A First-Principles Study on the Reaction Mechanisms of Electrochemical CO_2 Reduction to C_1 and C_2 Products on Cu(110)

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The supporting information (SI) complements some computational details and Figures. The optimized adsorption geometries of the intermediates in Figure 1 and 2 are shown. The potential energy diagram for CO* desorption from Cu(110) surface. The bond lengths of Cu-O and Cu-C in representative intermediates on Cu(110) surface are also shown. The density of state (DOS) of C atom of adsorption of intermediates in C-C coupling pathway on Cu(110) surface. Diagrams of the difference in charge densities of C-C coupling intermediates on Cu(110) surface. The Gibbs free energy diagrams for CO_2 reduction to CH_3OH and C_2H_4 on Cu(110) surface with applied potentials.

Computation Detail

Setting cut-off energy. We refer to the cut-off energy in previous literature on Cu catalyst for CO_2 reduction reaction [81,82] and tested the energy of our system. From these calculations based on first-principles, we find that the cut-off energy is set to 400 eV, 450 eV, and 500 eV. In order to determine the specific value of the cut-off energy, we test the cut-off energy. According to the values of cut-off energy in the references, we tested the energy of the system with the cut-off energy values of 400, 450, 500, 550, 600 and 650 eV, respectively. Comparing the results of the tests, we find that the system energy is almost unchanged at the cutoff energies of 450, 500, 550, and 600 eV.

In addition, the adsorption energy of key intermediate is an important descriptor in our work. Therefore, we also take the adsorption energy of CO on Cu(110) surface as an example to test the value of cut-off energy. We test the valve of cut-off energy of 400, 450, 500, 550, 600 and 650 eV, respectively. The adsorption energies of CO on the Cu(110) surface are shown in the Table S1.

Table S1. Calculated Adsorption Energies of CO with Different Cut-off Energy on the Cu(110) Surface (Units in eV)

Adsorption energy	Cut-off energy					
	400	450	500	550	600	650
CO	0.026	0.016	-0.004	-0.005	-0.005	-0.006

It is worth noting that the calculation method of adsorption energy is described in the computation detail section of our manuscript. Comparing the adsorption energy of CO, it can be seen that when the values of cut-off energy are set at 500, 550, 600, and 650 eV, the adsorption energy of CO is almost unchanged. This means that the accuracy of the calculation results can be guaranteed when the cut-off energy is set at 500, 550, 600, and 650 eV. Since most of the key intermediates are anchored to the Cu(110) surface by C atoms, the effect of cut-off energy on the adsorption energies of other key intermediates is similar to the effect on the adsorption energy of CO. Therefore, combined with our own computing resources, we set the cut-off energy value of 550 eV.

Setting slab thickness and the number of fixed layers. For the choice of slab thickness and the number of fixed layers, we considered two aspects: refer to publications and test our calculation. Firstly, we refer to the literature on calculating the CO_2 reduction process on Cu catalyst based on first-principles from [69,70] in this work. From these literature, we find that the slab of Cu(110) consists of 6 atomic layers (Cu atoms in the same atomic layer have the same coordinates on the z axis), and in general, only the top two Cu atoms are relaxed during geometry optimization. Considering the open structure of the Cu(110) surface, more slab layers are also required, i.e., more thicker of slab thickness. Thus, to ensure the reliability of the results, we chose eleven-layers slab model and fixed the bottom two layers of Cu atoms.

Secondly, for the fixed layers of slab model, we consider two parts: one is energy of system; other is adsorption energy of intermediate. For the energy of system, we tested the different fixed layers of slab models. The number of fixed layers is set at 2, 3, 4, and 5. The results indicate that the different fixed layers make the difference of system energy less than 0.002 eV. For the adsorption energy of intermediate, we take the adsorption energy of CO as an example. Likewise, the number of fixed layers is set at 2, 3, 4, and 5. The calculation results of adsorption energy of

CO are shown in Table S2. It is worth noting that the calculation method of adsorption energy is described in the computation detail section of our manuscript.

