Core-Shell ZnO@Cu2O as Catalyst to Enhance the Electrochemical Reduction of Carbon Dioxide to C2 Products

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Abstract: The copper-based catalyst is considered to be the only catalyst for electrochemical carbon dioxide reduction to produce a variety of hydrocarbons, but its low selectivity and low current density to C2 products restrict its development. Herein, a core-shell xZnO@yCu2O catalysts for electrochemical CO2 reduction was fabricated via a two-step route. The high selectivity of C2 products of 49.8% on ZnO@4Cu2O (ethylene 33.5%, ethanol 16.3%) with an excellent total current density of 140.1 mA cm−2 was achieved over this core-shell structure catalyst in a flow cell, in which the C2 selectivity was twice that of Cu2O. The high electrochemical activity for ECR to C2 products was attributed to the synergetic effects of the ZnO core and Cu2O shell, which not only enhanced the selectivity of the coordinating electron, improved the HER overpotential, and fastened the electron transfer, but also promoted the multielectron involved kinetics for ethylene and ethanol production. This work provides some new insights into the design of highly efficient Cu-based electrocatalysts for enhancing the selectivity of electrochemical CO2 reduction to produce high-value C2 products.

Keywords: CO2 electrochemical reduction; core-shell structure; ZnO@Cu2O; synergy effect; C2 products selectivity

1. Introduction

In recent years, great progress was made in the utilization of carbon dioxide (CO2), including the thermochemical, photochemical, and electrochemical methods. The electrochemical reduction of CO2 (ECR) is now the main research in the current stage due to its great advantages of simple reaction conditions [1–3]. Currently, the products obtained from ECR are mainly C1 products [4,5] (such as CO, HCOOH, and CH4) and C2 products (C2H4, C2H6, and C2H5OH, etc.) [6–9]. However, high overpotential, low product selectivity and low current density are still the main problems for the electrochemical reduction of CO2. Designing novel and efficient catalysts is now an effective way to solve the above problems.

Copper-based catalysts are the only known catalysts that can electrochemically reduce CO2 to a variety of hydrocarbons and oxygen-containing compounds because of their moderate binding energy with CO* [10,11], but the selectivity to products is low. Therefore, the research of high-selectivity copper-based catalysts for ECR is particularly important. To date, some effective strategies for modifying copper-based catalysts were widely investigated, including doping strategy (metal and non-metal) [12], defect engineering [13], oxide-derived copper [14,15], morphology control [16], and size control [17].

Metal oxides or metal oxide derivatives are effective strategies to improve the selectivity of electrochemical CO2 reduction to C2 products. Many works were carried out on Cu2O because Cu2O can strengthen the C–C coupling process for the formation of C2...
products. For example, Cu$_2$O films on a Cu disc catalyst was prepared for ECR to improve the selectivity of C$_2$ products. The optimum selectivity of 45% was obtained by adjusting the thickness of the oxide layer, but its partial current density was only 33 mA cm$^{-2}$ [18]. Li et al. [19] found that the high surface roughness Cu$_2$O catalyst formed at 500 °C would require 0.5 V less overpotential than polycrystalline Cu, to reduce CO$_2$. Furthermore, interface-induced Cu$_2$O nanocubes with controllable morphology and size also exhibited strong selectivity to ethylene (31.1%) in the H-cell at −1.15 V vs. RHE, but the current density was just 3.72 mA cm$^{-2}$ [20].

Moreover, the active sites and electron distribution of copper catalysts could be tailored by introducing the second element. The synergistic effect of the two elements could strengthen their activity and stability for CO$_2$ electrochemical reduction [21]. A Cu/CNT catalyst was applied for ECR in a flow cell, the main product of CO was obtained but the total current density was 15 mA cm$^{-2}$ [22]. Ning et al. [23] designed a new type of N-doped Cu$_2$O catalyst using the synergy between Cu$_2$O and pyridinic-N for boosting C$_2$H$_4$ selectivity and durability of Cu$_2$O. The selectivity of ethylene reached 19.7% (current density reached 12 mA cm$^{-2}$) in an H-type cell. Designing electrocatalysts with dual metal active sites of metal active sites and Cu$_2$O active sites are also an important strategy for enhancing ECR [24]. Gao et al. [25] prepared a bimetallic catalyst of Au uniformly supported on Cu$_2$O. The presence of Au active (an electrocatalyst for CO$_2$ to CO) helped to increase the coverage of *CO on Cu, thereby strengthening the production of C$_2$ products on Cu–Au catalysts. The total Faraday Efficiency of C$_2$ products reached 61.3% under −1.05 V vs. RHE in an H-type gas-tight electrolytic cell, and the current density of 42.87 mA cm$^{-2}$ was also nearly doubled, as compared to Cu. Similarly, the Ag/Cu foam catalyst also presented a good activity to produce ethanol with 33.7% FE in a glass beaker [26]. Furthermore, a ZnO deposited on CuO nanowire catalysts were synthesized by the atomic layer deposition method. Operando Raman spectroscopy showed that CO* binding on Cu sites was modified by Zn$^{2+}$. The key intermediate of ethanol products *COCH$_4$ was easily generated to enhance the product of ethanol (FE = 48.6%) with a current density of 98 mA cm$^{-2}$ in a flow cell [27]. A Cu oxide/ZnO-based catalyst showed high ethylene selectivity in the gas-phase CO$_2$ electro conversion [28]. Hence, the catalyst with dual active sites is an effective strategy for electrochemical CO$_2$ reduction, and it is a promising approach to achieve high selectivity and high current density for C$_2$ products in a flow cell.

Inspired by these works, we designed and synthesized a catalyst with ZnO core and Cu$_2$O shell through a wet chemical method. Due to the double active sites on the ZnO@Cu$_2$O catalyst. It is possible to make CO$_2$ first generate CO at the ZnO site, and then CO couples on Cu$_2$O, to generate C$_2$ product. The synergistic effect of Cu and Zn enhances the selectivity of C$_2$ products on the catalyst. This core-shell structure was used to enhance the multielectron reactions in electrochemical CO$_2$ reduction in a flow cell. The thickness of the Cu$_2$O shell was controlled to boost the coupling of CO on the Cu site to produce C$_2$ products. By tailoring the synergy of Cu and Zn oxides, a high Faradic efficiency of 49.8% for C$_2$ products at a high current density of 140.1 mA cm$^{-2}$ was achieved under the potential of −1.0 V vs. RHE. This work exceeded the selectivity of C$_2$ products with many jobs, while achieving a higher current density.

2. Results and Discussion
2.1. The Morphology and Structure of the Catalysts
2.1.1. ZnO Catalysts

The morphology, structure, and chemical state of the as-synthesized ZnO catalysts were characterized. Figure 1a–c shows the scanning electron microscopy (SEM) images of ZnO particles obtained at different calcination temperatures (400 °C, 600 °C, and 800 °C). All samples showed a similar sphere-like morphology. The particle size became bigger as the calcination temperature increased from 400 °C to 800 °C, probably due to the aggregation of particles. The smallest particle size was obtained at 24.4 ± 5 nm for the
ZnO-400 sample. The particle size distribution diagrams of ZnO catalyst are displayed in Figure S7.

