Supporting Information

Ag/Cu foam catalyst at lower potential selective reduction of CO_2 to CH_3OH

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Calculation formula

The potentials measured by Ag/AgCl electrode were converted to the RHE potentials by the following equation[1]:

$$E_{RHE} = E_{Ag/AgCl} + 0.0592 \times pH + E^{\theta}_{Ag/AgCl} \quad \text{(S1)}$$

where $E_{Ag/AgCl}$ is the experimentally measured potential and $E^{\theta}_{Ag/AgCl}$= 0.197 V (vs Ag/AgCl) at 25°C.

The Gibbs free energy change (ΔG) was calculated using the equation[2]:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + eU \quad \text{(S2)}$$

here, ΔE, ΔZPE, and ΔS correspond to the energy, zero-point energy, and entropy differences between the products and reactants, respectively. e represents the number of electrons transferred during the reaction, while U denotes the applied electrode potential. Due to limitations of the DFT approach in accurately calculating the energy of O_2, the free energy of O_2 was obtained by considering the free energy change of the reaction $2H_2 + O_2 \rightarrow 2H_2O$.

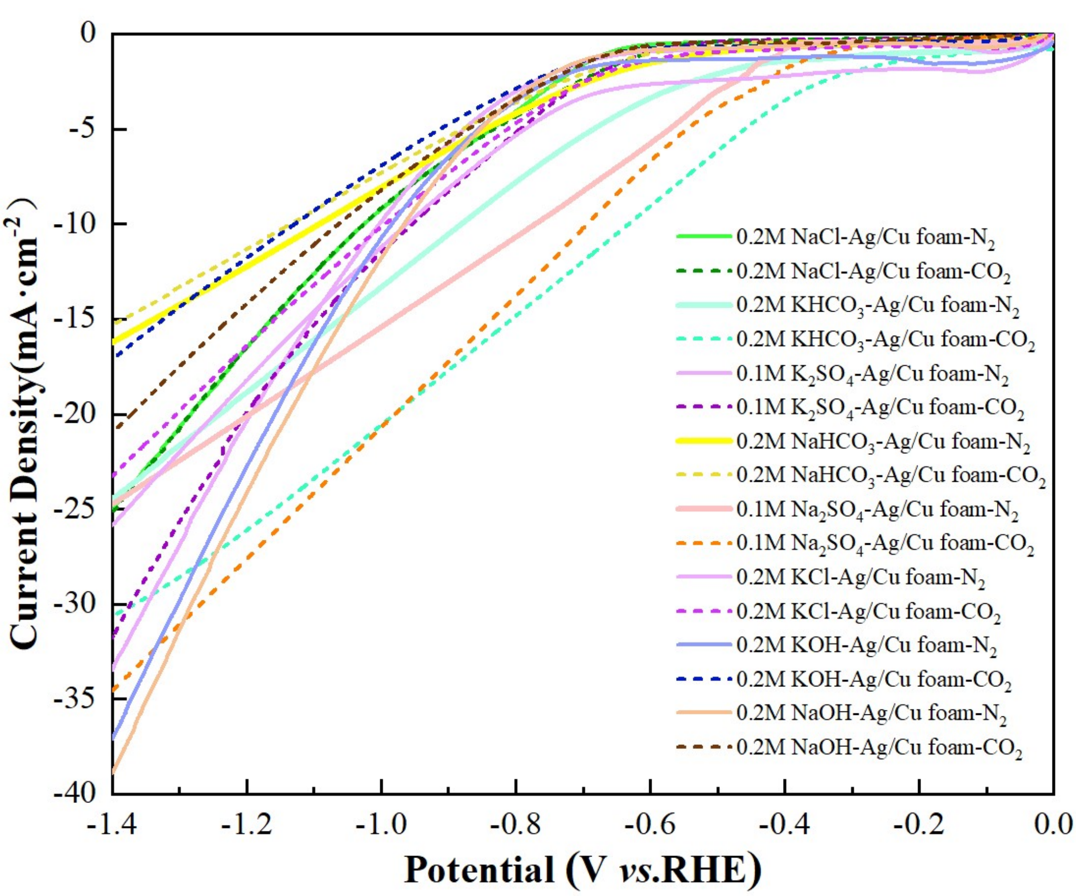


Figure S1. LSV curves for electrolyte screening.

