

Cerium Dioxide-Induced Abundant Cu^+/Cu^0 Sites for Electrocatalytic Reduction of Carbon Dioxide to C_{2+} Products

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In recent years, the electrochemical reduction of carbon dioxide (CO_2RR) has made many advances in C_{2+} production. Cu^+/Cu^0 site is beneficial for C–C coupling process, but the oxidation state of copper cannot be well maintained during the reaction process, resulting in a decrease in catalyst activity. Based on this consideration, in this work, transition metal oxide CeO_2 with a hollow cube structure and oxygen vacancies was introduced to stabilize and increase Cu^+/Cu^0 active sites (Ce_1Cu_2). The catalyst exhibits excellent CO_2RR performance, with $\text{FE}_{\text{C}_{2+}}$ achieving 73.52% and $j_{\text{C}_{2+}} > 280 \text{ mA/cm}^2$ at 1.26 V (vs. RHE). Ethanol is the main C_{2+} product and $\text{FE}_{\text{ethanol}}$ reaches 39% at 1.26 V. The

experimental results indicate that the presence of CeO_2 provides a large number of oxygen vacancies and forming $\text{Cu}^+-\text{O}^{2-}-\text{Ce}^{4+}$ structure by the strong interaction of CeO_2 and Cu NPs. The structure of $\text{Cu}^+-\text{O}^{2-}-\text{Ce}^{4+}$ and abundant oxygen vacancies lay a good foundation for the CO_2 adsorption. Moreover, it increases the content of Cu^+/Cu^0 sites, effectively inhibiting hydrogen evolution reaction, promoting the C–C coupling interaction, thereby facilitating the generation of C_{2+} products. The DFT theoretical calculation further demonstrates that Ce_1Cu_2 is more inclined towards the ethanol pathway, confirming its high selectivity for ethanol.

Introduction

With the massive global emissions of CO_2 , the resulting environmental pollution has a profound and far-reaching impact on human production and life. Among the myriad environmental issues exacerbated by the massive global emissions of CO_2 , the greenhouse effect stands out as a significant concern, leading to a cascade of critical issues, including global warming, rising sea levels, and land desertification. To solve this issue, extensive research has been conducted on the conversion of carbon dioxide, which can be converted into value-added chemicals/fuels through various methods such as electrocatalysis, photocatalysis, thermocatalysis and bio-catalysis.^[1–4] In the above conversion techniques, electrocatalytic carbon dioxide reduction reaction (CO_2RR) has been widely concerned because of its advantages such as mild reaction conditions, high selectivity and conversion rate.^[5–6]

Transition metals (TM) have been extensively employed as catalysts for CO_2RR , leveraging their distinctive properties to facilitate the efficient conversion of CO_2 into valuable chemical products. Different transition metals and their oxides exhibit distinct catalytic behaviors during the CO_2RR process, resulting

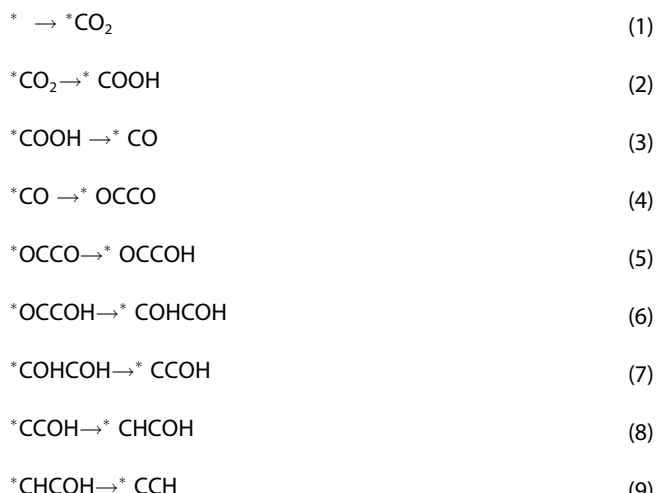
in different reduction products, thereby selecting appropriate catalysts for specific applications is important. For example, Zn, In, Sn, Bi, etc., the products in the CO_2RR are mostly C_1 products (carbon monoxide, methane, formic acid).^[7–11] Copper-based catalysts are the most extensively studied metal-based catalysts capable of producing C_{2+} products through electrocatalytic CO_2 reduction. Among them, Cu nanowires/nanosheets, Cu oxides (Cu_2O , CuO), CuM alloys (CuAg , CuPd , etc.), heteroatom-doped Cu (F–Cu, Cl–Cu, etc.), and Cu-based bifunctional catalysts are widely researched to enhance the production of C_{2+} products.^[12–18] Compared to C_1 products, C_{2+} products (including valuable chemicals such as ethylene, ethanol, acetic acid, and n-propanol) possess higher economic value. Therefore, the study of C_{2+} products has garnered extensive attention from researchers and industries alike, driven by the compelling economic incentives and the urgent need to develop sustainable and efficient CO_2 utilization technologies. The electrocatalytic conversion of carbon dioxide to C_{2+} products involve multi-proton-electron transfer, complex intermediates, and difficult carbon-carbon coupling steps.^[19–20] Ethylene and ethanol, as common C_{2+} products with great economic value, often coexist during the reaction process due to their close thermodynamic reaction potentials and similar reaction pathways, making it difficult to obtain a specific C_{2+} products.^[21–24] Thus, how to reasonably design catalysts to improve the Faraday efficiency of a specific C_{2+} product still faces significant challenges. Garza and Calle-Vallejo et al. proposed that in the C–C coupling step, the most important intermediate may be the $^*\text{OCCHO}$ or $^*\text{OCCOH}$ intermediate formed by coupling CO with hydrogenated CO ($^*\text{CHO}$ or $^*\text{COH}$).^[25–26] The formation mechanism of C_{2+} products ethylene and ethanol is generally believed to be as follows:

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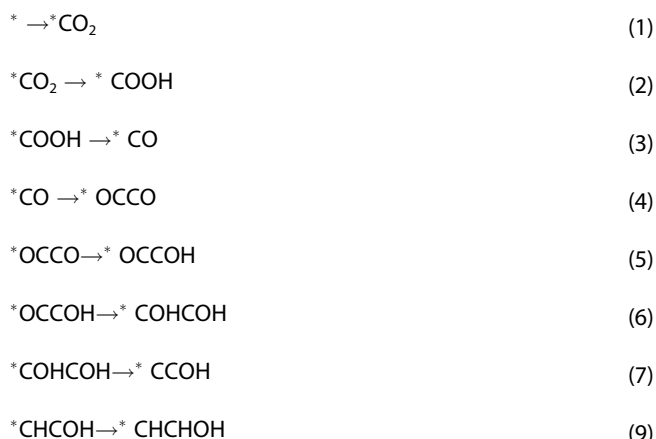
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The formation path of ethylene^[27] is



The formation path of ethanol^[28]



To achieve the production of C_{2+} products with high selectivity, it is imperative to delve into the intricate mechanisms of the CO_2RR process. From the above reaction mechanism, it can be concluded that $*CHCOH$ as a key intermediate of ethylene and ethanol, which is crucial for improving the Faraday efficiency of C_{2+} . At the same time, ethylene and ethanol are competing products in the reaction, and the step 1–8 reaction process is completely the same. After generating $*CHCOH$, the formation of ethylene requires breaking the C–O bond, while the formation of ethanol requires stabilizing the C–O bond.^[29–32] Therefore, stable $*CHCOH$ and C–O bonds should be beneficial for generating C_{2+} products, especially for improving the selectivity of ethanol.