![Figure 1. SEM images of (a) ZnO-400, (b) ZnO-600, and (c) ZnO-800. (d) XRD patterns and (e) (101) and (002) facets proportion of different ZnO catalysts. (f) Zn XPS spectrum of ZnO-400.](image)

The structure of ZnO particles was analyzed by XRD characterization. As shown in Figure 1d, all ZnO samples presented almost the same diffraction peaks at 2θ = 31.8°, 34.5°, 36.3°, 47.7°, 56.7°, 63.0°, and 68.1°, which were attributed to (100), (002), (101), (102), (110), (103), and (112) facets of hexagonal wurtzite ZnO (JCPDS No. 75-0576). Moreover, as shown in Figure 1e, the ZnO-400 sample illustrated the highest proportion of (101) and (002) facets, which would have a great impact on the ECR activity. The ratio of facets was calculated by comparing the intensities of the peak in XRD. The composition and chemical valence states of the ZnO samples were analyzed by X-ray photoelectron spectroscopy (XPS) technology. As shown in Figure 1f, the characteristic peaks of Zn 2p1/2 at 1045.63 eV and Zn 2p3/2 at 1022.47 eV were attributed to Zn2+ [29].

2.1.2. xZnO@yCu2O Catalyst

The core-shell xZnO@yCu2O catalysts were synthesized with ZnO-400 as the core, through the epitaxial growth method (Scheme 1). Figure 2a–d displays the morphology and structure of xZnO@yCu2O as well as the Cu2O catalysts. The surface composed of accumulated nano-spherical Cu2O was generated after growing the Cu2O shell, as compared to the pristine ZnO core. This coarse structure generally had a larger external surface area and could provide more active sites [30,31]. The Cu2O sample showed a similar morphology. The particle sizes of the xZnO@yCu2O samples were obviously larger than pristine ZnO particle and gradually grew up as the Cu2O shell thickness increased (101 ± 20 nm for 4ZnO@Cu2O, 129 ± 20 nm for ZnO@4Cu2O, and 227.9 ± 25 nm for ZnO@20Cu2O). Under similar conditions, the particle size of the obtained Cu2O particles was about 181.7 nm. The particle size distribution diagrams are displayed in Figure S8. The TEM image in Figure 2e shows that the Cu2O shell covered the ZnO particles uniformly. The surface composition of the ZnO@4Cu2O sample was analyzed by EDX along the arrow direction. The Cu signal was first monitored, and then the Zn signal was detected when close to the core [32], exhibiting an obvious core-shell distribution. In addition, the signal intensity of the Cu element was significantly stronger than that of the Zn element. Both the 4ZnO@Cu2O and ZnO@20Cu2O catalysts proved that a similar core-shell structure was shown in Figure S1. These results indicated that the core-shell xZnO@yCu2O structure was fabricated. Moreover, the size of the ZnO core was about 30 nm, which was consistent with the ZnO-400. The Cu2O shell thickness was approximately twice that of the ZnO core for the ZnO@4Cu2O catalyst. Furthermore, the element mapping showed that the Cu element was distributed uniformly on the surface of the catalyst, and Zn was mainly distributed in the center. The atomic ratio of Cu to Zn in transmission was 43:1, which was very different...
from ICP-OES (about 4:1, in Table S1) probably because most of the Zn element inside was not monitored. From Figure 2g, it could be found that three different distinct lattice fringes of the shell were observed. The lattice spacing was 0.30 nm, 0.21 nm, and 0.24 nm, assigned to the (110), (200), and (111) facets of Cu$_2$O, respectively [33]. These results indicated that the cuprous oxide shell was successfully formed on the ZnO core.

Figure 3a shows the XRD patterns of the xZnO@yCu$_2$O catalysts. Compared to the patterns of ZnO-400 (JCPDS:75-0576) and Cu$_2$O particles (JCPDS:78-2076) (Figure S2), the core-shell xZnO@yCu$_2$O showed a mixed one with the characteristic peaks at 2θ = 34.5°, 36.3° corresponding to the (002), (101) facets of ZnO and 2θ = 42.3° corresponding to the (200) facets of Cu$_2$O [34,35], respectively. The peak around 36.5° was obviously strengthened as compared to pristine ZnO, due to the diffraction overlapping of the ZnO (101) facet and Cu$_2$O (111) facet. No peaks assigned to the Cu/Zn alloys were found [36,37]. This indicated that the structure of ZnO was inherited in the xZnO@yCu$_2$O catalysts and the Cu$_2$O (101) shell enclosed with Cu$_2$O (111) and the Cu$_2$O (200) facets. As the binding energies of Cu$^+$ and Cu$^{2+}$ species are very close (only 0.1 eV), the Cu LMM spectrum was applied to distinguish the distribution of the Cu$^+$ and Cu$^{2+}$ species. No characteristic peaks appeared at the binding energy of 568.0 eV (Figure S3), indicating no presence of Cu$^+$ species. The Cu XPS spectra of the xZnO@yCu$_2$O catalysts in Figure 3c showed two characteristic peaks of Cu 2p$_{3/2}$ at binding energies of 933.4 eV and 935.2 eV mainly attributed to Cu$^+$ and Cu$^{2+}$, respectively [38]. According to the relative intensity of the Cu 2p peak in the spectrum, it
could be inferred that the Cu\(^+\) species dominated the Cu oxide shell. This result further proved that the Cu\(_2\)O shell was formed, consistent with the above characterization. Cu\(^{2+}\) species were also observed probably due to the easy oxidation of Cu\(_2\)O in the air. The proportion of Cu\(^+\) species in different catalysts was calculated; the result is shown in Figure S4. Although the particle size of 4ZnO@Cu\(_2\)O was much smaller than the Cu\(_2\)O particle, the core-shell sample with the thinnest shell exhibited almost the same level of Cu\(^+\) species. This was probably attributed to the Cu–Zn interaction in 4ZnO@Cu\(_2\)O, which resulted in part of the copper oxide being reduced to cuprous oxide. The ZnO@4Cu\(_2\)O catalysts showed a much higher level of Cu\(^+\) species, indicating the presence of the stronger Cu–Zn interaction. In order to prove this result, the chemical state of ZnO in xZnO@yCu\(_2\)O was also characterized by XPS. As shown in Figure 3d, all xZnO@yCu\(_2\)O samples presented the same characteristic peak of Zn \(2p_{3/2}\) with ZnO-400. This indicated that the valence state of the Zn species was kept during the growth of the Cu\(_2\)O shell in the second step. However, by carefully comparing these samples, it could be observed that the binding energy of Zn \(2p_{3/2}\) peak of 4ZnO@Cu\(_2\)O and ZnO@4Cu\(_2\)O shifted toward a higher one by 0.32 eV than that of ZnO (1022.82 eV vs.1022.50 eV). However, for ZnO@20Cu\(_2\)O (1022.58 eV), it only shifted about 0.08 eV. These results indicated that the redistribution of electrons between the metals occurred due to the interaction between Cu and Zn [39], and the thin Cu\(_2\)O shell in the xZnO@yCu\(_2\)O catalysts had a Cu–Zn interaction rather than the thick ones. These were in accordance with the Cu 2p XPS results.

