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A strategy to control grain boundary density and Cu⁺/Cu⁰ ratio of Cu-based catalysts for efficient electroreduction of CO₂ to C2 products

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Published on 13 February 2020. Downloaded by Universite Paris Descartes on 2/13/2020 11:42:49 AM

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Cu(OH)₂/CuO nanocomposites-derived Cu₂O/Cu were highly efficient for CO₂ electroreduction to C2 products. The highest faradaic efficiency and current density could reach 64.5% and 26.2 mA cm⁻², respectively. By changing calcination time, moderate grain boundary density and Cu⁺/Cu⁰ ratio in catalysts can be controlled, leading to large number of active sites and low interfacial charge transfer resistance.

Electrochemical CO₂ reduction has received wide attention, which not only reduces the greenhouse gases (CO_2) into chemical fuels and feedstock, but also provides an energy storage solution to the renewable energy sources.^[1-5] The activity of CO₂ reduction has been boosted by various methods, such as controlling morphology of nanostructured catalysts,^[6-9] manipulation of oxidation states,^[10-12] combing with other component,^[13-16] and choosing appropriate electrolyte.^[17-18] Among C-based products, C2 products have higher energy density and economic value, which are much more attractive and significant than C1 counterparts. Up to date, Cu-based materials have proved to be the most promising electrocatalysts for converting CO₂ to C2 products.^[19-27] In particular, previous research showed that oxide-derived copper (OD-Cu) could be prepared using a simple synthesized method. The surface Cu⁺ sites were suggested to act as the active sites for CO₂ reduction. They can

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facilitate CO2 molecules activation and C-C bond formation efficiently.[28]

It was discovered that the preparation method of OD-Cu catalysts played a crucial role for the distribution of the products. Generally, the methods can be divided into two categories,^[29-32] i.e. annealing and unannealing methods. The annealed Cu₂O exhibited high selectivity for C1 products, but low selectivity for C2 products at low overpotential. The total C1 faradic efficiency (FE) reached up 70% (40% CO and 30% formate).^[29] Meanwhile, it was reported that electroreductionannealed OD-Cu could be used to produce CO with FE up to 60%.^[30] Although annealing could decrease the overpotential for CO₂ reduction, the major product was CO and the FE of C2 products were low. Interestingly, OD-Cu prepared via the unannealed method was shown to be more inclined to produce C2 products. An electrodeposited Cu₂O exhibited high selectivity for ethylene, and the FE could reach up 40%.[31] In another case, O-plasma-treated Cu electrode achieved high ethylene selectivities, and the FE was about 60%.[32] Also, the total FE of ethanol and acetate reached up to 80% over Cu electrode derived from Cu-based complexes via in situ electrosynthesis.^[33] Recently, it was reported that a branched Cu₂O nanoparticles obtained in aqueous ammonia solution can effectively electroreduction CO₂ to ethylene, and the FE was about 70%.^[34] Further studies showed that Cu⁺ promoted CO₂ reduction to C2 products over the unannealed OD-Cu due to the enhancement of CO dimerization.^[35] However, they usually suffer from high overpotentials.

Bulk defects in metals, such as grain boundaries (GBs), can create regions of increased strain at the surface, which have previously been correlated with catalytic activity in some reactions.^[26, 36] It was demonstrated that the high densities of GBs in OD-Cu electrocatalysts could improve CO₂ reduction activity, including CO₂-to-CO^[29, 30] and CO-to-fuels.^[37] By annealing, larger GBs with appropriate types and distribution can be created. However, the ratio of Cu⁺/Cu⁰ active sites is difficult to tune, leading to a low stability and C2 product selectivity. Thus further modifying the local electronic

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI:10.1039/x0xx00000x

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structure of Cu with positive valence sites can keep the high Cu⁺ content on the OD-Cu surface. Combined with the high density of GBs, it probably enables control over CO generation, adsorption and dimerization, and makes preference for stable CO₂ reduction to C2 products possible.