Cu stands out as the sole metal-based catalyst capable of yielding C_{2+} products during the CO_2RR process, highlighting its unique and indispensable role in advancing the field of CO_2 utilization. However, in the electrocatalysis process, Cu-based catalysts often have problems such as agglomeration, higher overpotential, and poor stability, which hinder the stable and continuous production of C_{2+} products.^[33–34] To address these challenges, researchers have embarked on extensive investiga-

tions into Cu-based catalysts, aiming to optimize their performance for the efficient production of C_{2+} products in CO_2RR . By regulating the electronic structure (stress effect, ligand effect and synergistic effect),^[35–38] surface structure (unsaturated coordination number, exposed crystal surface, introduction of defects, etc.),^[39–41] and coordination environment (controlling the distance of Cu sites and the number and type of ligands) of the catalyst,^[42–44] the reactivity and directional selectivity of the catalyst can be significantly improved.

Despite extensive research and regulatory efforts, the reconfiguration of Cu-based catalysts during the electrocatalytic process remains an unavoidable reality. Therefore, it is crucial to investigate the valence changes of Cu throughout the electrocatalysis, as this understanding can pave the way for more stable and efficient catalysts. Yang et al. found that the ethanol selectivity of the catalyst was improved by co-adsorption of CO and hydroxyl at mixed grain boundaries Cu^+/Cu^0 .^[45] Wu et al. investigated the catalytic properties of different grains of copper oxide.^[46] The multi-grain copper oxide is in Cu^+/Cu^0 mixed state during the reaction, which is conducive to C–C coupling and the production of C_{2+} products. Current studies have shown the importance of Cu^+ and mixed valence states, so it is necessary to introduce other substances to increase the content of Cu^+ to promote the formation of C_{2+} products.

In recent years, the interaction between metal and carrier has emerged as a promising strategy to enhance CO_2 electrocatalytic activity, providing new avenues for the development of more efficient and durable catalysts. By constructing metal oxide and Cu composite catalysts and modifying copper with metal oxide supports, the selectivity of CO_2RR for various products can be significantly improved.^[47–50] Cerium dioxide, recognized as a prominent transition metal oxide, has garnered widespread application in the catalytic field, owing to its unique properties and potential to enhance various catalytic processes.^[51–52] Due to the unique electron configuration of CeO_2 , Ce exhibits two stable valence states of +3 and +4 in compounds.^[53–54] Accordingly, CeO_2 , with its robust redox capabilities, has shown significant potential and garnered favorable application in the realm of catalysis, particularly as a carrier, enhancing the performance of various catalytic systems. Therefore, it is reasonable to conjecture that the presence of CeO_2 can reduce Cu^{2+} produced in the CO_2RR , thereby increasing the content of Cu^+ .^[55] In addition, CeO_2 boasts a substantial number of oxygen vacancies, a characteristic attributed to its distinctive structural properties. A large number of oxygen vacancies facilitate the chemical adsorption of carbon dioxide molecules on the catalyst surface, thereby promoting the occurrence of subsequent reactions. Moreover, the recombination of CeO_2 with metal is conducive to the dispersion of the active site, making the Cu-based catalyst less prone to agglomeration.^[56]

Herein, Cu nanoparticles supported on cerium dioxide with a hollow cube structure (Ce_xCu_y) were prepared by electrostatic adsorption self-assembly method in this work. Compared with Cu nanoparticles, Ce_xCu_y exhibit better catalytic performance with higher $FE_{C_{2+}}$ and current density. The value of $FE_{C_{2+}}$ for the optimal material Ce_1Cu_2 reaches 73.52% and the current

density of C_{2+} product reaches more than 280 mA/cm^2 at 1.26 V (vs. RHE). More importantly, due to the unique structure of the synthesized sample Ce_1Cu_2 , there were significant changes in the reduction product. Compared to pure Cu NPs (with ethylene as the main product, $FE=30.18\%$), the introduction of carrier CeO_2 transforms the C_{2+} product into ethanol as the main component, with the ethanol Faraday efficiency up to 39% , effectively improving the selectivity of ethanol. The presence of CeO_2 provides a large number of oxygen vacancies and forming $Cu^+-O^{2-}-Ce^{4+}$ structure by the strong interaction of CeO_2 and Cu NPs. The structure of $Cu^+-O^{2-}-Ce^{4+}$ and a large number of oxygen vacancies lay a good foundation for the CO_2 adsorption. The structure of $Cu^+-O^{2-}-Ce^{4+}$ increases the content of Cu^+ , thereby increasing the ratio of Cu^+/Cu^0 . High Cu^+/Cu^0 sites within the catalyst effectively inhibit hydrogen evolution reaction and promote the C–C coupling interaction, thereby facilitating the generation of C_{2+} products. The DFT theoretical calculation further demonstrate that Ce_1Cu_2 is more inclined towards the ethanol pathway, confirming its high selectivity for ethanol.

Results and Discussion

Briefly, CeO_2 with a hollow cube structure was synthesized through the strategic etching of cuprous oxide cubes. Cu NPs were synthesized according to literatures.^[57–58] Then, Ce_xCu_y catalysts were prepared by electrostatic adsorption self-assembling from hollow cubes of cerium dioxide and copper nanoparticles. The contents of Ce and Cu in Ce_xCu_y were obtained by ICP-OES as shown in table S1. Among these, the Cu content in Ce_1Cu_2 is $27.5 \text{ wt}\%$, while the Ce content is $30.1 \text{ wt}\%$.

