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Effect of coordination environment of Cu in Cu₂O on the electroreduction CO₂ to ethylene

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Abstract: Cuprous oxide catalysts have attracted much attention because they exhibited high selectivity of C2+ products in CO₂ electroreduction, but the effect of the structure of catalysts on the reaction needs to be studied further. Herein, we studied the effect of Cu-Cu and Cu-O coordination number (CN) in Cu₂O on the catalytic performance of CO₂ electrocatalytic reduction to C₂H₄. It was demonstrated that the Cu-Cu CN and Cu-O CN, which could be tuned by changing the crystal surface and size of Cu₂O, influenced the current density and Faradaic efficiency (FE) of C₂H₄ significantly.

At suitable CNs, the FE of C_2H_4 could reach 50.6 % with a current density of 24.5 mA cm⁻². The CO₂ reduction reaction (CO₂RR) using renewable electricity has great potential of application because of its both controllable conversion into carbon-based products and the storage of intermittent electrical energy.^[1-5] Although much progress has been made in CO₂RR, the products are mainly focused on C1 such as

formic acid and carbon monoxide.[6-8] Recently, the generation of

C2+ products is attracting more and more attention due to their high

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energy densities and economic value.^[9-11] It is known that conversion of CO₂ to C2+ products requires intricate multielectron/proton coupling steps and C-C coupling steps. Therefore, the reaction usually suffers from poor selectivity and large overpotential.^[12-15] As a result, rational design of highly active electrocatalysts and the discovery of catalytic mechanism are critical for producing C2+ products via CO₂RR.

Generally, Cu-based catalysts are considered to be most promising materials for converting CO₂ to C2+ products due to the suitable adsorption energy of CO.[16-17] Many strategies have been applied to modify the activity of CO₂ to C2+ products over Cu-based catalysts, including changing morphology,^[18] using bimetallic alloys,[19-21] doping heteroatoms,[22] and modifying with other molecules.^[23] It has been known that altering surrounding structure of Cu is the useful method for enhancing generation of C2+ products.^[24] The surrounding structure can be understood through the coordination number (CN), the number of nearest neighbor atoms.^[25] The CN varies with different crystal surfaces, sizes and morphologies. It has been reported that the Cu (100) exhibited better selectivity of C₂H₄ than that of Cu (111).^[26] The cluster, edge and corner sites of Cu-based catalysts possessed significant activity for CO2RR due to the low Cu-Cu CN.[27] Therefore, the selectivity for C2+ products over Cu-based catalysts can be enhanced by optimization of the Cu CN.

In recent years, many researches have shown that cuprous oxide (Cu₂O) catalysts are selective towards C2+ products,^[28-33] but the detailed reasons need to be studied further. According to some previous work,^[34-35] the Cu oxides can be reduced and the metallic Cu was the real active sites during CO₂RR. However, some studies have shown that Cu oxide species existed and played crucial role in activating CO₂ and C-C coupling.^[36-37] Thus, to explore the effect of oxygen atom around the Cu atoms during CO₂RR is interesting, which not only can further reveal the mechanism of the reaction, but also can optimize high performance catalysts.

Herein, we design Cu₂O with different crystal surface and size to explore the effect of coordination environment on catalytic efficiency in CO₂RR. According to the results of operando X-ray absorption spectroscopy, we can deduce that the Cu-Cu CN and Cu-O CN are the main factor for the selectivity of C₂H₄, and they

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can be tuned by changing the crystal surface and size of Cu₂O. The highest faradaic efficiency (FE) for ethylene could reach 50.6% with a current density 24.5 mA cm⁻² by tuning the Cu-Cu CN and Cu-O CN.

In order to explore the effect of Cu surrounding structure on the selectivity of C2+ products, two different types of Cu₂O were selected as the research models. The Cu₂O with cubic morphology was surrounded by (100) facet and the Cu₂O with octahedral morphology was surrounded by (111) facet. [38] The different types of Cu₂O were prepared according to the reported methods.^[39, 40] As shown in Figure 1A, 1B and 1C, the cubic Cu₂O with size of 200 nm (C-200), the cubic Cu₂O with 500 nm (C-500) and the octahedral Cu₂O with 500 nm (O-500) were prepared, and the size uniform. Additional characterizations, including X-ray was photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) are provided in the supporting information, Figures S1-S2. It is clearly revealed that all catalysts showed similar XRD and XPS spectral information and no peak of Cu⁰ was found. The X-ray absorption fine structure spectroscopy (XAFS) study was conducted to identify the local coordination environment of different Cu₂O catalysts. Although the valence states are similar, the coordination structures are different (Figure S3), indicating that the surrounding structure of Cu depended on the size and facets.

