Electronic Supplementary Information

CO_2 reduction on *p*-block metal oxide overlayers on metal substrate — 2D MgO as a prototype

Nanshu Liu, Yanyan Zhao, Si Zhou*, Jijun Zhao

Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China

Contents

* Corresponding authors. Email: sizhou@dlut.edu.cn (S. Zhou)

Table S1. Zero-point energy (ZPE) and entropic corrections (TS) at T = 298 K to the free energies. The gas phases values were taken from Ref. 1, while those for the adsorbed species were calculated by vibrational frequencies from DFT calculations. Note that the energy corrections of –0.51 eV and –0.49 eV were added to the gas phase CO and CH_2O molecules due to the systematic error of DFT calculations with PBE functional, respectively, and such computed thermochemical reaction energies of CO_2 reduction to various C1 products were consistent with experimental results.[2] The (ZPE − *TS*) values for the adsorbed species on MgO/metal substrates were used as the same as the 1L/Ag(111) because the vibrational frequencies have been found to depend much less on the substrate surfaces than the molecular bond strength.

species	ZPE (eV)	*TS* (eV)	ZPE – *TS* (eV)
H_2	0.27	0.42	–0.15
H_2O	0.58	0.65	–0.07
CO_2	0.31	0.65	–0.34
CO	0.14	0.67	–0.53
HCOOH	0.90	1.02	–0.12
H_2CO	0.70	0.66	0.04
CH_3OH	1.35	0.79	0.56
CH_4	1.20	0.60	0.60
CO_2*	0.37	0.13	0.24
COOH*	0.69	0.15	0.54
HCOO*	0.62	0.24	0.38
HCOOH*	0.93	0.15	0.78
HCO*	0.55	0.11	0.44
H_2CO*	0.85	0.12	0.73
H_3CO*	1.09	0.20	0.89
O*	0.08	0.03	0.05
OH*	0.22	0.08	0.14
H_2O*	0.65	0.15	0.50

Table S2. Gibbs free energy of formation (ΔG) for each element steps of CO_2 reduction on MgO/metal(100) substrates.

step	Reaction	ΔG (eV)			
		1L/Ag(100)	2L/Ag(100)	1L/Au(100)	2L/Au(100)
R1	$CO_2 \rightarrow CO_2$*	0.04	0.11	−0.04	0.07
R2	CO_2* + H^+ + e^- → COOH*	0.92	1.16	0.22	0.63
R3	COOH* + H^+ + e^- → CO(g) + H_2O	−0.34	−0.65	0.44	−0.09
R2’	CO_2* + H^+ + e^- → HCOO*	−0.39	−0.51	0.00	−0.07
R3’	HCOO* + H^+ + e^- → HCOOH(g)	0.56	0.62	0.24	0.21

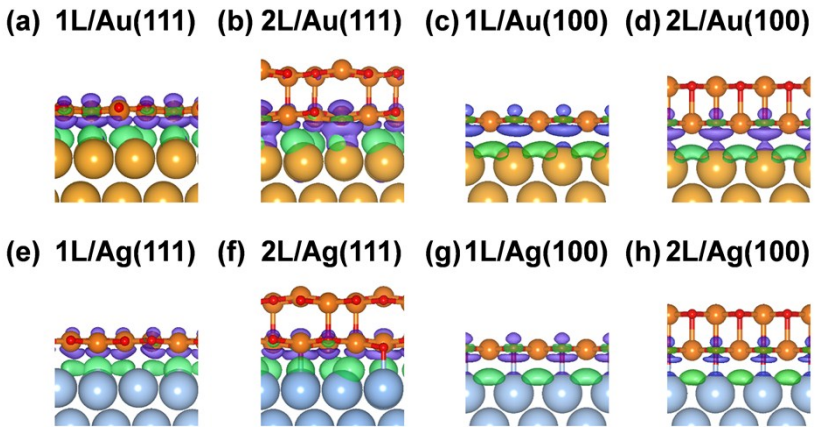

Figure S1. Differential charge density distributions between 1L and 2L MgO sheets on various substrates. The green and purple colors depict electron accumulation and depletion regions, respectively. The isosurface value is 1.5×10^{-3} e/Å^3.

