Supporting Information

Theoretical Understanding on the Effect of Specifically Adsorbed Halide Anions on Cu-Catalyzed CO_2 Electroreduction Activity and Product Selectivity

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1. Model and computational details

1.1 Surface and solvation model

The closed-packed Cu(111) crystal planes are generally chosen as the representative surfaces for both experimental and theoretical studies due to their high selectivity to CO_2 electroreduction into hydrocarbons. Considering the complexity of real CO_2 electroreduction systems, the aqueous-phase environment is included in the present study, in which 12 explicit H_2O 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 (See Figure S1). In fact, the formation of an ordered H_2O 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_2O. However, many different H_2O 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_2O as long as the same model is consistently used and a reasonable model in a local minimum structure is choose when calculating

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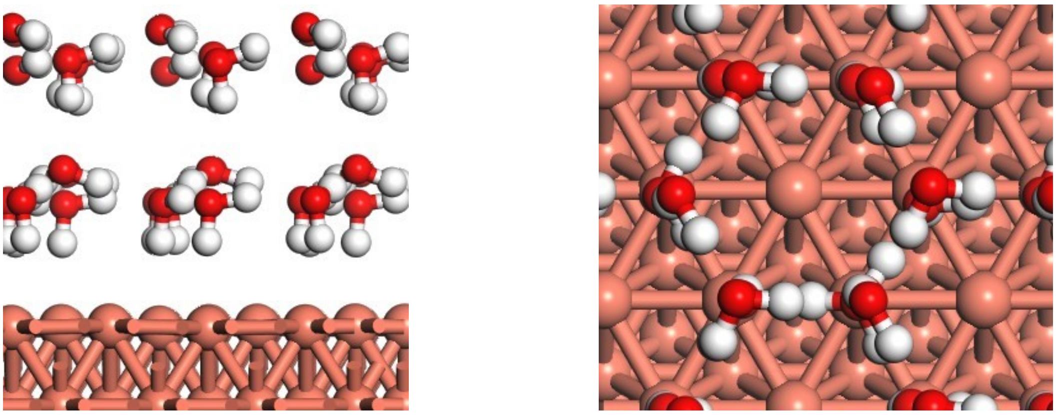
the energy differences. Considering the coverage is 2/3 of H_2O monolayer, thus, a (3x3) Cu(111) slab model with nine metal atoms per layer and theoretical equilibrium lattice constant of 3.66 Å by using four metal layers was created.



(a) (b)

Figure S1. The solvation model on Cu(111): (a) side view; (b) top view.

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.[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.[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.[7] The PWSCF codes in Quantum ESPRESSO distribution were employed to perform all calculations.[8] Brillouin-zone integrations were implemented using a (3×3×1) uniformly shifted k-mesh for (3×3) 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^{-3} Ry/Bohr and the total energy was converged to within 10^{-5} Ry. Using the climbing image nudged elastic band (CI-NEB) method, the saddle points and minimum energy paths (MEPs) were located.[9, 10] Zero point energy (ZPE) corrections were applied into the calculations of the activation and reaction free energies from MEP analysis, in which density functional perturbation theory within the linear response was used to study the vibrational properties.[11] The ZPEs were calculated using the PHONONS code that contained in the Quantum ESPRESSO distribution.[8]

The standard DFT approaches are unable to account for van der Waals dispersion forces properly. Taking an example of initial CO_2 electroreduction into COOH intermediate at F^- modified Cu(111)/H_2O interface, we examine the role of van der Waals interactions by using D2 scheme suggested by Grimme.[12] The calculated results showed that the reaction free energy is *ca*. -0.03 and -0.06 eV without and with van der Waals interactions, respectively. Thus, we can conclude that the effect of van der Waals interactions on energetics may be negligible at halide anions modified Cu(111)/H_2O interface due to subtle difference of reaction free energy.

For elementary reaction step of (A+H)* → AH* at halide anions modified Cu(111)/H_2O interfaces, the reaction free energy is calculated based on $\triangle G_{reac} = E(\text{AH*})\text{-}E[(\text{A+H})\text{*}]\text{+ZPE(AH*)-ZPE(A*)-ZPE(H*)}$, in which the asterisk (*) indicates that the species is adsorbed at halide anions modified Cu(111)/H_2O interfaces and the co-adsorption structures was optimized for steps involving co-adsorption of two species. The previous theoretical studies addressing systems in heterogeneous catalysis and surface science showed that any change of the adsorbed species including halogen atoms in entropy is negligible.[13-15] Thus, the entropy change of the adsorbed species are ignored in this paper.

