Efficient Electrocatalytic Reduction of CO2 to CO via Mechanochemical Synthesized Copper-based Composite Metallic Oxide Catalyst

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Abstract

Electrocatalysis serves as a highly effective approach to both mitigate greenhouse gas emissions and produce high-value chemicals. Copper-based catalysts have garnered considerable attention due to their immense potential in this domain, improving the selectivity and activity through optimizing preparation strategies is of paramount importance. In this study, mechanochemical method was first used for preparing copper-based composite metallic oxide electrocatalysts. Spherical CuO, Sn-CuO, and Sn-In-CuO catalysts were prepared and their electrochemical carbon dioxide reduction performance was evaluated. Among them, the Sn-In-CuO catalyst demonstrated the best performance in reducing carbon dioxide to carbon monoxide products. Within the potential range of -0.6 V to -1.1 V vs. RHE, the Faradaic efficiency of carbon monoxide product was consistently above 93.56%, with a maximum Faradaic efficiency of 96.11% achieved at -0.9 V vs. RHE. Sn-In-CuO also exhibits good stability with high Faradaic efficiency of carbon monoxide above 87.97% for a duration of 6 hours under the potential of -0.6 V vs. RHE in a 0.1 M KHCO$_3$ electrolyte. The excellent performance is speculated to be attributed to the generation of a large number of defects and the introduction of metal doping, which increases the number of active sites through the mechanochemical method.

1 Introduction

Electrocatalytic CO$_2$ reduction reaction (CO$_2$RR) is a promising strategy for converting CO$_2$ into important fuels and chemicals such as carbon monoxide (CO), formic acid (HCOOH), methanol (CH$_3$OH), and ethanol (C$_2$H$_5$OH). It not only reduces human reliance on fossil fuels but also holds the potential to achieve “carbon peak and carbon neutrality”, addressing energy crises and global environmental pollution [1–3]. Among the various products generated by CO$_2$ reduction reaction, CO produced through a two-electron reduction pathway serves as a fundamental building block for the production of multi-carbon chemicals [4, 5]. In recent years, there has been a dedicated effort to search for highly selective and active catalysts for electrocatalytic CO$_2$ reduction to CO. Noble metals such as Au [6], Ag [7], and Pd [8] have lower binding energies with the intermediate species CO*, leading to the tendency of generated CO* to directly detach from the electrode surface and exhibit high selectivity towards CO. However, the expensive and scarce nature of noble metals limits their further large-scale applications. The development of inexpensive and efficient catalysts for CO$_2$RR to CO holds great promise for practical applications.

Due to the unique electronic structure and the ability to provide appropriate active sites, Cu is widely regarded as a potential catalyst for CO$_2$ reduction with broad application prospects [9]. However, due to the fact that a mixture of various gases is produced by Cu catalysts during the electrocatalytic CO$_2$RR process, separation and purification are necessary. To avoid this costly necessity, improving the selectivity and activity of Cu catalysts is the key to produce valuable high-selectivity products. Currently, various strategies are being explored to enhance the performance, such as combining Cu with metal-organic frameworks [10], combination of Cu and carbon materials [11], doping other metals into copper-based catalysts [12]. The copper-based metal oxide catalysts by metal doping have been extensively...
investigated because doping can alter the electronic and geometric structure of the metal surface, which is closely related to catalytic performance\(^\text{[13]}\). Currently, the main methods for preparing composite metal oxide catalysts include atomic layer deposition (ALD)\(^\text{[14]}\), electrochemical deposition (ECD)\(^\text{[15]}\), chemical vapor deposition (CVD)\(^\text{[16]}\), and high-temperature pyrolysis\(^\text{[17]}\), among others. Recently, mechanochemical synthesis by ball milling have gained considerable attention for preparing catalysts as its significant advantages\(^\text{[18–20]}\). Firstly, ball milling enables the fabrication of catalyst with high density, quality, and volume performance\(^\text{[21]}\). Secondly, it does not require the addition of solvents or further thermal treatments, making it more environmentally friendly\(^\text{[22]}\). Additionally, ball milling is a simple and efficient technique with significant economic value\(^\text{[23]}\). Most importantly, it allows for the modulation of the catalyst's coordination environment by increasing defect density and oxygen content in the host material. These defect structures can serve as active sites for storing, capturing, and stabilizing metal atoms, thereby enhancing the catalyst's performance\(^\text{[24,25]}\). Therefore, mechanochemical methods may be suitable for the synthesis of high-performance copper-based composite metal catalysts for electrocatalytic \(\text{CO}_2\) reduction reactions. However, the development is limited as the corresponding investigations have been unexplored.

