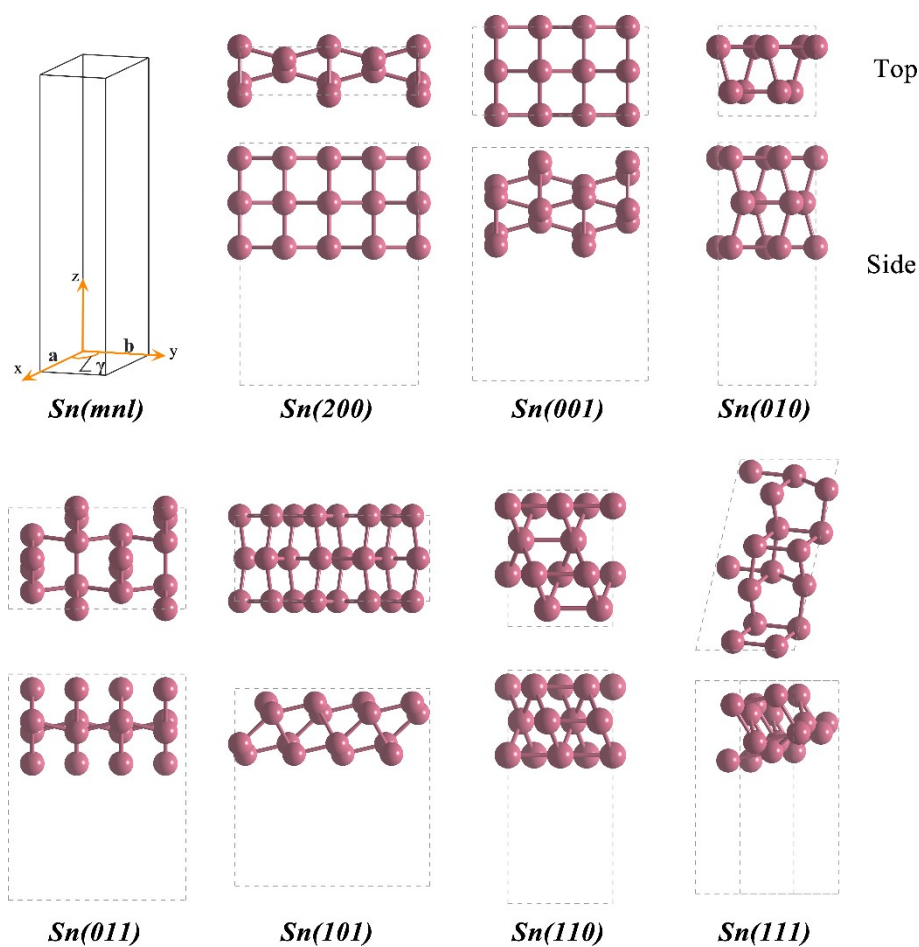


Supporting Information



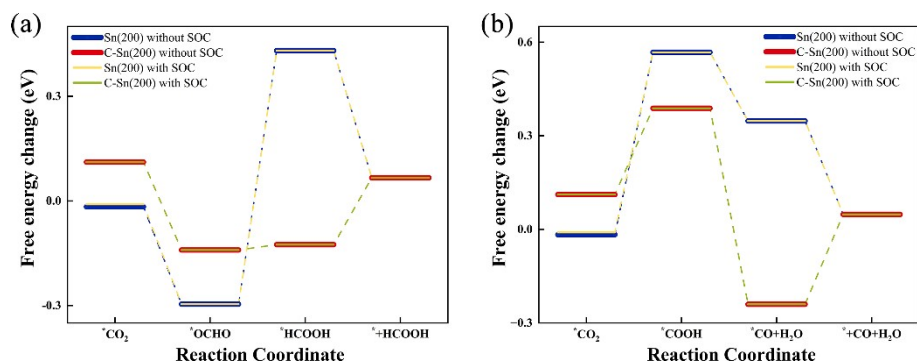
SI-Figure 1. The structure of Sn material in different low-index surfaces. The symbols m , n , and l denote the index of the surface in x , y , and z directions, respectively.

SI-Table 1. The surface energy (E_{sur}), lattice constant (a , b), lattice angle (γ), and surface area (S) corresponding to Sn in various low-index surfaces. The symbols a , b , γ , and S can be found in **SI-Figure 1**.

