Electronic Supplementary Information for Physical Chemistry Chemical Physics

Theoretical Understanding of Electrochemical Reaction Barrier: A Kinetic Study of CO_2 Reduction Reaction on Copper Electrodes

Shu-Ting Gao[a], Shi-Qin Xiang[a], Jun-Lin Shi[a], Wei Zhang*[b] and Liu-Bin Zhao*[a]

[a]Department of Chemistry, School of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, China

[b]Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing, 400714, China

Corresponding Authors

*E-mail: andyzhangwei@163.com.

*E-mail: lbzhao@swu.edu.cn.

Supplementary Figures and Tables

1. Derivation of Activation Barrier Energy E$_a$ of CPET process based on Marcus theory.

For a displaced oscillator model, free energy of transition state is expressed as

$$E_R = \frac{1}{2}kx^2 \rightarrow x^2 = \frac{2E_R}{k}$$

and

$$E_P = \frac{1}{2}k\left(x-q\right)^2 + \Delta G$$

Where *k* is force constants of reactant systems and product systems, respectively; Δ*G* is reaction free energy; *q* is the reaction coordinates.

We defined $\lambda = \frac{1}{2}kq^2$, then

$$E_R = E_P = E_a = \frac{\lambda}{4}\left(1+\frac{\Delta G}{\lambda}\right)^2$$

For a displaced-distorted oscillator model, free energy of transition state is expressed as

$$E_R = \frac{1}{2}k_R x^2 \rightarrow x^2 = \frac{2E_R}{k_R}$$

and

$$E_P = \frac{1}{2}k_P\left(x-q\right)^2 + \Delta G$$

Where k_R and k_P is force constants of reactant systems and product systems, respectively; Δ*G* is reaction free energy; *q* is the reaction coordinates.

We defined $\lambda_R = \frac{1}{2}k_R q^2, \lambda_P = \frac{1}{2}k_P q^2$,

Where λ_R is the total reorganization energy of reactant systems, λ_P is the total reorganization energy of product systems.

Finally, $E_a = \left(\frac{-\sqrt{\lambda_R}+\sqrt{\frac{\lambda_R}{\lambda_P}\left[\lambda_R+\Delta G(\frac{\lambda_R}{\lambda_P}-1)\right]}}{(\frac{\lambda_R}{\lambda_P}-1)}\right)^2$.

At $\Delta G = 0$, $E_a = \frac{\lambda_R\lambda_P}{(\sqrt{\lambda_R}+\sqrt{\lambda_P})^2}$

If $\lambda_R = \lambda_P$,

Then $E_a = \frac{\lambda_R}{4} = \frac{\lambda_P}{4} = \frac{\lambda}{4}$.

That is to say, the value of activation energy is determined by λ when reaction is spontaneous.

2. Correction of thermodynamic quantity G with the VASPKIT code.

Gibbs free energies were calculated from DFT total energies corrected by zero-point energy (ZPE), heat capacity (C_P), and entropy (TS).

$$G = E_{DFT} + E_{ZPE} + \int C_P dT - TS$$

The total electron energies E_{DFT} at 0 K were firstly calculated using the VASP program. Then, correction terms at 298.15 K were calculated by VASPKIT code. The internal energy of the system under 0 K is expressed:

$$U(0) = E_{DFT} + E_{ZPE}$$

For adsorbed molecules, we ignore PV contribution to translation. So H = U.

