

Increasing CO Binding Energy and Defects by Preserving Cu Oxidation State via O₂-Plasma-Assisted N Doping on CuO Enables High C₂₊ Selectivity and Long-Term Stability in Electrochemical CO₂ Reduction

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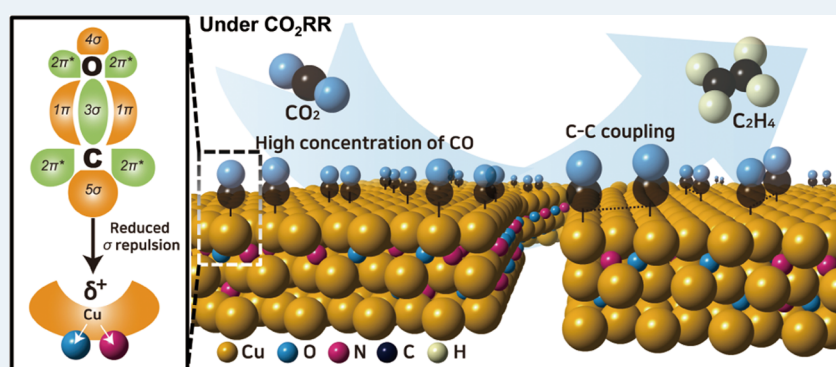
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ABSTRACT: Cu is considered as the most promising catalyst for the electrochemical carbon dioxide reduction reaction (CO₂RR) to produce C₂₊ hydrocarbons, but achieving high C₂₊ product selectivity and efficiency with long-term stability remains one of great challenges. Herein, we report a strategy to realize the CO₂RR catalyst allowing high C₂₊ product selectivity and stable catalytic properties by utilizing the benefits of oxygen-plasma-assisted nitrogen doping on CuO. It is exhibited that the defects such as oxygen vacancies and grain boundaries suitable for CO₂RR are generated by N₂ plasma radicals on CuO. Also, the oxidation state of Cu is maintained without Cu reduction by O₂ plasma. Indeed, ON–CuO synthesized through oxygen-plasma-assisted nitrogen doping is demonstrated to enable a high C₂₊ product selectivity of 77% (including a high C₂H₄ selectivity of 56%) with a high current density of -34.6 mA/cm^2 at -1.1 V vs RHE , as well as a long-term stability for 22 h without performance degradation. High CO₂RR performances are ascribed to the increased CO binding energy and catalytic sites in N-doped CuO. Furthermore, an in situ X-ray absorption near-edge structure analysis reveals that the defects in ON–CuO are favorable for C–C coupling leading to C₂₊ products.

KEYWORDS: electrochemical CO₂ reduction to C₂₊ product, O₂-plasma-assisted N doping, increasing CO binding energy and defect sites, preserving Cu oxidation state, in situ X-ray absorption spectroscopy

INTRODUCTION

There is a growing demand to achieve a sustainable carbon-neutral economy. The electrochemical carbon dioxide reduction reaction (CO₂RR) produces value-added fuels and feedstock from greenhouse CO₂ gas and reduces the CO₂ footprint; therefore, the reaction has attracted significant attention.^{1–7} In particular, multi-carbon (C₂₊) products and oxygenates, such as ethylene (C₂H₄) and ethanol (C₂H₅OH), are of a great demand because of their high-energy densities and economic and industrial values.^{8,9} Among the catalysts used for the CO₂RR, Cu is the only metal that can catalytically generate C₂₊ products.^{10–12} However, Cu has a wide distribution of CO₂RR products, including hydrogen and C₁

products, thus making the electrosynthesis of the desired C₂₊ products challenging.^{13–16} Several strategies have been used to tune the structural and chemical properties of Cu-based catalysts, such as the particle size,^{17–19} morphology,^{20,21} grain boundary,^{22–26} roughness,^{27,28} and oxidation state,^{29–33} to

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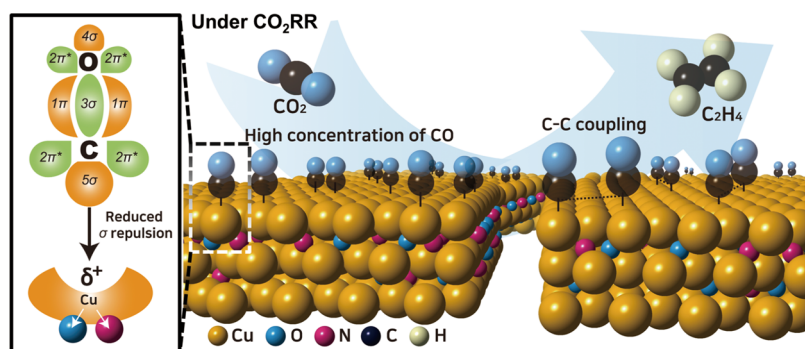


Figure 1. Schematic illustration of both increased CO binding energy ascribed to the reduced sigma repulsion and also defect sites favorable for C–C coupling leading to the efficient electrochemical carbon dioxide reduction reaction (CO₂RR) on ON–CuO synthesized through oxygen-plasma-assisted nitrogen doping.

improve their selectivity for C₂₊ products. Tailoring the electronic structure of Cu can promote C–C coupling by optimizing the binding energy between Cu and the CO intermediate, leading to enhanced selectivity for C₂₊ products. Also, the electronic structure of Cu can be regulated by creating Cu^{δ+} sites on the Cu surface via the oxide-derived Cu (OD–Cu), promoting the electroreduction of carbon dioxide.^{12,34–37} Moreover, the increased grain boundaries and undercoordinated Cu sites also play an important role in facilitating C–C coupling.^{21,38,39} To obtain high C₂₊ selectivity in a Cu-based catalyst for the CO₂RR, we chose a strategy of changing the bonding environment and the density of the catalytic active site simultaneously. First, to convert CO₂ to C₂₊ hydrocarbon products, such as ethylene, the existence of CO as an intermediate product at a high concentration on the catalytic surface is important. Therefore, obtaining appropriate binding energy between CO and Cu is essential. When Cu–CO has a strong binding energy, inducing C–C coupling is difficult. This leads to low C₂₊ product selectivity. In contrast, when the Cu–CO binding energy is significantly weak, the selectivity for CO increases, and the amount of C₂₊ products is traded off. Furthermore, it is well known that the oxidation state of Cu, which works as the catalytic reaction site, also plays an important role in the C₂₊ product pathway. In other words, controlling Cu–CO binding energy while maintaining an appropriate Cu oxidation number is essential. In addition, having many active sites on the catalytic surface is necessary for the reaction. In other words, with many defective sites, the grain boundaries may have high C₂₊ product selectivity.

