

Tuning interfacial water and CO–CHO coupling via Ag single atoms enhances ethylene production in CO₂ reduction

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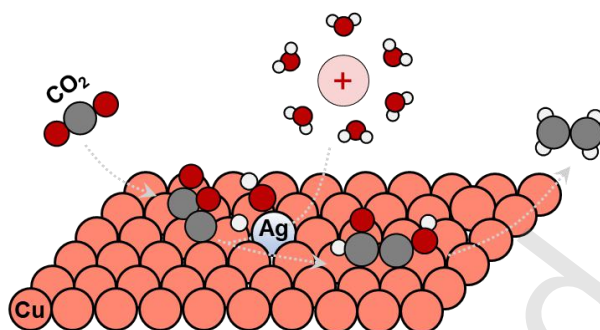
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The Ag₁-Cu interface promotes cation water dissociation and generates a localized proton-donating environment, which directs a favorable asymmetric CO-CHO coupling pathway and lowers the hydrogenation barrier of the key ethylene precursor *CH₂CHO.

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ABSTRACT: Single-atom site engineering has emerged as an effective strategy for enhancing the selectivity of multicarbon products in electrochemical CO₂ reduction reaction (CO₂RR), yet the synergistic roles of interfacial microenvironment regulation and key intermediate evolution remain poorly understood. Herein, Ag single-atom-modified porous CuO nanosheets (Ag₁-p-CuO) were constructed, and the mechanism by which Ag₁ atoms regulate the evolution of interfacial intermediates and water structure to promote ethylene formation, was systematically investigated through in situ shell-isolated nanoparticle enhanced Raman spectroscopy and advanced constant-potential density functional theory calculations. The atomically dispersed 0.2 % Ag species on porous CuO enabled a maximum C₂H₄ Faradaic efficiency of 54% and C₂₊ Faradaic efficiency of 78%. In situ Raman spectra reveal that, Ag₁ decoration enriches CO coverage at defective Cu step sites and reorganizes the interfacial water layer near the surface. The resulting Ag₁-Cu interface enhances cation-H₂O dissociation, establishing a local proton-donating environment that directs C–C bond formation toward a favorable asymmetric CO–CHO coupling pathway while lowering the hydrogenation barrier of the key ethylene precursor *CH₂CHO, thereby markedly improving ethylene selectivity. This work provides new insights into single-atom catalysis mediated interfacial microenvironment and intermediate behavior for promoting multicarbon product formation in CO₂RR.

KEYWORDS: single-atom catalysis, CO₂ reduction, surface enhanced Raman spectroscopy, Cu nanosheet

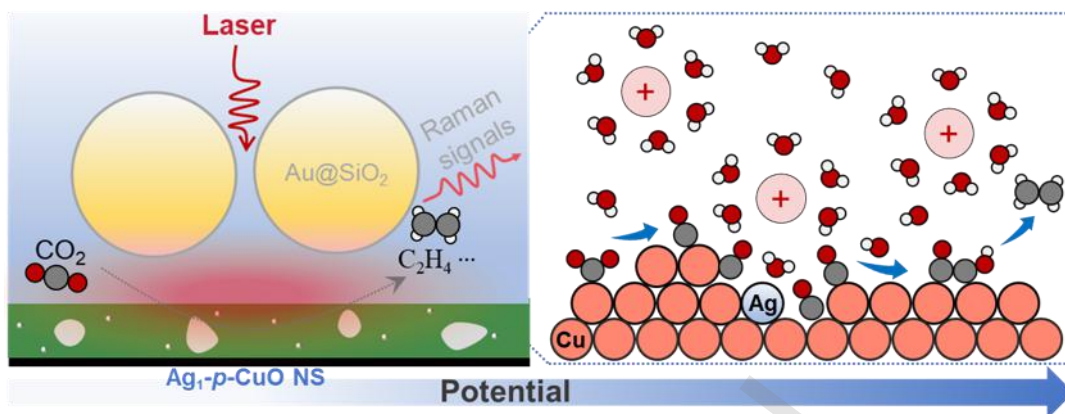
1 Introduction

Electrochemical CO₂ reduction reaction (CO₂RR) provides a promising route for converting intermittent renewable electricity into value-added chemicals and fuels, offering opportunities for both carbon neutrality and sustainable energy storage [1-4]. Among the diverse reduction products, multicarbon (C₂₊) compounds, particularly ethylene, are highly attractive because of their high energy density and broad industrial relevance [5,6]. Copper-based catalysts have been well established as promising electrocatalysts capable of producing appreciable amounts of C₂₊ products from CO₂ electroreduction [7,8]. However, the lack of selectivity remains an intrinsic issue as Cu often leads to the simultaneous generation of C₁, C₂₊ and H₂ byproduct.

To achieve highly selective C₂₊ production, extensive efforts have been devoted to regulating Cu surface facets, oxidation states, defects, and local electronic structures [11-10] to optimize the adsorption and dimerization of *CO intermediates [11-14]. Very recently, single-atom catalysts (SACs) [15-17] provide a unique opportunity to engineer the electrochemical interface at the atomic scale because of their well-defined coordination environments and highly tunable electronic structures for

CO₂RR [19-25]. Beyond simply modifying intermediate adsorption energies, isolated single-atom sites may simultaneously regulate *CO coverage, reconstruct the hydrogen-bonding network of interfacial water, and influence local proton transfer dynamics near active Cu sites [26-29]. Such synergistic regulation is expected to fundamentally alter the thermodynamics and kinetics of C–C coupling and subsequent hydrogenation pathways. Nevertheless, direct spectroscopic evidence correlating single-atom-induced interfacial intermediates and water evolution with key intermediate transformations during CO₂RR is still scarce [30,31].

Spectroscopic techniques [32] with molecular fingerprinting capability can provide direct evidence of reaction intermediates and their adsorption configurations at catalytic interfaces in real time, thereby offering deep insights into the relationship between interfacial structures and catalytic reaction mechanisms including CO₂RR [33-36]. Among them, Raman spectroscopy can probe the low-frequency region of 100-1000 cm⁻¹ that related to metal-adsorbate bonds, surface hydroxyls, and oxygen-containing species with minimal interference from water. In particular,



Scheme 1. Schematic depiction of in situ SHINERS for probing interfacial microenvironment regulation and key intermediate evolution during CO₂RR over Ag single-atom-modified porous CuO nanosheets.

surface-enhanced Raman spectroscopy (SERS), with ultrahigh surface sensitivity with excellent interfacial selectivity, is a powerful tool for mechanistic studies of electrocatalytic reactions including CO₂RR[37-41]. However, conventional SERS relies heavily on plasmonic Au, Ag, or Cu nanostructures of specific morphologies, limiting its application to most nanocrystal and single-atom catalytic systems. To overcome this long-standing challenge, Tian and co-workers developed shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), [42,43] which employs ultrathin, chemically inert SiO₂ shells on Au or Ag nanoparticles as Raman signal amplifiers. This isolation design prevents both interference signals originating from the surface of the enhancing nanoparticles and any potential electronic effect interference on the target surface. [33,44-46] Thus, SHINERS offers a promising strategy to correlate interfacial water activation, intermediate evolution, and product selectivity on single-atom catalysts. Motivated by these advances, we herein construct Ag single-atom-modified porous CuO nanosheets (Ag₁-p-CuO) and systematically investigate the role of Ag single atoms in regulating the interfacial intermediates and microenvironment during CO₂RR via in situ SHINERS (Scheme.1). The results reveal that an appropriate amount of Ag single atoms not only increase *CO coverage at Cu step sites and promote C-C coupling, but also significantly enhance the enrichment of non-hydrogen-bonded cation water dissociation at the interface. Such synergistic modulation of carbon intermediates and proton-transfer environments effectively lowers the energy barriers of key hydrogenation steps, ultimately promoting ethylene formation with enhanced selectivity. This work provides direct spectroscopic insights into single-atom site mediated CO₂RR over Cu-based catalysts, enabling efficient and highly selective C₂+ production.

2 RESULTS AND DISCUSSION

2.1 Characterization of Ag single-atom-modified porous CuO nanosheet

As illustrated in (Fig.1(a)), CuO nanosheets were first synthesized via a hydrothermal method. After calcination at 200 °C for 4 h, the residual carbonate species decomposed to generate porous CuO nanosheets (denoted as p-CuO). The obtained sample retained a two-dimensional porous nanosheet architecture (Figs.1 and Figs.2), featuring abundant pores and edge defect sites that are beneficial for exposing low-coordinated active sites. In addition, CuO nanosheets with calcination times of 2 h and 6 h were also prepared under otherwise identical conditions (Figs.3). The XRD patterns (Figs.4) reveal that the diffraction peak intensities first increase and then decrease with increasing calcination time, with the 4 h sample showing the highest peak intensity, indicating optimal crystallinity. Subsequently, a low loading amount of Ag was introduced through an impregnation-calcination process, yielding Ag single-atom-modified porous CuO nanosheets (denoted as Ag₁-p-CuO). Detailed synthetic procedures are provided in the Methods.

As shown in (Fig.1(b)), scanning electron microscopy (SEM) image reveal that the as-prepared Ag₁-p-CuO exhibits a micron-sized nanosheet morphology with an average lateral size of approximately ~1 μm and a thickness of ~35 nm characterized by atomic force microscopy measurement (Figs.5). High-resolution TEM images further confirm the formation of abundant porous structures after calcination. No Ag nanoparticles or clusters were observed in the aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) image (Fig.1(c)). Instead, isolated bright spots were clearly identified, indicating the atomic dispersion of Ag species. Consistently, X-ray diffraction (XRD) patterns (Figs.6) show only characteristic diffraction peaks of CuO without detectable Ag-related peaks, further suggesting the absence of Ag

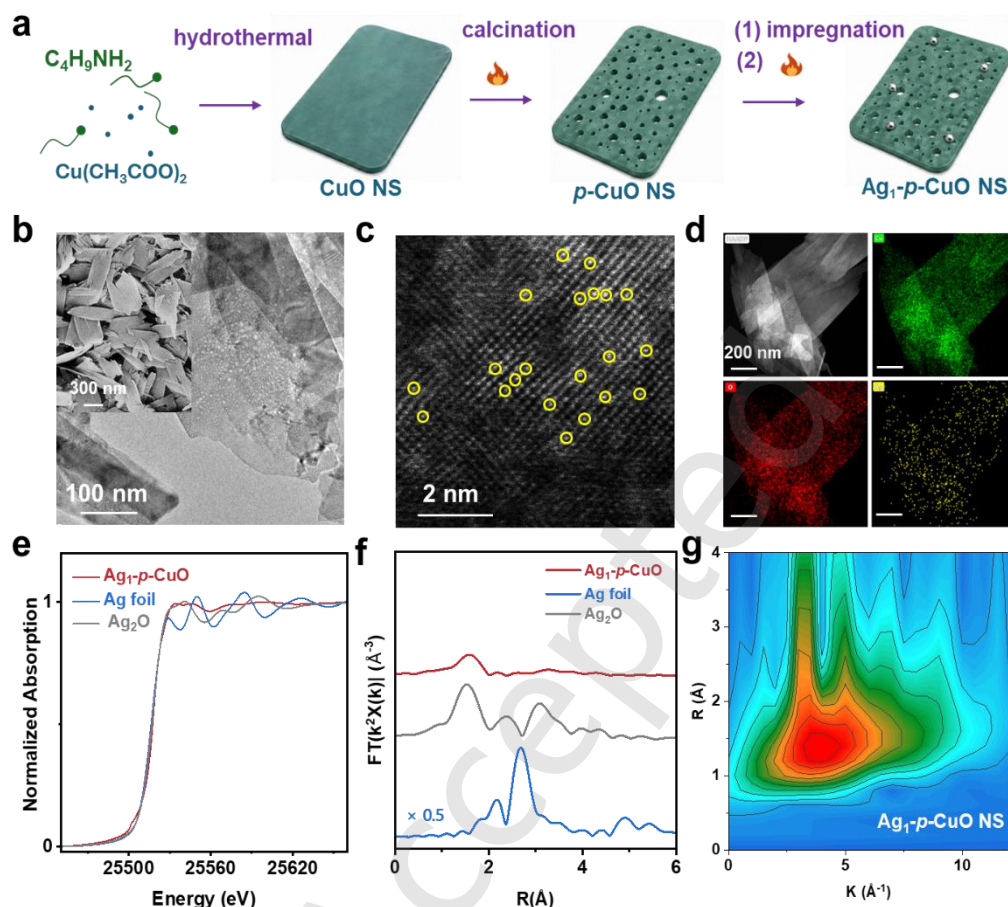


Figure 1 (a) Schematic illustration of the fabrication process of $\text{Ag}_1\text{-p-CuO}$ nanosheets. (b) SEM, TEM, and AC-HAADF-STEM images of the $\text{Ag}_1\text{-p-CuO}$ nanosheets. (c) AC-HAADF-STEM image of $\text{Ag}_1\text{-p-CuO}$ nanosheets (d) EDS elemental mapping images of the $\text{Ag}_1\text{-p-CuO}$ nanosheets. (e) Ag K-edge XANES spectra of CuO, $p\text{-CuO}$, and $\text{Ag}_1\text{-p-CuO}$ catalysts. (f) Ag K-edge FT-EXAFS spectra of the CuO, $p\text{-CuO}$, and $\text{Ag}_1\text{-p-CuO}$ catalysts. (g) Wavelet transform contour plot of the $\text{Ag}_1\text{-p-CuO}$ catalyst.

aggregates. Inductively coupled plasma optical emission spectroscopy analysis determined the Ag loading to be ~ 0.2 wt%. In addition, energy-dispersive X-ray spectroscopy (EDS) elemental mapping images (Fig.1(d)) demonstrate the uniform distribution of Cu, Ag, and O throughout the nanosheets. The electronic structure and local coordination environment of Ag species were further investigated by X-ray absorption spectroscopy (XAS). As shown in the XANES spectra (Fig.1(e)), the absorption edge position of $\text{Ag}_1\text{-p-CuO}$, determined by first-derivative analysis, lies between those of Ag foil and Ag_2O (Fig.S4), indicating a partially positively charged state of Ag species. In the Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra (Fig.1(f) and Figs.7), no Ag-Ag coordination peak analogous to that of Ag foil was detected at ~ 2.7 Å for the $\text{Ag}_1\text{-p-CuO}$ sample; instead, only a peak

(~ 1.5 Å) was observed at the position corresponding to the Ag-O coordination in Ag_2O . Furthermore, the k^2 -weighted wavelet transform (WT) analysis of $\text{Ag}_1\text{-p-CuO}$ (Fig.1(g) and Figs.8) reveals a dominant intensity signal centered at ~ 1.5 Å, which is in strong agreement with the Ag_2O reference and clearly distinguishable from Ag foil. EXAFS curve-fitting results reveal that the Ag-O bond distance in $\text{Ag}_1\text{-p-CuO}$ is 2.05 Å, consistent with that in Ag_2O (2.05 Å); however, the fitted Ag-O coordination number (0.7) is drastically reduced compared to bulk Ag_2O (2.0), providing strong evidence for the atomically dispersed nature of Ag species on the porous CuO nanosheets (Table.S1).

2.2 Ag Single-Atom Sites Promote Ethylene Product

The CO_2 electroreduction performance of CuO, $p\text{-CuO}$, and $\text{Ag}_1\text{-p-CuO}$ catalysts was systematically evaluated in

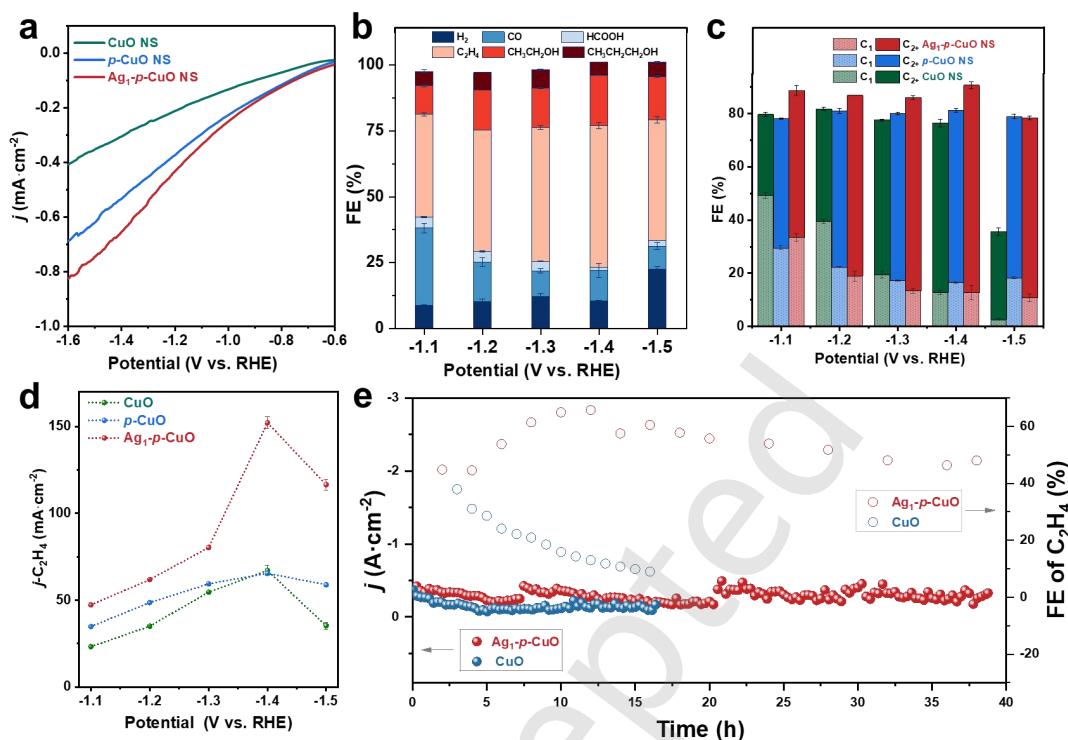


Figure 2 (a) LSV curves of CuO, *p*-CuO, and Ag₁-*p*-CuO measured in CO₂ atmosphere at a scan rate of 100 mV·s⁻¹ in flow-cell configuration. (b) Faradaic efficiency distributions of CO₂RR products over Ag₁-*p*-CuO measured in a flow-cell configuration. (c) Comparison of C₁ and C₂₊ Faradaic efficiencies and (d) partial current densities for C₂H₄ production on CuO, *p*-CuO, and Ag₁-*p*-CuO catalysts. (e) Long-term stability tests of CuO and Ag₁-*p*-CuO at 300 mA·cm⁻², showing stable C₂H₄ Faradaic efficiency and current density over 38 h continuous electrolysis.

both H-cell and flow-cell configuration over a potential range from -0.9 to -1.5 V versus RHE. The effect of annealing time on the CO₂RR performance was systematically investigated (Figs.9). The optimal C₂₊ selectivity was achieved at 4 h, which was selected for subsequent experiments. Under these cathodic potentials, the CuO-based catalysts underwent an in-situ reduction process and were transformed into metallic Cu during CO₂RR. Post-reaction XRD analyses (Figs.10) confirmed the complete disappearance of the CuO phase and the emergence of characteristic diffraction peaks corresponding to metallic Cu(111) and Cu(200), indicating the formation of Cu as the actual catalytic phase under operating conditions. Despite this structural reconstruction, SEM observations (Figs.10) revealed that the catalysts largely retained their nanosheet morphology after electrolysis, demonstrating good structural stability.

