Highlight

Carbon Future

Dynamic covalent organic framework linkages unlock efficient H_2O_2 photosynthesis

Yuheng Jiang and Bastian Mei

Laboratory of Industrial Chemistry, Ruhr University Bochum, 44780 Bochum, Germany

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Photocatalytic synthesis of H_2O_2 from H_2O and O_2 using solar energy has attracted increasing attention as a sustainable alternative to the industrial anthraquinone process, which suffers from safety concerns, a high energy consumption, and the use of organic solvents[1, 2]. Although semiconductor photocatalysts have been extensively studied[3–5], achieving efficient H_2O_2 production remains challenging due to insufficient visible-light utilization and rapid recombination of photogenerated charge carriers. Among emerging photocatalysts, covalent organic frameworks (COFs) have recently gained considerable interest because their ordered structures, tunable building blocks, and extended π-conjugation provide unique opportunities to engineer photocatalytic properties[6, 7]. Nevertheless, many COF-based systems still suffer from a poor charge separation efficiency, motivating the development of new COF architectures capable of facilitating directional charge transport while being catalytically active and selective.

Azole-linked COFs have recently emerged as a promising class of materials for photocatalytic H_2O_2 production owing to their superior chemical stability and the strong electron affinity of the azole rings[8]. These rings have been proposed to serve as electron-accepting sites for oxygen activation. However, a practical limitation lies in their synthetic complexity. In contrast to imine-, vinyl-, or azine-linked COFs, which can be obtained in a one-step synthesis, azole-linked frameworks typically require post-synthetic oxidation or cyclization of preformed imine COFs[9–11]. Such multistep transformations inevitably increase synthetic complexity, limit scalability, and restrict the structural diversity of azole-linked COFs. Consequently, the development of strategies that facilitate the direct or *in-situ* formation of azole linkages during catalytic operation would signify a substantial advancement in the field of high-performance COF photocatalysts.

In this context, Ao and co-workers recently reported a light-induced *in-situ* structural transformation of the imine linker, thereby enabling the formation of azole-linked COFs. Moreover, *in-situ* transformation was shown to significantly enhance the photocatalytic H_2O_2 production[12]. As a proof-of-concept, the authors employed an imine-linked OH-COF as the precursor and investigated its structural evolution during photocatalytic oxygen reduction in pure water under illumination (**Fig. 1a**). As the reaction proceeds, the imine linkages gradually transform into benzisoxazole linkages, thus generating a partially benzisoxazole-linked framework (OH-COF-E) *in-situ*. Importantly, the authors revealed that this dynamic reconstruction leads to a dramatic increase in the H_2O_2 production rate, from 88.20 μmol·g^{-1}·h^{-1} for the pristine COF to 1986.95 μmol·g^{-1}·h^{-1} after transformation (Fig. 1b). These measurements were performed under visible-light irradiation ($\lambda \geq 420$ nm, ~ 400 mW·cm^{-2}) using 5 mg of catalyst dispersed in 50 mL of water. Although the mass-normalized rate suggests a substantial enhancement in photocatalytic performance, direct comparison with other photocatalysts remains challenging due to differences in light intensity, reactor configuration, and catalyst loading. In this regard, future studies would benefit from reporting standardized metrics such as the apparent quantum efficiency (AQE) and solar-to-chemical conversion efficiency, which would enable more meaningful benchmarking across different photocatalytic systems[13].

Nevertheless, the work of Ao and co-workers provides valuable insights into the preparation of benzisoxazole-linked frameworks that represent a previously unexplored COF linkage motif, expanding the structural diversity of azole-based COFs. Importantly, the authors also convincingly demonstrated by a combination of powder X-ray diffraction (pXRD), Fourier transform infrared (FTIR) spectroscopy, ^{13}C and ^{15}N solid-state nuclear magnetic resonance (ssNMR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) that the overall structural integrity of the framework is maintained, i.e., *in-situ* transformation occurs without disrupting the overall framework structure, while selectively converting of imine linkages into benzisoxazole units. This structural evolution fundamentally alters the electronic architecture of the framework. Density functional theory (DFT) calculations reveal that the newly formed benzisoxazole moiety acts as an electron-deficient acceptor, whereas the original 2,5-dihydroxybenzene unit serves as an electron donor, thereby converting the parent donor–donor (D–D) system into a donor–acceptor (D–A) COF. The formation of this internal D–A heterojunction significantly lowers the exciton binding energy and promotes spatial separation of photogenerated carriers. Spectroscopic studies, including time-resolved photoluminescence and femtosecond transient absorption measurements, further demonstrate accelerated charge separation and carrier extraction in the transformed framework.