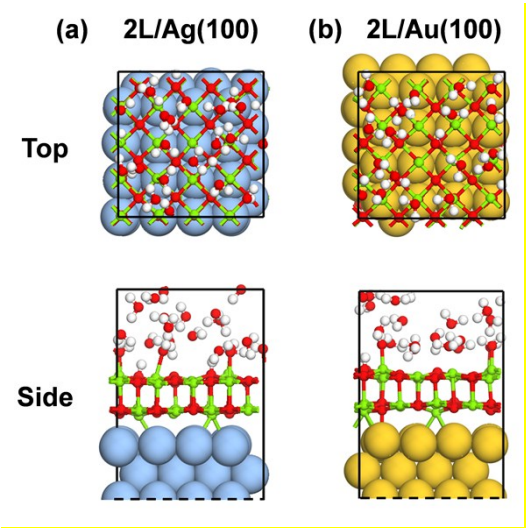

Figure S2. Geometrical structures for (a) 2L/Ag(100) and (b) 2L/Au(100) in water environment by AIMD simulation at 300 K after 10 ps. The supercells of Ag(111) and Au(111) surfaces (lateral dimensions of 10.00 × 11.56 Å and 11.54 × 11.54 Å) modelled by a four-layer slab were prepared, in which the Ag/Au atoms in the middle two layers were fixed and two bilayer MgO sheets were added to cover both upper and lower surfaces of the slab, respectively. The resulting 2L/Ag(111)/2L and 2L/Au(111)/2L heterostructures were placed in an explicit aqueous environment, which contained 35 water molecules with a density of 1 g/cm^3 for the liquid section.

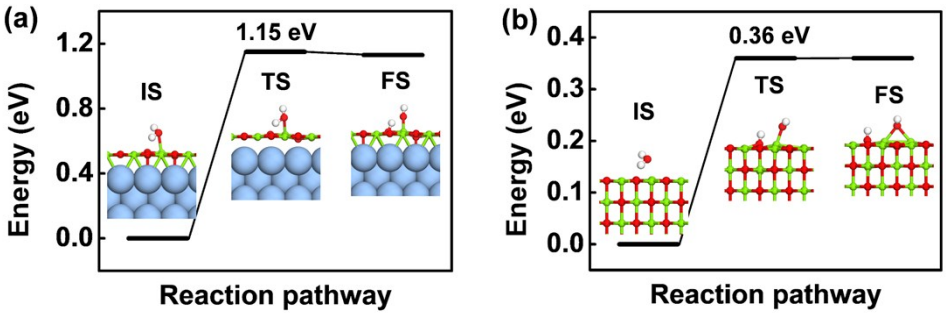

Figure S3. Kinetic barriers for water dissociation on (a) 1L/Ag(100) and (b) bulk MgO(100) surface. The black segments show the energies of the initial states (IS), transition states (TS), and final states (FS). The corresponding structures (side views) are presented next to each energy level. The H, O, Mg, and Ag atoms are shown in white, red, green, and blue colors, respectively.

