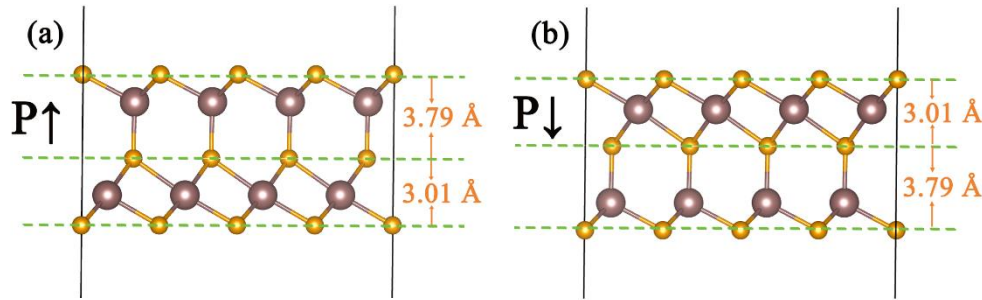


Tunable C₂ selectivity in CO electroreduction via charge-asymmetric dual-metal catalysts on ferroelectric In₂Se₃Dongqiu Zhao¹, Xiao Tang², Yixin Zhang¹, Shuli Liu¹, Di Yuan¹, Chen Long¹, Lin Ju^{1,†}, Liangzhi Kou^{3,‡}¹School of Physics and Electric Engineering, Anyang Normal University, Anyang 455000, China²College of Science, Nanjing Forestry University, Nanjing 210037, China³School of Mechanical, Medical and Process Engineering, Queensland University of Technology, Brisbane QLD 4001, AustraliaCorresponding authors. E-mail: [†]julin@aynu.edu.cn, [‡]liangzhi.kou@qut.edu.au

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**Fig. S1** The out-of-plane polarization in bare α -In₂Se₃ monolayer, (a) P $\uparrow$ and (b) P $\downarrow$.**Formation energy**The formation energy (E_{for}) for the ferroelectric DACs is calculated by the following equation,

$$E_{\text{for}} = E_{\text{total}} - E_{\text{sub}} - E_{\text{TM}_1} - E_{\text{TM}_2}, \quad (\text{ES1})$$

where E_{sub} and E_{total} are the total energies of the substrate without and with the added two transition metal single atoms, respectively. $E_{\text{TM}_1}/E_{\text{TM}_2}$ is calculated by dividing the energy of the most stable unit cell of a metal by the atomic stoichiometry inside the cell.

Desorption energyThe desorption energy (E_{des}) for the ferroelectric DACs is calculated by the following equation,

$$E_{\text{des}} = E_{\text{total}} - E_{\text{sub}} - E_{\text{TM}_1}^* - E_{\text{TM}_2}^*, \quad (\text{ES2})$$

where $E_{\text{TM}_1}^*/E_{\text{TM}_2}^*$ is the energy of isolated TM atom.**Table S1** The desorption energy (E_{des} , in eV) and formation energy (E_{for} , in eV) for three TM₁-TM₂@P $\uparrow$ -In₂Se₃ hetero-configurations (Ni-Nb, Pd-Nb, and Rh-Nb) and Nb-Nb@P $\uparrow$ -In₂Se₃ homo-configuration.

Catalyst	E_{des} (eV)	E_{for} (eV)
Ni-Nb@P $\uparrow$ -In ₂ Se ₃	-12.94	2.74
Pd-Nb@P $\uparrow$ -In ₂ Se ₃	-12.27	1.91
Rh-Nb@P $\uparrow$ -In ₂ Se ₃	-14.35	2.26
Nb-Nb@P $\uparrow$ -In ₂ Se ₃	-14.23	6.65

