

## Supporting Information

### Mechanistic Insights into Potential Dependence for CO Electrochemical Reduction into C<sub>1</sub> Products Based on an H Coverage-Dependent Cu(111)/H<sub>2</sub>O Interface Model

Lihui Ou\*, Zixi He, Yuandao Chen, Junling Jin

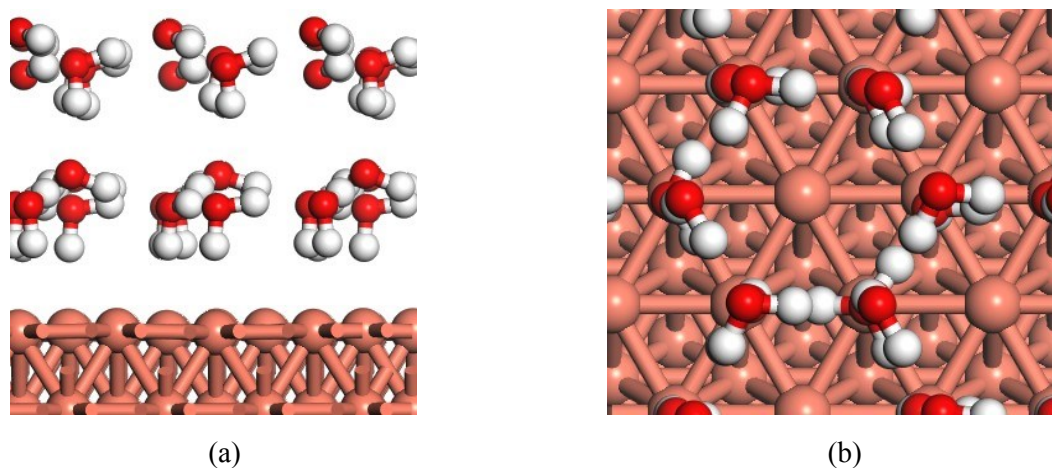
#### 1. Model and Computational Details

##### 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<sub>2</sub> electroreduction into CH<sub>4</sub>. Considering the complexity of real CO<sub>2</sub> electroreduction systems, the aqueous-phase environment is included in the present study, in which 12 explicit H<sub>2</sub>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 (See Figure S1). In fact, the formation of an ordered H<sub>2</sub>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 metal surface.<sup>1-3</sup> Our present solvation model is on the basis of the previous studies on structure and orientation of H<sub>2</sub>O. However, many different H<sub>2</sub>O solvation structures may also exist, which all are approximate in energy.<sup>4</sup> Since all energies of interest in this study are energy differences, which are not sensitive to the accurate model of H<sub>2</sub>O as long as the same model is consistently used and a reasonable model in a local minimum structure is chosen when calculating the energy differences. Considering the coverage is 2/3 of H<sub>2</sub>O monolayer, thus, a (3×3) 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.

---

\*Hunan Province Cooperative Innovation Center for the Construction & Development of Dongting Lake Ecologic Economic Zone, Hunan Provincial Key Laboratory of Water Treatment Functional Materials, Hunan Province Engineering Research Center of Electroplating Wastewater Reuse Technology, College of Chemistry and Materials Engineering, Hunan University of Arts and Science, Changde, 415000, China. E-mail: [oulihui666@126.com](mailto:oulihui666@126.com)



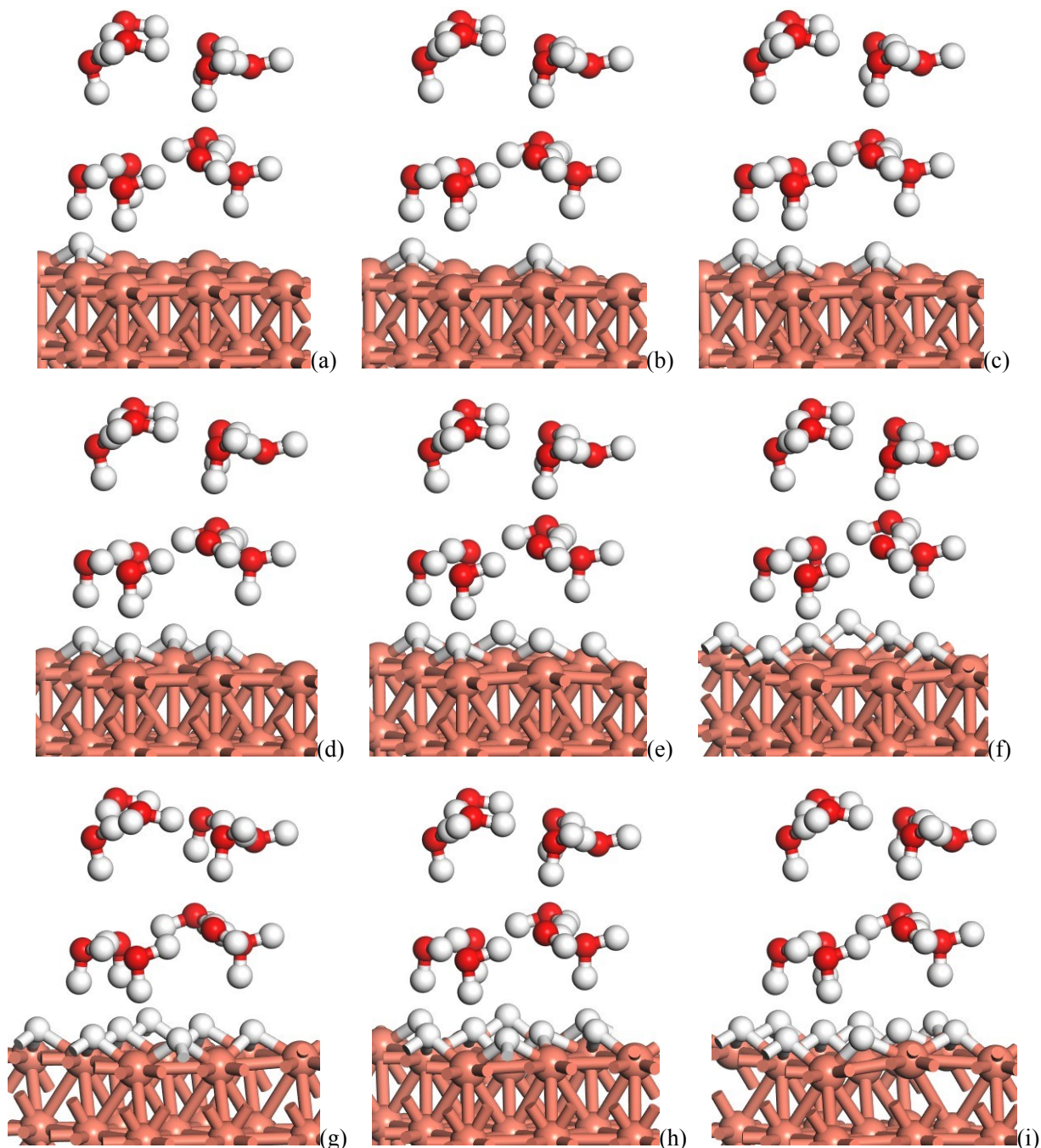
**Figure S1.** The Solvation Model on Cu(111): (a) Side View; (b) Top View.

