



Article Ag-Precipitated CuO Nanospheres for Enhanced Electrochemical Reduction of CO₂

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Abstract: An electrochemical CO₂ reduction reaction (CO₂RR) is an effective way to reduce greenhouse gases by converting CO₂ into high-value-added chemical products using electricity generated from renewable energy. In this paper, a Cu₂O spherical catalyst was prepared by ascorbic acid reduction. The precipitated Cu-Ag spherical catalyst (P-CuO-Ag) was successfully prepared by calcining Cu₂O-Ag with the introduction of an Ag component as the substrate. During the electrochemical reduction of CO₂, the FE of the P-CuO-Ag catalyst for C₂H₄ at a potential of -1.1 V vs. RHE was as high as 39.8%, which was nearly twice that of the CuO catalyst, while the local current density J_{C2H4} for C₂H₄ reached 6 mA cm⁻². The incorporation of Ag gives the spherical CuO catalyst higher electrochemical activity and better kinetic performance than the catalyst without Ag.

Keywords: electrochemistry; CO₂ reduction; C₂H₄; nanospheres; bimetallic copper-based derivatives

1. Introduction

Over the past few decades, the increasing global population and heavy reliance on fossil fuels have led to an alarming rise in CO_2 emissions, resulting in severe greenhouse effect problems [1–3]. This environmental challenge triggers events such as glacier melting, rising sea levels, climate anomalies, and more frequent oceanic storms [4,5]. These effects disrupt human life and development and pose significant threats to mankind [6]. Thus, capturing CO_2 and closing the anthropogenic carbon cycle is urgently needed to mitigate global warming. Carbon Capture, Utilization, and Storage (CCUS), achieved through chemical methods, is considered an effective strategy to reduce greenhouse gases in the short term [7–9]. Following the CCUS concept, the conversion of CO_2 into high-value-added products using electrochemical methods has sparked substantial interest in both the industrial and academic areas [10–12].

The electrochemical CO_2 reduction reaction (CO_2RR) serves as a pathway for converting CO_2 into value-added fuels and chemical products using renewable energy (like wind and solar energy) [13–16]. This conversion results in products like CO [17–21], formic acid [22,23], methanol [24], methane [25], ethylene [26,27], ethanol [28], acetic acid [29], and propanol [30]. Therefore, the process stores energy within these chemical products, aiming to lessen our dependence on traditional fossil fuels. Moreover, it addresses the power issues brought about by seasonal and climate factors [31] while also reducing greenhouse gas emissions. Despite these advantages, the CO_2RR process faces significant challenges,



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). notably the competitive Hydrogen Evolution Reaction (HER), which adversely affects the selectivity of the desired reduction products [32].

Single-metal catalysts play a crucial role in CO_2RR due to their specific properties and relatively straightforward synthesis. Among these, copper (Cu) is particularly notable for its ability to reduce CO_2 to multi-carbon products like C_2H_4 and C_2H_5OH [33]. Copper's intermediate binding strength with CO_2 intermediates facilitates the formation of C-C bonds necessary for multi-carbon products. However, Cu-based catalysts exhibit high overpotentials and slower reaction kinetics, with an activation energy for CO_2 decomposition of 67 kJ mol⁻¹ [34].

They also suffer from poor catalytic stability due to passivation and inactivation by ions present in the electrolyte, limiting their long-term efficiency. Gold (Au), another single-metal catalyst, excels in converting CO_2 to CO with a lower activation energy of 38 kJ mol⁻¹, often achieving Faraday efficiencies exceeding 90% [35]. However, the high cost of gold restricts its large-scale application, and its effectiveness is limited primarily to CO production. Tin (Sn) catalysts, especially in their oxide forms like SnO₂, are known for their high Faraday efficiency in producing formic acid (HCOOH) [22,23]. Nevertheless, their product range is limited, and their efficiency may decrease over time. Zinc (Zn) catalysts, which are cost-effective and selective for CO production, generally exhibit lower overall catalytic activity and a limited product range compared to more sophisticated bimetallic systems.