Figure 3. (a) XRD patterns of xZnO@yCu\(_2\)O catalyst. (b) The ratio of Cu\(_2\)O (200) facet/(111) facet on different catalysts. (c) Cu 2p XPS diagrams and (d) Zn 2p XPS diagrams of different shell thickness catalysts.

2.2. ECR Performance of ZnO Catalysts on the Catalyst
2.2.1. ZnO Catalysts

The electrochemical CO\(_2\) reduction performance of ZnO particles as the core was first measured by chronic amperometry in a flow cell with KOH as the electrolyte. As shown in Figure 4, all ZnO particles showed high CO selectivity. However, the H\(_2\) selectivity showed the opposite trend of CO, and almost no methane was produced. The ZnO-400 sample presented the best CO selectivity at \(-0.8\)–\(-1.0\) V (vs. RHE), and the highest CO Faraday efficiency of 89.8% was achieved due to its large specific surface area and the highest proportion of ZnO (101) and (002) facets. According to the literature [40], the (101) and (002) facets of ZnO have a strong COOH\(^*\) binding capacity and weak CO\(^*\) adsorption
capacity, therefore, they play a decisive role in the electroreduction of CO$_2$ to produce CO. As for the ZnO-600 and ZnO-800 samples, the CO selectivity was reduced significantly by 20% because of the increase of the particle size and the decrease of (101) and (002) facets. Among these ZnO samples, the ZnO-400 sample also exhibited the highest current density (Figure 4d). The increase of current density at a high overpotential was probably due to the reinforcement of the hydrogen evolution reaction [41].

2.2.2. ZnO-400, Cu$_2$O, and ZnO@4Cu$_2$O Catalysts

As a comparison, the ECR performance of Cu$_2$O and ZnO@4Cu$_2$O catalysts was carried out in Figure 5. The main product of the ZnO catalyst was CO, which was proved above. At the low overpotential, the CO and H$_2$ dominated the products over the Cu$_2$O catalysts. As the overpotential increased, the selectivity of HCOOH, C$_2$H$_4$, and C$_2$H$_5$OH increased significantly with the inhibition of hydrogen evolution reaction, and HCOOH became the main product. C$_2$H$_4$ and C$_2$H$_5$OH were also first monitored at $-0.6$ V vs. RHE and then gradually increased with applied potential. The best performance of 15.2% C$_2$H$_4$ and 10.5% C$_2$H$_5$OH on Cu$_2$O was obtained, which was similar to the report [42,43]. Compared to the Cu$_2$O and ZnO catalysts, the selectivity of C$_2$ products at a high overpotential was significantly boosted over the ZnO@4Cu$_2$O catalyst (49.8% at $-1.0$ V vs. RHE), with the inhibition of HCOOH. These results indicated that the introduction of ZnO with high activity of CO$_2$ to CO enhanced the CO–CO dimerization to generate C$_2$H$_4$, which was probably attributed to the high stability of OCCOH$^*$ intermediate on Cu$^+$ derived from the Zn–Cu interaction, and the high selectivity of the coordinating transfer electron to facilitate the C$_2$ products.

**Figure 4.** Faradaic efficiency on (a) ZnO-400, (b) Zn-600, and (c) ZnO-800. (d) The total current density of products on different ZnO catalysts.
2.2.3. xZnO@yCu2O Catalysts

The performance of the electrochemical CO2 reduction over the xZnO@yCu2O catalysts with different Cu2O shell thickness and ZnO~400 as the core was carried out. As shown in Figure 6, besides the H2, CO, CH4, and HCOOH, the C2 products including ethylene and ethanol were obtained. The selectivity of CH4 over all catalysts was maintained at a very low level (almost near zero). As for the 4ZnO@Cu2O catalyst, the main products were still CO and H2. The selectivity of CO increased with the increase of the applied overpotential and reached the maximum (ca. 60%) at −1.0 V vs. RHE. This result was similar to that of the ZnO core because the Cu2O shell was too thin. Almost the same selectivity of HCOOH (ca. 10%) in different overpotentials was achieved. Moreover, with an overpotential beyond −0.6 V vs. RHE, C2H5OH was detected and increased up to 10.2% at −0.8 V vs. RHE and then gradually decreased to zero at −1.2 V vs. RHE. Simultaneously, the C2H4 product appeared at −0.8 V vs. RHE and reached about 5.1~6.4% at high potential (−1.0 V~−1.2 V vs. RHE). When the thickness of the Cu2O shell increased, the selectivity of HCOOH, C2H4, and C2H5OH products increased significantly. As for the ZnO@4Cu2O and ZnO@20Cu2O catalysts, HCOOH and CO became the main products at a low overpotential. C2H4 and C2H5OH products were initially detected at a low potential of −0.4 V vs. RHE with the selectivity of C2H5OH being a little higher than that of C2H4 over the ZnO@4Cu2O catalyst, which quickly increased as the applied potential increased. With an applied potential over the −0.8 V vs. RHE, the Faradaic efficiency of C2H4 increased quickly and was significantly higher than that of C2H5OH. Thus, C2H4 became the main product over the ZnO@4Cu2O and the best faradaic efficiency of 33.5% was obtained at −1.0 V vs. RHE. As for the ZnO@20Cu2O catalyst, the C2H4 and C2H5OH products were first detected at −0.6 V vs. RHE and then gradually increased. When the applied potential was below −0.8 V vs. RHE, the selectivity of the C2H5OH product was a little higher than that of C2H4. At a high potential (−1.0~−1.2 V vs. RHE), the products were also dominated by CO and C2H4, and the faradaic efficiency of C2H4 was also significantly higher than that of C2H5OH. ZnO@20Cu2O exhibited almost the same product distribution with the Cu2O sample, which was due to the thick Cu2O shell, and the ZnO sites lose their function. Obviously, the xZnO@yCu2O catalysts showed different selectivity on C2H4 and C2H5OH at −0.8 V vs. RHE. As the shell thickness increased, the total current also increased, espe-
cially at a high overpotential. The highest total current density of 140.1 mA cm\(^{-2}\) with the partial current of C\(_2\) products at 70 mA cm\(^{-2}\) on ZnO@4Cu\(_2\)O was achieved at \(-1.0\) V vs. RHE (Figure 6d). The ZnO@20Cu\(_2\)O catalyst with a thick Cu\(_2\)O shell presented a much higher total current density than the Cu\(_2\)O catalyst at a high overpotential. These results indicated that the distribution of the product depended on the shell thickness, and the suitable shell thickness could significantly enhance the C–C coupling of CO. These could be probably attributed to the interaction and synergetic effect of the ZnO core and Cu\(_2\)O shell, where ZnO@4Cu\(_2\)O exhibited the strongest interaction between ZnO and Cu\(_2\)O.

![Figure 6](image-url)

**Figure 6.** Faradaic efficiency of products on xZnO@yCu\(_2\)O catalysts (a) 4ZnO@Cu\(_2\)O, (b) ZnO@4Cu\(_2\)O, and (c) ZnO@20Cu\(_2\)O. (d) The total current density of products on xZnO@yCu\(_2\)O catalysts.

