Improving catalytic activity by using strong metal support interactions and defect sites

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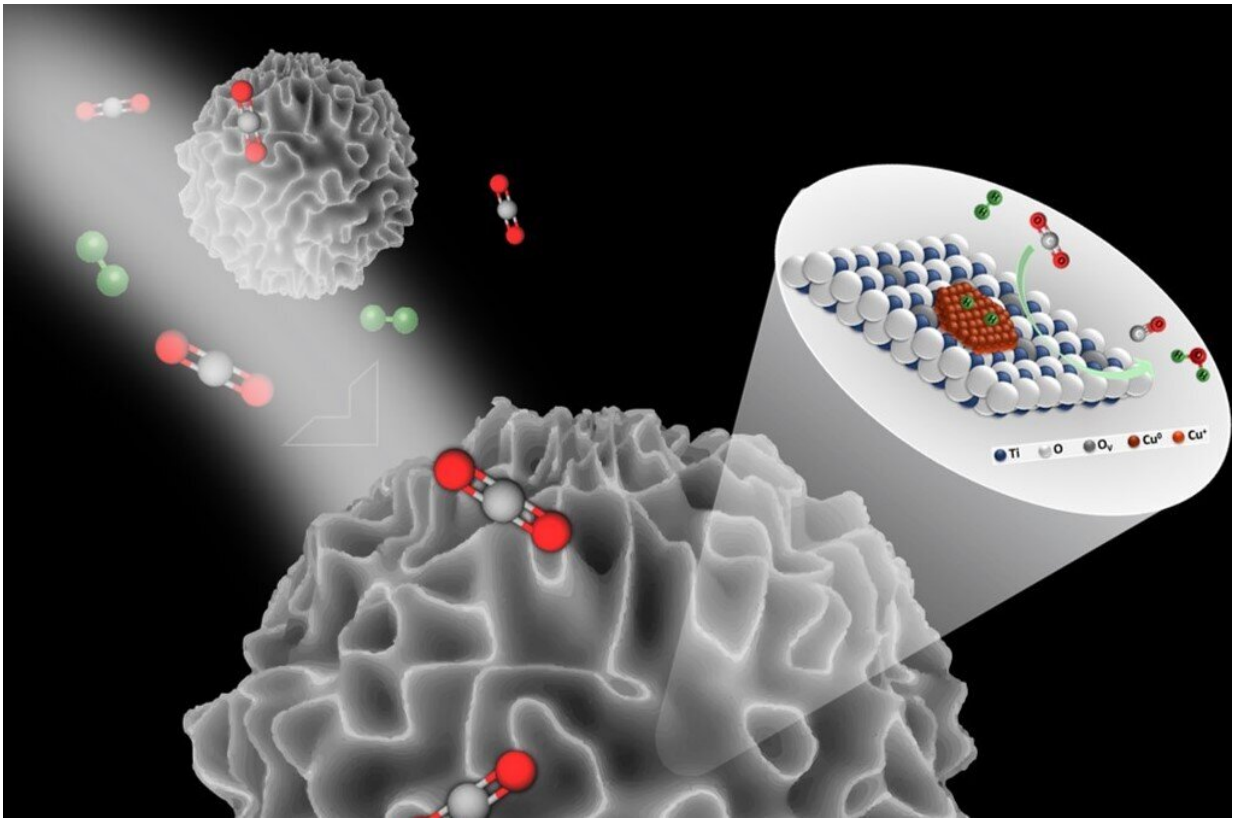

"Defects Tune the Strong Metal–Support Interactions", a unique approach to design CO_2 reduction nanocatalyst with excellent efficiency and stability. Credit: Mr. Rajesh Belgamwar and Prof. Vivek Polshettiwar

The heavy use of fossil fuels for driving industrial processes and human activities has resulted in increasingly excessive emissions of

anthropogenic CO_2 into our atmosphere, surpassing the 400 ppm level. This exceedingly high concentration of atmospheric CO_2 has led to a series of negative consequences for our planet's climate system. However, CO_2 can be a strategic carbon resource for synthesizing valued chemicals and fuels.

There have been numerous reports of noble metal catalysts, but their application was limited due to their moderate catalytic performance and high cost. In the non-noble metal catalyst family, Cu-based catalysts are among the most versatile, with good potential in many industrial processes. Unfortunately, the low Tammann temperature of copper and the resulting surface migration causes nanoparticles to sinter during the reaction, limiting their activity and long-term stability.

In this work, a team of researchers led by Prof. Vivek Polshettiwar at Tata Institute of Fundamental Research (TIFR), Mumbai, asked the question, how to improve the catalytic activity and stability of Cu-catalyst using the concept of strong metal support interactions (SMSI) and defect sites cooperativity?

They reported a catalyst with active copper sites loaded on titanium oxide-coated dendritic fibrous nanosilica (DFNS/TiO_2-Cu) for CO_2 to CO conversion. The fibrous morphology and high surface area of DFNS/TiO_2 allowed better dispersion and high loading of Cu NPs active sites.

This catalyst showed excellent catalytic performance for CO_2 reduction with CO productivity of 5350 mmol g^{-1} h^{-1} (i.e., 53506 mmol g_{Cu}^{-1} h^{-1}), superior to all copper-based thermal catalysts. Notably, DFNS/TiO_2-Cu10 showed 99.8% selectivity towards CO and was stable for at least 200 hours. The defect-controlled strong metal-support interactions between Cu and TiO_2 kept the copper nanoparticles firmly anchored on the surface of the support and imparted excellent catalyst

stability.

The EELS studies, in-situ diffuse reflectance infrared Fourier transform spectroscopy, H_2-temperature-programmed reduction, density functional theory calculations, and long-term stability indicated that there was a strong interaction between copper sites and the Ti^{3+} sites,which ensured good stability and dispersion of the active copper sites. In-situ studies provided insights into the role of defect sites (Ti^{3+} and O-vacancies) in tuning SMSI.

In-situ time-resolved Fourier transform infrared indicated that CO_2 did not directly dissociate to form CO, while the in-situ Raman and in-situ UV-DRS study demonstrated that the intensity of the oxygen vacancies and Ti^{3+} centers gradually decreased after introducing CO_2 gas into the reactor chamber and progressively increased when exposed to hydrogen. This indicated that CO_2 to CO conversion followed a redox pathway assisted by hydrogen.

Excellent catalytic performance of DFNS/TiO_2-Cu and in-situ mechanistic studies indicated the potential of defects in tuning the strong metal-support interactions. This approach may lead to the design of catalytic systems using various active sites and defective supports.

The paper is published in the *Journal of the American Chemical Society*.

More information: Rajesh Belgamwar et al, Defects Tune the Strong Metal–Support Interactions in Copper Supported on Defected Titanium Dioxide Catalysts for CO_2 Reduction, *Journal of the American Chemical Society* (2023). DOI: 10.1021/jacs.3c01336

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