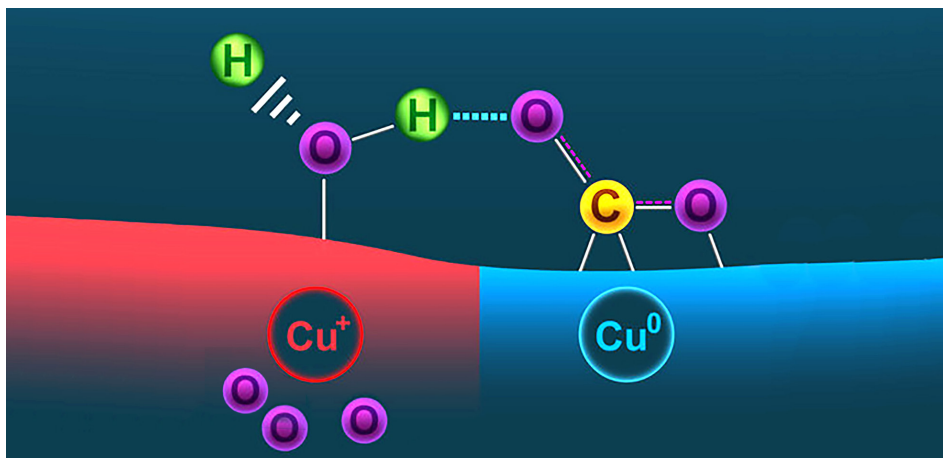
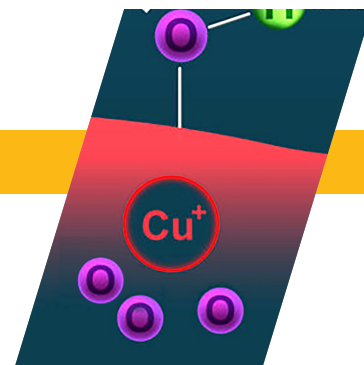


# Subsurface Oxygen Boosts Activity of Copper Catalysts



Researchers discovered that a sublayer of oxygen (purple) beneath the surface of a copper catalyst can help convert  $\text{CO}_2$  into more complex hydrocarbons such as ethanol. The oxygen causes some of the copper ( $\text{Cu}^0$ ) to become positively charged ( $\text{Cu}^+$ ), which stabilizes adsorbed  $\text{H}_2\text{O}$ . Adsorbed  $\text{CO}_2$  can then bind to the  $\text{H}_2\text{O}$ , a process that bends the normally linear  $\text{CO}_2$  molecule. Credit: Caltech/LBNL/JCAP

Scientists are seeking ways to reduce levels of carbon dioxide ( $\text{CO}_2$ ) in the atmosphere by improving the processes that convert  $\text{CO}_2$  gas into other compounds such as ethanol (a liquid fuel). Copper is currently considered the best catalyst for this process; however, it is not very efficient. Ambient-pressure x-ray photoelectron spectroscopy (APXPS) at the ALS, coupled with theoretical work by a team at the California Institute of Technology, revealed how oxygen atoms embedded very near the surface of a copper sample dramatically boost the early stages of the  $\text{CO}_2$  catalytic reaction. The information could prove useful in designing new types of materials to further enhance reactions and make them more efficient in converting  $\text{CO}_2$  into other products.

Large concentrations of  $\text{CO}_2$  are harmful to human health and the environment, so researchers have been pursuing ways to remove it from the atmosphere and safely store it or chemically convert it

into more beneficial forms. To convert  $\text{CO}_2$  into valuable hydrocarbons, a source of protons is needed, with water ( $\text{H}_2\text{O}$ ) being the favorite choice. However,  $\text{CO}_2$  is highly inert, and a catalyst is needed to initiate  $\text{CO}_2$  conversion reactions. Copper is the most promising pure-metal catalyst, but it is not very efficient or scalable, and its reaction pathways generally don't lead to the desired final products. Despite numerous experimental and theoretical studies, the role played by the copper surface structure in initiating chemical reactions is still unclear, and scientists lack a comprehensive understanding of how  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules adsorb on the copper surface and interact.

At ALS Beamline 9.3.2, researchers performed APXPS experiments on thin foils of copper exposed to pure  $\text{CO}_2$  gas as well as mixtures of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at room temperature. In some of the experiments, the sample was heated slightly in oxygen to increase the concentration of oxygen

