

Porous Organic Polymers for Photocatalytic Hydrogen Peroxide Production: Recent Advances and Future Perspectives

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Abstract Hydrogen peroxide (H₂O₂) is a green chemical with extensive applications in chemical synthesis and environmental remediation. While the industrial anthraquinone process remains the dominant production method, solar-driven photocatalytic H₂O₂ production has emerged as a promising strategy to complement or optimize current production models, particularly for on-site applications. Among various porous organic polymers (POPs), covalent organic frameworks (COFs), and covalent triazine frameworks (CTFs) have attracted significant attention as a premier platform due to their modular construction and precise molecular-level tunability. Here, we systematically summarize recent progress in POPs-based photocatalysts, with a primary focus on the structural and functional modification of COFs and CTFs. We first elucidate the fundamental principles and existing challenges of photocatalytic H₂O₂ production. Subsequently, the research landscape of various POPs materials in photocatalysis is discussed. Taking COFs and CTFs as representative examples, we then highlight advanced modification strategies, including the design of donor-acceptor (D-A) structures, functional group engineering, and the construction of heterostructures. These strategies effectively facilitate efficient charge separation, extend carrier lifetimes, and improve mass transport, thereby enhancing solar-to-chemical conversion efficiency. Finally, we summarize the current state of the field and offer perspectives on future research directions for POPs-based photocatalytic H₂O₂ production.

Keywords Porous organic polymers; Photocatalysis; Hydrogen peroxide; Molecular engineering; Structure-property relationship

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1 INTRODUCTION

Hydrogen peroxide (H₂O₂), a versatile oxidant with both strong redox properties and environmental friendliness, plays an irreplaceable role in fields such as fine chemical synthesis, environmental remediation, and biomedical disinfection.^[1–3] Given that its reduction product is exclusively H₂O and that it does not generate any pollutants, H₂O₂ is widely recognized as a core oxidant in green chemistry. Driven by the global transition toward sustainable energy and demand for green processes, the global demand for H₂O₂ is projected to exceed 5.7 million tons by

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2027.^[4] Currently, the industrial supply of H_2O_2 is heavily reliant on traditional anthraquinone cyclic processes. Although this process offers advantages for large-scale production, its complex indirect hydrogenation-oxidation cycle involves energy-intensive extraction and distillation stages, as well as significant solvent consumption, heavy environmental burdens, and potential explosion risks associated with the direct use of H_2 and O_2 .^[5] To overcome the inherent drawbacks of traditional technologies, researchers have explored various alternative pathways. Although the electrolysis method provides high-purity products, it is limited by extremely low current efficiency and insufficient raw material utilization, making it suitable only for small-scale, high-purity requirements;^[6,7] the isopropanol oxidation method operates under mild reaction conditions with recyclable by-products, but faces difficulties in product separation and challenges in scalability. Consequently, developing a distributed production technology that can directly utilize renewable energy, operate under safer and milder conditions, and have a lower carbon footprint has become a critical and urgent task in the field of chemical energy.

In contrast, solar-driven photocatalytic H_2O_2 synthesis inspired by natural photosynthesis demonstrates exceptional energy efficiency and environmental compatibility. Using only H_2O and O_2 as substrates, this technology enables the direct conversion and storage of chemical energy at room temperature and pressure, providing a highly competitive strategic path to establish a distributed, near-zero-emission H_2O_2 production model.^[8,9] However, the overall efficiency of photocatalytic H_2O_2 synthesis remains constrained by the complex multiphase photocatalytic kinetic processes. Specifically, the rapid recombination of photogenerated charge carriers, limited utilization of visible light, and sluggish interface reaction kinetics are the primary bottlenecks limiting efficiency improvements. Over the past decades, researchers have developed a variety of photocatalysts, including metal oxides,^[10–12] metal sulfides,^[13–15] graphitic carbon nitride ($\text{g-C}_3\text{N}_4$),^[16–19] and metal-organic frameworks (MOFs).^[20,21] Despite progress, these materials still face challenges such as limited light-responsive ranges, sparse distribution of active sites, and inadequate selectivity control toward H_2O_2 generation. Specifically, the structures of metal oxides limit fine-tuning of their structures and functions. $\text{g-C}_3\text{N}_4$ lacks functional groups and pore structures, so its catalytic activity depends on modification methods such as doping and defect control. For MOF materials, metal centers may lead to the decomposition of H_2O_2 ; therefore, there are many restrictions on the selection of metal centers and ligands. In comparison, POPs are entirely composed of covalent bonds and do not contain metallic elements in their frameworks. At the same time, they exhibit precisely controllable band structures, hydrophilic-hydrophobic structures, and pore structures, giving them unique advantages over other materials. Therefore, the development of novel semiconductor materials with highly tunable structures, abundant active centers, and superior charge-separation capabilities has become a key focus of research in this field.

As a burgeoning class of modular material systems, porous organic polymers (POPs) have demonstrated immense potential for applications in solar energy conversion and environmental remediation owing to their highly tunable molecular structures and excellent optoelectronic properties.^[22–24] Through diverse organic synthetic methodologies, the build-

ing blocks in POPs are connected *via* covalent bonds to form multidimensional networks characterized by intrinsic porosity and skeletal rigidity. This molecular-level customizability enables researchers to precisely modulate their optical band gaps, redox energy levels, and exciton dynamics (such as light absorption range and charge carrier lifetimes), thereby offering limitless possibilities for optimizing photocatalytic performance.^[25,26] Furthermore, a high degree of polymerization endows POPs with high chemical stability, which not only ensures structural integrity in complex reaction systems but also facilitates the recovery and recycling of the catalysts.^[27,28] Consequently, as efficient heterogeneous photocatalytic systems, POPs provide an ideal solution to overcome the challenges in the photocatalytic synthesis of H_2O_2 . Here, we systematically elucidate the underlying reaction mechanisms of photocatalytic H_2O_2 production and explore the structural advantages and design principles of POPs materials in depth. This work specifically highlights COFs and CTFs, two highly ordered and representative classes of POPs, and provides a detailed analysis of their modification strategies and structure-activity relationships for enhancing H_2O_2 yields based on the recent frontier literature. Finally, the current technical barriers in this field are summarized, and a forward-looking perspective on future research directions and application prospects is provided.

2 FUNDAMENTAL PRINCIPLES OF PHOTOCATALYTIC H_2O_2 SYNTHESIS

2.1 Photocatalytic Reaction Mechanisms

In recent decades, photocatalytic technology has received widespread attention and has been applied to numerous research fields. The physical essence of photocatalysis is a process in which semiconductor materials drive nonspontaneous chemical reactions by absorbing light energy. Generally, a complete heterogeneous photocatalytic cycle encompasses three critical kinetic stages, ranging from photon absorption to interfacial charge transfer^[29,30] (Fig. 1a): (1) photoexcitation and carrier generation, where photons with energy equal to or greater than the semiconductor bandgap (E_g) irradiate the catalyst surface, and electrons in the valence band (VB) absorb the light energy and undergo a stimulated transition, crossing the forbidden band into the conduction band (CB). This process generates reductive excited-state electrons (e^-) in the conduction band while leaving oxidative holes (h^+) in the valence band. The efficiency of this stage primarily depends on the light-absorption range and exciton concentration of the material. (2) Charge separation and migration: the photogenerated carriers produced in the bulk phase must migrate to the material surface within an extremely short time frame to participate in subsequent reactions. However, carrier recombination is a spontaneous exothermic process that competes energetically with the charge migration to the surface. Effective separation strategies (such as constructing internal electric fields or shortening diffusion distances) can significantly extend carrier lifetimes, ensuring that sufficient effective charges reach the catalytically active sites. (3) Interfacial redox reactions: the effective carriers that have migrated to the surface undergo charge exchange with the substrate molecules adsorbed on the material surface. The conduction band e^- undergoes reduction reactions with electron acceptor molecules, whereas the valence band h^+ drives the oxidation of donor molecules. The conversion efficiency of

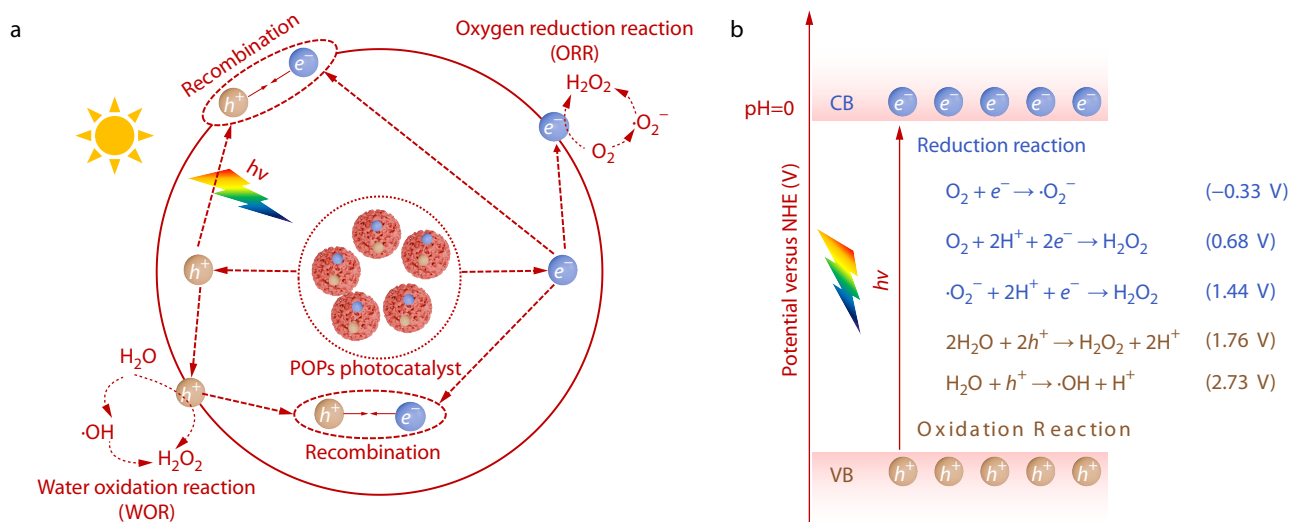


Fig. 1 (a) Schematic illustration of the photocatalytic H_2O_2 production process; (b) Oxidation and reduction products of photocatalytic H_2O_2 production and their corresponding redox potentials.

this stage depends not only on the carrier flux, but also on the distribution of active sites on the material surface and on the adsorption/desorption kinetics of the reactant molecules.

2.2 H_2O_2 Synthesis Pathways and Challenges

The photocatalytic generation of H_2O_2 primarily occurs via two pathways: the oxygen reduction reaction (ORR) and water oxidation reaction (WOR). This is illustrated in the Fig. 1(a), the photogenerated electrons drive the reduction of O_2 , whereas the photogenerated holes drive the oxidation of H_2O to produce H_2O_2 .

In photocatalytic H_2O_2 production, the rate of the WOR process is often much lower than that of the ORR process. The ORR mainly involves the adsorption and evolution of oxygen. Specifically, oxygen is first adsorbed onto electron-rich groups (such as imines and triazines). $\cdot O_2$ then interacts with protons in the water and photogenerated electrons on the catalyst to form H_2O_2 through a single-step two-electron process or through a two-step single-electron process to form $\cdot O_2^-$, which is reduced to $\cdot OOH$ and finally converted into H_2O_2 . A deep understanding of these pathways is beneficial for catalyst design and selection of reaction monomers.

From the perspective of reaction pathways, H_2O_2 can be generated through either a one-step two-electron process or stepwise single-electron process (Fig. 1b).^[31–33] Although the single-electron pathway appears kinetically easier owing to single charge transfer, its thermodynamic requirements are extremely high. For instance, the single-electron reduction of O_2 to form the O_2^- radical requires an extremely negative reduction potential (-0.33 V versus NHE, pH=0), while the single-electron oxidation of H_2O to form the $\cdot OH$ radical requires an extremely positive oxidation potential (+2.73 V versus NHE, pH=0). In contrast, the two-electron ORR (+0.68 V versus NHE, pH=0) and WOR (+1.76 V versus NHE, pH=0) pathways are more thermodynamically feasible.^[34–36] However, multi-electron transfer processes are often accompanied by higher kinetic barriers, which can lead to low generation efficiency.

In actual reaction systems, the efficient accumulation of H_2O_2 faces severe competition and decomposition issues: (1) Competing reactions: the $4e^-$ WOR to produce O_2 (+1.23 V

versus NHE, pH=0) is more thermodynamically advantageous than the $2e^-$ WOR to produce H_2O_2 (+1.76 V versus NHE, pH=0), and the H_2 evolution reaction (0 V versus NHE, pH=0) also competes for photogenerated electrons. (2) Side reactions and self-decomposition: as an unstable intermediate, H_2O_2 is highly susceptible to further reduction or oxidation by photogenerated carriers and exhibits intrinsic spontaneous instability. Therefore, the key to constructing efficient H_2O_2 photocatalysts lies in precisely modulating the energy band structure to match the two-electron transfer potential and optimizing the surface active sites to inhibit the ineffective decomposition of H_2O_2 , thereby enhancing the reaction selectivity and cumulative concentration.

In addition, competition occurred between the four-electron process (producing water) and the two-electron process (producing H_2O_2) during the reduction reaction. The reduction potential for the former is 1.23 V (versus NHE, pH=0), while the single-step two-electron process to H_2O_2 is 0.68 V (versus NHE, pH=0). The two-step single-electron processes are -0.33 V (versus NHE, pH=0) for $\cdot O_2^-$ and 1.44 V (versus NHE, pH=0) for H_2O_2 formation, respectively. Based on these redox potentials, it can be concluded that the single-step two-electron process is thermodynamically favorable. Therefore, the conduction band of the material can be adjusted to be close to or lower than -0.33 eV through bandgap engineering to inhibit the generation of superoxide radicals and promote the single-step two-electron process. Furthermore, the introduction of polar groups (such as carboxyl and sulfonic acid groups) to facilitate interfacial proton transfer is beneficial for the formation of $\cdot OOH$, thereby promoting $2e^-$ H_2O_2 production. In addition, the production of water involves the cleavage of the O—O bond. Therefore, the adsorption strength and density of active sites influence this process. Specifically, if the adsorption is too strong, the $\cdot OOH$ intermediate is difficult to desorb, making O—O bond cleavage more likely to occur and produce H_2O . If both the oxygen atoms in O_2 are simultaneously adsorbed on different active sites, bond cleavage is also favored. Therefore, choosing groups with moderate adsorption strengths and using elements with moderate adsorption strengths (such as nitrogen) as active

sites can facilitate product desorption and avoid H₂O formation. Selecting monomers with more dispersed active sites can effectively avoid dual-site adsorption. Furthermore, the design of hydrophilic-hydrophobic structures in POPs materials is beneficial for mass transport and product desorption. Understanding the electron transfer, mass transport, and adsorption/desorption processes of reactants and products is key to designing efficient and stable POPs-based photocatalysts.

