Water coordinated on Cu(I)-based catalysts is the oxygen source in CO₂ reduction to CO

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Catalytic reduction of CO₂ over Cu-based catalysts can produce various carbon-based products such as the critical intermediate CO, yet significant challenges remain in shedding light on the underlying mechanisms. Here, we develop a modified triple-stage quadrupole mass spectrometer to monitor the reduction of CO₂ to CO in the gas phase online. Our experimental observations reveal that the coordinated H₂O on Cu(I)-based catalysts promotes CO₂ adsorption and reduction to CO, and the resulting efficiencies are two orders of magnitude higher than those without H₂O. Isotope-labeling studies render compelling evidence that the O atom in produced CO originates from the coordinated H₂O on catalysts, rather than CO₂ itself. Combining experimental observations and computational calculations with density functional theory, we propose a detailed reaction mechanism of CO₂ reduction to CO over Cu(I)-based catalysts with coordinated H₂O. This study offers an effective method to reveal the vital roles of H₂O in promoting metal catalysts to CO₂ reduction.

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Catalytic reduction of CO₂ into high value-added carbon-based products is a promising strategy for tackling current energy demands and reducing greenhouse gas emissions. In the past few years, tremendous efforts have been made to explore CO₂ reduction reaction (CO₂RR), and several products, including CH₄, CO, CH₃OH, HCOOH, HCHO, C₂H₆, C₂H₅OH, and H₂C₂O₄, have been generated from CO₂ reduction via photo-, electro-, or thermal activation. To enhance the selectivity and the conversion efficiency of CO₂RR, focus has primarily been on exploring novel catalysts. Despite the progress, many details of the CO₂RR mechanisms on the surface of catalysts remain elusive. The techniques used to investigate CO₂RR mechanisms include Raman spectroscopy, X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, electron microscopy, and calculations using density functional theory (DFT). However, direct observation of the highly reactive intermediates is still a grand challenge.

Mass spectrometry (MS) is a formidable tool for chemical analysis and has also been used to explore the mechanisms of various chemical reactions. Nevertheless, there have been few reports on the use of MS to study CO₂RR mechanisms in operando. This could be attributed to the following obstacles: (i) CO₂ and its resulting products (e.g., CO, CH₄, and CH₃OH) are neutral molecules and rarely observed in mass spectra without adding charges through ionization; (ii) the lifetimes of reactive intermediates are typically less than milliseconds, making it challenging to capture them with off-line MS. To address these issues, this study proposes a strategy to explore CO₂RR mechanisms by adopting the features of triple-stage quadrupole (TSQ) mass spectrometer, in which different stages of quadrupoles in TSQ are used for separation of metal ions and related catalysts originating from nanoelectrospray ionization (nanoESI) (first stage), reaction unit of metal catalysts and CO₂ (second stage), and transmission of resulting ions (third stage) (Fig. 1). In the second stage, CO₂ and its resulting products could be charged favorably by interacting with metal ions and forming metal complexes. More importantly, the CO₂RR processes can be simultaneously carried out with online detection. As such, the reaction pathways of CO₂RR can be well identified.

To demonstrate the proof-of-concept, this study explores the reduction reaction of CO₂ to CO using copper (Cu) as the catalyst. Cu is the only metal catalyst known to generate hydrocarbons through CO₂RR, but poor selectivity and reaction efficiency for value-added products significantly limit its commercial applications. Although much effort has been made to understand the catalytic performance of Cu in CO₂RR, available techniques that can clarify the underlying reaction mechanisms remain limited. In the CO₂RR, CO has been widely identified as a significant product or a primary reaction intermediate for the formation of hydrocarbons. Therefore, understanding the reduction reaction of CO₂ to CO over Cu-based catalysts is necessary to promote conversion efficiency.

According to general understanding, there are three routes in CO₂ reduction to CO: (i) CO₂ + H₂ → CO + H₂O, (ii) CO₂ + 2e⁻ + H⁺ → CO + OH⁻, and (iii) CO₂ + 2e⁻ + 2H⁺ → CO + H₂O. For all three pathways, the O atom in the generated CO originated from CO₂. In contrast to the above routes, herein we discovered for the first time that the source of the O atom in CO originated from the H₂O coordinated on transition-metal-based catalysts (e.g., Cu, Ag, and Pd) rather than CO₂. H₂O is ubiquitous in nature and has been shown to be vital in many reactions such as alcohol oxidation to aldehyde, CH₄ oxidation to CH₃OH, and CO₂ reduction to CH₄, CH₃OH, and HCOOH. However, the role of H₂O in the reduction of CO₂ to CO is ambiguous. To elucidate the role of H₂O in CO₂RR, we investigated the behavior of Cu⁺ and [Cu(H₂O)]⁺ and found that the coordinated H₂O in [Cu(H₂O)]⁺ not only favored the adsorption of CO₂ onto Cu⁺, but also facilitated the reduction of CO₂ to CO. Isotope-labeling studies provided evidence suggesting that the origin of the O atom in CO was from the coordinated H₂O on Cu⁺. By combining experimental results and computational calculations with DFT, the detailed reaction mechanism of CO₂ reduction to CO over a [Cu(H₂O)]⁺ catalyst was proposed. The data presented in this work allowed us to elucidate the role of H₂O in CO₂RR and offered new insights for developing effective systems that enhanced the selectivity and conversion efficiency of CO₂ to CO and other carbon-based products.

