



Enhanced Active Hydrogen Absorption and Stabilized Cu(I) Species Over Cu-O-Ce Bridges Boosting Electrocatalytic CO₂ Reduction to Ethylene

Zhenwei Zhao⁺, Yu Zhang⁺, Junjun Li⁺, Bingqing Yao, Hui Zhang, and Zhicheng Zhang*

Abstract: Rational design of water activation center to promote active hydrogen (*H) generation and stabilize Cu(I) species are significant for the formation of multicarbon (C₂₊) products over Cu-based catalysts in electrocatalytic CO₂ reduction reaction (CO₂RR). Herein, CeO₂ nanograins and CuO nanothorns were selectively deposited on the edges of Cu₂O cubes through the seed-mediated growth method. The as-synthesized Cu_xO-CeO₂ composites exhibit enhanced Faradaic efficiency and partial current density of C₂H₄ compared with Cu₂O cubes. In situ spectroscopies and theoretical calculations confirm that the Cu-O-Ce bridges in Cu_xO-CeO₂ composite can effectively enhance *H absorption and stabilize Cu(I) species, facilitating subsequent C-C coupling and further protonation into the key *COCHO intermediate of C₂H₄. This work provides new insights into modulating *H absorption and stabilizing Cu(I) species for boosting CO₂ to C₂₊ products.

Introduction

The electrochemical reduction of CO₂ into multicarbon (C₂₊) products driven by renewable electricity has emerged as a promising strategy for achieving the carbon neutrality goal and alleviating the greenhouse effect.^[1-5] To date, Cu-based materials have been considered as efficient catalysts to electrochemically convert CO₂ into C₂₊ products.^[6-8]

Compared with metallic Cu, electron-deficient Cu(I) species have been demonstrated to show enhanced selectivity toward C₂₊ products.^[9-12] However, the redox process of the active Cu(I) species in electrocatalytic CO₂ reduction reaction (CO₂RR) usually leads to poor product selectivity and insufficient catalytic stability. Until now, various strategies have been developed to stabilize the Cu(I) species and achieve more efficient electrocatalytic CO₂RR, such as morphology regulation,^[13-15] atomic doping,^[16-18] and interface engineering.^[19-21]

Rare earth elements possess unique electronic structures and strong spin-orbit coupling effects.^[22,23] Particularly, the unique 4f orbital structure and adjustable valence state of the lanthanide element Ce are conducive to electron delocalization, promoting covalent interactions with adsorbed intermediate species and maintaining the surrounding atoms in a high-valence chemical state.^[24-26] As a result, the variable-valence Ce species may maintain the oxidation valence of Cu and enhance the stability of Cu(I) species in electrocatalytic CO₂RR process. In addition, in an alkaline electrolyte, water serves as the proton source for the CO₂RR reaction. Studies have shown that the presence of CeO₂ is beneficial for water activation.^[27-29] Accelerating the dissociation of water could provide an adequate supply of protons, and then regulate the reaction pathway and product selectivity toward specific C₂₊ products.^[30-33]

Herein, Cu_xO-CeO₂ composites were prepared with Cu₂O cubes as seeds, in which CuO nanothorns and CeO₂ nanograins grow on the edges of Cu₂O cubes. The as-synthesized Cu_xO-CeO₂ composites exhibited a maximum Faradaic efficiency (FE) of 51.7% with a partial current density of -102.8 mA cm⁻² toward C₂H₄. In situ spectroscopies and density functional theory (DFT) calculations confirm that the CeO₂ nanograins could promote the dissociation of H₂O to provide more *H, facilitating subsequent C-C coupling and further protonation to form the *COCHO intermediate. Note that CeO₂ nanograins can stabilize Cu(I) species as a sacrificial agent, and CuO nanothorns transformed into Cu₂O after the reaction, acting as a role in synergistically protecting Cu(I) species.

Results and Discussion

Cu_xO-CeO₂ composites were synthesized via a simple seed-mediated growth method with Cu₂O cubes as seeds (Figures 1a, S1 and S2). X ray diffraction (XRD) pattern shows typical peaks of Cu₂O for both Cu_xO-CeO₂ composites

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Additional supporting information can be found online in the Supporting Information section

