

Synergistic modulation of valence state and oxygen vacancy induced by surface reconstruction of the CeO₂/CuO catalyst toward enhanced electrochemical CO₂ reduction

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Funding information

Key Specialized Research and Development-International Science and Technology Cooperation Program in Henan Province, Grant/Award Number: 231111520500; Program for Science & Technology Innovation Talents in Universities of Henan Province, Grant/Award Number: 24HASTIT009; The 111 Project, Grant/Award Number: D17007; National Natural Science Foundation of China, Grant/Award Numbers: 52072114, 52271176; Henan Center for Outstanding Overseas Scientists, Grant/Award Number: GZS2022017

Abstract

Electrochemical CO₂ reduction reaction (CO₂RR) offers a promising strategy for CO₂ conversion into value-added C₂₊ products and facilitates the storage of renewable resources under comparatively mild conditions, but still remains a challenge. Herein, we propose the strategy of surface reconstruction and interface integration engineering to construct tuneable Cu⁰-Cu⁺-Cu²⁺ sites and oxygen vacancy oxide derived from CeO₂/CuO nanosheets (OD-CeO₂/CuO NSs) heterojunction catalysts and promote the activity and selectivity of CO₂RR. The optimized OD-CeO₂/CuO electrocatalyst shows the maximum Faradic efficiencies for C₂₊ products in the H-type cell, which reaches 69.8% at −1.25 V versus a reversible hydrogen electrode (RHE). Advanced characterization analysis and density functional theory (DFT) calculations further confirm the fact that the existence of oxygen vacancies and Cu⁰-Cu⁺-Cu²⁺ sites modified with CeO₂ is conducive to CO₂ adsorption and activation, enhances the hydrogenation of *CO to *CHO, and further promotes the dimerization of *CHO, thus promoting the selectivity of C₂₊ generation. This facile interface integration and surface reconstruction strategy provides an ideal strategy to guide the design of CO₂RR electrocatalysts.

KEYWORDS

active site, electrocatalytic CO₂ reduction reaction, Faraday efficiency, interface integration engineering and electrocatalysts, oxygen vacancy

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1 | INTRODUCTION

CO₂ can be regarded as an inexpensive, abundantly available, nontoxic, and reproducible resource; hence, use of an efficient method for CO₂ capture or conversion is a promising strategy to realize the carbon neutral process.^{1–3} Capture of CO₂ from flue gas provides a new solution to reduce carbon emissions and promote carbon economy. However, most CO₂ capture technologies still face significant drawbacks such as low efficiency, process complexity, regeneration energy loss, and shortage of adsorbents. In particular, these technologies cannot utilize CO₂ directly, which is not conducive to the long-term carbon cycle.^{4,5} Use electrochemical CO₂ reduction reaction (CO₂RR) to convert CO₂ into value-added chemicals has been proven to be an attractive approach because it can not only be implemented in a simple reaction device under comparatively mild conditions but can also be useful for energy storage of renewable energy sources (such as water energy and solar energy).^{6,7} Among various target compounds of CO₂RR, multi-carbon products (C₂₊) such as ethane and ethylene are used as chemical raw materials and energy carriers.⁸ However, because of the poor kinetics of the C–C coupling step due to complicated multi-proton and electron transfer, the activity and selectivity of C₂₊ products are severely limited.^{9,10} Therefore, efficient, active, and stable electrocatalysts are needed to realize the high activity and selectivity of C₂₊ products in CO₂RR.

Due to its unique electronic properties, it has been demonstrated that copper has moderate adsorption energy for crucial intermediates that produces C₂₊ products through a C–C coupling reaction during CO₂RR process.^{11–13} However, Cu itself is inherently limited by the proportional relationship of the adsorption energy of several reaction intermediates, resulting in a wide distribution of products and undesired hydrogen evolution reaction (HER),¹¹ thus hindering large-scale practical applications.¹⁴ To date, several efforts have been made to design Cu-based catalysts and achieve high activity of C₂₊ products, such as grain boundaries, microstructures and nanostructures, exposed lattices, doping, and structural defects/vacancy engineering.^{15–25} Among the various strategies for developing electrocatalysts, engineered heterojunctions are considered to be the general approach to boost molecular adsorption and activation.^{26–28} CeO₂ as a heterogeneous catalyst has attracted considerable attention because it has several O-vacancies and excellent redox properties derived from Ce³⁺/Ce⁴⁺ transformation, which represent unique properties that can promote the formation of Cu_xO/CeO₂ heterojunction electrocatalysts with highly active sites, promoting adsorption and activation of CO₂.^{29,30} In fact, CeO₂ has also been successfully applied in CO₂RR for the construction of highly efficient metal–CeO_x heterojunction electrocatalysts with the

best performance and excellent activity. For example, Bao et al. demonstrated that Au–CeO_x had higher activity and Faradic efficiency than Au or CeO_x for CO₂RR.³¹ Zhao et al. reported that coating a copper electrode with CeO₂ nanoparticles could greatly improve the selectivity of C₂₊ products during the electrochemical reduction of CO₂. Cu–CeO₂ had superior catalytic property, mainly attributed to the presence of Cu–CeO₂ interfaces, which stabilized the key intermediates by providing unique binding sites and/or adjusting the electronic structure of Cu.³²

Herein, CeO₂/CuO nanosheets (NSs) heterojunction electrocatalysts are obtained by hydrothermal synthesis using CeO₂-doped CuO. The as-obtained CeO₂/CuO NSs with well-dispersed CeO₂ on CuO NSs are reconstructed in situ to form oxide-derived interface/surfaces (CeO₂/CuO, CeO₂/Cu₂O, and CeO₂/Cu interface/surface) to expose more Cu⁰–Cu⁺–Cu²⁺ active sites and oxygen vacancies,⁸ which play a key role in determining the selectivity of C₂₊ products and show outstanding catalytic efficiency for converting CO₂ into C₂₊ products; also, the maximum Faraday efficiency (FE) of C₂₊ products is up to 69.8% in a 0.1 M KCl electrolyte with an H-type cell. The experimental results combined with density functional theory (DFT) calculations indicate that the Cu⁰–Cu⁺–Cu²⁺ sites and oxygen vacancies induced through interface/surface synergies are conducive to CO₂ adsorption and activation, accelerate the hydrogenation of *CO to *CHO, and further promote the dimerization of *CHO to facilitate C–C coupling and generate C₂₊ products.