The electrolyte with a higher current density of the catalyst was selected, and it exhibited a greater current density in the CO_2 atmosphere compared to the N_2 atmosphere, as depicted in Figure S1. Therefore, 0.1 M Na_2SO_4 proved to be more suitable for this purpose.

Figure S2. H-type cell diagram.

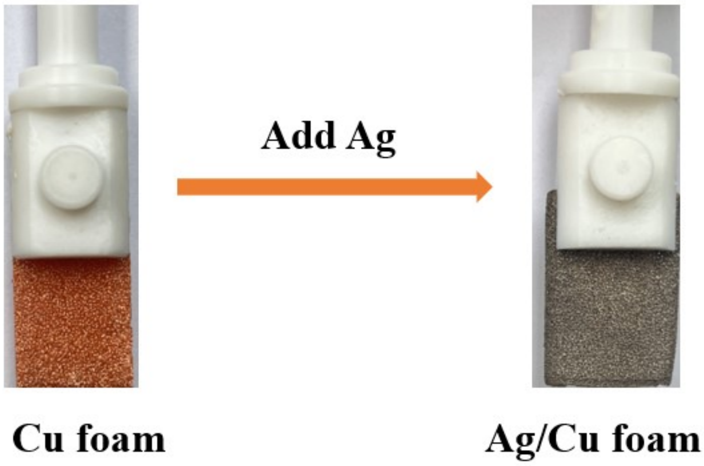


Figure S3. Electrode diagram.

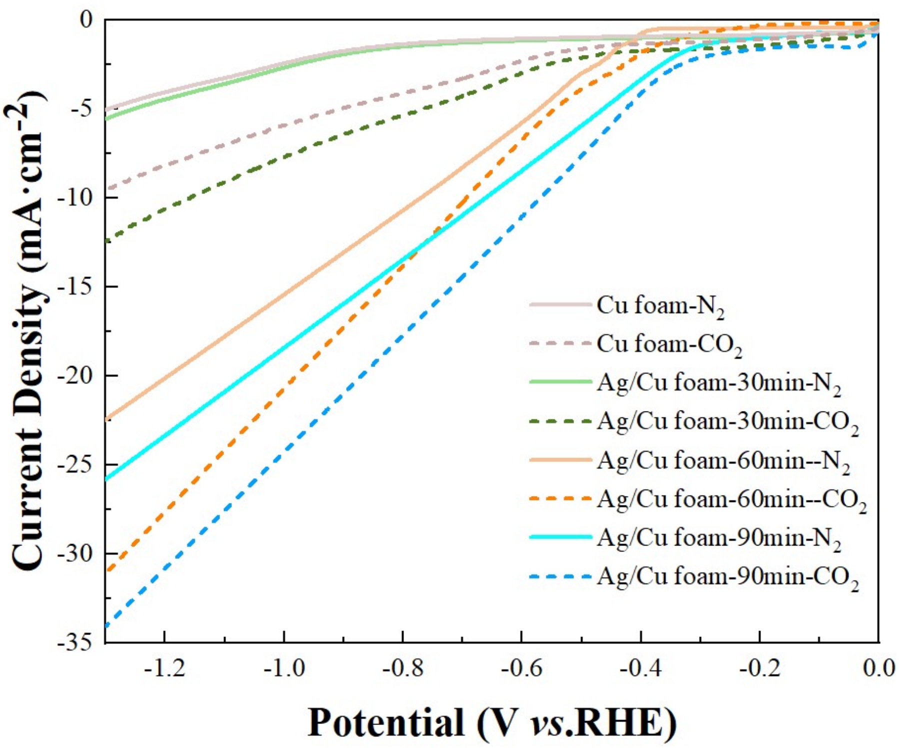


Figure S4. The LSV curves of Ag/Cu foam coated with varying durations of silver plating were investigated.