The enthalpy at temperature T is expressed:

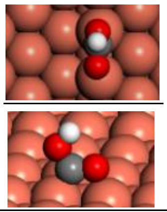
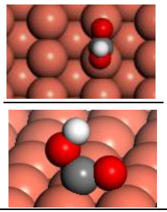
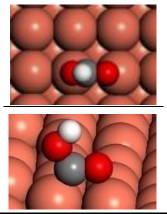
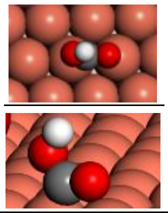
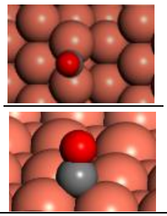
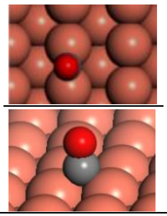
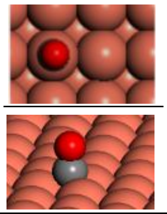
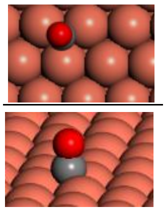
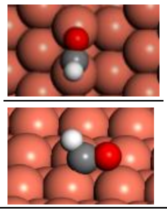
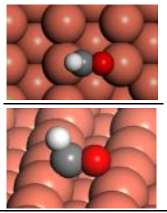
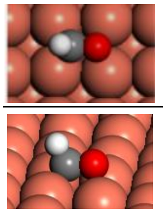
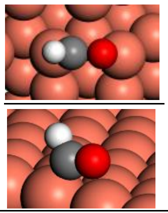
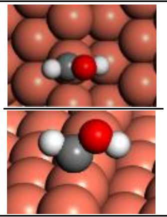
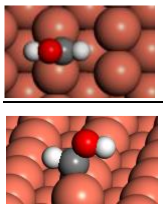
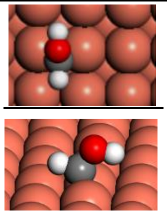
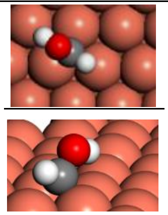
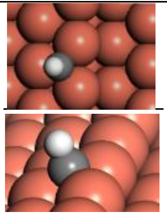
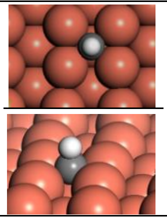
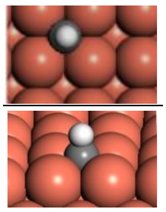
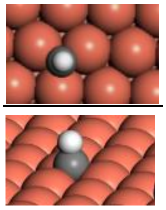
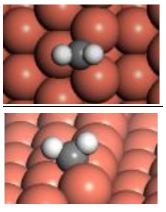
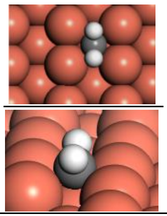
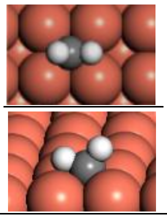
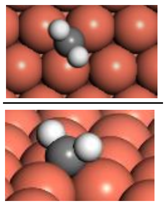
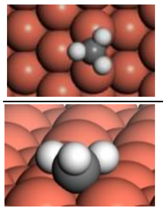
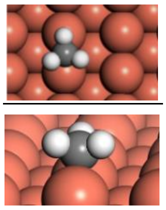
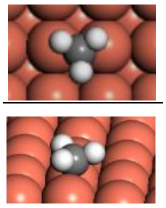
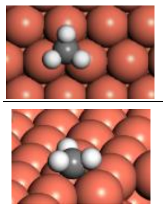
$$H(T) = E_{DFT} + E_{ZPE} + \int C_P dT$$

Where $\int C_P dT$ is the enthalpy contribution and expressed as E_H in the VASPKIT program, then the Gibbs free energy at temperature T is

$$G = H - TS = E_{DFT} + E_{ZPE} + \int C_P dT - TS$$

For correcting the Gibbs free energy data, we needed additional calculations at the Γ point, and they were carried out in the VASPKIT code.

Table S1. Calculated binding energy (in eV) and optimized structures of key adsorbates on the (111), (100), (110) and (211) crystal facets. The colors are Cu in orange, C in gray, O in red and H in white.

