## Supporting Information

## Computational Electrocatalysis beyond Conventional Hydrogen Electrode Model: CO<sub>2</sub> Reduction to C<sub>2</sub> Species on Copper Facilitated by Dynamically Formed Solvent Halide Ions at the Solid-Liquid Interface

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Figure S1. Radical distribution function of water from equilibrated AIMD trajectory. (a) The radical distribution function (RDF) of O-O and O-H and (b) the coordination number for O-O and O-H, which is integrated from RDF.



Figure S2. Charge transfer difference between copper surface and solvent. The iso-surface is set to be 0.003 e/Å<sup>3</sup>.



Figure S3. The calculated molecule orbitals for  $CO_2$  HOMO and LUMO on the left, 3s and 3p orbitals for halide ion on the right, and the LUMO and HOMO for  $CO_2$ -X compound in the middle.



Figure S4. The calculated Gibbs free energy change diagrams with energy barriers for the formation of CH<sub>3</sub>OH (orange line), CH<sub>4</sub> (black line), C<sub>2</sub>H<sub>5</sub>OH (green line), and C<sub>2</sub>H<sub>4</sub> (purple line), and some important reaction pathway to produce \*HCOO (red line) and \*C species (blue line) on the surface of Cu-H<sub>2</sub>O without halide ions in solvent.



Figure S5. Calculated concentration of carbon species of  $CO_{2(aq)}$ ,  $H_2CO_3$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $H^+$  OH<sup>-</sup>, and local pH change under different  $CO_2$  partial pressure.



Figure S6. Calculated NEB activation barriers for CO<sub>2</sub> hydrogenated to \*COOH species on Cu-H<sub>2</sub>O catalyst and I-assisted Cu-H<sub>2</sub>O catalyst.

Micro-kinetic calculation details

Inspired by previous theoretical studies, the microkinetic model has been explored here to study the current density change with and without anion in electric double layer. The reaction steps and rate equations for  $CH_4$  formation and  $C_2H_4$  formation are listed as follows in equation 1-14.

$$CO_{2(aq)} + * \bigoplus_{k_{-1}}^{k_{1}} CO_{2(aq)} \# (1)$$

$$* CO_{2(aq)} + * H \bigoplus_{k_{-2}}^{k_{2}} COOH + * \# (2)$$

$$* COOH + * H \bigoplus_{k_{-3}}^{k_{3}} CO + * H_{2}O \# (3)$$

$$* CO + * H \bigoplus_{k_{-4}}^{k_{4}} CHO + * \# (4)$$

$$* CHO + * H \bigoplus_{k_{-5}}^{k_{5}} CHOH + * \# (5)$$

$$* CHOH + * H \bigoplus_{k_{-6}}^{k_{6}} CH + * H_{2}O \# (6)$$

$${}^{*}CH + {}^{*}H \underset{k_{-7}}{\overset{k_{7}}{\Leftrightarrow}} {}^{*}CH_{2} + {}^{*}\#(7)$$

$${}^{*}CH_{2} + {}^{*}H \underset{k_{-8}}{\overset{k_{8}}{\leftrightarrow}} {}^{*}CH_{3} + {}^{*}\#(8)$$

$${}^{*}CH_{3} + {}^{*}H \underset{k_{-9}}{\overset{k_{9}}{\leftrightarrow}} {}^{*}CH_{4} + {}^{*}\#(9)$$

$${}^{*}CH_{4} \underset{k_{-10}}{\overset{k_{10}}{\leftrightarrow}} CH_{4} + {}^{*}\#(10)$$

Here,  $k_i$ , and  $k_i$  - *i* indicates the rate constant for forward, and backward reaction.

The coverage rate for each carbon species can be obtained by the following equation:

$$\theta_{*CO2} = K_1 p_{CO2} \theta_v \# (1-1)$$

Where  $\theta_{*CO2}$  is the adsorption coverage of CO<sub>2</sub>,  $p_{CO2}$  is the partial potential of CO<sub>2</sub>,  $\theta_{vis}$ vacancy coverage, which can be obtained using all other adsorbed species coverage subtract from overall coverage 1.0.

$$r_{2} = k_{2}\theta_{*CO2}\theta_{*H} - k_{-2}\theta_{*CO0H}\theta_{v}\#(2-2)$$

$$r_{3} = k_{3}\theta_{*CO0H}\theta_{*H} - k_{-3}\theta_{*CO}\theta_{*H2O}\#(3-3)$$

$$r_{4} = k_{4}\theta_{*CO}\theta_{H} - k_{-4}\theta_{*CHO}\theta_{v}\#(4-4)$$

$$r_{5} = k_{5}\theta_{*CHO}\theta_{*H} - k_{-5}\theta_{*CHOH}\theta_{v}\#(5-5)$$

$$r_{6} = k_{6}\theta_{*CHOH}\theta_{*H} - k_{-6}\theta_{*CH}\theta_{*H2O}\#(6-6)$$

$$r_{7} = k_{7}\theta_{*CH}\theta_{*H} - k_{-7}\theta_{*CH2}\theta_{v}\#(7-7)$$

$$r_{8} = k_{8}\theta_{*CH2}\theta_{*H} - k_{-9}\theta_{*CH3}\theta_{v}\#(8-8)$$

$$r_{9} = k_{9}\theta_{*CH3}\theta_{*H} - k_{-9}\theta_{*CH4}\theta_{v}\#(9-9)$$

$$\theta_{*CH4} = \frac{p_{CH4}\theta_{v}}{K_{10}}\#(10-10)$$

For the CO<sub>2</sub> adsorption and CH<sub>4</sub> removal steps, their rate constant can be obtained from  $k_i = Aexp^{[10]}(\frac{-G_i}{k_BT})$ , and thus, equilibrium constant  $K_i$  can be expressed as:  $K_i = exp^{(i)}(\frac{-\Delta G_i}{k_B T})$ 

Where A is the pre-exponential factor deduced by  $\overline{h}$ ,  $\Delta G$  is the free energy change, T is the room temperature, and  $k_B$  is Boltzmann constant.