In this work, we show that oxygen-plasma-assisted nitrogen doping on CuO is effective to tune CO binding energy and catalytically active sites for the CO₂RR, as schematically illustrated in Figure 1. The highly reactive N free radicals of N₂ plasma led to interstitial or substitutional nitrogen atoms in CuO crystals, thereby allowing to modulate the binding energy between Cu and the CO intermediate. We also show that O₂ plasma radicals help to effectively prevent the reduction of Cu by N₂ plasma radicals, thereby allowing to maintain the oxidation state of CuO. Indeed, ON–CuO synthesized through oxygen-plasma-assisted nitrogen doping on CuO is demonstrated to enable high C₂₊ product selectivity and long-term stability without performance degradation, which are proven to be ascribed to the increased binding energy between Cu and the CO intermediate owing to the reduced sigma repulsion in nitrogen-doped CuO as well as the additional catalytic reaction sites created by N₂ plasma radicals.

Additionally, an in situ X-ray spectroscopy analysis and density functional theory (DFT) calculations corroborate that the coexistence of N and O in ON–CuO is favorable for C–C coupling leading to the efficient production of C₂₊ products.

RESULTS AND DISCUSSION

CuO nanorods were first synthesized with carbon black as the starting material for plasma treatment. We then performed N₂ and O₂ and N₂ mixed plasma treatments to elucidate the effect of each plasma on CuO. The surface characteristics of CuO can determine the selectivity of the C₂₊ product by modulating the binding energy between the CO intermediate and Cu, which affects C–C coupling during CO₂RR. We performed the X-ray photoelectron spectroscopy (XPS) of Auger Cu LMM to reveal changes in the oxidation state of the Cu surface in CuO after plasma treatment (Figure 2a). The Cu LMM spectrum of CuO consists of a Cu²⁺ peak at 917.7 eV and a Cu⁺ peak at 916.3 eV. Compared to the content of Cu²⁺, there was a significantly greater amount of Cu⁰ (918.4 eV) and Cu⁺ in N–CuO. The spectra of ON–CuO are almost identical to those of CuO, indicating that O₂ plasma serves as an oxygen supplier. A similar trend was also confirmed in high-resolution Cu 2p XPS spectra (Figure S1). Although Cu⁺ and Cu⁰ are almost indistinguishable in Cu 2p, the difference in the ratio of the Cu²⁺ peak to the Cu⁺/Cu⁰ peak suggests that N–CuO was reduced and ON–CuO maintained its oxidation state. In addition, the X-ray diffraction (XRD) patterns (Figure S2) also indicate that all of the samples were composed of a CuO phase, except for N–CuO with a reduced Cu₂O phase. To further investigate the chemical state and coordination environment of the plasma-treated CuO, the Cu K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were performed. The XANES spectra (Figure S3a) show that CuO and plasma-treated CuO have three peaks at 8985, 8992, and 8997 eV, respectively, similar to those of the CuO reference. Only N–CuO had a small pre-edge peak at 8981 eV, corresponding to Cu₂O. The Fourier transform (FT) EXAFS spectra showed the main peak corresponding to Cu–O coordination at 1.55 Å (Figure S3b). N₂ plasma treatment drastically reduced the Cu–O peak intensity of N–CuO, and O₂ plasma treatment offset the decrease in the peak intensity of ON–CuO. Furthermore, we defined the coordination environment of Cu by fitting the EXAFS curve (Figure 2b and Table S1). N–CuO had the lowest coordination number of 3.4, whereas ON–CuO had a coordination number of 3.8, analogous to

