Supplementary Information

Enhancing the Electrocatalytic Performance of SnX_2 (X= S and Se) Monolayers for CO_2 Reduction to HCOOH via Transition Metal Atom Adsorption: A Theoretical Investigation

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Computational details of free energies for CO_2 reduction reduction (CRR)

In this work, the CO_2 reduction to HCOOH was assumed to take place along the following elementary step:

$$* + CO_2 \rightarrow *CO_2 \quad (1)$$

$$*CO_2 + H^+ + e^- \rightarrow *OOCH \quad (2)$$

$$*OOCH + H^+ + e^- \rightarrow *HCOOH \quad (3)$$

$$*HCOOH \rightarrow * + HCOOH \quad (4)$$

where * denotes the active site in the SnX_2 (X = S and Se) monolayers, and $*CO_2$, *OOCH and *HCOOH represent the adsorbed intermediates that are involved in CRR corresponding to two-electron transfer process. And the Gibbs free energies of these intermediates ($*CO_2$, *OOCH and *HCOOH) are calculated by the following equations:

$$\Delta G_{*CO_2} = G_{*CO_2} - G_* - G_{CO_2} \quad (5)$$

$$\Delta G_{*OOCH} = G_{*OOCH} - G_* - G_{CO_2} - \frac{1}{2} G_{H_2} \quad (6)$$

$$\Delta G_{*HCOOH} = G_{*HCOOH} - G_* - G_{CO_2} - G_{H_2} \quad (7)$$

where G_{*CO_2}, G_{*OOCH} and G_{*HCOOH} the free energy of the system with one adsorbed CO_2, OOCH and HCOOH, G_* is the free energy of the system itself, G_{H_2O}, G_{H_2} and G_{CO_2} are the free energy of H_2O, H_2 and CO_2 molecules, respectively.

To evaluate the catalytic activity, the CRR overpotential (η) is calculated from the change of free energy in the elementary step and limiting potential (U_L) at equilibrium state. And η is defined as $\eta = U_{equ} - U_L$, where U_{equ} is the equilibrium potential obtained from experimental data, U_L is calculated by $U_L = \frac{-\Delta G_{max}}{e}$, and ΔG and e are the difference of free energy of the reaction intermediate and the number of electrons transferred in the reaction. A catalyst with lower overpotential possesses better catalytic activity.