The CO₂ electroreduction activities of catalysts were tested in a typical H-type cell.[41-44] Controlled potential electrolysis of CO2 at each given potential was performed. Gas-phase and solutionphase products were quantified by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy, respectively. Various products, including ethylene, CO, formic acid and H₂, were detected with a combined FE of around 100 % for all the catalysts (Figure S4). As shown in Figure 1D, 1E and 1F, the C-200 exhibited the highest FE of ethylene, and the FE of ethylene could reach 41.5% at -1.2 V vs. RHE. Meanwhile, the C-500 exhibited higher FE of ethylene than that of O-500. The cube and small size of Cu₂O possessed higher activity of C₂H₄ than that of octahedral and large size of Cu₂O, which is consistent with the previous literatures.^[26, 44]



Figure 1. A, B and C) SEM images for C-200, C-500 and O-500, respectively. D, E and F) Faradaic efficiency of C₂H₄ over C-200, C-500 and O-500, respectively.

In order to further study the mechanism, the operando-XAFS measurements were investigated to identify the local coordination environment of Cu₂O during the CO₂RR at -1.2 V vs. RHE (Figure S5). According to previous report, the XAFS can provide insight into the electronic structures and chemical bonding of surface metal atoms in their local environment.^[45-48] As shown by the normalized Cu K-edge X-ray absorption near edge structure (XANES), the valence state of Cu during the CO₂RR is between Cu⁰ and Cu⁺,

indicating that the Cu₂O can be partially reduced to Cu. (Figure 2A and 2B). The local order of the coordination environment around copper atoms is expressed by the oscillations from 0 to 12 Å⁻¹ in the k³ weighted EXAFS (Figure 2B), the Cu-O and Cu-Cu coordination had different changes for different catalysts. The changes in the CN of Cu-O and Cu-Cu were further showed in the Fourier-transform (FT) of EXAFS (Figure 2C), we can observed that an obvious Cu-Cu peak located at 2.3 Å⁻¹ appeared and the Cu-O became weaken during CO₂RR. Moreover, we used the ARTEMIS programs of IFEFFIT to fit the Cu-O and Cu-Cu CN of the as-prepared materials. The EXAFS data fitting results are provided in Figure S6 and Table S1. The correlations between the maximal FE of C₂H₄ and Cu-Cu CN or Cu-O CN are shown in Figure 2D and 2E. We can know that the low Cu-O CN and high Cu-Cu CN are favorable to producing C₂H₄. It can be known from Figures 1D-1F and Figure 2F that the ratios of Cu-Cu CN/Cu-O CN is also related to the activity of C2 products. These results indicated that the activity of catalysts is



related with Cu-Cu CN and Cu-O CN.

Figure 2. A) XANES spectra at the Cu K-edge for different Cu₂O catalysts at -1.2V vs. RHE. B) The apparent valence states from the XANES. C) Cu K-edge extended XAFS oscillation function k³w(k). D) The corresponding Fourier transforms FT(k³w(k)). E) The Cu-Cu CN and Cu-O CN for different catalyst. F) The ratio of Cu-Cu CN/Cu-O CN for different catalysts.

From the above experimental data, we reasonably believe that the selectivity of C2+ products can be improved by tuning the Cu-Cu CN and Cu-O CN. We can observe that the Cu-Cu CN and Cu-O CN varies with the crystal surface. The (100) facet possesses high Cu-Cu CN, and the (111) facet has high Cu-O CN. Thus the Cu-Cu CN and Cu-O CN can be optimized by tuning the ratio of (100) and (111) facets. According to the literatures, the (100) and (111) facets can be exposed on octahedral Cu₂O at the same by the method of acid etching, due to the (100) of Cu₂O is more acid resistant than that of the (111) crystal planes.^[49] The ratio of (100) and (111) can be changed by the time of acid etching.

Thus, the O-500 was modified via acid etching with different times, and the catalysts are named as O-500-x, and x represents the time of acid etching. From the scanning electron microscopy (SEM) and transmission electron microscope (TEM) images, as shown in Figure 3A and Figure 3B, we can observe that the surface of O-500 become rough after etching 90 min, and the roughness increased with the etching time (Figure S7). From the high resolution (HR)-TEM image (Figure 3C), the (100) and (111) facets can be observed on O-500-90, indicating that the method of acid etching can produce (100) facet on the O-500. Furthermore the XRD and XPS characterizations were also carried out, it is clear that all samples show similar spectral information and no peak of Cu⁰ was found (Figure S8-S9).

Journal Name

Journal Name

Page 3 of 5

The CO₂ electroreduction activities of O-500-45, O-500-90 and O-500-135 were also tested in H-type cell. The linear sweep voltammetry (LSV) results are given in Figure S10. O-500-90 exhibited a more positive onset potential and higher total current density than the other catalysts, suggesting that O-500-90 was most active catalyst for CO2 reduction. Controlled potential electrolysis of CO₂ at each given potential was then performed. From Figure 3D and Figure S11, we can find that the acid etching can significantly enhance the selectivity of C2 products, and the O-500-90 yielded the highest FE of C_2H_4 . The FE of C_2H_4 over O-500-90 could reach 50.6% at -1.2 V vs. RHE, which exceeded that of O-500 under identical conditions by a factor of about 2.1. Moreover, the current density over O-500-90 was 24.5 mA cm⁻², and the partial current density of C₂H₄ was 12.5 mA cm⁻², which is 5.2 times of that over O-500 (Figure S12). Compared with other state-of-the-art Cubased electrocatalysts, O-500-90 also showed high selectivity for C₂H₄ (Table S2). The results indicate that the catalytic performance can be tuned by the time of acid etching, which results in change of ratio of (100) and (111) facets or Cu-Cu CN and Cu-O CN. In addition, no obvious change in morphology were observed after reaction (Figure S13), indicating the excellent stability of O-500-90.



