

## Supporting Information

### **Glycine Modified Copper Promotes CO<sub>2</sub> Electroreduction to Multi-Carbon Products: A Computational Study**

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## Computational Methods

DFT calculations were performed using the Vienna ab initio Software (VASP).<sup>[1,2]</sup> The generalized gradient approximation (GGA) with Perdew, Burke, and Ernzerh (PBE) functional is adopted to describe the electron exchange-correlation interaction.<sup>[3, 4]</sup> Electron wave functions are expanded in plane waves with a kinetic energy cutoff of 450 eV. The method of Methfessel-Paxton (MP) with a smearing width of 0.20 eV was employed to transition metal surfaces and interfaces.<sup>[5]</sup> The convergence criterion for the electronic self-consistent iteration and force was set to  $10^{-5}$  eV and  $0.02 \text{ eV \AA}^{-1}$ , respectively. A vacuum layer of 15 Å was introduced to avoid the interactions between periodic images. Dispersopm cprrection was included using the DFT-D3 method for Grimme.<sup>[6]</sup> The k-points sampling was  $2 \times 2 \times 1$ , generated by Monkhorst–Pack grids with the origin at the  $\Gamma$ -point<sup>[7]</sup> due to the large supercell (The Cu slab model was constructed with four atomic layers and a  $6 \times 6$  supercell containing a total of 144 Cu atoms). The transition state search was conducted with the climbing image nudged elastic band (CI-NEB) method<sup>[8,9]</sup>, followed by the dimer method <sup>[10]</sup> to converge the saddle point within  $0.05 \text{ eV \AA}^{-1}$ .

Binding energies between glycine and Cu were computed with the energetic correction terms according to the following equation:

$$\Delta G = E_{Cu-glycine} - E_{slab} - E_{glycine} + ZPE + \int C_p dT - TS$$

Free energies were computed with the energetic correction terms according to the following equation:

$$\Delta G = E_{slab-intermediate} - E_{slab} - E_{intermediate} + ZPE + \int C_p dT - TS$$

The reaction energy of \*CO-\*CHO coupling is calculated according the follow equation:

$$\Delta E = E_{*OCCHO} - E_{*CO \text{ and } *CHO \text{ co-adsorption}}$$

Where the  $E_{Cu-glycine}$ ,  $E_{slab-intermediate}$ ,  $E_{glycine}$ ,  $E_{slab}$  and  $E_{intermediate}$  were obtained by DFT calculations. The entropy ( $S$ ) and zero-point energies ( $ZPE$ ) of adsorbates and the heat capacity ( $C_p$ ) were derived form the vibrational frequency calculations.<sup>[10]</sup> The temperate ( $T$ ) were set to be 298.15 K. For the vibrational frequency calculations, the convergence criterion of electronic relaxation was  $10^{-7}$  eV. The computational hydrogen electrode (CHE) approach was used for proton–electron transfer steps.<sup>[11]</sup>

For the calculation considered solvation effect, the solvent environment was modeled by the VASPsol code. The relative permittivity was set to 80 to model the aqueous electrolyte. The effective surface tension parameter was assigned to 0 in VASPsol to neglect the

cavitation energy contribution. The linearized Poisson–Boltzmann model with a Debye length of 3.0 Å mimics the compensating charge.

For the constant potential method calculation, electrode potential referenced to the standard hydrogen electrode (SHE) scale is formulated in

$$U = -4.6 + \Phi_q$$

where  $-4.6$  V is the absolute electrode potential of the SHE,  $\Phi_q$  is the work function of the charged system.

The  $E-U_q$  points follow a quadratic function as

$$E_{Uq} = -\frac{1}{2}C(U_q - U_0)^2 + E_0$$

where  $U_0$ ,  $C$ , and  $E_0$  are the fitted values of the potential of zero charge (PZC), capacitance of the corresponding system, and the energy of the system at the PZC, respectively.

