Article

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

Shuaikang Zhu ¹, Xiaona Ren ¹, Xiaoxue Li ¹, Xiaopo Niu ¹, Miao Wang ¹, Shuang Xu ¹, Zheyuan Wang ¹, Yunxi Han ¹ and Qingfa Wang ^{2,*}

- ¹ Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China; zhushk@tju.edu.cn (S.Z.); xna_ren@tju.edu.cn (X.R.); lixiaoxue@tju.edu.cn (X.L.); xiaoponiu@tju.edu.cn (X.N.); miaowang@tju.edu.cn (M.W.); shuangxu@tju.edu.cn (S.X.); 2018207501@tju.edu.cn (Z.W.); hyx_602002@tju.edu.cn (Y.H.)
- ² Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
- * Correspondence: qfwang@tju.edu.cn; Tel.: +86-139-2037-9125

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

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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, C₂H₆OH, and C₂H₆, 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, Cu₂O films on a Cu disc catalyst was prepared for ECR to improve the selectivity of C₂ 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 Cu₂O catalyst formed at 500 °C would require 0.5 V less overpotential than polycrystalline Cu, to reduce CO₂. Furthermore, interface-induced Cu₂O 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 CO₂ 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 Cu₂O catalyst using the synergy between Cu₂O and pyridinic-N for boosting C₂H₄ selectivity and durability of Cu₂O. 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 Cu₂O active sites are also an important strategy for enhancing ECR [24]. Gao et al. [25] prepared a bimetallic catalyst of Au uniformly supported on Cu₂O. The presence of Au active (an electrocatalyst for CO₂ to CO) helped to increase the coverage of *CO on Cu, thereby strengthening the production of C₂ products on Cu–Au catalysts. The total Faraday Efficiency of C₂ 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 AgCu 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 Zn²⁺. The key intermediate of ethanol products *COCH₃ 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 CO₂ electro conversion [28]. Hence, the catalyst with dual active sites is an effective strategy for electrochemical CO₂ reduction, and it is a promising approach to achieve high selectivity and high current density for C₂ products in a flow cell.

Inspired by these works, we designed and synthesized a catalyst with ZnO core and Cu₂O shell through a wet chemical method. Due to the double active sites on the ZnO@Cu₂O catalyst. It is possible to make CO₂ first generate CO at the ZnO site, and then CO couples on Cu₂O, to generate C₂ product. The synergistic effect of Cu and Zn enhances the selectivity of C₂ products on the catalyst. This core-shell structure was used to enhance the multielectron reactions in electrochemical CO₂ reduction in a flow cell. The thickness of the Cu₂O shell was controlled to boost the coupling of CO on the Cu site to produce C₂ products. By tailoring the synergy of Cu and Zn oxides, a high Faradic efficiency of 49.8% for C₂ 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 C₂ 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.

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 $2\theta = 31.8^\circ$, 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 $2p_{1/2}$ at 1045.63 eV and Zn $2p_{3/2}$ at 1022.47 eV were attributed to Zn^{2+} [29].

2.1.2. $x\text{ZnO}@y\text{Cu}_2\text{O}$ Catalyst

The core-shell $x\text{ZnO}@y\text{Cu}_2\text{O}$ 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 $x\text{ZnO}@y\text{Cu}_2\text{O}$ as well as the Cu_2O catalysts. The surface composed of accumulated nano-spherical Cu_2O was generated after growing the Cu_2O 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 Cu_2O sample showed a similar morphology. The particle sizes of the $x\text{ZnO}@y\text{Cu}_2\text{O}$ samples were obviously larger than pristine ZnO particle and gradually grew up as the Cu_2O shell thickness increased (101 ± 20 nm for $4\text{ZnO}@\text{Cu}_2\text{O}$, 129 ± 20 nm for $\text{ZnO}@4\text{Cu}_2\text{O}$, and 227.9 ± 25 nm for $\text{ZnO}@20\text{Cu}_2\text{O}$). Under similar conditions, the particle size of the obtained Cu_2O 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 Cu_2O shell covered the ZnO particles uniformly. The surface composition of the $\text{ZnO}@4\text{Cu}_2\text{O}$ 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 $4\text{ZnO}@\text{Cu}_2\text{O}$ and $\text{ZnO}@20\text{Cu}_2\text{O}$ catalysts proved that a similar core-shell structure was shown in Figure S1. These results indicated that the core-shell $x\text{ZnO}@y\text{Cu}_2\text{O}$ structure was fabricated. Moreover, the size of the ZnO core was about 30 nm, which was consistent with the ZnO-400. The Cu_2O shell thickness was approximately twice that of the ZnO core for the $\text{ZnO}@4\text{Cu}_2\text{O}$ 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_2O , respectively [33]. These results indicated that the cuprous oxide shell was successfully formed on the ZnO core.