## 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.<sup>5</sup> 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.<sup>6</sup> 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.<sup>7</sup> The PWSCF codes in Quantum ESPRESSO distribution were employed to perform all calculations.<sup>8</sup> Brillouin-zone integrations were implemented using a  $(3 \times 3 \times 1)$  uniformly shifted k-mesh for  $(3 \times 3)$  supercell with the special-point technique, which was tested to converge to a subset of the relative energies reported herein. A vacuum layer of  $16 \text{ \AA}$  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.<sup>9, 10</sup> 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.<sup>11</sup> The ZPEs were calculated using the PHONONS code that contained in the Quantum ESPRESSO distribution.<sup>8</sup>

## 2. H Adsorption Configuration on Cu(111)

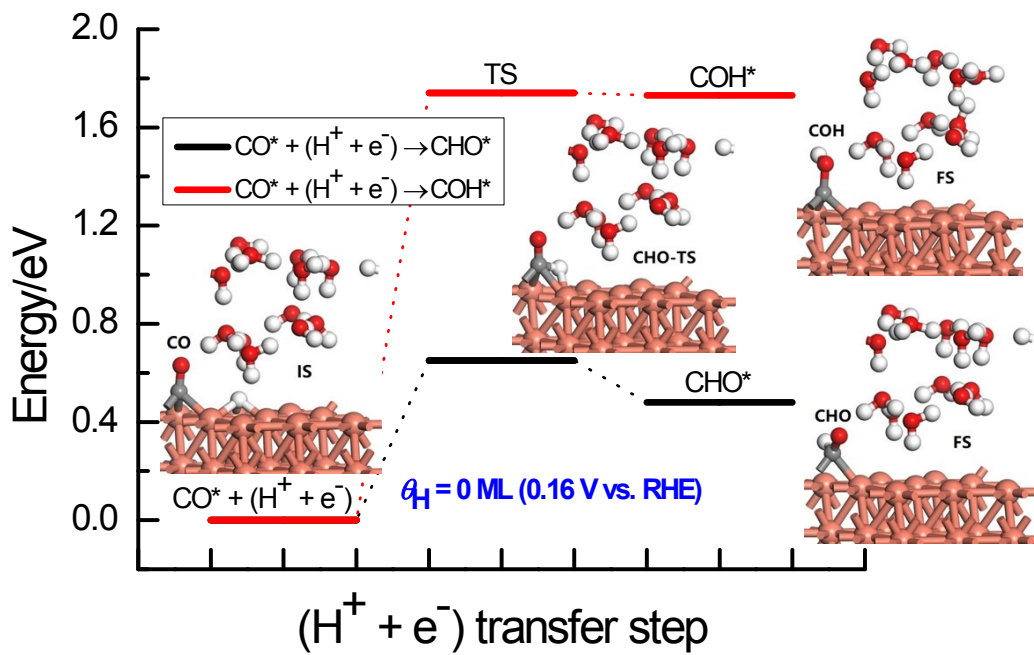
Various possible surface adsorption sites of H atoms and coverage dependence are considered in our present study, as shown in Figure S2. It is observed that H atoms prefer to adsorb at 3-fold face-centered cubic hollow (fcc) sites on Cu(111) so that they can stay away from each other to minimize the repulsive reactions in our present research scope on  $\theta_H$ .



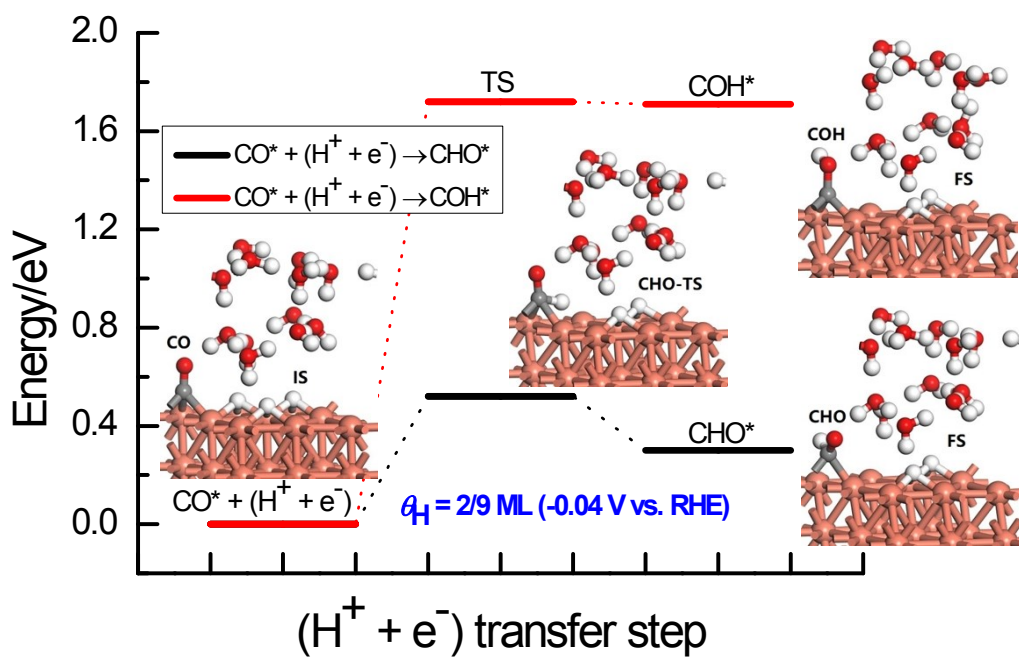
**Figure S2.** Various possible surface H adsorption configurations on Cu(111) at different H coverage: (a) 1/9 ML; (b) 2/9 ML; (c) 1/3 ML; (d) 4/9 ML; (e) 5/9 ML; (f) 2/3 ML; (g) 7/9 ML; (h) 8/9 ML; (i) 1ML.

### 3. Minimum Energy Pathways of Various Elementary Reaction Steps

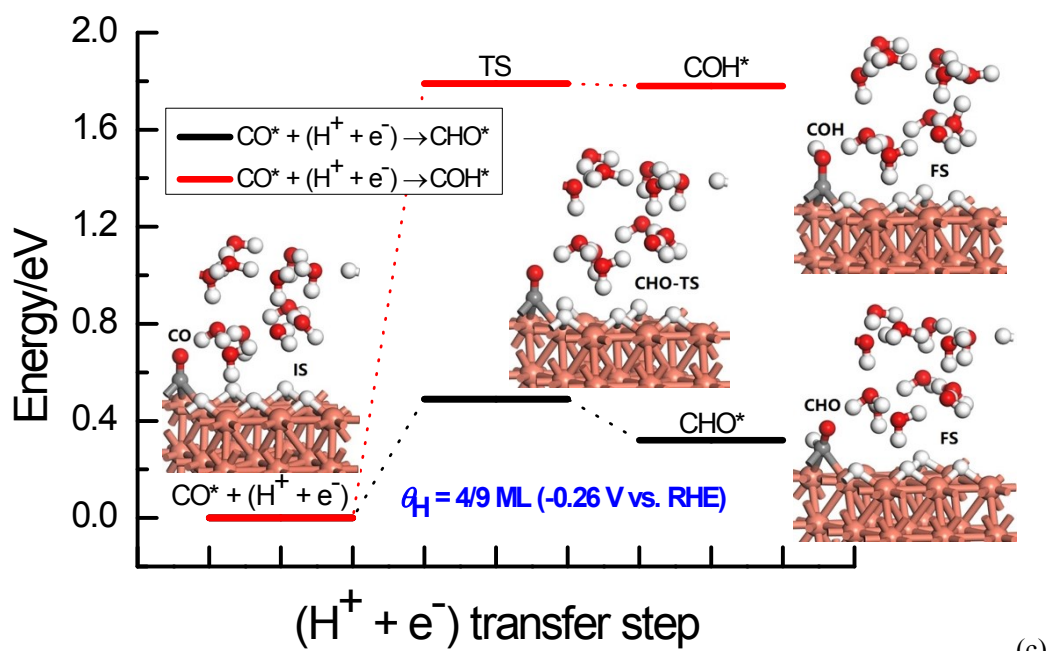
#### 3.1 CO Electroreduction into CHO and COH



