

Atomically dispersed Zn regulates Cu nanosheets for ampere-level CO₂ electroreduction to C₂₊ products

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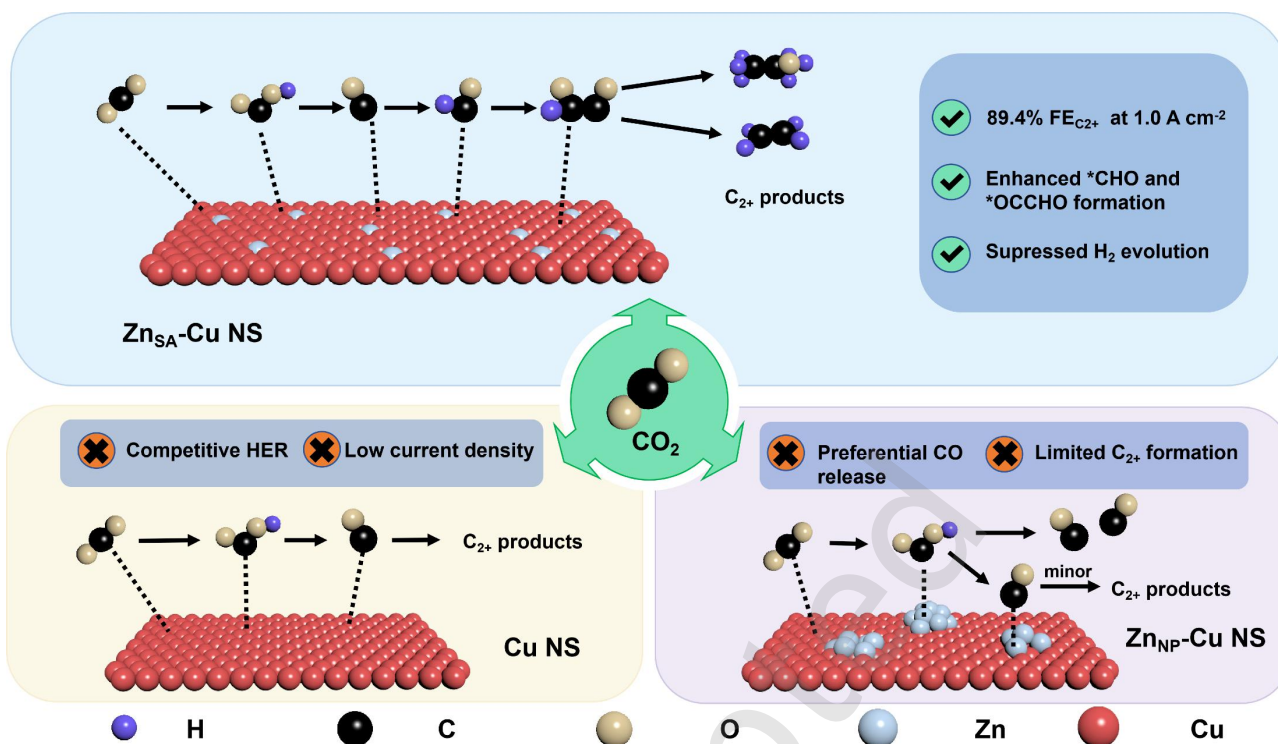
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Atomically dispersed Zn-regulated Cu nanosheets sustain efficient C–C coupling during ampere-level CO₂ electroreduction, achieving a C₂+ Faradaic efficiency of 89.4% at 1.0 A cm⁻². Atomic Zn–Cu coordination regulates *CO adsorption and promotes the formation of *CHO and *OCCHO intermediates, whereas Zn-rich particulate domains are associated with preferential CO release.

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ABSTRACT: Maintaining efficient C–C coupling at ampere-level current density remains challenging because the rates of *CO generation and consumption become kinetically mismatched at Cu interfaces. Here, atomically dispersed Zn-regulated Cu nanosheets (Zn_{SA}-Cu NS) were generated via *in situ* electrochemical reconstruction of low-Zn-loaded Cu-based oxide nanosheet precursors. Zn nanoparticle-modified Cu nanosheets (Zn_{NP}-Cu NS), reconstructed from high-Zn-loaded precursors, were used as a control to evaluate the influence of the reconstructed Zn state. In a flow cell with a neutral electrolyte, Zn_{SA}-Cu NS delivers a Faradaic efficiency for multicarbon (C₂₊) products (FE_{C₂₊}) of 89.4% at 1.0 A cm⁻², outperforming most reported Cu-based catalysts at high current density. Quasi-*in situ* X-ray absorption spectroscopy, together with *in situ* Raman and infrared spectroscopy, reveals a structurally stable Cu framework, regulated *CO adsorption behavior, and enhanced formation of *CHO and *OCCO intermediates. These results indicate that atomic Zn–Cu coordination facilitates *CO hydrogenation and subsequent C–C coupling, whereas Zn-rich particles dominated by Zn–Zn coordination are associated with preferential CO release. This work identifies the Zn dispersion state as a key structural parameter for sustaining C–C coupling during ampere-level CO₂ electroreduction.

KEYWORDS: CO₂ electroreduction; atomically dispersed Zn; C–C coupling; C₂₊ products

1 Introduction

Electrocatalytic CO₂ reduction reaction (CO₂RR) offers a viable route for carbon recycling by converting CO₂ into CO, formate, hydrocarbons, and alcohols [1–4]. Among these products, C₂₊ products, including ethylene, ethanol, and n-propanol, are particularly attractive because of their high energy density and economic value [5–7]. Cu-based catalysts are among the most effective systems for promoting CO₂-to-C₂₊ conversion under ambient conditions, owing to their moderate binding affinity for carbon-containing intermediates and their ability to facilitate C–C coupling [8–12]. Accordingly, tailoring the local coordination and electronic structure of Cu sites, regulating the surface coverage of key intermediates, and directing C–C coupling pathways have become central strategies for improving C₂₊ selectivity [13–20].

Although many Cu-based catalysts exhibit high FE_{C₂₊} at low or moderate current density, the corresponding C₂₊ production rates remain insufficient for high-rate electrosynthesis. Therefore, increasing the current density toward the ampere level is important for improving C₂₊ productivity, although C₂₊ selectivity typically decreases and sustaining stable active sites over prolonged operation becomes increasingly challenging under such high-current-

density conditions [21–26]. At high reaction rates, rapid CO₂ consumption intensifies interfacial CO₂ depletion and perturbs the local pH, proton availability, ion transport, and gas-liquid-solid three-phase microenvironment [27,28]. These coupled interfacial changes further affect the formation, residence, and subsequent conversion of *CO, making it difficult to sustain the *CO-derived intermediates required for C–C coupling [29,30]. Accordingly, effective catalyst design should not only maintain stable Cu active sites and continuous electron transport at high current density, but also regulate the interfacial fate of *CO on Cu while preserving adjacent Cu ensembles favorable for C–C coupling. Multicomponent catalytic systems can leverage the synergistic interactions among different active components to fulfill complementary functions, thereby facilitating reactant activation and intermediate conversion processes [31–33]. Among them, atomically dispersed heterometallic sites or single-atom catalysts can precisely regulate the local coordination structure and adsorption environment of neighboring Cu sites, and therefore hold considerable promise for simultaneously achieving high current density, high C₂₊ selectivity, and excellent structural stability [34–39].

Herein, we report Zn_{SA}-Cu NS for CO₂-to-C₂₊ conversion at ampere-level current density in a neutral electrolyte. Unmodified Cu nanosheets (Cu NS) and Zn_{NP}-Cu NS are

employed as controls to compare the influence of the reconstructed Zn state on $^*\text{CO}$ conversion and C–C coupling. Comparative structural and spectroscopic analyses reveal that atomically dispersed Zn forms isolated Zn–Cu coordination sites that facilitate $^*\text{CO}$ hydrogenation and the formation of C–C coupled intermediates. In contrast, $\text{Zn}_{\text{NP}}\text{-Cu}$ NS contains Zn-rich particles dominated by Zn–Zn coordination and exhibits a higher CO product fraction. Consequently, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS delivers a $\text{FE}_{\text{C}_2^+}$ of 89.4% at 1.0 A cm^{-2} in a neutral electrolyte, highlighting its favorable C_2^+ selectivity under high-current-density conditions. These findings identify the Zn dispersion state as a key structural

parameter for regulating the interfacial fate of CO and sustaining C–C coupling over Cu-based catalysts under ampere-level conditions.

2 Results and discussion

2.1 Synthesis and structural evolution of Zn-regulated Cu nanosheets

Zn-regulated Cu-based nanosheet precursors were synthesized through an alkaline precipitation and aging process followed by hydrothermal treatment, as illustrated in Fig. 1(a).