The morphology of the synthesized samples Ce_1Cu_2 , CeO_2 , and Cu NPs were characterized by transmission electron microscopy (TEM). As shown in figure 1a, CeO_2 exhibits a clear and regular hollow cube structure with lattice spacing 0.312 nm corresponding to the (111) crystal plane of CeO_2 (figure 1d). Figure 1b shows that Cu NPs are uniformly dispersed and the particle size distribution indicates that the particle size of Cu nanoparticles is about 6 nm (figure S1). It is worth noting that the (111) crystal planes of Cu_2O with a lattice spacing of 0.246 nm and (111) crystal planes of Cu with a lattice spacing of 0.208 nm were observed in Cu NPs, as shown in figure 1e, indicates the coexistence of Cu^+/Cu^0 sites in the sample Cu NPs. The morphology of the composite catalyst Ce_1Cu_2 , as illustrated in figure 1c, reveals the distribution of Cu NPs on the surface of hollow cube CeO_2 . The lattice fringes of 0.312 nm and 0.246 nm can be observed by high-resolution transmission electron microscopy (figure 1f), which corresponding to CeO_2 (111) and CuO_2 (111), respectively. Notably, the clear interface proves the formation of nano-heterostructures. As depicted in figures 1g–i, the Ce, O, and Cu elements are uniformly distributed throughout the composite catalyst, indicating a well-integrated and homogeneous structure. For other Ce_xCu_y composites, as the Cu loading increases, there are certain structural differences observed among catalysts with different Ce/Cu ratios. The morphologies of Ce_1Cu_3 and Ce_1Cu_4 become

increasingly unstable and fail to maintain the hollow cube structure well. This may be due to the partial filling of the hollow cubes by Cu NPs, leading to structural instability as the Cu loading increases. In contrast, Ce_1Cu_2 exhibiting the most favorable morphology, highlighting its superior structural integrity and potential for enhanced catalytic performance (figure S2–5).

Furthermore, X-ray diffraction (XRD) analysis was employed to elucidate the crystalline structure of the materials, providing valuable insights into their atomic arrangements and phase compositions. As depicted in figure 2a, the diffraction peak of Cu NPs appears at 36.4° , 61.4° and 43.3° , corresponding to Cu_2O (111), (220) and Cu (111) respectively, further indicating that the prepared Cu NPs exists in the form of Cu^+/Cu^0 mixed state. The diffraction peak of CeO_2 appears at 28.5° , 47.4° and 56.2° , corresponding to CeO_2 (111), (220) and (311), respectively. Ce_1Cu_2 exhibits the characteristic diffraction peaks of CeO_2 , indicating that the incorporation of Cu NPs did not significantly alter the structural integrity of CeO_2 . However, no characteristic peak of copper was observed in the sample Ce_1Cu_2 , possibly due to the dispersion of copper in the form of nanometers and its low content. This conjecture can be illustrated by comparing the XRD of other Ce_xCu_y . As shown in figure S6, with the increase of copper content, the diffraction peak intensity of Cu_2O and Cu gradually increases.

To further elucidate the structural characteristics of the catalyst (Ce_xCu_y), the chemical compositions and valence states of the constituent elements were meticulously investigated using X-ray photoelectron spectroscopy (XPS), offering a comprehensive understanding of the material's electronic and chemical properties. In Ce 3d XPS spectra, the characteristic peaks located at 882.5 , 888.7 , 898.2 , 900.9 , 907.2 , 916.7 eV and 885.0 , 902.6 eV , which belongs to Ce^{4+} (v , u , $v_{2/3}$, $v_{3/2}$, $u_{3/2}$) and Ce^{3+} (v_1 , u_1) can be observed as shown in figure 2b. Compared to pure CeO_2 , the content of Ce^{3+} in the composite material Ce_1Cu_2 is significantly increased. Because the ionic radius of Ce^{3+} is slightly larger than Ce^{4+} , an increase in Ce^{3+} content will inevitably generate more vacancy oxygen. This result indicates that the addition of copper in the composite material induces the transformation of some Ce^{4+} ions into Ce^{3+} ions, thereby generating more oxygen vacancies, which induced the formation of $Cu^+-O^{2-}-Ce^{4+}$. The unique structural features and the presence of oxygen vacancies in the catalyst provide a robust foundation for the efficient adsorption of CO_2 during the CO_2RR process.

To demonstrate the variation in oxygen vacancy content, we further conducted O 1s XPS analysis on the samples. As shown in figure 2c, the catalysts Ce_1Cu_2 and pure CeO_2 exhibit absorption peaks at 529.5 eV , 531.2 eV , and 533.1 eV , respectively, attributed to lattice oxygen (O_l), oxygen vacancies (O_v), and adsorbed oxygen. Comparing these two samples, we found that the vacancy oxygen content in Ce_1Cu_2 is higher than that in CeO_2 , which is consistent with the conclusion of Ce 3d XPS. Additionally, for the sample Cu NPs, there is also a small amount of vacancy oxygen, which further indicates the presence of Cu^+/Cu^0 sites in the synthesized copper nanoparticles. The EPR results further indicate the presence of