Linear sweep voltammetry (LSV) measurements were first conducted under a CO₂ atmosphere in flow-cell configuration. As shown in (Fig.2(a)), the current density (*j*) followed the order of CuO < *p*-CuO < Ag₁-*p*-CuO after -0.8 V, indicating that both the porous structure and Ag single-atom modification significantly enhanced the catalytic activity toward CO₂ reduction. The gaseous products were quantified using online gas chromatography (Figs.11), while

the liquid products were analyzed by proton nuclear magnetic resonance (¹H NMR) spectroscopy (Figs.12). According to the product distributions over CuO (Figs.13a), *p*-CuO (Figs.13(b)), and Ag₁-*p*-CuO (Fig.2(b)) in flow-cell configuration, the Faradaic efficiency (FE) for H₂ evolution decreased markedly after Ag modification, whereas the FE of carbonaceous products increased substantially.

Among the C₂₊ products, C₂H₄ was identified as the dominant product. Notably, Ag₁-*p*-CuO exhibited a high C₂H₄ FE ranging from 39% to 54% over a wide potential window from -1.1 to -1.5 V vs. RHE. The highest C₂H₄ FE of 54% was achieved at -1.4 V vs. RHE. In addition, the total FE for C₂₊ products reached 55%-78% in (Fig.2(c)), which was 14 %-35% higher than that of pristine CuO and 7%-13% higher than that of *p*-CuO under the same conditions. Similarly results could also be found in H-cell (Figs.14). These results demonstrate that Ag single-atom modification effectively promotes C-C coupling and enhances multicarbon product selectivity. As shown in (Fig.2(d)), the partial current density for C₂H₄ over Ag₁-*p*-CuO reached ~150 mA·cm⁻² at -1.4 V vs. RHE, which was nearly three times higher than those of CuO and *p*-CuO (~50 mA·cm⁻²). The significantly enhanced C₂H₄ partial current density further confirms the superior intrinsic activity of the Ag₁-*p*-CuO catalyst toward multicarbon product formation.

In addition, CO₂RR measurements

performed on Ag-modified *p*-CuO catalysts with varying Ag loadings (0.1, 0.2, 0.5, and 1.0 wt%) (Figs.15) revealed a volcano-type dependence of C₂H₄ selectivity on Ag content, with the 0.2 wt% sample delivering the highest FE for C₂H₄ production. Notably, Ag nanoparticles were detected when the loading increased to 1 wt%, accompanied by enhanced CO formation. This observation suggests that low-loading Ag predominantly exists as isolated atomic sites, which can regulate the interfacial water structure and local reaction environment without substantially sacrificing the Cu surface area required for C–C coupling. Furthermore, long-term electrolysis was performed in the flow-cell system at a current density of 300 mA·cm⁻² to evaluate catalytic stability. As shown in (Fig.2(e)), the Ag₁-*p*-CuO catalyst maintained a high FE of C₂H₄ fluctuating between 45% and 66% over 38 h of continuous operation. In contrast, the C₂H₄ FE of pristine CuO rapidly decreased from 38% to 9% after only 16 h. The significantly improved stability of Ag₁-*p*-CuO indicates that Ag single-atom modification not only enhances catalytic activity and C₂⁺ selectivity but also effectively stabilizes the interfacial active sites and reaction microenvironment during prolonged CO₂ electroreduction.

2.3 In Situ Raman Monitoring of the CO₂RR Process

To elucidate the role of Ag single atoms during CO₂RR, in situ Raman measurements were further performed using SHINERS technique. ~55 nm Au core~2 nm SiO₂ shell nanoparticles (details shown in Figs.16) were deposited onto the catalyst surface to enhance the Raman signals. (Fig.3(a)) shows the potential-dependent Raman spectra acquired on the Ag₁-*p*-CuO catalyst in a CO₂-saturated electrolyte from -0.8 to -1.5 V vs. RHE with a potential interval of 0.1 V. At open-circuit potential (OCP), two characteristic Raman bands located at 619 and 515 cm⁻¹ were observed, which can be assigned to surface Cu_{2-x}O according to the literature [42,47]. Upon applying -0.8 V vs. RHE, a pronounced linearly adsorbed *CO signal emerged in the high-frequency region at 2010–2090 cm⁻¹. Meanwhile, in the low-frequency region, a Raman band at 306 cm⁻¹ corresponding to the Cu–C stretching vibration of adsorbed *CO was detected. As the potential became more negative, several new Raman bands appeared at 397, 485, and 548 cm⁻¹, indicating the formation of new surface intermediates during CO₂RR.

To further identify these species, isotope-labeling experiments were conducted using D₂O. As shown in (Fig.3(b)), the corresponding Raman peaks shifted to 371, 438, and 506 cm⁻¹, respectively, confirming the involvement of hydrogen-containing intermediates. To determine their assignments, density functional theory (DFT) calculations were performed to simulate the vibrational frequencies of several key oxygenated intermediates, including *COCHO, *CH₂CHO, and *COHCHO on the Ag₁Cu(100) surface in (Fig.3(c)). The calculated coupled vibrational modes involving C–C, C–O, C–H, and O–H vibrations, appeared at 415, 510, and 584 cm⁻¹, respectively, in good agreement with

the experimental observations. Therefore, these Raman features are reasonably assigned to *COCHO, *CH₂CHO, and *COHCHO intermediates, which are key hydrogenated species formed after C–C coupling. Previous theoretical and experimental studies [42,48] have also identified *CH₂CHO as a critical intermediate in the rate-determining pathway toward ethylene formation on Cu-based catalysts, with a reported Raman feature around 529 cm⁻¹, which is close to our observations on CuO (Figs.17).

In addition, a Raman band at 1614 cm⁻¹ corresponding to the bending vibration of interfacial water (δH₂O) was clearly observed. Notably, the δH₂O intensity on Ag₁-*p*-CuO was significantly stronger than those on CuO and *p*-CuO (Fig.S13). (Fig.3(d)) compares the integrated Raman intensity of the δH₂O feature at different applied potentials for CuO, *p*-CuO, and Ag₁-*p*-CuO catalysts, indicating enhanced interfacial water adsorption after Ag single-atom modification. Moreover, the intensity continuously increased with decreasing potential and reached a maximum at -1.4 V vs. RHE, consistent with the highest Faradaic efficiencies for both C₂H₄ and total C₂⁺ products, followed by a slight decrease at -1.5 V, likely due to the intensified hydrogen evolution reaction. These results suggest that Ag single atoms significantly enhance interfacial water adsorption and activation, thereby facilitating water dissociation to provide active protons for CO₂RR hydrogenation processes.

Detailed analysis of the Raman band feature of *CO was further conducted. As shown in (Fig.3(e) and Fig.18), the *CO band at -0.8 V could be deconvoluted into two Gaussian peaks centered at 2080 and 2040 cm⁻¹. According to previous reports[49,50], these two bands are generally assigned to *CO adsorbed on step sites and terrace sites, respectively. The step sites, possessing lower coordination environments, are capable of stabilizing higher local*CO coverage. Some studies have also attributed the higher-frequency band at ~2080 cm⁻¹ to *CO dimer species [42]. Considering the abundant defect-rich step sites in the porous nanosheet structure, the step-site-related *CO signal became dominant and significantly enhanced on *p*-CuO, and Ag₁-*p*-CuO. (Fig.3(e)) further compares the proportion of step-site *CO relative to the total *CO peak area for the three catalysts at different potentials. *p*-CuO exhibited substantially higher step-site *CO ratios than pristine CuO, indicating that the porous structure effectively increases the density of defect-rich step sites and strengthens *CO adsorption. More importantly, Ag single-atom modification further enhanced the step-site *CO signal, likely because the lower electronegativity of Ag induces electron transfer from Cu to Ag, generating more Cu⁺ species, as further confirmed by post-reaction X-ray photoelectron spectra (XPS) and Cu LMM Auger spectra analysis (Figs.19). Furthermore, as the potential became more negative, the step-site *CO signal

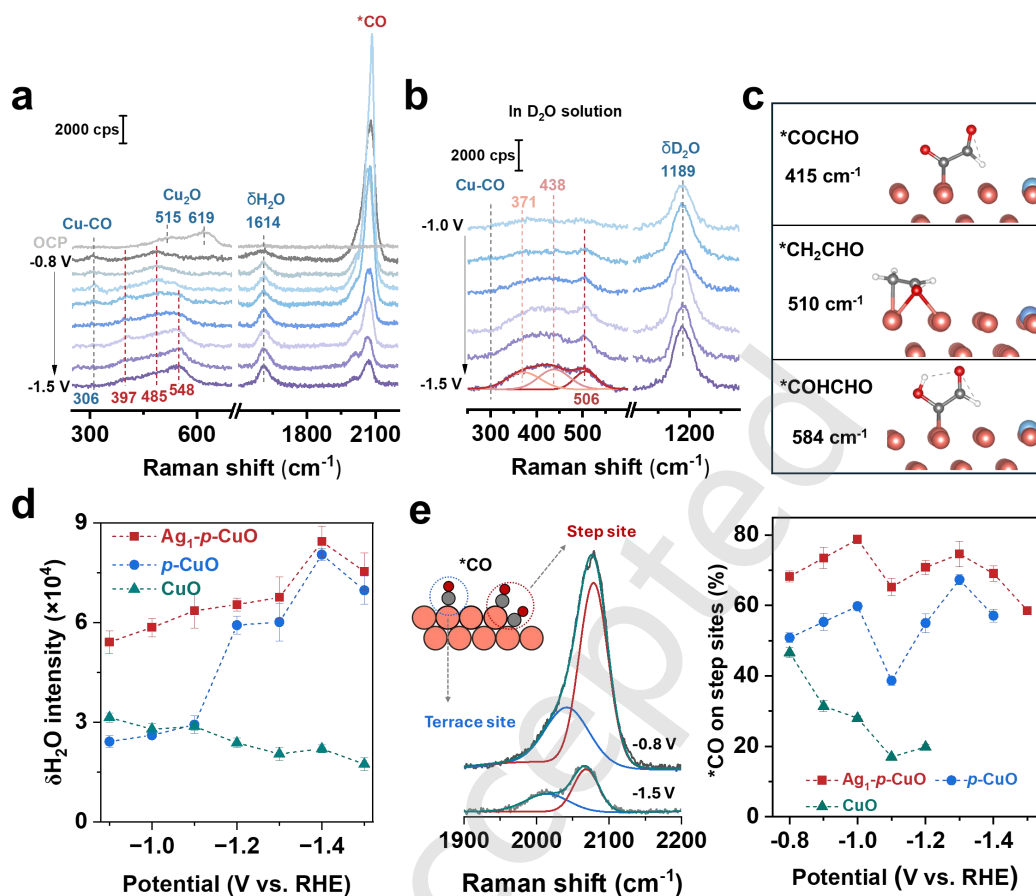


Figure 3 (a) In situ Raman spectra acquired on the $\text{Ag}_1\text{-p-CuO}$ catalyst in a CO_2 -saturated solution, recorded from -0.8 to -1.5 V vs. RHE with a potential interval of 0.1 V. (b) In situ Raman spectra obtained from isotopic experiments using D_2O solution. (c) DFT-calculated adsorption configurations of the $^*\text{COCHO}$, $^*\text{CH}_2\text{CHO}$ and $^*\text{COHCHO}$ intermediate on the $\text{Ag}_1\text{-Cu}(100)$ surface. (d) Potential-dependent intensity variations of the $\delta\text{H}_2\text{O}$ vibrational feature on CuO , $p\text{-CuO}$, and $\text{Ag}_1\text{-p-CuO}$ catalysts. (e) CO adsorption-related Raman features and comparison of the high-frequency step-site $^*\text{CO}$ ratio among CuO , $p\text{-CuO}$, and $\text{Ag}_1\text{-p-CuO}$ catalysts.

on pristine CuO decreased markedly, whereas $\text{Ag}_1\text{-p-CuO}$ maintained relatively strong $^*\text{CO}$ adsorption, suggesting that Ag single atoms effectively stabilize interfacial $^*\text{CO}$ adsorption and facilitates C–C coupling toward multicarbon product formation under highly reducing conditions.

2.4 Probing Interfacial Water Structure

To further understand the influence of Ag single atoms on the interfacial microenvironment, in situ Raman spectroscopy was employed to probe the interfacial water structure during CO_2RR . Typically, the O–H stretching region of interfacial H_2O appears within $3100\text{--}3600\text{ cm}^{-1}$ and can be deconvoluted into three overlapping components corresponding to water species with different hydrogen-bonding configurations: four-hydrogen-bonded water (4HB- H_2O), two-hydrogen-bonded water (2HB- H_2O), and hydrogen-bond-free cation-associated water (K- H_2O), centered at ~ 3200 , ~ 3400 , and $\sim 3550\text{ cm}^{-1}$, respectively[42].

To better distinguish these interfacial water structures, D_2O was employed to replace H_2O because isotope substitution lowers the vibrational frequency and suppresses quantum fluctuations[51,52], thereby slowing hydrogen-bond network dynamics and weakening vibrational coupling. As a result, the spectral resolution of different local water structures in Raman spectra can be significantly improved.

(Fig. 4(a)) shows the in-situ potential-dependent Raman spectra of interfacial water on the $\text{Ag}_1\text{-p-CuO}$ catalyst in a CO_2 -saturated solution, recorded from -1.0 to -1.5 V vs. RHE with a potential interval of 0.1 V. At -1.0 V, three distinct Raman bands corresponding to 4HB- D_2O , 2HB- D_2O , and K- D_2O were clearly observed at ~ 2350 , ~ 2480 , and $\sim 2620\text{ cm}^{-1}$, respectively. As the potential became more negative, the relative proportions of these water species evolved significantly, accompanied by obvious redshifts. These gave out a Stark slopes from -1.1 to -1.4 V

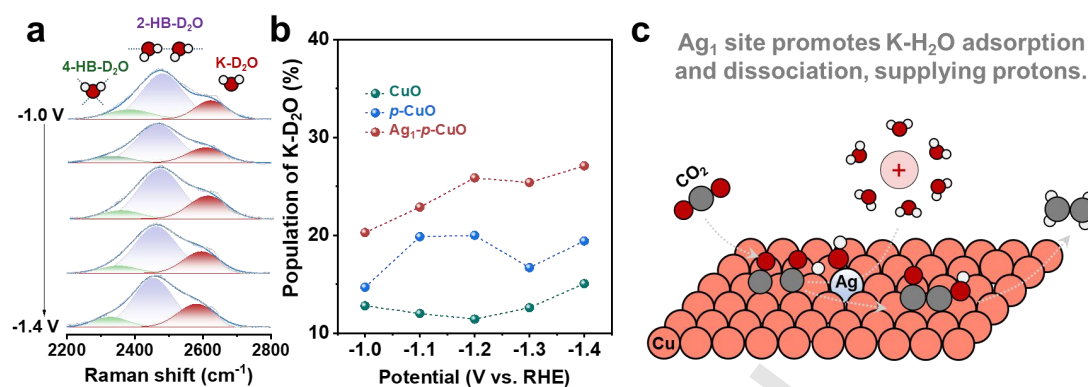


Figure 4 (a) In situ potential-dependent Raman spectra of interfacial water on the Ag₁-p-CuO catalyst in a CO₂-saturated solution, recorded from -1.0 to -1.5 V vs. RHE with a potential interval of 0.1 V. Gaussian deconvolution of the interfacial water bands is shown in green (4HB-D₂O), purple (2HB-D₂O), and red (K-D₂O), respectively. (b) Variations in the proportion of K-D₂O species on CuO, p-CuO, and Ag₁-p-CuO at different applied potentials. (c) Schematic illustration of Ag single-atom sites promoting interfacial K-H₂O dissociation to provide protons for CO₂ reduction.

follow the order of 4HB-D₂O (132 cm⁻¹/V) > K-D₂O > (100 cm⁻¹/V) 2HB-D₂O (62 cm⁻¹/V) under the interfacial electric field, consistent with previous result [53].