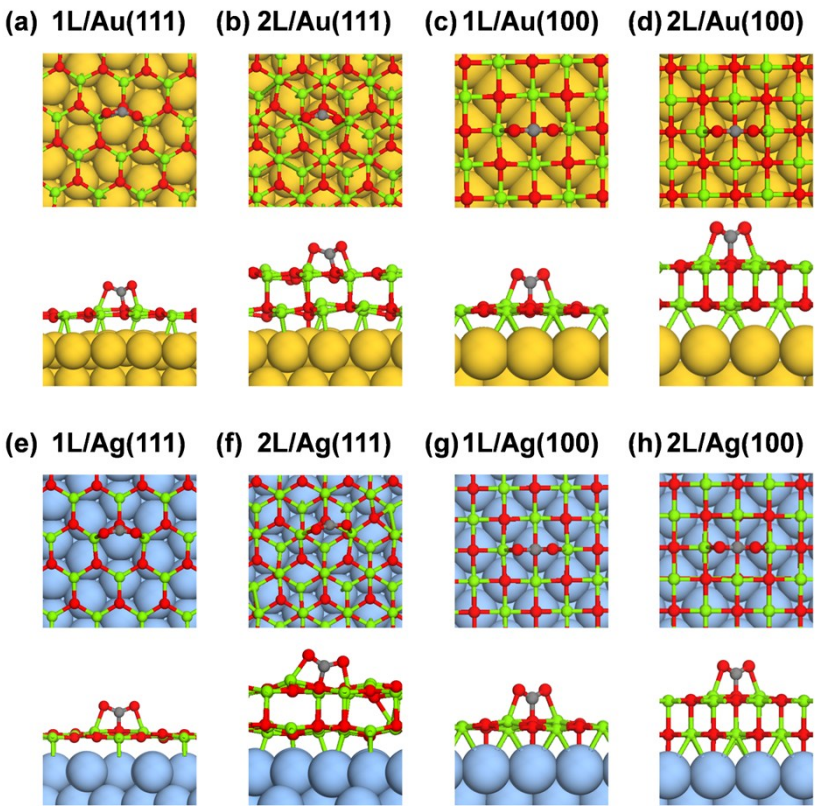

Figure S4. Most stable CO_2 adsorption configurations on various 2D MgO/metal heterostructures. The C, O, Mg, Ag and Au atoms are represented by grey, red, green, blue and yellow balls, respectively.

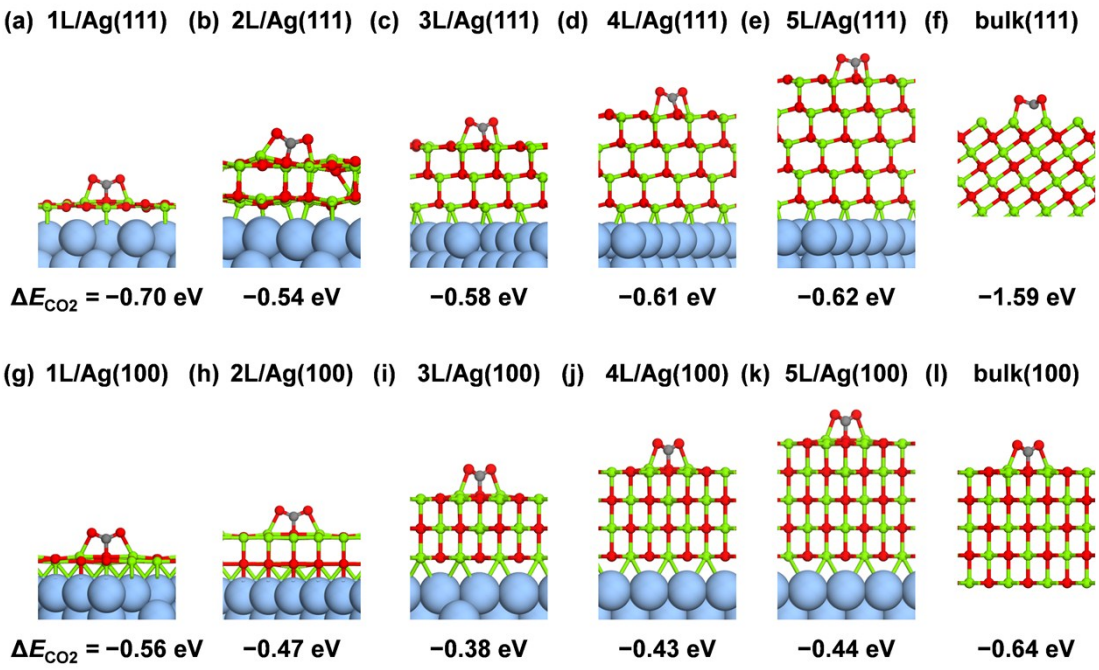

Figure S5. Side-view structures of one to five MgO layers on Ag(111) and Ag(100) substrate, with a CO_2 molecule chemisorbed on the MgO surface. The adsorption energy of CO_2 (ΔE_{CO2}) is given for each system. For comparison, the side-view structures of bulk MgO along the (111) and (100) orientation are shown on the right. The C, O, Mg and Ag atoms are shown in grey, red, green and blue colors, respectively.

