Supporting Information

Directing CO₂ electroreduction to ethanol via delicate geometrical modification of copper-based alloys

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Computational Methods

Neural network (NN) potential calculation

We used Large-Scale Atomic Simulation via Machine Learning Potentials^{1,2} (LASP) to make all Molecular dynamic simulation.

- 5 LASP is a commercial software, which is developed by Prof. Zhipan Liu group at Fudan University (http://www.lasphub.com/index.asp). LASP code is developed for large-scale simulation of complex systems with neural network (NN) potential. By learning the first principles dataset of global potential energy surface (PES), which is obtained from stochastic surface walking (SSW) global optimization, global neural
- 10 network potential is generated. PES exploration for complex materials can be achieved by combining the SSW method and NN potential. Apart from SSW-NN global optimization, the software implements standard interfaces to dock with other energy/force evaluation package and can perform tasks for PBS properties like molecular dynamics simulation.
- 15 The NN potential used in this calculation is provided by LASP software, here are the basic data of the potential (**Table S1**).

To train the NN potential, a series of random structures were generated, where atoms were placed in different chemical environments. These data were used to train the NN potential so that it could handle the complex atomic systems of CuZnCHO. Due to commercial software licensing agreements, we only selected some of the training structures to address your comments. Images of selected structures can be found in **Figure S27**, the atomic structure is represented using different colored spheres: oxygen (red), copper (orange), zinc (blue), carbon (grey), and hydrogen (white).

We also calculated the adsorption energy of key intermediates (*CO and *OCCOH)
using both VASP and LASP NN potential, with the results shown in Figure S26. The RMSEs are 0.09 eV/atoms and 0.14 eV/atoms, which are sufficiently accurate for this work. The training dataset used for the NN-potential is partially shown in Figure S27. The specific strategy for the oxidation of the OD-CuZn alloy is as follows:

First is the O adsorption simulation strategy. In this process, we identify the active sites on the catalyst surface through the Alpha-shape algorithm. After locating the active sites, O adsorption energies are calculated sequentially (Figure S2).

The calculation method for O adsorption energies on the catalyst surface is as follows:

$$E_{0} = E_{*0} - \frac{1}{2}E_{0_{2}} - E_{slab}$$

Furthermore, we sort the O adsorption energies from high to low and calculate the average O adsorption energy sequentially using the following formula:

$$E_{avg_0} = \frac{1}{N} (E_{N*0} - \frac{N}{2} E_{0_2} - E_{slab})$$

As the surface coverage increases, the average adsorption energy of surface oxygen will gradually decrease. When the average O adsorption energy approaches 0 eV, it can be considered that O adsorption on the catalyst surface reaches saturation in this step (Figure S3).

Subsequently, after obtaining the O-saturated surface, we employ kinetic simulations to model O diffusion, in which we observe the diffusion of O into the bulk 15 structure. We use the total energy of the system as a descriptor, monitoring the trend of total energy change. When the total energy change stabilizes, it is considered that sufficient diffusion of O atoms has occurred (Figure S4).

Similarly for the reduction process, we calculated the oxygen vacancy formation energies for all O atoms on the surface, using the formula below:

$$E_{0v} = E_{N*0} - (E_{H_20} - E_{H_2}) - E_{(N-1)*0}$$

Accordingly, we computed all the oxygen vacancy formation energies on the surface, and removed all O atoms with vacancy formation energies below 0 eV simultaneously (Figure S5).

After obtaining the surface with oxygen vacancies, we again employed kinetic 25 simulations to model O diffusion, where we observed the diffusion of O atoms back to the surface. The total energy of the system was used as the descriptor, monitoring its change during the simulation. When the total energy change stabilized, sufficient diffusion of O atoms was considered to have occurred. Then, we will get the oxide derived CuZn catalysts (Figure S6-11).

Basic parameters for calculation

Density functional theory calculations were performed using the plane-wave-based Vienna Ab Initio Simulation package³ (VASP). The electron exchange and correlation effects were described by the generalized gradient approximation (GGA) in the form of

- 5 the Perdew-Burke-Ernzerhof (PBE) functional⁴. The D3 correction method was employed to illustrate the long-range dispersion interactions between the adsorbates and CuZn surface⁵. The interaction between atomic cores and electrons was described by the projector augmented wave (PAW) method⁴. A cutoff energy of 400 eV for the plane-wave basis set and an atomic force convergence of 0.02 eV/Å were employed.
- 10 The transition state search was conducted with climbing image nudged elastic band (CI-NEB) method⁶, followed by the dimer method to converge the saddle point within 0.05 eV/Å.

The electronic band calculations were performed with density functional theory (DFT) by combining the Vienna ab initio Simulation package (VASP) with post-15 processing VASPKIT package⁷.