Scheme 1. Illustration of formation of $x\text{ZnO}@y\text{Cu}_2\text{O}$.

Figure 2. SEM images of (a) Cu_2O , (b) $4\text{ZnO}@ \text{Cu}_2\text{O}$, (c) $\text{ZnO}@4\text{Cu}_2\text{O}$, and (d) $\text{ZnO}@20\text{Cu}_2\text{O}$. (e) TEM image of $\text{ZnO}@4\text{Cu}_2\text{O}$ and (f) line EDX analysis along the arrow. (g) HR-TEM image of $\text{ZnO}@4\text{Cu}_2\text{O}$. (h) Cu K and (i) Zn K mappings of $\text{ZnO}@4\text{Cu}_2\text{O}$.

Figure 3a shows the XRD patterns of the $x\text{ZnO}@y\text{Cu}_2\text{O}$ catalysts. Compared to the patterns of ZnO -400 (JCPDS:75-0576) and Cu_2O particles (JCPDS:78-2076) (Figure S2), the core-shell $x\text{ZnO}@y\text{Cu}_2\text{O}$ showed a mixed one with the characteristic peaks at $2\theta = 34.5^\circ$, 36.3° corresponding to the (002), (101) facets of ZnO and $2\theta = 42.3^\circ$ corresponding to the (200) facets of Cu_2O [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_2O (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 $x\text{ZnO}@y\text{Cu}_2\text{O}$ catalysts and the Cu_2O (110) shell enclosed with Cu_2O (111) and the Cu_2O (200) facets. As the binding energies of Cu^0 and Cu^+ species are very close (only 0.1 eV), the Cu LMM spectrum was applied to distinguish the distribution of the Cu^0 and Cu^{1+} species. No characteristic peaks appeared at the binding energy of 568.0 eV (Figure S3), indicating no presence of Cu^0 species. The Cu XPS spectra of the $x\text{ZnO}@y\text{Cu}_2\text{O}$ 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_2O shell was formed, consistent with the above characterization. Cu^{2+} species were also observed probably due to the easy oxidation of Cu_2O 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 $4\text{ZnO}@\text{Cu}_2\text{O}$ was much smaller than the Cu_2O 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 $4\text{ZnO}@\text{Cu}_2\text{O}$, which resulted in part of the copper oxide being reduced to cuprous oxide. The $\text{ZnO}@\text{Cu}_2\text{O}$ 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 $x\text{ZnO}@y\text{Cu}_2\text{O}$ was also characterized by XPS. As shown in Figure 3d, all $x\text{ZnO}@y\text{Cu}_2\text{O}$ 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_2O 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 $4\text{ZnO}@\text{Cu}_2\text{O}$ and $\text{ZnO}@\text{Cu}_2\text{O}$ shifted toward a higher one by 0.32 eV than that of ZnO (1022.82 eV vs. 1022.50 eV). However, for $\text{ZnO}@\text{Cu}_2\text{O}$ (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_2O shell in the $x\text{ZnO}@y\text{Cu}_2\text{O}$ 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 $x\text{ZnO}@y\text{Cu}_2\text{O}$ catalyst. (b) The ratio of Cu_2O (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 $-0.8\sim-1.0$ 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].

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.

2.2.2. ZnO-400, Cu_2O , and $\text{ZnO}@4\text{Cu}_2\text{O}$ Catalysts

As a comparison, the ECR performance of Cu_2O and $\text{ZnO}@4\text{Cu}_2\text{O}$ 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_2O catalysts. As the overpotential increased, the selectivity of HCOOH , C_2H_4 , and $\text{C}_2\text{H}_5\text{OH}$ increased significantly with the inhibition of hydrogen evolution reaction, and HCOOH became the main product. C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$ were also first monitored at -0.6 V vs. RHE and then gradually increased with applied potential. The best performance of 15.2% C_2H_4 and 10.5% $\text{C}_2\text{H}_5\text{OH}$ on Cu_2O was obtained, which was similar to the report [42,43]. Compared to the Cu_2O and ZnO catalysts, the selectivity of C_2 products at a high overpotential was significantly boosted over the $\text{ZnO}@4\text{Cu}_2\text{O}$ 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_2H_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 5. Faradaic efficiency of products on different catalysts (a) ZnO-400, (b) Cu₂O, and (c) ZnO@4Cu₂O. (d) The total current density of products on different 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 Faradic 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 $\text{ZnO@4Cu}_2\text{O}$ was achieved at -1.0 V vs. RHE (Figure 6d). The $\text{ZnO@20Cu}_2\text{O}$ catalyst with a thick Cu_2O shell presented a much higher total current density than the Cu_2O 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_2O shell, where $\text{ZnO@4Cu}_2\text{O}$ exhibited the strongest interaction between ZnO and Cu_2O .

