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Project Title: Cu-Containing Bimetallic Nanoparticles for Electrocatalytic CO₂ Reduction into Fuels

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In the past year, which is also the second year of this project, we built on the progress we had achieved in the prior year and continued to investigate new strong metal-metal and metal-oxide interactions for more selective, active and stable electrocatalytic CO₂ reduction to fuels and chemicals. We have understood the mechanisms for noble metal atoms (Pd, Pt and Rh) stabilizing CO₂ electroreduction to hydrocarbons on Cu surface. We have developed a sample transfer procedure to realize *quasi-in-situ* X-ray photoelectron spectroscopy (XPS) characterization of catalyst surfaces exposed under reduction reaction conditions. Utilizing win-win metal-oxide interactions, we have developed a Ag/SnO_x catalyst that can operate in two modes and selectively convert CO₂ to two different products (CO and formate).

While Cu metal catalysts have received substantial attention due to their distinct capabilities to catalyze CO₂ electroreduction to hydrocarbons, they still suffer from fast deactivation. Developing a Cu electrocatalyst with long-term catalytic durability for CO₂ reduction remains a big challenge. We have invented a surface-restructuring strategy to realize self-cleaning Cu catalyst electrodes with unprecedented catalytic stability toward CO₂ reduction (Figure 1). Under the working conditions, the Pd atoms pre-deposited on Cu surface induce continuous morphological and compositional restructuring of the Cu surface, which constantly refreshes the catalyst surface and thus maintains the catalytic properties for CO₂ reduction to hydrocarbons. Our Pd-decorated Cu electrode can catalyze CO₂ reduction with relatively stable selectivity and current density for up to 16 h, representing one of the best catalytic durability performances among all Cu electrocatalysts for effective CO₂ conversion to hydrocarbons. The generality of this approach of utilizing foreign metal atoms to induce surface restructuring toward stabilizing Cu catalyst electrodes for CO₂ reduction is further demonstrated by replacing Pd with Rh.

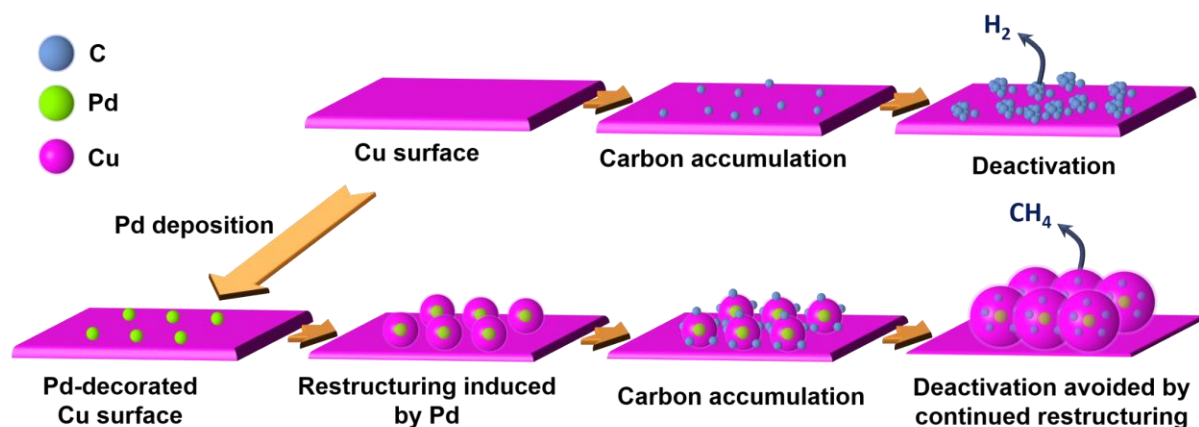


Figure 1. Schematic illustration of Pd-induced surface restructuring that can avoid the accumulation of carbonaceous species on Cu surface. Pink: Cu; green: Pd; blue: carbonaceous species.

Probing and understanding surface restructuring-induced electrocatalytic reactivity is an essential but challenging step toward rational prediction of electrocatalytic properties and design of high-performance catalysts. CoP nanoparticles are state-of-the-art electrocatalysts for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). However, the structure-reactivity correlations are not straightforward because the nanoparticles will restructure under working conditions. Employing a protective sample transfer procedure (Figure 2), we use simple lab XPS to unveil the changes in oxidation state and composition of the nanoparticle surface induced by electrochemical reaction conditions. CoP nanoparticles are naturally oxidized on their surface. In alkaline electrolyte under HER conditions, a Co-rich phosphide surface is generated as a result of polyphosphate dissolution and reduction of the oxidized P and Co species. In alkaline electrolyte under OER conditions, an oxidation and dissolution process occurs and the surface evolves into hydroxide/oxide with a subtle amount of phosphate residue. In acidic electrolyte under HER conditions, the surface oxidation layer is dissolved by the electrolyte and a fresh CoP surface is exposed. These surface restructuring results help rationalizing the electrocatalytic reactivity of CoP nanoparticles for water splitting under various electrochemical conditions.