Species	Cu(211)		Cu(110)		Cu(100)		Cu(211)	
	structure	E_b	Structure	E_b	structure	E_b	structure	E_b
COOH		−2.54		−2.47		−2.27		−1.99
CO		−1.02		−0.94		−0.86		−0.81
CHO		−2.07		−2.01		−1.86		−1.59
CHOH		−1.99		−2.08		−1.90		−1.66
CH		−5.56		−5.70		−6.13		−5.34
CH_2		−3.92		−3.78		−3.79		−3.55
CH_3		−2.42		−2.36		−2.10		−2.04

$E_b = E_{total} - E_{substrate} - E_{molecule}$

where E_{total} is the total energy of the complete system (surface + adsorbates), $E_{substrate}$ is the energy of the substrate (i.e., slab only), and $E_{molecule}$ is the energy of a single molecule in the unit cell.

Table S2. Calculated the bond lengths and bond angles of *COOH, *CO and *CHO on the (111), (100), (110) and (211) crystal facets are summarized. The colors are Cu in orange, C in gray, O in red and H in white.

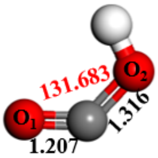
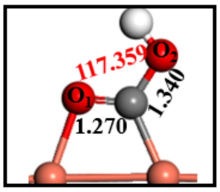
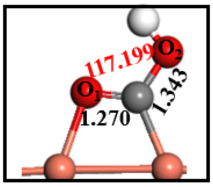
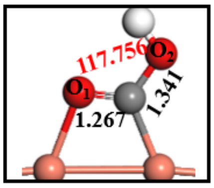
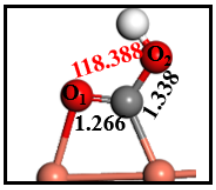
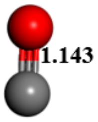
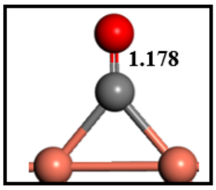
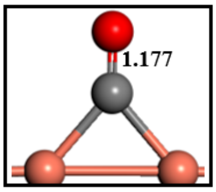
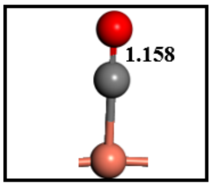
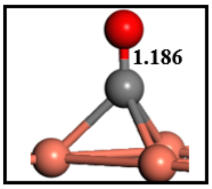
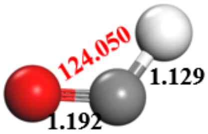
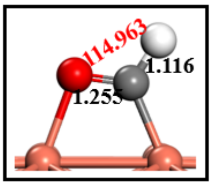
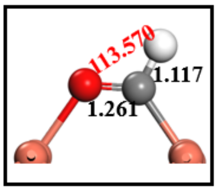
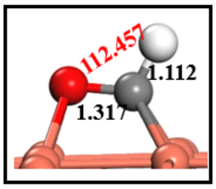
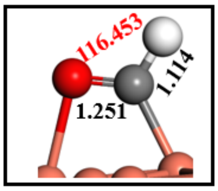
	Free molecule	Cu(211)	Cu(110)	Cu(100)	Cu(111)
Structure of COOH					
d_{Cu-C}/Å		1.934	1.937	1.943	1.950
d_{Cu-O1}/Å		2.033	2.051	2.068	2.123
E_b / eV		−2.54	−2.47	−2.28	−2.00
Structure of CO					
d_{Cu-C}/Å		1.960, 1.961	1.960, 1.959	1.842	2.045,2.045,2.046
E_b / eV		−1.02	−0.94	−0.86	−0.81
Structure of CHO					
d_{Cu-C}/Å		1.919	1.922	2.024, 2.037	1.936
d_{Cu-O}/Å		2.060	2.048	2.139, 2.100	2.168
E_b / eV		−2.07	−2.01	−1.86	−1.59

Table S3. The zero-point energy correction, enthalpy correction, and entropy correction for adsorbates on four different structures. All values are given in eV.