Results and Discussion

Reaction apparatus and generation of Cu(I) species. To reveal the underlying roles of H₂O in the reduction of CO₂ to CO via copper-based catalysis, we employed a modified TSQ apparatus for online observation of the CO₂RR and detection of the reaction intermediates and products. As shown in Fig. 1, nanoESI was used as an ionization source to generate Cu-based ions. As the catalyst ions were introduced into the TSQ apparatus, the desired Cu species were isolated from Q1 and then transferred to Q2. In the reaction unit of Q2, Cu-based ions interacted with CO₂ upon the applied voltage of 5 V and formed CO. Due to the low reaction efficiency at low temperatures (as discussed below), CO₂ gas was heated to 280°C using a heating tape in the gas circuit system prior to reacting with the Cu catalyst in the gas phase. After the reduction reaction was completed, the resulting products were transferred directly to Q3 followed by online detection.

![Fig. 1 Schematic diagram of the apparatus for CO₂ reduction and detection of reaction products.](https://doi.org/10.1038/s41467-022-30289-5)
Many previous studies have demonstrated that the different oxidation states, Cu(I)-related species are one of the most important catalysts in CO₂RR. Considering that the current study investigated different Cu-based complexes in the reduction of CO₂, nanoESI was utilized to generate Cu(I) species rather than inductively coupled plasma (ICP), which only produces Cu(I). In the nanoESI process, the types of Cu species and solvent were found to have a pronounced effect on the resulting mass spectra. When CuX (X = Cl, Br, or I) was dissolved into acetonitrile, comparable and intensive peaks of Cu-based ions appeared in the mass spectra (e.g., [63Cu(CO)⁺] and [63Cu(H₂O)⁺]), and few non-Cu species emerged (Supplementary Figs. 1–3). Thus, CuCl was used to generate different Cu(I)-based ions.

**Effect of H₂O on the reduction of CO₂ to CO**

The above MS setup allowed us to investigate the reduction of CO₂ to CO in situ. As [63Cu⁺] or [65Cu⁺] ions were isolated to interact with CO₂, no obvious resultant species were observed, and only Cu⁺ itself and [Cu(H₂O)⁺] appeared in the mass spectra (Fig. 2a, b). Remarkably, when [63Cu(H₂O)⁺] or [65Cu(H₂O)⁺] was introduced to the reaction unit along with CO₂, not only did the reaction product, CO, emerge in the forms of [63Cu(CO)⁺] and [63Cu(CO)⁺], but so did the reactant, CO₂, as complexes of [63Cu(CO₂)⁺] and [65Cu(CO₂)⁺], addition to [63Cu(H₂O)⁺], [65Cu(H₂O)⁺], and their fragment ions [63Cu⁺] and [65Cu⁺] (Fig. 2c, d). These results suggested that in contrast to the bare Cu⁺, the coordinated H₂O in [Cu(H₂O)⁺] played a vital role in the interaction with CO₂, which both rendered the adsorption of CO₂ and the reduction of CO₂ to CO on the Cu(I) catalyst. We also found that the coordinated H₂O favored other metal-based ions (e.g., [Ag(H₂O)⁺] and [Pd(H₂O)⁺]) to carry out the CO₂RR (Supplementary Figs. 4 and 5), revealing that H₂O molecules on the metal catalysts were active sites for facilitating the effective reduction of CO₂ to CO. The effect of H₂O could also be mirrored by a reversed water-gas shift reaction (WGSR) using Cu/ZnO/Al₂O₃ as catalyst (Supplementary Fig. 6a–c) and in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) using Cu/γ-Al₂O₃ and Pt/γ-Al₂O₃ as catalysts (Supplementary Fig. 7). It hinted that dosing a suitable amount of H₂O could promote heterogeneous thermal catalytic conversion of CO₂ to CO in realistic conditions.