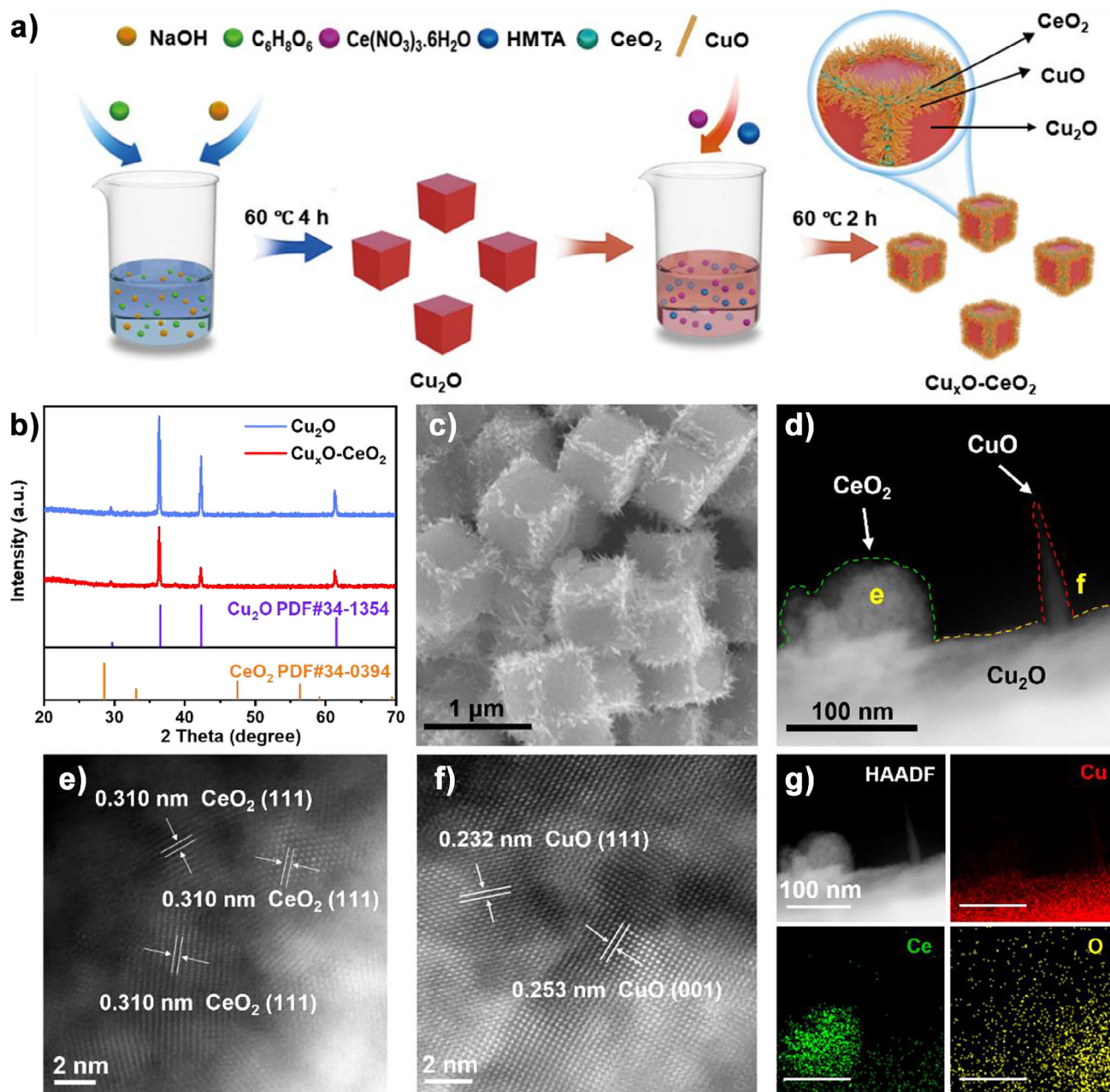


Figure 1. Synthesis and structural characterization. a) Schematic illustration for the preparation of $\text{Cu}_x\text{O}-\text{CeO}_2$ composites. b) XRD patterns of Cu_2O cubes and $\text{Cu}_x\text{O}-\text{CeO}_2$ composites. c) SEM, d)–f) AC-HAADF-STEM images and g) corresponding EDS element mappings of $\text{Cu}_x\text{O}-\text{CeO}_2$ composites. Note that (e–g) are taken from (d).

and Cu_2O cubes (Figure 1b). There are no prominent peaks corresponding to CeO_2 nanograins, which could be attributed to their small grain size. Scanning electron microscopy (SEM) image shows that well-defined spiny structures grow on the edges of cubes for $\text{Cu}_x\text{O}-\text{CeO}_2$ composites (Figure 1c). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) image indicates that spiniform CuO and CeO_2 nanograins grow on the edge of Cu_2O cubes (Figure 1d–f), which could be further confirmed by the corresponding energy-dispersive spectroscopy (EDS) mapping images (Figures 1g and S3). As

shown in Figure 1e, the lattice spacing of 0.310 nm could be assigned to the (111) plane of CeO_2 . The lattice spacings of 0.232 and 0.253 nm can be attributed to the (111) plane and (001) plane of CuO, respectively (Figure 1f).

