Electronic Supplementary Information

Two-dimensional ZnO for selective photoreduction of CO_2

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Table S1 Zero-point energy (ZPE) and entropic correction (*TS*) at T = 298 K for the molecules and intermediate species involved in CO_2 reduction on ZnO(*n*L) sheets to form various C_1 products. The ZPE and *TS* values of gaseous molecules were obtained from the NIST-JANAF thermodynamics table.[1] For the reaction intermediates, we calculated their vibrational frequencies and derived ZPE and *TS* using the thermodynamics model within the harmonic approximation.[2] The (ZPE – TS) values of intermediates are very similar for ZnO(*n*L) with different number of layers

Species	ZPE (eV)	*TS* (eV)	ZPE − *TS* (eV)
H_2	0.29	0.41	−0.12
H_2O	0.60	0.59	0.01
CO	0.14	0.62	−0.48
CO_2	0.31	0.67	−0.35
CH_2O	0.72	0.68	0.04
HCOOH	0.92	1.02	−0.10
CH_3OH	1.39	0.79	0.60
CH_4	1.20	0.58	0.62
CO_2*	0.37	0.13	0.24
COOH*	0.68	0.19	0.49
HCOO*	0.62	0.15	0.47
CO*	0.17	0.16	0.01
HCOOH*	0.96	0.25	0.71
HCO*	0.56	0.10	0.46
H_2CO*	0.84	0.11	0.73
H_2COH*	1.17	0.16	1.01
CH_2*	0.72	0.05	0.67
CH_3*	1.04	0.11	0.93

Table S2 Formation energy (ΔH) per formula unit, intralayer and interlayer Zn–O bond order, and adsorption energies of HCOOH and CO molecules (ΔE_{HCOOH*}, ΔE_{CO*}). The formation energy of ZnO(nL) is defined as $\Delta H = (E_{nL} - n/2\ E_{bulk}) / n$, where E_{nL} and E_{bulk} are the energies of ZnO(nL) film and bulk ZnO, respectively

ZnO(nL)	ΔH (eV)	Bond order		ΔE_{HCOOH*} (eV)	ΔE_{CO*} (eV)
		Intralayer	Interlayer		
1L	0.74	1.13	--	−0.09	−0.14
2L	0.48	1.19	−0.03	−0.08	−0.22
3L	0.38	1.20	−0.03	−0.47	−0.20
4L	0.32	1.23	−0.01	−0.48	−0.27
5L	0.29	1.25	0.00	−0.52	−0.36
6L	0.26	1.25	0.02	−0.94	−0.84
7L	0.24	1.25	0.03	−1.73	−0.96
8L	0.26	1.21	0.04	--	--
bulk	0	1.07	0.18	−0.75	−0.58

Table S3 Band gap (E_g) calculated by the PBE functional, Mulliken (Bader) charge on O and Zn atoms from surface and interior ZnO layers, and effective masses of electron and hole carriers calculated by the HSE06 functional for ZnO(nL) sheets. Negative charge means electron accumulation. m_0 is the electron rest mass

ZnO(nL)	E_g (eV)	Mulliken (Bader) charges (e)				Effective masses (m_0)	
		Surface		Interior		electron	hole
		O	Zn	O	Zn		
1L	1.67	−0.96 (−1.19)	+0.96 (+1.19)	--	--	0.32	0.31
2L	1.44	−0.89 (−1.22)	+0.89 (+1.22)	--	--	0.28	0.32
3L	1.31	−0.88 (−1.20)	+0.84 (+1.20)	−0.87 (−1.21)	+0.94 (+1.19)	0.26	0.31
4L	1.25	−0.87 (−1.9)	+0.82 (+1.18)	−0.86 (−1.19)	+0.91 (+1.19)	0.25	0.30
5L	1.20	−0.86 (−1.18)	+0.80 (+1.18)	−0.85 (−1.89)	+0.98 (+1.22)	0.25	0.30
6L	1.17	−0.86 (−1.21)	+0.79 (+1.20)	−0.85 (−1.20)	+0.94 (+1.21)	0.24	0.29
7L	1.14	−0.86 (−1.21)	+0.78 (+1.20)	−0.85 (−1.20)	+0.92 (+1.21)	0.24	0.29
8L	--	−0.84 (−1.21)	+0.77 (+1.11)	−0.84 (−1.20)	+0.88 (+1.24)	--	--
bulk	0.47	−0.87[3]	+0.82[3]	−0.83	+0.83	0.25	0.56