In this study, we employed the ball milling method for the first time to prepare a series of Cu-based composite metallic oxide catalysts for electrocatalytic \(\text{CO}_2\)RR. The prepared CuO, Sn-CuO, and Sn-In-CuO catalysts were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area analysis, and hydrogen temperature-programmed reduction (H\(_2\)-TPR). The electrocatalytic performance was evaluated and the results demonstrate that the Sn-In-CuO catalyst exhibits the best performance in converting \(\text{CO}_2\) into CO products with CO Faradaic efficiencies (FE) of 96.11\% under −0.9 V vs. RHE. The Sn-In-CuO catalyst also possesses good catalytic stability with FE\(_{\text{CO}}\) remains above 93.56\% within 6 h. Furthermore, a possible catalytic mechanism is speculated based on the experimental results.

2 Experimental Section

2.1 Materials and reagents

Copper nitrate trihydrate (\(\text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O}\)), indium trichloride tetrahydrate (\(\text{InCl}_3 \cdot 4\text{H}_2\text{O}\)), tin tetrachloride pentahydrate (\(\text{SnCl}_4 \cdot 5\text{H}_2\text{O}\)), potassium hydroxide (KOH), and sodium chloride (NaCl) are commercially available and were used as supplied without further purification. The \(\text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O}\), \(\text{SnCl}_4 \cdot 5\text{H}_2\text{O}\), and \(\text{InCl}_3 \cdot 4\text{H}_2\text{O}\) were subjected to dehydration treatment. The ultrapure water used in the experiment was generated using an ultrapure water system produced by Millipore Elix (USA).

2.2 Mechanochemical preparation of CuO
Firstly, Cu(NO$_3$)$_2$·3H$_2$O, KOH, and NaCl are added in a certain proportion into a zirconia jar. Then, zirconia grinding balls are added in a ratio of 1:15 (based on the mass of materials to zirconia grinding balls), and the grinding is carried out at 260 r min$^{-1}$ for 30 minutes. Finally, the ground sample is placed into a muffle furnace and heated to 500 °C at a rate of 5 °C min$^{-1}$ for 2 hours. The resulting sample is washed, dried, and obtained as black CuO.

2.3 Mechnochemical preparation of Sn-CuO and Sn-In-CuO

The procedure is the same as above and the preparation process is shown in Scheme 1. Firstly, Cu(NO$_3$)$_2$·3H$_2$O, KOH, NaCl, and SnCl$_4$·5H$_2$O are added in a certain proportion into a zirconia jar. Then, zirconia grinding balls are added in a ratio of 1:15 (based on the mass of materials to zirconia grinding balls), and the grinding is carried out at 260 r min$^{-1}$ for 30 minutes. Finally, the ground sample is placed into a muffle furnace and heated to 500 °C at a rate of 5 °C min$^{-1}$ for 2 hours. The resulting sample is washed, dried, and obtained as black Sn-CuO. The preparation process for Sn-In-CuO (Cu:Sn:In = 50:1:1 of molar ratio) is the same as for Sn-CuO. The preparation process of Sn-In-CuO is shown in Scheme 1.