Previous studies [52–54] have indicated that K-H₂O species play a crucial role in promoting the C₂ pathway during CO₂RR because their low-coordination hydrogen-bonding environment lowers the kinetic barrier for water activation to provide proton. (Fig. 4(b)) compares the potential-dependent variations in the proportion of K-D₂O species on CuO, p-CuO, and Ag₁-p-CuO catalysts. The corresponding interfacial water Raman spectra collected on p-CuO and CuO at different potentials are shown in (Figs. 20). Notably, the Ag₁-p-CuO interface exhibited a significantly higher proportion of K-D₂O species together with a reduced fraction of strongly hydrogen-bonded water, indicating that Ag single atoms substantially reconstruct the interfacial hydrogen-bonding network. The increased population of low-coordination K-H₂O species is expected to facilitate water dissociation and accelerate proton-coupled hydrogenation processes during CO₂RR.

Based on these observations, a molecular-level mechanism for interfacial water regulation by Ag single atoms is proposed, as schematically illustrated in (Fig. 4(c)). The Ag single-atom sites promote the enrichment and activation of interfacial K-H₂O species, facilitating their dissociation into reactive hydrogen species. These activated protons can subsequently participate in the hydrogenation of C-C coupling intermediates, thereby accelerating the formation of key oxygenated intermediates such as *COHCHO and *CH₂CHO and ultimately promoting the selective production of ethylene.

2.5 Ag₁-Mediated Ethylene Formation Mechanism

To elucidate the selectivity regulation mechanism of CO₂RR, spin-polarized DFT calculations within the constant-

potential hybrid-solvation dynamic model (CP-HS-DM) [55,56], combined with ab initio molecular dynamics (AIMD) simulations, were performed to investigate the interfacial water microenvironment and thermodynamic pathways toward ethylene formation. First, solid-liquid interfacial water models of Ag single-atom-modified Cu(100) (denoted as Ag₁-Cu(100)) were constructed (Fig. 5(a)) to simulate the catalyst-electrolyte interface under realistic CO₂RR conditions, with pure Cu(100) used as a reference (Figs. 21).

As shown in (Fig. 5(b)), the average distances between surface Cu or Ag sites and adjacent water molecules were compared at two representative potentials of -0.8 and -1.2 V. Compared with the pristine Cu substrate, the introduction of Ag₁ significantly modulates the spatial distribution of the interfacial water layer. On the one hand, the average distance between Cu sites and water molecules in the Ag₁-Cu(100) system is noticeably increased, which effectively weakens the disordered strong adsorption of water molecules on Cu active sites, thereby reducing solvent occupation and steric hindrance toward CO₂RR intermediates. On the other hand, under the same potential, the distance (1.91 Å) between Ag sites and neighboring water molecules is substantially shorter than that at Cu site (2.41 Å). Furthermore, the radial distribution function (RDF) results (Figs. 22) exhibit a pronounced characteristic peak at approximately 3.3 Å between Ag atoms and the oxygen atoms of water molecules, indicating localized enrichment of water molecules around the Ag active sites. Notably, the peak intensity at -1.2 V is nearly three times higher than that at -0.8 V, suggesting that strongly reductive potentials significantly enhance the adsorption affinity of Ag toward water molecules. These findings are highly consistent with

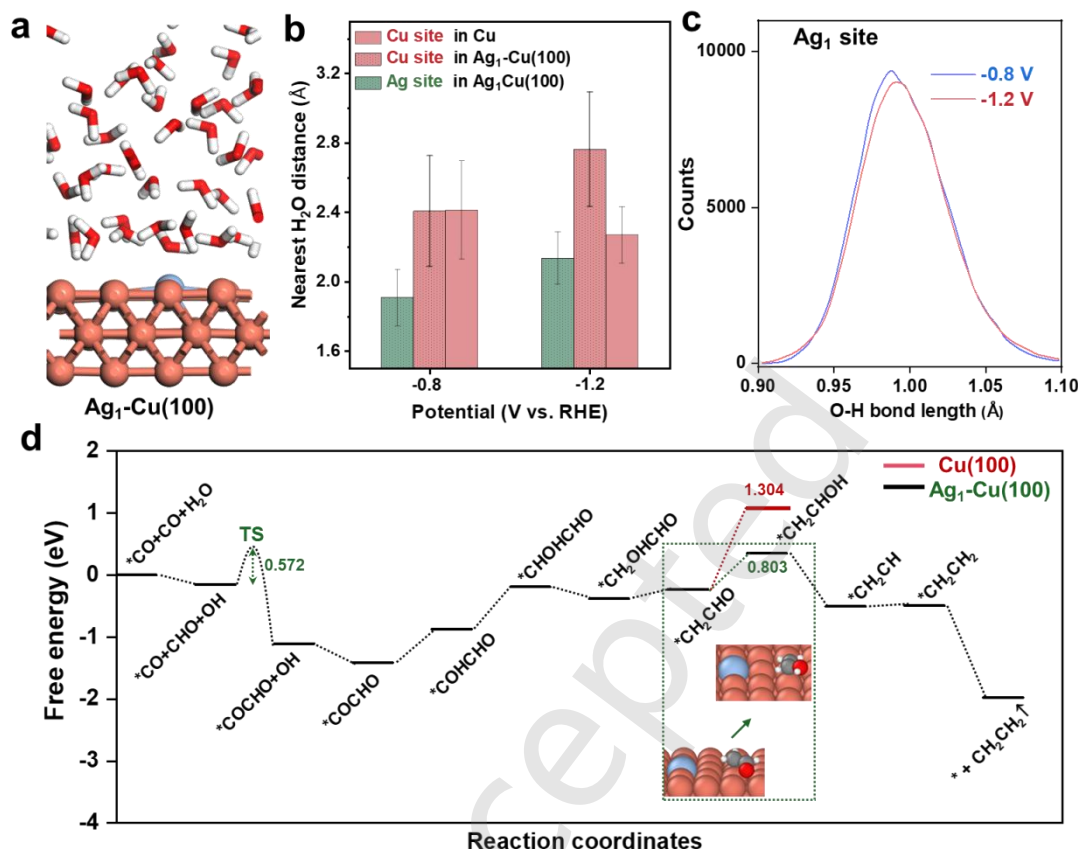


Figure 5 (a) Interfacial aqueous models of Cu(100) and Ag₁-Cu(100) surfaces under realistic CO₂RR conditions. (b) Average distances between active sites and interfacial water molecules at -0.8 V and -1.2 V vs. RHE. (c) O-H bond length distribution of water molecules near Ag sites at different applied potentials. (d) Free energy profiles for ethylene production via CO₂RR over pristine Cu(100) and Ag₁-Cu(100) surfaces at -1.2 V vs. RHE.

the in-situ Raman observations and the enhanced K-H₂O results, both of which indicate strengthened interfacial water adsorption induced by Ag₁ sites.

Further analysis of the O-H bond lengths of localized water molecules surrounding the Ag sites (Fig.5(c)) reveals that the overall O-H bond length of adsorbed water molecules increases under the more negative potential of -1.2 V. The strong localized adsorption of water on Ag sites weakens the O-H bond interaction, thereby enabling preferential water activation and providing abundant local proton sources for the multi-step proton-transfer and hydrogenation processes during CO₂RR [57]. In addition, statistical analysis of the orientation-angle distribution of water molecules adjacent to the Ag sites (Figs.23) shows a clear rightward shift of the distribution peak at -1.2 V compared with that at -0.8 V, indicating that water molecules tend to adsorb on Ag sites with a larger and flatter orientation angle under strongly negative potentials. Such a lying-down adsorption configuration is favorable for electron transfer and thus facilitates water activation. These results collectively confirm that isolated Ag atoms exhibit strong localized affinity toward water molecules and drive the directional aggregation of water species around Ag sites.

This unique interfacial structure with localized water enrichment promotes water adsorption and activation on Ag₁ sites, thereby creating favorable conditions for subsequent electrocatalytic reactions.

Based on our experimental observations, we further proposed the key reaction pathway for CO₂RR toward C₂ products over the Ag₁- Cu(100) single-atom catalyst. Initially, adsorbed *CO intermediates are generated through CO₂RR on neighboring Cu sites, while H₂O preferentially adsorbs on the Ag atoms and serves as the source of active hydrogen species. One hydrogen atom from the activated H₂O is subsequently transferred to *CO to form the *CHO intermediate, which then couples with another *CO species to generate the key precursor for ethylene formation. Notably, this asymmetric CHO-CO coupling pathway exhibits a lower energy barrier (0.57 eV vs 0.78 eV) and higher occurrence probability than the

conventional symmetric CO–CO coupling process (Figs. 24) [58].

To further clarify the catalytic role of Ag single atoms, the free-energy profiles for the major ethylene-production pathways on pure Cu(100) and Ag₁-Cu(100) surfaces were systematically compared (Fig. 5(d)) and Figs. 25). After Ag₁ incorporation, both the potential-determining step and the corresponding Gibbs free energy barrier (ΔG) exhibit significant changes. For the hydrogenation step of *CH₂CHO during ethylene formation, the pristine Cu surface shows a high ΔG of 1.304 eV. Ag₁ doping effectively breaks this thermodynamic bottleneck, lowering the ΔG of the *CH₂CHO hydrogenation step sharply to 0.803 eV on the Ag₁Cu(100) surface. In addition, the dimerization transition-state barrier for CO–CHO coupling on the Ag₁-Cu(100) surface is only 0.572 eV (Figs. 24), which is highly favorable for C–C coupling. Localized water activation at the Ag₁ sites optimizes proton supply, alleviates steric hindrance, and stabilizes key reaction intermediates. This synergistic effect significantly promotes both C–C coupling and the subsequent hydrogenation processes, ultimately enabling highly efficient electrocatalytic CO₂ reduction toward ethylene production.

3 CONCLUSIONS

In summary, we developed Ag single-atom-modified porous CuO nanosheets for electrochemical CO₂ reduction to ethylene and elucidated the mechanistic role of isolated Ag sites at the catalyst–electrolyte interface. The 0.2 % Ag loading achieved maximum Faradaic efficiencies of 54 % for C₂ H₄ and 78 % for C₂₊ products, highlighting the strong effect of trace single atoms on multicarbon selectivity. Combined in situ SHINERS and DFT reveal that Ag sites simultaneously modulate surface intermediates and interfacial water: the Ag₁–Cu interface enriches *CO coverage at defective Cu steps to facilitate C–C coupling, while Ag₁ sites restructure the water hydrogen-bonding network, increasing weakly H-bonded cation-associated water and promoting a flat-lying configuration with elongated O–H bonds. This restructuring aids cation–H₂O dissociation and provides localized proton donation near active sites. The cooperative regulation of *CO and proton availability steers the pathway toward asymmetric CO–CHO coupling and lowers the hydrogenation barrier of *CH₂CHO, accelerating ethylene formation while suppressing side reactions. This work underscores the interplay between intermediate evolution and interfacial water in governing C₂₊ selectivity, offering a paradigm for single-atom microenvironment engineering in CO₂ electroreduction.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Wang Ya-Hao and Li Yadong designed the experiments, Peng Xiao-Hui performed the experiments; Ran Haiyan and Ren Chunjing performed the theoretical calculations; Peng Xiaohui and Ran Haiyan wrote the paper with support from Wang Ya-Hao, Ren Chunjing, and Zhou Xiao-Shun. All authors contributed to the general discussion.

Use of AI statement

None.

References

- De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S. A.; Jaramillo, T. F.; Sargent, E. H. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* 2019, 364, 70–74.
- Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; Seger, B.; Stephens, I. E. L.; Chan, K.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F.; Chorkendorff, I. Progress and perspectives of electrochemical CO₂ reduction on copper in aqueous electrolyte. *Chem Rev* 2019, 119, 7610–7672.
- Zhu, P.; Wu, Z.-Y.; Elgazzar, A.; Dong, C.; Wi, T.-U.; Chen, F.-Y.; Xia, Y.; Feng, Y.; Shakouri, M.; Kim, J. Y.; Fang, Z.; Hatton, T. A.; Wang, H. Continuous carbon capture in an electrochemical solid-electrolyte reactor. *Nature* 2023, 618, 959–966.
- Liu, J.; Wang, Y.; Mo, P.; Yang, F.; Jiang, K.; Cheng, Z.; Liu, Y.; Sun, Z.; Liu, Z.; Zhang, Y.; Chen, W. In situ reconstruction induced oxygen-deficient multiphase Cu based species hybridized with Ni single atoms as tandem platform for CO₂ electroreduction. *Nano Res* 2024, 17, 3888–3894.
- Zheng, Y.; Vasileff, A.; Zhou, X.; Jiao, Y.; Jaroniec, M.; Qiao, S.-Z. Understanding the roadmap for electrochemical reduction of CO₂ to multi-carbon oxygenates and hydrocarbons on copper-based catalysts. *J Am Chem Soc* 2019, 141, 16429–16440.
- Calle - Vallejo, F.; Koper, M. T. M. Theoretical Considerations on the Electroreduction of CO to C₂ Species on Cu(100) Electrodes. *Angew Chem Int Ed* 2013, 52, 7282–7285.
- Hori, Y. Electrochemical CO₂ reduction on metal electrodes. In *Modern Aspects of Electrochemistry*; Springer: New York, 2008, pp 89–189.
- Li, C. W.; Kanan, M. W. CO₂ reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu₂O films. *J Am Chem Soc* 2012, 134, 7224–7227.
- Lin, Y.; Yao, Y.; Zhuo, Z.; Niu, J.; Gu, J.; Mao, J.; Liu, Y. Protective Shield for Interfacial Cu⁺/Cu⁰ Sites Enhances Multicarbon Production Toward Electrochemical Reduction of Carbon Dioxide. *Angew Chem Int Ed* 2026, 65, e24602.
- Cao, X.; Liu, Y.; Yu, R.; Yang, Y.; Li, A.; Li, X.; Mao, J. Breaking Ampere-Level Current Density Limitations in Multi-Carbon Products through Crystal Facet Engineering. *Chem* 2026, 12, 102824.
- Popović, S.; Smiljanić, M.; Jovanović, P.; Vavra, J.; Buonsanti, R.;