The valence states and electronic structure of the Cu_2O cubes and $\text{Cu}_x\text{O}-\text{CeO}_2$ composites were analyzed via X-ray absorption fine structure spectroscopy (Table S1, Figures 2a–e, S4, and S5). The Cu K-edge X-ray absorption near edge structure (XANES) of $\text{Cu}_x\text{O}-\text{CeO}_2$ composites coincides with that of the standard Cu_2O sample, indicating that the valence state of Cu in $\text{Cu}_x\text{O}-\text{CeO}_2$ composites is

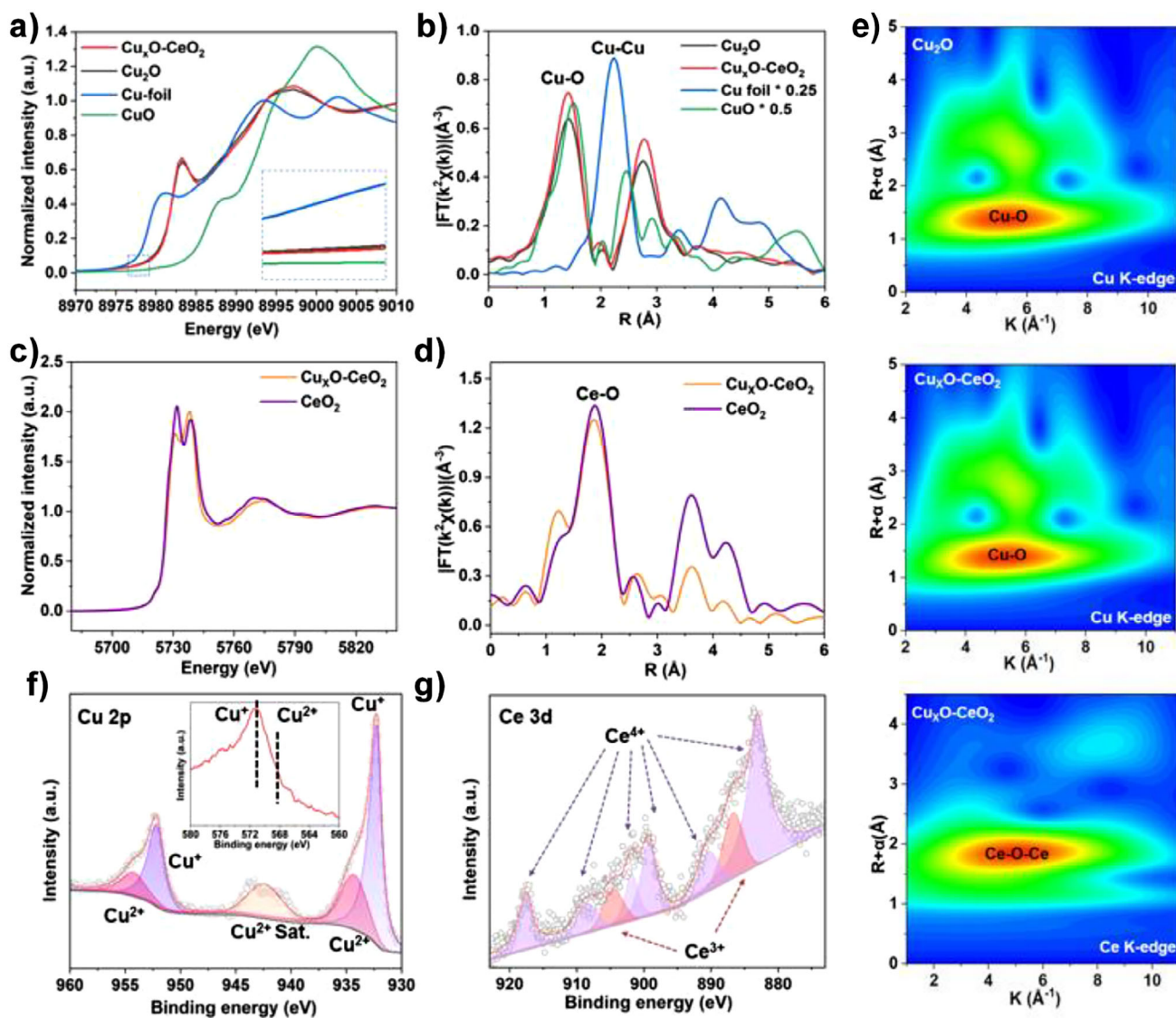


Figure 2. Spectral characterization. Cu K-edge a) XANES and b) FT-EXAFS spectra of Cu_xO – CeO_2 composites with reference to Cu foil, Cu_2O , and CuO. Ce K-edge c) XANES and d) FT-EXAFS spectra of Cu_xO – CeO_2 with reference to CeO_2 . e) Wavelet transform of Cu_2O cubes and Cu_xO – CeO_2 composites. XPS spectra of f) Cu 2p and g) Ce 3d of Cu_xO – CeO_2 composites. The inset in (f) is Cu Auger LMM of Cu_xO – CeO_2 composites.

