

Synergistic promotion of proton relay and *CO hydrogenation in Cu-Zn tandem catalysts for highly efficient electrocatalytic CO₂-to-CH₄ conversion

Zhixin Dai, Ruichao Bian, Yanping Qiu, Linping Li, Ning Li, Lei Ge(✉)

State Key Laboratory of Heavy Oil Processing, College of New Energy and Materials, China University of Petroleum Beijing, No. 18 Fuxue Rd., Beijing 102249, China

Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94908916>

<https://www.sciopen.com/journal/1998-0124> on Jun. 8, 2026

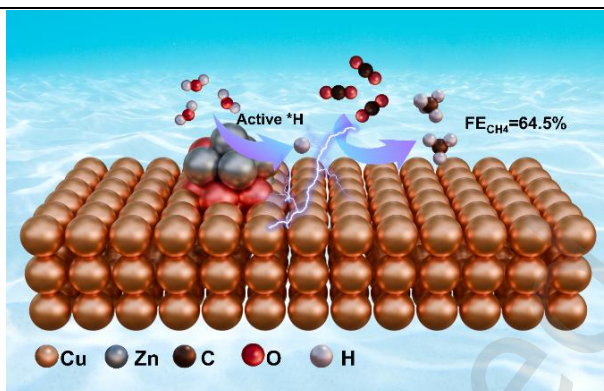
© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research*, **2025**, *18*, 94906990). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.

Synergistic promotion of proton relay and $^*\text{CO}$ hydrogenation in Cu-Zn tandem catalysts for highly efficient electrocatalytic CO_2 -to- CH_4 conversion

TABLE OF CONTENTS (TOC)



CuZn800@C was constructed via solvothermal method and utilizes the high-temperature volatility of zinc to prepare through calcination at different temperatures. achieves, which displays a high methane Faradaic efficiency of 64.5% and a remarkable partial current density of -551.3 mA/cm^2 at -1.7 V vs. RHE, along with excellent stability.

Synergistic promotion of proton relay and *CO hydrogenation in Cu-Zn tandem catalysts for highly efficient electrocatalytic CO₂-to-CH₄ conversion

Zhixin Dai, Ruichao Bian, Yanping Qiu, Linping Li, Ning Li, and Lei Ge  

State Key Laboratory of Heavy Oil Processing, College of New Energy and Materials, China University of Petroleum Beijing, No. 18 Fuxue Rd., Beijing 102249, China

Received: 20 March 2026; Revised: 8 May 2026; Accepted: 8 June 2026

 Address correspondence to gelei@cup.edu.cn, gelei08@sina.com

 **Cite this article:** *Nano Research*, 2026, 19, 94908916 <https://doi.org/10.26599/NR.2026.94908916>

ABSTRACT: The eight-electron transfer pathway required for CH₄ formation in eCO₂RR is kinetically slow, which leads to poor reaction selectivity. In this work, a CuZn-BDC-NH₂ precursor was synthesized via a facile solvothermal method, and a series of CuZn@C materials were prepared by calcination under varying temperature conditions (700°C, 800°C, 900°C) utilizing the high-temperature volatility of Zn. Among them, the CuZn800@C sample demonstrates the best CH₄ electro-reduction performance, achieving a methane Faradaic efficiency (FE) of 64.5% and a partial current density of -429.1 mA/cm² at a potential of -1.7 V vs. RHE, along with excellent stability, showing only a slight performance decline after a 24-hour test. Through in situ infrared spectroscopy and DFT calculations, electrocatalytic mechanism investigations reveal that Zn and Cu form a tandem reaction system. Zn sites promote water splitting to provide protons, while Cu sites reduce the energy barrier for *CO hydrogenation. Moreover, Zn and Cu can constitute dual active sites that enhance CO₂ adsorption, thereby boosting subsequent reactions. This work develops a new strategy for designing high performance Cu-based methanation catalysts.

KEYWORDS: methane production, tandem reaction system, Cu-Zn bimetallic catalyst, DFT calculations.

1 Instruction

Driven primarily by excessive CO₂ emissions from human activities, the escalating energy crisis and greenhouse effect have emerged as one of the most severe challenges to global sustainable development. [1-4]. Converting captured CO₂ into high value fuels and chemicals not only contributes to achieving carbon cycle balance, but also enables the storage of intermittent sustainable energy (such as solar and wind) in the form of chemical energy, making it a highly promising "two-for-one" solution [5-9]. Among various CO₂ conversion technologies, the electrocatalytic carbon dioxide reduction reaction, which uses renewable electrical energy as a driving force, can be carried out under ambient temperature and pressure in an aqueous solution [10-12]. Its widespread recognition as an ideal CO₂ resource utilization pathway originates from the precise control it offers over reaction rate and product selectivity, achievable by adjusting parameters like potential, electrolyte, and catalyst structure [13-15].

Among the diverse array of products generated from electrocatalytic CO₂ reduction, methane (CH₄) occupies a distinct niche due to its exceptionally high mass energy density [16]. As the primary component of natural gas, CH₄ is fully compatible with existing energy infrastructure and can be utilized directly as a clean fuel—a fact that underscores

its considerable importance [17]. The conversion of CO₂ to CH₄ is a complex, multi-step process involving the transfer of eight electrons and protons, which makes it kinetically demanding [18-19]. Consequently, the development of electrocatalysts capable of steering the CO₂ reduction reaction toward CH₄ with both high efficiency and high selectivity represent a central challenge and a key research objective in this field [20]. Among all explored catalysts, Cu-based materials are capable of not only producing multi-carbon products (e.g., ethylene, ethanol) but also driving the deep reduction of CO₂ to hydrocarbons like methane [21-23]. This unique capability stems from their moderate adsorption energy for the *CO intermediate, which facilitates subsequent C-C coupling or hydrogenation steps [24-27]. The distinctive property has established Cu-based materials as the primary platform for researching CO₂ reduction to CH₄ [28-30]. However, existing Cu-based catalysts still exhibit several drawbacks in selectively generating CH₄ [31]. Firstly, their Faradaic efficiency is usually low with a narrow potential window, making it difficult to maintain high selectivity over a broad potential range, as competing reactions producing by-products (especially hydrogen, ethylene and carbon monoxide) are severe; Secondly, the Cu-based catalysts suffer from insufficient stability, as active sites are prone to deactivation during the reaction due to oxidation, re-construction or carbon deposition [32-33]. On

a deeper level, the understanding of the key active site structures and reaction pathways on Cu surfaces that determine CH₄ selectivity remains unclear, which severely hinders the rational design of highly performance catalysts.

Researchers have addressed the limitations of copper-based materials in the eCO₂RR through various strategies, including morphology and nanostructure control [21, 34], alloying [35–37], oxide derived strategy [38, 39], constructing single atom alloys or dispersed sites [40, 41], surface modification and molecular regulation [42, 43], as well as tandem catalysis. Researches have revealed that doping with elements creates synergistic multi active sites on Cu, enabling atomic-scale cascade catalysis that enhances the CO₂ reduction reaction. Jin et al. [35] reported a breakthrough in atomic scale tandem catalysis via a Mo1Cu single atom alloy (SAA). This catalyst features three distinct sites within the Cu lattice: Mo atoms for H₂O dissociation to generate H, distal Cu atoms (Cu⁰) for CO₂ activation to CO, and adjacent Cu atoms (Cu^{δ+}) capturing these intermediates, thereby orchestrating the C-C coupling in an efficient atom scale cascade process. As a promising approach, bimetallic catalysts enable precise tuning of electronic structures via controlled formations like heterostructures, alloys, defects and surface modifications. Currently, researchers have synthesized various types of bimetallic catalysts, such as Ce [13], Co [44], Ag [45], Pd [46], La [28] and Zn [36], to enhance the performance of CO₂ electroreduction. Among them, Zn can regulate the electron occupancy of the Cu d orbitals and then effectively modulate the adsorption of reaction intermediates on the active copper sites, thereby enhancing the performance of electrochemical CO₂ reduction. Wan et al. [47] prepared core-shell and phase-separated CuO_x-ZnO nanowire (NW) catalysts, which were electrochemically reduced in situ into corresponding Cu-Zn bimetallic NWs. Density functional theory (DFT) simulations discovered that the phase separated Cu-Zn NWs presented a lower energy barrier for *COOH formation—the rate-determining step—compared to the core-shell structure, confirming their superior CO₂ reduction reaction (CO₂RR) activity. In the core-shell NWs, Zn leaching induced by strain from *COOH adsorption led to elemental redistribution, structural deformation and instability. Instead of employing premixed catalysts, Peerlings et al. [48] found that initially distinct CuO and ZnO phases underwent in-situ reconstruction during CO₂RR, leading to atomic level mixing. Cu promotes the reduction of ZnO, while the partially reduces ZnO, in turn, stabilizes the oxidation state of Cu. This modification suppresses ethylene formation while simultaneously promoting the production of H₂ and CO on Cu.

Therefore, leveraging the property of zinc to spill over at high temperatures, the CuZn-BDC-NH₂ sample was first synthesized and Cu-Zn bimetallic electrocatalysts with different zinc contents were then prepared by calcining at various temperatures. Among them, CuZn800@C sample presents outstanding methane electrocatalytic production performance, achieving a methane selectivity of 64.5% at a voltage of -1.7 V vs. RHE. DFT theoretical computations illustrate that the incorporation of zinc forms a tandem reaction system with copper, where Zn boosts water

splitting to generate a large number of protons. Under the influence of Zn, activation energy of the *CO hydrogenation reaction on Cu sites is significantly lowered. The synergistic effect of the Cu-Zn contributes to the excellent electrocatalytic performance. Additionally, CuZn800@C demonstrates notable stability, maintaining high level of catalytic performance after a 24-hour durability test.

2 Experimental

2.1 Chemicals

Cu(NO₃)₂ (99.0 % metals basis), Zn(NO₃)₂·6H₂O (99.0 % metals basis) and 2-Aminoterephthalic acid were purchased from Aladdin. KOH was provided by Shanghai Titan Technology Co., LTD. Nafion solution (5 wt %) and hydrophobic carbon paper were purchased from Suzhou Sinero Technology Co., LTD.

2.2 Synthesis of CuZn@C catalysts

First, CuZn-BDC-NH₂ was synthesized. The 2-aminoterephthalic acid (2.3 mmol) was dissolved in 15 ml of solvent (ethanol: DMF: DI = 1:1:1) to prepare Solution A. Then, the metal salts (2.6 mmol, Zn:Cu = 10:1) were dissolved in 15 ml of solvent (ethanol: DMF: DI = 1:1:1) to prepare Solution B. Solution B was added dropwise into Solution A with stirring for 30 minutes. The mixture was then reacted in an oven at 100°C for 24 hours. The product was collected by centrifugation and dried to obtain CuZn-BDC-NH₂. The collected powder was calcined in a tube furnace under an argon atmosphere at a heating rate of 5°C/min. It was first heated at 500°C for 3 hours, followed by further calcination at 700°C, 800°C, and 900°C, respectively. The resulting products were designated as CuZn700@C, CuZn800@C, and CuZn900@C accordingly. Under the same reaction conditions, Cu700@C, Cu800@C and Cu900@C were obtained without the addition of Zn. The synthesis methods for the Cu:Zn = 1:5 and Cu:Zn = 1:20 samples are the same as those for the other catalysts, differing only in the initial molar ratios of added Cu and Zn salts, which are 1:5 and 1:20, respectively.

3 RESULTS

3.1 Synthesis and characterizations

The Cu-Zn bimetallic CuZn800@C sample was obtained following the facile synthesis route illustrated in Fig. 1(a). Specifically, CuZn-BDC-NH₂ was first synthesized at room temperature, followed by calcination at 800 °C to yield CuZn800@C. Additionally, leveraging the volatility of Zn at high temperatures, CuZn700@C and CuZn900@C with different Zn contents were obtained by calcination at 700 °C and 900 °C. The mass percentages of elements in the materials were determined by ICP-OES (Table S1). The results demonstrate that CuZn700@C, CuZn800@C and CuZn900@C contain Cu at 5.91 wt%, 22.36 wt%, 32.77 wt%, and Zn contents are determined to be 46.02 wt%, 3.19 wt%, 1.45 wt%, respectively. This phenomenon displays that the relative contents of Zn and Cu elements can be regulated by adjusting the heat treatment temperature, thereby controlling the electrocatalytic performance. The XRD patterns shown in Fig. 1(b) reveal the phase composition of the bimetallic materials. For CuZn700@C, the diffraction peaks located at approximately 31.6°, 34.2°, 36.1°, 47.3°,

56.5°, 62.7°, 66.3°, 67.9° and 69.1° correspond to ZnO (JCPDS #36-0451). Moreover, relatively weak diffraction peaks belonging to Cu (JCPDS #04-0836) are observed at 42.9°, 50.4°, 73.7° and 89.4°. In CuZn800@C, CuZn900@C,

Cu700@C, Cu800@C and Cu900@C samples, no diffraction peaks of ZnO are observed, while only the characteristic peaks of Cu appear. Fig. 1(c) and Fig. S2 illustrate the TEM images of CuZn800@C,

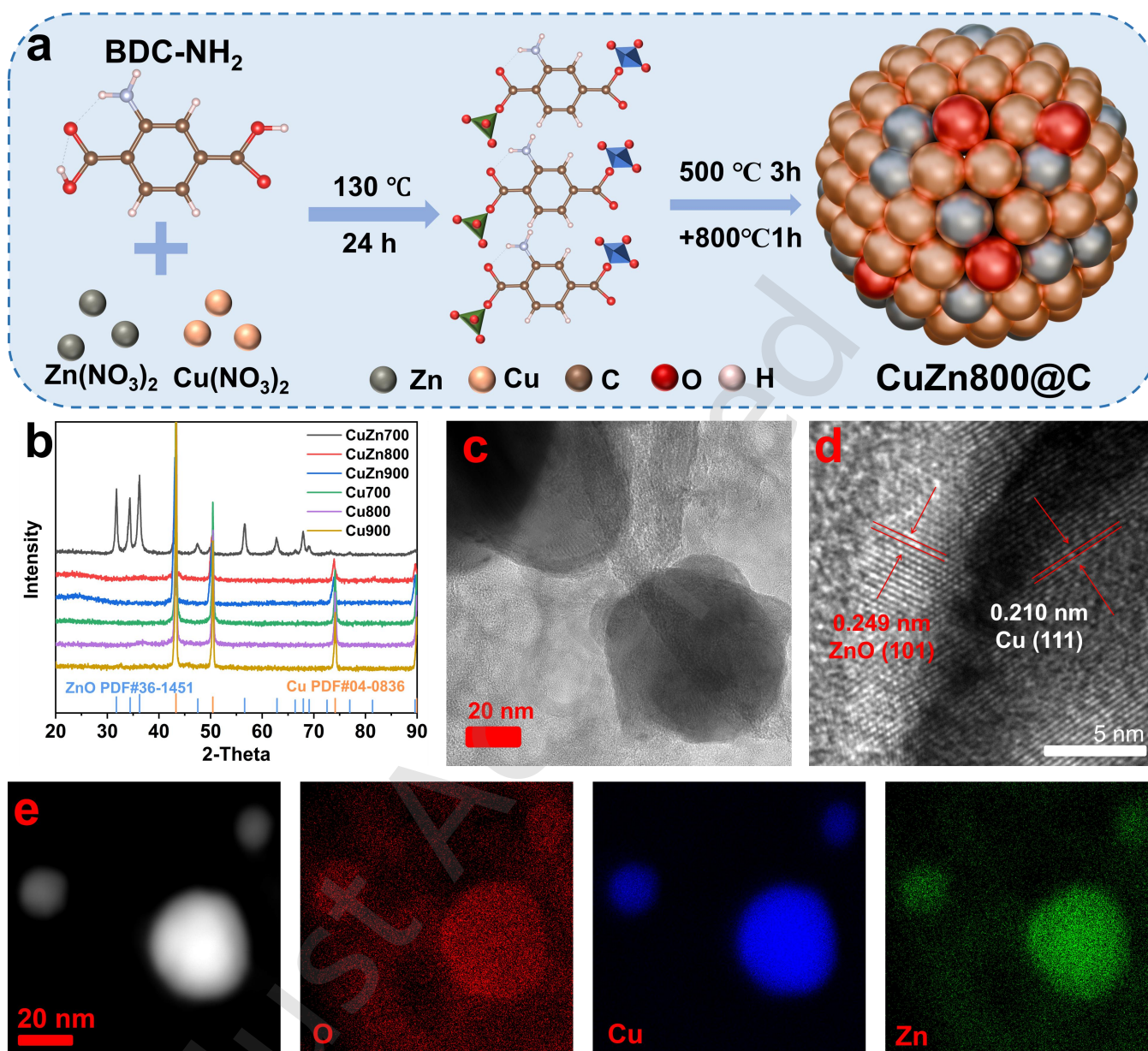


Fig. 1. (a) Synthetic pathway of bimetallic CuZn@C samples; (b) XRD patterns of CuZn700@C, CuZn800@C, CuZn900@C, Cu700@C, Cu800@C and Cu900@C; (c) TEM image of CuZn800@C; (d) HR-TEM image of CuZn800@C; (e) EDS elemental mapping images of CuZn800@C.

revealing that CuZn800@C primarily presents a nanosphere-like morphology. Fig. 1(d) shows an HR-TEM image featuring lattice fringes with spacings of 0.210 nm and 0.249 nm, assignable to the (111) plane of Cu and the (101) plane of ZnO, respectively. The lattice fringes of ZnO are not well-defined, indicating poor crystallinity of ZnO in CuZn800@C. Combined with the reduced Zn content, this phenomenon explains why no ZnO diffraction peaks are observed in the XRD patterns.

