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Electrochemical CO_2 reduction: water/catalyst interface versus polymer/catalyst interface

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Supporting Information

Computational details

To simulated copper electrode surface, a four-layer Cu slab (two layers fixed) model was used based on a 4×4 periodic cell. Aqueous interface models contain the Cu slab and three-layer water molecules. In the charged aqueous-phase system, one H atom was located in bulk water as a solvated H^+ in the solution with an electron entering the slab. The quaternary ammonia poly (Nmethyl-piperidine-co-p-terphenyl) (QAPPT) polymer[1] was simplified by taking its minimum repeating unit structure with the key functional group, i.e. quaternary ammonia ($-NR_3^+$) retained, and placed above the copper surface to simulate the QAPPT-polymer/Cu(100) interface. At the polymer/copper interface, the quaternary ammonia serves as cation to capture dissociative OH^- ion, while other groups in the polymer do not contribute to the CO_2RR. Two water molecules were placed between QAPPT-polymer and Cu(100) to supply the proton for reduction reaction and transfer hydroxide ion. The pathway towards CH_4 formation in water/Cu(100) interface and the corresponding free energy profiles have been reported by Sheng, et al.[2-4] The free energy of the missing elementary step, $COH+H^++e^- \rightarrow C+H_2O$, is calculated by the same constrained molecular dynamics method in ref. 2. The reaction paths of all elementary steps at the QAPPT-polymer/Cu(100) interface were generated by the slow-growth approach, and the potential of mean force (PMF) was calculated by constrained molecular dynamics. Electrochemical reaction energetics at constant potential were determined using the energy differences between the initial work function (Φ_1) and final work function (Φ_2) using the correction proposed by Chan et al.[5] An increment of 0.0005 Å/step to collective variables was applied to drive the reactions. Simulations of 5 ps were carried out at each window of constrained molecular dynamics to produce the PMF. The electrode potential (U) was obtained by referring the work function (Φ) of the system to the experimental work function of the standard hydrogen electrode (SHE) according to the following equation, $U = \Phi/e - 4.44V$.[6,7] The relative saturated concentrations and diffusion coefficients for CO_2 in aqueous solution and humidified gaseous CO_2 are 0.033 M, 0.0016 mm^2/s, 0.041 M, and 16 mm^2/s, respectively.[8]

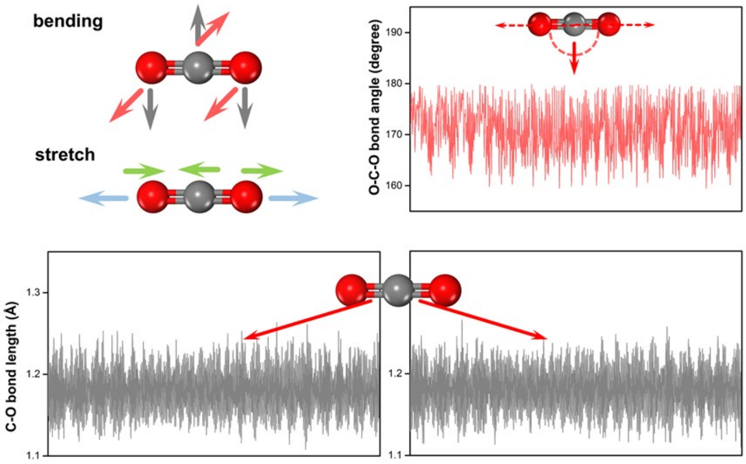

Figure S1. CO_2 vibrational modes in the gas-phase; symmetric/antisymmetric stretch and in-plane/out off-plane bending. Changes of O-C-O bond angles and C-O bond lengths along the simulation steps.

