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Boosting CO₂ Electroreduction to Multi-carbon Products via Oxygen-rich Vacancies and Ce⁴⁺—O^{2−}—Cu⁺ Structure in Cu/CeO₂ for Stabilizing Cu⁺

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Cu is a promising electrocatalyst for the CO₂ reduction reaction (CO₂RR) to produce high-value C₂₊ products. Due to the fierce competition of the hydrogen evolution reaction, the slow diffusion of CO₂, and the high energy barrier of the C—C coupling reaction, it is still challenging to achieve high activity and high selectivity to produce multi-carbon products on copper-based electrocatalysts. In this work, we synthesized Cu/CeO₂ catalysts with varying amounts of Cu doping, aiming at effectively converting CO₂ into C₂₊ products through electroreduction. At a copper doping level of 9.77 wt%, the catalyst exhibited a current density of 16.8 mA cm^{−2} using a standard H-

type cell, achieving a C₂₊ faradaic efficiency (FE) of 78.3%. Through additional experiments and material characterization, we confirmed that controlling the Cu loading on the surface of CeO₂ is an effective way to regulate the ratio of Cu⁺ to Cu⁰ active sites and the number of oxygen vacancies. Furthermore, the strong electron interaction between Ce⁴⁺—O^{2−}—Cu⁺ structure can stabilize Cu⁺ species and enhance the overall stability of the catalyst. This strategy enhances the selectivity towards C₂₊ products and effectively suppresses the competing hydrogen evolution reaction.

Introduction

Electrochemical conversion of CO₂ into value-added chemicals, known as CO₂ reduction reactions (CO₂RR), is widely recognized as a promising strategy to achieve the objective of “carbon neutrality.” This approach not only helps mitigate global climate change but also enables the storage and utilization of renewable energy, and offers a sustainable pathway for transforming carbon dioxide into valuable products.^[1–3] Chemicals and fuels

that contain two or more carbon atoms (C₂₊ products), such as ethylene, acetic acid, and ethanol, have significant economic value and have various applications in industry.^[4–7] However, direct production of high value-added multi-carbon products through CO₂RR faces various challenges, including competitive hydrogen evolution reaction, slow kinetic, high overpotential and reaction energy barrier due to the stable structure of CO₂, and multiple electron-proton transfer and C—C coupling.^[4,8–12] Therefore, enhancing the selectivity towards high-value multi-carbon products in electrocatalytic CO₂ reduction is highly desired.^[13]

Cu has been studied widely as electrocatalyst for generating valuable C₂₊ products through the CO₂RR.^[14,15] Various approaches have been explored to enhance the reactivity and selectivity of copper-based catalysts in CO₂RR.^[16,17] These strategies encompass alloying, morphology manipulation, surface functionalization, atom doping, defect engineering, and in-situ reconstruction.^[18–23] However, further advancements are still required to overcome the challenges associated with improving both the activity and selectivity of these catalysts.

Previous theoretical and experimental investigations have indicated that the active species Cu⁺ on the catalyst surface plays a crucial role in facilitating the highly efficient reduction of CO₂ into valuable products.^[24] Specifically, in the initial step of C₂₊ formation through CO₂ activation, Cu⁺ species dilute the negative charge generated by *CO₂—Cu⁰, thereby stabilizing the transition and final states of CO₂ activation. In the subsequent C—C dimerization process, representing the rate-determining step for C₂₊ formation, the C atom of *CO—Cu⁺ carries a positive charge, while the C atom of *CO—Cu⁰ carries a negative charge. This charge distribution facilitates the formation of C—C

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bonds between the two C atoms through electrostatic attraction.^[25] Hence, the cooperative effect between Cu^+ and Cu enhances the activation of CO_2 and facilitates C–C coupling, effectively suppressing the formation of hydrogen and C_1 products.^[26] For example, a Faraday efficiency (FE) of 62.5% was reported for the electrocatalytic reduction of CO_2 to C_2H_4 at the Cu^+/Cu^0 interface formed by in-situ reconstructed CuO nano-sheets at grain boundaries.^[27] Unfortunately, maintaining the stable presence of Cu^+ sites at high overpotential during CO_2RR is still tricky.^[28] Therefore, finding a general strategy that effectively stabilizes Cu^+ species is still challenging.

CeO_2 , with its highly tunable properties, including metal-support interaction and abundant oxygen vacancies, is an excellent potential material for the CO_2 conversion reaction.^[29] On the one hand, the presence of CeO_2 can improve the dispersion and stability of Cu^+ species on the catalyst surface through strong electron interaction, thereby improving the overall electrocatalytic performance.^[30] On the other hand, the abundant oxygen vacancies (O_v) formed by CeO_2 can regulate the electronic structure and promote CO_2 adsorption and activation, which play a crucial role in CO_2RR activity.^[31] Therefore, using reducible metal oxide CeO_2 as an additive or carrier is one of the most promising approaches to enrich and stabilize the Cu^+ species on the catalyst surface and improve the performance of electrocatalytic CO_2 reduction to C_{2+} products.