Table S2. Calculated Adsorption Energies of CO with Different Fixed Layers of Slab Models (Units in eV)

Adsorption energy	Fixed Layers			
	2	3	4	5
CO	-0.004	-0.005	-0.005	-0.005

Comparing the adsorption energy of CO, it can be seen that when the number of fixed layers is 2, 3, 4, and 5, the adsorption energy of CO is almost unchanged. This means that the accuracy of the calculation results can be guaranteed when the number of fixed layers is 2. Since most of the key intermediates are anchored to the Cu(110) surface by C atoms, the effect of cut-off energy on the adsorption energies of other key intermediates is similar to the effect on the adsorption energy of CO. Therefore, the slab thickness and the number of fixed layers can accurately reflect our calculation results.

The effect of different number of fixed layers on reaction barriers. We choose the number of fixed layers is 2, 3, 4, and 5 in eleven-layer slab model. We take the steps of $CO^* + H^* \rightarrow CHO^*$ and $CO^* + CH_2O^* \rightarrow CO\text{-}CH_2O^*$ steps as examples, and the results are shown in Table S3.

Table S3. Calculated Reaction Barriers of $CO^*+H^* \rightarrow CHO^*$ and $CO^* + CH_2O^* \rightarrow CO\text{-}CH_2O^*$ Step with Different Fixed Layers of Slab Models (Units in eV)

Reaction Barriers	Fixed Layers			
	2	3	4	5
$CO^* + H^* \rightarrow CHO^*$	1.10	1.08	1.08	1.08
$CO^* + CH_2O^* \rightarrow CO\text{-}CH_2O^*$	0.19	0.16	0.15	0.15

It is worth noting that the calculation method of reaction barriers is described in the computation detail section of our manuscript. Comparing the reaction barriers of $CO^*+H^* \rightarrow CHO^*$ step, it can be seen that when the number of fixed layers is 2, 3, and 4, the reaction barrier of this step is almost unchanged. A similar situation can also be seen in calculation of reaction barrier of $CO^* + CH_2O^* \rightarrow CO\text{-}CH_2O^*$ step. This means that the accuracy of the calculation results can be guaranteed when the number of fixed layers is 2. Therefore, we believe that the different number of fixed layers do not significantly affect our calculation results.

Calculation method of transition state. For the identified transition states, ever though we cannot absolutely identify the transition state as indeed the highest energy points along the reaction pathway, we think that our calculation results are sufficient to reflect transition states in elementary steps. The reasons are as follows.

First, we choose an odd number of images to search the transition state since we know from symmetry that the transition state must lie in the middle of the reaction coordinate.

Secondly, although fitting a smooth curve through the CI-NEB calculated enough images can obtain maximum value, our calculation can also get a result close to the exact value of transition states. Because the number of intermediate images we choose can almost reflect the whole picture of a reaction process. Due to all the intermediate images are evenly distributed throughout the whole process. Therefore, the energy value we fit through calculation is generally close to the real maximum value, so we think that our calculation method and using number of intermediate images are reasonable. Our method and using number of intermediate images are

consistent with previous literature [83,84], which indicates the correctness of our calculation method.

Testing thickness of vacuum layer. Since van der Waals forces is taken into account in calculation system, we tested the thickness of vacuum layer. We refer to the thickness of vacuum layer in the previous literature [85-87], and set at 15, 20, and 25 Å, respectively. The adsorption energy of CO on the Cu(110) surface is calculated as an example. The adsorption energies of CO on the Cu(110) surface are shown in the Table S4.