The integration of copper with other metals to form bimetallic catalysts could enhance their catalytic activity and selectivity compared to single-metal catalysts. Bimetallic catalysts like CuAu, CuSn, and CuZn leverage the strengths of individual metals to enhance activity, selectivity, and stability [36–38]. For example, the addition of silver (Ag) to copper significantly increases the Faraday efficiency for CO, facilitating C-C coupling and improving efficiency for C_2 products. Controlling the structure of these catalysts is critical for optimizing their performance [39]. Moreover, Niu et al. prepared a Cu₂O-Ag nanocube catalyst that shows a high local current density and Faraday efficiency for C2 reduction products. The local current density reaches up to 243.2 mA cm⁻², and a maximum of 72.9% FE is reached for C_2 reduction products. This high performance is a result of the addition of Ag, which enhances the Faraday efficiency of CO compared to Cu₂O. High CO content reduces the energy barrier of the C-C coupling reaction, leading to a decrease in the Faraday efficiency of C_1 class CH_4 and a consequent increase in C_2 product Faraday efficiency [40]. Zhu et al. demonstrated that an 8 nm Au nanoparticle catalyst achieved a Faraday efficiency of approximately 90% for CO, attributed to the prevalence of edge sites over corner sites [41]. Similarly, Choi et al. developed an Ag-Cu dendritic catalyst with a layered structure that enhanced catalytic activity, achieving a Faraday efficiency of 64.6% for CO [42].

To address challenges such as high overpotentials and slow reaction kinetics, we focus on developing copper-based bimetallic oxide catalysts. By carefully selecting and preparing catalysts with highly stable structures and enhanced electrochemical activity and selectivity, we aim to refine their performance through structural morphology adjustments [43,44]. In this study, we introduced a precipitated Ag on a CuO spherical catalyst. The morphological structure, composition, and electrochemical reduction performance of this catalyst were analyzed using techniques such as SEM, TEM, XRD, and XPS. The results demonstrated that the catalyst exhibited enhanced performance as a cathode material for CO_2 reduction, showcasing its potential in advancing the field of CO_2RR . The incorporation of bimetallic catalysts in CO_2RR research has shown significant promise in enhancing catalytic activity, selectivity, and stability. By leveraging the synergistic effects of different metal components and optimizing the structural morphology of the catalysts, researchers can develop more efficient and effective catalysts for CO_2 reduction.

2. Materials and Methods

2.1. Materials

All of the following reagents are analytical-grade reagents. Copper(II) acetate monohydrate (Cu(CO₂CH₃)₂·H₂O, AR), ascorbic acid (C₆H₈O₆, AR), silver nitrate (AgNO₃, AR), sodium bicarbonate (NaHCO₃, AR), sodium chloride (NaCl, AR), nano-copper oxide (CuO, AR), Nafion 117 solution (C₉HF₁₇O₅S, AR), isopropanol (C₃H₈O, AR), potassium bicarbonate (KHCO₃, AR), and polyvinylpyrrolidone (PVP, (C₆H₉NO)n, AR) were purchased from Shanghai Aladdin Biochemical Technology Co. (Shanghai, China); carbon dioxide (CO₂) from Tianjin Huanyu Co., Tianjin, China; and deionized water and hydrophobic carbon paper from Toray, Japan.

2.2. Preparation of Catalysts and Electrodes

A total of 0.56 g of copper acetate monohydrate and 1.69 g of PVP were dissolved in 50 mL of deionized water and sonicated for 30 min to obtain a blue solution. Then, 2.25 mL of 0.085 mol L⁻¹ sodium chloride solution was added, and after 10 min of reaction, 2.5 mL of 1.28 mol L⁻¹ ascorbic acid solution was quickly added. After 20 min, a brown-red solution was obtained. This solution was centrifuged at 10,000 r s⁻¹ and washed three times with water and alcohol. Finally, the solid catalyst obtained by centrifugation was dried in a vacuum oven at 50 °C for 10 h to obtain the Cu₂O catalyst [27,43]. Then, 30 mL of 3 mmol AgNO₃ solution was added to the brown-red solution, and a black solution was obtained by reacting for 10 min, then centrifuged and mixed with the Cu₂O catalyst to obtain spherical Cu₂O-Ag. Finally, Cu₂O and Cu₂O-Ag were calcined in a muffle furnace at 500 °C for 2 h to obtain CuO and precipitated CuO-Ag (P-CuO-Ag) black powder.