Table S4 Gibbs free energy of formation (ΔG) for each elementary steps of CO_2 reduction on ZnO(nL) sheets and bulk ZnO(0001) surface, given in the unit of eV

step	Reaction	ΔG^{1L}	ΔG^{2L}	ΔG^{3L}	ΔG^{4L}	ΔG^{5L}	ΔG^{6L}	ΔG^{bulk}
R1	$CO_2 \rightarrow CO_2$*	0.61	0.48	0.25	0.23	0.01	−0.36	−0.77
R2	CO_2* + H^+ + e^- → COOH*	1.12	0.75	0.43	0.11	−0.23	−0.37	0.52
R2’	CO_2* + H^+ + e^- → HCOO*	2.32	2.16	2.39	2.37	2.41	2.42	−0.67
R3	COOH* + H^+ + e^- → CO + H_2O	−1.62	−1.13	−0.57	−0.23	0.33	0.84	0.36
R3’	COOH* + H^+ + e^- → HCOOH*	−0.80	−0.29	−0.14	0.22	0.73	0.79	0.46
R4	HCOOH* → HCOOH	−0.72	−0.73	−0.33	−0.35	−0.29	0.15	0
R4’	HCOOH* + H^+ + e^- → HCO* + H_2O	0.74	0.23	0.06	−0.30	−0.79	−0.85	--
R5	HCO* + H^+ + e^- → H_2CO*	−0.58	−0.28	0.05	0.21	0.87	0.95	--
R6	H_2CO* → CH_2O	−0.90	−0.70	−0.45	−0.28	−0.39	0.04	--
R6’	H_2CO* + H^+ + e^- → H_2COH*	0.73	0.29	0.19	−0.19	−0.73	−0.55	--
R7	H_2COH* + H^+ + e^- → CH_3OH	−1.72	−1.09	−0.74	−0.18	0.24	0.50	--
R7’	H_2COH* + H^+ + e^- → CH_2* + H_2O	−0.52	−0.03	0.03	0.69	0.86	0.65	--
R8	CH_2* + H^+ + e^- → CH_3*	−0.10	−0.54	−0.66	−1.16	−1.43	−1.42	--
R9	CH_3* + H^+ + e^- → CH_4	−2.36	−1.77	−1.36	−0.97	−0.45	0.01	--

Table S5 Reduction potentials of CO_2 reduction with water to various C_1 products at pH = 7 relative to the vacuum level, which can be derived from the values referred to the normal hydrogen electrode (NHE) via $E_{VAC} = -E_{NHE} - 4.44$[4, 5]

Reaction	E_{VAC} (eV)
$CO_2 + 2H^+ + 2e \rightarrow CO + H_2O$	−3.91
$CO_2 + 2H^+ + 2e \rightarrow HCOOH$	−3.83
$CO_2 + 4H^+ + 4e \rightarrow CH_2O + H_2O$	−3.96
$CO_2 + 6H^+ + 6e \rightarrow CH_3OH + H_2O$	−4.06
$CO_2 + 8H^+ + 8e \rightarrow CH_4 + 2H_2O$	−4.20
$2H^+ + 2e \rightarrow H_2$	−4.03
$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e$	−5.26