(111), (100) and (211) facets were used to model Zn doped on 111 faces, Zn doped on square sites and Zn doped on step sites. The size of the model is $(4 \times 4 \times 5)$, where the three bottom layers were kept fixed in optimization. $(3 \times 3 \times 1)$ k-points grid was used.

Cluster analysis on oxide derived CuZn catalysts

- 20 On oxide-derived CuZn catalysts, we employed both geometric parameters and energetic descriptors (E_{*CO} and E_{*OCCO}) for cluster analysis. The active sites were categorized into three distinct structural motifs: Zn-doped (111) facets, Zn-modified step-square configurations, and Zn-incorporated planar-square arrangements. Specifically, we extracted the active sites from existing structural models (**Figure S6**-
- 25 11) and supplemented these with algorithmically generated surface configurations.(Figure S12-14)

The specific atomic cluster selection procedure was implemented as follows (Figure S13):

For each simulated OD-CuZn slab, we established a coordinate system where
 the slab edges were defined along x and y axes, with values normalized from 0 to 1.

2: We created a selection box of fixed dimensions to extract atomic clusters from the slab.

3: Using a random number generator, we generated coordinate pairs (x, y) to determine the center position of the selection box. For example, if the random
5 coordinates were (0.4, 0.5), we would position the selection box's center at that location.

4: The atoms within the selection box boundaries were then extracted to create the smaller computational model.

10 Experimental Section

Synthesis of Oxide-derived CuZn catalysts

We synthesized a batch of catalysts using a spray coating method, and the synthesis process is described as follows:

- First, the purchased polycrystalline CuZn alloy powder was milled in a ball mill,
 15 using zirconia ceramic balls with a diameter of 1 mm. After milling, the catalyst particles underwent oxidation in air atmosphere at 675 K for 5 hours in a muffle furnace. In subsequent preparation, we added 50.0 mg catalyst, 200.0 μL Nafion solution (5 wt% EtOH solution) into 15.0 mL isopropanol. The suspension was ultrasonically treated in a 0°C water bath for 2 hours, and sprayed onto carbon paper (5 cm × 5 cm)
- 20 using a N₂ gas stream, then dried at 80°C for 2 hours. The average loading amount of the CuZn alloy was 2mg/cm². (Figure S18)

To determine the optimal composition of CuZn alloys, we initially employed H-cell experiments (Figure S1). The results indicated that the most effective ratio is approximately Cu₃Zn.

25 Characterization

The crystal structure of the catalysts was determined using an x-ray diffractometer (XRD, Bruker D8 Focus, Cu Ka radiation, $\lambda = 1.54056$ Å) with a voltage of 40 kV and a current of 40 mA. XRD spectra was collected at a scanning speed of 8°/min in the 20 range from 10 to 80°. In Figure S19, the XRD data shows that the Cu diffraction peaks

30 shifted as the Zn ratio increased. All the diffraction peaks are in good agreement with

the standard pattern for pure face centered cubic phase of copper nanoparticles (JCPDS No. 040836).

The morphology of the catalysts was observed using a field emission scanning electron microscope (FESEM, Hitachi S4800) with an accelerating voltage of 5 kV.

5 XPS analysis was got on a Physical Electronics PHI 1600 ESCA system with an x-ray source with AI (1486.6 eV) to determine the surface composition of the catalysts, the peak position of the binding energy was calibrated with the C 1s signal at 284.8 eV as the reference.

In the XPS pattern, the Cu oxide has strong satellite peaks, indicating that the surface 10 Cu is oxidized to Cu²⁺, whereas for the surface of the catalyst after electroreduction, Cu, Zn are presented in metallic form. Auger electron spectroscopy (AES) analysis revealed the presence of metallic Cu (Cu⁰) and Zn (Zn⁰) species in the reduced catalyst.

In-situ Raman spectroscopy was carried out in a custom-designed flow cell, which was manufactured by Gaossunion Co., Ltd⁸., Tianjin. The electrode was exposed

15 circular geometric surface area of ~1 cm². A platinum wire and an Ag/AgCl electrode (saturated KCl, Gaossunion Co., Ltd., Tianjin) were used as the counter and the reference electrode, respectively. In situ Raman spectroscopy was performed with a Raman microscopy system (LabRAM HR Evolution, Horiba Jobin Yvon). A He–Ne laser ($\lambda = 532$ nm) served as the excitation source.

