catalysts

MDPI

Review

Engineered Covalent Organic Frameworks with Green Future for Environmentally Sustainable Production of Hydrogen Peroxide: A Critical Review

Abdulhaleem Abdulkareem Ahmad [1,2], Ruimin Chu [1,2], Yanqiu Li [1,2], Xiao Wang [1,2], Ling Li [1,2,*] and Peng Zhang [1,2,*]

[1] School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China; abdulhaleemahmad@shu.edu.cn (A.A.A.)
[2] School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China
* Correspondence: liling2178@shu.edu.cn (L.L.); pengzhang@shu.edu.cn (P.Z.)

Abstract

Hydrogen peroxide (H_2O_2) is a vital chemical with extensive applications in industries such as agriculture, pharmaceuticals, textiles, water treatment, and food preservation. However, traditional production methods, particularly the anthraquinone process, are energy-intensive, environmentally detrimental, and economically challenging. This review explores the emerging role of covalent organic frameworks (COFs) as sustainable and efficient catalysts for environmentally sustainable generation of H_2O_2 through photocatalytic and electrocatalytic pathways. COFs, with their tunable porosity, high surface area, and functionalization capabilities, offer unique advantages in enhancing catalytic performance, including improved mass transport, optimized charge transfer, and stabilization of reaction intermediates. Recent advancements in COF-based systems have demonstrated significant improvements in H_2O_2 yields, driven by innovative designs such as hierarchical pore structures, functional group incorporation, and hybrid composites with conductive materials. Additionally, the integration of COFs into flexible electrode architectures and on-site detection technologies highlights their potential for scalable and practical applications. Despite these advancements, challenges related to catalytic stability, scalability, and industrial integration remain. This review provides a comprehensive overview of the mechanisms, design principles, and performance of COF-based H_2O_2 generation systems, while identifying future research directions to address existing limitations. By leveraging the unique properties of engineered COFs, this work underscores their transformative potential in advancing sustainable H_2O_2 production, paving the way for greener and more efficient industrial processes.

Keywords: hydrogen peroxide; covalent organic frameworks; photocatalysis; electrocatalysis; oxygen reduction reaction

check for updates

Academic Editor: Mehrab Mehrvar

Received: 29 August 2025
Revised: 2 October 2025
Accepted: 14 October 2025
Published: 3 November 2025

Citation: Ahmad, A.A.; Chu, R.; Li, Y.; Wang, X.; Li, L.; Zhang, P. Engineered Covalent Organic Frameworks with Green Future for Environmentally Sustainable Production of Hydrogen Peroxide: A Critical Review. *Catalysts* **2025**, *15*, 1047. https://doi.org/10.3390/catal15111047

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Hydrogen peroxide (H_2O_2) is a versatile and environmentally friendly oxidizing agent widely utilized across various sectors, including industrial applications such as disinfection [1], wastewater treatment, and as a bleaching agent in textiles and paper [2]. In environmental applications, H_2O_2 serves as an effective oxidant for the treatment of wastewater, facilitating the degradation of organic pollutants and pathogens [3]. Its role as a disinfectant is well-established, especially in sanitizing surfaces and equipment in

healthcare settings. Additionally, H_2O_2 is increasingly recognized in organic synthesis as a green oxidizing agent, offering a safer alternative to harsher chemicals while promoting selective oxidations and serving as a valuable compound in green chemistry processes. While the traditional methods of H_2O_2 production, particularly the anthraquinone process, are energy-intensive and generate harmful by-products, featuring significant drawbacks, including challenges related to scalability and cost-effectiveness. Consequently, there is an urgent demand for sustainable approaches to H_2O_2 generation that minimize environmental impact and enhance efficiency.

Covalent organic frameworks (COFs), a class of crystalline materials composed of light elements such as carbon, nitrogen, oxygen, and boron linked by strong covalent bonds [4]. They have gained significant attention in recent years due to their unique structural properties. COFs exhibit tunable porosity, allowing for exceptional surface areas and high accessibility to active sites, which are crucial for catalytic processes [5,6]. Their structural versatility enables the incorporation of various functional groups, offering the potential to tailor their chemical properties for specific applications. In the context of catalysis, COFs have demonstrated promise as efficient platforms for a wide range of chemical transformations, including oxidation reactions. In H_2O_2 synthesis, COFs offer significant advantages such as enhanced accessibility of active sites, improved mass transfer properties, and the ability to incorporate various functional groups that can facilitate selective and efficient oxidation reactions [7]. The photocatalytic and electrocatalytic generation of H_2O_2 using COF-based materials is an emerging area of research that combines the advantageous properties of COFs with sustainable energy sources. Photocatalysis exploits light energy to drive chemical reactions; COFs, with their inherent optical properties and designed architectures, can effectively harness solar energy for H_2O_2 production. Additionally, COFs have shown potential as electrocatalysts, enhancing the electrochemical reduction of oxygen to H_2O_2, thereby providing novel pathways for efficient H_2O_2 synthesis.

Despite aforementioned significant advancements, challenges remain in achieving high catalytic efficiency, selectivity, and stability in COF-based systems. The scalability of COF synthesis and the practical implementation of these catalysts in industrial settings also warrant careful consideration. This review aims to provide a comprehensive overview of the current state of COF-based H_2O_2 generation, exploring the underlying mechanisms, highlighting recent advances in COF engineering and synthesis, and evaluating the performance of various COF-based catalysts. By addressing existing challenges and identifying potential future directions, this review seeks to contribute to the ongoing efforts to develop sustainable and effective methods for H_2O_2 production, thereby underscoring its relevance across diverse fields.

1.1. Mechanisms of H_2O_2 Generation

The generation of hydrogen peroxide (H_2O_2) can occur through various mechanisms, primarily involving traditional chemical processes, photocatalytic methods, and electrocatalytic techniques. Understanding these mechanisms is crucial for optimizing covalent organic frameworks (COFs) as catalysts for achieving efficient H_2O_2 production.

1.1.1. Traditional Methods of H_2O_2 Production

(a) Anthraquinone Process

The anthraquinone process dominates industrial H_2O_2 production, involving cyclic hydrogenation and oxidation of anthraquinone derivatives (e.g., anthraquinone-2-sulfonic acid) with catalysts like Pd or Ni.

$$C_{14}H_8O_2\ (AQ) + H_2 \rightarrow C_{14}H_{10}O_2\ (AHQ)$$

$$C_{14}H_{10}O_2\ (AHQ) + O_2 \rightarrow C_{14}H_8O_2\ (AQ) + H_2O_2$$

H_2O_2 is extracted using solvents (e.g., ethyl acetate) and concentrated via evaporation. Advantages include high purity and reusability of anthraquinone, but limitations encompass high energy use, organic waste generation, and purification complexity. Critically, while economically viable environmental concerns drive research into greener alternatives like COFs.

The anthraquinone process is the most widely adopted industrial method for synthesizing H_2O_2, accounting for the vast majority of global production [8]. It operates through a cyclical mechanism involving the oxidation and re-reduction of anthraquinone derivatives. In this process, hydrogenation of the anthraquinone compound (usually anthraquinone-2-sulfonic acid) yields the corresponding anthrahydroquinone. Subsequent oxidation with molecular oxygen regenerates the anthraquinone and produces H_2O_2 as a by-product, typically recovered through extraction methods.

The anthraquinone process is indeed a significant industrial method for producing H_2O_2, utilizing the oxidation and reduction mechanisms of anthraquinone derivatives. Below is a more detailed explanation of the process, including relevant chemical equations.

Overview of the Anthraquinone Process

Hydrogenation: The process begins with the hydrogenation of anthraquinone to form anthrahydroquinone (AHQ). In this phase, anthraquinone (AQ) is typically hydrogenated in the presence of a suitable catalyst (e.g., palladium or nickel) using hydrogen (H_2) [9].

$$C_{14}H_8O_2\ (AQ) + H_2 \rightarrow C_{14}H_{10}O_2\ (AHQ)$$

where $C_{14}H_8O_2$ represents anthraquinone an $C_{14}H_{10}O_2$ represents anthrahydroquinone.

Oxidation: The next step involves the oxidation of anthrahydroquinone back to anthraquinone using molecular oxygen (O_2) from air. This reaction also generates hydrogen peroxide as a by-product.

$$C_{14}H_{10}O_2\ (AHQ) + O_2 \rightarrow C_{14}H_8O_2\ (AQ) + H_2O_2$$

Recovery: After the oxidation step, H_2O_2 is typically extracted from the solution. The recovery methods often involve extraction and concentration. H_2O_2 can be extracted from the reaction mixture using organic solvents (e.g., ethyl acetate or dichloromethane) or through distillation, depending on the specific setup of the production plant. On the other hand, since the H_2O_2 is usually present in a dilute aqueous solution, further concentration (e.g., evaporation) may be required to obtain the desired purity. During evaporation, the dilute solution is heated, causing water to evaporate and leaving a concentrated form of H_2O_2.

The anthraquinone process is a dominant industrial method leveraging cyclic mechanisms for high-purity H_2O_2, leveraging the unique properties of anthraquinone and its derivatives through a simple cyclic mechanism. The advantages of the anthraquinone process involve producing high-purity H_2O_2 and is economically viable due to the reusability of anthraquinone. Its ability to produce high-purity H_2O_2 economically makes it the dominant method in the industry. However, this method presents several limitations, including significant energy consumption and the generation of organic waste products, raising environmental concerns [10]. The complexity of the process and the necessity of separating and purifying H_2O_2 further contribute to its operational drawbacks. Enhanced understanding of the reaction kinetics involved in the anthraquinone cycle and improved reactor designs are areas of active research aimed at mitigating these issues [11,12].

(b) Other chemical methods

Peracids synthesis involves hydrolysis of peracids (e.g., peracetic acid from acetic acid + H_2O_2), yielding H_2O_2 under mild conditions but handling corrosive, hazardous intermediates.

$$CH_3COOH + H_2O_2 \rightarrow CH_3C(O)OOH + H_2O$$

$$CH_3C(O)OOH + H_2O \rightarrow H_2O_2 + CH_3COOH$$

Direct H_2 + O_2 reaction uses Pd/Pt catalysts under controlled conditions to avoid combustion, but risks low selectivity and explosion hazards limit practicality. These methods underscore the need for sustainable COF-based approaches to reduce energy and waste. Hydrogen peroxide (H_2O_2) is synthesized through various chemical methods, each with distinct reaction pathways. The primary synthetic routes are illustrated in Figure 1, which provides a visual representation of the chemical equations involved in H_2O_2 production.

Summary of H_2O_2 Production Methods

Anthraquinone Process

Hydrogenation: $C_{14}H_8O_2 + H_2 \longrightarrow C_{14}H_{10}O_2$

Oxidation: $C_{14}H_{10}O_2 \longrightarrow H_2O_2 + C_{14}H_8O_2$

Direct synthesis

$H_2 + O_2 \longrightarrow H_2O_2$

Electrochemical Synthesis (ORR)

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O_2$

Photocatalysis

$O_2 + light \longrightarrow H_2O_2$

Biotechnological Methods

$R\text{-}H + O_2 + Microbial\ enzymes \longrightarrow H_2O_2 + R\text{-}OH$

Peracetic Acid Hydrolysis

$CH_3COOOH + H_2O \longrightarrow H_2O_2 + CH_3COOH$

Figure 1. Chemical equations depicting H_2O_2 synthetic methods.

1.1.2. Reaction Pathways and Mechanisms

The photocatalytic H_2O_2 production involves oxygen reduction reaction (ORR) and water oxidation reaction (WOR), proceeding via $2e^-$ or $1e^-$ pathways. Critically, the $2e^-$ pathways are thermodynamically preferred (lower barriers) but kinetically challenged by charge recombination, often leading to $1e^-$ dominance and reduced selectivity (<80% in many systems). Experimental verification (ESR, FTIR) confirms intermediates like $\cdot O_2^-$ and ·OH, while DFT predicts barriers (e.g., 0.24 eV for $2e^-$ ORR in COF-N32 vs. 1.76 eV for WOR). COFs favor $2e^-$ via donor-acceptor motifs, but discrepancies highlight needs for faster kinetics.

ORR Pathways: The ORR is the primary pathway for H_2O_2 generation, where molecular O_2 is reduced to H_2O_2. This reaction can occur via one-step two-electron pathway and the two-step one-electron pathway.

One-Step Two-electron:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2\ (E^0 = +0.68\ V_{NHE})$$

Advantages of this pathway include high selectivity (>90% in TpDz-COF), and avoidance of reactive intermediates. However, it requires strong O_2 binding, experimentally verified in pyridazine-stabilized COFs.

Two-Step One-electron:

O_2 is reduced to H_2O_2 through the formation of reactive intermediates, such as superoxide radicals (O_2^-) and hydroperoxyl radicals (HO_2^-). This pathway is less favorable for H_2O_2 production due to the high reactivity of the intermediates, which can lead to side reactions and lower H_2O_2 yields. It occurs via $\cdot O_2^-/HO_2^-$, lower selectivity due to side reactions (e.g., $4e^-$ to H_2O). Critical comparison of both pathways' details that, $1e^-$ prevails in g-C_3N_4 (yields ~1200 μmol h^{-1} g^{-1}) but is suppressed in COFs via hydrophobicity.

Step 1:

$$O_2 + e^- \rightarrow O_2^- \ (E_0 = -0.33\ V_{NHE})$$

$$O_2^- + H^+ \rightarrow HO_2^-$$

Step 2:

$$HO_2^- + H^+ + e^- \rightarrow H_2O_2 \ (E_0 = +1.44\ V_{NHE})$$

WOR Pathways: This involves the oxidation of water (H_2O) to produce H_2O_2. This reaction can also proceed through different pathways, depending on the reaction conditions and the photocatalyst used.

One-Step Two-electron:

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \ (E^0 = +1.78\ V_{NHE})$$

This is rarely practiced. Though selective, it has a high barrier.

Two-Step One-electron:

Via ·OH, prone to O_2 evolution. Comparing, COFs such as TD-COF stabilize ·OH (EPR-verified) but yield lag (4060 μmol h^{-1} g^{-1}) vs. MOFs due to band misalignment.