The selectivity of C\(_2\) products (C\(_2\)H\(_4\) and C\(_2\)H\(_5\)OH) over different xZnO@yCu\(_2\)O catalysts is further summarized in Figure 7a. The selectivity of the C\(_2\) product showed a clear volcanic curve on all catalysts. Only low selectivity of C\(_2\) products was achieved beyond the 4ZnO@Cu\(_2\)O catalyst, probably because the Cu\(_2\)O shell was too thin to provide enough residence time for C–C coupling of CO. The ZnO@4Cu\(_2\)O catalyst exhibited the highest Faradaic efficiency of C\(_2\) products (49.8%, FE \(_{\text{ethylene}} = 33.5\%\) and FE \(_{\text{ethanol}} = 16.3\%) under \(-1.0\) V vs. RHE, which was almost twice that of the Cu\(_2\)O catalyst. The ZnO@20Cu\(_2\)O catalyst showed a similar selectivity of C\(_2\) products with the Cu\(_2\)O catalyst at a low overpotential. However, at a high overpotential, ZnO@20Cu\(_2\)O had a higher selectivity of C\(_2\) products than the Cu\(_2\)O catalyst (30% for ZnO@20Cu\(_2\)O and 25.7% for Cu\(_2\)O at \(-1.0\) V vs. RHE). The C\(_2\) products selectivity on ZnO@20Cu\(_2\)O was lower than ZnO@4Cu\(_2\)O at high potential (30% vs. 49.8%). ZnO@20Cu\(_2\)O had too thick a Cu\(_2\)O shell and the function of ZnO core might be reduced, accounting for less intermediate CO* and inhibition of the C–C coupling process. The selectivity of C\(_2\) products corresponded to the ratio of the Cu\(_2\)O (200)/(111) facet analyzed earlier. The interface of the Cu\(_2\)O (200) facet and (111) could strengthen the CO–CO coupling, due to the strong *CO binding capacity and weak C\(_2\)H\(_4\) adsorption capacity. The FE values of the C\(_2\) products and the total current over ZnO@4Cu\(_2\)O were among the best reported in flow-cell and surpassed most reports in the H-cell (Figure 7b, Table S4) [18,37,44–47].
The comparison of total current density and selectivity of C2 products between this work with others.

2.3. Electrochemical Characterization on xZnO@yCu2O Catalysts

To gain insights into the role of the ZnO core on the ECR performance of xZnO@yCu2O and enhancement of the C2 products (C2H4 and C2H5OH), the electrochemical active surface area (ECSA), electrochemical impedance, and electrokinetic were further determined. As shown in Figure 8a, the ZnO@4Cu2O catalyst showed the highest ECSA value (0.47 mF cm−2), indicating that more active sites were generated. The electrochemical impedance spectroscopy in Figure 8b showed that the ZnO@4Cu2O catalyst had the smallest charge transfer resistance of 2.84 Ω. This result suggested that the introduction of the ZnO core facilitated the electron transfer between the electrolyte and the electrocatalysts. Moreover, the LSV curves in Figure 8c illustrate that the ZnO@4Cu2O catalyst had the lowest initial overpotential for ECR. Additionally, the lower overpotential and higher current density were obtained in the KHCO3 electrolyte saturated with CO2 than in the electrolyte saturated with Ar. This indicated that the core-shell ZnO@4Cu2O catalyst could inhibit the hydrogen evolution reaction better than Cu2O, facilitating the improvement of C2 products selectivity and current density. As shown in Figure 8d, the ratio of C2 products/HCOOH on the ZnO@4Cu2O catalyst was almost two times higher than that on Cu2O (2.07 vs. 0.73). This indicated that the introduction of the ZnO core could significantly promote the selectivity of the coordinating transfer electron to generate the C2 products [48]. As previously reported, the Tafel slopes could provide some insights into the reaction mechanism. Tafel analyses of ethylene and ethanol production from electrochemical CO2 reduction on the xZnO@yCu2O catalysts were also carried out. As shown in Figure 8e, the ZnO@4Cu2O catalysts gave the smallest slopes of 46.9 mV dec−1 for C2H4 production, indicating that it had a faster electrode kinetic than other samples. Similar slopes for C2H4 production were also observed on the ZnO@20Cu2O, Cu2O, and 4ZnO@Cu2O catalysts, suggesting that the thickness of the Cu2O shell changed the overall rate-determining step. The same trend of Tafel slopes for ethanol production on these catalysts were also observed. The ZnO@4Cu2O catalyst still gave the smallest slope of 46.5 mV dec−1 for C2H6O. Additionally, the Tafel slopes of 46.9 and 46.5 mV dec−1 also suggested that the electron transfer to CO2 was not the rate-determining step for CO2 reduction [49]. The higher C2H4 and C2H5O production rate on the ZnO@4Cu2O catalyst indicated that C–C coupling was fast once the electrocatalytic CO2 reduction initiated.
Based on the above discussion, the high ECR activity of ZnO@4Cu2O could be attributed to several factors. As shown in Figure 3b, the ZnO@4Cu2O catalyst exposed a more enhanced joint interface between the (200) and (111) facets, due to the highest ratio of (200)/(111) facets, which could facilitate the C–C coupling to produce C2+ products [50]. The introduction of the ZnO core in the core-shell ZnO@4Cu2O catalyst enlarged the electrochemically active surface, lowered the electron transfer resistance between the electrolyte and the electrocatalysts, and enabled the ZnO@4Cu2O catalyst to have a higher overpotential of HER to inhibit H2O reduction and improve the efficiency of CO2 electroreduction to C2 products. Additionally, it also significantly promoted the selectivity of the coordinating transfer electron to generate C2+ products, probably due to the high CO production activity of the ZnO core. Moreover, the core-shell ZnO@4Cu2O catalysts had the faster electrode kinetic for C2 production. Therefore, the high electrochemical activity of ZnO@4Cu2O for ECR to C2 products most likely originated from the synergetic effects of the ZnO core and the Cu2O shell, which could not only generate a large electrochemical surface area, improve the HER overpotential, and fasten electron transfer, but could also promote the multielectron involved kinetics for ethylene and ethanol production.
3. Materials and Methods

3.1. Materials

Zinc acetate (C$_4$H$_6$O$_4$Zn, 99.99%, Macklin, Shanghai, China), deuterium oxide (D$_2$O, 99.9%, Macklin), potassium hydrogen carbonate (KHCO$_3$, 99.7–100% (dried basis), Alfa, Stony Brook, NY, USA), and dimethyl sulfoxide (DMSO, AR > 99.9%, Alfa) were used as received. Methoxy polyethylene glycol (CH$_3$O(C$_2$H$_4$O)$_n$H, M$_n$ = 5000), ammonium citrate (C$_6$H$_5$O$_7$(NH$_4$)$_3$, AR 98.5%), ammonia solution (NH$_3$·H$_2$O, AR, 25%~28%), copper nitrate trihydrate (Cu(CH$_3$COO)$_2$, 99.5%), potassium hydroxide (KOH, 99.99%), isopropyl alcohol (C$_3$H$_8$O, AR ≥ 99.5%, Aladdin, Seattle, WA, USA), and potassium chloride (KCl, AR, 99.5%) were purchased from Aladdin. Ethanol (C$_2$H$_6$O, 99.9%, Tianjin Yuanli Chemical Co., Ltd., Tianjin, China), hydrazine hydrate (N$_2$H$_4$·H$_2$O, 35% of volume fraction), Nafion 117 solution (5%, Sigma-Aldrich, St. Louis, MO, USA), and carbon-based gas diffusion layer (GDL, China, Wuhan, Gaoshiruilian Technology Co., Ltd., Wuhan, China) were purchased from the specified suppliers. Ultrapure water (18.2 MΩ cm$^{-1}$) was homemade by a Millipore system (Milli-Q Advantage A10).

