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Optimizing Sn Loading in CuO Catalysts for CO_2 Reduction to CO

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Abstract

The increasing concentration of CO_2 in the atmosphere poses urgent environmental challenges, driving the need for sustainable carbon utilization strategies. Electrochemical CO_2 reduction reaction (CO_2RR) offers a promising route to convert CO_2 into valuable fuels and chemicals. In this study, we investigate the effect of Sn loading on CuO-based electrodes, aiming to enhance selectivity and efficiency in CO_2RR. A series of Sn–CuO catalysts with varying Sn contents were synthesized via a hydrothermal method followed by thermal treatment. Structural and morphological characterizations (XRD, SEM, HRTEM) confirmed the successful incorporation of Sn, leading to nanosheet morphologies with high surface area. Electrochemical testing revealed that optimized Sn loading significantly redirected the reaction pathway toward CO formation while suppressing competing H_2 evolution. The Sn–CuO-3 composition achieved the highest CO faradaic efficiency (~86%) at –0.67 V vs RHE. These results demonstrate that controlled Sn loading can tune catalyst performance by modifying active sites and reaction pathways, providing valuable insights into catalyst design for CO_2 utilization and sustainable energy applications.

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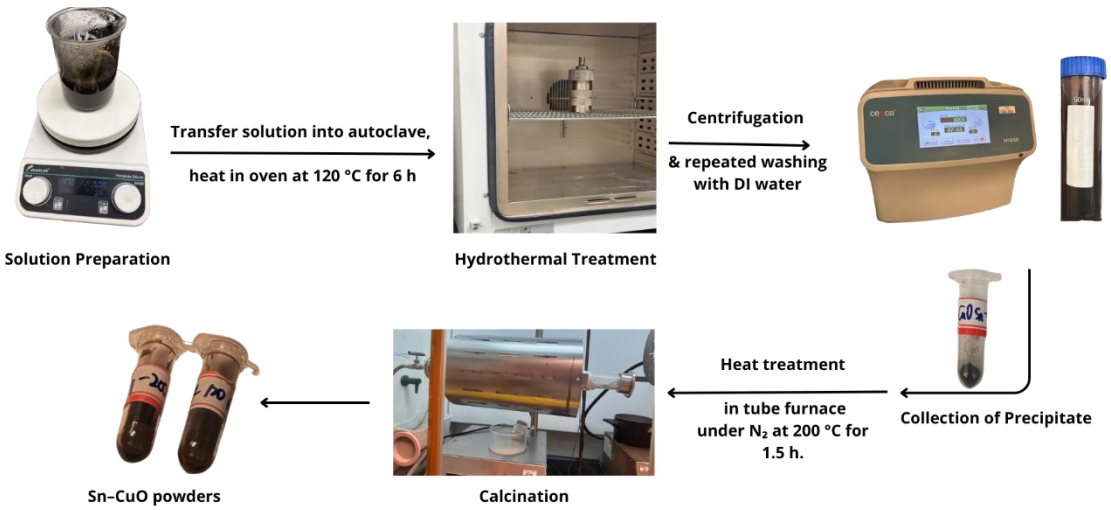
1 Introduction

This project was carried out within the KAUST Academy Energy Transition Specialization Program under the supervision of Prof. Huabin Zhang and guided by Changle Yue, with the main contributions in synthesis, electrochemical testing, and analysis performed by Raghd Hantoush. The motivation for this work stems from the urgent need to mitigate CO_2 emissions, a major driver of climate change, by converting them into valuable fuels and chemicals through the electrochemical CO_2 reduction reaction (CO_2RR). Despite its promise, this reaction faces challenges of poor selectivity and competition with the hydrogen evolution reaction (HER). The central assumption of this study is that CuO catalysts can be tuned by incorporating tin (Sn), though the timeframe of the project limited extended durability testing and focused primarily on CO, H_2, and HCOOH as products. The main objective was to investigate how varying Sn loading affects the catalytic pathway, with the goal of enhancing CO selectivity while suppressing H_2 formation. The problem addressed is that while Cu-based catalysts are widely studied, the effect of different Sn loading levels on redirecting the CO_2RR pathway remains underexplored. To address this, Sn–CuO electrodes with different Sn contents were synthesized via hydrothermal and calcination methods, characterized using XRD, SEM, and HRTEM, and tested electrochemically. The results indicate that controlled Sn loading significantly improves CO selectivity, offering a pathway toward efficient