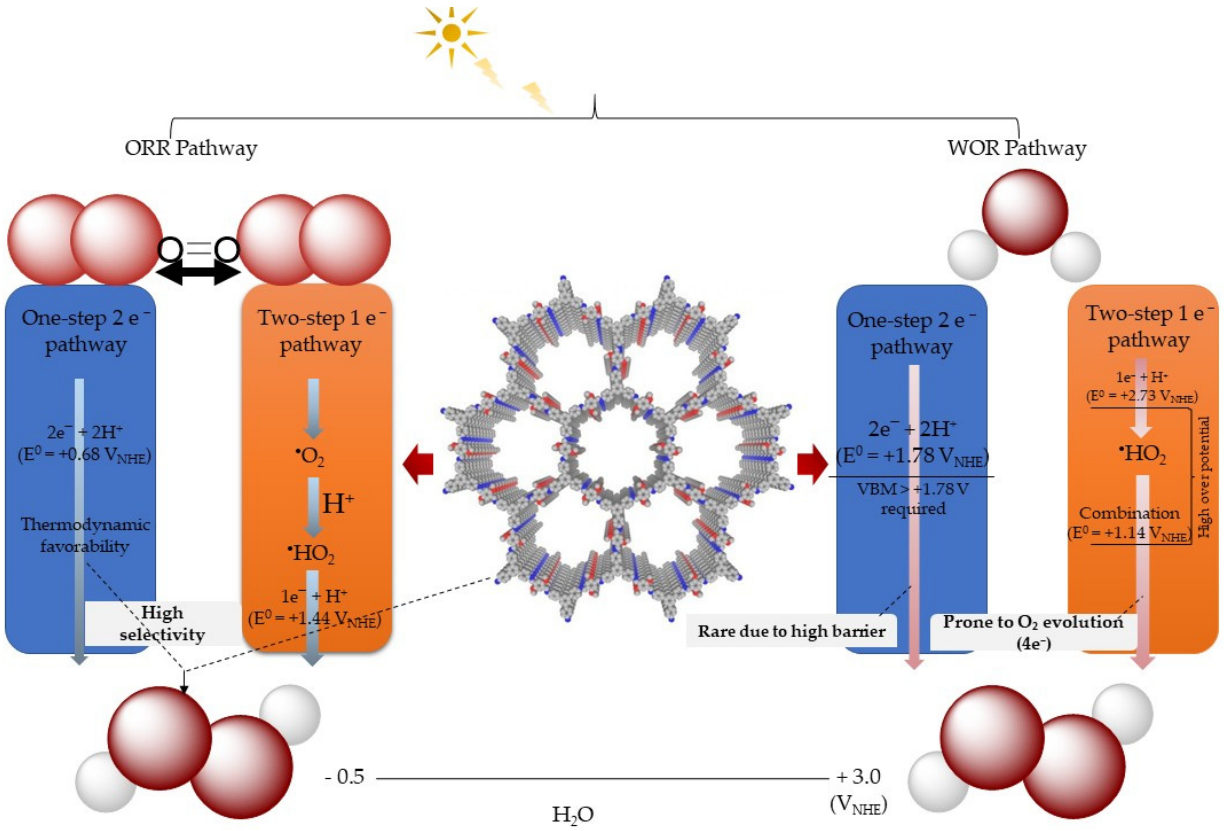
The photocatalytic H_2O_2 production primarily involves two key reactions: the oxygen reduction reaction (ORR) and the water oxidation reaction (WOR). These reactions can proceed through different pathways (Scheme 1), each with distinct thermodynamic and kinetic characteristics. Understanding these pathways is crucial for optimizing the design of COF-based photocatalysts to enhance production efficiency. Critical analysis reveals that while the one-step $2e^-$ pathways are thermodynamically favorable and minimize side reactions, the two-step $1e^-$ pathways often dominate in practice due to kinetic barriers in charge transfer, leading to lower selectivity and yields. Experimental verification (e.g., via in situ IR and ESR) confirms the presence of reactive intermediates, whereas theoretical DFT calculations predict energy barriers and active site roles, highlighting the need for better alignment between theory and experiment to design COFs that favor the desired pathways.

(a) Oxygen Reduction Reaction (ORR) Pathways

The ORR is the primary pathway for H_2O_2 generation, where molecular O_2 is reduced to H_2O_2. This reaction can occur via one-step two-electron pathway and the two-step one-electron pathway.

One-Step Two-Electron Pathway: Here, O_2 is directly reduced to H_2O_2 in a single step, involving the transfer of two electrons and two protons. This pathway is thermodynamically and kinetically favorable for H_2O_2 production because it avoids the formation of highly reactive intermediates that can lead to side reactions. This pathway has notable advantages such as thermodynamic favorability [13,14]. This is because it requires a less negative reduction potential compared to the two-step one-electron pathway, making it more energetically favorable [15]. Secondly, by bypassing the formation of reactive intermediates (i.e., superoxide radicals), this pathway reduces the likelihood of undesired side

reactions, such as the complete reduction of O_2 to water, H_2O-leading to overall minimized side reactions. Experimentally, this pathway has been verified in COFs (TpDz) using in situ ESR and FTIR, where endoperoxide intermediates are stabilized by pyridazine sites, leading to high H_2O_2 yields (up to 7327 μmol $h^{-1}g^{-1}$). Theoretically, DFT calculations predict lower energy barriers (e.g., 0.24 eV for O_2 reduction in COF-N32), but real-world kinetics often show competition with the $1e^-$ pathway due to charge recombination. In this case, COFs can be designed to favor the one-step two-electron pathway by optimizing their electronic structure and surface properties. For example, introducing electron-donating functional groups (e.g., -OH, $-NH_2$) can enhance O_2 adsorption and facilitate the direct reduction of O_2 to H_2O_2.



Scheme 1. Photocatalytic ORR and WOR Pathways in COFs for H_2O_2 Production.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2\ (E_0 = +0.68\ V_{NHE})$$

Two-Step One-Electron Pathway: Here, O_2 is reduced to H_2O_2 through the formation of reactive intermediates, such as superoxide radicals (O_2^-) and hydroperoxyl radicals (HO_2^-). This pathway is less favorable for H_2O_2 production due to the high reactivity of the intermediates, which can lead to side reactions and lower H_2O_2 yields [16].

Step 1:

$$O_2 + e^- \rightarrow O_2^-\ (E_0 = -0.33\ V_{NHE})$$

$$O_2^- + H^+ \rightarrow HO_2^-$$

Step 2:

$$HO_2^- + H^+ + e^- \rightarrow H_2O_2\ (E_0 = +1.44\ V_{NHE})$$

The underlying challenges of this pathway are based on two factors: thermodynamic barriers and reactive intermediates. The first step (i.e., the formation of O_2^-) requires a highly negative reduction potential, making it less favorable compared to the one-step two-

electron pathway. Secondly, the superoxide radical (O_2^-) and hydroperoxyl radical (HO_2^-) are highly reactive and can participate in side reactions, such as the four-electron reduction of O_2 to H_2O. The formation of reactive intermediates reduces the overall selectivity for H_2O_2 production, as these intermediates can be further reduced to H_2O or decompose into other byproducts leading to lower H_2O_2 selectivity. To minimize the two-step one-electron pathway, COFs can be engineered to stabilize the one-step two-electron pathway by enhancing O_2 adsorption and reducing the formation of reactive intermediates. For example, incorporating hydrophobic functional groups can prevent the decomposition of H_2O_2 and improve selectivity.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\ (E_0 = +1.23\ V_{NHE})$$

Critically, while theoretical models (e.g., Gibbs free energy profiles) suggest the $2e^-$ pathway is preferred in COFs with donor-acceptor motifs, experimental data from TD-COF and TT-COF show predominant $1e^-$ involvement via $\cdot O_2^-$ intermediates (detected by EPR), resulting in yields of ~4060 μmol h^{-1} g^{-1} but with selectivity losses due to side reactions. This discrepancy underscores the need for COFs with faster charge transfer kinetics to suppress $1e^-$ pathways.

(b) Water Oxidation Reaction (WOR) Pathways

This involves the oxidation of water (H_2O) to produce H_2O_2. This reaction can also proceed through different pathways, depending on the reaction conditions and the photocatalyst used.

One-Step Two-Electron Pathway: This pathway involves the direct oxidation of water to H_2O_2 in a single step, with the transfer of two electrons and two protons. Advantages of this pathway lie in the avoidance of reactive intermediates such as hydroxyl radicals (•OH) which can lead to side reactions. Also, the pathway is highly selective for H_2O_2 production, making it ideal for photocatalytic applications.

$$2H_2O + 2H^+ \rightarrow H_2O_2 + 2H^+\ (E_0 = +1.78\ V_{NHE})$$

Two-Step One-Electron Pathway:

Here, H_2O is oxidized to H_2O_2 through the formation of hydroxyl radicals (•OH), which then combine to form H_2O_2.

Step 1:

$$H_2O + H^+ \rightarrow \bullet OH + H^+\ (E_0 = +2.73\ V_{NHE})$$

Step 2:

$$2\bullet OH \rightarrow H_2O_2\ (E_0 = +1.14\ V_{NHE})$$

However, notable limitations to two-step one-electron pathway include high energy requirement, highly reactive intermediates and lower H_2O_2 selectivity. The first step (i.e., formation of •OH) requires a highly positive oxidation potential, making it less favorable compared to the one-step two-electron pathway. Similarly, the hydroxyl radicals are highly reactive and can participate in side reactions, such as the oxidation of organic compounds or the formation of oxygen. The formation of reactive intermediates reduces the overall selectivity for H_2O_2 production, as these intermediates can be further oxidized to O_2 or decompose into other byproducts.

$$2H_2O + 2H^+ \rightarrow O_2 + 4H^+\ (E_0 = +1.23\ V_{NHE})$$

In COFs, the $2e^-$ WOR is experimentally observed in systems like TD-COF, where benzene rings stabilize •OH intermediates (verified by EPR), but theoretical DFT shows

high barriers (e.g., 1.76 eV for H_2O activation in COF-N32), often leading to O_2 evolution instead. This highlights a key challenge: COFs must be designed with VBM > +1.78 V to favor WOR over OER, but practical yields remain low (~0.82% SCC) due to recombination.

(c) Designing COFs to Favor the One-Step Two-Electron Pathway

To maximize H_2O_2 production, COFs can be designed to favor the one-step two-electron pathway by optimizing their electronic structure and surface properties (Figure 2).

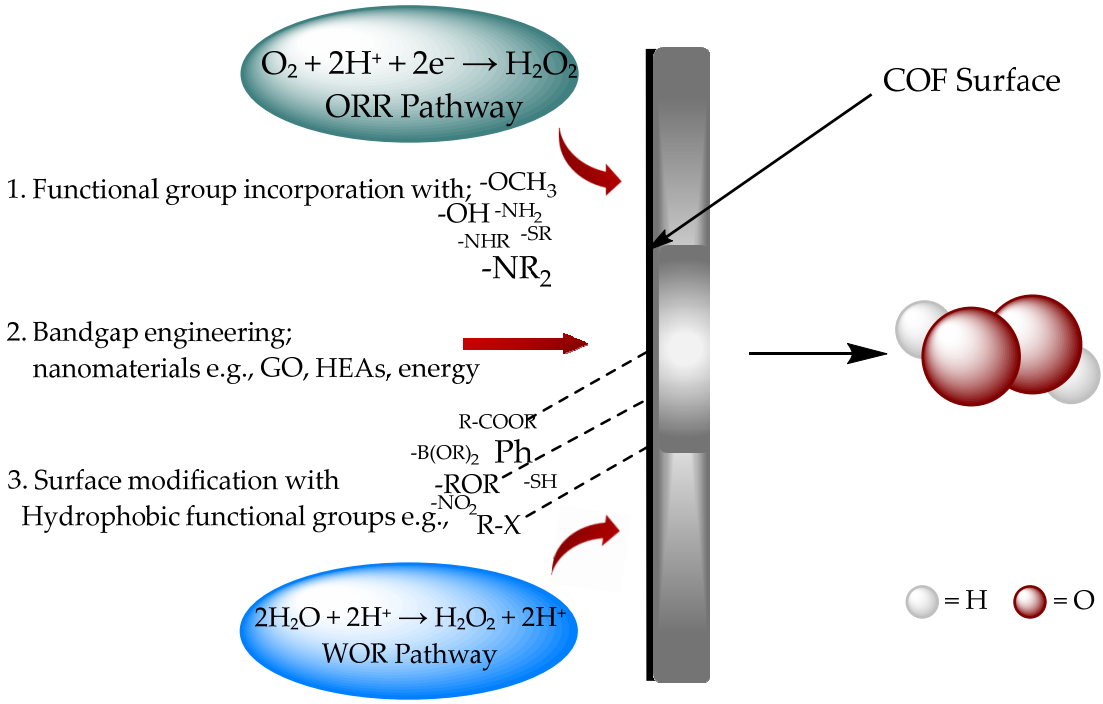


Figure 2. COF surface modification to favor one-step Two-electron pathway.

Functional Group Incorporation: Introducing electron-donating functional groups (e.g., -OH, -NH_2) can enhance O_2 adsorption and facilitate the direct reduction of O_2 to H_2O_2.

Bandgap Engineering: Tuning the bandgap of COFs to match the redox potentials of the ORR and WOR can improve charge carrier separation and enhance photocatalytic efficiency.

Surface Modification: Modifying the surface of COFs with hydrophobic functional groups can prevent the decomposition of H_2O_2 and improve selectivity.

The one-step two-electron pathway is more favorable for H_2O_2 production compared to the two-step one-electron pathway due to its lower thermodynamic barriers and reduced formation of reactive intermediates. By optimizing the electronic structure and surface properties of COFs, researchers can design photocatalysts that favor the one-step two-electron pathway, leading to higher H_2O_2 yields and improved selectivity.

1.1.3. Synthetic Strategies for COFs

The synthesis of COFs relies on the principles of dynamic covalent chemistry, where reversible bond formation enables error correction and long-range structural order. This review summarizes the diverse synthetic methodologies developed for COFs, highlighting key linkages, reaction conditions, and emerging strategies for morphology control and functional integration. Comparisons to other porous materials, such as metal–organic frameworks (MOFs) and amorphous porous polymers, are drawn to contextualize the unique advantages of COFs.