Table S4. Calculated Adsorption Energies of CO with Different Vacuum Thickness on the Cu(110) Surface (Units in eV)

Adsorption energy	Vacuum Thickness (Å)		
	15	20	25
CO	-0.005	-0.009	-0.008

Comparing the adsorption energy of CO, it can be seen that when the vacuum thickness is set at 15, 20, and 25 Å, respectively, the adsorption energy of CO is almost unchanged. This means that the vacuum thickness is set at 15 Å already enough for van der Waals forces. Since most of the key intermediates are anchored to the Cu(110) surface by C atoms, the effect of cut-off energy on the adsorption energies of other key intermediates is similar to the effect on the adsorption energy of CO. Therefore, combined with our own computing resources, we believe that the vacuum thickness of 15 Å is sufficient to meet our calculation.

Solvation Model. As we know, applying different solvation models may change the absolute value of Gibbs free energy, but in the calculation process we should pay attention to the relative value of Gibbs free energy. Only the relative value of Gibbs free energy can reflect the trend of CO_2 reduction reaction. We have used a single water molecule to explain the solvation effects. In addition, we have also calculated the adsorption energies and activation energies of typical reaction step with two water molecules. Even though two water molecules are not enough to represent the full solvation environment, we can access the difference of error, thus to know the magnitude of the error considered for full solvation molecules are consider. If the difference in reaction energy, adsorption energy and activation energy between the single water and two water solvation models are small, we believe that our solvation model can obtain similar or slightly different calculation results compared with a full solvation model. The reaction energy of formation CO* on Cu(110) surface is calculated and the result are shown in Table S5.The adsorption energy of CO on Cu(110) surface are calculated and the result are shown in Table S6. The activation energy of CO hydrogenation to CHO on Cu(110) surface are calculated and the result are shown in Table S7.

Table S5. Calculated Reaction Energy of Steps of COOH* → CO* and CO* + CH_2O*→ CO-CH_2O* with Two Water Solvation Molecules Model and Comparison with a Single Water Solvation Molecule Model.

Reaction Energy	Solvation model	
	A single water molecule	Two water molecules
COOH* → CO*	-0.016	-0.07
CO-CH_2O* → CHO-CH_2O*	-0.18	-0.13

Table S6. Calculated Adsorption Energy of CO with Two Water Solvation Molecules Model and Comparison
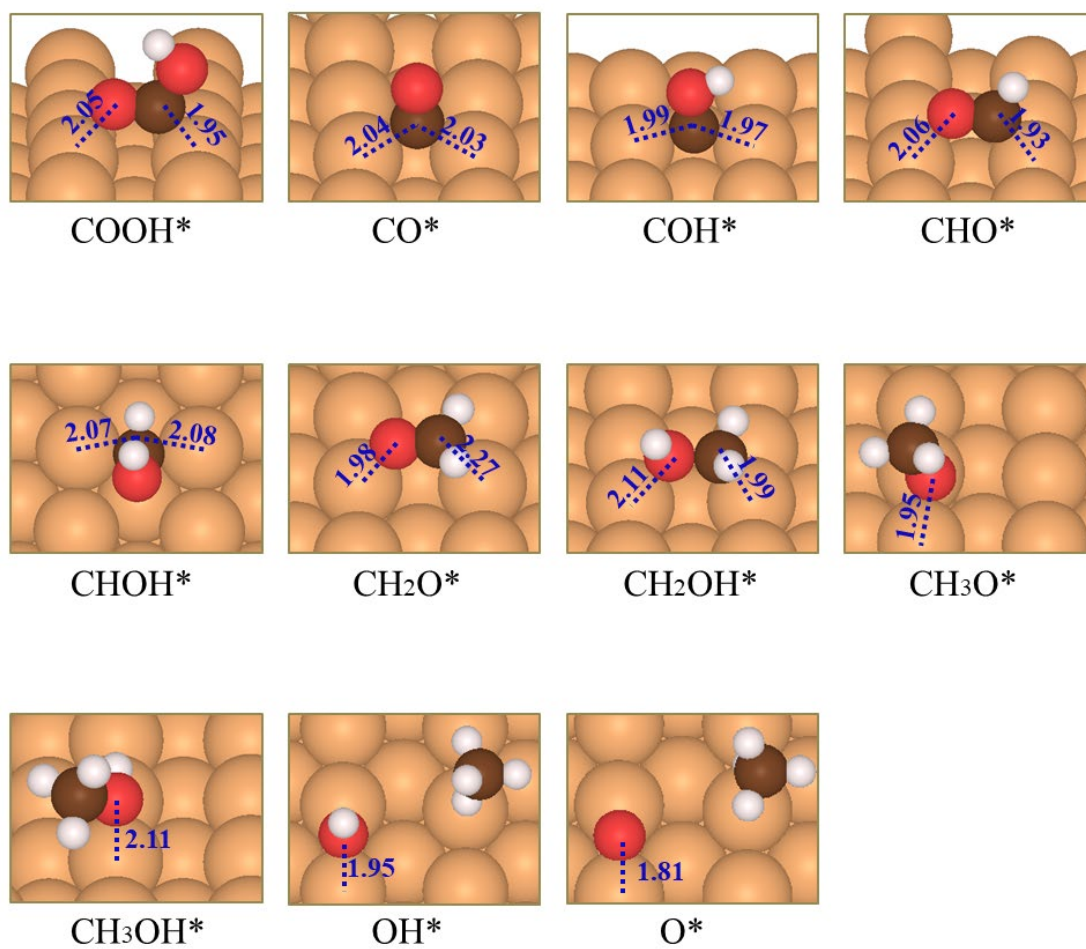
with a Single Water Solvation Molecule Model.