2 | RESULTS AND DISCUSSION

CeO₂/CuO catalysts with controllable compositions were synthesized via a simple hydrothermal reaction by changing the metal precursor ratios, and the compositions of Cu/Ce were quantitatively analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). The CeO₂/CuO catalyst is named CCX (X is equal to the molar ratio of Ce to Cu+Ce multiplied by CC3, CC10, CC17, and CC49). We systematically investigate the effects of the metal precursor ratios on the formation of CeO₂/CuO NSs. The morphology and structure of CeO₂/CuO catalysts and CuO NSs are obtained by transmission electron microscopy (TEM). Representative TEM images of the synthesized CuO NSs and CeO₂/CuO catalysts are shown in Figures 1A–C and S1, indicating that the catalysts of CC3 (Figure S1A), CC10 (Figure S1D), and CC17 (Figure 1B) have a morphology of smooth nanosheets decorated with CeO₂ nanoparticles less than 5 nm in size, while CuO NSs (Figure 1A) have the same morphology as the CeO₂/CuO NSs, except for the presence of CeO₂ nanoparticles. Interestingly, a Cu precursor must be present in sufficient quantities for the nanoparticles to grow into nanosheets. Nanosheet structures will not form if a Cu

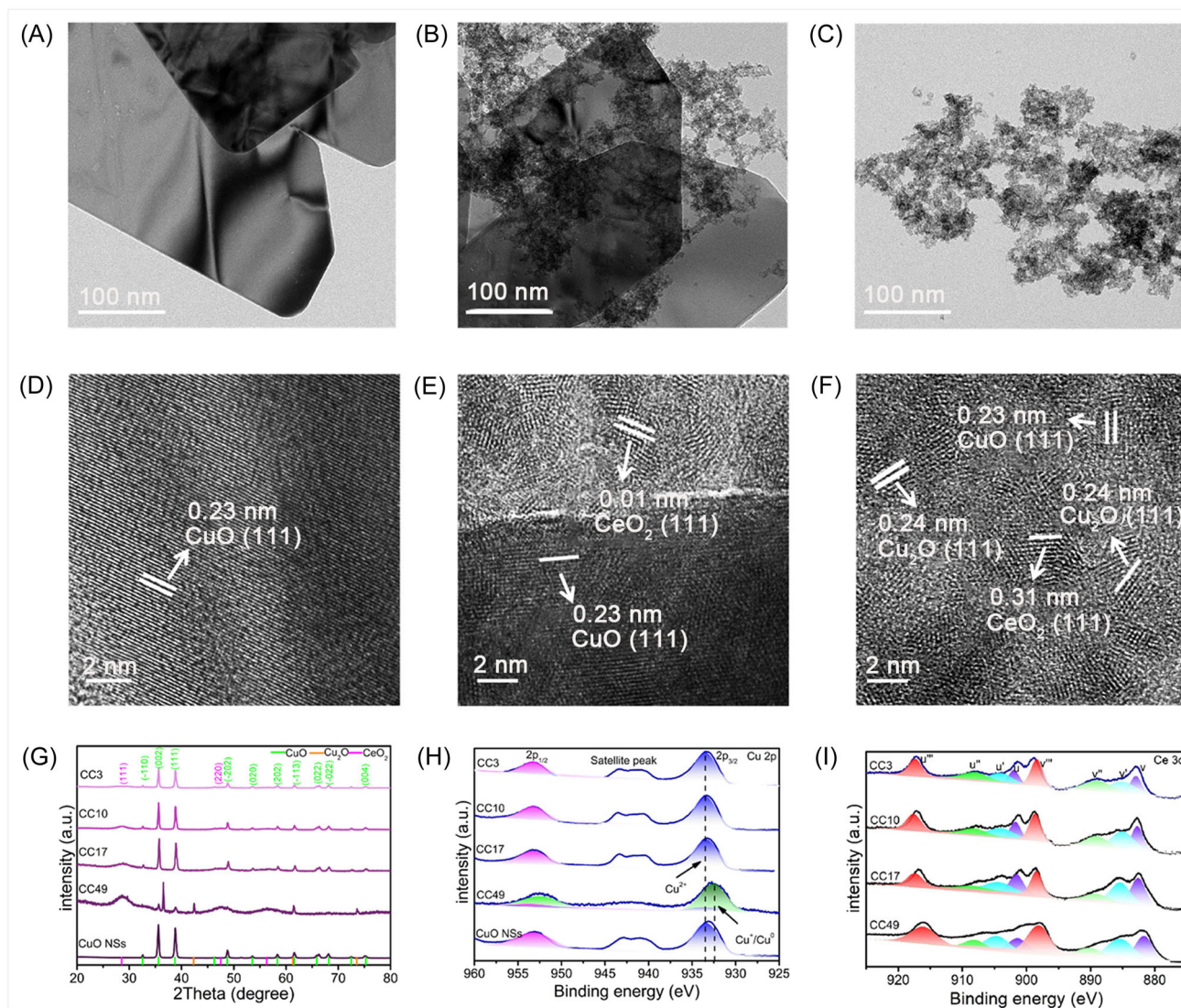


FIGURE 1 Structural characterization of CeO₂/CuO catalysts. (A–C) TEM images, (D–F) HR-TEM images of CuO NSs, CC17, and CC49, respectively, and (G) XRD patterns and XPS spectra of (H) Cu 2p and (I) Ce 3d for CeO₂/CuO catalysts.

precursor is not present in sufficient quantities. For example, from the TEM image of the CC49 catalyst shown in Figure 1C, it is clear that no nanosheet structure is formed. Two typical lattice fringes are observed in high-resolution TEM (HR-TEM) images with planar spacings of 0.23 and 0.31 nm for CC3 (Figure S1B), CC10 (Figure S1E), CC17 (Figure 1E), and CC49 (Figure 1F) corresponding to CuO(111) and CeO₂(111), respectively. An interplane spacing of 0.24 nm is observed on CC49 (Figure 1F), which can be attributed to the (111) lattice fringes of Cu₂O. The selected area electron diffraction (SAED) image also further confirms the formation of Cu₂O and CuO, as shown in Figure S2, and the diffracted rings correspond well with Cu₂O(111) and CuO(111). For CuO NSs, the inter-plane spacing is 0.23 nm (Figure 1D). Besides, the energy-dispersive spectroscopy (EDS) elemental mapping (Figures S1C,F and S3) and EDS spectrum (Figure S4)

results for CeO₂/CuO catalysts also provide evidence that the catalysts consist of CeO₂ and CuO crystallites.