To quantitatively describe the roles of coordinated H₂O over metal surfaces to CO₂ adsorption and reduction to CO, we used Cu-based catalysts as an example. Fig. 3a and Supplementary Fig. 8a show the effect of reaction gas pressure on the adsorption of CO₂ to Cu⁺. The adsorption performance was examined by the absolute peak intensities of generated [Cu(CO₂)⁺] in mass spectrometric analysis. When bare Cu⁺ was employed, the adsorption ability of CO₂ onto the Cu⁺ catalyst gradually increased with the increasing reaction gas pressure from 0 to 4 mTorr. However, in the presence of [Cu(H₂O)⁺], the adsorption of CO₂ onto Cu⁺ increased with increasing reaction gas pressure and reached a maximum value in the range of 1.5–2.5 mTorr, then decreased thereafter. More interestingly, in the presence of [63Cu(H₂O)⁺], the peak intensity of [63Cu(CO₂)⁺] was 48.6-fold higher than that with [65Cu⁺] in their optimal conditions. This demonstrated that after H₂O was coordinated to

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**Fig. 2 Mass spectra of CO₂ reduction to CO under different Cu-based catalytic systems.** 

- a) [63Cu⁺] b) [65Cu⁺].
- c) [63Cu(H₂O)⁺] d) [65Cu(H₂O)⁺] (gas circuit temperature: 280 °C; reaction pressure: 1.5 mTorr).
the presence of either $^{63}$Cu (gas circuit temperature: 280°C). Effect of the gas circuit temperature on (c) adsorption of CO2 onto Cu$^+$ and (d) CO generation by CO2 reduction in the presence of either $^{63}$Cu$^+$ or $[^{63}$Cu(H2O)]$^+$. catalysts (reaction pressure: 1.5 mTorr).}

Cu$^+$, CO2 was more prone to interact with $[^{63}$Cu(H2O)]$^+$ to generate $[^{63}$Cu(CO)]$^+$ compared to bare Cu$^+$. Besides CO2, we also found that in contrast to Cu$^+$, $[\text{Cu(H}_2\text{O)}]$$^+$ was likely to form Cu-based complexes with other molecules such as methanol (Supplementary Fig. 9), ethanol (Supplementary Fig. 10), acetonitrile (Supplementary Fig. 11), benzene (Supplementary Fig. 12), toluene (Supplementary Fig. 13), and dichloromethane (Supplementary Fig. 14). Such a fact suggests that the coordinated H2O in the structure of $[\text{Cu(H}_2\text{O)}]$ is a uniquely active site for adsorbing different molecules. To our knowledge, it could be speculated as the following reasons. As H2O was bound to Cu$^+$, the resulting $[\text{Cu(H}_2\text{O)}]$$^+$ more likely tended to form hydrogen bond or OH-π interactions with those studied molecules than bare Cu$^+$. After undergoing further structural rearrangements, Cu(I)-based complexes were favorably generated. Despite this, detailed reasons need to be further studied.

It is well known that adsorption onto catalyst surfaces is a very crucial step for CO2 reduction, and a more favorable CO2 adsorption can facilitate a more efficient reduction to CO15. To evaluate the reduction ability of CO2 to CO in the presence of Cu$^+$ and $[\text{Cu(H}_2\text{O)}]$$^+$, we compared the difference in quantity of generated $[\text{Cu(CO)}]$$^+$ at varying gas pressures (Fig. 3b and Supplementary Fig. 8b). For bare Cu$^+$, the peak intensity of $[^{63}$Cu(CO)]$^+$ sharply increased at 0 – 0.5 mTorr, followed by a gradual increase at 1 – 4 mTorr. A different pattern was observed for $[\text{Cu(H}_2\text{O)}]$$^+$, where the peak intensity first increased to a maximum value at 1.5 mTorr, and then decreased thereafter. Comparing both systems with Cu$^+$ and $[\text{Cu(H}_2\text{O)}]$$^+$, it was remarkable that $[\text{Cu(CO)}]$$^+$ was generated more favorably for $[\text{Cu(H}_2\text{O)}]$$^+$. Similar to the amount of adsorbed CO2, the amount of CO generated in the presence of $[^{63}$Cu(H2O)]$^+$ was 84.7-fold higher than that in the presence of $^{63}$Cu$^+$ under optimal conditions. These results indicated that the coordinated H2O in $[^{63}$Cu(H2O)]$^+$ not only greatly facilitated CO2 adsorption to Cu$^+$, but also significantly promoted CO generation. A similar process was also conducted to compare the adsorption of CO2 and generation of CO at different temperatures, which was controlled by varying the temperature of heating tape around the gas circuit (Fig. 1). As the temperature increased from room temperature (20°C) to 350°C, CO2 adsorption using $[^{63}$Cu(H2O)]$^+$ demonstrated a gradual increasing pattern. However, a different pattern was observed for the system using $[^{63}$Cu(H2O)]$^+$, in which an initial steady increasing trend from room temperature to 280°C was observed, followed by a slight decreasing one within the range of 280 – 350°C (Fig. 3c and Supplementary Fig. 8c). In the optimal temperature range, the CO2 adsorption amount in the presence of $[^{63}$Cu(H2O)]$^+$ was more than two orders of magnitude (158.7-fold) higher than $^{63}$Cu$^+$. For the generation of CO, both $^{63}$Cu$^+$ and $[^{63}$Cu(H2O)]$^+$ catalytic systems demonstrated a comparable pattern, in which the formation of CO first increased and reached a maximum value at 280°C, then decreased thereafter (Fig. 3d and Supplementary Fig. 8d). By comparing both systems, it was found that the use of $[^{63}$Cu(H2O)]$^+$ resulted in more than two orders of magnitude (160.9-fold) of CO formation than using $^{63}$Cu$^+$. Thus, we can conclude in confident that the coordinated H2O in $[^{63}$Cu(H2O)]$^+$ was a governing factor in CO2 adsorption and CO generation.