The TEM results demonstrate that CuZn800@C is composed predominantly of Cu with a small amount of ZnO. Fig. S1 presents the TEM results of CuZn700@C. As shown in Fig. S1a and S1b, the material consists of ZnO nanorods [49].

Lattice fringes matching the ZnO (101) plane and the Cu (111) can be observed in Fig. S1c. This result displays that CuZn700@C is a composite material of ZnO and Cu. Fig. S3 presents the TEM results of CuZn900@C. Fig. S3a and S3b present that the material exhibits nanosphere morphology. Lattice fringes attributable to the (111) plane of Cu can be observed in Fig. S3c. Additionally, crystallographic plane spacings belonging to the (101) plane of ZnO are also appeared on the surface of the nanospheres. Fig. S4 presents the TEM results of Cu800@C. The images in Fig. S4a and S4b illustrate that the material is composed of nanospheres. Meanwhile, the lattice fringes consistent with the (111) plane of Cu are observable in Fig. S4c. As shown by the EDS

mapping in Fig. 1(e), S1d, S3d, and S4d, all elements are uniformly distributed across the material.

The valence states of elements in the catalysts were characterized by XPS. Fig. 2(a) and (b) display the Cu 2p spectra of CuZn700@C, CuZn800@C, CuZn900@C and Cu800@C. The XPS peaks located at 932.7, 932.6, 932.6 and 932.5 eV are assigned to Cu 2p_{1/2} orbital of Cu⁰/Cu⁺ species, while the characteristic peaks at 952.5, 952.5, 952.5 and 952.4 eV correspond to Cu 2p_{3/2} orbital of Cu⁰/Cu⁺ [50]. The Cu Auger spectra shown in Fig. 2(c) are used to determine the specific oxidation state of Cu. In both CuZn800@C and Cu800@C, Cu presents a mixed oxidation state of +1 and 0, which may be attributed to partial surface oxidation of Cu upon exposure to air. Comparative analysis indicates that introducing Zn tends to cause a positive shift in the binding energy of Cu. Figs. 2(d) and (e) demonstrate the Zn 2p XPS spectra of CuZn700@C, CuZn800@C, CuZn900@C and ZnO@C. The XPS peaks located at 1022.1, 1022.0, 1021.9 and 1022.6 eV are assigned to Zn²⁺ species [51]. By comparing the binding energies, a trend opposite to that observed for the Cu spectra can be identified: as the Cu content increases, the Zn peak positions shift negatively. Collectively, the results point to a transfer of electrons from Cu to Zn in the catalyst. This electron transfer phenomenon suggests that the in-corporation of Zn can effectively tailor the electron density of the Cu sites, thereby favoring the adsorption of

reaction intermediates and ultimately improving the efficiency of the CO₂ reduction reaction. The Bader charge calculation results shown in Fig. S16 indicate that a charge of 0.58 eV is transferred from Cu to Zn, which is in agreement with the experimental results. Fig. S5 shows the O 1s XPS signals of CuZn700@C, CuZn800@C and CuZn900@C. The deconvoluted peaks, labeled O1, O2 and O3, correspond to adsorbed H₂O, surface -OH/O²⁻ species and Zn-O/Cu-O bonds, respectively [52]. The intensity of the O3 peak decreases with the reduction of Zn content, indicating that oxygen is primarily bonded to Zn. Combined with the Zn XPS spectra, this result confirms that Zn exists predominantly in oxide form. The C 1s XPS spectrum (Fig. 2(f)) can be deconvoluted into three peaks, attributable to C-C, C-O, and C=O bonds [53]. Fig. 2(g) presents the Raman spectra of CuZn700@C, CuZn800@C, CuZn900@C and Cu800@C. The measured ID/IG ratios are determined to be 0.95, 0.95, 0.86 and 0.9, respectively. Both the Raman and C 1s XPS results confirm the presence of a carbon layer [54]. N₂ adsorption-desorption isotherms in Fig. 2(h) give that CuZn800@C possesses a specific surface area of 889.9 m²/g, which is substantially greater than that of CuZn700@C (178.2 m²/g), CuZn900@C (55.7 m²/g) and Cu800@C (24.9 m²/g). Analysis indicates that the adsorption-desorption isotherm of the material can be classified as Type IV, with an H4-type hysteresis loop,

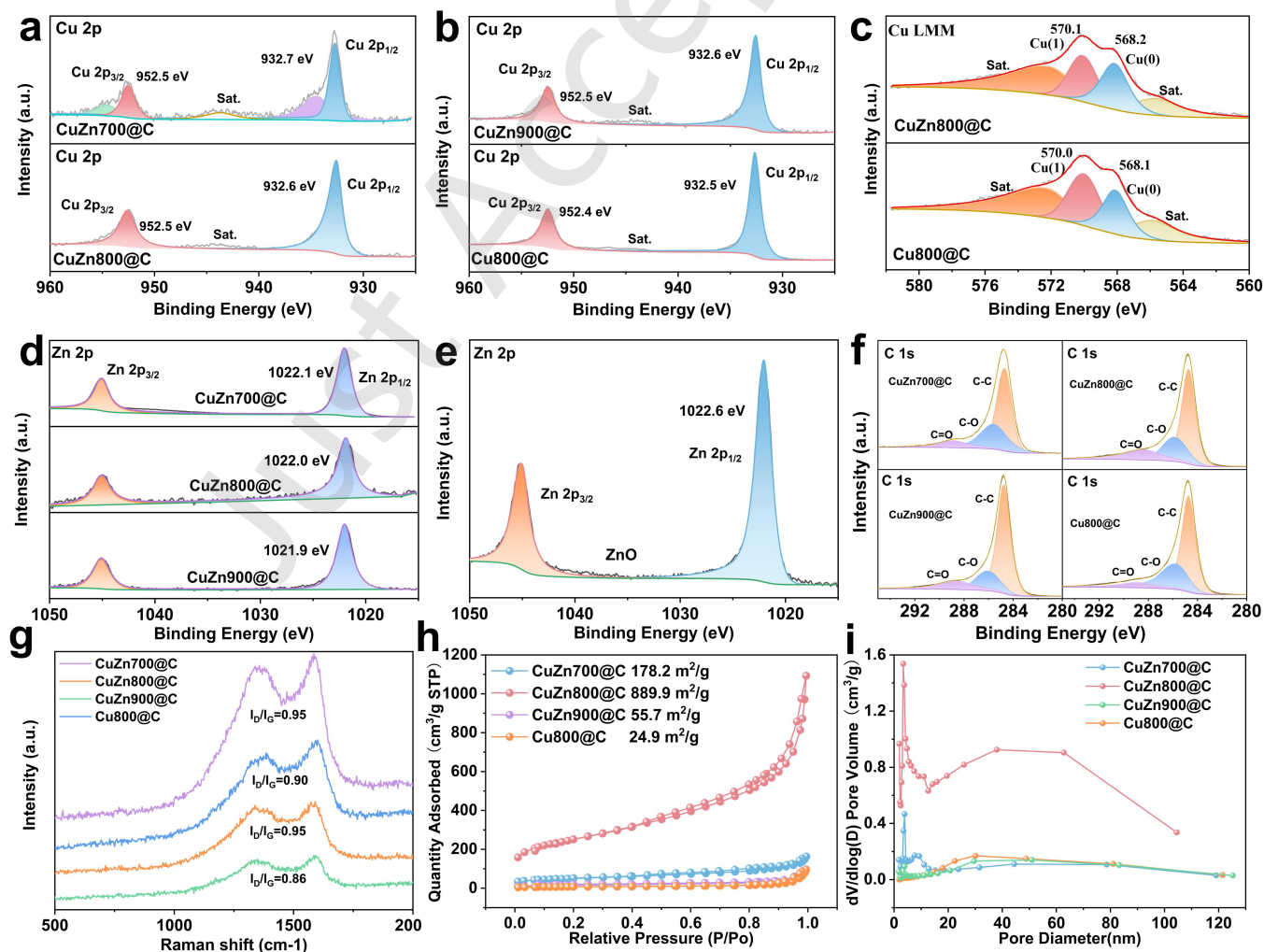


Fig. 2. Cu 2p XPS spectra of (a) CuZn700@C and CuZn800@C; (b) CuZn900@C and Cu800@C; (c) Cu LMM spectra of CuZn800@C and Cu800@C; Zn 2p XPS spectra of (d) CuZn700@C, CuZn800@C and CuZn900@C, (e) ZnO; (f) C 1s XPS spectra; (g) Raman spectra; (h) N₂ adsorption-desorption

isotherms; (i) The pore size distribution of CuZn700@C, CuZn800@C, CuZn900@C and Cu800@C.

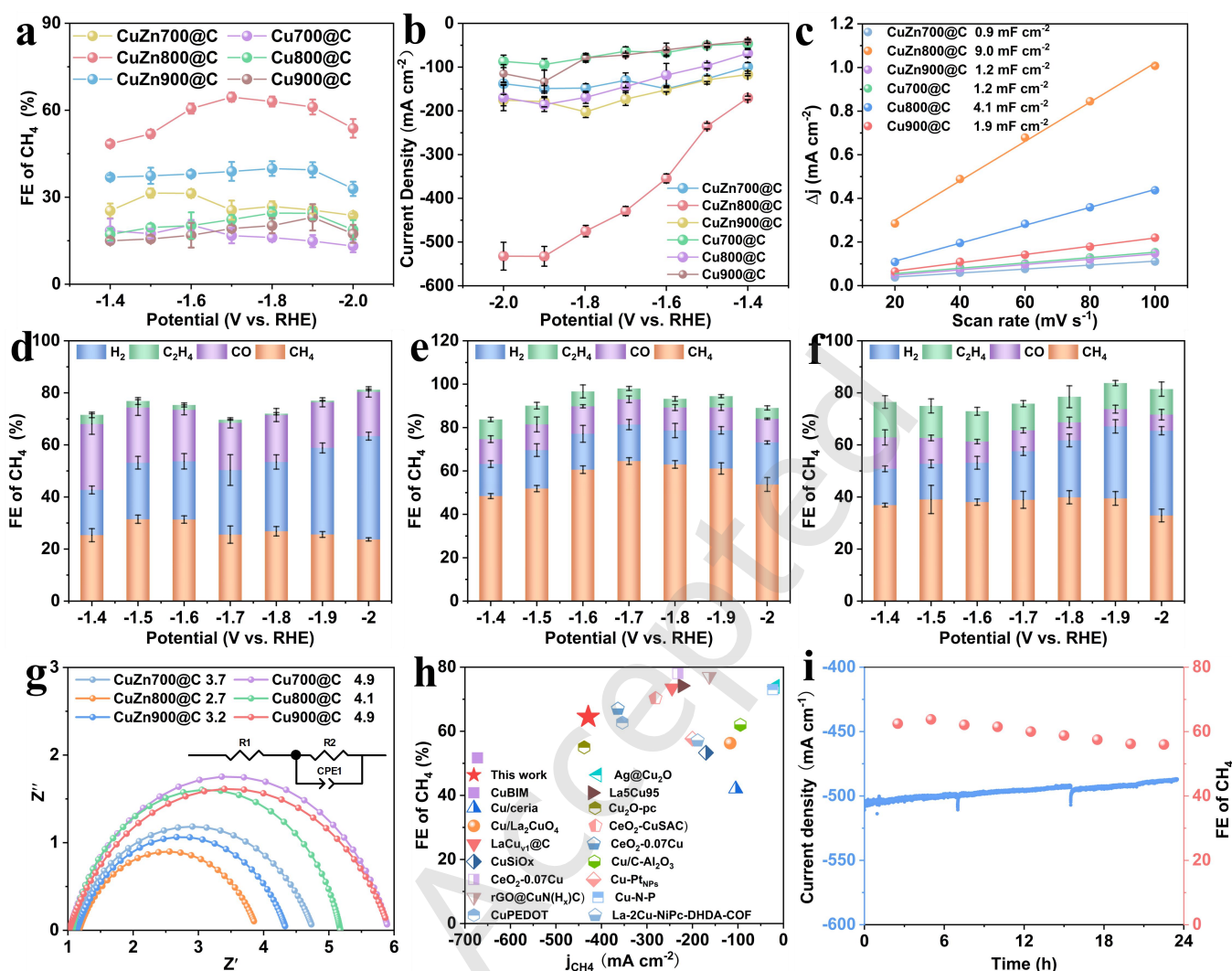


Fig. 3. (a) FE of CH₄; (b) The comparison of CH₄ partial current density; (c) C_{dl} of CuZn700@C, CuZn800@C, CuZn900@C, Cu700@C, Cu800@C and Cu900@C; (d) The FEs of products on CuZn700@C; (e) The FEs of products on CuZn800@C; (f) The FEs of products on CuZn900@C; (g) Nyquist plots of CuZn700@C, CuZn800@C, CuZn900@C, Cu700@C, Cu800@C and Cu900@C; (h) Evaluating the CH₄ current density and Faradaic Efficiency of different electrocatalysts; (i) Stability test of the CuZn800@C at -1.7 V (vs. RHE).

which is characteristic of typical mesoporous materials. Combined with the pore size distribution shown in Fig. 2(i), it can be confirmed that a significant number of mesopores exist within the catalyst. The abundant and well-developed pore network not only facilitates the mass transport of CO₂, but also effectively enhances CO₂ adsorption with the presence of numerous mesopores. These characteristics endow CuZn800@C with the fundamental attributions of a promising electrocatalyst for the eCO₂RR.

3.2 Electrochemical performance of CO₂RR

The electrochemical performance of CuZn800@C and the comparative catalysts was tested in a flow cell with 1.0 M KOH electrolyte. Fig. 3(a) presents a comparison of the Faraday efficiency for methane in the potential window of -1.4 to -2.0 V vs. RHE. It can be observed that CuZn800@C gives electrocatalytic performance of methane production far exceeding that of other comparative samples. At a potential of -1.7 V, it achieves a methane selectivity of 64.5%, while the highest FE_{CH₄} values for CuZn700@C, CuZn900@C, Cu700@C, Cu800@C and Cu900@C are determined to be

31.4%, 39.8%, 20.4%, 24.5% and 23.0%, respectively. Fig. 3(b) illustrates the comparison curves of the methane partial current density for each material. CuZn800@C demonstrates the most superior electrocatalytic performance with a high partial current density of -429.1 mA/cm² under a constant potential of -1.7 V vs. RHE, significantly exceeding that of the other comparative materials. Figs. 3(d), 3(e), 3(f) and S6 respectively present the detailed product distribution for CuZn700@C, CuZn800@C, CuZn900@C, Cu700@C, Cu800@C and Cu900@C. Comparing the hydrogen selectivity of CuZn800@C and Cu800@C leads to the conclusion that an appropriate Zn content can effectively suppress the competing hydrogen evolution reaction (HER) reaction. Additionally, samples with feedstock ratios of Cu:Zn=1:5 and Cu:Zn=1:20 were synthesized for comparison (Fig. S7), with their FE_{CH₄} being 49.6% and 59.6%, respectively. The comparative experiments demonstrate that Cu:Zn=1:10 is the optimal feedstock ratio.