- Hodnik, N. Stability and degradation mechanisms of copper-based catalysts for electrochemical CO₂ reduction. *Angew Chem Int Ed* 2020, 132, 14844–14854.
- 12 Yang, J.; Jin, C.; Si, D.; Kang, F.; Qiao, F.; Wang, J.; Liu, D.; Zhang, L.; Tian, T.; Zhao, X.; Yu, Z.; Chen, K.; Chen, H.-Q.; Zhou, X.-S. Tailoring solvent-mediated CO₂ reservoirs at heterointerfaces for enhanced electrochemical CO₂-to-C₂H₄ conversion. *J Am Chem Soc* 2025, 147, 7102–7111.
 - 13 Gao, J.; Bahmanpour, A.; Kröcher, O.; Zakeeruddin, S. M.; Ren, D.; Grätzel, M. Electrochemical synthesis of propylene from carbon dioxide on copper nanocrystals. *Nat Chem* 2023, 15, 705–713.
 - 14 Teh, W. J.; Romeo, E.; Xi, S.; Rowley, B.; Illas, F.; Calle-Vallejo, F.; Yeo, B. S. Selective electroreduction of acetylene to 1,3-butadiene on iodide-induced Cu^{δ+}-Cu⁰ sites. *Nat Catal* 2024, 7, 1382–1393.
 - 15 Liang, X.; Fu, N.; Yao, S.; Li, Z.; Li, Y. The progress and outlook of metal single-atom-site catalysis. *J Am Chem Soc* 2022, 144, 16855–16874.
 - 16 Qiao, B.; Wang, A.; Yang, X.; Allard, L. F.; Jiang, Z.; Cui, Y.; Liu, J.; Li, J.; Zhang, T. Single-atom catalysis of CO oxidation using Pt₁/FeO_x. *Nat Chem* 2011, 3, 634–641.
 - 17 Kaiser, S. K.; Chen, Z.; Faust Akl, D.; Mitchell, S.; Pérez-Ramírez, J. Single-atom catalysts across the periodic table. *Chem Rev* 2020, 120, 11703–11809.
 - 18 Wu, Y.; Jiang, J.; Chen, Q.; Zhu, C.; Yu, D.; Lu, N.; Mao, J. Synergistic Interplay of Ni Single Atoms and Neighboring Mn₂ Dual Atoms Enabling Selective Photocatalytic Reduction of CO₂ to Propane. *Angew Chem Int Ed* 2026, 65, e21193.
 - 19 Zhao, J.; Liu, D.; Wei, F.; Ip, W. F.; Hui, P.; Lin, S. How water molecules occupying the active site of a single-atom catalyst affect the electrochemical reduction of carbon dioxide. *Nano Res* 2023, 16, 9091–9098.
 - 20 Ma, Z.; Wang, B.; Yang, X.; Ma, C.; Wang, W.; Chen, C.; Liang, F.; Zhang, N.; Zhang, H.; Chu, Y.; Zhuang, Z.; Xu, H.; Wang, Y.; Liu, J. P-block aluminum single-atom catalyst for electrocatalytic CO₂ reduction with high intrinsic activity. *J Am Chem Soc* 2024, 146, 15648–15656.
 - 21 Zheng, T.; Jiang, K.; Ta, N.; Hu, Y.; Zeng, J.; Liu, J.; Wang, H. Large-scale and highly selective CO₂ electrocatalytic reduction on nickel single-atom catalyst. *Joule* 2018, 2, 2652–2666.
 - 22 Arcudi, F.; Đorđević, L.; Schweitzer, N.; Stupp, S. I.; Weiss, E. A. Selective visible-light photocatalysis of acetylene to ethylene using a cobalt molecular catalyst and water as a proton source. *Nat Chem* 2022, 14, 716–723.
 - 23 Zhang, Y.; Wei, C.; Nan, B.; Frauenheim, T.; Yang, J.; Mao, J. Atomically isolated Cd sites boosting CO electroreduction to C₂+ alcohols at ampere-level current densities. *Angew Chem Int Ed* 2025, 64, e202418927.
 - 24 Zhang, N.; Zhang, X.; Tao, L.; Jiang, P.; Ye, C.; Lin, R.; Huang, Z.; Li, A.; Pang, D.; Yan, H.; Wang, Y.; Xu, P.; An, S.; Zhang, Q.; Liu, L.; Du, S.; Han, X.; Wang, D.; Li, Y. Silver single-atom catalyst for efficient electrochemical CO₂ reduction synthesized from thermal transformation and surface reconstruction. *Angew Chem Int Ed* 2021, 60, 6170–6176.
 - 25 Li, Z.; Wang, P.; Lyu, X.; Kondapalli, V. K. R.; Xiang, S.; Jimenez, J. D.; Ma, L.; Ito, T.; Zhang, T.; Raj, J.; Fang, Y.; Bai, Y.; Li, J.; Serov, A.; Shanov, V.; Frenkel, A. I.; Senanayake, S. D.; Yang, S.; Senftle, T. P.; Wu, J. Directing CO₂ electroreduction pathways for selective C₂ product formation using single-site doped copper catalysts. *Nat Chem Eng* 2024, 1, 159–169.
 - 26 Chen, Y.; Wang, P.; Mao, Y.; Su, G.; Liu, H.; Peng, B.; Liu, Z.; Ze, H.; Wang, Y.; Hu, X.; Li, J.; Fan, L.; Alahmed, A.; Jamal, A.; Gereige, I.; Lee, S.; Dunn, J. B.; Wang, Z.; Xie, K.; Sargent, E. H. Dilute alloy electrocatalysts enable asymmetric C–C coupling for ethylene production from a CO₂ post-capture liquid. *Nat Synth* 2026, 5, 421–430.
 - 27 Jin, C.; Lin, Y.; Wang, Y.; Shi, J.; Li, R.; Liu, Y.; Yue, Z.; Leng, K.; Zhao, Y.; Wang, Y.; Han, X.; Qu, Y.; Bai, J. Engineering atom - scale cascade catalysis via multi - active site collaboration for ampere - Level CO₂ electroreduction to C₂+ products. *Adv Mater* 2025, 37, 2408968.
 - 28 Wang, M.; Fang, M.; Liu, Y.; Chen, C.; Zhang, Y.; Jia, S.; Wu, H.; He, M.; Han, B. Enhanced intermediates inter-migration on Ag single-atom alloys for boosting multicarbon product selectivity in CO₂ electroreduction. *J Am Chem Soc* 2025, 147, 9861–9869.
 - 29 Wang, S.; Li, F.; Zhao, J.; Zeng, Y.; Li, Y.; Lin, Z.-Y.; Lee, T.-J.; Liu, S.; Ren, X.; Wang, W.; Chen, Y.; Hung, S.-F.; Lu, Y.-R.; Cui, Y.; Yang, X.; Li, X.; Huang, Y.; Liu, B. Manipulating C-C coupling pathway in electrochemical CO₂ reduction for selective ethylene and ethanol production over single-atom alloy catalyst. *Nat Commun* 2024, 15, 2896.
 - 30 Li, D.; Zheng, X.; Zhao, Y.; Zhang, J.; Wang, G. Deciphering the interaction patterns of intermediates on single atom catalysts during electrocatalytic CO₂ conversion reactions. *Chem Soc Rev* 2026, 55, 1890–1921.
 - 31 Ren, X.; Zhao, J.; Li, X.; Shao, J.; Pan, B.; Salamé, A.; Boutin, E.; Groizard, T.; Wang, S.; Ding, J.; Zhang, X.; Huang, W.-Y.; Zeng, W.-J.; Liu, C.; Li, Y.; Hung, S.-F.; Huang, Y.; Robert, M.; Liu, B. In-situ spectroscopic probe of the intrinsic structure feature of single-atom center in electrochemical CO/CO₂ reduction to methanol. *Nat Commun* 2023, 14, 3401.
 - 32 Birdja, Y. Y.; Pérez-Gallent, E.; Figueiredo, M. C.; Göttle, A. J.; Calle-Vallejo, F.; Koper, M. T. M. Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels. *Nat Energy* 2019, 4, 732–745.
 - 33 Wang, Y. H.; Le, J. B.; Li, W. Q.; Wei, J.; Radjenovic, P. M.; Zhang, H.; Zhou, X. S.; Cheng, J.; Tian, Z. Q.; Li, J. F. In situ spectroscopic insight into the origin of the enhanced performance of bimetallic nanocatalysts towards the oxygen reduction reaction (ORR). *Angew Chem Int Ed* 2019, 58, 16099–16103.
 - 34 Pérez - Gallent, E.; Figueiredo, M. C.; Calle - Vallejo, F.; Koper, M. T. M. Spectroscopic observation of a hydrogenated CO dimer intermediate during CO reduction on Cu(100) electrodes. *Angew Chem Int Ed* 2017, 56, 8234–8238.
 - 35 Dunwell, M.; Lu, Q.; Heyes, J. M.; Rosen, J.; Chen, J. G.; Yan, Y.; Jiao, F.; Xu, B. The central role of bicarbonate in the electrochemical reduction of carbon dioxide on gold. *J Am Chem Soc* 2017, 139, 3774–3783.
 - 36 Zhu, S.; Li, T.; Cai, W.-B.; Shao, M. CO₂ electrochemical reduction as probed through infrared spectroscopy. *ACS Energy Lett* 2019, 4, 982–996.
 - 37 Zhan, C.; Dattila, F.; Rettenmaier, C.; Herzog, A.; Herran, M.; Wagner, T.; Scholten, F.; Bergmann, A.; López, N.; Roldan Cuenya, B. Key intermediates and Cu active sites for CO₂ electroreduction to ethylene and ethanol. *Nat Energy* 2024, 9, 567–576.
 - 38 Liu, Q.; Yang, W. Resolving non-covalent interactions between surface hydroxyl on Cu and interfacial water in alkaline CO electroreduction. *Nat Catal* 2025, 8, 412–421.
 - 39 Chernyshova, I. V.; Somasundaran, P.; Ponnuram, S. On the origin

- of the elusive first intermediate of CO₂ electroreduction. *PNAS* 2018, 115, E9261–E9270.
- 40 Pinilla-Sánchez, A.; Panja, S.; Polesso, B.; Haldar, P.; Ram, R.; Seemakurthi, R. R.; Guha, A.; López, N.; García de Arquer, F. P. Interfacial adsorbate competition regulates intermediate stabilization and onset potential in acidic CO₂ electroreduction. *J Am Chem Soc* 2026, 148, 10026–10036.
 - 41 Ma, H.; Ibáñez-Alé, E.; You, F.; López, N.; Yeo, B. S. Electrochemical formation of C₂₊ products steered by bridge-bonded *CO confined by *OH domains. *J Am Chem Soc* 2024, 146, 30183–30193.
 - 42 Wang, Y.-H.; Zheng, S.; Yang, W.-M.; Zhou, R.-Y.; He, Q.-F.; Radjenovic, P.; Dong, J.-C.; Li, S.; Zheng, J.; Yang, Z.-L.; Attard, G.; Pan, F.; Tian, Z.-Q.; Li, J.-F. In situ Raman spectroscopy reveals the structure and dissociation of interfacial water. *Nature* 2021, 600, 81–85.
 - 43 Li, J. F.; Huang, Y. F.; Ding, Y.; Yang, Z. L.; Li, S. B.; Zhou, X. S.; Fan, F. R.; Zhang, W.; Zhou, Z. Y.; Wu, D. Y.; Ren, B.; Wang, Z. L.; Tian, Z. Q. Shell-isolated nanoparticle-enhanced Raman spectroscopy. *Nature* 2010, 464, 392–395.
 - 44 Li, X.-C.; Wang, B.; Yu, Z.; Wan, Q.; Zheng, J.-F.; Maisonhaute, E.; Zhou, X.-S.; Wang, Y.-H. Deciphering dynamic surface of PtRu alloy nanocatalysts to revisit their synergistic effects during the electrooxidation. *Sci China Chem* 2024, 67, 1123–1132.
 - 45 Yu, Z.; Li, J.-P.; Xu, X.-K.; Ding, Z.-C.; Peng, X.-H.; Gao, Y.-J.; Wan, Q.; Zheng, J.-F.; Zhou, X.-S.; Wang, Y.-H. Uncovering interfacial oxygen-bridged binuclear metal centers of heterogenized molecular catalyst for water electrolysis. *Adv Sci* 2025, 12, 2417607.
 - 46 Yu, Z.; Xu, Y.-X.; Su, J.-Q.; Radjenovic, P. M.; Wang, Y.-H.; Zheng, J.-F.; Teng, B.; Shao, Y.; Zhou, X.-S.; Li, J.-F. Probing interfacial electronic effects on single-molecule adsorption geometry and electron transport at atomically flat surfaces. *Angew Chem Int Ed* 2021, 60, 15452–15458.
 - 47 de Ruiter, J.; An, H.; Wu, L.; Gijsberg, Z.; Yang, S.; Hartman, T.; Weckhuysen, B. M.; van der Stam, W. Probing the dynamics of low-overpotential CO₂-to-CO activation on copper electrodes with time-resolved Raman spectroscopy. *J Am Chem Soc* 2022, 144, 13674–13682.
 - 48 Zhao, Y.; Zhang, X.-G.; Bodappa, N.; Yang, W.-M.; Liang, Q.; Radjenovic, P. M.; Wang, Y.-H.; Zhang, Y.-J.; Dong, J.-C.; Tian, Z.-Q.; Li, J.-F. Elucidating electrochemical CO₂ reduction reaction processes on Cu(hkl) single-crystal surfaces by in situ Raman spectroscopy. *Energy Environ Sci* 2022, 15, 3968–3980.
 - 49 Wu, Z.-Z.; Zhang, X.-L.; Niu, Z.-Z.; Gao, F.-Y.; Yang, P.-P.; Chi, L.-P.; Shi, L.; Wei, W.-S.; Liu, R.; Chen, Z.; Hu, S.; Zheng, X.; Gao, M.-R. Identification of Cu(100)/Cu(111) Interfaces as Superior Active Sites for CO Dimerization During CO₂ Electroreduction. *J Am Chem Soc* 2021, 143, 15273–15282.
 - 50 Gunathunge, C. M.; Li, J.; Li, X.; Hong, J. J.; Waegle, M. M. Revealing the predominant surface facets of rough Cu electrodes under electrochemical conditions. *ACS Catal* 2020, 10, 10171–10180.
 - 51 De Marco, L.; Carpenter, W.; Liu, H.; Biswas, R.; Bowman, J. M.; Tokmakoff, A. differences in the vibrational dynamics of H₂O and D₂O: Observation of symmetric and antisymmetric stretching vibrations in heavy water. *J Phys Chem Lett* 2016, 7, 2163–2168.
 - 52 Xu, Y.; Shi, Z.; Zhu, S.; Zhao, Y.; Sun, M.; Wang, H.; Deng, Y.; Zhai, T.; Yu, L.; Liu, Y. Electrified interfacial oxygen-down water boosts efficient and durable electrolysis. *Nat Commun* 2026, 17, 1942.
 - 53 Zhao, Y.; Li, Q.-Q.; He, Q.-F.; Ren, P.-W.; Zhang, D.-A.; Wang, Y.-H.; Dong, J.-C.; Zheng, S.; Zhang, Y.-J.; Yang, Z.-L.; Li, J.-F. In situ Raman spectroscopy reveals the multifunctional role of interfacial water in CO₂-to-C₂ electroreduction on Cu(hkl) Surfaces. *J Am Chem Soc* 2025, 147, 30230–30238.
 - 54 Zhang, H.; Raciti, D.; Hall, A. S. Disordered interfacial H₂O promotes electrochemical C–C coupling. *Nat Chem* 2025, 17, 1161–1168.
 - 55 Zhao, X.; Liu, Y. Origin of Selective Production of Hydrogen Peroxide by Electrochemical Oxygen Reduction. *J. Am. Chem. Soc.* 2021, 143, 9423–9428.
 - 56 Zhao, X.; Levell, Z. H.; Yu, S.; Liu, Y. Atomistic understanding of two-dimensional electrocatalysts from first principles. *Chem. Rev.* 2022, 122, 10675–10709.
 - 57 Ma, W.; Xie, S.; Liu, T.; Fan, Q.; Ye, J.; Sun, F.; Jiang, Z.; Zhang, Q.; Cheng, J.; Wang, Y. Electrocatalytic reduction of CO₂ to ethylene and ethanol through hydrogen-assisted C–C coupling over fluorine-modified copper. *Nat Catal* 2020, 3, 478–487.
 - 58 Du, C.; Mills, J. P.; Yohannes, A. G.; Wei, W.; Wang, L.; Lu, S.; Lian, J.-X.; Wang, M.; Guo, T.; Wang, X.; Zhou, H.; Sun, C.-J.; Wen, J. Z.; Kendall, B.; Couillard, M.; Guo, H.; Tan, Z.; Siahrostami, S.; Wu, Y. A. Cascade electrocatalysis via AgCu single-atom alloy and Ag nanoparticles in CO₂ electroreduction toward multicarbon products. *Nat Commun* 2023, 14, 7612.

Tuning interfacial water and CO–CHO coupling via Ag single atoms enhances ethylene production in CO₂ reduction

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Experiments and methods

Catalyst Synthesis

Butylamine (20 mL, ca. 0.20 mol) and copper(II) acetate monohydrate (5 g, ca. 25 mmol) were dissolved in 450 mL and 180 mL of ultrapure water, respectively. Under vigorous magnetic stirring, the butylamine solution was added dropwise into the copper acetate solution via a peristaltic pump at a rate of 4 mL/min. After the addition, the mixture was stirred for an additional 1 h, yielding a blue suspension.

The suspension was then transferred to an 80 °C water bath and vigorously stirred for 4 h. The resulting brown-black precipitate was collected by centrifugation, washed several times with ultrapure water and ethanol sequentially, and dried at 60 °C in a forced-air oven to obtain CuO nanosheets (denoted as CuO NS).

The as-obtained CuO NS were calcined in a muffle furnace at 200 °C for 4 h with a ramping rate of 5 °C/min to afford porous CuO nanosheets (denoted as *p*-CuO NS).

A certain amount of *p*-CuO NS was dispersed in 50 mL of ultrapure water, followed by the addition of AgNO₃ solution with different mass fractions. The mixture was stirred overnight. After centrifugation, the solid was dried at 60 °C in a forced-air oven and subsequently calcined in air at 200 °C for 1 h to obtain Ag-loaded porous CuO nanosheets.

Electrochemical Measurements

All CO₂ electroreduction performance tests were conducted on an Autolab PGSTAT302N electrochemical workstation under ambient temperature and pressure. In the H-type cell configuration, the cathodic and anodic compartments were separated by an anion exchange membrane (YLS-30T). A carbon rod and an Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. All potentials were converted to the reversible hydrogen electrode (RHE) scale using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197 \text{ V}$$

0.1 M KHCO₃ was used as the electrolyte. CO₂ gas was continuously bubbled into the cathodic compartment at a flow rate of 20 sccm.

Flow cell tests were performed on the same Autolab PGSTAT302N workstation. A flow cell equipped with an anion exchange membrane (Fumasep FAB-3-PK-130) was used. Ni foam and Hg/HgO were employed as the counter and reference electrodes, respectively. Potentials were converted to RHE using the following equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098 \text{ V}$$

The electrolyte (1 M KOH) was circulated through the cathodic and anodic compartments at 20 mL/min using a peristaltic pump. CO₂ gas was supplied to the gas chamber at 30 sccm using a digital mass flow controller.

Product Analysis

The CO₂ reduction products were evaluated by chronoamperometry at various applied potentials. CO₂ gas was fed into the cathodic compartment at 20 sccm and directly introduced into an online gas chromatograph (GC-2022) for analysis.

Liquid products (formic acid and ethanol) were analyzed by nuclear magnetic resonance (NMR) spectroscopy. ¹H NMR spectra were recorded using water suppression mode in 10% D₂O with dimethyl sulfoxide (DMSO) as an internal standard.