3.2. Preparation of Catalysts

3.2.1. Synthesis of ZnO Catalysts

The ZnO core was prepared by a sol–gel method according to the reference [51]. A total of 0.015 mol of zinc acetate powder, 0.0076 mol of ammonium citrate, and 15 mL of ultrapure water were dissolved into a 100 mL beaker. These mixtures were mixed at room temperature. Then, 2 mL of ammonia solution and 25 mL of ethanol was added to the mixture and stirred at 75°C for 120 min, and then the mixture was cooled to room temperature and aged for an additional 120 min. Finally, ammonia aqueous was dropped into the obtained solution under stirring, until the precipitate disappeared completely to form a wet gel. Then, the gel was dried at 90°C for 720 min and calcined at different temperatures for 120 min in a muffle furnace. The size of ZnO was controlled by calcination at different temperatures (400°C, 600°C, and 800°C), the heating rate was 5°C/min. The final products were denoted as ZnO-400, ZnO-600, and ZnO-800, respectively.

3.2.2. Preparation of the ZnO@Cu$_2$O Catalyst

The cuprous oxide shell was prepared using the epitaxial shell growth approach [52]. A total of 120 mL (2 wt.%) of polyethylene glycol methyl ether, 0.0002 mol as-synthesized ZnO core, and 2 mL of 0.1 M Cu(NO$_3$)$_2$ were mixed under stirring at room temperature. A total of 0.1 mL of hydrazine hydrate (35 wt.%) was then added under stirring for an additional 5 min. Then, after the same post-treatment with ZnO@Cu$_2$O, the Cu$_2$O samples were obtained.

3.2.3. Synthesis of Cu$_2$O Catalyst

A reference Cu$_2$O sample was also prepared in the same method with the Cu$_2$O shell in ZnO@Cu$_2$O. A total of 120 mL of polyethylene glycol methyl ether (2 wt.%) and 2 mL of 0.1 M Cu(NO$_3$)$_2$ were mixed under stirring at room temperature. A total of 0.1 mL of hydrazine hydrate (35 wt.%) was then added under stirring for an additional 5 min. Then, after the same post-treatment with ZnO@Cu$_2$O, the Cu$_2$O samples were obtained.

3.2.4. Preparation of Gas Diffusion Electrode

The gas diffusion electrode (GDE) was prepared according to the reference [53]. A total of 3 mL of isopropanol, 0.066 mL of Nafion solution, and 50 mg of the above as-synthesized powder was added to the beaker and well mixed. The mixture was handled
by ultrasonication for 60 min to obtain the catalyst ink. Then, the ink was dropped on a gas diffusion layer (GDL, 3.5 cm × 1.5 cm) with a catalyst loading of 1 mg cm⁻². The prepared gas diffusion electrode (GDE) was dried overnight for use.

3.3. Characterizations

The morphology and structure of the catalysts were characterized by scanning electron microscope (SEM, Hitachi S-4800, Tokyo, Japan), transmission electron microscope (TEM, JEM-F200, JEOL, Tokyo, Japan), and high-resolution TEM (HRTEM). The element distribution was analyzed by energy dispersive spectroscopy (EDS, Oxford Industries, Atlanta, GA, USA). The X-ray diffraction (XRD) pattern was collected on a D/MAX-2500 (Rigaku, Tokyo, Japan) equipped with a Cu Kα X-ray source (λ = 0.1541 nm) at 40 kV and 40 mA, the scanning range was 20–90°, and the scanning speed was 5°/min. The atomic ratio of Zn and Cu was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, VISTA-MPX, Varian, Palo Alto, CA, USA). The X-ray photoelectron spectroscopy (XPS, Thermal Fisher, Waltham, MA, USA) was determined by ESCALAB 250Xi (Thermal Fisher, Waltham, MA, USA), using Al Kα X-ray source (hν = 1486.6 eV) and the binding energy was calibrated with C 1s spectra (binding energy = 284.8 eV).

3.4. Electrochemical CO₂ Reduction

The electrochemical CO₂ reduction was carried out in a flow electrolyzer. The cathode compartment and anode compartment of the flow cell were separated by ion-exchange membranes. The prepared GDE was used as the working electrode. GDL (3.5 cm × 1.5 cm) loaded with IrO₂ and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. All experiments were performed on the AutoLab (Model PGSTAT302 N, Metrohm AG, Herisau, Switzerland). The electrolyte, 1 M KOH, was pumped through the cell at the flow rate of 1.5 mL min⁻¹. CO₂ was introduced at a flow rate of 20 mL min⁻¹ to exhaust the air and saturated the electrolyte solution. The Faraday efficiency of the product on all samples was calculated using Equations (1–3) in the supplementary materials. Equipment should be checked for leaks of gas and liquid before starting the experiment.

During the electrochemical CO₂ reduction process, the gas product was quantitatively analyzed by online gas chromatography (GC, GC-2010, Shimadzu, Kyoto, Japan) equipped with a BID detector. After the reaction, the cathode liquid products were quantitatively analyzed with a liquid nuclear magnetic resonance spectrometer (400 MHz). The electrochemical analysis was carried out in an H-Cell. The cathode chamber and anode chamber were separated by a proton exchange membrane. Platinum mesh and the Ag/AgCl electrode were used as the counter electrode and the reference electrode. The 0.1 M KHCO₃ solution was used as the electrolyte. Cyclic voltammetry in the range of 0.45~0.84 V vs. RHE was carried out to measure the double-layer capacitance of the catalyst for the electrochemical CO₂ reduction at the scanning rate of 50 mV s⁻¹, 100 mV s⁻¹, 150 mV s⁻¹, 200 mV s⁻¹, 250 mV s⁻¹, and 300 mV s⁻¹. The redox peaks of the catalysts were explored by cyclic voltammetry at −1.31 V~0.69 V vs. RHE, with a scan rate of 100 mV s⁻¹. Linear sweep voltammetry was carried out at −1.31 V~0.69 V vs. RHE with a sweep rate of 10 mV s⁻¹ in the electrolyte saturated with CO₂ and Ar, respectively. The electrochemical impedance spectroscopy of the catalyst was performed in the 0.1 M KHCO₃ electrolyte saturated with CO₂ at −1.0 V vs. RHE from 0.01 Hz to 10⁵ Hz.