In an effort to understand the factors driving the exceptional catalytic activity, the electrochemical active

surface area (ECSA) metric was employed to evaluate the samples [55]. In simple terms, the ECSA is directly proportional to the double-layer capacitance [56]. Typically, the double-layer capacitance is measured to reflect the electrochemically active surface area, with a higher double-layer capacitance value indicating a larger ECSA. Fig. 3(c) displays the C_{dl} plot, CuZn800@C displays a C_{dl} of 9.0 mF cm^{-2} , which is the highest among the six tested materials. It is 10 times that of CuZn700@C (0.9 mF cm^{-2}), 1.5 times that of CuZn900@C (1.2 mF cm^{-2}) and 2.2 times that of Cu800@C (4.1 mF cm^{-2}). The far superior ECSA of CuZn800@C also accounts for its high current density. Fig. S9 presents the ECSA-normalized partial current density curves of CuZn800@C and Cu800@C. The normalized current density of CuZn800@C is higher than that of Cu800@C, demonstrating that the introduction of Zn enhances the intrinsic catalytic activity of the catalyst. As another key indicator of electrochemical performance, the EIS data presented in Fig. 3(g) provide critical insights into the charge transfer characteristics of the materials. By fitting the data points obtained from the EIS measurements, the charge transfer resistance of each material was determined [57]. The charge transfer resistance (R_{ct}) of CuZn800@C is determined to be 2.7Ω , which is lower than that of CuZn700@C (3.7Ω), CuZn900@C (3.2Ω), Cu700@C (4.9Ω), Cu800@C (4.1Ω) and Cu900@C (4.9Ω). Fig. S10 presents the Bode plots of CuZn800@C measured at various potentials. The high-frequency region relates to electron transfer within the catalyst, while the low-frequency region corresponds to charge transfer at the electrolyte-catalyst interface. The clear trend in the low-frequency phase angle, compared to the minimal change at high frequencies, indicates that the dominant charge-transfer resistance arises from the interface rather than the catalyst bulk. In the Bode plot, the low-frequency ($1\text{--}10 \text{ Hz}$) and mid-frequency ($10\text{--}10^2 \text{ Hz}$) regions correspond to the kinetics of the Volmer and Heyrovsky steps, respectively, whereas the Tafel step, which does not involve electron transfer, cannot be directly observed by EIS. At lower potentials, sluggish Heyrovsky kinetics result in accumulated H, which holds the Volmer step near equilibrium and limits electron transfer. As the potential becomes more negative, H species is consumed by CO_2 reduction intermediates to form CH_4 , disrupting the Volmer equilibrium. This result is evidenced by a distinct shift of the phase angle peak to higher frequencies along with decreased peak intensity, indicating faster CO_2 reduction kinetics, which is in agreement with experimental observations. Clearly, the fast electron transfer efficiency and high ECSA of CuZn800@C are the key reasons for its superior performance [58, 59]. Fig. 3(h) and Table S2 compare the electro-catalytic performance of the catalyst in this work with that of other previously reported methane catalytic materials. Overall, CuZn800@C demonstrates outstanding performance in terms of FE_{CH_4} and partial current density. In addition to excellent performance, the ability to stably catalyze CO_2 reduction over extended periods is also crucial for an outstanding electrocatalytic CO_2 reduction catalyst. A long-term stability test was conducted, as shown in Fig. 3(i), where the reaction was performed at a potential of -1.7 V vs. RHE for 24 hours. Throughout the entire test,

both the current density and the FE for methane demonstrate slight decrease, indicating relatively excellent stability.

To furthermore explore whether the properties of the material changed after the reaction, additional characterization was performed on CuZn800@C following the 24-hour test. Fig. S11 presents the XRD pattern of CuZn800@C after the stability test. No new phase formation is observed after the prolonged reaction, and the material remains as metallic copper. Fig. S12 displays the XPS spectra used to verify whether the elemental states in the material changed after the reaction. The comparison reveals that the oxidation states of Cu and Zn remain unchanged even after 24 h testing. Fig. S13 presents a comparison of the SEM images prior to and following the reaction. In Fig. S13a, the material can clearly be seen as stacked nanoparticles. After 24 hours of reaction (Fig. S13b), slight agglomeration of the material is observed, but it still overall exhibits the characteristics of nanoparticles. Fig. S14 gives the TEM characterization and EDS mapping images after the stability test. It can be observed that lattice fringes belonging to Cu (111) and ZnO (101) are still visible in the material after the reaction. Given that ZnO is highly susceptible to in situ reduction or electrolyte leaching at the strong reduction potential of -1.7 V vs. RHE, the ICP-OES analysis was conducted on the electrolyte after stability testing (Table S1). The electrolyte contains 0.0007 mg of Zn, while the Zn content on the electrode surface is 0.0128 mg . This phenomenon indicates that the Zn content in the catalyst remains stable even after prolonged testing.

Throughout the material, the elements also present a uniform distribution. Above results demonstrate that the synthesized material not only possesses excellent methane catalytic performance, but also maintains its material properties unchanged during prolonged stability testing, exhibiting remarkable stability.

3.3 Electrocatalytic CO_2 reduction mechanism investigation

To investigate the reaction process of electrocatalytic conversion of CO_2 into CH_4 , in situ infrared technology was applied to detect the intermediates involved. As shown in Fig. 4(a) and S15, the in-situ FT-IR spectrum demonstrates characteristic peaks corresponding to key reaction intermediates. The FT-IR spectrum displays characteristic bands at 1495 cm^{-1} , which can be assigned to the C–O stretching vibrations of the $^*\text{OCH}_3$ intermediate [60]. The band observed at 1214 cm^{-1} corresponds to the C–O stretching mode of $^*\text{COOH}$ [61]. A band at 1620 cm^{-1} is attributed to the H–O–H bending mode of adsorbed H_2O [37]. Additionally, the distinct feature at 1672 cm^{-1} is assigned to the C–O stretching vibration of the $^*\text{CHO}$ [62]. Among these intermediates, $^*\text{OCH}_3$ and $^*\text{CHO}$ are identified as key intermediates in the electrochemical CO_2 reduction to methane. The peaks located at 1318 cm^{-1} and 1356 cm^{-1} are associated with the C–O stretching vibrations of CO_3^{2-} and HCO_3^- [63]. As observed in the spectra, the intensity of the peak corresponding to CO_3^{2-} increases with the applied voltage, whereas that assigned to HCO_3^- decreases. This trend can be explained by the accelerated reaction kinetics

on the material surface under higher voltages, which boosts water dissociation and leads to an elevated local concentration of OH^- . As a result, HCO_3^- is progressively

converted into CO_3^{2-} , which is consistent with the potential-dependent transformation of surface adsorbed carbonate species

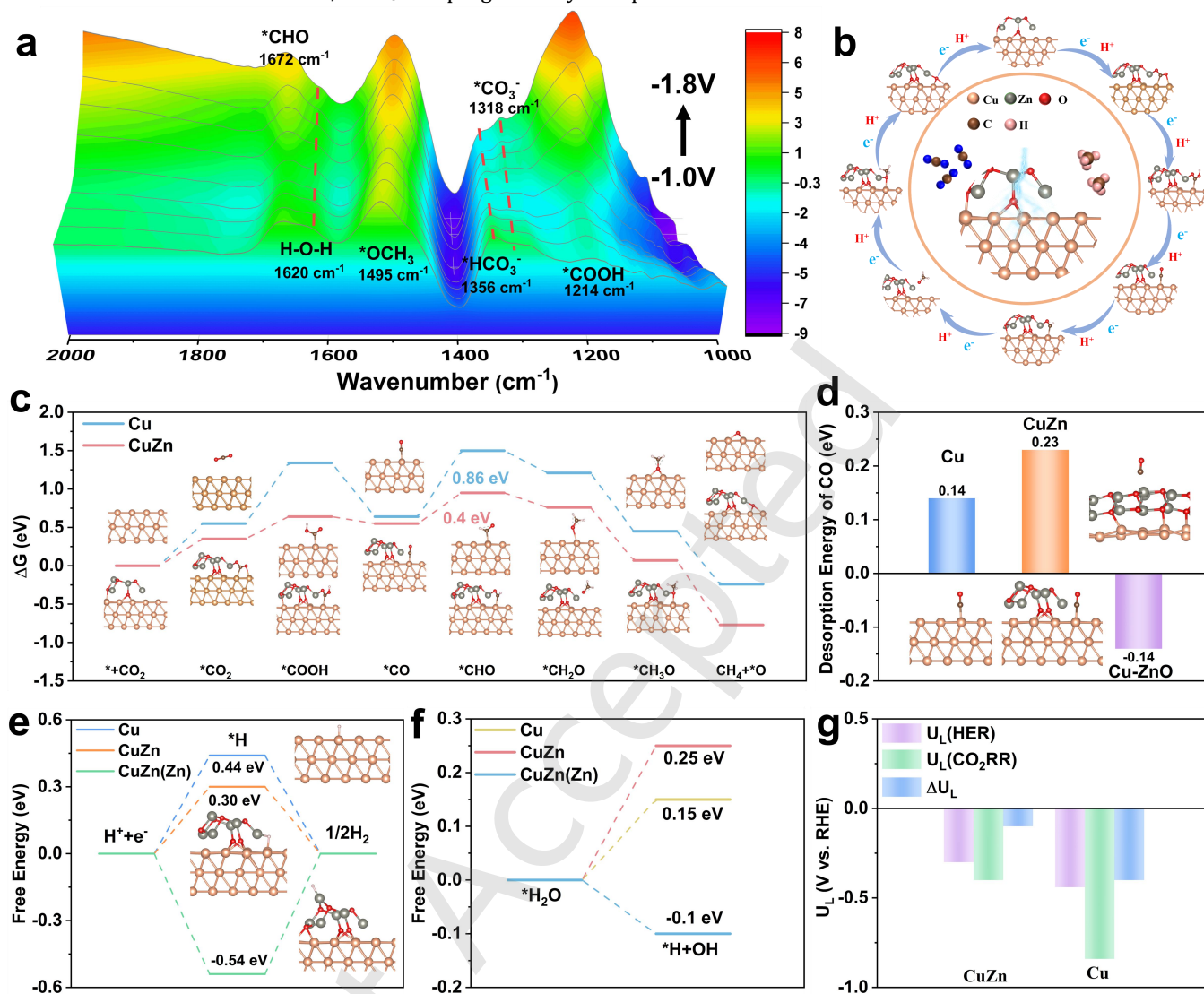


Fig. 4. (a) In-situ ATR-FTIRS spectrum of CuZn800@C; (b) Reaction pathway diagram of CuZn800@C; (c) ΔG for CO₂ reduction to CH₄ on Cu and CuZn; (d) Desorption energy of CO on Cu, CuZn and Cu-ZnO; (e) H₂ free energy profiles; (f) Dissociation energy of water on Cu, CuZn and Cu-ZnO; (g) U_L(HER), U_L(CO₂RR) and ΔU_L of Cu and CuZn.

evidenced by infrared spectroscopy. On the basis of the in situ FTIR results, it is evident that the pathway for CO₂ electro-reduction to methane on CuZn800@C proceeds as follows: $^*\text{CO}_2 \rightarrow ^*\text{COOH} \rightarrow ^*\text{CO} \rightarrow ^*\text{CHO} \rightarrow ^*\text{CH}_2\text{O} \rightarrow ^*\text{CH}_3\text{O} \rightarrow ^*\text{CH}_4$ (Fig. 4(b)) [64, 65].

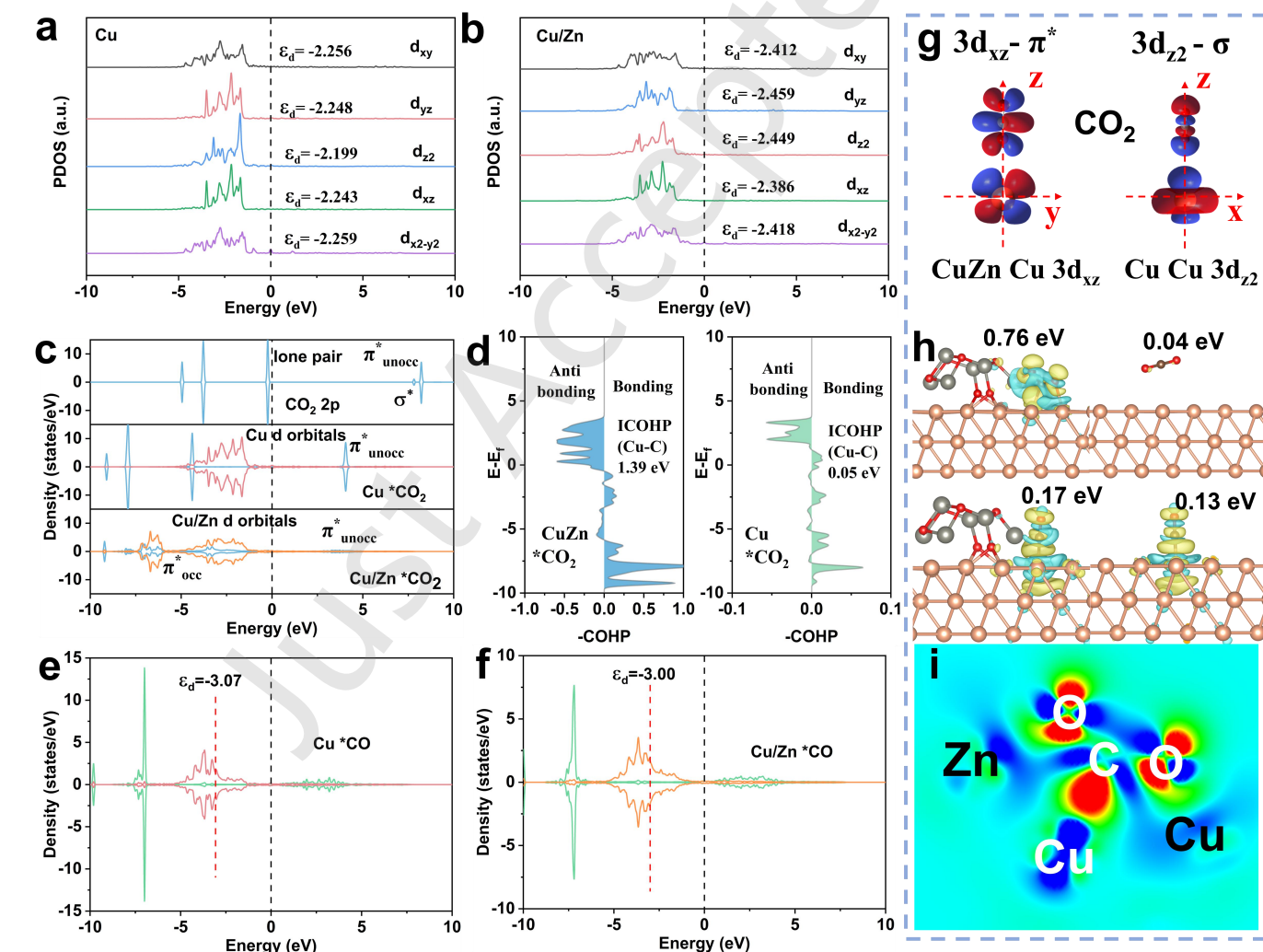
To further investigate the impact of Zn on the catalytic kinetics of CO₂RR on Cu, DFT theoretical calculations were performed to elucidate the reaction kinetics. Based on the characterization results from XRD and TEM, ZnO clusters on the Cu (111) crystal plane were constructed to simulate the CuZn. For comparison, models of Cu (111) (named Cu) and a heterostructure of Cu (111) and ZnO (101) were also constructed (Figs. S16 and S17). Guided by in situ infrared spectroscopy, the Gibbs adsorption free energy of each reaction intermediate was also calculated. Fig. 4(c) demonstrates the results of the volcano plot calculations. The rate-determining step on both Cu and CuZn is $^*\text{CO} \rightarrow ^*\text{CHO}$ with an energy barrier of 0.86 eV for the former and 0.4 eV for the latter. The conversion of CO₂ to CH₄ proceeds

via the hydrogenation of $^*\text{CO}$ to $^*\text{CHO}$, which is a pivotal step in the mechanism. The marked lowering of the reaction energy barrier for $^*\text{CO}$ hydrogenation on Cu sites, achieved by Zn introduction, directly enhances the catalytic efficiency toward methane production. Furthermore, the introduction of Zn can also form dual sites with Cu, thereby promoting the adsorption of CO₂. This phenomenon is specifically manifested as $\Delta G_{\text{CO}_2} = 0.55$ eV on Cu and $\Delta G_{\text{CO}_2} = 0.38$ eV on CuZn. The promoting effect of Zn on the hydrogenation reaction at Cu sites is also evident in the step $^*\text{CO}_2 \rightarrow ^*\text{COOH}$, where the energy profile decreases from 0.79 eV to 0.26 eV. Therefore, Zn can significantly enhance the hydrogenation reactions on Cu, thereby promoting the reduction of CO₂ to CH₄ on CuZn. As mentioned earlier, the hydrogenation of $^*\text{CO}$ to $^*\text{CHO}$ is a critical step in methane formation. Therefore, the particularly crucial. If the adsorption capacity is weak, $^*\text{CO}$ tends to desorb and form gaseous CO. Fig. 4(d) provides the calculated CO desorption energies on Cu, CuZn and Cu-ZnO. The desorption energy on CuZn is 0.23 eV, while that on