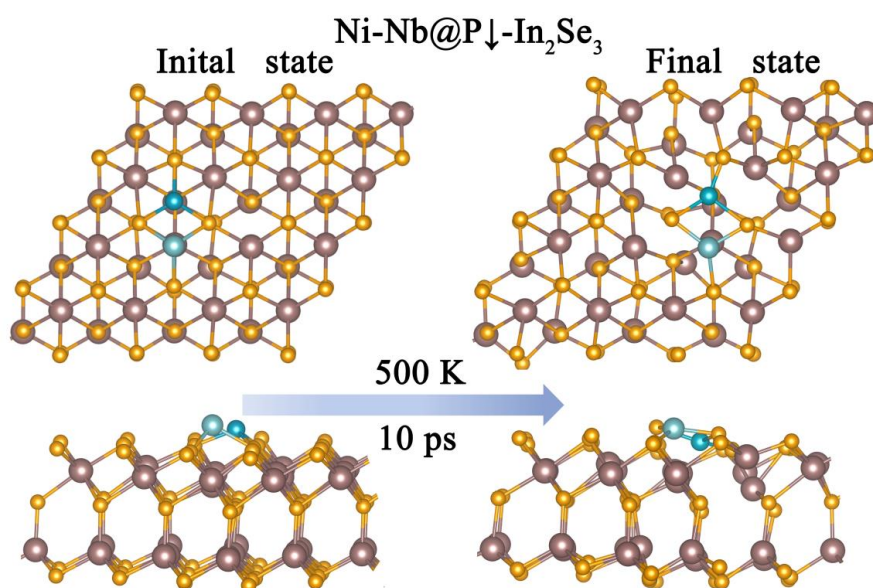


Fig. S2 Top and side views of the initial and final states of the Ni-Nb@P↓-In₂Se₃ configuration from AIMD simulations at 500 K and a duration of 10 ps.

Table S2 The number of electrons transferred (in e) between the adsorbed TM single atoms and the ferroelectric substrates for Pd-Nb@In₂Se₃, Rh-Nb@In₂Se₃, Ni-Nb@In₂Se₃ and Nb-Nb@In₂Se₃ under P↓ and P↑ states. Negative and positive values represent electron loss and gain, respectively.

Catalyst	Pd-Nb@-In ₂ Se ₃		Rh-Nb@-In ₂ Se ₃		Ni-Nb@In ₂ Se ₃		Nb-Nb@In ₂ Se ₃	
TM atoms	Pd	Nb	Rh	Nb	Ni	Nb	Nb	Nb
P↓	0.16	-2.01	0.24	-1.96	-0.12	-1.91	-1.75	-1.37
P↑	0.15	-1.87	0.11	-2.07	-0.06	-1.81	-1.96	-1.79

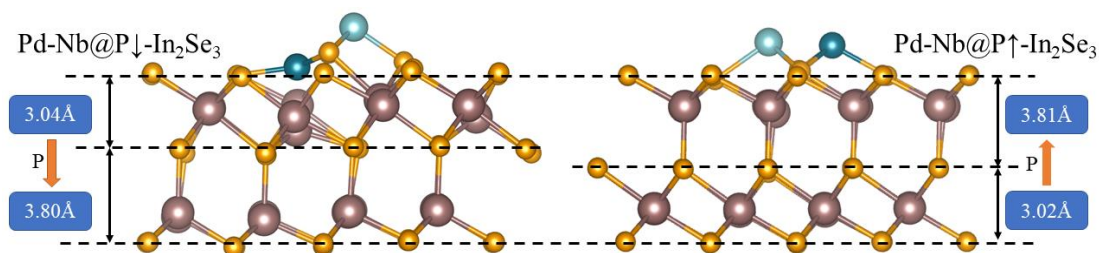


Fig. S3 The out-of-plane polarization in Pd-Nb@In₂Se₃ systems (P↓ and P↑).