The power X-ray diffraction (XRD) patterns of as-obtained CeO₂/CuO catalysts together with individual CuO NSs are shown in Figure 1G. The XRD patterns of CC3, CC10, and CC17 show the characteristic diffraction of CeO₂ and CuO. The diffraction peaks at 28.54°, 47.48°, and 56.34° are assigned to the (110), (002), (111), and (202) planes of CeO₂ (PDF# 43-1002), respectively. Besides, the diffraction peaks at 32.49°, 35.49°, 38.73°, and 48.72° are assigned to the (002), (111), and planes of CuO (PDF# 45-0937), respectively. These results indicate that a face-centered cubic (fcc) structure of fluorite (*Fm* $\bar{3}$ *m*) CeO₂ has been formed,³³ unlike the pure CuO NSs that display representative monoclinic CuO peaks. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical state and surface compositions of CuO/CeO₂ catalysts and CuO NSs. The Cu 2p

signals of CeO_2/CuO catalysts and CuO NSs are shown in Figure 1H. The Cu 2p core-level spectra of all the catalysts reveal obvious CuO features, namely, Cu^{2+} 2p_{3/2} and 2p_{1/2} peaks with binding energies (BEs) of 933.5 and 953.0 eV, respectively.³⁴ Strong Cu^{2+} satellites at 941.0 and 943.5 eV are also clearly observed,³⁵ whereas no apparent peaks assigned to Cu^+ can be identified, except the CC49. Two other peaks located at 932.5 and 952.0 eV are observed in CC49, which can be attributed to Cu^+ 2p_{3/2} and 2p_{1/2}, respectively, confirming the formation of Cu^+ at CC49, which is consistent with XRD results.³⁴ The Ce 3d signals of CeO_2/CuO catalysts are obtained to further identify the oxidation state of Ce. Due to the hybridization of the Ce 4f level and the O 2p valence band, the Ce 3d-level spectrum is considered to be a complex spectrum ranging from 880 to 920 eV. As shown in Figure 1I, the Ce 3d spectrum consists of eight peaks, labeled v and u, due to the presence of spin orbital twin peaks in the 3d_{5/2} and 3d_{3/2} orbits. The Ce^{4+} of 3d_{3/2} is labeled u (901 eV), u'' (908 eV), and u''' (917 eV), and the Ce^{4+} of 3d_{5/2} is labeled v (883 eV), v'' (889 eV), and v''' (898 eV).³⁶ The other two peaks u'(902 eV) and v' (885 eV) belong to Ce^{3+} ions and are derived from the ionization of Ce 3d_{5/2} and Ce 3d_{3/2}, indicating the presence of Ce_2O_3 in the sample.³⁷ These observations confirm the existence of Ce^{4+} and Ce^{3+} ions in the ceria lattice. The conversion of Ce^{4+} into Ce^{3+} will generate more oxygen vacancies, which is conducive to the improvement of catalytic activity.³⁸ To confirm the oxygen vacancies of CeO_2/CuO catalysts, we

study the O 1s XPS spectrum and the contents of all samples, as shown in Figure S5 and Table S1. The analysis of O 1s XPS spectra shows that there are three different forms of surface oxygen. The BE at 528.3–530 eV is attributable to lattice oxygen,⁸ and the BE at 532.0–531.8 eV is assigned to characteristic oxygen vacancy. The O 1s XPS spectra are in good agreement with Ce 3d XPS results.

The oxide-derived catalyst is generally produced by partially reducing the pre-formed metal oxides in situ to the metal state to generate the metal/metal oxide interface during CO_2RR , and it shows good performance; the in situ reduction of metal oxides on the surface of electrode can result in morphological changes, and residual metastable oxides can alter the environment and electronic structure of the active sites, thus regulating the catalytic behavior.¹⁵ In order to obtain the oxide-derived CCX (OD-CCX) and OD-Cu catalysts, the CCX and CuO catalysts are partially reduced by in situ electroreduction at -1.45 V (vs. RHE) for 1 h. The electrocatalytic performances of OD-CCX catalysts and OD-Cu NSs in a CO_2 -saturated 0.1 M KCl electrolyte are investigated in a typical gas-tight three-electrode H-type cell.²³ The catalytic ability of the obtained OD-CCX and OD-Cu NSs toward CO_2 reduction is assessed in N_2 - and CO_2 -saturated 0.1 M KCl electrolytes by linear sweep voltammetry (LSV), which is recorded in the range of 0 to -1.55 V (vs. RHE) at a scanning speed of 20 mVs^{-1} . Obviously, the total current density of OD-CC17 and OD-Cu NSs in the CO_2 -saturated electrolyte is higher than that of