From the above, it was noticeable that there was a maximum CO2 adsorption capacity and a maximum CO production rate when $[\text{Cu(H}_2\text{O)}]$$^+$ was used as catalyst throughout the studied temperature and pressure ranges (Fig. 3). This phenomenon was presumably due to the instability of $[\text{Cu(H}_2\text{O)}]$$^+$ with increasing
reaction pressures and temperatures. As an example of increasing reaction pressures, the content of CO$_2$ in the Q2 of mass spectrometer (Fig. 1) steadily increased and therefore, high yields of [Cu(CO$_2$)]$^+$ and [Cu(CO)]$^+$ should be generated, whereas an opposite trend was observed within the range of 2 – 4 mTorr (Fig. 3a, b). As aforementioned, [Cu(H$_2$O)]$^+$ was more favorable for the generation of [Cu(CO$_2$)]$^+$ and [Cu(CO)]$^+$ than Cu$^+$. However, the generated amount of [Cu(H$_2$O)]$^+$ demonstrated a decreasing pattern with increasing reaction pressures from 2 to 4 mTorr (Supplementary Fig. 15a). A lower amount of [Cu(H$_2$O)]$^+$ would result in a lower generation efficiency to [Cu(CO$_2$)]$^+$ and [Cu(CO)]$^+$. As a compromise between reaction pressure and the amount of [Cu(H$_2$O)]$^+$, 1.5 mTorr gave the optimal performance. As to the temperature, the same pattern as the reaction pressure was observed (Fig. 3c, d), and 280 °C offered the highest generation efficiency to both [Cu(CO$_2$)]$^+$ and [Cu(CO)]$^+$. This case may be associated with the compromise of [Cu(H$_2$O)]$^+$ stability (Supplementary Fig. 15b) and the thermodynamic reaction activity between CO$_2$ and [Cu(H$_2$O)]$^+$ under increasing temperatures.

Origin of the O atom in generated CO. Isotope-labeling experiments (H$_2$O, H$_2$O, C$_{16}$O$_2$, and C$_{18}$O$_2$) allowed us to conclude that the origin of the O atom in the generated CO was from the coordinated H$_2$O, rather than CO$_2$ itself. In previous studies$^{1,17,34,43}$, different mechanistic scenarios were proposed to elucidate the reduction pathway of CO$_2$ to CO, and the generation of CO was conventionally contributed to the loss of an O atom in CO$_2$. However, no direct experimental evidence generated through isotopic labeling has been supported thus far. MS has been demonstrated to be a very powerful tool that offers the opportunity to derive the origin of the O atom in generated CO from CO$_2$.

As expected, monitoring of the reaction between [${}^{63}$Cu(H$_2$O)]$^+$ and C$_{16}$O$_2$ resulted in the observation of [${}^{63}$Cu(C$_{16}$O)]$^+$ (Fig. 4a). The inability to isolate [${}^{63}$Cu(H$_2$O)]$^+$, by dissolving CuCl or other Cu-based chemicals into the mixture of acetonitrile and H$_2$O$_2$, meant that it was impossible to probe the reaction products in the presence of [${}^{63}$Cu(H$_2$O)]$^+$ and C$_{16}$O$_2$. This case could be attributed to the fact that there are plenty of H$_2$O in air, and the H$_2$O in generated [${}^{63}$Cu(H$_2$O)]$^+$ would be quickly exchanged by H$_2$O in the plume of nanoESI or the transfer process to the Q1 of mass spectrometer (Fig. 1). As a result, insufficient [${}^{63}$Cu(H$_2$O)]$^+$ ions could be generated and were not favorable for MS detection. To resolve this issue, [${}^{63}$Cu(H$_2$O)]$^+$ was first isolated in Q1, and H$_2$O$_2$ or H$_2$O was then injected into the CO$_2$ gas circuit (Fig. 1). After interaction among the reactants in the reaction region Q2, the resulting products were analyzed. As H$_2$O$_2$ was injected (Fig. 4b), the mass spectrum was analogous to that of only [${}^{63}$Cu(H$_2$O)]$^+$ and C$_{16}$O$_2$ (Fig. 4a). Noticeably, when H$_2$O was added to the system containing [${}^{63}$Cu(H$_2$O)]$^+$ and C$_{16}$O$_2$ (Fig. 4c), not only did [${}^{63}$Cu(H$_2$O)]$^+$ appear in the mass spectrum, but so did [${}^{63}$Cu(C$_{16}$O)]$^+$ and [${}^{63}$Cu(C$_{18}$O)]$^+$. These results indicated that it was an effective strategy for generating [${}^{63}$Cu(H$_2$O)]$^+$, and more importantly, the origin of the O atom in CO was presumed from the coordinated water.

