Atomically Precise Au $_{25}$ – based Alloy Nanoclusters for Electrochemical CO$_2$ Conversion

The researchers investigated the catalytic activity of a unique class of nanomaterials known as ligand-protected Au nanoclusters (NCs) for the electrochemical conversion of CO$_2$ to CO. They were able to explain the experimentally observed high stability of the well-known Au$_{25}$ NC upon ligand removal, thus confirming an earlier hypothesis on active site generation. Then, they identified heterometal doped Au NCs, such as the Au$_{19}$Cd$_2$ and Au$_{24}$Pd NCs, that exhibited significantly improved CO$_2$R performance compared to their monometallic precursors. They elucidated the electronic structure of these bimetallic NCs through DFT and TD-DFT while also probing their catalytic activity and selectivity for CO$_2$R and hydrogen evolution reaction (HER). The thermodynamics of active site formation and the mechanism of CO$_2$R on bimetallic Au-based NCs were investigated, showing that partial ligand removal (-R removal) from the surface of bimetallic Au NCs is essential and responsible for their high activity and selectivity towards CO$_2$R to CO. Importantly, they showed that partial ligand removal on bimetallic Au-based NCs can change the electronic interaction of reaction intermediates with the active site, which in turn can boost their CO$_2$R activity and selectivity.

Relaxed structures of the NCs upon hydrogen adsorption on Au active site.
Color labels: magenta = Au, light grey = Ag, yellow = S, cyan = adsorbed H, grey = C, and white = H.
**Benefits:**
Overall, this UCFER project has contributed to developing a fundamental understanding of the CO$_2$R performance of atomically precise Au-based NCs through a combination of experiment, theory, and computation. Such information will play a key role in advancing the field of nanoscale catalysis and materials discovery, resulting in practical solutions that can address the challenge posed by increasing levels of CO$_2$.

**Accomplishments:**
The research showed that 1) it is possible to generate a stable partially protected NC with either a S or Au atom exposed on the NC surface, 2) the reaction intermediates formed during the reaction play an important role in stabilizing the Au$_{25}$ NC, 3) the single-atom substitution can largely improve the electrocatalytic activity of NCs through electronic structure modification, 4) the mass activity of Au$_{19}$Cd$_2$ (2200 mA mg$^{-1}$) for CO$_2$R was one of the highest among reported LPNCs, 5) the structural integrity of the NC is due to species bonded to an S atom, and 6) the detailed mechanism and active sites for CO$_2$R on Au-based NCs was elucidated through a combination of theory and experiments.

**NETL Collaboration:**
Collaboration with NETL was highly successful and productive, demonstrating a fruitful synergy between theory and experiment. Bimetallic Au-based NC candidates for CO$_2$R were synthesized and tested by a team of NETL scientists. Using state-of-the-art experimental techniques, the exact geometric and electronic structure of the catalysts was revealed as well as their electrocatalytic CO$_2$R activity, selectivity, and stability. An excellent agreement between experimental and computational results was observed, providing deep mechanistic insight into CO$_2$R pathways and the electronic properties of ligand-protected bimetallic NCs that result in enhancing the CO$_2$R to chemicals. Overall, this work has provided a framework for accelerated catalyst discovery for the electrochemical conversion of CO$_2$ to fuels and chemicals.

**Relevant Publications:**


Frontier molecular orbitals of Au$_{36}$Ag$_2$(SCH$_3$)$_{18}$ and their corresponding energy levels.