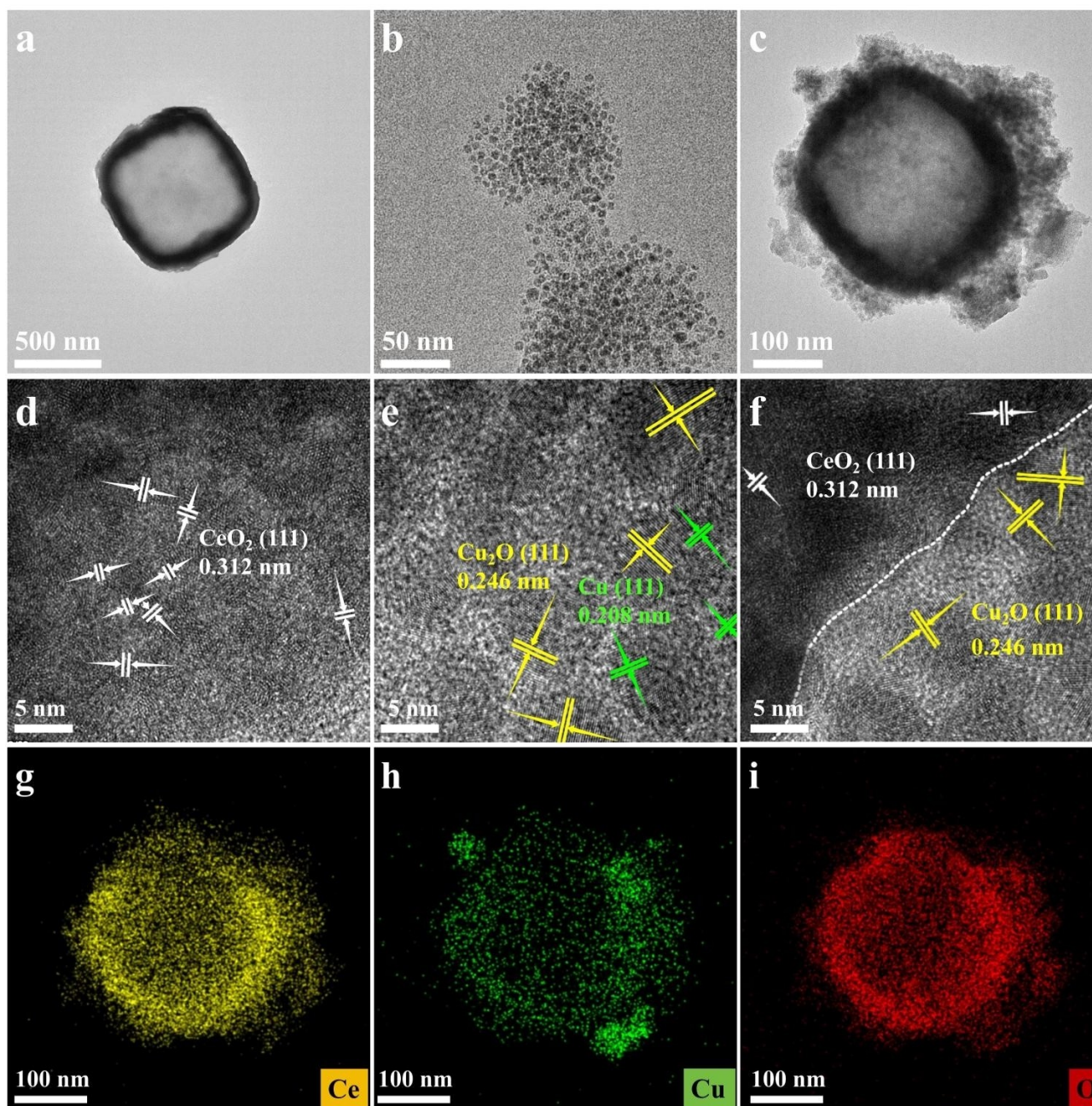


Figure 1. The morphology characterization of CeO₂, Cu NPs and Ce₁Cu₂. (a, d). TEM images of CeO₂; (b, e). TEM images of Cu NPs; (c, f). TEM images of Ce₁Cu₂; (g–i). Elemental mapping image of Ce₁Cu₂.

oxygen vacancies in the Cu NPs and composite material Ce₁Cu₂ as shown in figure 2d. Due to the introduction of carrier CeO₂, the composite material Ce₁Cu₂ exhibits a higher peak intensity at $g=2.0$, indicating a significant increase in oxygen vacancies. As shown in figure 2e, it can be seen that there are two pairs of peaks for Ce₁Cu₂, which belong to Cu⁺ or Cu⁰ (932.2 and 952.2 eV) and Cu²⁺ (934.2 and 954.4 eV), respectively. This observation suggests that Cu⁺ or Cu⁰ and Cu²⁺ coexist within the Ce₁Cu₂ composite. However, since the binding energies of Cu⁺ and Cu⁰ are close to each other, it cannot be determined by the Cu 2p XPS spectrum. To further elucidate the distinction between Cu⁺ and Cu⁰, Cu LMM Auger spectroscopy was

conducted, providing detailed insights into the electronic states and distribution of copper within the composite catalyst. In figure 2f, the presence of both Cu⁺ and Cu⁰ is evident, indicating a dynamic and interactive electronic environment within the catalysts, which may contribute to its enhanced catalytic performance. To further investigate the electronic interaction between Cu NPs and CeO₂, we conducted a detailed XPS analysis of Ce₁Cu_y samples with different ratios as shown in figure S7 and table S2–3. The peak area ratio of Cu⁺/Cu⁰ was compared in Cu 2p XPS spectra as shown in figure 2e–f and figure S7c–d. The ratio of Cu⁺/Cu⁰ increases first and then decreases with the load of copper as shown in table S2. The

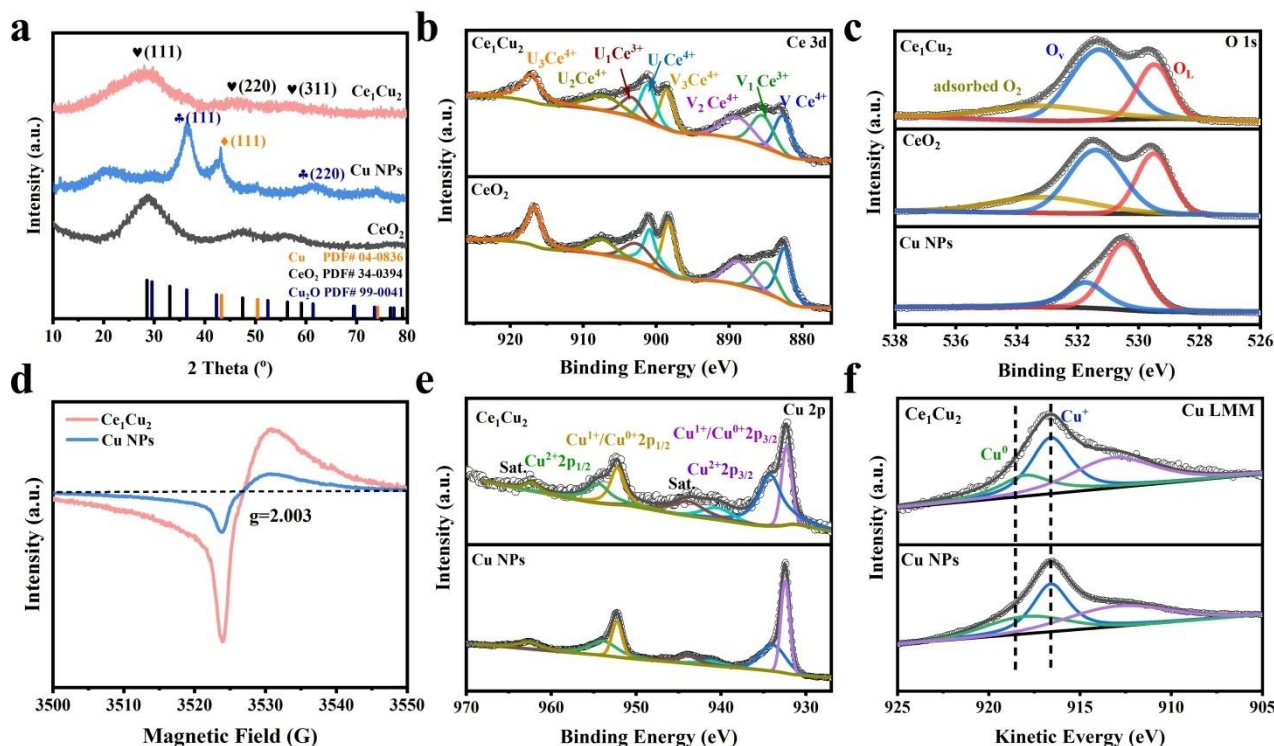


Figure 2. The structural characterization of different catalysts. (a). XRD patterns of CeO₂, Cu NPs and Ce₁Cu₂; (b). Ce 3d XPS of CeO₂ and Ce₁Cu₂; (c). O 2p XPS of CeO₂, Cu NPs and Ce₁Cu₂; (d). EPR of Cu NPs and Ce₁Cu₂; (e). Cu 2p XPS of Cu NPs and Ce₁Cu₂; (f) Cu LMM Auger spectra of Cu NPs and Ce₁Cu₂.