More convincing evidence was gained from the reaction between [${}^{63}$Cu(H$_2$O)]$^+$, C$_{18}$O$_2$, and H$_2$O$_2$/H$_2$O. Interestingly, as [${}^{63}$Cu(H$_2$O)]$^+$ interacted with C$_{18}$O$_2$ (Fig. 4d), [${}^{63}$Cu(C$_{18}$O)]$^+$, rather than [${}^{63}$Cu(C$_{16}$O)]$^+$, was formed, indicating that the O atom in CO was indeed from the H$_2$O. The same result was obtained from the system with [${}^{63}$Cu(H$_2$O)]$^+$, C$_{18}$O$_2$, and H$_2$O$_2$ (Fig. 4e). However, as H$_2$O$_2$ was injected into the C$_{18}$O$_2$ gas circuit system (Fig. 4f), the mass spectrum was analogous to the system with [${}^{63}$Cu(H$_2$O)]$^+$, C$_{16}$O$_2$, and H$_2$O$_2$ (Fig. 4c), in which both [${}^{63}$Cu(C$_{16}$O)]$^+$ and [${}^{63}$Cu(C$_{18}$O)]$^+$ were generated. This phenomenon, as well as [${}^{65}$Cu (Supplementary Fig. 16), $^{107}$Ag, and $^{109}$Pd (Supplementary Fig. 17)]-based reactions, allowed us to draw a definite conclusion that in the CO$_2$RR process, the two O atoms in CO$_2$ were eliminated completely by losses of two molecules of H$_2$O$^{46,48,70}$, and the O atom in CO originated from the coordinated H$_2$O. Moreover, H$_2$O$_2$-labeling experiments in tandem with off-line GC-MS
Fig. 5 Influence of the number of coordinated H$_2$O, free H$_2$O, and extraneous acid on the generation of CO. a Effects of the number of coordinated H$_2$O and free H$_2$O on CO$_2$ reduction to CO under different Cu-based catalytic systems ([$^{63}$Cu$^+$], [$^{64}$Cu(H$_2$O)], and [$^{65}$Cu(H$_2$O)$_2$]). b Effect of extraneous acid on the reduction of CO$_2$ to CO under different Cu-based catalytic systems. Note: The free H$_2$O and HOAc (acetic acid) were injected into the gas circuit system by an injector; gas circuit temperature: 280 °C; reaction pressure: 1.5 mTorr; n = 5).

Identifying the effect of H$_2$O on CO generation. The number of coordinated H$_2$O in [$^{62}$Cu(H$_2$O)$_n$]$^+$ (x = 0, 1, or 2) was observed to have a significant influence on the reduction of CO$_2$ to CO. The reaction efficiency was evaluated by comparing the absolute peak intensities of generated [$^{63}$Cu(CO)]$^+$ in mass spectrometric analysis. When bare [$^{63}$Cu$^+$] was used as the catalyst, a low signal was observed (Fig. 5a and Supplementary Fig. 22). Noticeably, a significant improvement was observed for [$^{63}$Cu(H$_2$O)]$^+$, and the reaction efficiency was 193.8 times higher than with [$^{63}$Cu$^+$]. However, further increasing the number of coordinated H$_2$O to 2 (e.g., [$^{63}$Cu(H$_2$O)$_2$]$^+$) resulted in a comparable reaction efficiency to [$^{63}$Cu(H$_2$O)]$^+$, indicating that one coordinated H$_2$O molecule was sufficient for high-efficiency reduction of CO$_2$ to CO.

In the reaction between [$^{63}$Cu(H$_2$O)]$^+$ and CO$_2$, it was unclear how H$_2$O molecules interacted with CO$_2$, namely whether it was a (i) direct interaction between [$^{63}$Cu(H$_2$O)]$^+$ and CO$_2$, or if (ii) CO$_2$ first interacted with the dissociated H$_2$O molecule from [$^{63}$Cu(H$_2$O)]$^+$, then reacted with dissociated [$^{63}$Cu$^+$] or [$^{63}$Cu(H$_2$O)$_2$]$^+$. To probe the above assumptions, 2 μL of free H$_2$O was injected into the CO$_2$ gas circuit system at a temperature of 280 °C (Fig. 1). After being injected, the free H$_2$O molecules immediately evaporated and interacted with CO$_2$ in the gas circuit by forming H$_2$CO$_3$ (H$_2$O + CO$_2$ → H$_2$CO$_3$)$^{71-73}$, which was indirectly confirmed by the isotope-labeling experiments, namely H$_2^{18}$O and C$^{16}$O$_2$ (Supplementary Fig. 23). If route (ii) was taken in the CO$_2$RR, the involved free H$_2$O would facilitate CO$_2$ reduction to CO. However, a comparable reaction efficiency to the system without free H$_2$O was observed (Fig. 5a and Supplementary Fig. 22), indicating that CO$_2$ reduction to CO occurred through route (i). Namely, [$^{63}$Cu(H$_2$O)]$^+$ first interacted with CO$_2$ by a formation of [$^{63}$Cu(H$_2$O)(CO$_2$)]$^+$, which was supported by isotope-labeling experiments (Supplementary Fig. 24), and then a reduction reaction occurred to convert CO$_2$ to CO. The above results also indicated that the coordinated H$_2$O on the Cu$^+$, rather than free H$_2$O, played crucial roles for the reduction of CO$_2$ to CO. The transition metals such as Cu$^+$ not only provided efficient active sites for the generation of [$^{63}$Cu(H$_2$O)]$^+$ or other H$_2$O-based metal complex ions, but also offered opportunity to charge neutral species such as CO$_2$ and CO for favorable mass spectrometric analysis by the forms of [$^{63}$Cu(CO)$_2$]$^+$ and [$^{63}$Cu(CO)]$^+$ (Figs. 2 and 4).