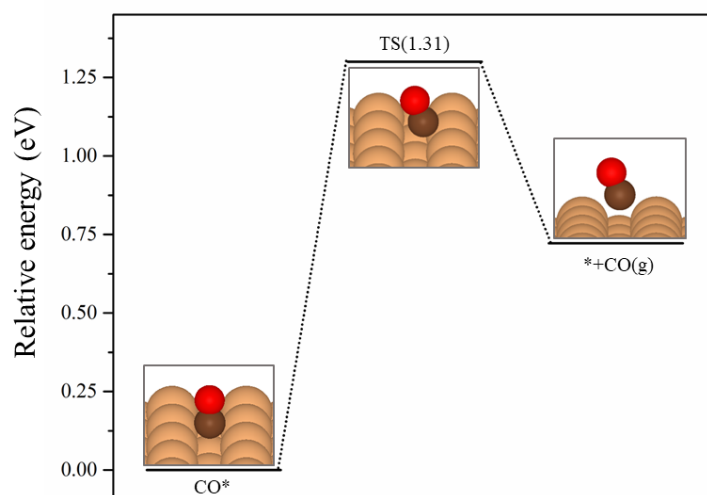| Adsorption Energy	Solvation model	
	A single water molecule	Two water molecules
CO	-0.005	-0.013

Table S7. Calculated Activation Energies of CO Hydrogenation to CHO and CO and CH₂O Coupling with Two Water Solvation Molecules Model and Comparison with a Single Water Solvation Molecule Model.

Activation Energy	Solvation model	
	A single water molecule	Two water molecules
CO* + H* → CHO*	1.10	1.02
CO* + CH₂O* → CO-CH₂O*	0.19	0.11

Compared with two water molecules solvation model, a single water molecule slightly overestimates the reaction energy, adsorption energy and activation energies. However, these differences are small enough (less than 0.1 eV). Considering that the solvent effect has small enough effect on the reaction energies, adsorption energies and activation energies, we think that it has small enough effect on our calculation results. Thus, we believe that a single water molecule solvation model employed our calculations is still reasonable.