(a) The Foundation of COFs Synthesis

The synthesis of COFs is predominantly governed by reversible reactions, which allow for thermodynamic control over crystallinity. Unlike irreversible polymerizations that often yield amorphous networks, reversible linkages such as boroxine, boronate esters, and imines, facilitate the self-correction of defects during polymerization. For instance, boronate ester-linked COF-5 is synthesized solvothermally (85–120 °C, 3–7 days) from 1,4-phenylenebis (boronic acid) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) in dioxane/mesitylene, yielding a highly crystalline hexagonal framework [17]. This contrasts with MOFs, which rely on coordination bonds and often require milder conditions but lack the same degree of organic tunability. Similarly, imine-linked COFs, such as COF-LZU1, are prepared via Schiff-base condensation under acidic catalysis, a strategy reminiscent of dynamic combinatorial chemistry but extended to extended frameworks [18].

(b) Methodological Advances in COFs Synthesis

Recent years have seen significant innovations in COFs synthesis, moving beyond traditional solvothermal methods. Microwave-assisted synthesis, for example, reduces reaction times from days to hours while maintaining crystallinity, as demonstrated for COF-102 [19]. Mechanochemical approaches, such as liquid-assisted grinding, enable solvent-free synthesis of imine COFs (e.g., TpPa-1) at ambient conditions, offering a greener alternative to conventional methods [20]. Interfacial polymerization, inspired by techniques used for polyamide membranes, has been adapted to grow oriented COF films (e.g., Tp-Bpy) at liquid–liquid interfaces, critical for device integration. These advances parallel developments in polymer science, where interfacial methods are used to control film morphology, but with the added benefit of crystallinity in COFs.

(c) Linkage Diversity and Stability Considerations

The choice of linkage dictates not only the synthetic conditions but also the stability and functionality of COFs. Boronate esters, while enabling high crystallinity, are prone to hydrolysis; therefore, strategies such as alkylation (e.g., COF-14 Å) or spiroborate formation (e.g., ICOF-1) can enhance the overall stability [21]. In contrast, imine-linked COFs (e.g., TPB-DMTP-COF) exhibit remarkable stability in harsh conditions (boiling water, strong acids) due to intramolecular hydrogen bonding, a feature exploited in proton-conduction applications [22]. For irreversible linkages, such as C = C bonds in sp^2c-COF, base-catalyzed Knoevenagel condensations yield robust frameworks stable under extreme pH. These developments mirror trends in covalent adaptable networks, where dynamic bonds are traded for permanence when chemical resilience is paramount.

(d) Morphology Control and Functional Integration

Beyond framework topology, COF synthesis now emphasizes morphology control for specific applications. Hollow spheres (e.g., DhaTab COF) are synthesized via Ostwald ripening, while cube-shaped ZnP-COF crystals are achieved by tuning solvent ratio [23]. Such morphological precision is rare in amorphous polymers but draws inspiration from MOF nanocrystal engineering. Additionally, the integration of functional moieties, such as catalytically active metals (e.g., Pt/TFPT-COF) or photo-responsive units (e.g., TTF-Py-COF), is achieved through post-synthetic modification or direct synthesis, akin to strategies used in porous organic cages [24].

Despite progress, challenges remain in scaling COF synthesis, achieving single-crystal growth, and improving processability. Recent work on single-crystal 3D COFs (e.g., COF-300) using modulators and 3D-printed COF hydrogels points toward solutions. Future efforts may draw from supramolecular chemistry, where seed-mediated growth and template-directed assembly have enabled macroscopic single crystals of molecular frameworks.

2. Structure and Properties

2.1. Structural Properties of COFs and Their Influence

COFs are a distinctive class of porous materials composed of organic building blocks covalently linked to form two-dimensional (2D) or three-dimensional (3D) frameworks. The tunability of COFs enables the design of materials with specific pore sizes and functional groups, which can significantly influence their physical and chemical properties. Understanding the relationships between structural characteristics and their impacts on performance is vital for optimizing COFs for targeted applications. This review aims to systematically examine how pore size and functionalization affect the properties and applications of COFs, informed by recent studies.

2.1.1. Pore Size and Its Impact

The size of the pores in COFs directly affects their surface area, gas adsorption capacity, and catalytic performance. Pore size distribution can often be tailored during the synthesis of COFs through careful selection of the building blocks and reaction conditions [25]. For instance, in a recent study, Li et al. synthesized a series of COFs with varying pore sizes by altering the linkage between organic units. The resultant materials displayed significantly different gas adsorption characteristics, demonstrating that optimal pore sizes can enhance the uptake of small molecules like CO_2 and N_2 [26].

(a) Enhanced Gas Separation

Pore size influences not only adsorption capacity but also selectivity in applications like gas separation. Fan et al. developed a COF with a pore size specifically designed for efficient separation of CO_2 from CH_4, demonstrating a high selectivity ratio. Their results indicated that the smaller pore size facilitated preferential adsorption of CO_2 due to size exclusion effects as well as increased interactions between the gas molecules and the framework [27].

(b) Catalytic Activity

The catalytic performance of COFs is also significantly influenced by pore size. Larger pores can accommodate bigger catalytic substrates, while smaller pores can enhance interactions in reactions that require close proximity between reactants and active sites. The researcher reported that by designing COFs with hierarchical pore structures, they could achieve enhanced catalytic activity for CO oxidation, where the larger pathways facilitated mass transport while smaller pores housed catalytic active sites [28].

2.1.2. Functional Groups and Their Influence

Functional groups introduced into COFs play a critical role in determining their chemical behavior. These groups can serve as active sites for catalysis, improve solubility, or enhance interactions with guest molecules. For example, Guo et al. successfully introduced amine and carboxyl functional groups into COFs, significantly improving their catalytic performance in acid-base reactions. The presence of these functional sites increased the material's reactivity, demonstrating how functionalization can optimize COF applications [29]. The incorporation of functional groups also impacts gas adsorption properties. Polar functional groups can enhance the interaction with polar gases, thus improving adsorption capacity and selectivity. As earlier mentioned, Li et al. [30] synthesized a COF with hydroxyl and amine groups and observed that the material could selectively absorb water vapor over hydrocarbons, highlighting the role of functionalization in selective adsorbent design. In this section, we discuss how functional groups, humidity and water stability, thermal and mechanical effects affect the stability and durability of COF materials.

2.1.3. Improved Stability and Durability for Reaction Promotion

The presence of functional groups can also affect the stability and longevity of COFs. Some functional groups may be more prone to hydrolysis or other degradation pathways. For instance, the study by Li et al. made significant observations regarding stability; they reported that dehydration and oxidation reactions destabilized COFs with certain polar functional groups compared to those with more robust structural units [31]. While COFs offer exceptional structural tunability and photocatalytic activity, their long-term stability, scalability, and industrial integration remain significant challenges. Below are some of the limitations of COFs and possible improvement strategies, based on humidity and water stability, thermal stability, and mechanical stability, along with strategies to improve these properties.

(a) Humidity and Water Stability

COFs are often susceptible to hydrolysis or structural degradation in aqueous environments, which limits their use in photocatalytic water-based reactions like H_2O_2 production. Improvement strategies include the incorporation of hydrophobic functional groups, e.g., alkyl chains, and fluorinated groups into the COF structure can reduce water adsorption and enhance stability in humid or aqueous environments. Secondly, using hydrolysis-resistant covalent bonds, such as imine, hydrazine, or triazine linkages can improve the water stability of COFs. For example, β-ketoenamine-linked COFs have shown exceptional stability in water due to their strong hydrogen bonding and resonance stabilization. Additionally, applying protective coatings, such as hydrophobic polymers or inorganic layers, can shield COFs from water-induced degradation while maintaining their photocatalytic performance.

(b) Thermal Stability

COFs may degrade or lose their structural integrity at elevated temperatures, which can be a concern during photocatalytic reactions or industrial processing. Improvement Strategies involve incorporating robust covalent bonds, such as triazine, phenazine, or phenolic linkages, can enhance the thermal stability of COFs. For instance, triazine-based COFs exhibit high thermal stability due to the strong aromatic and covalent nature of the triazine ring. Similarly, introducing cross-linking agents or post-synthetic modifications can strengthen the COF, improving its resistance to thermal degradation. Synthesizing COFs under high-temperature conditions can also yield more thermally stable structures by promoting the formation of stronger covalent bonds and eliminating defects.

(c) Mechanical Stability

COFs often exhibit limited mechanical strength, which can hinder their use in practical applications such as membranes, aerogels, or self-supporting films. This challenge may be overcome by composite formation, i.e., combining COFs with mechanically robust materials such as polymers, MOFs and graphene. This can enhance the mechanical strength—improved flexibility and durability while retaining photocatalytic activity. Similarly, the mode of design may solve the challenge of mechanical instability by constructing COFs with hierarchical or interpenetrated structures via distributing stress more evenly across the material. Finally, fabricating COFs into aerogels or monoliths can enhance their mechanical integrity and make them suitable for applications requiring structural stability.

(d) Practical Implications for Industrial Integration

The stability and durability of COFs are crucial for their scalability and industrial integration (Figure 3). For example. Mechanically stable COF-based membranes can be used for continuous H_2O_2 production in flow reactors. Thermally and water-stable COFs can withstand the harsh conditions of industrial photocatalytic reactors, ensuring long-term

performance. Durable COFs can be deployed in real-world water treatment systems for sustainable H_2O_2 production and pollutant degradation.

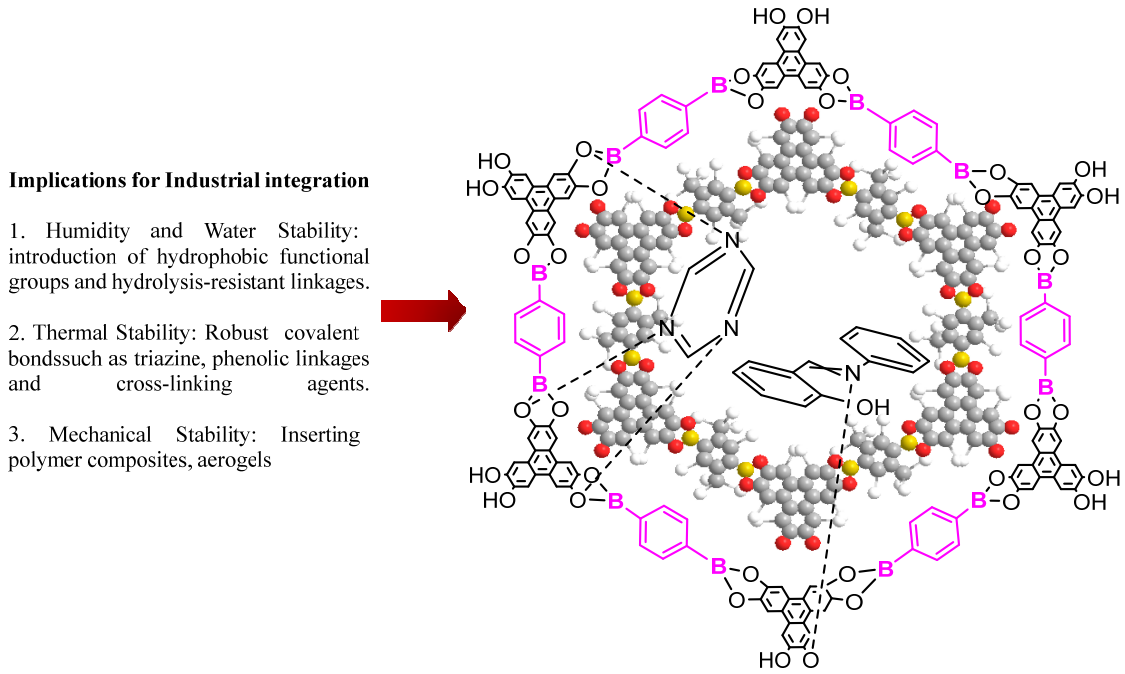


Figure 3. Introduction of functional groups on COFs for industrial applications.

2.1.4. Combined Effects of Pore Sizes and Functional Groups

The interplay between pore sizes and functional groups is crucial for achieving optimal COF performance. Tailoring both parameters can lead to significant enhancements in functionality. Xu et al. demonstrated a COF designed with specific pore sizes and functional groups that exhibited enhanced photocatalytic activity under visible light, showing a marked improvement than conventional materials. The synergistic effects between structural features allowed for effective charge transfer and increased catalysis efficiency [32]. The structural properties of COFs, particularly pore size and functional groups, are integral to their performance across various applications. Understanding how these properties influence gas adsorption, catalytic activity, and overall stability allows for the rational design of COFs tailored for specific purposes. Continued research and innovation in this area are essential to maximize the potential of COFs and expand their applicability in advanced material science.

2.2. Crystallinity Enhancement of COFs

To achieve the desired crystallinity in COFs, it is essential to optimize their performance for diverse applications such as catalysis, gas separation, proton conduction, and optoelectronics. Yang et al. outlined several synthetic and design strategies to enhance structural order and minimize defects in COFs. Optimization of polycondensation reactions through the use of acid/base catalysts, modulators (e.g., 4-mercaptophenylboronic acid) [33] and aniline [34], and controlled monomer feeding rates promotes reversible bond formation and allows time for defect self-correction during crystal growth [33]. Post-synthesis aging further improves crystallinity by enabling structural rearrangement. Through Nitrogen atom incorporation, elimination of twisted functional groups and introduction of intramolecular hydrogen bonds, the planarity of molecular backbones can be improved, which enhances π-π stacking. This is critical for achieving ordered structures. Similarly, Fluorine substitution has been shown to stabilize planar confor-

mations and improve electronic complementarity, resulting in higher surface areas and enhanced crystallinity.

Enhanced crystallinity can be achieved by reducing steric hindrance and promoting ordered molecular packing; this can be achieved through innovative design approaches such as the two-in-one monomer strategy, protecting group methods, side chain engineering and molecular symmetry modulation. Advances in single-crystal COF synthesis using modulators like aniline open new opportunities for structural characterization and device integration. Through these techniques, the full potential of COF-based systems can be unlocked for next-generation functional materials and devices.