Based on the prior experiments, the origin of the O atom in CO was from H$_2$O rather than CO$_2$. Thus, the two O atoms in CO$_2$ needed to be eliminated prior to the formation of CO. According to the previous CO$_2$RR mechanisms$^{46,48,70}$, the generation of CO was achieved by first proton-electron (H$^+$/e$^-$) transfer processes to CO$_2$, followed by the elimination of H$_2$O. To promote the formation of CO, an efficient step to proton generation and capture was necessary$^{46}$. In this study, a proton (H$^+$) was also found to be crucial to the generation of CO. For the reaction of [$^{63}$Cu(H$_2$O)]$^+$ and CO$_2$, the generation of H$^+$ was believed to be caused by water dissociation. However, further dissociation of water might affect its ability to participate in the formation of [$^{63}$Cu(H$_2$O)(CO$_2$)]$^+$ and reduce the reaction efficiency. Addition of supplementary H$^+$ could mitigate water dissociation and boost CO generation. To confirm this hypothesis, 2 μL of acetic acid (HOAc) was injected into the CO$_2$ gas circuit system. For the system containing [$^{63}$Cu(H$_2$O)]$^+$, a 8.9-fold increase of CO formation was observed with the addition of HOAc, whereas no significant difference was observed for bare Cu$^+$ (Fig. 5b and Supplementary Figs. 25 and 26). These results indicated that supplementary H$^+$ was indeed important for boosting the reduction efficiency of CO$_2$ to CO in the presence of [$^{63}$Cu(H$_2$O)]$^+$ catalyst, in which H$^+$ from the coordinated H$_2$O participated into the elimination of O atoms in CO$_2$.$^{46,48,70}$

Analysis were carried out to confirm the source of O atom in resulting CO from the reversed WGSR. As shown in Supplementary Fig. 6f–h, in comparison with the system of introducing H$_2^{16}$O, an abundant peak of m/z 30 (C$^{18}$O) emerged in the mass spectrum for the system of H$_2^{18}$O. This fact indicated that the involved H$_2$O was the oxygen source of the resulting CO. More importantly, the observed results of CO$_2$ reduction in the TSQ mass spectrometer could be extrapolated to realistic heterogeneous catalysis. Those gas-phase results also correlated directly to solution-phase CO$_2$RR. To gain insight into this point, we performed the electrochemical reduction of CO$_2$ in KCl aqueous solution using Au electrode, because the produced amount of CO was below the limit of detection using Cu or Ag electrode. The reaction products were monitored using an online differential electrochemical mass spectrometer (Supplementary Fig. 18). In contrast to the system of H$_2^{16}$O, a considerable amount of C$^{18}$O (m/z 30) was generated in the presence of H$_2^{18}$O (Supplementary Figs. 19–21). This further indicated that H$_2$O was the oxygen source of resulting CO from CO$_2$ reduction and provided solid evidence on the generalization of the current finding to related reactions in the condensed phase (Supplementary Table 1).
According to experimental observations, the pathway of CO2 reduction to CO involves the interaction among 1Cu(I), 1H2O, and 1CO2. However, in contrast to the Cu(I) system where the reduction of CO2 to CO was mainly on the singlet reaction path with a lower energy, the activation of CO2 in the presence of Cu(II) was initialized with the collision interaction among 1CO2, 1Cu(I), and 1H2O (Supplementary Fig. 30). All calculations on bimolecular interactions indicated that 1Cu-OH2+ (1MS1), through the collision of 1Cu+ and 1H2O, was the most preferred possibility in contrast to others, such as 1Cu+ and 1CO2 or 1Cu+ and 1H2O. The binding energy of 1Cu+ and 1H2O in 1MS1 was as high as \(-40.18\) kcal mol\(^{-1}\), which is higher than those of 1Cu+ and 1CO2 (\(\{1Cu-O=O=C=O\}^+\), \(-19.68\) kcal mol\(^{-1}\)) and 1CO2 and 1H2O (\(\{1H2CO3-O=O=C=O\}^+\), 2.53 kcal mol\(^{-1}\)). In the collision between 1Cu+ and 1H2O, 1Cu+ was prone to interact with the central O atom in H2O to form 1Cu(OH2)+ through O-Cu coupling with a bond length of 1.90 Å.