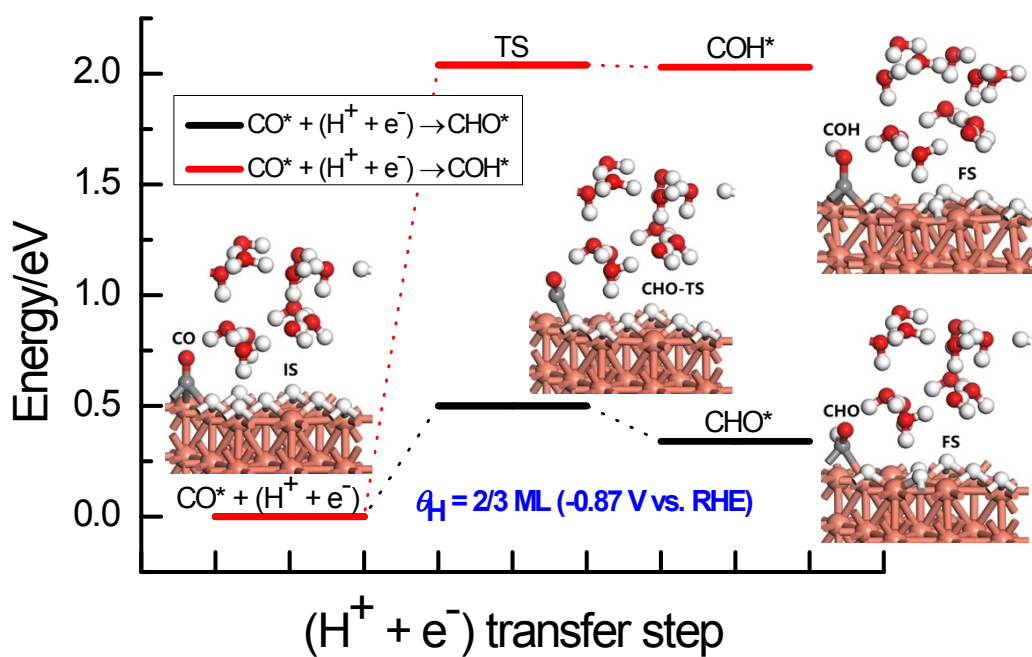
(a)



(b)



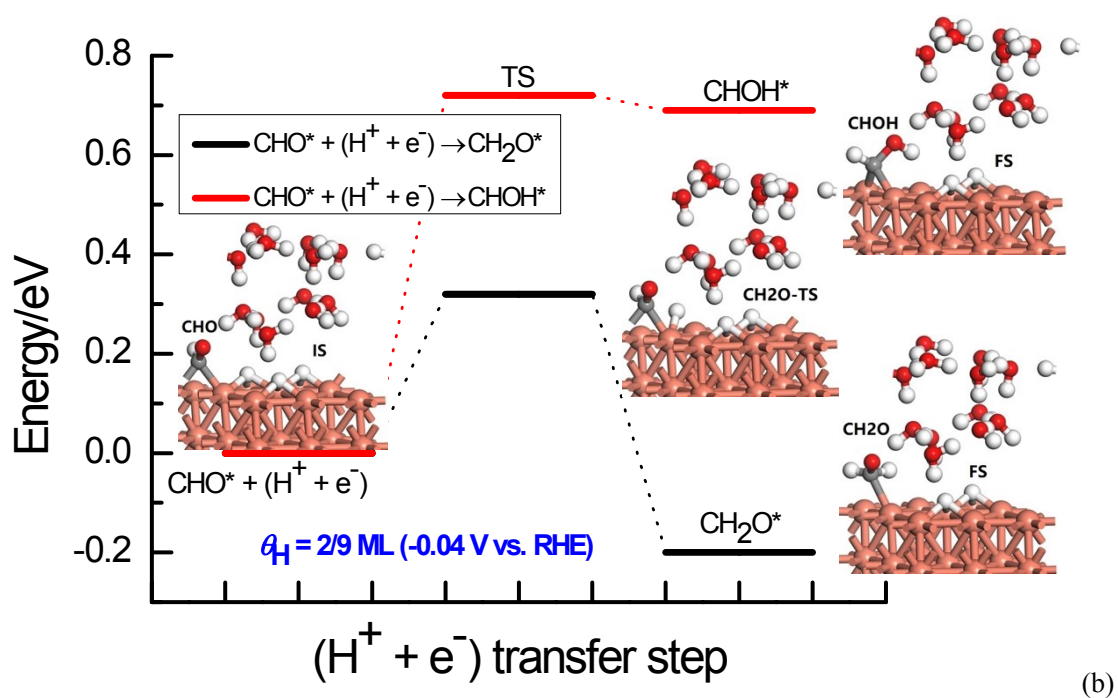
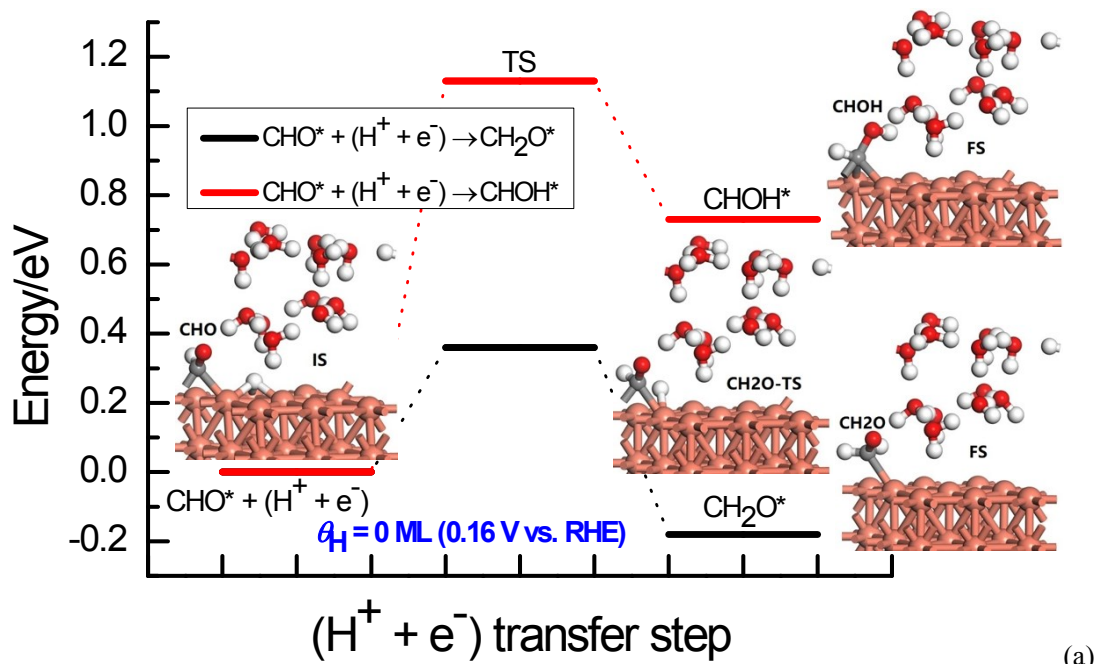
(c)