2.4 Characterizations

XRD analysis is performed using the Smart Lab X-ray analyzer (Nippon Corporation, Japan). XPS analysis is performed using the ESCALAB Xi$^+$ spectrometer (Thermo Fisher Scientific, USA). The appearance and morphology of the sample are observed using the Zeiss EVO18 SEM (Zeiss, Germany). The elemental composition of the sample is detected using a high-resolution TEM (FEI, USA). The measurement of the specific surface area and pore size of the sample is performed using the ASAP2010 low-temperature nitrogen physisorption analyzer (Micromeritics, USA). The sample was subjected to vacuum treatment at 150°C for 6 hours and then analyzed for N$_2$ adsorption-desorption isotherms at liquid nitrogen temperature using high-purity nitrogen as the adsorbate. The specific surface area was calculated using the BET method, and the pore structure parameters were determined using the BJH theory. The reducibility of the sample was measured using the AutoChem II 2920 fully automated programmable temperature chemical adsorption analyzer (Micromeritics, USA).

2.5 Electrochemical performance testing

The electrocatalytic performance was studied using a three-electrode system on the Shanghai Chenhua CHI660E electrochemical workstation. A silver/silver chloride (Ag/AgCl) electrode was chosen as the reference electrode, and a platinum mesh electrode was used as the working electrode, with the catalysts coated on carbon paper (1 cm$^2$). The electrochemical performance of all catalysts was tested in an H-type electrolysis cell. The electrocatalytic CO$_2$ reduction reaction took place in the cathodic electrolysis cell, with both the cathode and anode electrolytes consisting of 20 mL of 0.1 M KHCO$_3$ aqueous solution with a pH of 6.8. A gas mass flow controller was used to control the flow rate of CO$_2$ at 20 mL·min$^{-1}$ in the cathodic electrolysis cell. The gas outlet of the cathodic electrolysis cell was connected to a gas...
chromatography system. The entire reaction was conducted at room temperature and atmospheric pressure.

In this study, all potentials \((E, V)\) were measured against the Ag/AgCl reference electrode (in saturated KHCO\(_3\) solution) and then converted to the Reversible Hydrogen Electrode (RHE) reference scale using the following equation:

\[
E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197 + 0.0591 \times \text{pH}
\]

The FE is determined by dividing the charge passed by each product generated by the total charge passed throughout the entire operation. FE is calculated using the following equation:

\[
FE = \frac{ZnF}{Q_{\text{total}}}
\]

Where, \(Z\) represents the number of transferred electrons \((Z = 2\) for CO, HCOOH, and H\(_2\) products), \(n\) (mol) is the molar quantity of the product, \(F\) (96485 C mol\(^{-1}\)) is Faraday's constant, and \(Q_{\text{total}}\) (C) is the total charge transferred throughout the entire electrolysis process.

The partial current density of the product in electrocatalytic CO\(_2\)RR or H\(_2\) can be obtained by multiplying the corresponding FE by the total current density \((j, \text{mA cm}^{-2})\). The following equation:

\[
j_{(\text{ECR products or H}_2)} = j \times FE_{(\text{ECR products or H}_2)}
\]

The calculation formula for Electrochemical Surface Area (ECSA) is as follows:

\[
\text{ECSA} = R_f \times S
\]

The roughness factor, \(R_f\) is given by the following equation:

\[
R_f = \frac{\text{Cdl}}{Z}
\]

Where Cdl is the double-layer capacitance and \(Z\) is a constant.
3 Results and discussion

The X-ray diffraction patterns of CuO, Sn-CuO, and Sn-In-CuO catalysts are shown in Fig. 1(a). Several characteristic diffraction peaks were observed at 35.2°, 38.5°, 48.6°, 53.3°, 58.0°, 61.3°, 65.9°, 67.8°, and 75.0°, which correspond to the (-111), (111), (-202), (020), (202), (-113), (311), (220), and (-222) crystal planes of monoclinic CuO, respectively. No characteristic diffraction peaks of Cu and Cu$_2$O were observed in the XRD, indicating the absence of corresponding crystalline phases. Additionally, no diffraction peaks related to Sn and In were observed in the XRD, suggesting that the doping levels of Sn and In may be insufficient to be detected. It was observed that the doping of Sn led to changes in the intensity and width of the CuO (-111) and CuO (111) peaks in Sn-CuO and Sn-In-CuO. This indicates that the doping does not affect the formation of the final product but alters its morphology. The crystal grain size (D) of the CuO (111) crystal plane in CuO, Sn-CuO, and Sn-In-CuO can be calculated using the well-known Debye-Scherrer equation $^{[26,27]}$:

$$D = \frac{K\lambda}{\beta\cos\theta}$$

In this equation, $D$ represents the crystallite size (nm), $K$ is a constant equal to 0.9, $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum (FWHM) of the diffraction peak, and $\theta$ is the diffraction angle given in degrees. As shown in Table 1, the crystallite sizes of the CuO (111) crystal plane in CuO, Sn-CuO, and Sn-In-CuO are 16.51 nm, 11.59 nm, and 10.80 nm, respectively, which are consistent with the corresponding XRD diffraction patterns. When Sn is doped into CuO, both Sn-CuO and Sn-In-CuO exhibit a decrease in peak intensity and broadening of the peaks. This indicates that Sn replaces the lattice sites of CuO, leading to an increase in disorder, an increase in lattice parameter, and a decrease in crystallite size $^{[28]}$. Therefore, the incorporation of Sn and In into CuO promotes intermolecular interactions and may enhance the catalytic efficiency.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$2\theta$</th>
<th>FWHM</th>
<th>Crystallite Size (nm)</th>
<th>(hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>38.67</td>
<td>0.46</td>
<td>16.51</td>
<td>(111)</td>
</tr>
<tr>
<td>Sn-CuO</td>
<td>38.63</td>
<td>0.66</td>
<td>11.59</td>
<td>(111)</td>
</tr>
<tr>
<td>Sn-In-CuO</td>
<td>38.71</td>
<td>0.70</td>
<td>10.80</td>
<td>(111)</td>
</tr>
</tbody>
</table>

Due to the significant impact of surface composition on the performance of materials, XPS was employed to investigate the surface composition and oxidation states of CuO, Sn-CuO, and Sn-In-CuO catalysts. The XPS full spectra of the catalyst are shown in Fig. 1(b). Cu and O elements were detected in CuO, Cu, O, and Sn elements were present in Sn-CuO, and Cu, O, Sn, and In elements were found in Sn-In-
CuO, indicating the successful synthesis of the catalysts. No other impurity-related elements were detected in the three samples, indicating a high purity of the samples. Figure 1(c) displays the Cu 2p signals of CuO, Sn-CuO, and Sn-In-CuO. The peaks at 933.0 eV and 953.0 eV correspond to Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2}, respectively, indicating the presence of Cu(II) in the samples. The strong Cu\textsuperscript{2+} satellite peaks at 962.6 eV, 943.9 eV, and 941.0 eV were also clearly observed, exhibiting clear CuO characteristics\[^{29}\]. Compared to CuO, Sn-CuO and Sn-In-CuO exhibited a slight shift towards higher binding energy in the peak located at 953.0 eV. This could be attributed to the doping of Sn and In resulted in electron transfer within the Cu\textsuperscript{2+} and consequently altered the electronic structure\[^{30}\]. The detailed spectrum of O 1s and the ratio of O elements are shown in Fig. 1(d), clearly demonstrating the presence of two oxygen peaks at 529.8 eV and 531.5 eV. These peaks correspond to lattice oxygen (O\textsubscript{latt}) and oxygen adsorption (O\textsubscript{ads}), respectively\[^{31}\]. It is noteworthy that the O\textsubscript{ads}/O\textsubscript{latt} ratio of Sn-CuO and Sn-In-CuO is 0.72 and 0.96, respectively, which is significantly lower than the value of 2.45 for CuO. According to the literature\[^{32,33,34}\], an appropriate concentration of oxygen vacancies not only reduces the recombination rate between electrons and holes but also facilitates the adsorption and activation of CO\textsubscript{2}, thereby promoting electrocatalytic CO\textsubscript{2}RR. The fine spectrum of Sn 3d in Sn-CuO and Sn-In-CuO catalysts is shown in Fig. 1(e), exhibiting two distinct peaks at 495.0 eV and 486.5 eV, corresponding to Sn 3d\textsubscript{3/2} and Sn 3d\textsubscript{5/2} of Sn\textsuperscript{4+} doping state\[^{35}\], respectively. This indicates that Sn atoms tend to release charge to Cu and O atoms, resulting in charge delocalization\[^{36}\]. Meanwhile, the fine spectrum of In is depicted in Fig. 1(f), revealing two prominent peaks at 444.6 eV and 452.2 eV, corresponding to the binding energies of In 3d\textsubscript{5/2} and In 3d\textsubscript{3/2}, respectively\[^{37}\]. The above results demonstrate that the Cu-based composite metallic oxide catalysts with doped Sn and In into CuO are successful synthesized though the mechanochemical method.