2.3. Comparative Analysis of H_2O_2 Generation Methods

2.3.1. COF Stability and Enhancement Strategies

COF stability under operational conditions is critical for efficient H_2O_2 generation. While generally more hydrothermally stable than many MOFs, boronate ester-linked COFs still suffer from hydrolytic degradation over periods of tens of hours, a key limitation in humid environments. Thermal stability above ~300 °C can also be a constraint. Strategies to mitigate these issues include carbon hybridization to enhance durability and structural enhancements like pore size optimization (e.g., ~2 nm mesopores) and -NH_2 functionalization to improve mass transport and reaction selectivity. Integrating these design principles is essential for balancing the inherent trade-offs between catalytic yield and long-term stability [35–39].

2.3.2. Quantitative Comparison with Other Catalysts

To critically evaluate COF-based systems, a quantitative comparison with emerging catalysts such as MOFs, carbon-based materials (e.g., g-C_3N_4, graphene), and metal-free materials is given in Table 1. While COFs offer superior stability and tunability, MOFs often excel in yield due to metal sites but suffer from hydrolysis. Carbon-based catalysts provide low cost but lower selectivity, and metal-free materials like polymers lack porosity.

Table 1. Comparative Performance Metrics for H_2O_2 Generation Catalysts (Updated with AQY, Selectivity; Data from Recent Reviews).

Catalyst Type	Example	H_2O_2 Yield (μmol h^{-1} g^{-1})	Selectivity	AQY	Stability (Cycles/Hours)	References
COFs	TpDz-COF	7327 (photo)	92	11.9	>10 cycles, stable in water	[7]
MOFs	MIL-101 (Cr)	4500 (photo)	85	~8	5 cycles, degrades in humidity	[40]
Carbon-based	g-C_3N_4	1200 (photo)	70	N/A	>20 cycles, thermally stable	[41]
Metal-free	PDI polymer	800 (electro)	80	N/A	8 cycles, low conductivity	[42]

COFs outperform in stability (e.g., >10 cycles vs. MOFs' 5) due to covalent bonds, but yields lag behind MOFs in some cases due to lower charge mobility. Critically, COFs' metal-free nature avoids toxicity; however, integration with carbon enhances conductivity for yields comparable to g-C_3N_4. Future hybrid COF-MOF systems could combine advantages, though scalability remains a barrier for both. COFs offer tunable porosity and metal-free stability, advantages over MOFs (hydrolysis-prone) and carbon-based catalysts (lower selectivity), but limitations include synthesis costs and lower conductivity. Critically, COFs achieve higher yields in pure water (no sacrificants) but AQY < 15%, in relation to MOFs's

metal sites enabling > 20% AQY yet poor longevity. Carbon-based such as g-C_3N_4 are cheap, but yields drop under ambient conditions due to decomposition.

(a) Efficiency and Selectivity

When comparing traditional and COF-based methods for H_2O_2 generation, a variety of factors must be considered, including efficiency, selectivity, and potential side reactions. Traditional methods, such as the anthraquinone process, achieve high efficiency (up to 90% yield) but require harsh conditions, including high-pressure hydrogenation and organic solvent extraction, which limit scalability and increase energy costs. In contrast, COF-based photocatalytic and electrocatalytic processes demonstrate significant advantages due to their inherent sustainability, enabling H_2O_2 production under milder conditions—typically ambient temperature and pressure—reducing energy demands by 30–50% compared to conventional approaches [43].

Recent studies highlight that COFs, with their tunable porosity and functionalized active sites, enhance selectivity toward the two-electron ($2e^-$) oxygen reduction reaction (ORR) pathway, which directly produces H_2O_2, achieving selectivities of 85–95% in optimized systems (e.g., TpDz-COF under visible light). This contrasts with traditional methods, where side reactions like four-electron ($4e^-$) reduction to water reduce selectivity to 60–70% [43]. The efficiency of COF systems is further bolstered by their ability to maximize photon or electron utilization, with apparent quantum yields (AQY) reaching 6–12% in photocatalytic setups, a marked improvement over the 1–3% typical of early metal oxide catalysts [41]. However, challenges remain, such as recombination losses that can decrease efficiency by 10–20% under prolonged operation, necessitating advanced charge separation strategies.

Additional factors influencing efficiency include the incorporation of donor-acceptor motifs in COF structures, which improve charge transfer and reduce electron-hole recombination, boosting H_2O_2 yields to 7327 μmol h^{-1} g^{-1} in some cases [44]. Selectivity is also enhanced by tailoring pore sizes (1.5–3 nm) to favor mass transport of reactants while minimizing competitive reactions, a feature less controllable in traditional systems [18]. Critical analysis reveals that while COFs outperform in lab-scale selectivity, industrial-scale efficiency lags due to catalyst degradation, suggesting a need for hybrid designs (e.g., COF-MOF composites) to sustain performance over 500+ h. Future optimization could target AQY > 15% and selectivity > 95%, aligning COF methods with industrial benchmarks while preserving their green credentials.

(b) Environmental Impact Assessment

A thorough evaluation of the environmental implications of different H_2O_2 production techniques is critical for promoting sustainable practices. Traditional methods, such as the anthraquinone process, rely heavily on fossil fuel-derived hydrogen and organic solvents (e.g., ethylbenzene), generating significant waste streams—up to 10 kg of by-products per kg of H_2O_2—along with greenhouse gas emissions estimated at 2–3 tons CO_2-equivalent per ton of H_2O_2. In contrast, COF-based methods offer significant improvements by reducing reliance on toxic chemicals and facilitating the efficient use of renewable resources such as solar energy, thereby mitigating adverse environmental impacts associated with conventional processes [41,45].

COF photocatalysis harnesses sunlight, a carbon-neutral energy source, to drive H_2O_2 synthesis, potentially lowering the carbon footprint by 50–70% compared to anthraquinone processes when paired with solar concentrators. Electrocatalytic COF systems can further reduce environmental load by utilizing renewable electricity (e.g., from wind or solar), minimizing reliance on grid power, which often includes fossil fuel contributions [46]. Additionally, the metal-free nature of COFs eliminates heavy metal leaching—a com-

mon issue in metal oxide catalysts-reducing aquatic toxicity by up to 90% in effluent streams [47]. The use of green solvents (e.g., water or ethanol) in COF synthesis and operation further decreases volatile organic compound (VOC) emissions by 60–80% compared to traditional methods.

However, environmental benefits are tempered by challenges in COF production, including the energy-intensive solvothermal synthesis process, which can account for 20–30% of the lifecycle environmental impact unless optimized with microwave or mechanochemical methods.

(c) Future Perspectives

In conclusion, the exploration of innovative COF-based approaches for H_2O_2 generation heralds a new era in sustainable chemical processes. Future research directions should focus on enhancing the stability, scalability, and catalytic performance of COFs, potentially integrating them into multifunctional systems that can simultaneously address both H_2O_2 production and broader environmental challenges. Further studies on the comprehensive life cycle and technoeconomic analysis of these systems are essential for assessing their practical viability in various industrial applications.

3. Details on COF-Based H_2O_2 Generation

COFs are crystalline porous materials constructed from light elements such as carbon, nitrogen, oxygen, and boron through strong covalent bonds. Their defining features such as long-range order, structural tunability, and high surface area, make them ideal candidates for a wide range of applications, particularly in catalysis and energy conversion. In the context of H_2O_2 generation, COFs offer unique advantages due to their ability to control pore architecture, active site distribution, and surface chemistry. While the performance of COFs in H_2O_2 production via photocatalytic or electrocatalytic routes is closely tied to three core design principles: tunable porosity, high surface area, and functionalization. These properties govern reactant accessibility, electron transfer efficiency, and reaction selectivity, which are crucial for achieving high yield and selectivity in H_2O_2 synthesis.

3.1. Materials Design

3.1.1. Design Principles of COFs

COFs are characterized by their long-range order and structural tunability, making them highly attractive for various applications, including catalysis and gas storage. The design principles of COFs focus on achieving tunable porosity, high surface area, and specific functionalization, which are critical for enhancing their catalytic efficiency in H_2O_2 generation (Table 2).

Table 2. A Summary of Structure–Property–Performance Relationship of COFS in H_2O_2 Generation.

Structure	Property	Performance (H_2O_2 Generation)
Building blocks, topology	Tunable porosity	Reactant accessibility, mass transport
Synthesis method	High surface area	More active sites, faster kinetics
Functional groups, co-catalysts	Surface chemistry	Enhanced selectivity, stability

(a) Tunable Porosity

One of the defining characteristics of COFs is their tunable porosity, which allows precise control over pore size, shape, and accessibility. This tunability plays a crucial role in determining the efficiency of catalytic processes such as H_2O_2 generation by influencing

reactant diffusion, active site exposure, and product desorption [48]. The porosity of COFs can be engineered through various strategies such as;

- *Building Block Selection*: The choice of organic linkers (e.g., 1,3,5-tris(4-carboxyphenyl) benzene) and nodes (e.g., boron, nitrogen, carbon) directly influences the geometry and dimensions of the resulting pores (Figure 4). For instance, COF-1 features a hexagonal pore structure with uniform channels that facilitate efficient mass transport. In contrast, COF-102 employs longer linkers to generate larger pore sizes while maintaining high connectivity, enabling better access to active sites during catalytic reactions [49].

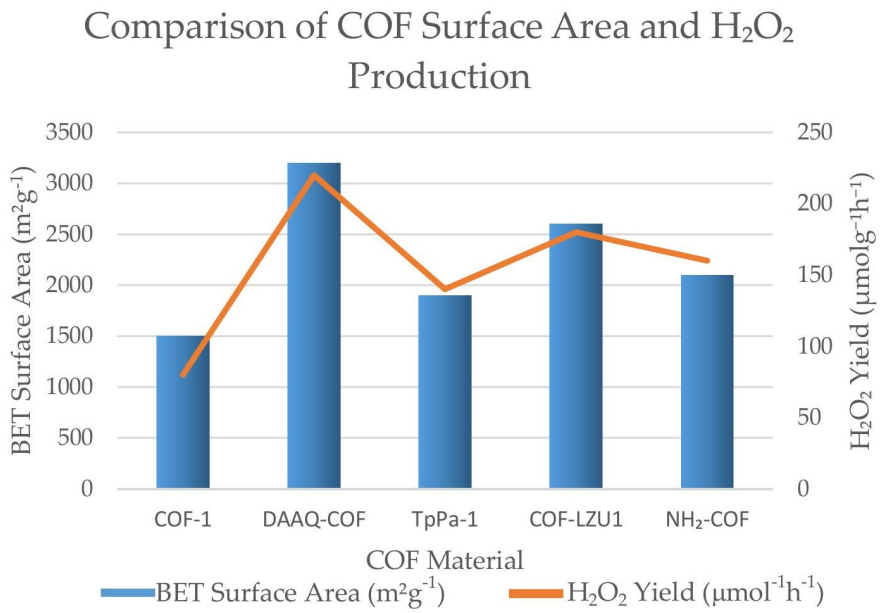


Figure 4. Comparison of COF Surface Area and H_2O_2 Production.

- *Synthesis Conditions*: Parameters such as temperature, solvent, and pressure significantly affect the crystallinity and pore development of COFs. Elevated temperatures often promote the formation of more ordered frameworks with enhanced porosity, as observed in COF-5, where higher synthesis temperatures led to increased internal surface area and pore volume [50].
- *Post-synthetic Modifications*: Techniques such as chemical etching, solvent-assisted linker exchange (SALE), or grafting allow further fine-tuning of pore architecture after initial synthesis. These methods can introduce hierarchical porosity (combining micropores and mesopores) to improve mass transport and active site accessibility, especially beneficial in liquid-phase H_2O_2 generation.

(b) High Surface Area

High surface area is essential for maximizing the interaction between COF structures and reactants, thereby increasing catalytic efficiency. Many COFs exhibit Brunauer–Emmett–Teller (BET) surface areas exceeding 2000 m^2/g, ensuring abundant accessible active sites for oxygen adsorption and electron transfer processes critical for H_2O_2 generation (Figure 4).

- *Surface Area Optimization*: Certain COFs, such as DAAQ-COF, demonstrate surface areas above 3000 m^2/g, enabling superior oxygen adsorption capacity and facilitating rapid charge transfer kinetics, both of which enhance H_2O_2 production rates [51,52].
- *Pore Volume Utilization*: Larger pore volumes not only accommodate more reactants but also reduce diffusion limitations and improve access to active sites. Studies have shown that doubling the pore volume in certain COFs can lead to a two-fold increase in H_2O_2 yield [53].

- *Directed Assembly Techniques*: Advanced synthesis strategies, such as template-directed growth or solvothermal methods, can be employed to engineer additional porosity and interconnected channels within COFs. These techniques enable the creation of highly tailored architectures optimized for specific catalytic functions.

(c) Functionalization

Functionalization enables precise tailoring of COF surfaces to promote specific reaction pathways. Electron-donating or electron-withdrawing groups can be introduced during or after synthesis to modulate the electronic environment around active sites (Figure 5), influence redox behavior, and stabilize intermediates involved in the oxygen reduction reaction (ORR) [54]. The combination of these design principles makes COFs highly versatile materials suitable for efficient photocatalytic and electrocatalytic H_2O_2 production. Functionalization of COFs may involve the following:

- *Incorporation of Active Groups*: Functional groups such as -NH_2, -COOH, or –SO_3H provide specific sites for interaction with oxygen molecules and reaction intermediates. For example, amino-functionalized COFs have been shown to enhance the selectivity for H_2O_2 production by stabilizing superoxide species, which are key intermediates in the two-electron ORR pathway [55]. During ORR, molecular oxygen (O_2) undergoes electron transfer processes to form either water (H_2O) via a four-electron pathway or H_2O_2 via a two-electron pathway. COFs with tailored functional groups can selectively promote the two-electron pathway, favoring H_2O_2 production over water formation.