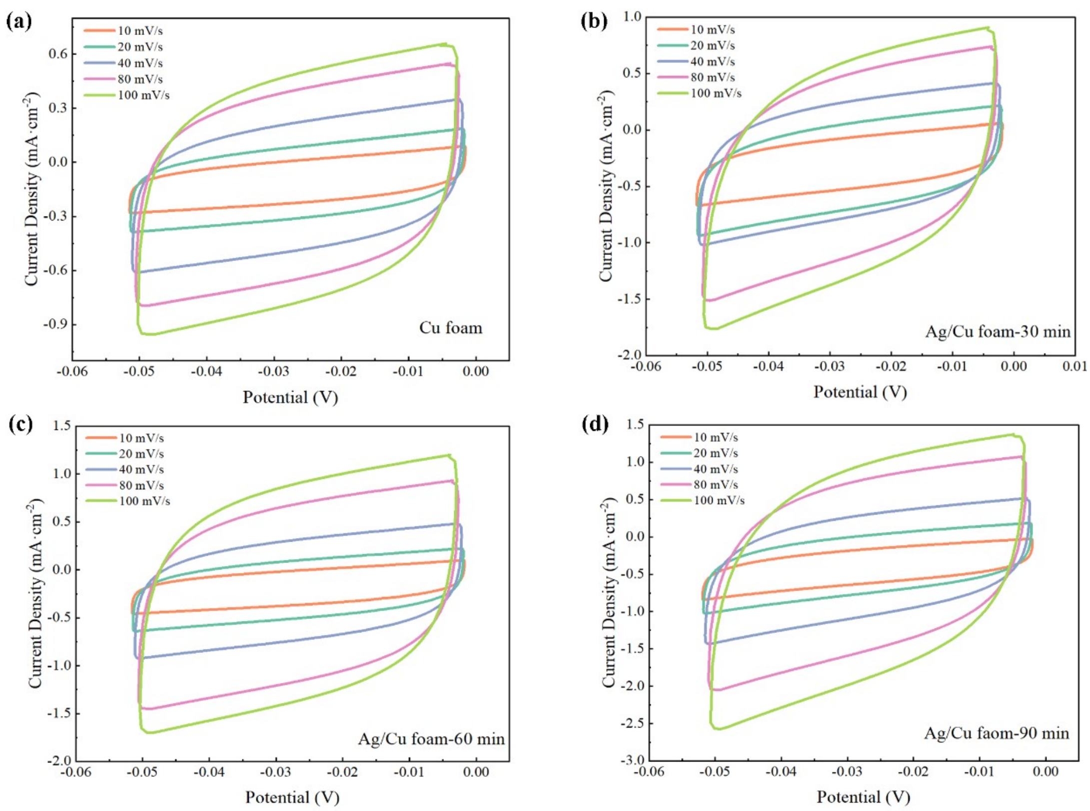


Figure S5. CV curves of Cu-based catalysts. The voltage range for the selected CV curve was set within the interval of 0 V (V *vs*. RHE) and 0.05 V (V *vs*. RHE).

Table S1. Electrochemical impedance spectroscopy (EIS) analysis of catalysts with varying durations of silver plating.

Sample	R_s (Ω)	R_{ct} (Ω)	CPE
Cu foam	1.609	103.8	0.003309
Ag/Cu foam-30 min	1.643	39.91	0.002951
Ag/Cu foam-60 min	1.631	7.343	0.004532
Ag/Cu foam- 90 min	1.831	3.358	0.01166

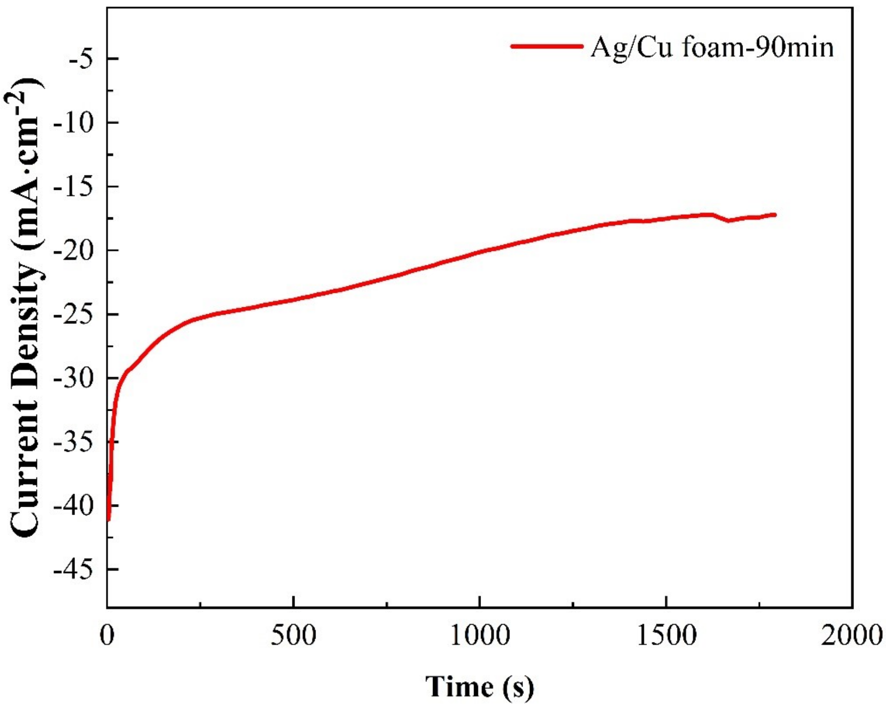


Figure S6. The IT curve of Ag/Cu foam-90 min.