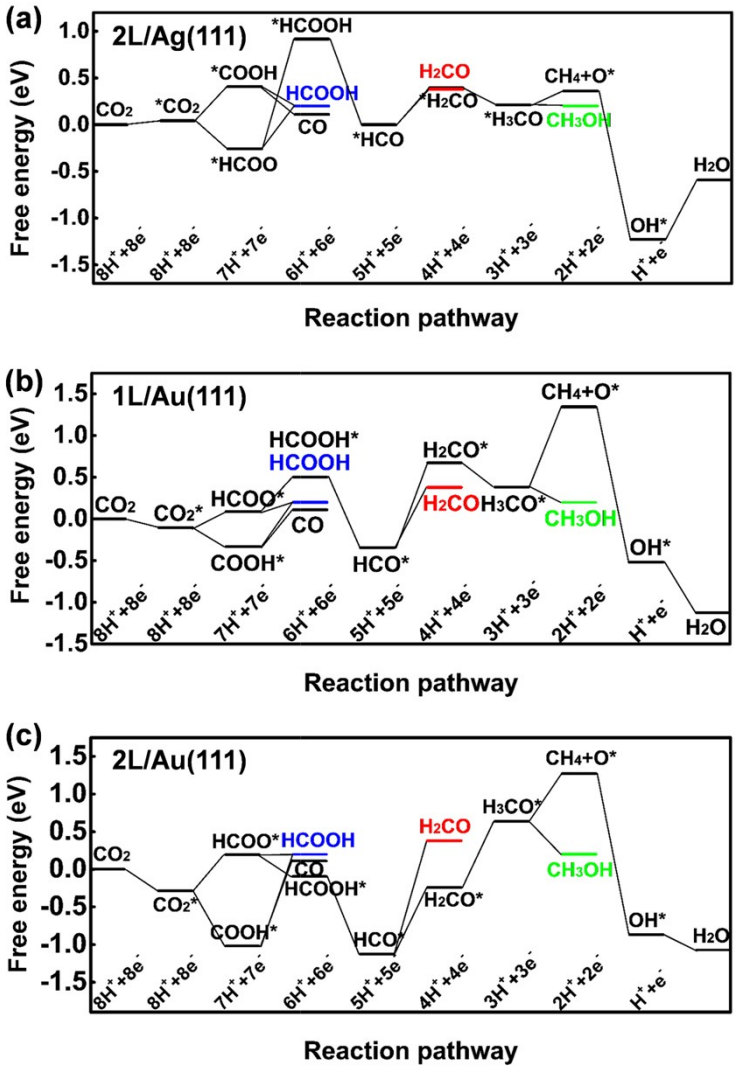

Figure S6. (a) Free energy profile for CO_2 reduction on (a) 2L/Ag(111), (b) 1L/Au(111), and (c) 2L/Au(111) heterostructures, respectively. The colored lines indicate the formation of the products.

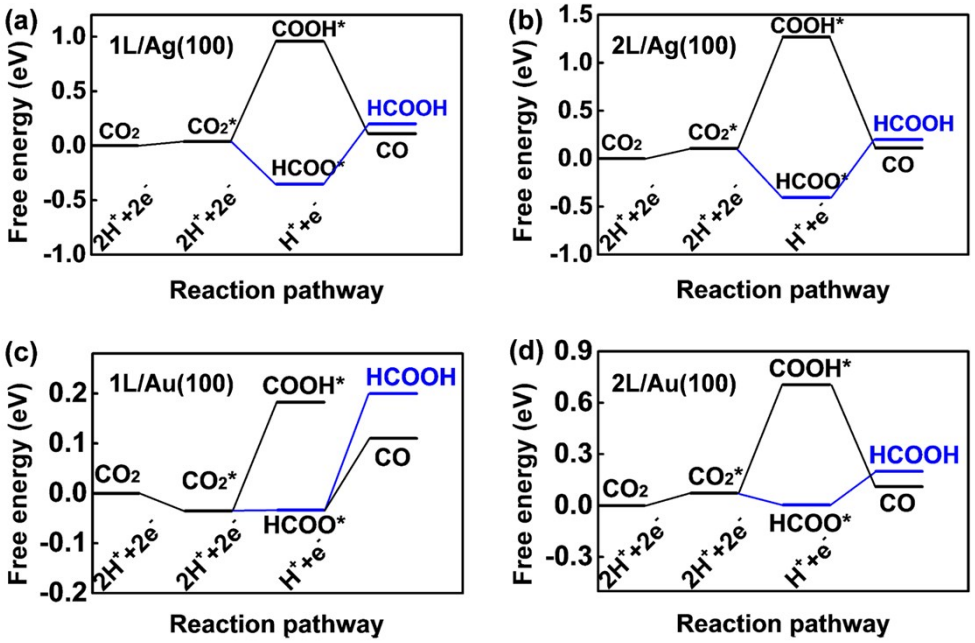

Figure S7. Free energy diagrams for CO_2 reduction on (a) 1L/Ag(100), (b) 2L/Ag(100), (c) 1L/Au(100), and (d) 2L/Au(100), respectively.