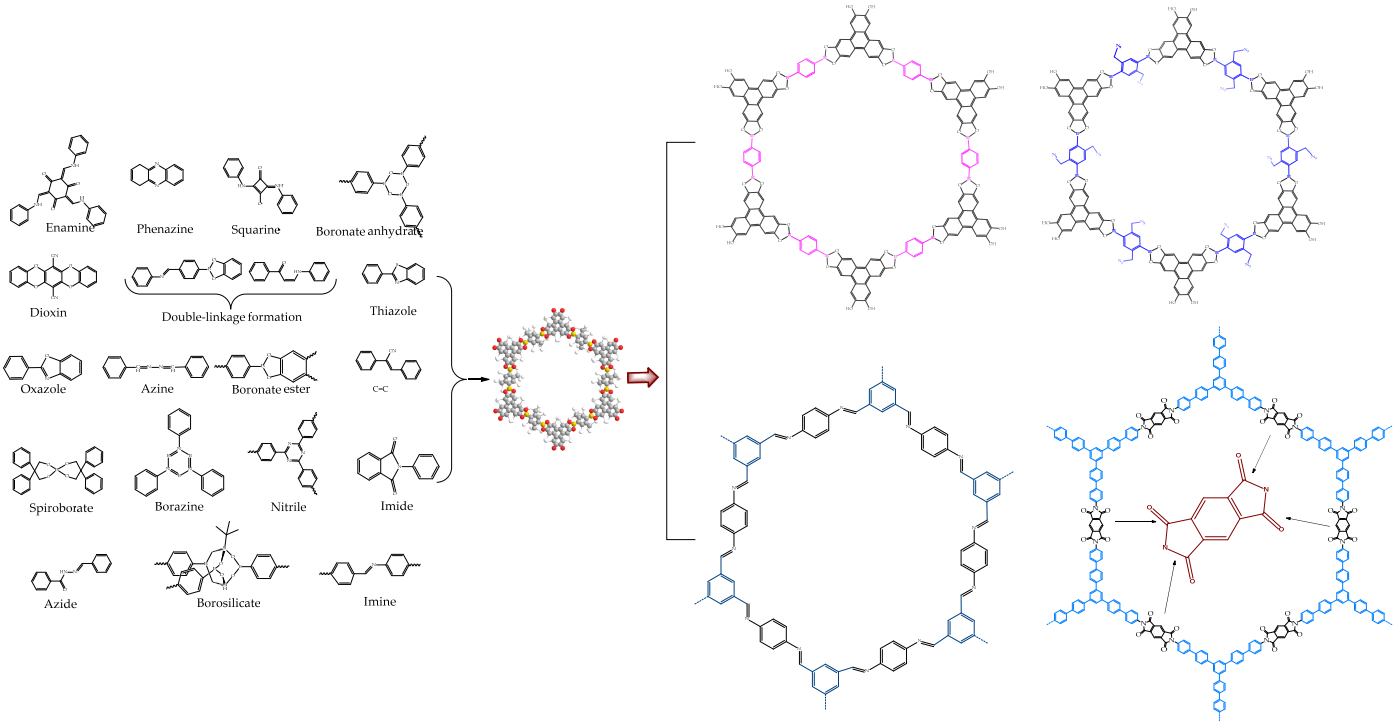


Figure 5. Various linkers for COF synthesis.

Step 1 (Oxygen Adsorption): Oxygen molecules (O_2) are adsorbed onto the COF surface at active sites. Electron-donating functional groups such as -NH_2 (amine) or -OH (hydroxyl) enhance O_2 adsorption by creating a more electron-rich environment.

$$\text{COF-NH}_2 + O_2 \rightarrow \text{COF-NH}_2 \cdots O_2 \text{ (adsorbed complex)}$$

Step 2 (First Electron Transfer): the adsorbed O_2 accepts one electron to form a superoxide intermediate (O_2^-). This step is facilitated by the presence of electron-rich functional groups, which stabilize the negatively charged species through electrostatic of hydrogen bonding interactions.

$$\text{COF-NH}_2\cdots\text{O}_2 + \text{e}^- \rightarrow \text{COF-NH}_2\cdots\text{O}_2^-$$

Step 3 (Protonation and Second Electron Transfer): The superoxide intermediate undergoes protonation and gains a second electron to form hydroperoxyl species (HO_2^-), which remains loosely bound to the COF surface.

$$\text{COF-NH}_2\cdots\text{O}_2^- + \text{H}^+ + \text{e}^- \rightarrow \text{COF-NH}_2\cdots\text{HO}_2^-$$

Step 4 (Release of H_2O_2): Finally, HO_2^- reacts with protons in the solution to form H_2O_2, which desorbs from the COF surface into the bulk solution.

$$\text{COF-NH}_2\cdots\text{HO}_2^- + \text{H}^+ \rightarrow \text{COF-NH}_2 + \text{H}_2\text{O}_2$$

- *Co-catalyst Integration*: Embedding metallic or non-metallic co-catalysts (e.g., Pt, Pd, or Fe-based complexes) within the COF can significantly boost electron transfer efficiency and catalytic activity. For instance, COF-Pt composites have demonstrated enhanced H_2O_2 yields due to synergistic interactions between the COF support and the metal nanoparticles [56,57].
- *Tailored Properties for Specific Reactions*: By designing COFs with controlled surface chemistries, researchers can direct reaction outcomes. Electron-deficient environments may favor the four-electron ORR (leading to water), whereas electron-rich environments promote the two-electron pathway (favoring H_2O_2). Strategic functionalization thus allows selective tuning of reaction mechanisms.

3.1.2. Green Design Approach to COF Synthesis

Green synthesis strategies focus on environmentally friendly approaches to chemical production by minimizing the use of toxic solvents, reducing energy consumption, and eliminating harmful waste. These methods, including green solvents, room-temperature synthesis, mechanochemistry, and electrochemistry, aim to achieve sustainable and scalable material fabrication. By adhering to green chemistry principles, these strategies enable the development of functional materials like COFs for industrial applications while promoting environmental sustainability. A study by Zhang et al. comprehensively studied the green and large-scale synthesis of COFs, aiming to overcome the challenges posed by harsh synthesis conditions and limited scalability [58]. Several works have been carried out to develop environmentally friendly and scalable synthesis strategies to facilitate their industrial applications. Summarily, four green strategies were explored; (1) Green solvents (2) Room-temperature synthesis (3) Mechanochemistry, and (4) Electrochemistry. Each approach was designed to minimize environmental impact, reduce energy consumption and enable large-scale production.

Green Solvents: Water, ionic liquids, and molten salts are proven alternatives to traditional toxic organic solvents. These solvents not only reduced environmental hazards but also enabled a scalable synthesis method for COFs. For instance, water-based systems demonstrated the feasibility of gram-scale COF production, while ionic liquids facilitated the formation of COF membranes with controlled morphology (Figure 6).

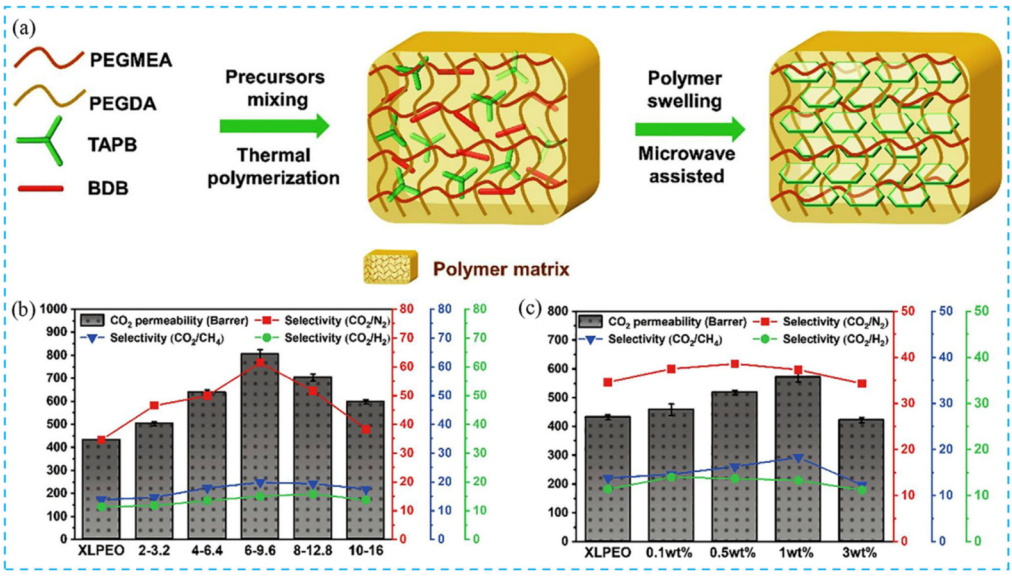


Figure 6. (**a**) Schematic diagrams of 2D COF-based mixed matrix membranes. Gas separation performance of (**b**) COF−(3 wt.%)@XLPEO MMM and (**c**) COF (10–16)-based MMM.

Room-Temperature Synthesis: By eliminating the need for high-temperature and high-pressure conditions, this strategy significantly reduces pollution and energy consumption, as well as cost of production. Through this method, highly crystalline COFs were generated under mild conditions.

Mechanochemistry: This is a solvent-free approach leveraging mechanical force to drive chemical reactions, offering an environmentally sustainable pathway for COF synthesis. In recent works, mechanochemical processes have been successfully utilized to produce COFs with high thermal and chemical stability, as well as demonstrating scalability and reduced waste generation [59–62].

Electrochemistry: Electrochemical synthesis is a highly efficient and environmentally friendly method for producing thin COF films on conductive substrates. It allows precise control of film thickness and structure by adjusting electrical parameters. For example, Wang et al. created defect-free ionic TpEB COF membranes using electrochemical condensation, while Shirokura et al. developed an electrogenerated acid (EGA) method to synthesize COF films with adjustable thickness (Figure 7) [63,64]. This approach minimizes environmental impact, reduces byproducts, and lowers energy consumption, making it a sustainable option for large-scale COF production.

The findings highlight the effectiveness of these green synthesis strategies in producing COFs with tailored properties and scalable yields. The studies also validated the practical applications of COFs in key industrial areas. For example, COFs were synthesized as catalysts for chemical reactions, photocatalysis, and electrocatalysis, showcasing their versatility and efficiency. In separation technologies, COFs demonstrated excellent gas purification and water treatment capabilities. Additionally, COFs were employed in sensors and batteries, emphasizing their potential for environmental monitoring and energy storage. It can be concluded that, while significant progress has been made, further development is needed to optimize synthesis methods, scale up production and ensure consistent material properties. The related studies suggested proposed interdisciplinary collaboration, artificial intelligence-assisted modeling, and real-world testing as future directions to accelerate the transition of COFs from laboratory to industrial scale.

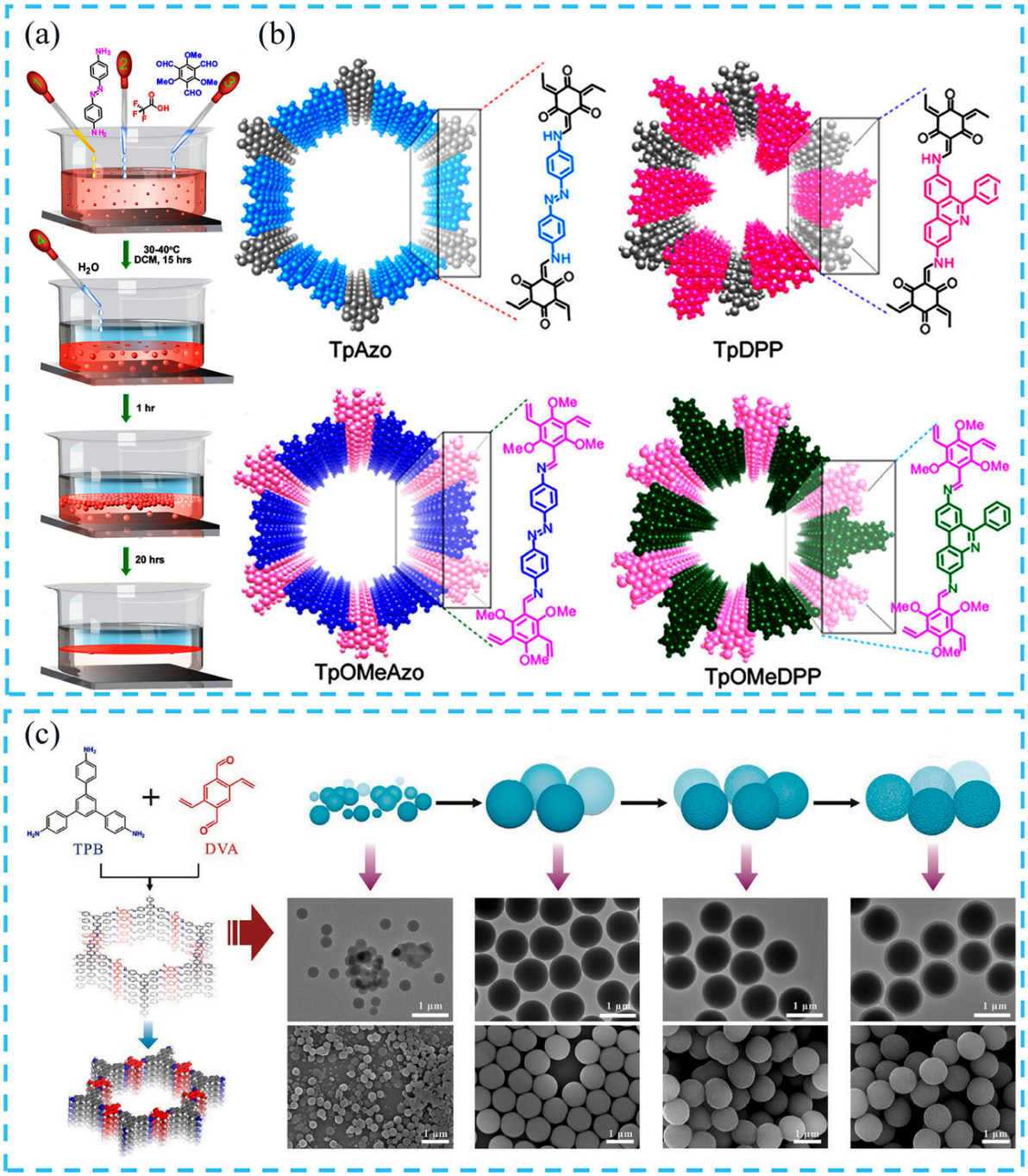


Figure 7. (**a**) The synthetic diagram of different COF films. (**b**) The chemical structure of COFs and (**c**) TEM/SEM images at different reaction times.

