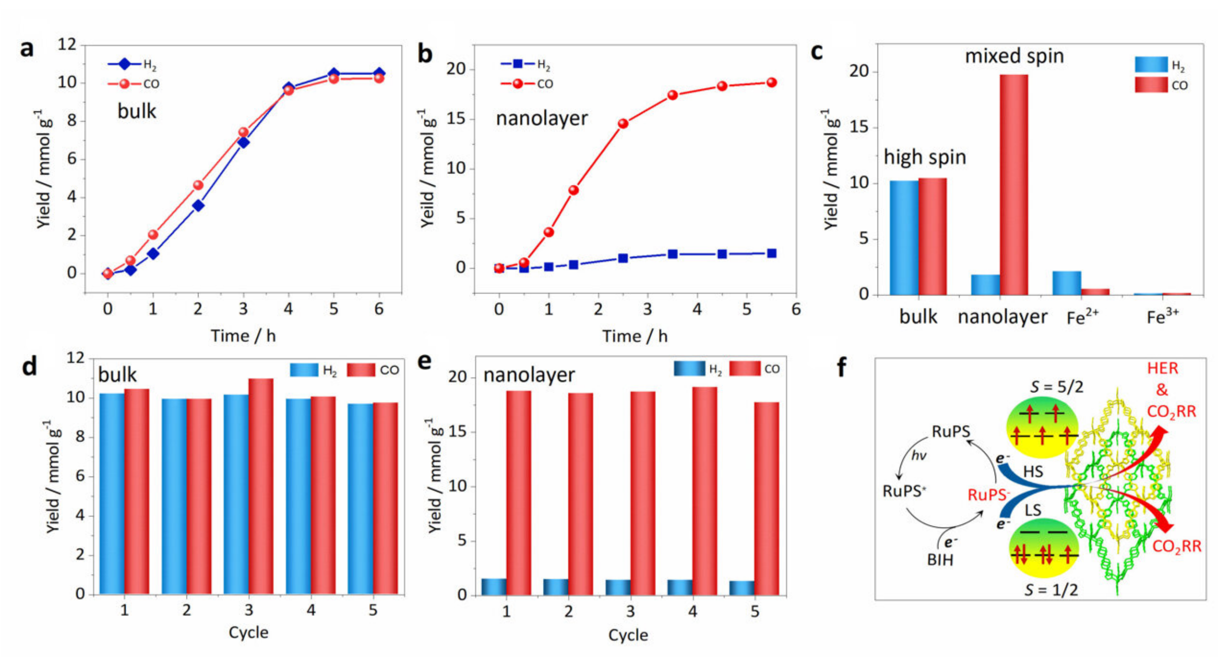
New method for designing efficient biomimetic catalysts

April 25 2023, by Zhao Weiwei



Catalytic performance. Time-dependent H_2 and CO yield with (a) HS bulk and (b) MS nanolayer o-1. (c) H_2 and CO yields through HS bulk o-1, MS nanolayer and control samples as catalysts after 4 h irradiation. Recycle experiments for H_2 and CO production with (d) HS bulk o-1 and (e) MS nanolayer o-1 as catalysts. (f) Proposed photocatalytic mechanism in this work. Credit: Wu Dayu

Recently, Professor Wu Dayu of Changzhou University, the user of China's Steady High Magnetic Field Facility (SHMFF), Hefei Institutes of Physical Science (HFIPS) of the Chinese Academy of Sciences

(CAS), together with his collaborators proposed a facile mechanical strategy to optimize the electronic structures of the catalytic center by mechanically induced spin transition, and realized a new method for designing efficient biomimetic catalysts.

The results were published in *Angewandte Chemie International Edition*.