Figure S1. The optimized adsorption geometries of the intermediates in Figure 1 and the bonding distances between them and the Cu(110) surface are shown. Cu: yellow, C: brown, O: red, H: white.
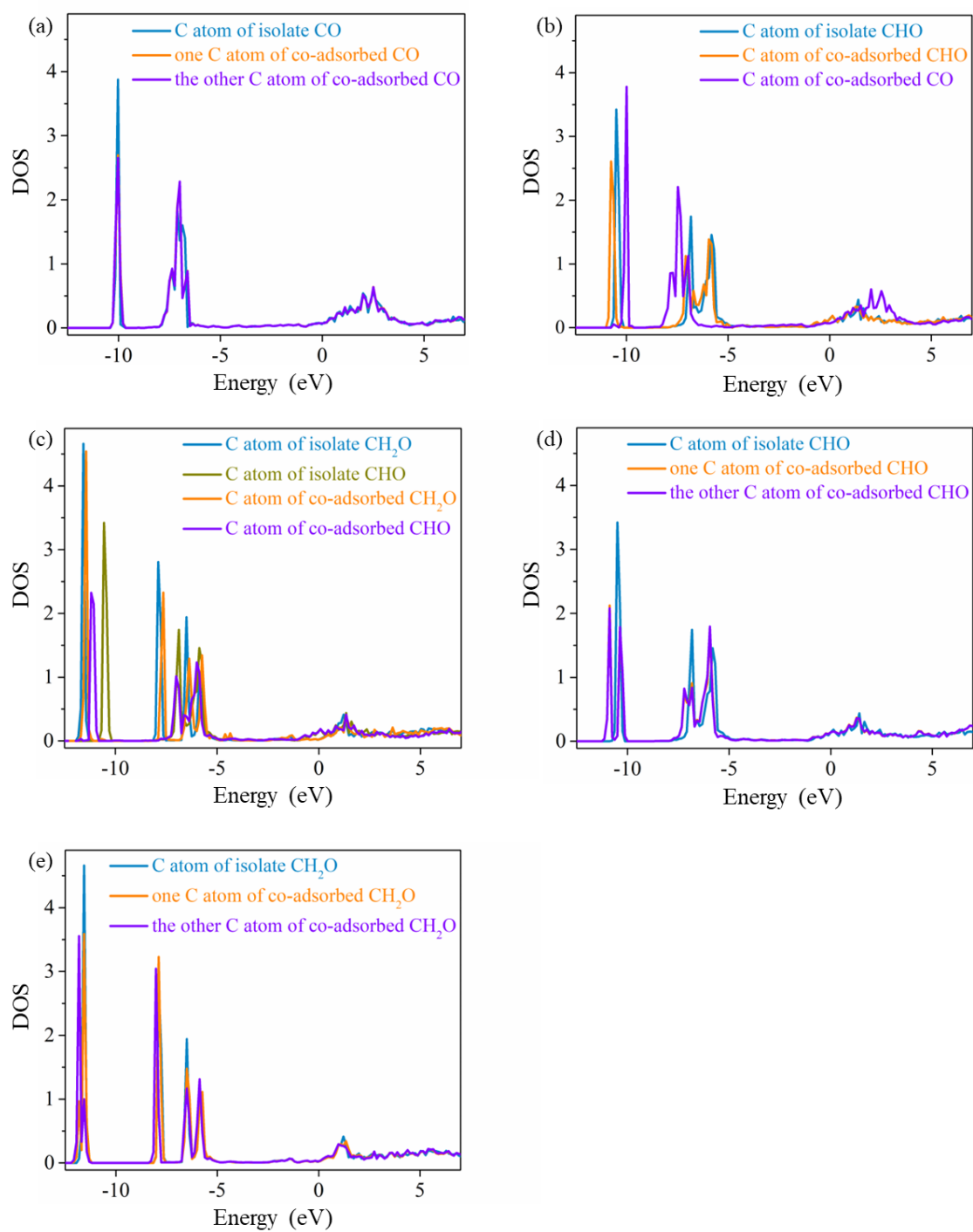
Figure S2. Schematic potential energy diagram for CO* desorption from Cu(110) surface. The optimized adsorption geometries of the initial state, transition state, and finial state are shown in the insets. Cu: yellow, C: brown, O: red.