In this work, we tried to combine the advantages to achieve high selectivity for C2 products with low overpotentials. We successfully prepared five reduced $Cu(OH)_2/CuO$ composites (R-Cu). By adjusting the calcination time, $Cu(OH)_2/CuO$ composites with different ratios of $Cu(OH)_2$ and CuO were first prepared. After electrochemically reducing, a series of R-Cu composites with different GB densities and Cu^+/Cu^0 ratios was obtained. The catalytic performance of these composites for electrochemical CO_2 reduction was studied. It was discovered that the highest FE for C2 products could reach 64.5% with a current density of 26.2 mA cm⁻² at -0.9 V vs. RHE. This is one of the highest FE for C2 products at such low applied potential. The high catalytic activity resulted mainly from the synergistic effect of GB densities and Cu^+ species, which could be tuned easily by changing the calcination time. images for R-Cu-2, R-Cu-5, R-Cu-10 and R-Cu-20, respectively. N) XRD patterns of Composites-x. O) XRD patterns of BCu_{120.1039}/D0GC00247J

The procedures to synthesize R-Cu-x composites are shown schematically in Figure 1A. A polished Cu foil was used as the substrate, and Cu(OH)₂ nanosheets were firstly synthesized through modified chemical immersion method.^[15] Then, it was calcined in the muffle at 500 °C for desired time. Cu(OH)₂ was partially transformed to CuO, and Cu(OH)₂/CuO composites were formed. For clarity, Composites-x refers to different $Cu(OH)_2/CuO$ composites, and x represents the calcination time (min). Finally, Cu(OH)₂/CuO-x were electrochemically reduced at -2.0 V vs. RHE for 500 s, leading to the formation of R-Cu-x. During the electrochemically reducing, we can observe that the current density decreased before 500 s, while the current density was stable after 500 s, indicating that Cu(OH)₂/CuO-x was completely reduced. Figure S1 shows optical pictures of the samples, displaying an observable color change and uniformity during the process.



Fig. 1 A) Schematic illustration of the process to prepare R-Cu-x. B, E, H and K) SEM images for Composites-2, Composites-5, Composites-10 and Composites-20, respectively. C, F, I and L) SEM images for R-Cu-2, R-Cu-5, R-Cu-10 and R-Cu-20, respectively. D, G, J and M) HR-TEM



Fig. 2 Electrocatalytic results in CO_2 -saturated 0.1 M KHCO₃ electrolyte. A) LSV curves on different electrodes with a scan speed of 20 mV s⁻¹. B) FE for C2 products over different electrodes at different potentials. C) The distribution of C2 products at different potentials over R-Cu-5. D) The long-term stability of R-Cu-5 at -0.9 vs. RHE during 24 h electrolysis.

The morphologies of Composites-x and R-Cu-x were first characterized by scanning electron microscopy (SEM). The obtained Cu(OH)₂ had a sheet-like morphology (Figure S2). After calcination, Composites-2 remained to have the sheet-like morphology (Figure 1B). However, with the increased calcination time, a three-dimensional (3D) structure was formed for Composites-5 and Composites-10 (Figure 1E and 1H). Then the 3D structure collapsed to the dense films when the calcination time extended to 20 minutes (Figure 1K). After Composites-x was electrochemically reduced, the structure of R-Cu-x became more porous compared with Composites-x (Figure 1C, 1F, 1I and 1L). Transmission electron microscopy (TEM) images of R-Cu-x are presented in Figure 1D, 1G, 1J and 1M, demonstrating that GBs existed in the bulk of the

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composites. The as-obtained samples were then characterized by X-ray diffraction (XRD). For the Composites-x (Figure 1N), with increasing calcination time, the characteristic peaks of CuO were strengthened (36.0° and 41.8°) and the characteristic peaks of Cu(OH)₂ were weakened (35.5° and 38.6°). It indicated that Cu(OH)₂ transformed to CuO gradually. For R-Cu-x, the characteristic peaks of Cu(OH)₂ and CuO disappeared. A new peak around 36.5° was observed, which can be assigned to Cu₂O. It demonstrated that Cu⁺ species was generated after the electroreduction of Composites-x (Figure 1O). The strong peaks at about 50° were corresponding to the Cu foil, which were not changed after electrochemical reduction.