The microstructure and morphology of the catalysts prepared by mechanochemical synthesis are analyzed using SEM. The differences in microstructure and particle size distribution of CuO, Sn-CuO, and Sn-In-CuO are shown in Fig. 2(a-c). From SEM analysis, it can be observed that there is not a significant difference in the morphology of CuO, Sn-CuO, and Sn-In-CuO. However, Sn-CuO, and Sn-In-CuO exhibit smaller and more uniformly distributed particles compared to CuO, which may result in a significantly increased effective surface area of the catalyst. This observation is consistent with the characterization results obtained from BET analysis. The particle size of the catalyst was calculated using the "Image J software", as shown in Fig. 2(d). The particle sizes of CuO, Sn-CuO, and Sn-In-CuO were determined to be 34.89 nm, 17.65 nm, and 16.07 nm, respectively. These results indicate that the addition of Sn and In significantly reduces the particle size of CuO, while the difference in particle size between Sn-CuO and Sn-In-CuO is negligible. Furthermore, we characterized the EDS elemental distribution of the Sn-In-CuO sample using TEM, as shown in Fig. 2(e-i). It can be observed that Sn and In are uniformly distributed on CuO, further verifying the successful doping of Sn and In into CuO by the mechanochemical method.

The specific surface area and pore size distribution of the catalyst were characterized using N\textsubscript{2} adsorption-desorption measurements. Figure 3 depicts the N\textsubscript{2} adsorption-desorption isotherms and pore
size distribution graphs (inset) of CuO, Sn-CuO, and Sn-In-CuO catalysts. According to the BET classification, all three catalysts exhibit type IV isotherms and H3 hysteresis loops, indicating the presence of mesoporous characteristics in all the catalysts. The values of the BET specific surface area, pore volume, and average pore diameter of the catalysts are shown in Table 2. The analysis results indicate that the Sn-In-CuO catalyst has the highest specific surface area of 57.44 m² g⁻¹, while the specific surface areas of CuO and Sn-CuO are 21.78 m² g⁻¹ and 48.89 m² g⁻¹, respectively. This suggests that the simultaneous doping of Sn and In into CuO significantly enhances its surface area, exposing more active sites and increasing the adsorption capacity for CO₂ molecules. Further analysis revealed that the doping of Sn leads to an increase in the pore volume and a decrease in the average pore diameter of CuO. The pore volumes of CuO, Sn-CuO, and Sn-In-CuO are 0.15 cm³ g⁻¹, 0.27 cm³ g⁻¹, and 0.32 cm³ g⁻¹, respectively. The average pore diameters are 26.31 nm, 20.69 nm, and 20.62 nm, respectively. In summary, the doping of Sn and In allows for the control of the specific surface area, pore volume, and average pore size and distribution of the samples.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Textural property of the catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalysts</td>
<td>Surface Area (m²/g)</td>
</tr>
<tr>
<td>CuO</td>
<td>21.78</td>
</tr>
<tr>
<td>Sn-CuO</td>
<td>48.89</td>
</tr>
<tr>
<td>Sn-In-CuO</td>
<td>57.44</td>
</tr>
</tbody>
</table>

### 4 Electrocatalytic CORR performance

To investigate the electrocatalytic activity of CuO, Sn-CuO, and Sn-In-CuO catalysts for CO₂ reduction, linear sweep voltammetry (LSV) was performed in the potential range of 0 V to -1.2 V vs. RHE at a scan rate of 10 mV s⁻¹. As shown in Fig. 4(a), at potentials ranging from −0.6 V to -1.2 V vs. RHE, a sharp increase in current density was observed for CuO, Sn-CuO, and Sn-In-CuO, indicating the occurrence of CO₂RR. Compared to CuO and Sn-CuO, Sn-In-CuO exhibits higher current density and lower onset potential, indicating higher activity in the electrocatalytic reduction of CO₂.