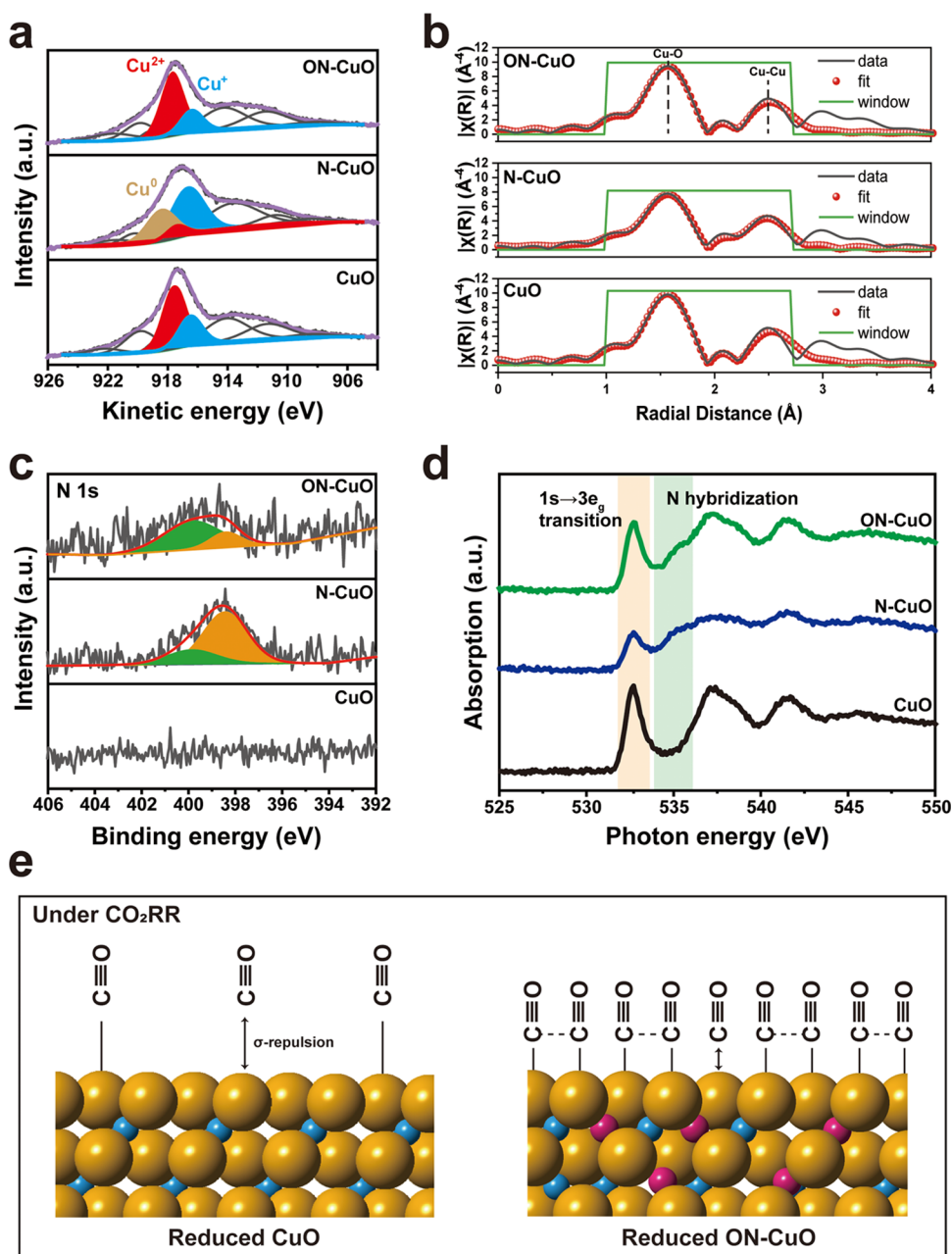


Figure 2. Chemical and structural characterizations of ON-CuO. (a) Auger Cu LMM XPS, (b) FT k^3 -weighted Cu K-edge EXAFS fitting, (c) N 1s XPS, and (d) O K-edge NEXAFS spectra of CuO, N-CuO, and ON-CuO. (e) Schematic illustration of the change in the CO intermediate concentration by reducing sigma repulsion.

CuO. The Cu–Cu bond lengths of CuO and ON-CuO were 2.876 and 2.880 Å, respectively. On the other hand, N-CuO has a Cu–Cu bond length of 2.837 Å. These confirm that N_2 plasma plays a role in breaking Cu–O bonds and forming oxygen vacancy, and O_2 plasma retains Cu–O bonds. In addition, to examine the existence of nitrogen in nitrogen-doped CuO, the high-resolution XPS spectra of N 1s were measured. As shown in Figure 2c, N 1s spectra were deconvoluted into two characteristic peaks, which were obtained for N-CuO and ON-CuO. The peak at 398 eV corresponds to the N–Cu bond owing to the substitutional doping of nitrogen in the oxygen sites.^{40,41} Moreover, the peak at 400 eV indicates the interstitial doping of nitrogen in a CuO lattice, corresponding to Cu–N–O or Cu–O–N bonding. Thus, it can be interpreted that owing to the different

atmospheres of N_2 and O_2/N_2 plasma treatments, nitrogen is doped differently on N-CuO and ON-CuO. In the case of N-CuO, lattice oxygen atoms were dissipated because of the reductive atmosphere of N_2 plasma, followed by substitutional nitrogen doping on the oxygen vacancy sites. However, the N_2/O_2 mixed plasma treatment has a relatively less reductive atmosphere; therefore, oxygen atoms were rarely substituted, and nitrogen was mainly doped interstitially. Through the mixed plasma treatment, nitrogen was interstitially doped while maintaining the oxidation state of Cu. To elucidate whether doped nitrogen can change the electronic structure, the O K-edge NEXAFS analysis was performed (Figure 2d). The O K-edge NEXAFS indirectly provides information of the electronic structure. The characteristic peaks at 532.7, 537.4, 541.5, and 546.2 eV, respectively, were observed. The peak at 532.7 eV

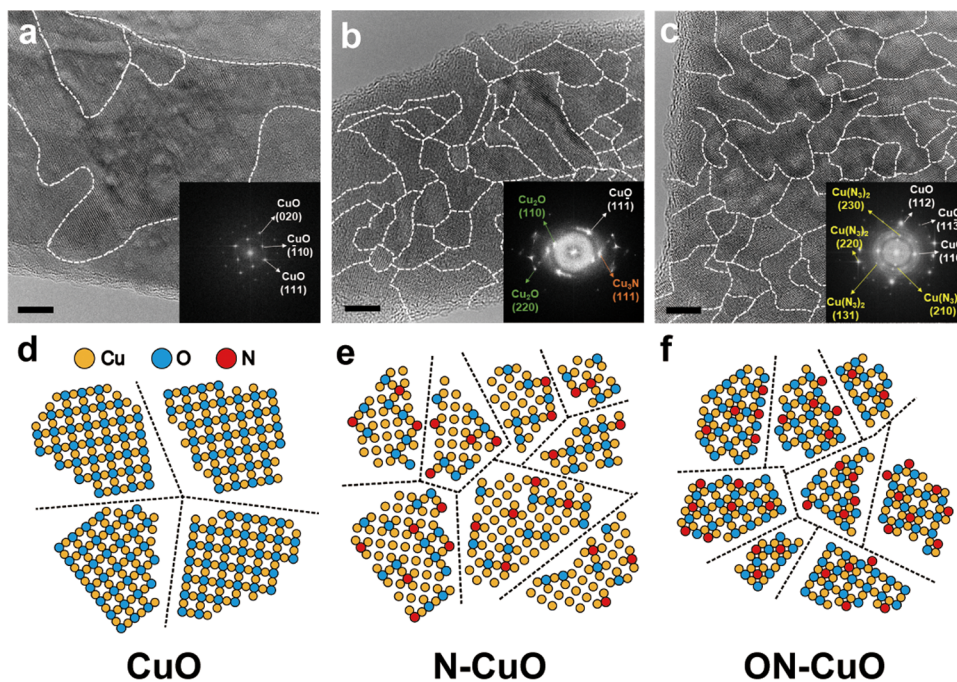


Figure 3. Crystal structure and morphology changes in plasma treated samples. TEM images and proposed lattice structures of (a, d) CuO, (b, e) N–CuO, and (c, f) ON–CuO, where the insets of TEM images are the corresponding FFT patterns (scale bar = 5 nm).

corresponds to the $1s \rightarrow 3e_g$ electron transition of CuO, which is generated by the electron transition to the hybridized state of O 2p and Cu 3d.⁴² In CuO, the electron configuration of Cu^{2+} was partially filled because of the d^9 configuration. The higher energy peaks at 537.4, 541.5, and 546.2 eV result from the electron transition to the hybridized orbital of O (2p and 3p) and Cu (4s and 4p). There was a slight difference in the peak characteristics between each sample. N–CuO exhibited the reduced intensities of the first and second peaks at 532.7 and 537.4 eV, respectively, due to the reduced $1s \rightarrow 3e_g$ transition by the electron configuration of d^{10} of Cu^+ or $4s^1$ of Cu^0 , which contained more electrons than d^9 of Cu^{2+} . The peaks in the higher energy region were also broadened compared to those of pristine CuO, which is attributed to the hybridization of O 2p and Cu ($n + 1$) sp. This was also the result of additional complex hybridization with Cu ($n + 1$) sp and N 2p.⁴² Similarly, in the case of ON–CuO, Cu was reduced relatively less, and a peak shape similar to that of pristine CuO was observed. However, the second peak of ON–CuO had a shoulder peak in the same low-energy region as that in the case of N–CuO. These different peak characteristics are attributed to additional hybridization with the N 2p orbital, as well as with the O 2p orbital. This confirms that ON–CuO inhibits Cu reduction while being doped with nitrogen to form additional orbitals through the hybridization of the O, N, and Cu orbitals.^{43–45} This can lead to a change in Cu–CO binding energy. According to the Blyholder model, the surface bonding of CO and Cu is related to the interplay between the d orbital of Cu and the frontier orbital of CO, which corresponds with the electron donation of the $5-\sigma$ orbital (HOMO) and the back-donation of the $2\pi^*$ orbital (LUMO), resulting in a sigma bond and a pi bond, respectively.⁴⁶ Because the $2\pi^*$ orbital is empty and antibonding, electron back-donation weakens C–O internal bonds. When CO molecules are adsorbed on the surface of Cu, depending on the degree of electron back-donation, the length