3 DESIGN STRATEGIES

3.1 Classifications of POPs

As a class of highly designable porous materials, porous organic polymers (POPs) have demonstrated unique competitive advantages in the field of photocatalytic energy conversion owing to their exceptional specific surface area, highly tunable pore size distribution, and molecular-level customizability. Depending on the differences in synthesis strategies, bonding nature, and structural regularity, the POPs family encompasses various subcategories, primarily including (Fig. 2): (1) polymers of intrinsic microporosity (PIMs);^[37,38] (2) hypercrosslinked polymers (HCPs);^[39,40] (3) conjugated microporous polymers (CMPs);^[41–44] (4) hydrogen-bonded organic frameworks (HOFs);^[45–49] (5) covalent organic frameworks (COFs);^[50,51] (6) covalent triazine frameworks (CTFs);^[52,53] and (7) porous aromatic frameworks (PAFs).^[54–56]

3.2 Classification of COFs and CTFs Based on Chemical Link

Yaghi *et al.* successfully prepared highly porous crystalline organic frameworks through the condensation reaction of benzeneboronic acid, laying the foundation for the subsequent re-

search and development of COFs.^[57] Since then, COF materials based on various bonding modes have been developed. The successful preparation of extended crystalline materials requires the following conditions: the formation of bonds between building units must be reversible under the given conditions, and the rate of bond formation must be slow enough to ensure that the associated structural defects can be adequately repaired. A wide variety of COFs has been developed based on different bonding modes, as shown in Fig. 3. The main types include boronate ester COFs synthesized from TPBA monomers,

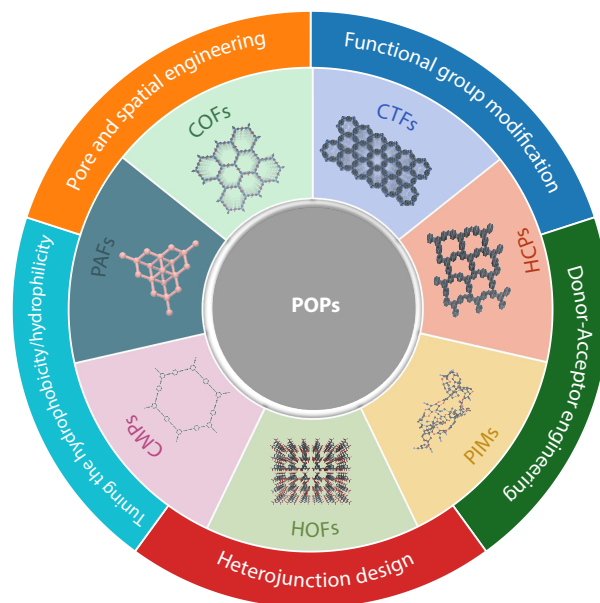
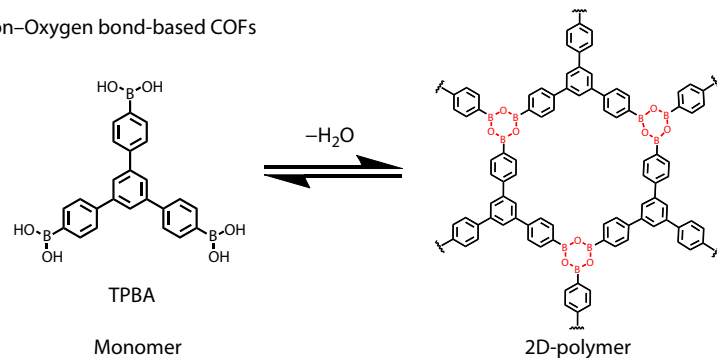
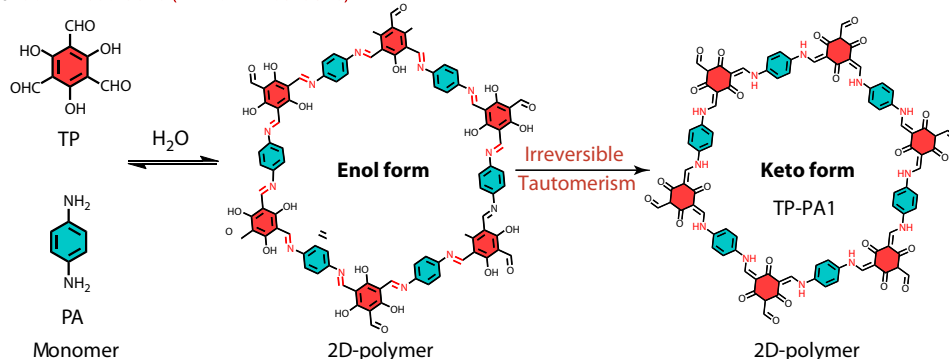


Fig. 2 Classifications and characteristics of POPs.

a Boron–Oxygen bond-based COFs



b Schiff Base COFs (Imine-Linked COFs)



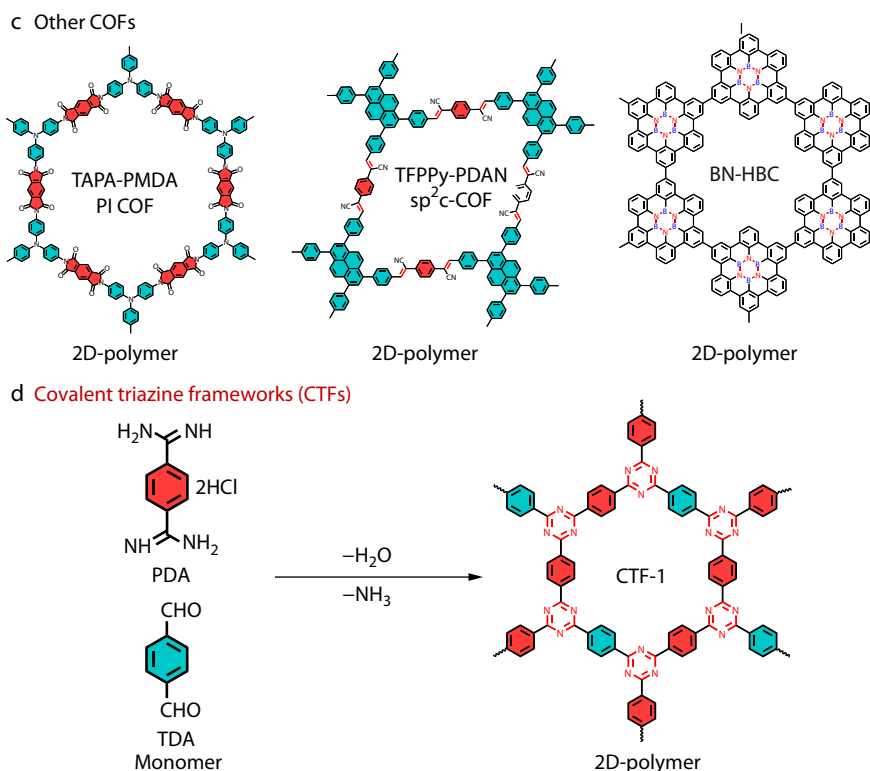
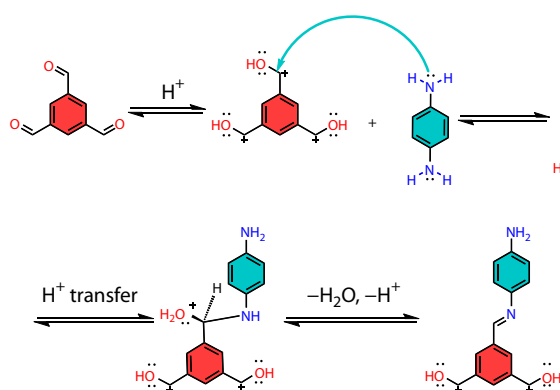


Fig. 3 COFs synthesized *via* different linkage chemistries: (a) COFs linked by boroxine bonds; (b) COFs linked by imine bonds; (c) COFs linked by amide, acrylonitrile, and boron-nitrogen (BN) heterocyclic linkages; and (d) CTFs synthesized *via* dehydration and deamination of amidines (PDA) and aldehydes (TDA).

a Synthesis mechanism of imine-linked COFs



b Synthesis mechanism of CTFs

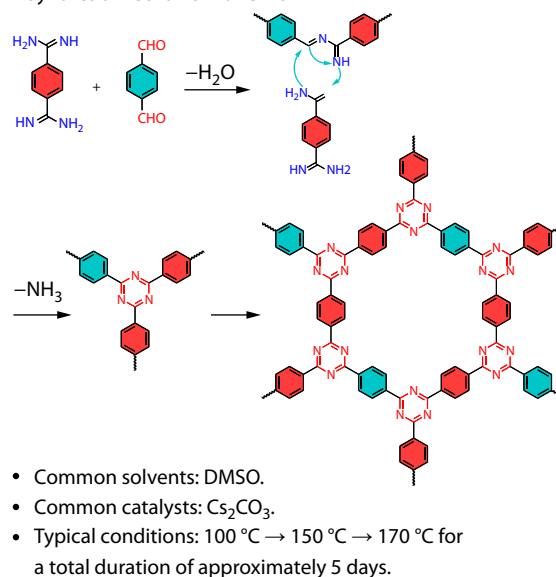


Fig. 4 (a) Reaction mechanism of imine-linked COFs; (b) Reaction mechanism of CTFs.

imine COFs prepared *via* Schiff base reactions using TP and PA monomers, and other types, such as PI-COF, sp²C-COF, and BN-HBC.

For traditional CTFs, the benzonitrile monomer was prepared at high temperatures *via* the ion thermal method. In contrast, in 2017, our team discovered in 2017^[58] that crys-

talline CTFs can be prepared under relatively mild conditions *via* a dehydration-deamination reaction between terephthalimidine and terephthalaldehyde, catalyzed by cesium carbonate. This has expanded the applications of CTFs in the field of photocatalysis.

Regarding the synthesis mechanism of imine COFs (Fig. 4a),

under acidic conditions, the aldehyde is protonated, followed by attack of the lone pair of electrons from the amine on the aldehyde to form a transition state. After proton transfer and dehydration, COF was generated. This reaction is partially reversible in water; therefore, by adjusting the solvent and water content, the equilibrium can be controlled and products with high crystallinity can be obtained. Typically, we used aqueous solutions of acetic acid or trifluoromethanesulfonic acid as catalysts, and mesitylene, dioxane, *o*-dichlorobenzene, or *n*-butanol as solvents, and heated at 120 °C for three days to ensure complete crystallization.

In CTFs (Fig. 4b), diamines and aldehydes undergo dehydration and deamination reactions to form triazine rings. The reversibility of this reaction is much lower than that of imine COFs, making it more difficult to obtain highly crystalline products. To address this issue, our research group developed a slow-dropping and programmed temperature-rising method,^[58] which enables the preparation of large quantities of highly crystalline CTFs catalysts.

3.3 Design Strategies of POPs

3.3.1 Functional group modification

Functional groups play a pivotal role in determining the physicochemical properties of POPs. By incorporating specific functional moieties, the electronic environment of the catalytic sites and the subsequent reaction pathways can be directly modulated. Numerous studies have demonstrated that the introduction of nitrogen-containing groups, such as piperazine,^[59] pyridine,^[60] bipyridine,^[61] triazine,^[62] tetrazine,^[63] and heptazine^[64], can significantly enhance the capture of dissolved oxygen by acting as Lewis base sites. Furthermore, these nitrogenous units serve as robust anchoring sites for metal catalysts, while their electron-deficient nature facilitates charge transfer and separation, effectively regulating energy band structures.

Meanwhile, the integration of sulfur-containing heterocycles, including sulfone units,^[65] thiophene,^[66] and thiazole,^[67] can effectively increase the local electron density, thereby strengthening the adsorption and interaction with oxygen species, accelerating charge transport, and broadening the visible light response range. Additionally, the strong electronegativity of halogens (F, Cl, Br, and I)^[68,69] enables the precise regulation of charge distribution on adjacent carbon atoms, providing highly active sites for O₂ adsorption while enhancing exciton dissociation. Moreover, oxygen-containing groups such as hydroxyl (—OH),^[70] carboxyl (—COOH),^[71] and sulfonate (—SO₃H)^[72] not only improve the dispersibility and wettability of POPs in aqueous media to ensure efficient reactant diffusion, but also function as proton sources or reservoirs. These groups accelerate proton transfer to the ORR sites, thereby promoting the overall photocatalytic kinetics.

3.3.2 Donor-acceptor structure engineering

A primary challenge in photocatalysis is the rapid recombination of photogenerated charge carriers. Thus, enhancing the separation efficiency and extending the carrier lifetime are critical for photocatalyst design. By incorporating donor (D) and acceptor (A) units into the polymer backbone (Fig. 5), an alternating D-A architecture generates an internal molecular dipole that drives the spatial separation of the electrons and holes. Particularly in highly crystalline POPs such as COFs and CTFs, long-range ordered structures establish continuous pathways for charge transport. This effectively suppresses carrier recombination, enhances charge mobility and lifetime, and ultimately maximizes the utilization efficiency of photogenerated carriers.

The construction of D-A structures typically follows two distinct methods. The most prevalent approach involves judicious selection of monomers with inherent D-A characteristics during the initial design phase. This strategy allows for a

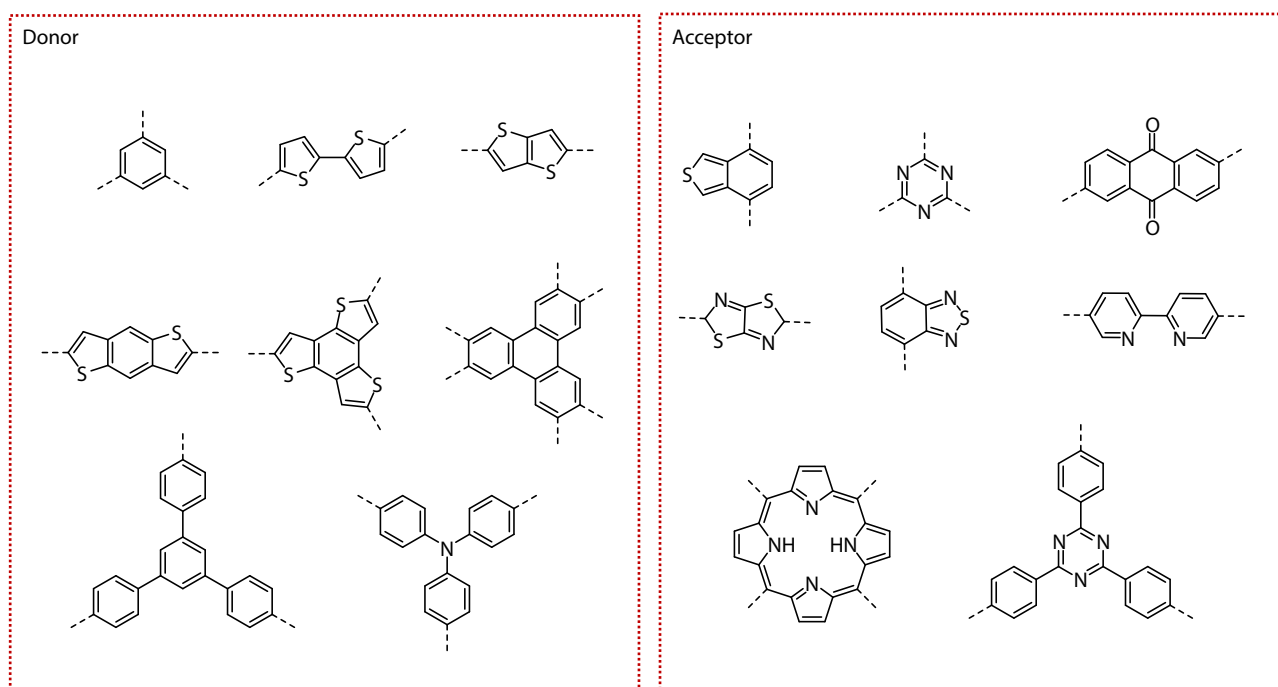


Fig. 5 The donor and acceptor units of POPs.

systematic investigation of how different heteroatoms (e.g., O, S, Se) or side chains influence the material properties by tuning the relative strengths of the donor or acceptor moieties.^[73,74] However, this method requires careful consideration of the polymerization reactivity of different monomers. An alternative strategy focuses on the post-synthetic modification of the pre-synthesized photocatalysts. This involves converting weak D-A systems into strong D-A architectures.^[75] The primary advantage of this post-synthetic approach is its ability to enhance the chemical stability and optoelectronic performance while preserving the high porosity and crystallinity of the parent framework. Nevertheless, this method is limited by the need to maintain structural integrity during the modification process and the challenge of controlling the degree of functionalization.