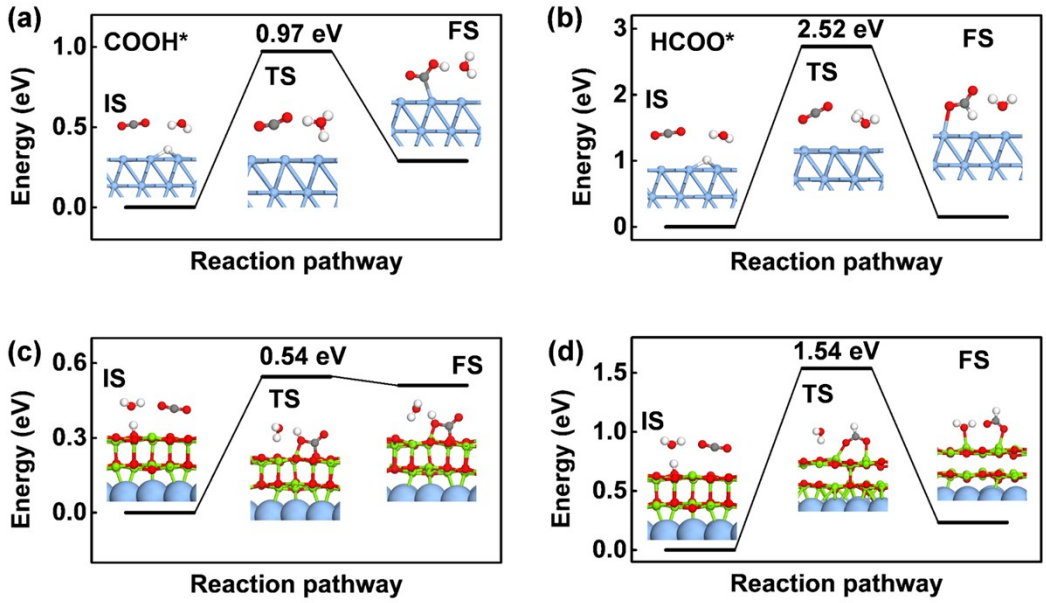

Figure S8. Reaction of CO_2 with a H adatom to form COOH* and HCOO* on (a, b) clean Ag(111) and (c, d) 2L/Ag(111) in the presence of a H_2O molecule. The black segments show the energies of the initial states (IS), transition states (TS), and final states (FS). The corresponding structures (side views) are presented next to each energy level. The H, C, O, Mg and Ag atoms are shown in white, grey, red, green and blue colors, respectively.

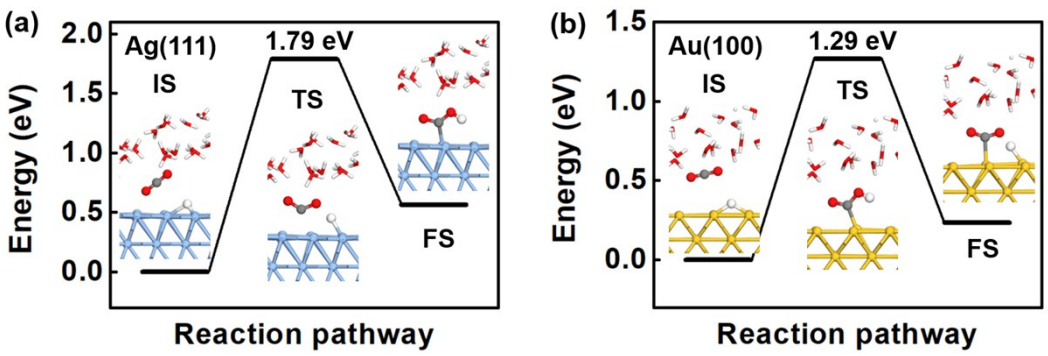

Figure S9. Reaction of CO_2 with a H adatom to form COOH* on (a) bare Ag(111) and (b) bare Au(100) surfaces in aqueous environment. The black segments show the energies of the initial states (IS), transition states (TS), and final states (FS). The corresponding structures (side views) are presented next to each energy level. The H, C, O, Ag, and Au atoms are shown in white, grey, red, blue and yellow colors, respectively.