In order to further evaluate the selectivity of different catalysts towards CO products, the FE₇CO were tested at different potentials, as shown in Fig. 4(b). Within the wide potential range of -0.6 to -1.1 V vs. RHE, the FE₇CO of Sn-In-CuO catalyst remains above 93.56%. Moreover, at the optimum potential of -0.9 V vs. RHE, the FE₇CO reaches a maximum value of 96.11%. In contrast, the CuO and Sn-CuO catalysts reach their maximum FE₇CO at different optimal potentials. CuO catalyst achieves its maximum FE₇CO of 44.18% at -0.6 V (vs. RHE), while Sn-CuO catalyst achieves its maximum FE₇CO of 95.59% at -0.8 V (vs. RHE). Comparing the FE₇CO values throughout the entire range of tested potentials, Sn-In-CuO exhibits the highest FE₇CO compared to CuO and Sn-CuO catalysts. At a potential of -0.9 V vs. RHE, the FE₇H₂ for CuO,
Sn-CuO, and Sn-In-CuO are 61.53%, 5.32%, and 3.89% respectively. This observation suggests a synergistic effect among the three elements, which effectively suppresses the hydrogen evolution reaction (HER) and promotes CO$_2$RR.

Current density is another key metric for evaluating the electrochemical performance of catalysts in CO$_2$RR. The CO partial current density ($j_{\text{CO}}$) of catalysts CuO, Sn-CuO, and Sn-In-CuO at different potentials was compared, as shown in Fig. 4(c). The $j_{\text{CO}}$ of Sn-CuO and Sn-In-CuO catalysts are nearly identical and both higher than that of CuO. At -1.1 V vs. RHE, the $j_{\text{CO}}$ values for CuO, Sn-CuO, and Sn-In-CuO catalysts are 2.3 mA cm$^{-2}$, 9.8 mA cm$^{-2}$, and 12.4 mA cm$^{-2}$, respectively. The $j_{\text{CO}}$ of Sn-In-CuO is approximately 6 times higher than that of CuO, which is consistent with the observed FE of CO. This indicates that Sn-In-CuO catalyst exhibits excellent catalytic activity.

Next, we focused on studying the reasons behind the enhanced CO$_2$RR performance of Sn-In-CuO. As shown in Fig. 5(a), H$_2$-TPR profiles of CuO, Sn-CuO, and Sn-In-CuO catalysts are displayed. Typically, the reduction peak for pure CuO occurs around 300 °C [38]. Except for the Sn-In-CuO sample, both CuO and Sn-CuO samples exhibit two distinct reduction peaks in the region below 300 °C. The $\alpha$ peak ($T_1$) corresponds to the reduction of CuO with smaller particle size, while the $\beta$ peak ($T_2$) corresponds to the reduction of CuO with larger particle size [39, 40]. It can be observed that the addition of Sn does not cause significant changes in the reduction peak of CuO. However, when both Sn and In are simultaneously added to CuO, the reduction peaks of CuO shift towards the high-temperature end. This shift is particularly prominent for larger CuO particles, indicating that they are being reduced. Small particles have more surface area and lattice defects, providing more reduction sites, making it easier for CuO to be reduced to Cu [41, 42]. This indicates that the simultaneous introduction of Sn and In in the temperature range of 200–300°C weakens the interaction forces between CuO, resulting in the presence of CuO in larger particles, which is beneficial for preventing the reduction of CuO.

By conducting Tafel slope measurements on the catalyst, the reaction kinetics of electrocatalytic CO$_2$ reduction to CO were revealed for the catalyst material. The Tafel slopes of CuO, Sn-CuO, and Sn-In-CuO are shown in Fig. 5(b). The Sn-In-CuO catalyst exhibits a smaller Tafel slope value of 229.62 mV dec$^{-1}$, significantly lower than that of CuO (337.52 mV dec$^{-1}$) and Sn-CuO (267.71 mV dec$^{-1}$). This indicates that the rate-determining step for electrocatalytic CO$_2$ reduction to CO on Sn-In-CuO and Sn-CuO catalysts is the first step involving proton-coupled electron transfer. The significant reduction in Tafel slope implies that Sn-In-CuO catalyst has faster CO$_2$RR kinetics, accelerating the production of CO. This could be attributed to the reaction kinetics that promote protonation and subsequent formation of COOH*, which plays a crucial role in CO generation [43–45].