catalyst Ce₁Cu₂ exhibits the highest ratio of Cu⁺/Cu⁰, indicating an optimal balance of copper species that may contribute to its superior catalytic performance and selectivity in CO₂ reduction processes. This further proves that the presence of Cu⁺-O²⁻-Ce⁴⁺ structure regulates the ratio of Cu⁺/Cu⁰. The peak area ratio of Ce³⁺/(Ce³⁺ + Ce⁴⁺) was compared in Ce 3d XPS spectra (figure 2b and figure S7a). This result shows that Ce³⁺ and Ce⁴⁺ exist in Ce_xCu_y, as well as in CeO₂. A larger ratio of Ce³⁺/(Ce³⁺ + Ce⁴⁺) corresponds to a higher concentration of oxygen vacancies and unsaturated bonds within the catalyst. These factors are critical for enhancing its ability to adsorb and activate CO₂ molecules during the CO₂RR process. By comparing Ce³⁺/(Ce³⁺ + Ce⁴⁺) of Ce_xCu_y, it can be concluded that the value of Ce³⁺/(Ce³⁺ + Ce⁴⁺) increases first and then decreases with the load of copper (table S2). Ce₁Cu₂ has the highest ratio of Ce³⁺/(Ce³⁺ + Ce⁴⁺), which means it has the most oxygen vacancies. The presence of lattice oxygen indicates the presence of Ce-O or Cu-O in Ce₁Cu₂, but the binding energy of lattice oxygen of Ce-O is close to that of Cu-O. As shown in figure S7b, the binding energy of lattice oxygen shifts first negatively and then positively with the increase of copper loading. The lattice oxygen binding energy of Ce₁Cu₂ is the lowest (529.5 eV), which indicating some interaction between CeO₂ and Cu NPs. It exists in Cu⁺-O²⁻-Ce⁴⁺ structure, which inhibits the formation of lattice oxygen and promotes the formation of O_v. According to table S3, it can be seen that Ce₁Cu₂ has the largest content of O_v. The result is the same as the conclusion on the ratio of Ce³⁺/(Ce³⁺ + Ce⁴⁺) in Ce 3d XPS. The catalysts were subsequently subjected to Brunauer-

Emmett-Teller (BET) surface area analysis, as shown in figure S8. Based on these results, the specific surface areas and pore size distributions of the catalysts were compared in table S4. The results indicate that Ce₁Cu₂ has a higher specific surface area and moderate pore size compared to Cu NPs, which is beneficial for CO₂ adsorption, thereby enhancing the selectivity and yield of C₂₊ products.

The electrocatalytic performance of Ce_xCu_y on CO₂RR was investigated in a flow cell (figure S9) with 1.0 M KOH solution as electrolyte and carbon paper as a gas diffusion electrode. The distribution of gaseous and liquid products generated within the potential range of -0.86 V to -1.36 V (vs. RHE) can be accurately detected and analyzed using gas chromatography (GC) and ¹H nuclear magnetic resonance (NMR) spectroscopy, providing comprehensive insights into the catalytic performance and selectivity of the CO₂RR process. As shown in figure 3a, compared to CeO₂ and Cu NPs, the LSV curve of Ce₁Cu₂ shows the highest current density and more positive initial potential, indicating that the formation of nano-hetero-junctions significantly improves the conductivity and intrinsic activity of the material. The product distribution of the catalyst during the CO₂RR process encompasses a diverse array of valuable chemicals, rather than being confined to a single compound (table S5-6). As shown in figure 3b-c and figure S10, the gas phase products of Cu NPs and Ce_xCu_y in the CO₂RR are mainly hydrogen, carbon monoxide, methane and ethylene; the liquid phase products are ethanol, acetic acid and formic acid. In addition, as shown in figure 3d and figure S11, the C₂₊ Faraday efficiency of Ce₁Cu₂ is higher than other Ce_xCu_y.