The CO₂ electroreduction activities of R-Cu-x were tested in a typical H-type cell^{[38]} and CO_2-saturated 0.1 M $\rm KHCO_3$ solution (pH 6.8) was used as electrolyte. As revealed by linear sweep voltammetry (LSV) in Figure 2A, R-Cu-5 exhibited a more positive onset potential and higher total current density than other catalysts, suggesting that R-Cu-5 was most active catalyst for CO₂ reduction. Controlled potential electrolysis of CO₂ at each given potential was then performed. Solutionphase and gas-phase products were quantified by nuclear resonance (NMR) spectroscopy and magnetic gas chromatography (GC), respectively. Under these conditions, various products, including ethylene, ethane, ethanol, CO, formate and H₂, were detected with a combined FE of around 100 % for all the studied catalysts (Figure S3 and S4). From Figure 2B, we can observe that R-Cu-5 could yield the highest total FE of 64.5 % for C2 products at -0.9 V vs. RHE, and a FE of 22.5 % at -0.6 V vs. RHE. As shown in Figure S5, the onset potential of C2 products for R-Cu-5 was -0.45V (ethane), -0.50V (ethanol) and -0.51V (ethylene), respectively. The onset potential of C2 products over other R-Cu-x catalysts were also calculated (Table S1), and we can observe that R-Cu-5 exhibited lowest onset potential in the five catalysts. As far as we known, this is one of the highest FE for C2 products with such low applied potential (Table S2 and Table S3). However, the maximum FE for C2 products over R-Cu-10 and R-Cu-20 were 55.3% and 35.2%, respectively. Interestingly, for R-Cu-2 and R-Cu(OH)₂, C2 products could not be detected under low potentials, and the maximum FE for C2 products were only 32.1% and 23.6% at -1.1 V vs. RHE, respectively. In detail, the whole distribution of C2 products were presented in Figure 2C and Figure S4. The results indicate that the appropriate calcination time could not only increase the selectivity of C2 products, but also reduced the overpotential. 500 °C is an optimal calcination temperature. Catalysts would fall off from the Cu foil when the temperature was 600 °C, while the catalytic activity became lower when the temperature was 400 °C (Figure S6). Moreover, R-Cu-5 also had higher current density and partial current density for C2 products than those of other catalysts (Figure S7-S8). The long-term stability of R-Cu-5 was tested at -0.9 V vs. RHE for 24 h (Figure 2D). It can be seen that both the current density and the FE for C2 products kept stable with time during the entire period.

According to the cyclic voltammograms (CV) curves under different scan rates (Figure S9), the electrochemical active

surface areas (ECSA) were determined by measuring double layer capacitance (C_{dl}; Table S4). The ECSA0 #879 R2C6-90 Was higher than that of other catalysts (Figure 3A). The increased ECSA indicated larger number of active sites and increased apparent concentration of reactant at the surface of R-Cu-5, leading to the higher efficiency for CO₂ reduction. For R-Cu-x, the partial current density for C2 products were also normalized by ECSA (Figure 3B). Similar to the geometric partial current density, the normalized partial current density for C2 products of R-Cu-5 was also highest among the five catalysts. Therefore, the increased activity of R-Cu-5 was not only attributed to the increasing number of active sites. Moreover, the total current densities normalized by ECSA were similar (Figure 3C), indicating a nearly identical consumption rate of local protons during CO₂ reduction. We can conclude that the high C2 selectivity for R-Cu-5 cannot ascribed to the local pH.[39-40]

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The electrochemical impedance spectroscopy (EIS) was also conducted, and the Nyquist plots were obtained by running the experiment at an open circuit potential (Figure 3D). R-Cu-5 showed the lowest interfacial charge transfer resistance, suggesting that electron transfer on R-Cu-5 electrode surface was more facile than others. Therefore, R-Cu-5 showed significant advantages in all the key steps for CO_2 electroreduction to C2 products.



Fig. 3 A) Charging current density differences plotted against the scan rates: R-Cu-5 (a), R-Cu-10 (b), R-Cu-20 (c), R-Cu-2 (d) and R-Cu(OH)₂ (e). B) The partial current density for C2 products normalized by ECSA. C) The total current density normalized by ECSA. D) Nyquist plots for different electrodes in CO₂-saturated 0.1 M KHCO₃ electrolyte.