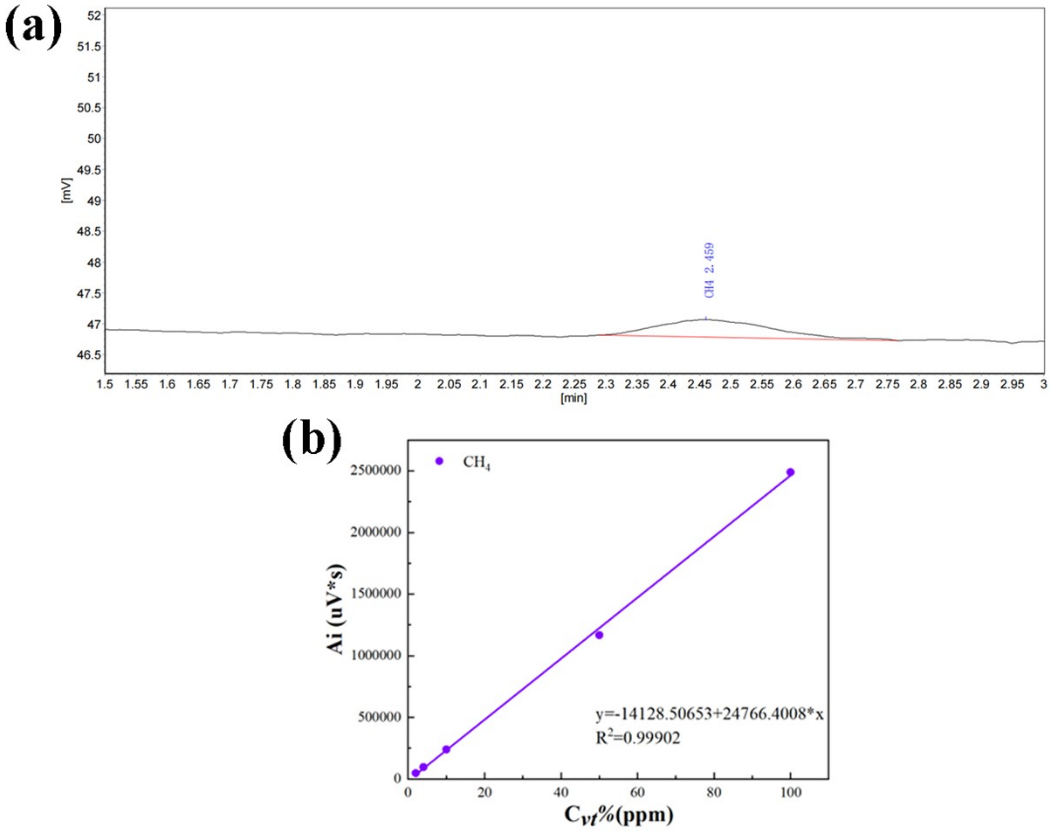


Figure S7. (a) Standard gas chromatographic diagram of CH_4, (b) Gas chromatographic diagram of CH_4 standard sample.