Many previous studies\(^8,26,55–59,74,75\) illustrated that the Cu(I) surface was the active site anchoring the CO2RR. Because of this, several strategies, including the addition of copper nitride support\(^55\) or copper oxide support\(^56\), boron-element doping\(^58\), plasma treatment\(^57\), catalyst electro-redistribution\(^78\), and covering the catalyst surface with nanocavities\(^75\), have been used to stabilize the active Cu(I) oxidation state. Despite these efforts, the precise effect of a single Cu valence state on the reduction of CO2 to CO remains ambiguous. Ions can be easily isolated through MS, enabling the investigation of the interaction between CO2 and Cu with different oxidation states. In this study, we not only investigated the effect of Cu(I) in CO2RR, but also explored the performance of Cu(II) on CO production. Taking the copper oxidation state and the reduction of CO2 to CO were suggested in Fig. 6a. This is based on the thermodynamic and kinetic feasibility of the suggested pathway.

Mechanistic studies. Based on the overwhelming evidence from the experimental observations, the pathway of CO2 reduction to CO over Cu(I)-based catalyst was suggested in Fig. 6a. This process started with the formation of [Cu(H2O)]+. As aforementioned, H2CO3 formed after the reaction of CO2 and H2O, thereby the occurrence of transition from [Cu(H2O)]+ to [Cu(H2CO3)]+, which was similar to the direct CO2 capture and conversion to fuels over magnesium nanoparticles\(^54\). Subsequent H\(^+/e^-\) transfer reactions\(^46,48,70\) led to the generation of [Cu(CO)]+, along with the elimination of two H2O molecules. In the CO2RR, H\(^+\) ions originated from the dissociation of H2O/H2CO3 or added acid, and the necessary electrons involved in the reduction of CO2 to CO were likely from the generated H2CO3 (Supplementary Fig. 28 and related discussion). Upon the CO2 reduction, the O atom in [Cu(H2O)]+ combined with the C atom in CO2 by the formation of CO, whereas the two O atoms in CO2 were eliminated by loss of two H2O molecules. The released H2O molecules could combine with Cu\(^+\) to form [Cu(H2O)]+ for the next cycle of CO2 reduction. Despite this, the oxidation state of copper persisted +1, in good agreement with the previous reports\(^77\).

To gain detailed insight into the reaction mechanism, DFT calculations were carried out to explore the key reaction intermediates and possible reaction pathways. Both the singlet and triplet reaction paths had been considered to understand all possibilities. The singlet reaction pathway was more thermodynamically favorable than the triplet reaction pathway, and both paths were similar (Fig. 6b, Supplementary Fig. 29, and Supplementary Table 2–4). Because of this fact, the discussion herein focused mainly on the singlet reaction path with a lower energy. The activation of CO2 was initialized with the collision interaction among 1CO2, 1Cu+, and 1H2O (Supplementary Fig. 30). All calculations on bimolecular interactions indicated that 1Cu+ and 1H2O was the most preferred possibility in contrast to others, such as 1Cu+ and 1CO2 or 1Cu+ and 1H2O. The binding energy of 1Cu+ and 1H2O in 1MS1 was as high as \(-40.18\) kcal mol\(^{-1}\), which is higher than those of 1Cu+ and 1CO2 (\(\{1Cu-O=O\}^+\), \(-19.68\) kcal mol\(^{-1}\)) and 1CO2 and 1H2O (\(\{1H2CO3-O=O\}^+\), 2.53 kcal mol\(^{-1}\)). In the collision between 1Cu+ and 1H2O, 1Cu+ was prone to interact with the central O atom in H2O to form 1Cu(OH2)+ through O-Cu coupling with a bond length of 1.90 Å.