of the C–Cu bond also changes. Although both the π bond and σ repulsion are affected by the position of the metal d-band, σ repulsion is more affected by the occupancy of the Cu sp orbital. Therefore, the electron acceptor can reduce the σ repulsion by attracting electrons from the Cu sp band.⁴⁷ Similarly, copper with subsurface oxygen has been reported to increase the CO binding energy.³⁴ Through the increased CO binding energy, the concentration of the CO intermediate on the surface kinetically increased the C–C coupling (Figure 2e). In this work, we doped nitrogen into copper oxide using plasma. The doped nitrogen and trapped oxygen on the subsurface make it possible to reduce the σ repulsion. Consequently, it was possible to obtain an improved C_{2+} product selectivity compared to that of pristine CuO.

Moreover, more catalytic active sites could be obtained by generating defective sites through nitrogen plasma treatment. We investigated the changes in the crystal structure and morphology of CuO after plasma treatment. No morphological transformation was observed in the scanning electron microscopic (SEM) and low-magnification transmission electron microscopic (TEM) images, as shown in Figures S4 and S5. However, the high-resolution transmission electron microscopic images (Figure 3a–c) show obvious differences in the lattice structure according to the type of plasma treatment. Pristine CuO (Figure 3a,d) has a polycrystalline structure composed of a few grains of the CuO phase, as confirmed by the TEM image and fast Fourier transform (FFT) patterns. On the other hand, as shown in Figure 3b,e, the CuO crystal after N_2 plasma treatment was fragmented, and nitrogen was simultaneously doped on the CuO lattice. The N–CuO crystal attacked by the reactive N radicals was broken, and more grain boundaries were formed. The FFT ring pattern indicates randomly oriented grains, and interestingly, Cu_2O and Cu_3N phases were observed, which are based on reduced and nitrogen-doped phases, respectively. This result confirms that N_2 plasma treatment results in nitrogen species on the

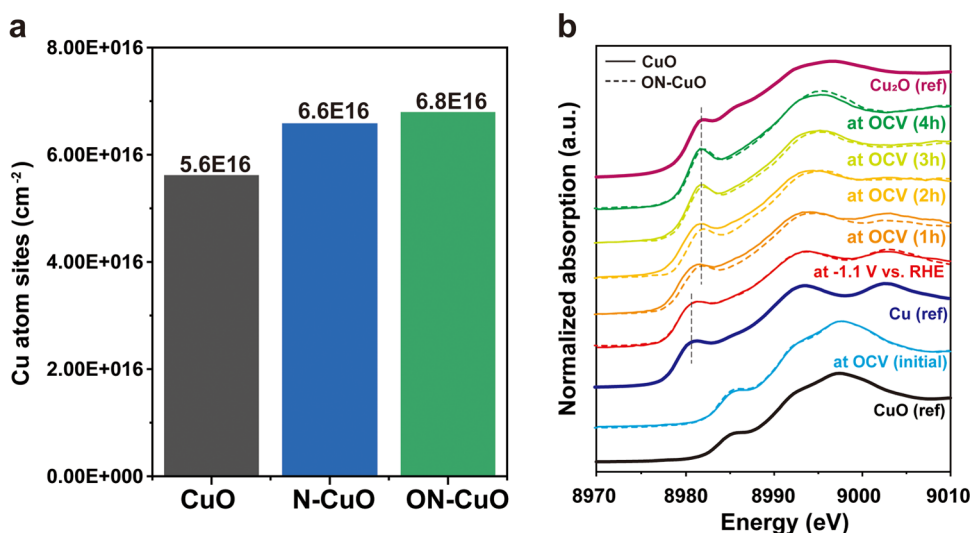


Figure 4. Characterizations of the catalytic sites of plasma treated samples. (a) Electrochemical active surface area analysis by Pb underpotential deposition and (b) in situ Cu K-edge XANES analysis of CuO and ON–CuO.

