High-loading single cobalt atoms on ultrathin MOF nanosheets for efficient photocatalytic carbon dioxide reduction

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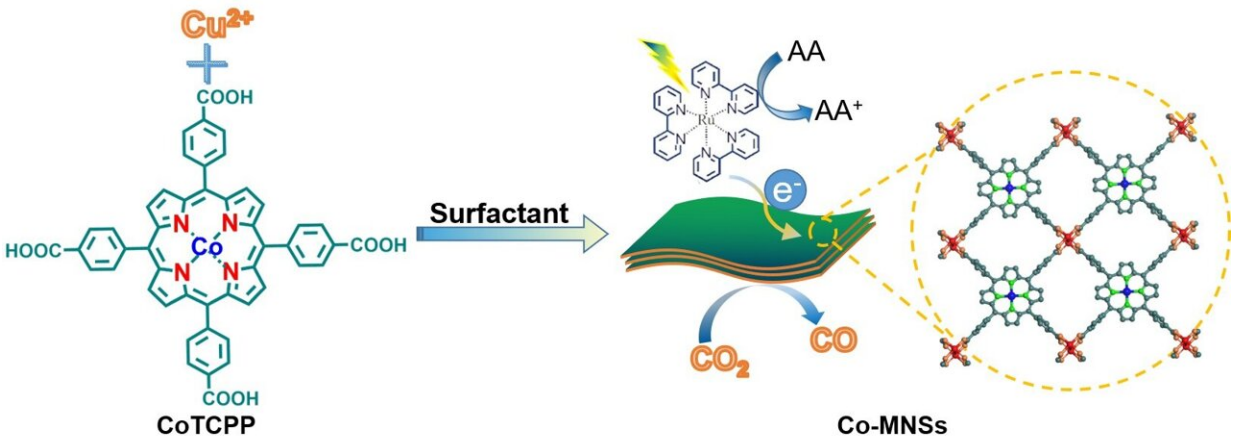


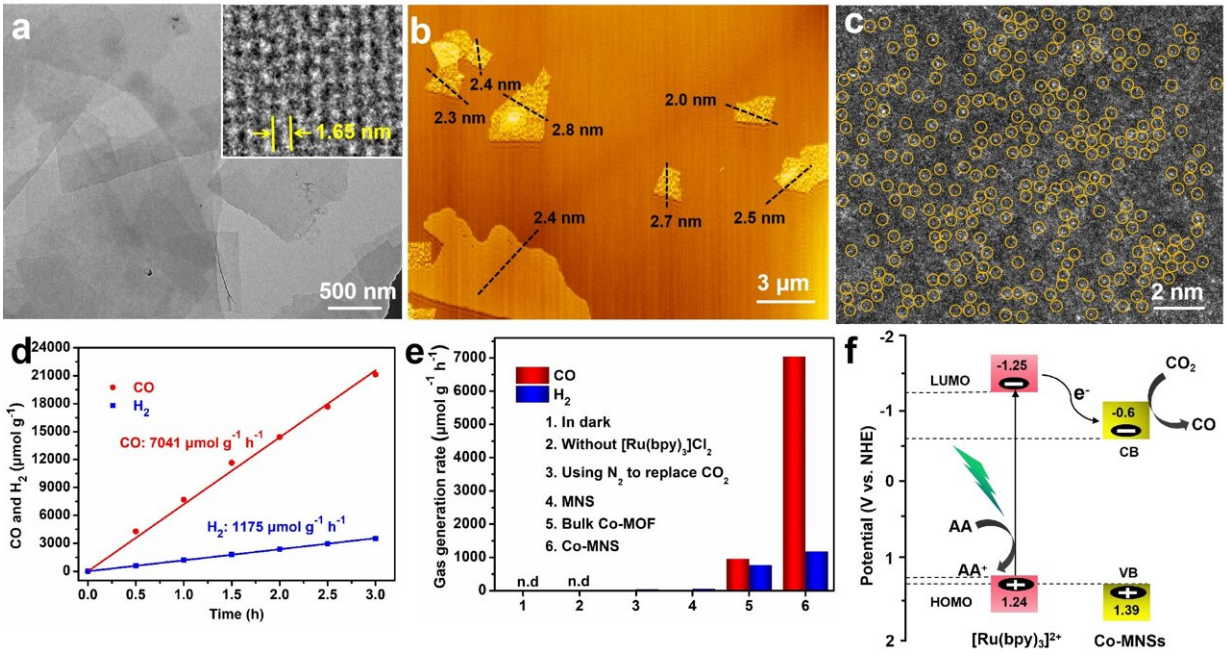
Synthetic illustration of the ultrathin MOF nanosheet-based cobalt single-atom catalyst for visible-light-driven photocatalytic CO_2-to-CO conversion. Credit: Science China Press

Using solar energy to convert CO_2 into synthetic fuels is currently one of the most promising technologies to achieve carbon neutrality with the embedment of sustainable energy into our modern economy. However, the efficiency of photocatalytic CO_2 conversion is greatly limited due to the high thermodynamic stability of CO_2 molecules and their multiple-electron-reduction process.