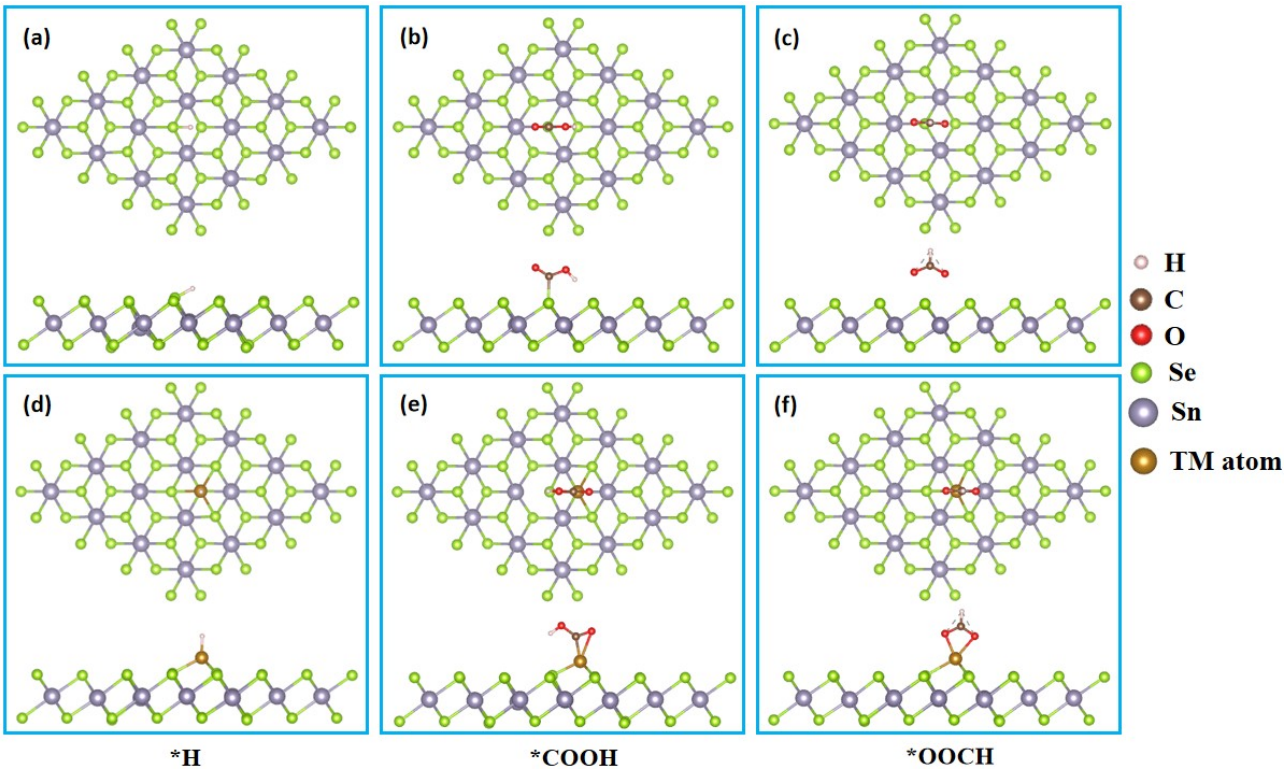

Figure S1. Side and top views of key intermediates (*H, *COOH and *OOCH) adsorption on the surface of (a)-(c) pristine $SnSe_2$ and (d)-(f) TM/$SnSe_2$ monolayers.

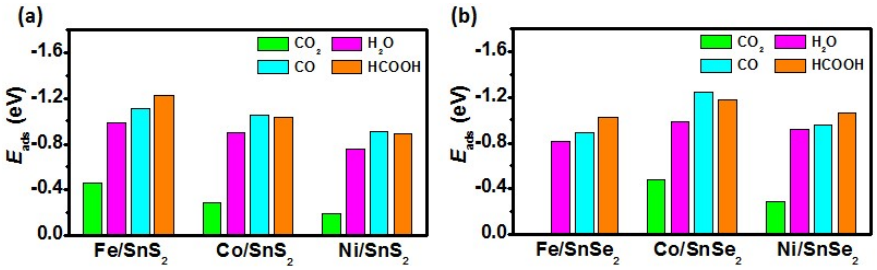

Figure S2. The adsorption energies of CO_2, H_2O, CO and HCOOH adsorbed on the surface of (a) SnS_2 and (b) $SnSe_2$ monolayers.

Table S1. The Adsorption Energies for the CO_2, H_2O, CO and HCOOH Adsorption on the Surface of SnX_2 (X=S and Se) Monolayers

surface	Adsorption Energy (eV)			
	CO_2	H_2O	CO	HCOOH
pristine SnS_2	-0.13	-0.12	-0.09	-0.02
Fe/SnS_2	-0.46	-0.99	-1.83	-1.05
Co/SnS_2	-0.29	-0.90	-1.77	-0.85
Ni/SnS_2	-0.19	-0.76	-1.63	-0.71
pristine $SnSe_2$	-0.22	-0.06	-0.19	-0.19
Fe/$SnSe_2$	-0.001	-0.81	-1.61	-0.84
Co/$SnSe_2$	-0.48	-0.99	-1.97	-1.01
Ni/$SnSe_2$	-0.29	-0.92	-1.68	-0.88