Herein, we prepared Cu/ CeO_2 catalysts with different Cu doping amounts by the impregnation-calcination two-step method. By combining material characterization and a series of

control experiments, we further confirmed that the strong electron interaction of $\text{Ce}^{4+}-\text{O}^{2-}-\text{Cu}^+$ structure can stabilize Cu^+ . In addition, with the increase in Cu loading, the ratio of Cu^+ to Cu active sites, oxygen vacancy concentration, and C_{2+} product selectivity all show volcanic trend. When the copper doping amount is 9.77 wt%, the FE of C_{2+} can reach 78.3% at a current density of 16.8 mA cm^{-2} .

Results and Discussion

The Cu/ CeO_2 catalysts with different amounts of Cu loading were synthesized by a simple impregnation-calcination two-step method (see the Supporting Information for experimental details). The amounts of Cu loading were adjusted by varying the concentration of the Cu precursor (Cupric nitrate trihydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) during the impregnation process.^[32] In this work, the samples are named Cu_x/CeO_2 , with x being the mass fraction of Cu, which are 4.73 wt%, 6.97 wt%, 9.77 wt% and 14.69 wt%, respectively as determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Table S1).

The scanning electron microscopy (SEM) images show that the morphological features of the pure CeO_2 (Figure S1) and the Cu/ CeO_2 catalysts (Figure S2) with different amounts of Cu loading are similar. The related Transmission electron microscopy (TEM) images are shown in Figures 1a and S3, which reveal the porous nature of the Cu/ CeO_2 nanoparticles. The HR-TEM image for the $\text{Cu}_{9.77}/\text{CeO}_2$ catalyst in Figure 1b shows the

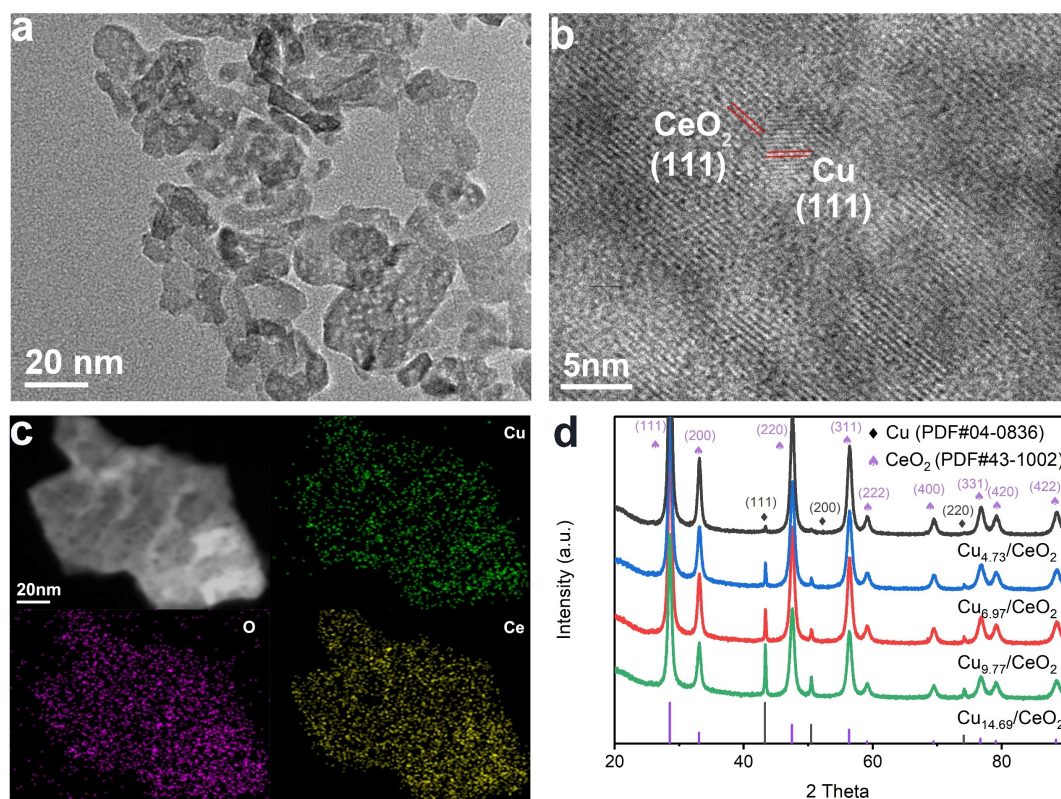


Figure 1. Structural characterizations. Morphology and atomic structure of the $\text{Cu}_{9.77}/\text{CeO}_2$ catalyst: **a.** TEM image. **b.** HRTEM image. **c.** Elemental mappings. **d.** XRD patterns of the Cu/ CeO_2 catalysts.

lattice spacing of 3.1 Å and 2.08 Å, corresponding to the (111) planes of CeO₂ and the (111) planes of Cu, respectively. Moreover, the elemental mapping of Cu, O, and Ce in the Cu_{9.77}/CeO₂ catalyst was determined by energy-dispersive X-ray spectroscopy (EDS), which showed that the Cu nanoparticles were uniformly distributed over the CeO₂ support without significant agglomeration (Figure 1c). Furthermore, the high density of Cu nanoparticles on the CeO₂ support was severely agglomerated and unevenly distributed when the Cu loading increased to 14.69 wt% (Figure S4).^[33] As shown in Figure 1d, the diffraction peaks of the X-ray diffraction (XRD) patterns of the synthesized Cu/CeO₂ samples correspond to CeO₂ (JCPDS no. 04-0836) and metallic Cu (JCPDS no. 34-0394), which is consistent with the above HR-TEM. In addition, the diffraction peaks of metallic Cu are gradually enhanced with the increase in Cu loading. The positions of these diffraction peaks did not change significantly.