2 Methodology

2.1 Catalyst Preparation

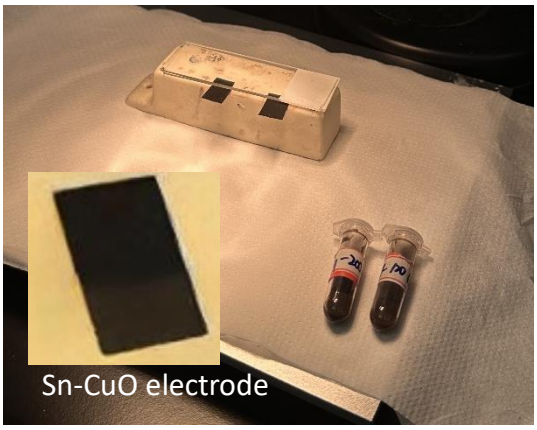
The Sn–CuO catalysts were synthesized via a hydrothermal-assisted method followed by post-treatment. In a typical process, aqueous solutions of copper and tin precursors were mixed under continuous stirring at elevated temperature in the presence of polyvinylpyrrolidone (PVP) as a stabilizing agent. Sodium hydroxide solution was then added to initiate precipitation, and the mixture was stirred further to ensure complete reaction. The resulting suspension was transferred into a Teflon-lined autoclave and heated hydrothermally for several hours. After cooling, the solid precipitate was collected by centrifugation, washed repeatedly with deionized water, and dried overnight in a vacuum oven. The obtained powder was ground and subsequently annealed in a tube furnace under nitrogen atmosphere at 200 °C to enhance crystallinity and stabilize the Sn–CuO structure.



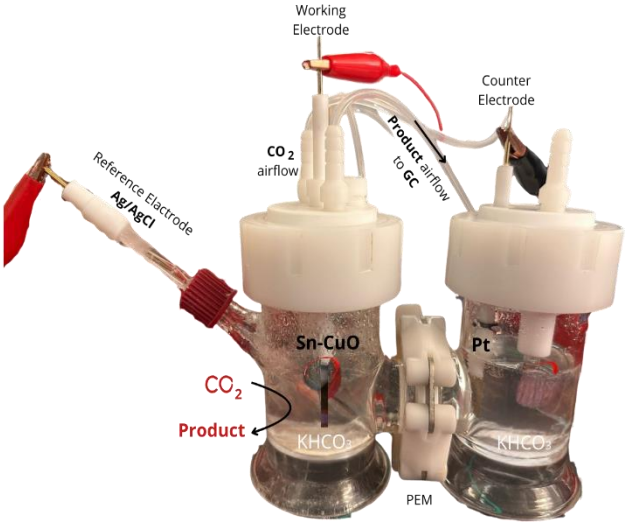
(Figure1: Catalyst Preparation)

2.2 Electrode & Cell Setup

The synthesized Sn–CuO powders were dispersed in ethanol with Nafion binder to form a homogeneous ink. A measured volume was drop-cast onto carbon paper and dried at room temperature to obtain a uniform catalyst layer (working electrode). Electrochemical tests were carried out in a three-electrode H-type cell separated by a proton-exchange membrane, using Ag/AgCl as the reference and a Pt wire as the counter electrode. The electrolyte was CO_2-saturated 0.1 M $KHCO_3$. CO_2 was bubbled for ≥30 min prior to measurements to ensure full saturation.



(Figure2: Working Electrode Preparation)



(Figure3: cell setup)

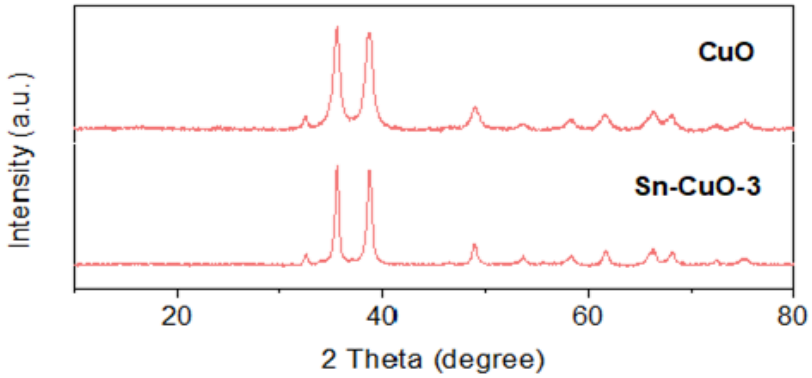
2.3 Evaluation Procedure

Catalytic activity was first assessed by linear sweep voltammetry (LSV) to determine the onset potential and overall current response. Product-selective tests were performed by chronoamperometry (CA) at fixed potentials. Gaseous products (CO, H_2) were quantified by gas chromatography (GC), while liquid products (HCOOH) were analyzed by ^{1}H NMR. Each condition was measured in triplicate for reproducibility.