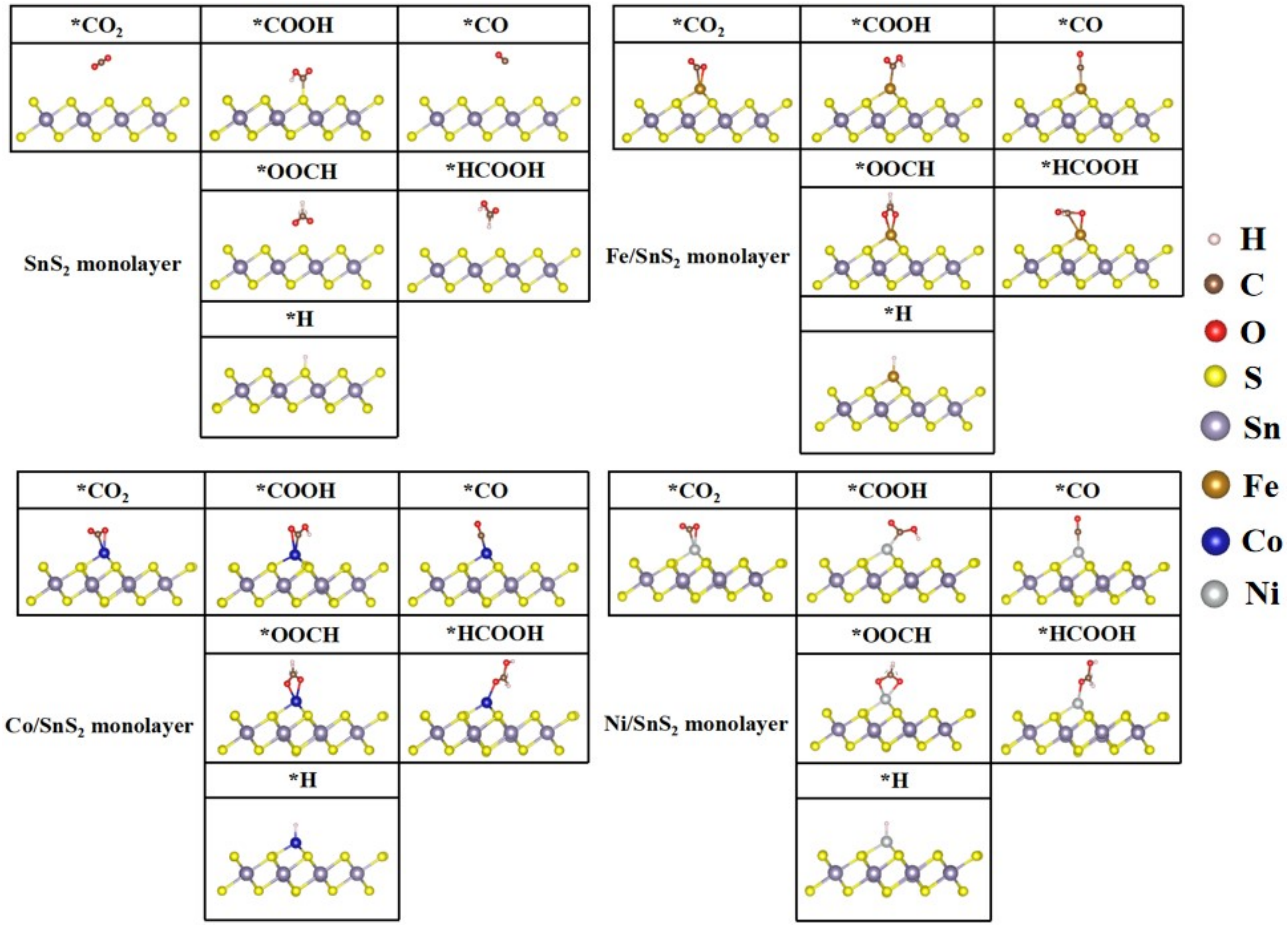

Figure S3. Key reaction intermediate species for the CO_2 reduction reaction with two electrons transfer on SnS_2 monolayers.