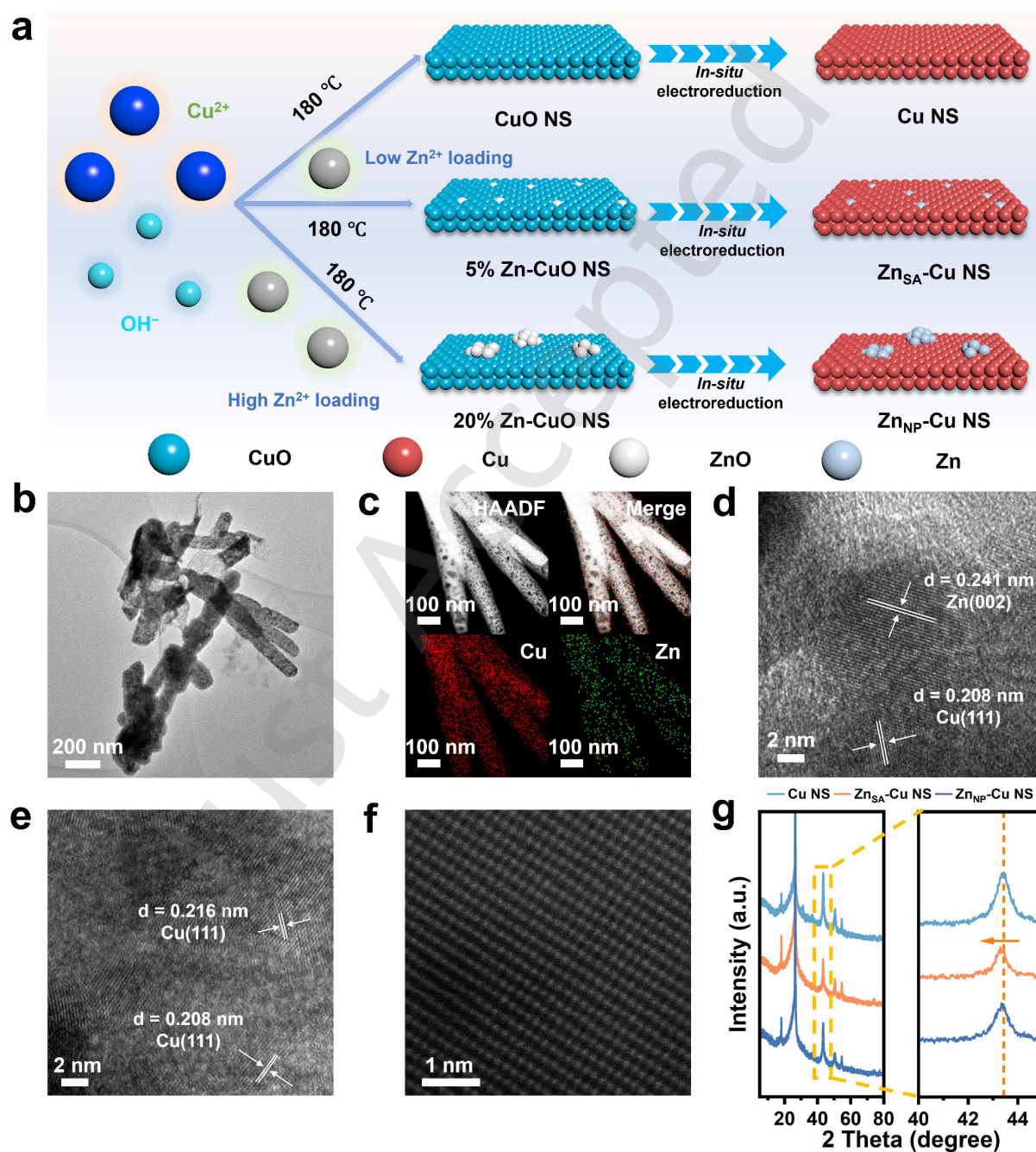


Figure 1 Preparation and structural characterization of Cu NS, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS, and $\text{Zn}_{\text{NP}}\text{-Cu}$ NS. (a) Schematic illustration of precursor synthesis and electrochemical reconstruction. (b) TEM image of $\text{Zn}_{\text{SA}}\text{-Cu}$ NS. (c) The EDS mappings of $\text{Zn}_{\text{SA}}\text{-Cu}$ NS. HRTEM image of (d) $\text{Zn}_{\text{NP}}\text{-Cu}$ NS and (e) $\text{Zn}_{\text{SA}}\text{-Cu}$ NS. (f) Aberration-corrected HAADF-STEM image of $\text{Zn}_{\text{SA}}\text{-Cu}$ NS. (g) XRD patterns of Cu NS, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS, and $\text{Zn}_{\text{NP}}\text{-Cu}$ NS.

In the absence of Zn^{2+} , Cu^{2+} was converted into CuO nanosheet precursors under alkaline conditions. 5% Zn-CuO

and 20% Zn-CuO were prepared using Zn/Cu precursor mass ratios of 5% and 20%, respectively. Transmission

electron microscopy (TEM) images of the fresh precursors show that CuO, 5% Zn-CuO, and 20% Zn-CuO all retain nanosheet-like or nanosheet-assembled morphologies, indicating that Zn^{2+} incorporation does not appreciably disrupt the CuO nanosheet framework (Fig. S1 in the Electronic Supplementary Material (ESM)). The X-ray diffraction (XRD) patterns of all three precursors are dominated by the characteristic diffraction peaks of CuO. A small amount of ZnO phase is also observed in 5% Zn-CuO, whereas ZnO-related diffraction peaks become more pronounced in 20% Zn-CuO (Fig. S2 in the ESM). X-ray absorption fine structure (XAFS) further shows that the Cu K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) features of the fresh samples closely resemble those of CuO and are dominated by Cu-O coordination, with Zn addition accompanied by subtle changes in the local Cu coordination environment (Fig. S3 in the ESM). After *in situ* electrochemical reduction under CO_2 reduction reaction conditions, the CuO, 5% Zn-CuO, and 20% Zn-CuO precursors were reconstructed into Cu NS, Zn_{SA} -Cu NS and Zn_{NP} -Cu NS, respectively. TEM images show that Cu NS, Zn_{SA} -Cu NS, and Zn_{NP} -Cu NS largely preserve their nanosheet-like or nanosheet-assembled morphologies, indicating that electrochemical reconstruction largely preserves the nanosheet-like framework (Fig. 1(b) and Fig. S4 in the ESM). High-resolution transmission electron microscopy (HRTEM) and elemental mapping further reveal distinct reconstructed

local structures after reconstruction of precursors with different Zn loadings (Fig. 1(c) and Figs. S5 and S6 in the ESM). Cu NS displays clear lattice fringes with an interplanar spacing of 0.208 nm, assigned to Cu (111). For Zn_{NP} -Cu NS, lattice fringes with interplanar spacings of 0.208 and 0.241 nm are resolved and assigned to Cu (111) and Zn (002) (Fig. 1(d)). Zn_{SA} -Cu NS exhibits an enlarged Cu (111) spacing of approximately 0.216 nm (Figs. 1(e) and 1(f)), suggesting that low-loading Zn species become incorporated into the Cu lattice during reconstruction, thereby inducing lattice expansion and local strain. For Zn_{NP} -Cu NS, Zn-related particulate structures or locally enriched regions are observed, indicating that higher Zn loading promotes the formation of particulate Zn species during electrochemical reconstruction. The XRD patterns of the reconstructed samples are dominated by diffraction peaks associated with metallic Cu. Relative to Cu NS, the Cu diffraction peaks of Zn_{SA} -Cu NS show a clear shift, further supporting the interpretation that low-loading Zn interacts with and perturbs the Cu lattice during electrochemical reconstruction (Fig. 1(g)) [40]. This observation agrees with the enlarged Cu (111) spacing measured by HRTEM and further supports the interaction of atomically dispersed Zn with the local Cu lattice environment following electrochemical reconstruction of the low-Zn-loading precursor.

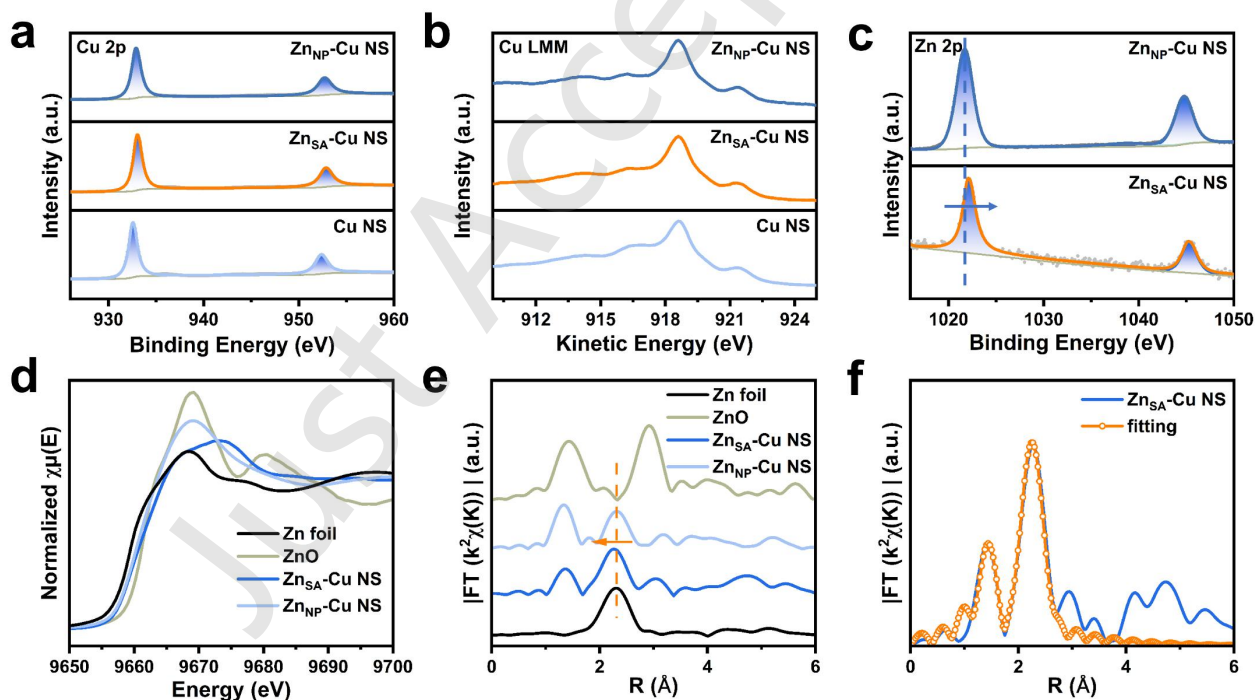


Figure 2 Surface electronic structure and local coordination analysis of Zn-regulated Cu nanosheets. (a) Cu 2p XPS spectra. (b) Cu LMM Auger spectra. (c) Zn 2p XPS spectra. (d) Zn K-edge XANES spectra of Zn_{SA} -Cu NS and Zn_{NP} -Cu NS with Zn foil and ZnO as references. (e) k^2 -weighted Zn K-edge FT-EXAFS spectra of Zn_{SA} -Cu NS and Zn_{NP} -Cu NS with Zn foil and ZnO as references in R space. (f) EXAFS fitting result for Zn_{SA} -Cu NS.

2.2 Zn dispersion state and local coordination structure

Correlating structural evolution, valence states, and functional species is broadly important for understanding energy-related materials with dynamic phase or coordination changes [34,35,40,41]. X-ray photoelectron spectroscopy (XPS) and XAFS spectroscopy were subsequently used to examine the surface electronic structure and local coordination environment of the

reconstructed samples. The Cu 2p XPS spectra show no distinct Cu^{2+} satellite peaks, suggesting that Cu after reconstruction is present mainly as Cu^0/Cu^+ (Fig. 2(a)). The Cu LMM Auger spectra further display dominant Cu^0 features, confirming that the Cu-based precursors are largely reduced to metallic Cu under CO_2 RR conditions (Fig. 2(b)) [21]. The Zn 2p XPS peak of Zn_{SA} -Cu NS is clearly shifted relative to that of Zn_{NP} -Cu NS, indicating that Zn species are not present

simply as particulate Zn but instead interact strongly with the Cu lattice (Fig. 2(c)) [21,40].