Cu is 0.14 eV. Thus, Zn can enhance the adsorption of the *CO on Cu, consequently promoting its catalytic performance. Furthermore, in the constructed Cu-ZnO structure, the desorption of *CO is a thermodynamically favorable reaction, thus promoting the generation of CO. This is also in agreement with the results shown in Fig. 3(d). HER is a competitive reaction to methane formation. Fig. 4(e) presents the calculated volcano plots for HER on Cu, CuZn (Cu) and CuZn (Zn). The ΔG for *H on Cu is 0.44 eV, site in CuZn is 0.30 eV, and on the Zn site in CuZn is -0.54 eV. In comparison, the Zn site in CuZn is not favorable for HER, the introduction of Zn accelerates hydrogen generation on the Cu site, which contradicts experimental findings. Therefore, the dissociation energy of H₂O on Cu, CuZn (Cu) and CuZn (Zn) was calculated (Fig. 4(f)). The dissociation energies of H₂O on Cu, CuZn (Cu) and CuZn (Zn) are 0.15 eV, 0.25 eV and -0.1 eV, respectively. It can be clearly seen that the introduction of Zn suppresses the dissociation of H₂O on Cu to some extent (0.25 > 0.15). Therefore, although the Cu sites in CuZn favor H₂ production, the addition of Zn can suppress

facilitating the CO₂ reduction reaction. Moreover, it can be observed that the H₂O dissociation energy on the Zn sites in CuZn is as low as -0.1 eV, which is highly favorable for H₂O dissociation. Meanwhile, H₂ generation on the Zn sites of CuZn is unfavorable. Therefore, it can be concluded that Zn in CuZn promotes the dissociation of H₂O, thereby supplying protons for hydrogenation reactions on the Cu sites. The synergy between the dual sites enhances the electro-reduction of CO₂ on CuZn. The thermodynamic limiting potential difference (ΔU_L) between the two reactions can be used to compare the selectivity of eCO₂RR versus HER. A more positive ΔU_L value typically indicates higher selectivity toward eCO₂RR. Fig. 4(g) illustrates a comparison of the ΔU_L values on CuZn and Cu. The ΔU_L on CuZn is -0.1 V, which is greater than the -0.4 V on Cu, indicating that CuZn provides more favorable electrochemical conditions for eCO₂RR.

The d-band centers of the Cu 3d_{xy}, 3d_{yz}, 3d_{z²}, 3d_{xz} and 3d_{x²-y²} orbitals shown in Fig. 5(a) are determined to be -2.256, -2.248, -2.199, -2.243, and -2.259 eV, respectively.



the HER by inhibiting the dissociation of H₂O, thus

Fig. 5. DFT calculations; The PDOS of Cu 3d_{xy}, 3d_{yz}, 3d_{z²}, 3d_{xz}, and 3d_{x²-y²} on (a) Cu, (b) CuZn; (c) The PDOS of CO₂ on Cu and CuZn surfaces is compared to freestanding CO₂ molecules; (d) The COHP curves of Cu-C bonds in Cu and CuZn. Projected density of states (PDOS) of d orbitals associated with *CO on (e) Cu, (f) CuZn; (g) Charge density differences for the *CO₂ and *CO adsorption configurations on Cu and CuZn; (h) Illustrative two-dimensional contour plots of the charge density difference in asymmetric activation of CO₂ in CuZn; (i) The binding modes of CO₂ interacting with Cu site. (The color scheme is as follows: orange for Cu, gray for Zn, red for O, and brown for C atoms. Yellow and blue correspond to electron gain and loss,

respectively.)

In Fig. 5(b), the corresponding values are -2.412, -2.459, -2.449, -2.386 and -2.418 eV. The highest occupied orbitals of and π^* orbitals of CO_2 . Compared to the isolated molecule, the adsorbed CO_2 on both Cu and CuZn surfaces exhibits an overall downward shift in its occupied orbitals, as shown by the PDOS comparison in Fig. 5(c). In the CuZn system, the interaction between the d-orbitals and the π^* antibonding orbitals of CO_2 is particularly pronounced, resulting in a pronounced decrease in the energy of the π^* orbitals. This robust d- π^* coupling further causes the π^* orbitals to split with one component shifting upward the Fermi level and the other reorganizing below, forming occupied d- π^* hybridized states. In contrast, this orbital splitting and energy redistribution are not observed in the PDOS of CO_2 adsorbed on pure Cu. COHP was employed to further evaluate the adsorption capacity of CO_2 on Cu and CuZn. Fig. 5(d) gives that the Cu-C strength on CuZn is 1.39 eV, whereas on Cu it is 0.05 eV. This phenomenon demonstrates that the addition of Zn significantly enhances the material's adsorption capacity for CO_2 [66]. Furthermore, as shown in Fig. S18, the bond angle of CO_2 adsorbed on Cu is 179.8° , while on CuZn it is 127.6° . The dual adsorption sites of Cu and Zn alter the linear structure of CO_2 , making it more susceptible to activation and thereby favoring subsequent hydrogenation reactions. The differential charge density in the 2D sectional view of CuZn* CO_2 (Fig. 5(i)) further reveals the interaction with CO_2 localized at the CuZn dual sites. The Bader charge analysis in Fig. 5(h) also supports this conclusion. The charge transfer from Cu to CO_2 is 0.04 eV, while that from CuZn is 0.76 eV. This result further demonstrates that CuZn has a stronger adsorption capacity for CO_2 . Figs. 5(e) and 5(f) provide the PDOS diagrams of *CO adsorbed on Cu and CuZn, respectively. It is established that a d-band center positioned closer to the Fermi level enhances the catalyst's binding ability toward reactants, thus promoting easier bond formation. The d-band center of Cu*CO is -3.07 eV, while that of CuZn*CO is -3.00 eV. Therefore, CuZn exhibits stronger adsorption capacity for the *CO intermediate. The Bader charge analysis in Fig. 5(h) also shows that CuZn transfers 0.17 eV to *CO, while Cu transfers 0.13 eV. This result further confirms that Zn doping enhances the adsorption of the *CO reaction intermediate on the Cu site. As mentioned above, the process of *CO to *CHO is a key step in methane formation. Therefore, stable adsorption of *CO is crucial. The calculations indicate that incorporating Zn into the Cu catalyst lowers the activation energy barrier for the electrocatalytic CO_2 reduction reaction, thereby enhancing CO_2 adsorption. Additionally, Zn and Cu form a tandem reaction, where Zn facilitates water splitting and provides protons for the hydrogenation of *CO on Cu, thereby accelerating the reaction. Consequently, CuZn800@C exhibits excellent methane catalytic performance.

4 CONCLUSIONS

In summary, the CuZn bimetallic catalysts with different zinc contents were synthesized using a solvothermal method and followed by high temperature calcination, taking advantage of the spillover characteristics of zinc at high temperatures. CuZn800@C presents outstanding electrocatalytic

Cu and CuZn are d_{z^2} and d_{yz} , respectively, which form bonds with the σ performance for the process of CO_2 to methane, achieving a FE of 64.5% for methane at a potential of -1.7 V vs. RHE, with a partial current density as high as -429.1 mA/cm^2 . Furthermore, the material demonstrates excellent stability, showing only a slight decrease in catalytic performance after a prolonged 24-hour test. DFT theoretical calculations show that the dual adsorption sites formed by Zn and Cu greatly boost the adsorption and activation of CO_2 . Moreover, Zn can modulate the charge density around Cu, thus reducing the energy barrier for hydrogenation reactions on Cu. Therefore, Zn sites promote water splitting, providing abundant protons for the hydrogenation reactions occurring at Cu sites. The tandem reaction system formed by the two components greatly enhances the material's ability to electro-reduce CO_2 to methane. This experiment provides new insights for constructing Cu-based catalysts with high methane catalytic performance.

Electronic Supplementary Material: Supplementary material (electrochemical test details, catalyst structure characterization, comparative catalyst activity tests, computational models.) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908916>.

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."

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (Grant No. 52473327, 51572295 and 21273285) and National Key R&D Program of China (Grant No. 2021YFA1501300, 2019YFC1907602).

Declaration of competing interest

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

Author contribution statement

Dai ZX participated in the data analysis and participated in editing and review of the manuscript; Bian RC carried out the DFT calculations and editing of the manuscript; Qu YP carried out the experiments; Li LP assisted in the experiments and took part in the format editing of the manuscript; Li N assisted in the experiments and data analysis; Ge L supervised the project, provided resources, and directed the research. All authors contributed to the general discussion.

Use of AI statement

None.

References

- [1] An, B. H.; Li, X.; Li, L. P.; Dai, Z. X.; Li, N.; Gao, Y. Q.; Ge, L. Review and perspective on the rational design and structural modulation of transition metal phosphides for efficient electrocatalytic water splitting. *Coord. Chem. Rev.* **2026**, 550, 217406.
- [2] An, B. H.; Li, X.; Liu, W. L.; Dong, J. P.; Bian, R. C.; Zhang, L. Y.; Li,