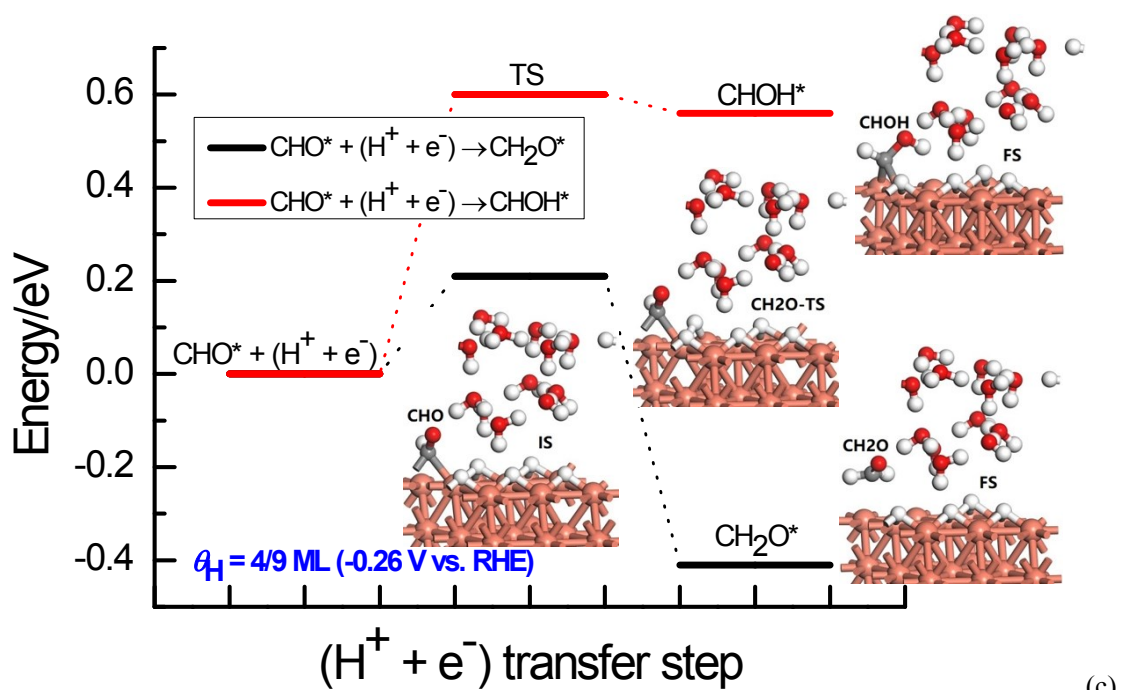


(d)

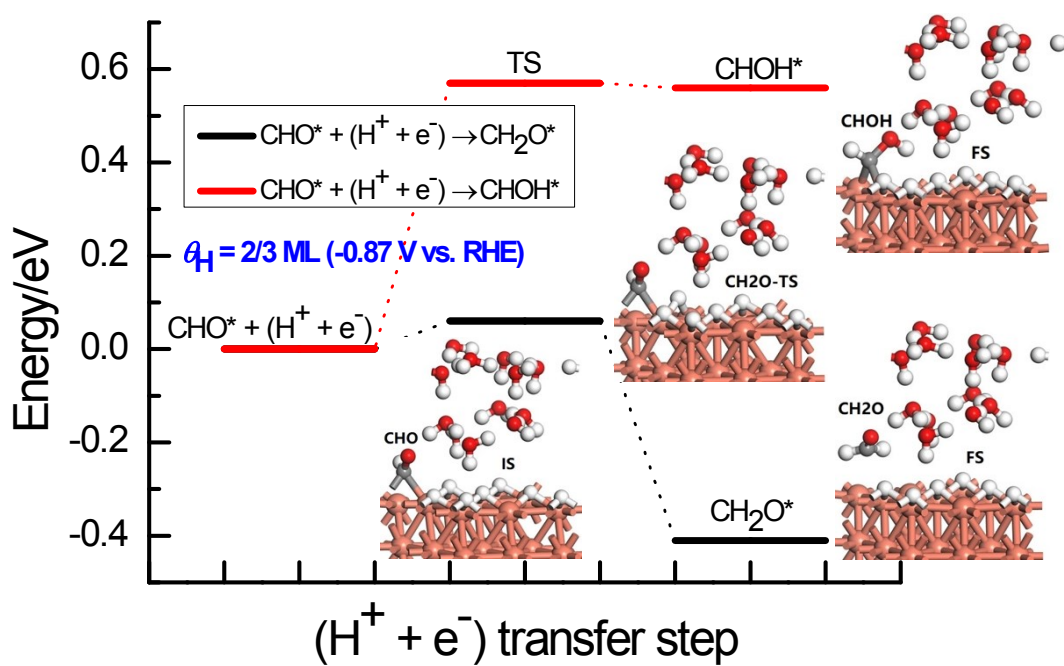
**Figure S3.** The Minimum energy pathway analysis of CO electroreduction into CHO and COH intermediates on Cu(111) at various applied potentials (an asterisk \* indicates adsorption to the Cu surface; IS represents Initial State; TS represents Transition State; FS represents Final State): (a) 0.16 V; (b) -0.04 V; (c) -0.26 V; (d) -0.87 V.

