

Abstract

Oxide-derived copper catalysts have been shown to enhance CO₂ reduction reaction (CO₂ RR) activity with high selectivity toward hydrocarbon products. However, the chemical state of oxide-derived copper during CO₂ RR has remained elusive and lacked *in-situ* observations. Herein, a two-step process was developed to synthesize Ag nanowires coated with various thicknesses of CuO_x layer for CO₂ RR. By employing the *in-situ* X-ray absorption spectroscopy, a strong correlation between the chemical state under reaction conditions and the CO₂ RR product profile can be revealed to validate another competing reaction (i.e., the spontaneous oxidation of Cu(0) in aqueous electrolyte) that significantly governs the chemical state of active centers of Cu. Quantification analysis of reoxidized behavior is revealed to indicate that the reoxidation rate is independent of surface morphology and strongly proportional to the electrochemically surface area. The steady oxidation state of Cu in *in-situ* condition is the paramount key and dominates the products profile of CO₂ RR rather than other factors (e.g., crystal facets, atomic arrangements, morphology, elements) that have been investigated in numerous reports.