please include level 3 milestone(s) that your work is addressing

Molecular tuning of Cu electrodes promotes CO_2-to-ethylene electroconversion

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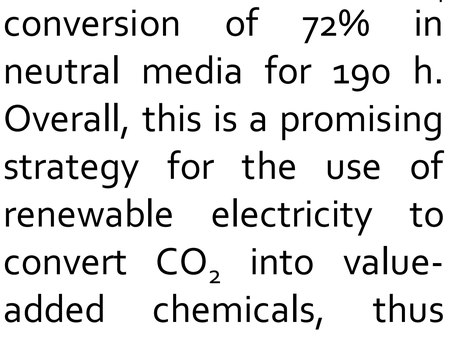
Abstract:

The highly selective generation of economically desirable products such as ethylene (C_2H_4) from the carbon dioxide reduction reaction (CO_2RR) remains a challenge. Here we present a molecular tuning strategy - the functionalization of the surface of electrocatalysts with organic films - that promotes the CO_2RR to ethylene conversion. We report the triple role of a simple N-substituted additives: first by forming nanocubes by corrosion of the copper surface; secondly, by stabilizing them during catalysis by forming a protective organic layer; and finally by promoting the formation of $C_{\geq 2}$ products.

Introduction

Cu electrodes are one of the few materials capable of converting CO_2 into $C_{\geq 2}$ products, including hydrocarbons, alcohols and aldehydes, with significant efficiencies. In the presence of organic additives, such as ionic liquids and pyridines, the selectivity is further enhanced towards C-C coupled products. Nevertheless, the mode of action of such additives is still unclear

Team



Outlook

This work presents a strategy to form and stabilize nanostructued Cu electrocatalysts using organic films. While anions can corrode Cu surfaces to form nanostructures, the *in-situ* electrodeposited *N*-substituted tetra-hydro-bipyridine films stabilized them under reduced conditons. Using a gas diffusion type flow cell, we maintained a CO_2-to-C_2H_4 conversion of 72% in neutral media for 190 h. Overall, this is a promising strategy for the use of renewable electricity to convert CO_2 into value-added chemicals, thus storing the renewable energy in the form of chemical energy.

Acknowledgments

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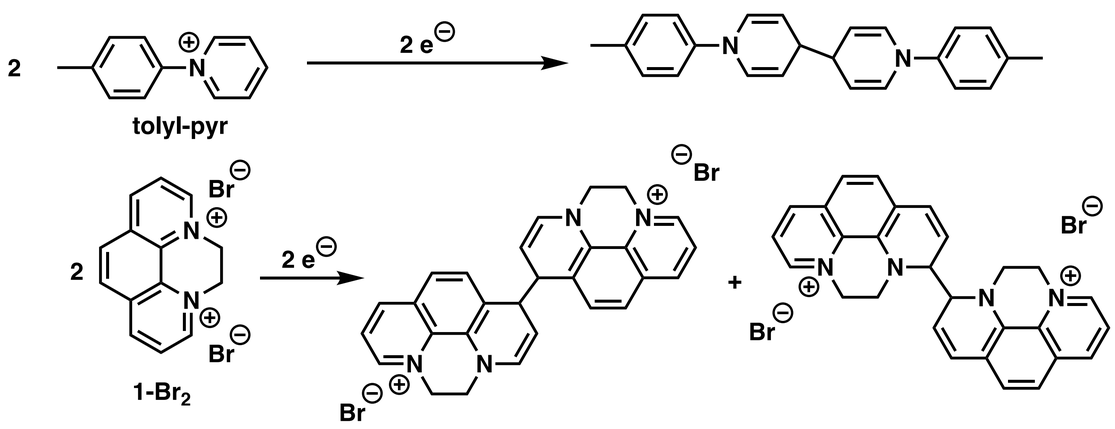
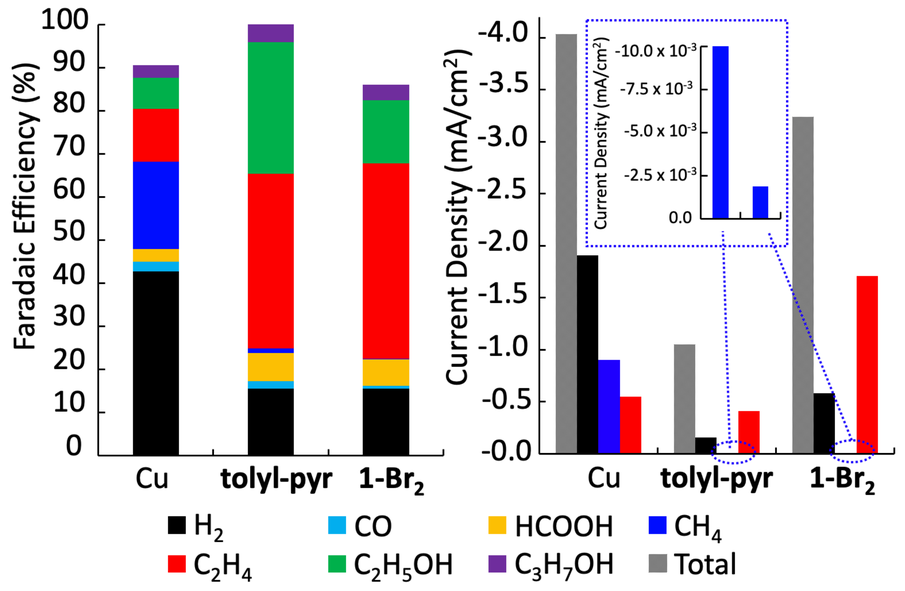
Results, Highlights, and Accomplishments