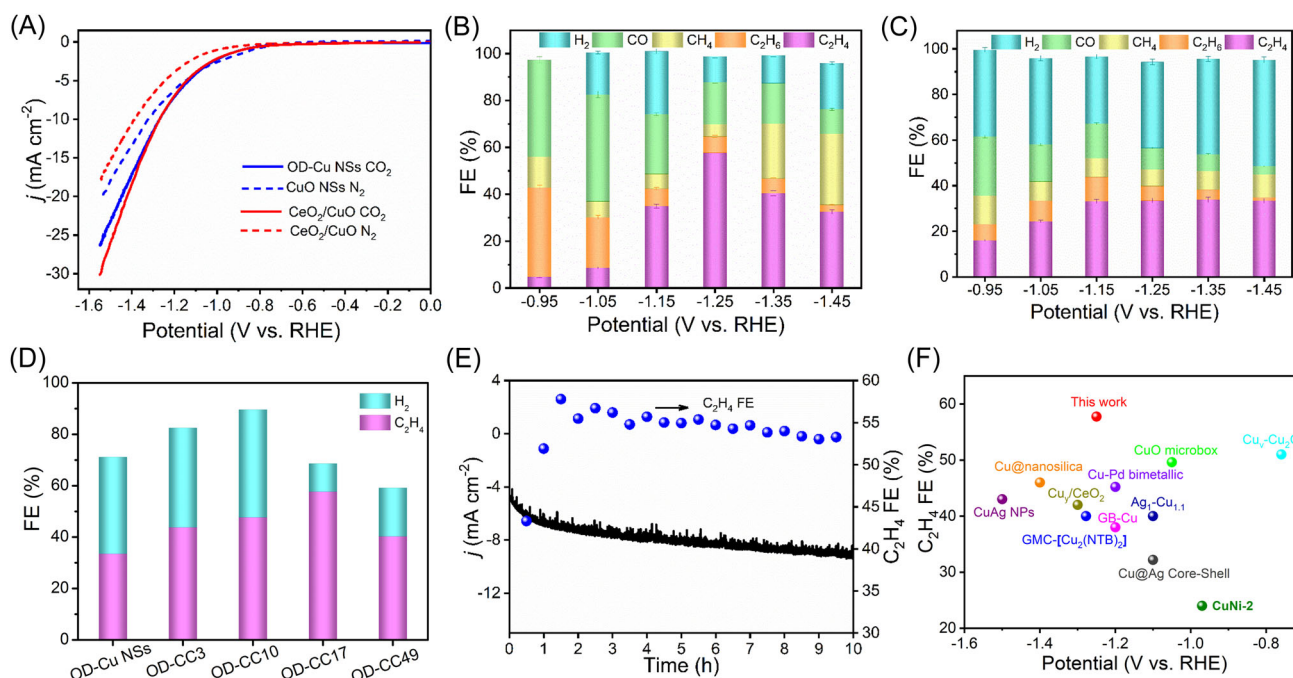


FIGURE 2 Electrochemical CO_2 reduction performance. (A) LSV curves. (B, C) FE of the gas reduction products of OD-CC17 and OD-Cu NSs, respectively. (D) FE for C_2H_4 and H_2 obtained on different OD-CCX catalysts at -1.25 V versus RHE. (E) Stability of OD-CC17 at a potential of -1.25 V versus RHE during 10 h. (F) C_2H_4 FE of OD-CC17 compared with reported electrocatalysts for reduction of CO_2 into C_2H_4 .

the N₂-saturated electrolyte, as shown in Figure 2A, indicating that the catalysts are more beneficial for CO₂RR than HER. Moreover, the current density of OD-CC17 is higher than that of other OD-CCX catalysts during CO₂RR from −0.05 V to −1.55 V vs. RHE (Figure S6). The gaseous products of CO₂RR are analyzed by gas chromatography (GC) in the range of −0.95 to −1.45 V (vs. RHE). The obtained reduction products' distribution as a function of applied potentials for OD-CC17 and OD-Cu NSs is displayed in Figure 2B,C, respectively. It is noteworthy that the main product of CO₂RR on OD-CC17 is C₂H₄, accompanied by C₂H₆, CH₄, H₂, and CO. It is obvious that the CO₂RR performance of OD-CC17 is significantly enhanced compared with OD-Cu NSs. Specifically, the C₂H₄ FE on OD-CC17 reaches the highest value of 57.8%, and the FE of C₂₊ products reaches the highest value of 69.8% at −1.25 V (vs. RHE). More importantly, the performance of OD-CC17 in 0.1 M KCl and 0.1 M KHCO₃ electrolytes was almost the same (Figure S7), suggesting that Cl[−] adsorption is not the main factor responsible for the different performance on the surface of the catalyst.³⁹ In contrast, OD-Cu NSs show low reduction efficiency of CO₂ with a low C₂₊ products FE of 37.9%, and C₂H₄ FE is only 33.5% at the same applied potential. The results show that the selectivity of the product is different when OD-CC17 is applied at different potentials. At relatively low overpotentials (−0.95 to −1.15 V [vs. RHE]), CO is the main product on OD-CC17. The FE of the produced CO decreases and the FE of the generated C₂H₄ increases with an increase in the applied potential. The evolution of H₂ is suppressed on OD-CC17 compared with that on OD-Cu NSs throughout the potential range examined. Therefore, the OD-CC17 electrode shows excellent selectivity for the electroreduction of CO₂ to C₂₊ products.

We also compare the catalytic performance of CO₂RR among OD-CC3, OD-CC10, OD-CC17, OD-CC49, and OD-Cu NSs to evaluate the relationship between the factors (different compositions and Cu chemical state) and electrocatalytic performance. The CO₂RR performance of the catalysts is measured under the same experimental conditions. The incorporation of various amounts of CeO₂ is more conducive to inhibiting HER and promoting C₂H₄ generation than OD-Cu NSs; also, the optimal loading of CeO₂ is 17.0%, as shown in Figures 2D and S8A–C. Then, the C₂H₄ FE is decreased when the doped amount of CeO₂ nanoparticles is further increased. The main reason for the decrease of electrocatalytic CO₂ reduction performance with the increase of the CeO₂ content is the decrease of effective active sites. The enhanced electrocatalytic selectivity of the OD-CC17 catalyst for CO₂ reduction can also be attributed to the synergistic effect between different valence Cu ions at the interface. In addition, compared with OD-Cu NSs and other OD-CCX

electrocatalysts (Figure S9), the electrochemical surface area (ECSA) of OD-CC17 is significantly increased because of the abundant oxygen vacancies on the surface of OD-CC17. Furthermore, electrochemical impedance spectroscopy (EIS) measurements are performed to obtain the interfacial resistance of catalysts during CO₂RR. The EIS result (Figure S10) reveals that the OD-CC17 catalyst has a lower charge-transfer resistance, indicating faster electron transfer on its surface.

We will focus on the performance of OD-CC17. The catalytic stability of OD-CC17 for CO₂RR in 0.1 M KCl is investigated for 10 h at −1.25 V (vs. RHE) using the chronopotentiometry technique. The stability of CO₂RR on OD-CC17 is shown in Figure 2E. It can be seen that the current density increases gradually with the reduction process and then tends to remain unchanged. It is also noticeable that small amounts of ethylene are detected during the first hour, indicating that CO₂RR is inhibited. After 1 h, the performance of CO₂RR is improved, because the in situ reconstructed surface improves the catalytic activity and the FE of C₂H₄ decreases slightly after 10 h, indicating that OD-CC17 has better stability, which is also confirmed by TEM after 10 h, as the morphology remains stable (Figure S11). In addition, the catalytic performance of OD-CC17 is the same as or even better than those of the previously reported Cu-based catalysts under similar experimental conditions (Figure 2F).^{38,40–49}

To further clarify the structure and compositions of CeO₂ and CuO during CO₂RR, we also performed TEM measurements immediately after the reduction reaction. The TEM images of OD-CCX catalysts are displayed in Figures 3A–C and S12A,B, which clearly indicate that the bulk structures of OD-CCX are well preserved. The HR-TEM images at the edge region of OD-CCX catalysts indicate the formation of Cu and Cu₂O on the surfaces of nanosheets (Figures 3D–F and S12C,D). The SAED images also further confirm the formation of Cu and Cu₂O, as shown in Figure S13, and the diffracted rings correspond well with Cu(111) and Cu₂O(111). The EDS mapping in Figures 3G–I and S12E,F suggests that CeO₂ nanoparticles are distributed uniformly and densely on the surface of nanosheets after surface reconstruction. Interestingly, Cu and Cu₂O small particles emerge and many atomic defects are formed on the surface of the catalyst during CO₂RR, which improves C₂₊ selectivity and inhibits HER.¹⁴ Consequently, the integration area between the CeO₂ and CuO interface is enlarged, thus resulting in a strong synergistic effect. Besides, the morphology of the surface-reconstructed OD-Cu NSs is less stable than that of the OD-CCX heterojunction catalyst, indicating that CeO₂ can maintain the stability of the electrocatalysts.