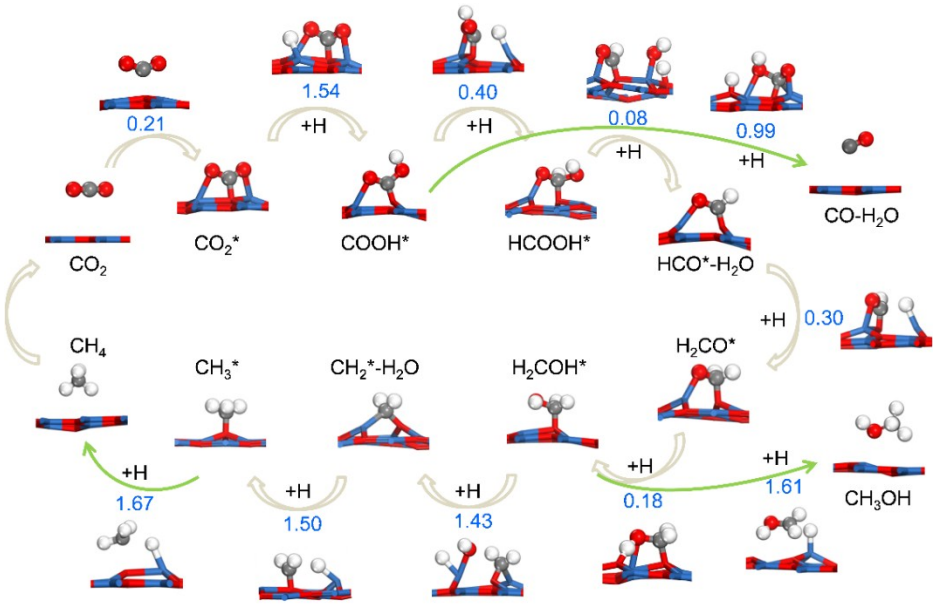

Fig. S1 Atomic structures of reactants, intermediate species, transition states and products of CO_2 reduction on the ZnO(1L) surface. The blue numbers show the kinetic barrier (in eV) calculated by the nudged elastic band method.[6] The H, C, O and Zn atoms are shown in white, grey, red and blue colors, respectively.

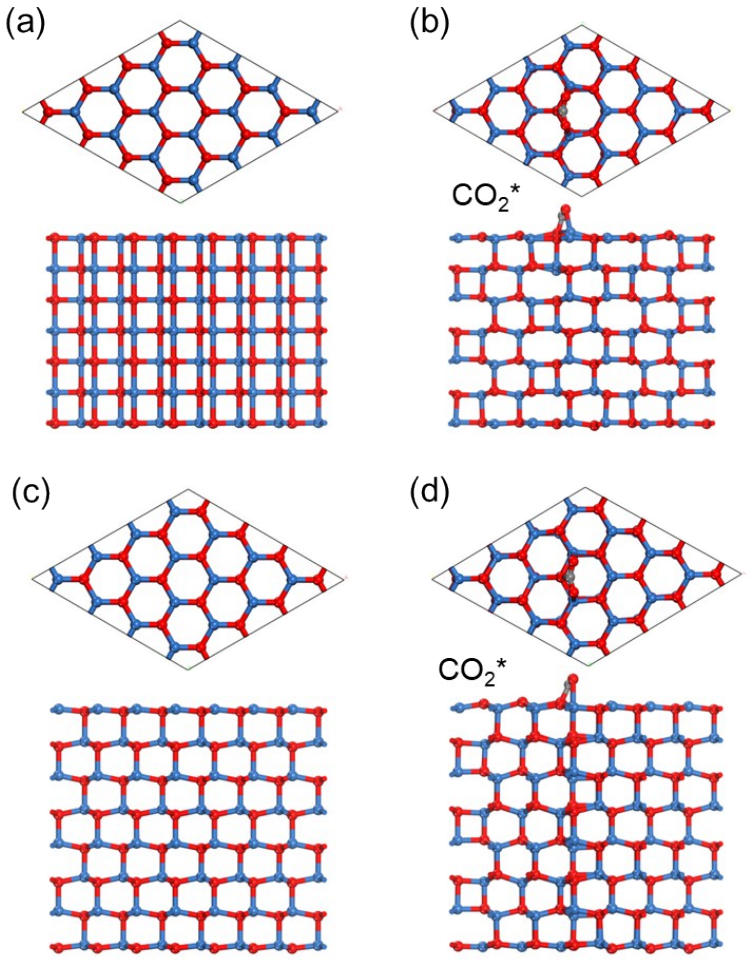

Fig. S2 (a), (b) Atomic structures of ZnO(7L) without and with adsorption of a CO_2 molecule, respectively. (c), (d) Atomic structures of ZnO(7L) without and with adsorption of a CO_2 molecule, respectively. The C, O and Zn atoms are shown in grey, red and blue colors, respectively. For both systems, severe structure reconstructions are induced by the molecular adsorption.