The Zn K-edge XANES spectrum indicates that the average oxidation state of Zn in Zn_{SA}-Cu NS lies between Zn⁰ and Zn²⁺, which may result from partial surface oxidation of Zn species during exposure to air (Fig. 2(d)). In the EXAFS spectrum, Zn_{SA}-Cu NS exhibits both Zn-O coordination and a distinct metallic coordination feature. This feature appears at a lower R value than the Zn-Zn peak of Zn foil, indicating that it originates predominantly from Zn-Cu rather than Zn-Zn coordination (Fig. 2(e)) [21,40]. The corresponding EXAFS fitting further confirms the presence of Zn-Cu coordination in Zn_{SA}-Cu NS (Fig. 2(f) and Table S1 in the ESM). By contrast, the metallic coordination feature of Zn_{NP}-Cu NS is consistent with a Zn-Zn bond, indicating that Zn is present mainly as particulate species in the high-Zn-loading sample (Fig. S8 in the ESM) [40]. Cu K-edge XANES, EXAFS, and fitting results show that Cu in Cu NS, Zn_{SA}-Cu NS, and Zn_{NP}-Cu NS predominantly retains metallic Cu⁰ characteristics (Figs. S9, S10 and Table S2 in the ESM) [21,40]. For Zn_{SA}-Cu NS, the Zn K-edge results reveal atomic Zn-Cu coordination, indicating that atomically dispersed Zn interacts with the Cu lattice, although the low Zn content makes this subtle structural perturbation difficult to resolve from the Cu K-edge spectra. For Zn_{NP}-Cu NS, the combined Zn and Cu K-edge analyses indicate that Zn mainly exists as particulate species and has no obvious influence on the metallic Cu framework. Taken

together, these results support that atomically dispersed Zn in Zn_{SA}-Cu NS interacts with the metallic Cu lattice through local Zn-Cu coordination, whereas higher Zn loading preferentially leads to particulate Zn species [21,40].

2.3 Ampere-level CO₂RR performance toward C₂₊ products

To assess the CO₂RR performance of Zn_{SA}-Cu NS, electrochemical measurements were conducted in a flow cell (Fig. S11 in the ESM). The current responses of Cu NS, Zn_{SA}-Cu NS, and Zn_{NP}-Cu NS were first compared using linear sweep voltammetry (LSV) measurements (Fig. 3(a)). Under CO₂-saturated conditions, Zn_{SA}-Cu NS exhibits a higher cathodic current density than Cu NS and Zn_{NP}-Cu NS at the same potential. The distinct cyclic voltammetry (CV) profiles further reflect different electrochemical response characteristics among the three precursor-derived electrodes (Fig. S12 in the ESM).

The product distributions and C₂₊ selectivity of Zn_{SA}-Cu NS were subsequently examined under galvanostatic conditions (Figs. 3(b), 3(c) and S13, and Table S3 in the ESM). As the current density increases from 100 to 1000 mA cm⁻², the FE for C₂₊ products rises from approximately 26% to 89.4%, while the FE for H₂ remains low. This value highlights the strong capability of Zn_{SA}-Cu NS to achieve highly selective C₂₊ production under ampere-level conditions, placing its performance above that of most reported Cu-based catalysts at high current density.

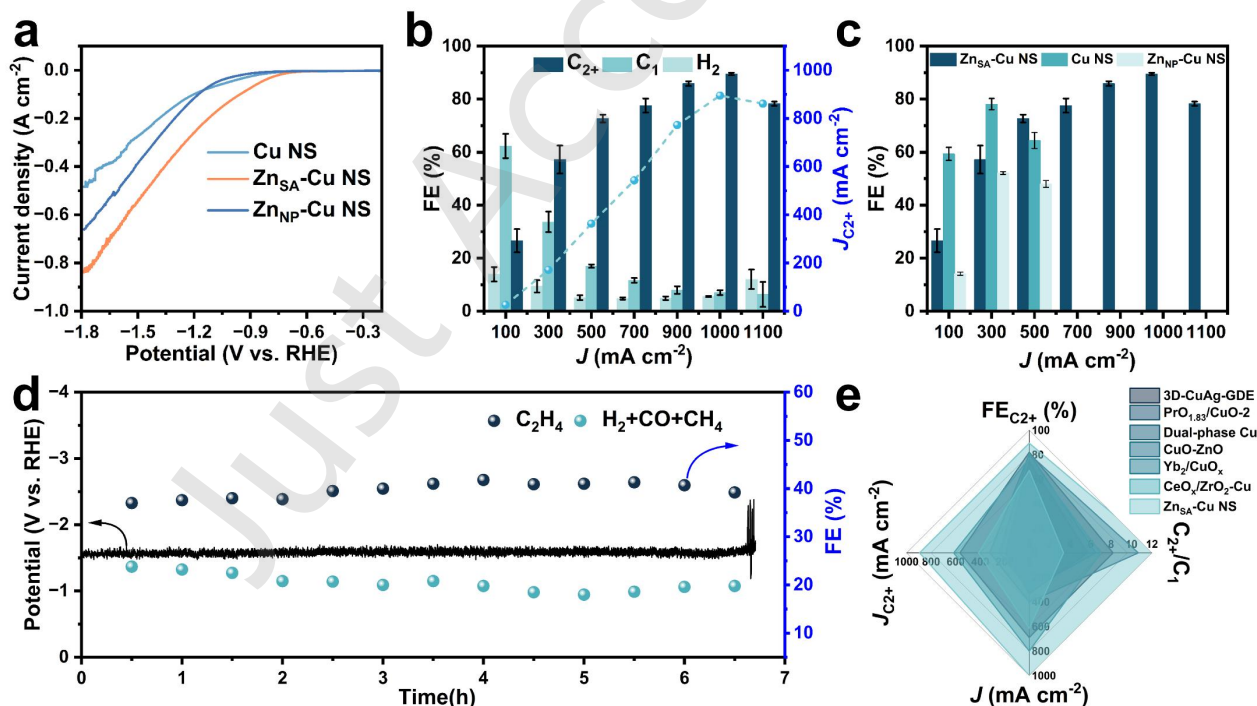


Figure 3 CO₂RR performance in a flow cell. (a) LSV curves of Cu NS, Zn_{SA}-Cu NS and Zn_{NP}-Cu NS in CO₂. (b) FE of H₂, C₁, and C₂₊ products and the corresponding C₂₊ partial current density for Zn_{SA}-Cu NS at different current density. (c) FE of C₂₊ for Cu NS, Zn_{SA}-Cu NS and Zn_{NP}-Cu NS. (d) Approximately seven-hour galvanostatic operation of Zn_{SA}-Cu NS at 500 mA cm⁻² in a flow cell using 1.0 M KCl electrolyte without electrolyte recirculation. (e) Comparison of Zn_{SA}-Cu NS with the reported representative Cu-based electrocatalysts.

The control samples further highlight the importance of Zn speciation (Fig. S14 and Fig. S15 in the ESM). At 300 mA cm⁻², Cu NS affords a FE_{C2+} of 78.1%, whereas Zn_{NP}-Cu NS reaches only 52.1%, together with a substantially higher CO fraction. A direct comparison among the three samples shows that Zn_{SA}-Cu NS maintains superior C₂₊ selectivity across a broad

current-density range and sustains high C₂₊ partial current density from 700 to 1100 mA cm⁻². Taken together, these results indicate that the presence of atomically dispersed Zn, rather than particulate Zn species, is associated with more sustained C-C coupling under high-current CO₂RR conditions.

The operational stability of Zn_{SA}-Cu NS was evaluated by

galvanostatic electrolysis at 500 mA cm^{-2} for approximately 7 h in a flow cell using 1.0 M KCl electrolyte without electrolyte recirculation (Fig. 3(d)). During this period, the electrode potential and the monitored gas-phase Faradaic efficiencies remain relatively stable, indicating long-term operational stability under the tested high-current conditions. When benchmarked against previously reported Cu-based catalysts, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS combines a FE_{C_2+} close to 90% with a C_{2+} partial current density of approximately 900 mA cm^{-2} , showing that $\text{Zn}_{\text{SA}}\text{-Cu}$ NS combines high C_{2+} selectivity with a high C_{2+} partial current density (Fig. 3(e) and Table S4 in the ESM) [22,42–46].

2.4 Spectroscopic analysis of structural stability and reaction intermediates

To elucidate the origin of the high FE_{C_2+} maintained by $\text{Zn}_{\text{SA}}\text{-Cu}$ NS under ampere-level CO_2RR conditions, we combined quasi-*in situ* XAFS with *in situ* Raman and infrared spectroscopy to track catalyst structural evolution and key reaction intermediates. Cu K-edge XANES spectra acquired at different current density remain characteristic of metallic Cu, with no discernible shift toward higher oxidation states during CO_2RR (Fig. 4(a)). Consistently, the corresponding Fourier-transformed EXAFS spectra are dominated by Cu–Cu coordination, with no pronounced Cu–O contribution (Fig. 4(b) and Table S2 in the ESM).