Moreover, XRD patterns of the surface-reconstructed OD-CCX catalysts confirm the coexistence of Cu, Cu₂O,

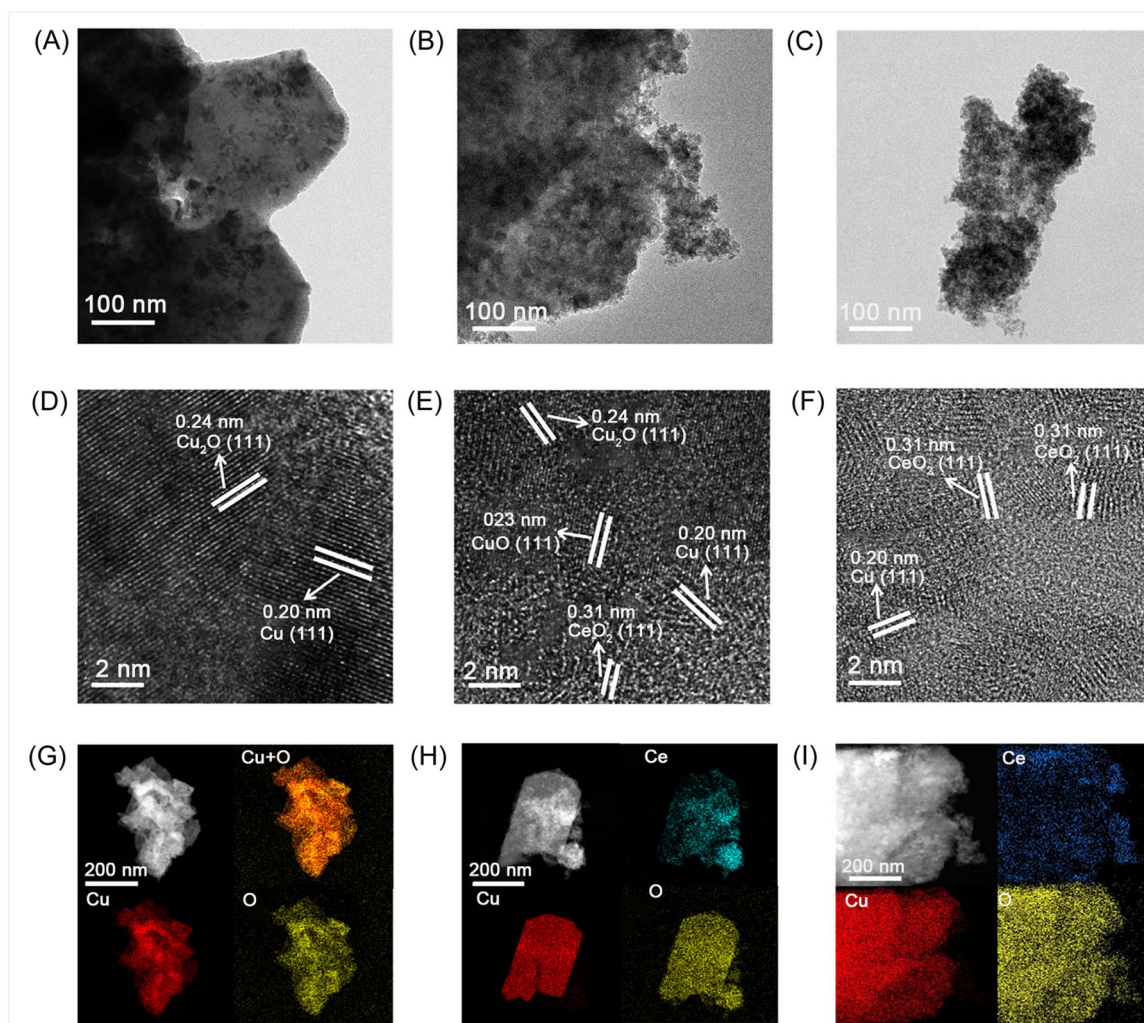


FIGURE 3 Structural characterizations of reconstructed OD-CCX catalysts. (A–C) TEM images, (D–F) HR-TEM images, and (G–I) EDS elemental mappings of OD-Cu, OD-CC17, and OD-CC49, respectively.

CuO, and CeO₂, except for the OD-CC49 catalyst, as shown in Figure 4A. Therefore, it is speculated that the CuO was only partly reduced, which further demonstrates that CeO₂ nanoparticles can maintain the stability of the catalyst. By contrast, the XRD pattern of reconstructed OD-Cu NSs shows that CuO peaks disappear and Cu⁰ and Cu⁺ signals appear, indicating that CuO has been completely reduced. The peak of Cu²⁺ still exists in the surface-reconstructed OD-CCX catalysts and a new Cu phase appears after electrochemical reduction, as shown in the XPS spectra of Cu 2p (Figure 4B) and Cu LMM Auger spectra (Figure 4C and Table S2), which is consistent with HR-TEM and XRD results. As for OD-Cu NSs, the peak of Cu²⁺ disappears and the signal peaks of Cu⁰ and Cu⁺ emerge after electrochemical reduction. It is reported that part of the CuO is not reduced due to the self-sacrifice mechanism of CeO₂.³⁸ First, the electrons preferentially reduce Ce⁴⁺ to Ce³⁺ in CeO₂/CuO during the

reconstruction process. Meanwhile, Ce³⁺ provides a rapid electron transport channel in the NSs region covered by CeO₂ nanoparticles. More oxygen vacancies are created through the conversion of Ce⁴⁺ into Ce³⁺ during electrochemical reduction, which promotes improvement of catalytic activity. The increased Ce³⁺ concentration in OD-CCX catalysts is also confirmed by XPS analysis (Figure 4D and Table S3). Moreover, with the increase of the Ce³⁺ concentration, the oxygen vacancies also increase because of the peak formed by the electrochemical reduction of Ce⁴⁺ into Ce³⁺. The surface-reconstructed OD-CCX catalysts show a significant increase in the vacancy oxygen/lattice oxygen ratio relative to the sample after CO₂RR (Figure S14 and Table S4), indicating that there are a large number of oxygen vacancies on the surface of the heterojunction catalyst.⁴⁶ Combined with catalytic activity, the presence of Cu²⁺ can inhibit HER, Cu⁰ can enhance the formation of *CHO from *CO,²³ and the higher content of Cu⁺ and