### 3.2 CHO Electroreduction into CH<sub>2</sub>O and CHOH





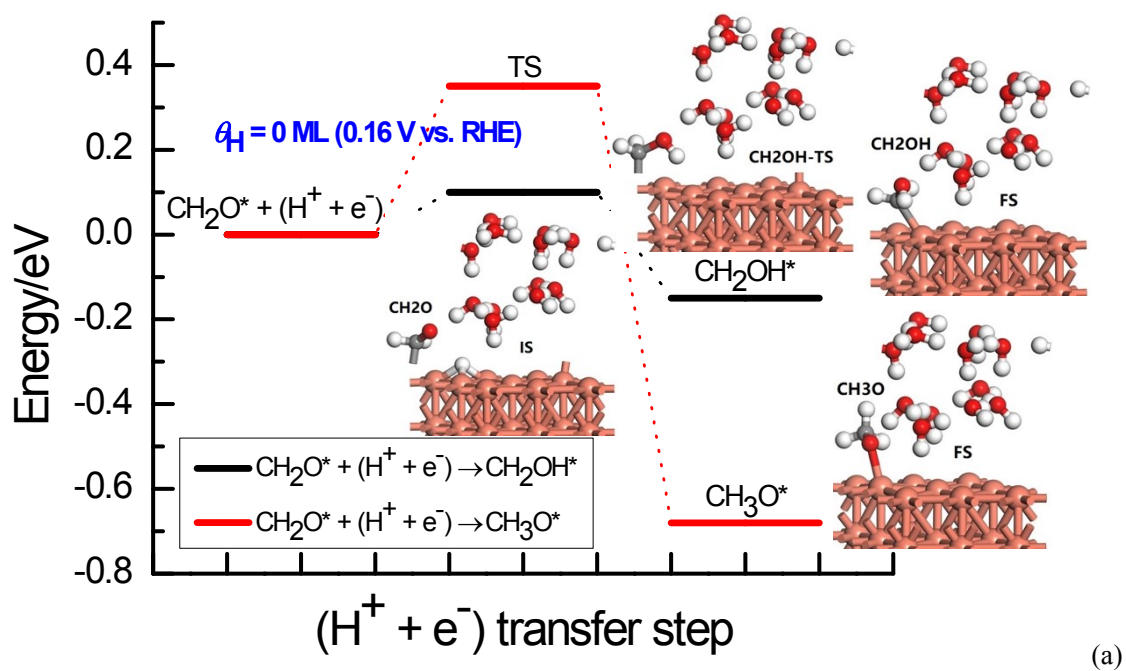
(c)



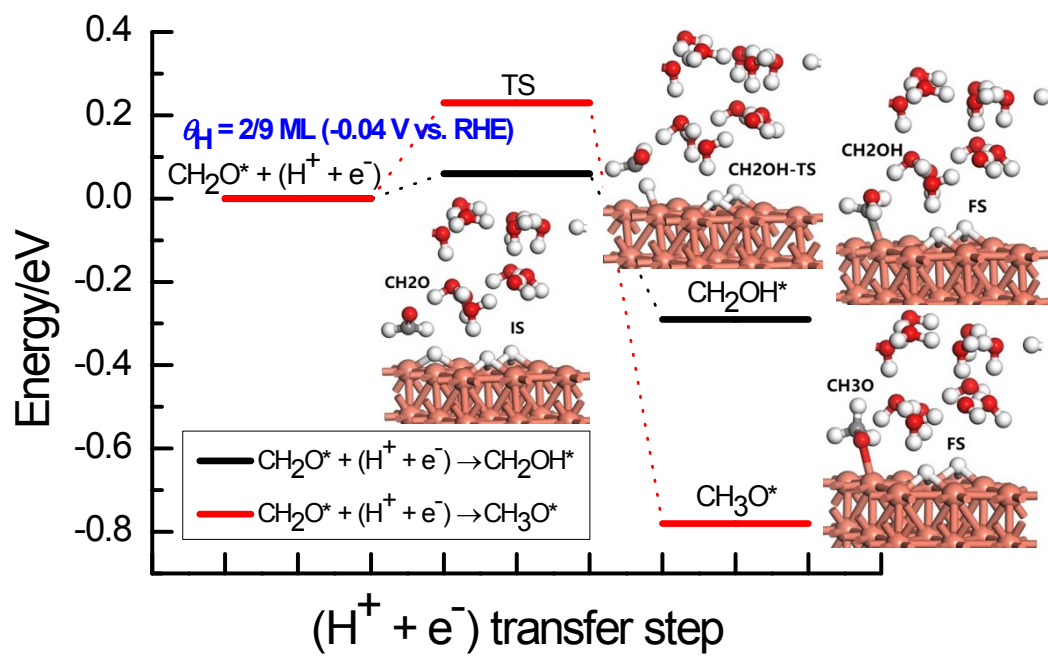
(d)

**Figure S4.** The Minimum energy pathway analysis of CHO electroreduction into CH<sub>2</sub>O and CHOH intermediates on Cu(111) at various applied potentials (an asterisk \* indicates adsorption to the Cu surface; IS represents Initial State; TS represents Transition State; FS represents Final State): (a) 0.16 V; (b) -0.04 V; (c) -0.26 V; (d) -0.87 V.

### 3.3 CH<sub>2</sub>O Electroreduction into CH<sub>2</sub>OH and CH<sub>3</sub>O

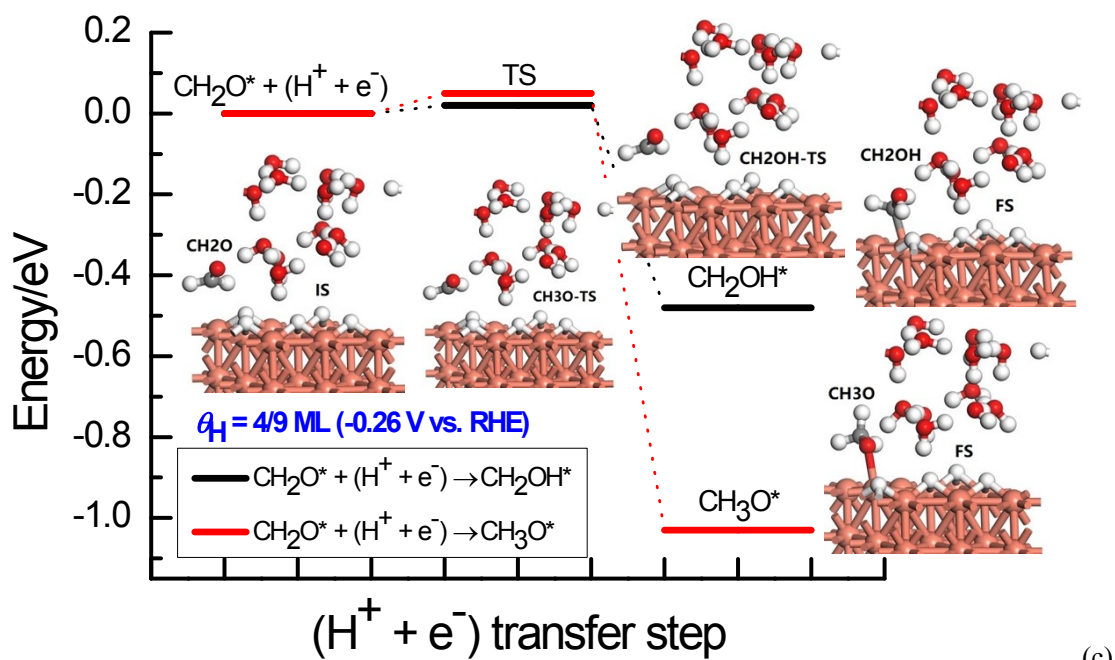


(a)