- N.; Gao, Y. Q.; Ge, L. Developing a stable and high-performance W-CoMnP electrocatalyst by mitigating the Jahn-Teller effect through W doping strategy. *Chin. J. Catal.* **2025**, 74, 264-278.
- [3] Bian, L.; Zhang, Z.-Y.; Tian, H.; Tian, N.-N.; Ma, Z.; Wang, Z.-L. Grain boundary-abundant copper nanoribbons on balanced gas-liquid diffusion electrodes for efficient CO₂ electroreduction to C₂H₄. *Chin. J. Catal.* **2023**, 54, 199-211.
- [4] Bui, T. S.; Lovell, E. C.; Daiyan, R.; Amal, R. Defective Metal Oxides: Lessons from CO₂RR and Applications in NO_xRR. *Adv. Mater.* **2023**, 35, e2205814.
- [5] Chen, R.; Zhao, J.; Li, Y.; Cui, Y.; Lu, Y.-R.; Hung, S.-F.; Wang, S.; Wang, W.; Huo, G.; Zhao, Y.; Liu, W.; Wang, J.; Xiao, H.; Li, X.; Huang, Y.; Liu, B. Operando Mössbauer Spectroscopic Tracking the Metastable State of Atomically Dispersed Tin in Copper Oxide for Selective CO₂ Electroreduction. *J. Am. Chem. Soc.* **2023**, 145, 20683-20691.
- [6] Li, N.; Qiu, Y. P.; Li, L.; Zhang, J.; Gao, Y. Q.; Ge, L.; L Vacancy and the Se/S Ratio Regulate the p-Band Center of Hollow NiS₂/Se_{2-x}/Phase Junction CdS to Achieve High Efficiency and Broad-Spectrum Photocatalytic Performance. *Small* **2025**, 21, 2408057.
- [7] Sun, Y. X.; Lai, K. Z.; Shi, X. Q.; Li, L. P.; Li, N.; Gao, Y. Q.; Ge, L. Engineering Cu/V asymmetric sites for photocatalytic CO₂-to-C₂H₄ conversion by promoting C-C coupling: Achieving 98.24% selectivity through electronic synergy. *J. Mater. Sci. Technol.* **2026**, 252, 301-312.
- [8] Sun, Y. X.; Lai, K. Z.; Shi, X. Q.; Li, N.; Gao, Y. Q.; Ge, L. Regulating metal cation Cu vacancies on ZnIn₂S₄/Cu_{1.8}S to achieve high selectivity for the photocatalytic reduction of CO₂ to CH₄. *Appl. Catal., B* **2025**, 365, 124907.
- [9] Chen, W. T.; Shiu, H. W.; Chen, Y. X.; Batsaikhan, E.; Lai, Y. L.; Cheng, S. L.; Araki, T.; Lee, J. F.; Hayashi, M.; Hsu, Y. J. Highly Selective Toward HER or CO₂RR by Regulating Cu Single and Dual Atoms on g-C₃N₄. *Adv. Funct. Mater.* **2025**, 36, e14183.
- [10] Li, Y. C.; Wang, Z.; Yuan, T.; Nam, D.-H.; Luo, M.; Wicks, J.; Chen, B.; Li, J.; Li, F.; de Arquer, F. P. G.; Wang, Y.; Dinh, C.-T.; Voznyy, O.; Sinton, D.; Sargent, E. H. Binding Site Diversity Promotes CO₂ Electroreduction to Ethanol. *J. Am. Chem. Soc.* **2019**, 141, 8584-8591.
- [11] Lai, K. Z.; Sun, Y. X.; Li, L. P.; Shi, X. Q.; Zhou, X.; Li, N.; Gao, Y. Q.; Ge, L. Defect-mediated dual-site synergy in Zn-CuInS₂ enables orbital-tailored high performance photocatalytic CO₂-to-ethylene conversion. *Chin. J. Catal.* **2026**, 85, 153-167.
- [12] Liu, M.; Liu, S.; Xu, Q.; Miao, Q.; Yang, S.; Hanson, S.; Chen, G. Z.; He, J.; Jiang, Z.; Zeng, G. Dual atomic catalysts from COF-derived carbon for CO₂RR by suppressing HER through synergistic effects. *Carbon Energy* **2023**, 5, e300.
- [13] Shan, J.; Shi, Y.; Li, H.; Chen, Z.; Sun, c.; Shuai, Y.; Wang, Z. Effective CO₂ electroreduction toward C₂H₄ boosted by Ce-doped Cu nanoparticles. *Chem. Eng. J.* **2022**, 433, 133769.
- [14] Zu, X.; Li, X.; Liu, W.; Sun, Y.; Xu, J.; Yao, T.; Yan, W.; Gao, S.; Wang, C.; Wei, S.; Xie, Y. Efficient and Robust Carbon Dioxide Electroreduction Enabled by Atomically Dispersed Sn⁶⁺ Sites. *Adv. Mater.* **2019**, 31, 1808135.
- [15] Huo, S.; Lu, J.; Wang, X. Electrodeposition of Ni on MWNTs as a promising catalyst for CO₂RR. *Energy Sci. Eng.* **2021**, 9, 1042-1047.
- [16] Shi, X. Q.; Sun, Y. X.; Lai, K. Z.; Li, L. P.; Li, N.; Gao, Y. Q.; Ge, L. Mn induced adsorption and orbital hybridization synergistically promote C-C coupling for highly selective photocatalytic CO₂-to-C₂H₄ conversion. *Appl. Catal., B* **2026**, 382, 126001.
- [17] Zhao, P.; Jiang, H.; Shen, H.; Yang, S.; Gao, R.; Guo, Y.; Zhang, Q.; Zhang, H. Construction of Low-Coordination Cu-C₂ Single-Atoms Electrocatalyst Facilitating the Efficient Electrochemical CO₂ Reduction to Methane. *Angew. Chem. Int. Ed.* **2023**, 62, e202314121.
- [18] Xu, Z.; Peng, C.; Luo, G.; Yang, S.; Yu, P.; Yan, S.; Shakouri, M.; Wang, Z.; Sham, T. K.; Zheng, G. High-rate CO₂-to-CH₄ Electrosynthesis by Undercoordinated Cu Sites in Alkaline-Earth-Metal Perovskites with Strong Basicity. *Adv. Energy Mater.* **2023**, 13, 2204417.
- [19] Ma, J.; Xu, B.; Cao, S.; Li, S.; Chu, W.; Perathoner, S.; Centi, G.; Liu, Y. Structural dynamics of Ni/Mo₂CT MXene catalysts under reaction modulate CO₂ reduction performance. *Chin. J. Catal.* **2025**, 72, 243-253.
- [20] Cui, S.; Yu, C.; Tan, X.; Li, W.; Zhang, Y.; Qiu, J. A tandem catalyst with high CO₂ capture capability to achieve a promoted CO₂-to-CH₄ electrochemical conversion. *Chem. Eng. J.* **2023**, 470, 144083.
- [21] Wang, P.; Meng, S.; Zhang, B.; He, M.; Li, P.; Yang, C.; Li, G.; Li, Z. Sub-1 nm Cu₂O Nanosheets for the Electrochemical CO₂ Reduction and Valence State-Activity Relationship. *J. Am. Chem. Soc.* **2023**, 145, 26133-26143.
- [22] Onajah, S.; Sarkar, R.; Islam, M. S.; Lalley, M.; Khan, K.; Demir, M.; Abdelhamid, H. N.; Farghaly, A. A. Silica-Derived Nanostructured Electrode Materials for ORR, OER, HER, CO₂RR Electrocatalysis, and Energy Storage Applications: A Review. *Chem. Rec.* **2024**, 24, e202300234.
- [23] Song, D.; Wu, Y.; Hua, J.; Shao, C.; Wei, Z.; Wang, J.; Dai, K. Insight into the role of imidazolium cations in regulating Ag electrode interface for enhancing electrochemical CO₂ reduction. *Chin. J. Catal.* **2026**, 81, 206-215.
- [24] Liu, Z.; Liu, Y.; Zhang, J.; Cao, T.; Sun, Z.; Liu, J.; Shang, H. Asymmetrically coordinated single atom Cu catalyst with unsaturated C-Cu-N structure for CO₂ reduction to CO. *Nano Res.* **2024**, 17, 3911-3918.
- [25] Lai, K. Z.; Sun, Y. X.; Li, L. P.; Shi, X. Q.; Ge, L.; Liu, Z. Q. Cu Sites d Orbital Regulation Enables Highly Efficient Photocatalytic CO₂-to-Ethylene Conversion. *Adv. Funct. Mater.* **2026**, 36, e24582.
- [26] Lai, K. Z.; Sun, Y. X.; Li, N.; Gao, Y. Q.; Li, H.; Ge, L.; Ma, T. Y. Photocatalytic CO₂-to-CH₄ conversion with ultrahigh selectivity of 95.93% on S-vacancy modulated spatial In₂S₃/In₂O₃ heterojunction. *Adv. Funct. Mater.* **2024**, 34, 2409031.
- [27] Wang, J.; Zhu, F.; Chen, B.; Deng, S.; Hu, B.; Liu, H.; Wu, M.; Hao, J.; Li, L.; Shi, W. B atom dopant-manipulate electronic structure of CuIn nanoalloy delivering wide potential activity over electrochemical CO₂RR. *Chin. J. Catal.* **2023**, 49, 132-140.
- [28] Dai, Z. X.; Lai, K. Z.; Li, X.; Ge, L.; Li, L. P.; Liu, Z. F.; Li, N. Asymmetric Adsorption Site and Cu Vacancy Regulation in La-Cu Nanospheres to Promote CO₂ Electroreduction Performance with Ultrahigh CH₄ Selectivity. *Adv. Funct. Mater.* **2025**, 36, e202514227.
- [29] Wang, M.; Xie, Q.; Chen, H.; Liu, G.; Cui, X.; Jiang, L. Surface regulated Ni nanoparticles on N-doped mesoporous carbon as an efficient electrocatalyst for CO₂ reduction. *Chin. J. Catal.* **2021**, 42, 2306-2312.
- [30] Xiong, L.; Fu, X. Recent advances and challenges in electrochemical CO₂ reduction to CH₄. *Chin. J. Catal.* **2025**, 73, 39-61.
- [31] Zhang, Y.; Zhang, X.-Y.; Sun, W.-Y. In Situ Carbon-Encapsulated Copper-Doped Cerium Oxide Derived from MOFs for Boosting CO₂-to-CH₄ Electro-Conversion. *ACS Catal.* **2023**, 13, 1545-1553.
- [32] Zhu, J.; Zhang, Y.; Chen, Z.; Zhang, Z.; Tian, X.; Huang, M.; Bai, X.; Wang, X.; Zhu, Y.; Jiang, H. Superexchange-stabilized long-distance Cu sites in rock-salt-ordered double perovskite oxides for CO₂ electromethanation. *Nat. Commun.* **2024**, 15, 1565.
- [33] Xu, Y.; Wang, L.; Liu, Q.; Teng, B.; Wu, C.; Ge, B.; Bi, W.; Gu, M.; Zhang, M.; Yan, H.; Lu, J. Integrating controlled synthesis and theory for revealing of active site structure of single-atom nickel catalysts in electrochemical CO₂ reduction. *Chin. J. Catal.* **2025**, 79, 68-77.
- [34] Sun, M.; Rocabado, D. S. R.; Cheng, J.; Noguchi, T. G.; Donoshita, M.; Matsui, T.; Higashi, M.; Fujigaya, T.; Ishimoto, T.; Yamauchi, M. In Situ Observation of Post-CO Intermediates to Decode C-C Coupling Pathways in CO₂ Electroreduction. *Angew. Chem. Int. Ed.* **2025**, 64, e202502740.
- [35] 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, 2412658.
- [36] Min, Z.; Shao, C.; Chang, B.; Wang, N.; Zhao, Y.; Gao, S.; Zhang, X.-G.; Fan, M.; Zhang, S.; Wang, J. Constructing Triple-Atom sites for H₂O Participated Electrocatalytic CO₂ Reduction. *Chem. Eng. J.* **2024**, 502, 157813.
- [37] Chen, Y.; Wang, X.; Li, X.-Y.; Miao, R. K.; Dong, J.; Zhao, Z.; Liu, C.; Huang, J. E.; Wu, J.; Chu, S.; Ni, W.; Guo, Z.; Xu, Y.; Ou, P.; Xu, B.; Hou, Y.; Sinton, D.; Sargent, E. H. Electrified synthesis of n-propanol using a dilute alloy catalyst. *Nat. Catal.* **2025**, 8, 239-247.
- [38] Liu, X.; Liu, T.; Ouyang, T.; Deng, J.; Liu, Z. Q. Ce³⁺/Ce⁴⁺ Ion Redox Shuttle Stabilized Cu^{δ+} for Efficient CO₂ Electroreduction to C₂H₄. *Angew. Chem. Int. Ed.* **2024**, 64, e202419796.
- [39] Li, Y.; Zou, J.; Sun, L.; Liu, S.; Li, H.; Song, Z.; Yu, J.; Zhang, L.; Guo, Z. Strong Electronic Interactions of the Abundant Cu/Ce Interfaces Stabilized Cu₂O for Efficient CO₂ Electroreduction to C₂₊ Products under Large Current Density. *Adv. Funct. Mater.* **2025**, 35, 2509899.
- [40] Gao, X.; Wang, D.; Bai, R.; Lin, D.; Zhang, J.; Li, Z.; Hou, Y.; Lei, L.; Yang, B. Highly Efficient and Selective Electrocatalytic Semihydrogenation of Acetylene to Ethylene via Continuous Proton Feeding and Accelerated Transfer on Cu NP/FeNC Composite. *Adv. Funct. Mater.* **2024**, 35, 2415384.
- [41] Zhang, Y.; Chen, F.; Yang, X.; Guo, Y.; Zhang, X.; Dong, H.; Wang, W.; Lu, F.; Lu, Z.; Liu, H.; Liu, H.; Xiao, Y.; Cheng, Y. Electronic metal-support interaction modulates Cu electronic structures for CO₂ electroreduction to desired products. *Nat. Commun.* **2025**, 16, 1965.
- [42] Wei, Y.; Zhang, J.; Li, B.; Yu, F.; Li, M.; Wang, Y.; He, T.; Zhu, J.; Chen, S.; Su, Y.; Ding, S.; Xiao, C.; Xia, B. Y. Self-Assembled Monolayer Interface with Reconstructed Hydrogen-Bond Network for Enhanced CO₂ Electroreduction. *Adv. Mater.* **2025**, 37, 2504515.

- [43] Cai, H.; Yang, H.; Feng, J.; Zhou, K.; Liu, C.; Hu, Q.; He, C. Ionic Liquid-Induced Product Switching in CO₂ Electroreduction on Copper Reaction Interface. *Adv. Funct. Mater.* **2024**, 34, 2404102.
- [44] Yi, J. d.; Gao, X.; Zhou, H.; Chen, W.; Wu, Y. Design of Co-Cu Diatomic Site Catalysts for High-efficiency Synergistic CO₂ Electroreduction at Industrial-level Current Density. *Angew. Chem. Int. Ed.* **2022**, 61, e202212329.
- [45] 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, 10247.
- [46] Wei, W.; Li, Z.; Shang, J.; Xia, C.; Hu, X.; Hu, Y.; Xu, J.; Zhao, Y.; Ding, M. Modulating *CO adsorption configuration over the CuPd/Cu interfaces to improve C-C coupling for enhanced acetate production. *Appl. Catal., B* **2025**, 371, 125220.
- [47] Wan, L.; Zhang, X.; Cheng, J.; Chen, R.; Wu, L.; Shi, J.; Luo, J. Bimetallic Cu-Zn Catalysts for Electrochemical CO₂ Reduction: Phase-Separated versus Core-Shell Distribution. *ACS Catal.* **2022**, 12, 2741-2748.
- [48] Peerlings, M. L. J.; Han, K.; Longo, A.; Helfferich, K. H.; Ghiassi, M.; de Jongh, P. E.; Ngene, P. Synthesis and Catalytic Performance of Bimetallic Oxide-Derived CuO-ZnO Electrocatalysts for CO₂ Reduction. *ACS Catal.* **2024**, 14, 10701-10711.
- [49] Zhang, F.; Li, Y.-H.; Qi, M.-Y.; Tang, Z.-R.; Xu, Y.-J. Boosting the activity and stability of Ag-Cu₂O/ZnO nanorods for photocatalytic CO₂ reduction. *Appl. Catal., B* **2020**, 268, 118380.
- [50] Qiu, Y. P.; Ge, L. Low-coordination Cu₃ motif for selective photocatalytic conversion of CO₂ to ethanol. *Chin. J. Struct. Chem.* **2025**, 44, 100716.
- [51] Xiang, T.; Liu, T.; Ouyang, T.; Zhao, S.; Liu, Z. Q. Tuning the selectivity of CO₂ conversion to CO on partially reduced Cu₂O/ZnO heterogeneous interface. *Interdiscip. Mater.* **2024**, 3, 380-388.
- [52] Li, L. P.; Su, J. H.; Qiu, Y. Q.; Gao, Y. Q.; Li, N.; Ge, L. Design and fabrication of ternary Au/Co₃O₄/ZnCdS spherical composite photocatalyst for facilitating efficient photocatalytic hydrogen production. *Chin. J. Struct. Chem.* **2024**, 43, 100472.
- [53] Qiu, Y. Q.; Zhang, J. T.; Li, L. P.; Gao, Y. Q.; Li, N.; Ge, L. MOF-derived g-C₃N₄/ZnIn₂S₄ S-scheme heterojunction: Interface-engineering enhanced photocatalytic NO conversion. *Acta Phys.-Chim. Sin.* **2026**, 42, 100175.
- [54] Chang, F.; Zhu, K.; Liu, C.; Wei, J.; Yang, S.; Zhang, Q.; Yang, L.; Wang, X.; Bai, Z. Construction of Cu-Ni Atomic Pair with Bimetallic Atom-Cluster Sites for Enhanced CO₂ Electroreduction. *Adv. Funct. Mater.* **2024**, 34, e202400893.
- [55] An, B. H.; Liu, W. L.; Dong, J. P.; Li, N.; Gao, Y. Q.; Ge, L. Atomic orbitals modulated dual functional bimetallic phosphides derived from MOF on MOF structure for boosting high efficient overall water splitting. *Chin. J. Catal.* **2024**, 65, 113-125.
- [56] Zhou, X.; Liang, Z.; Wu, Z.; Zhou, X.; Ning, X.; Zhan, L.; Luo, J. Reasonably constructing BiVO₄/CoNiFe-LDH S-scheme heterojunction with fast interface charge transfer for efficient photodegradation of tetracycline. *Adv. Powder Technol.* **2025**, 36, 104858.
- [57] Liu, W. L.; Teng, Z. Y.; An, B. H.; Dong, J. P.; Li, N.; Gao, Y. Q.; Ge, L. Asymmetric electronic structure effects in Co₉S₈@FeS₂ core-shell nanostructures for highly efficient overall water splitting by modulating d-p orbital hybridization. *J. Colloid Interface Sci.* **2025**, 504, 158932.
- [58] Liu, W. L.; Dong, J. P.; Zhang, L.; Li, N.; Gao, Y. Q.; Ge, L. Dynamic tuning of d-p orbital hybridization during sulfur vacancy evolution in Co₉S₈ toward efficient overall water splitting. *Chin. J. Struct. Chem.* **2025**, 44, 100661.
- [59] Li, X.; Dong, Y.; Dai, Z. X.; Zhang, L. Y.; An, B. H.; Li, N.; Gao, Y. Q.; Ge, L. Electronic modulation of CoFeP@NiFe LDH hierarchical nanosheets for industrial water electrolysis at an ultra-low voltage of 1.67 V. *J. Colloid Interface Sci.* **2026**, 706, 139632.
- [60] Li, P.; Liu, J.; Wang, Y.; Zhang, X.D.; Hou, Y.; Zhang, Y.; Sun, X.; Kang, X.; Zhu, Q.; Han, B. Manipulation of Oxygen Species on an Antimony-Modified Copper Surface to Tune the Product Selectivity in CO₂ Electroreduction. *J. Am. Chem. Soc.* **2024**, 146, 26525-26533.
- [61] Liang, S.; Xiao, J.; Zhang, T.; Zheng, Y.; Wang, Q.; Liu, B. Sulfur Changes the Electrochemical CO₂ Reduction Pathway over Cu Electrocatalysts. *Angew. Chem. Int. Ed.* **2023**, 62, e202310740.
- [62] Shi, X. Q.; Lai, K. Z.; Sun, Y. X.; Li, L. P.; Shi, J.; Qiu, Y. P.; Li, N.; Gao, Y. Q.; Ge, L. Synergistic promotion of charge transfer and CO₂ activation over CoS_{1.097}/ZnIn₂S₄ heterojunction for photocatalytic CO₂ reduction. *Appl. Catal., B* **2026**, 394, 126808.
- [63] Tong, X.; Zhang, P.; Chen, P.; He, Z.; Kang, X.; Yin, Y.; Cheng, Y.; Zhou, M.; Jing, L.; Wang, C.; Xu, B.; Zheng, L.; Xing, X.; Wu, Z.; Han, B. Switching CO₂ Electroreduction Pathways between Ethylene and Ethanol via Tuning Microenvironment of the Coating on Copper Nanofibers. *Angew. Chem. Int. Ed.* **2024**, 64, e202413005.
- [64] Tong, X.; Zhang, P.; Chen, P.; He, Z.; Kang, X.; Yin, Y.; Cheng, Y.; Zhou, M.; Jing, L.; Wang, C.; Xu, B.; Zheng, L.; Xing, X.; Wu, Z.; Han, B. Switching CO₂ Electroreduction Pathways between Ethylene and Ethanol via Tuning Microenvironment of the Coating on Copper Nanofibers. *Angew. Chem. Int. Ed.* **2024**, 64, e202413005.
- [65] Sun, Y. X.; Lai, K. Z.; Li, N.; Gao, Y. Q.; Ge, L. Efficient photocatalytic CO₂ reduction to CH₄ via electric field-regulated d-band center on Ga₂S₃/CuS S-type heterojunction interface structures. *Appl. Catal., B* **2024**, 357, 124302.
- [66] Su, H.; Song, S.; Gao, Y. Q.; Li, N.; Fu, Y.; Ge, L.; Song, W.; Liu, J.; Ma, T. Y. In situ electronic redistribution tuning of NiCo₂S₄ nanosheets for enhanced electrocatalysis. *Adv. Funct. Mater.* **2022**, 32, 2109731.