mainly + 1 (Figure 2a). The Fourier transformed extended X-ray absorption fine structure (FT-EXAFS) spectrum shows a peak at approximately 1.5 Å, which can be attributed to the Cu–O bond (Figure 2b). The Ce L_3 -edge XANES spectrum and FT-EXAFS spectrum are shown in Figure 2c,d. Compared with the spectrum of the standard CeO_2 , no obvious differences were observed, indicating that CeO_2 is the dominant phase for Ce species. The wavelet transform contour plots further confirm the structure of Cu_xO – CeO_2 composites (Figure 2e). According to the high-resolution XPS spectrum of Cu 2p, the two prominent peaks located at 932.6 and 952.4 eV are attributed to Cu(I) species for both Cu_2O cubes and Cu_xO – CeO_2 composites (Figures 2f and S6). Impressively, compared with Cu_2O cubes, stronger characteristic peaks of Cu^{2+} and corresponding satellite peaks were observed in Cu_xO – CeO_2 composites. The Cu^{2+} species could be attributed to CuO nanothorns grown on the edges

of Cu_2O cubes (Figure 1d,f). For the Cu Auger LMM spectra, the peak at 570.4 eV is the characteristic peak of Cu(I) species, and there is no characteristic peak of Cu^0 , further proving that Cu mainly exists in the form of Cu(I) species for both Cu_2O cubes and Cu_xO – CeO_2 composites. According to the XPS spectrum of Ce 3d, Ce in the Cu_xO – CeO_2 composites exists with a mixed trivalent and tetravalent valence state, and the peak area of Ce^{4+} is much higher than that of Ce^{3+} , indicating that Ce mainly exists in the form of Ce^{4+} (Figure 2g).

The electrocatalytic CO_2RR performance test of the prepared Cu_2O cubes and Cu_xO – CeO_2 composites was conducted in a flow cell (Figure S7). Linear sweep voltammetry (LSV) curves show that the Cu_xO – CeO_2 composites possess a higher current density compared with Cu_2O cubes at the same potential, indicating the enhanced electrochemical CO_2RR activity for Cu_xO – CeO_2 composites (Figure 3a). Gas-phase chromatography and ^1H nuclear magnetic resonance