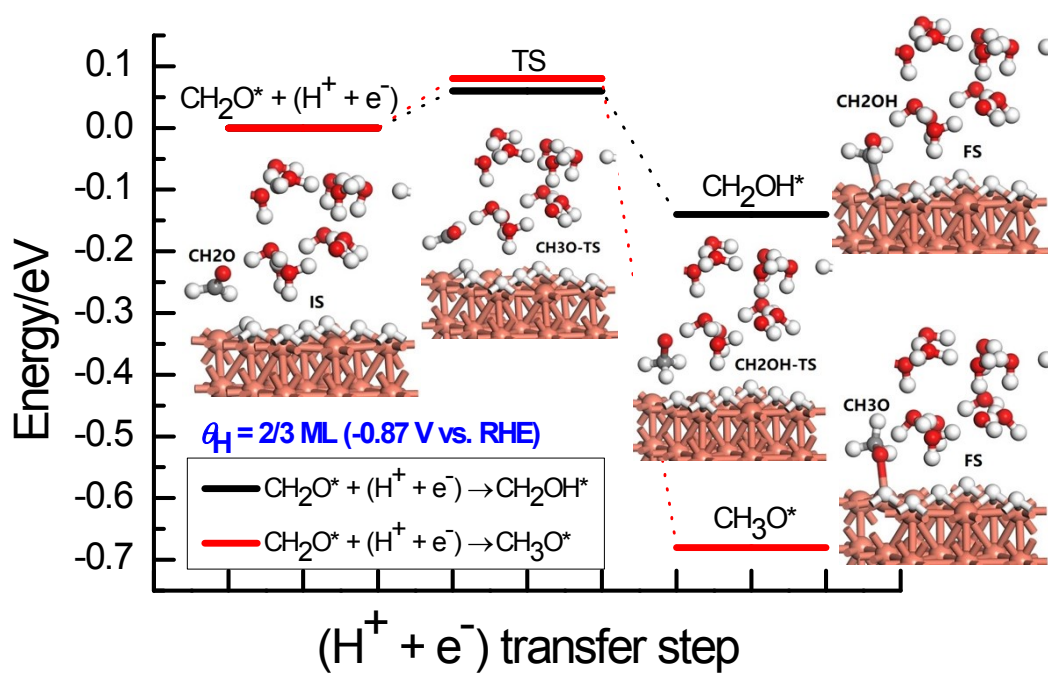


(b)





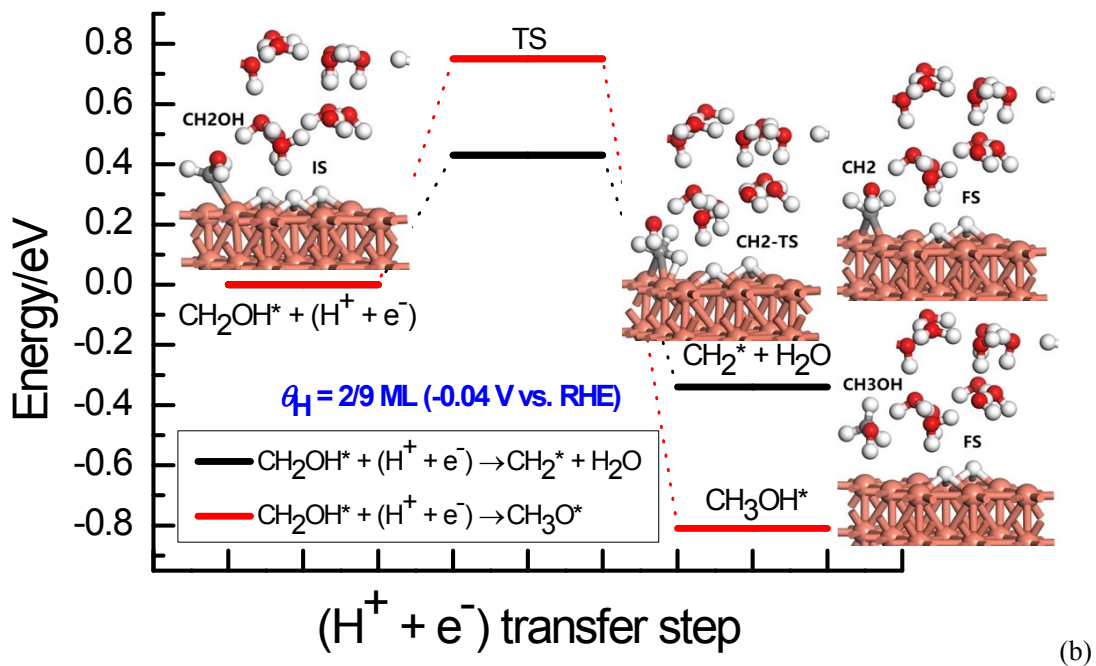
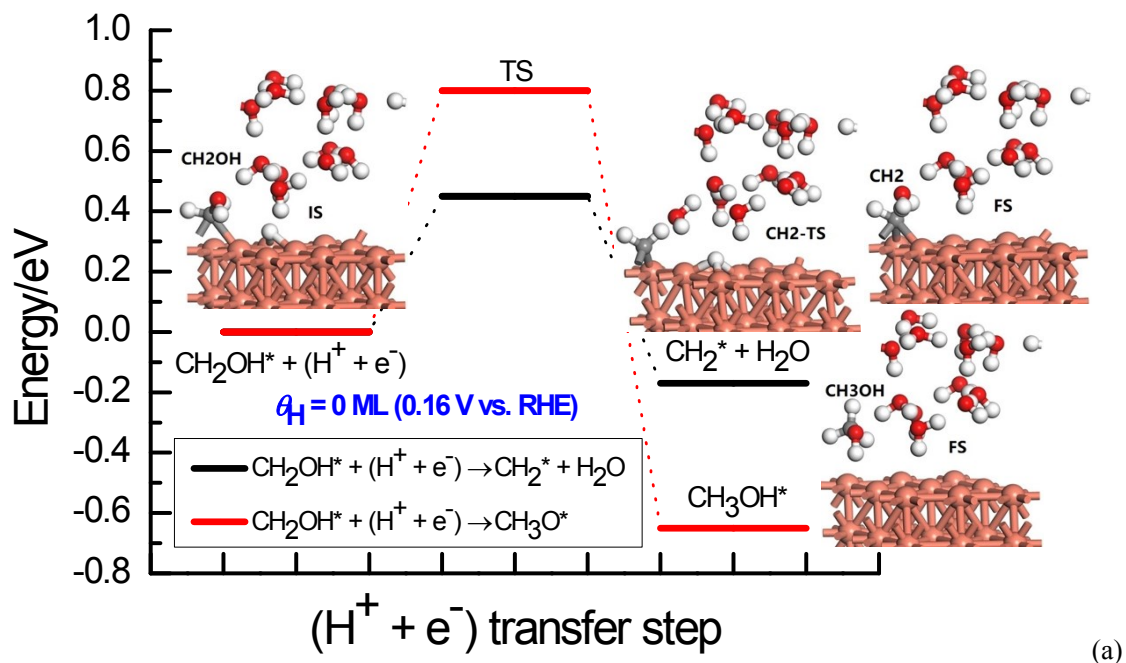
(c)