© The Author(s) 2026. *Nano Research* published by Tsinghua University Press. The articles published in this open access journal are distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits use, distribution and reproduction in any medium, provided the original work is properly c

Electronic Supplementary Material

Synergistic promotion of proton relay and $^*\text{CO}$ hydrogenation in Cu-Zn tandem catalysts for highly efficient electrocatalytic CO_2 -to- CH_4 conversion

Zhixin Dai, Ruichao Bian, Yanping Qiu, Linping Li, Ning Li, and Lei Ge^{id} 

State Key Laboratory of Heavy Oil Processing, College of New Energy and Materials, China University of Petroleum Beijing, No. 18 Fuxue Rd., Beijing 102249, China

Supporting information to <https://doi.org/10.26599/NR.2026.94908916>

Just Accepted

Preparation of electrodes

The hydrophobic carbon paper (YLS-30T) was cut into 1×3 cm pieces, and the surface was cleaned with deionized water. A catalyst (2.5 mg) was dispersed in a solution containing 40 μL Nafion and 760 μL of isopropanol, followed by ultrasonication for 10 minutes. The resulting slurry was uniformly sprayed onto the cleaned hydrophobic carbon paper using a handheld spray gun. The electrode coating was subsequently subjected to 60-minute vacuum desiccation. The catalyst loading was 0.4 mg/cm².

Electrochemical performance tests

The electrochemical measurements were performed in a flow cell featuring a working area of $2 \times 0.5 \text{ cm}^2$. The cell assembly comprised three distinct compartments: a gas-fed cathode chamber housing the working electrode and reference electrode, and an anode chamber containing a platinum foil counter electrode. These two chambers were separated by an anion exchange membrane (FAA-3-50). During the electrochemical process, CO₂ was precisely delivered to the gas-fed chamber at 30 sccm using a calibrated mass flow controller. Simultaneously, the alkaline electrolyte (1.0 M KOH, pH=13.6) was continuously circulated through both cathode and anode compartments via a peristaltic pump maintaining a flow rate of 4 mL/min. A mass flow meter (MFM) was connected between the gas chamber outlet and the gas chromatograph (G(C) to measure the gas flow rate at the outlet.

All electrochemical experiments were performed using a computer-controlled potentiostat/galvanostat system (CHI 760E, CH Instruments, US(A)). All electrode potentials were converted to the reversible hydrogen electrode (RHE) scale using the following Nernstian relationship:

$$E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.0591 \times \text{pH} + 0.197\text{V}$$

Linear sweep voltammetry (LSV) polarization curves were acquired in the potential range of 0 to -2.8 V versus Ag/AgCl (3 M KCl) using a staircase scan mode (20 mV s⁻¹ step potential, 2 s equilibration), while cyclic voltammetry (CV) between -0.3 V and -0.4 V vs. RHE at incrementally varied scan rates (100–200 mV s⁻¹) provided the electrochemical double-layer capacitance (C_{dl}) values through linear regression analysis of capacitive current differentials ($\Delta j = j_{anodic} - j_{cathodic}$), which quantitatively correlates with the electrochemically active surface area (ECS(A)). Electrochemical impedance spectroscopy (EIS) was conducted under open-circuit potential conditions, applying a sinusoidal AC signal with an amplitude of 5 mV across a frequency range of 0.1 Hz to 10⁵ Hz.

Gaseous and liquid products analysis

Gas chromatography (GC FULI 9790 II) is online connected to the outlet of the flow cell for analyzing the composition of gaseous products.

The Faradaic efficiency (FE) of the product is:

$$FE = \frac{n}{Q/NF} \times 100\%$$

Where Q is the charge ((C), F is the Faradaic constant (96485 C mol⁻¹), N is the number of electrons required to generate the product, and n is the moles of products. For the H₂, CO, CH₄ and C₂H₄, the N is 2, 2, 8 and 12, respectively.

Material characterization

X-ray diffraction (XRD) was performed using the X-ray diffractometer (Bruker D8 Advance) with 2θ range from 5° to 90°. The morphology was examined using Field-emission transmission electron microscopy (TEM) and field-emission scanning electron microscopy (SEM) with FEI Tecnai F20 and FEI SU8010, respectively. X-ray Photoelectron Spectroscopy (XPS) analysis and Auger Electron Spectroscopy (AES) were conducted using a Thermo Fisher Scientific Nexsa instrument. Laser confocal Raman spectroscopy (Raman) analysis was performed using a DXR3 system (Thermo Fisher Scientific).

Density functional theory (DFT) calculation

All the spin-unrestricted density functional theory (DFT) calculations were performed using Vienna Ab-initio Simulation Package (VASP). The exchange and correlation potential were determined with the Perdew, Burke, and Ernzerhof within the generalized gradient approximation (PBE-GG(A) functional. The interaction between electrons and ions were described by using projector augmented wave (PAW) method. The geometrical configurations and charge density difference plots were illustrated with VESTA software.

In Materials Studio (MS), copper (Cu) is cleaved along the Cu(111) plane (with lattice parameters $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $a = 5.059 \text{ \AA}$, $b = 5.059 \text{ \AA}$). After conversion, the γ angle of Cu(111) is transformed to 90° . The converted parameters are: $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $a = 8.762 \text{ \AA}$, $b = 5.059 \text{ \AA}$. Finally, a 3×2 supercell expansion is performed, resulting in $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $a = 26.2886 \text{ \AA}$, $b = 10.118 \text{ \AA}$. The slab consists of three atomic layers, with the bottom layer constrained in bulk positions and the top layer fully relaxed. The interaction between atomic nuclei and electrons is described using the projected augmented wave method. The energy cutoff for the plane wave basis set is set to 520 eV. The Brillouin zone is sampled using a $1 \times 2 \times 1$ grid centered at the k-point to achieve geometric relaxation. The sampling vacuum spacing for all slab models is approximately 15 Å, ensuring

that lateral interactions of adsorbates can be neglected. About half of the bottom layer, constituting the structure, is kept fixed at lattice positions. All structures with dynamic magnetic moments are fully relaxed without any constraints until their total energy converges to 1×10^{-6} eV. The unit cell parameters were determined.

Operando ATR FT-IR measurements

Operando attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR) was conducted using a Bruker VERTEX 70V spectrometer (Bruker Optik GmbH). The catalyst ink was drop-cast onto an ITO-coated silicon microgroove wafer at a 55° incident angle, air-dried, and subsequently analyzed. The electrolyte consisted of 1.0 M KOH continuously purged with CO_2 . Potentials were applied from -1.0 to -1.8 V vs. RHE. Infrared absorption spectra were recorded with a temporal resolution of 1 minute per spectrum.

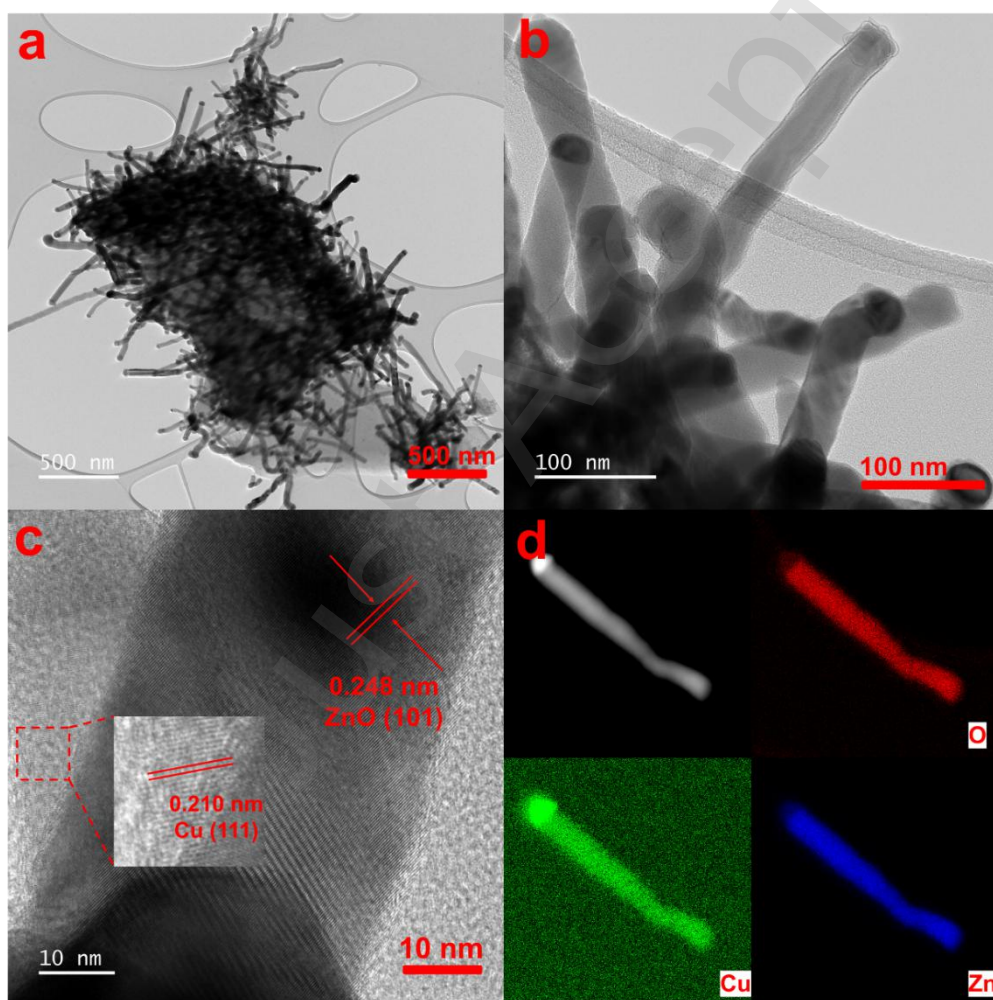


Fig. S1. (a) and (b) TEM images of CuZn700@C, (c) HR-TEM images of CuZn700@C, (d) EDS elemental mapping images of CuZn700@C.

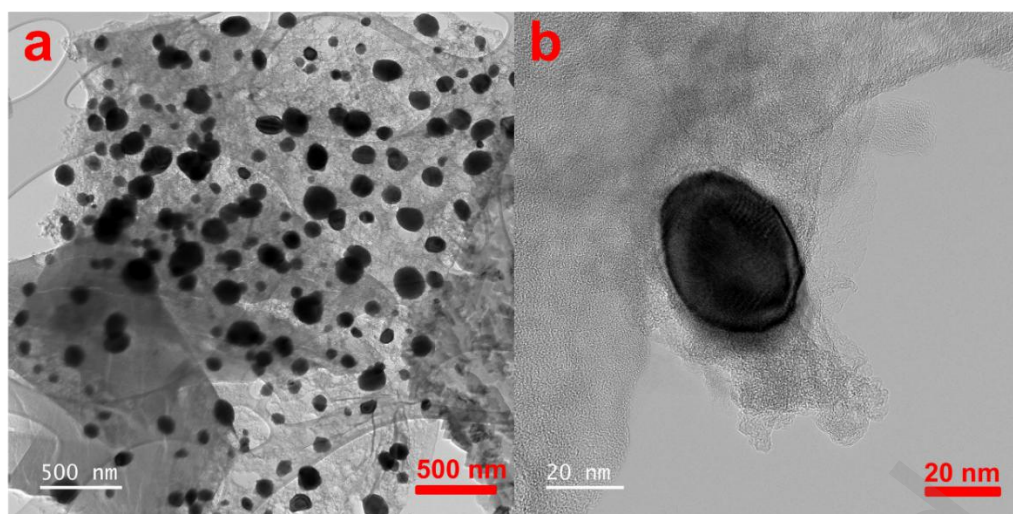


Fig. S2. (a) and (b) TEM images of CuZn800@C.

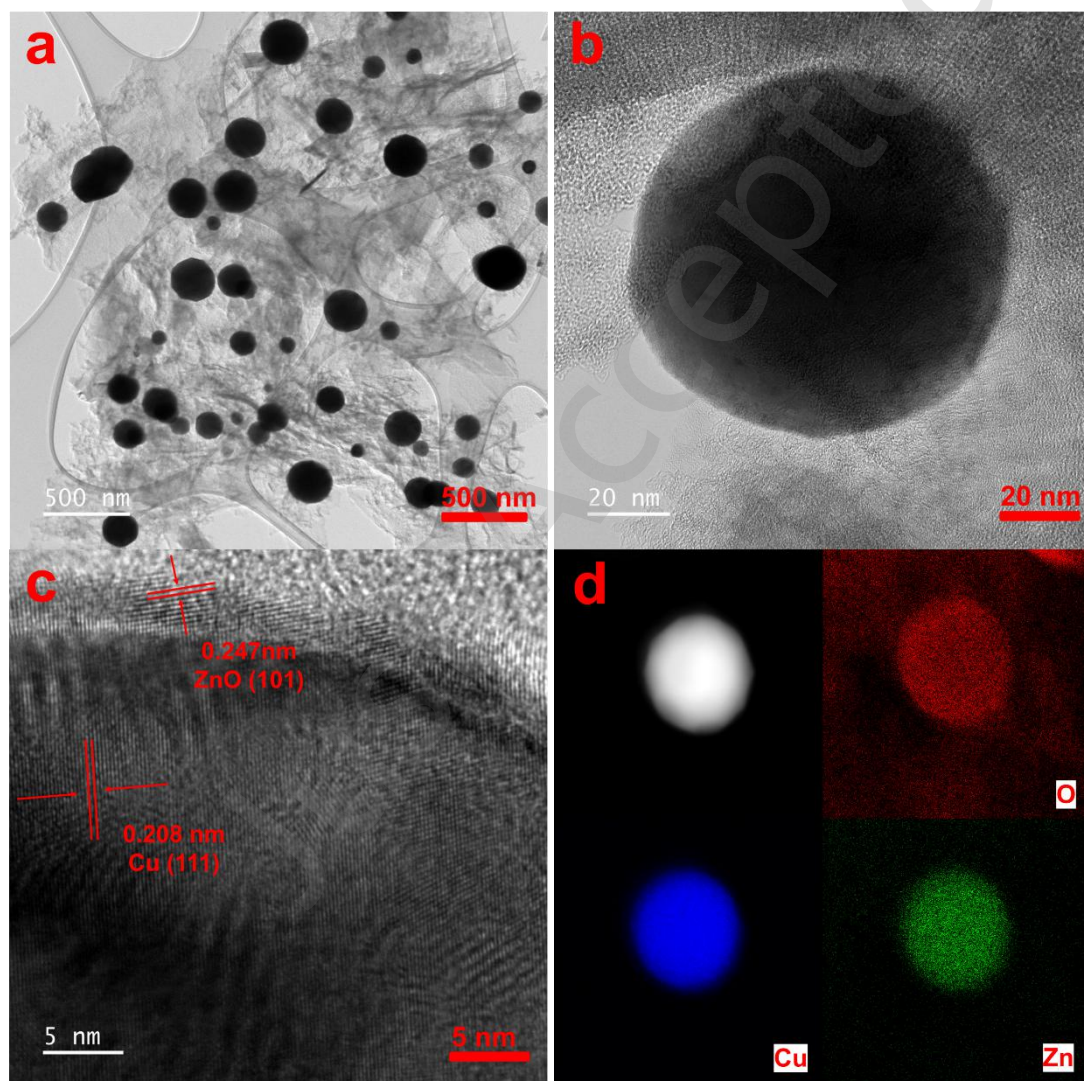


Fig. S3. (a) and (b) TEM images of CuZn900@C, (c) HR-TEM images of CuZn900@C, (d) EDS elemental mapping images of CuZn900@C.

