Confinement Effect of Carbon Support on Carbon-Based Cu-Ag Bimetallic Catalysts for Efficient Electroreduction of CO_2

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ABSTRACT

Electrochemical reduction of CO_2 is a promising approach for storing the green electricity from intermittent solar and wind energy into chemical fuels. The direct production of energy-dense renewable synthetic fuels that is highly compatible with the existing transportation infrastructures is particularly important yet extraordinarily challenging. In this work, bimetallic Cu-Ag catalysts confined in a nitrogen-doped carbon octahedral shell are developed by a facile MOF-mediated synthesis for this grand objective. By correlative microscopic characterizations, the hierarchical nitrogen-doped carbon confined structure was identified and Cu-Ag bimetallic nanoparticles were successfully confined in the porous octahedral shell. It is discovered through systematic experiments and further theoretical investigations that nanoconfined bimetallic Cu-Ag nanoparticles work in synergy with the nitrogen-doped porous carbon octahedral shell for efficient electrocatalytic CO_2 reduction reaction (CO_2RR) towards high-order products. Owing to the geometric and electronic benefits, the as-designed electrocatalyst is favorable for migration of *CO intermediate from Ag domain to Cu-Ag interface and subsequently promote C-C coupling through an interesting *CHO-*CO pathway with significantly lower energy barrier, which leading to high activity and selectivity towards energy-dense products. The total faradaic efficiency of high-order products i.e., CH_4, C_2H_4, C_2H_5OH and CH_3COOH reaches 55.3% with a high current density of 5.3 mA/cm^2 at a relatively low overpotential of -1.2 V versus reversible hydrogen electrode (RHE), exceeding the most common primary products e.g., H_2, CO and HCOOH. By removing porous carbon octahedral shell via air calcination, non-confined Cu-Ag nanoparticles with aggregated morphology were obtained, which exhibits much worsened CO_2RR performance. Through finite-element method (FEM) simulations, confinement effect of porous carbon octahedral shell was further investigated. Compared to bare Cu-Ag nanoparticles, nanoconfined structure of hierarchical nitrogen-doped carbon confined Cu-Ag nanoparticles enables faster mass transport of CO_2 and the adsorption of CO_2 reactant is thus enhanced. The enriched local feeding of CO_2 facilitates the generation of intermediates. Moreover, the local concentration of the intermediates like CO is significantly enriched through confinement effect of hierarchical nitrogen-doped carbon confined structure. The enriched reactant and intermediates benefited from confinement effect of carbon support further promotes CO_2RR towards high-order products. This study presents that the rational assembly of Cu-derived bimetallic catalysts with confined nitrogen-doped carbon architecture to produce high-order products from electrocatalytic CO_2 reduction.

KEY WORDS

Confinement effect; Bimetallic Cu-Ag catalysts; Nitrogen-doped carbon confinement; CO_2 electroreduction; High-order synthetic fuels