3 Results Discussion

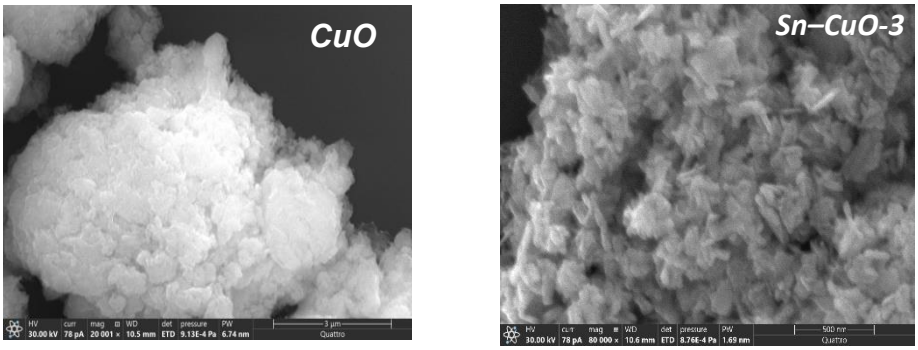
3.1 Structural Characterization

- **XRD:**
  The XRD patterns of pristine CuO and Sn–CuO composites exhibit the characteristic peaks of monoclinic CuO. Upon Sn incorporation, no additional phases are observed, suggesting successful Sn incorporation without forming separate tin oxide phases. The slight peak broadening indicates reduced crystallite size and lattice distortion, which can facilitate CO_2 activation.



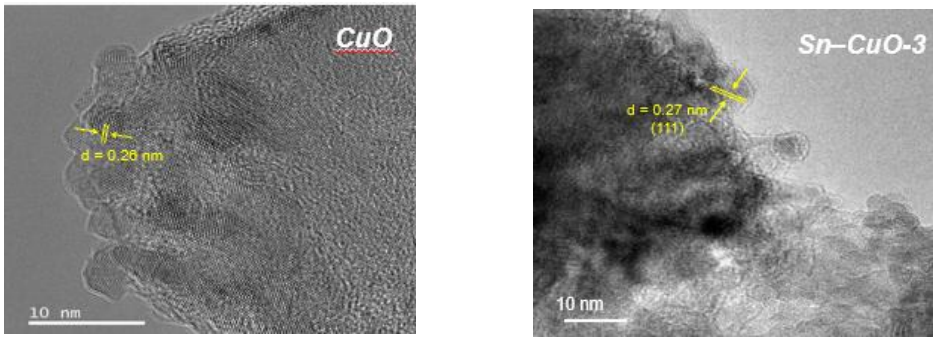
(Figure4: XRD patterns of CuO and Sn–CuO-3)

- **SEM:**
  Pure CuO shows agglomerated microscale particles with rough morphology. In contrast, Sn–CuO-3 displays nanosheet-like structures (~200 nm), which increase surface area and expose more active sites.



(Figure5: SEM images of CuO and Sn–CuO-3)

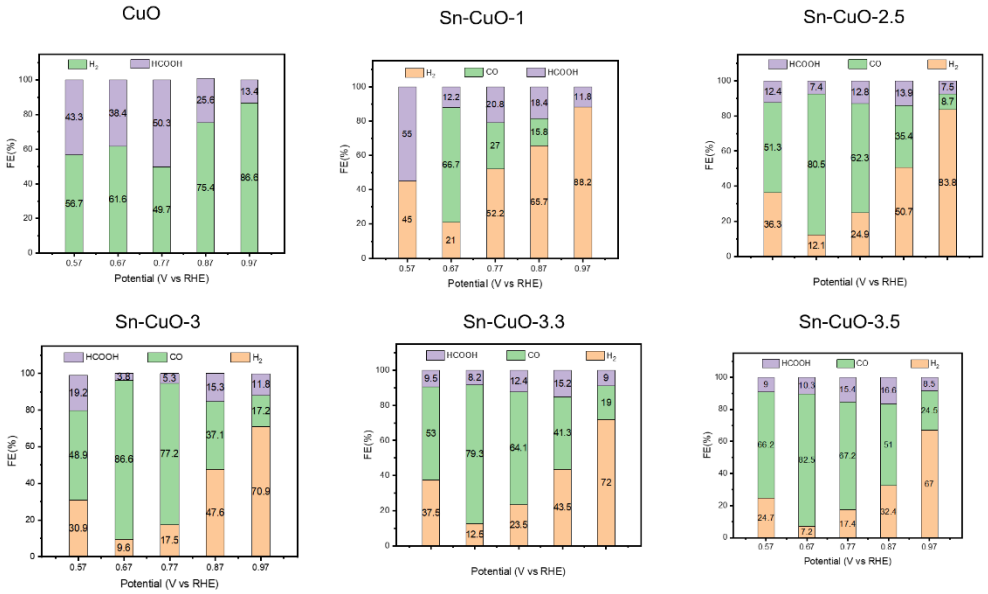
- **HRTEM:**
  HRTEM images confirm nanosheet morphology decorated with ~4 nm CuO nanoparticles. The lattice fringes (d ≈ 0.26–0.27 nm) correspond to CuO (111), verifying crystallinity. Sn incorporation leads to well-dispersed nanoparticles, supporting enhanced catalytic activity.