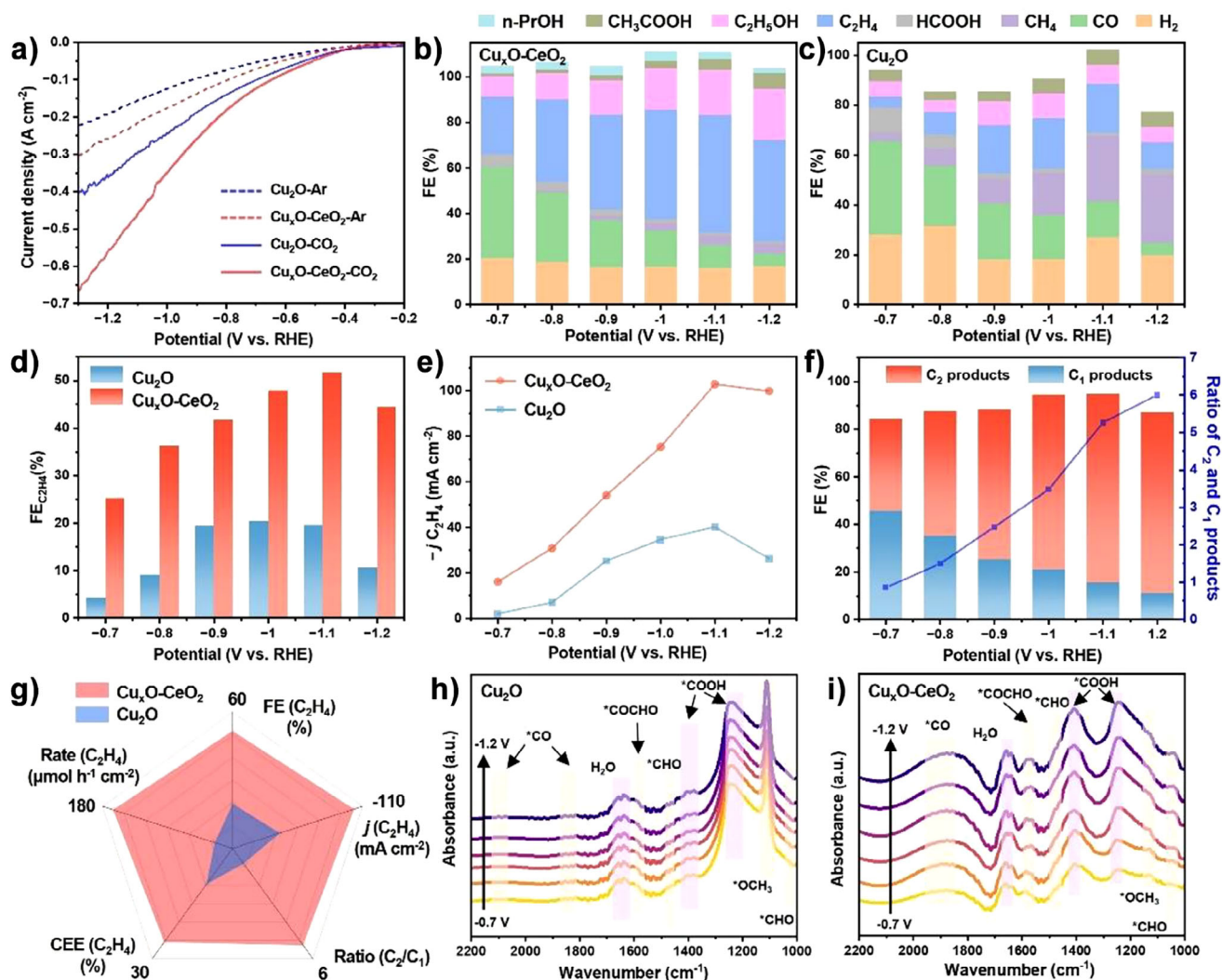


Figure 3. CO₂RR performance. a) LSV curves of Cu_xO–CeO₂ composites and Cu₂O cubes in CO₂-saturated or Ar-saturated in 1.0 M KOH electrolyte. FEs of various products over b) Cu_xO–CeO₂ composites and c) Cu₂O cubes. d) FE of C₂H₄ and e) $j_{\text{C}_2\text{H}_4}$ over Cu_xO–CeO₂ composites and Cu₂O cubes. f) FE and the C₂/C₁ ratio over Cu_xO–CeO₂ composites. g) Overall performance comparison between Cu_xO–CeO₂ composites and Cu₂O cubes for CO₂RR performance. In situ ATR-FTIR characterization at different potentials for h) Cu₂O cubes and i) Cu_xO–CeO₂ composites at –0.7, –0.8, –0.9, –1.0, –1.1, –1.2 V versus RHE, respectively.

spectroscopy were used to detect the gas and liquid-phase products and further quantify the products, respectively (Figures S8 and S9). Compared with Cu₂O cubes, Cu_xO–CeO₂ composites exhibited higher activity and selectivity for C₂H₄ products. Specifically, at –1.1 V versus RHE, the FE for C₂H₄ products exceeded 50%, which is approximately 2.6 times that of the Cu₂O cubes (Figure 3b–d). The Cu_xO–CeO₂ composites exhibited higher partial current density of C₂H₄ ($j_{\text{C}_2\text{H}_4}$) across the entire potential range, with a maximum $j_{\text{C}_2\text{H}_4}$ of –102.8 mA cm^{–2} at –1.1 V versus RHE, which is much higher than that of the pure Cu₂O cubes (Figure 3e). Meanwhile, the FE for C₂₊ products of the Cu_xO–CeO₂ composites could exceed 80%, and the maximum C₂/C₁ ratio could reach up to 6 (Figure 3f). In addition, the Cu_xO–CeO₂ composites displayed higher formation rate of C₂H₄, higher cathode energy efficiency (CEE) (Figures 3g). Specifically, at different potentials ranging from –0.7 to

–1.1 V versus RHE, the selectivity of pure CeO₂ toward H₂ is higher than 80%, demonstrating that CeO₂ does not have the ability to electrochemically produce C₂₊ products through CO₂RR and is not the active site for C–C coupling. The CO₂RR performance of the physically mixed sample of Cu₂O and CeO₂ was similar to that of pure Cu₂O cubes (Figure S10), indicating the unique heterostructural Cu_xO–CeO₂ composites could facilitate the C–C coupling to form the C₂₊ products.

