Computational Nanoscale Electrocatalyst Design for CO­2 Reduction

Atomically precise Au nanoclusters, stabilized by organic ligands, exhibit well-defined structure (size/shape), but the accessibility of reactants to the metal is limited by the presence of ligands. Experiments have shown that these nanoclusters are active for CO2 electrochemical reduction, but the catalytic active sites are elusive. In this work, we apply first principles calculations to understand the CO2 reduction mechanism to CO on thiolate protected Au-based nanoclusters. We demonstrate that partial ligand loss from the nanocluster under electrochemical conditions generates active sites, significantly stabilizing the COOH intermediate that produces CO. Inherently, the reaction intermediates act as stabilizing ligands on the nanocluster. We apply nanoscale design rules combining catalyst stability and activity/selectivity trends to identify heterometal dopants that lead to the discovery of highly active and selective CO2 reduction electrocatalysts. We demonstrate how heterometal dopants and doping positions alter the electronic properties of the nanoclusters to finely tune electrocatalytic behavior. Our computational findings both rationalize and guide experimental studies and introduce novel paths for the discovery of active and tunable electrocatalysts.