The synthesis of stable single-atom catalysts with high metal loading is desirable to boost photocatalytic CO_2 performance, which, however, has remained a great challenge. To overcome this challenge, a study was performed by the groups of Prof. Yongfeng Zhou and Prof. Yiyong Mai (School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University).

They developed a bottom-up synthetic strategy for the construction of ultrathin MOF nanosheets coordinated with Co single atoms, by directly using Co^{II} tetrakis(4-carboxyphenyl) porphyrin (CoTCPP) as the linkers and Cu_2–$(COO)_4$ paddlewheel cluster as the metal nodes. The bottom-up strategy avoids the tedious exfoliation processes and low yields encountered in top-down synthetic approach.

Moreover, because the Co sites were coordinated within the porphyrin rings before the MOF formation, Co single atoms with a high loading of 6.0 wt.% were achieved on the MOF nanosheets. The obtained MOF nanosheets showed an ultrathin thickness of 2.4 ± 0.5 nm and micron-sized lateral dimension.

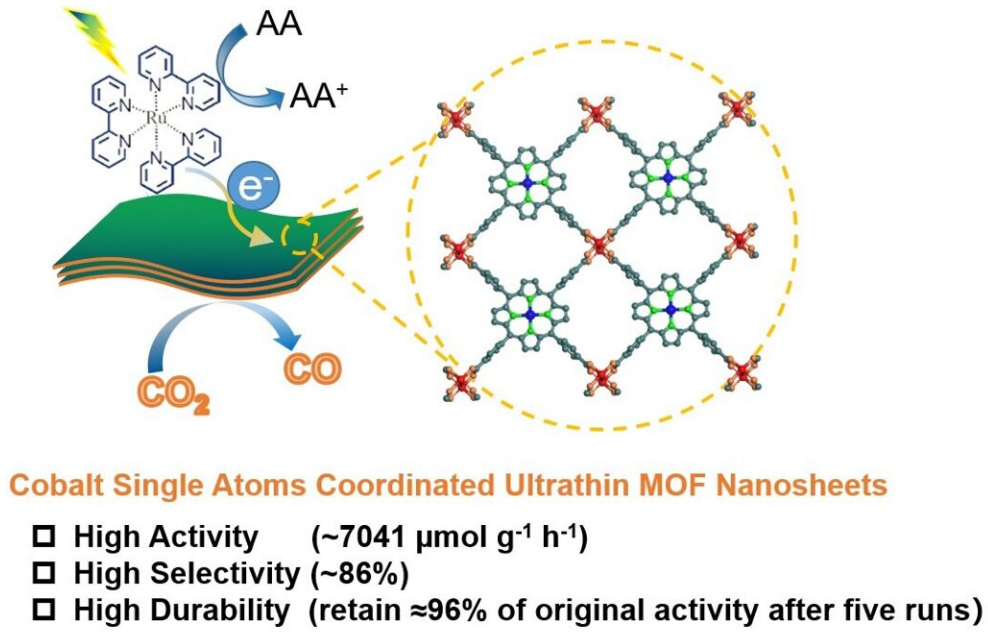


a) TEM images of Co-MNSs (inset: high resolution TEM image showing the lattice information); b) AFM height profile of Co-MNSs, the heights of the sheets are marked; c) HAADF-STEM image of Co-MNSs, the yellow circles highlight the tiny bright spots in the nanosheets; d) Photocatalytic time-dependent CO and H_2 yields by Co-MNSs; e) Comparison of CO_2 photocatalytic performance under various reaction conditions; f) A proposed electronic band diagram for the photocatalytic system. Credit: Science China Press

Such a large aspect-ratio 2-D morphology coupled with the high content of Co single atoms enabled abundant accessible active sites on the catalyst surfaces, and also effectively inhibited the electron–hole recombination by shortening the diffusion length of charge carriers from the material interior to the surface.

As a catalyst for visible-light-driven photocatalytic CO_2 reduction, Co-MNSs exhibited a high CO_2-to-CO production rate of 7,041 μmol g^{-1} h^{-1} and a remarkable selectivity of 86% in aqueous media under $\lambda > 420$

nm light irradiation, which is among the top-level performances of the reported MOF-based photocatalysts.



Ultrathin MOF nanosheet-based cobalt single-atom catalyst for visible-light-driven photocatalytic CO_2-to-CO conversion. Credit: Science China Press

This study opens a new avenue for the synthesis of 2-D stable single-atom catalysts with high loading of single metal atoms, and also stimulates future endeavors to develop efficient photocatalysts for important yet thermodynamically uphill reactions.

The study is published in the journal *Science China Chemistry*.

More information: Quan Zuo et al, High-loading single cobalt atoms on ultrathin MOF nanosheets for efficient photocatalytic CO_2 reduction, *Science China Chemistry* (2023). DOI: 10.1007/s11426-022-1498-y

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