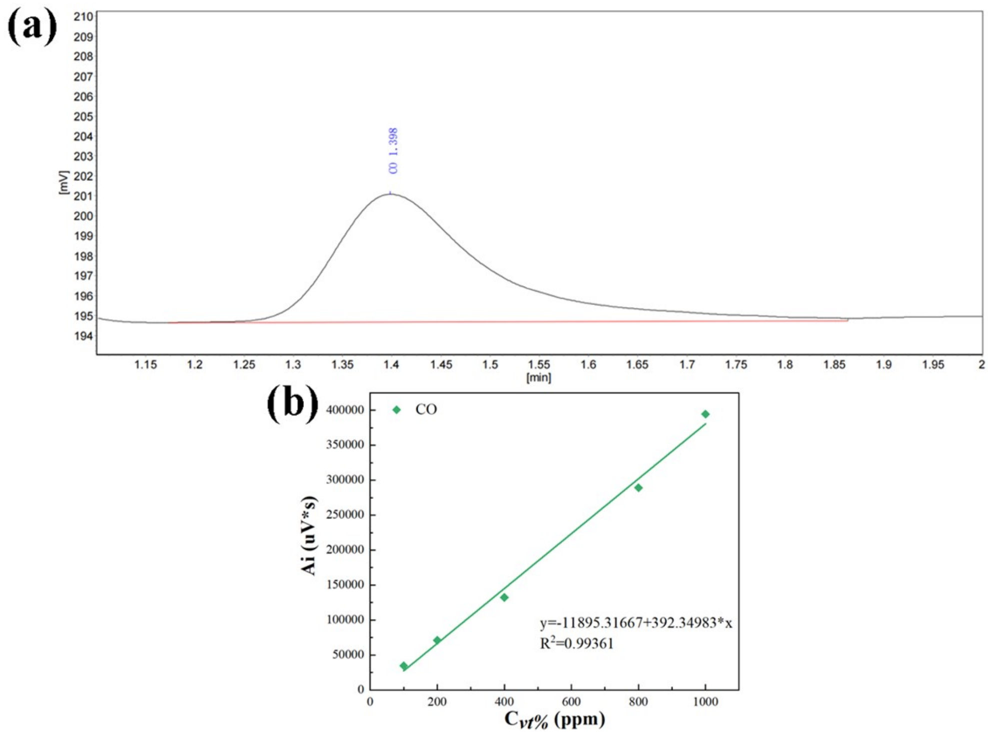
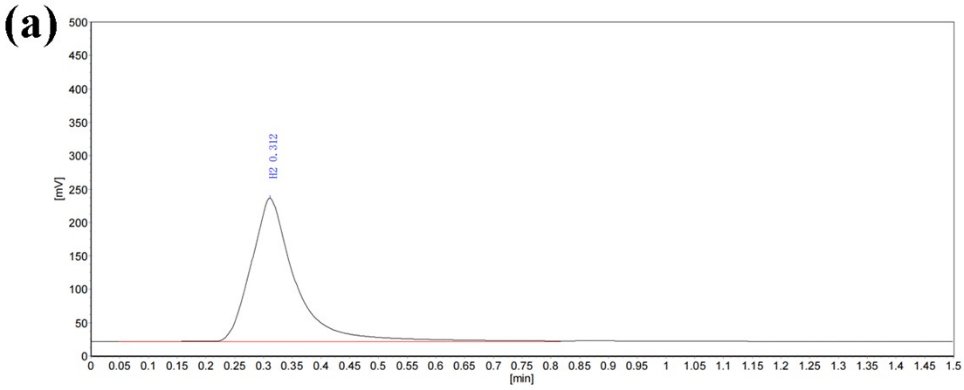


Figure S8. (a) Standard gas chromatographic diagram of CO, (b) Gas chromatographic diagram of CO standard sample.



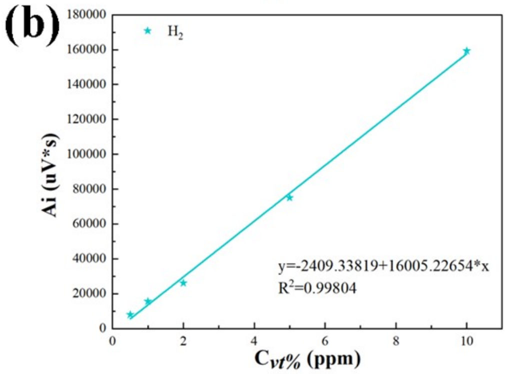


Figure S9. (a) Standard gas chromatographic diagram of H_2, (b) Gas chromatographic diagram of H_2 standard sample.

