1. COMPUTATIONAL DETAILS

1.1 Surface and Solvation Model

Considering the complexity of real CO$_2$ electroreduction systems, the aqueous-phase environment is included in the present study, in which 12 explicit H$_2$O molecules with two relaxed bilayer structures chosen to fill up the vacuum region were used to model the solvation effect in order to better simulate the interactions between solvent and adsorbates and decrease the size of the simulated systems as much as possible. In fact, the formation of an ordered H$_2$O bilayer structure in a hexagonal arrangement with 2/3 monolayer saturation coverage with respect to the surface normal had been demonstrated by X-ray absorption spectroscopy, thermal desorption spectroscopy, low-energy electron diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy along with DFT calculations in previous experimental and theoretical studies on the meal surface.$^{1-3}$ Our present solvation model is on the basis of the previous studies on structure and orientation of H$_2$O. However, many different H$_2$O solvation structures may also exist, which all are approximate in energy.$^4$ Since all energies of interest in this study are energy differences, which are not sensitive to the accurate model of H$_2$O as long as the same model is consistently used.
used and a reasonable model in a local minimum structure is choose when calculating the energy differences. Considering the coverage is 2/3 of H\textsubscript{2}O monolayer, thus, a (3x3) Cu(100) slab model with nine metal atoms per layer and theoretical equilibrium lattice constant of 3.66 Å by using four metal layers was created.

1.2 Computational Parameters

Using the generalized gradient approximation of the Perdew–Burke–Ernzerhof exchange correlation functional, calculations were performed in the framework of DFT.\textsuperscript{5} Ultrasoft pseudopotentials were employed to describe the nuclei and core electrons and the Kohn-Sam equations were self-consistently solved using a plane-wave basis set.\textsuperscript{6} A kinetic energy cutoff of 30 Ry and a charge-density cutoff of 300 Ry were used to make the basis set finite. The Fermi surface has been treated by the smearing technique of Methfessel–Paxton with a smearing parameter of 0.02 Ry.\textsuperscript{7} The PWSCF codes in Quantum ESPRESSO distribution were employed to perform all calculations.\textsuperscript{8} Brillouin-zone integrations were implemented using a (3x3x1) uniformly shifted k-mesh for (3x3) supercell with the special-point technique, which was tested to converge to a subset of the relative energies reported herein. A vacuum layer of 16Å was placed above the top layer of slab, which is sufficiently large to ensure that the interactions are negligible between repeated slabs in a direct normal to the surface. The Cu atoms in the bottom two layers are fixed at the theoretical bulk positions, whereas the top two layers and all adsorbates including solvent are allowed to relax to minimize the total energy of the system. Structural optimization was performed until the Cartesian force components acting on each atom were brought below 10\textsuperscript{-3} Ry/Bohr and the total energy was converged to within 10\textsuperscript{-5} Ry. Using the climbing image nudged elastic band (CI-NEB) method, the saddle points and minimum energy paths (MEPs) were located by initially setting initial state and final state.\textsuperscript{9, 10} Zero point energy (ZPE) corrections were applied into the calculations of the activation and reaction energies from MEP analysis, in which density functional perturbation theory within the linear response was used to study the vibrational properties.\textsuperscript{11} The ZPEs were calculated using the PHONONS code that contained in the Quantum ESPRESSO distribution.\textsuperscript{8}

1.3 CO Coverage-Dependent Electrode/Solution Interface Model

We have reported the methodology for CO coverage-dependent equilibrium potentials on Cu(111) in our recent work,\textsuperscript{12} which was used to model reduction pathways of CO\textsubscript{2} into CH\textsubscript{4} products at the low overpotentials. In this paper, the corresponding method is again employed to study the potential-dependent
C-C bond formation mechanisms on Cu(100). As abovementioned, CO had been identified as a key intermediate during CO\textsubscript{2} reduction, which can be formed by following reaction (S1):

\[
\text{CO}_2 + \ast + 2(\text{H}^+ + \text{e}^-) \rightarrow \text{CO}^\ast + \text{H}_2\text{O} \quad (\text{S1})
\]

On the basis of the approach proposed by Nørskov et al. and Chen et al. for hydrogen evolution and oxygen reduction reactions\textsuperscript{13-17}, equation (S2) can be used to calculate the Gibbs free energy of reaction (1), \(\Delta G(\theta)\) at various surface CO coverage, in which \(\Delta E(\theta), \Delta S(\theta), \Delta \text{ZPE}\) and \(k_B T \ln(\theta/1-\theta)\) are the differential adsorption energy of CO, entropy, zero-point energy and configurational entropy contributions to \(\Delta G(\theta)\), respectively. Here coverage \(\theta = n/N\), in which \(n\) is the number of surface adsorbed CO molecule and \(N\) is the total number of the surface Cu atoms.