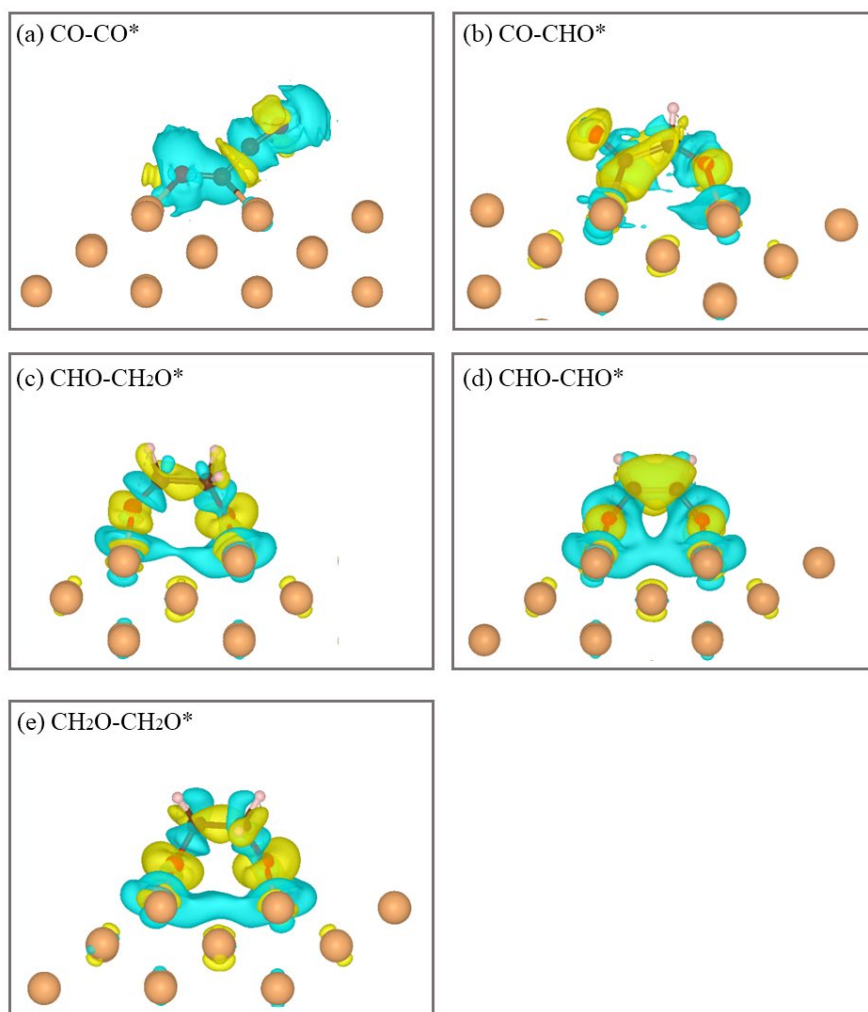
Figure S3. The optimized adsorption geometries of initial states, transition states, and finial states involved in CO*
reduction to CH₃O* in Figure 2. The bonding distances between them and the Cu(110) surface are also shown. Cu:
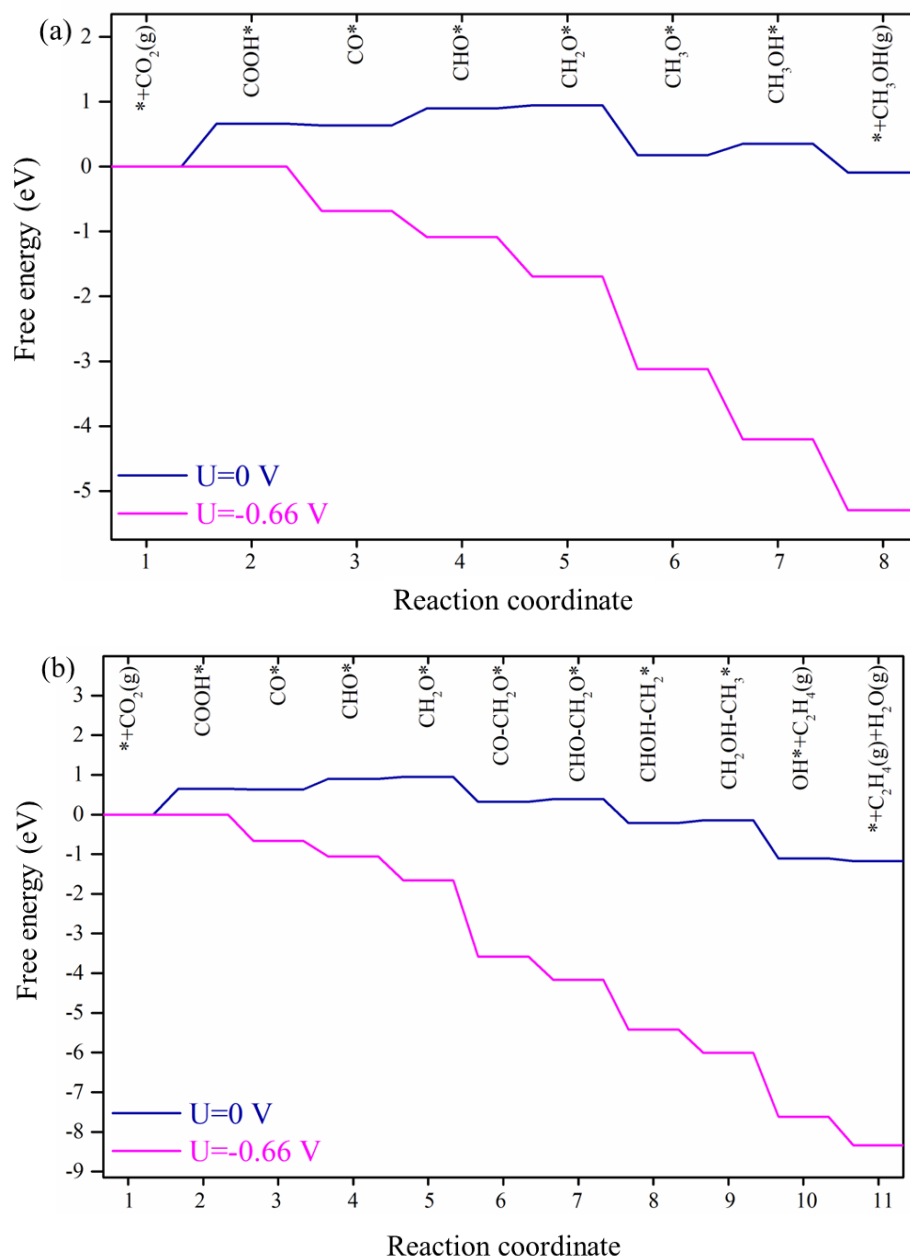yellow, C: brown, O: red, H: white.

Figure S4. Density of states (DOSs) plots of C atoms of adsorbed intermediates in (a) two CO* (b) CO* and CHO*; (c) CHO* and CH₂O*; (d) CHO* and CHO*; and (e) CH₂O* and CH₂O* pathways on Cu(110) surface.

Figure S5. Diagrams of the difference in charge densities of (a) CO-CO*; (b) CO-CHO*; (c) CHO-CH$_2$O*; (d) CHO-CHO*; and (e)CH$_2$O-CH$_2$O* on Cu(110) surface by an isosurface of 0.002 eV/Å.

Figure S6. Gibbs free energy diagrams for CO_2 reduction to (a) CH_3OH and (b) C_2H_4 on the Cu(110) surface with applied potentials of 0 V and −0.66 V versus RHE.