Structures	Adsorbate	ZPE	$\int C_p \mathrm{d}T$	TS	$\int C_p \mathrm{d}T - TS$	$ZPE + \int C_p \mathrm{d}T - TS$
Cu(211)	*CO$_2$[a]	0.32	-	-	−0.14	0.18
	*COOH	0.60	0.10	0.21	−0.11	0.49
	*CO	0.17	0.08	0.15	−0.07	0.10
	*CHO	0.48	0.08	0.15	−0.07	0.41
	*CHOH	0.80	0.09	0.19	−0.10	0.70
	*CH	0.34	0.03	0.04	−0.01	0.33
	*CH$_2$	0.59	0.06	0.09	−0.03	0.56
	*CH$_3$	0.90	0.08	0.16	−0.08	0.82
	*CH$_4$[a]	1.19	-	-	−0.16	1.03
Cu(110)	*CO$_2$[a]	0.33	-	-	−0.14	0.19
	*COOH	0.61	0.10	0.20	−0.10	0.51
	*CO	0.17	0.08	0.17	−0.09	0.08
	*CHO	0.46	0.07	0.14	−0.07	0.39
	*CHOH	0.77	0.09	0.18	−0.09	0.68
	*CH	0.32	0.04	0.06	−0.02	0.30
	*CH$_2$	0.58	0.06	0.10	−0.04	0.54
	*CH$_3$	0.90	0.08	0.16	−0.08	0.82
	*CH$_4$[a]	1.19	-	-	−0.16	1.03
Cu(100)	*CO$_2$[a]	0.31	-	-	−0.14	0.17
	*COOH	0.60	0.08	0.16	−0.08	0.52
	*CO	0.18	0.06	0.11	−0.05	0.13
	*CHO	0.43	0.08	0.14	−0.06	0.37
	*CHOH	0.77	0.09	0.17	−0.08	0.69
	*CH	0.34	0.03	0.04	−0.01	0.33
	*CH$_2$	0.56	0.06	0.10	−0.04	0.52
	*CH$_3$	0.90	0.06	0.10	−0.04	0.86
	*CH$_4$[a]	1.19	-	-	−0.16	1.03
Cu(111)	*CO$_2$[a]	0.31	-	-	−0.14	0.17
	*COOH	0.59	0.11	0.23	−0.12	0.47
	*CO	0.17	0.08	0.15	−0.07	0.10
	*CHO	0.45	0.08	0.17	−0.08	0.37
	*CHOH	0.75	0.10	0.19	−0.10	0.66
	*CH	0.34	0.03	0.05	−0.02	0.32
	*CH$_2$	0.58	0.06	0.11	−0.05	0.53
	*CH$_3$	0.91	0.07	0.12	−0.05	0.86
	*CH$_4$[a]	1.20	-	-	−0.16	1.04

[a] Physical adsorption

Table S4. The zero-point energy correction, enthalpy correction, and entropy correction for free modules. All values are given in eV.

Species	Fugacity (Pa)	ZPE	$\int C_p \mathrm{d}T$	TS	$ZPE + \int C_p \mathrm{d}T - TS$
CO_2(g)	101325	0.31	0.10	0.66	−0.26
H_2(g)	101325	0.27	0.09	0.40	−0.05
CH_4(g)	20467	1.19	0.10	0.62	0.68
H_2O(l)	3534	0.56	0.10	0.67	−0.01