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Address correspondence to Yuheng Jiang, Yuheng.Jiang@ruhr-uni-bochum.de; Bastian Mei, Bastian.Mei@ruhr-uni-bochum.de

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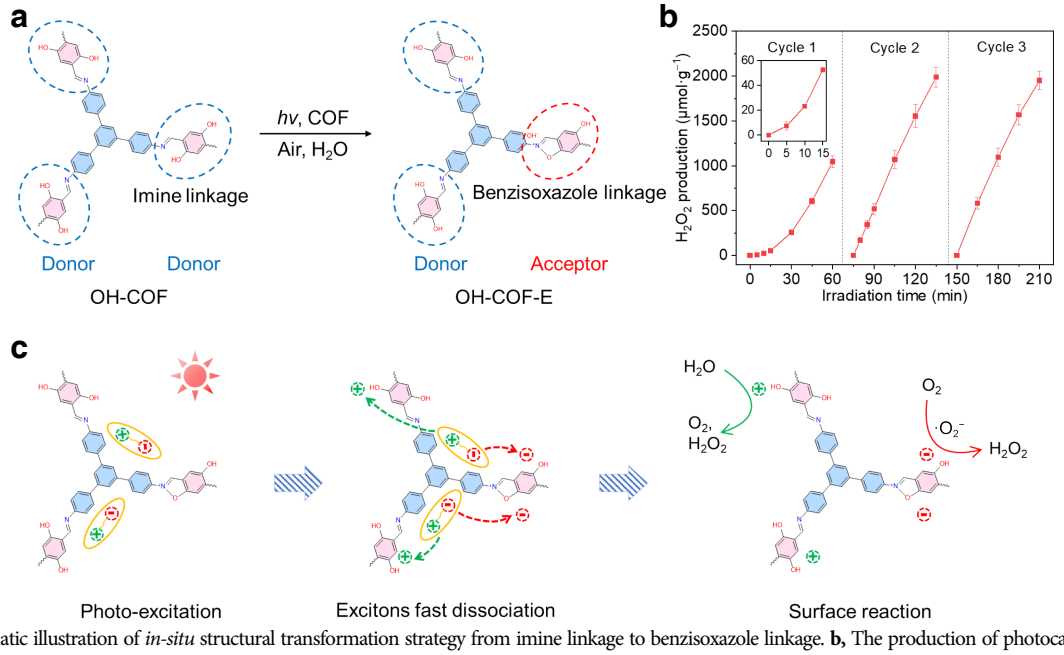

Fig. 1. **a,** Schematic illustration of *in-situ* structural transformation strategy from imine linkage to benzisoxazole linkage. **b,** The production of photocatalytic H_2O_2 over OH-COF as a function of time. **c,** Schematic illustration of the photocatalytic H_2O_2 generation pathway over OH-COF-E. Reproduced with permission from Ref.[12], © Zhang, P. et al. 2026.

Beyond improving charge dynamics, the benzisoxazole units also function as catalytic sites for oxygen activation. Their electron-deficient nature enhances O_2 adsorption and facilitates its reduction to the superoxide radical ($\cdot O_2^-$), the key intermediate in the two-electron oxygen reduction pathway toward H_2O_2 formation (Fig. 1c). Consequently, the *in-situ* reconstructed COF integrates improved charge separation with more favorable catalytic sites for oxygen reduction, thereby enabling substantially enhanced photocatalytic performance.

In summary, the study by Ao et al. introduces a novel concept: the utilization of structural evolution during photocatalysis for the fabrication of more active catalytic frameworks. The authors demonstrated a viable route to access azole-linked COFs without complex post-synthetic modifications by coupling photocatalytic reactions with linkage transformation. Beyond COFs, this study contributes to the broader understanding of dynamic reconstruction in catalysis, where catalysts evolve under operating conditions to form the true active phase. Such behavior has been widely recognized in the fields of themalcatalysis[14] and electrocatalysis[15]. However, it remains comparatively underexplored in the context of photocatalytic systems. In this context, the present work suggests that light-driven structural evolution may represent a general strategy to enhance catalytic performance. While further studies are needed to evaluate the generality of this approach across different COF systems and reactions, it may also have important implications for other classes of photocatalysts that exhibit induction periods, where *in-situ* restructuring could govern activity. This viewpoint unveils novel avenues for the design of adaptive photocatalysts and has the potential to catalyze the discovery of structures with unprecedented functionalities that were previously inaccessible.

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Data availability

Not applicable.

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Y. H. J. and B. M. jointly wrote and revised the manuscript.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

Use of AI statement

During the preparation of this work, the authors used ChatGPT in order to check the grammar. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.