Figure 6. Faradaic efficiency of products on $x\text{ZnO}@y\text{Cu}_2\text{O}$ catalysts (a) $4\text{ZnO@Cu}_2\text{O}$, (b) $\text{ZnO@4Cu}_2\text{O}$, and (c) $\text{ZnO@20Cu}_2\text{O}$. (d) The total current density of products on $x\text{ZnO}@y\text{Cu}_2\text{O}$ catalysts.

The selectivity of C_2 products (C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$) over different $x\text{ZnO}@y\text{Cu}_2\text{O}$ 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 over the $4\text{ZnO@Cu}_2\text{O}$ catalyst, probably because the Cu_2O shell was too thin to provide enough residence time for C–C coupling of CO. The $\text{ZnO@4Cu}_2\text{O}$ catalyst exhibited the highest Faradaic efficiency of C_2 products (49.8%, $\text{FE}_{\text{ethylene}} = 33.5\%$ and $\text{FE}_{\text{ethanol}} = 16.3\%$) under -1.0 V vs. RHE , which was almost twice that of the Cu_2O catalyst. The $\text{ZnO@20Cu}_2\text{O}$ catalyst showed a similar selectivity of C_2 products with the Cu_2O catalyst at a low overpotential. However, at a high overpotential, $\text{ZnO@20Cu}_2\text{O}$ had a higher selectivity of C_2 products than the Cu_2O catalyst (30% for $\text{ZnO@20Cu}_2\text{O}$ and 25.7% for Cu_2O at -1.0 V vs. RHE). The C_2 products selectivity on $\text{ZnO@20Cu}_2\text{O}$ was lower than $\text{ZnO@4Cu}_2\text{O}$ at high potential (30% vs. 49.8%). $\text{ZnO@20Cu}_2\text{O}$ had too thick a Cu_2O 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_2O (200)/(111) facet analyzed earlier. The interface of the Cu_2O (200) facet and (111) could strengthen the CO–CO coupling, due to the strong $^*\text{CO}$ binding capacity and weak C_2H_4 adsorption capacity. The FE values of the C_2 products and the total current over $\text{ZnO@4Cu}_2\text{O}$ were among the best reported in flow-cell and surpassed most reports in the H-cell (Figure 7b, Table S4) [18,37,44–47].

Figure 7. (a) Selectivity towards C₂ products on xZnO@Cu₂O catalysts with different shell thickness. (b) 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 C₂H₅O. 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.

Figure 8. Electrochemical characterizations of different catalysts. (a) Double-layer capacitance measured by cyclic voltammetry in 0.1 M KHCO_3 saturated by CO_2 . (b) Electrochemical impedance spectroscopy (EIS) plots were carried at -1.0 V vs. RHE in 0.1 M KHCO_3 saturated with CO_2 . (c) Linear sweep voltammetry (LSV) curves measured in 0.1 M KHCO_3 solution saturated by CO_2 and Ar with a scan rate of 10 mV s^{-1} . (d) The ratio of Faraday efficiency of C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$ to Faraday efficiency of HCOOH on catalysts with different shell thickness. Tafel Kinetics over different catalysts of (e) C_2H_4 and (f) $\text{C}_2\text{H}_5\text{OH}$.