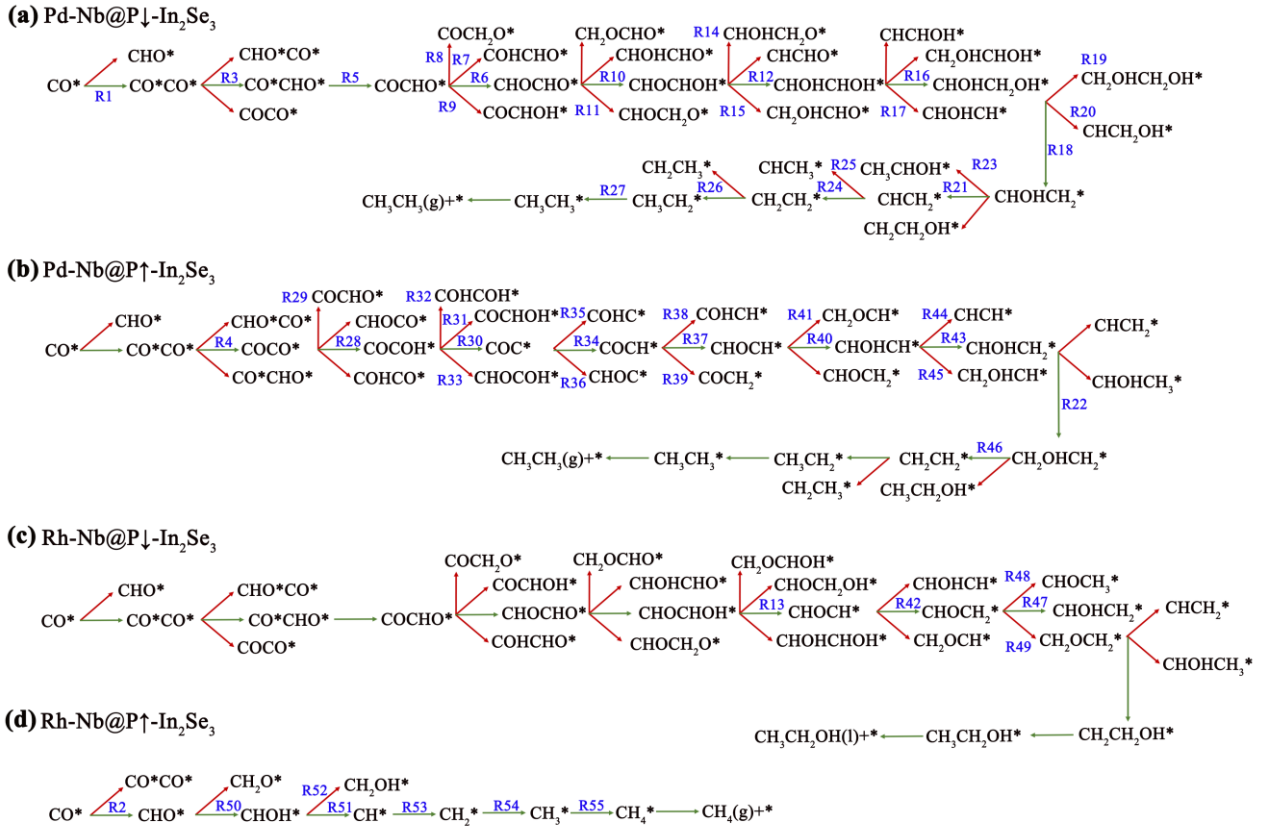


Fig. S4 The search process for the minimum energy reaction pathways of the CO reduction reactions on (a) $\text{Pd-Nb@P}\downarrow\text{-In}_2\text{Se}_3$, (b) $\text{Pd-Nb@P}\uparrow\text{-In}_2\text{Se}_3$, (c) $\text{Rh-Nb@P}\downarrow\text{-In}_2\text{Se}_3$, and (d) $\text{Rh-Nb@P}\uparrow\text{-In}_2\text{Se}_3$. The red arrows denote disallowed reaction paths, while the green arrows stand for the enabled ones.

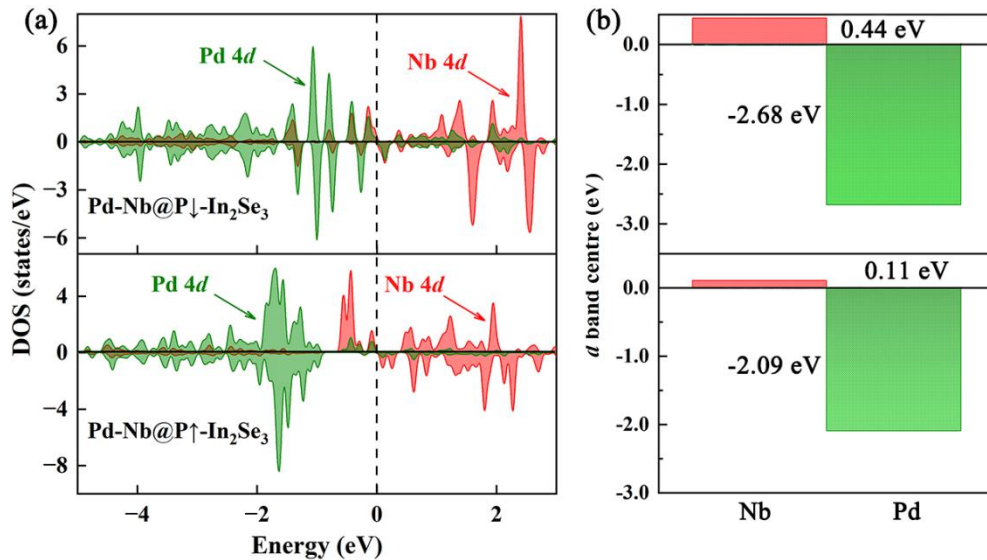


Fig. S5 Projected density of states (PDOS) of 4d orbitals for the Pd (red) and Nb (green) in $\text{Pd-Nb@In}_2\text{Se}_3$ under $\text{P}\downarrow$ and $\text{P}\uparrow$ states. The dashed lines indicate the Fermi level. (b) The corresponding d band center positions for the Pd (red) and Nb (green), showing their shifts with polarization switching.