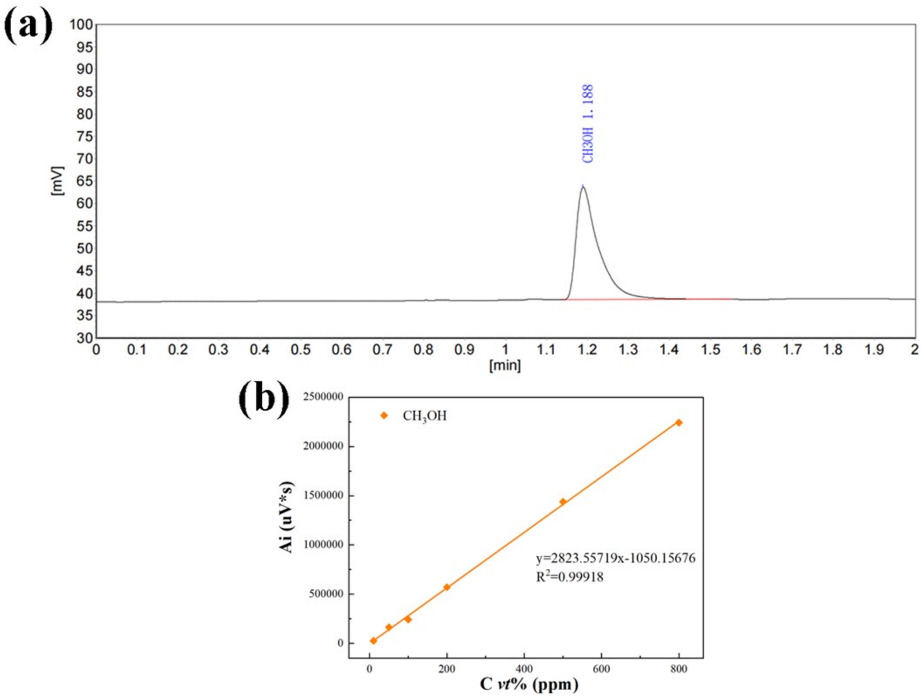


Figure S10. (a) Standard gas chromatographic diagram of CH_3OH, (b) Gas chromatographic diagram of CH_3OH standard sample.

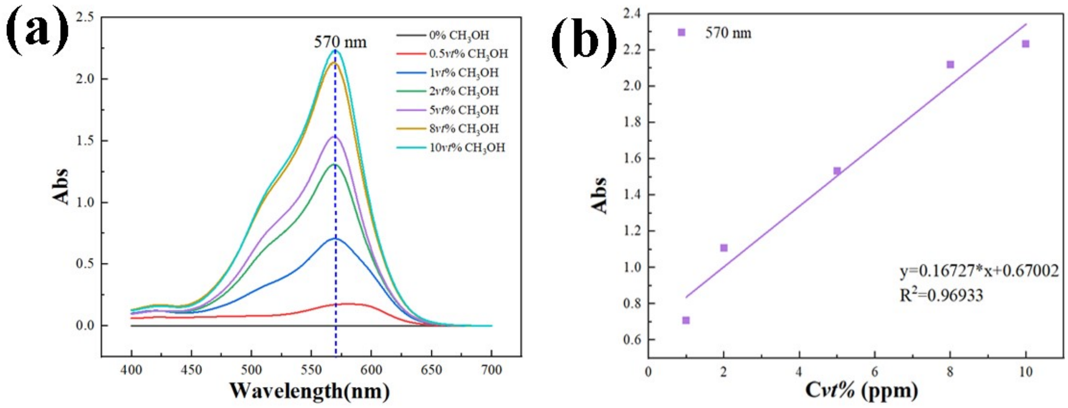


Figure S11. Quantification of methanol was performed using UV-1780 spectrophotometry. (a) the UV-VIS absorption spectra of methanol at 570 nm, (b) the UV-1780 absorption spectrum standard diagram of methanol at 570 nm.