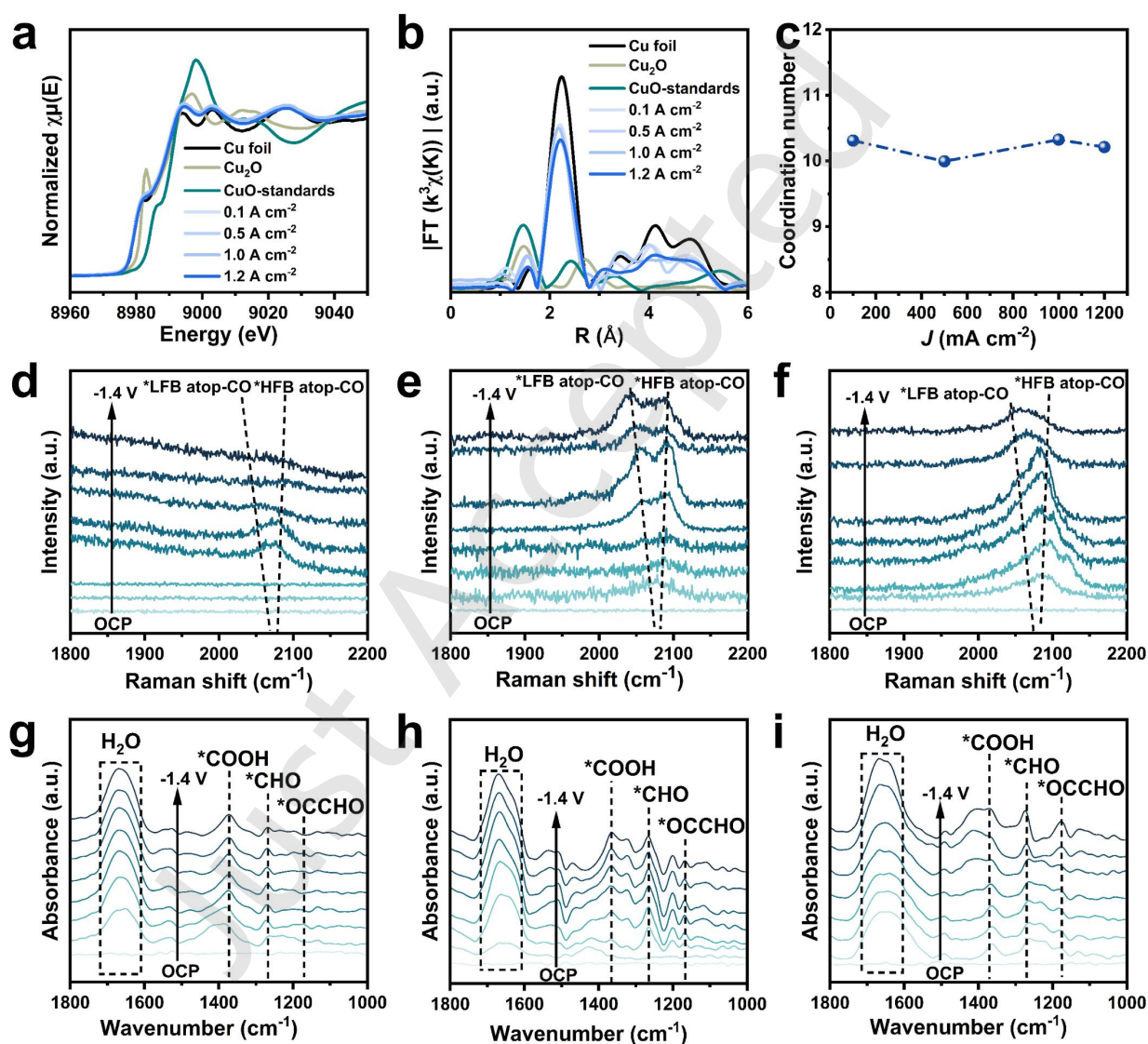


Figure 4 *In situ* and quasi-*in situ* spectroscopic analysis. (a) Quasi-*in situ* Cu K-edge XANES spectra of $\text{Zn}_{\text{SA}}\text{-Cu}$ NS collected after CO_2RR at different current density. (b) Corresponding Fourier-transformed Cu K-edge EXAFS spectra in R space. (c) Evolution of the Cu–Cu coordination number for $\text{Zn}_{\text{SA}}\text{-Cu}$ NS at various current density. (d–f) *In situ* Raman spectra recorded at different applied potentials for Cu NS, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS and $\text{Zn}_{\text{NP}}\text{-Cu}$ NS under CO_2 , respectively. (g–i) *In situ* ATR-SEIRAS spectra recorded at different applied potentials for Cu NS, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS and $\text{Zn}_{\text{NP}}\text{-Cu}$ NS under CO_2 , respectively.

Quantitative fitting further shows that the Cu coordination number remains close to 10 across a broad current range (Fig. 4(c) and Fig. S16 in the ESM), indicating that $\text{Zn}_{\text{SA}}\text{-Cu}$ NS largely preserves a metallic Cu coordination environment during high-current CO_2RR [21].

In situ Raman spectroscopy was subsequently employed to examine surface-adsorbed *CO on Cu NS, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS, and

$\text{Zn}_{\text{NP}}\text{-Cu}$ NS during CO_2RR (Figs. 4(d)–4(f) and Fig. S17 in the ESM). Cu NS exhibits relatively weak atop- *CO signals, consistent with limited steady-state *CO availability under the investigated conditions, particularly as the cathodic bias becomes more negative. In contrast, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS shows moderate and progressively enhanced *CO signals from 0 to -1.4 V vs. RHE, together with the gradual development of

distinguishable low- and high-frequency atop-*CO components at approximately 2040–2060 and 2080–2100 cm^{-1} , respectively [8,22]. These spectral characteristics indicate that atomically dispersed Zn modifies the local electronic and coordination environments of neighboring Cu sites, thereby regulating the adsorption state and interfacial availability of *CO rather than simply maximizing its surface accumulation [22,38]. $\text{Zn}_{\text{NP}}\text{-Cu}$ NS exhibits a stronger *CO-related Raman response than Cu NS at relatively mild cathodic potentials, but the *CO signal becomes weaker at more negative potentials; together with its higher CO fraction in the product distribution, this behavior is consistent with preferential CO release and less efficient downstream utilization of CO-derived intermediates for C–C coupling [21,47].

In situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) spectroscopy provides complementary evidence for the enhanced formation of CO_2RR -related intermediates on $\text{Zn}_{\text{SA}}\text{-Cu}$ NS (Figs. 4(g)–4(i) and Fig. S18 in the ESM). As the cathodic bias becomes more negative, the band at approximately 1380 cm^{-1} , assigned to *COOH, progressively intensifies, indicating enhanced *COOH formation and accumulation, consistent with facilitated initial CO_2 activation [21,38,47]. The feature near 1260 cm^{-1} , tentatively assigned to a *CHO-related vibration, suggests that $\text{Zn}_{\text{SA}}\text{-Cu}$ NS facilitates the hydrogenation of *CO-derived intermediates. More importantly, the *OCCHO-related band at approximately 1185 cm^{-1} is substantially more prominent on $\text{Zn}_{\text{SA}}\text{-Cu}$ NS than on Cu NS or $\text{Zn}_{\text{NP}}\text{-Cu}$ NS, supporting the preferential formation of key C–C coupling intermediates in the presence of atomic Zn–Cu coordination [47]. Deconvolution of the $\delta(\text{HOH})$ region reveals two components associated with weakly hydrogen-bonded water (w-HB- H_2O) at lower wavenumbers and strongly hydrogen-bonded water (s-HB- H_2O) at higher wavenumbers (Fig. S19 in the ESM) [48,49]. With increasing Zn content, the relative contribution of w-HB- H_2O progressively increases, indicating a redistribution of interfacial water toward relatively weaker hydrogen-bonding environments. Compared with the s-HB- H_2O -dominated Cu NS and the strongly w-HB- H_2O -biased $\text{Zn}_{\text{NP}}\text{-Cu}$ NS, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS exhibits a more balanced distribution of w-HB- H_2O and s-HB- H_2O , which may provide a favorable compromise between interfacial proton transfer and stabilization of CO-derived intermediates for subsequent C–C coupling [49,50].

3 Conclusions

In summary, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS was generated through the *in situ* electrochemical reconstruction of low-Zn-loaded Cu-based oxide nanosheet precursors for C_{2+} production at ampere-level current density in a neutral electrolyte. Compared with unmodified Cu NS and $\text{Zn}_{\text{NP}}\text{-Cu}$ NS, $\text{Zn}_{\text{SA}}\text{-Cu}$ NS features atomically dispersed Zn–Cu coordination, an expanded Cu lattice, and a largely preserved metallic Cu coordination environment, thereby achieving a C_{2+} Faradaic efficiency of nearly 90% and a C_{2+} partial current density of 894 mA cm^{-2} at 1.0 A cm^{-2} . Mechanistic analyses indicate that atomically dispersed Zn enhances *CO adsorption and activation and promotes the formation of *COOH, *CHO, and *OCCHO intermediates, thereby facilitating C–C coupling while

suppressing the hydrogen evolution reaction. This work provides a useful design reference for the atomic-scale coordination engineering of Cu-based catalysts and for sustaining high $\text{FE}_{\text{C}_{2+}}$ under ampere-level conditions.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Declaration of competing interest

The authors declare no conflict of interest.

Author contribution statement

Zhu Chengyang and Mao Junjie conceived the idea and supervised the research; Liu Enhe designed and prepared the samples, performed the experiments and data analysis, and wrote the manuscript; Wu Wenjie revised the manuscript; Yu Dongyang provided guidance for the research; Yu Wenqian contributed to data validation and manuscript formatting. All authors contributed to the general discussion and approved the final manuscript.

Use of AI statement

None.

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Atomically dispersed Zn regulates Cu nanosheets for ampere-level CO₂ electroreduction to C₂₊ products

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Experimental section

Chemicals. Copper(II) sulfate pentahydrate (CuSO₄·5H₂O) was obtained from Sinopharm Chemical Reagent Co., Ltd., and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) was obtained from Xilong Scientific Co., Ltd. Potassium hydroxide (KOH, 95%) was obtained from Shanghai Macklin Biochemical Co., Ltd., and anhydrous ethanol (C₂H₅OH, 99.7%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout the synthesis and washing procedures. All chemicals were used as received without further purification.

Preparation of 5% Zn-CuO NS. The synthesis of the Cu-based oxide nanosheet precursors was adapted from the method reported by Zhang et al., with minor modifications [1]. Here, “5% Zn-CuO NS” denotes a precursor-salt mass ratio of $m[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]/m[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}] \times 100\% = 5\%$, rather than the Zn content in the final catalyst. In a typical synthesis, 1.0 g of CuSO₄·5H₂O and 50 mg of Zn(NO₃)₂·6H₂O were dissolved in 50 mL of deionized water. The mixture was stirred for 30 min to obtain a homogeneous precursor solution. Subsequently, 0.7 g of KOH was added to the solution, followed by continuous stirring for an additional 30 min. The resulting suspension was then aged at 5 °C for 24 h, transferred into a hydrothermal autoclave, and maintained at 180 °C for 18 h. After the autoclave had cooled naturally to room temperature, the solid product was collected and washed twice with deionized water and twice with anhydrous ethanol. Finally, the product was dried in an oven, and the resulting sample was denoted as 5% Zn-CuO NS.

Preparation of CuO NS. The CuO NS control sample was synthesized following the same procedure used for 5%-Zn-CuO NS, except that Zn(NO₃)₂·6H₂O was omitted from the precursor solution. All other reagent quantities, aging conditions, hydrothermal-treatment parameters, washing procedures, and drying conditions were kept unchanged.

Preparation of 20% Zn-CuO NS. The 20% Zn-CuO NS control sample was prepared using the same procedure, except that 200 mg of Zn(NO₃)₂·6H₂O was used with 1.0 g of CuSO₄·5H₂O, corresponding to a precursor-salt mass ratio of 20%. All other reagent quantities and experimental conditions were kept unchanged.