Fig. 6 The mechanism of CO2 reduction to CO in the presence of Cu(I) catalyst and water. a Schematic representation of the reduction of CO2 to CO according to experimental observations. b The DFT microscopic reaction pathway [the singlet reactants of 1Cu\(^+\)+1H2O+1CO2 (1ISO, 0.00) was taken to be zero as a reference], demonstrating the thermodynamic and kinetic feasibility of the suggested pathway.
The existence of activated $[\text{Cu(OH)}_2]^+$ ($\text{MS1}$) promoted the reduction of $\text{CO}_2$. First, $\text{CO}_2$ interacted with $\text{MS1}$ to form the $[\text{Cu}-(\text{O})-(\text{H})-\cdot \text{O}-(\text{O})\cdot \text{CO}]^+$ ($\text{MS2}$, $-40.33$ kcal mol$^{-1}$) intermediate by a weak O–H–O hydrogen bond. The O–C bond length of $\text{CO}_2$ changed from 1.16 Å to 1.17 and 1.15 Å in $\text{MS2}$. Subsequently, $\text{MS2}$ isomerized into $[\text{Cu}-(\text{O})-(\text{C})-(\text{O})\cdot \text{OH}]^+$ ($\text{MS3}$, $-2.84$ kcal mol$^{-1}$) through a transition state, $\text{TS2/3}$ ($10.08$ kcal mol$^{-1}$). It is worth noting that in the conversion from $\text{TS2/3}$ to $\text{MS3}$, the breaking of the O–H and O–C bonds formed between the H$_2$O and CO$_2$ (Supplementary Fig. 31–34). This process was the rate-limiting step of CO$_2$ reduction with an activation barrier as high as $50.41$ kcal mol$^{-1}$, completing the catalytic cycle and releasing $\text{H}_2\text{O}$, suggesting the efficiency of CO$_2$ reduction with a high activation barrier as high as $50.41$ kcal mol$^{-1}$.

Preparation of glass capillary with a tip orifice of 1μm. A glass capillary with a tip orifice of 1μm was pulled from borosilicate glass capillary with filament (Sutter Instrument, USA, 1.5 mm o.d., 0.86 mm i.d., 10 cm length) using a micropipette puller (Model P-97, Sutter Instrument Co., Novato, CA, USA). The tip orifice was then polished with a metallographic scope equipped with a Vortex oscillator (Haimen Qilin Beier Instrument Manufacturing Co., Ltd., Haimen, China) for 1 min.

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(4 mL min⁻¹, 5% CO₂/95% Ar) were introduced sequentially. To investigate the effect of water on CO₂/Ra, a syringe needle fulfilled with 1 μL of water was inserted into the gas containing flow, establishing the introduction of trace water into the reaction system. The employed catalyst, Cu₆Al₂O₃, was prepared by an incipient-wetness impregnation method using the precursors of Cu(NO₃)₂ (>99.9%, Guangzhou Chemical Reagent Factory, Guangzhou, China) and γ-Al₂O₃ powder (99.9%, Energy Chemical Co., Guangzhou, China).

Electrochemical reduction of CO₂ and online mass spectrometer monitoring. For the electrochemical reduction of CO₂ to CO, the reaction products and CO₂ were monitored with an online differential electrochemical mass spectrometer (DEMS, LingLu Instrument Co., Ltd, Shanghai, China). The configuration of the electrochemical cell is shown in Supplementary Fig. 18. The cell was fulfilled with 2.5 M KCl solution, which was saturated with CO₂ gas. During the electrochemical test, a continuous CO₂ flow was introduced into KCl solution. The reference electrode was an Ag/AgCl electrode in saturated KCl solution, and the counter electrode was Pt wire electrode. The linear sweeping voltammogram was conducted on a electrochemical workstation (CHI Instruments, Inc., Austin, TX, USA) with the sweeping rate of 10 mV s⁻¹ from −0.8 V to −1.6 V. Simultaneously, the MS signals with the mass/charge ratios of 44, 30, and 18 were recorded by the MS. The 18O-labelled H₂O (purity: 99.0%, 18O abundance: 298.0%) was purchased from Wuhan Isotope Technology Co., Ltd (Wuhan, China).

Computational details. All electronic structure calculations were performed with the Gaussian 09 package (revision B01; Gaussian, Inc., Wallingford CT, 2010). For geometry optimization, we used the B2PLYP double hybrid density functional method in conjunction with the augmented-concentration correlated-polarized triple zeta (aug-cc-pVTZ) basis set with the implicit treatment of scalar-relativistic corrections to the enthalpy were calculated for structures optimized at the B2PLYP/cc-pVTZ level. The thermodynamic functions (ΔH) were estimated within the ideal gas, rigid-rotor, and harmonic oscillator approximations at 298 K and 1 atm. For ease of discussion, the symbols “95C” and “298S” are used to describe the initial state (IS), intermediate state (MS), and final state (FS), while “S+T/S/m” is used for the interconversion transition state between the intermediate states, 3m and n. The left superscript “S” denotes the spin multiplicity (1 and 3 for singlet and triplet, respectively).

Data availability. Source data are provided with this paper, which can also be available from the corresponding authors on reasonable request.

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Author contributions

Z.Z., Y.Z. Q.W., and G.Y. devised the initial concept for the work. Z.Z. and Y.Z. designed the experiments, H.Y., R.D., Z.X., F.L., G.Y., and Y.L. carried out the experiments and performed the experiments, H.Y., R.D., Z.X., F.L., G.Y., and Y.L. carried out the experiments and characterization of the experiments, and Z.Z. and Y.Z. designed the experiments and characterized the experiments. The authors declare no competing interests.
analyzed the data. Z.Z., Q.W., Y.Z., G.Y., and Q.M. co-wrote the manuscript. All authors discussed the results and commented on the manuscript at all stages.

Competing interests
The authors declare no competing interests.

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