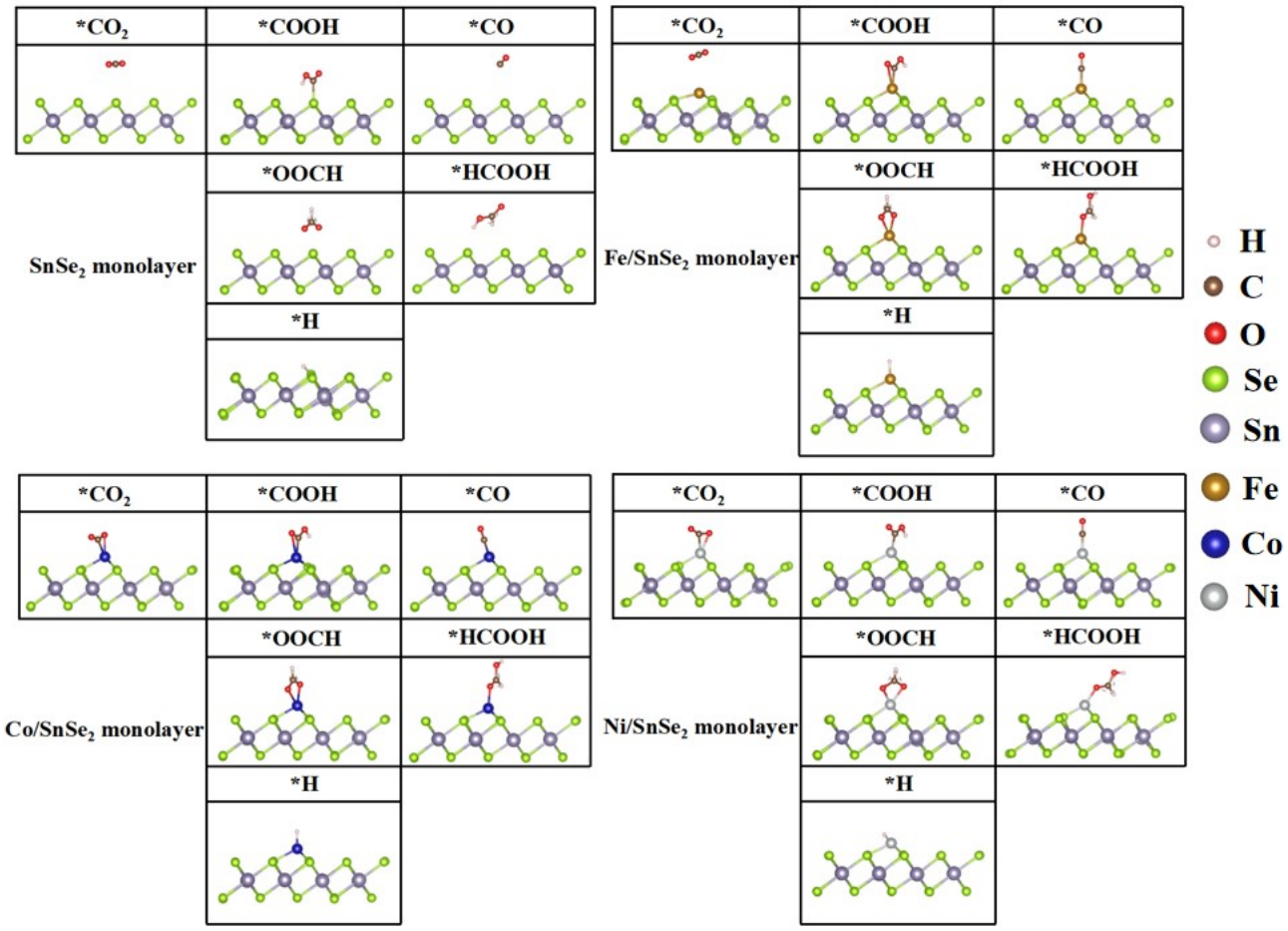

Figure S4. Key reaction intermediate species for the CO_2 reduction reaction with two electrons transfer on $SnSe_2$ monolayers.

