Hybrid Assemblies for the Electrocatalysis of Oxygen and Nitrogen Reduction: Mechanistic Studies and the Design of New Catalysts

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In this talk, we discuss aspects of our work related to the structure and reactivity of electrode surfaces. We report first on our efforts directed at establishing the mechanism of oxygen and peroxide reduction on many different metal surfaces. By using a combination of spectroscopic, imaging, and x-ray scattering techniques combined with detailed calculations, we show that a crucial step involves the spontaneous clevage of the O-O bond to form a mixed metal-hydroxide complex. This hydroxide complex is reduced during the electron transfer event, leading to the product water. The understanding derived from the mechanistic work provides directions for synthesis of advanced catalysts for oxygen reduction. In particular, we have synthesized a series of bio-insipired metal coordination polymers exhibiting oxygen reduction activity,and developed a series of correlations between the strucuture of these materials and their activity. A recent extension uses similar constructs to enhance CO_2 reduction.

In the area of nitrate reduction – performed on Cu single crystal surfaces -- characterization techniques reveal the interplay between the surface structure and reactivity. In particular, access to surface oxides yields a high performing catalyst, while inhibition of surface oxide formation leads to diminished activity and a completely different set of products relative to the oxide accessible case.

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