4. Conclusions

In summary, we synthesized a new type of catalyst with zinc core-copper shell by the sol–gel method and epitaxial shell growth method. Due to the double active sites on the ZnO@4Cu₂O catalyst, it was possible to get the CO₂ to first generate CO at the ZnO site, and then the CO coupled on Cu₂O to generate the C₂ product. The synergistic effect of Cu and Zn enhanced the selectivity of C₂ products on the catalyst. The core-shell ZnO@4Cu₂O enclosed with the enhanced joint interface of Cu₂O (111) and Cu₂O (200)
facets and high ECSA, exhibited the best C\textsubscript{2} product selectivity of 49.8\% (ethylene 33.5\%, ethanol 16.3\%) and a high total current density of 140.1 mA cm\textsuperscript{-2}. This core-shell structure could strengthen the synergy between Cu and Zn oxides to simultaneously improve the selectivity of C\textsubscript{2} products and the total current. The product distribution depended on the shell thickness, and the suitable shell thickness could significantly enhance the C–C coupling of CO. The thickness of the Cu\textsubscript{2}O shell in xZnO@yCu\textsubscript{2}O could change the overall rate-determining step. Our work might provide some new insights for developing novel high-efficiency catalysts and enhancing the selectivity of electrochemical CO\textsubscript{2} reduction to produce high-value C\textsubscript{2} products.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/catal11105035/s1. Figure S1: TEM image of (a) 4ZnO@Cu\textsubscript{2}O and (b) ZnO@20Cu\textsubscript{2}O. The line EDX analysis along the arrow (c) 4ZnO@Cu\textsubscript{2}O and (d) ZnO@20Cu\textsubscript{2}O. Figure S2: XRD pattern of Cu\textsubscript{2}O and its PDF card. Figure S3: Cu LMM Auger spectra of xZnO@yCu\textsubscript{2}O catalysts with different shell thickness. Figure S4: The ratio of Cu\textsuperscript{2+}/Cu\textsuperscript{0} with different shell thickness catalysts. Figure S5: The current density of C\textsubscript{2} products on xZnO@yCu\textsubscript{2}O catalysts with different shell thickness. Figure S6: Cyclic voltammograms of different catalysts in 0.1 M KHCO\textsubscript{3} (CO\textsubscript{2}-saturated) at scan rates of 50 mV s\textsuperscript{-1}, 100 mV s\textsuperscript{-1}, 150 mV s\textsuperscript{-1}, 200 mV s\textsuperscript{-1}, 250 mV s\textsuperscript{-1}, and 300 mV s\textsuperscript{-1}. (a) Cu\textsubscript{2}O; (b) ZnO@20Cu\textsubscript{2}O; (c) ZnO@4Cu\textsubscript{2}O; (d) ZnO@8Cu\textsubscript{2}O; (e) ZnO; and (f) double-layer capacitance measured by cyclic voltammetry in 0.1 M KHCO\textsubscript{3} saturated by CO\textsubscript{2} on the catalysts with different shell thickness. Figure S7: The particle size distribution of (a) ZnO-400, (b) ZnO-600, and (c) ZnO-800. Figure S8: The particle size distribution of (a) Cu\textsubscript{2}O, (b) ZnO@4Cu\textsubscript{2}O, (c) ZnO@8Cu\textsubscript{2}O, and (d) ZnO@20Cu\textsubscript{2}O. Figure S9: The flow cell used for electrochemical reduction of CO\textsubscript{2}. Table S1: Proportion of elements in the sample measured by ICP-OES. Table S2: The intensity and proportion of different facets of ZnO in the xZnO@yCu\textsubscript{2}O catalyst. Table S3: The intensity and proportion of significant facets of Cu\textsubscript{2}O in xZnO@yCu\textsubscript{2}O catalyst. Table S4: Comparison of multicarbon product formation from various Cu-based catalysts. Table S5: The distribution of products at different applied potentials on ZnO@4Cu\textsubscript{2}O catalyst. Table S6: The distribution of products at different applied potentials on Cu\textsubscript{2}O catalyst. Table S7: The resistance of different catalysts.

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**References**

1. Goeppert, A.; Czaun, M.; Jones, J.P.; Prakash, G.K.S.; Olah, G.A. Recycling of carbon dioxide to methanol and derived products—closing the loop. *Chem. Soc. Rev.* 2014, 43, 7995–8048. [CrossRef]

2. Zhang, H.C.; Chang, X.X.; Chen, J.G.G.; Goddard, W.A.; Xu, B.J.; Cheng, M.J.; Lu, Q. Computational and experimental demonstrations of one-pot tandem catalysis for electrochemical carbon dioxide reduction to methane. *Nat. Commun.* 2019, 10, 3340. [CrossRef]

3. Zhu, D.D.; Liu, J.L.; Qiao, S.Z. Recent advances in inorganic heterogeneous electrocatalysts for reduction of carbon dioxide. *Adv. Mater.* 2016, 28, 3423–3452. [CrossRef]

4. Liu, Y.M.; Fan, X.F.; Nayak, A.; Wang, Y.; Shan, B.; Quan, X.; Meyer, T.J. Steering CO\textsubscript{2} electroreduction toward ethanol production by a surface-bound Ru polypryidyl carbene catalyst on N-doped porous carbon. *Proc. Natl. Acad. Sci. USA* 2019, 116, 26353–26358. [CrossRef]

5. Li, D.; Liu, T.T.; Huang, L.L.; Wu, J.J.; Li, N.; Zhen, L.; Feng, Y.J. Selective CO\textsubscript{2}–to–formate electrochemical conversion with core–shell structured Cu\textsubscript{2}O/Cu@C composites immobilized on nitrogen-doped graphene sheets. *J. Mater. Chem. A* 2020, 8, 18302–18309. [CrossRef]

6. Li, J.C.; Kuang, Y.; Meng, Y.T.; Tian, X.; Hung, W.H.; Zhang, X.; Li, A.W.; Xu, M.Q.; Zhou, W.; Ku, C.S.; et al. Electroreduction of CO\textsubscript{2} to formate on a copper-based electrocatalyst at high pressures with high energy conversion efficiency. *J. Am. Chem. Soc.* 2020, 142, 7276–7282. [CrossRef]
Catalysts 2021, 33. Tsai, Y.H.; Chanda, K.; Chu, Y.T.; Chiu, C.Y.; Huang, M.H. Direct formation of small Cu nanowires for low-overpotential CO₂ reduction. Nano Lett. 2015, 15, 6829–6835. [CrossRef] [PubMed]

25. Gao, J.; Ren, D.; Guo, X.Y.; Zakeeruddin, S.M.; Gratzel, M. Sequential catalysis enables enhanced C–C coupling towards multi-carbon alkenes and alcohols in carbon dioxide reduction: A study on bifunctional Cu/Au electrocatalysts. ChemElectroChem 2020, 7, 204–212. [CrossRef]

23. Ning, H.; Mao, Q.H.; Wang, W.H.; Yang, Z.X.; Wang, X.S.; Zhao, Q.S.; Song, Y.; Wu, M.B. N-doped reduced graphene oxide to C₂H₂OH at low potential. Small 2020, 16, 1901981. [CrossRef] [PubMed]

22. Han, H.; Noh, Y.; Kim, Y.; Park, S.; Yoon, W.; Jiang, D.; Choi, S.M.; Kim, W.B. Selective electrochemical CO₂ conversion to multi-carbon alcohols on highly efficient N-doped porous carbon-supported Cu catalysts. Green Chem. 2020, 22, 71–84. [CrossRef]