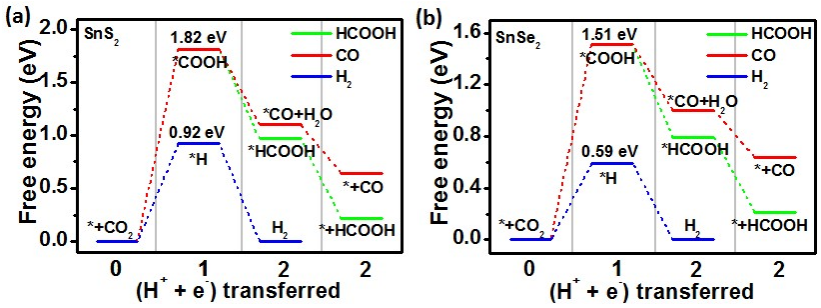

Figure S5. Free energy diagram for electroreduction of CO_2 to HCOOH (green), CO (red) and H_2 (blue) on the surface of pristine (a) SnS_2 and (b) $SnSe_2$ monolayers.

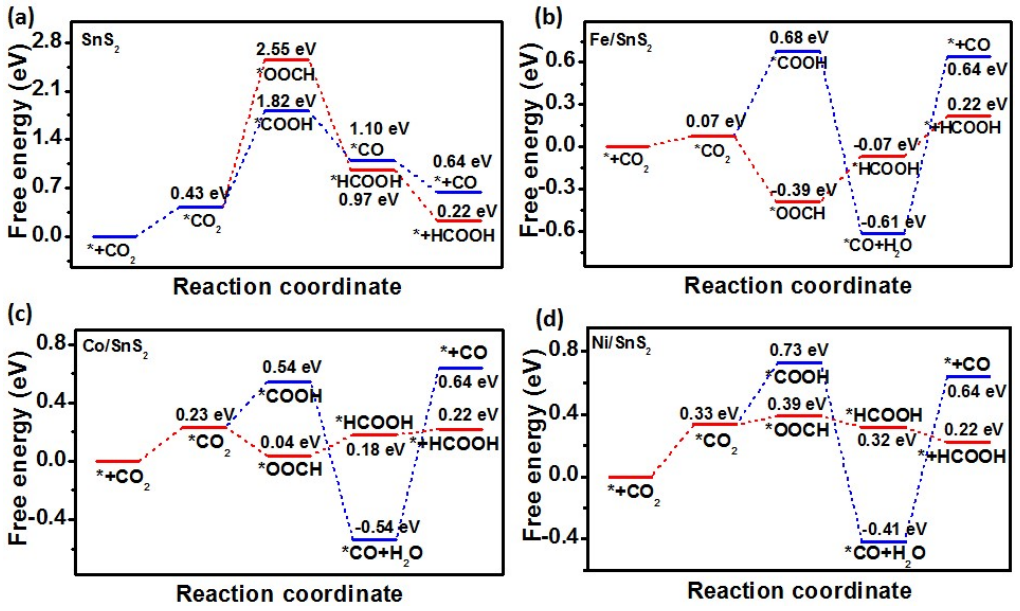

Figure S6. Free energy diagram for electroreduction of CO_2 to HCOOH (red line) and CO (blue line) on the surface of (a) pristine SnS_2, (b) Fe/SnS_2, (c) Co/SnS_2 and (d) Ni/SnS_2 monolayers.