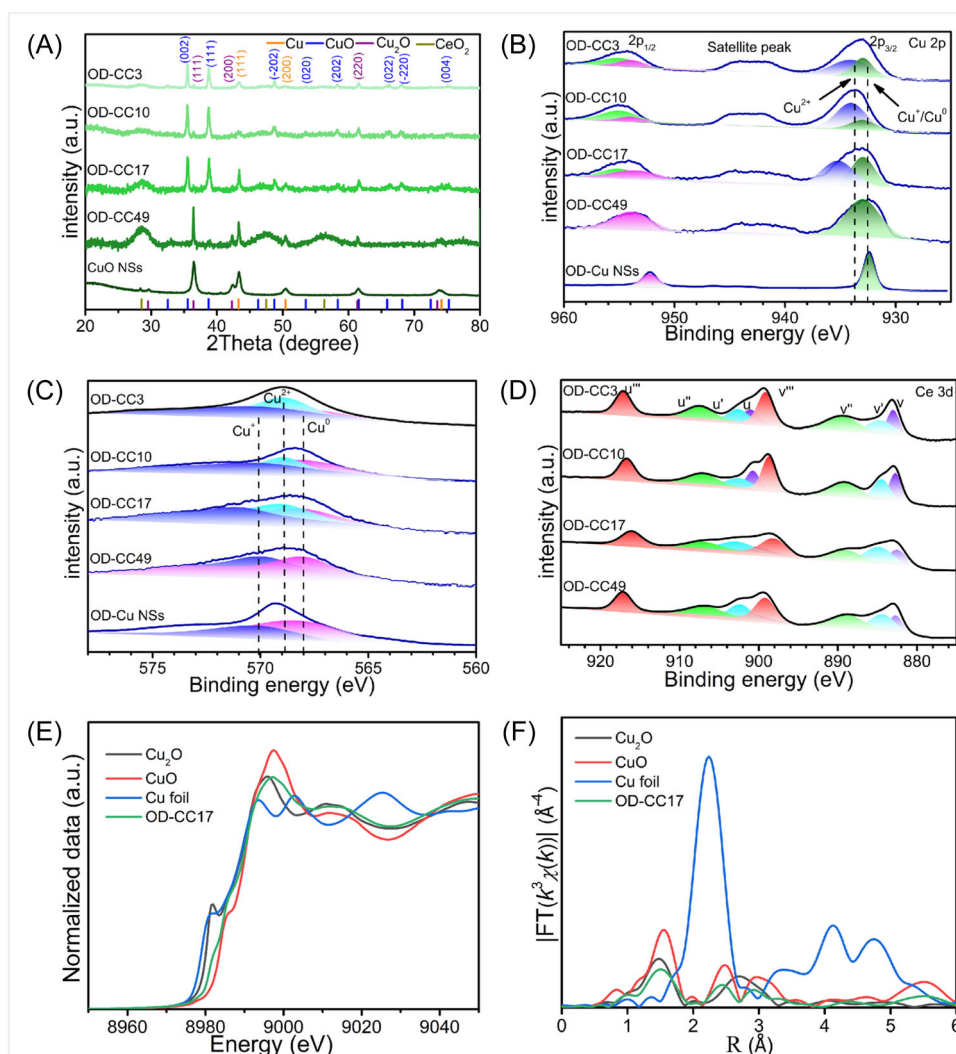


FIGURE 4 (A) XRD patterns, (B) XPS spectra and deconvoluted peaks of Cu 2p, (C) Cu LMM Auger spectra, (D) Ce 3d of OD-CCX samples, (E) Cu K-edge XANES spectrum, and (F) Cu K-edge Fourier transformed EXAFS spectrum of OD-CC17.

oxygen vacancies can promote the formation of C_{2+} products. The CO_2RR performance of OD-CCX catalysts is improved by introducing oxygen vacancies during in situ reduction. Cu K-edge X-ray absorption near edge structure (XANES) is performed to further characterize the detailed structural and electronic properties of OD-CC17 after surface reconstruction. After a long period of electrochemical reduction, the XANES spectrum shows the typical characteristics of low-oxidation Cu, but the electrode is still dominated by CuO state, as shown in Figure 4E. The k^3 -weighted Fourier-transformed (FT) extended X-ray absorption fine structure (EXAFS) spectra are shown in Figure 4F, and it is clear that the first shell coordination of Cu transforms into a mixture of different Cu species on OD-CC17. The chemical states of 0, +1, and +2 of Cu in OD-CC17 are evidenced by their absorption edge located between those of Cu, $Cu_2O(I)$, and CuO, which is further confirmed by

Cu EXAFS analysis that provides both the k and R space resolution (Figure S15). The coordination configuration of OD-CC17 is studied by quantitative EXAFS curve fitting, as shown in Figure S16 and Table S5. The fitting analysis shows that the coordination number (CN) of OD-CC17 is lower than that of the reference CuO. The results prove that OD-CC17 has an unsaturated coordination structure, because of which there are more active sites and the catalytic efficiency for CO_2RR has improved. These results indicate that the introduction of CeO_2 nanoparticles can stabilize the CuO phase, which is ascribed to the interaction between Ce and Cu.

To further explore the surface-reconstructed mechanism and the valence state of Cu elements during electrolysis, in situ Raman spectroscopy is carried out to monitor the structural evolution of the OD-CC17 electrode. The Raman peaks at 286 and 327 cm^{-1} ascribed to CuO at the open circuit potential (OCP), and the spectrum at