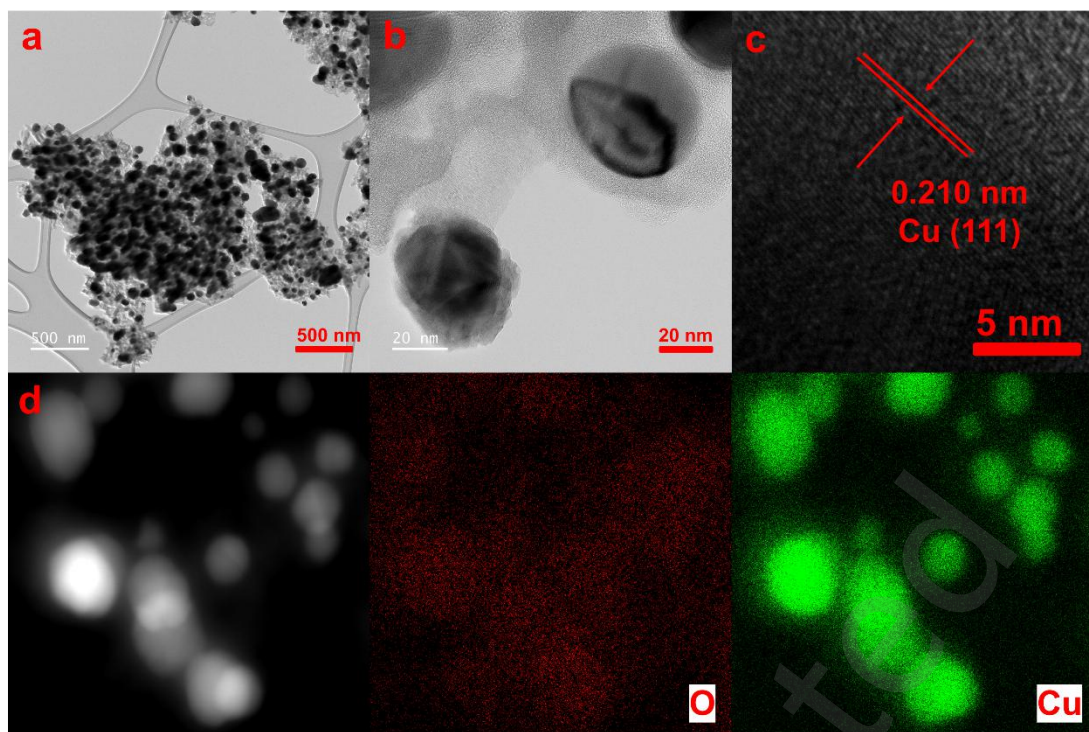


Fig. S4. (a) and (b) TEM images of Cu800@C, (c) HR-TEM images of Cu800@C, (d) EDS elemental mapping images of Cu800@C.

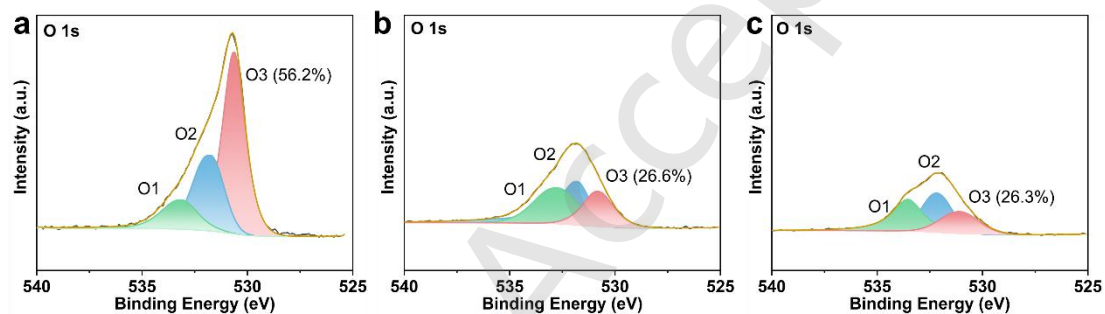


Fig. S5 O 1s XPS spectra of CuZn700@C, CuZn800@C and CuZn900@C.

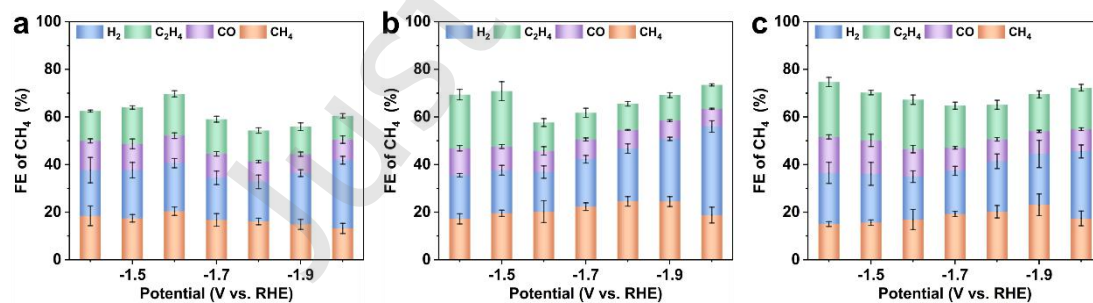


Fig. S6. CH₄ FE of (a) Cu700@C, (b) Cu800@C and (c) Cu900@C.

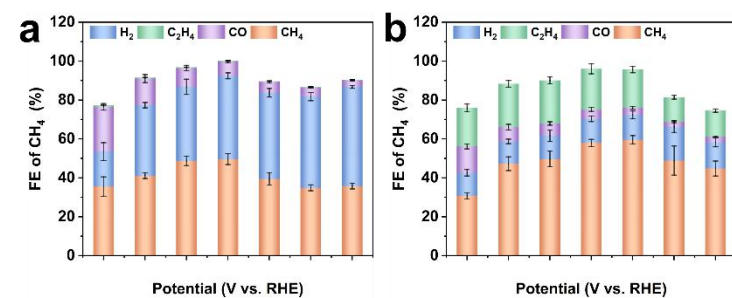


Fig. S7. CH₄ FE of (a) Cu:Zn=1:5, (b) Cu:Zn=1:20.

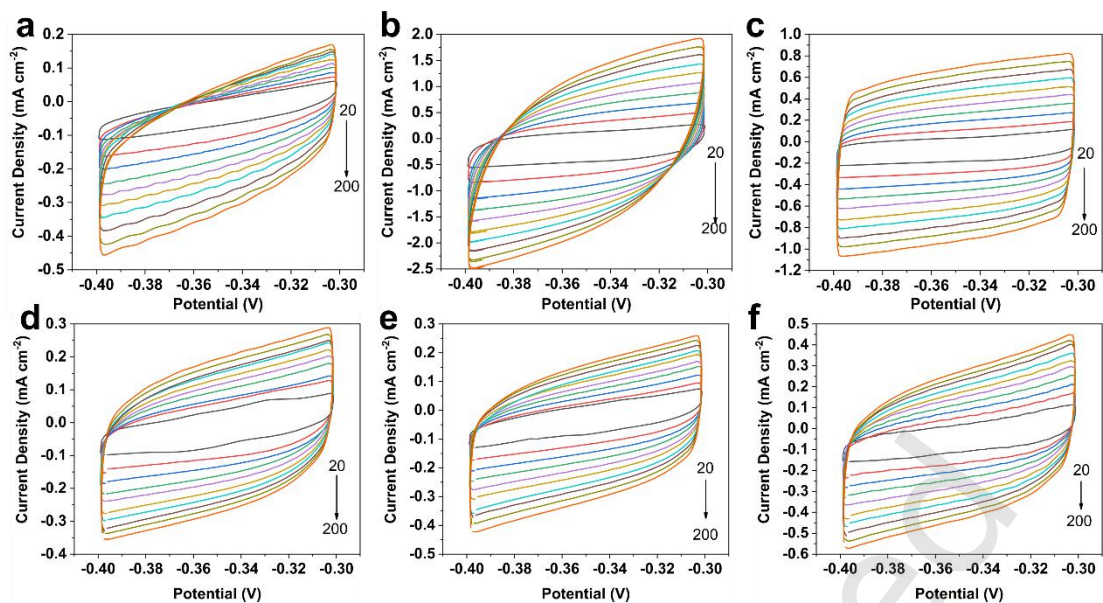


Fig. S8. CV test from 20 mV/s to 200 mV/s of (a) CuZn700@C; (b) CuZn800@C ; (c) CuZn900@C; (d) Cu700@C; e) Cu800@C and f) Cu900@C.

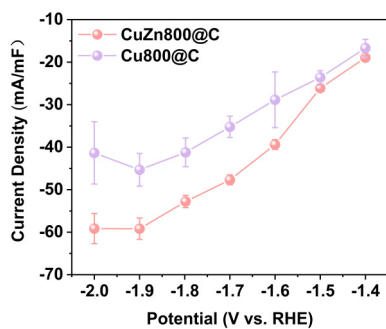


Fig. S9 ECSA-normalized polarization curves of CuZn800@C and Cu800@C.

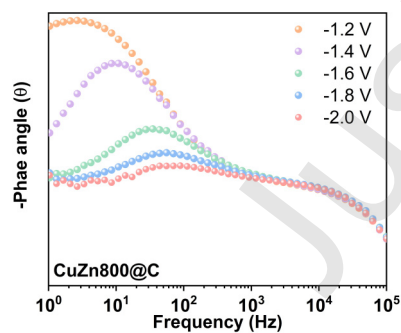


Fig. S10 Bode plots recorded at various potentials for CuZn800@C.

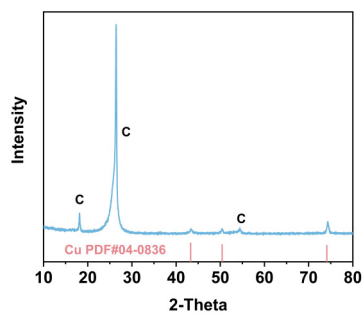


Fig. S11. XRD pattern of CuZn800@C after test.

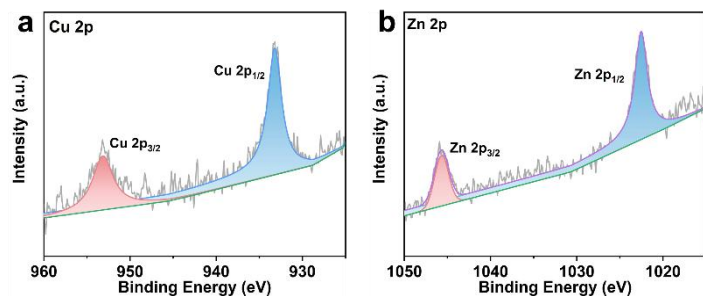


Fig. S12. (a) Cu 2p, (b) Zn 2p XPS spectra of CuZn800@C after test.

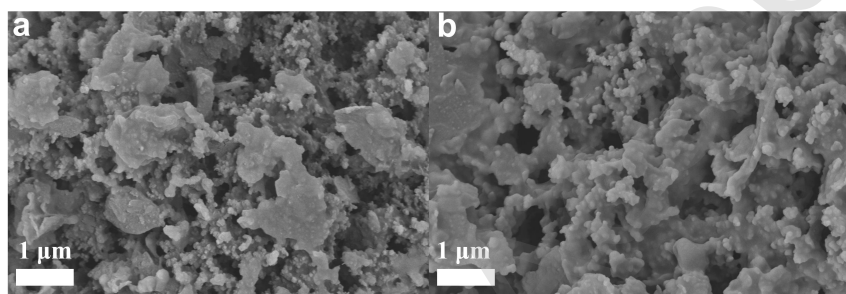


Fig. S13. SEM images of CuZn800@C (a) before test, (b) after test

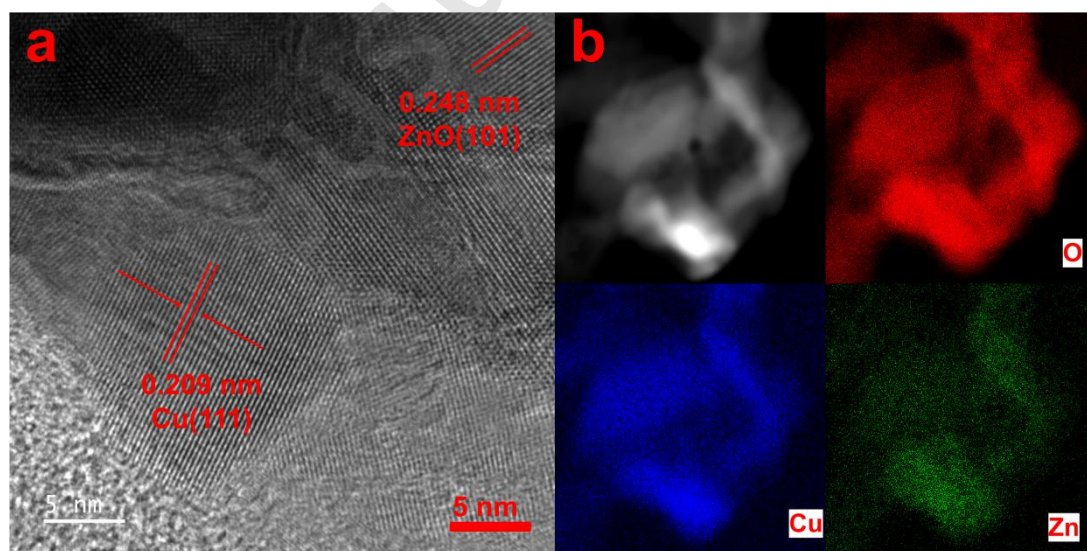


Fig. S14. (a) TEM images of CuZn800@C after test; (b) EDS elemental mapping images of CuZn800@C after test.