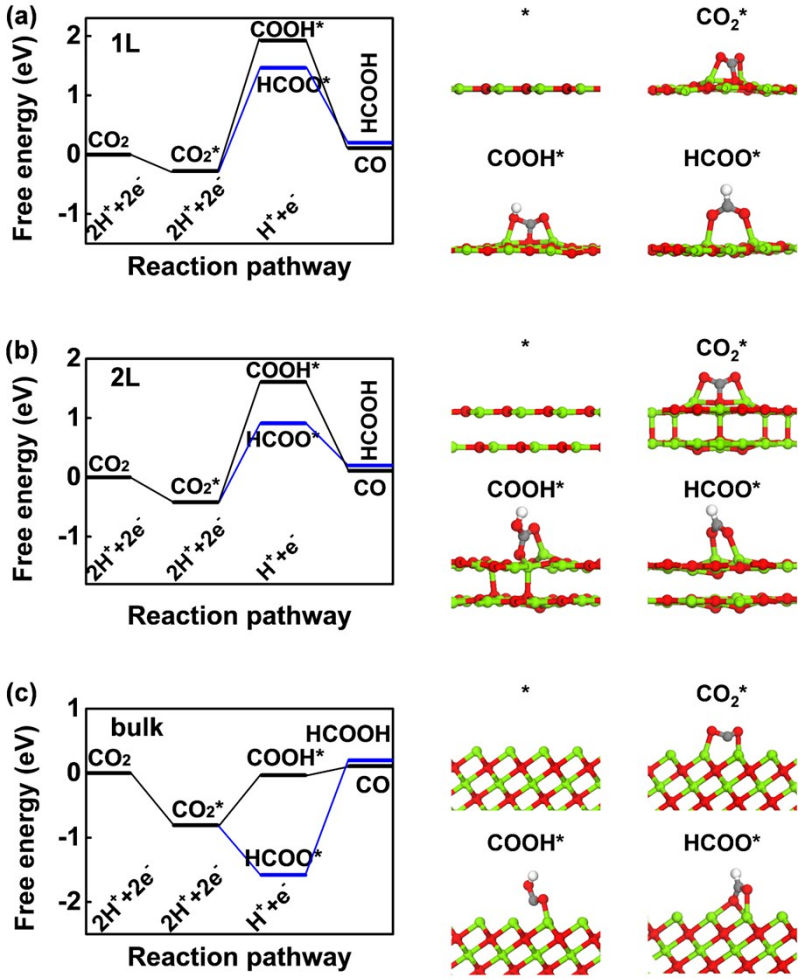

Figure S10. Left panels: free energy diagrams for CO_2 reduction on freestanding (a) 1L, (b) 2L and (c) bulk MgO(111) surface, which is modeled by a five-layer slab with the bottom layer O atoms terminated by H atoms. Right panel: corresponding structures of reaction intermediates, the H, C, O, and Mg atoms are represented by white, grey, red, and green balls, respectively.