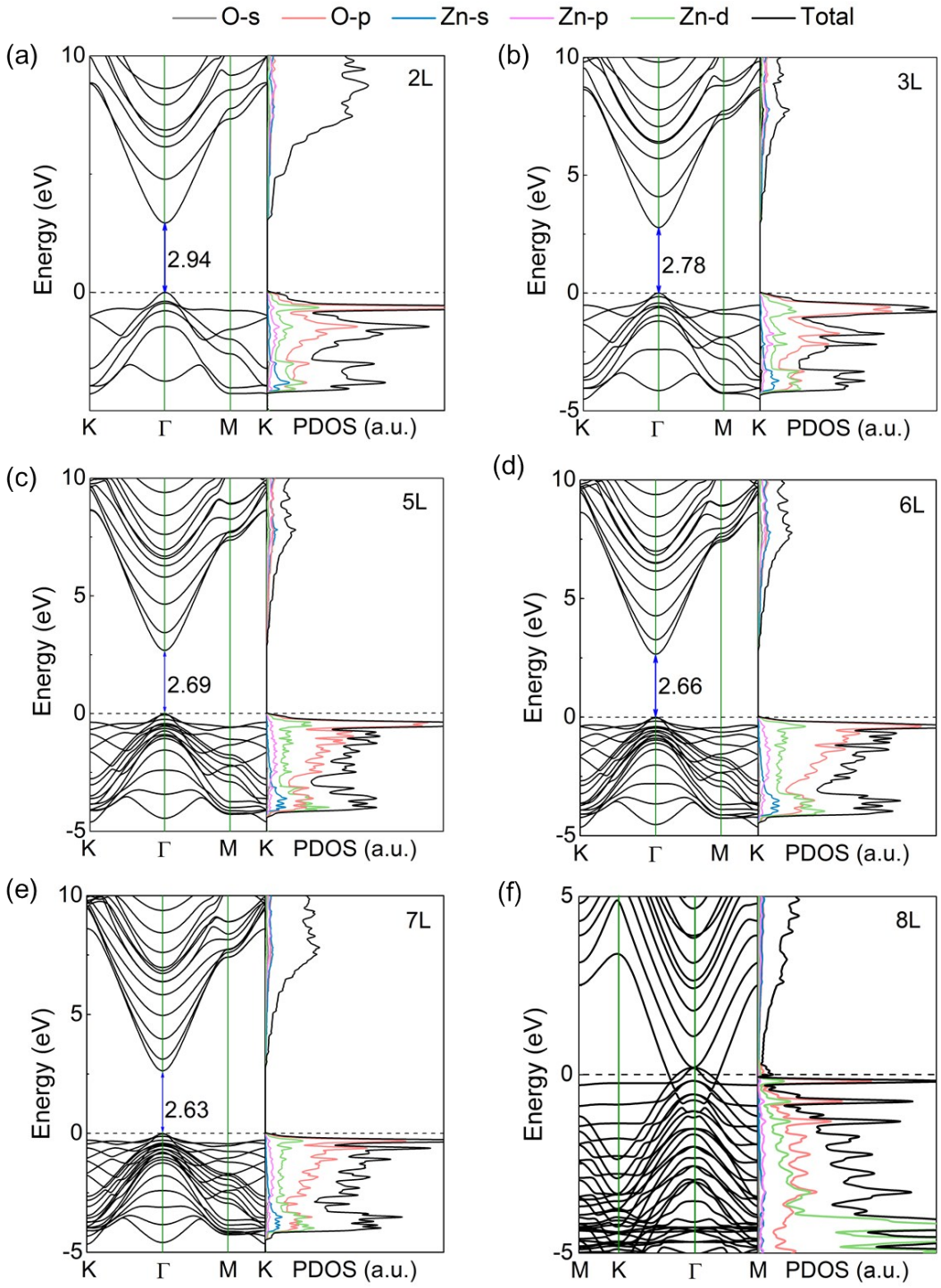

Fig. S3 Electronic band structures and projected density of states (PDOS) of (a) ZnO(2L), (b) ZnO(3L), (c) ZnO(5L), (d) ZnO(6L), (e) ZnO(7L) and (f) ZnO(8L) calculated using the HSE06 functional. The Fermi level is set to zero (black dotted lines).