The structures of the catalysts after the electrochemical CO₂RR test were also characterized (Figure S11). SEM images indicate that the cubic morphology of both Cu₂O cubes and the Cu_xO–CeO₂ composites could be well maintained. Cu₂O cubes surface was almost completely reduced to metallic Cu, while the Cu₂O phase of the Cu_xO–CeO₂ composites could exist stably as confirmed by the HRTEM images. The EDS elemental mappings indicated the uniform

distribution of Cu and O elements, and CeO₂ nanograins were still located at the edges of Cu₂O cubes. The XRD pattern further demonstrated that the characteristic peak intensity of Cu₂O in the Cu_xO–CeO₂ composites was stronger, and the characteristic peak of Cu was more obvious in Cu₂O cubes after the reaction (Figure S12). From the Cu Auger LMM spectrum, the Cu_xO–CeO₂ composites possess a stronger characteristic peak of Cu(I) species at 570.4 eV, proving that Cu mainly existed in the form of Cu(I) species, which is consistent with the results of HRTEM and XRD. The Ce 3d XPS spectrum of the Cu_xO–CeO₂ composites after the CO₂RR showed that the characteristic peak area of Ce³⁺ was increased, indicating that Ce⁴⁺ was partly reduced to Ce³⁺ (Figure S13). Therefore, it might be speculated that the construction of the Cu_xO–CeO₂ composites have the electron-withdrawing interaction between Ce and Cu, which could stabilize Cu(I) species, thereby promoting the C–C coupling to C₂₊ products.

To investigate the reaction pathways and mechanisms of electrochemical CO₂RR for Cu₂O cubes and Cu_xO–CeO₂ composites, in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was employed to analyze the intermediates (Figures 3h,i and S14–S15). The bands located at approximately 1400 and 1250 cm^{−1} belong to the C–O stretching vibration and symmetric vibration of *COOH (a key intermediate of *CO), respectively. The Cu_xO–CeO₂ composites exhibited a strong infrared absorption peak at approximately 1850 cm^{−1} within the entire potential range from −0.7 to −1.2 V versus RHE, which is attributed to the *CO intermediate. In contrast, the absorption peak of the *CO intermediate over the Cu₂O cubes is relatively weak, demonstrating that the Cu_xO–CeO₂ composites are more conducive to the generation and stabilization of the *CO intermediate. Specifically, the absorption peak of the Cu_xO–CeO₂ composites at approximately 1480 cm^{−1} corresponds to the *CHO intermediate, and the absorption peak at approximately 1590 cm^{−1} could be ascribed to the *COCHO (a key intermediate of C₂H₄). Therefore, it could be speculated that CeO₂ can promote the dissociation of H₂O to produce *H, facilitating the protonation of the *CO intermediate to form *CHO, and further promoting the asymmetric C–C coupling of *CO and *CHO to generate C₂H₄. In contrast, the Cu₂O cubes has a strong infrared absorption peak at approximately 1140 cm^{−1} within the entire potential range from −0.7 to −1.2 V versus RHE, which is attributed to the *OCH₃ intermediate (a key intermediate of CH₄). In addition, in situ Raman spectroscopy tests were conducted on the Cu₂O cubes and Cu_xO–CeO₂ composites to track the evolution of the valence state of Cu during the electrocatalytic CO₂RR process (Figures S16–S17). The Raman spectra of both the Cu₂O cubes and Cu_xO–CeO₂ composites exhibited characteristic Raman peaks of Cu(I) species at 146, 221, 412, 534, and 628 cm^{−1}. Apparently, for the Cu₂O cubes, these Raman signals gradually weakened as the applied reduction potential became more negative, arising from the reduction of the Cu₂O cubes to metallic Cu. In contrast, these characteristic peaks of the Cu_xO–CeO₂ composites were basically maintained. The above results demonstrate that the introduction of CeO₂ can inhibit the

electron aggregation around the Cu(I) species sites, thereby protecting them from electrochemical reduction and enabling the stable existence of Cu(I) species.

To elucidate the effect of CeO₂ on the electronic structure of Cu₂O (111), the projected density of states (PDOS) of Cu₂O (111) and CeO₂–Cu₂O (111) systems are calculated (Figure 4a). Upon CeO₂ introduction, the main Cu d-band peak shifts significantly below the Fermi level, indicating a lowered d-level and enhanced electron binding, which improves the system's thermodynamic stability.^[34] In the −4 to 0 eV region, enhanced Cu 3d–O 2p hybridization suggests increased covalency of Cu–O bonds, which reinforces interfacial mechanical stability and facilitates CO₂ adsorption and activation.^[35] Additionally, Ce 4f orbitals, through O–2p bridging, form high-energy unoccupied hybridized states in the range of 1 to 3.5 eV, effectively suppressing lattice oxygen loss, stabilizing Cu⁺ and enabling dynamic interfacial charge regulation, thereby enhancing CO₂RR activity and selectivity.^[26,36] Furthermore, delocalized Ce 5d–O 2p states with weak hybridization, may also serve as electron transport channels, promoting efficient multi-electron reaction processes.^[37]