3.2. Photocatalytic COF-Based H_2O_2 Generation

Photocatalysis leverages light energy to trigger chemical reactions, making it a promising approach for H_2O_2 generation. The process involves semiconductor materials that absorb light, leading to the excitation of electrons from the valence band to the conduction band, resulting in the formation of electron-hole pairs. These photo-excited charge carriers can then interact with reactants like molecular oxygen and water to facilitate the generation of H_2O_2 and reactive oxygen species (ROS) [65,66]. COFs have gained attention as potential photocatalysts for H_2O_2 generation due to their unique structural properties, including tunable porosity, high surface area, and the ability to incorporate chromophores for enhanced light absorption [67].The structural design of COFs allows for fine-tuning

their band gap, facilitating efficient solar energy harvesting and making them suitable candidates for photocatalytic applications. In photocatalytic H_2O_2 generation using COFs, several pathways are typically involved. Upon light irradiation, COFs absorb photons, leading to the generation of electron-hole pairs. The photo-excited electrons can reduce molecular oxygen to superoxide anions (O_2^-), which subsequently react with protons to form H_2O_2 [68]. Moreover, hydroxyl radicals generated from the oxidation of water can also react with superoxide to yield H_2O_2, highlighting the intricacies of this photocatalytic process [69]. The balance of these reactions emphasizes the importance of optimizing COFs structures to maximize photocatalytic efficiency and selectivity. Recent studies have showcased the potential of various COF materials in photocatalytic H_2O_2 production. For instance, Wang et al. demonstrated that incorporating functional groups such as amine or carbonyl groups within the COF structure significantly enhanced photocatalytic activity by facilitating charge transfer processes and improving light absorption efficiency [70]. The development of composite COFs, integrating other semiconductor materials like titanium dioxide (TiO_2) and graphitic carbon nitride (g-C_3N_4), has also been explored to improve light absorption and charge separation, ultimately leading to higher H_2O_2 yields [44,71].

$$O_2 + e^- \rightarrow O_2^-$$

$$O_2^- + 2H^+ \rightarrow H_2O_2$$

In addition to COFs, other semiconductor materials such as TiO_2 or g-C_3N_4 have been widely studied for their photocatalytic properties. TiO_2 with its strong oxidative capabilities and favourable band alignment, is often used in hybrid systems to promote enhanced charge separation and prolonged electron lifetime, critical for effective H_2O_2 generation [72,73]. Likewise, g-C_3N_4 has exhibited unique photocatalytic properties due to its relatively narrow band gap, which facilitates visible light absorption and subsequent charge carrier generation [74,75]. The photocatalytic generation of H_2O_2 utilizing COFs and other semiconductor materials represents a rapidly advancing field. Enhanced understanding of the mechanistic aspects of these reactions and the development of innovative photocatalyst designs will be critical in optimizing the efficiency and selectivity of H_2O_2 production through photocatalysis.

3.3. Electrocatalytic H_2O_2 Generation

Electrocatalysis involves the reduction of molecular oxygen to H_2O_2 at the cathode in an electrochemical cell. The selectivity of this reaction is heavily influenced by the properties of the electrocatalyst, including its surface morphology and electronic structure [76]. The overall reaction typically involves a four-electron reduction of oxygen to yield H_2O_2 as an intermediate product. Managing the reaction conditions, such as pH and potential, can further enhance the selectivity of H_2O_2 formation over water.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

3.3.1. Influence of Electrocatalyst Properties and Compositions on H_2O_2 Generation

Electrocatalysis is a significant process in electrochemical systems, playing a crucial role in the reduction of O_2 at the cathode of electrochemical cells to generate H_2O_2. The overall electrochemical reaction is represented by the following equation: The selectivity of this reaction towards H_2O_2 formation is influenced by the electrocatalyst's properties, particularly its surface morphology and electronic structure. Therefore, enhanced catalyst design can significantly improve the efficiency of the reaction, resulting in a higher yield of H_2O_2 as opposed to the complete reduction to H_2O. Recent studies have highlighted the

importance of tailoring the surface properties of electrocatalysts to enhance their performance. For instance, Sun et al. demonstrated that engineering carbon-based nanomaterials with optimized pore sizes and surface functionalities could effectively direct the reduction pathway of O_2 towards H_2O_2 production, yielding substantial improvements in selectivity and efficiency [77]. Moreover, the reaction mechanism for electrocatalytic reduction typically involves two main electron transfer steps. The selectivity towards H_2O_2 formation compared to complete reduction to water hinges on the catalyst's ability to stabilize reaction intermediates. McCrory et al. elucidated these mechanistic pathways, underscoring the decisive role of the surface electronic structure in determining whether H_2O_2 or H_2O emerges as the primary product [78]. The choice of metals and alloys used in catalyst formulations is another critical factor affecting selectivity. Transition metal catalysts have been extensively studied for their ability to enhance H_2O_2 production through strategic electronic tuning. Chanussot et al. explored the use of platinum-copper alloys, finding that the alloying effect not only improved surface electron transfer kinetics but also significantly increased the formation rates of H_2O_2 [79]. The electrocatalytic reduction of O_2 to H_2O_2 presents a viable pathway for sustainable production. The optimization of electrocatalysts through careful consideration of surface morphology, electronic structure, and catalyst composition remains a vital area of research for improving the efficiency and selectivity of this reaction.

The intermediates in $2e^-$ ORR include $OOH^\bullet$, experimentally detected by in situ FTIR, with binding energies theoretically optimized via $\Delta G_{OOH\bullet}$~0.8–1.2 eV for high selectivity. Active sites are metal-free (e.g., F-doped for charge redistribution) or metalated (e.g., Co-porphyrin), with experimental FE > 99% but theoretical models showing stability issues under acidic conditions.

3.3.2. Role of COFs as Electrocatalysts

COFs can serve as effective electrocatalysts for H_2O_2 production due to their tunable porous architecture, which allows for enhanced mass transport and accessibility of reaction sites. The ability to functionalize COFs enables researchers to fine-tune their electronic properties, leading to improved charge transfer capabilities and catalytic efficiency [80]. Furthermore, the inherent stability of COFs under electrochemical conditions positions them as favourable candidates for sustainable H_2O_2 production. The configuration of the electrode plays a vital role in the electrocatalytic generation of H_2O_2. Various strategies, including optimizing COF film thickness, modifying electrode surface area, and incorporating conductive materials, can significantly enhance the electrochemical performance [81]. Studies have shown that hybrid systems combining COFs with conductive carbon materials result in improved conductivity and electrochemical reactivity, making COF-based electrocatalysts more viable for practical applications. Recent advancements have highlighted the potential of COFs in electrochemical systems for efficient H_2O_2 generation. For example, it reported a COF-based electrocatalyst with high selectivity and stability for H_2O_2 production, achieved through strategic incorporation of active sites tailored for oxygen reduction reactions [82]. Furthermore, the integration of COFs into flexible, scalable electrode architectures has shown promise for the development of next-generation electrochemical cells [83].

COFs are crystalline porous materials constructed entirely from light elements (e.g., carbon, nitrogen, oxygen) linked by strong covalent bonds. They are characterized by their tunable porosity, high surface area, and metal-free nature, making them ideal candidates for sustainable photocatalytic applications. There is no need for metal ions, and their modular design allows for precise control over their pore size, functionality, and electronic properties. These factors eliminate adverse environmental impact and enable optimization

for specific photocatalytic reactions. Their conjugated structures also facilitate efficient charge carrier separation and transport, which is critical for enhancing photocatalytic performance. However, their synthesis often requires precise control of reaction conditions which can complicate large-scale production. Also, while generally stable, COFs may degrade under extreme conditions, e.g., high temperatures and strong acids limiting their applications in certain environmental conditions. To compare with other porous framework materials, including Metal–Organic Frameworks (MOFs) and Hydrogen-Bonded Organic Frameworks (HOFs) are highly efficient catalysts for H_2O_2 production. Each class offers unique advantages and challenges, making them suitable for various applications. Here, these materials' structural properties, stability, photocatalytic performance are compared (Table 1).

MOFs are crystalline materials composed of metal ions or clusters coordinated with organic ligands. They are known for their high tunability and porosity, which can be tailored by varying the metal nodes and organic linkers. MOFs have been widely explored for photocatalytic applications due to their large surface areas and excellent light absorption properties. MOFs allow for precise control of their structural and electronic properties, making them highly adaptable for specific catalytic applications. Having abundant active sites and versatile functionality due to high surface areas, MOFs are excellent photocatalytic reactants. However, many MOFs are prone to hydrolysis, leading to structural degradation in the presence of water, resulting in their inactivity in aqueous photocatalytic systems. Also, their activity depends on metal nodes, which can introduce challenges relating to cost, toxicity and environmental impact. Additionally, HOFs are porous materials formed through hydrogen-bonding interactions between organic molecules. They are known for their self-healing properties and superior water stability, making them promising candidates for applications in aqueous environments. The reversible nature of H-bonds in HOFs allows for self-repair. This gives them enhanced durability and longevity in photocatalytic applications. They also have excellent stability in aqueous environments leading to a suitable H_2O_2 production in water-based systems. However, they have lower mechanical strength than MOFs and COFs due to the weak H-bonding limiting their application in reactions requiring high structural integrity. Additionally, they are new and hence need extensive studies prior to realistic photocatalytic applications. Table 3 summarizes the comparison of photocatalytic applications of COFs, MOFs and HOFs.

Table 3. Comparison of MOFs, COFs, and HOFs for Photocatalytic H_2O_2 Production.

Property	MOFs	COFs	HOFs
Composition	Metal ions/clusters + organic ligands	Organic building blocks (C, N, O)	Organic building blocks (H-bonded)
Tunability	High (via metal nodes and ligands)	High (via organic building blocks)	Moderate (via H-bonding interactions)
Surface Area	Very high	High	Moderate to high
Stability in Water	Poor (prone to hydrolysis)	Moderate	Excellent
Charge Separation	Moderate	Excellent	Moderate
Synthesis Conditions	Moderate	Strict	Mild
Mechanical Strength	High	Moderate	Low
Environmental Impact	Metal-dependent (potential toxicity)	Metal-free (low toxicity)	Metal-free (low toxicity)
Applications	Gas storage, catalysis, sensing	Photocatalysis, gas separation	Aqueous catalysis, self-healing

Summarily, each class of porous framework materials offers unique advantages and challenges for photocatalytic H_2O_2 production. MOFs excel in tunability and surface area but often suffer from poor water stability. COFs provide a metal-free alternative with efficient charge carrier separation, though their synthesis can be challenging. HOFs stand out for their self-healing properties and superior water stability, but their mechanical strength and photocatalytic potential remain underexplored. By leveraging the strengths of each material class, researchers can design more efficient and sustainable systems for H_2O_2 production [84].

3.4. Characterization Techniques for COFs

Characterization techniques are essential for understanding COF performance. Table 3 summarizes methods such as Transient Absorption Spectroscopy (TAS) for charge dynamics and Fourier Transform Infrared (FTIR) for intermediates, providing insights into catalytic efficiency.

3.4.1. Typical Characterization

COFs are made up of light elements such as carbon, nitrogen, oxygen, and boron, linked by strong covalent bonds. The unique structural properties of COFs, including their tunable porosity, high surface area, and the ability for functionalization, make them suitable for various applications, including gas storage, catalysis, and drug delivery. To understand their properties and optimize their performance, various characterization techniques are employed to characterize COFs, and further demonstrate their effectiveness.

X-ray Diffraction (XRD): This is a fundamental method used to determine the crystallinity and phase purity of COFs. It provides information about the arrangement of atoms in the crystal structure and can confirm the formation of the desired COF phase. Deriving from several studies, Yang et al. investigated the XRD patterns of newly synthesized COF, which showed sharp peaks indicative of a crystalline structure (Figure 8), confirming the successful formation of the desired framework. The observed d-spacings aligned with the calculated values derived from the proposed structure, validating the structural integrity of the COF [85–87].

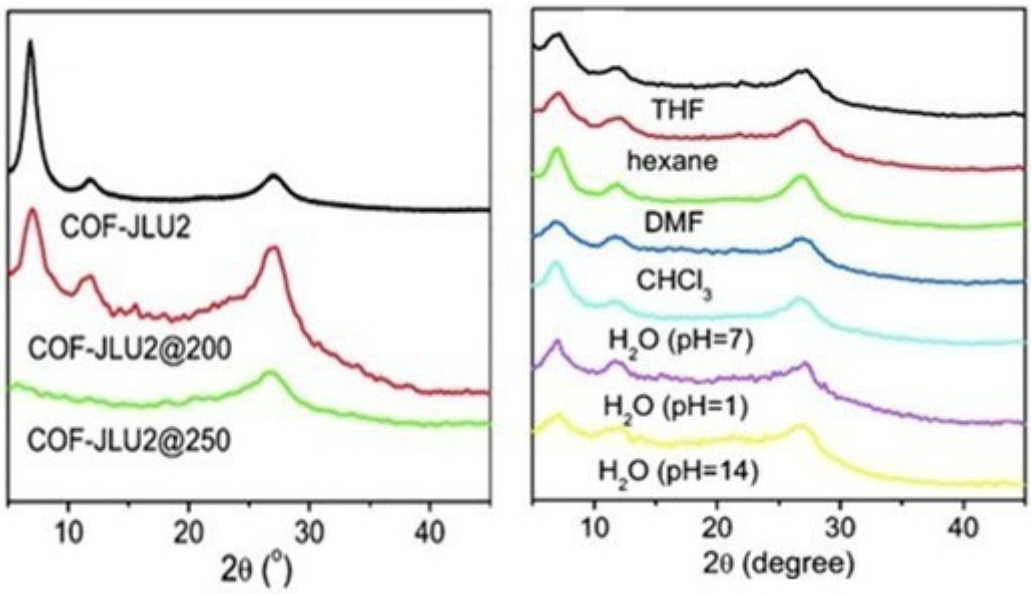


Figure 8. XRD patterns of newly synthesized COF showed sharp peaks indicative of a crystalline structure in the solid state and upon treatment at different conditions.

Brunauer–Emmett–Teller (BET) Surface Area Analysis: This method is utilized to measure the specific surface area and porosity of COFs by adsorbing gases (typically nitrogen) onto the material's surface. This analysis is crucial for understanding the framework's ability to store gases or other entities. Li et al. characterized a COF with BET surface area measurements, revealing a high surface area of over 600 m^2 g^{-1} (Figure 9). This indicated the potential application of the COF in gas adsorption and storage [88].