Faradaic efficiencies (FEs) of the products were calculated using the following equation:

$$\text{FE}_i = \frac{Q_i}{Q_{\text{total}}} = \frac{Z_i \times F \times N_i}{I \times t} = \frac{Z_i \times v_i \times G \times F \times P_0}{I \times R \times T_0 \times 60000}$$

where $Q_i = z_i \times F \times N_i$, and $Q_{\text{total}} = I \times t$. The parameters are defined as follows:

z_i : number of electrons transferred to form one molecule of product i ;

F : Faraday constant (96485.3 C·mol⁻¹);

N_i : amount of substance of product i in the GC sampling loop, calculated as $N_i = N_{\text{total}} \times v_i$;

N_{total} : total amount of gas in the GC sampling loop, calculated from the ideal gas law: $N_{\text{total}} = \frac{P_0 \times V_0}{R \times T_0}$;

V_0 : volume of the GC sampling loop, $V_0 = G \times t$;

v_i : volume fraction of product i determined by GC;

G : gas flow rate;

I : measured current;

t : time required to fill the GC sampling loop;

P_0 : atmospheric pressure (1.01×10^5 Pa);

T_0 : temperature of the sampling loop (298 K);

R : ideal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

Raman measurements

Synthesis of 55 nm Au nanoparticles: A seed-mediated growth method was employed to prepare the Au nanoparticles. First, 1.5 mL of 1 wt% sodium citrate solution was added into 50 mL of boiling 0.01 wt% HAuCl₄ aqueous solution under vigorous stirring to obtain 16 nm Au seeds. Subsequently, 1.5 mL of the as-prepared 16 nm Au seed solution, 300 μL of 1 wt% ascorbic acid, 100 μL of 1 wt% sodium citrate, and 10 mL of Milli-Q water were mixed in a flask in an ice-water bath. After stirring for 5 min, 550 μL of 1 wt% HAuCl₄ solution was added dropwise, and the mixture was transferred to a 70 °C water bath for 30 min to obtain 50 nm Au NPs. To further grow the particles to 55 nm, 2 mL of the 50 nm Au seed solution, 400 μL of 1 wt% ascorbic acid, 100 μL of 1 wt% sodium citrate, and 20 mL of Milli-Q water were combined in an ice-water bath with stirring. After 5 min, 654 μL of 1 wt% HAuCl₄ solution was added dropwise, followed by heating at 70 °C for 30 min, yielding 55 nm Au NPs.

Silica shell coating and SHINs preparation: To form the silica shell, 400 μL of 1 mM (3-aminopropyl)trimethoxysilane (APTMS) solution was added dropwise into 30 mL of the pre-synthesized 55 nm Au sol under stirring at room temperature. The reaction proceeded for 15 min. Subsequently, 3.2 mL of Na₂ SiO₃ solution (0.54 wt%) was added all at once, and the mixture was allowed to react for another 3 min at room temperature. The mixture was then heated to 99 °C in a water bath for 30 min and rapidly cooled in an ice-water bath to terminate the reaction, yielding the Au@SiO₂ SHINs.

Electrode modification for in situ Raman measurements: For the Raman experiments, 1.5 mL of the as-prepared SHINs solution was concentrated by centrifugation at 4500 rpm for 10 min, and the supernatant was removed. This centrifugation step was repeated twice. The concentrated SHINs were then redispersed in 200 μL of ultrapure water. Finally, 3 μL of the concentrated Au@SiO₂ SHINs suspension was drop-cast onto the catalyst-coated glassy carbon electrode for in situ Raman measurements.

In situ Raman spectroscopy measurements and data acquisition parameters: The Raman spectra were acquired on a confocal Raman microscope (Renishaw InVia) using a 633 nm excitation laser. A 50 $\times$ microscope objective with a numerical aperture of 0.55 was employed throughout all measurements. A CHI-660D electrochemical workstation was used to control the applied potential. A Pt and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. To ensure the reliability and reproducibility of the spectral data, each spectrum was collected three times at each applied potential, and no significant differences were observed among the repeated measurements. Each Raman spectrum presented in this work was acquired with an integration time of 10 s.

DFT calculations

All density functional theory (DFT) calculations in this work were performed using the Vienna Ab initio Simulation Package (VASP)^[1] to systematically investigate the electrocatalytic CO₂ reduction reaction (CO₂RR) on Cu(100) and Ag₁-Cu single-atom catalysts. The calculations involved geometric optimization of catalysts and adsorbed reaction intermediates, ab initio molecular dynamics (AIMD) simulations, thermodynamic corrections, and slow-growth^[2] free energy calculations. Solvation effects and external electric potentials were fully considered to accurately reproduce realistic electrocatalytic environments.

The exchange-correlation functional was described by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)^[31] parametrization, and Grimme's D3 dispersion correction was employed to account for weak interfacial interactions^[4,5]. Projector-augmented wave (PAW)^[6,7] pseudopotentials were adopted to describe the interactions between valence electrons and core electrons, with a plane-wave energy cutoff of 400 eV. Spin-polarized calculations were performed with ISPIN = 2 to properly account for possible spin-dependent effects in the Cu-based catalyst systems. The energy convergence threshold for geometric optimization was set to 1×10^{-5} eV, and the atomic force convergence criterion was less than $0.03 \text{ eV} \text{ \AA}^{-1}$. A $3 \times 3 \times 1$ Monkhorst–Pack k-point grid was used for structural optimizations and single-point energy calculations of the $5 \times 5 \times 3$ slab models, while the Γ -point was used for AIMD simulations of the $4 \times 4 \times 3$ slab models. A 15 Å vacuum layer perpendicular to the surface was introduced to eliminate spurious periodic interactions.

Catalyst Models

Two sets of catalyst models were constructed for different simulation tasks:

1. For static optimization and CHE free energy calculations:

A Cu(100) surface with a $5 \times 5 \times 3$ slab;

An Ag₁-Cu single-atom catalyst obtained by replacing one surface Cu atom with Ag in the $5 \times 5 \times 3$ slab.

2. Considering the high requirement for computational resources in AIMD simulations, we adopted a smaller supercell model. For explicit-solvent AIMD simulations:

A Cu(100) surface with a $4 \times 4 \times 3$ slab;

An Ag₁-Cu single-atom catalyst obtained by replacing one surface Cu atom with Ag in the $4 \times 4 \times 3$ slab.

In all models, the bottom layer was fixed, while surface atoms, adsorbates, and water molecules were fully relaxed.

Ab Initio Molecular Dynamics (AIMD) Simulations

To explore the dynamic evolution of interfacial solvent structures, coordination environments of active sites, and adsorbed species on Ag₁-Cu and Cu(100) surfaces under realistic CO₂RR conditions, AIMD simulations were performed at 300 K under constant potentials of -0.8 V and -1.2 V versus reversible hydrogen electrode (vs. RHE). Explicit solvation and constant external electric potentials were incorporated throughout the simulations to faithfully replicate the electrocatalytic interface. The NVT canonical ensemble was employed, with temperature controlled via the Nosé–Hoover thermostat. A time step of 1 fs was adopted, with a total simulation duration of 10 ps. Explicit solvation was modeled by constructing a 10 Å-thick water layer containing 39 H₂O molecules on each catalyst surface, reproducing the water arrangement and hydrogen-bond network at the electrolyte–electrode interface.

The Γ -point was used for Brillouin zone sampling in AIMD simulations, with all other parameters identical to those for static structural optimizations. The first 2 ps of each simulation were used for system relaxation and thermodynamic equilibrium, and the subsequent 8 ps of trajectories were analyzed to characterize the interfacial water distribution and dynamic variations in the local structure of active sites under the two applied potentials for both catalyst systems.

Structural Optimization, Zero-Point Energy Corrections, and Free Energy Calculations for CO₂RR Intermediates

Geometric optimizations of key CO₂RR reaction intermediates were performed with full atomic relaxation until convergence criteria were satisfied. Implicit solvation effects and external electric potentials were included to accurately describe the realistic electrochemical interface. Implicit solvation was modeled using the VASPsol solvent model for aqueous environments. The constant-potential CP-VASP module was employed to apply a potential of -1.2 V vs. RHE by adjusting the Fermi level of the system, which allowed us to determine stable intermediate configurations and adsorption strengths under working conditions.

Vibrational frequency calculations at the Γ -point were performed for all optimized intermediates to obtain zero-point energy (ZPE) corrections. In these frequency calculations, only the adsorbed reaction intermediates (adsorbates) were included, while the slab substrate atoms were kept fixed, as the vibrational contributions from the rigid substrate are nearly identical under different adsorption conditions and can be effectively canceled out in the relative free energy calculations. Adsorption free energies of elementary reaction intermediates were then calculated using the computational hydrogen electrode (CHE) model at 300 K, incorporating ZPE corrections as well as entropic and enthalpic contributions. The corrected free energies were further used to establish the free energy profile of the CO₂RR pathway at a constant potential of -1.2 V vs. RHE.

Slow-Growth Free Energy Calculations for Reaction Coupling

The slow-growth constrained molecular dynamics method was applied to investigate the microscopic mechanism and free energy barrier of key intermediate coupling steps in CO₂RR, with implicit solvation effects and constant potentials incorporated throughout the calculations. The C–C bond distance was selected as the reaction coordinate for constrained dynamics simulations, which were performed in the NVT ensemble at 300 K. Implicit solvation was described by the VASPsol solvent model for aqueous environments, and the CP-VASP^[8,9] module fixed the system potential at -1.2 V vs. RHE to probe potential-dependent coupling barriers and reaction selectivity. The potential of mean force (PMF) was calculated via thermodynamic integration to construct the free energy profile, enabling determination of thermodynamic trends and kinetic barriers for the C–C coupling process.

Constant-potential simulations were performed using the CP-VASP method. In this framework, the electron chemical potential (μ_e) is fixed by the following relation:

$$\mu_e = \mu_{\text{SHE}} - |e|U_{\text{SHE}}$$

where μ_{SHE} (-4.6 eV) is the work function of the standard hydrogen electrode (SHE) in VASPsol^[10], and U_{SHE} is the applied potential relative to SHE. All constant-potential calculations were performed at pH = 6.8 to match the experimental condition of 0.1 mol/L KHCO₃ electrolyte^[11]. The experimentally relevant potential versus the reversible hydrogen electrode (RHE) was converted using the Nernst relation:

$$U_{\text{RHE}} = U_{\text{SHE}} + 0.059 \times \text{pH}$$

Supplementary Figures

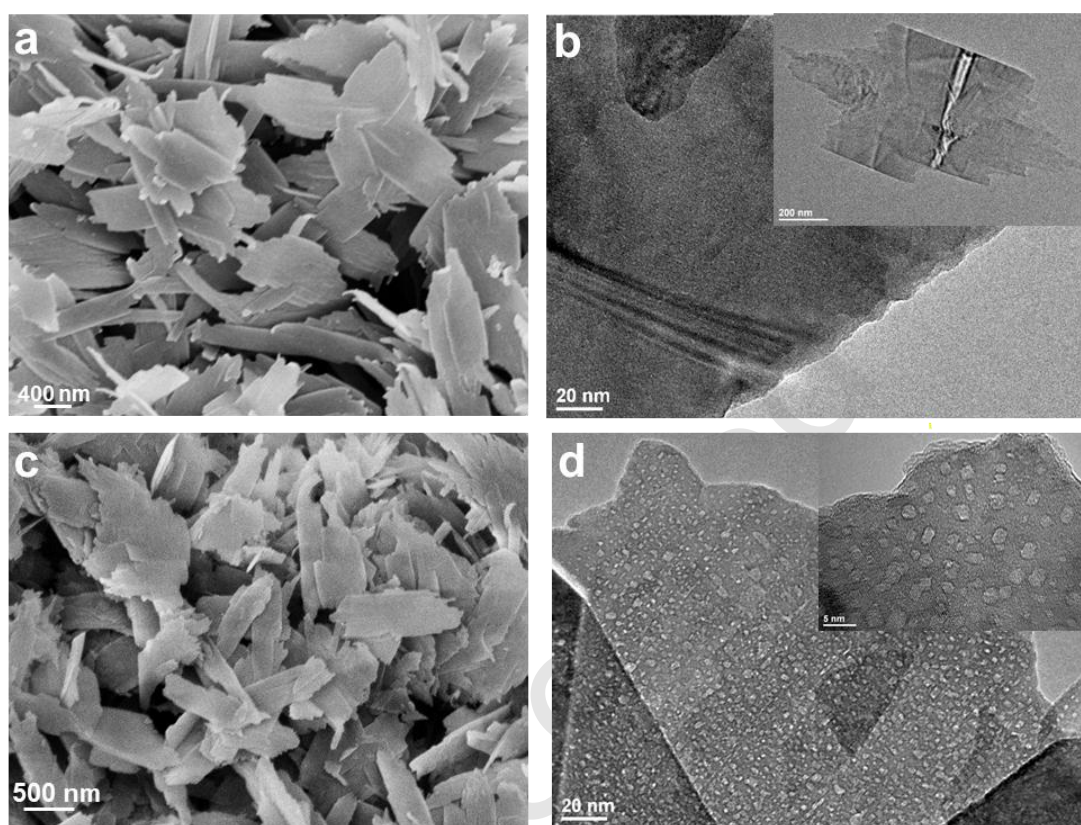


Figure S1. (a, b) SEM and TEM images of as-prepared CuO nanosheets. (c, d) SEM and TEM images of p-CuO nanosheets obtained by calcining the CuO nanosheets at 200 °C for 4 h.

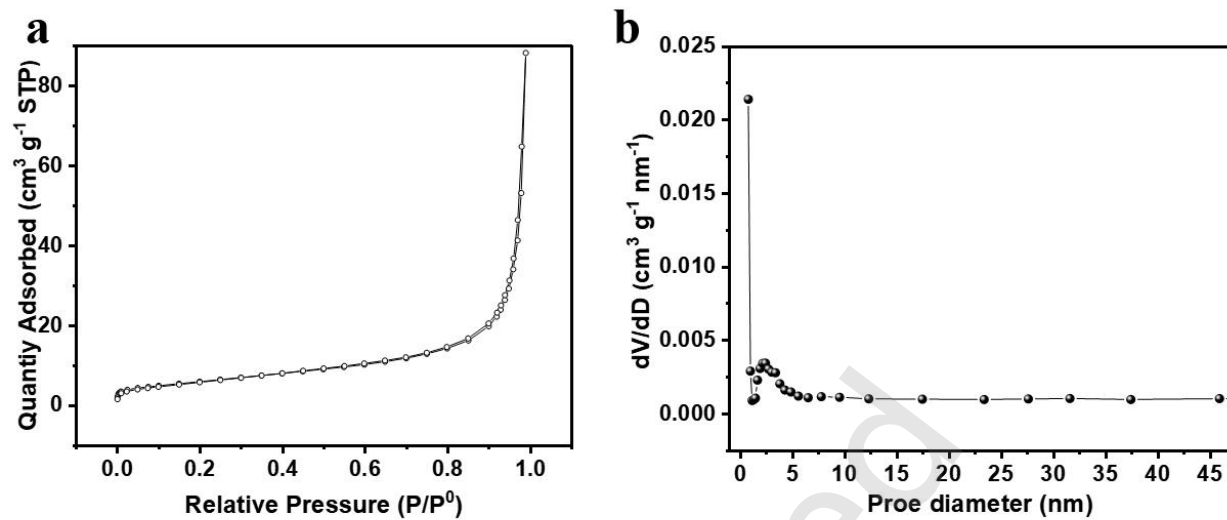


Figure S2. (a) N_2 adsorption-desorption isotherm and (b) corresponding pore size distribution curve of p-CuO (4 h).

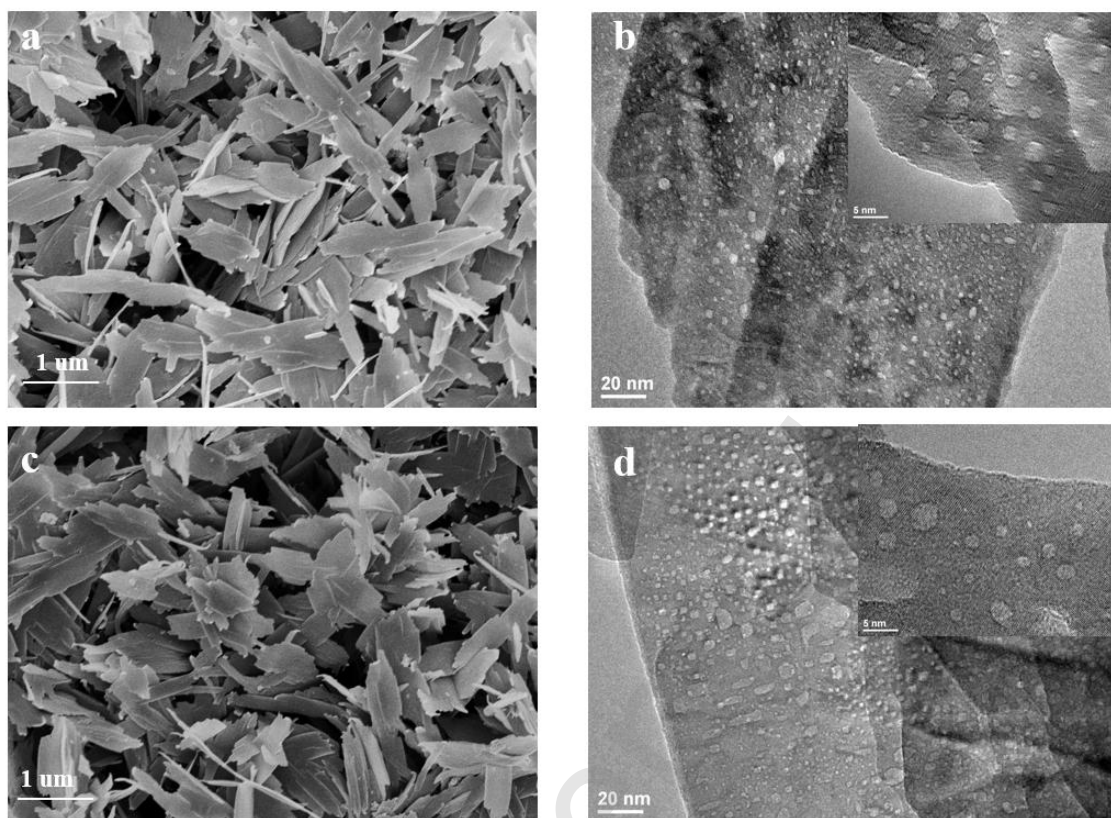


Figure S3. (a, b) SEM and TEM images of as-prepared CuO nanosheets obtained by calcining the CuO nanosheets at 200 $^{\circ}\text{C}$ for 2 h. (c, d) SEM and TEM images of p-CuO nanosheets obtained by calcining the CuO nanosheets at 200 $^{\circ}\text{C}$ for 6 h.