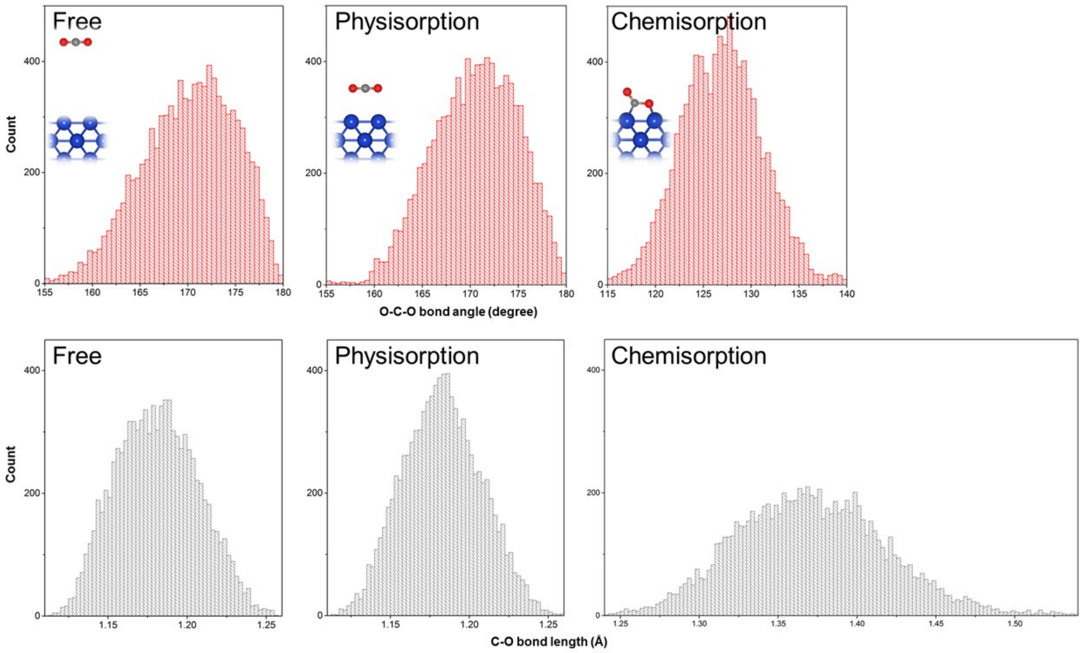

Figure S2. Distributions of O-C-O bond angle and C-O bond length in the gas-fed system.

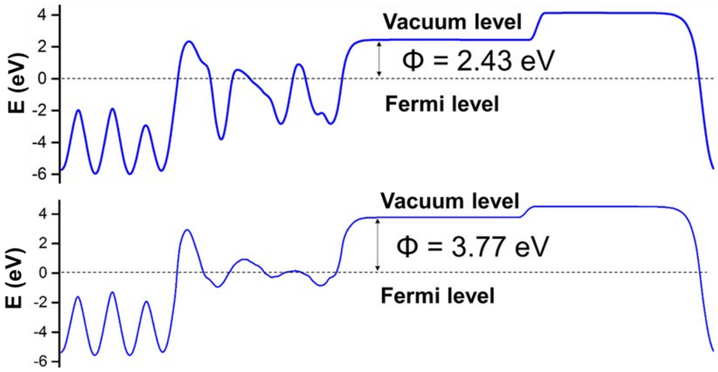

Figure S3. Electrostatic potential profile averaged on the surface plane as a function of the z-axis.

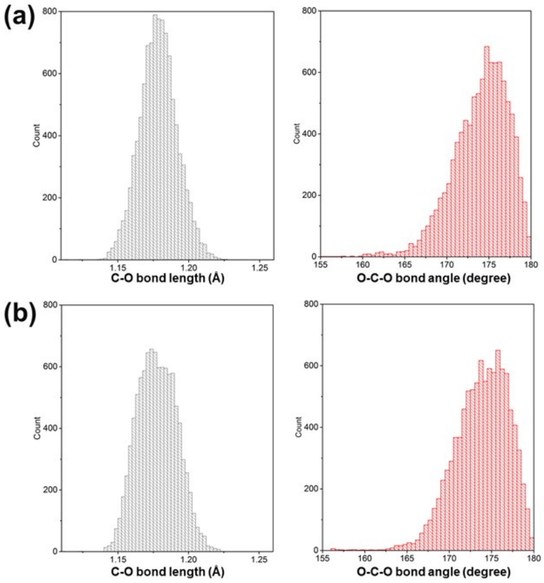

Figure S4. Distributions of O-C-O bond angle and C-O bond length in the aqueous-phase system with/without solvated proton.