Preparation of Cu NS, Zn_{SA}-Cu NS, and Zn_{NP}-Cu NS electrodes. In a typical electrode preparation, 5 mg of the synthesized CuO NS, 5% Zn-CuO NS, or 20% Zn-CuO NS precursor was accurately weighed and ultrasonically dispersed in 475 μL of a water-ethanol mixed solvent. Subsequently, 25 μL of Nafion binder solution was added dropwise, and the resulting suspension was further sonicated for 30 min to obtain a homogeneous catalyst ink. The catalyst ink was then uniformly spray-coated onto a carbon paper substrate with a geometric area of 2.5 cm × 1.0 cm and dried under an infrared lamp. The resulting electrodes were assembled as cathodes in a flow cell electrolyzer and activated *in situ* under CO₂RR conditions by potential cycling for five cycles between -0.8 and -2.0 V versus Ag/AgCl. The electrodes were subsequently electrochemically reconstructed at a current density of 50 mA cm⁻² for 30 min. After electrochemical reconstruction, the electrodes derived from CuO NS, 5% Zn-CuO NS, and 20% Zn-CuO NS were denoted as Cu NS, Zn_{SA}-Cu NS, and Zn_{NP}-Cu NS, respectively.

Characterizations. The crystal structure and morphology of the prepared catalysts were characterized by XRD on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation (λ = 1.5406 Å). HRTEM measurements were performed on an

aberration-corrected JEM-ARM300F microscope. XPS analysis was carried out on a Nexsa photoelectron spectrometer (Thermo Fisher Scientific) equipped with a monochromatic Al K α X-ray source (1486.6 eV) to obtain detailed chemical-composition information. ATR-SEIRAS measurements were performed on a Bruker INVENIO-R spectrometer equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector.

Electrochemical measurements. All electrochemical measurements were performed at room temperature and ambient pressure using a CHI electrochemical workstation (1140 series). CO₂RR was conducted in a gas-diffusion-electrode (GDE)-based flow cell with a continuous feed of CO₂. At each applied current density, CO₂RR was operated for 15 min to ensure steady-state product formation. The prepared GDE was used as the cathode, and an IrO_x-coated titanium mesh was used as the anode. CO₂ was introduced into the flow cell at a flow rate of 100 sccm using a mass flow controller. Gas-phase and liquid-phase products were quantified based on three independent electrolysis experiments, and the data are reported as the mean $\pm$ standard deviation. Electrochemical measurements were carried out in a three-electrode flow cell configuration. Potentials were measured against an Ag/AgCl reference electrode (1.0 M KCl) and converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation. Unless otherwise specified, all potentials were reported without internal resistance compensation.

The working electrode was prepared as follows. First, 5 mg of catalyst was dispersed in a mixed solution containing 475 μ L of Millipore ultrapure water/ethanol mixed solvent and 25 μ L of Nafion dispersion, followed by sonication to form a homogeneous ink. The ink was then brush-coated onto carbon fiber paper at 60 $^{\circ}$ C, giving a catalyst loading of 1.0 mg cm⁻². The cathodic and anodic compartments were separated by a cation-exchange membrane (N117), and 1.0 M KCl and 1.0 M KOH aqueous electrolytes were circulated through the cathode and anode chambers, respectively, at a flow rate of 5 mL min⁻¹ using a peristaltic pump.

CO₂RR products quantification. The gaseous products were collected in a gas-tight sample bag and analyzed by gas chromatography (F60, Fuli) equipped with a thermal conductivity detector (TCD) using nitrogen as the carrier gas. The Faradaic efficiency (FE) of a gaseous product *i* was determined using the equation:

$$FE_i = \frac{Q_i}{Q_{\text{total}}} \times 100\% = \frac{n_i \times C_i \times v \times t \times F}{I \times t \times V_M} = \frac{n \times C_x \times v \times F}{I \times V_M}$$

where FE_{*i*} is the Faradaic efficiency for the gas product *i*; Q_{*i*} is the charge transferred for the product *i* formation; Q_{total} is the charge passed through the working electrode; n_{*i*} is the electrons transferred for reduction to a molecule product *i*; C_{*i*} is the volume fraction of the product *i* detected by GC; v is the outlet gas flow rate; t is the CO₂ electrolysis time; F is the Faradaic constant, 96,485 C mol⁻¹; I is the total current during CO₂ electrolysis; and V_M is the gas molar volume at room temperature, 24.5 L mol⁻¹.

Liquid products were collected from the catholyte, anolyte, and the condensate trapped from the gas outlet stream, and analyzed by ¹H NMR (Bruker Advance III 400 HD spectrometer). For quantification, a 500 μ L aliquot of each collected sample was taken to mix with 200 μ L D₂O containing 50 ppm (m/m) dimethyl sulfoxide (DMSO) as the internal standard. The same spectral acquisition parameters were used for all measurements to ensure complete relaxation and accurate quantification. The FEs of liquid products were then calculated by the following formula

$$FE_i = \frac{Q_i}{Q_{\text{total}}} \times 100\% = \frac{n_i \times C_i \times V \times F}{I \times t}$$

where FE_{*i*} is the Faradaic efficiency for the liquid product *i*; Q_{*i*} is the charge transferred for product *i* formation; Q_{total} is the charge passed through the working electrode; n_{*i*} is the electrons transferred for reduction to a molecule product *i*; C_{*i*} is the concentration of the product *i* in the catholyte gained by NMR; V is the volume of the catholyte; t is the CO₂ electrolysis time; F is the Faradaic constant, 96,485 C mol⁻¹; I is the total current during CO₂ electrolysis; and t is the CO₂ electrolysis time [2].

In situ ATR-SEIRAS measurements. *In situ* ATR-SEIRAS was performed on the ATR-SEIRAS spectrometer (INVENIO-R, Bruker). Pt foil and Ag/AgCl electrode (Gaossunion Co., Ltd.) was used as the counter electrode and reference electrode, respectively. Before performing the experiment, 5 sccm (standard cubic centimeter per minute) N₂ was used to purge the

optical path system for 5 h to reduce the impact of CO₂ (g) and H₂O (g) in the air. The background was taken in a CO₂-saturated electrolyte for each electrode. Later, 20 mL of electrolyte was bubbled with CO₂ for 30 min before the test. Electrochemical measurements were conducted on a potentiostat (CHI760f). Before spectrum acquisition, the catalysts underwent electrochemical reduction for 30 min.

***In situ* Raman spectroscopy measurements.** To investigate the evolution of catalyst structure and intermediates on the electrode surface during CO₂RR, *in situ* Raman spectra were acquired using a confocal Raman microscope (WITec Alpha 300R). For the analysis of catalyst structure changes, a 488 nm laser with a 600 grooves/mm and a 50×objective (Zeiss LD EC Epiplan-Neofluar Dic) was employed. Each spectrum was recorded with a 30-second acquisition time and 1 times of accumulation. The catalyst loading was 5 mg cm⁻², and the electrolyte consisted of 1.0 M KCl and KOH aqueous were circulated through the cathodic chamber and anodic chamber by peristaltic pumps at a rate of 5 mL min⁻¹, respectively. Before spectrum acquisition, the catalysts underwent electrochemical reduction for 30 min. For studying the behavior of intermediates, a 633 nm laser was used.

***Quasi-in situ* XAFS measurement.** The working electrodes were prepared by drop-casting the catalyst ink onto carbon paper. Prior to XAFS measurements, the catalyst electrodes were operated in a flow cell under CO₂ at different current density for 30 min. After electrolysis, the carbon paper electrodes were removed from the flow cell and immediately subjected to Cu and Zn K-edge XAFS data collection to preserve the post-reaction catalyst state as much as possible.

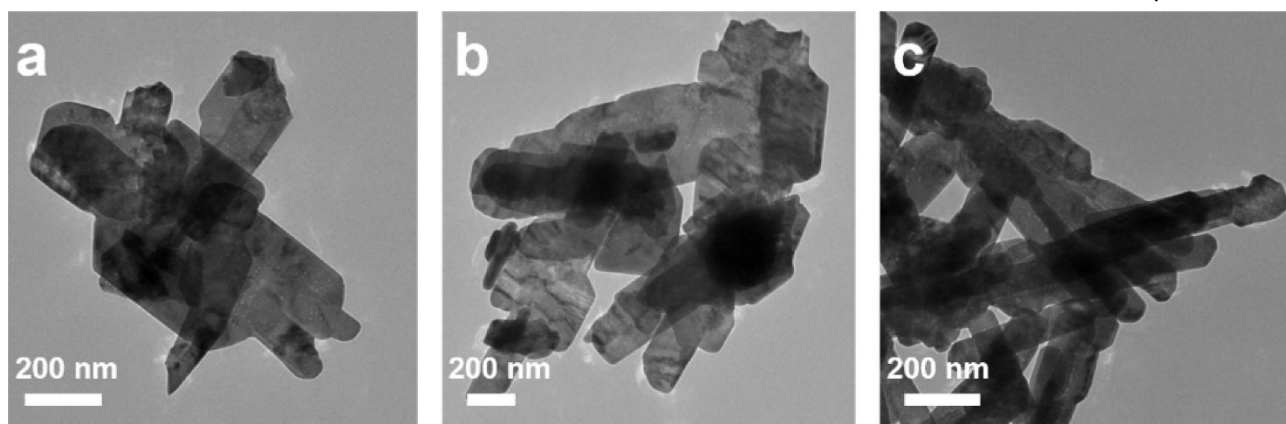


Figure S1. TEM images of (a) CuO NS, (b) 5% Zn-CuO NS, and (c) 20% Zn-CuO NS.

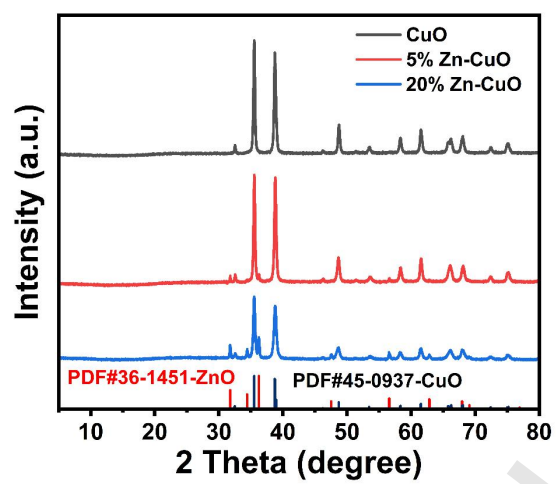


Figure S2. XRD patterns of CuO, 5% Zn-CuO NS and 20% Zn-CuO NS.