The electrocatalytic performance of Cu/CeO₂ catalysts is frequently related to the presence of Ce³⁺, oxygen vacancies,

and Ce–O–Cu structure.^[2,34,35] X-ray photoelectron spectroscopy (XPS) was performed to characterize the chemical environment of the Cu/CeO₂ catalysts. Figure 2a shows the XPS spectrum of Ce 3d, consisting of nine characteristic peaks attributed to Ce 3d_{5/2} (V⁰, 880 eV; V, 881.8 eV; V', 886.7 eV and V'', 896.7 eV) and Ce 3d_{3/2} (U⁰, 898.7 eV; U, 901.2 eV; U', 905.6 eV; U'', 909.3 eV and U''', 914.7 eV). The peaks V, U, and U'' belong to the Ce³⁺ species, while the others belong to the Ce⁴⁺ species.^[36] The XPS spectrum of Ce 3d indicates that the valency of the Ce species is mainly composed of Ce⁴⁺. Moreover, Figure 2b shows three peaks in the O 1s spectra of Cu/CeO₂ with different Cu loading amounts located at 529.3, 531.4, and 533.1 eV, respectively. These three peaks correspond one by one to different chemical environments of oxygen, namely lattice oxygen (O²⁻), vacancy oxygen (O_v), and adsorbed oxygen (–OH).^[37] Due to the small difference in the binding energy of the lattice oxygen O of Ce–O and Cu–O, the XPS spectra are completely overlapped and cannot be distinguished. The binding energy of lattice oxygen shifts negatively and then positively with the increase

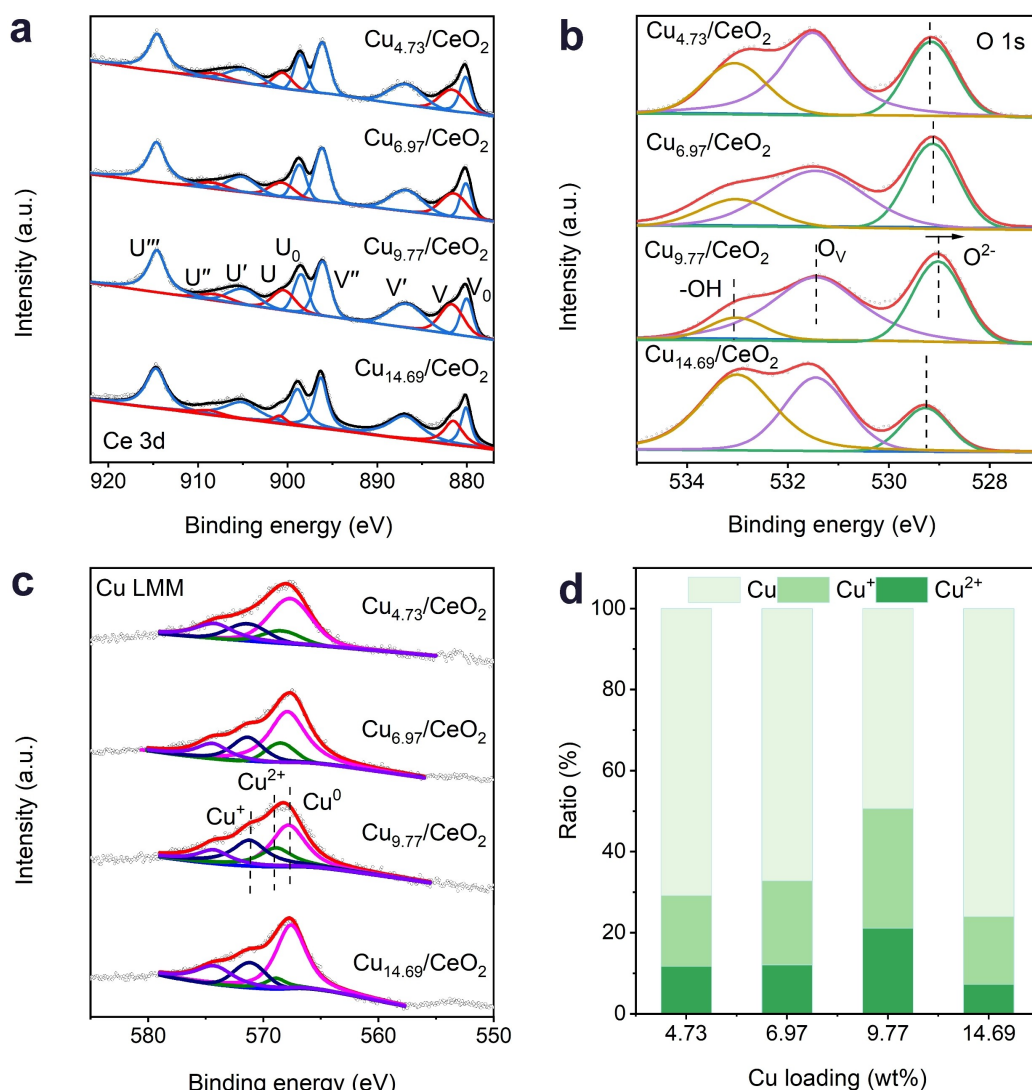


Figure 2. XPS spectra of Cu/CeO₂ catalysts in a. Ce 3d, b. O 1s region, and c. Cu LMM. d. The ratios of surface Cu with different valence states for the Cu/CeO₂ catalysts.