The catalysts prepared with 10 mg (Cu₂O, CuO, Cu₂O-Ag, CuO-Ag) and 80 μ L of Nafion 117 solution were dispersed in 2 mL of isopropanol, and the catalyst ink was obtained by ultrasonic dispersion for 30 min. The catalyst ink was evenly sprayed on carbon paper (size: 2 × 2 cm) using a spraying device, and the working electrode was obtained after natural drying at room temperature.

2.3. Characterization

The micromorphology of the catalyst was characterized using a scanning electron microscope (SEM, Hitachi SU8010, HITACHI CO., Tokyo, Japan) equipped with energy-dispersive spectroscopy (EDS) and a transmission electron microscope (USA-FEI-Tecnai G2 F20, Thermo Fisher Scientific, Waltham, MA, USA). The crystal structure of the catalyst was characterized using an X-ray diffractometer (XRD, D8 ADVANCE, BRUKER, Billerica, MA, USA) with Cu K α radiation (λ = 1.5405 Å) at scan step of 10° min⁻¹ in the 2 θ range of 10–80°. X-ray photoelectron spectroscopy (XPS, NEXSA, Thermo Fisher, Waltham, MA, USA) was used to analyze the elements on the catalyst surface.

2.4. Electrochemical Performance Testing

A CHI760E electrochemical workstation (CH Instruments, Chenhua Co, Shanghai, China) was used for electrochemical performance testing in an H-type electrolytic cell with a Nafion proton exchange membrane as the diaphragm. The carbon paper loaded with the catalyst served as the working electrode, with a platinum sheet as the anode, and an Ag/AgCl electrode as the reference electrode. In CO₂-saturated KHCO₃, linear sweep voltammetry (LSV) and cyclic voltammetry (CV) tests were performed at a potential sweep range of -0.6 V to -2.0 V (vs. Ag/AgCl) at a sweep speed of 10 mV s⁻¹. The electrochemically active surface area was evaluated by testing CVs with different scan rates.

2.5. CO₂ Electrochemical Reduction Device

The electrochemical reduction of CO_2 was performed in a typical H-type electrolytic cell where 45 mL of 0.5 M KHCO₃ is used as the electrolyte for both the anode and cathode chambers. The carbon paper loaded with the catalyst served as the working electrode

(size: 1×1.7 cm, Toray, Japan), with an Ag/AgCl reference electrode placed in the cathode chamber. A gas tube leading into CO₂ was placed on the side near the working electrode, with another gas tube discharging the reducing gas product connected to the drying device and the gas flow meter, and then to a gas chromatograph. A platinum sheet electrode was placed in the anode chamber (size: 1×1.7 cm, Ledonlab, Zhengzhou, China) with openings for discharging O₂ above the anode chamber. We separated the cathode chamber and anode chamber with a Nafion proton exchange membrane to prevent the cathode and anode chamber products from crossing. The reaction potential was provided using the CHI760E electrochemical workstation.

2.6. Analytical Methods

The CO₂ reduction gas-phase products were detected by a gas chromatograph (Agilent, 7890B, Agilent Technologies Ltd., New York, NY, USA) equipped with an FID detector and a TCD detector. All gases to be measured in this experiment were calibrated by the standard gas using the external standard method, with the calibration curve determined by standard gas of known concentration, and the calibration results averaged by at least three results. The Faraday efficiency of the gas phase product is calculated as follows:

$$FE = \frac{QF_{10^6}^{P} * \frac{v}{60*22,400}}{I_{\text{total}}} * 100\%$$
(1)

where *Q* is the number of transferred electrons required to generate the target product; *F* is Faraday's constant (96,485 C mol⁻¹); *P* is the proportion of the target gas product in the reaction gas (ppm); v is the flow rate of the reaction gas (SCCM); and I_{total} is the current obtained by the experiment, A [28].