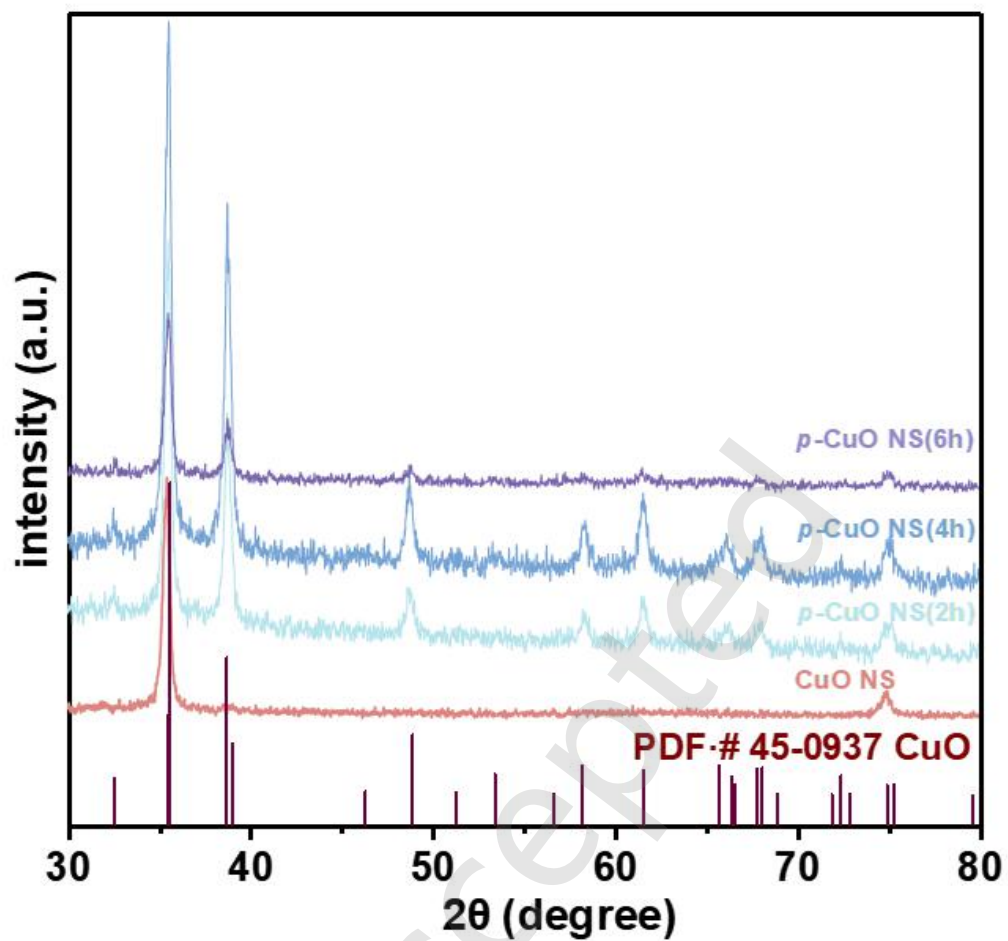


Figure S4. XRD patterns of CuO nanosheets before (0 h) and after calcination at 200 °C for 2, 4, and 6 h.

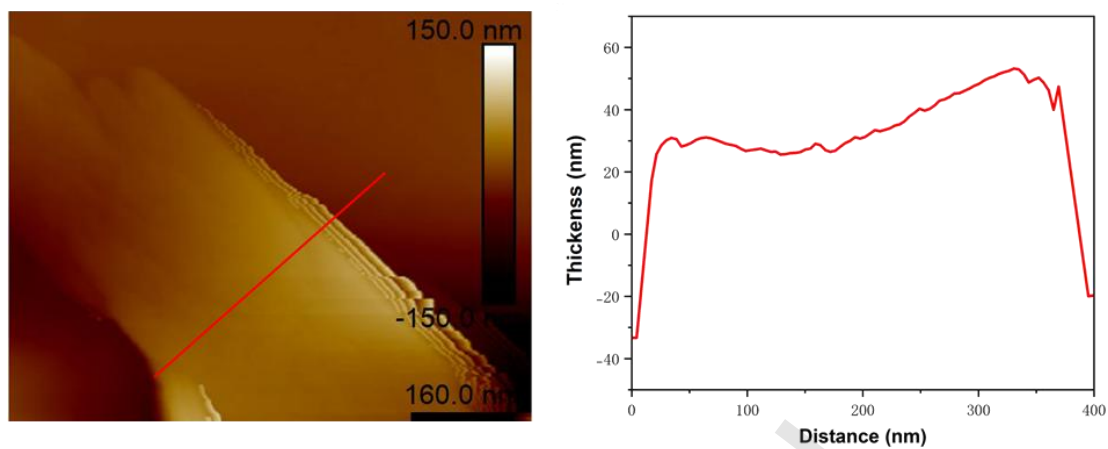


Figure S5. AFM images of as-prepared Ag₁-*p*-CuO nanosheets on mica and the corresponding height analysis to obtain the nanosheet thickness.

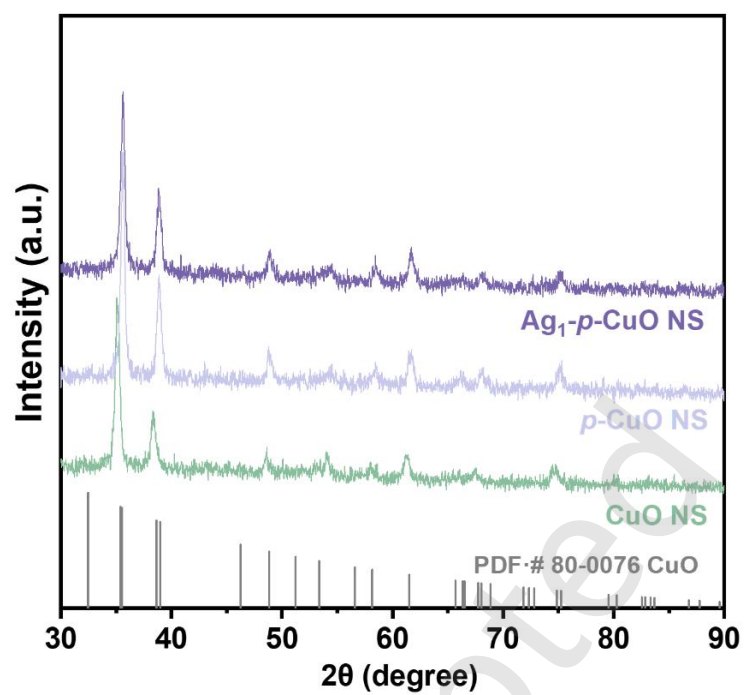


Figure S6. XRD patterns of as-prepared CuO, *p*-CuO, and Ag₁-*p*-CuO.

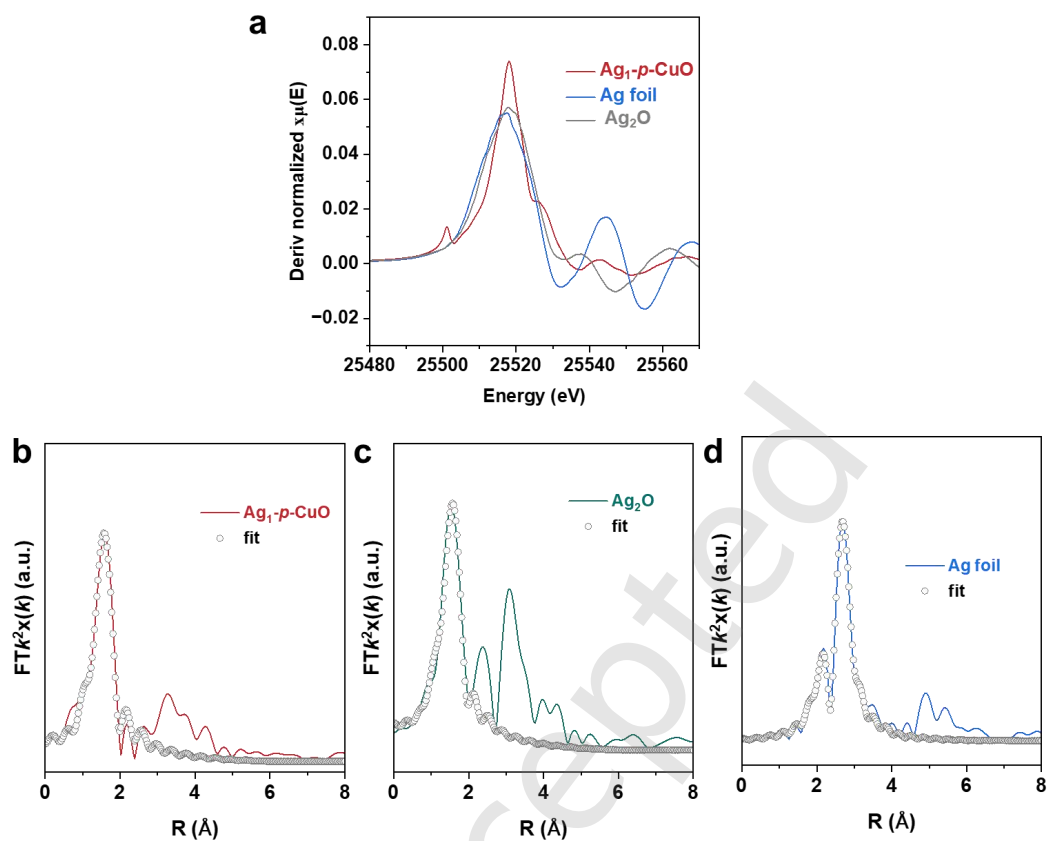


Figure S7. (a) The absorption edge position of $\text{Ag}_1\text{-p-CuO}$, determined by first-derivative analysis, lies between those of Ag foil and Ag_2O . The corresponding EXAFS fitting curves of as-prepared (b) $\text{Ag}_1\text{-p-CuO}$, (c) Ag_2O and (d) Ag foil .

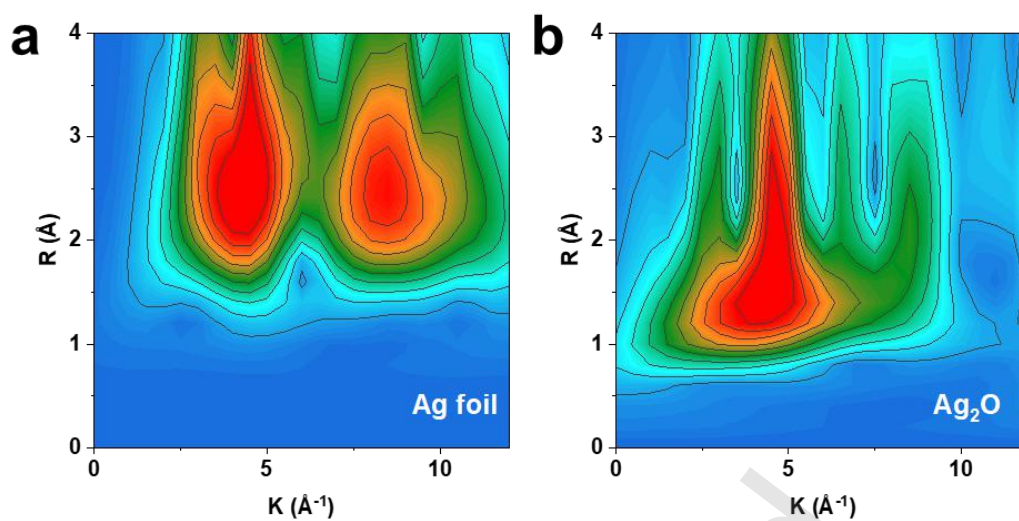


Figure S8. Ag K-edge WT-EXAFS of (a)Ag foil and (b) Ag_2O .

Table S1 EXAFS Fitting results of Ag K-edge

Sample	Scattering path	C. N.	R(Å)	σ^2 (x0.001)	ΔE (eV)	R factor
Ag _{1-p} -CuO	Ag-O	0.7	2.05	2.60	7.92	0.022
Ag foil	Ag-Ag	12	2.86	9.9	3.08	0.005
Ag ₂ O	Ag-O	2.0	2.05	4.63	7.06	0.031

k range for Fourier transform: 3-12 Å⁻¹ (for Ag Foil), 3-11.5 Å⁻¹ (for Ag₂O), 3-11 Å⁻¹ (for Ag_{1-p}-CuO). R range for EXAFS fitting: 1-3.2 Å⁻¹ (for Ag Foil), 1-3.2 Å⁻¹ (for Ag₂O), 1-2.5 Å⁻¹ (for Ag_{1-p}-CuO). $S_0^2=0.89$. Error bounds (accuracies) that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as C. N., $\pm 20\%$; R, $\pm 1\%$; σ^2 , $\pm 30\%$; ΔE_0 , $\pm 30\%$.

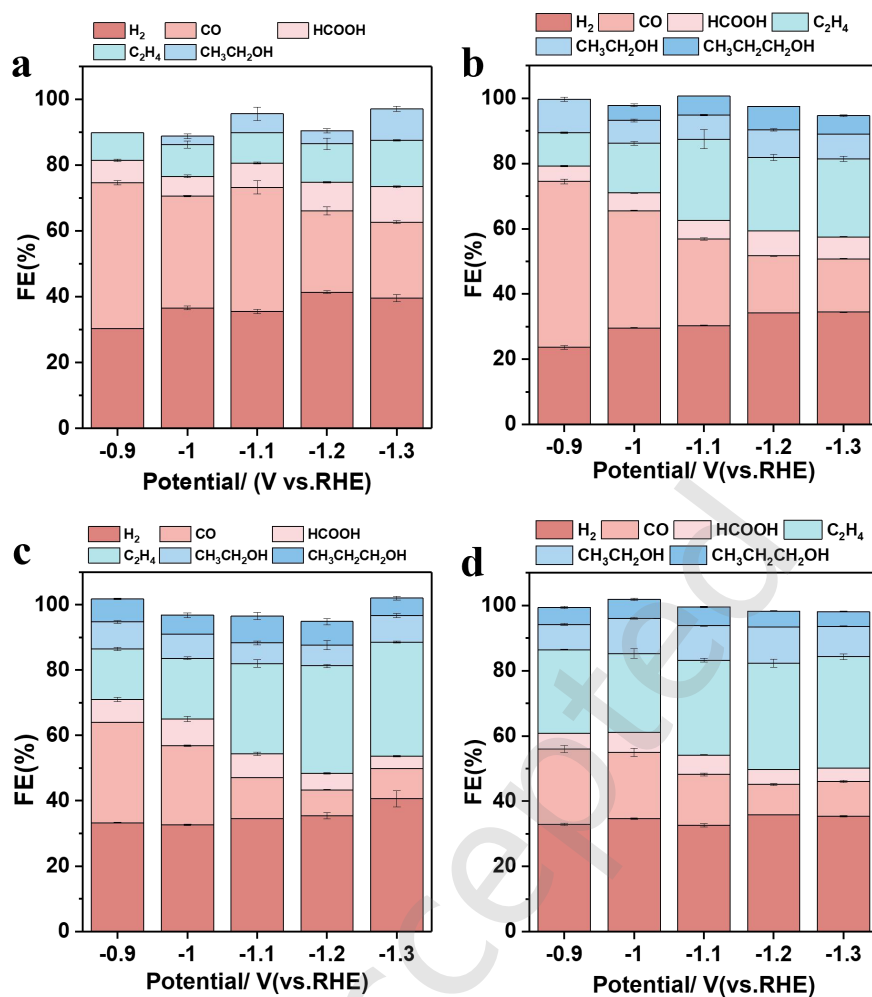
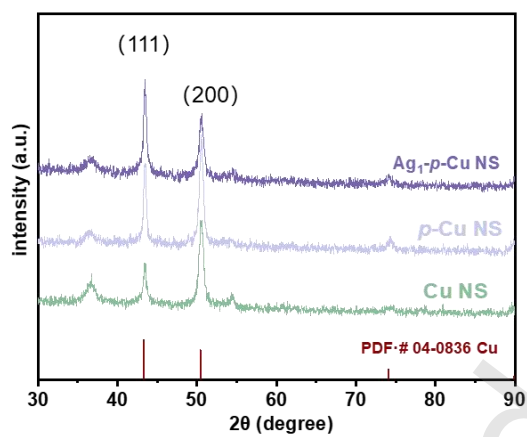


Figure S9. H⁻ cell CO₂ reduction performance of p- CuO catalysts with varying annealing durations: (a) 0 h, (b) 2 h, (c) 4 h, and (d) 6 h.