of copper loading. When the copper loading is 9.77 %, the binding energy of lattice oxygen is the lowest. Based on the aforementioned findings, it is inferred that the $\text{Ce}^{4+}\text{--O}^{2-}\text{--Cu}^+$ structure, which is established and stabilized through the incorporation of Cu into CeO_2 , exhibits robust electronic interactions. These interactions play a pivotal role in suppressing the generation of lattice oxygen, thereby promoting the stabilization of Cu^+ .^[38]

The high-resolution Cu 2p XPS spectrum displays two pairs of peaks attributed to Cu^0/Cu^+ (932.2 and 952.2 eV) and Cu^{2+} (934.5 and 954.3 eV), suggesting the presence of Cu^0/Cu^+ and Cu^{2+} in Cu/ CeO_2 catalysts (Figure S5).^[39] In addition, since the binding energy of Cu^0 and Cu^+ in the Cu 2p spectra were similar, the samples were analyzed using X-ray photoelectron spectroscopy to distinguish them.^[40] Figure 2c shows the Auger Cu LMM spectra of Cu/ CeO_2 catalysts with different Cu doping amounts. In the peak fitting of Cu LMM, as shown in Figure 2c, there are three peaks at 568.3 eV (Cu^0), 569.8 eV (Cu^{2+}) and 570.6 eV (Cu^+), and another peak at 573.7 eV, representing other transition states of Cu LMM spectrum.^[41] A strong signal corresponding to Cu^+ was observed in the XPS of the Cu LMM region, further demonstrating the presence of Cu^+ species. Specifically, a volcano-type relationship exists between the ratio of Cu^+ to Cu^0 and the amount of Cu loading peaking at 9.77 wt % (Figure 2d), consistent with the relative concentrations of Ce^{3+} and oxygen vacancies.

As shown in Figure S6, oxygen vacancies increase with the increase of Cu loading and then decrease. When the Cu loading

is 9.77 wt%, the proportion of oxygen vacancies is the highest. In addition, the relative concentrations of Ce^{3+} are also highest at 9.77 wt% Cu loading. The reason is that when Ce^{4+} is reduced to Ce^{3+} , it is accompanied by the introduction of oxygen vacancies. The more Ce^{3+} generated, the more oxygen vacancies are introduced.^[42,43] Therefore, by doping an appropriate amount of Cu, the $\text{Ce}\text{--O}\text{--Cu}$ bond formed promotes the reduction of Cu^{2+} to Cu^+ in the catalyst, effectively regulates the ratio of Cu^+/Cu^0 in the catalyst, and forms the $\text{Ce}^{3+}\text{--O}_v\text{--Cu}^+$ bond to promote the formation of oxygen vacancy. In addition, Cu doping in CeO_2 can form a strong electronic interaction of $\text{Ce}^{4+}\text{--O}^{2-}\text{--Cu}^+$ structural connection to stabilize Cu^+ .^[44]

The electrocatalytic CO_2RR performance was evaluated in an H-cell with 0.1 M CsI aqueous solution as the electrolyte. The linear sweep voltammetry (LSV) curves of $\text{Cu}_{9.77}/\text{CeO}_2$ in N_2 and CO_2 saturated 0.1 M CsI electrolyte are presented in Figure 3a. In the CO_2 -saturated electrolyte, a much higher current density was generated over $\text{Cu}_{9.77}/\text{CeO}_2$, indicating its high activity for the CO_2RR .^[45] Controlled potential electrolysis of CO_2 was conducted to investigate the reduction products at potentials ranging from -0.9 to -1.3 V vs. RHE. Gas chromatography (GC) and ^1H NMR spectroscopy were utilized to analyze the gas phase and liquid products, respectively. The quantitative results of nuclear magnetic resonance (NMR) spectroscopy and gas chromatography (GC) showed that the detected liquid products were formate, ethanol (EtOH), and acetate, while the gaseous products were H_2 , CO , CH_4 , and C_2H_4 . First, no hydrocarbons