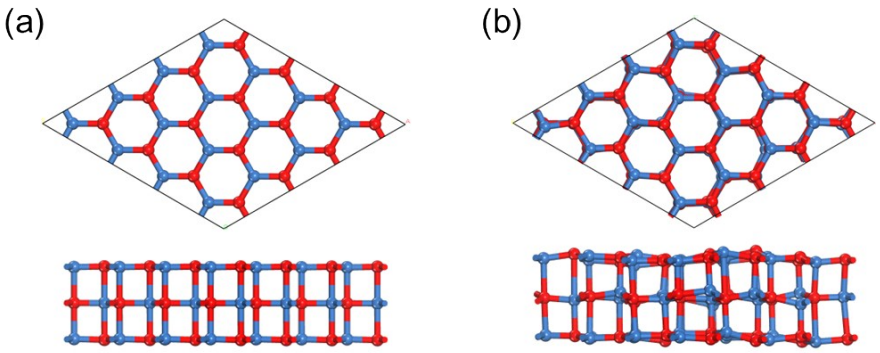

Fig. S4 (a) Atomic structures of ZnO(3L) at 0 K. (b) Atomic structures of ZnO(3L) by *ab initio* molecular dynamic simulations at 300 K for 10 ps, showing slight buckling with average vertical displacement of atoms less than 0.18 Å from their equilibrium positions. The O and Zn atoms are shown in by red and blue colors, respectively.

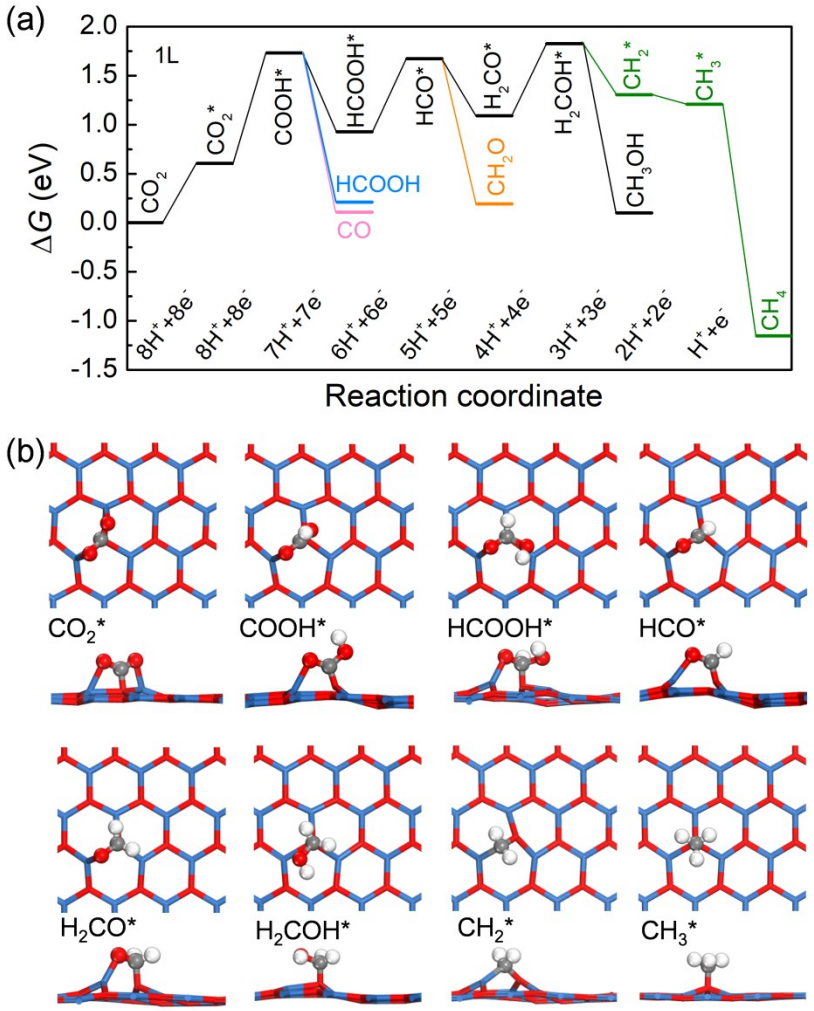

Fig. S5 (a) Free energy diagram of CO_2 reduction on ZnO(1L). Different products are color-coded. (b) Atomic structures of intermediate species of CO_2 reduction on ZnO(1L). The H, C, O and Zn atoms are shown in white, grey, red and blue colors, respectively.