To further understand the reasons for the excellent performance of the Sn-In-CuO catalyst, the electrochemical double layer capacitance (Cdl) was determined to assess the electrochemically active surface area (ECSA). First, CV curves of CuO, Sn-CuO, and Sn-In-CuO were obtained at different scan rates (10 ~ 60 mV s$^{-1}$), and then the corresponding double layer capacitance was calculated using the
formula. As shown in Fig. 5(c), the results show that the Cdl of Sn-In-CuO (9.50 mF cm$^{-2}$) is approximately twice that of CuO (4.91 mF cm$^{-2}$) and Sn-CuO (3.72 mF cm$^{-2}$). This indicates that Sn-In-CuO possesses a larger ECSA compared to CuO and Sn-CuO, which confirms that simultaneous doping of Sn and In can modulate the electronic structure of CuO, thereby increasing the number of active sites and promoting the CO$_2$ reduction reaction$^{[46,47]}$.

Further elucidation of the kinetic differences of the CuO, Sn-CuO, and Sn-In-CuO catalysts was achieved through testing electrochemical impedance spectroscopy (EIS). The decrease in charge transfer impedance ($R_2$) in EIS reflects faster interfacial charge transfer between the reactants in the working electrode and the electrolyte, leading to an accelerated CO$_2$ conversion$^{[48,49]}$. As shown in Fig. 5(d), Sn-In-CuO exhibits a smaller semicircle diameter, indicating that it has the lowest charge transfer resistance. Based on the above analysis, the Sn-In-CuO electrode exhibits the fastest charge transfer rate, indicating the most favorable charge transfer kinetics during the CO$_2$ electroreduction process.

In addition, durability performance is also an indispensable parameter for catalysts. The stability of the Sn-In-CuO catalyst in generating CO at -1.2 V vs. RHE was evaluated using chronoamperometry, as shown in Fig. 6. Even after continuous electrolysis for 6 hours, the FE$_{CO}$ remains above 87%, and there is no significant loss in current density, indicating that Sn-In-CuO exhibits excellent catalytic stability.

According to literature reports$^{[50,51]}$, the commonly accepted mechanism for CO$_2$ reduction to produce CO is as follows:

$$\text{CO}_2(g) + H^+ + e^- \rightarrow \text{COOH}^*$$  

7

$$\text{COOH}^* + H^+ + e^- \rightarrow \text{CO}^* + \text{H}_2\text{O} \; (l)$$  

8

$$\text{CO}^* \rightarrow \text{CO}$$  

9

Based on above results, the electrocatalytic CO$_2$RR pathway of the Sn-In-CuO catalyst to CO can be inferred. As shown in Fig. 7, the first step involves the diffusion of CO$_2$ from the electrolyte to the surface of the Sn-In-CuO catalyst and its adsorption onto the catalyst. The application of mechanochemical method leads to a finer structure of Sn-In-CuO, increasing its surface area. Introducing Sn and In into CuO simultaneously helps to expose more active sites, promoting the adsorption of CO$_2$. In the second step, through chemical activation, CO$_2$ is transformed into the excited state CO$_2$$^*$ intermediate species. In the third step, electron or proton transfer occurs, leading to the cleavage of the carbon-oxygen bond and formation of a carbon-hydrogen bond, resulting in the formation of COOH$^*$ as shown in Eq. (7). In the
fourth step, COOH* undergoes electron transfer, leading to the cleavage of the carbon-oxygen bond, resulting in the formation of CO* as shown in Eq. (8). Finally, the adsorbed CO* further reacts in the electrolyte to form CO. According to the electrocatalytic CO₂RR testing, Sn-In-CuO exhibits a high FE_{CO} of up to 96.11% at -0.9 V vs. RHE. In conclusion, the improved performance and selectivity of Sn-In-CuO in electrocatalytic CO₂RR can be attributed to two main factors. Firstly, the mechanical ball milling generates defects on the CuO support, facilitating the doping of Sn and In metals and creating abundant defect structures that serve as active sites for metal atom storage, capture, and stabilization. Secondly, the introduction of Sn and In allows for the formation of tri-metallic active centers, leading to higher metal loading and a greater number of active sites. This optimization of the active centers greatly enhances the adsorption and desorption behavior, resulting in the observed high selectivity towards CO.