In addition, adsorption free energy analysis (Figure 4b) reveals that the CeO₂–Cu₂O (111) interface exhibits superior CO₂ capture ability ($G_{\text{ads}} = -0.77$ eV) compared to Cu (111) (0.22 eV) and Cu₂O (111) (0.13 eV). For *CO, adsorption strength follows a gradient: overly strong on Cu (111) (−1.16 eV), too weak on Cu₂O (111) (−0.43 eV), and optimally balanced on CeO₂–Cu₂O (111) (−0.87 eV), favoring intermediate stabilization and C–C coupling. Differential charge density and Bader charge analyses (Figure 4c) further confirm that CeO₂–Cu₂O (111) transfers more electrons upon CO₂ adsorption (0.38e) than Cu (111) (0.24e) and Cu₂O (111) (0.07e), while maintaining moderate charge transfer for *CO, indicating balanced electron regulation.^[38] Additionally, on the pure Cu₂O (111) surface, the O sites show a relatively high hydrogen adsorption free energy (0.69 eV), indicating weak hydrogen adsorption. After introducing CeO₂, the Ce–O–Cu interface significantly tunes the hydrogen adsorption behavior, and the O1 site at the interface exhibits strong hydrogen adsorption capability (−1.23 eV), effectively suppressing the hydrogen evolution reaction (HER),^[39] while the O2 site shows a moderate adsorption energy (−0.25 eV), favoring proton transfer and intermediate stabilization (Figure S22).^[40] Moreover, the lattice oxygen structure of the CeO₂–Cu₂O interface, together with the adsorbed water molecules, could form a hydrogen-bond network that supports continuous proton migration through the Grotthuss mechanism,^[41] significantly improving proton accessibility and transfer efficiency during CO₂ reduction.^[42]

To elucidate the enhancement mechanism of CeO₂-modified Cu₂O (111), the Gibbs free energy profiles for the complete CO₂-to-C₂H₄ pathway were systematically compared on three different catalyst surfaces (Figures 4e and S18), with the optimized configurations in Figures S19–S21. The CeO₂–Cu₂O (111) surface exhibits the lowest CO₂ adsorption free energy, indicating enhanced CO₂ activation. The symmetric *CO dimerization pathway shows an ultralow energy barrier of 0.015 eV, significantly lower than that