21. Bai, X.W.; Li, Q.; Shi, L.; Niu, X.H.; Ling, C.Y.; Wang, J.L.; Hu, H.; et al. Interface-induced controllable synthesis of Cu₂O nanocubes as high active catalyst for CO₂ reduction. J. Alloys Compd. 2020, 8681–8689. [CrossRef] [PubMed]

20. Wang, W.H.; Ning, H.; Yang, Z.X.; Feng, Z.X.; Wang, J.L.; Wang, X.S.; Mao, Q.H.; Wu, W.T.; Zhao, Q.S.; Hu, H.; et al. Interface-induced controllable synthesis of Cu₂O nanocubes for electroreduction CO₂ to C₂H₄. Electrochim. Acta. 2019, 306, 360–365. [CrossRef]

19. Lee, S.Y.; Jung, H.; Kim, N.K.; Oh, H.S.; Min, B.K.; Hwang, Y.J. Mixed copper states in anodized Cu electrocatalyst for stable and selective ethylene production from gas-phase CO₂. Faraday Discuss. 2019, 215, 282–296. [CrossRef] [PubMed]

18. Ren, D.; Gao, J.; Guo, X.Y.; Zakeeruddin, S.M.; Gratzel, M. Sequential catalysis enables enhanced C–C coupling towards multi-carbon alkenes and alcohols in carbon dioxide reduction: A study on bifunctional Cu/Au electrocatalysts. Faraday Discuss. 2019, 215, 282–296. [CrossRef] [PubMed]

17. Lomuscio, D.; Scricciolo, C.; Belser, C.; Cicala, C.; Zanotti, D.; Boaro, M.; Bruni, F.; Di Fabrizio, A. Hierarchically porous Cu/Nb bimetallic catalysts for highly selective CO₂ electroreduction to liquid C₂ products. Appl. Catal. B Environ. 2020, 269, 118800. [CrossRef]

16. Wang, W.H.; Ning, H.; Yang, Z.X.; Feng, Z.X.; Wang, J.L.; Wang, X.S.; Mao, Q.H.; Wu, W.T.; Zhao, Q.S.; Hu, H.; et al. Interface-induced controllable synthesis of Cu₂O nanocubes for electroreduction CO₂ to C₂H₄. Electrochim. Acta. 2019, 306, 360–365. [CrossRef]

15. Zhuang, T.T.; Liang, Z.Q.; Seifitokaldani, A.; Li, Y.; De Luna, P.; Burdyny, T.; Che, F.L.; Meng, F.; Min, Y.M.; Quintero-Bermudez, R. Selectivity roadmap for electrochemical CO₂ reduction. Angew. Chem. Int. Ed. 2018, 57, 5789–5792. [CrossRef]

14. Kim, D.; Lee, S.; Ocon, J.D.; Jeong, B.; Lee, J.K.; Lee, J. Insights into an autonomously formed oxygen-activated Cu₂O electrode for the selective production of C₂H₄ from CO₂. Phys. Chem. Chem. Phys. 2015, 17, 824–830. [CrossRef]

13. Liu, Y.; Zheng, Y.; Vasileff, A.; Qiao, S.Z. Selectivity roadmap for electrochemical CO₂ reduction. ChemElectroChem 2020, 7, 204–212. [CrossRef]

12. Han, H.; Noh, Y.; Kim, Y.; Park, S.; Yoon, W.; Jiang, D.; Choi, S.M.; Kim, W.B. Selective electrochemical CO₂ conversion to multi-carbon alcohols on highly efficient N-doped porous carbon-supported Cu catalysts. Green Chem. 2020, 22, 71–84. [CrossRef]

11. Bai, X.W.; Li, Q.; Shi, L.; Niu, X.H.; Ling, C.Y.; Wang, J.L. Hybrid Cu²⁺ and Cu⁺ as atomic interfaces promote high-selectivity conversion of CO₂ to C₂H₂OH at low potential. Small 2020, 16, 1901981. [CrossRef] [PubMed]

10. Wang, W.H.; Ning, H.; Yang, Z.X.; Feng, Z.X.; Wang, J.L.; Wang, X.S.; Mao, Q.H.; Wu, W.T.; Zhao, Q.S.; Hu, H.; et al. Interface-induced controllable synthesis of Cu₂O nanocubes for electroreduction CO₂ to C₂H₄. Electrochim. Acta. 2019, 306, 360–365. [CrossRef]

9. Chen, C.J.; Sun, X.F.; Lu, L.; Yang, D.X.; Ma, J.; Zhu, Q.G.; Qian, Q.L.; Han, B.X. Efficient electroreduction of CO₂ to C₂ products over B-doped oxide-derived copper. Green Chem. 2018, 20, 4579–4583. [CrossRef] [PubMed]

8. Ren, D.; Deng, Y.L.; Handoko, A.D.; Chen, C.S.; Malkhandi, S.; Yeo, B.S. Selective electrochemical reduction of carbon dioxide to ethylene and ethanol on copper(I) oxide catalysts. ACS Catal. 2015, 5, 2814–2821. [CrossRef] [PubMed]

7. Tan, Z.H.; Peng, T.Y.; Tian, X.J.; Wang, W.H.; Wang, X.S.; Yang, Z.X.; Ning, H.; Zhao, Q.S.; Wu, M.B. Controllable synthesis of Leaf-Like CuO Nanosheets for Selective CO₂ Electroreduction to Ethylene. ChemElectroChem 2020, 7, 2020–2025. [CrossRef] [PubMed]

6. Wang, M.; Ren, X.N.; Yuan, G.; Niu, X.P.; Xu, Q.L.; Gao, W.L.; Zhu, S.K.; Wang, Q.F. Selective electroreduction of CO₂ to CO over co-electrodeposited dendritic core-shell indium-doped Cu₂CuO catalyst. J. CO₂ Util. 2020, 37, 204–212. [CrossRef] [PubMed]

5. Payra, S.; Shenoy, S.; Chakraborty, C.; Taranedde, K.; Roy, S. Structure-sensitive electrocatalytic reduction of CO₂ to methanol over carbon-supported intermetallic PtZn nano-arrays. ACS Appl. Mater. Inter. 2020, 12, 19042–19144. [CrossRef] [PubMed]

4. Han, J.; Li, S.S.; Chen, J.Y.; Liu, Y.Q.; Geng, D.S.; Wang, D.W.; Zhang, L.C. Dendritic Ag/Pd Alloy Nanostructure Arrays for Electrochemical CO₂ Reduction. ChemElectroChem 2020, 7, 2608–2613. [CrossRef] [PubMed]

3. Zhi, X.; Jiao, Y.; Zheng, Y.; Vasileff, A.; Qiao, S.Z. Selectivity roadmap for electrochemical CO₂ reduction on copper-based alloy catalysts. Nano Today 2020, 71, 103180. [CrossRef] [PubMed]