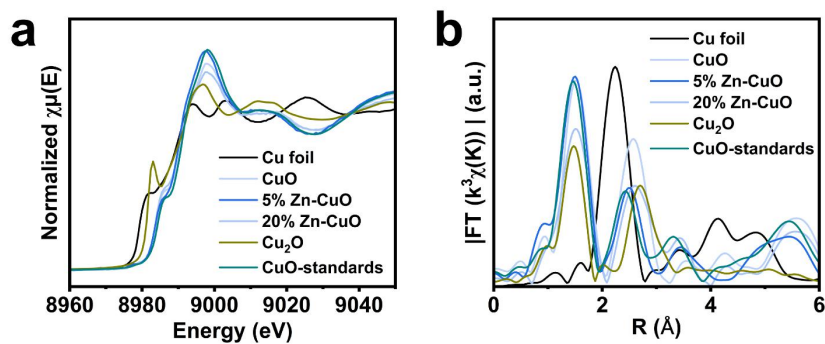


Figure S3. (a) Cu K-edge XANES spectra and (b) k^3 -weighted Fourier-transformed Cu K-edge EXAFS spectra in R space.

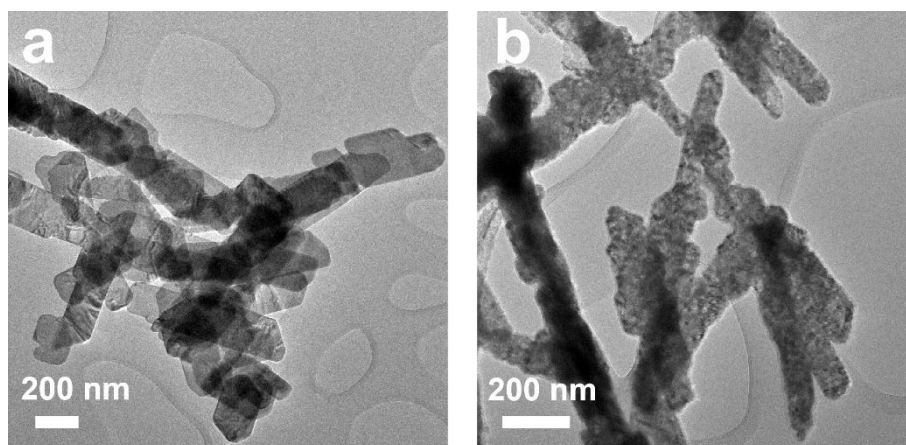


Figure S4. TEM images of (a) Cu NS and (b) Zn_{NP}-Cu NS.

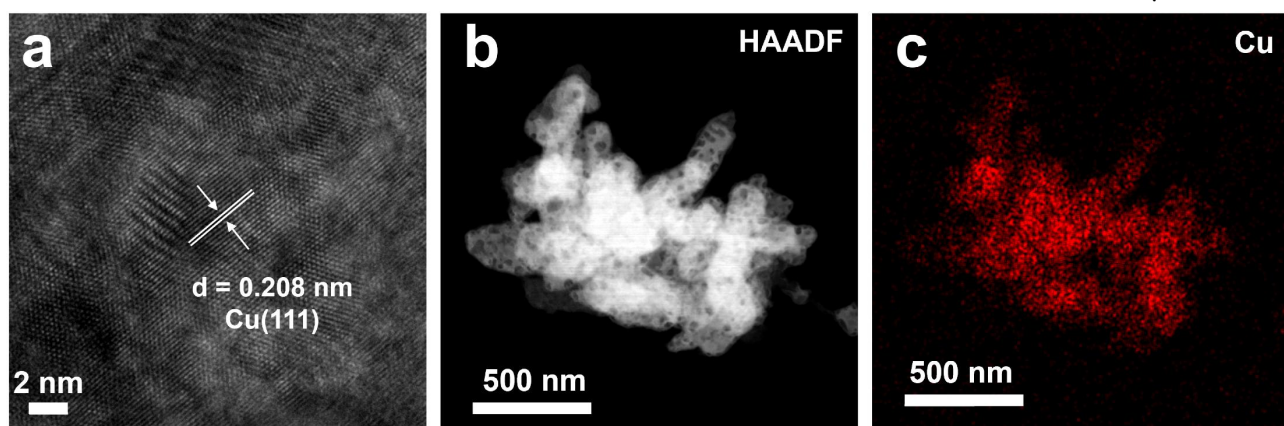


Figure S5. (a) HRTEM image, (b) HAADF-STEM image and (c) EDS mapping of Cu NS.

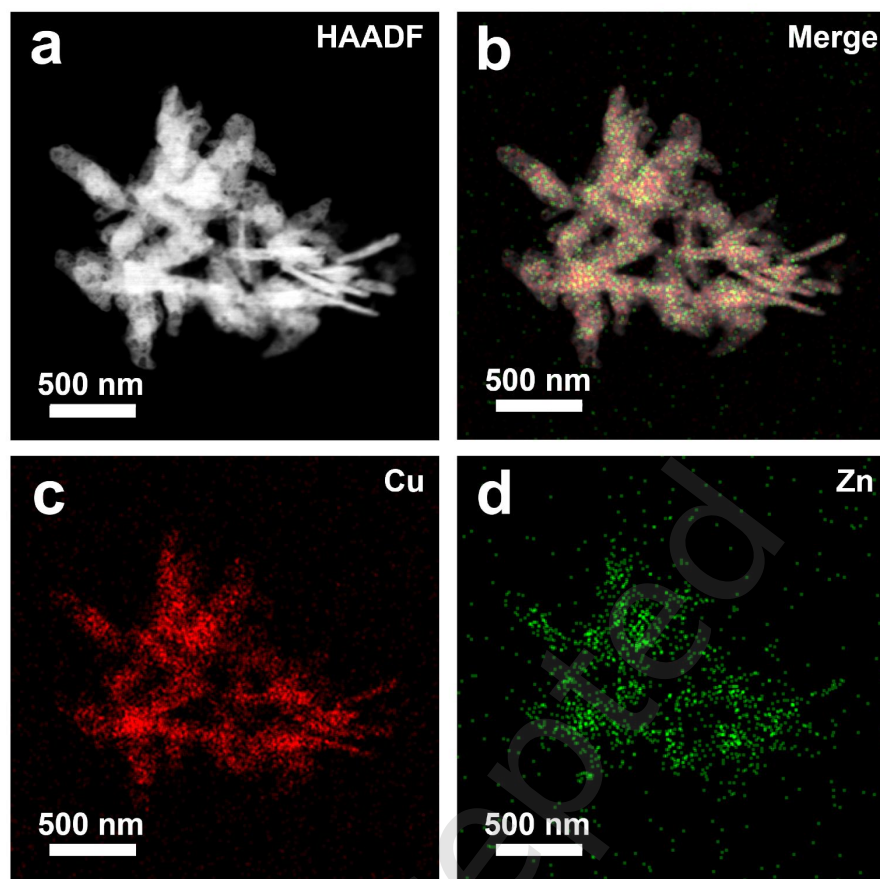


Figure S6. The EDS mappings of Zn_{NP}-Cu NS.

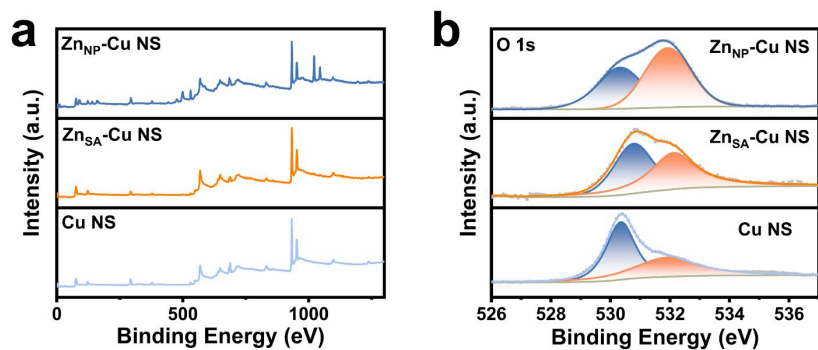


Figure S7. (a) XPS survey spectra and (b) high-resolution O 1s XPS spectra of Cu NS, Zn_{SA}-Cu NS, and Zn_{NP}-Cu NS.

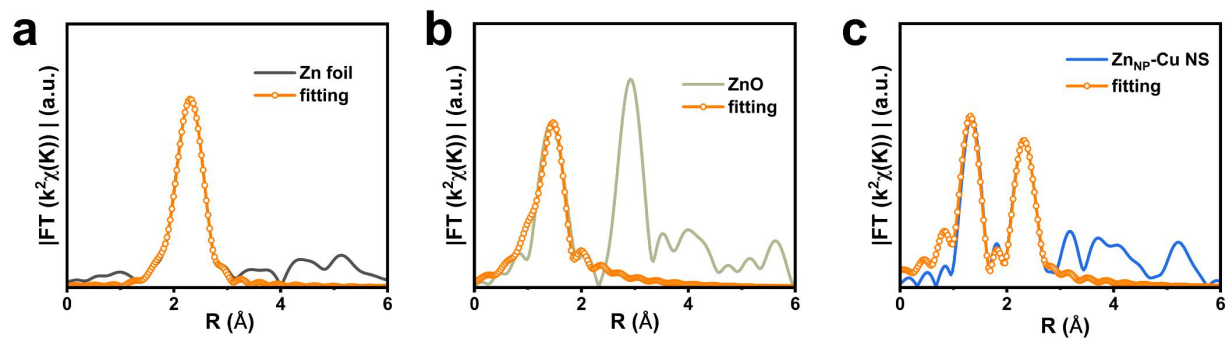


Figure S8. Zn K-edge EXAFS fitting results in R space for (a) Zn foil, (b) ZnO, and (c) Zn_{NP}-Cu NS.

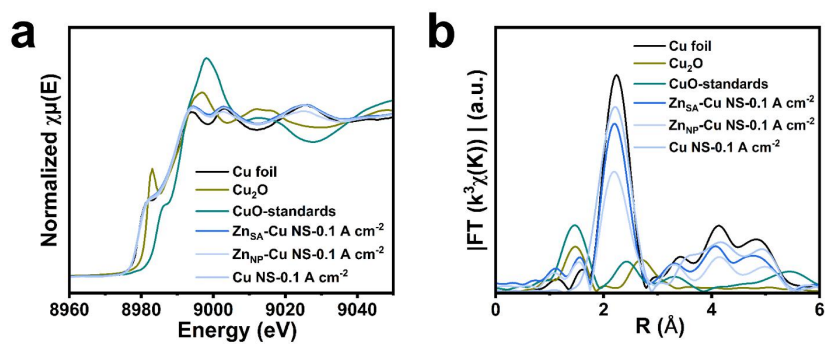


Figure S9. (a) Cu K-edge XANES spectra of Cu NS, Zn_{SA}-Cu NS, and Zn_{NP}-Cu NS after electrochemical reduction at 0.1 A cm⁻² under CO₂RR conditions. (b) Corresponding Fourier-transformed Cu K-edge EXAFS spectra in R space.