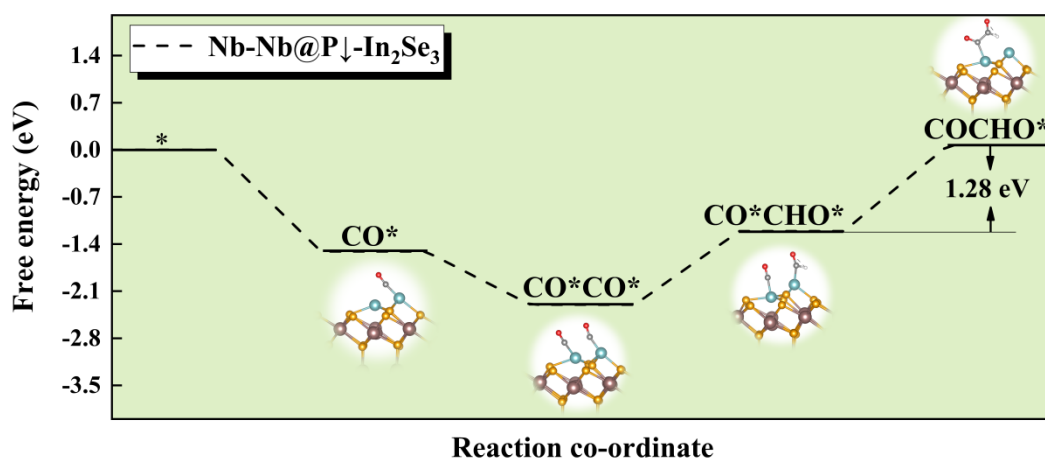


Fig. S6 Nb-Nb@P↓-In₂Se₃ carries the CORR path, which ends in a C-C coupling step.

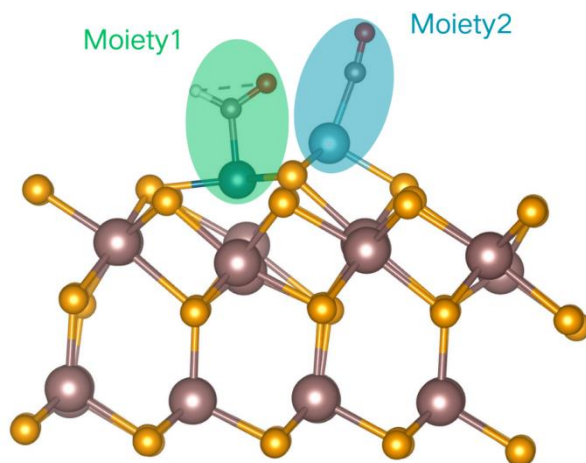


Fig. S7 Schematic for the partition of the two moieties on the intermediates before C-C coupling reaction. Moiety1 and moiety2 separately consist of the single TM atoms with their attached C_xH_yO_z group.

Reaction free energy change

The reaction free energy change (ΔG) for each elementary step is calculated based on the computational hydrogen electrode (CHE) model proposed by Nørskov and co-workers by the following equation:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + eU + \Delta G_{\text{pH}}, \quad (\text{ES2})$$

where ΔE is the reaction energy obtained from DFT calculations. ΔE_{ZPE} and $T\Delta S$ are the contributions of the zero-point energy and entropy to ΔG , respectively, which are obtained from the vibrational frequency. T is the temperature and taken as 298.15 K, and ΔS is the entropy change.

Table S3 Zero-point energy correction (E_{ZPE}) and entropy contribution (TS , $T=298.15$ K) of molecules.

Species	TS (eV)	E_{ZPE} (eV)
CO	0.11	0.14
H ₂ O	0.18	0.57

CH ₄	0.17	1.19
C ₂ H ₄	0.15	1.38
CH ₃ CH ₂ OH	0.25	2.11
C ₃ H ₆	0.20	1.98

Table S4 The total energy (E), zero-point energy correction (E_{ZPE}), entropy contribution (TS , $T=298.15$ K), and the Gibbs free energy (G) of adsorbates along the reaction pathway on Pd-Nb@P↓-In₂Se₃, where * represents the adsorption site.