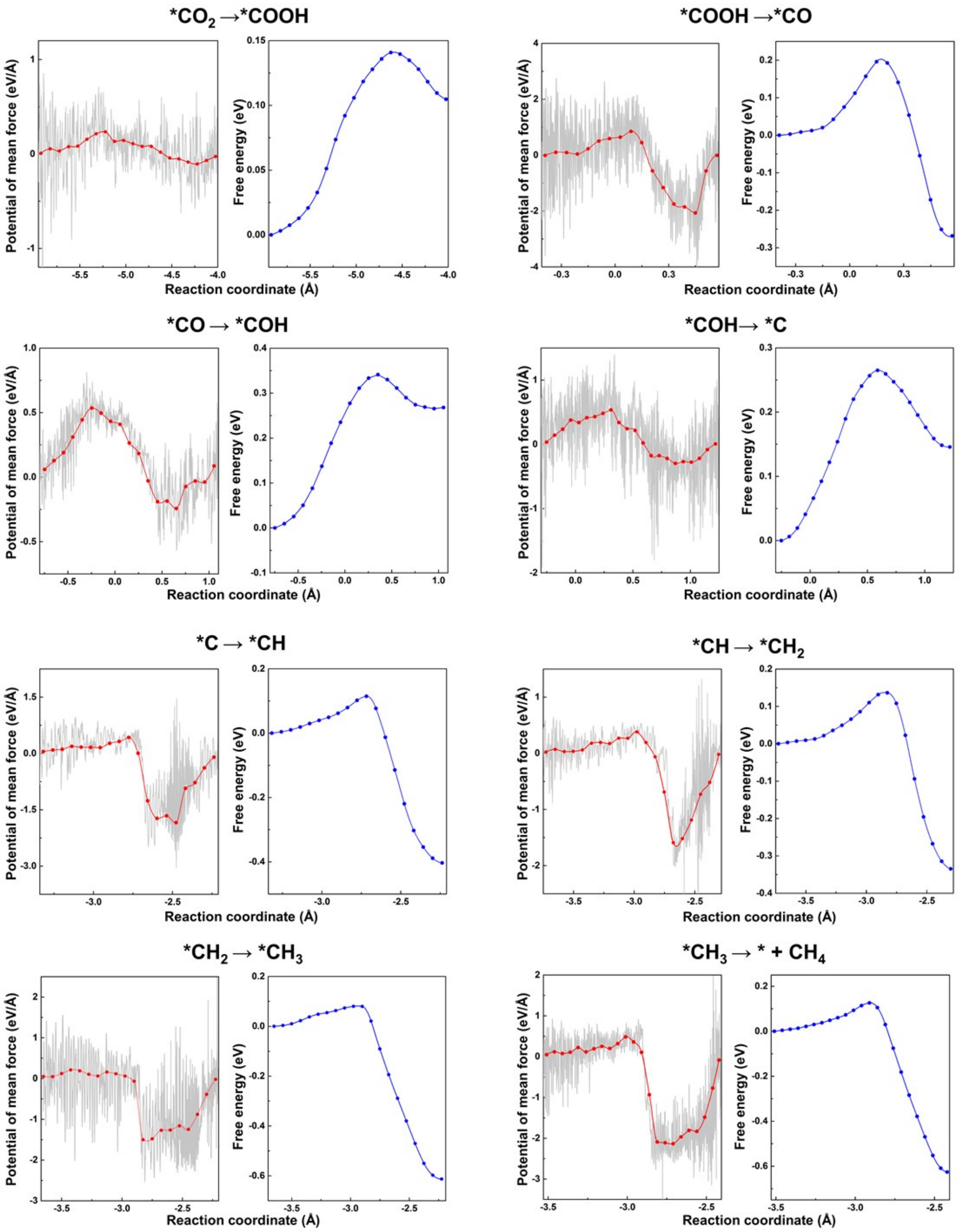

Figure S5. Potential of mean forces (PMF) and corresponding free energy changes for the elementary steps of CO_2 reduction at the QAPPT-polymer/Cu(100) interface.

Table S1. Work functions Φ, changes in q and charge-extrapolated constant potential corrections.

Reaction	Φ_{FS} (eV)	Φ_{IS}-Φ_{FS} (eV)	Φ_{TS}-Φ_{FS} (eV)	q_{IS}-q_{FS}	q_{TS}-q_{FS}	$\Delta G_{(IS-FS)}$ (eV)	$\Delta E_{a(TS-FS)}$ (eV)
$*CO_2 \rightarrow *COOH$	2.36	-0.76	-0.24	0.16	0.32	-0.12	-0.02
$*COOH \rightarrow *CO$	2.59	-0.94	-0.46	0.21	0.38	-0.18	-0.05
$*CO \rightarrow *COH$	2.35	-0.72	-0.25	0.28	0.31	-0.11	-0.04
$*COH \rightarrow *C$	2.61	-0.99	-0.48	0.17	0.31	-0.15	-0.04
$*C \rightarrow *CH$	2.35	-0.76	-0.20	0.24	0.43	-0.17	-0.02
$*CH \rightarrow *CH_2$	2.43	-0.83	-0.36	0.19	0.42	-0.17	-0.03
$*CH_2 \rightarrow *CH_3$	2.47	-0.88	-0.33	0.20	0.33	-0.14	-0.03
$*CH_3 \rightarrow *CH_4$	2.57	-0.90	-0.47	0.19	0.28	-0.13	-0.04

References

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