Nature-Inspired Solid-State Electrocatalysts: The Oxidation of Water and the Reduction of CO₂ to Fuels

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Objective
This research aims to develop novel catalyst design principles for two of the most relevant electrochemical reactions for the production of liquid fuels: water oxidation for the production of hydrogen from water splitting and CO₂ electro-reduction for the synthesis of alkanes, alkenes, or alcohols from CO₂. The reaction rate and the selectivity of these two reactions will be improved by tailoring catalytically active sites at the atomic scale.

Figure 1: Scheme of the envisioned carbon-neutral cycle for the use of electrochemically synthesized carbon-based liquid fuels

Background
Liquid fuels are a medium of choice to convert into and store the energy from intermittent energy sources such as sunlight and wind. They present multiple advantages including high energy density and ease of storage over other options. Additionally, liquid fuels benefit from the existing distribution infrastructure, which would ease the utilization of renewable sources to power the transportation sector. The most relevant liquid fuel options in this context are hydrogen, light hydrocarbons, and alcohols, all of which can be synthesized electrochemically and combusted in a carbon-free or carbon-neutral scheme. Hydrogen can be produced by water splitting, where water molecules get oxidized and reduced into oxygen and hydrogen respectively using an external source of electrons. Subsequently, energy from hydrogen can be extracted by combustion either in a fuel cell or an internal combustion engine, resulting in the emission of water. Light hydrocarbons and alcohols can be synthesized by reducing CO₂ electrochemically. By using high-concentration CO₂ emissions from existing fossil-fueled power plants and chemical facilities and CO₂ eventually extracted from the atmosphere, carbon fuels may be used in a carbon-neutral or even carbon-negative cycle, as depicted in Figure 1.
Currently, both water oxidation and the electro-reduction of CO₂ suffer from considerable inefficiencies even in the presence of state-of-the-art catalysts. Their improvement requires the development of novel classes of catalysts with enhanced activity and selectivity. This research effort focuses on developing design principles for robust, purely inorganic catalysts with features mimicking natural enzymes. The emphasis is put on the fundamental understanding of the effects of the morphological tailoring at the atomic scale of the catalyst active sites on the surface chemistry and physics involved in the above reactions. The chemical structure and morphology of the active sites are engineered at the atomic level, based on results from Density Functional Theory (DFT) models on reactive surfaces and experimental investigation of well-defined, atomically resolved catalyst surfaces.

**Approach**

The scientific approach adopted to understand the influence of atomic-scale tailoring of the catalytic active sites in this research effort is rooted in the fundamentals of surface chemistry and physics. First, ab initio calculations are performed to understand the water oxidation and CO₂ reduction reactions on enzyme active centers and other active catalyst surfaces. Based on the results derived from simulation, model catalyst surfaces are synthesized and their active sites identified and quantified using atomically-resolved imaging, both in-situ and ex-situ. The fundamental knowledge gained from experiment and theory is subsequently used to establish design principles for ideal active sites in terms of their atomic and electronic structure. Nanostructures with the desired surface properties are finally fabricated by implementing these design principles. Figure 2 depicts this same experimental approach adopted for the development of nanostructured MoS₂ catalysts for the reduction of water into hydrogen [T. F. Jaramillo et al., Science 317, 100, July, 2007].

Materials of choice for this study are manganese oxide thin films and nanoparticles for water oxidation and Fe-Ni-S composites in all of their stoichiometries for the reduction of CO₂. Both materials will be studied considering their numerous crystal structures that engender multiple and unique surface properties for electrochemical reactions.