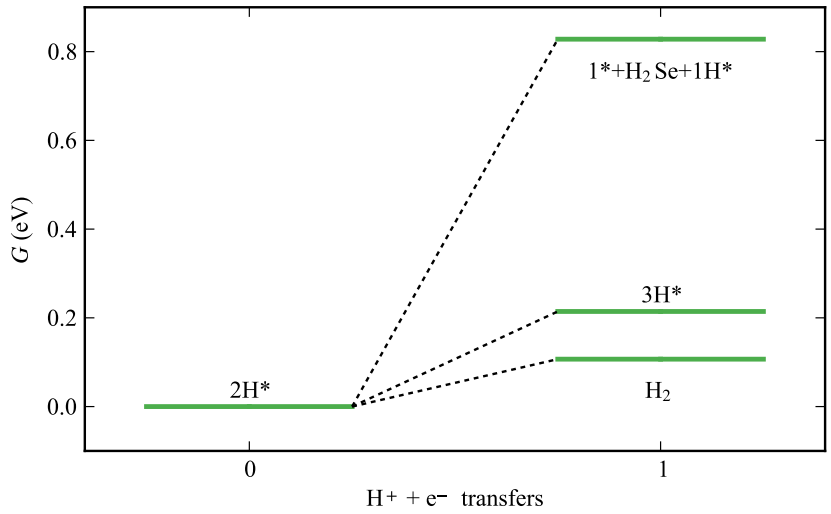


Figure S9: Free energy diagram for H_2 evolution, H adsorption, and H_2Se evolution on the Se-edge of WSe_2 with $\theta_{Se} = 1.0$ ML and $\theta_H = 0.50$ ML. Here, H* denotes an adsorbed hydrogen, and * denotes a selenide vacancy.

1.4.1 WSe_2 Se-edge reconstruction upon hydrogen adsorption

At the stable Se coverage on the Se-edge of WSe_2 (as circled in Table S4), there is a reconstruction in the edge structure when the final hydrogen is adsorbed. When θ_H is increased from 0.25 ML to 0.5 ML, the Se-Se dimer bond is broken in order to form the Se-H bond, increasing the Se-Se distance from 2.39 Å to 3.03 Å. To determine the energetic cost of this reconstruction, we take the stable edge structure ($\theta_{Se} = 1.0$ ML, $\theta_H = 0.5$ ML), remove the final adsorbed hydrogen, and perform a fixed single point calculation on the resulting structure. We are then able to determine the reconstruction relative to the stable edge structure at $\theta_H = 0.25$ ML, as well as the S−H bond formation energy. These values are $\Delta E_{\text{reconstruction}} = 0.10$ eV and $\Delta G_{S-H} = -0.15$ eV.

References

(S1) Peterson, A. A.; Abild-Pedersen, F.; Studt, F.; Rossmeisl, J.; Nørskov, J. K. How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. *Energy & Environmental Science* **2010**, *3*, 1311.