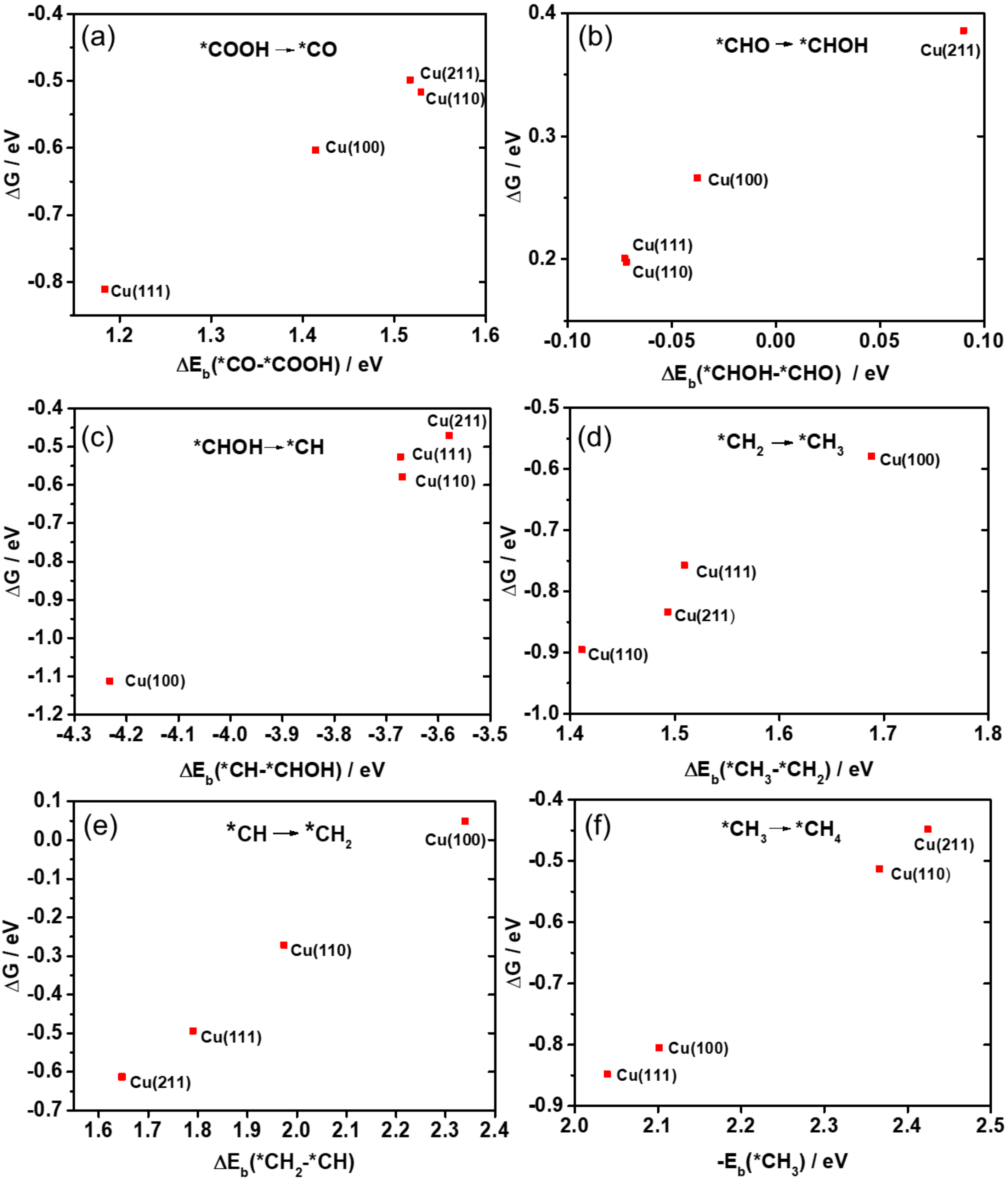


Fig. S1. The relationship between the Gibbs free energy change and the corresponding binding energy difference for (a)

$^*COOH \rightarrow {}^*CO+H_2O$, (b) $^*CHO \rightarrow {}^*CHOH$, (c) $^*CHOH \rightarrow {}^*CH+H_2O$, (d) $^*CH \rightarrow {}^*CH_2$, (e) $^*CH_2 \rightarrow {}^*CH_3$ and (f) $^*CH_3 \rightarrow {}^*CH_4$ on four Cu surfaces.