a



b

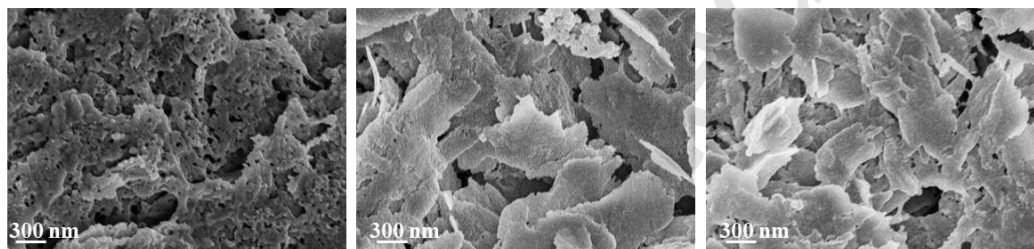


Figure S10. (a) Post-reaction XRD patterns of as-prepared CuO , p-CuO , and $\text{Ag}_1\text{-p-CuO}$. (b) Post-reaction SEM image of as-prepared CuO , p-CuO , and $\text{Ag}_1\text{-p-CuO}$

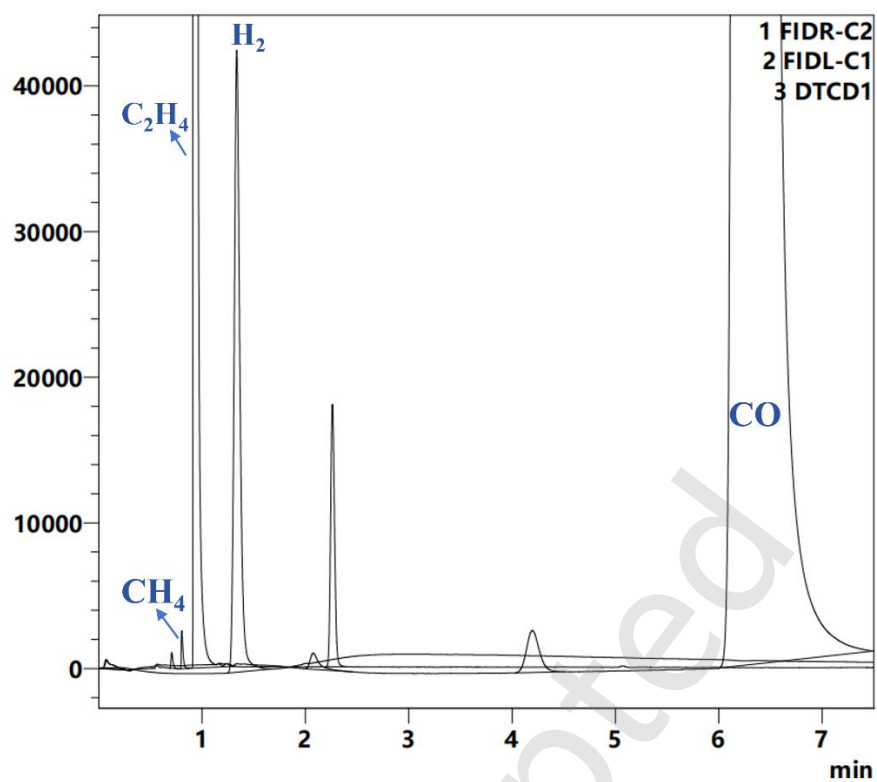


Figure S11. Typical GC curve of the gaseous products collected for the $\text{Ag}_1\text{-}p\text{-CuO}$ catalyst.

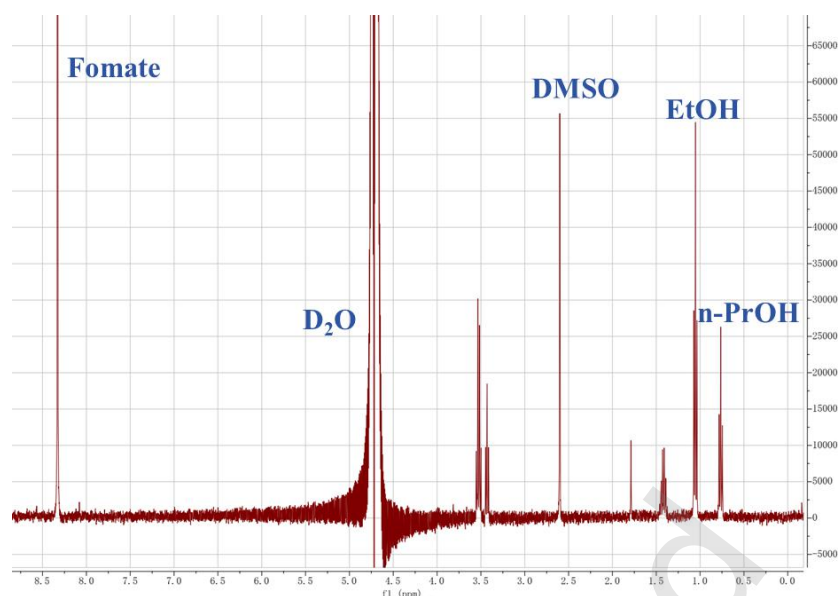


Figure S12. Typical ^1H -NMR spectra of the collected post-reaction solution of the $\text{Ag}_1\text{-}p\text{-CuO}$ catalyst.

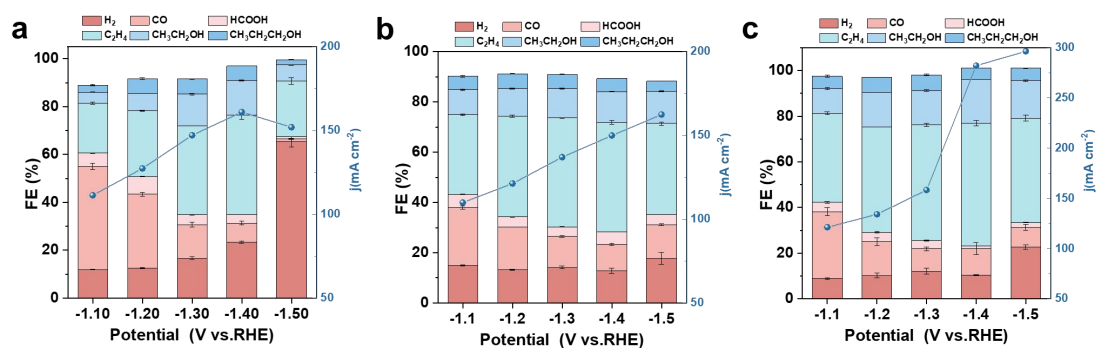


Figure S13. Flow cell CO₂ reduction performance of (a) CuO, (b) *p*-CuO, and (c) Ag₁-*p*-CuO.

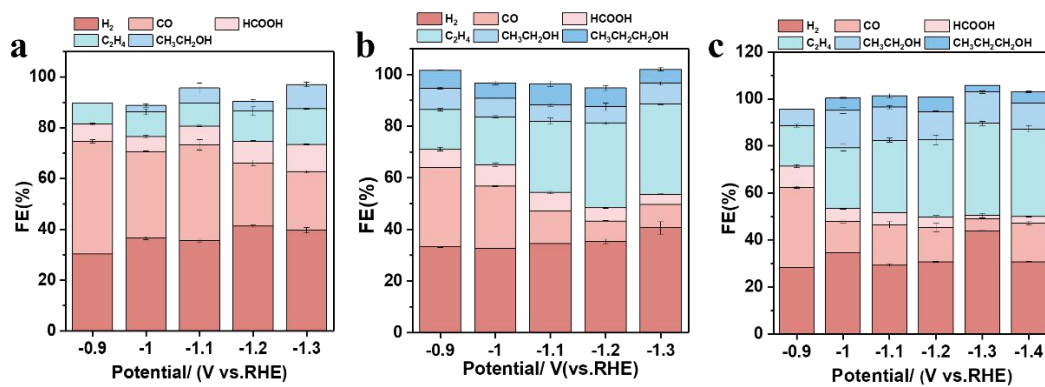


Figure S14. H-cell CO₂ reduction performance of (a) CuO NS (b) *p*-CuO, and (c) Ag₁-*p*-CuO.

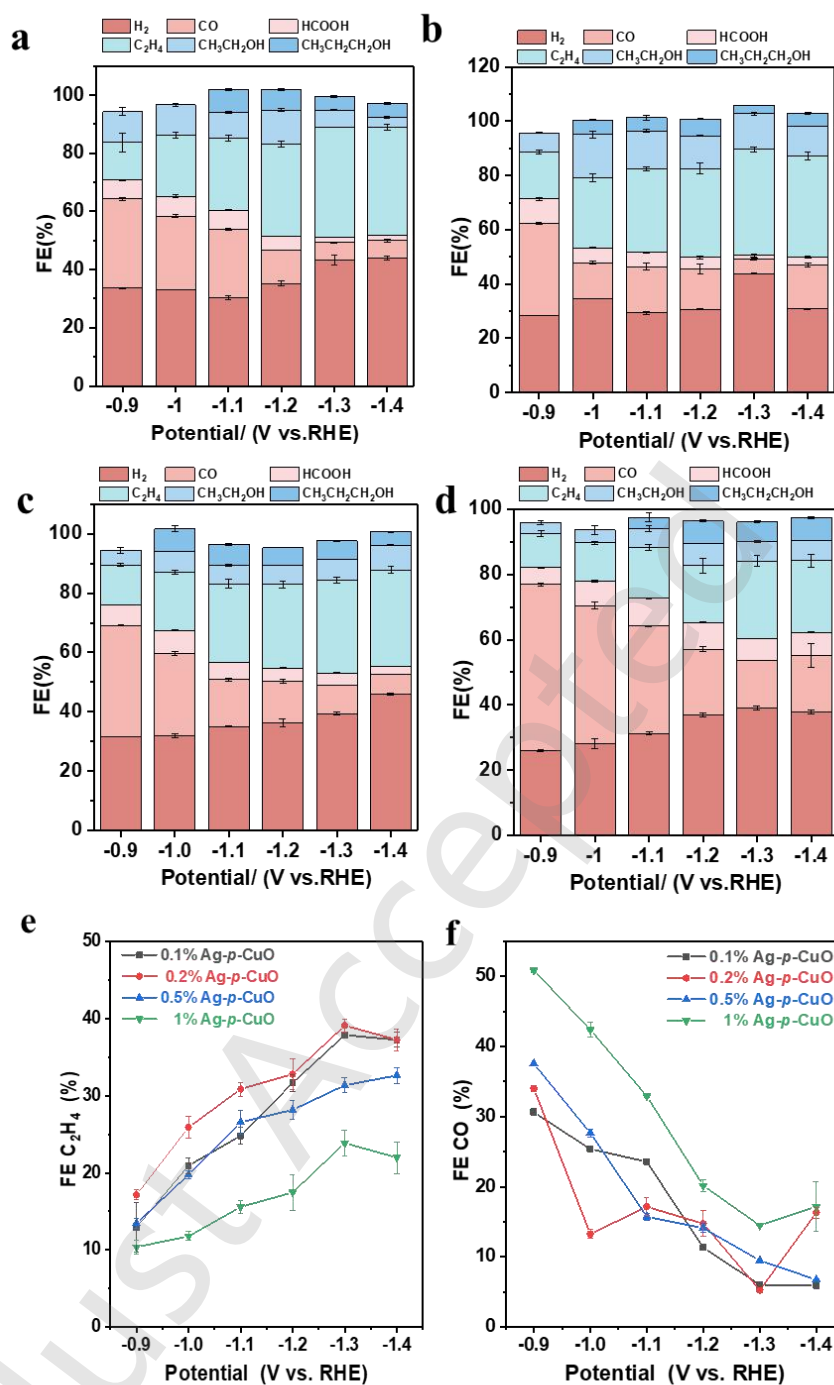


Figure S15. H-cell CO₂ reduction performance of Ag-modified *p*-CuO catalysts with varying Ag loadings (a) 0.1, (b) 0.2, (c) 0.5, and (d) 1.0 wt%. Comparison of (e) C₂H₄ and (f) CO Faradaic efficiencies.

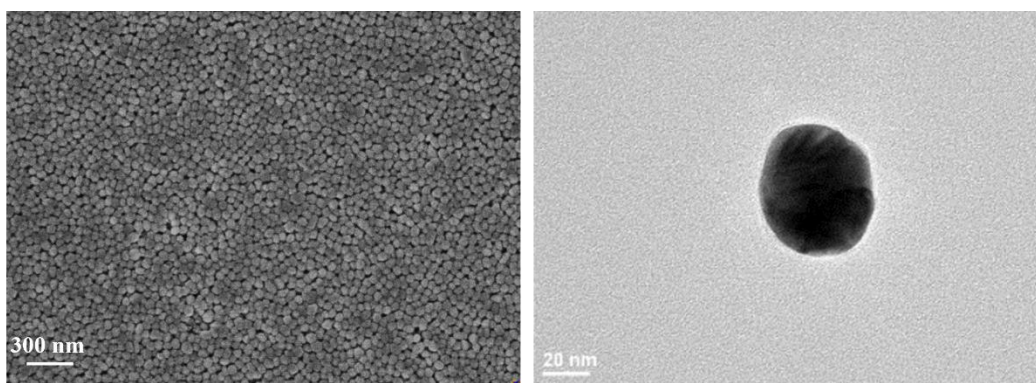


Figure S16. SEM and TEM images of as-prepared ~ 55 nm Au core ~ 2 nm SiO₂ shell nanoparticles.

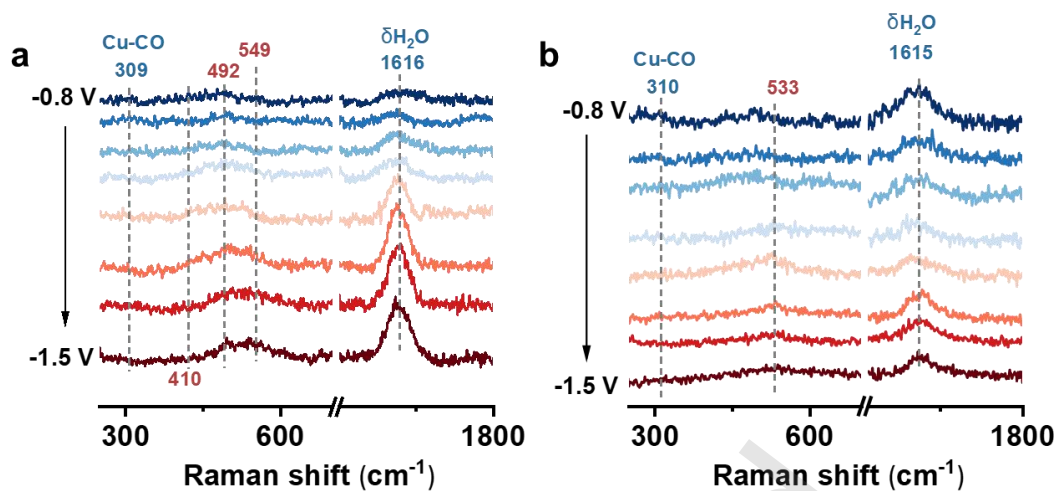


Figure S17. In situ Raman spectra acquired on the (a) $p\text{-CuO}$ and (b) CuO catalyst in a CO_2 -saturated solution, recorded from -0.8 to -1.5 V vs. RHE with a potential interval of 0.1 V.

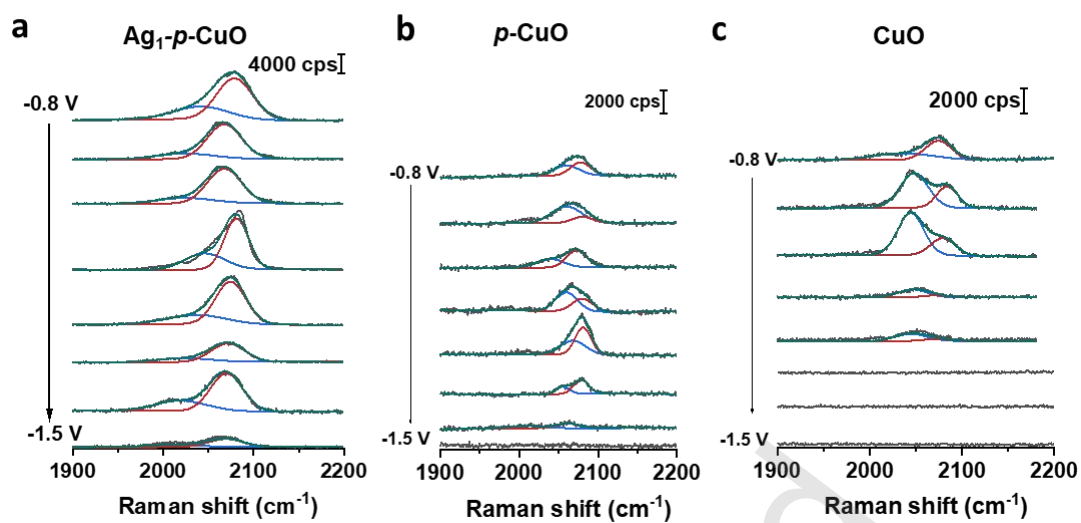


Figure S18. Potential-dependent CO adsorption-related Raman bands of (a) Ag₁-p-CuO, (b) p-CuO, and (c) CuO catalysts.