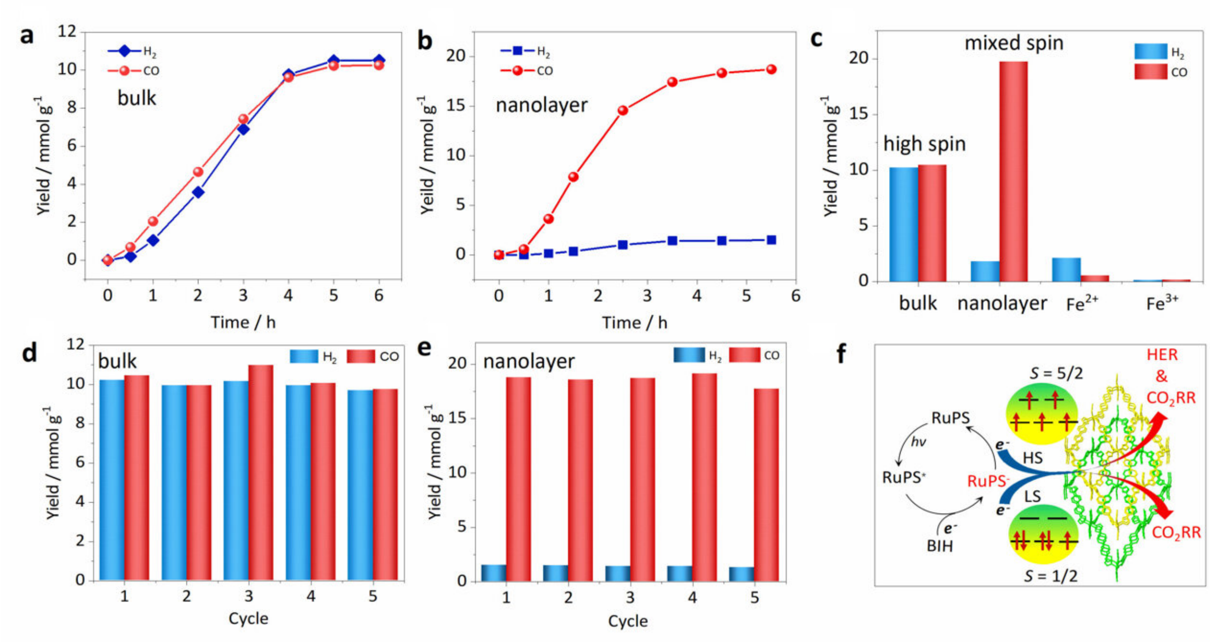
In recent years, the synthesis of transition-metal catalysts has received extensive attention. However, to improve catalytic activity/selectivity, it's urgent to precisely control the electronic structure of the catalytic center at the atomic level.

Wu's team in-situ induced partial spin crossover (SCO) of the iron catalytic active center around the grid-like lattice from high spin (HS, S = 5/2) to low spin (LS, S = 1/2). Due to the partial SCO of the iron center, the mixed-spin (MS) nanosheet catalyst exhibited a high CO yield of 19.7 mmol g^{-1} and a selectivity of 91.6%, far above the high-spin counterpart.

SHMFF experimental conditions were employed in this study to confirm the spin transition of the catalytic active center.

Density functional theory (DFT) calculations showed that the electron configuration of low-spin 3d orbitals effectively increased the overlap of bonding orbitals between O-2p and Fe-$3d_{xy}/d_{yz}$, thereby significantly promoting the selective adsorption of CO_2. However, the high-spin 3d orbital overlapped with the O-2p orbital through the $3dz^2$ anti-bond orbital, which greatly weakened the bonding interaction between the catalyst and the substrate, and reduced the catalytic activity.

In addition, DFT calculations showed that low-spin state played a key role in reducing the activation barrier. Researchers used electron paramagnetic resonance spectrometer, Mossbauer, magnetic [susceptibility](#) and other experimental methods to analyze and characterize the electronic structure of catalysts before and after mechanical exfoliation.



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Aside from that, they calculated the physicochemical mechanism behind spin catalysis through DFT calculation.

This study laid a foundation for the development of highly active, inexpensive and environmentally friendly CO_2 reduction catalysts, and further provided an important guarantee for solving the current energy and environmental crisis and achieving the goal of dual carbon.

More information: Dayu Wu et al, Spin Manipulation in a Metal–Organic Layer through Mechanical Exfoliation for Highly Selective CO2 Photoreduction, *Angewandte Chemie International Edition* (2023). DOI: 10.1002/anie.202301925

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