### Group electronegativity calculations

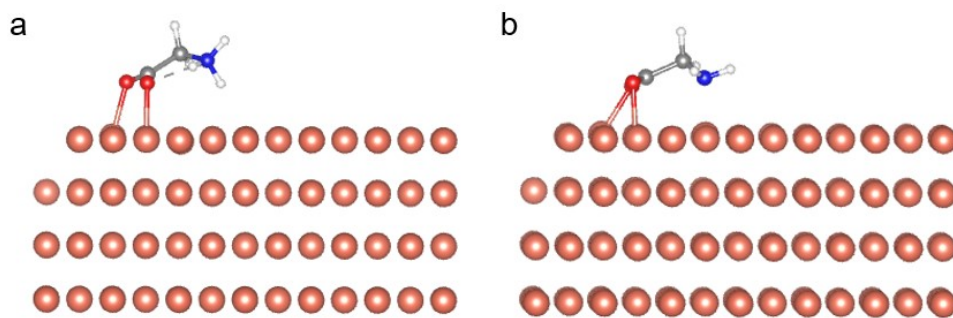
The group electronegativity was defined by Sanderson method<sup>12,13</sup>.

Based on the Principle of Electronegativity Equalization, when two or more atoms unite to form a compound, their electronegativities become adjusted to the same intermediate value within the compound. A corollary is, the intermediate electronegativity within the compound is the geometric mean of all the atomic electronegativities. So, the group electronegativity could be calculated according to the follow equation:

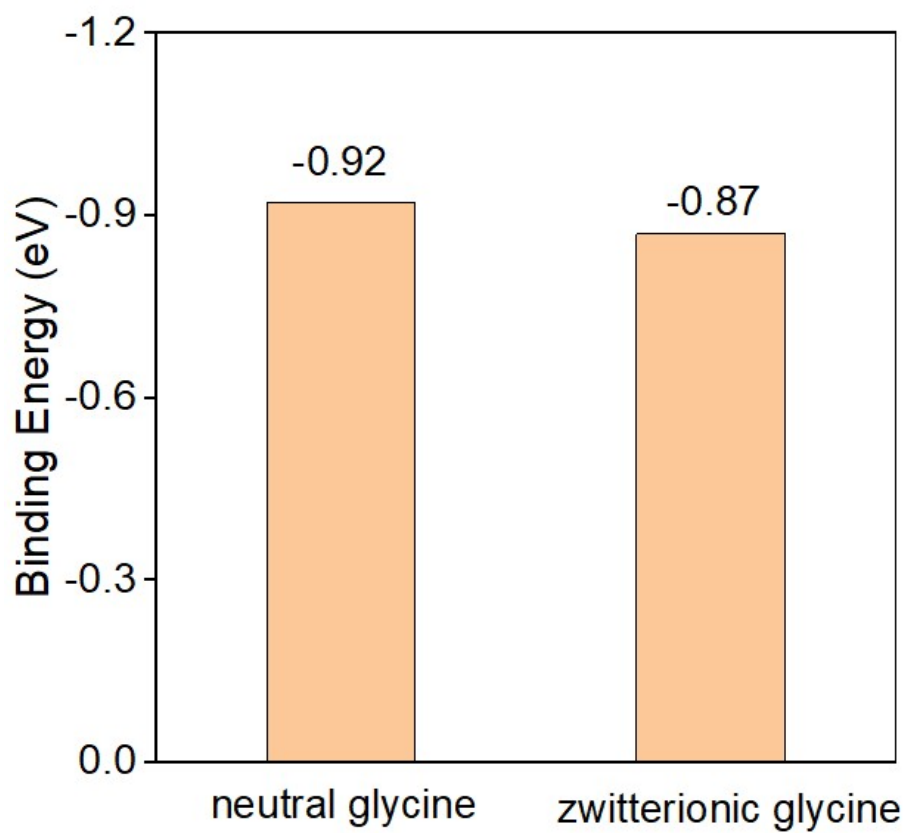
$$S_{eq} = \frac{m \times S_A + n \times S_B + o \times S_C + \dots}{m + n + o + \dots}$$

Where the  $S_{eq}$  is the group electronegativity,  $S_A$ ,  $S_B$  and  $S_C$  are the electronegativity of A, B and C atom, the  $m$ ,  $n$  and  $o$  are the number of A, B, C atoms in the group.