3. Results

3.1. Morphological and Structural Characterization of Catalysts

The crystal structure of the catalyst was analyzed using XRD. As shown in Figure 1a, the diffraction peaks of the catalyst Cu₂O-Ag at $2\theta = 29.5^{\circ}$, 36.4° , 42.2° , 61.3° , 73.5° , and 77.3° correspond to the (110), (111), (200), (220), (311), (311), (222), and (222) crystal faces of Cu₂O, respectively, which correspond to the Cu₂O (#05-0667) standard card. Typical Ag diffraction peaks appear at 38.1° , 44.2° , 64.4° , and 77.3° , which correspond to the (111), (200), (220), and (311) crystallographic planes of Ag, respectively, and correspond to the (#87-0597) standard PDF card of Ag, which proves the successful synthesis of Cu₂O-Ag [40]. For P-CuO-Ag, the diffraction peaks at $2\theta = 35.2^{\circ}$, 35.5° , 38.5° , 38.9° , 48.7° , and 67.4° correspond to the (002), (111), (200), (200), (220) crystal faces of CuO, respectively, corresponding to the CuO (#89-2530) standard card. Typical Ag diffraction peaks appear at 37.7° , 43.8° , 63.7° , and 76.4° , which correspond to the (111), (200), (220), and (311) crystal planes of Ag, respectively, which are in accordance with the standard card of Ag (#65-8428), which indicates the successful synthesis of CuO-Ag [44].

Figure S1a and Figure 1b illustrate SEM images of spherical CuO catalysts and spherical Cu₂O-Ag tandem catalysts. The prepared spherical CuO catalyst presents a multilayered structure, with pore size mostly ranging from 6 to 100 nm. The addition of Ag does not change the overall catalyst structure. With the addition of a silver nitrate solution, Ag⁺ displaces and adheres to the Cu₂O surface with a rougher surface. Commercial CuO exhibits an irregular, fragmented morphology (Figure S1b). In contrast, CuO prepared by the reduction method has a spherical structure, with an overall size ranging between 1 and 3 μ m.



Figure 1. (a) XRD patterns of Cu₂O-Ag and P-CuO-Ag; SEM images of (b) Cu₂O-Ag and (c) P-CuO-Ag; (d) EDS mapping image of P-CuO-Ag, and element mappings of (e) Cu and (f) Ag; (g) Survey spectra, (h) Cu 2p, and (i) Ag 3d XPS spectra of Cu₂O-Ag and P-CuO-Ag.

Figure 1c shows an SEM image of the spherical CuO-Ag catalyst. After calcinating Cu₂O-Ag at 500 °C, significant changes are observed in its surface morphology. It now possesses a distinctive layered structure. These differently sized pores provide the catalyst with a larger array of potential catalytic active sites, not only increasing the reaction area but also allowing pre-reduced CO₂ gas to stay longer within the catalyst. This extended stay aids in the enrichment of the reduction intermediate CO* within the catalyst. The structure is primarily a result of the Kirkendall effect [45], with the differing diffusion rates of outward-diffusing Cu atoms and inward-diffusing O atoms leading to various gap formations. These gaps gradually enlarge, forming noticeable pores in the material.

To further analyze the elemental distribution of the synthesized P-CuO-Ag catalyst, SEM EDS mapping was conducted, as shown in Figure 1d–f. The mapping reveals the presence of Cu and Ag elements in the material. Cu elements show minor agglomeration, whereas Ag elements are evenly distributed, demonstrating the successful incorporation and distribution of Ag within the CuO spheres.

The P-CuO-Ag catalyst was further characterized using TEM to verify its composition. As observed in Figure S2a, the P-CuO-Ag catalyst exhibits a spherical structure, whereas the CuO catalyst without Ag (Figure S2c) displays a rough surface morphology. This roughness might be attributed to the adhesion of Ag. High-resolution TEM of the lattice fringes (Figure S2b,d) showed that the synthesized catalysts exhibit clear lattice fringes. The fringe spacing of the P-CuO-Ag catalyst is 0.25 nm, aligning with the CuO (112) crystal plane. At the edge of the catalyst, Ag lattice fringes are noticeable, with a spacing of

0.24 nm, corresponding to the Ag(200) crystal plane. These observations further confirm the synthesized catalyst as P-CuO-Ag. The CuO catalyst also exhibits clear lattice fringes (Figure S2d) with a fringe spacing of 0.215 nm corresponding to the standard CuO(200) crystal plane, further confirming its composition as CuO.