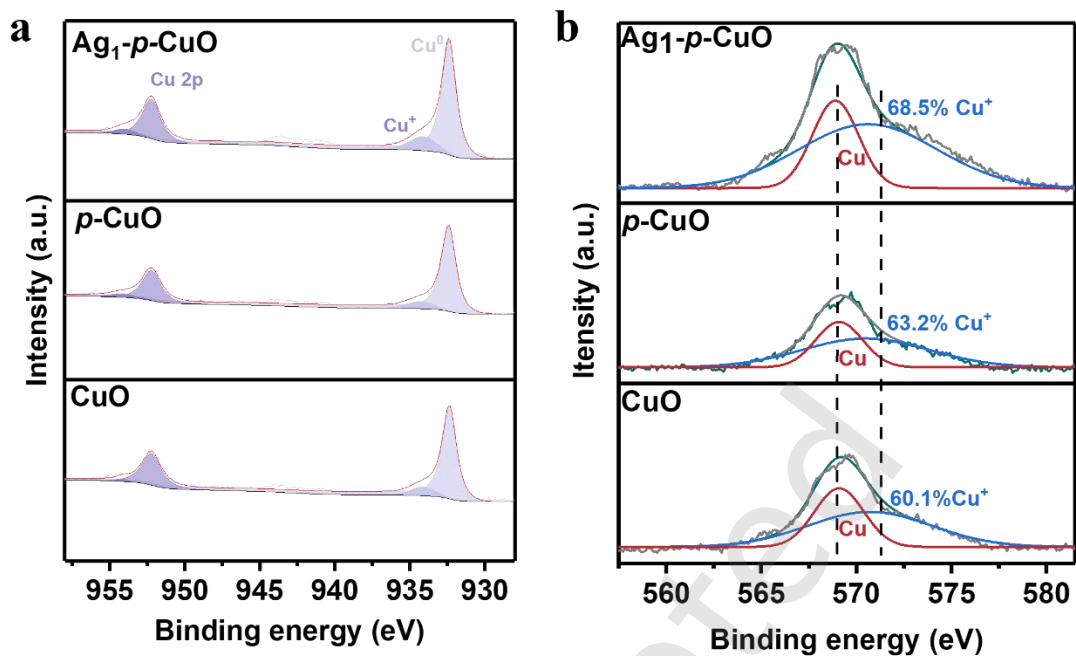


Figure S19. (a) Post-reaction Cu 2p XPS spectra of as-prepared CuO , p-CuO , and $\text{Ag}_1\text{-p-CuO}$. (b) Post-reaction Cu LMM Auger spectra of as-prepared CuO , p-CuO , and $\text{Ag}_1\text{-p-CuO}$.

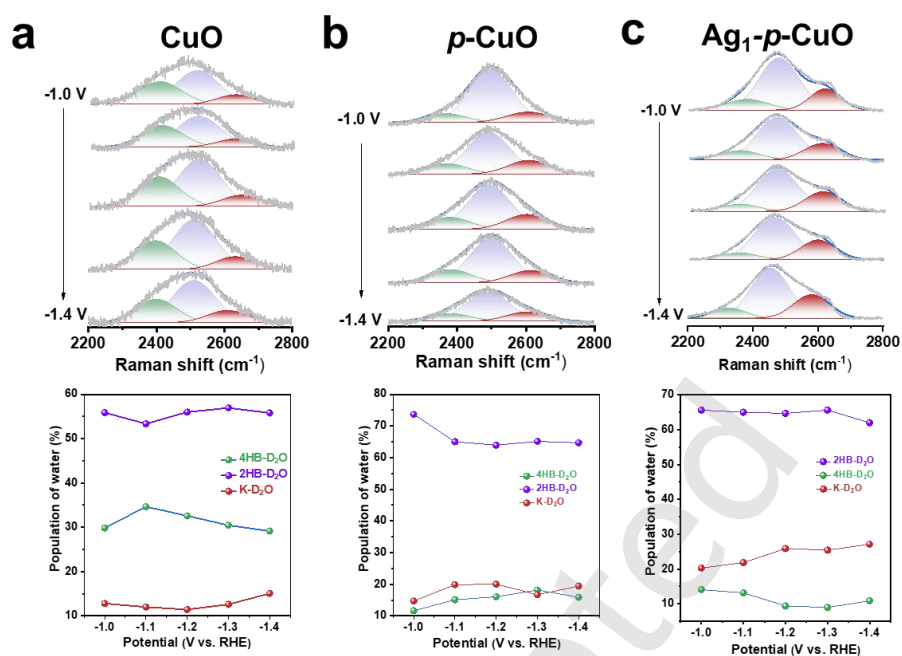


Figure S20. In situ potential-dependent Raman spectra (top panel) of interfacial water on (a) CuO, (b) *p*-CuO, and (c) Ag₁-*p*-CuO, along with the corresponding populations of 4-HB-D₂O, 2HB-D₂O, and K-D₂O water (bottom panel) estimated from Raman peak intensities.

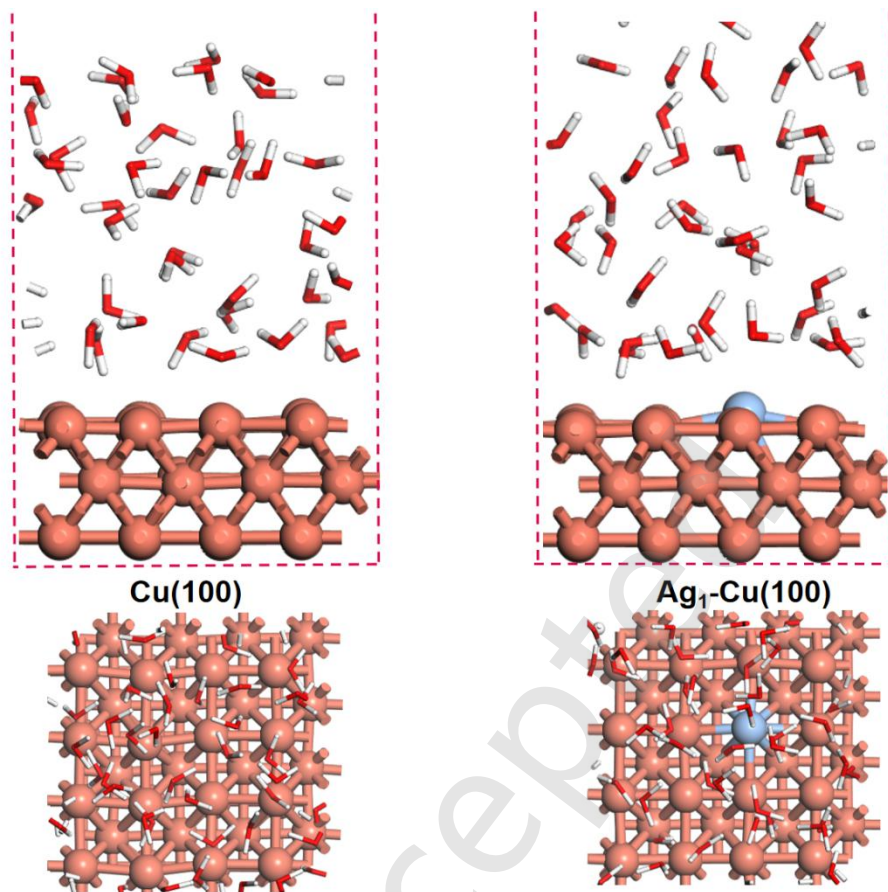


Figure S21. Solid-liquid aqueous models of Cu(100) and Ag₁-Cu(100)

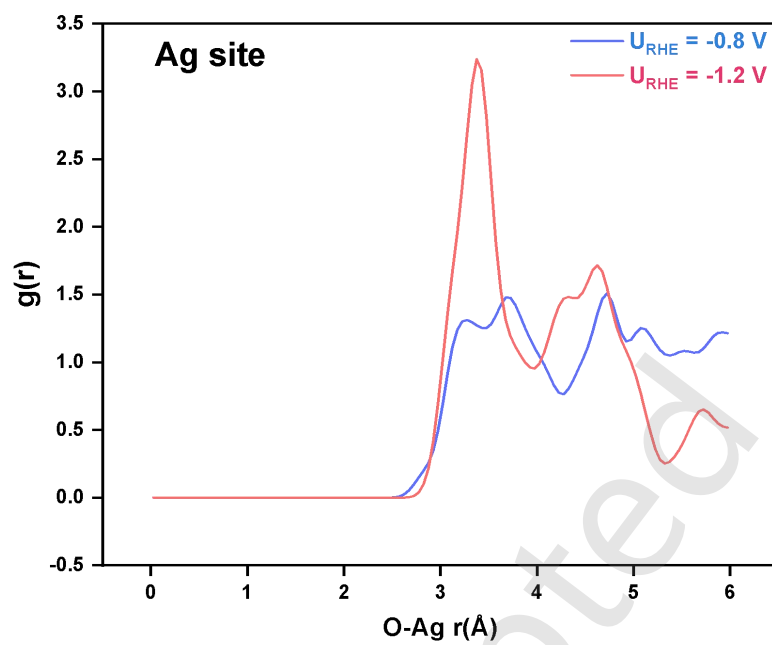


Figure S22. Radial distribution function (RDF) between Ag Atoms and O atoms of water molecules

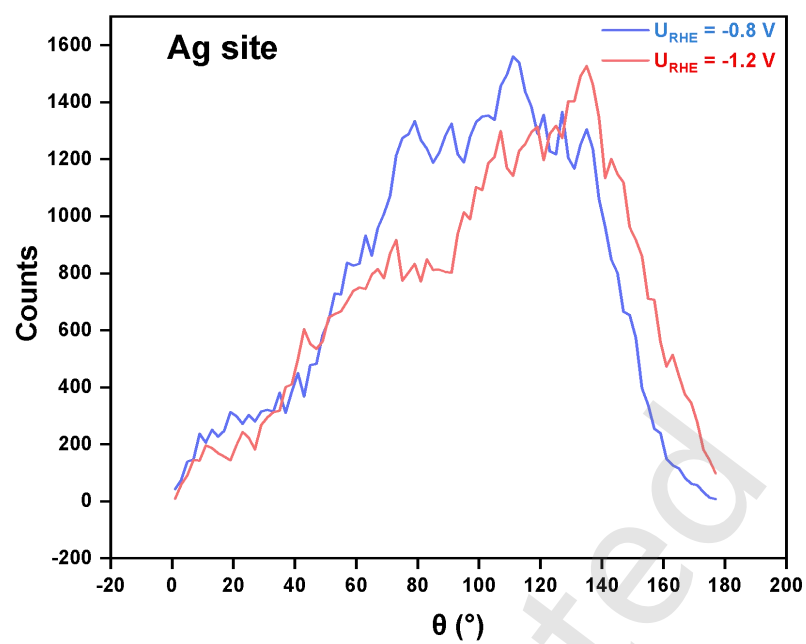


Figure S23. Orientation angle distribution of water molecules near Ag sites on Ag₁-Cu(100) surface.

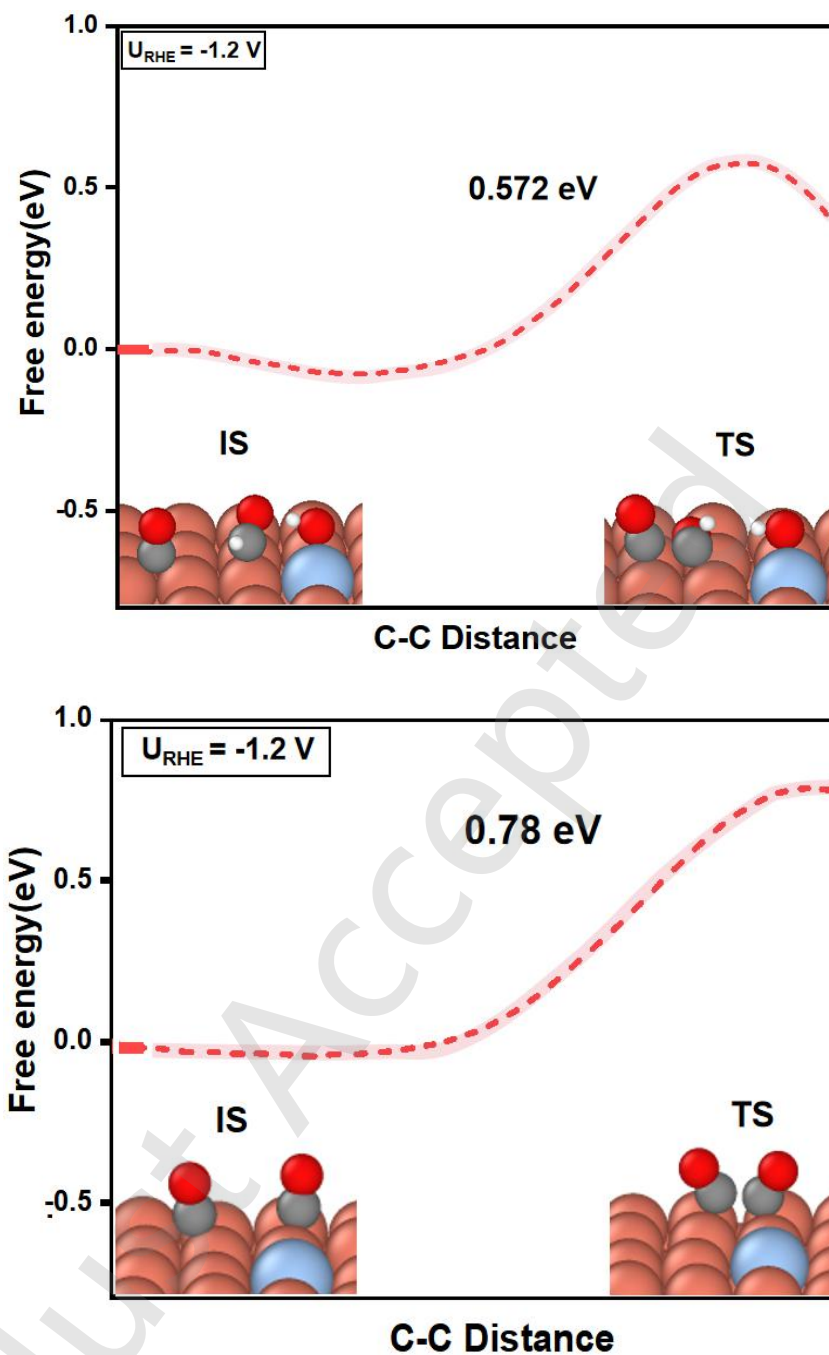


Figure S24. (a) Energy barrier of $*CHO + *CO \rightarrow *CHOCO$ coupling process on Ag₁-Cu single-atom catalyst surface. (b) Energy barrier of $*CO + *CO \rightarrow *COCO$ coupling process on Ag₁-Cu single-atom catalyst surface.

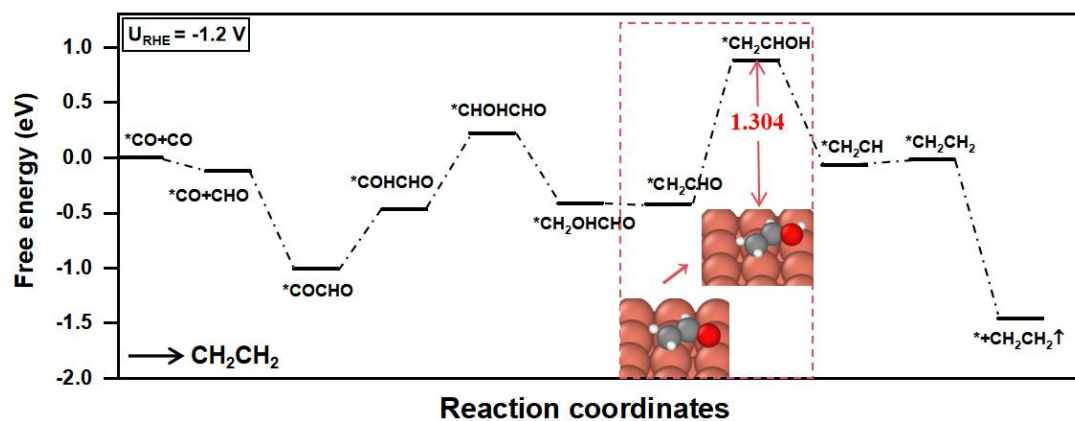


Figure S25. Free energy diagram for CO conversion to C₂H₄ on pristine Cu(100) surface at -1.2 V.

Reference

- [1] Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1996, 54, 11169–11186.
- [2] Jarzynski, C. Nonequilibrium equality for free energy differences. *Phys. Rev. Lett.* 1997, 78, 2690–2693.
- [3] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77 (18), 3865–3868.
- [4] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* 2010, 132 (15), 154104.
- [5] Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* 2011, 32 (7), 1456–1465.
- [6] Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1999, 59, 1758–1775.
- [7] Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1994, 50 (24), 17953–17979.
- [8] Zhao, X.; Liu, Y. Origin of Selective Production of Hydrogen Peroxide by Electrochemical Oxygen Reduction. *J. Am. Chem. Soc.* 2021, 143 (25), 9423–9428.
- [9] Yu, S.; Levell, Z.; Jiang, Z.; Zhao, X.; Liu, Y. What Is the Rate-Limiting Step of Oxygen Reduction Reaction on Fe-N-C Catalysts? *J. Am. Chem. Soc.* 2023, 145 (46), 25352–25356.
- [10] Mathew, K.; Kolluru, V. S. C.; Mula, S.; Steinmann, S. N.; Hennig, R. G. Implicit self-consistent electrolyte model in plane-wave density-functional theory. *J. Chem. Phys.* 2019, 151 (23), 234101.
- [11] Ju, W.; Bagger, A.; Hao, G.-P.; Varela, A. S.; Sinev, I.; Bon, V.; Roldan Cuenya, B.; Kaskel, S.; Rossmeisl, J.; Strasser, P. Understanding activity and selectivity of metal-nitrogen-doped carbon catalysts for electrochemical reduction of CO₂. *Nat. Commun.* 2017, 8 (1), 944.