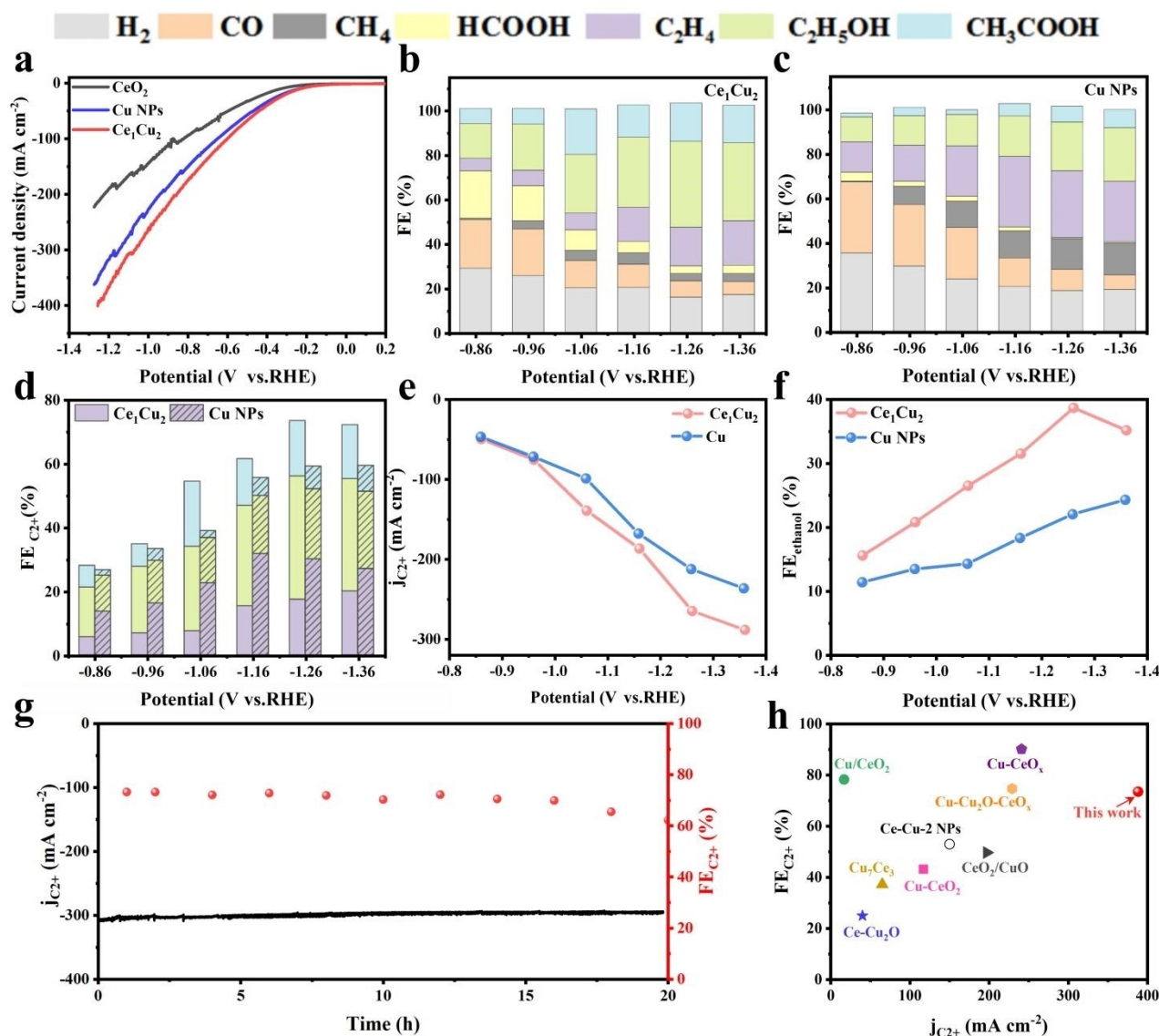


Figure 3. Electrochemical properties of different catalysts under CO₂RR in Flow-cell. (a). LSV of CeO₂, Cu NPs and Ce₁Cu₂; (b). FE of Ce₁Cu₂; (c). FE of Cu NPs; (d). FE_{C₂+} of Cu NPs and Ce₁Cu₂; (e). j_{C₂+} of Cu NPs and Ce₁Cu₂; (f). FE_{ethanol} of Cu NPs and Ce₁Cu₂; (g). the stability test by chronoamperometry; (h). Comparison of properties of Ce₁Cu₂ and Cu/Ce materials in other literatures.

catalysts and Cu NPs. Compared the FE_{C₂+} of Cu NPs (59.48%), the FE_{C₂+} of Ce₁Cu₂ reaches a maximum value of 73.52% at the potential of −1.26 V (vs. RHE). The current density (j_{C₂+}) of C₂ products of CeO₂, Cu NPs and Ce₁Cu₂ under CO₂RR are shown in figure 3e. Compared with CeO₂ and Cu NPs, Ce₁Cu₂ has the highest current density of C₂ products, j_{C₂+} can reach 288 mA cm^{−2} at −1.36 V (vs. RHE), much higher than the j_{C₂+} of Cu NPs. Compared with other Ce_xCu_y, the j_{C₂+} of Ce₁Cu₂ is highest as shown in figure S12. By comparing the ratio of FE_{C₂+} and FE_{C₁}, it can be seen that the value of FE_{C₂+}/FE_{C₁} of other Ce_xCu_y is around 1, while the value of FE_{C₂+}/FE_{C₁} of Ce₁Cu₂ is the largest (figure S13), is up to 5. The results indicate that Ce₁Cu₂ is more inclined to C–C coupling to produce C₂ production in the CO₂RR process. This result may be attributed to the significant influence of the high oxygen vacancies and elevated ratio of Cu⁺/Cu⁰ in Ce₁Cu₂, which collectively contrib-

ute to the catalyst's enhanced ability to facilitate multiple reaction pathways and produce C₂ chemicals.

To further investigate the effect of CeO₂ on Cu NPs, the Faraday efficiency of each product of different catalysts is compared. The main C₂ product of Cu NPs under CO₂RR is ethylene, and the FE_{ethylene} can reach 30% at a potential of −1.16 V (vs. RHE). While, the main C₂ product of Ce₁Cu₂ under CO₂RR is ethanol, and the FE_{ethanol} can reach 39% at −1.26 V (vs. RHE) as shown in figure 3d and f. Ce₁Cu₂ exhibits a preference for the ethanol formation pathway during the CO₂RR process, indicating that the unique structural and electronic properties are optimized for the selective production of ethanol from CO₂. This result may be due to the fact that the structure of Cu⁺-O²⁻-Ce⁴⁺ increases the content of Cu⁺, which increases the ratio of Cu⁺/Cu⁰ sites. High Cu⁺/Cu⁰ sites can effectively inhibit HER and promote the C–C coupling interaction to generate C₂. As

shown in figure S14, The C_1 product (carbon monoxide, methane, formic acid) of Ce_1Cu_2 has the lowest Faraday efficiency compared to other Ce_xCu_y catalysts. Moreover, as depicted in figure S15, the Faraday efficiency of H_2 did not increase at high negative potentials, and even at 1.36 V (vs. RHE), FE_{H_2} remained below 17%, indicating that side reactions HER were well suppressed and contributing to the improvement of CO_2 electrocatalytic reduction efficiency. With the increase of negative potential, the Faraday efficiency of ethylene and ethanol of Ce_1Cu_2 increased, which was significantly higher than that of other Ce_xCu_y catalysts (figure S16 and S17). This outcome further substantiates the exceptional catalytic activity and stability of Ce_1Cu_2 , reinforcing its potential as a superior catalyst for CO_2 reduction processes and the production of valuable chemical products.

Subsequently, the reaction kinetics of various catalysts were compared, providing a comprehensive understanding of their relative performance, efficiency, and potential for optimization in CO_2 reduction applications. The Cyclic voltammetry (CV) tests were performed on different catalysts at different scanning speeds (20~100 mV/s) as shown in figure 4a-c and figure S18. The double layer capacitance (C_{dl}) of various catalysts was evaluated and compared based on their CV curves, offering insights into their electrochemical behavior, surface area. The C_{dl} of Ce_1Cu_2 is 0.066 mF/cm², much higher than the value of Cu NPs (0.026 mF/cm²) and CeO_2 (0.025 mF/cm²) as shown in figure 4d. However, the C_{dl} value of Ce_1Cu_2 is lower than other Ce_xCu_y in figure S19. The electrochemical surface area of Ce_1Cu_2 is higher than that of CeO_2 and Cu NPs, and lower than that of

other Ce_xCu_y catalysts. Subsequently, we compared the LSV normalized by electrochemical surface area (ECSA), as shown in figure S20. The analysis revealed that Ce_1Cu_2 demonstrates superior catalytic performance, with its actual catalytic activity surpassing that of Cu NPs and other Ce_xCu_y catalysts. It is worth noting that the ECSA is not the only criterion to evaluate its catalytic kinetics, so other parameters were compared. Tafel slope is another important parameter to evaluate the performance of electrocatalysis. By comparing this parameter as shown in figure 4e and figure S21, it is found Ce_1Cu_2 (598 mV/dec) has the lowest tafel slope compared with Cu NPs and other Ce_xCu_y . This indicates that Ce_1Cu_2 possesses a relatively low over-potential and demonstrates commendable catalytic activity, making it a promising candidate for efficient and selective CO_2 reduction applications. Electrochemical impedance spectroscopy (EIS) is used to further evaluate catalyst activity and charge transfer rate. As shown in figure 4f and figure S22, Ce_1Cu_2 exhibits a smaller semicircle in the EIS plot, indicating that its electrochemical impedance is significantly lower compared to Cu NPs, CeO_2 , and other Ce_xCu_y catalysts. This observation underscores the exceptionally fast charge transfer rate of Ce_1Cu_2 , which is crucial for its superior catalytic performance in CO_2 reduction processes.

