High-loading Single Cobalt Atoms on Ultrathin MOF Nanosheets for Efficient Photocatalytic CO2 Reduction

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Researchers have developed a bottom-up synthetic strategy for the construction of ultrathin MOF nanosheets coordinated with Co single atoms.

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 CoII 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.

Ultrathin MOF nanosheet-based cobalt single-atom catalyst for visible-light-driven photocatalytic CO2-to-

CO conversion

The obtained MOF nanosheets showed an ultrathin thickness of 2.4 ± 0.5 nm and micron-sized lateral dimension. Such a large aspect-ratio 2D 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 CO2 reduction, Co-MNSs exhibited a high CO2-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.

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

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