Based on the above discussion, the high ECR activity of $\text{ZnO}@4\text{Cu}_2\text{O}$ could be attributed to several factors. As shown in Figure 3b, the $\text{ZnO}@4\text{Cu}_2\text{O}$ 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 C_{2+} products [50]. The introduction of the ZnO core in the core-shell $\text{ZnO}@4\text{Cu}_2\text{O}$ catalyst enlarged the electrochemically active surface, lowered the electron transfer resistance between the electrolyte and the electrocatalysts, and enabled the $\text{ZnO}@4\text{Cu}_2\text{O}$ catalyst to have a higher overpotential of HER to inhibit H_2O reduction and improve the efficiency of CO_2 electroreduction to C_2 products. Additionally, it also significantly promoted the selectivity of the coordinating transfer electron to generate C_{2+} products, probably due to the high CO production activity of the ZnO core. Moreover, the core-shell $\text{ZnO}@4\text{Cu}_2\text{O}$ catalysts had the faster electrode kinetic for C_2 production. Therefore, the high electrochemical activity of $\text{ZnO}@4\text{Cu}_2\text{O}$ for ECR to C_2 products most likely originated from the synergetic effects of the ZnO core and the Cu_2O 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 ($C_4H_6O_4Zn$, 99.99%, Macklin, Shanghai, China), deuterium oxide (D_2O , 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 ($CH_3O(C_2H_4O)_nH$, $M_n = 5000$), ammonium citrate ($C_6H_5O_7(NH_4)_3$, AR 98.5%), ammonia solution ($NH_3 \cdot H_2O$, AR, 25%–28%), copper nitrate trihydrate ($Cu(CH_3COO)_2 \cdot 3H_2O$, 99.5%), potassium hydroxide (KOH, 99.99%), isopropyl alcohol (C_3H_8O , AR $\geq 99.5\%$, Aladdin, Seattle, WA, USA), and potassium chloride (KCl, AR, 99.5%) were purchased from Aladdin. Ethanol (C_2H_6O , 99.9%, Tianjin Yuanli Chemical Co., Ltd., Tianjin, China), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 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 ($18.2 M\Omega cm^{-1}$) 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@Cu₂O 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 0.1 M $Cu(NO_3)_2$ were added into a 250 mL beaker, under stirring, for 30 min, and then 0.1 mL hydrazine hydrate (35 wt.%) was added. After stirring for an additional 5 min, the catalyst was separated by centrifugation at 8000 rpm for 20 min. The obtained ZnO@Cu₂O particles were washed twice with water and then washed twice with ethanol. The products were separated at 12,000 rpm for 15 min for each wash. Finally, the ZnO@Cu₂O particles were dried at 50 °C in a vacuum drying oven for 1200 min. The different shell thickness of the catalyst was tailored by controlling the different amounts of $Cu(NO_3)_2$ (0.5 mL, 8 mL, 40 mL), the obtained samples were named xZnO@yCu₂O (4ZnO@Cu₂O, ZnO@4Cu₂O, and ZnO@20Cu₂O), based on the ICP results.

3.2.3. Synthesis of Cu₂O Catalyst

A reference Cu₂O sample was also prepared in the same method with the Cu₂O shell in ZnO@Cu₂O. 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@Cu₂O, the Cu₂O 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 K α 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 K α X-ray source ($h\nu$ = 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 C₂ product selectivity of 49.8% (ethylene 33.5%, ethanol 16.3%) and a high total current density of 140.1 mA cm^{−2}. This core-shell structure could strengthen the synergy between Cu and Zn oxides to simultaneously improve the selectivity of C₂ 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 Cu₂O shell in xZnO@yCu₂O 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 CO₂ reduction to produce high-value C₂ products.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11050535/s1>. Figure S1: TEM image of (a) 4ZnO@Cu₂O and (b) ZnO@20Cu₂O. The line EDX analysis along the arrow (c) 4ZnO@Cu₂O and (d) ZnO@20Cu₂O. Figure S2: XRD pattern of Cu₂O and its PDF card. Figure S3: Cu LMM Auger spectra of xZnO@yCu₂O catalysts with different shell thickness. Figure S4: The ratio of Cu¹⁺/Cu_{total} with different shell thickness catalysts. Figure S5: The current density of C₂ products on xZnO@Cu₂O catalysts with different shell thickness. Figure S6: Cyclic voltammograms of different catalysts in 0.1 M KHCO₃ (CO₂-saturated) at scan rates 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}. (a) Cu₂O; (b) ZnO@20Cu₂O; (c) ZnO@4Cu₂O; (d) 4ZnO@Cu₂O; (e) ZnO; and (f) double-layer capacitance measured by cyclic voltammetry in 0.1 M KHCO₃ saturated by CO₂ 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) Cu₂O, (b) 4ZnO@Cu₂O, (c) ZnO@4Cu₂O, and (d) ZnO@20Cu₂O. Figure S9: The flow cell used for electrochemical reduction of CO₂. 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@yCu₂O catalyst. Table S3: The intensity and proportion of significant facets of Cu₂O in xZnO@yCu₂O 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@4Cu₂O catalyst. Table S6: The distribution of products at different applied potentials on Cu₂O catalyst. Table S7: The resistance of different catalysts.

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