

Carbon-Neutral Fuels Move a Step Closer

Single-atom catalysts with high efficiency and selectivity demonstrate outstanding performance in electrocatalytic conversion and reactions.

To achieve high energy efficiency and scalability, the reaction must occur rapidly and selectively at low overpotentials. The electrochemical reduction of CO_2 could play an important role in addressing climate-change issues and global energy demands as part of a carbon-neutral energy cycle. The most active electrocatalysts for the conversion of CO_2 to CO are currently gold-based nano-materials, whereas non-precious metal catalysts have shown little or modest activity. Many single-atom catalysts have recently been developed in which numerous catalytic metal sites separated from each other were chemically and electronically constrained on solid supports. These catalysts exhibit properties and activity distinct from both nanoparticles and molecular complexes of the same metal elements. Single-atom catalysts can display outstanding electrocatalytic performance, but, given their single-site nature, they are typically amenable only to reactions that involve single molecules. For processes that involve multiple molecules, improved catalytic properties could be achieved through the development of atomically dispersed catalysts with greater complexities.

Xile Hu (Ecole polytechnique fédérale de Lausanne) and Hao-Ming Chen (National Taiwan University) have recently made a landmark discovery, successfully developing a highly efficient catalyst that converts dissolved CO_2 into CO —an essential ingredient of all synthetic fuels, as well as plastics and other materials. Employing operando X-ray ab-

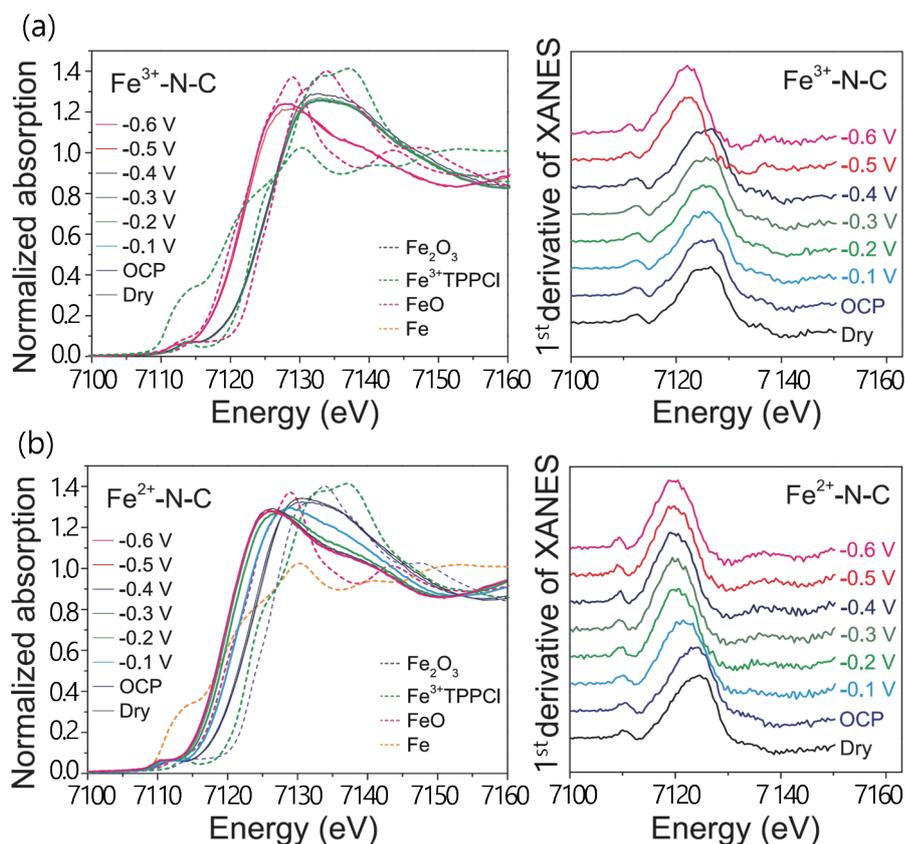


Fig. 1: Operando XAS characterization. (a)–(b) Fe K-edge XANES spectra (left) and first derivative of the spectra (right) of (a) Fe^{3+} -N-C and (b) Fe^{2+} -N-C as dry powder (black) and loaded on glassy carbon electrodes at open circuit potential (OCP) (blue), -0.1 V (light blue), -0.2 V (green), -0.3 V (dark green), -0.4 V (dark blue), -0.5 V (red), and -0.6 V (pink) vs. RHE, with spectra of Fe_2O_3 (blue dashed), Fe^{3+} TPPCI (green dashed), FeO (pink dashed), and Fe foil (orange dashed) as references. [Reproduced from Ref. 1]

sorption spectra (XAS) at **SP 12B1** and **TLS 20A1**,¹ the authors clarified the active sites to be discrete Fe^{3+} ions, coordinated to pyrrolic nitrogen (N) atoms of the N-doped carbon support. Operando XAS measurements in the CO_2 -saturated KHCO_3 catholyte (0.5 M) are illustrated in **Fig. 1**. The results imply that Fe^{3+} sites are more active for generating CO ; furthermore, the reduction of Fe^{3+} sites is accompanied by a change of local structure around the Fe ions. A reference sample (Fe^{2+} -N-C) was also prepared and operando XAS characterization performed. The results indicate that ligands of pyrrolic type are important to maintain Fe sites in oxidation state +3 during electroreduction of CO_2 , and consequently to retain the high activity and stability of these Fe^{3+} sites.