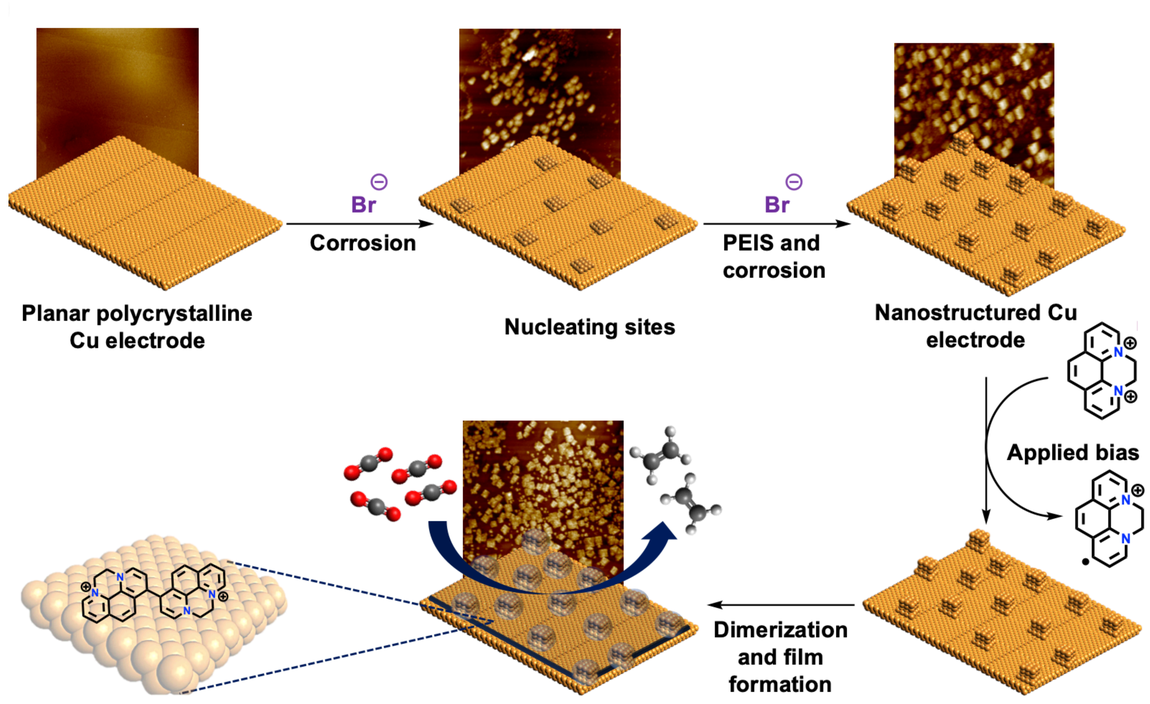
1. Organic salt additive for CO_2RR

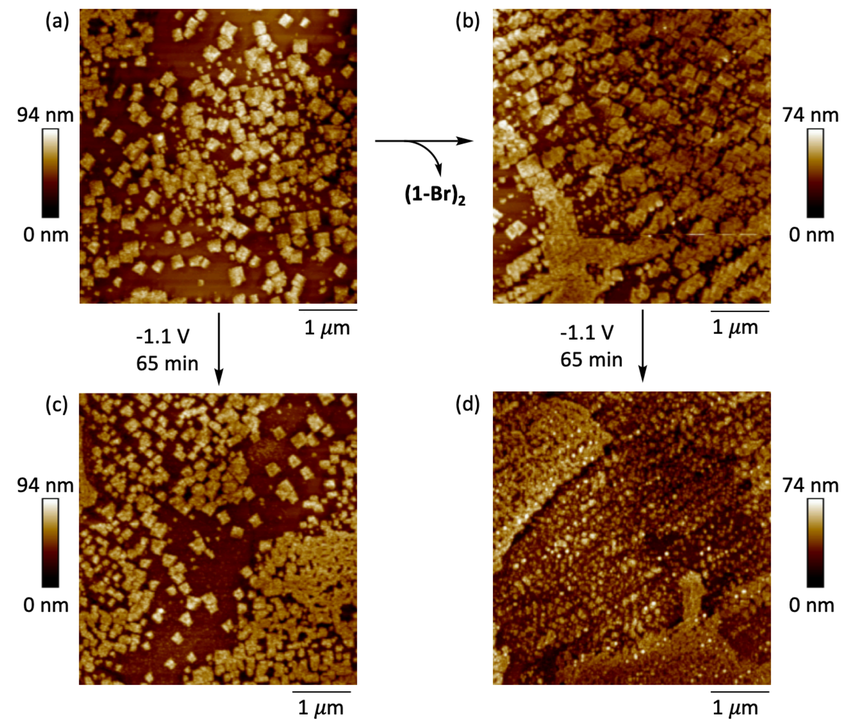




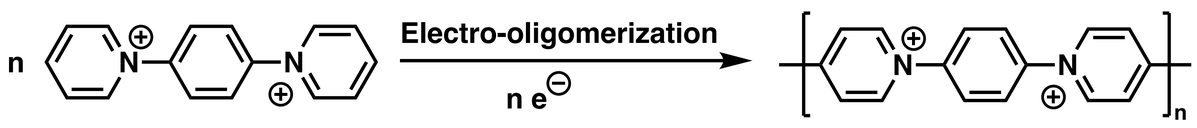
CO_2RR conditions: Polycrystalline Cu electrode, 0.1 M $KHCO_3$ buffer, pH: 6.8, [**1**]: 10 mM, flow CO_2: 5 ml/min, duration: 65 min.

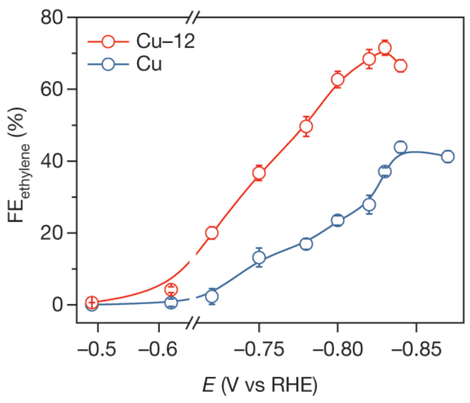
2. Formation and stabilization of nanostructures in presence of phenanthrolinium dibromide additive