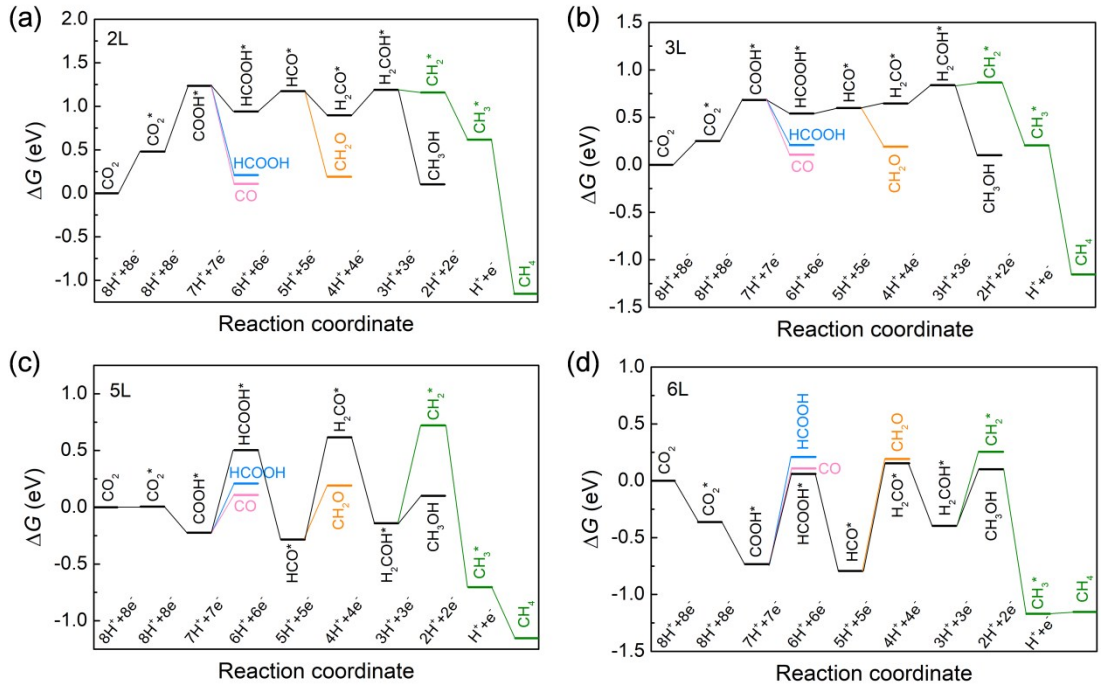

Fig. S6 Free energy diagrams of CO_2 reduction on (a) ZnO(2L), (b) ZnO(3L), (c) ZnO(5L) and (d) ZnO(6L).