2. Raciti, D.; Livio, K.J.; Wang, C. Highly dense Cu nanowires for low-overpotential CO₂ reduction. Nano Lett. 2015, 15, 6829–6835. [CrossRef] [PubMed]
34. Chen, C.J.; Yan, X.P.; Liu, S.J.; Wu, Y.H.; Wan, Q.; Sun, X.F.; Zhu, Q.G.; Liu, H.Z.; Ma, J.; Zheng, L.R.; et al. Highly efficient electroreduction of CO\(_2\) to C\(_2\)\(_2\), alcohols on heterogeneous dual active sites. *Angew. Chem. Int. Ed.* 2020, 59, 16439–16464. [CrossRef] [PubMed]

35. Schouten, K.J.P.; Qin, Z.S.; Gallent, E.P.; Koper, M.T.M. Two Pathways for the Formation of Ethylene in CO Reduction on Single-Crystal Copper Electrodes. *J. Am. Chem. Soc.* 2012, 134, 9864–9867. [CrossRef]

36. Xu, H.P.; Rebollar, D.; He, H.Y.; Chong, L.N.; Liu, Y.Z.; Li, C.; Sun, C.J.; Li, T.; Muntean, J.V.; Winans, R.E.; et al. Highly selective electrocatalytic CO(2) reduction to ethanol by metallic clusters dynamically formed from atomically dispersed copper. *Nat. Energy* 2020, 5, 623–632. [CrossRef]

37. Song, H.; Song, J.T.; Kim, B.; Tan, Y.C.; Oh, J. Activation of C\(_2\)H\(_4\) reaction pathways in electrochemical CO\(_2\) reduction under low CO\(_2\) partial pressure. *Appl. Catal. B Environ.* 2020, 272, 119049. [CrossRef]

38. Shao, Q.; Wang, P.T.; Liu, S.H.; Huang, X.Q. Advanced engineering of core/shell nanostructures for electrochemical carbon dioxide reduction. *J. Mater. Chem. A.* 2019, 7, 20478–20493. [CrossRef]

39. Liu, K.H.; Wang, J.Z.; Shi, M.M.; Yan, J.M.; Jiang, Q. Simultaneous Achieving of High Faradaic Efficiency and CO Partial Current Density for CO\(_2\) Reduction via Robust, Noble-Metal-Free Zn Nanosheets with Favorable Adsorption Energy. *Adv. Energy Mater.* 2019, 9, 1900276. [CrossRef]

40. Birdja, Y.Y.; Perez-Gallent, E.; Figueiredo, M.C.; Gottle, A.J.; Calle-Vallejo, F.; Koper, M.T.M. Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels. *Nat. Energy* 2019, 4, 732–745. [CrossRef]

41. Tan, X.Y.; Yu, C.; Zhao, C.T.; Huang, H.W.; Yao, X.C.; Han, X.T.; Guo, W.; Cui, S.; Huang, H.L.; Qiu, J.S. Restructuring of Cu\(_2\)O to Cu\(_2\)O@Cu-Metal-Organic Frameworks for Selective Electrochemical Reduction of CO\(_2\). *ACS Appl. Mater. Inter.* 2019, 11, 9904–9910. [CrossRef]

42. Suen, N.T.; Kong, Z.R.; Hsu, C.S.; Chen, H.C.; Tung, C.W.; Lu, Y.R.; Dong, C.L.; Shen, C.C.; Chung, J.C.; Chen, H.M. Morphology Manipulation of Copper Nanocrystals and Product Selectivity in the Electrocatalytic Reduction of Carbon Dioxide. *ACS Catal.* 2019, 9, 5217–5222. [CrossRef]

43. Zhang, J.; Luo, W.; Zuttel, A. Self-supported copper-based gas diffusion electrodes for CO\(_2\) electrochemical reduction. *J. Mater. Chem. A.* 2019, 7, 26285–26292. [CrossRef]

44. Reller, C.; Krause, R.; Volkova, E.; Schmid, B.; Neubauer, S.; Rucki, A.; Schuster, M.; Schmid, G. Selective Electroreduction of CO\(_2\) toward Ethylene on Nano Dendritic Copper Catalysts at High Current Density. *Adv. Energy Mater.* 2017, 7, 1602114. [CrossRef]

45. Shen, S.B.; Peng, X.Y.; Song, L.D.; Qin, Y.; Li, C.; Zhuo, L.C.; He, J.; Ren, J.Q.; Liu, X.J.; Luo, J. AuCu Alloy Nanoparticle Embedded Cu Submicrocone Arrays for Selective Conversion of CO\(_2\) to Ethanol. *Small* 2019, 15, 1902229. [CrossRef] [PubMed]

46. Song, Y.; Peng, R.; Hensley, D.K.; Bonnesen, P.V.; Liang, L.B.; Wu, Z.L.; Meyer, H.M.; Chi, M.F.; Ma, C.; Sumpter, B.G.; et al. High-Selectivity Electrochemical Conversion of CO\(_2\) to Ethanol using a Copper Nanoparticle/N-Doped Graphene Electrode. *ChemistrySelect* 2016, 1, 6055–6061. [CrossRef]

47. Balamurugan, M.; Jeong, H.Y.; Choutipalli, V.S.K.; Hong, J.S.; Sao, H.; Saravanan, N.; Jang, J.H.; Lee, K.G.; Lee, Y.H.; Im, S.W.; et al. Electrocatalytic Reduction of CO\(_2\) to Ethylene by Molecular Cu-Complex Immobilized on Graphitized Mesoporous Carbon. *Small* 2020, 16, 2000955. [CrossRef]

48. Wang, S.; Kou, T.; Baker, S.E.; Duoss, E.B.; Li, Y. Recent progress in electrochemical reduction of CO\(_2\) by oxide-derived copper catalysts. *Mater. Today Nano* 2020, 12, 100096. [CrossRef]

49. Liu, Y.M.; Chen, S.; Quan, X.; Yu, H.T. Efficient Electrochemical Reduction of Carbon Dioxide to Acetate on Nitrogen-Doped Nanodiamond. *J. Am. Chem. Soc.* 2015, 137, 11631–11636. [CrossRef]

50. Gao, Y.G.; Wu, Q.; Liang, X.Z.; Wang, Z.Y.; Zheng, Z.K.; Wang, P.; Liu, Y.Y.; Dai, Y.; Whangbo, M.H.; Huang, B.B. Cu\(_2\)O Nanoparticles with Both (100) and (111) Facets for Enhancing the Selectivity and Activity of CO\(_2\) Electroreduction to Ethylene. *Adv. Sci.* 2020, 7, 1902820. [CrossRef]

51. Liu, Z.F.; Jin, Z.G.; Li, W.; Qiu, J.J. Preparation of ZnO porous thin films by sol-gel method using PEG template. *Mater. Lett.* 2005, 59, 3620–3625. [CrossRef]

52. Zhang, L.; Jing, H.; Boisvert, G.; He, J.Z.; Wang, H. Geometry Control and Optical Tunability of Metal-Cuprous Oxide Core-Shell Nanoparticles. *ACS Nano* 2012, 6, 3514–3527. [CrossRef] [PubMed]

53. Ma, S.C.; Sadakiyo, M.; Luo, R.; Heima, M.; Yamauchi, M.; Kenis, P.J.A. One-step electrolysytion of ethylene and ethanol from CO\(_2\) in an alkaline electrolyzer. *J. Power Sources* 2016, 301, 219–228. [CrossRef]