3.3.3 Heterojunction design

Constructing heterojunctions by combining two photocatalytic materials is an effective strategy for suppressing charge carrier recombination and facilitating their separation. Traditional heterojunctions are generally classified into types I and II based on the direction of charge migration and band structure. In a type-II heterojunction, electrons migrate from the CB with higher energy to those with lower energy, while holes move in the opposite direction within the VB. This spatial separation significantly enhances the charge separation efficiency and carrier utilization; however, it inevitably leads to diminished overall redox capacity of the composite system.^[76]

To circumvent this limitation, recently proposed Z-scheme and S-scheme heterojunctions^[77] utilize mechanisms such as internal electric fields and band bending to retain electrons with stronger reduction ability and holes with higher oxidation ability. Consequently, the construction of S-scheme or Z-scheme heterojunctions has emerged as a prominent research focus, as they preserve high redox activity while improving charge separation. Nevertheless, heterojunction materials currently face significant challenges. First, the precise integration of two components at the molecular level remains a major hurdle. Second, the direct characterization and in-depth mechanistic exploration of the synergistic effects at these interfaces remain difficult.

3.4 Tuning the Hydrophobicity/Hydrophilicity

Photocatalytic H₂O₂ production is a characteristic tri-phase reaction involving a gas-phase reactant (O₂), liquid-phase reactant and product (H₂O and H₂O₂), and solid-phase catalyst. In this process, O₂ and H₂O must diffuse and be adsorbed onto the active sites of the catalyst for subsequent electron transfer. Beyond charge-transfer kinetics, mass transport significantly dictates the overall catalytic performance. A primary physical constraint in this system stems from the low solubility and sluggish diffusion kinetics of O₂ in aqueous media, which typically creates a significant mass transfer barrier and leads to concentration polarization at the catalyst-liquid interface. Wettability is a key determinant of mass transport efficiency; specifically, hydrophilic structures facilitate intimate contact between the catalyst and H₂O, whereas hydrophobic regions promote the accessibility of O₂ to the catalyst surface and aid in the timely desorption of the generated H₂O₂. By meticulously tailoring the hydrophilic-hydrophobic balance, it is possible to construct stable "gas-liquid-solid" tri-phase microenvironments. Such configura-

tions allow gaseous O₂ to bypass the bulk liquid phase and reach the active sites directly, effectively shortening the diffusion path of the gaseous reactants. This ensures a high local reactant flux and enhances mass transfer kinetics even under ambient conditions.

Modulation of hydrophilic-hydrophobic properties can be achieved during the initial design phase by incorporating specific functional groups into the polymer backbone.^[78] Alternatively, interfacial polymerization techniques can be employed to construct architectures with distinct wettability profiles.^[79] Furthermore, post-synthetic treatments of pre-formed catalysts offer another route to reconfigure the surface structure and tune its wettability.^[80] By optimizing the contact between the reactants and solid catalyst, these approaches ensure that the gas, liquid, and solid phases are brought into effective contact at the interface, thereby maximizing the active interfacial area and accelerating the overall reaction kinetics. These strategies have proven effective in enhancing the mass transport across the tri-phase interface, thereby significantly improving the overall photocatalytic efficiency by ensuring a continuous and rapid supply of oxygen to the catalyst surface.

A porous structure is a defining characteristic of a POPs. The strategic design of pores encompasses both topological and microenvironmental regulations. The former involves tailoring the length and geometry of the monomers to create POPs with diverse pore sizes and architectures.^[81] These structural variations can facilitate charge carrier separation and transport by spatially isolating the oxidation and reduction reactions, thereby maximizing carrier utilization.

However, the electronic structure can be precisely tuned through the selection of monomeric side chains^[82] or post-synthetic modifications.^[83] These approaches enhance electronic delocalization, promote charge separation and transport, and modulate the microenvironment within pores. Such modifications improve the mass transport efficiency and increase the accessibility of active sites. Consequently, the design and modification of pore structures represent a highly effective strategy; they not only boost photocatalytic activity from the perspective of charge dynamics (separation and migration) but also enhance the overall catalytic efficiency by optimizing mass transport kinetics.

4 RECENT ADVANCES

Covalent triazine frameworks (CTFs) and covalent organic frameworks (COFs), which are typical representatives of highly crystalline POPs, have sparked a research boom in the field of photocatalytic H₂O₂ synthesis owing to their well-defined molecular structures, long-range ordered pore systems, and excellent photoelectric properties. Compared with amorphous polymers, the core advantage of COFs lies in their structural pre-designability and high regularity, making them ideal model materials for studying the intrinsic mechanisms of photocatalytic reactions.^[93,94]

4.1 Progress Overview

Reviewing the evolution of H₂O₂ photocatalysis, the research focus has gradually shifted from early inorganic semiconductors, such as TiO₂ to organic semiconductor materials, such as g-C₃N₄

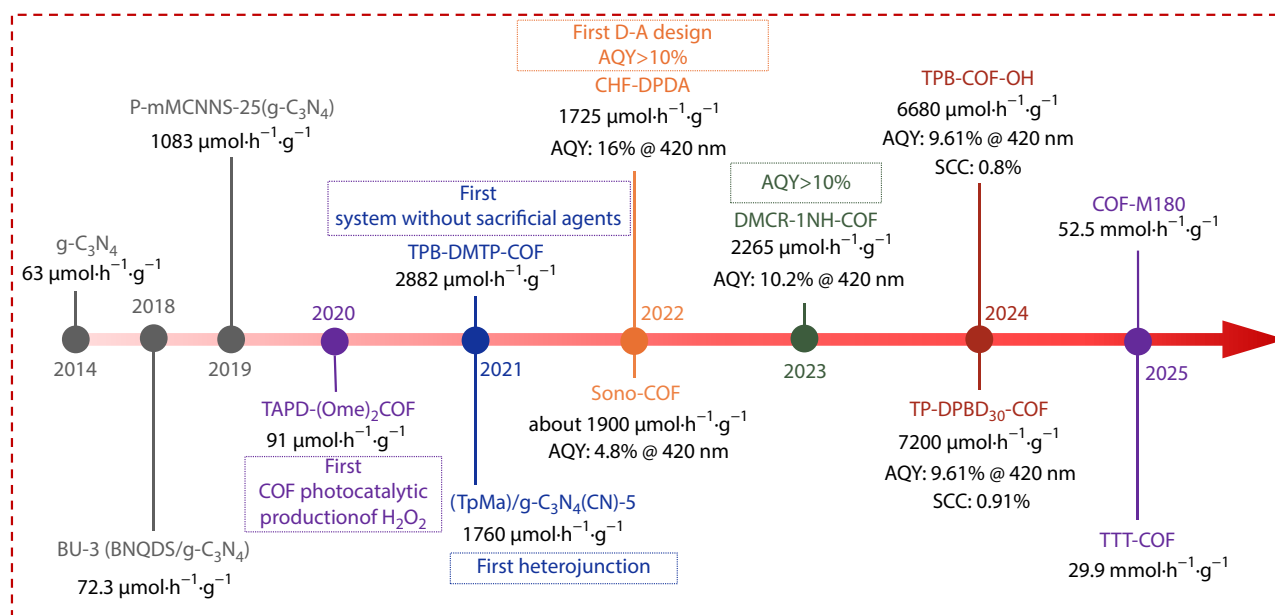


Fig. 6 Development of photocatalytic H_2O_2 production over the past decade.^[4,75,79,84–92] AQY = apparent quantum yield; SCC = solar-to-chemical conversion efficiency.

and COFs (Fig. 6 and Table 1). Over the past decade, the performance of new catalytic systems has improved by nearly three orders of magnitude, and production rate records continue to be refreshed. This highlights their immense potential for future research.

4.2 Case Studies

COFs possess high specific surface areas and tunable energy band characteristics, providing ideal physical channels for directional separation and efficient transport of photogenerated charge carriers. Currently, photocatalytic systems based on COFs and CTFs have demonstrated excellent potential to have activity in the field of H_2O_2 synthesis. To further explore their performance limits, researchers have developed a series of regulation strategies, including functional group modification, atomic-level metal anchoring, D-A structure construction, heterojunction integration, and hydrophilic/hydrophobic microenvironment regulation.

The core objective of these strategies is to precisely regulate the density of active sites at the molecular level, optimize the electronic band structure, and clear the charge transfer pathways, thereby fundamentally overcoming bottlenecks in photocatalytic kinetics. This section systematically discusses the enhancement mechanisms of the modification strategies on catalytic performance. By analyzing the intrinsic correlations between the material structure and catalytic activity (*i.e.*, structure-activity relationships), we aimed to reveal the underlying physicochemical roots of the improved H_2O_2 production rates in photocatalysis.

4.2.1 Functional group modification

In photocatalytic systems, the functional groups on the benzene ring influence the catalytic performance by regulating the electronic structure and behavior of photogenerated charge carriers. Electron-donating groups (such as $-\text{OH}$, $-\text{NH}_2$, and $-\text{OR}$) can increase the electron density of the aromatic ring, promote the separation of photogenerated electron-hole pairs,

and enhance reactivity. Conversely, electron-withdrawing groups (such as $-\text{NO}_2$, $-\text{CN}$, and $-\text{COOH}$) reduce the electron density, thereby improving the selectivity of oxidation reactions. Functional groups also influence the light absorption properties, molecular polarity, and pore environment, thereby playing a key role in reactions such as the photocatalytic production of H_2O_2 .

Hydroxyl ($-\text{OH}$) functionalized COFs can serve as proton reservoirs, effectively coordinating proton transport between the WOR and ORR, thereby significantly enhancing the efficiency of photocatalytic H_2O_2 synthesis. For example, Chenglong *et al.* synthesized a TFBP-DHBD COF (containing $-\text{OH}$), which exhibited approximately 3.3-fold higher photocatalytic H_2O_2 production activity than the non-functionalized TFBP-BD COF (Fig. 7).^[95] Mechanistic studies indicate that the $-\text{OH}$ groups can provide protons to the ORR and be replenished by protons released from the WOR, achieving timescale matching between the two half-reactions while reducing the formation energy barrier of the $^*\text{OOH}$ intermediate and promoting the proton-coupled electron transfer process. Furthermore, when loaded into a microreactor, this material can simultaneously achieve H_2O_2 generation and bacterial inactivation in water under ambient temperature, air, and natural water conditions, representing a typical strategy for functional group regulation of electron and proton transport to enhance photocatalytic performance.

Similarly, Amin *et al.* demonstrated that regulating the electronic structure and configuration of COFs through functional group engineering can significantly enhance the photocatalytic H_2O_2 production performance (Fig. 8).^[96] They synthesized four tetrazine-based DT-COF-*n* (*n*=0–3, corresponding to the number of $-\text{OH}$ groups). By adjusting the number of hydroxyl substituents on the aldehyde monomer, systematic regulation of framework configuration, degree of order, and charge separation behavior. DT-COFs possess an extremely high nitrogen content (72 N atoms per pore, account-

Table 1 Summary of representative POPs-based photocatalysts for photocatalytic H₂O₂ production.

