Homogeneous Investigation of N-Heterocyclic Carbene Stabilized Au-Nanoclusters for Electrocatalysis

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Gold nanoclusters (AuNC) are among the most well studied type of NCs and are reputable for their ability to catalyze several reactions of energy importance electrochemically, such as hydrogen evolution reaction (HER) and CO_2 reduction reaction (CO_2RR). Typically, AuNCs are stabilized by either phosphine or thiol-based ligands, however, our lab has recently spearheaded the synthesis and characterization of several new AuNCs stabilized by N-heterocyclic carbenes (NHC).[1-5] Interestingly, regardless of ligand identity, the electrochemical nature of AuNCs remains surprisingly understudied. Despite the molecular nature of AuNCs, examples of electrochemical homogeneous characterization are scarce and most electrocatalytic experiments are performed heterogeneously.[1,6,7] The evaluation of the heterogeneous performance of molecular catalysts is valuable, however, homogeneous electrochemical studies of molecular catalysts provide a wealth of information important for benchmarking catalytic performance, understanding reaction mechanisms, and structural optimization.

As such, our group is interested in expanding the current AuNC catalytic field through the implementation of in-depth homogeneous studies for various reactions of energy importance. Herein, we report the investigation of a family of atomically precise Au_{13}NCs supported by Bis-NHC ligands for electrocatalytic homogeneous HER. From our investigation, we have determined that the mechanism for HER is influenced by the NHC ligand functionality, acid pka, and applied potential. As such, various stepwise catalytic EC reaction mechanisms can be accessed by the manipulation of these parameters. Utilizing this knowledge, we have extended our study towards CO_2RR to optimize reaction conditions for selective CO production and H_2 evolution suppression, a deleterious side reaction for CO_2RR. To the best of our knowledge, this is the first in-depth homogeneous study for HER utilizing AuNCs.

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