High-performance catalysts for applications in fuel cell, battery and water splitting electrodes require careful design of nanostructures and surfaces that form through either direct or post synthesis processing. The conventional impregnation method typically does not have the level of control to meet various requirements, such as catalytic surface with controlled single atom position or sub-monolayer atoms. Approaches are being developed to address preparation challenges in nanocrystal size, facet, composition and fine structures (e.g., site specific bimetallic catalysts). I will present our latest understandings on the design and post-synthesis treatment of several classes of electrocatalysts. The focus of this presentation will be on a) ligand chemistry in the design and controlled synthesis of metal catalysts, b) in situ liquid transmission electron microscopy (LTEM) in the understanding of nucleation and growth of heterogeneous bimetallic nanoparticle catalysts, c) in-situ variable temperature environmental TEM (ETEM) study of structural dynamics of oxygen reduction reaction (ORR) catalysts, d) structure-property relationship and e) density functional theory (DFT) calculation in understanding the observed new phenomena.