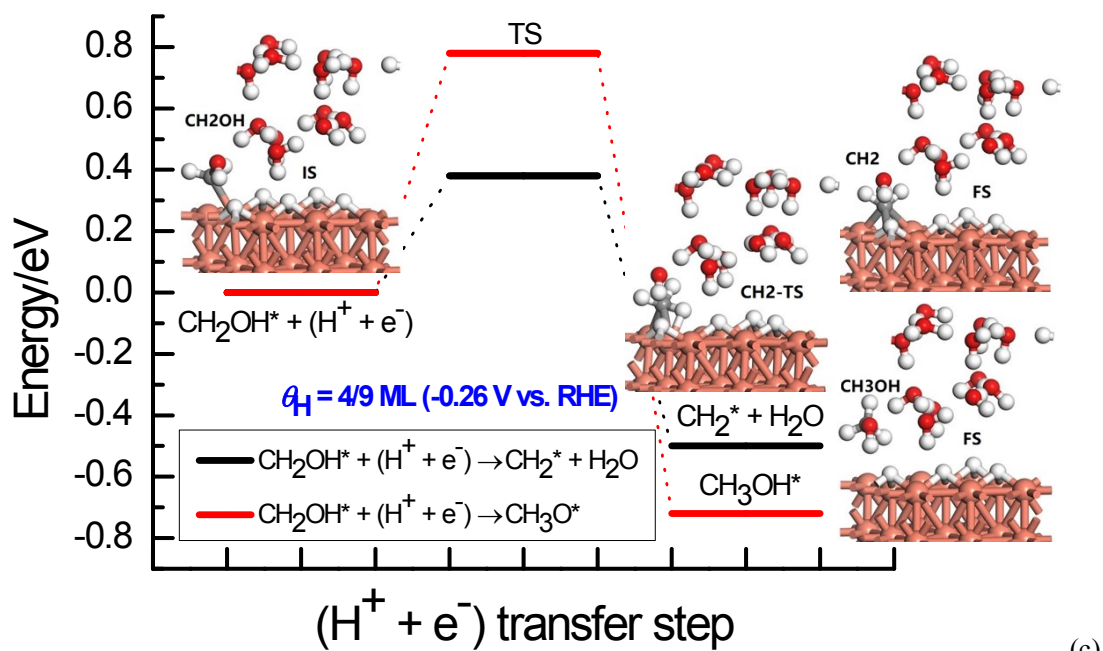


(d)

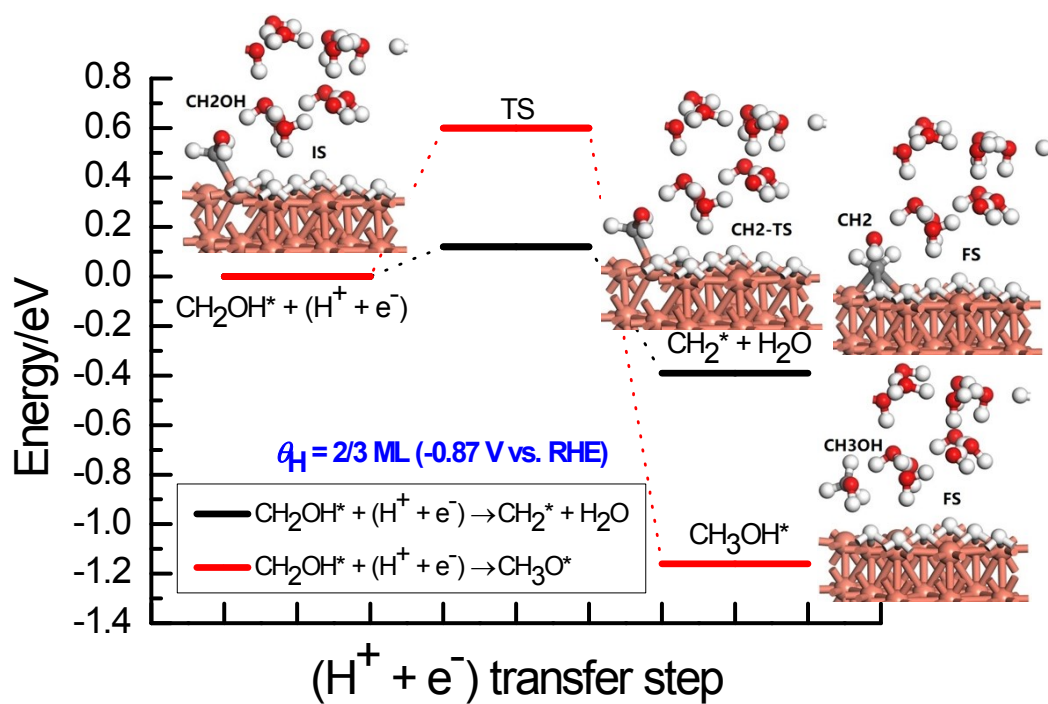
**Figure S5.** The Minimum energy pathway analysis of  $\text{CH}_2\text{O}$  electroreduction into  $\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{O}$  intermediates on Cu(111) at various applied potentials (an asterisk \* indicates adsorption to the Cu surface; IS represents Initial State; TS represents Transition State; FS represents Final State): (a) 0.16 V; (b) -0.04 V; (c) -0.26 V; (d) -0.87 V.

### 3.4 CH<sub>2</sub>OH Electroreduction into CH<sub>2</sub> and CH<sub>3</sub>OH





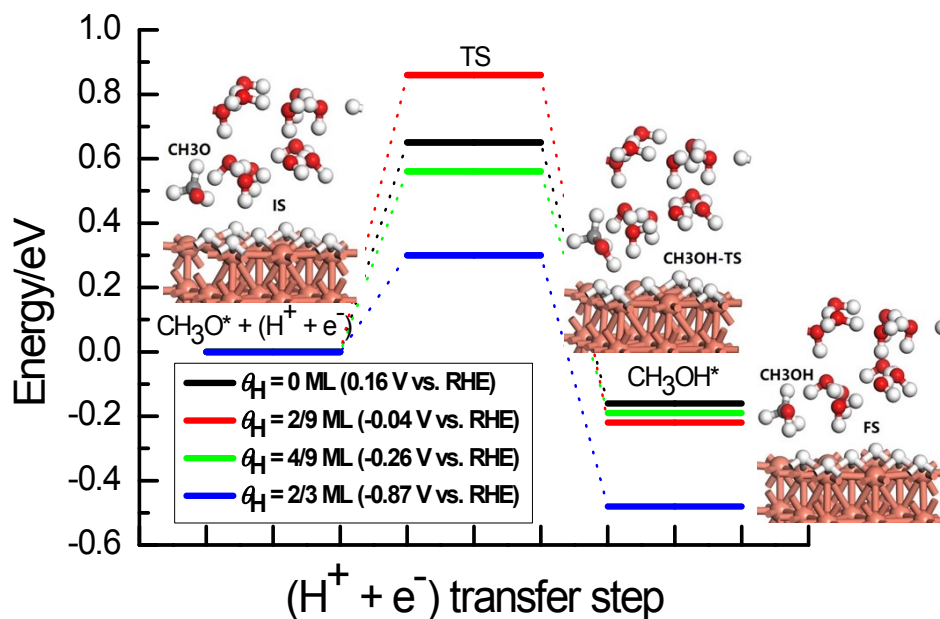
(c)



(d)