Species	E (eV)	TS (eV)	E_{ZPE} (eV)	G (eV)
CO*	-334.16	0.15	0.18	-334.13
CO*CO*	-349.39	0.24	0.39	-349.24
CO*CHO*	-352.35	0.20	0.64	-351.91
COCHO*	-352.55	0.20	0.68	-352.07
CHOCHO*	-355.89	0.17	0.92	-355.14
CHOHCHO*	-360.15	0.19	1.30	-359.04
CHOHCHOH*	-364.45	0.26	1.65	-363.06
CH ₂ OHCHOH*	-367.88	0.29	1.92	-366.25
CH ₂ OHCH*	-357.09	0.23	1.47	-355.85
CH ₂ CH*	-346.49	0.19	1.08	-345.60
CH ₂ CH ₂ *	-350.66	0.19	1.37	-349.48
CH ₂ CH ₃ *	-353.31	0.16	1.60	-351.87
CH ₃ CH ₃ *	-358.91	0.20	2.00	-357.11

Table S5 The total energy (E), zero-point energy correction (E_{ZPE}), entropy contribution (TS , $T=298.15$ K), and the Gibbs free energy (G) of adsorbates along the reaction pathway on Pd-Nb@P↑-In₂Se₃, where * represents the adsorption site.

Species	E (eV)	TS (eV)	E_{ZPE} (eV)	G (eV)
CO*	-331.60	0.07	0.19	-331.49
CO*CO*	-346.98	0.21	0.37	-346.82
COCO*	-347.81	0.21	0.42	-347.60
COCOH*	-350.43	0.22	0.72	-349.94
COC*	-340.24	0.13	0.34	-340.04
COCH*	-344.06	0.18	0.60	-343.64
CHOCH*	-347.82	0.15	0.94	-347.04
CHOHCH*	-350.79	0.22	1.22	-349.79
CHOHCH ₂ *	-356.24	0.24	1.51	-354.96
CH ₂ OHCH ₂ *	-358.58	0.20	1.83	-356.94
CH ₂ CH ₂ *	-348.99	0.12	1.39	-347.72
CH ₂ CH ₃ *	-351.90	0.20	1.69	-350.41

CH ₃ CH ₃ *	-355.85	0.15	1.98	-354.02
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Table S6 The total energy (E), zero-point energy correction (E_{ZPE}), entropy contribution (TS , $T=298.15$ K), and the Gibbs free energy (G) of adsorbates along the reaction pathway on Rh-Nb@P↓-In₂Se₃, where * represents the adsorption site.

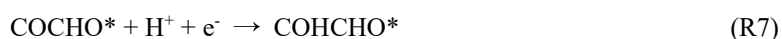
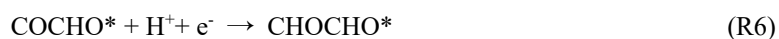
Species	E (eV)	TS (eV)	E_{ZPE} (eV)	G (eV)
CO*	-336.28	0.14	0.21	-336.21
CO*CO*	-351.48	0.24	0.38	-351.34
CO*CHO*	-354.73	0.25	0.65	-354.33
COCHO*	-355.00	0.27	0.71	-354.56
CHOCHO*	-359.56	0.20	1.03	-358.73
CHOHCHO*	-363.35	0.25	1.36	-362.24
CHOHCHOH*	-352.28	0.15	0.94	-351.49
CH ₂ OHCHOH*	-356.47	0.25	1.21	-355.51
CH ₂ OHCH*	-359.33	0.16	1.51	-357.98
CH ₂ OHCH ₂	-362.56	0.30	1.82	-361.04
CH ₂ OHCH ₃	-367.30	0.27	2.13	-365.44