The valence states of Cu elements between the Cu₂O-Ag and P-CuO-Ag catalysts were analyzed by XPS. Figure 1g shows the full spectrum of the XPS test, revealing the spectral characteristic information of Cu, O, Ag, and C. As shown in Figure 1h, for the Cu_{2p} signal spectra of Cu₂O-Ag and P-CuO-Ag catalysts, P-CuO-Ag exhibits $2p_{3/2}$ and Cu2 $p_{1/2}$ photoelectron peaks of Cu²⁺ at 933.8 eV and 953.7 eV, respectively [28]. The peaks around 943.0 eV and 941.0 eV are typical satellite peaks of CuO, suggesting that the form of Cu in P-CuO-Ag is Cu²⁺. In contrast, Cu₂O-Ag exhibits $2p_{3/2}$ and $2p_{1/2}$ photoelectron peaks of CuO, respectively [46]. It lacks the typical satellite peaks of CuO, indicating that the form of Cu in Cu₂O-Ag is Cu⁺. The fine spectroscopy of Ag (Figure 1i) shows that both Cu₂O-Ag and P-CuO-Ag catalysts have two strong typical Ag $3d_{3/2}$ and $3d_{5/2}$ characteristic peaks at 374.2 eV and 368.2 eV [47]. Thus, Ag exists in elemental form in both Cu₂O-Ag catalysts.

3.2. Characterization of Electrochemical Properties

Figure 2a shows the LSV results for five different electrode materials in CO₂-saturated electrolyte conditions. Pure carbon paper exhibits the least electrochemical activity, with its current density only reaching -39.0 mA cm^{-2} at a potential of -1.4 V vs. RHE. The other four catalysts show better electrochemical activity due to their CO₂ reduction ability. Notably, the P-CuO-Ag catalyst shows the highest electrochemical activity among the catalysts, with a peak current density of $-150.8 \text{ mA cm}^{-2}$ at the same potential of -1.4 V vs. RHE. The overall electrochemical activity order is P-CuO-Ag > Cu₂O-Ag > Cu₂O. This suggests that the addition of Ag to Cu₂O enhances its electrochemical activity. The catalyst's electrochemical activity can be significantly improved through the design of its composite structure.



Figure 2. (a) LSV curves of four different catalyst-prepared electrodes and pure carbon paper under CO₂-saturated electrolyte KHCO₃; (b) Tafel slopes of four different electrodes.

The Tafel slopes from the LSV curves of the catalysts reflect their kinetic differences. As illustrated in Figure 2b, the P-CuO-Ag catalyst has a Tafel slope of 251 mV dec⁻¹, which is lower than those of the other three catalysts, indicating faster reaction rates. This improvement is consistent with the LSV results. Compared with Cu₂O catalyst. The addition of Ag improves the reaction kinetics, and also improves the reaction kinetics of the catalyst itself by designing the composite structure of the catalyst.

To further investigate the electrochemically active surface area (ECSA) of the catalyst, different electrodes were tested via cyclic voltammetry (CV) at various scan rates, as shown in Figure 3a–d. Scan rates of 10 mV s⁻¹, 20 mV s⁻¹, 30 mV s⁻¹, 40 mV s⁻¹, 50 mV s⁻¹, and 60 mV s⁻¹ were tested. The current density of each catalyst increased with the scan

rate, indicating enhanced electrochemical activity. The ECSA of the catalysts was measured using the double-layer capacitance method, where the charging and discharging current densities linearly correlated with the scan rate. This relationship demonstrates that a larger slope indicates a larger ECSA, providing insights into the availability of active sites for catalysis. The surface morphology, roughness, and porosity of the catalyst play a crucial role in the electrochemical reaction's dynamics. These physical characteristics directly impact the distribution of active sites and electron transfer kinetics across the electrode's surface. This effect is evident in the case of the porous CuO-Ag (P-CuO-Ag) catalyst, where the porous structure, despite increasing the electrochemically active surface area, introduces complexity in the reaction kinetics and electron transfer processes. The composition and structural integrity of composite or bimetallic catalysts, such as Cu₂O-Ag, add another layer of complexity to the electrochemical reactions. These catalysts combine different metals to enhance catalytic activity and selectivity towards certain products. However, the interaction between different metal components can lead to varying electron transfer rates and reaction pathways at different potential ranges. This can significantly affect the CV curve's smoothness, as the electrochemical behavior of composite catalysts is influenced by the synergy and interaction between the constituent metals.