Type of catalyst	Year	Photocatalyst	H ₂ O ₂ yield (mmol·g ⁻¹ ·h ⁻¹)	AQY @ Wavelength	Sacrificial agent	Band gap (eV)	Band structure (eV) (versus NHE pH=7)	Fluorescence lifetime	Ref.
COF	2025	PyNTB-2SO ₃	15.16 2.76	N/A	Benzyl Alcohol None	1.93	-0.66 to 1.27	N/A	[83]
COF	2025	COF-M180	52.5	N/A	None	1.74	-0.33 to 1.41	N/A	[79]
COF	2025	DT-COF-1	4.3	14.1% @ 420 nm	None	2.15	-5.63 to -3.48	N/A	[96]
COF	2025	TTT-COF	4.75	N/A	None	2.66	-1.34 to 1.32	0.33 ns	[75]
COF	2025	TFBP-DHBD	29.9 1.44	12% @ 400 nm N/A	Benzyl Alcohol None	2.26	-0.79 to 1.47	N/A	[95]
COF	2024	QP-HPTP-COF	4.39	N/A	None	2.63	-1.75 to 0.88	N/A	[81]
COF	2024	SO ₃ H-COF	4.97	15% @ 400 nm	Methanol	2.23	-0.43 to 1.80	7.5 ns	[99]
COF	2024	TP- DPBD ₃₀ -COF	7.2	18.0% @ 420 nm	None	2.84	-0.77 to 2.07	0.67 ns	[90]
COF	2024	TPB-COF-OH	6.68	9.61% @ 420 nm	None	1.97	-0.63 to 1.34	N/A	[89]
COF	2023	TZ-COF	4.95	N/A	Benzyl alcohol	1.98	-1.04 to 0.94	N/A	[94]
COF	2023	Py-Da-COF	0.268 3.67	0.6% @ 475 nm 4.5% @ 420 nm	None Benzyl alcohol	2.53	-0.51 to 2.02	N/A	[100]
COF	2023	DMCR-1NH- COF	0.461 2.26	N/A 10.2% @ 420 nm	None Ethanol	2.60	-2.37 to 0.23	N/A	[88]
COF	2022	sono-COF	about 1.90	4.8% @ 420 nm	None	2.68	-2.41 to 0.27	N/A	[4]
COF	2022	TAPB-PDA-OH	2.12	2.99% @ 420 nm	Ethanol	2.10	-0.94 to 1.16	2.91 ns	[101]
COF	2022	CHF-DPDA	1.725	16% @ 420 nm	None	2.35	0.46 to 1.89	17.2 ns	[92]
COF	2021	TPB-DMPT- COF	1.565	N/A	None	2.30	-0.83 to 1.47	<1 ns	[78]
COF	2020	TAPD- (Ome) ₂ COF	0.091	N/A	Ethanol	2.63	-1.21 to 0.89	N/A	[84]
CTF	2025	CTF-TPCZ	10.33	3.02% @ 420 nm	None	2.75	-0.39 to 2.36	3.99 ns	[62]
CTF	2024	CTF-Th	4.77	8.2% @ 420 nm	None	1.90	-0.77 to 1.13	2.39 ns	[102]
CTF	2023	CTF-LTZ	4.07	4.5% @ 400 nm	Ethanol	2.22	-0.96 to 1.26	25.1 ns	[103]
CTF	2022	Bpt-CTF	3.27	8.6% @ 400 nm	None	2.23	-1.25 to 1.05	5.05 ns	[104]
CTF	2019	CTF-BDBBN	0.048	N/A	None	2.43	0.15 to 2.28	2.82 ns	[31]
Heterojunction	2026	MIL-125- NH ₂ @COF	2.92	N/A	None	2.34	-1.97 to +0.76	0.35 ns	[105]
Heterojunction	2025	AZC-2	4.43	3.66% @ 450 nm	None	1.28	-1.19 to 1.31	N/A	[97]
Heterojunction	2025	20BTB	4.09	1.95% @ 365 nm	None	3.52	-0.91 to +2.79	3.88 ns	[106]
Heterojunction	2024	COF/In ₂ S ₃	5.71	N/A	None	1.94	-1.15 to 1.60	N/A	
Heterojunction	2023	COFs@Pd ICs	2.14	6.5% @ 400 nm	Ethanol	2.54	-0.74 to 1.78	1.11 ns	[107]
Heterojunction	2021	(TpMa)/g- C ₃ N ₄ (CN)-5	1.76	N/A	Isopropanol	2.27	-1.01 to +1.51	6.78 ns	[91]

Note: for convenient comparison of the H₂O₂ production efficiency of all catalysts, the reported values were normalized, with the unit being mmol·g⁻¹·h⁻¹. For ease of comparison of the band structures, the reported data were normalized and uniformly converted to values referenced to the NHE at pH=7. AQY=Apparent quantum yield.

ing for 50.3% of the framework), which, combined with the strong electron-withdrawing properties of the tetrazine units and azo bonds, effectively promotes the separation and stabilization of the photogenerated charge carriers. Among them, DT-COF-1, containing only one hydroxyl group, exhibited a higher structural order and extended π -conjugation owing to a moderate electron-donating effect and an optimized keto-enol tautomeric equilibrium. The H₂O₂ production rate reached 4300 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, with an AQY of 14.1% (420 nm). Mechanistic studies showed that a single —OH group acting as an activating substituent enhanced charge transfer to the tetrazine acceptor, narrowed the bandgap, and promoted HOMO-LUMO overlap, enabling ultrafast electron transfer (<500 fs) and extending the excited-state lifetime. Meanwhile, the nitrogen-rich framework facilitates the adsorption and stabilization of O₂⁻ intermediates, driving the 2e⁻ ORR pathway. This work demonstrates that fine-tuning the number of hydroxyl groups and nitrogen-enriched structures can syner-

gistically optimize the electronic structures and reaction intermediate behavior, serving as a typical example of using functional group engineering to improve the photocatalytic H₂O₂ performance of COFs.

4.2.2 Donor-acceptor engineering

In photocatalytic systems, donor-acceptor (D-A) structural design is widely recognized as a key strategy for improving the separation efficiency of photogenerated charge carriers and reaction selectivity. By introducing electron donor and acceptor units at the molecular or framework level, an internal electric field can be generated within the material. This facilitates the directional migration of photogenerated electrons and holes and inhibits recombination, thereby enhancing the synergistic efficiency of the reduction and oxidation half-reactions in photocatalysis. Especially in photocatalytic H₂O₂ production systems, a rational D-A architecture helps promote the synergy between the 2e⁻ ORR process and the 4h⁺ WOR process, while optimizing electron transport and energy level matching, which serves

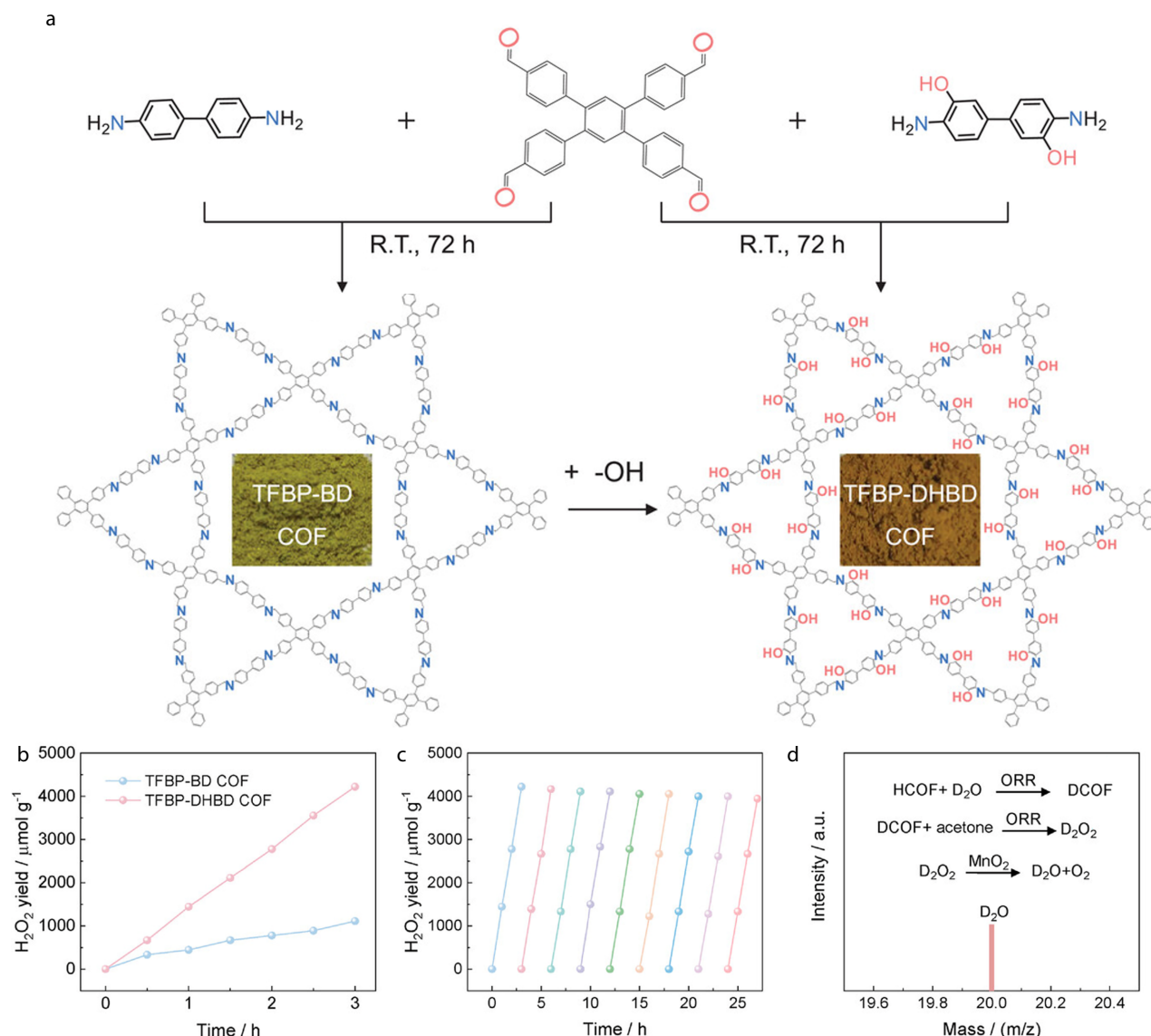


Fig. 7 (a) Schematic diagram of TFBP-BD and TFBP-DHBD COFs; (b) H₂O₂ yields of TFBP-BD and TFBP-DHBD COFs; (c) Photocatalytic stability of TFBP-DHBD COF for Photocatalytic H₂O₂ production; (d) Mass spectra of the produced D₂O for the isotope labeling experiment: TFBP-DHBD COF, i.e., HCOF, deuterated COF, i.e., DCOF, DCOF is used as the photocatalyst for D₂O₂ production. The produced D₂O₂ was catalytically decomposed into D₂O and then analyzed by mass spectrometry.^[95] (Reproduced with permission from Ref. [95]; Copyright (2025), Wiley-VCH).

as an important design principle for improving the overall quantum efficiency.

Based on this concept, in 2024, our team prepared two novel carbazole-containing D-A type covalent CTFs as photocatalysts (Fig. 9).^[62] By introducing carbazole as a strong electron donor to construct a sophisticated D-A charge transport system with the triazine ring as the electron acceptor, deep regulation of photogenerated charge-carrier behaviour was achieved at this level.

This D-A structure effectively addressed the bottleneck of difficult exciton dissociation in traditional polymer photocatalysts, significantly reducing the exciton binding energy (E_b decreased from 130 meV in non-D-A types to 55 meV). This not only greatly promoted the rapid separation and migration of photogenerated electrons and holes but also significantly extended the carrier lifetime through polarization effects. More-

over, a unique and efficient synergistic catalytic mechanism was established: the triazine rings underwent a two-step single-electron ORR to produce H₂O₂, whereas the carbazole groups performed a one-step two-electron WOR as an auxiliary reaction. This allowed the catalyst to operate stably in pure water without sacrificial agents. Compared to the non-D-A control sample CTF-HUST-1 (with a yield of only 292 μmol·g⁻¹·h⁻¹), the D-A-structured CTF-TPCZ exhibited an H₂O₂ yield of 3764 μmol·g⁻¹·h⁻¹ under visible light, representing a massive 12.9-fold increase in performance. Moreover, its yield under simulated sunlight reached 10331 μmol·g⁻¹·h⁻¹, with a solar-to-chemical conversion (SCC) efficiency of 0.68%, far exceeding the photosynthetic efficiency of natural plants (approximately 0.1%). This fully demonstrates the central role and broad prospects of the D-A design in the construction of efficient and sustainable industrial-grade photocatalytic ma-

terials.

Similarly, Jiani *et al.* constructed a thiazole-based homozygous heteroaromatic covalent organic framework (TTT-COF) through heteroatom regulation and post-cyclization, systematically demonstrating the reinforcing effect of D-A structures on the photocatalytic performance (Fig. 10).^[75] This work utilized a sulfur vapor-induced post-cyclization reaction to convert imine bonds into thiazole structures. The introduc-

tion of S heteroatoms not only significantly enhanced the chemical stability of the framework, but also constructed a continuous π -conjugated backbone. The introduction of thiazole units effectively increased the molecular polarity of the framework and strengthened the internal D-A characteristics, promoting the separation and migration of photogenerated charges, thereby significantly improving intrinsic photocatalytic activity. Compared with the original imine-type COFs,

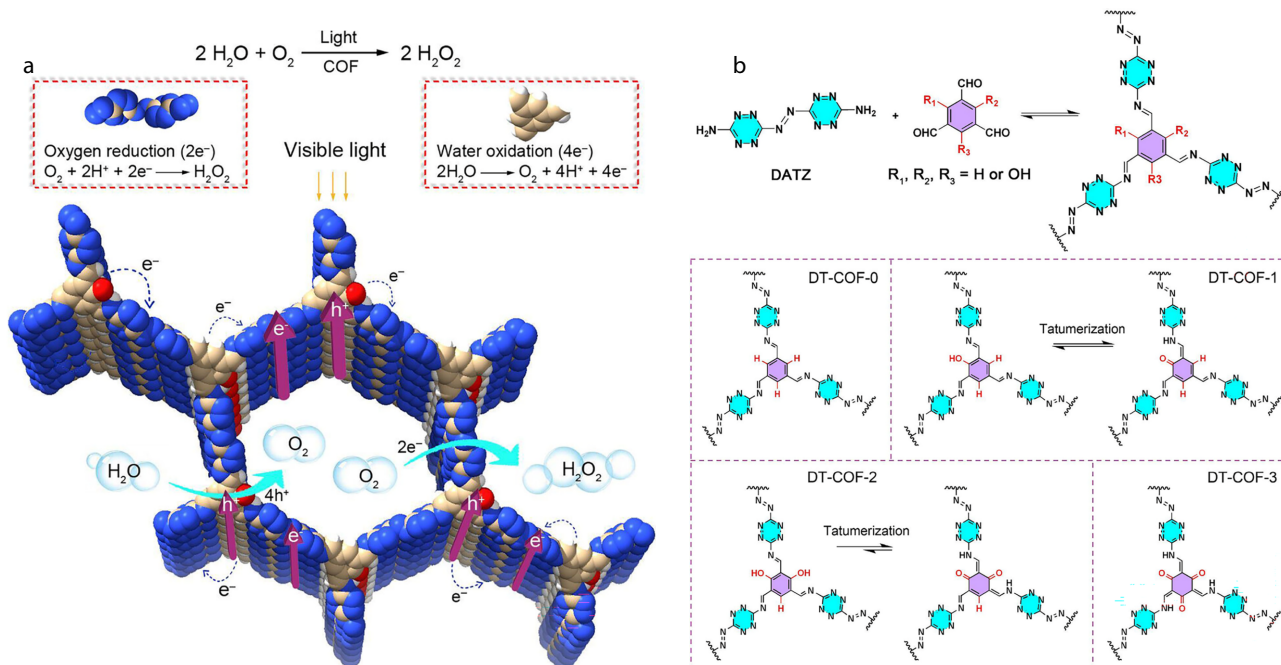


Fig. 8 (a) Reaction pathways for photocatalytic H_2O_2 production over DT-COFs, highlighting a tetrazine-enabled two-electron water oxidation route; (b) Synthesis and structural features of DT-COFs, emphasizing hydroxyl proton tautomerism. (Reproduced with permission from Ref. [96]; Copyright (2025), Wiley-VCH.)