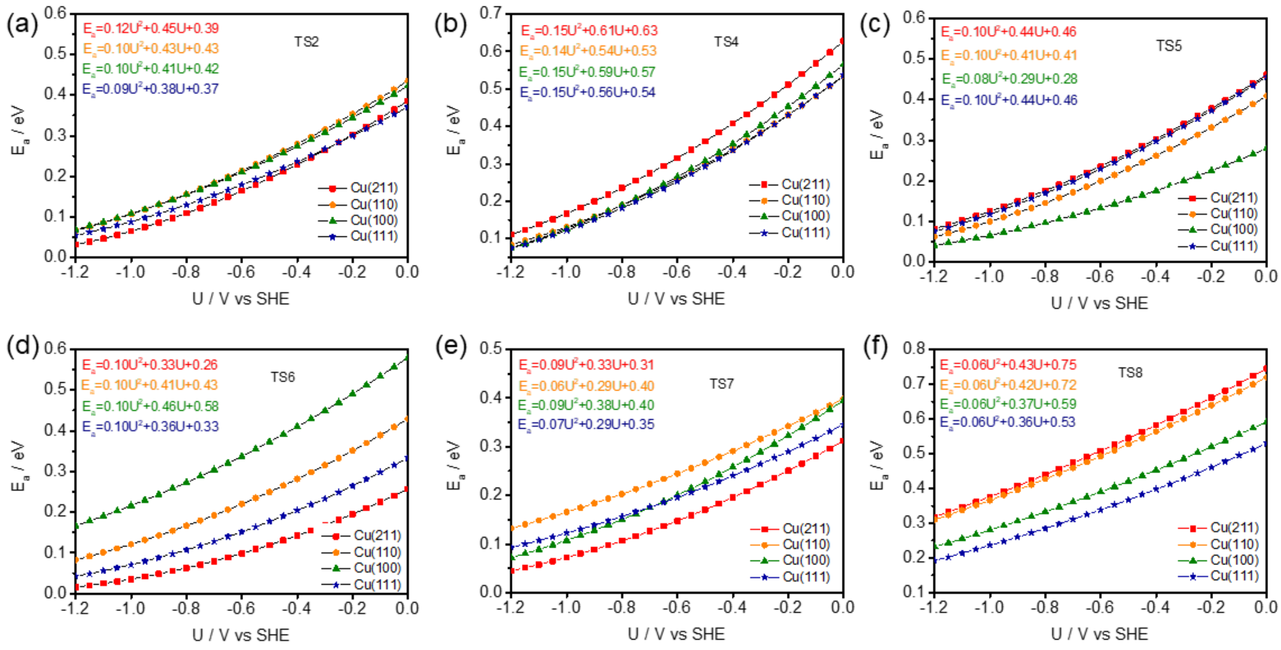


Fig. S2. Reaction barriers for (a) $^*COOH \rightarrow {}^*CO+H_2O$, (b) $^*CHO \rightarrow {}^*CHOH$, (c) $^*CHOH \rightarrow {}^*CH+H_2O$, (d) $^*CH \rightarrow {}^*CH_2$, (e) $^*CH_2 \rightarrow {}^*CH_3$ and (f) $^*CH_3 \rightarrow {}^*CH_4$ on different crystal facets as a function of applied electrode potential.