Figure 3. A, B) SEM and TEM images of O-500-90.C) The HR-TEM image of O-500-90. D) Faradaic efficiency of C₂H₄ over different catalysts. E) The Cu-Cu CN and Cu-O CN for different catalyst. F) The ratio of Cu-Cu CN/Cu-O CN for different catalysts.

In order to verify our hypothesis, the operando-XAFS measurements were also investigated to identify the local coordination environment of O-500-x during the CO₂RR at -1.2V vs. RHE. As shown by XANES and EXAFS spectra (Figure S14 and Figure S15), the valence state of Cu is between Cu^{0} and $\text{Cu}^{\text{+}},$ and the Cu-O and Cu-Cu coordination changed with the time of etching. The valence state of O-500-90 was tested by the semi-in-situ XPS after reaction (Figure S16). It can be known that the Cu(1) and Cu (0) existed in the catalyst (Figure S17), indicating that a portion of Cu₂O was reduced to Cu(0). This was consistent with the results of XAFS. Moreover, the correlation between the selectivity of C_2H_4 and Cu-Cu CN or Cu-O CN is demonstrated in Figure 3E. As can be shown from Figures 3D and 3F, the trend of FE_{C2H4} is consistent with the ratios of Cu-Cu CN/Cu-O CN.

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Figure 4. A) The correlation between the maximal FE_{C2H4} and the ratio Cu-Cu CN/Cu-O CN over different catalyst. B) The possible synergistic mechanisms between the Cu-Cu and Cu-O.

These results indicated that the FE of C₂H₄ can be controlled by the ratio of Cu-Cu CN and Cu-O CN of the O-500-based catalysts. Figure 4A shows the dependence of FE on the ratio of Cu-Cu CN and Cu-O CN of all the catalysts in this work, and the ratio of about 6 yielded the best selectivity of C₂H₄. Moreover, we can observe that the valence state of catalysts increase with the Cu-O CN, and the valence state of catalysts decreases with the Cu-Cu CN (Figure S18). Based on the above datum analysis and previous literatures,^[50-53] the Cu-Cu and Cu-O provide two intrinsically different sites to bind the CO₂ and the H₂O, and a possible mechanism was proposed (Figure 4B). H₂O is more likely to attach to Cu-O sites and CO₂ is more likely to attach to Cu-Cu sites. The adsorbed H₂O can stabilizes the negative charge on chemisorbed CO₂, promoting reduction CO₂ to CO, and the selectivity of C₂H₄ can be enhanced by the increase of CO, due to the CO is the key C1 intermediate to produce C2+ products.[54] Thus the Cu-Cu and Cu-O exhibited synergistic effect for enhancing the activity of CO₂RR to C₂H₄.

Moreover, the other factors to influence the reaction were also investigated. According to cyclic voltammograms (CV) curves under different scan rates, the electrochemical active surface areas (ECSAs) of catalysts were determined by measuring double layer capacitance. The O-500-90 exhibited the largest ECSAs among the four catalysts (Figure S19). The partial current density for C₂H₄ was further normalized by ECSA (Figure S20). Similar to the geometric current density, the O-500-90 showed the highest normalized current density among the catalysts. The adsorption isotherms of CO₂ on different catalysts were determined, the O-500-90 exhibited the highest CO₂ adsorption capacity (Figure S21). Furthermore, the valence band spectra were obtained to further clarify the chargetransfer process for CO₂ adsorption and activation on O-500-90 in electrolysis via the semi-in-situ XPS (Figure S16). As shown in Figure S22, the significant change in the valence band can be observed after CO₂ reduction, which results from the formation and adsorption of CO₂ • - species on O-500-90. The Electrochemical impedance spectroscopy (EIS) was used to measure the interfacial charge transfer resistance (Rct) between the electrolyte and electrode at an open circuit potential. As shown in Figure S23, O-500-90 showed the lowest interfacial Rct, indicating that electron transfer to O-500-90 is easier than to others during CO₂RR.

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In summary, The Cu₂O catalysts with different Cu-Cu CN and Cu-O CN were preapared by varying the crystal surface and size. The performance of the catalysts for CO₂ electrocatalytic reductin to C₂H₄ was studied. It was found that the coordination environment of Cu affected the current density and FE of C₂H₄ the atalysts. The effeciency of the catalysts was highest as Cu-Cu CN/Cu-O CN ratio was about 6, and the FE of C₂H₄ could reach 50.6 % with a current density of 24.5 mA cm⁻². The high effeciency results mainly from the higher electrochemical active area, strong CO₂ adsorption, and small interfacial charge transfer resistance between the electrolyte and electrode. We believe that the results of our work are valuable for designing efficient catalysts of CO₂ electroreduction.

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