\[
\Delta G(\theta) = \Delta E(\theta) + 2eU - T\Delta S(\theta) + \Delta \text{ZPE} + 2k_B T \ln(\theta/1-\theta) \quad (\text{S2})
\]

\(\Delta E(\theta)\) can be calculated according to equation (S3) by differentiating the plots of \(\partial E(\theta)_M\text{CO}_n / n\) against \(\theta\), in which \(E(\theta)_M\text{CO}_n\) is the total energy of the surface with different CO coverage, \(E_{\text{H}_2\text{O}}, E_{\text{CO}_2}\) and \(E_{\text{H}_2}\) are the total energy of isolated \text{H}_2\text{O}, \text{CO}_2 and \text{H}_2\) molecules, respectively, and they are directly available through DFT calculations.

\[
\Delta E(\theta) = \left[\partial E(\theta)_M\text{CO}_n / \partial n + E_{\text{H}_2\text{O}} - E_{\text{CO}_2} - E_{\text{H}_2}\right] \\
= \left[\partial E(\theta)_M\text{CO}_n / N \partial \theta + E_{\text{H}_2\text{O}} - E_{\text{CO}_2} - E_{\text{H}_2}\right] \quad (\text{S3})
\]

Considering that the entropies of the adsorbed molecules are small when compared with the entropies of gaseous and that the zero-point energy of the surface adsorbed CO molecules is little according to our calculations, the contributions from the changes of entropy and ZPE together to \(\Delta G(\theta)\) has been estimated to be -0.42 eV for standard temperature (298 K) based on the available data from Nørskov et al.\textsuperscript{18} Combining equation (S2) with (S3), we can obtain the following form of equation (S4). Accordingly, the CO coverage-dependent equilibrium potential \(U\) (vs. RHE) can be determined when \(\Delta G(\theta)\) is equal to zero.

\[
\Delta G(\theta) = \left[\partial E(\theta)_M\text{CO}_n / N \partial \theta + E_{\text{H}_2\text{O}} - E_{\text{CO}_2} - (E_{\text{H}_2} - 2eU)\right] + 0.42 \\
+ 2k_B T \ln(\theta/1-\theta) \quad (\text{S4})
\]
2. CO adsorption Configurations on Cu(100)

Figure S1. Various possible surface CO adsorption configurations on Cu(100) at different CO coverage: (a) 1/16 ML; (b) 1/12 ML; (c) 1/9 ML; (d) 2/9 ML; (e) 1/3 ML; (f) 4/9 ML; (g) 5/9 ML; (h) 2/3 ML; (i) 7/9 ML; (j) 8/9 ML; (k) 1 ML; (l) 10/9 ML.
3. CO Coverage-Dependent Equilibrium Potentials

Figure S2. (a) The polynomial relationships between CO coverage ($\theta_{CO}$) and the differential adsorption energy of CO, $\Delta E(\theta)$; (b) The polynomial dependence of the calculated equilibrium potentials ($U$) on $\theta_{CO}$ on Cu(100).

4. Geometry for C-C Bond Formation Pathways

4.1 Initial CO Electreduction Pathways on Cu(111)

4.1.1 Condition of Low Overpotential ($\theta_{CO} = 1/9$ ML)

Figure S3. The geometries of CO electreduction into CHO species on Cu(111) at the low overpotential ($\theta_{CO} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S4. The geometries of CO electroreduction into COH species on Cu(111) at the low overpotential ($\theta_{CO} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S5. The geometries of CO dimerization into OCCO species on Cu(111) at the low overpotential ($\theta_{CO} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

4.1.2 Condition of Medium Overpotential ($\theta_{CO} = 2/9$ ML)

Figure S6. The geometries of CO electroreduction into CHO species on Cu(111) at the medium overpotential ($\theta_{CO} = 2/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S7. The geometries of CO electroreduction into COH species on Cu(111) at the medium overpotential ($\theta_{\text{CO}} = 2/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S8. The geometries of CO dimerization into OCCO species on Cu(111) at the medium overpotential ($\theta_{\text{CO}} = 2/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

4.1.3 Condition of High Overpotential ($\theta_{\text{CO}} = 1/3$ ML)

Figure S9. The geometries of CO electroreduction into CHO species on Cu(111) at the high overpotential ($\theta_{\text{CO}} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S10. The geometries of CO electroreduction into COH species on Cu(111) at the high overpotential ($\theta_{\text{CO}} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S11. The geometries of CO dimerization into OCCO species on Cu(111) at the high overpotential ($\theta_{\text{CO}} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