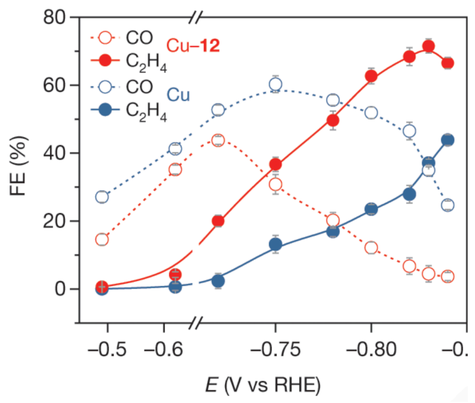


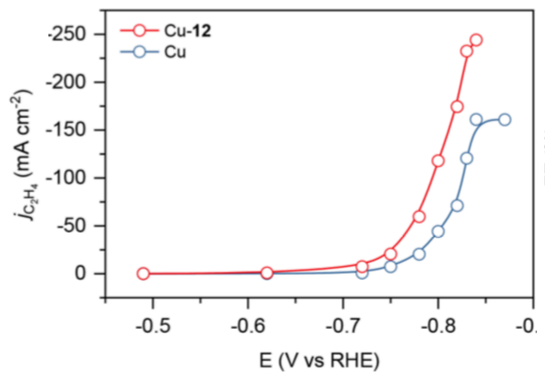


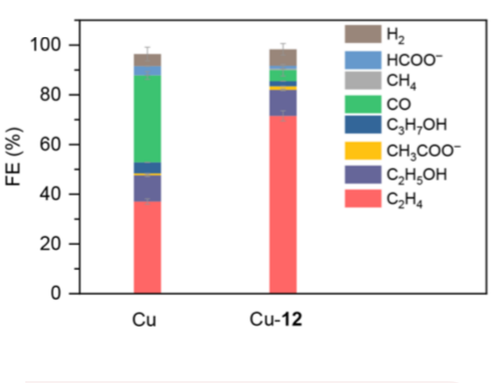
3. CO_2RR performance in gas diffusion type flow cell (in collaboration with the University of Toronto).

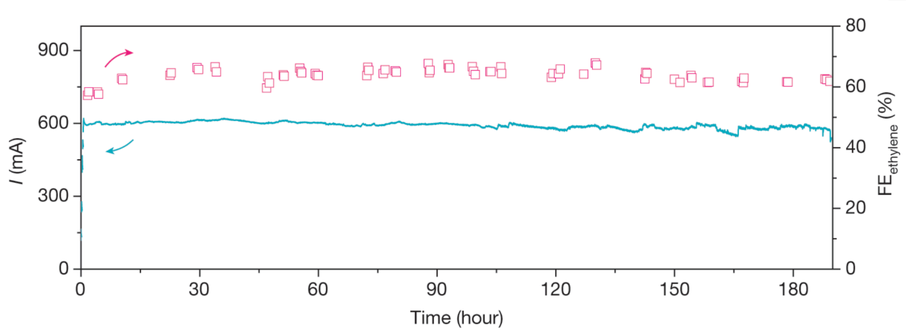












- The bispyridinium additve has similar Bader charge and CO_{atop}/CO_{bridge} ratio as the tolyl-pyridinium additive (additive **1**)
- Most of the CO is converted to C_2H_4 in presence of the organic film
- **Faradaic efficiency for C_2H_4 as high as 72%** in 1 M $KHCO_3$ at -0.80 V_{RHE}
- **C_2H_4 current density as high as 250 mA/cm²** at -0.80 V_{RHE}
- High production of C_2H_4 maintained over 190 h using a MEA cell
- Energy efficiency above: 20%

References: F. Li, A. Thevenon, A. Rosas-Hernández et al., *Nature*, **2020**, 577, 509; A. Thevenon, A. Rosas-Hernández, J. C. Peters, T. Agapie, *Angew. Chem. Int. Ed.*, **2019**, 58, 16952; Z. Han, R. Kortlever et al. *ACS Cent. Sci.*, **2017**, 3, 853