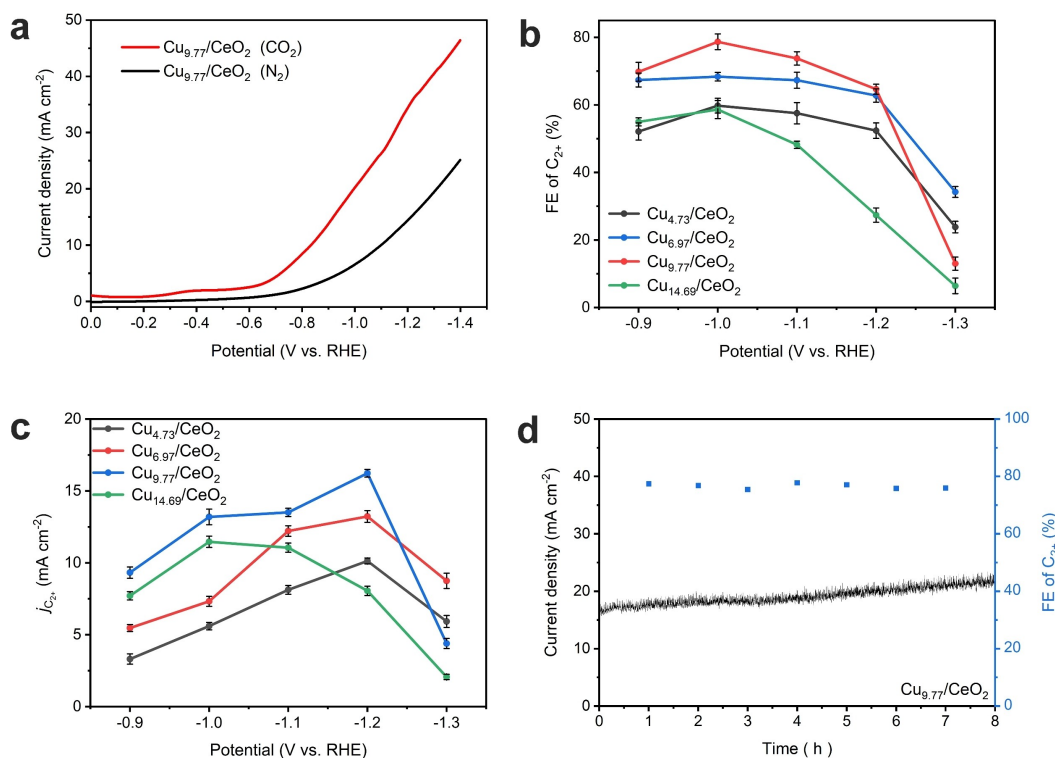


Figure 3. Electrocatalytic CO_2RR measurement. **a.** LSVs of $\text{Cu}_{9.77}/\text{CeO}_2$ in N_2 and CO_2 saturated 0.1 M CsI/ K_2SO_4 at 0 to -1.4 V vs. RHE (scan rate, 10 mV s^{-1}). **b.** Comparison of the C_2^+ FE and partial current density of the $\text{Cu}_{4.73}/\text{CeO}_2$, $\text{Cu}_{6.97}/\text{CeO}_2$, $\text{Cu}_{9.77}/\text{CeO}_2$, $\text{Cu}_{14.69}/\text{CeO}_2$. **c.** Stability test on $\text{Cu}_{9.77}/\text{CeO}_2$: Current density (left axis) and FE of C_2^+ (right axis) as a function of time during chronoamperometric electrolysis at -1.0 V vs. RHE.

were detected over the pure CeO_2 catalyst under the above test conditions, and the Faradaic Efficiency (FE) of H_2 was calculated to be close to 100%, which indicates that the catalyst matrix CeO_2 cannot catalyze the production of hydrocarbons. (Figure S7).

The hydrogen evolution reaction (HER) is strongly inhibited on Cu/CeO_2 , and the doping of copper leads to a significant improvement in the FE of the hydrocarbon (Figure S8). These indicate that Cu^+/Cu^0 has excellent catalytic ability. Figure 3b shows the FEs for C_{2+} as functions of applied potentials from -0.9 to -1.3 V vs. RHE over $\text{Cu}_{4.73}/\text{CeO}_2$, $\text{Cu}_{6.97}/\text{CeO}_2$, $\text{Cu}_{9.77}/\text{CeO}_2$, and $\text{Cu}_{14.69}/\text{CeO}_2$. The $\text{Cu}_{9.77}/\text{CeO}_2$ achieved the highest C_{2+} selection from -0.9 to -1.3 V vs. RHE. For $\text{Cu}_{9.77}/\text{CeO}_2$, the FE of C_{2+} products followed a volcano trend with the increase of the applied potential, reaching the highest value of 78.36% at -1.0 V vs. RHE, with a total current density of 16.8 mA cm^{-2} (Figure S8). A volcano relation could be recognized between the Cu^+/Cu^0 contents and C_{2+} faradaic efficiencies as well as C_{2+} partial current densities. Furthermore, the $\text{Cu}_{9.77}/\text{CeO}_2$ also exhibited the highest C_{2+} partial current density (Figure 3c), indicating that the coexisting Cu^+ and Cu^0 active sites could inhibit hydrogen generation and promote the formation of C_{2+} products during CO_2RR .