To evaluate the stability of Ce_1Cu_2 , a chronoamperometry test was conducted, providing valuable insights into the long-term performance and durability of the catalyst in CO_2 reduction applications. As illustrated in figure 3g, the j_{C_2+} remains nearly unchanged, and the FE_{C_2+} exceeds 60% over a span of 20 hours in the flow cell. This demonstrates the

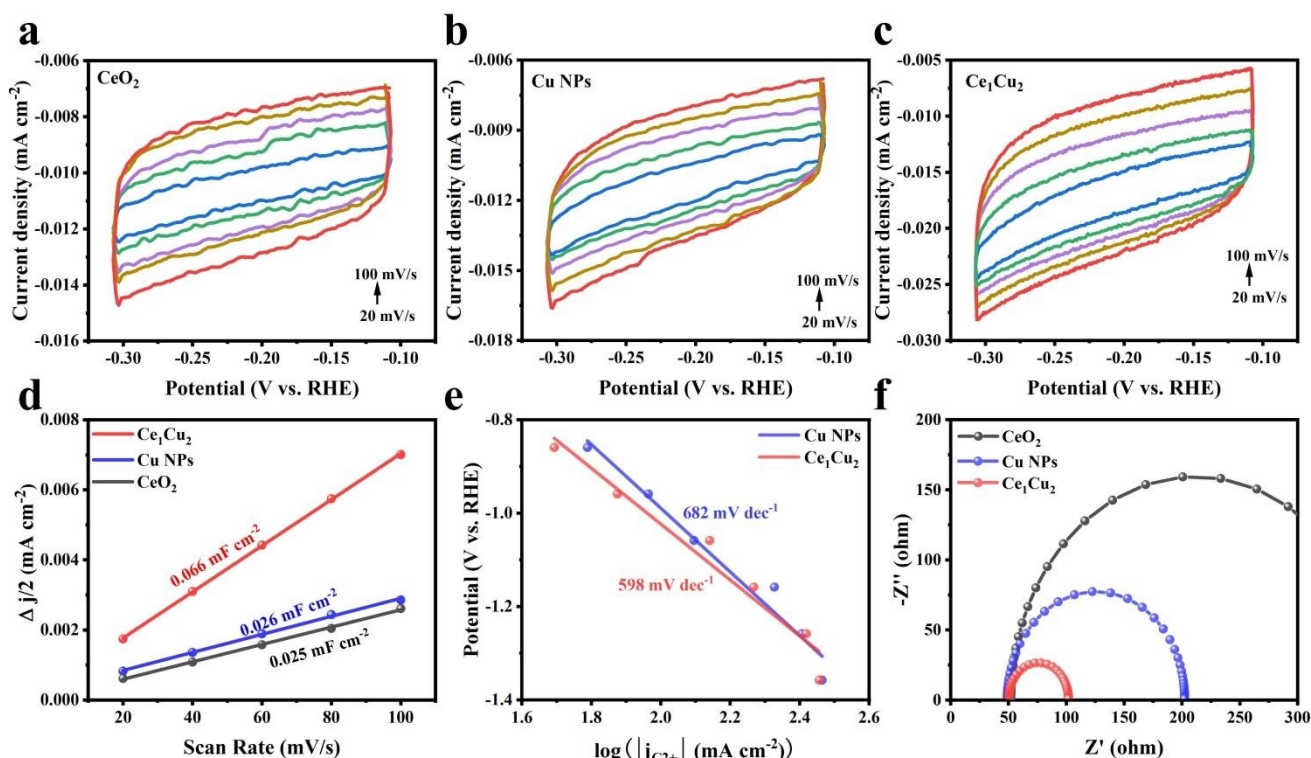


Figure 4. (a–c). The cyclic voltammetry curves at different sweep speeds of CeO_2 (a), Cu NPs (b) and Ce_1Cu_2 (c); (d). Double layer capacitor (C_{dl}); (e). Tafel slope; (f). EIS curves of CeO_2 , Cu NPs and Ce_1Cu_2 .

exceptional stability and sustained performance of Ce_1Cu_2 in CO_2 reduction processes. Following electrochemical tests, Ce_1Cu_2 was characterized through morphology analysis and XPS analysis, providing detailed insights into its structural integrity, surface composition, and electronic environment. As shown in figure S23a, it can be seen that the morphology of Ce_1Cu_2 after the reaction is unchanged, where Cu NPs loaded on the surface of hollow cubic CeO_2 . The lattice fringes of 0.312 nm and 0.246 nm observed by high-resolution transmission electron microscopy correspond to CeO_2 (111) and CuO_2 (111), respectively (figure S23b). And the elements are evenly distributed as shown in the figure S23d-e. The XPS spectra before and after the reaction were also compared. In Ce 3d XPS spectra as shown in figure S24a, the absorption peaks of Ce^{4+} (v_1, u_1, v_2, v_3, u_3) and Ce^{3+} (v_1, u_1) can also be observed. In figure S24b, the absorption peaks at 529.6 eV, 530.7 eV, and 533.4 eV, which can contribute to lattice oxygen (O_L), oxygen vacancy (O_V), and adsorbed oxygen, is similar to the absorption peaks of Ce_1Cu_2 before reaction. It can be seen from the Cu 2p XPS and Cu LMM Auger spectra that Cu^+ , Cu^0 and Cu^{2+} exist after the reaction. The ratio of $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$, Cu^+/Cu^0 and the O_V content of Ce_1Cu_2 after the reaction did not show significant changes after the reaction. This observation underscores the remarkable long-term stability of Ce_1Cu_2 in both structural integrity and performance, reinforcing its potential for sustained and efficient CO_2 reduction applications over extended periods.