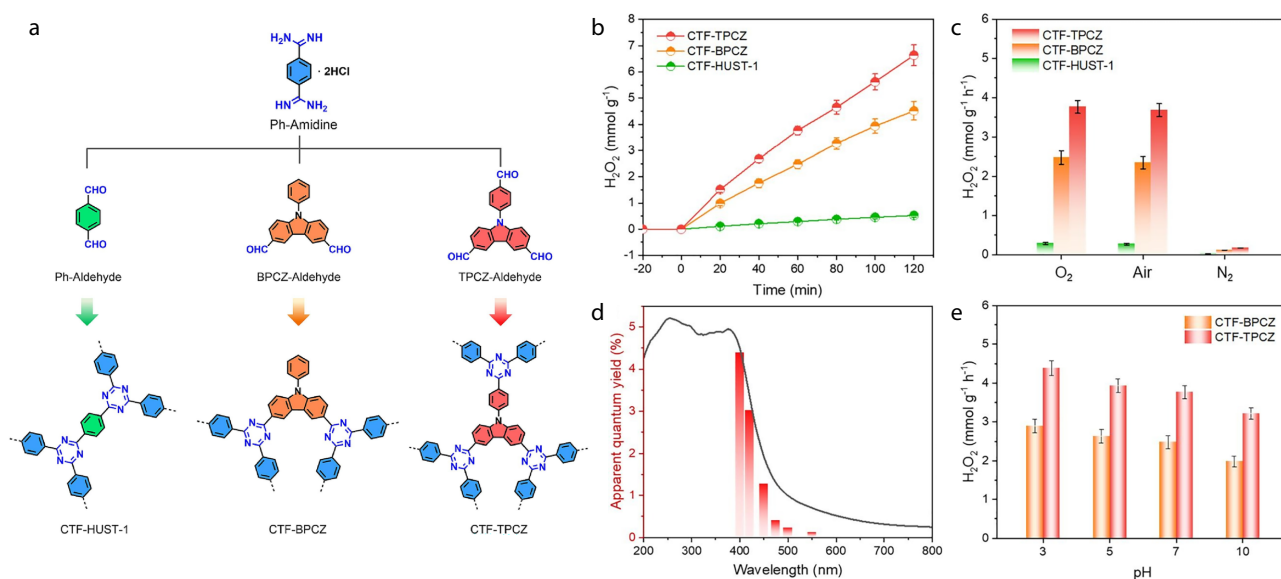


Fig. 9 Synthesis, characterization, and photocatalytic H_2O_2 performance of CTFs. (a) Synthesis and chemical structures of CTF-HUST-1, CTF-BPCZ, and CTF-TPCZ; (b) Photocatalytic H_2O_2 production under various atmospheres; (c) Extended atmosphere-dependent H_2O_2 production tests; (d) H_2O_2 production at different wavelengths; (e) pH-dependent H_2O_2 production rates for CTF-PCZs. (Conditions: 5 mg of catalyst, 50 mL of water, 300 W Xe lamp, $100 \text{ mW} \cdot \text{cm}^{-2}$, $\lambda \geq 420 \text{ nm}$). (Reproduced with permission from Ref. [62]; Copyright (2024), Elsevier.)

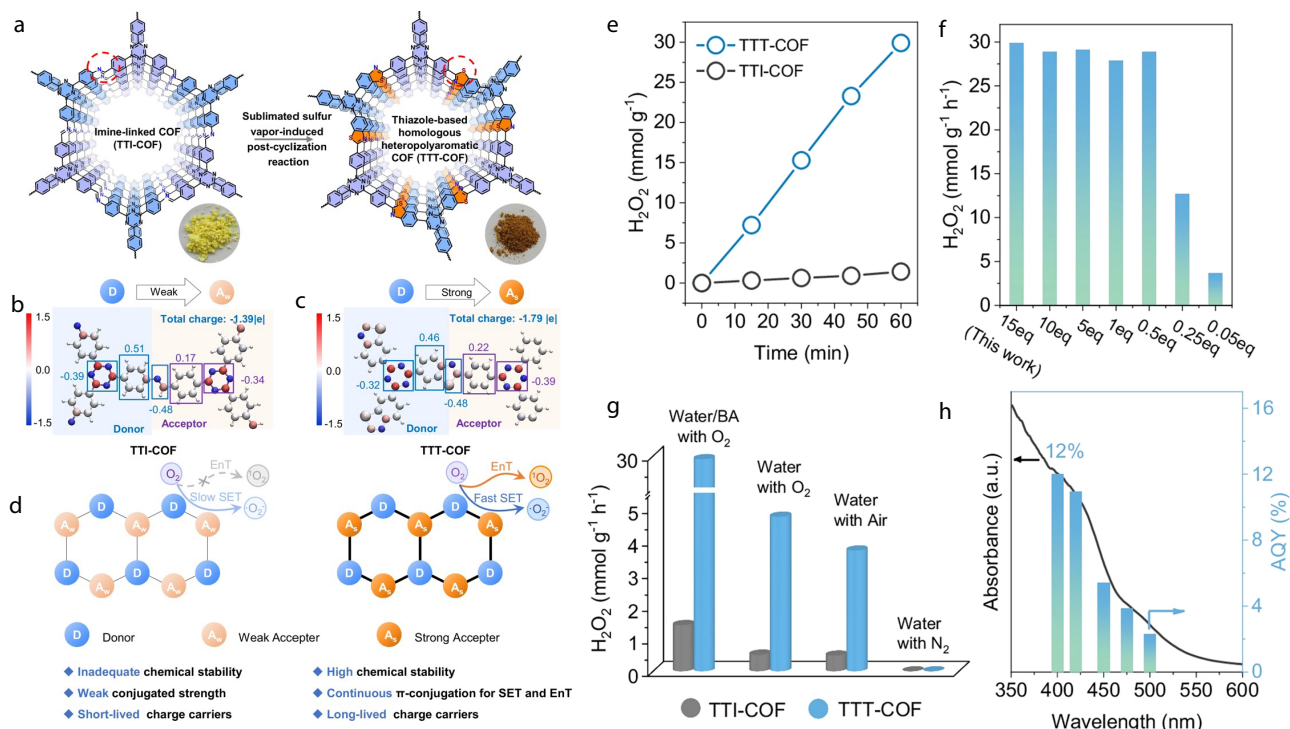


Fig. 10 (a) Post-cyclization synthesis of TTT-COF from TTI-COF induced by sulfur vapor (insets: synthesized COFs); (b, c) Bader charge distribution maps of TTI-COF and TTT-COF; (d) Structural advantages of homologous heteropoly aromatic COFs (TTT-COF); (e) Photocatalytic H_2O_2 production of TTI-COF and TTT-COF under visible light; (f, g) Effects of sulfur dosage and gas atmosphere on H_2O_2 generation; (h) Wavelength-dependent AQY of TTT-COF. (Reproduced with permission from Ref. [75]; Copyright (2025), Springer Nature.)

the photocatalytic H_2O_2 production rate of TTT-COF increased approximately 20-fold, reaching $29.9 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, and it could operate stably for over 200 h in the presence of sacrificial agents. Furthermore, its continuous π -conjugation and enhanced D-A structure endowed the material with efficient electron and energy transfer capabilities, enabling it to exhibit excellent activity in the aerobic oxidation of $\text{C}(\text{sp}^3)\text{-H}$ bonds. This study indicates that synergistically enhancing D-A characteristics through heteroatom introduction and structural reconstruction is an effective way to achieve photocatalytic COFs with high activity and stability.

4.2.3 Heterojunction design

In COF-based photocatalytic systems, the rapid recombination of photogenerated charge carriers is a key bottleneck limiting the efficient production of H_2O_2 . Constructing heterojunctions, especially those with well-defined energy-band alignments, is considered an effective strategy. This approach establishes an internal electric field at the interface, promoting spatial separation and directional migration of photogenerated electrons and holes, thereby significantly enhancing the efficiency of photocatalytic H_2O_2 production. Consequently, heterojunction design has gained increasing attention for the performance optimization of COF-based photocatalysts.

In the design of COF-based heterojunction systems, Meng *et al.*^[97] proposed a synergistic strategy combining S-scheme heterojunction construction with ion-doping engineering to enhance the efficiency of photocatalytic H_2O_2 production (Fig. 11). In this study, a bipyridine-based COF (TpBpy) was loaded onto the surface of Ag-doped ZnIn_2S_4 (Ag-ZIS) nanoflowers through room-temperature cation exchange

and subsequent hydrothermal treatment, successfully constructing an Ag-ZIS/TpBpy COF S-scheme heterojunction. Ag doping not only induced atomic-level regulation of the ZnIn_2S_4 lattice, achieving bandgap narrowing and a red-shift in visible-light absorption, but also effectively enhanced the internal electric field (IEF) within the heterojunction, thereby promoting directional migration and efficient separation of photogenerated charge carriers. Benefiting from the strong electronic coupling at the interface between the Ag-ZIS and TpBpy COF, the system significantly inhibited carrier recombination and established an efficient electron transport channel. As a result, the optimized sample achieved a H_2O_2 production rate as high as $4425 \text{ } \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ in a pure water system. Further characterization and DFT calculations indicated that Ag doping plays a key role in regulating the energy band structure and interface charge dynamics. From the perspective of synergistically optimizing atomic-scale bandgap regulation and interface charge transport, this work provides a new design paradigm for constructing efficient MS/COF type S-scheme heterojunction photocatalytic systems and lays an important theoretical and methodological foundation for green and sustainable H_2O_2 synthesis technology.

Similarly, Yu *et al.* developed a novel COF/ In_2S_3 organic/inorganic S-scheme heterojunction photocatalyst (Fig. 12).^[98] By *in situ* growth of In_2S_3 nanosheets on a covalent organic framework (COF) substrate, this study achieved extremely high utilization efficiency of photogenerated charge carriers through the regulation of the energy band structure and interfacial interactions of the S-scheme heterojunction. This D-A type interaction (with COF as the electron donor and In_2S_3

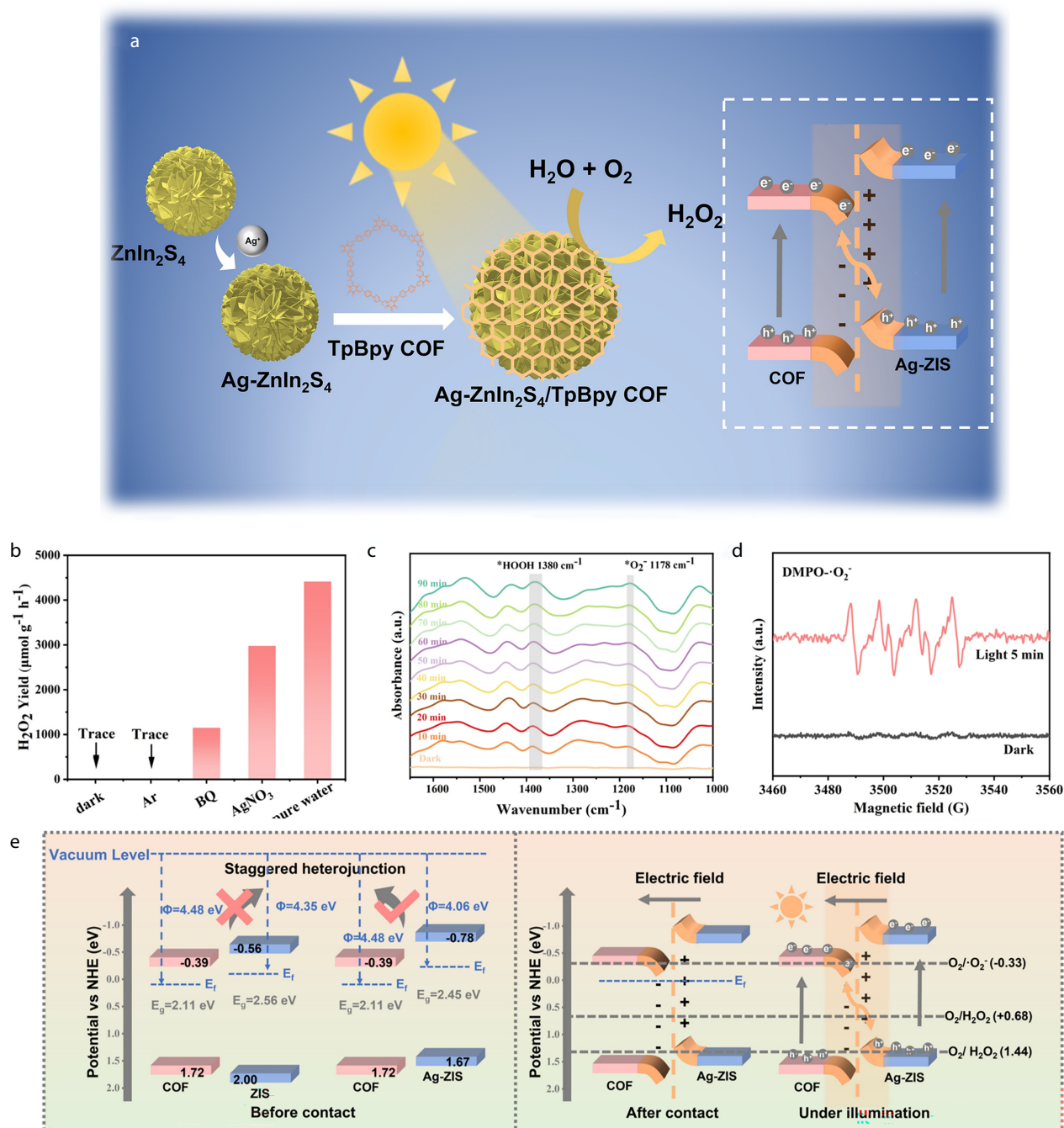


Fig. 11 Photocatalytic mechanism and performance analysis of AZC-2. (a) Photocatalytic mechanism of AZC-2 for H₂O₂ production; (b) Effects of various reaction conditions and scavengers on H₂O₂ production over AZC-2; (c) *In situ* FTIR spectra of AZC-2 during photocatalytic H₂O₂ generation (the dark spectrum was collected under a He atmosphere); (d) EPR spectra of DMPO-·O₂⁻ radicals over AZC-2 under illumination; (e) Schematic comparison of ZC and AZC heterojunctions and the proposed S-scheme heterojunction photocatalytic mechanism of AZC. (Reproduced with permission from Ref. [97]; Copyright (2025), Elsevier).

as the acceptor) and the resulting S-scheme structure significantly broadened the light absorption range. Owing to the formation of intermediate hybrid energy levels that narrow the bandgap, the issues of limited light absorption and rapid carrier recombination in single-component materials have been effectively addressed. By leveraging the S-scheme mechanism, the spatial separation of electrons and holes was achieved while maintaining strong redox capabilities, en-

abling efficient photosynthesis of H₂O₂ in pure water through synergistic oxygen reduction (ORR) and water oxidation (WOR) pathways. Compared with the monomeric COF without the heterojunction structure (yield of 727 μmol·g⁻¹·h⁻¹) or pure In₂S₃ (yield of 534 μmol·g⁻¹·h⁻¹), the H₂O₂ yield of the optimized COF/In₂S₃ heterojunction under visible light increased to 2651 μmol·g⁻¹·h⁻¹. This performance represents an approximately 3.6-fold increase compared to that of the