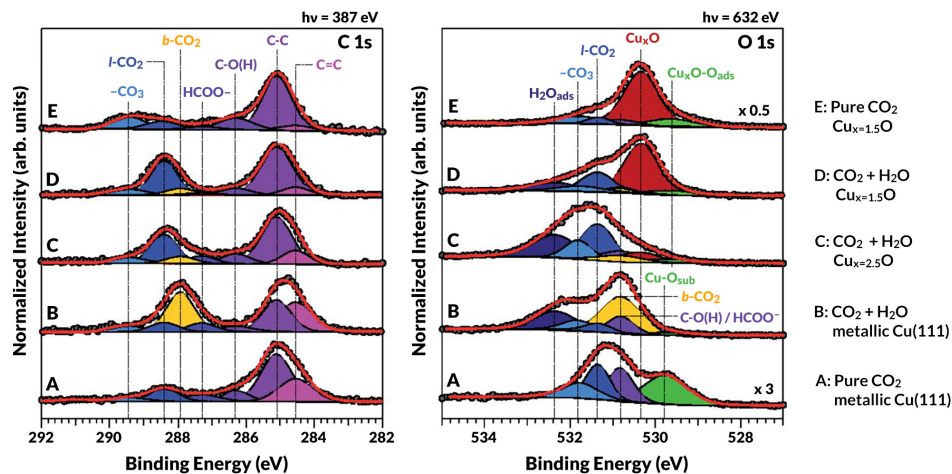
## A Sun-Powered Liquid Fuel

In the United States, the transportation sector (fossil-fueled vehicles) accounts for over a quarter of the energy directly used by consumers—clearly a major part of modern American life. Because the infrastructure to support that sector has been designed around the use of liquid hydrocarbon fuels, the development of an alternative, renewable source of such compounds is key to reducing our dependence on fossil fuels. Ethanol, for example, is a liquid fuel that's currently derived mostly from biomass—unused material from plants such as corn, sugar cane, and switchgrass. Plants, through photosynthesis, use energy from the sun to transform carbon dioxide and water into chemical fuel.

The Joint Center for Artificial Photosynthesis (JCAP) is a U.S. Department of Energy program whose mission is to create the scientific foundation for a scalable technology that, like plants, can convert carbon dioxide, water, and sunlight into renewable transportation fuels. In this work by Favaro et al., the back-and-forth between theory and experiment is a good example of the JCAP strategy of fostering a collaborative and cross-disciplinary team-science approach. The Caltech group used computers to help understand how electrons and atoms rearrange themselves in the reaction, while the Berkeley group used x-rays from the ALS to provide experimental data. As a result, we now have fresh insights into how to more efficiently catalyze the production of a sun-powered liquid fuel.

embedded in the foil. The APXPS data then revealed the various species of carbon and oxygen at the copper surface in the presence of water and different amounts of subsurface oxide. The probe depth (determined by the mean free path of the escaping photoelectrons) was about 1.2 nm from the topmost layer. At Caltech, members of the research team worked to develop and refine a quantum mechanical theory that unraveled the x-ray observations and explained the behavior of the molecules in the reaction.

The results showed that when there is little to no subsurface oxygen, CO<sub>2</sub> molecules (in their usual linear O=C=O arrangement) hover above the copper surface in a weakly bound, physisorbed state (adsorption involving van der Waals forces). A modest amount of subsurface oxygen causes some of the copper near the surface to become positively charged. This has the effect of stabilizing any adsorbed H<sub>2</sub>O molecules, which can then interact with nearby CO<sub>2</sub> molecules to facilitate chemisorption (adsorption involving chemical bonds), bending them through an angle of about 120°. This chemisorption is a key step in the transformation of CO<sub>2</sub> and H<sub>2</sub>O into formate (HCOO<sup>-</sup>) and formic acid (HCOOH),



**Carbon 1s (left) and oxygen 1s (right) APXPS data (black circles) for five different experimental conditions (A–E). All measurements were taken at 0.7 Torr and 298 K (room temperature). A multi-peak fitting procedure was used to disentangle the overlapping contributions from various carbon and oxygen species (multicolored peaks). Note that the peak representing the bent form of CO<sub>2</sub> (*b*-CO<sub>2</sub>, yellow) is most prominent under condition B, where it was exposed to both CO<sub>2</sub> and H<sub>2</sub>O and with just a small amount of subsurface oxygen (O<sub>sub</sub>, green) present.**

which are basic building blocks for more complex hydrocarbons such as ethanol. Too much subsurface oxygen, however, decreases the stability of the CO<sub>2</sub> and lowers the catalytic activity. The calculations indicated that an optimum amount of subsurface oxygen is (at most) one oxygen per every four copper atoms, or Cu(111)O<sub>x=0.25</sub>.

The researchers expect that it should be possible to mix and match different catalysts (e.g., other copper surfaces, copper alloys, or other metals) with subsurface atoms other than oxygen (e.g., sulfur or chlorine). The insights gained in this work have thus provided a foundation for the rational development of improved CO<sub>2</sub> catalysis as well as unique active electrocatalysts in general.

**Publication about this research:** M. Favaro, H. Xiao, T. Cheng, W.A. Goddard, III, J. Yano, and E.J. Crumlin, "Subsurface oxide plays a critical role in CO<sub>2</sub> activation by Cu(111) surfaces to form chemisorbed CO<sub>2</sub>, the first step in reduction of CO<sub>2</sub>," *PNAS* **114**, 6706 (2017). doi: 10.1073/pnas.1701405114

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