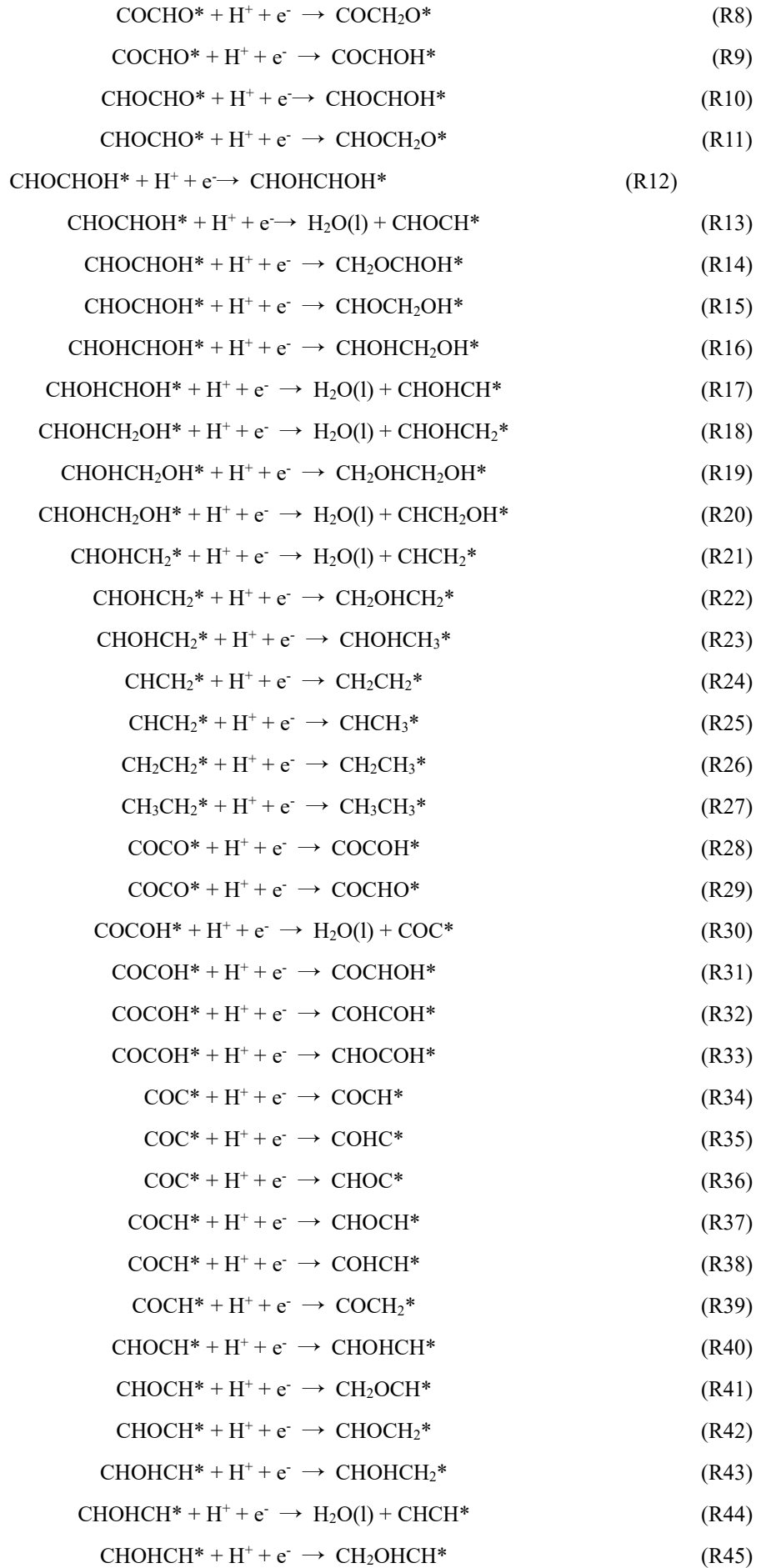
Table S7 The total energy (E), zero-point energy correction (E_{ZPE}), entropy contribution (TS , $T=298.15$ K), and the Gibbs free energy (G) of adsorbates along the reaction pathway on Rh-Nb@P↑-In₂Se₃, where * represents the adsorption site.

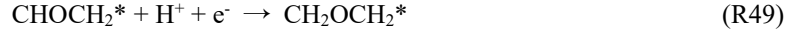
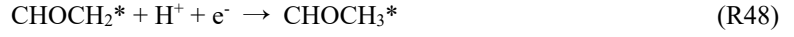
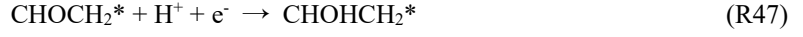
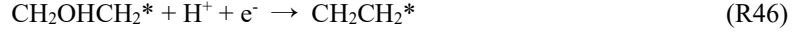
Species	E (eV)	TS (eV)	E_{ZPE} (eV)	G (eV)
CO	-333.52	0.09	0.20	-333.41
CHO	-337.20	0.15	0.46	-336.89
CHOH	-340.59	0.18	0.78	-339.99
CH	-329.77	0.08	0.34	-329.51
CH ₂	-334.08	0.14	0.59	-333.63
CH ₃	-337.77	0.13	0.91	-336.99
CH ₄	-341.53	0.12	1.21	-340.44

Elementary steps in CORR and HER

All the hydrogenation reactions (R1~R56) considered in the search process for the minimum energy reaction pathways of the CO reduction reactions can be written as:







The hydrogenation reactions (R57~R59) for HER can be written as:



Therefore, when $U = 0$ V and $\text{pH} = 0$, ΔG for each elementary step (R1-R56) can be rewritten as:

$$\Delta G_{R1} = G_{\text{CO}^*\text{CO}^*} - G_{\text{CO}^*} - G_{\text{CO}} \quad (\text{ES3})$$

$$\Delta G_{R2} = G_{\text{CHO}^*} - G_{\text{CO}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES4})$$

$$\Delta G_{R3} = G_{\text{CO}^*\text{CHO}^*} - G_{\text{CO}^*\text{CO}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES5})$$

$$\Delta G_{R4} = G_{\text{COCO}^*} - G_{\text{CO}^*\text{CO}^*} \quad (\text{ES6})$$

$$\Delta G_{R5} = G_{\text{CO}^*\text{CHO}^*} - G_{\text{COCHO}^*} \quad (\text{ES7})$$

$$\Delta G_{R6} = G_{\text{CHOCHO}^*} - G_{\text{COCHO}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES8})$$

$$\Delta G_{R7} = G_{\text{COHCHO}^*} - G_{\text{COCHO}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES9})$$

$$\Delta G_{R8} = G_{\text{COCH}_2\text{O}^*} - G_{\text{COCHO}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES10})$$

$$\Delta G_{R9} = G_{\text{COCHOH}^*} - G_{\text{COCHO}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES11})$$

$$\Delta G_{R10} = G_{\text{CHOCHOH}^*} - G_{\text{CHOCHO}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES12})$$

$$\Delta G_{R11} = G_{\text{CHOCH}_2\text{O}^*} - G_{\text{CHOCHO}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES13})$$

$$\Delta G_{R12} = G_{\text{CHOHCHOH}^*} - G_{\text{CHOCHOH}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES14})$$

$$\Delta G_{R13} = G_{\text{CHOCH}^*} + G_{\text{H}_2\text{O}} - G_{\text{CHOCHOH}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES15})$$

$$\Delta G_{R14} = G_{\text{CH}_2\text{OCHOH}^*} - G_{\text{CHOCHOH}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES16})$$

$$\Delta G_{R15} = G_{\text{CHOCH}_2\text{OH}^*} - G_{\text{CHOCHOH}^*} - \frac{1}{2}G_{\text{H}_2} \quad (\text{ES17})$$

$$\Delta G_{R16} = G_{CHOHCH_2OH*} - G_{CHOHCHOH*} - \frac{1}{2}G_{H_2} \quad (ES18)$$

$$\Delta G_{R17} = G_{CHOHCH*} + G_{H_2O} - G_{CHOHCHOH*} - \frac{1}{2}G_{H_2} \quad (ES19)$$

$$\Delta G_{R18} = G_{CHOHCH_2OH*} + G_{H_2O} - G_{CHOHCH_2*} - \frac{1}{2}G_{H_2} \quad (ES20)$$

$$\Delta G_{R19} = G_{CH_2OHCH_2OH*} - G_{CHOHCH_2OH*} - \frac{1}{2}G_{H_2} \quad (ES21)$$

$$\Delta G_{R20} = G_{CHCH_2OH*} + G_{H_2O} - G_{CHOHCH_2OH*} - \frac{1}{2}G_{H_2} \quad (ES22)$$

$$\Delta G_{R21} = G_{CHCH_2*} + G_{H_2O} - G_{CHOHCH_2*} - \frac{1}{2}G_{H_2} \quad (ES23)$$

$$\Delta G_{R22} = G_{CH_2OHCH_2*} - G_{CHOHCH_2*} - \frac{1}{2}G_{H_2} \quad (ES24)$$

$$\Delta G_{R23} = G_{CHOHCH_3*} - G_{CHOHCH_2*} - \frac{1}{2}G_{H_2} \quad (ES25)$$

$$\Delta G_{R24} = G_{CH_2CH_2*} - G_{CHCH_2*} - \frac{1}{2}G_{H_2} \quad (ES26)$$

$$\Delta G_{R25} = G_{CHCH_3*} - G_{CHCH_2*} - \frac{1}{2}G_{H_2} \quad (ES27)$$

$$\Delta G_{R26} = G_{CH_2CH_3*} - G_{CH_2CH_2*} - \frac{1}{2}G_{H_2} \quad (ES28)$$

$$\Delta G_{R27} = G_{CH_3CH_3*} - G_{CH_2CH_3*} - \frac{1}{2}G_{H_2} \quad (ES29)$$