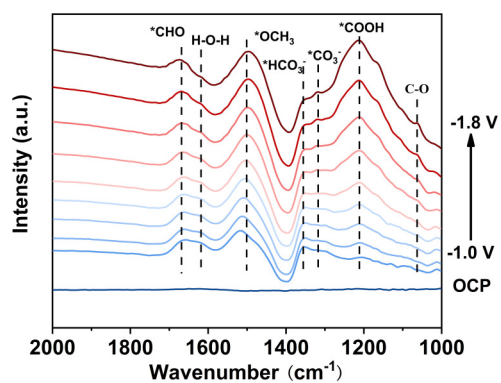


Fig. S15. In-situ ATR-FTIRS spectrum of CuZn800@C

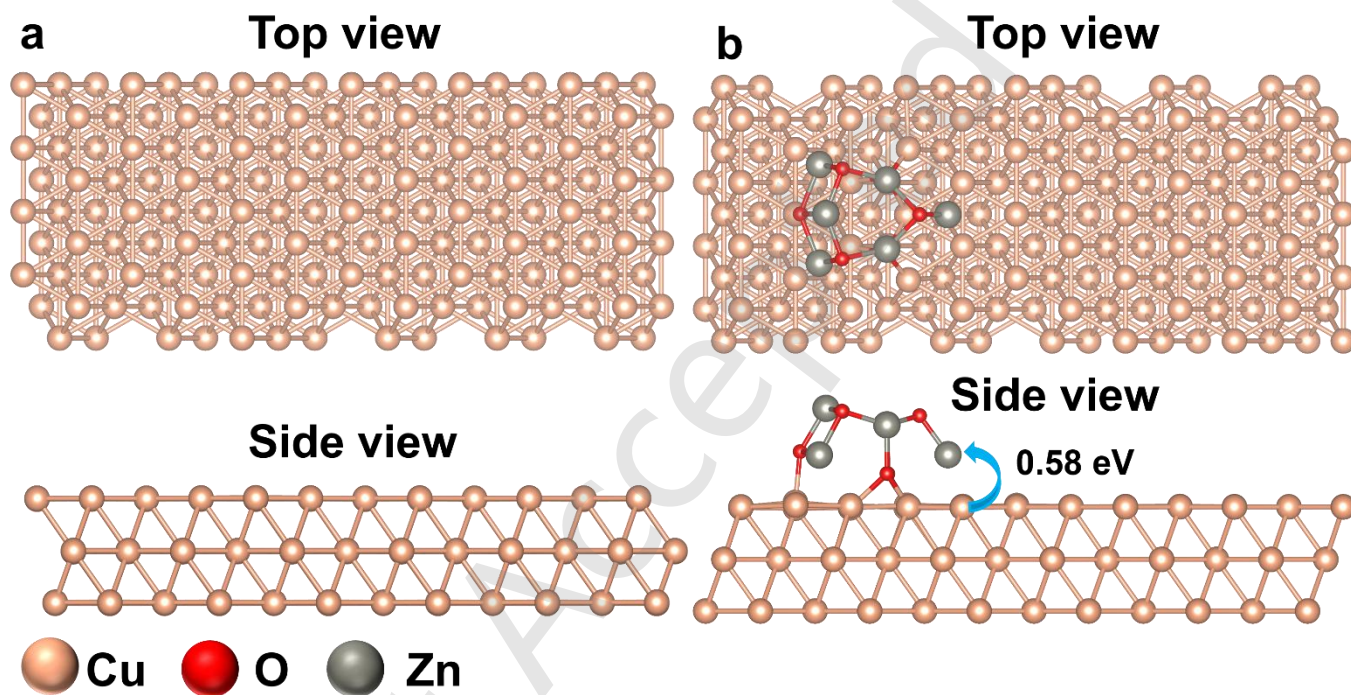


Fig. S16 (a) Top view and side view of Cu (b) Top view and side view of CuZn and Bader charge transferred from Cu to Zn.

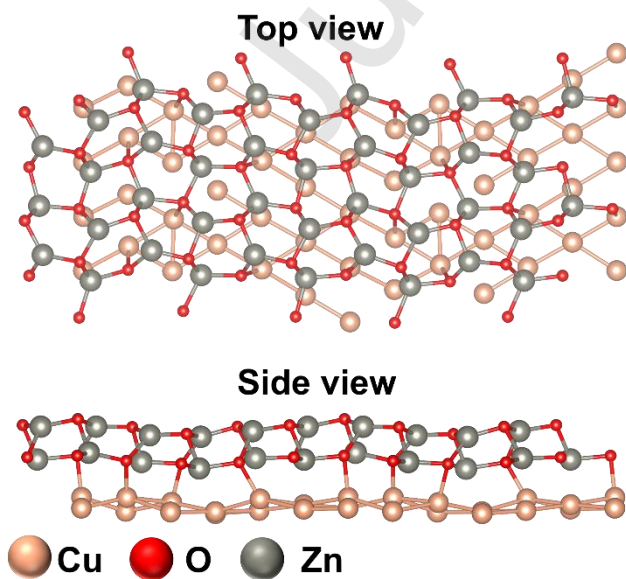


Fig. S17 Top view and side view of Cu-ZnO.

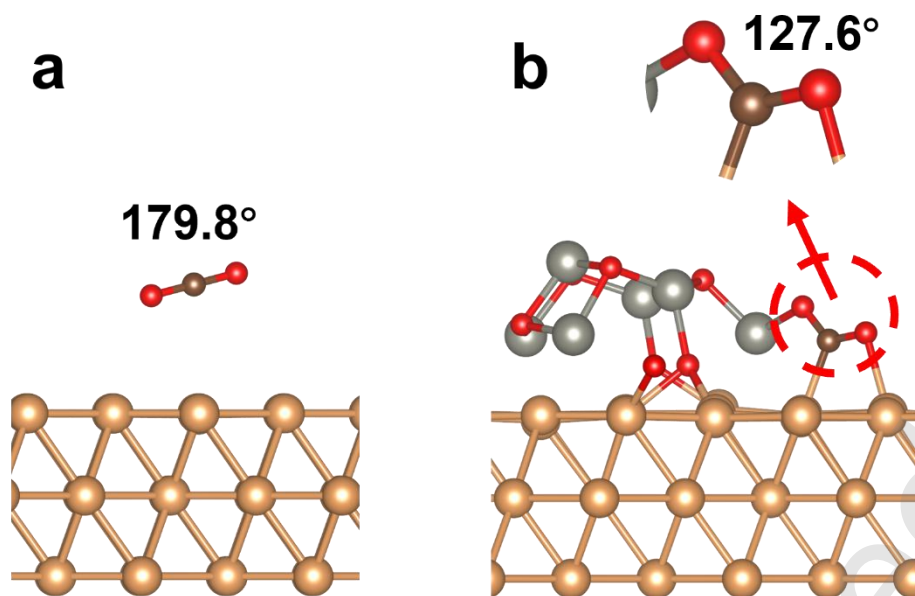


Fig. S18 CO₂ adsorbed on (a) Cu, (b) CuZn.

Table S1. Mass percent of Zn and Cu elements from ICP-OES, Zn element concentration in the electrolyte after stability test.

Sample	Zn	Cu
CuZn700@C	46.02%	5.91%
CuZn800@C	3.19%	22.36%
CuZn900@C	1.45%	32.77%
electrolyte after test	0.014 mg/L	-

Table S2. CH₄ Faradaic efficiency comparison of the recently reported Cu electrocatalysts derived from other precursors.

Sample	Electrolyte	Potential (V vs.RHE)	Current density (mA cm ⁻²)	CH ₄ FE (%)	Ref
CuZn800@C	1 M KOH	-1.70	-429.1	64.5	This work
CuBIM	1 M KOH	-1.08	-672.4	51.7	[1]
Cu/ceria	1 M KOH	-1.49	-105	42	[2]
Cu/La ₂ CuO ₄	1 M KOH	-1.40	-117	56.3	[3]
LaCu _{v1} @C	1 M KOH	-1.60	-245	73.5	[4]
CuSiOx	1 M KOH	-1.60	-170.4	53.3	[5]
Ag@Cu ₂ O	1 M KOH	-1.2	-178	74.0	[6]
La ₅ Cu ₉₅	1 M KOH	-1.72	-222.6	74.2	[7]
Cu ₂ O-pc	1 M KOH	-1.58	-438.0	55.0	[8]
CeO ₂ -CuSAC	1 M KOH	-1.89	-281.2	70.3	[9]

CeO ₂ -0.07Cu	1 M KOH	-1.00	-364.0	67.0	[10]
Cu/CeO ₂	1 M KOH	-1.80	-232.1	78.0	[11]
Cu/C-Al ₂ O ₃	1 M KOH	-1.20	-94.8	62.0	[12]
Cu-Pt _{NPs}	1 M KOH	-1.2	-200	57.7	[13]
rGO@CuN(H _x)C	1 M KOH	-1.4	-163	77.1	[14]
La-2Cu-NiPc-DHDA-COF	1 M KOH	-1.7	-188.5	57.1	[15]
Cu-N-P	0.5 M KHCO ₃	-1.6	-23.4	73	[16]
CuPEDOT	1 M KOH	-1.58	-354	62.7	[17]

Table S3. Free energies changes for forming intermediates of Cu and CuZn

Adsorbed species	Free energies changes for forming intermediates (eV)	
	Cu	CuZn
CO ₂	0.55	0.38
COOH	0.79	0.26
CO	-0.7	-0.09
CHO	0.86	0.4
CH ₂ O	-0.29	-0.19
CH ₃ O	-0.76	-0.69
CH ₄	-0.69	-0.84

- [1] Hu, S.; Chen, Y.; Zhang, Z.; Liu, H.; Kang, X.; Liu, J.; Li, S.; Luo, Y.; Liu, B. Simultaneous High Current Density and Selective Electrocatalytic CO₂ - to - CH₄ through Intermediate Balancing. *Angew. Chem. Int. Ed.* **2025**, 64, e202423951.
- [2] Huang, F.; Chen, X. Y.; Sun, H. H.; Zeng, Q. D.; Ma, J. J.; Wei, D.; Zhu, J. L.; Chen, Z. J.; Liang, T. Y.; Yin, X. C.; Liu, X. J.; Xu, J.; He, H. B. Atmosphere Induces Tunable Oxygen Vacancies to Stabilize Single-Atom Copper in Ceria for Robust Electrocatalytic CO₂ Reduction to CH₄. *Angew. Chem. Int. Ed.* **2025**, 64, 2415642.
- [3] Chen, S. H.; Su, Y. Q.; Deng, P. L.; Qi, R. J.; Zhu, J. X.; Chen, J. X.; Wang, Z. T.; Zhou, L.; Guo, X. P.; Xia, B. Y. Highly Selective Carbon Dioxide Electroreduction on Structure-Evolved Copper Perovskite Oxide toward Methane Production. *ACS Catal.* **2020**, 10, 4640-4646.
- [4] Dai, Z.; Lai, K.; Li, X.; Ge, L.; Li, L.; Liu, Z.; Li, N. Asymmetric Adsorption Site and Cu Vacancy Regulation in La-Cu Nanospheres to Promote CO₂ Electroreduction Performance with Ultrahigh CH₄ Selectivity. *Adv. Funct. Mater.* **2025**, 36, e202514227.
- [5] Tan, X.; Sun, K. A.; Zhuang, Z. W.; Hu, B. T.; Zhang, Y.; Liu, Q. G.; He, C.; Xu, Z. Y.; Chen, C.; Xiao, H.; Chen, C. Stabilizing Copper by a Reconstruction-Resistant Atomic Cu-O-Si Interface for Electrochemical CO₂ Reduction. *J. Am. Chem. Soc.* **2023**, 145, 8656-8664.
- [6] Xiong, L. K.; Zhang, X.; Chen, L.; Deng, Z.; Han, S.; Chen, Y. F.; Zhong, J.; Sun, H.; Lian, Y. B.; Yang, B. Y.; Yuan, X. Z.; Yu, H.; Liu, Y.; Yang, X. Q.; Guo, J.; Rummeli, M. H.; Jiao, Y.; Peng, Y. Geometric Modulation of Local CO Flux in Ag@Cu₂O Nanoreactors for Steering the CO₂RR Pathway toward High-Efficacy Methane Production. *Adv. Mater.* **2021**, 33, e2101741.
- [7] Zhao, J.; Zhang, P.; Yuan, T. H.; Cheng, D. F.; Zhen, S. Y.; Gao, H.; Wang, T.; Zhao, Z. J.; Gong, J.

- L. Modulation of *CH_xO Adsorption to Facilitate Electrocatalytic Reduction of CO₂ to CH₄ over Cu-Based Catalysts. *J. Am. Chem. Soc.* **2023**, 145, 6622-6627.
- [8] Wang, J.; Chen, Y. S.; Zhang, S. S.; Yang, C.; Zhang, J. Y.; Su, Y. Q.; Zheng, G. F.; Fang, X. S. Controllable States and Porosity of Cu-Carbon for CO₂ Electroreduction to Hydrocarbons. *Small* **2022**, 18, 2202238.
- [9] Zhang, Y.; Chen, F.; Yang, X.; Guo, Y.; Zhang, X.; Dong, H.; Wang, W.; Lu, F.; Lu, Z.; Liu, H.; Liu, H.; Xiao, Y.; Cheng, Y. Electronic metal-support interaction modulates Cu electronic structures for CO₂ electroreduction to desired products. *Nat. Commun.* **2025**, 16, 1965.
- [10] Liu, J. Y.; Li, P. S.; Bi, J. H.; Jia, S. Q.; Wang, Y.; Kang, X. C.; Sun, X. F.; Zhu, Q. G.; Han, B. X. Switching between C₂⁺ Products and CH₄ in CO₂ Electrolysis by Tuning the Composition and Structure of Rare-Earth/Copper Catalysts. *J. Am. Chem. Soc.* **2023**, 145, 23037–23047.
- [11] Huang, F.; Xu, A.; Chen, X.; Sun, H.; He, S.; Wei, D.; Wang, B.; Guan, A.; Yin, X.; Xu, J.; He, H. Constructing f-p-d Orbital Coupling Using Cu-Doped Frustrated Lewis Acid–Base Pairs in CeO₂ to Boost CO₂ Electroreduction. *ACS Catal.* **2025**, 15, 20864-20878.
- [12] Wu, Q. J.; Si, D. H.; Sun, P. P.; Dong, Y. L.; Zheng, S.; Chen, Q.; Ye, S. H.; Sun, D.; Cao, R.; Huang, Y. B. Atomically Precise Copper Nanoclusters for Highly Efficient Electroreduction of CO₂ towards Hydrocarbons via Breaking the Coordination Symmetry of Cu Site. *Angew. Chem. Int. Ed.* **2023**, 62, e202306822.
- [13] Hou, T.; Zhu, J.; Gu, H.; Li, X.; Sun, Y.; Hua, Z.; Shao, R.; Chen, C.; Hu, B.; Mai, L.; Chen, S.; Wang, D.; Zhang, J. Switching CO(2) Electroreduction toward C(2⁺) Products and CH(4) by Regulating the Dimerization and Protonation in Platinum/Copper Catalysts. *Angew. Chem. Int. Ed.* **2025**, 64, e202424749.
- [14] Cai, R.; Zhu, H.; Yang, F.; Ju, M.; Huang, X.; Wang, J.; Gu, M. D.; Gao, J.; Yang, S. The Proximal Protonation Source in Cu-NH(x)-C Single Atom Catalysts Selectively Boosts CO(2) to Methane Electroreduction. *Angew. Chem. Int. Ed.* **2025**, 64, e202424098.
- [15] Dong, X. Y.; Chen, H.; Wang, S.; Zou, R. Y.; Zang, S. Q.; Cai, J. Introducing La into a Customized Dual Cu Covalent Organic Framework to Steer CO(2) Electroreduction Selectivity from C(2)H(4) to CH(4). *Adv. Mater.* **2025**, 37, e2413710.
- [16] Li, Z.; Yuan, Y.; Qu, G.; Xiang, K.; Ning, P.; Du, W.; Pan, K.; Cai, Y.; Li, J. Preparation of phosphorus-doped Cu-based catalysts by electrodeposition modulates *CH_xO adsorption to facilitate electrocatalytic reduction of CO₂ to CH₄. *Appl. Catal., B* **2025**, 360, 124525.
- [17] Chen, X.; Jia, S.; Chen, C.; Jiao, J.; Zhai, J.; Deng, T.; Xue, C.; Cheng, H.; Dong, M.; Xia, W.; Zeng, J.; Xing, X.; Wu, H.; He, M.; Han, B. Highly Stable Layered Coordination Polymer Electrocatalyst toward Efficient CO(2) -to-CH(4) Conversion. *Adv. Mater.* **2024**, 36, e2310273.