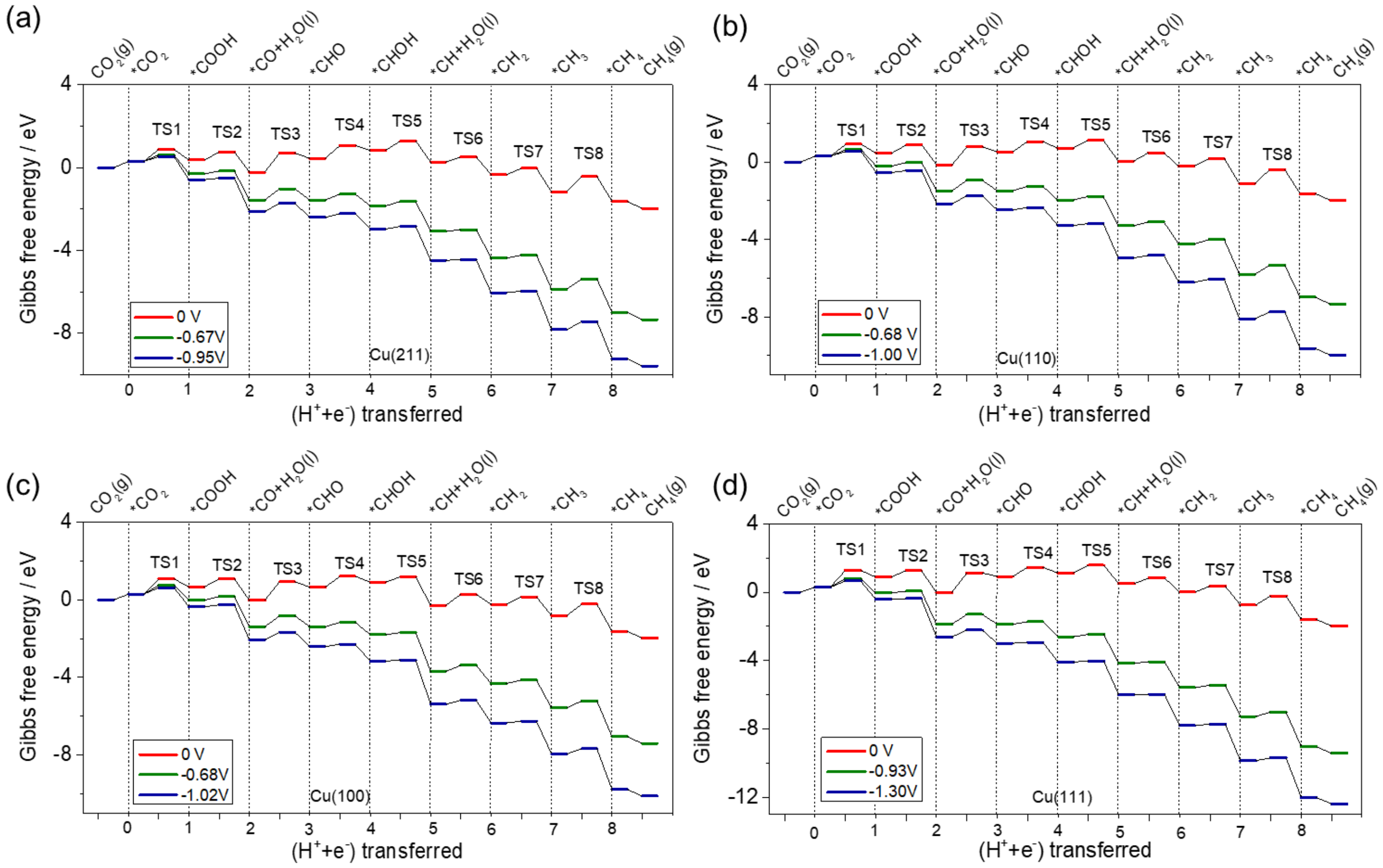


Fig. S3. Calculated Gibbs free energies of electroreduction of CO_2 as a function of the applied potential in pH = 0 solution on (a) Cu(211), (b) Cu(110), (c) Cu(100), (d) Cu(111) surfaces. The electrode potentials are referred to the standard hydrogen electrode.

Table S5. Calculated internal reorganization energy, solvent reorganization energy related to electron transfer, and solvent reorganization energy related to proton transfer for Electroreduction of CO_2 to CH_4 on four different structures. All values are given in eV.