$$\Delta G_{R28} = G_{COCO*} - G_{COCO*} - \frac{1}{2}G_{H_2} \quad (ES30)$$

$$\Delta G_{R29} = G_{COCHO*} - G_{COCO*} - \frac{1}{2}G_{H_2} \quad (ES31)$$

$$\Delta G_{R30} = G_{COC*} + G_{H_2O} - G_{COCO*} - \frac{1}{2}G_{H_2} \quad (ES32)$$

$$\Delta G_{R31} = G_{COCHOH*} - G_{COCO*} - \frac{1}{2}G_{H_2} \quad (ES33)$$

$$\Delta G_{R32} = G_{COHCOH*} - G_{COCO*} - \frac{1}{2}G_{H_2} \quad (ES34)$$

$$\Delta G_{R33} = G_{CHOCO*} - G_{COCO*} - \frac{1}{2}G_{H_2} \quad (ES35)$$

$$\Delta G_{R34} = G_{COCH*} - G_{COC*} - \frac{1}{2}G_{H_2} \quad (ES36)$$

$$\Delta G_{R35} = G_{COHC*} - G_{COC*} - \frac{1}{2}G_{H_2} \quad (ES37)$$

$$\Delta G_{R36} = G_{CHOC*} - G_{COC*} - \frac{1}{2}G_{H_2} \quad (ES38)$$

$$\Delta G_{R37} = G_{CHOCH*} - G_{COCH*} - \frac{1}{2}G_{H_2} \quad (ES39)$$

$$\Delta G_{R38} = G_{COHCH*} - G_{COCH*} - \frac{1}{2}G_{H_2} \quad (ES40)$$

$$\Delta G_{R39} = G_{COCH_2^*} - G_{COCH^*} - \frac{1}{2}G_{H_2} \quad (ES41)$$

$$\Delta G_{R40} = G_{COHCH_2^*} - G_{COHCH^*} - \frac{1}{2}G_{H_2} \quad (ES42)$$

$$\Delta G_{R41} = G_{CHOHCH_2^*} - G_{CHOCH^*} - \frac{1}{2}G_{H_2} \quad (ES43)$$

$$\Delta G_{R42} = G_{CHOCH_2^*} - G_{CHOCH^*} - \frac{1}{2}G_{H_2} \quad (ES44)$$

$$\Delta G_{R43} = G_{CHOHCH_2^*} - G_{CHOHCH^*} - \frac{1}{2}G_{H_2} \quad (ES45)$$

$$\Delta G_{R44} = G_{CHCH^*} + G_{H_2O} - G_{CHOHCH^*} - \frac{1}{2}G_{H_2} \quad (ES46)$$

$$\Delta G_{R45} = G_{CH_2OHCH^*} - G_{CHOHCH^*} - \frac{1}{2}G_{H_2} \quad (ES47)$$

$$\Delta G_{R46} = G_{CH_2CH_2^*} - G_{CH_2OHCH_2^*} - \frac{1}{2}G_{H_2} \quad (ES48)$$

$$\Delta G_{R47} = G_{CHOHCH_2^*} - G_{COHCH_2^*} - \frac{1}{2}G_{H_2} \quad (ES49)$$

$$\Delta G_{R48} = G_{CHOCH_3^*} - G_{COHCH_2^*} - \frac{1}{2}G_{H_2} \quad (ES50)$$

$$\Delta G_{R49} = G_{CH_2OCH_2^*} - G_{COHCH_2^*} - \frac{1}{2}G_{H_2} \quad (ES51)$$

$$\Delta G_{R50} = G_{CHOH^*} - G_{CHO^*} - \frac{1}{2}G_{H_2} \quad (ES52)$$

$$\Delta G_{R51} = G_{CH^*} + G_{H_2O} - G_{CHOH^*} - \frac{1}{2}G_{H_2} \quad (ES53)$$

$$\Delta G_{R52} = G_{CH_2OH} - G_{CHOH^*} - \frac{1}{2}G_{H_2} \quad (ES54)$$

$$\Delta G_{R53} = G_{CH_2} - G_{CH^*} - \frac{1}{2}G_{H_2} \quad (ES55)$$

$$\Delta G_{R54} = G_{CH_3} - G_{CH_2^*} - \frac{1}{2}G_{H_2} \quad (ES56)$$

$$\Delta G_{R55} = G_{CH_4} - G_{CH_3^*} - \frac{1}{2}G_{H_2} \quad (ES57)$$

$$\Delta G_{R56} = G_{H^*} - G_* - \frac{1}{2}G_{H_2} \quad (ES58)$$

$$\Delta G_{R57} = G_{H_2} + G_* - \frac{1}{2}G_{H_2} \quad (ES59)$$