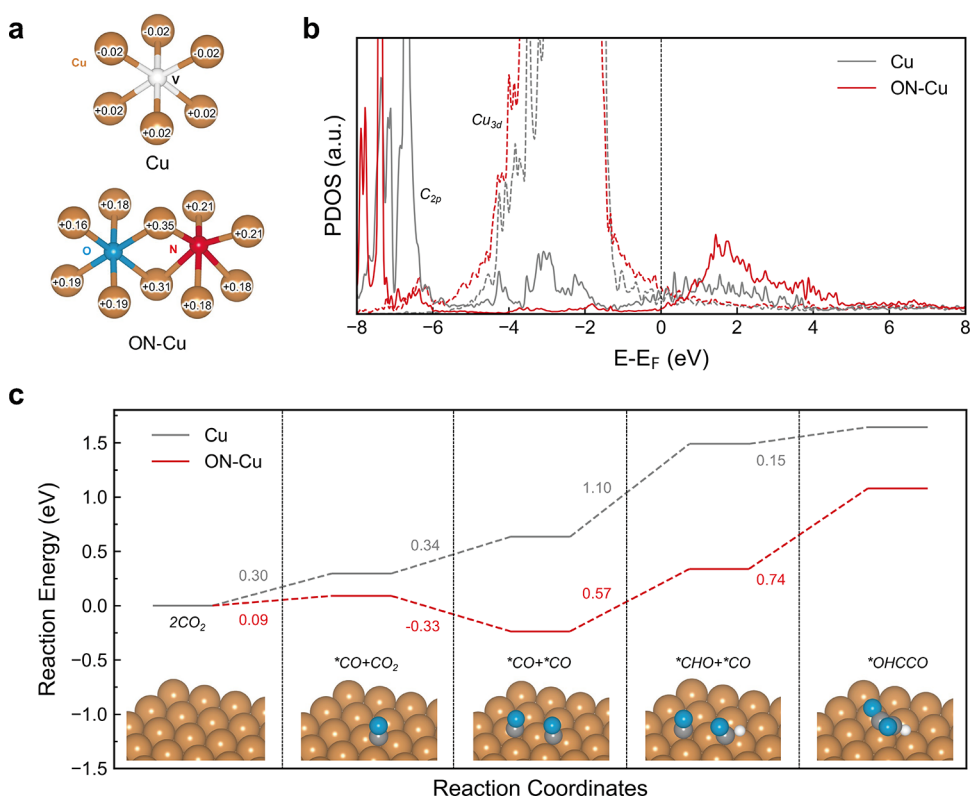


Figure 5. DFT calculations on enhancing the formation of C_{2+} products. (a) Atomic charges on Cu for the bare Cu (111) and ON–Cu surfaces, where V represents the octahedron site in the Cu (111) surface. (b) PDOS of CO-adsorbed surfaces. The dashed lines represent 3d bands for Cu, while the solid lines represent the hybridized 2p orbitals for C. (c) Free-energy diagram of key hydrogenation intermediates to form $*OHCCO$ at $U = 0$ V.

CuO lattice coupled with the reduction of Cu. O_2/N_2 -mixed-plasma-treated CuO (ON–CuO) exhibited significantly different characteristics from those of the pristine samples (Figure 3c,f). N_2 plasma promoted grain fragmentation and doping of nitrogen atoms on CuO, while O_2 plasma prevented Cu reduction so that the CuO phase can exist predominantly. The grain size of ON–CuO was significantly reduced, as shown in the TEM image and the ring pattern of the FFT (Figure 3f). In addition, nitrogen was doped in the form of a $Cu(N_3)_2$ phase

with a Cu^{2+} valence state, as shown in the FFT pattern, demonstrating suppressed Cu reduction.

Moreover, the electrochemical active surface area (ECSA) analysis was performed to confirm the increase of the catalytic active sites due to the plasma effect (Figure S6). The ECSA analysis was performed by Pb underpotential deposition in an Ar-saturated 0.1 M $HClO_4$ with 1 mM $PbCl_2$ electrolyte to determine the ECSA of the catalyst (Figure 4a). Compared to pristine CuO, the surface roughness factor increased after the

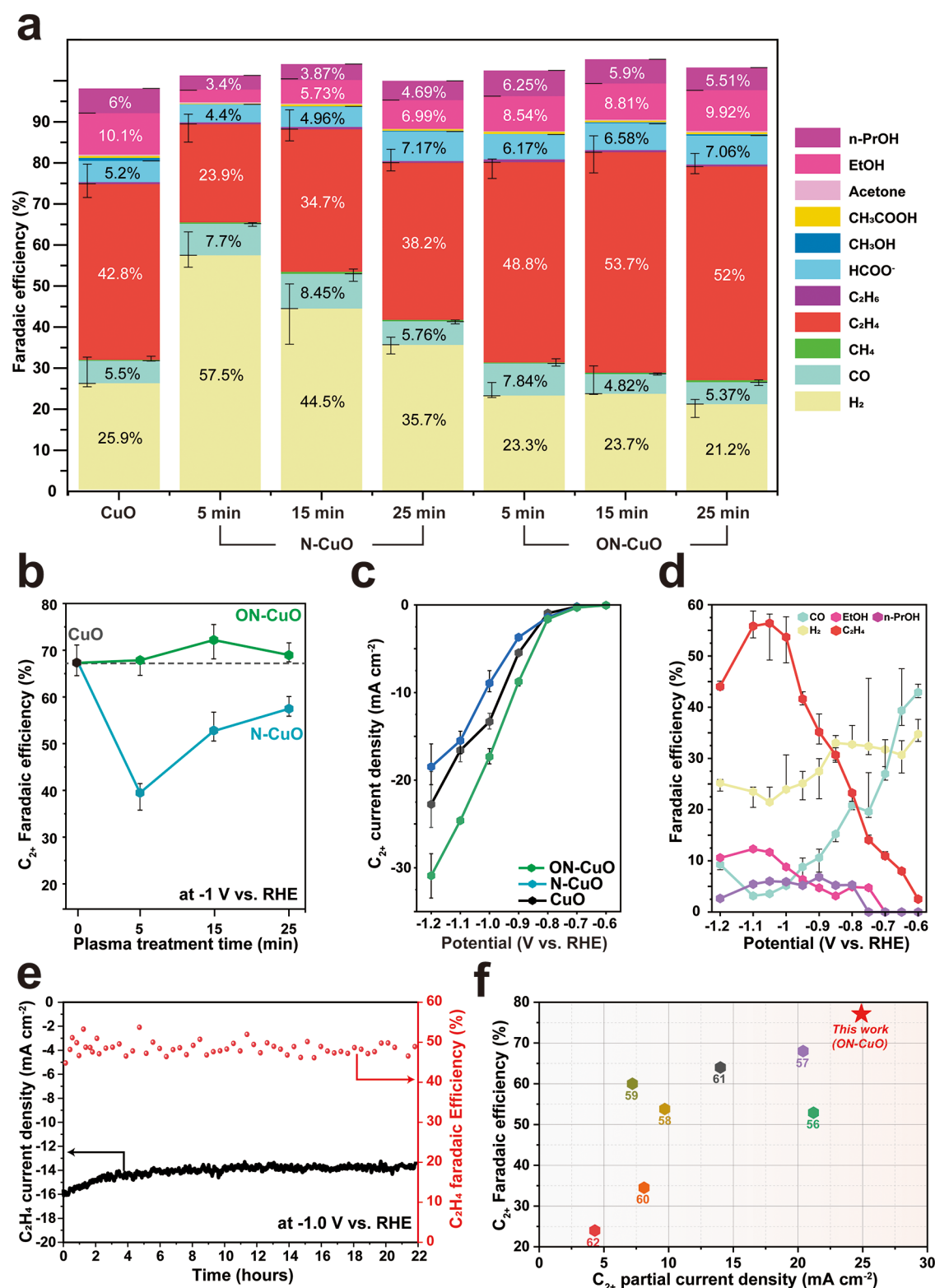


Figure 6. Characterizations of CO₂RR performances in ON-CuO. (a) Faradaic efficiency of different plasma-treated CuO for different products according to the plasma treatment time. (b) Faradaic efficiency for C₂₊ products according to the plasma treatment time. (c) Partial current densities of C₂₊ products for CuO, N-CuO, and ON-CuO, respectively. (d) Faradaic efficiency of ON-CuO for major products at different potentials. (e) Results of the stability test for ON-CuO at -1.0 V vs RHE for 22 h. (f) Comparison of C₂₊ faradaic efficiency and partial current density with previously reported works. The details of the reported results are provided in Table S2.