It is important to investigate the contributors for the outstanding catalytic activity of R-Cu-5 in CO₂ reduction to C2 products. Firstly, R-Cu-5 possesses a high density of GBs, which can enhance the activity of CO₂ reduction.^[29, 41] In our work, GB density was analyzed by imaging ~30 particles of R-Cu-x (Figure S10) and the detailed calculation method is provided in the supporting information. From the HR-TEM images (Figure S10C), we can observe that there was an obvious interface

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between two crystallites in the grain boundary area. The (111) plane of Cu and (110) plane of Cu₂O were observed in the catalysts, which was consistent with the XRD results. From Table S5, we can find that GB density increased with the increasing calcination time. For example, R-Cu-5 had a GB density of 64.8 μ m⁻¹ and R-Cu-10 had the highest value of 86.4 μ m⁻¹. It indicated that the anneal method can accelerate the formation of GBs. However, GB density of R-Cu-20 was only 57.2 μ m⁻¹, which was less than that of R-Cu-10. This may result from the agglomeration, and is consistent with the results from SEM study. We tried to establish a quantitative correlation between GB density and CO₂ reduction activity. From Figure 2B and Figure 4A, we found that the FE for C2 products first increased with the increasing GB density on R-Cu-x and reached highest on R-Cu-5. However, the FE for C2 products decreased on R-Cu-10, although it had a higher GB density. It indicated that there are other influence factors except GB density for the enhancement of CO₂ reduction to C2 products.

Moreover, high Cu⁺/Cu⁰ ratio of R-Cu-5 was favorable to both CO₂ activation and CO dimerization to generate C2 products. We attempted to compare the valence state of Cu for R-Cu-x by using the semi-in-situ X-ray photoelectron spectroscopy (XPS), which can prevent the samples to be oxidized by the air (Figure S11).^[42] As shown in Figure S12, a small peak was observed around 934.6 eV in the spectra of Cu 2p orbits, which can be assigned to Cu2+. It indicated that Cu+ or Cu⁰ was the major Cu species in R-Cu-x. The Cu LMM in Auger electron spectroscopy was further used to confirm Cu+ and Cu⁰.^[43] It can be seen that both Cu⁺ and Cu⁰ existed in R-Cu-x (Figure 4B), and the ratio of Cu⁺/Cu⁰ decreased with the increase of calcination time (Figure S13). However, the ratio of Cu⁺/Cu⁰ had no obvious change with the increase the electrolysis time (Figure S14). In other words, Cu⁺ content in the final catalyst could be controlled by the calcination time of Cu(OH)₂/CuO composites. It can be known from Figure 2B and Figure 4A, the selectivity for C2 products decreased with the decreasing Cu⁺ content after the calcination time exceeded 5 min. Although R-Cu(OH)₂ and R-Cu-2 had higher Cu⁺/Cu⁰ ratio, the FE for C2 products was still low. It may be caused by the low GB density in these two composites.



Fig. 4 A) The synergistic effect of GB density and Cu^+/Cu^0 ratio on the C2 products selectivity for R-Cu-x. B) LMM Auger spec-tra of Cu for R-Cu-x.

Furthermore, we can observe that the catalysts with high GB density (R-Cu-5 and R-Cu-10) exhibited high activity of CO_2

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reduction at low potential (-0.6 V), indicating that the GB was favorable for activating CO₂. However, \mathbb{R}^{2} Cu² With figh Cu³ content exhibited higher selectivity of C2 products than that of R-Cu-20 and R-Cu-10 at high potential (-1.1 V), indicating that Cu⁺ was favorable for C-C coupling. Thus, we can make a conclusion that the GB was favorable for activating CO₂, and the surface Cu⁺ sites were favorable for C-C coupling. The superior activity of CO₂ reduction over R-Cu-5 was contributed to the synergistic effect of GB densities and Cu⁺ species.

Conclusion

In summary, by simple thermal calcination and electrochemical reduction of Cu(OH)2, we have designed five Cubased composites with distinct GB densities and Cu⁺/Cu⁰ ratios. R-Cu-5 exhibited excellent electrocatalytic performance for CO2 reduction to C2 products in aqueous solution. The maximum total FE of C2 products could reach 64.5 % with a current density of 26.2 mA cm⁻² at a low electrolysis potential (-0.9 V vs. RHE). It also showed excellent durability after the long-term chronoamperometry test. The excellent catalytic activity of R-Cu-5 originated mainly from the abundant GBs and high Cu⁺/Cu⁰ ratio. These result in large number of active sites and low interfacial charge transfer resistance, which were favorable to CO₂ activation and CO dimerization to generate C2 products. This work provides a further understanding for OD-metal catalysts. We believe that the method can also be used to prepare some other efficient electrocatalysts for CO₂ reduction to useful chemicals and fuels.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work was supported by National Key Research and Development Program of China (2017YFA0403101), National Natural Science Foundation of China (21890761, 21733011), and Chinese Academy of Sciences (QYZDY-SSW-SLH013).

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