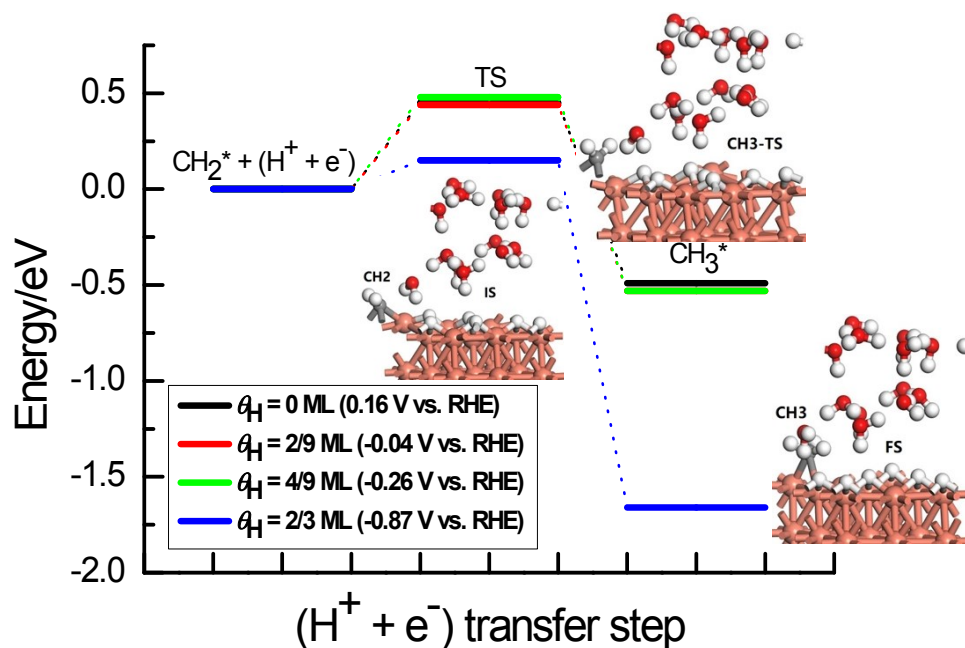
**Figure S6.** The Minimum energy pathway analysis of CH<sub>2</sub>OH electroreduction into CH<sub>2</sub> and CH<sub>3</sub>OH on Cu(111) at various applied potentials (an asterisk \* indicates adsorption to the Cu surface; IS represents Initial State; TS represents Transition State; FS represents Final State): (a) 0.16 V; (b) -0.04 V; (c) -0.26 V; (d) -0.87 V.

### 3.5 CH<sub>3</sub>O Electroreduction into CH<sub>3</sub>OH



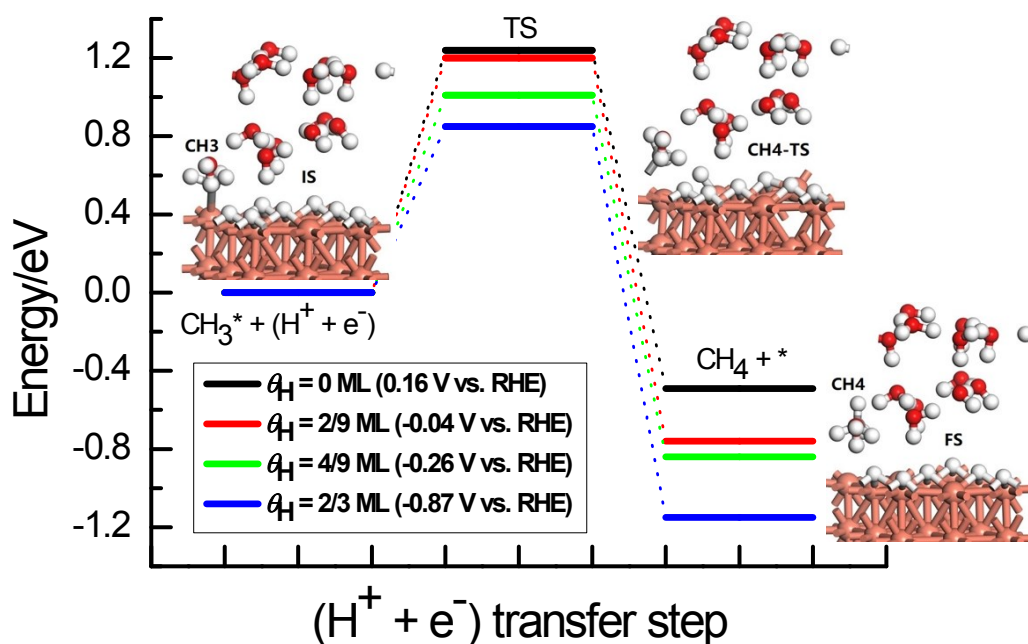
**Figure S7.** The Minimum energy pathway analysis of CH<sub>3</sub>O electroreduction into CH<sub>3</sub>OH product on Cu(111) at various applied potentials (an asterisk \* indicates adsorption to the Cu surface; IS represents Initial State; TS represents Transition State; FS represents Final State).

### 3.6 CH<sub>2</sub> Electroreduction into CH<sub>3</sub>



**Figure S8.** The Minimum energy pathway analysis of CH<sub>2</sub> electroreduction into CH<sub>3</sub> intermediate on Cu(111) at various applied potentials (an asterisk \* indicates adsorption to the Cu surface; IS represents Initial State; TS represents Transition State; FS represents Final State).

### 3.7 CH<sub>3</sub> Electroreduction into CH<sub>4</sub>



**Figure S9.** The Minimum energy pathway analysis of CH<sub>3</sub> electroreduction into CH<sub>4</sub> product on Cu(111) at various applied potentials (an asterisk \* indicates adsorption to the Cu surface; IS represents Initial State; TS represents Transition State; FS represents Final State).

### References

- (1) E. Skúlason, V. Tripković, M. E. Björketun, S. Gudmundsdóttir, G. Karlberg, J. Rossmeisl, T. Bligaard, H. Jónsson and J. K. Nørskov, Modeling the Electrochemical Hydrogen Oxidation and Evolution Reactions on the basis of Density Functional Theory Calculations, *J. Phys. Chem. C*, 2010, **114**, 18182-18197.
- (2) M. A. Henderson, Interaction of Water with Solid surfaces: Fundamental Aspects Revisited, *Surf. Sci. Rep.*, 2002, **46**, 1-308.
- (3) H. Ogasawara, B. Brena, D. Nordlund, M. Nyberg, A. Pelmenschikov, L. G. M. Pettersson and A. Nilsson, Structure and Bonding of Water on Pt(111), *Phys. Rev. Lett.*, 2002, **89**, 276102.
- (4) S. Haq, C. Clay, G. R. Darling, G. Zimbitas and A. Hodgson, Growth of Intact Water Ice on Ru(0001) between 140 and 160 K: Experiment and Density-Functional Theory Calculations, *Phys. Rev. B*, 2006, **73**, 115414.
- (5) J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- (6) D. Vanderbilt, Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism, *Phys. Rev.*

*B*, 1990, **41**, 7892-7895.

- (7) M. Methfessel and A. T. Paxton, High-Precision Sampling for Brillouin-Zone Integration in Metals. *Phys. Rev. B*, 1989, **40**, 3616-3621.
- (8) S. Baroni, A. Dal Corso, S. de Gironcoli and P. Giannozzi, PWSCF and PHONON: Plane-Wave Pseudo-Potential Codes, <http://www.quantum-espresso.org/>, **2001**.
- (9) G. Henkelman and H. Jonsson, Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points, *J. Chem. Phys.*, 2000, **113**, 9978-9985.
- (10) G. Henkelman, B. P. Uberuaga and H. Jonsson, A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths, *J. Chem. Phys.*, 2000, **113**, 9901-9904.
- (11) S. Baroni, S. Gironcolli, A. Corso and P. Giannozzi, Phonons and Related Properties of Extended Systems from Density Functional Perturbation Theory, *Rev. Mod. Phys.*, 2001, **73**, 515-562.