

## Abstract

Electrochemical reaction of CO<sub>2</sub> could play important role in addressing global warming issues. It offers a promising strategy to directly reduce CO<sub>2</sub> and replace fossil fuels. Single-atom catalysts (SACs) display outstanding performance to convert CO<sub>2</sub> into carbon monoxide. However, carbon monoxide is valueless and toxic so tuning the metal-nitrogen interaction to change the catalytic ability of SACs is an urgent issue for the development of favorable SACs.

Herein, the atomically dispersed Cu atoms on nitrogenated graphene-like carbon were synthesized through a two-stage carbonization and acid treatment and exhibited an efficient conversion of CO<sub>2</sub> to HCOOH, reaching a specific turnover frequency of 672 h<sup>-1</sup> at mild overpotential of 0.69 V for HCOOH formation. Based on X-ray photoelectron spectroscopy and near-edge X-ray absorption spectra, X-ray absorption spectroscopy measurements, the 2D mixed-valence Cu atomic center with a  $d_{x^2-y^2}$  electronic configuration was identified as the catalytically active site. The conventional catalyst, which converted CO<sub>2</sub> into CO, was further compared. By means of in-situ K-edge XAS, it is found that the differences of the coordinated environment of Cu-N during electrocatalysis are mainly attributed to the selectivity of CO<sub>2</sub>RR. These results could provide an effective approach to advance the performance of CO<sub>2</sub>RR.