20 Electrochemical reduction of CO₂ in a flow cell

 CO_2 reduction was conducted in a custom-designed three-chamber flow cell manufactured by Gaossunion Co., Ltd. (details in our previous work⁸), where the CO_2 gas was supplied directly to the catalyst layer (cathode, working electrode). The CO_2 gas flow rate was controlled using a mass flow controller (MC-Series, Alicat Scientific)

- 25 and set to 20 sccm. We used flowmeter (M-Series, Alicat Scientific) to detect the CO₂ flow rate at the outlet of the reactor and used this number as the basis for calculating F.E. Aqueous KOH solution (1 M) was used as both the catholyte and the anolyte. Activated Ni foam was used as the anode (counter electrode). Peristaltic pumps (EC200-01, Gaossunion Co., Ltd.) were used to control the flow rate of the electrolytes
- 30 at ~15 ml min⁻¹. An AEM (FAA-3-PK-75, Fumatech) was used to separate the cathode

and anode chambers. Electrolysis experiments were conducted using chronoamperometry with a potentiostat (CompactStat.e20250, IVIUM). The cathode potentials were measured against a Hg/HgO reference electrode (1 M KOH, Gaossunion Co., Ltd., Tianjin). For each measurement, products were quantified after

5 the amount of electron flowing through the cathode achieved 50 C and at least three replicates were conducted to obtain an average value with the standard deviation.

Supplemental Figures and Tables

RMS Energy	2.991	RMS Force	0.08(eV/Ang)
Version	20200510052346	Dataset size	63539

Fable	S1	Basic	data	of	CuZnCHO.	pot
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Table S2 Surface Elemental Composition

Element	Line types	Percentage by weight	Wt % Sigma	Percentage by
				atoms
Cu	L	71.03	1.27	71.61
Zn	L	28.97	1.27	28.39
Total		100.00		100.00



Figure S1 The CO₂ reduction performance of OD-CuZn alloy catalysts with different CuZn ratios in H-cells shows that the C₂₊ product activity data is highest when the CuZn ratio is close
to 3:1.



Figure S2 strategy for oxidation simulation process.

The diagrams for variation of total energy in NN-SSW global optimization and energy profiles in the 1 ns MD simulation of global minimum. Meanwhile, in the 1 ns, nearly all the atoms oscillated near their equilibrium position without obvious movement.



Figure S3 O Adsorption and Diffusion Process



Figure S4 Total Energy Change in Kinetic Simulations



5 Figure S5 Schematic illustration of O reduction steps (each step in the figure encompasses multiple actual reduction steps due to the large number of steps)



Figure S6 Distribution of surface sites on the catalyst after OD treatment



Figure S7 Distribution of surface sites on the catalyst after OD treatment



Figure S8 Distribution of surface sites on the catalyst after OD treatment



Figure S9 Distribution of surface sites on the catalyst after OD treatment



Figure S10 Distribution of surface sites on the catalyst after OD treatment



Figure S11 Distribution of surface sites on the catalyst after OD treatment



Figure S12 Correspondence between the geometry of the alloy surface and the model surfaces

used in calculations



Figure S13 Workflow of random selection process



Figure S14 Some example model surfaces used in the calculations



5 Figure S15 Clustering results of the OD alloy surface based on E_{*CO} and E_{*OCCO} . The stars points are calculated by VASP, the dot points are calculated by LASP



Reaction Coordinate

Figure S16 Reaction pathway for CO₂ electroreduction on step-square sites.



5 Figure S17 Charge density difference of adsorbed *OC₂H₃ intermediate on different active sites. Blue and yellow contours represent the iso-surfaces of electronic charge depletion and accumulation, respectively, with an iso-surface value of 0.01 eÅ⁻³ implemented.



Figure S18 Schematic diagram of catalyst synthesis



5 **Figure S19** XRD patterns of Cu-Zn nanoparticles with Zn ratios. (The diffraction peaks are indexed according to JCPDS Card No. 040836.)



Figure S20 Surface Structure and Elemental Distribution



Figure S21 Elemental Mapping



Figure S22 XPS spectra of the a: Oxidised Cu 2p, b: Reduced Cu 2p, c: Oxidised Zn 2p, d: Reduced Zn 2p



Figure S23 Cu and Zn LMM Auger spectrum of the reduced catalyst.



Figure S24 Comparison between OD-Cu and OD-CuZn alloy shows that after introducing Zn atoms, the total productivity of C_{2+} products and the ratio of C_2H_5OH to C_2H_4 increased significantly.





Figure S25 a: Catalysts surface after OD process, b: Catalysts surface after annealing.



Figure S26 The comparison of NN potential predicted energy and that from DFT calculation. (a) *CO adsorption energy, (b) *OCCOH adsorption energy



Figure S27 Representative atomic configurations from the LASP neural network potential training set. Color code: oxygen (red), copper (orange), zinc (blue), carbon

(grey), and hydrogen (white).

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