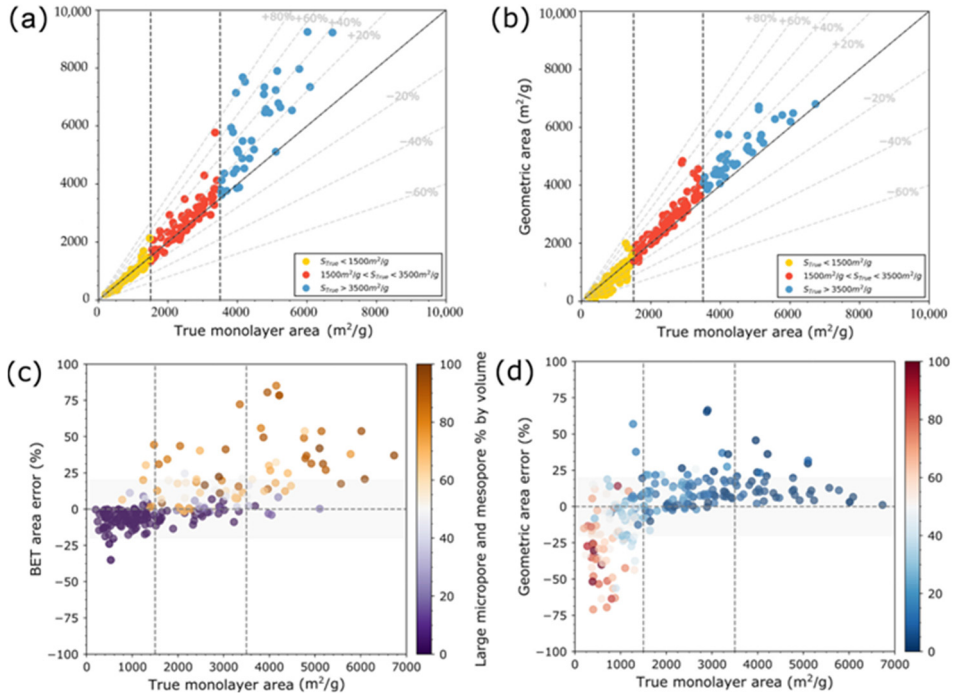


Figure 9. Comparisons of BET and geometric area with true monolayer area for MOFs. (**a**) BET area vs true monolayer area. (**b**) Geometric area vs true monolayer area. (**c**) Deviation of the BET area from true monolayer area vs true monolayer area. (**d**) Deviation of the geometric area from the true monolayer area vs the true monolayer area. In (**a**,**b**), the gray lines represent deviation from true monolayer area in steps of 20%. For results shown in (**c**,**d**), each point is further color coded to represent the volume fraction of large micropores and mesopores (i.e., pore diameter > 10 Å) and micropores with a pore diameter less than 4 Å, respectively.

Fourier Transform Infrared Spectroscopy (FTIR): This spectroscopy is employed to identify functional groups within the COF structure and confirm the formation of covalent linkages between the building blocks. In the research, Akinnawo reported the synthesis of high-grade imine-linked COF-LZU1 membrane supported on α-Al_2O_3 tubes, with improved thermal and chemical stabilities [81,89]. The study used FTIR to characterize a COF synthesized via imine linkages. The observed peaks corresponding to the C = N stretching vibrations confirmed the successful formation of imine bonds, corroborating the proposed synthesis mechanism (Figure 10).

Nuclear Magnetic Resonance (NMR) Spectroscopy: particularly solid-state NMR, is useful for elucidating the connectivity and environment of atoms within COFs. It helps in understanding the local geometry and spatial arrangement of structural units. Lyle et al. employed solid-state NMR to study a COF's topology, revealing distinct chemical shifts that provided insights into the bonding environment and aromaticity of the framework. Their analysis confirmed the successful integration of different building blocks (Figure 11), providing a deeper understanding of the COF's structural features [90].

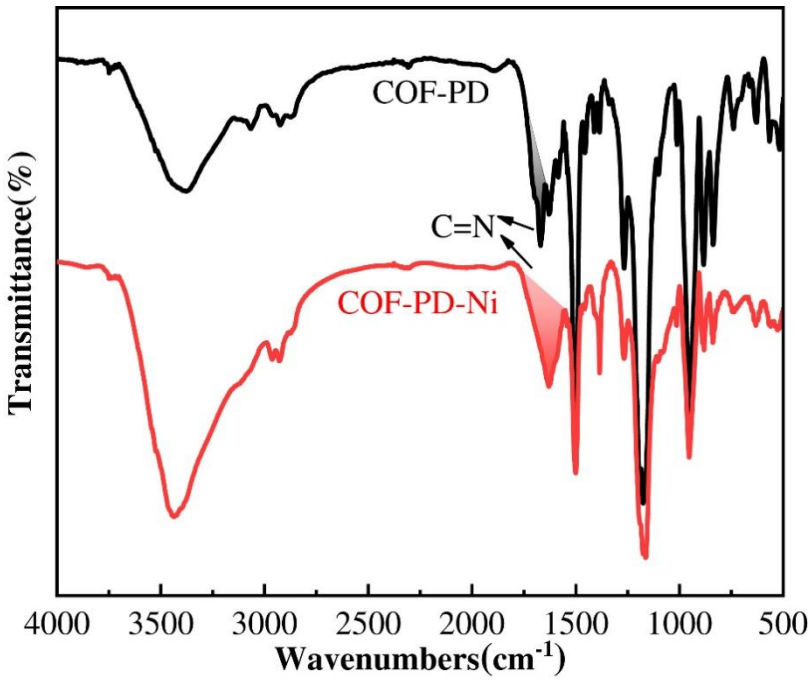


Figure 10. FTIR measurements of some synthesized COF materials [81].

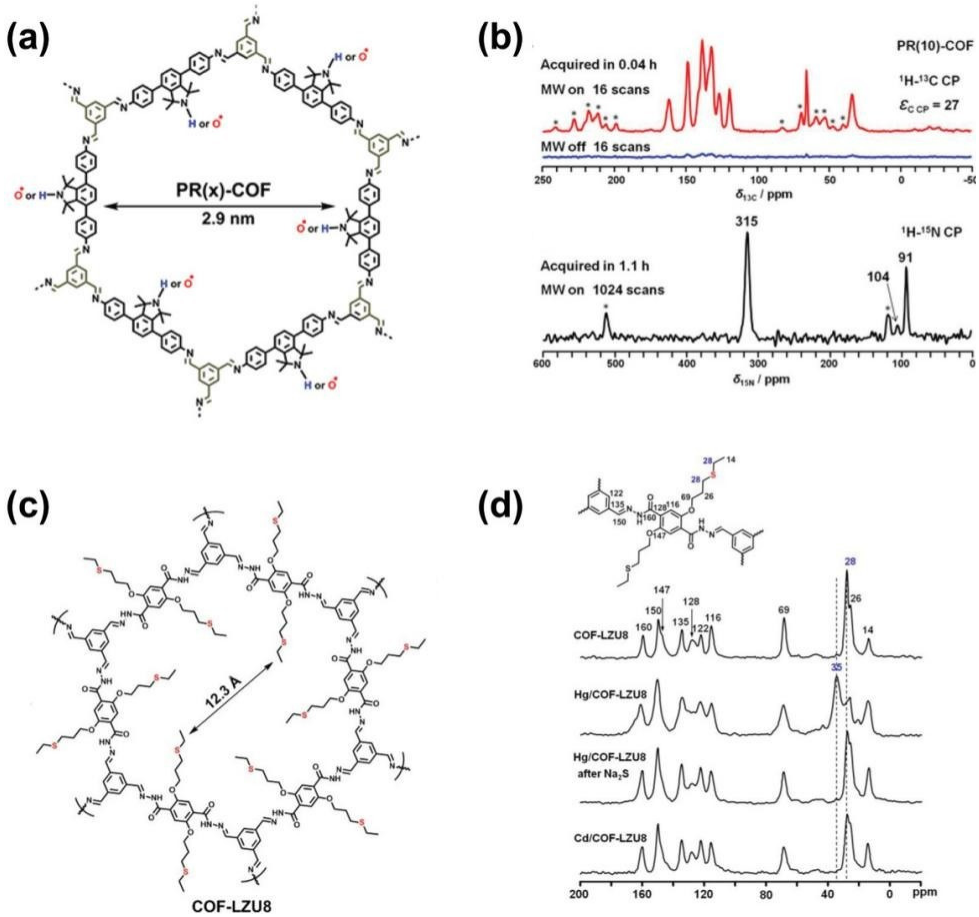


Figure 11. Solid state NMR Spectra showing (**a**) Structure of PR(x)-COF at 29nm and (**b**) corresponding spectra with notable imine linkage (=N-) and ^{15}N asterisk peaks at ~120 and ~510 ppm, and (**c**) Structure of COF-LZU8, and (**d**) spectra in comparison with Hg-COF-LZU8, Hg/COF-LZU8 after Na_2S treatment and Cd/COF-LZU8 [91].

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM): They are critical for investigating the morphology, particle size, and overall structural integrity of COFs at high resolutions. These techniques provide visual confirmation of the framework's structural features. Zhu et al. utilized SEM and TEM to examine the surface morphology and particle size of their synthesized COF (Figure 12), demonstrating a uniform distribution of nanostructures. Their imaging results showed a well-defined morphology in line with the predicted structure, corroborating the successful synthesis of the COF [92].

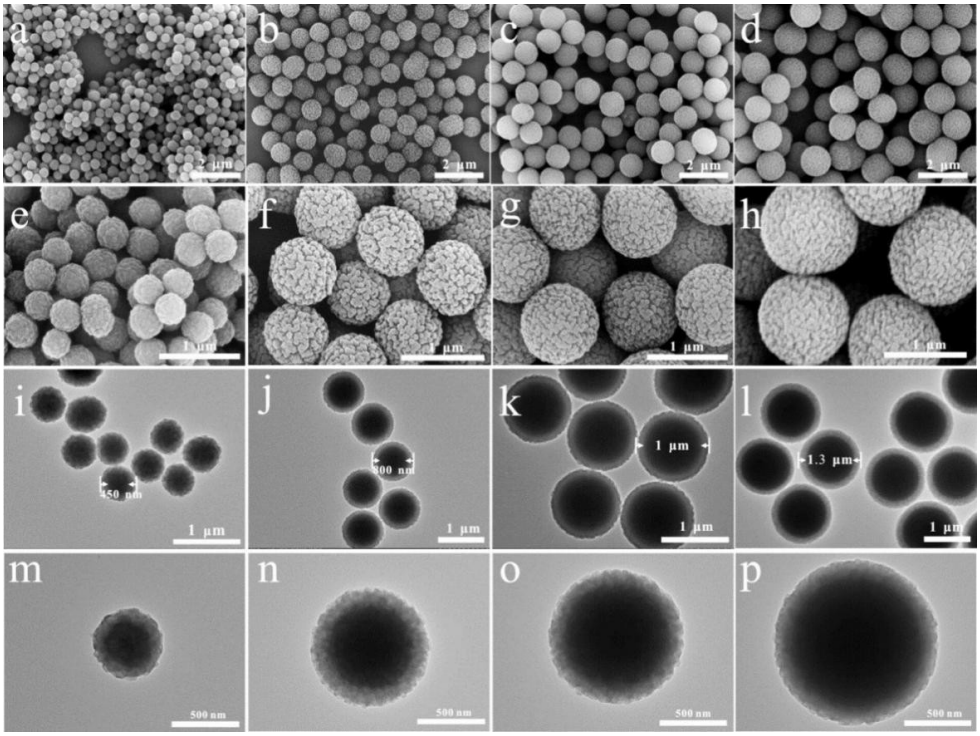


Figure 12. SEM and TEM images of the uniform spherical COFs prepared in 0.7, 0.5, 0.4 and 0.3 mL HAc, and with different sizes: ((**a**,**e**,**i**,**m**): 450 nm), ((**b**,**f**,**j**,**n**): 800 nm), ((**c**,**g**,**k**,**o**): 1.0 μm), ((**d**,**h**,**l**,**p**): 1.3 μm), respectively, [93].

Thermogravimetric Analysis (TGA): this measures the thermal stability and composition of materials by tracking weight changes as a function of temperature. This technique is essential for assessing the thermal stability and robustness of COFs, especially when considering their practical applications. The thermal stability of a COF was assessed by Yue et al. using TGA (Figure 13), which showed a weight loss of less than 5% up to 300 °C, indicating excellent thermal stability. This result is crucial for applications in catalysis and gas separation [94].

X-ray Photoelectron Spectroscopy (XPS): this is used to analyze the surface chemistry of COFs, providing information about elemental composition, oxidation states, and chemical environments. Son et al. reported using XPS to investigate the surface functionalization of a COF (Figure 14). Their results showed distinct binding energy peaks corresponding to the expected elements, confirming the chemical composition and functionalization of the framework [95–97].

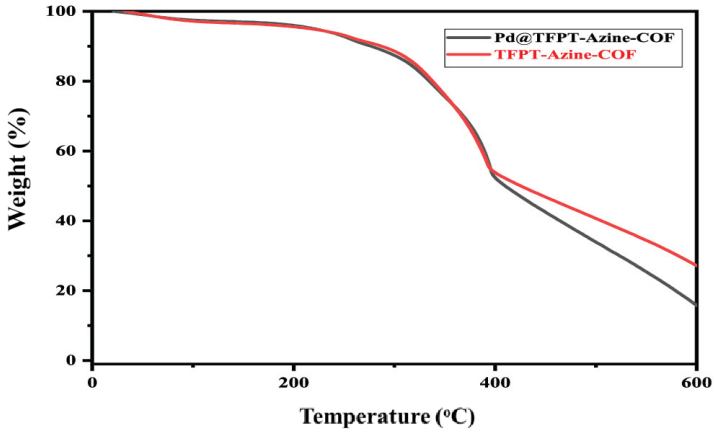


Figure 13. TGA Thermograms showing weight loss in % for synthesized COFs.