Elementary Reaction	Facet	λ_R	λ_P	λ_R^i	λ_P^i	$\lambda_R^{o,ET}$	$\lambda_P^{o,ET}$	$\lambda_R^{o,PT}$	$\lambda_P^{o,PT}$
$*CO_2+H^++e^-\rightarrow *COOH$	Cu(211)	1.81	2.71	0.56	1.53	1.20	1.14	0.05	0.04
	Cu(110)	1.86	2.58	0.61	1.40				
	Cu(100)	2.18	2.69	0.93	1.51				
	Cu(111)	2.45	2.89	1.20	1.71				
$*COOH+H^++e^-\rightarrow *CO+H_2O$	Cu(211)	3.37	2.23	2.24	1.17	1.14	1.06	0.00	0.00
	Cu(110)	3.39	2.53	2.26	1.47				
	Cu(100)	3.41	2.66	2.27	1.60				
	Cu(111)	3.46	2.82	2.32	1.76				
$*CO+H^++e^-\rightarrow *CHO$	Cu(211)	2.25	2.04	0.97	0.82	1.25	1.19	0.03	0.03
	Cu(110)	2.24	2.18	0.96	0.96				
	Cu(100)	2.48	2.06	1.20	0.83				
	Cu(111)	2.41	2.18	0.78	1.02				
$*CHO+H^++e^-\rightarrow *CHOH$	Cu(211)	1.62	1.69	0.43	0.55	1.19	1.15	0.00	0.00
	Cu(110)	1.65	1.81	0.46	0.66				
	Cu(100)	1.74	1.61	0.55	0.46				
	Cu(111)	1.73	1.71	0.54	0.56				
$*CHOH+H^++e^-\rightarrow *CH+H_2O$	Cu(211)	3.34	2.59	2.19	1.48	1.15	1.10	0.00	0.00
	Cu(110)	3.23	2.60	2.08	1.49				
	Cu(100)	2.83	3.15	1.68	2.05				
	Cu(111)	3.62	2.58	2.47	1.47				
$*CH+H^++e^-\rightarrow *CH_2$	Cu(211)	1.83	2.22	0.47	0.96	1.35	1.27	0.00	0.00
	Cu(110)	1.98	2.46	0.63	1.19				
	Cu(100)	1.89	2.66	0.54	1.39				
	Cu(111)	1.98	2.38	0.63	1.11				
$*CH_2+H^++e^-\rightarrow *CH_3$	Cu(211)	2.44	2.78	1.12	1.53	1.27	1.21	0.05	0.04
	Cu(110)	2.22	3.90	0.90	2.65				
	Cu(100)	2.50	2.68	1.18	1.43				
	Cu(111)	1.87	3.40	0.55	2.15				
$*CH_3+H^++e^-\rightarrow *CH_4$	Cu(211)	3.69	3.94	2.48	2.57	1.21	1.37	0.00	0.00
	Cu(110)	3.56	4.07	2.35	2.71				
	Cu(100)	3.44	4.08	2.24	2.71				
	Cu(111)	3.17	3.94	1.96	2.58				

As seen from Table S5, the calculated reorganization energies of C1, C2, C5, and C8 are much larger than the other elementary reactions. The most important contribution of reorganization energies for these reactions arise from the inner reorganization term. For C1 and C8 reactions, the reactant CO_2 and product CH_4 are physisorbed on copper surfaces while COOH and CH_3 are strongly chemisorbed on copper surfaces. The molecular geometry changes significantly from the equilibrium configuration of the reactant to the equilibrium configuration of the product, which leads to a large inner reorganization energy. Similarly, C2 and C5 reaction are dehydration reactions with cleavage of C-O bond. The large molecular geometry change during electrochemical reduction results to a great inner reorganization energy. Alternatively, the molecular geometry change is quite tiny for C3, C4, C6, and C7, which produces relative smaller inner reorganization energies.