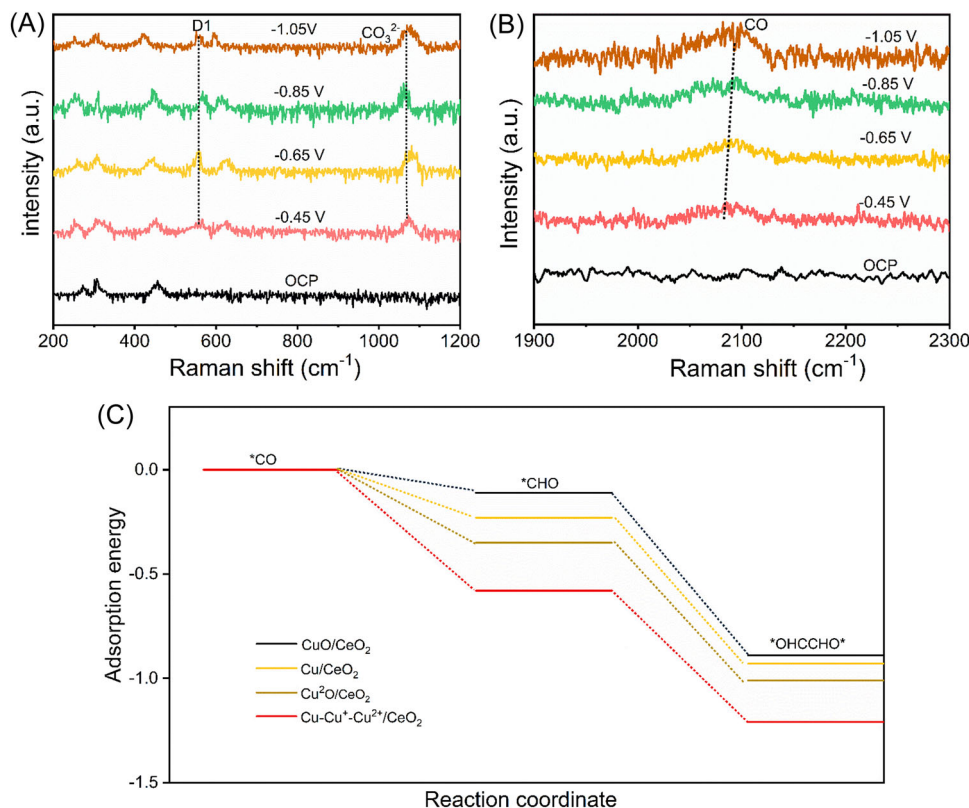


FIGURE 5 Compositional analysis of OD-CC17 during CO₂RR. (A, B) In situ Raman spectra on OD-CC17 collected at different potentials. (C) Reaction energy diagram for *CO hydrogenation to *CHO on CeO₂/CuO, CeO₂/Cu₂O, CeO₂/Cu, and Cu⁰-Cu⁺-Cu²⁺/CeO₂.

463 cm⁻¹ on OD-CC17 is assigned to the symmetric stretching vibration mode of the oxygen atoms around Ce⁴⁺ shown in Figure 5A.⁴⁵ The characteristic peaks of CuO weaken and begin to appear at ~624 and ~1070 cm⁻¹ related to Cu and Cu₂O on OD-CC17 at -0.45 V (vs. RHE). Meanwhile, a new peak appears at ~560 cm⁻¹ during the negative scanning, assigning to the D1 bond of defective CeO₂.³⁸ The peak is the result of electrochemical reduction of Ce⁴⁺ to Ce³⁺ and the creation of an oxygen vacancy.³⁸ The Raman peaks at 2085 cm⁻¹ is ascribed to the C≡O stretching vibration of *CO on Cu surface (Figure 5B).⁵⁰ Oxygen vacancy, as a Lewis site, can improve the surface adsorption capacity of CO₂ molecules and increase the binding energy of intermediate products (CO*),⁵¹ thereby improving the efficiency of CO₂RR. Therefore, OD-CC17 can effectively absorb and transform CO₂, therefore enhancing the catalytic efficiency. The intensities of two Raman peaks of CuO (286 and 327 cm⁻¹) are weakened to a certain degree but do not disappear completely, indicating that the surface of CuO is not reduced completely under the reduction potential.⁵⁰ Therefore, it can be shown that the Cu⁰-Cu⁺-Cu²⁺ ions act together to promote electrocatalytic carbon dioxide reduction. The catalyst after stability at -1.25 V (vs. RHE) for 10 h is characterized by TEM (Figure S11). The initial

morphology of OD-CC17 is basically maintained but with a wrinkled surface and edge, confirming the generally existing structural evolution during CO₂RR.⁵²

We further conducted DFT calculations to elucidate the mechanism of ethylene over Cu⁰-Cu⁺-Cu²⁺ sites modified with CeO₂ and high C₂H₄ selectivity on the surface-reconstructed OD-CC17 surface in CO₂RR. Based on TEM, XPS, XRD, XANES, and in situ Raman results, the introduction of CeO₂ can lead to the formation of an interface/surface among Cu, Cu₂O, CuO, and CeO₂, and prevent complete reduction of Cu²⁺. Cu/CeO₂, Cu₂O/CeO₂, CuO/CeO₂, and Cu⁰-Cu⁺-Cu²⁺/CeO₂ models are shown in Figure S17A–D, which are built to represent Cu⁰, Cu⁺, Cu²⁺, and Cu⁰-Cu⁺-Cu²⁺ active sites, respectively. CO₂ is generally first reduced into *CO by the *COOH path, and the adsorbed *CO intermediate is considered to be an important intermediate of C₂₊ products in CO₂RR. The introduction of CeO₂ can enhance water activation and form an interface with active sites.⁵³ Han and co-workers have confirmed that *CO easily formed *CHO on Cu/CeO₂ and facilitated C–C coupling via coupling between *CHO in the presence of CeO₂, thus endowing the CeO₂/CuO catalyst with excellent catalytic property of CO₂RR for C₂₊ products.²³ It is very important to establish sufficient *CO coverage to facilitate *CHO formation that promotes C–C

coupling kinetics in order to produce C_{2+} products (Figure S17E–L). As shown in Figure 5C, the adsorption energy of $^*CHO$ at Cu^+ and $Cu^0-Cu^+-Cu^{2+}$ sites is relatively stronger than that at Cu^0 and Cu^{2+} sites, which enhances the coverage of $^*CHO$ and promotes coupling between $^*CHO$ and $^*OHCCHO^*$. On the other hand, near the surface of CeO_2 and $Cu^0-Cu^+-Cu^{2+}$ sites, the energy for 2^*CHO coupling to $^*OHCCHO^*$ decreases sharply to -1.21 eV, indicating that $Cu^0-Cu^+-Cu^{2+}/CeO_2$ could facilitate C–C coupling from $^*OHCCHO^*$ to produce C_{2+} products. Thus, $Cu^0-Cu^+-Cu^{2+}$ sites with sufficient $^*CO$ coverage and relatively low $^*OHCCHO^*$ formation energy are most preferable for C–C coupling and the further production of C_2 products.

3 | CONCLUSION

In summary, the surface-reconstructed CeO_2/CuO heterojunction electrocatalyst significantly improves the selectivity and activity toward C_{2+} products in CO_2RR . The reconstructed CeO_2/CuO NSs show prominent selectivity for the reduction of CO_2 to C_2H_4 , and the C_2H_4 FE is up to 57.8% in the H-type cell. The reason for the high reduction efficiency is that the surface-reconstructed CeO_2/CuO NSs maximize the interfacial integration of components, promote the formation of oxygen vacancies, and increase the surface active site density. Compared with pure CuO nanosheets with a weak binding site of CO_2 molecular adsorption, the CeO_2 decoration induces a new stable-binding site at the CuO and CeO_2 interface, promoting the activation of CO_2 and the C–C coupling reaction on nearby surfaces. Most importantly, DFT calculations prove that the C–C coupling on reconstructed OD- CeO_2/CuO NSs follows the $^*CHO$ path and interface effects promote the thermodynamic and kinetic processes of $^*OHCCHO^*$. These findings provide a novel strategy for regulating the interface of heterostructure catalysts and contribute to the rational design of efficient catalysts for CO_2RR target products.