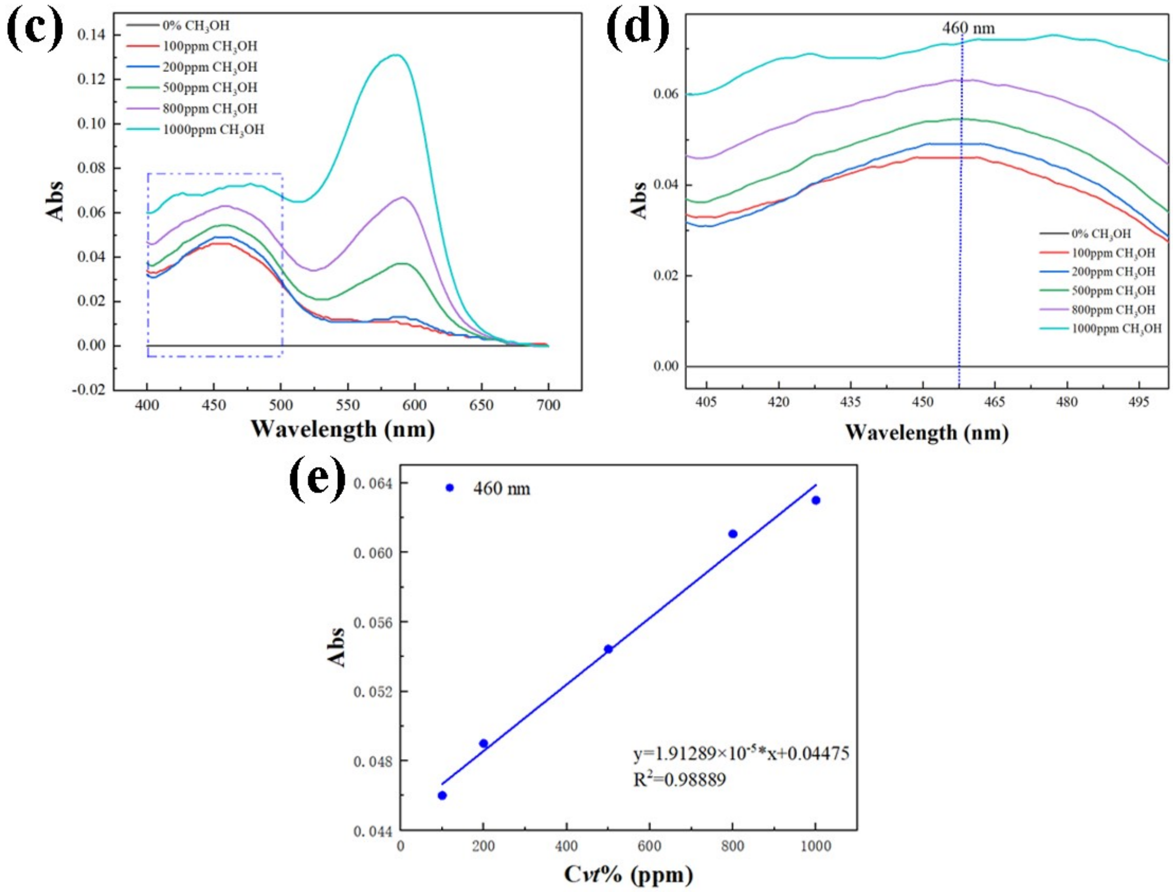


Figure S12. Quantification of methanol was performed using UV-1780 spectrophotometry. (a) the UV-VIS absorption spectra of methanol at 460 nm, (b) the UV-1780 absorption spectrum standard diagram of methanol at 460 nm.

(1) Principle: After methanol is oxidized to formaldehyde, it reacts with fuchsin sulfite to produce blue-purple compounds, which are quantified compared with standard series.

(2)Method: Add water to 5 mL in each sample tube and standard tube, then add 2 mL of acidic potassium permanganate solution in turn, mix it well, leave it for 10 min, add 2 mL of oxalic acid and sulfuric acid mixed solution, mix it well to make it fade, then add 5 mL of fuchsin and sulfuric acid mixed solution, mix it well, and let it stand for 0.5 h above 24℃, use a 20 mm colorimetric cup, and adjust the zero point with zero tube. Measure absorbance at 590 nm, draw a standard curve for comparison, or visually compare with the standard series. The linear curve is obtained by linear fitting with the standard curve drawn. The sample is measured according to the above method, and the methanol concentration of the sample can be obtained by inserting the absorbance into the equation.

(3) The specific peak of methanol with low concentration is not obvious at the wavelength of 570 nm, but a relatively obvious peak is found at the wavelength of 460nm. The linear fitting of methanol with low concentration at 460 nm shows that the error of methanol testing at 460 nm is 31.76% smaller than that at 570 nm. Therefore, we chose to test low concentration methanol at a wavelength of 460 nm.

The electrochemical properties of Ag /Cu are shown in the experimental results (Figure 5). Ag /Cu can promote methanol production at different voltages. After increasing the voltage, the formation of methane is promoted, but the simple Cu cannot produce methanol and methane. In order to further illustrate the above experimental results, the catalyst was simulated. The results of simulation under pure Cu component are shown in supplementary information Figure S12. Originally, there were 6 equivalent positions that could be adsorbed, but the bond length of two positions was too long, so it was not included in the calculation process. The best position of pure Cu component was position 1.