(Figure6: HRTEM images of CuO and Sn–CuO-3)

3.2 Electrochemical Performance

- **Faradaic Efficiency (FE):**
  The FE distribution for CO, HCOOH, and H_2 varies significantly with Sn loading.
  - Pristine CuO mainly produces **H_2** (61.6%), with limited CO selectivity (38.4%).
  - Sn–CuO composites suppress H_2 formation and enhance CO selectivity.
  - Sn–CuO-3 exhibits the highest CO FE (~86.6% at –0.67 V vs RHE), confirming optimal Sn loading for selective CO_2RR to CO.
  - At higher Sn loadings (Sn–CuO-3.5), CO selectivity decreases slightly, and H_2 reappears, suggesting overloading may block active sites.



(Figure7: Faradaic efficiency of Sn–CuO-x catalysts at different applied potentials)

Discussion Summary

- Sn incorporation modifies the reaction pathway, steering CO_2RR from H_2 evolution toward CO production.
- Optimal Sn loading (Sn–CuO-3) provides the best balance of active sites, high conductivity, and stabilized intermediates.
- Excessive Sn reduces performance, highlighting the importance of controlled loading.
- These results demonstrate that catalyst composition is a key driver in tuning selectivity toward valuable CO production for sustainable energy applications.

4 Reflections on Challenges

- **Technical challenges:**
  During the synthesis, controlling Sn loading precisely was challenging, as excess Sn tended to destabilize the CuO surface. Ensuring uniform dispersion required repeated optimization of reaction conditions (temperature and precursor ratios).
- **Process/coordination challenges:**
  Time constraints were significant due to the limited duration of the program. Balancing synthesis, characterization, and electrochemical testing within the available timeline required strict scheduling.
- **Unexpected findings:**
  While Sn incorporation enhanced CO selectivity, at higher loadings (e.g., Sn–CuO-3.5), the selectivity dropped due to excessive surface coverage—an observation that was not initially anticipated.
- **How challenges were overcome:**
  These issues were mitigated by systematically varying Sn loading and conducting careful cross-validation using XRD, SEM, and HRTEM to ensure structural consistency. Effective time management and task prioritization allowed the team to complete all required characterizations and analyses within the deadline.

5 Conclusion and Future Work

Conclusion

This study demonstrated that optimizing Sn loading on CuO electrodes significantly influences the CO_2 reduction reaction (CO_2RR) pathway. Moderate Sn incorporation (e.g., Sn–CuO-3) enhanced CO selectivity while suppressing H_2 evolution, confirming the critical role of Sn in steering product distribution. Structural analyses (XRD, SEM, HRTEM) further validated the uniform dispersion of Sn and the formation of nanosheet morphologies, which contributed to improved catalytic activity. These findings highlight the potential of controlled catalyst composition in advancing sustainable CO_2 utilization.

Future Work
Future studies should focus on:

- Exploring broader Sn loading ranges and fine-tuning ratios for maximum CO selectivity.
- Conducting long-term stability and durability tests under continuous electrolysis conditions.
- Expanding the product scope to C_2^+ products by coupling Sn with other promoters.
- Employing advanced in-situ characterization techniques (e.g., in-situ TEM, XPS) to monitor real-time structural and electronic changes during CO_2RR.
- Integrating these catalysts into scaled-up electrochemical systems to evaluate industrial feasibility.

6 References

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