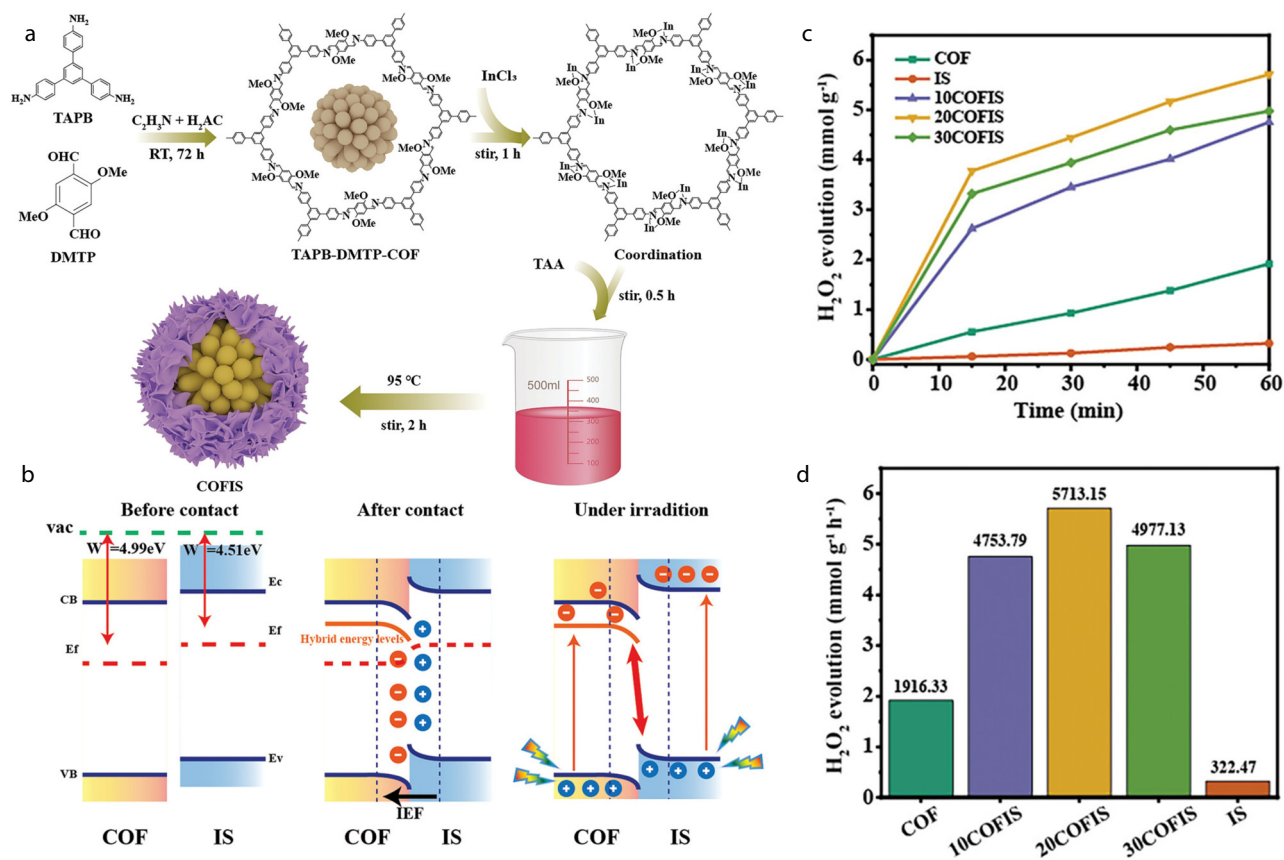


Fig. 12 Synthesis and photocatalytic H_2O_2 production performance of COF/ In_2S_3 (COFIS) S-scheme heterojunction. (a) Schematic diagram for the synthesis of COF/ In_2S_3 composites (COFIS); (b) Charge carrier transfer mechanism in the COF/ In_2S_3 S-scheme heterojunction; (c) Photocatalytic H_2O_2 evolution rates of various samples; (d) Comparison of H_2O_2 yields for different samples after 1 h of illumination. (Reproduced with permission from Ref. [98]; Copyright (2024) Wiley-VCH).

monomeric COF and a 5-fold increase compared to pure In_2S_3 , with an apparent quantum efficiency (AQE) as high as 16.3% at 420 nm. This work demonstrates the enormous potential of heterojunction construction for enhancing the solar energy conversion efficiency and environmentally friendly chemical production.

4.2.4 Tuning the hydrophobicity/hydrophilicity

Recent studies have shown that the hydrophilic and hydrophobic properties of catalysts exert a significant influence on photocatalytic H_2O_2 generation, primarily by modulating interfacial mass transfer resistance. Appropriate hydrophobic or hydrophilic functionalization can regulate the distribution of reactants (such as O_2 and H_2O) on the catalyst surface at the microscale, which is crucial for overcoming the inherent mass-transport bottleneck caused by the low solubility of O_2 . By strategically introducing hydrophobic regions, these designs provided low-resistance pathways for gaseous O_2 diffusion, effectively bypassing the sluggish transport process through the bulk aqueous phase. This optimization ensured a rapid and continuous supply of gaseous reactants to the catalyst surface, thereby improving the local reactant concentrations and overall mass transfer efficiency.

For instance, O_2 can be enriched in hydrophobic regions, whereas hydrophilic regions facilitate the adsorption and activation of water molecules, creating a localized high-concentration reaction environment. Simultaneously, the differ-

ences in hydrophilicity and hydrophobicity can affect the migration and separation of photogenerated charge carriers, reducing the electron-hole recombination rates. By employing this strategy, the H_2O_2 yield and quantum efficiency of photocatalytic systems can be significantly enhanced, with particularly notable effects under air-water interfaces or oxygen-limited conditions. Overall, the hydrophilic-hydrophobic design provides a dual optimization approach for photocatalytic H_2O_2 production, ranging from interface engineering to reaction kinetics, which is a vital strategy for improving catalytic efficiency.

Qiao *et al.* proposed an efficient photocatalytic strategy based on triphase interface engineering by constructing COF membranes with asymmetric hydrophilic-hydrophobic characteristics. This approach effectively addressed the mass transfer limitations of O_2 and H_2O in air/water systems (Fig. 13).^[79] By transforming traditional COF powders into nanostructured membranes, researchers not only significantly enhanced light absorption and energy band alignment, but also concurrently enriched O_2 and H_2O in localized regions through hydrophilic-hydrophobic partitioning. This structural refinement fundamentally alters the oxygen transport the asymmetric wettability creates a dedicated gaseous diffusion pathway that facilitates the rapid delivery of O_2 from the atmosphere to the active sites, effectively minimizing the diffusion distance within the liquid phase. The optimized AZC-2

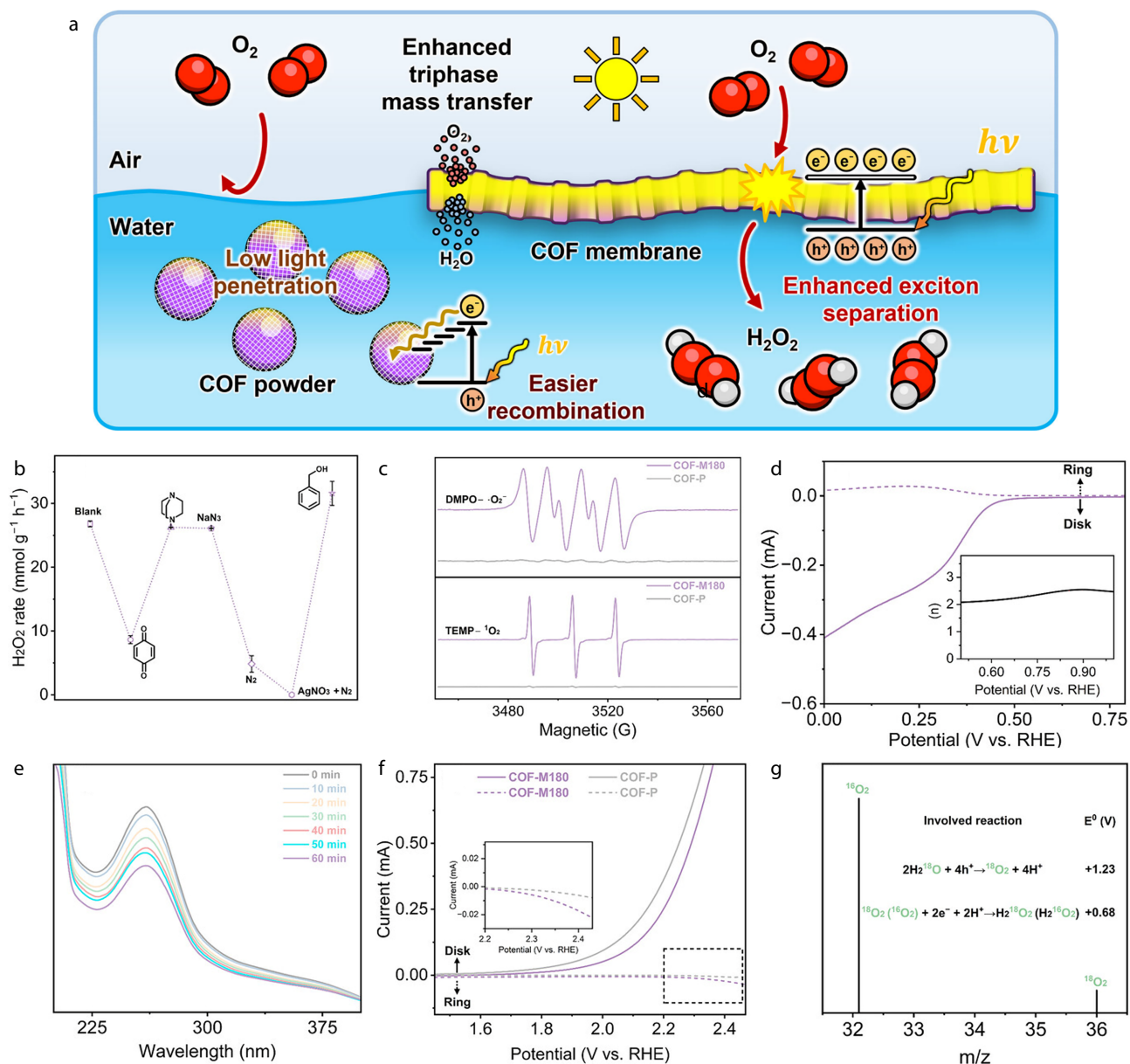


Fig. 13 (a) Comparison of COF powder and COF-M180 membrane with asymmetric wettability for enhanced H_2O_2 production; the membrane forms a gas-liquid-solid interface, enabling localized O_2 enrichment and efficient reactant diffusion, while the powdered system suffers from limited O_2 accessibility. (b) Photocatalytic H_2O_2 generation mechanism and effect of different scavengers on COF-M180 activity. (c) Comparison of EPR spectra of COF-M180 and COF-P under visible-light irradiation using DMPO and TEMP spin-trapping agents. (d) RRDE polarization curves for H_2O_2 detection (disk and ring currents used to calculate electron transfer number). (e) Time-dependent degradation of NBT to monitor $\cdot\text{O}_2^-$ formation over COF-M180. (f) RRDE voltammograms obtained in 0.1 mol L^{-1} phosphate buffer solution with a scan rate of 10 mV s^{-1} and a rotation rate of 1600 r min^{-1} . The potential of the Pt ring electrode is set at -0.23 V versus Ag/AgCl to detect O_2 . Inset: Enlarged ring current spectra within the black dashed box. (g) GC-MS analysis of H_2O_2 decomposition products in the H_2^{18}O isotope experiment, confirming direct two-electron water oxidation over COF-M180. (Reproduced with permission from Ref. [79]; Copyright (2025), Wiley-VCH.)

membrane achieved an H_2O_2 production rate of 52.5 $\text{mmol g}^{-1} \text{h}^{-1}$ under oxygen-rich conditions. Its apparent quantum efficiency exhibited a 27.8-fold increase compared to its powder counterpart and a remarkable 148.9-fold enhancement under ambient air conditions. Moreover, these membrane-based COFs can be seamlessly integrated into continuous-flow reactors, enabling the simultaneous degradation of pollutants *via in situ*-generated H_2O_2 , which demonstrates superior application potential over traditional batch

systems. Further investigations revealed that this design strategy is highly versatile, yielding tens-to-hundred-fold performance improvements in other COF systems, such as TapbDva and TapbHta. This work provides critical insights into overcoming mass transfer bottlenecks through hydrophilic-hydrophobic regulation and triphase interface intensification, laying a robust theoretical foundation for the development of scalable COF-based photocatalytic membrane reactors.

Complementarily, beyond the membrane engineering

strategies discussed previously, molecular-level functionalization of the framework represents another vital approach. Li *et al.* reported a class of highly crystalline triazine-based COFs featuring distributed polar oxygen functional groups such as $-\text{SO}_3\text{H}$ or $-\text{COOH}$.^[99] The incorporation of these polar groups significantly enhances the surface hydrophilicity of the catalyst, which in turn facilitates the separation and rapid transport of both photogenerated electrons and interfacial protons (Fig. 14). This optimized interfacial environment is crucial for managing the complex charge-transfer requirements of the reaction. This study reveals that the targeted

placement of polar groups not only optimizes the electronic structure, but also creates a localized proton-rich microenvironment, which is essential for accelerating proton mass transport to the adsorbed oxygen species. This process effectively facilitates a polarity-driven proton-coupled electron transfer (PCET) mechanism. This process effectively accelerates the formation of $^*\text{OOH}$, which is the key intermediate in the $2e^-$ oxygen reduction reaction (ORR) pathway. By lowering the thermodynamic barriers associated with this intermediate, polar-functionalized COFs significantly enhanced the overall Photocatalytic H_2O_2 production rate. Experimental da-