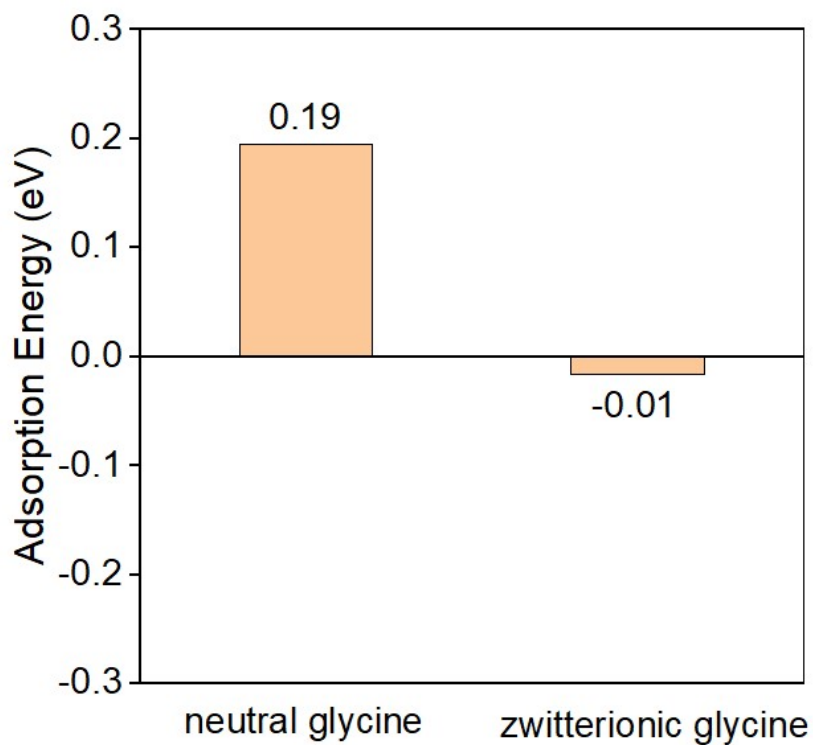
The electronegativity of different element was shown in Table S1.



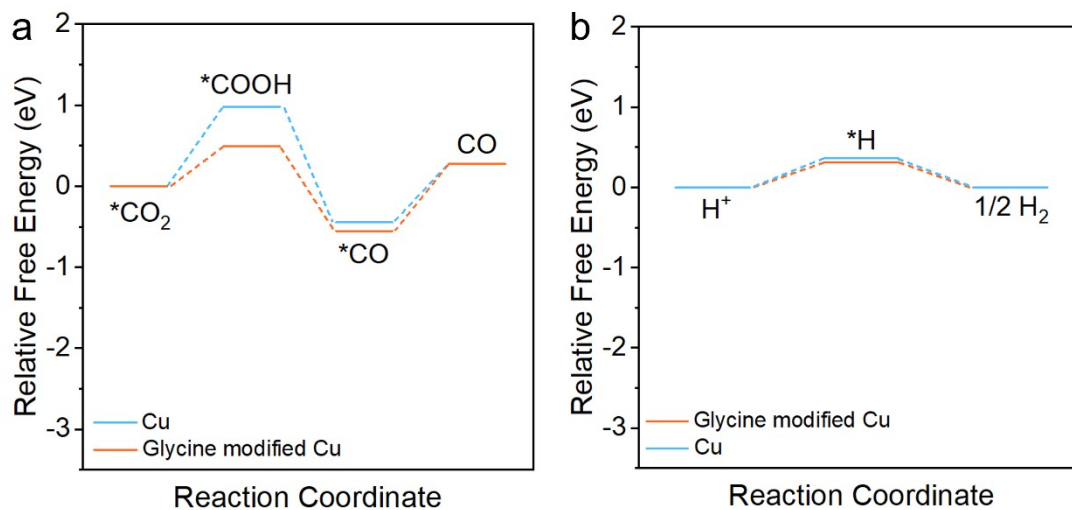
**Fig. S1** The model of (a) zwitterionic glycine modified Cu and (b) neutral glycine modified Cu.