plasma treatment. ON-CuO exhibited the largest ECSA, which is ascribed to the increase in the number of defective sites and surface roughness, resulting in its largest CO₂RR

current density.^{48,49} We performed an in situ XANES analysis to reveal the origin of the improved faradaic efficiency of the C₂₊ products of ON-CuO (Figure 4b). CuO and ON-CuO

showed the same profile as that of CuO reference at the open circuit voltage (OCV) before applying the reduction potential. However, they were reduced to Cu⁰ after the potential was applied at -1.1 V vs RHE for 2 h. Subsequently, the XANES spectra of CuO and ON-CuO were measured at 1 h intervals for 4 h at the OCV. After 1 h, ON-CuO, which was reduced to Cu⁰, was reoxidized to a Cu₂O phase, while CuO was observed to maintain Cu⁰. CuO was reoxidized to a Cu₂O phase after 3 h. The defect sites, such as oxygen vacancies and grain boundaries, created by O₂ and N₂ plasma improved the surface oxygen mobility,⁵⁰ indicating that oxygen is more readily accessed on the surface of ON-CuO than CuO.

To gain atomistic insights into the effects of coordination environments and oxidation states of Cu on the binding strength of CO and C₂₊ product formation, we performed the DFT calculations. We modeled N₂- and O₂-plasma-treated samples as O and N co-doped into the interstitial sites of the Cu (111) surface (ON-Cu) and the reference sample as pristine Cu (111) surface because the surface oxygen atoms are highly likely to be removed under the reducing environments with prolonged reactions (Figure S7). We calculated the projected density of states (PDOS) of the bare surfaces to conjecture the binding affinity toward CO, which is a key intermediate for the formation of C₂₊ products (Figure S8). The overall trends of the Cu *d*-band are similar to those of bare surfaces, but the *d*-band center energy (-2.36 eV) of the ON-Cu surface shifts away from the Fermi level compared to that (-2.25 eV) of the Cu surface. This indicates that Cu atoms in the ON-Cu surface are more positively charged compared to those in the bare surface. As shown in Figure 5a, the atomic charges obtained by Bader charge analysis show that the partial positive charges increased for the ON-Cu surface compared to those of the bare Cu surface. The results reveal that the co-doping of O and N radicals induces the oxidation state of Cu to be Cu^{δ+}. Considering the symmetrically distinct sites in pristine Cu (111) and ON-Cu surfaces, the binding energies of CO were -0.93 and -1.13 eV for the thermodynamically most stable sites on pristine Cu and ON-Cu surfaces, respectively (Table S3). CO is likely to be adsorbed at a face-center crystal site in the bare Cu surface while it is adsorbed at the atop site in between O and N in the subsurface of ON-Cu in which the Cu site becomes reduced by interacting with O and N atoms in the subsurface to attract CO molecules more strongly. As shown in Figure 5b, the PDOS of hybridized C_{2p} peaks also reveals that the splitting between bonding and antibonding is larger in the ON-Cu surface compared to that in the Cu (111) surface. The strong binding affinity toward CO in the ON-Cu surface indicates that the reduction reaction to form C₂₊ products can be facilitated. To further elucidate the reason for selectivity for C₂₊ products, we evaluated the free-energy diagram of key intermediates to form *OHCCO as shown in Figure 5c. The formation of *CO from CO₂ (g) undergoes two-electron pathways whose thermodynamic-limiting steps involve in the formation of *COOH.⁵¹ *CO can have diverged reaction pathways with various reaction intermediates. Previous studies^{52–54} showed that the C–C coupling from the *CHO–*CO state is more facile than the direct C–C coupling from *CO–*CO. Hence, we only considered the constrained reaction pathway of C–C coupling forming *OHCCO in this work. The overall reaction profile of the ON-Cu surface lies below the pristine one. It is notable that the co-adsorption state of CO (*CO+*CO) is thermodynamically

stable, which indicates the favorable adsorption of CO leading to the high concentration of the CO intermediate on the surface. Also, the rate-determining step can be attributed to hydrogenation or C–C coupling.⁵⁵ The thermodynamic barrier for hydrogenation from *CO (*CO+*CO → *CHO+*CO) is much lower in the ON-Cu surface than that in the pristine one, thus supporting that the formation of C₂₊ products is more favorable to ON-Cu. As a result, the ON-Cu surface facilitates the formation of C₂₊ products with the high binding energy of CO as well as the low thermodynamic barriers for hydrogenation and C–C coupling.

We also explored the effect of plasma on CuO via electrochemical CO₂RR experiments at -1.0 V vs RHE for various plasma treatment times according to the type of plasma (Figure 6a,b). N-CuO showed a noticeable change in faradaic efficiency. N-CuO, which was plasma-treated for 5 min, showed lower C₂₊ and higher H₂ faradaic efficiency than pristine CuO due to the reductive atmosphere of N₂ plasma. However, as the plasma treatment time increased, the faradaic efficiency of H₂ decreased and that of C₂₊ products, such as ethylene, increased. This suggests that nitrogen doping can increase the selectivity for the generation of C₂₊ products. Nonetheless, when treated with nitrogen plasma alone, Cu was reduced and the oxidation number of Cu approached zero. It is known that Cu shows higher C₂₊ selectivity when the oxidation number is positive rather than zero. To confirm the effect of the Cu oxidation state, an electrochemical CO₂RR was performed on the sample treated with H₂ plasma, which is a strong reductive atmosphere (Figures S9–S11). As shown in the results, H₂-plasma-treated H-CuO majorly generates C₁ products, such as formate, rather than C₂₊ products, confirming that the reduction of Cu has a negative effect on the formation of C₂₊ products. It can be seen that C₂₊ selectivity significantly decreases when Cu is excessively reduced. In addition, H-CuO shows invariable faradaic efficiencies despite the increase in the treatment time. We also determined CO₂RR with O₂-plasma-treated CuO (O-CuO) to clarify the effect of nitrogen doping (Figures S12, S13). Although the oxidation state of CuO was further stabilized by O₂ plasma treatment, the faradaic efficiencies of O-CuO exhibit no significant change depending on the O₂ plasma treatment time and the lower C₂₊ selectivity compared to those of ON-CuO. These results demonstrate that nitrogen doping through N₂ plasma treatment improves C₂₊ selectivity in electrochemical CO₂RR. Therefore, O₂/N₂ mixed plasma was treated to obtain N-doped samples while maintaining the oxidation number of Cu appropriately. Considering these findings, the highest C₂₊ faradaic efficiency of ON-CuO can be achieved by the synergistic effect of nitrogen doping and the prevention of Cu reduction by the O₂/N₂ mixed plasma. The total current densities of plasma-treated CuO were -29.3 , -28.7 , and -34.6 mA cm⁻² at -1.1 V vs RHE for CuO, N-CuO, and ON-CuO, respectively (Figure S14). ON-CuO treated with mixed plasma exhibited the largest current density because of the increased number of active sites owing to grain size reduction and nitrogen doping. The total current density of ON-CuO exhibited an increase of 18% compared to pristine CuO. The partial current densities of C₂₊ products for CuO, N-CuO, and ON-CuO, were -17.8 , -16.9 , and -24.9 mA cm⁻², respectively (Figure 6c). N-CuO showed slightly smaller values than pristine CuO. This trend is similar to that of the total current density, indicating that treatment with N₂ plasma alone does not have a significant positive effect on the