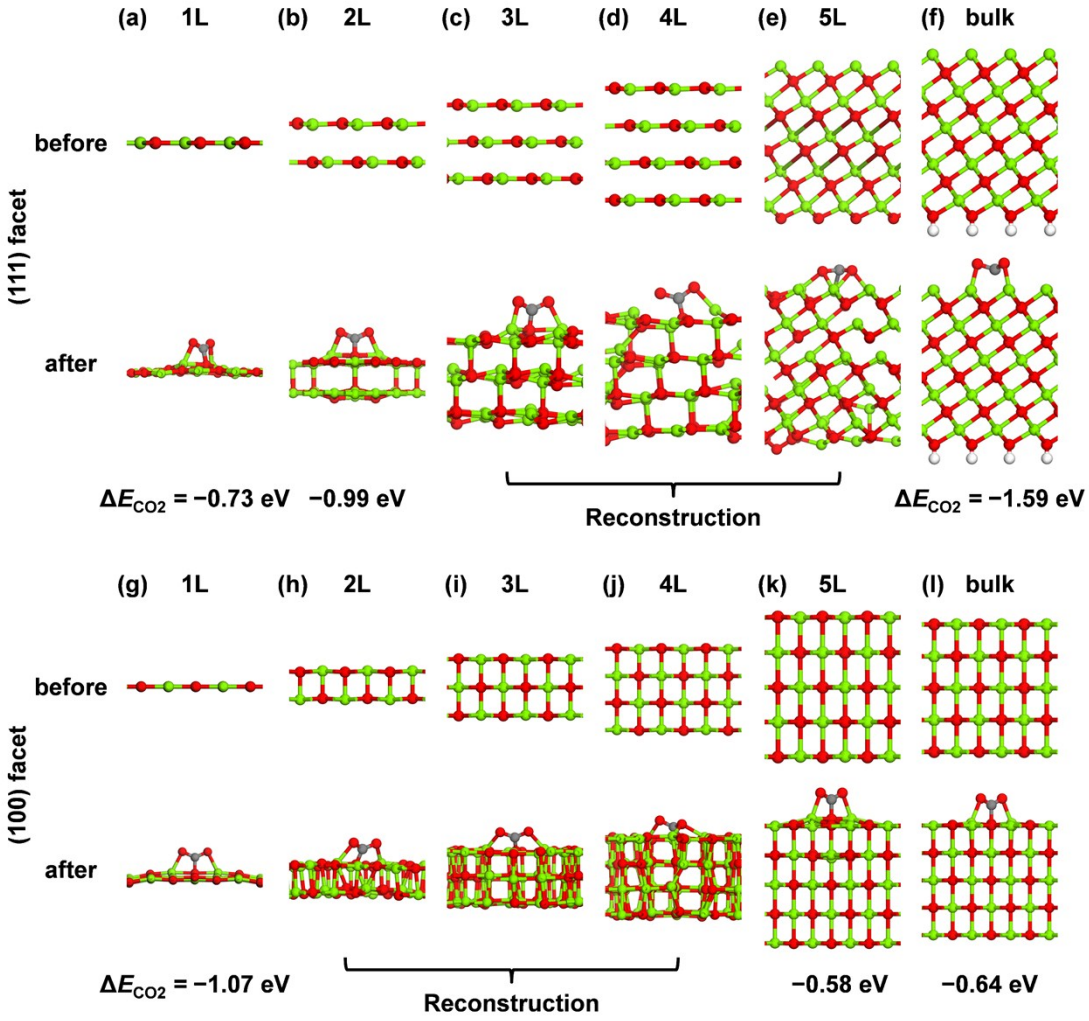

Figure S11. Side-view structures of freestanding MgO ultrathin films (one to five layers) with the (111) and (100) facets exposed before (upper panels) and after (bottom panels) adsorption of a CO_2 molecule, as well as for bulk MgO(111) and (100) surfaces. The adsorption energy of CO_2 (ΔE_{CO2}) is given for some structure-maintained systems, while the other systems undergo severe deformation upon molecular adsorption. The H, C, O, and Mg atoms are shown in white, grey, red, and green colors, respectively.

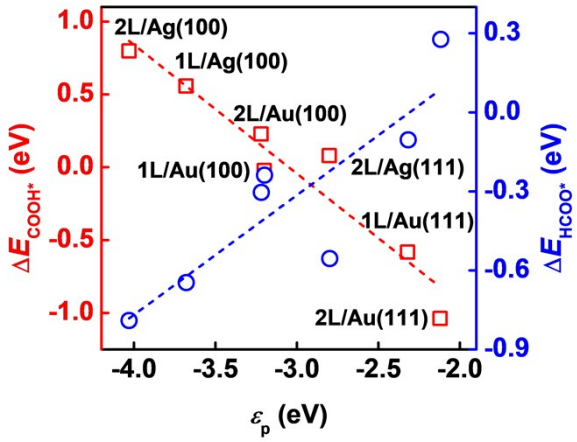

Figure S12. Adsorption energies of COOH* and HCOO* intermediates (ΔE_{COOH*}, red symbol; ΔE_{HCOO*}, blue symbol) as a function of the *p*-band center (ε_p) for various 2D MgO/metal heterostructures. We define $\Delta E_{COOH*/*HCOO} = E_{COOH*/*HCOO} - E_{MgO/metal} - E_{CO2} - ½\ E_{H2}$.

Reference

1. M. W. Chase Jr, *NIST-JANAF Thermochemical Tables*, American Chemical Society, American Institute of Physics for the National Institute of Standards and Technology, Washington, DC, New York, 1998.
2. J. Varley, H. Hansen, N. L. Ammitzbøll, L. Grabow, A. Peterson, J. Rossmeisl and J. Nørskov, *ACS Catal.*, 2013, **3**, 2640–2643.