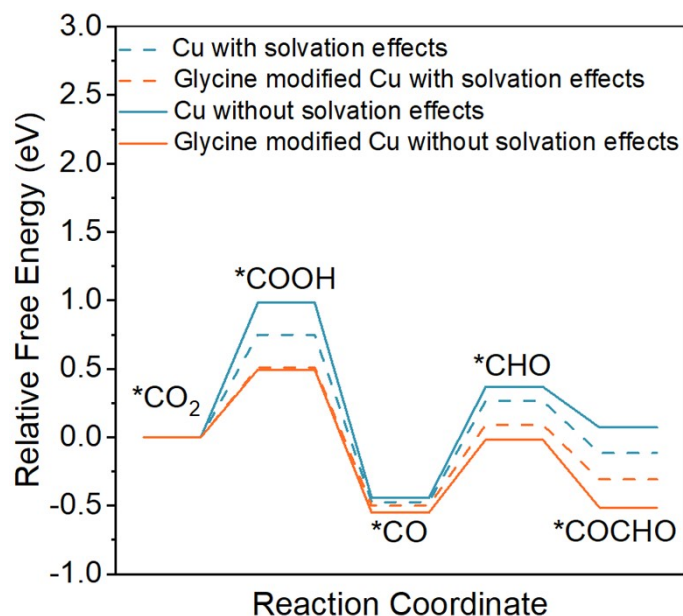
**Fig. S2** Binding energy between neutral/zwitterionic glycine and Cu slab



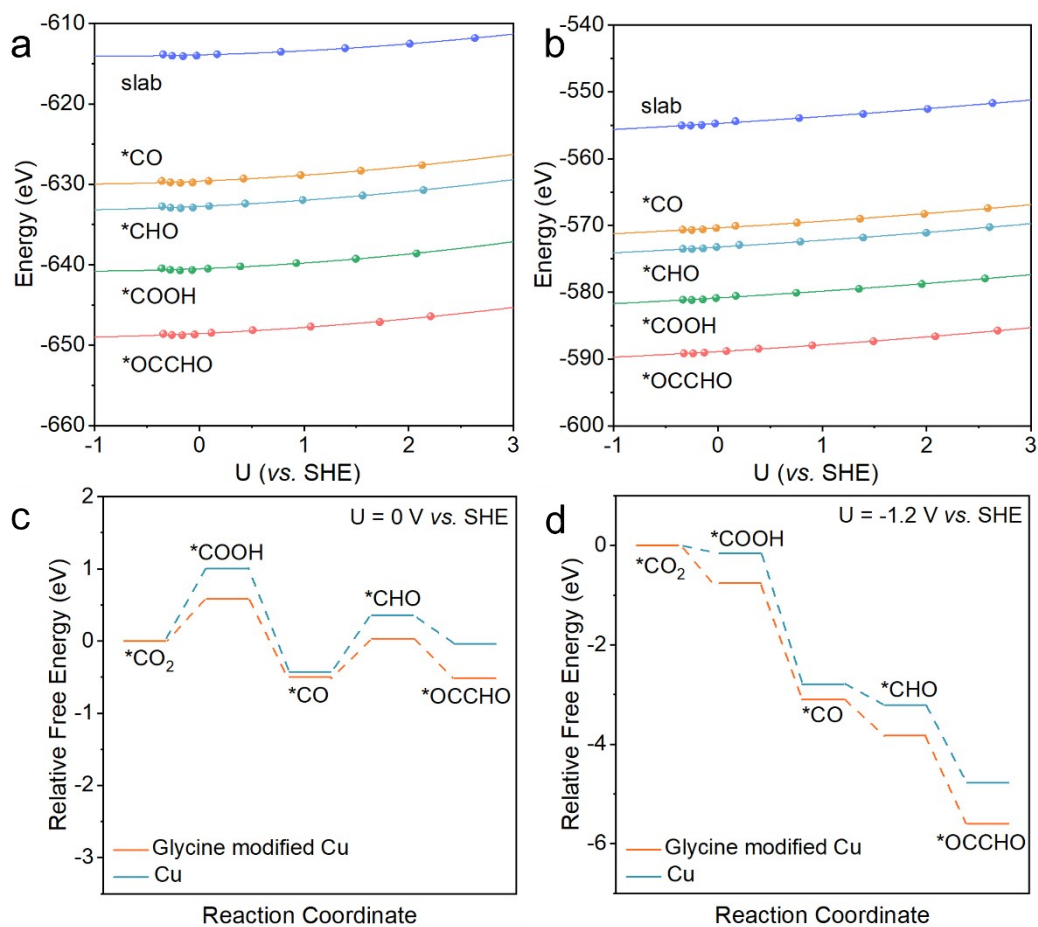
**Fig. S3** Adsorption energy of \*CHO adsorbed on neutral/zwitterionic glycine and Cu slab