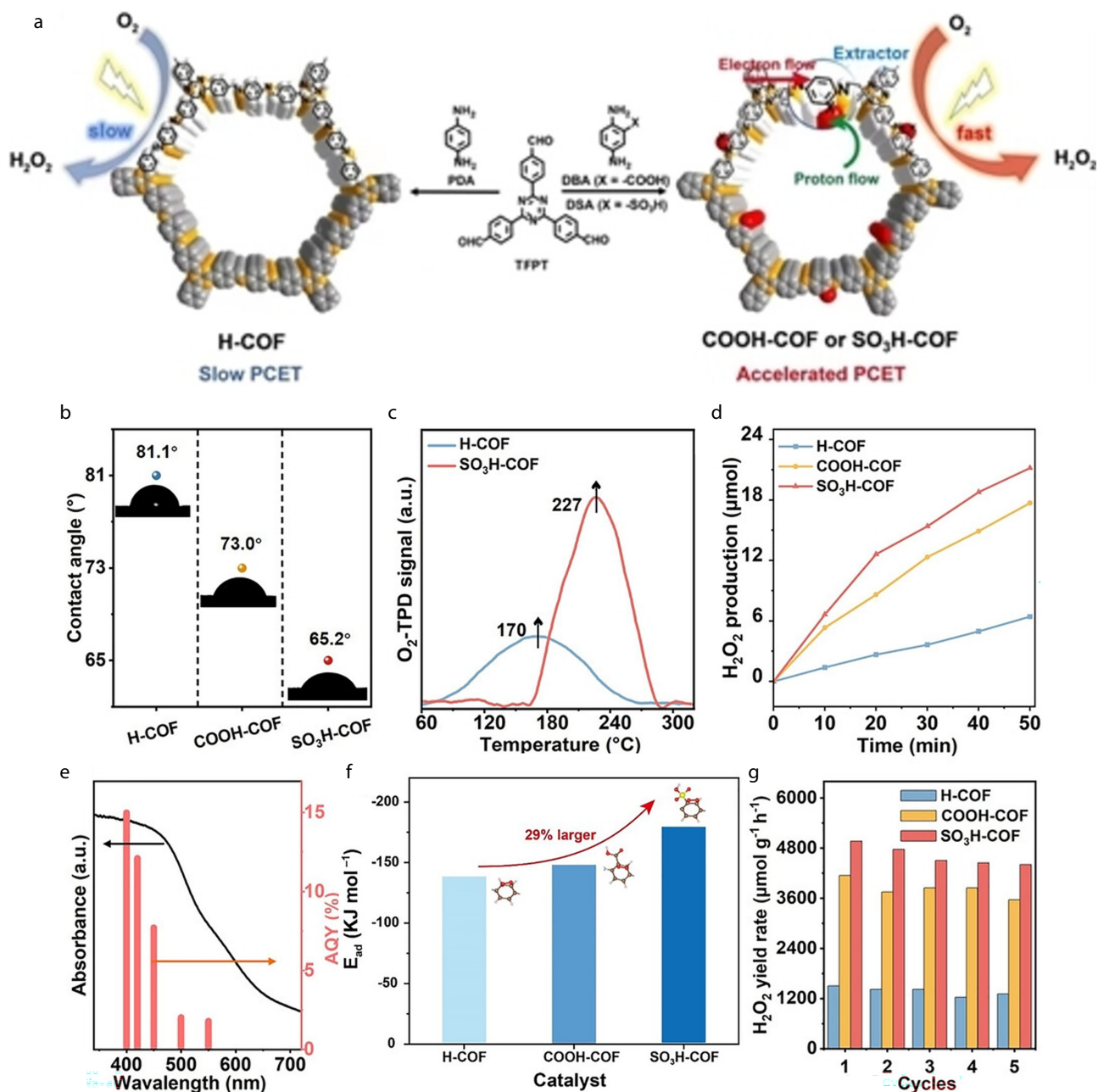


Fig. 14 Characterization and H_2O_2 production performance of polar-functionalized COFs. (a) Schematic of $\text{SO}_3\text{H-COF}$ and COOH-COF as electron/proton extractors to boost carrier transfer; (b) Water contact angle measurements and (c) O_2 -TPD analysis; (d) Wavelength-dependent H_2O_2 yields and AQY of $\text{SO}_3\text{H-COF}$; (e) Comparison of H_2O_2 yield and AQY with typical COF photocatalysts; (f) O_2 adsorption energies and (g) stability test of $\text{SO}_3\text{H-COF}$ ($\lambda > 400$ nm). (Reproduced with permission from Ref. [99]; Copyright (2024), Wiley-VCH.)

ta showed that the SO_3H -COF derivative achieved an H_2O_2 production rate of $4971 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ under visible-light irradiation, with an apparent quantum yield (AQY) of 15% at 400 nm. This research clearly demonstrates that the rational design of a catalyst's polarity and hydrophilic-hydrophobic characteristics can simultaneously optimize charge carrier transport and O_2 adsorption. Consequently, this work provides an important reference for the molecular engineering of high-performance COF photocatalysts, highlighting how targeted functional group placement can fundamentally improve solar-to-chemical conversion efficiency.

Various strategies exist for the modification of hydrophilic and hydrophobic properties, including the fabrication of films with gradient amphiphilicity and incorporation of polar functional groups, as previously discussed. Although these approaches differ in execution, their primary objective is to construct efficient tri-phase mass transfer channels that facilitate the transport of water and oxygen to catalytically active sites. The literature suggests that the optimal balance between hydrophilicity and hydrophobicity must be evaluated within the context of specific reaction systems, as neither property is inherently superior. Specifically, hydrophilicity enhances the catalyst dispersibility in aqueous media, promotes the diffusion of water reactants to active sites, and facilitates the desorption of H_2O_2 products. Conversely, hydrophobic structures accelerate the diffusion of oxygen toward active sites, a critical factor given that the low solubility of oxygen in water often limits the oxygen reduction reaction (ORR) rate. Consequently, many catalyst designs incorporate hierarchical structures that integrate both hydrophilic and hydrophobic domains. Such structural engineering is instrumental for simultaneously enhancing the overall catalytic activity and long-term stability of the material.

4.2.5 Pore and spatial engineering

Pore and spatial engineering represent indispensable dimensions in the design of high-performance POP-based photocatalysts. The unique porous nature of these frameworks provides a versatile platform for optimizing mass transport kinetics and tailoring the reaction microenvironment. By precisely controlling the pore size, dimensionality, and spatial arrangement, it is possible to facilitate the rapid diffusion of reactants to active sites while ensuring the timely removal of the produced H_2O_2 , thereby suppressing undesired secondary decomposition. Crucially, the rational design of the topological framework plays a decisive role in regulating the internal electronic environment, and an optimized topology can establish efficient pathways for charge migration, significantly enhancing the separation and transfer efficiencies of the photogenerated carriers. Consequently, integrated pore and spatial engineering serve as a critical strategy for boosting both the charge dynamics and mass transport flux, ultimately leading to superior catalytic activity and solar-to-chemical conversion (SCC) efficiency in photocatalytic H_2O_2 production systems.

Cheng *et al.* designed and synthesized three π -conjugated 2D sp^2 carbon-linked COFs with distinct topologies by selecting building blocks (Fig. 15).^[81] Despite possessing similar chemical compositions and band structures, these three COFs exhibited significant disparities in charge separation and transfer efficiencies, which were attributed to their different topological frameworks. Among them, QP-HPTP-COF demonstrated superior photocatalytic performance, with H_2O_2 production rates that were 4.7-fold and 2.3-fold higher than those of QP-TPB-COF and QP-BPT-COF, respectively. Furthermore, the optimal catalyst achieved a remarkable solar-to-chemical conversion (SCC) efficiency of 1.41%.

Luan *et al.* introduced varying amounts of sulfonate groups ($-\text{SO}_3$) onto PyNTB-COF *via* a post-synthetic modification

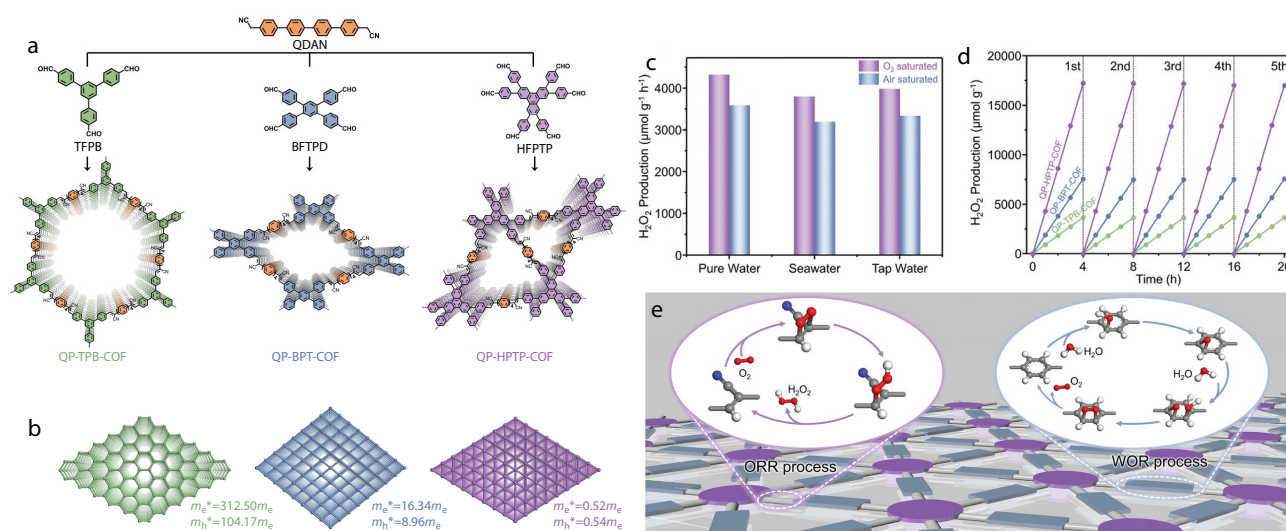


Fig. 15 Synthesis, porous structure, and charge carrier dynamics of QP-functionalized COFs. (a) Synthetic schemes and corresponding chemical structures of QP-TPB-COF, QP-BPT-COF, and QP-HPTP-COF; (b) Schematic illustration of the correlation between topology and effective masses (m_e^* and m_h^*) in different COFs; (c) Overall photosynthetic H_2O_2 production performance of QP-HPTP-COF in O_2 and air saturated pure water, seawater, and tap water under visible light irradiation ($\lambda > 420$ nm, 300 W Xe lamp); (d) Typical time course of overall photosynthetic H_2O_2 production by QP-HPTP-COF in O_2 saturated pure water under the same conditions; (e) Schematic illustration of the photocatalytic reaction pathways for H_2O_2 formation on QP-HPTP-COF under visible light irradiation. (Reproduced with permission from Ref. [81]; Copyright (2025), Wiley-VCH.)

strategy (Fig. 16).^[83] This approach significantly optimized the pore microenvironment of PyNTB-COF, effectively enhancing the mass transport kinetics of both the reactants and products. Meanwhile, the incorporation of sulfonate moieties modulated the intrinsic charge distribution of the framework, thereby improving the charge-carrier separation and transfer efficiencies. Consequently, the photocatalytic performance was enhanced up to 20-fold, demonstrating that the regulation of the pore microenvironment is a crucial means of boosting the catalytic activity of photocatalysts.

5 CONCLUSIONS & FUTURE PERSPECTIVES

5.1 Conclusions

Here, we provide a systematic review of recent progress in POPs for the photocatalytic production of H_2O_2 . Through precise molecular-level engineering, covalent COFs and CTFs have demonstrated significant advantages in enhancing light utilization, charge separation efficiency, and mass transfer capabilities, as summarized below.

5.2 Light Harvesting and Bandgap Regulation

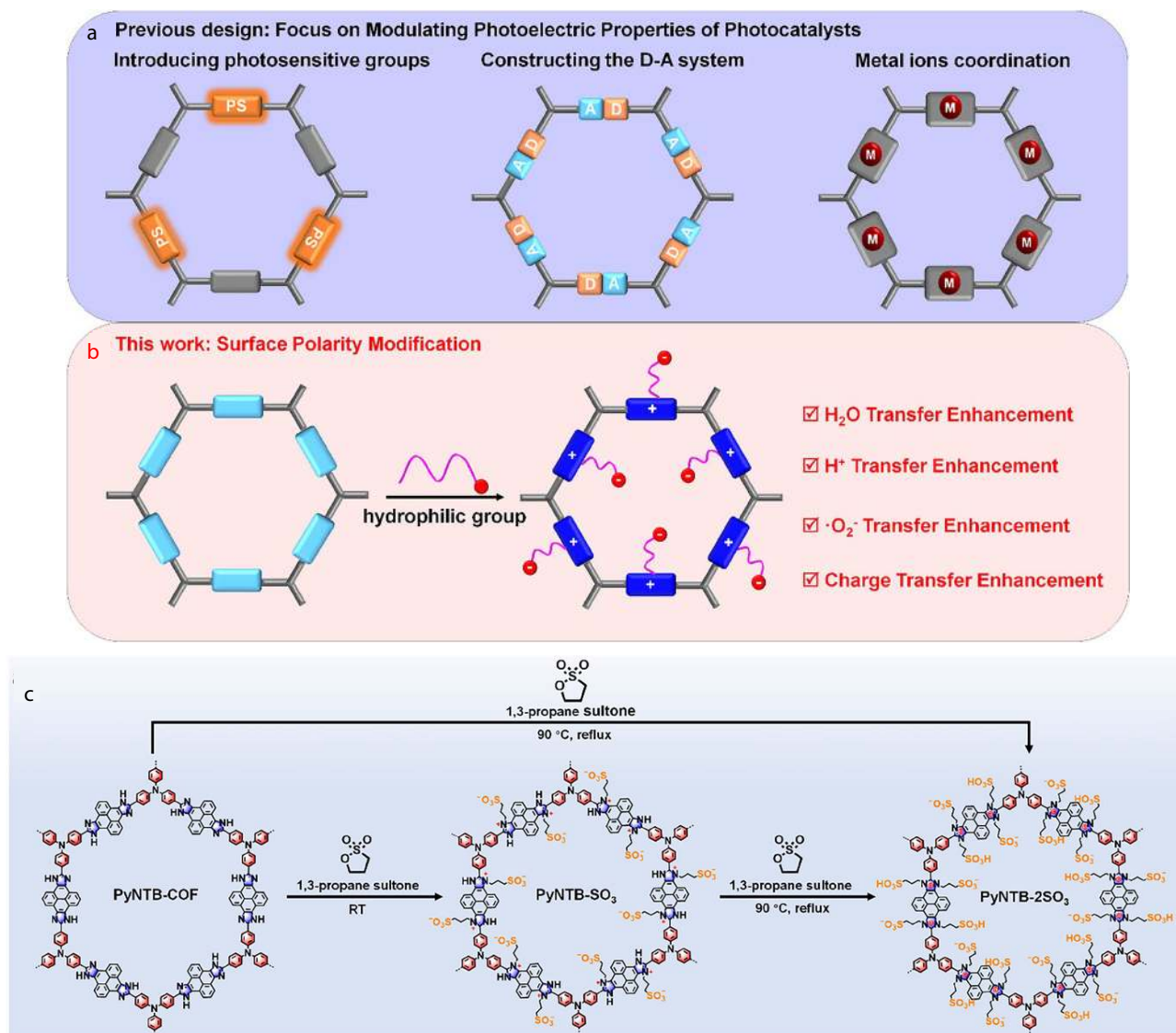
By integrating photoactivity and employing D-A engineering, broad-spectrum visible-light absorption was achieved. Furthermore, the band structures of these polymers can be finely tuned to meet the specific thermodynamic requirements of the reaction.

5.2.1 Optimization of charge dynamics

Efficient charge carrier management was achieved through a two-fold approach involving charge separation and recombination inhibition. The inherent electronic push-pull effect generated by D-A architectures, complemented by strategic hetero-junction design, promotes the directional migration of photo-generated electrons and holes. Moreover, by spatially separating the redox-active sites and incorporating co-catalysts to rapidly consume sacrificial agents or holes, the probability of non-radiative carrier recombination is significantly reduced, thereby extending the lifetime of the reactive species.