Figure 3. CV test curves of (**a**) P-CuO, (**b**) Cu₂O, (**c**) Cu₂O-Ag, and (**d**) P-CuO-Ag at different scan rates; (**e**) electrochemical impedance curves of P-CuO-Ag, Cu₂O-Ag, P-CuO, and Cu₂O; (**f**) stability test of P-CuO-Ag catalyst in 0.5 mol/L KHCO₃ electrolyte.

The electrochemically active surface area is positively correlated with the double-layer capacitance, and by calculating the magnitude of the double-layer capacitance, we evaluate the electrochemically surface active area [48]. As shown in Figure 3e, the linear slope magnitude corresponds with the double-layer capacitance value, indirectly reflecting the ECSA of the material. The double-layer capacitance of P-CuO-Ag is 4.77 mF cm^{-2} , the highest among the four catalysts, meaning it also has the largest ECSA. This might be due to the composite structure that exposes more active sites and accelerating the diffusion rate of Cu²⁺. Figure 3f shows the results of a stability test for the P-CuO-Ag catalyst at -1.1 V vs. RHE using the chronoamperometry (i-t) method. During the continuous 5 h test, the current density of P-CuO-Ag remained stable at around 16.0 mA cm⁻². Moreover, the FE for the main product, C_2H_4 , consistently remained between 30 and 35% without significant reduction. In addition, we also characterized the used catalysts of Cu₂O-Ag and P-CuO-Ag, as shown in Figures S3–S5, and the results showed that they were basically the same as the catalysts before use. After the reaction, the condition of the catalyst materials showed minimal changes, indicating their robustness and stability. The XRD patterns further confirmed the stability of the crystalline phases of Cu₂O and CuO, with no new phases detected, reinforcing the conclusion that the catalyst's chemical composition remained stable (Figure S3). Similarly, the XPS spectra provided detailed insights into the surface chemistry, indicating that the surface oxidation states were consistent with the bulk material, further evidencing minimal alteration (Figure S4). Moreover, the TEM images in Figure S5 indicate that the overall morphology of the catalyst post-reaction was essentially unchanged compared to its pre-reaction state. This observation suggests that the structural integrity of the catalyst was maintained throughout the process, and no significant agglomeration or sintering occurred. These findings, included in the supporting information in Figures S3–S5, demonstrate that the catalyst maintained its chemical and physical properties effectively after the reaction. The minimal changes in both the chemical states and physical structure highlight the catalyst's durability, making it suitable for repeated use in similar conditions. This stability is crucial for catalytic applications, as it ensures consistent performance and reduces the need for frequent regeneration or replacement of the catalyst. Overall, the catalyst's resilience under reaction conditions underscores its potential for practical applications in catalytic processes.

These results suggest that the P-CuO-Ag catalyst maintains its electrocatalytic activity and selectivity towards the production of ethylene over prolonged electrolysis, indicating good long-term stability. The catalyst exhibits stability in maintaining its activity and selectivity over time, which signifies stable morphology and composition under the tested conditions. The active sites for CO₂RR in these copper-based catalysts are primarily the surface atoms that interact with CO₂ and intermediates during the reduction process. The incorporation of Ag alters the electronic structure and surface properties of the catalysts, thereby influencing the binding strength of intermediates and the activation of CO₂. The presence of Ag promotes the formation of CO intermediates, which are essential for the synthesis of C₂⁺ products through C-C coupling reactions.