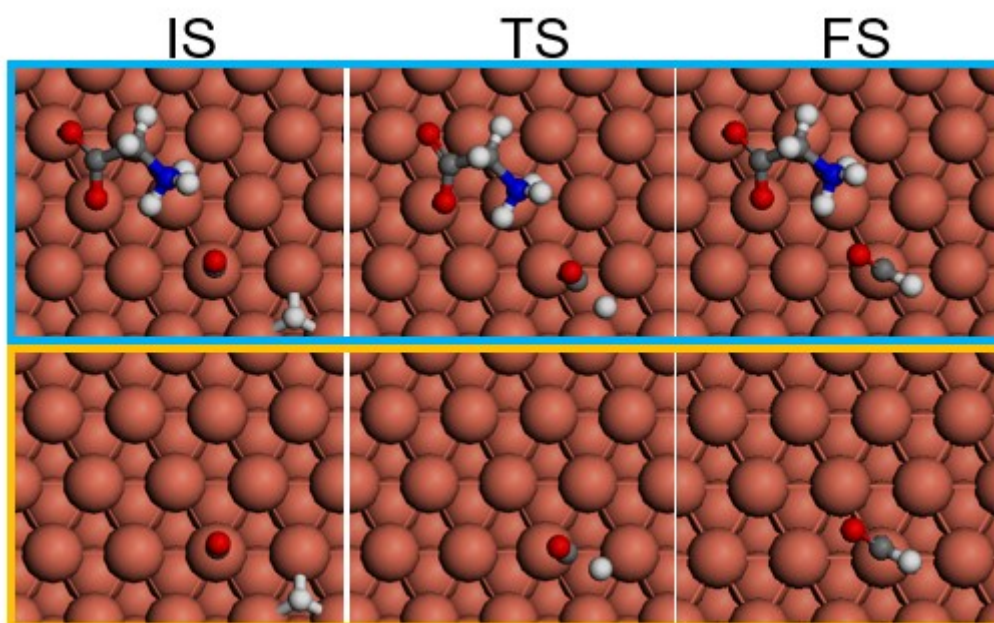
**Fig. S4** (a)  $ECO_2R$  reaction pathway of CO, (b) HER reaction pathway.



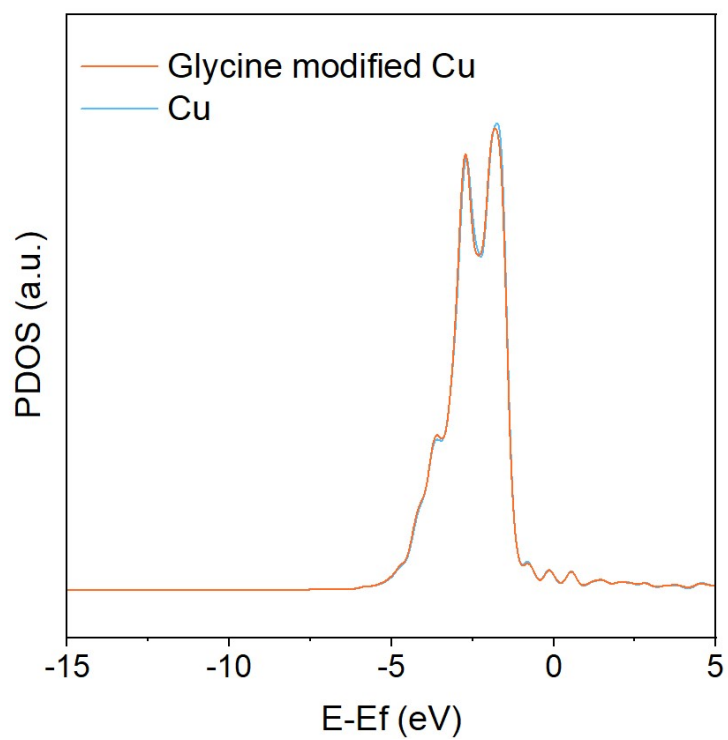
**Fig. S5** ECO<sub>2</sub>R reaction pathway of CO<sub>2</sub> to \*COCHO with/without solvation effects



