

Research Highlight

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Dynamic structural twist in metal-organic framework twists the clockwork spring of photocatalytic overall water splitting

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Photocatalytic overall water splitting (OWS) is considered as the Holy Grail reaction in chemistry. Despite notable advancements^[1,2], the materials that can carry out photocatalytic OWS directly are still limited. One of the difficulties lies in the fast recombination of photogenerated charge carriers^[3-5]. Diverse strategies, such as doping, constructing heterojunctions, and crystal facet engineering^[6], have been proposed to suppress the recombination, whereas most center on the ground state rather than the excited state of the catalyst. Inspired by natural photosynthesis, it is imperative to develop a novel photocatalyst with structural change in the excited state to avoid radiative relaxation. Metal-organic frameworks (MOFs) have garnered wide attention in the field of photocatalysis^[7-9]. Given the diverse compositions of MOFs, incorporating flexible building units can emulate biomimetic dynamic behavior. Moreover, the well-defined structure of MOFs allows for precise design and regulation at molecular scale, providing great convenience for further research on catalytic mechanisms.

Very recently, Sun *et al.* adopted a MOF named Coordination Framework Augsburg-Zn (CFA-Zn) in photocatalytic OWS^[10]. In CFA-Zn, the crystallographically completely independent ligands act as the



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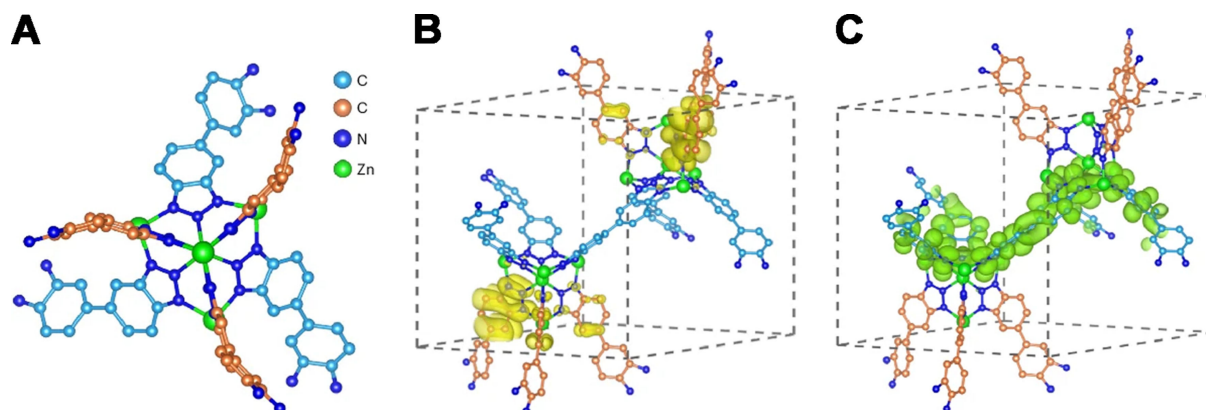


Figure 1. (A) The secondary building unit in CFA-Zn with hydrogen atoms and acetate omitted. The orange and light blue benzene rings represent crystallographically different ligands; (B and C) Spatial distribution of the (B) VBM and (C) CBM of the ground state in the MOF single cell with the isosurface value of $0.003 e \text{ \AA}^{-3}$. The yellow bubbles and green bubbles represent the electron clouds^[10]. CFA-Zn: Coordination Framework Augsburg-Zn; VBM: valence band maximum; CBM: conduction band minimum; MOF: metal-organic framework.

electron donor-acceptor pair [Figure 1A]. The closed-shell Zn^{2+} nodes with d^{10} configuration serve as the electronic insulators, preventing the overlap of the electron clouds of the valence band maximum (VBM) and the conduction band minimum (CBM) [Figure 1B and C]. Consequently, the CBM ligand will accept the energy of excited electrons alone and transition to the high energy state. For system stability, the structure of CFA-Zn will twist dynamically due to the flexibility of the ligand. Further analysis demonstrates that the excited electrons on CBM cannot recombine with the holes on the VBM, extending the lifetime of the charge carriers.

After introducing Pt and Co_3O_4 as cocatalysts, H_2 and O_2 were detected under visible light over CFA-Zn without sacrificial agents. In ten consecutive tests lasting 100 h, only slight activity decay can be observed, attesting to the stability of CFA-Zn. The apparent quantum efficiency (AQE) of photocatalytic OWS at 365 nm is $3.09\% \pm 0.32\%$. The AQE and stability of CFA-Zn position it among the top photocatalysts for OWS under visible light [Figure 2A].

To investigate the influence of structural twist, the $-\text{CH}_3$ group is introduced into the ligand. The density functional theory (DFT) calculations and time-resolved photoluminescence spectra suggest that the $-\text{CH}_3$ group impedes the structural twist in the excited state, resulting in the recombination of charge carriers and reduced activity in photocatalytic OWS. In addition, the CFA-Zn/Co was synthesized by a postsynthetic exchange strategy, in which closed-shell Zn^{2+} was partially substituted with open-shell Co^{2+} . With increasing Co^{2+} content, the photocatalytic OWS activity of CFA-Zn/Co decreased markedly [Figure 2B]. The *in situ* soft X-ray absorption spectroscopy characterizations reveal that the Co^{2+} nodes participate in electron transfer. Therefore, the changed energy is not enough to trigger the structural twist of excited CFA-Zn/Co [Figure 2C]. The control experiments certificate the significant importance of dynamic structural twist. In addition, the compositions of the two MOFs named Cd(5-BrIP)(TIB) and JNU-402- NH_2 determine the possibility of dynamic structural twists, which is confirmed by DFT calculations. Their photocatalytic OWS activities and stabilities prove the universality of dynamic structural twist in photocatalysis.