3.3. Performance Test of Electrocatalytic Reduction of CO₂

To investigate the selectivity and stability of the catalysts in the electrochemical reduction of CO₂, the prepared P-CuO-Ag, Cu₂O-Ag, and CuO catalysts were tested. These catalysts served as working electrodes, with platinum sheets as counter electrodes and Ag/AgCl electrodes as reference electrodes. The tests were conducted within the potential range of -1 V to -1.4 V vs. RHE using typical H-type electrolytic cells. The results, displayed in Figure 4a–c, indicate that all catalysts produce CH₄, C₂H₄, CO, and H₂. However, C₂H₄, a C₂ product, is the primary output of the reduction reaction for all three catalysts. During the CO₂ reduction reaction (CO₂RR) process, an unwanted hydrogen evolution reaction (HER) also occurs. As a competing reaction, HER not only reduces the quantity of reduction products but also impairs the selectivity of the reduction. Thus, an effective catalyst should minimize HER.



Figure 4. FE versus potential for CO₂ reduction product of (a) P-CuO-Ag, (b) Cu₂O-Ag, and (c) CuO; (d) FE distribution of C_2H_4 at different potentials for the four catalysts; (e) plot between the partial current density and electrode potential for the reduction of CO₂ to C₂H₄ product by P-CuO-Ag, Cu₂O-Ag, and CuO; (f) plot between FE and electrode potential for the reduction of CO₂ to CO product by P-CuO-Ag, Cu₂O-Ag, and CuO catalysts.

As shown in Figure 4a–c, the CuO catalyst consistently exhibits a Faraday efficiency for HER above 30%. At -1 V vs. RHE, the Faraday efficiency of HER reaches 44.3%, decreasing to its lowest point of 32.4% at -1.1 V vs. RHE. However, as the potential becomes more negative, the Faraday efficiency of HER increases, peaking at 53.4% at the maximum potential of -1.4 V vs. RHE. This pattern indicates that within the range of -1 V to -1.4 V vs. RHE, the CuO catalyst maintains a relatively high HER side reaction Faraday efficiency. For the Cu₂O-Ag catalyst, the FE of its HER is consistently lower than that of the CuO catalyst at equivalent potentials. The FE for the HER shows a trend of slight decline followed by an increase as the potential becomes more negative. It shows its lowest point of 18.1% at -1.1 V vs. RHE, and its highest point of 41.6% at -1.4 V vs. RHE. In comparison, the P-CuO-Ag catalyst presents a lower HER side reaction FE than the other two catalysts. The FE for its HER shows a fluctuating trend, with its minimum value of 17.2% occurring at -1 V vs. RHE. For the main product, C₂H₄, the P-CuO-Ag catalyst displays the highest Faraday efficiency, as depicted in Figure 4d. Its FE is superior to the other two catalysts at identical potentials, peaking at 39.8% with a potential of -1.1 V, before gradually decreasing to a minimum of 29.1% at -1.4 V. The Cu₂O-Ag catalyst has the second-best FE for C_2H_4 , hitting a minimum of 23.5% at -1.3 V. The CuO catalyst exhibits a generally lower Faraday efficiency for C_2H_4 , consistently under 30%, peaking at 29.6% at the initial potential of -1.0 V. For the C₁ product CH₄, the FE of CuO exceeds that of the other two catalysts. This suggests that compared to P-CuO-Ag, the active sites of CuO tend to generate the by-product H₂, thereby reducing the C-C coupling process. Thus, the CO intermediate in the C_2 product C_2H_4 is more likely to combine with H^+ to form the C_1 product CH_4 . Based on the heterogeneous characteristics of CO_2RR , the structure of the catalysts, including their porosity, surface area, and crystal facets, plays a crucial role in determining their electrocatalytic properties. The composite structure of P-CuO-Ag facilitates a higher number of active sites, increases the reaction area, and allows pre-reduced CO_2 gas to stay longer within the catalyst, enriching the reduction intermediate CO*. This is evident from the Kirkendall effect observed in the formation of the catalyst, where the structure is formed due to differing diffusion rates of atoms. Additionally, the synergistic effects between Cu and Ag improve the catalyst's performance, where Ag incorporation enhances CO₂RR towards specific products. The incorporation of Ag alters the electronic structure and surface properties of the catalysts, thereby influencing the binding strength of intermediates and the activation of CO_2 . The presence of Ag promotes the formation of CO intermediates, which are essential for the synthesis of C_2^+ products through C-C coupling reactions. The spherical structure of the P-CuO-Ag catalyst, as evidenced by TEM and SEM analysis, also contributes to its high catalytic performance.