5.2.2 Mass transfer and interfacial control

Beyond electronic modulation, the synergistic design of hy-



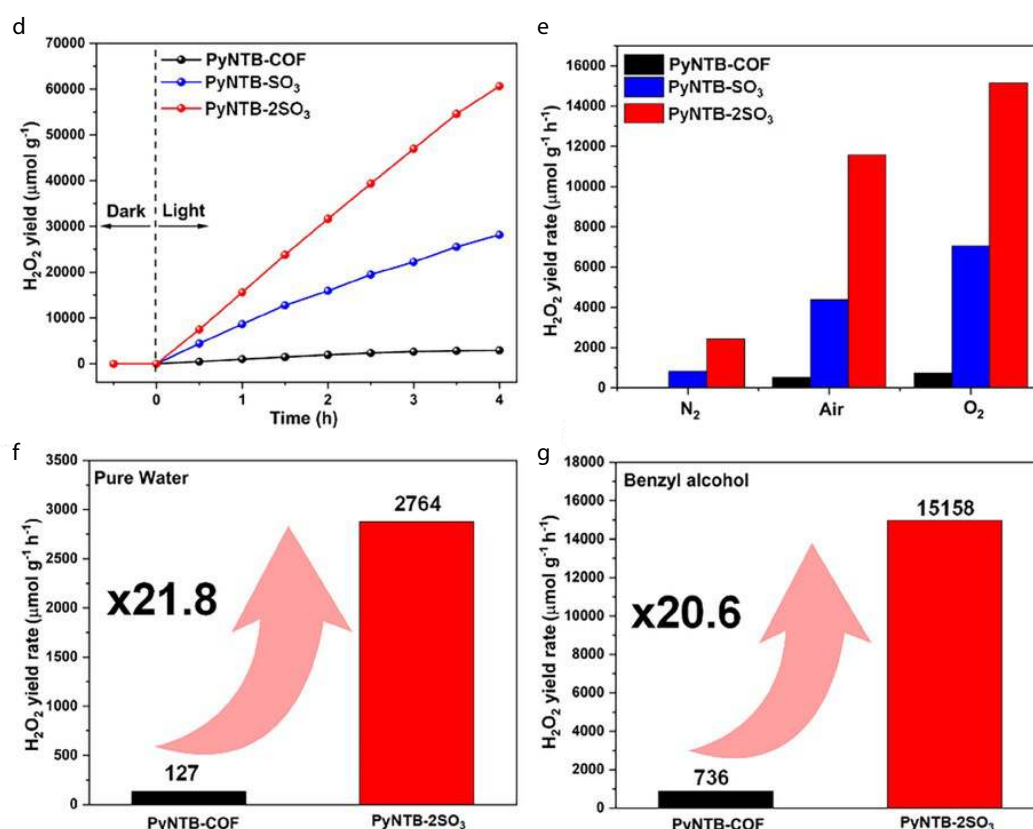


Fig. 16 Synthesis, pore environment modulation, and photocatalytic H_2O_2 production performance. (a) Synthesis strategies of the reported COF-based photocatalysts; (b) Schematic illustration of pore microenvironment modulation to increase mass transfer in the fabricated photocatalysts; (c) Synthetic routes for PyNTB- SO_3 and PyNTB- 2SO_3 ; (d) Time profiles of H_2O_2 generation catalyzed by PyNTB-COF, PyNTB- SO_3 , and PyNTB- 2SO_3 . The H_2O_2 generation rate with PyNTB-COF, PyNTB- SO_3 , and PyNTB- 2SO_3 as catalysts: (e) under different atmospheres, (f) in pure water, (g) in the presence of benzyl alcohol. (Reproduced with permission from Ref. [83]; Copyright (2026), Wiley-VCH.)

drophilic-hydrophobic structures plays a critical role in optimizing O_2 diffusion channels, thereby facilitating the transport of reactants to catalytically active sites and enhancing the mass transfer efficiency at the gas-liquid-solid tri-phase interface. Specifically, the low solubility of oxygen in water inherently restricts the rate of oxygen reduction reaction (ORR) in photocatalytic H_2O_2 production. The strategic integration of the hydrophobic domains within the catalyst can result in gas diffusion pathways, ensuring efficient contact between oxygen and the active sites. Concurrently, the incorporation of hydrophilic or polar functional groups improves the dispersibility of the catalyst in aqueous media, promotes charge carrier separation, and facilitates both the transport of water to active sites and rapid desorption of the H_2O_2 product. This dual-functional approach prevents the recombination of H_2O_2 with photogenerated charge carriers, thereby avoiding unwanted over-oxidation or reduction and shields the catalyst from structural damage. Collectively, these structural designs significantly accelerate mass transport in the tri-phase system, leading to marked improvements in both the catalytic activity and long-term stability.

In summary, porous organic polymers (POPs) show great potential for photocatalytic H_2O_2 production because of their designable structures and tunable bandgap positions. However, they are still in the laboratory research stage and have not yet been used in industrial applications. The main rea-

sons for this phenomenon are as follows: the concentration of H_2O_2 produced is low, making it difficult to meet industrial concentration and purification requirements; the stability of the catalyst itself in the photocatalytic reaction is insufficient; the synthesis cost of the catalyst is high; and the synthesis steps are complex, making large-scale production difficult. In terms of laboratory applications, some are applied in flow cells for the degradation of organic pollutants; however, the sustainability and degradation efficiency of flow cells remain very limited. In photo-enzyme coupled systems, light intensity and temperature must be specifically controlled to avoid enzyme inactivation, while the limited light intensity restricts the occurrence of the photocatalytic reaction. Regarding wound disinfection, issues such as the biocompatibility of POPs, impact of photogenerated charge carriers on biological tissues, and light penetration depth in tissues all limit the photocatalytic reaction. Therefore, although many related studies have attempted to promote photocatalytic reactions for practical applications, there are still many problems to be solved before photocatalytic H_2O_2 production can truly serve practical needs.

5.3 Future Perspectives

Despite the breakthrough progress achieved thus far, COFs and CTFs still face several severe challenges in their transition to industrial applications, which simultaneously define key direc-

tions for future research. Addressing these bottlenecks is essential for moving beyond laboratory-scale demonstrations to large-scale solar fuel production. In the following sections, we provide a detailed elaboration of the specific challenges and critical issues encountered during the research and practical application processes, as analyzed below.

5.3.1 Stability enhancement and inhibition of H_2O_2 decomposition

Achieving high concentrations of H_2O_2 in photocatalytic systems remains challenging, primarily because of its inherent instability at elevated levels, the limited robustness of catalysts under such conditions, and the presence of competing side reactions. At higher concentrations, H_2O_2 can readily consume photogenerated charge carriers, resulting in decreased photocatalytic efficiency. Meanwhile, its interaction with the catalyst surface may induce structural damage. Consequently, once the H_2O_2 concentration surpasses a certain threshold, the production rate often declines markedly and eventually reaches a dynamic balance between formation and decomposition, making further accumulation difficult.

To overcome this limitation, catalyst optimization should be approached from two perspectives: structural design and interfacial microenvironment regulation. From the standpoint of structural design, priority should be given to enhancing the inherent stability of catalyst frameworks. For instance, transforming imine linkages into π -conjugated structures can reinforce framework robustness. In addition, the development of linkage chemistry with improved resistance to oxidative degradation is of equal importance. Together, these approaches contribute to strengthening the intrinsic stability of the catalysts.

In addition, introducing hydrophilic–hydrophobic structures into the catalyst can promote mass transfer at three-phase interfaces. On the one hand, this increases the diffusion rate of oxygen in water, ensuring the continuous participation of active sites in the reaction. On the other hand, by introducing polar functional groups to improve the local charge distribution and form hydrogen-bonding networks, the adsorption strength of intermediates can be regulated and the rapid desorption of the product H_2O_2 can be promoted. Consequently, while achieving high photochemical and chemical stability of the catalyst, structural damage caused by locally high concentrations can be effectively avoided. Photocatalytic systems with high stability are of key significance for increasing the H_2O_2 concentration and promoting the transition from laboratory research to practical applications.

5.3.2 Efficient modification processes

Future research should also explore milder and more efficient modification techniques for these materials.^[108,109] Achieving precise functionalization of COF pores under milder conditions not only aligns with the principles of green chemistry but is also conducive to preserving the intrinsic activity of the crystalline material. Developing advanced post-synthetic or bottom-up strategies will facilitate the creation of multifunctional catalysts without compromising their structural integrity or porosity.

Beyond the development of advanced photocatalysts, several critical challenges in the field of photocatalytic H_2O_2 production remain unaddressed.

5.3.3 Standardization of testing protocols

The efficiency of photocatalytic H_2O_2 production is highly sensitive to experimental parameters, including the catalyst dosage, reactor configuration, reaction temperature, and the type and intensity of the light source. Currently, catalyst dosages vary widely (from several to dozens of milligram), which leads to inconsistent mass transport efficiencies of reactants and products. Moreover, variations in the reactor geometry, light sources (e.g., Xe lamps versus LED lamps), and illumination directions (top-down, side-on, or ambient) create significant discrepancies. The lack of standardized protocols makes it difficult to directly compare the performances of different photocatalysts, hindering the field's development.

5.3.4 Measurement and calculation of solar-to-chemical conversion (SCC)

Solar-to-chemical conversion (SCC) efficiency is a pivotal metric typically calculated as

$$\text{SCC} = \frac{[\Delta G \text{ for } \text{H}_2\text{O}_2 \text{ generation (J} \cdot \text{mol}^{-1})][\text{H}_2\text{O}_2 \text{ formed (mol)}]}{[\text{Total input power (W)}][\text{Reaction time (s)}]} \times 100\% \quad (1)$$

Most studies adopt $\Delta G = 117 \text{ kJ} \cdot \text{mol}^{-1}$, representing the standard Gibbs free energy change for H_2O_2 production from water and oxygen. However, in practical systems, the ORR rate significantly exceeds that of the WOR. If the WOR process generates oxygen or other byproducts, the SCC may be underestimated. Conversely, the use of sacrificial agents bypasses the high-energy barrier and sluggish kinetics of the WOR process, leading to a serious overestimation of the SCC. Furthermore, the choice of light sources, use of filters, and illumination geometry all affect the energy input calculation. For instance, using monochromatic light or specific filters only accounts for energy in the absorbable band, leading to inflated SCC values, whereas improper illumination might reduce the effective light-reception area, resulting in underestimation. Additionally, as the H_2O_2 concentration increased over time, the production rate tended to plateau; thus, selecting different time intervals for calculation can lead to significant variations in the reported SCC values. These inconsistencies prevent parallel comparisons of the catalytic activity across different studies.

5.3.5 Discrepancies between pure water and sacrificial systems

Photocatalytic H_2O_2 production involves two primary pathways: the relatively fast ORR and kinetically sluggish WOR, the latter being the rate-determining step. This kinetic mismatch results in a surplus of photogenerated holes, which not only facilitates carrier recombination but also oxidizes the organic framework, leading to structural damage. Although sacrificial agents can rapidly scavenge these holes and substantially enhance their efficiency, they also complicate the reaction system. The introduction of such agents makes the separation, concentration, and purification of H_2O_2 significantly more challenging.

5.3.6 Selection of active species capture agents

Various capture agents are available for specific active species in radical-trapping experiments for pathway validation. Typically, *p*-benzoquinone (PBQ) and superoxide dismutase (SOD) are

used for superoxide radicals ($\cdot\text{O}_2^-$), isopropanol (IPA), benzyl alcohol for hydroxyl radicals ($\cdot\text{OH}$), 1,4-diazabicyclo[2.2.2]octane (DABCO) and sodium azide (NaN_3) for singlet oxygen ($^1\text{O}_2$), silver nitrate (AgNO_3) for electrons (e^-), and EDTA-2Na and methanol for photogenerated holes (h^+). Although one or more agents are usually selected for verification, the current research remains primarily qualitative. Quantitative analysis is significantly hindered by the varying selectivities of different agents, their potential competitive relationships with the primary reaction, and the possibility of their consumption by H_2O_2 . Therefore, establishing standardized selection criteria and in-depth quantitative correlations is essential to enhance the reliability and robustness of these mechanistic validation experiments in future studies.

5.3.7 Large language models (LLMs) and machine learning (ML)

Numerous monomers can form COFs/CTFs, and the design of catalysts and screening of reaction conditions often requires a large amount of time. However, with current technologies such as machine learning, large language models, and high-throughput robotics, it is possible, on the one hand, to achieve rapid screening of reaction conditions, reducing the synthesis difficulty of highly crystalline COFs and greatly shortening the discovery time of new materials.^[110] On the other hand, by summarizing the reported literature, it is also possible to design catalysts with high efficiency and stability, achieving the synthesis of efficient catalysts.^[111] Therefore, the application of these tools will effectively improve the work efficiency of researchers and is of great significance for the design and synthesis of catalysts with high efficiency, stability, and selectivity.

In summary, photocatalytic H_2O_2 production is at the stage of rapid evolution. Addressing these bottlenecks and establishing standardized experimental protocols are essential steps in the transition of this technology from laboratory research to practical applications.

BIOGRAPHY

Bi-En Tan is a professor at the School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST). He received his PhD in 1999 from the College of Materials at South China University of Technology. He then joined Beijing Institute of Aeronautical Materials for postdoctoral research in National Laboratory of Advanced Composites (1999–2001). He worked as a PDRA at the University of Liverpool (2001–2007). He then returned to China and joined HUST in September 2007 as a professor. His main research interests include polymeric materials, microporous materials, hydrogen storage, metal nanoparticles, emulsion-templated materials, and high through-put materials methodology.

Conflict of Interests

The authors declare no interest conflict.

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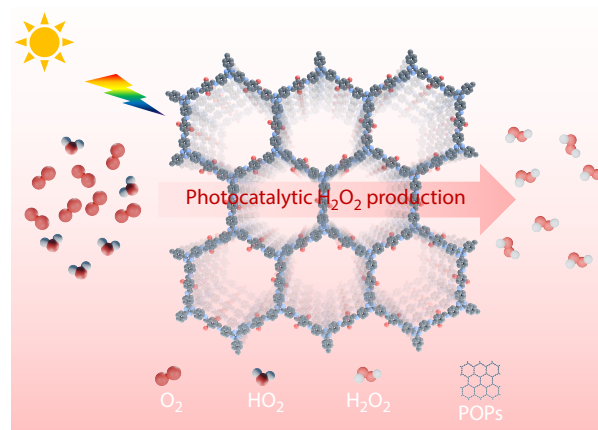
Graphical Abstract

Porous Organic Polymers for Photocatalytic Hydrogen Peroxide Production: Recent Advances and Future Perspectives

Jia-Wei Xie and Bi-En Tan

Huazhong University of Science and Technology

This review systematically summarizes modification strategies of porous organic polymers (POPs) (covalent organic frameworks (COFs)/covalent triazine frameworks (CTFs)) for photocatalytic H_2O_2 production, highlights structure-activity relationships, and offers forward-looking perspectives on this field.



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