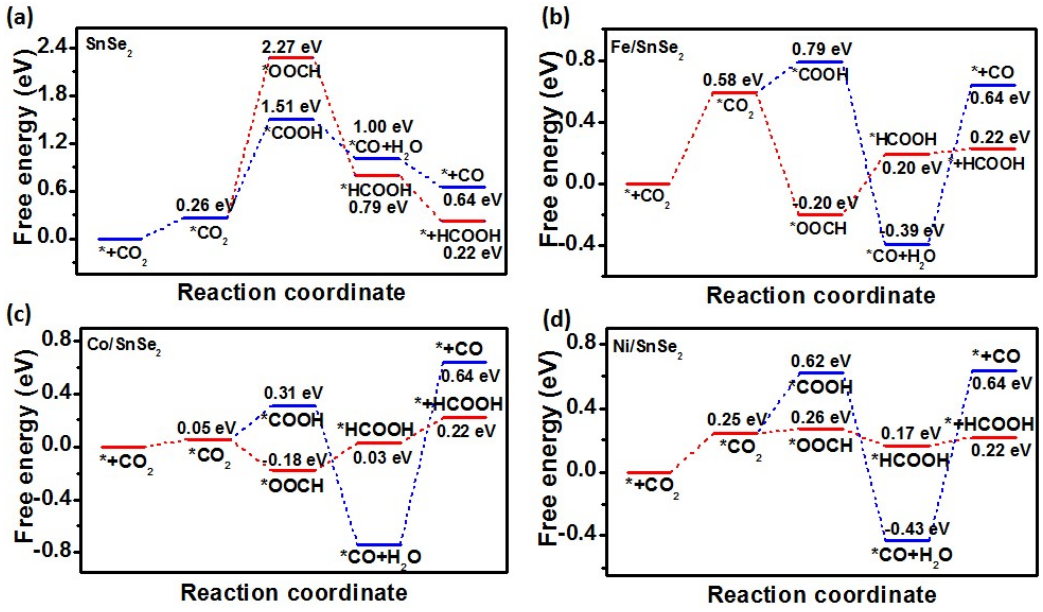

Figure S7. Free energy diagram for electroreduction of CO_2 to HCOOH (red line) and CO (blue line) on the surface of (a) pristine $SnSe_2$, (b) $Fe/SnSe_2$, (c) $Co/SnSe_2$ and (d) $Ni/SnSe_2$ monolayers.