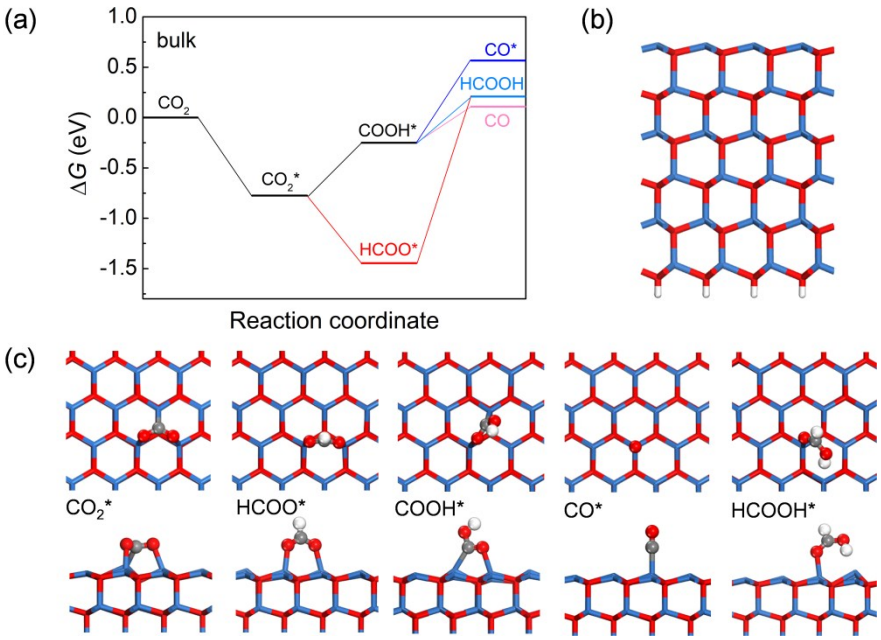

Fig. S7 (a) Free energy diagram of CO_2 reduction on the bulk ZnO(0001) surface, which is modeled by a 6-layer slab with the bottom layer O atoms terminated by H atoms,[7, 8] as shown in (b), and 4 × 4 ZnO unit cells for the lateral dimensions. (c) Atomic structures of intermediate species on the ZnO(0001) surface. The H, C, O and Zn atoms are shown in white, grey, red and blue colors, respectively.

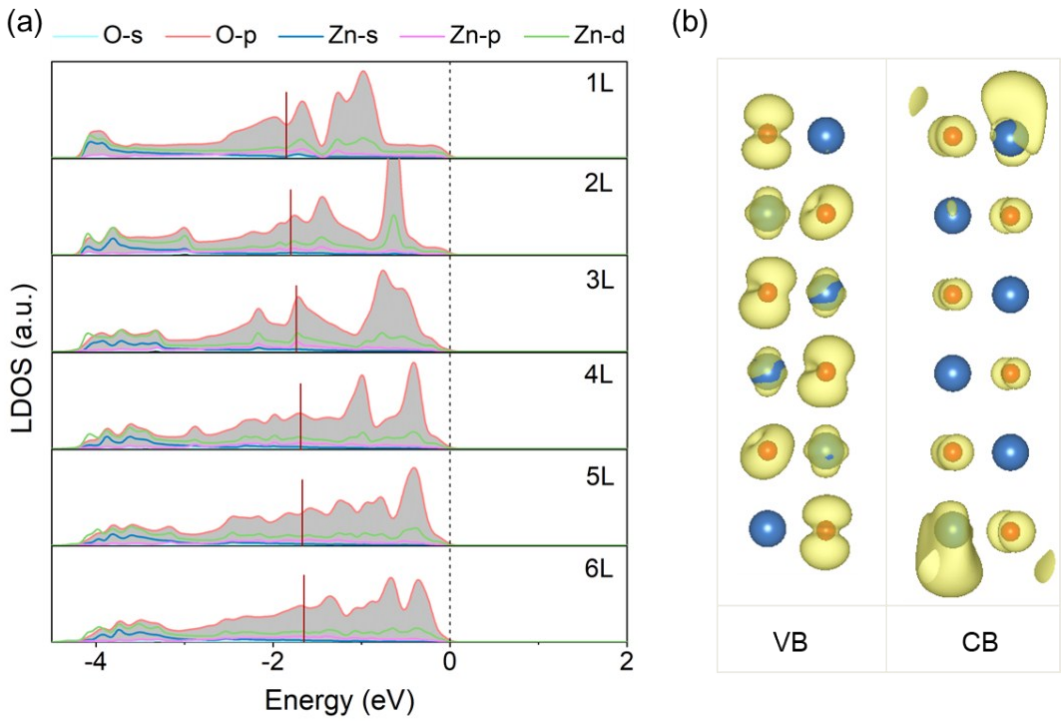

Fig. S8 (a) Local density of states (LDOS) of surface layers of ZnO(*n*L) sheets. The O 2*p* band center (ε_p) is indicated by the dark red line for each system. The Fermi level is set to zero (black dashed lines). (b) Band decomposed charge density of the top valence band (VB) and bottom conduction band (CB) for ZnO(6L), with an isosurface value of 0.003 e/Å^3.

Reference

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