4 | EXPERIMENTAL SECTION

4.1 | Materials

Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) was purchased from Macklin. Sodium hydroxide ($NaOH$) and potassium chloride (KCl) were obtained from Aladdin Chemical Reagents. Copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) was purchased from Kermel. Nafion (5 wt.%) was obtained from Aldrich. CO_2 and N_2 were purchased from Airgas.

4.2 | Synthesis of CeO_2/CuO NSs catalysts

CeO_2/CuO NSs catalysts with various contents of CeO_2 (3, 10, 17, and 51 wt%, named CC3, CC10, CC17, and CC51, respectively) were prepared using a hydrothermal synthesis method with some modifications.⁵⁴ Briefly, in a specific synthesis of CC17 catalyst, 0.469 g of $Cu(NO_3)_2 \cdot 3H_2O$, and 0.361 g of $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in deionized water (30 mL) and stirred for 20 min. Subsequently, 10 mL of $NaOH$ (9.6 M) was slowly dropped into the above solution and aged for 1 h with intense stirring to obtain ink-blue color precipitates. The above precipitates were then transferred to an autoclave (100 mL) and reacted at $100^\circ C$ for 24 h. The precipitation was then centrifuged several times with distilled water and ethanol. Then, the as-collected catalysts were dried at $70^\circ C$ overnight. During the synthesis of CCX, the total molar number of Cu^{2+} and Ce^{3+} and the concentration of $NaOH$ were constant, and the different compositions were obtained by tuning the molar ratio of Cu^{2+} and Ce^{3+} . With the increase of the Ce^{3+} concentration, the consumption of $NaOH$ increased, which resulted in the decomposition of the obtained $Cu(OH)_4^{2-}$ to form Cu_2O at high temperature, as shown in Scheme S1.⁵⁵ The synthesis of CeO_2 and CuO catalysts was performed using the same method as that of the CeO_2/CuO NSs catalyst, except for the addition of $Ce(NO_3)_3 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$.

4.3 | Physical characterizations

TEM and HR-TEM results were used to characterize the morphologies and size of the catalysts.⁵⁶ XRD patterns, XPS, and AES were measured to characterize the catalyst structure and chemical valence state.⁵⁷ The compositions of CeO_2/CuO NSs were analyzed by ICP-MS. In situ Raman spectroscopy was performed with a 532 nm laser on LabRAM HR Evolution in a flow cell. XANES experiments were carried out on BSRF beam line 1W1B at Shenzhen Synchrotron.⁵⁸

4.4 | Preparation of the working electrode

The catalyst ink was prepared by dispersing 20.0 mg of CeO_2/CuO with 5.0 μL of Nafion solution (5 wt%) in 1.0 mL of isopropyl alcohol and then performing ultrasonic treatment for at least 30 min.⁵⁹ Subsequently, 10 μL of catalyst ink was coated on the surface of a polished glass carbon electrode with a diameter of 3 mm, which was then dried as the working electrodes for subsequent CO_2RR tests.

4.5 | Electrochemical measurement

The electrochemical tests were carried out on the electrochemical workstation (760e, CHI) using a gas-tight three-electrode system with a working electrode, in which a Ag/AgCl electrode, a Pt sheet, and a 0.1 M KCl solution were used as the reference electrode, the counter electrode, and the electrolyte during CO₂RR, respectively. Before the electrochemical test, the electrolyte in the cathode compartment was foamed with CO₂ or N₂ to obtain a CO₂- or N₂-saturated solution. EIS measurements were conducted under a bias of −0.5 V versus RHE with a frequency that ranged from 0.01 to 10⁵ Hz.³⁰ The double-layer capacitance C_{dl} value was associated with ECSA, which was estimated based on the scan rate dependence of cyclic voltammetry curves (CVs) to measure the capacitance current in relationship with the double layer. The CV curves were in the range 0.25–0.35 V versus RHE. By plotting the C_{dl} value of Δj ($j_a - j_c$) against the scanning rates (j_a = anodic current density, j_c = cathodic current density) at −0.15 V versus RHE, the slope was twice that of the C_{dl} value. The scanning rates ranged from 40 to 120 mV s^{−1}.⁶⁰ The measured electrode potentials were converted into the RHE scale as follows:

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

Gas chromatograph (PANNA) was used to quantify the gas products (i.e., H₂, CO, CH₄, C₂H₄, and C₂H₆) using a flame ionization detector (FID) and a thermal conductivity detector (TCD). GC was directly connected to the H-type cell for on-line analysis. The FE of each gas product was calculated using the following equation⁶¹:

$$\text{FE} = \frac{n \cdot F \cdot v_i \cdot V \cdot P}{R \cdot T \cdot I},$$

where F is the Faraday constant (96,485 C mol^{−1}), I and V are the cell current and gas flow, respectively, n is the number of electrons required to generate molecular products (e.g., 2e[−], 2e[−], 8e[−], 12e[−], and 14e[−] for CO, H₂, CH₄, C₂H₄, and C₂H₆), and ppm is the product concentration measured by gas chromatography. $T = 273.15 \text{ K}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and $P = 1.013 \times 10^5 \text{ Pa}$.

4.6 | Computational method

Spin polarization DFT was performed using the Perdew–Burke–Ernzerhof functional under generalized gradient approximation. The model used was a hybrid

structure of Cu, CuO, Cu₂O, and CeO₂ connected by (111) facets, respectively.⁵⁶

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 52072114 and 52271176), the 111 Project (Grant No. D17007), the Henan Center for Outstanding Overseas Scientists (Grant No. GZS2022017), the Key Specialized Research and Development–International Science and Technology Cooperation Program in Henan Province (Grant No. 23111520500), and the Program for Science & Technology Innovation Talents in Universities of Henan Province (24HASTIT009).

CONFLICT OF INTEREST STATEMENT

The authors declare that there are no conflicts of interests.

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SUPPORTING INFORMATION

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How to cite this article: Chang F, Zhang Z, Zhang Y, et al. Synergistic modulation of valence state and oxygen vacancy induced by surface reconstruction of the CeO_2/CuO catalyst toward enhanced electrochemical CO_2 reduction. *Carbon Energy*. 2024;6:e588. doi:10.1002/cey2.588