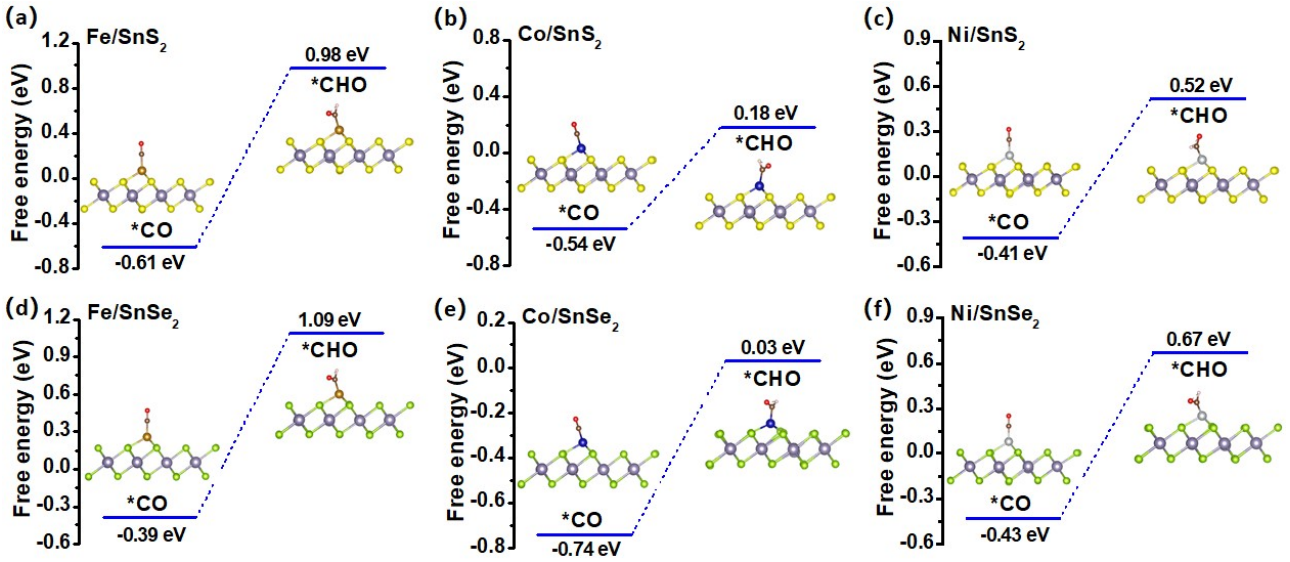

Figure S8. The calculated free energy changes of *CO to *CHO during the CRR for Fe, Co and Ni adsorbed on (a)-(c) SnS_2 and (d)-(f) $SnSe_2$ monolayers.

The *CO intermediate added one H^+ and one e can form *CHO intermediate during the CO_2 reduction reaction (CRR). And the Gibbs free energy of *CHO is calculated by the equation of $\Delta G_{*\mathrm{CHO}} = G_{*\mathrm{CHO}} + G_{\mathrm{H_2O}} - G_{*} - G_{\mathrm{CO_2}} - \frac{1}{2}G_{\mathrm{H_2}}$, where $G_{*\mathrm{CHO}}$ the free energy of the system with one adsorbed CHO, G_{*} is the free energy of the system itself, $G_{\mathrm{H_2O}}$, $G_{\mathrm{H_2}}$ and $G_{\mathrm{CO_2}}$ are the free energy of H_2O, H_2 and CO_2 molecules, respectively. Our calculated results show that the free energy barrier (from *CO + H^+ + e to *CHO) is high in this protonation step during CRR for TM/SnX_2 (X= S and Se) monolayers (shown in Figure S8), indicating unfavorable formation of formaldehyde and methanol product. Moreover, the first protonation step (* + CO_2 + H^+ + e to *COOH) of TM/SnX_2 (X= S and Se) monolayers is endothermic and the free energy barrier is high, suggesting the difficulty of this process.

Table S2. The Potential Determining Steps (PDS), Limiting Potentials U_L (V) and Overpotentials (η/V) for CO_2 Reduction to CO on the Different Surface of SnX_2 (X=S and Se) Monolayers

surface	PDS	U_L	η
pristine SnS_2	$*CO_2 \rightarrow *COOH$	−1.39	1.27
Fe/SnS_2	$*CO \rightarrow CO$	−1.25	1.13
Co/SnS_2	$*CO \rightarrow CO$	−1.18	1.06
Ni/SnS_2	$*CO \rightarrow CO$	−1.05	0.93
pristine $SnSe_2$	$*CO_2 \rightarrow *COOH$	−1.24	1.12
Fe/$SnSe_2$	$*+CO_2 \rightarrow *CO_2$	−1.03	0.91
Co/$SnSe_2$	$*CO \rightarrow CO$	−1.38	1.26
Ni/$SnSe_2$	$*CO \rightarrow CO$	−1.07	0.95

Table S3. **The Limiting Potentials U_L (V) and Overpotentials (η/V) for CRR and HER on the Different Surface of SnX_2 (X=S and Se) Monolayers**

surface	U_L/V(HCOOH)	η/V(HCOOH)	U_L/V(CO)	η/V(CO)	U_L/V(H_2)
pristine SnS_2	–1.39	1.19	–1.39	1.27	–0.92
Fe/SnS_2	–0.32	0.12	–1.25	1.13	–0.31
Co/SnS_2	–0.23	0.03	–1.18	1.06	–0.49
Ni/SnS_2	–0.33	0.13	–1.05	0.93	–0.80
pristine $SnSe_2$	–1.24	1.04	–1.24	1.12	–0.59
Fe/$SnSe_2$	–0.59	0.39	–1.03	0.91	–0.47
Co/$SnSe_2$	–0.21	0.01	–1.38	1.26	–0.30
Ni/$SnSe_2$	–0.25	0.05	–1.07	0.95	–0.45