5 Conclusion

In summary, we have successfully confirmed that mechanochemical synthesis is an effective approach for the fabrication of high-performance composite metallic oxide electrocatalysts. The Sn-In-CuO catalyst possesses excellent performance in reducing CO₂ to CO product, effectively suppressing the competing HER and enhancing the production of CO. In the potential range of -0.6 V to -1.1 V vs. RHE, the FE_{CO} of the catalyst remain above 93.56%. and the maximum Faradaic efficiency can of achieve at 96.11% under −0.9 V vs. RHE. The excellent performance is speculated to be attributed to the generation of a large number of defects and the introduction of metal doping, which increases the number of active sites through the mechanochemical method. This study can provide some guidance for further improving the selectivity of Cu-based catalysts in electrocatalytic CO₂ reduction to CO, and may inspire more interest in the mechanochemical synthesis methods.

Declarations

Author contributions

H. L., T. S. and Z. Y. conceived and designed the experiment. T. S. conducted experiments. H. L. and T. L. provided experimental conditions. X. Z., Y. W. and L. C. helped some results analysis and discussion. T. S. and Z. Y. collaborated on the paper. All authors reviewed the manuscript.

Conflicts of interest

The authors declare that they have no competing interests.

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References


**Scheme 1**
Scheme 1 is available in Supplementary Files section.

Figures

Figure 1
(a) XRD diffraction patterns of CuO, Sn-CuO, and Sn-In-CuO. (b) XPS full spectra of CuO, Sn-CuO, and Sn-In-CuO. (c) Cu 2p fine spectra of CuO, Sn-CuO, and Sn-In-CuO. (d) O 1s fine spectra of CuO, Sn-CuO, and Sn-In-CuO (O$_{ads}$/O$_{latt}$ ratio of O element). (e) Sn 3d fine spectra of Sn-CuO and Sn-In-CuO. (f) In 3d fine spectra of Sn-In-CuO.

Figure 2

SEM images of the catalysts: (a) CuO, (b) Sn-CuO, (c) Sn-In-CuO. (d) Size comparison of CuO, Sn-CuO, and Sn-In-CuO particles. (e) EDS of Sn-In-CuO: (f) Cu, (g) O, (h) Sn, (i) In.
Figure 3

N$_2$ adsorption and desorption isotherms and pore size distribution curves (inset): (a) CuO, (b) Sn-CuO, (c) Sn-In-CuO.

Figure 4

(a) LSV curves of CuO, Sn-CuO, and Sn-In-CuO in a 0.1 M KHCO$_3$ solution saturated with CO$_2$ at a scan rate of 10 mV s$^{-1}$. (b) Comparison of FE$_{CO}$ for CuO, Sn-CuO, and Sn-In-CuO at different potentials. (c) Comparison of $j_{CO}$ for CuO, Sn-CuO, and Sn-In-CuO at different potentials.
Figure 5

(a) H₂-TPR profiles of CuO, Sn-CuO, and Sn-In-CuO. (b) Tafel slope plots of CuO, Sn-CuO, and Sn-In-CuO. (c) Comparison of double-layer capacitance plots of CuO, Sn-CuO, and Sn-In-CuO at different scan rates. (d) EIS spectra of CuO, Sn-CuO, and Sn-In-CuO.
Figure 6

Stability performance testing of Sn-In-CuO at -0.6 V vs. RHE.
Figure 7

Mechanistic pathway diagram for the electrocatalytic CO$_2$RR to CO by Sn-In-CuO.

Supplementary Files

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- Scheme1.png