In addition to catalytic activity and selectivity, catalytic stability is also an important index to evaluate the performance of catalysts.^[46] The stability of $\text{Cu}_{9.77}/\text{CeO}_2$ was then evaluated (Figure 3d). After 8 h of CO_2RR catalytic stability test at -1.0 V vs. RHE, the total current density and the C_{2+} FE did not change notably during electrolysis. The structure and chemical state of

$\text{Cu}_{9.77}/\text{CeO}_2$ catalyst before and after electrolysis for 8 h at -1.0 V vs. RHE in 0.1 M CsI electrolyte were characterized. The XRD pattern shows that the structure of the $\text{Cu}_{9.77}/\text{CeO}_2$ catalyst did not change significantly (Figure S9a). The SEM and TEM images show that the structure of the $\text{Cu}_{9.77}/\text{CeO}_2$ catalyst was stable in the electrochemical reaction (Figure S10 and S11a). The HR-TEM result shows that the lattice spacing of Cu and the separated Cu species structure are difficult to find.^[47] This is due to the poor scattering ability of Cu, and the Cu species are still highly dispersed on the $\text{Cu}_{9.77}/\text{CeO}_2$ nanointerface (Figure S11b). In addition to the characteristic peak of Cu^0 , the characteristic peak of Cu^+ is also retained in the Auger spectrum of Cu LMM after long-term electrolysis, indicating that the strong electron interaction between $\text{Ce}^{4+}-\text{O}^{2-}-\text{Cu}^+$ structure can stabilize Cu^+ species (Figure S9b). Due to the XPS test under ex-situ conditions, some copper species were oxidized, and a low-intensity characteristic peak related to Cu^{2+} appeared.^[48] The results of XPS after long-time electrolysis show that the chemical state of Ce and O for $\text{Cu}_{9.77}/\text{CeO}_2$ catalyst remain basically unchanged (Figure S9c and S9d). The above results indicate that the strong interaction between $\text{Ce}^{4+}-\text{O}^{2-}-\text{Cu}^+$ structure in the catalyst played an important role in stabilizing Cu^+ species and confirming the electrochemical stability of the Cu/CeO_2 catalyst.^[49]

To further reveal the inherent origins of the superiority of $\text{Cu}_{9.77}/\text{CeO}_2$ for CO_2RR , the electrochemical properties and CO_2 adsorption capacities of Cu/CeO_2 with different Cu loading amounts were analyzed. As observed in the linear sweep voltammetry (LSV) analysis (Figure 4a), the $\text{Cu}_{9.77}/\text{CeO}_2$ catalyst

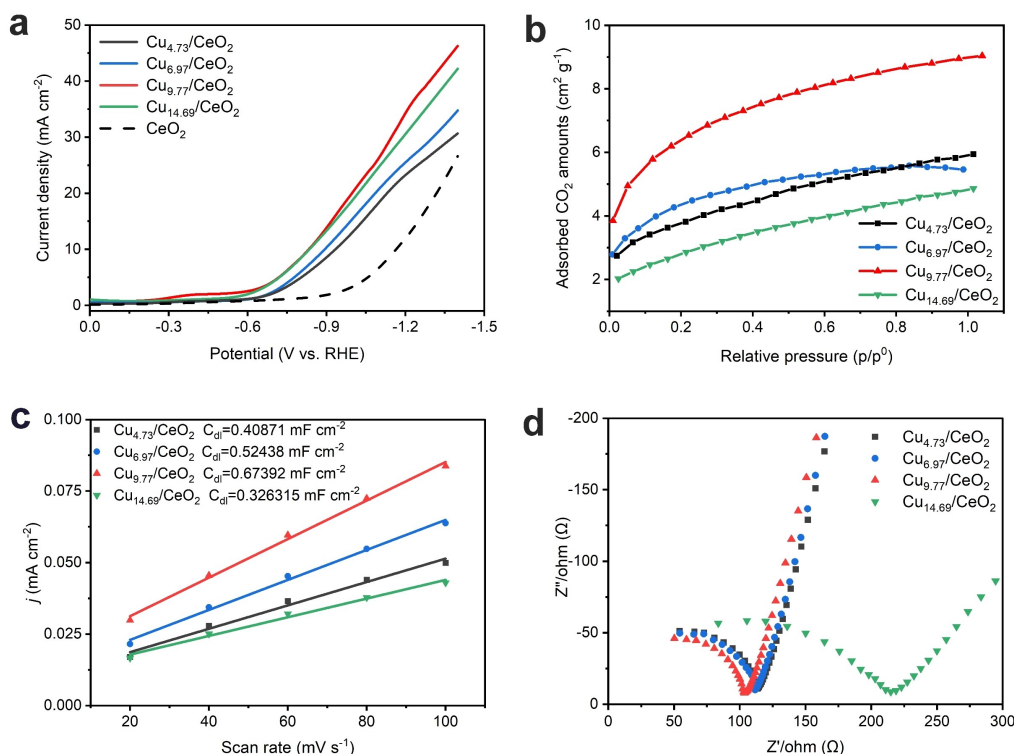


Figure 4. Characterizations of electrochemical performance. **a.** LSVs of Cu/CeO_2 catalyst in CO_2 saturated $0.1 \text{ M CsI}/\text{K}_2\text{SO}_4$ at electrochemical potential (E) from 0 to -1.4 V versus RHE (scan rate, 10 mV s^{-1}). **b.** CO_2 adsorption isotherms for Cu/CeO_2 catalyst at 25°C . **c.** ECSA patterns of Cu/CeO_2 catalyst. **d.** Nyquist plots of Cu/CeO_2 catalyst.

