Abstract: Sustainable energy utilization and carbon emission reduction are critical challenges for the world. Solving these challenges requires precise control of many important chemical reactions with sluggish kinetics and myriad possible reaction pathways and associated products. There is a critical need for selective, active, durable and low-cost catalysts. This talk presents our research efforts aimed at bridging the gap between homogenous catalysis and heterogeneous catalysis to realize materials with new or improved electrocatalytic properties for the carbon dioxide reduction reactions. We have developed heterogenized metal-complex electrocatalysts allowing for mechanism-based optimization at the molecular level. We have discovered interesting phenomena including ligand-mediated electron transfer, beyond two-electron reduction via a domino process, and reversible restructuring under reaction conditions. We have also designed reactors to enhance electrochemical performance, study surface/interface phenomena, and perform thermodynamically challenging reactions.