electrochemical CO₂RR. In contrast, the partial current density of the C₂₊ product for ON–CuO was increased by 40% compared to that of pristine CuO. This indicates that the mixed plasma treatment, rather than N₂ plasma treatment alone, improves C₂₊ product selectivity in the CO₂RR. It was confirmed that nitrogen doping was possible while maintaining the oxidation number of Cu through the mixed plasma, and that the C₂₊ product can be promoted by increasing the number of defective sites and the grain boundary density. Regarding the faradaic efficiency of the product for each voltage of ON–CuO, hydrogen and CO were found to be the major products at a low voltage (Figure 6d). However, as the voltage increases, we found that the generation of hydrogen decreased and that of CO decreased significantly. Moreover, at the same time, the generation of C₂H₄ was observed to be increased rapidly at –1.1 V (vs RHE) and the faradaic efficiencies of ethylene and the C₂₊ product were 56 and 77%, respectively. It can be seen that ON–CuO has an appropriate CO binding energy to create an appropriate environment for generating C₂₊ products. We also calculated the turnover frequency (TOF) of C₂H₄ per Cu atom to prove that high TOF values are mainly not attributed to the surface roughness effect, as confirmed in Figure S15 showing that ON–CuO leads to a higher TOF than pristine CuO. In addition, Tafel slopes in Figure S16 show 132, 119, and 110 mV/dec for CuO, N–CuO, and ON–CuO, respectively. A low Tafel slope indicates a low kinetic barrier and fast electron transfer. From these results, N–CuO and ON–CuO are shown to have a lower kinetic barrier and faster electron transfer for C₂H₄ formation than pristine CuO, thus explaining the reason for the high C₂H₄ selectivity of ON–CuO.

A study that employed oxide-derived Cu for electrochemical CO₂RR reported that if the reaction time is prolonged due to a reducing environment, the oxidation state of Cu is eventually completely reduced to Cu⁰ and the catalytic properties deteriorate. Therefore, we investigated the current density and faradaic efficiency of C₂H₄ generation through an electrochemical CO₂RR experiment for approximately 22 h (Figure 6e). Consequently, although a slight decrease in the current density occurred during the first few hours, the current remained constant in the subsequent reaction. In addition, it was confirmed that the faradaic efficiency of ethylene production was stable and that the current density and selectivity of the C₂₊ product increased when nitrogen was doped through the mixed plasma. Moreover, the catalytic properties were maintained even in a long-term reductive environment without any degradation or aggregation of grains as shown in the TEM images (Figure S17). As shown in the XRD patterns in Figure S18, ON–CuO shows no crystallinity after the stability test. However, it is revealed that most of the nitrogen in ON–CuO was well maintained in the form of interstitial N even after the long-term CO₂RR (Figure S19). Furthermore, Cu LMM Auger spectra indicate that the surface of ON–CuO is reoxidized to Cu⁺, which is consistent with the FFT pattern of the TEM image in Figure S12 and in situ XANES data. The results of this study were compared with those of previous studies conducted in H-cell-type experiments under neutral electrolyte conditions (Figure 6f).^{56–62} As shown in this figure, it was confirmed that the mixed plasma-treated sample conducted in this study showed excellent results not only in C₂₊ partial current density but also in faradaic efficiency.

CONCLUSIONS

In summary, we demonstrated a high-performance CO₂RR electrocatalyst (ON–CuO) that enables high C₂₊ product selectivity and long-term stability. Oxygen-assisted nitrogen doping on CuO was employed to utilize the advantages of oxide-derived CuO and the effect of heteroatom doping. The highly reactive N radicals of N₂ plasma led to interstitial or substitutional nitrogen atoms in CuO crystals, thereby allowing to modulate the binding energy between Cu and the CO intermediate. Also, they resulted in defects such as oxygen vacancies and grain boundaries in CuO. Besides, O₂ plasma radicals effectively prevented the reduction of Cu by N₂ plasma radicals, thereby allowing to maintain the oxidation state of CuO. Moreover, CuO treated with oxygen and nitrogen plasma radicals (ON–CuO) was shown to enable a high C₂₊ product selectivity of 77% (including a high C₂H₄ selectivity of 56%) with a total current density of –34.6 mA/cm² at –1.1 V vs RHE, as well as a long-term stability for 22 h. High CO₂RR performance was ascribed to the increased binding energy between Cu and the CO intermediate owing to the reduced sigma repulsion in nitrogen-doped CuO, as well as the additional catalytic reaction sites created by N₂ plasma radicals. Additionally, an in situ XANES analysis proved that the ON–CuO with defect sites is easily oxidized and favorable for C–C coupling. Consequently, this study supports that modulating CO binding energy and C–C coupling sites through oxygen-plasma-assisted nitrogen doping could pave a route to realize high-performance CO₂RR catalysts.

EXPERIMENTAL SECTION

Synthesis of CuO. First, 10 mg of Ketjen Black and 170.48 mg of CuCl₂·2H₂O (1.0 mmol) were dissolved in a solution mixed with 5 mL of ethanol and 10 mL of distilled water in a 50 mL vial. Then, 880 mg of solid NaOH (22.0 mmol) was dissolved in 25 mL of water in the vial. Subsequently, 25 mL of NaOH aqueous solution was added into the precursor vial. After stirring for 10 min, the precipitate of CuO was obtained. The precipitate was harvested by centrifugation at 8000 rpm for 5 min, washed with distilled water, and then dried at 60 °C in a vacuum oven. Finally, this dried sample was heat-treated in a CVD at 200 °C for 4 h in an Ar atmosphere.