The electrochemical test results indicate that Ce_1Cu_2 has high catalytic activity sites and rapid reaction kinetics, which promote the conversion of CO_2 to C_{2+} products. Compared with the currently reported CuCe catalysts, the synthesized Ce_1Cu_2 has the highest $\text{FE}_{\text{C}_{2+}}$ and $j_{\text{C}_{2+}}$ as shown in figure 3h and table S7. This result further demonstrates that cerium dioxide significantly enhances the catalytic performance of Cu NPs, highlighting the synergistic effects and potential of the composite catalyst for efficient CO_2 reduction processes.

Based on the comprehensive electrochemical characterization and XPS results, the catalytic mechanism of Ce_xCu_y was deduced, providing a detailed understanding of the interplay between the constituent elements and their roles in facilitating the efficient CO_2 reduction process. The catalytic mechanism of Ce_1Cu_2 is shown in figure 5. Because cerium dioxide is rich in a large number of oxygen vacancies, CeO_2 and Cu NPs have strong interaction after the addition of copper, forming Cu^+

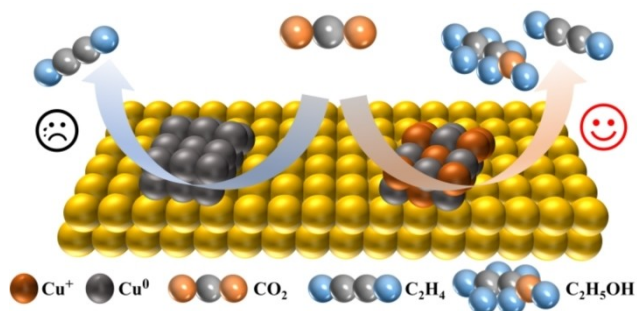


Figure 5. The mechanism of Ce_1Cu_2 under CO_2RR .

$-\text{O}^{2-}-\text{Ce}^{4+}$ structure. The structure of $\text{Cu}^+-\text{O}^{2-}-\text{Ce}^{4+}$ and a large number of oxygen vacancies lay a good foundation for the CO_2 adsorption. This results in the CO_2 enrichment at the active site of the catalyst, increasing the local concentration of the reactants, and improving the efficiency and product selectivity of CO_2RR . In addition, the strong interaction between CeO_2 and Cu NPs regulates the valence state of Cu NPs, which makes Cu^+ exists stable. The structure of $\text{Cu}^+-\text{O}^{2-}-\text{Ce}^{4+}$ increases the content of Cu^+ , thereby increasing the ratio of Cu^+/Cu^0 sites. High Cu^+/Cu^0 sites within the catalyst effectively inhibit hydrogen evolution reaction (HER) and promote the C–C coupling interaction, thereby facilitating the generation of C_{2+} products. Maintaining the Cu^+ species and the mixed state of Cu^+/Cu^0 of the Cu-based catalyst during the catalytic process can effectively improve the selectivity of its multi-carbon products, which makes Ce_1Cu_2 further proceed to the ethanol reaction path in addition to the ethylene reaction path. In addition, the catalyst Ce_1Cu_2 containing mixed grain boundary Cu^+/Cu^0 have uniformly dispersed active sites that are not prone to agglomeration, which makes Ce_1Cu_2 maintains stability during CO_2RR .

Then a model of Ce_1Cu_2 was constructed using Density Functional Theory (DFT), as illustrated in figure S25, to further elucidate the mechanism behind the high selectivity of C_{2+} products in the electrocatalytic reduction of CO_2 over the Ce_1Cu_2 catalyst. The reaction pathways for ethanol and ethylene on the Ce_1Cu_2 catalyst was constructed as shown in figure 6, which share the same reaction pathway before the key intermediate $^*\text{CHCOH}$. The shared $^*\text{CHCOH}$ intermediate can form ethanol via carbon protonation ($^*\text{CHCOH}$ to $^*\text{CHCHOH}$) or ethylene via C–O bond cleavage and dehydration to $^*\text{CCH}$. We observed that both the pathway for forming $^*\text{CHCHOH}$ (red line) and the pathway for forming $^*\text{CCH}$ are endothermic (blue line). The formation of $^*\text{CHCHOH}$ on Ce_1Cu_2 is relatively more favorable compared to the formation of $^*\text{CCH}$. Specifically, the energy barrier (1.13 eV) that needs to be overcome for the formation of $^*\text{CHCHOH}$ is smaller than the energy barrier (1.40 eV) for the formation of $^*\text{CCH}$. This ensures a high Faradaic efficiency of ethanol.

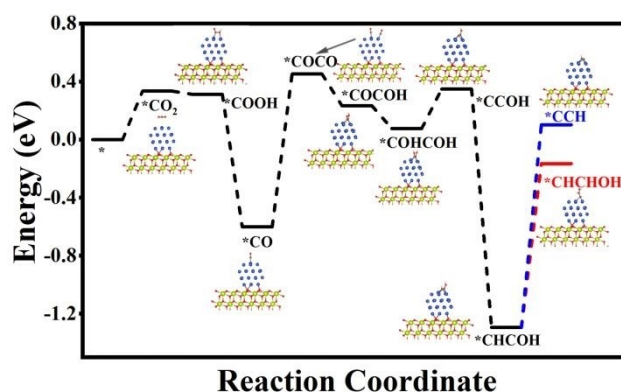


Figure 6. The free energy diagram of CO_2RR showing the pathways alongside the key intermediates toward ethanol and ethylene products on Ce_1Cu_2 .

Conclusions

In summary, Cu nanoparticles supported on hollow cube cerium dioxide were prepared by electrostatic adsorption self-assembly method in this paper. Compared with Cu nanoparticles, Ce_xCu_y exhibits better catalytic performance with higher FE_{C_2+} and current density. The value of FE_{C_2+} for Ce_1Cu_2 reaches 73.52% and the current density of C_2+ product reaches more than 280 mA/cm^{-2} at 1.26 V (vs. RHE). The CeO_2 with a hollow cube structure provides a large number of oxygen vacancies for Cu NPs. The strong interaction between CeO_2 and Cu forms a $\text{Cu}^+-\text{O}^{2-}-\text{Ce}^{4+}$ structure. The $\text{Cu}^+-\text{O}^{2-}-\text{Ce}^{4+}$ structure increases the content of Cu^+ , the high Cu^+/Cu^0 sites within the catalyst effectively suppress the hydrogen evolution reaction and promote C–C coupling interactions, thus facilitating the formation of C_2+ products. The DFT theoretical calculation further demonstrate that Ce_1Cu_2 has high selectivity for ethanol. This work provides a new approach for designing efficient Cu-based catalysts for CO_2RR .

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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 in the supplementary material of this article.

Keywords: CO_2RR · CeO_2 · Copper · Cu^+/Cu^0 sites · C_2+ products

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