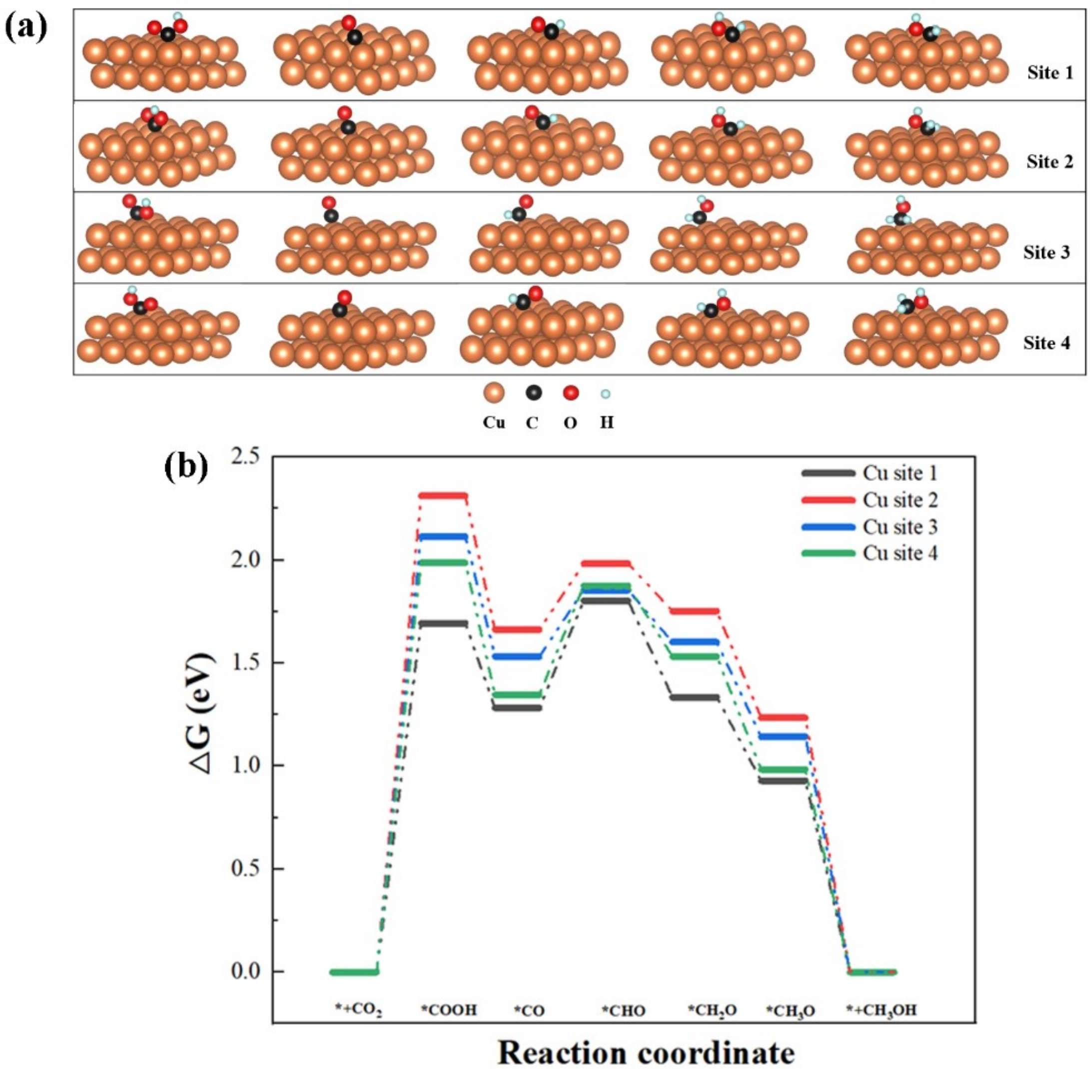


Figure S13. Carbon dioxide reduction on the (111) crystal plane of Cu in the (a) site 1-4, (b) Calculated CO_2 reduction free energy diagram. The cyan atoms in the model symbolize the adsorbed H atoms, the light brown Cu atoms, red O atoms and black C atoms denoting the sites of adsorption, respectively.

References

1. Y. Cui, A. Dong, Y. Zhou, Y. Qu, M. Zhao, Z. Wang and Q. Jiang, *Small*, 2023, **19**, e2207661.
2. Y. R. Wang, H. M. Ding, S. N. Sun, J. W. Shi, Y. L. Yang, Q. Li, Y. Chen, S. L. Li and Y. Q. Lan, *Angew Chem Int Ed Engl*, 2022, **61**, e202212162.