2. Minimum Energy Pathways

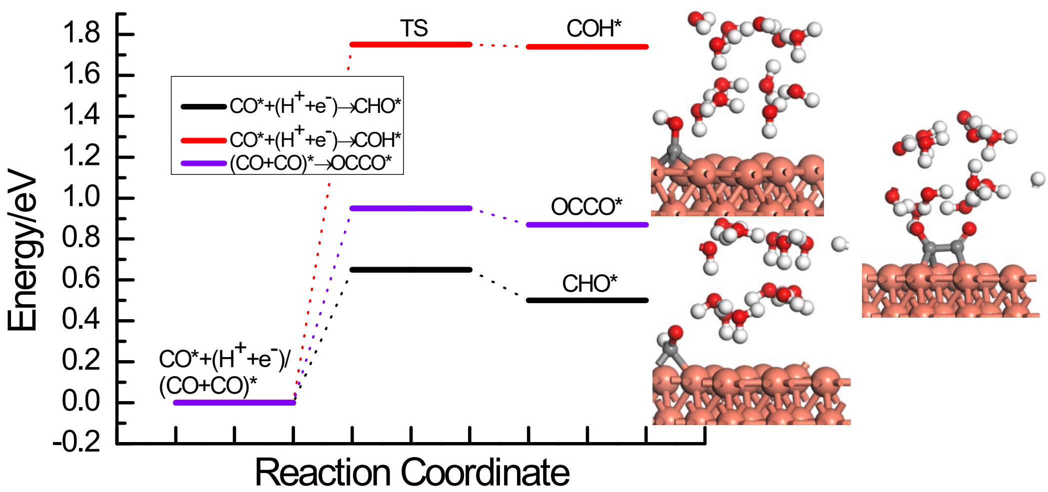


Fig. S2. The minimum energy pathway diagram of CO electroreduction into CHO, COH and OCCO intermediates at clean Cu(111)/H_2O interface.

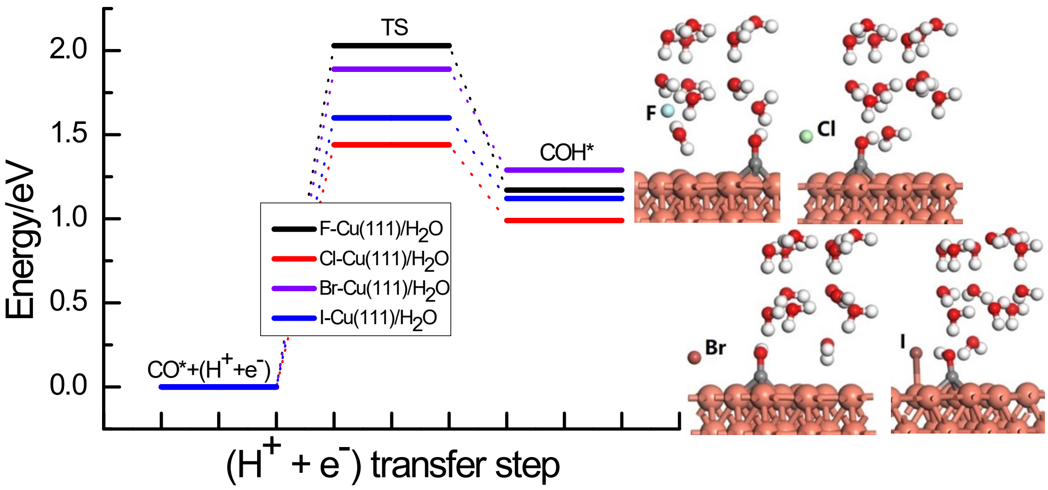


Fig. S3. The minimum energy pathway diagram of CO electroreduction into COH intermediate at specifically adsorbed F^-, Cl^-, Br^- and I^- modified Cu(111)/H_2O interfaces.

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