exhibits significantly higher current density compared with $\text{Cu}_{4.73}/\text{CeO}_2$, $\text{Cu}_{6.97}/\text{CeO}_2$, and $\text{Cu}_{14.69}/\text{CeO}_2$, indicating optimal electrocatalytic activity.^[50] In addition, $\text{Cu}_{9.77}/\text{CeO}_2$ shows the most robust CO_2 adsorption ability (Figure 4b), which is advantageous for CO_2RR . As the Cu doping continues to increase, the CO_2 adsorption decreases. Previous studies have shown that the more oxygen vacancies introduced in CeO_2 samples with different Cu contents, the higher the CO_2 adsorption amount and the greater the adsorption capacity of the resulting intermediates, which can lead to excellent C_{2+} selectivity under the synergistic effect of Cu^0 and Cu^+ active sites to promote C–C coupling.^[28,51,52] In short, with the change in Cu content, the oxygen vacancy content changed, significantly affecting the CO_2 adsorption amount and the adsorption capacity of intermediates on the catalyst surface, resulting in the difference in CO_2 reduction activity in this series of samples. The electrochemical active surface area (ECSA) and electrochemical impedance spectroscopy (EIS) of the catalyst were investigated to reveal the reason for the high catalytic performance of the $\text{Cu}_{9.77}/\text{CeO}_2$ catalyst in CO_2RR .^[53] As shown in Figure 4c and S12, $\text{Cu}_{9.77}/\text{CeO}_2$ exhibits the highest electrochemical surface area (ECSA) according to the double-layer capacitance (C_{dl}) results from cyclic voltammograms. According to the Nyquist plots (Figure 4d), $\text{Cu}_{9.77}/\text{CeO}_2$ exhibits the lowest interfacial electron transfer resistance (R_{ct}), which is conducive to the occurrence of CO_2RR . These results demonstrate the optimal strong electron interaction of the $\text{Cu}_{9.77}/\text{CeO}_2$ catalyst containing the most excellent Cu^+/Cu^0 ratio and oxygen vacancies, thus facilitating the adsorption, activation, and conversion of the reactants and intermediates.

Conclusions

In summary, Cu/CeO_2 catalysts with different Cu doping amounts have been prepared in this study, which can efficiently convert CO_2 to C_{2+} by electroreduction. At a copper doping of 9.77 wt%, the FE of C_{2+} can reach 78.3% with a current density of 16.8 mA cm^{-2} . The detailed study indicates that adjusting the amount of Cu loading on the CeO_2 surface is an effective strategy to regulate the ratio of Cu^+ to Cu^0 active sites and the concentration of oxygen vacancy to improve the selectivity of C_{2+} products and inhibit competing HER. In addition, the reduction of Cu^+ can be inhibited by strong electron interaction of $\text{Ce}^{4+}-\text{O}^{2-}-\text{Cu}^+$ structure, thus stabilizing Cu^+ to improve the stability of the catalyst. Based on these results, our work provides an effective strategy for designing copper-based catalysts to enhance CO_2RR .

Experimental Section

Materials

Cupric (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd.), Cerium(III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Shanghai Aladdin Biochemical Technology Co., Ltd.), Toray Carbon Paper (CP, TGP-H-60, $19 \text{ cm} \times 19 \text{ cm}$), Nafion D-521 dispersion (5%

w/w in water and 1-propanol, $\geq 0.92 \text{ meq g}^{-1}$ exchange capacity) and Nafion N-117 membrane (0.180 mm thick, $\geq 0.90 \text{ meq g}^{-1}$ exchange capacity) were purchased from Alfa Aesar China Co., Ltd. Both carbon dioxide (CO_2 , 99.999%) and nitrogen (N_2 , 99.999%) were supplied by Shanghai Chemistry Industrial Zone Pujiang Special Type Gas Co., Ltd. No further purification is required when all reagents are used.

Catalyst Preparation

Synthesis of CeO_2

A certain amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was placed in a muffle furnace and heated to 500°C for 4 h, then stopped heating and cooled down naturally to obtain CeO_2 .

Synthesis of Cu/CeO_2

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.41 g, 0.58 g, 0.85 g, and 1.36 g) was dissolved in 20 mL water, and 2 g CeO_2 powder was added under magnetic stirring. The mixture was stirred at room temperature for 5 h, and then heated slowly at 60°C under stirring to concentrate the solvent. The obtained sample was dried and calcined at 500°C at a heating rate of 5°C min^{-1} and maintained for 4 h in an air atmosphere. After cooling, it was placed in a tubular furnace and reduced at 300°C under 5% H_2/Ar atmosphere for 2 h. The prepared catalysts were named $\text{Cu}_{4.73}/\text{CeO}_2$, $\text{Cu}_{6.97}/\text{CeO}_2$, $\text{Cu}_{9.77}/\text{CeO}_2$ and $\text{Cu}_{14.69}/\text{CeO}_2$, respectively, in which the Cu loading was calculated by mass fraction.

