High-performance photocatalytic water oxidation realized via ultrathin covalent organic framework nanosheets

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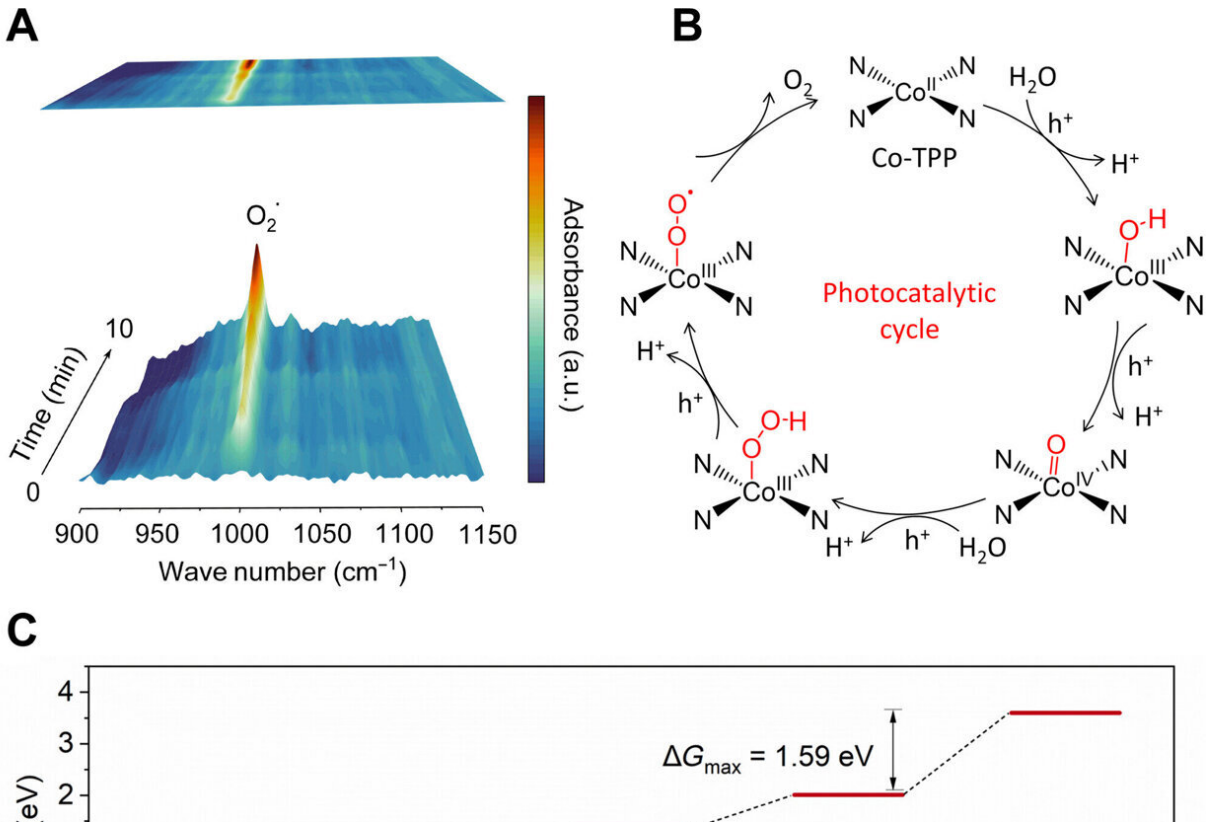

In situ ATR-IR characterizations and density functional theory calculations. Credit: *Science Advances* (2024). DOI: 10.1126/sciadv.adk8564

The photocatalytic water oxidation process plays a vital role in attaining

efficient solar-to-chemical process by enabling photocatalytic water splitting and CO_2/N_2 fixation. However, the lack of well-designed photocatalysts to overcome the sluggish kinetics of water oxidation has impeded the ongoing research. Therefore, it is important to develop an efficient water oxidation photocatalyst.

In a study published in *Science Advances*, Prof. Wang Yaobing's team from Fujian Institute of Research on the Structure of Matter of the Chinese Academy of Sciences has proposed a novel approach for the rational design of an ionic-type covalent organic framework (CoTPP-$CoBpy_3$) with atomic ultrathin nanosheets morphology, high water-affinity, efficient charge separation, and kinetic favored water oxidation mechanism. The CoTPP-$CoBpy_3$ water oxidation photocatalyst outperforms most of the reported COF-based photocatalysts.

The researchers demonstrated the ultrathin nanosheet morphology of CoTPP-$CoBpy_3$ in various solvents by atomic force microscopy (AFM) and cryo-TEM (transmission electron microscopy). They confirmed the superhydrophilicity by contact angle measurements (CAs), zeta potential tests and density functional theory (DFT) calculations.

Based on the analysis of the charge separation property by femtosecond transient absorption (fs-TA) spectra, the researchers realized the ultrafast intramolecular charge transfer (ICT) between two triplet states, a prolonged excited state lifetime and the relayed electron transfer pathway.

By combining DFT calculations and in situ attenuated total reflectance infrared spectrum (in situ ATR-IR) spectroscopy, they demonstrated an end-on type superoxide radical adsorption in the single cobalt active site for the first time, suggesting a kinetically-favored water oxidation pathway.

The researchers propose an electron-intermediate cascade mechanism of synergistic coupling of the relayed electron transfer pathway and catalytic water oxidation intermediate evolutions. Such an electron-intermediate cascade mechanism emphasizes that the electron-relayed state of the Co active site could be more beneficial for water oxidation rather than an extreme hole accumulation.

This study presents an efficient water oxidation photocatalyst design, which offers a promising example for exploration on high-performance water oxidation photocatalysts.

More information: Enbo Zhou et al, Ultrathin covalent organic framework nanosheets for enhanced photocatalytic water oxidation, *Science Advances* (2024). DOI: 10.1126/sciadv.adk8564

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