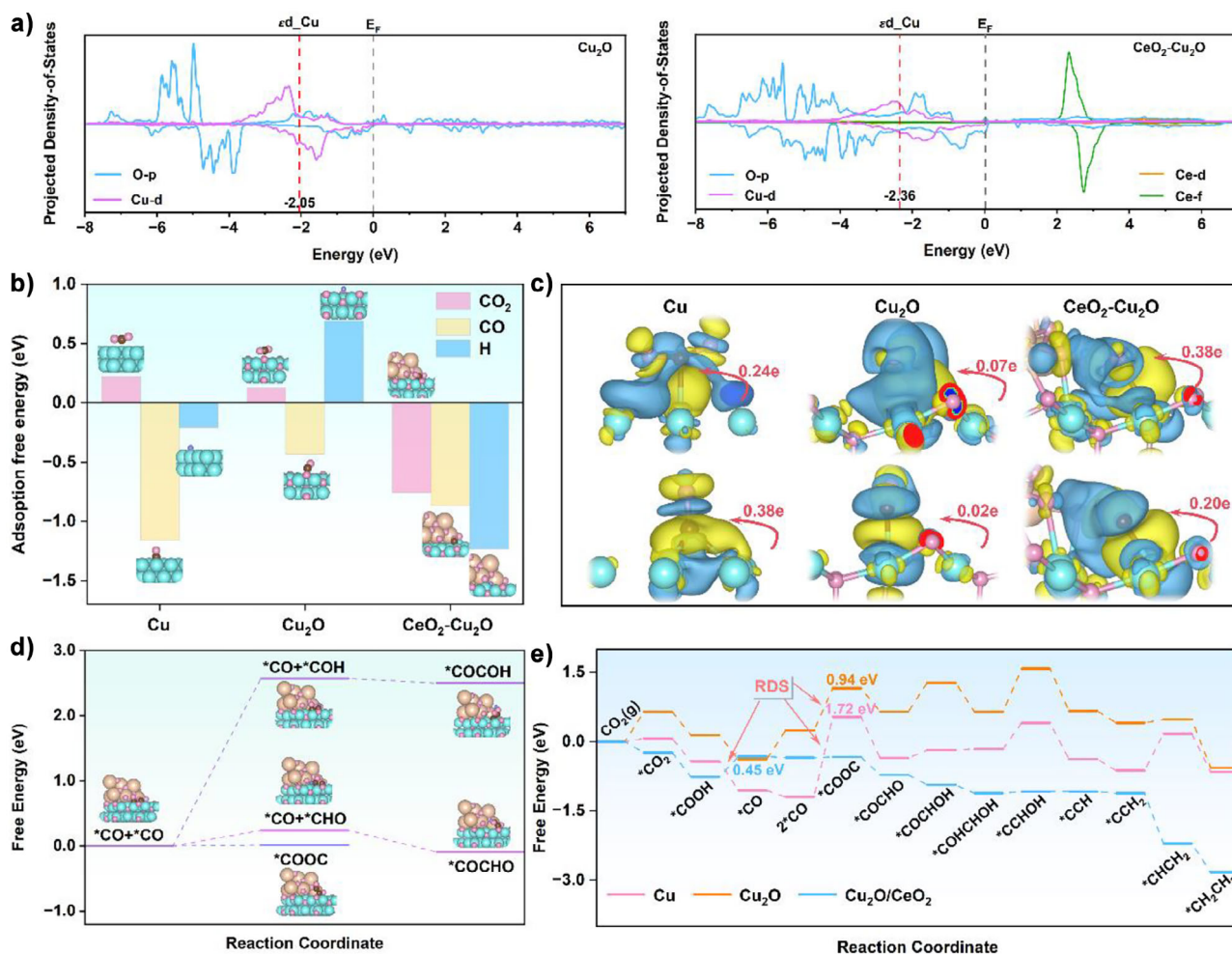


Figure 4. DFT calculations. a) PDOS of pure Cu₂O (111) and CeO₂-Cu₂O (111) systems. O p peak intensity here is 10 times b) Adsorption free energies of key intermediates CO₂, CO, and H during the CO₂RR process on Cu (111), Cu₂O (111), and CeO₂-Cu₂O (111) catalysts. c) Differential charge density analysis and corresponding Bader charge analysis of CO₂ and CO adsorbed on Cu (111), Cu₂O (111), and CeO₂-Cu₂O (111) catalyst surfaces. Yellow and deep blue regions represent electron accumulation and depletion, respectively. d) Free energy diagram for the selection of C-C coupling step on CeO₂-Cu₂O (111). e) Gibbs Free-energy diagram of CO₂RR to C₂H₄ paths on Cu (111), Cu₂O (111), and CeO₂-Cu₂O (111) catalysts.

of the *CO protonation routes (*COH, 2.57 and *CHO, 1.03 eV) (Figure 4d) and C-C coupling barriers on Cu (111) (1.73 eV) and Cu₂O (111) (0.91 eV). The rate-determining step, i.e., *COOH dehydration to *CO (0.40 eV), demonstrates the dual role of CeO₂ in tuning intermediate adsorption and lowering energy barriers. Furthermore, interfacial charge redistribution and geometric synergy promote spontaneous hydrogenation, improving ethylene selectivity and C-C coupling efficiency.

Conclusion

In summary, the unique Cu_xO-CeO₂ composites composed of CeO₂ nanograins in conjunction with CuO nanothorns on the edges of Cu₂O cubes have been fabricated via the seed-mediated growth method. Importantly, the as-synthesized Cu_xO-CeO₂ composites exhibit a maximum FE (C₂H₄) of 51.7% with a *j*_{C₂H₄} of -102.8 mA cm⁻², which is approximately 2.6 times that of Cu₂O. In situ spectroscopies and

DFT calculations confirm that the Cu_xO-CeO₂ composite is more conducive to the generation and stabilization of the *CO intermediate, arising from the stabilization of the Cu⁺ active sites. CeO₂ could promote the dissociation of H₂O, providing more *H, and facilitating C-C coupling and further protonation into the *COCHO intermediate, which enhances the thermodynamic favorability of C₂H₄ production. In the future, it is imperative to identify the real active sites and the structure of the reconstructive phase during CO₂RR with the aid of in situ and operando characterization techniques. This work is expected to provide profound insights into the stabilization of copper-based catalysts by lanthanide metals for boosting CO₂ electroreduction to specific C₂+ products.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: Active hydrogen • CO₂ reduction • Cu(I) species • Electrocatalysis • Ethylene

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Research Article

CO₂ Electroreduction

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Enhanced Active Hydrogen Absorption
and Stabilized Cu(I) Species Over Cu-O-
Ce Bridges Boosting Electrocatalytic CO₂
Reduction to Ethylene

The as-synthesized Cu_xO–CeO₂ composites exhibit enhanced Faradaic efficiency and partial current density of C₂H₄ compared with Cu₂O cubes. In situ spectroscopies and theoretical calculations confirm that the Cu–O–Ce bridges in Cu_xO–CeO₂ composite can effectively enhance *H adsorption and stabilize Cu(I) species, facilitating subsequent C–C coupling and further protonation into the key *COCHO intermediate of C₂H₄.

