Citrus Waste to Carbon Catalysts: A Sustainable Approach to CO_2 Reduction

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Significance and Relevance

This study explored the use of citrus waste as a sustainable and cost-effective precursor for CO_2 reduction electrocatalysts. Active Cu-based catalysts were successfully synthesized by leveraging the inherent reducing properties and porosity of citrus peels, particularly orange peels. The study revealed that the type of copper precursor and citrus peel significantly influenced the catalyst performance. Orange peel-derived catalysts, especially those prepared with sulfate precursors, exhibited superior activity and selectivity towards multi-electron reduction products like methane. This novel approach demonstrates the potential of waste biomass to contribute to sustainable energy solutions.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion/Advanced process with electrocatalysis and plasma utilization
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Within the framework of a circular economy, there exists the potential to enhance the economic value of waste materials, such as biomass, by repurposing them as precursors for carbon supports in electrocatalytic applications. Carbon derived from waste biomass offers a sustainable alternative due to its inherent renewability and low cost. The valorization of citrus waste provides a compelling case study for this approach. By investigating the utilization of citrus waste as a feedstock for the production of carbon-supported copper-based electrocatalysts, we have demonstrated its two-fold advantages: (i) it serves as the carbon support for copper nanoparticles (CuNPs), and (ii) it provides the reducing agents (e.g., ascorbic acid) necessary for the reduction of cationic copper species. This study aims to validate the feasibility of directly employing citrus waste in a one-pot synthesis of carbon-supported Cu nanoparticles and their subsequent application in CO_2 electroreduction.

Materials and Methods

Catalysts were synthesized via microwave-assisted hydrothermal treatment. A copper precursor ($CuSO_4$, $CuCl_2$, or $Cu(NO_3)_2$) was dissolved in distilled water at 50 °C. Finely ground orange or lemon peels were suspended in the copper precursor solution and further diluted with distilled water. The mixture was then subjected to microwave irradiation at 68 °C. The resulting catalysts were thermally annealed in an argon atmosphere at 500 °C, and characterized by XPS, SEM, XRD and TEM.

An ink was prepared by sonicating a mixture of the catalyst, Nafion, and absolute ethanol for 2 hours. This ink was subsequently deposited onto a gas diffusion layer (GDL) via spray coating. The resulting electrodes, serving as working electrodes, were evaluated using chronoamperometric detection in a three-electrode electrochemical cell. Experiments were conducted at two different potentials (-1.8 and -2 V vs. Ag/AgCl) in a 0.1 M $KHCO_3$ solution saturated with CO_2.

Results and Discussion

This work investigated the influence of copper precursors ($CuCl_2$, $Cu(NO_3)_2$, $CuSO_4$) and citrus peel type (orange, lemon) on the performance of C-supported Cu-based electrocatalysts for CO_2 reduction. While the copper precursor marginally affected the initial catalyst structure, it significantly impacted

the final carbon support structure. Sulfate-based precursors favored the formation of a more porous carbon structure, leading to enhanced CO_2 reduction, including multi-electron products such as CH_4. The type of citrus peel played a crucial role in catalyst performance. Orange peel-derived catalysts outperformed lemon peel-derived catalysts. Also, the redox properties of the peel constituents, particularly the higher reducing compounds present in orange peels, combined with the redox properties of the counter anions (Cl^-, NO_3^-, SO_4^{2-}), controlled the thermal restructuring of the peel. This process generated intrinsic porosity, more enhanced in the case of SO_4^{2-} anion, and facilitated the formation of Cu_2O/Cu core-shell nanoparticles also confirmed by XPS and TEM analysis. The resulting high porosity and strong reducing properties of orange peel-derived catalysts led to well-dispersed, stabilized Cu_2O/Cu nanoparticles, enhancing electrochemical surface area (ECSA) and promoting a diverse range of CO_2 reduction products, including CO, CH_4, and HCOOH. As reported in figure 1, the T-$CuSO_4$-O (sulfate precursor and orange peel) catalyst achieved the highest faradaic efficiency (FE) for both CO (12.8%) and CH_4 (4%) production at -2V Vs Ag/AgCl. In contrast, lemon peel-derived catalysts, with less favorable redox properties, exhibited poor nanoparticle stabilization and favored formic acid production, potentially due to excessive Cu exposure and hydrogen evolution reaction (HER).

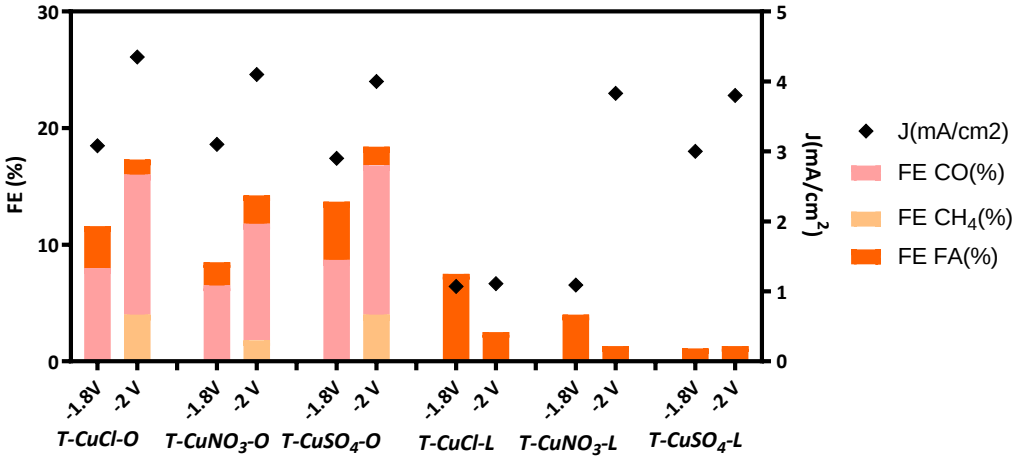

Figure 1: Current density (J), and faradaic efficiency of carbon monoxide (CO), formic acid (FA) and methane (CH_4) of orange peel-derived samples, and lemon peel derived samples after 1 hours of testing at an applied potential of -1.8 and -2 V vs Ag/AgCl.

These findings demonstrate the potential of valorizing citrus waste, particularly orange peels, as a sustainable and cost-effective precursor for efficient CO_2 reduction electrocatalysts. The insights gained from this study can guide the development of advanced electrocatalysts from various waste biomass sources for clean energy applications.

Acknowledgements

The project is funded by the ERC Grant “Surface-Confined Fast Modulated Plasma for Process and Energy Intensification" (SCOPE), Grant No. 810182