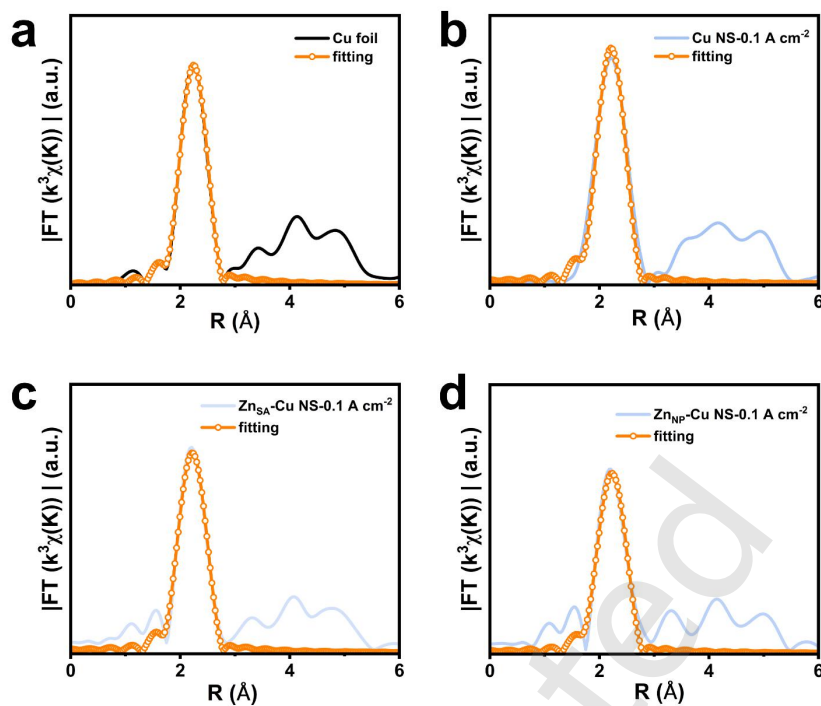


Figure S10. Cu K-edge EXAFS fitting results in R space for (a) Cu foil, (b) Cu NS, (c) Zn_{SA}-Cu NS, and (d) Zn_{NP}-Cu NS.

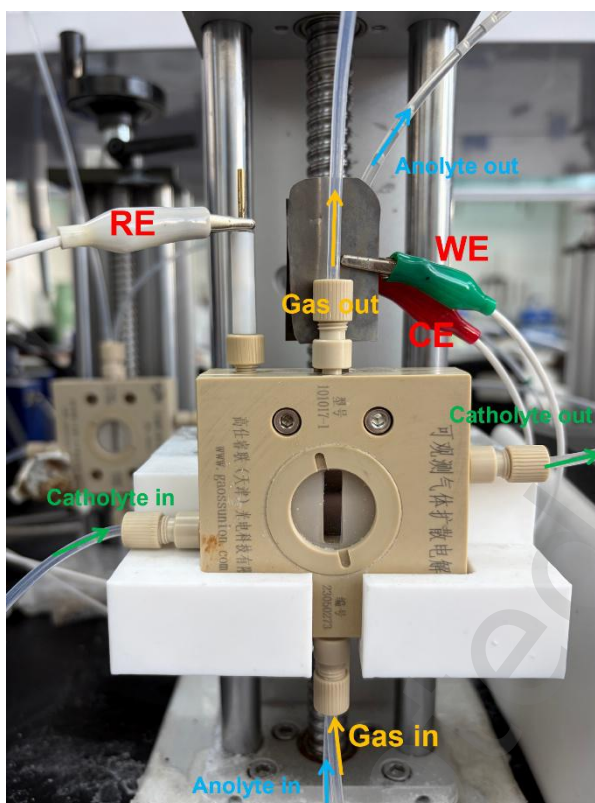


Figure S11. Photograph of the flow cell configuration used for CO₂RR measurements.

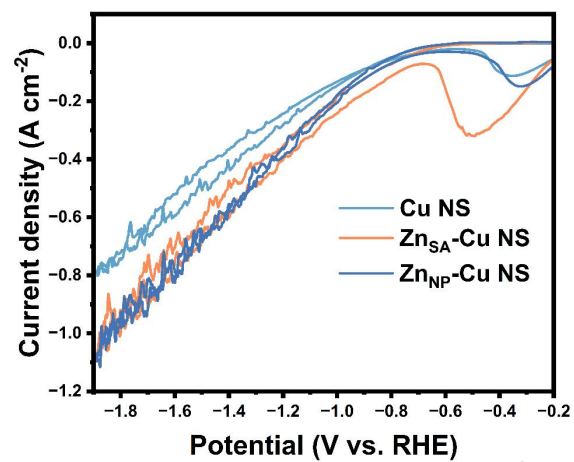


Figure S12. CV curves of Cu NS, Zn_{SA}-Cu NS, and Zn_{NP}-Cu NS under CO₂.

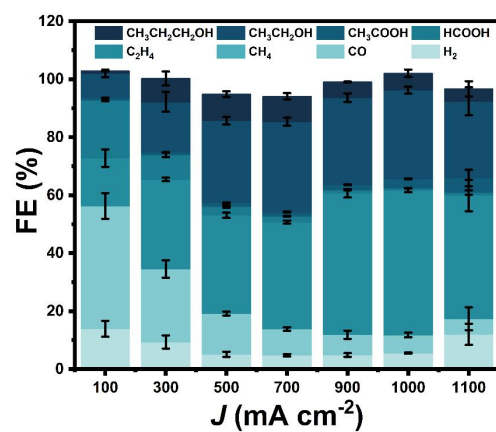


Figure S13. FE of all individually detected products over Zn_{SA}-Cu NS at different current density in 1.0 M KCl.

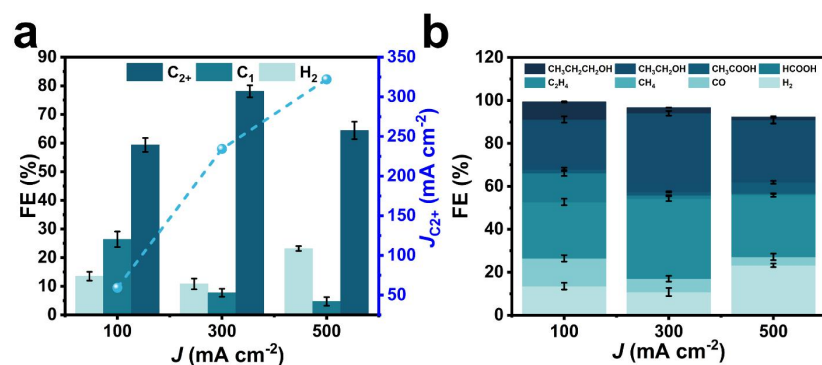


Figure S14. (a) FE of H₂, C₁, and C₂₊ products and the corresponding C₂₊ partial current density for Cu NS at different current density. (b) FE of all individually detected products over Cu NS at different current density in 1.0 M KCl.

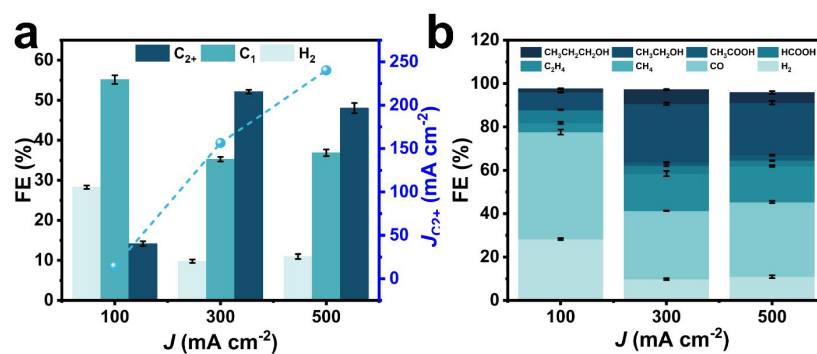


Figure S15. (a) FE of H₂, C₁, and C₂₊ products and the corresponding C₂₊ partial current density for Zn_{NP}-Cu NS at different current density. (b) FE of all individually detected products over Zn_{NP}-Cu NS at different current density in 1.0 M KCl.

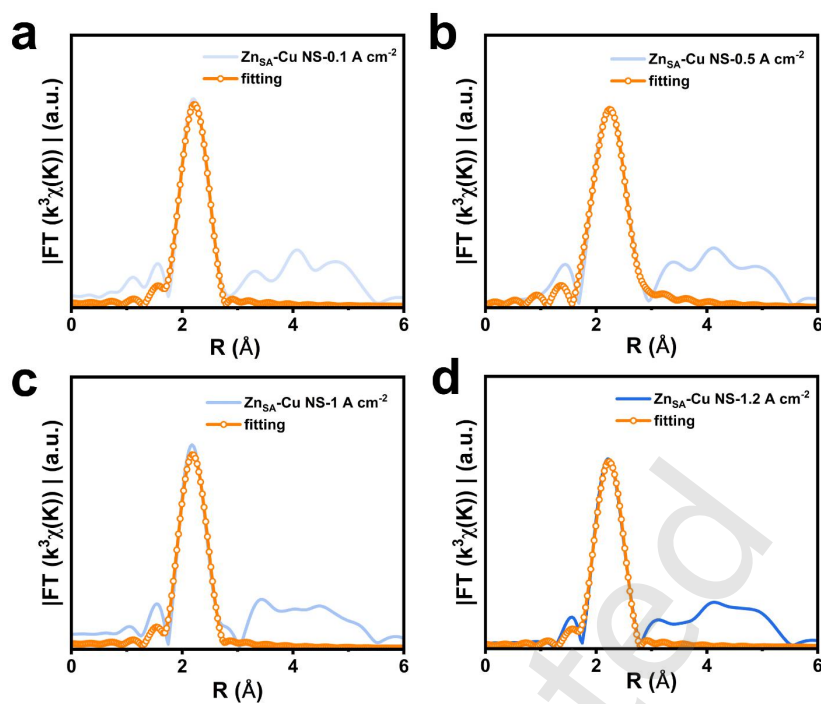


Figure S16. Cu K-edge EXAFS fitting results for Zn_{SA}-Cu NS after CO₂RR at (a) 0.1, (b) 0.5, (c) 1.0, and (d) 1.2 A cm⁻².