To assess the selectivity and stability of the electrochemical CO₂ reduction catalyzed by P-CuO-Ag, Cu₂O-Ag, and CuO, these prepared catalysts were utilized as working electrodes, with platinum sheets as counter electrodes and Ag/AgCl electrodes as reference electrodes. Figure 4e presents a comparison of the partial current density for C_2H_4 production versus the electrode potential for the three catalysts. As shown in the figure, the P-CuO-Ag catalyst exhibits a trend of gradual increase in the partial current density for C_2H_4 . It is lower than that of Cu_2O -Ag within the -1 V to -1.2 V range, but reaches a maximum of 18.9 mA cm⁻² at a potential of -1.4 V. The CuO catalyst shows a lower partial current density for C₂H₄, peaking at 10.7 mA cm⁻² at -1.3 V. Figure 4f provides further exploration into why the addition of Ag enhances the production of C_2H_4 by the catalysts. It charts the relationship between the Faraday efficiency (FE) for CO production and the electrode potential during CO₂ reduction by the P-CuO-Ag, Cu₂O-Ag, and CuO catalysts. The P-CuO-Ag catalyst causes a more significant decrease in FE for CO production compared to the other two catalysts. Given that CO is a critical intermediate for C-C coupling and necessary for C_2 production, a substantial reduction indicates a higher efficiency in transforming the FE to C_2H_4 . Thus, P-CuO-Ag presents a decreased FE for CO and an increased FE for C_2H_4 . This also demonstrates that the presence of Ag species in P-CuO-Ag catalysts can indeed promote the selectivity of CO_2 conversion to C_2H_4 products [42,44].

The novel P-CuO-Ag catalyst is achieved through the integration of silver (Ag) into CuO followed by a calcination process. The distinctive morphological structure and composition, as confirmed by SEM and TEM analysis, features a multilayered structure, which aids in increasing the reaction surface area and promotes CO_2 reduction. The addition of Ag to copper-based catalysts notably improves their catalytic performance in CO_2RR by enhancing their selectivity and activity towards specific reduction products.

Additionally, the XPS analysis results confirm the successful doping of Cu and Ag elements, which are critical for the electrochemical activity and stability of P-CuO-Ag. In terms of other products, the electrochemical reduction of CO_2 can lead to a variety of products, including CO, formic acid, methanol, methane, ethylene, ethanol, acetic acid, and propanol. The presence and yield of these products depend on the catalytic material used, its structure, and the operational conditions of the CO_2RR process, with selectivity

influenced by the catalyst composition and structure [21]. Hence, the catalytic performance of CuO in the electrochemical CO₂ reduction process is enhanced when combined with Ag, as demonstrated by the improved FE for C₂ reduction products. While the overall FE might not be very high, the selectivity towards valuable products such as C_2H_4 is significantly improved, which is crucial for the practical application of CO₂RR processes [49].

4. Conclusions

In this study, the ascorbic acid method was employed to fabricate a Cu₂O spherical catalyst. Ag was then introduced into Cu₂O to yield a Cu₂O-Ag spherical catalyst, which was further calcined to produce a P-CuO-Ag spherical catalyst. An electrode modified with this catalyst was utilized in the electrochemical CO₂ reduction reaction. The P-CuO-Ag catalyst demonstrated a Faraday efficiency (FE) for C₂H₄ as high as 39.8% at a potential of -1.1 V vs. RHE. The introduction of Ag resulted in the spherical CuO catalyst having higher electrochemical activity and enhanced kinetic performance compared to the catalyst without Ag. The inclusion of Ag in the P-CuO-Ag catalyst led to an elevated CO FE.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/su16145888/s1, Figure S1: SEM images of (a) spherical CuO catalysts and (b) commercial CuO. Figure S2: (a) TEM and (b) HRTEM of P-CuO-Ag; (c) TEM (d) HRTEM of CuO. Figure S3: XRD patterns of used Cu₂O-Ag and used P-CuO-Ag. Figure S4: (a) Survey spectra; (b) Cu 2p; (c) Ag 3d XPS spectra of used Cu₂O-Ag and used P-CuO-Ag. Figure S5: TEM of used Cu₂O-Ag (a) and used P-CuO-Ag (b).

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