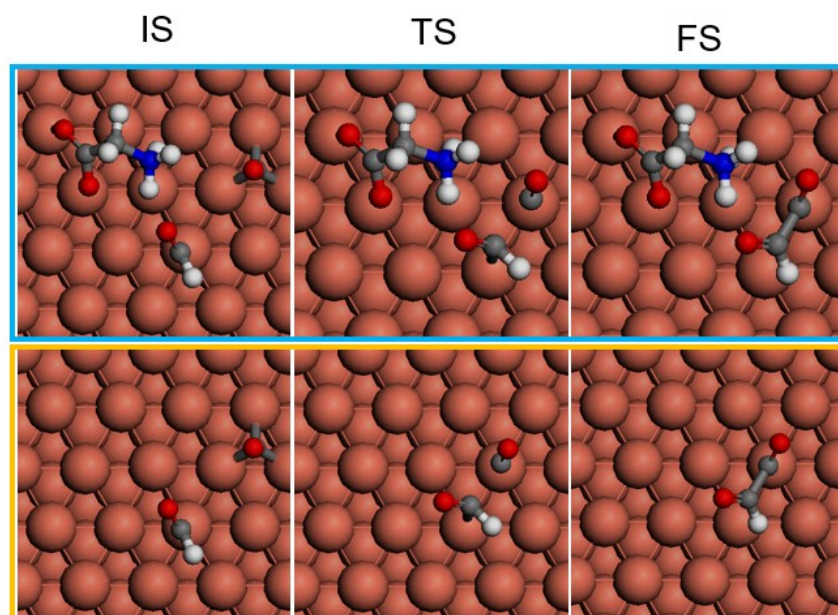
**Fig. S6** (a) Calculated energies of glycine modified Cu and corresponding three reaction intermediates. (b) Calculated energies of Cu and corresponding three reaction intermediates. ECO<sub>2</sub>R reaction pathway of CO<sub>2</sub> to \*COCHO at (c) 0 V vs. SHE and (d) -1.2V vs. SHE.



**Fig. S7** Calculation models of \*CO hydrogenation with/without glycine modification.



**Fig. S8** PDOS of Cu atom which \*CO adsorbed with/without glycine modification.



**Fig. S9** Calculation models of \*CO-\*CHO coupling with/without glycine modification.

**Table. S1** Electronegativities of differene element<sup>12</sup>.

element	<i>S</i>	elemen	<i>S</i>	elemen	<i>S</i>
H	2.592	S	2.957	Ag	1.826
Li	0.670	Cl	3.475	Cd	1.978
Be	1.810	K	0.445	In	2.138
B	2.275	Ca	0.946	Sn	2.298
C	2.746	Cu	2.033	Sb	2.458
N	3.194	Zn	2.223	Te	2.618
O	3.654	Ga	2.419	I	2.778
F	4.000	Ge	2.618	Cs	0.220
Na	0.560	As	2.816	Ba	0.651
Mg	1.318	Se	3.014	Hg	2.195
Al	1.714	Br	3.219	Tl	2.246
Si	2.138	Rb	0.312	Pb	2.291
P	2.515	Sr	0.721	Bi	2.342



Table. S2  $E_{*CO}$  and  $*CHO$  co-adsorption,  $E_{*OCCHO}$  and  $\Delta E$  of  $*CO-*$ CHO coupling on Cu modified with glycine where  $-NH_2$  is replaced by  $-X$

X	$E_{*CO}$ and $*CHO$ co-adsorption (eV)	$E_{*OCCHO}$ (eV)	$\Delta E$ of $*CO-*$ CHO coupling (eV)
NO <sub>2</sub>	-648.013	-647.582	0.431
CH <sub>3</sub>	-649.350	-649.042	0.308
CH <sub>2</sub> CH <sub>3</sub>	-665.930	-665.620	0.310
SH	-636.713	-636.280	0.433
NH <sub>2</sub>	-644.477	-644.033	0.444

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