Chen Chen (Tsinghua University) and his coworkers recently also developed a new catalyst that features two adjacent copper atoms, which they call an atom-pair catalyst, that work together to implement the critical

bimolecular step in CO₂ reduction. Employing an operando XAS technique at **SP 12B1**,² Chen's team learned that CuO_x (Cu–O) species could retain their stability during the electrochemical tests (even under potential -0.98 V). According to the XANES spectra (Fig. 2), the Cu₄–O_x structure is inferred to be the essential active site for conversion of CO₂ into CO during reduction of CO₂.

In summary, these two works here offer an ideal model of interface design at an atomic level for the reduction of CO₂. The concept of atomically dispersed catalyst is believed to provide an effective and competent supplement to single-atom catalysis, and will provide numerous new opportunities for atomic-level dispersed catalysts to be applied in more complicated catalytic reactions. (Reported by Yan-Gu Lin)

This report features the work of (1) Xile Hu and his collaborators published in Science 364, 1091 (2019); (2) Chen Chen and his collaborators published in Nat. Chem. 11, 222 (2019).

TLS 20A1 BM – (H-SGM) XAS

SP 12B1 BM – Material X-ray Study

- XANES, EXAFS
- Materials Science, Chemistry, Condensed-matter Physics, Environmental and Earth Science

References

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2. J. Jiao, R. Lin, S. Liu, W.-C. Cheong, C. Zhang, Z. Chen, Y. Pan, J. Tang, K. Wu, S.-F. Hung, H. M. Chen, L. Zheng, Q. Lu, X. Yang, B. Xu, H. Xiao, J. Li, D. Wang, Q. Peng, C. Chen, Y. Li, *Nat. Chem.* **11**, 222 (2019).

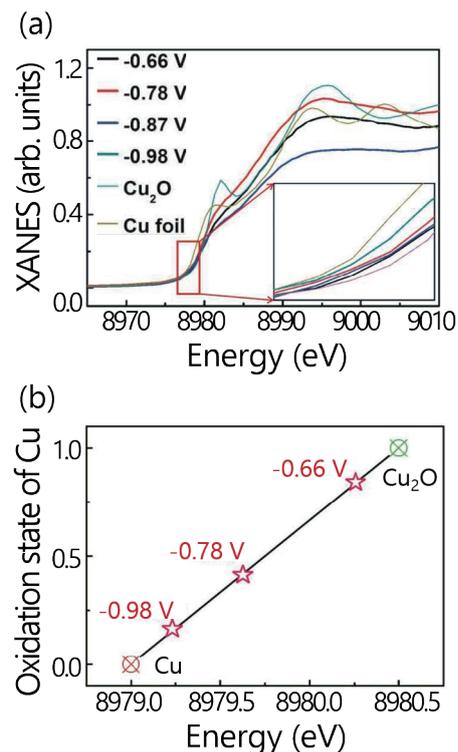


Fig. 2: XAS spectra of catalyst with Cu (0.20 wt%). (a) Cu K-edge XANES spectra *in situ* with various voltages. (b) Oxidation states of Cu with varied voltages from Cu K-edge XANES. [Reproduced from Ref. 2]

Metal Chalcogenide Molecular Accelerates Hydrogen Evolution

An active immobilized single molecular molybdenum disulfide on carbon support was developed.

The production of hydrogen through water splitting using earth-abundant metal catalysts is a promising pathway for converting solar energy into chemical fuels. However, existing approaches for fine stoichiometric control, structural and catalytic modification of materials by appropriate choice of earth abundant elements are either limited or challenging. For example, platinum-based catalytic systems are the most efficient hydrogen evolution reaction (HER) electrocatalysts. However, the low abundance and high cost of precious metals ultimately restricts their large-scale commercial applications. Therefore, the development and pursuit of cheap, noble-metal free electrocatalysts is highly desirable.

Bing-Joe Hwang (National Taiwan University of Science and Technology) and his co-workers recently developed a synthetic approach to fabricate immobilized single molecular molybdenum disulfide (MoS₂) on the surface of carbonized polyacrylonitrile (cPAN), and the electrocatalytic HER of the MoS₂-cPAN composite was performed and benchmarked. Employing X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and X-ray photoemission spectra at **TPS 09A**, **TLS 07A1**, and **TLS 24A1**,¹ the team found that the as-prepared material has no metal–metal scattering and it resembles MoS₂ with a molecular state. The local atomic structure of the MoS₂-cPAN catalyst was characterized by XAS of the Mo K-edge, as shown