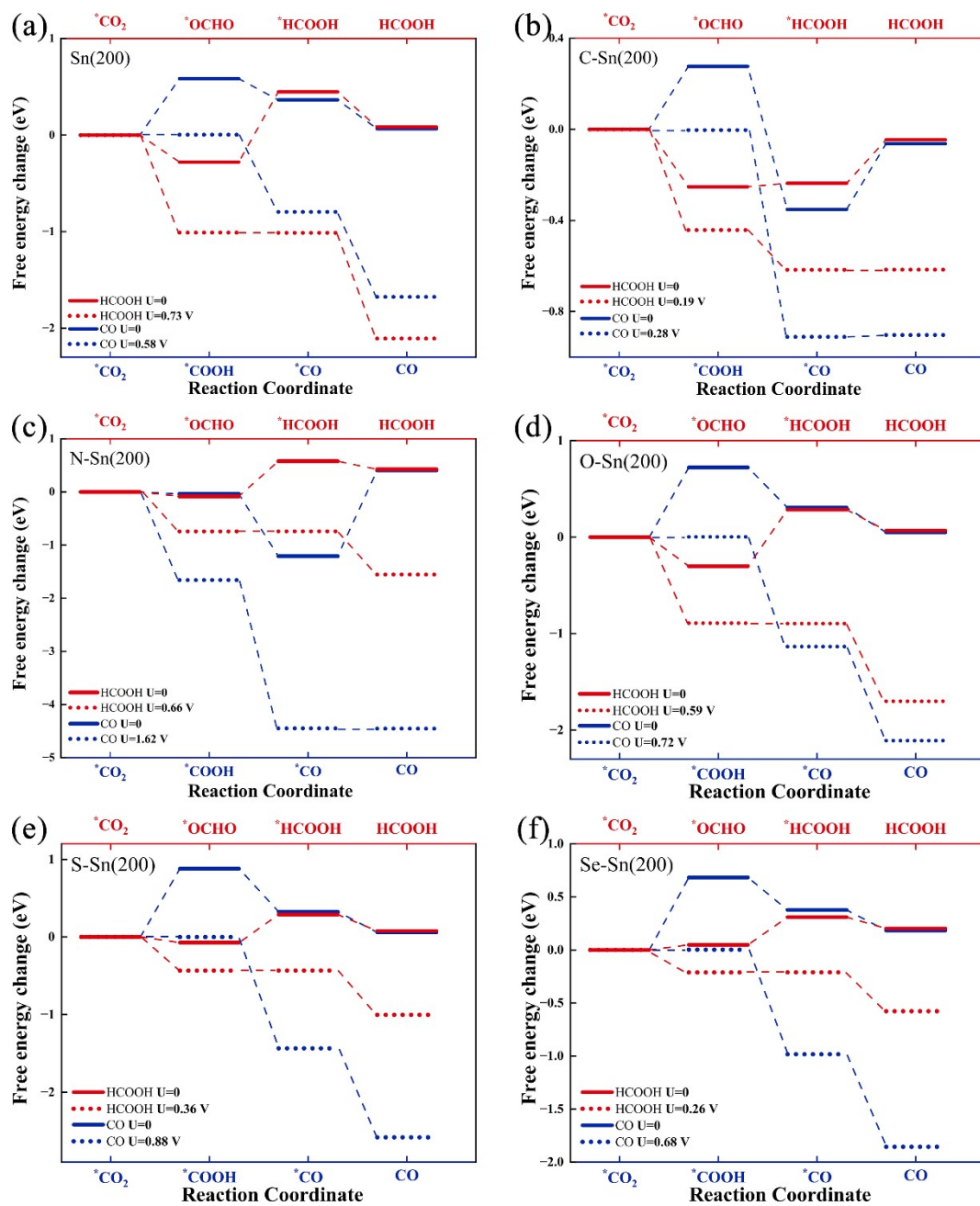
Sn Surface	E_{sur} (meV)	a (Å)	b (Å)	γ (°)	S (Å ²)
(001)	45.75	5.84	5.84	90.00	34.13
(010)	40.28	3.17	5.84	90.00	18.53
(011)	36.90	5.84	6.65	90.00	38.83
(100)	37.88	5.84	3.17	90.00	18.53
(101)	36.86	6.65	5.84	90.00	38.83
(110)	47.54	3.17	8.26	90.00	26.21
(111)	41.22	6.65	6.65	76.80	43.03
(200)	36.50	5.84	3.18	90.00	18.58

SI-Table 2. The change of Gibbs free energy (ΔG) at possible overpotentials during the CO_2 reduction process.

Product	Reaction process	ΔG (eV) associated overpotential					
		Sn(200)	C-Sn(200)	N-Sn(200)	O-Sn(200)	S-Sn(200)	Se-Sn(200)
HCOOH	$^*\text{CO}_{2(\text{ads})} + (\text{H}^+ + \text{e}^-) \rightarrow ^*\text{OCHO}_{(\text{ads})}$		0.02				0.05
	$^*\text{OCHO}_{(\text{ads})} + (\text{H}^+ + \text{e}^-) \rightarrow ^*\text{HCOOH}_{(\text{ads})}$	0.73		0.66	0.59	0.36	0.26
	$^*\text{HCOOH}_{(\text{ads})} \rightarrow ^* + \text{HCOOH}_{(\text{g})}$		0.19				
	$^*\text{CO}_{2(\text{ads})} + (\text{H}^+ + \text{e}^-) \rightarrow ^*\text{COOH}_{(\text{ads})}$	0.58	0.28		0.72	0.88	0.68
CO	$^*\text{COOH}_{(\text{ads})} + (\text{H}^+ + \text{e}^-) \rightarrow ^*\text{CO}_{(\text{ads})} + \text{H}_2\text{O}_{(\text{g})}$						
	$^*\text{CO}_{(\text{ads})} \rightarrow \text{CO}_{(\text{g})}$		0.29	1.62			



SI-Figure 2. The influence of spin-orbit coupling (SOC) on CO_2RR activity. The reduction of CO_2 to HCOOH (a) and CO (b) at Sn(200) and C-Sn(200) surfaces.



SI-Figure 3. The effect of electrode potential U on the two-electronic CO₂ reduction to form HCOOH and CO at different Sn(200) related substrates, as (a) Sn(200), (b) C-Sn(200), (c) N-Sn(200), (d) O-Sn(200), (e) S-Sn(200) and (f) Se-Sn(200). It should be mentioned that the reductions to form HCOOH and CO are denoted in red and dark blue lines, respectively.