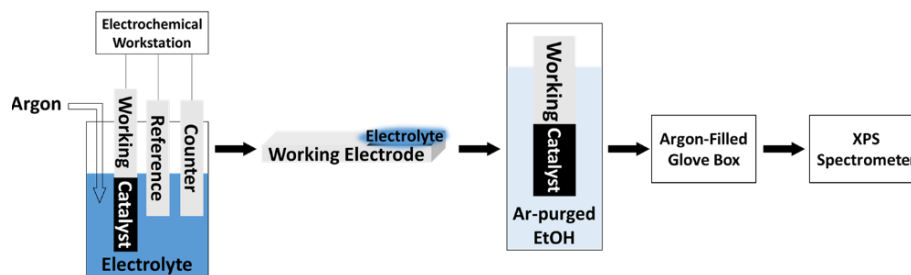


Figure 2. *Quasi-in-situ* XPS measurement enabled by a protective sample transfer procedure. Schematic illustration for the protective sample transfer procedure.

Understanding how remarkable properties of materials emerge from complex interactions of their constituents and designing advanced material structures to render desired properties are a grand challenge. Metal-oxide interactions are frequently utilized to improve catalytic properties, but are often limited to situations where only one component is facilitated by the other. In our work (manuscript submitted for publication), we demonstrate highly-cooperative win-win metal-oxide interactions that enable unprecedented catalytic functionalities for electrochemical CO₂ reduction reactions (Figure 3). In a single Ag/SnO_x catalyst, the oxide promotes the metal in the CO production mode, and meanwhile the metal promotes the oxide in the HCOOH production mode, achieving potential-dependent bi-functional CO₂ conversion to fuels and chemicals, with H₂ evolution suppressed in the entire potential window. Spectroscopic studies and computational simulations reveal that electron transfer from Ag to SnO_x and dual-site cooperative binding for reaction intermediates at the Ag/SnO_x interface are responsible for stabilizing the key intermediate in the CO pathway, changing the rate-determining step in the HCOOH pathway, and increasing the kinetic barrier in the H₂ evolution pathway, all together leading to highly synergistic CO₂ electroreduction.

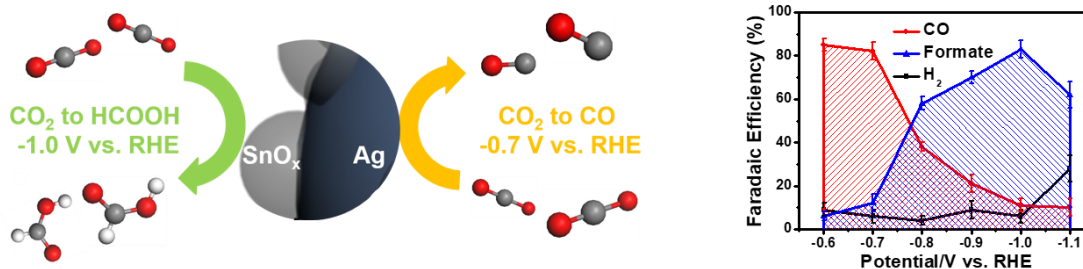


Figure 3. Bi-functional electrocatalytic CO₂ conversion to CO and formate by Ag/SnO_x.

With this project, we have obtained fundamental understanding of how metal-metal and metal-oxide interactions influence the electrocatalytic properties of materials for the electrochemical CO₂ reduction reactions; we have also formulated strategies for utilizing such interactions to design catalysts with new functions and/or improved properties. Working on this project had enormous effects advancing my faculty career and my students' PhD study. Both students have advanced to PhD candidacy at Yale.

Related Publications:

1. Zhe Weng, Xing Zhang, Yueshen Wu, Shengjuan Huo, Jianbing Jiang, Wen Liu, Guanjie He, Yongye Liang*, Hailiang Wang*, "Self-Cleaning Catalyst Electrodes for Stabilized CO₂ Reduction to Hydrocarbons", *Angew. Chem. Int. Ed.* 2017, 56, 13135-13139.
2. Zishan Wu, Quan Gan, Xiaolin Li, Yiren Zhong, Hailiang Wang*, "Elucidating Surface Restructuring-Induced Catalytic Reactivity of Cobalt Phosphide Nanoparticles under Electrochemical Conditions", *J. Phys. Chem. C* 2018, 122, 2848-2853.