Material Characterization

The samples were analyzed for morphology using a Hitachi S4800 scanning electron microscope (SEM) operating at 3 kV and a FEI Tecnai G2 F30 transmission electron microscope (TEM) operating at 300 kV. A Rigaku Ultima VI X-ray diffractometer equipped with $\text{Cu}-\text{K}\alpha$ radiation was used to perform power X-ray diffraction (XRD) analysis. The scan range was set between 20° and 90° with a scan speed of $10^\circ \text{ min}^{-1}$. An AXIS Supra (XPS) surface analysis instrument equipped with a monochromatic X-ray source was used to acquire X-ray photoelectron spectroscopy (XPS) data (combined Al/Ag anode, energy $1486.6/2984.2 \text{ eV}$). The binding energy was calibrated using the C 1s peak at 284.6 eV as a reference. The Agilent 5100 SVDV model of Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) was employed to quantify the relative copper content. The CO_2 adsorption isotherms of the catalysts were obtained using the BELSORP-max II apparatus within the pressure range of 0–1 atm at 298 K .

Electrode Preparation

To prepare the catalyst ink, 1 mg of the catalyst powder was dispersed in a mixture of $350 \mu\text{L}$ isopropyl alcohol and $30 \mu\text{L}$ Nafion solution (5 wt%). The mixture was then sonicated for 30 min to obtain a homogenous catalyst ink. Subsequently, the catalyst ink was carefully dispensed onto the surface of a carbon paper ($1 \times 1 \text{ cm}^2$) using a micropipette. The electrode was then allowed to dry naturally at room temperature. The amount of the catalyst on the electrode was 1 mg cm^{-2} .

Linear Sweep Voltammetry (LSV) and Electrolysis

Linear sweep voltammetry (LSV) measurements were conducted using a three-electrode system on a potentiostat (CHI 660E, Shanghai CH Instruments Co., China) in a gas-tight two-compartment H-cell, which was divided by an ion exchange membrane (Nafion117). The system consisted of a working electrode, a platinum gauze serving as the counter electrode, and an Ag/AgCl electrode (3 mol L⁻¹ KCl) used as the reference electrode. A Nafion-117 proton exchange membrane was employed to partition the cathode and anode compartments, facilitating the selective transfer of H⁺ ions from the anode compartment to the cathode compartment. The cathodic electrolyte used in the experiment was 0.1 M CsI solution, while the anodic electrolyte was 0.1 M K₂SO₄ solution. Linear sweep voltammetry (LSV) measurement was conducted in the range of 0.2 V to -1.2 V vs. RHE (reversible hydrogen electrode) at a scan rate of 20 mVs⁻¹. In all measurements, the reference electrode was Ag/AgCl. The potential (vs. Ag/AgCl) was then converted to the reversible hydrogen electrode (RHE) scale using the following equation: E(RHE) = E(Ag/AgCl) + 0.197 + 0.059 × pH.

Before the experiment, the electrolyte was purged with nitrogen (N₂) or carbon dioxide (CO₂) for a minimum of 30 minutes. The experiment was conducted with a continuous flow of CO₂ (15 mL min⁻¹) while maintaining a constant applied potential. The CO₂ flow rate was regulated using a mass flow controller (SevenStar D07-19B). Cyclic voltammetry (CV) measurements were conducted in gas-saturated electrolytes over a potential range of 0.6 V to -1.4 V vs. RHE with a sweep rate of 50 mVs⁻¹.

Product Analysis

Gas chromatography (GC) analysis was performed using an Agilent 8890D system with a flame ionization detector (FID) and thermal conductivity detector (TCD) for the detection of gaseous products. From the peak areas obtained from GC and calibration curves of the thermal conductivity detector (TCD), the molar quantity of gaseous products can be calculated. The quantification of liquid products was performed using a nuclear magnetic resonance (NMR) spectrometer (Bruker; Ascend 400-400 MHz) in D₂O (deuterated water) with phenol as the internal standard. The moles of the liquid product were determined based on the integral areas obtained from NMR spectra and calibration curves. The Faradaic efficiency (FE) of each product was determined using the following calculation method [Eq. (1)]:

$$FE = \frac{n \times F \times n_{\text{product}}}{Q} \times 100\% \quad (1)$$

(Q: the amount of charge passed through the working electrode; F: The Faraday constant (96485 C mol⁻¹); n: number of moles of electrons to participate in the Faradaic reaction).

Double-layer Capacitances (C_{dl}) Measurement

The capacitance value (C_{dl}) was obtained by analyzing the capacitive current related to double-layer charging, which was determined from the scan rate dependence of the cyclic voltammogram (CV) recorded in an H-type cell. To perform cyclic voltammetric stripping, the potential window was set between -0.24 V and -0.34 V (vs. RHE). The estimation of C_{dl} involved plotting the difference in the current density at -0.29 V vs. RHE against scan rates, which were set at 20, 30, 50, 80, and 100 mVs⁻¹.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements were performed in a CO₂-saturated 0.1 M CsI aqueous solution at the open circuit potential (OCP). The frequency range of the measurements spanned from 0.1 Hz to 100,000 Hz, and the applied amplitude was set at 5 mV.

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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: Copper-ceria · C₂₊ production · Electrocatalyst · Electrochemical CO₂ reduction · Oxygen vacancy

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