For adsorption and desorption process, they are non-electrochemical steps, which is independent on electrode potential. However, for other elementary steps and carbon species, such as \*COOH, \*CHO, and so on, these formation process depends on electrode potential (U), which can be calculated by:

$$k_i = A_i exp^{[i0]}(\frac{-E_{ai}}{k_B T}) exp^{[i0]}(\frac{-e\beta_i(U-U_i)}{k_B T})$$

 $U_i = \frac{-\Delta G_i}{e} E_{aiis}$ Where  $U_{i}$  is the reversible potential of elementary step I deduced by activation barrier of each elementary step, which can be calculated from CI-NEB calculations,  $\beta_{i}$  is the symmetric factor taken as 0.50.

For electrochemical steps, the  $k_{-i}$  can be calculated from rate constant and equilibrium constant, thus:

$$k_{-i} = \frac{k_i}{K_i}$$

In addition, for equilibrium constant for electrochemical steps,  $K_i = exp^{[iii]}(\frac{-\Delta G_i - eU}{k_B T})$ All the approximation is the formula of the step of All the approximation and derivation methods are based on our previous work, then all the other elementary steps are in equilibrium apart from  $r_4$ :

$$r_2 = r_3 = r_5 = r_6 = r_7 = r_8 = r_9 = 0$$

Besides, based on the conservation law, these coverages should be satisfied as

$$\theta_{*CO2} + \theta_{*CO0H} + \theta_{*H} + \theta_{*CO} + \theta_{*H2O} + \theta_{*CHO} + \theta_{*CHOH} + \theta_{*CH} + \theta_{*CH2} + \theta_{*CH3} + \theta_{*CH4} + \theta_{v} = 1$$

Overall, these rate equations are solved at fast reaction apart from rate limiting step eq4, then we can get the turnover frequency (TOF), and  $\text{TOF}=r_4$ .

The current density of CH<sub>4</sub> formation can expressed as:

$$j_{CH4} = e\rho TOF$$

Where, e is  $1.602*10^{-19}$  C,  $\rho$  is surface density of active site, which can be calculated by using surface active sites divided by surface area, for the model we used in this work, each layer is 221.6 \*10<sup>-16</sup> cm<sup>-2</sup>. Thus, the density of exposed Cu atoms is as high as 1.083\*10<sup>15</sup> per cm<sup>2</sup>. In this regard,  $e\rho$  can be estimated as 173.60  $\mu C/cm^2$ . Then we can obtain the current density for CH<sub>4</sub> formation is about 0.1575 mA/cm<sup>2</sup> at a working potential of -1.0 V vs. RHE for I-assisted Cu-H<sub>2</sub>O. However, without I presence in Cu-H<sub>2</sub>O, the calculated current density is only  $2.038*10^{-8}mA/cm^2$ .

For C<sub>2</sub>H<sub>4</sub> formation, the elementary steps are as follows:

$$CO_{2(aq)} + * \bigoplus_{k_{-1}}^{k_{1}} CO_{2(aq)} \# (1)$$

$$* CO_{2(aq)} + * H \bigoplus_{k_{-2}}^{k_{2}} COOH \# (2)$$

$$* COOH + * H \bigoplus_{k_{-3}}^{k_{3}} CO + * H_{2}O \# (3)$$

$$* CO + * CO \bigoplus_{k_{-11}}^{k_{11}} COCO + * \# (11)$$

$$* COCO + * H \bigoplus_{k_{-12}}^{k_{12}} COCOH + * \# (12)$$

$$* COCOH + * H \bigoplus_{k_{-12}}^{k_{13}} COHCOH + * \# (12)$$

$$* COHCOH + * H \bigoplus_{k_{-13}}^{k_{13}} COHCOH + * \# (13)$$

$$* COHCOH + * H \bigoplus_{k_{-14}}^{k_{14}} COHC + * H_{2}O \# (14)$$

$$* COHC + * H \bigoplus_{k_{-15}}^{k_{15}} COHCH + * \# (15)$$

$$* COHC + * H \bigoplus_{k_{-15}}^{k_{16}} COHCH + * \# (15)$$

$$* COHCH + * H \bigoplus_{k_{-16}}^{k_{16}} CCHCH + * H_{2}O \# (16)$$

$$* CCH + * H \bigoplus_{k_{-17}}^{k_{16}} CCH_{2} + * \# (17)$$

$$* CCH_{2} + * H \bigoplus_{k_{-18}}^{k_{19}} CHCH_{2} + * \# (18)$$

$$* CHCH_{2} + * H \bigoplus_{k_{-19}}^{k_{19}} CH_{2}CH_{2} + * \# (19)$$

$$* CH_{2}CH_{2} \bigoplus_{k_{-20}}^{k_{20}} CH_{2}CH_{2} + * \# (20)$$

As discussed above, we can get the current density for  $C_2H_4$  formation on I-assisted Cu-H2O is 35.43 mA/cm<sup>2</sup> at a working potential of -1.0 V vs. RHE, which is comparable to the reference value of 50.0-42.1 mA/cm<sup>2</sup>. However, as for the pure Cu-H<sub>2</sub>O, the obtained current density is

only  $1.489*10^{-4}$  mA/cm<sup>2</sup>. Therefore, the current density has significantly enhanced by orders of magnitude for I-assisted Cu-H<sub>2</sub>O and pure Cu-H<sub>2</sub>O without halide ions in the solvent.