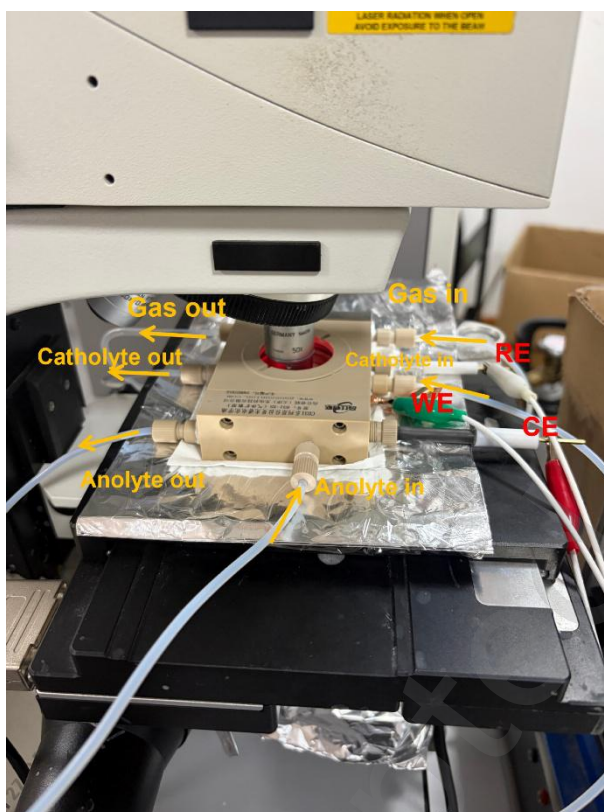


Figure S17. Photograph of the electrochemical cell for *in situ* Raman measurements.

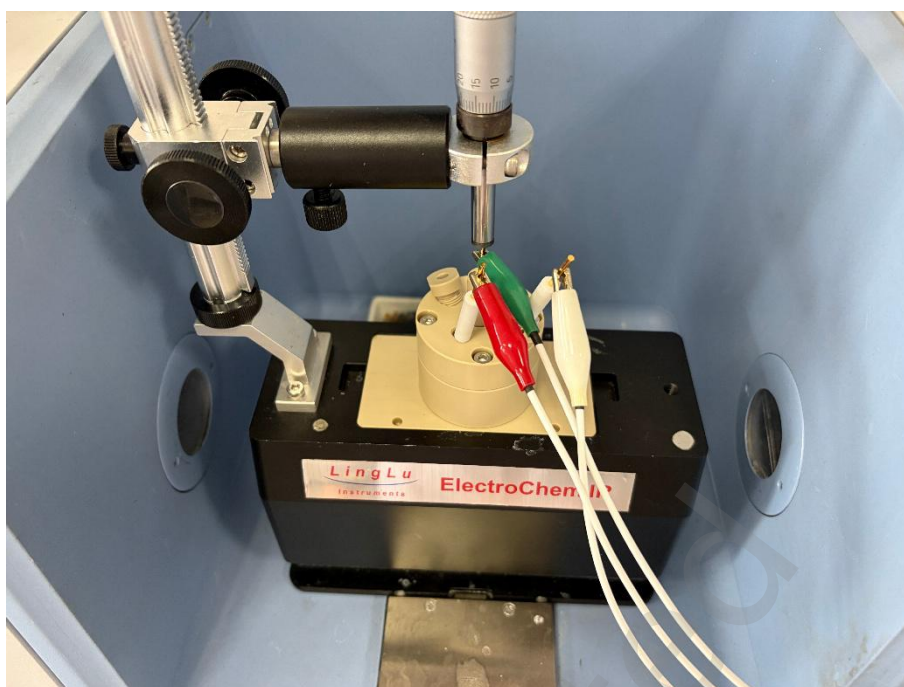


Figure S18. Photograph of the electrochemical cell for *in situ* ATR-SEIRAS measurements.

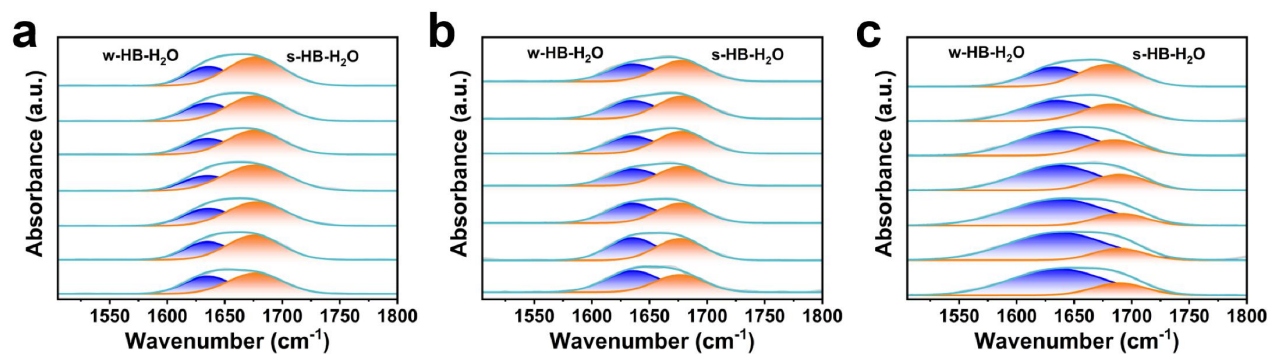


Figure S19. Deconvolution of the $\delta(\text{HOH})$ bending region in the *in situ* ATR-SEIRAS spectra of (a) Cu NS, (b) Zn_{SA} -Cu NS, and (c) Zn_{NP} -Cu NS. The lower- and higher-frequency components are assigned to w-HB- H_2O and s-HB- H_2O , respectively.

Table S1. Structural parameters extracted from the Zn K-edge EXAFS fitting. ($S_0^2=0.759$)

sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3} \text{ Å}^2)$	$\Delta E_0(\text{eV})$	R factor
Zn foil	Zn-Zn	6*	2.64	9.1±1.2	2.8±0.8	0.003
	Zn-Zn	6*	2.75	9.3±0.7		
Zn_{SA}-Cu NS	Zn-O	0.54	1.88	5.2±0.5	4.9±0.6	0.0017
	Zn-Cu	2.91	2.54	3.8±0.2		
Zn_{NP}-Cu NS	Zn-O	1.11	1.89	9.4±1.8	9.8±2.2	0.010
	Zn-Zn	5.85	2.60	8.3±2.7		
	Zn-Zn	4.95	2.70	9.9±1.9		
ZnO	Zn-O	6	1.91	4.7±0.4	2.9±0.7	0.019

S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

* This value was fixed during EXAFS fitting, based on the known structure.

Table S2. Structural parameters extracted from the Cu K-edge EXAFS fitting. ($S_0^2=0.821$)

sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3} \text{ Å}^2)$	$\Delta E_0(\text{eV})$	R factor
Cu foil	Cu–Cu	12*	2.54	8.4±0.4	4.9±0.6	0.003
Zn_{SA}-Cu NS 0.1 A cm⁻²	Cu–Cu	10.31	2.54	9.9±1.1	3.3±0.8	0.010
Zn_{SA}-Cu NS 0.5 A cm⁻²	Cu–Cu	9.99	2.55	9.6±1.5	5.2±1.7	0.007
Zn_{SA}-Cu NS 1.0 A cm⁻²	Cu–Cu	10.33	2.53	8.8±1.8	3.1±0.7	0.016
Zn_{SA}-Cu NS 1.2 A cm⁻²	Cu–Cu	10.21	2.54	9.0±0.9	4.2±1.4	0.007
Cu NS 0.1 A cm⁻²	Cu–Cu	11.21	2.54	9.7±1.6	2.7±0.4	0.009
Zn_{NP}-Cu NS 0.1 A cm⁻²	Cu–Cu	8.92	2.54	9.9±1.9	3.9±0.9	0.016

S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

* This value was fixed during EXAFS fitting, based on the known structure.

Table S3. CO₂RR performance of the Zn_{SA}-Cu NS, Zn_{NP}-Cu NS and Cu NS in flow cell.

Catalyst	J _{total} (mA cm ⁻²)	FE (%)								
		C ₃ H ₇ OH	CH ₃ COOH	C ₂ H ₅ OH	C ₂ H ₄	HCOOH	CH ₄	CO	H ₂	C ₂₊
Zn_{SA}-Cu NS	100	0.85	0.84	8.39	16.53	19.99	0	42.34	13.94	26.61
	300	8.06	0.80	17.46	30.90	8.50	0	25.18	9.38	57.22
	500	9.14	1.24	28.39	33.92	2.98	0	14.04	5.13	72.68
	700	8.72	1.46	31.17	36.88	2.01	0	9.04	4.82	78.23
	900	5.43	1.93	30.00	48.81	1.02	0	6.97	4.91	86.18
	1000	5.68	3.26	30.62	49.84	0.77	0	6.26	5.54	89.40
	1100	4.28	5.06	26.42	42.55	0.97	0	5.38	12.02	78.31
Zn_{NP}-Cu NS	100	1.59	0.28	8.03	4.26	5.82	0	49.34	28.28	14.17
	300	6.54	1.46	27.03	17.11	3.76	0	31.52	9.80	52.14
	500	4.71	2.53	24.22	16.59	2.46	0	34.43	10.96	48.04
Cu NS	100	8.17	1.78	23.19	26.23	13.45	0	12.96	13.52	59.37
	300	2.61	1.61	36.62	37.27	1.56	0	6.18	10.81	78.12
	500	1.39	5.23	29.03	28.76	0.73	0	3.97	23.19	64.41

Table S4. Comparison of CO₂ Electroreduction to C₂+ Products over Reported Electrocatalysts.

Electrocatalyst	Electrolyte	FE _{C2+} (%)	J _{C2+} (mA cm ⁻²)	C ₂ /C ₁	J (mA cm ⁻²)	Ref.
Zn_{SA}-Cu NS	1.0 M KCl	89.4	894	12.7	1000	This work
3D-CuAg-GDE	3.0 M KOH	82.04	565.18	8.2	689	[3]
PrO _{1.83} /CuO-2	1.0 M KOH	74.4	246	5.4	330	[4]
Dual-phase Cu	3.0 M KCl	80.52	322.08	10.68	400	[5]
Cu-400	0.5 M KHCO ₃	69.33	242.88	3.59	300	[6]
Yb ₂ /CuO _x	0.5 M K ₂ SO ₄ (pH = 7)	77	616	7	800	[7]
CeO _x /ZrO ₂ -Cu	1.0 M KCl	67.2	413.0	3.36	615	[8]

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