In summary, the structural twist in the excited state modulates the microenvironment of CFA-Zn and prolongs the lifetime of photogenerated charge carriers. The mechanism is comprehensively elucidated by rigorous characterizations and theoretical calculations. This work encourages researchers to utilize the

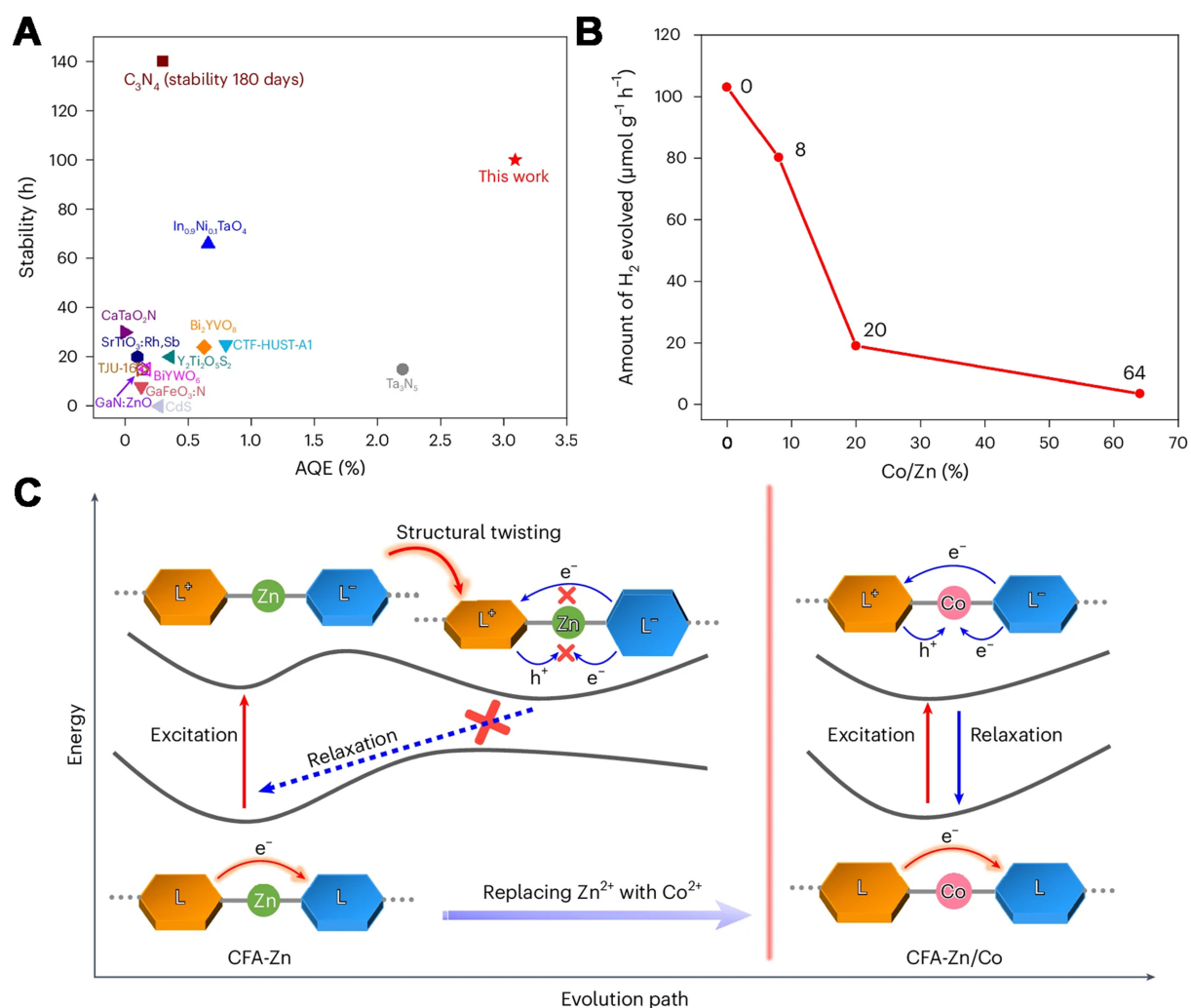


Figure 2. (A) The AQE and the stability of the photocatalytic OWS materials; (B) The photocatalytic H_2 production rates in OWS of CFA-Zn/Co with different Co/Zn molar percentages; (C) (left) the long-lived charge-separated state of the MOF with Zn nodes, and (right) the rapid charge recombination of the MOF with Zn/Co nodes^[10]. AQE: Apparent quantum efficiency; OWS: overall water splitting; CFA-Zn: Coordination Framework Augsburg-Zn; MOF: metal-organic framework.

precise structure of MOFs, capturing the dynamic behavior of photocatalyst structures by advanced characterization in order to determine the detailed reaction mechanisms and bring new perspectives and inspirations to the future development of photocatalysis. Dynamic structural twist winds the clockwork spring of photocatalytic OWS, unlocking potential for its further development.

DECLARATIONS

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Authors' contributions

Wrote the draft manuscript: Cao K

Revised and rewrote the manuscript: Zhang C, Zhang J

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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