Plasma Treatment. The sample was coated on a glass slide and dried in a vacuum oven. Then, the sample was placed in the chamber of the microwave plasma enhanced-chemical vapor deposition equipment. A plasma ball was generated above the sample at a microwave power of 500–600 W, and the plasma had a gas flow of H₂ (99.999%), O₂ (99.999%), N₂ (99.999%), or O₂ and N₂. The pressure and flow rate of gas were kept constant, and the exposure time to plasma was controlled with a temperature not exceeding 100 °C. After the exposure to the plasma ball, the color of the samples changed based on the type of plasma.

Material Characterization. SEM images were taken using a field emission scanning electron microscope (JEM-7600F, JEOL, Japan, SU8230, Hitachi, Japan) operated at 15 kV. TEM images were also obtained by a transmission electron microscope (Tecnai F20, FEI Company, Titan G2, FEI company) at an acceleration voltage of 200 kV. Moreover, powder X-ray diffraction patterns were obtained using an X-ray diffractometer (Smartlab, Rigaku, Japan) with a Cu K α radiation source at 1200 W (40 kV, 30 mA). X-ray photoelectron spectroscopy spectra were also obtained using

an X-ray photoelectron spectroscope (K- α , Thermo Scientific) with an Al-K α radiation at a beam current of 3 mA and a beam size of 0.4 mm. X-ray absorption spectroscopy including XANES and the EXAFS were conducted at a multipole-wiggler 10C beamline, and NEXAFS measurement was performed at the 4D beam line at the Pohang Accelerator Laboratory (PAL). The synchrotron radiations were monochromatized using a Si (111) double-crystal monochromator. The incident beams were detuned with proper rates for harmonic rejection. The Cu K-edge spectra obtained in the transmission mode were analyzed using Athena and Artemis software from the IFEFFIT library.

Characterization of the Electrochemical CO₂RR. The catalyst was coated on a glassy carbon substrate, which was then used as a cathode for electroreduction of CO₂ in a 0.1 M KHCO₃ solution. The electrolyte was first purged with CO₂ to attain a pH of 6.8. Electrochemical measurements were conducted using a Biologic SP-300 potentiostat. CO₂ electrolysis was performed in a custom-made H-type electrochemical cell, in which the working electrode is parallel to the counter electrode and the geometric area for the working electrodes was 0.2 cm². The average mass loading of samples on the working electrode is 300 $\mu\text{g cm}^{-2}$. In order to separate the anodic and cathodic chambers, a Selemion AMVN anion-exchange membrane was used. The electrolyte of the cathodic compartment was saturated with CO₂ for at least 15 min prior to conducting electrolysis. CO₂ was sparged during the electrolysis at a flow rate of 20 sccm. A platinum mesh and a Ag/AgCl electrode (leak free series) were used as the counter electrode and the reference electrode, respectively. Pt mesh has a high surface area not to limit current of the working electrode. All collected data were rescaled to the RHE using the following equation

$$E \text{ vs RHE} = E \text{ vs Ag/AgCl} + 0.197 \text{ V} + 0.0591 \times \text{pH} \quad (1)$$

The solution and charge transfer resistances were measured using electrochemical impedance spectroscopy by scanning from 1 MHz to 10 Hz prior to the electrolysis and all reported CVs and electrolysis measurements were made 95% IR-compensated. The ECSA of a catalyst was estimated from Pb underpotential method.

$$\Delta J_{\text{non-faradaic}} = (J_{\text{anodic}} - J_{\text{cathodic}}) = \nu \cdot C_{\text{dl}} \quad (2)$$

Electrochemical Surface Area. Pb underpotential deposition (UPD) method was used following previous studies.^{63–65} The electrolyte of 0.1 M HClO₄ and 1 mM PbCl₂ aqueous solution (pH 1.54) was purged with Ar gas. Cyclic voltammetry was measured from -0.1 to -0.5 V vs the Ag/AgCl reference electrode at a scan rate of 10 mV/s.

Product Analysis. Gaseous products were analyzed with a gas chromatograph (Young Lin instruments) equipped with a packed Porapak Q column, a packed MolSieve 5A column, and a capillary Gaspro column. CO, CH₄, C₂H₄, and C₂H₆ were detected using a flame ionization detector (FID) with a methanizer in He as the carrier gas. H₂ was analyzed using a thermal conductivity detector (TCD) in argon carrier gas. Calibration of the gas chromatograph was performed using a calibration gas with various concentrations. Online gas product analysis was carried out every 25 min by flowing CO₂ directly into the gas-sampling loop of the gas chromatograph during 1.6 h electrolysis. Faradaic efficiencies were obtained by averaging the individual product analysis. Liquid products were

collected from the cathodic compartments after electrolysis and subsequently analyzed by ¹H-NMR (Bruker AVANCE III HD, 9.4T) equipped with a 400 MHz 5 mm BBFO probe with z-gradients. Topspin software was used for spectrometer control. MestreNova software was used for the quantitative analysis to obtain faradaic efficiency.

First-Principles Calculations. All DFT calculations were performed with Vienna Ab-initio Simulation Package (VASP) with the revised Perdew-Burke Ernzerhof (RPBE)⁶⁶ generalized gradient approximation (GGA) exchange-correlation functional. The projector-augmented-wave (PAW) basis set⁶⁷ with a cutoff energy of 520 eV was used to consider core–electron interaction. Spin polarization and van der Waals (vdW) interaction with the DFT-D3 method by Grimme⁶⁸ were considered for all calculations. Slab models of 5 atomic layers, of which 2 atomic layers were fixed, were constructed with a 3 × 3 × 1 supercell and a 15 Å vacuum space. All surfaces were optimized until the total energy and forces were converged within 10^{−4} and 0.02 eV Å^{−1}, respectively. A Γ -centered 3 × 3 × 1 *k*-point grid was used for geometry optimization, and a 9 × 9 × 1 *k*-point grid was used for the electronic structure calculations. More details about the model systems and reaction free energy diagram can be found in Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.3c01441>.

Method details; characterization details; computational details; XPS spectra; SEM images; TEM images; XRD spectra; XANES spectra; cyclic voltammograms; faradaic efficiency; current density; TOF analysis; Tafel plot; projected density of states; EXAFS fitting parameter table; previously reported results table; CO adsorption energy table; ZPE-TS correction table (PDF)

Web Enhanced Object Figure 1 (TIF)

Web Enhanced Object Figure 2 (TIF)

Web Enhanced Object Figure 3 (TIF)

Web Enhanced Object Figure 4 (TIF)

Web Enhanced Object Figure 5 (TIF)

Web Enhanced Object Figure 6 (TIF)

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Notes

The authors declare no competing financial interest.

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