4.2 Initial CO Electroreduction Pathways on Cu(100)

4.2.1 Condition of Low Overpotential ($\theta_{\text{CO}} = 1/9$ ML)

Figure S12. The geometries of CO electroreduction into CHO species on Cu(100) at the low overpotential ($\theta_{\text{CO}} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S13. The geometries of CO electroreduction into COH species on Cu(100) at the low overpotential ($\theta_{\text{CO}} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S14. The geometries of CO dimerization into OCCO species on Cu(100) at the low overpotential ($\theta_{\text{CO}} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

4.2.2 Condition of Medium Overpotential ($\theta_{\text{CO}} = 2/9$ ML)

Figure S15. The geometries of CO electroreduction into CHO species on Cu(100) at the medium overpotential ($\theta_{\text{CO}} = 2/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S16. The geometries of CO electroreduction into COH species on Cu(100) at the medium overpotential ($\theta_{\text{CO}} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S17. The geometries of CO dimerization into OCCO species on Cu(100) at the medium overpotential ($\theta_{\text{CO}} = 2/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

4.2.3 Condition of High Overpotential ($\theta_{\text{CO}} = 1/3$ ML)

Figure S18. The geometries of CO electroreduction into CHO species on Cu(100) at the high overpotential ($\theta_{\text{CO}} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S19. The geometries of CO electroreduction into COH species on Cu(100) at the high overpotential ($\theta_{\text{CO}} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S20. The geometries of CO dimerization into OCCO species on Cu(100) at the high overpotential ($\theta_{\text{CO}} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

4.3 CHO/COH Electroreduction Pathways on Cu(100)

4.3.1 Condition of Low Overpotential ($\theta_{\text{CO}} = 1/9$ ML)

Figure S21. The geometries of CHO electroreduction into CH$_2$O species on Cu(100) at the low overpotential ($\theta_{\text{CO}} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S22. The geometries of CHO electroreduction into CHOH species on Cu(100) at the low overpotential ($\theta_{CO} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S23. The geometries of dimerization of CHO with CO into COCHO species at the low overpotential ($\theta_{CO} = 1/9$ ML) on Cu(100) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S24. The geometries of CHO dimerization into CHOCHO species on Cu(100) at the low overpotential ($\theta_{CO} = 1/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).
4.3.2 Condition of Medium Overpotential ($\theta_{\text{CO}} = 2/9$ ML)

**Figure S25.** The geometries of COH electroreduction into CHOH species on Cu(100) at the medium overpotential ($\theta_{\text{CO}} = 2/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

**Figure S26.** The geometries of COH electroreduction into C species along with H$_2$O on Cu(100) at the medium overpotential ($\theta_{\text{CO}} = 2/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

**Figure S27.** The geometries of dimerization of COH with CO into COCOH species at the medium overpotential ($\theta_{\text{CO}} = 2/9$ ML) on Cu(100) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S28. The geometries of COH dimerization into COHCOH species on Cu(100) at the medium overpotential ($\theta_{CO} = 2/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

4.3.3 Condition of High Overpotential ($\theta_{CO} = 1/3$ ML)

Figure S29. The geometries of CHO electroreduction into CH$_2$O species on Cu(100) at the high overpotential ($\theta_{CO} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S30. The geometries of CHO electroreduction into CHOH species on Cu(100) at the high overpotential ($\theta_{CO} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S31. The geometries of dimerization of CHO with CO into COCHO species at the high overpotential ($\theta_{CO} = 1/3$ ML) on Cu(100) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S32. The geometries of CHO dimerization into CHOCHO species on Cu(100) at the high overpotential ($\theta_{CO} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S33. The geometries of dimerization of CHO with COH into CHOCHO species at the high overpotential ($\theta_{CO} = 1/3$ ML) on Cu(100) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S34. The geometries of COH electroreduction into CHOH species on Cu(100) at the high overpotential ($\theta_{CO} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S35. The geometries of COH electroreduction into C species along with H$_2$O on Cu(100) at the high overpotential ($\theta_{CO} = 1/3$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

Figure S36. The geometries of dimerization of COH with CO into COCOH species at the high overpotential ($\theta_{CO} = 1/3$ ML) on Cu(100) (IS represents initial state, TS represents transition state and FS represents final state).
Figure S37. The geometries of COH dimerization into COHCOH species on Cu(100) at the high overpotential ($\theta_{CO} = 2/9$ ML) (IS represents initial state, TS represents transition state and FS represents final state).

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