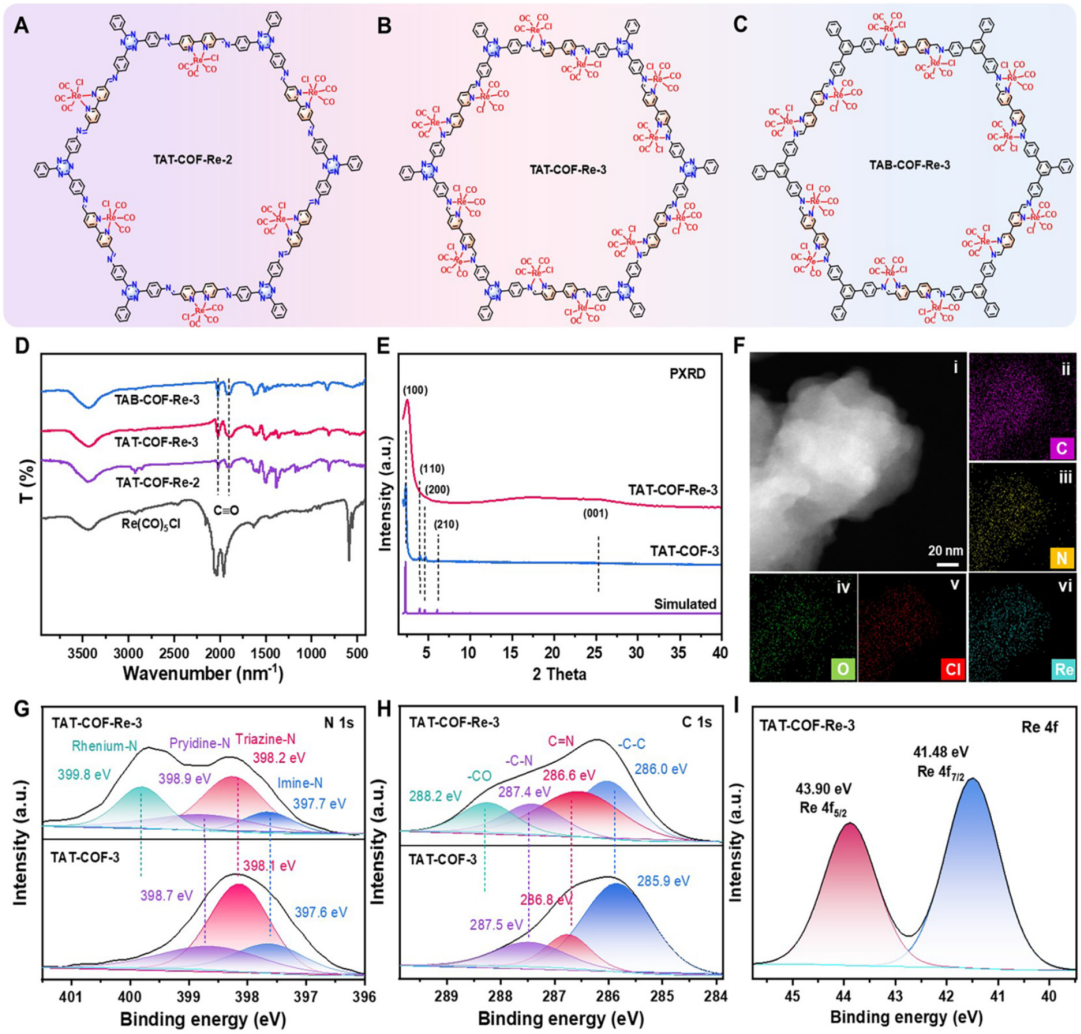


Figure 14. Molecular structures of (**A**) TAT-COF-Re-2, (**B**) TAT-COF-Re-3, and (**C**) TAB-COF-Re-3. (**D**) FT-IR spectra of TAT-COF-Re-2, TAT-COF-Re-3, TAB-COF-Re-3 and their Re complex. (**E**) PXRD patterns and simulated results. (**F**) Dark-field HR-TEM (**i**) EDX elemental mappings of TAT-COF-Re-3; C (**ii**), N (**iii**), O (**iv**), Cl (**v**) and Re (**vi**). The scale bar is 20 nm. (**G**) Full XPS spectra and (**H**) the defined N 1 s XPS spectra of TAT-COF-Re-2 (up) and TAT-COF-2 (down). (**I**) The defined Re 4f XPS spectra of TAT-COF-Re-3.

3.4.2. Advanced Characterization Techniques

The use of various characterization techniques is pivotal in the comprehensive analysis of COFs. Each method contributes essential information regarding structural integrity, surface properties, chemical composition, and functionality. Ongoing research continues to expand the capabilities and applications of COFs, making an understanding of these characterization techniques increasingly relevant in the field of material science. For a comprehensive understanding of the photocatalytic mechanisms in COFs for H_2O_2 production, advanced characterization techniques are essential. These methods provide detailed insights into the structural, electronic, and dynamic properties of COFs under operational conditions. Below, several advanced techniques and their applications in studying COF-based photocatalysts are discussed.

In Situ Infrared (IR) Spectroscopy: this allows the observation of the formation and transformation of surface-bound species, such as adsorbed water, oxygen, and reaction intermediates, during the photocatalytic process. This technique is particularly useful for identifying key reaction steps and understanding how surface chemistry influences H_2O_2 production. By tracking the vibrational modes of specific functional groups, changes in the IR spectrum with reaction progress and catalyst performance can be correlated (Figure 15).

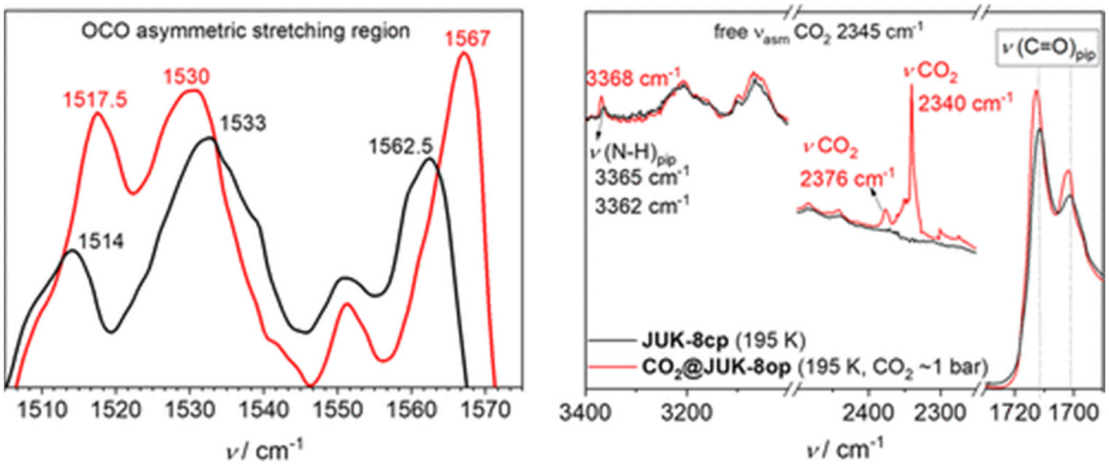


Figure 15. In situ Infrared spectroscopy of COF [98].

Temperature-dependent photoluminescence (TDPL): it measures the photoluminescence (PL) emission of COFs as a function of temperature, providing insights into the behavior of excitons (electron-hole pairs) and their recombination processes. By analyzing the PL intensity and peak positions at different temperatures, the efficiency of charge carrier separation and the presence of trap states that may hinder photocatalytic activity can be determined (Figure 16). This information is critical for optimizing COF structures to minimize exciton recombination and enhance H_2O_2 production.

Kelvin Probe Force Microscopy (KPFM): this is a scanning probe technique that measures the contact potential difference (CPD) between a conductive atomic force microscopy (AFM) tip and the sample surface. This allows for the visualization of charge distribution and transfer at the nanoscale. In COF-based photocatalysts, KPFM can reveal how charges migrate across the material and identify regions of high or low charge density. This information is invaluable for designing COFs with efficient charge transport pathways, which are essential for maximizing photocatalytic efficiency (Figure 17). The figure shows the Kelvin probe force microscopy (KPFM) images of COFs prepared within PVDF for different COF samples.

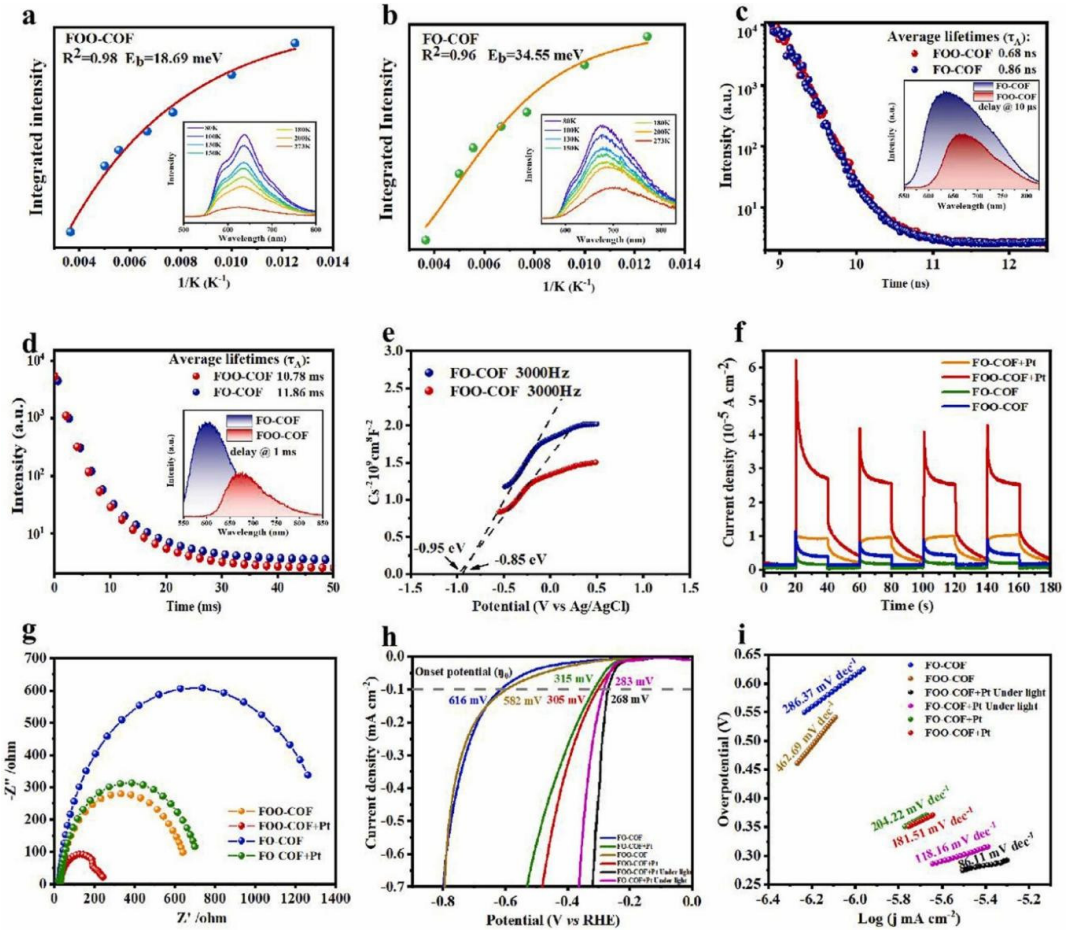


Figure 16. Temperature-dependent photoluminescence spectrum of integrated PL intensity as a function of the temperature for different COF samples. (**a**) FOO-COF and (**b**) FO-COF from 80 to 273 K). (**c**) Time-resolved photoluminescence spectra of FOO-COF and FO-COF samples monitored at a delayed time of 10 μs for FOO-COF and FO-COF at 300 K). (**d**) Time-resolved phosphorescence spectra for FOO-COF and FO-COF samples (recorded at a delayed time of 1 ms for FOO-COF and FO-COF). (**e**) Mott−Schottky curves for FO-COF (blue) and FOO-COF (red). (**f**) Transient photocurrent spectra of FOO-COF, FO-COF, FOO-COF, FO-COF/Pt and FOO-COF/Pt. (**g**) EIS Nyquist plots of FOO-COF, FO-COF, FOO-COF, FO-COF/Pt and FOO-COF/Pt. (**h**) LSV polarization curves and (**i**) Tafel plots of FOO-COF, FO-COF, FO-COF/Pt and FOO-COF/Pt.

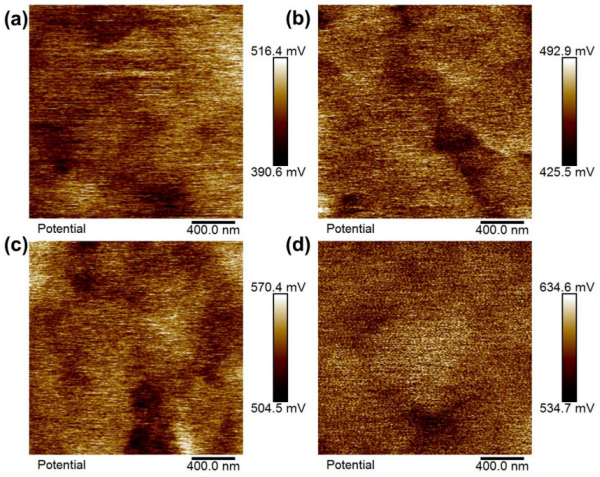


Figure 17. Kelvin probe force microscopy (KPFM) images of (**a**) H-COF@PVDF (**b**) CH3-COF@PVDF (**c**) 2F-COF@PVDF and (**d**) 4FCOF@PVDF [99].

Transient Absorption Spectroscopy (TAS): This is a pump-probe technique that monitors the absorption changes in a material following photoexcitation. It provides temporal resolution on the femtosecond to nanosecond timescales, enabling the observation of ultrafast processes such as charge transfer, exciton dissociation, and carrier relaxation. For COF-based photocatalysts, TAS can reveal how quickly photogenerated charges are transferred to reactive sites and how long they remain active. This knowledge helps in optimizing COF structures to prolong charge carrier lifetimes and improve photocatalytic performance. For instance, studies have used TAS to elucidate charge dynamics in donor-acceptor COFs, showing efficient charge separation that enhances material efficiency for applications like H_2O_2 generation. Similarly, investigations into fully conjugated 2D COFs have revealed rapid exciton dissociation and charge migration, implying improved photocatalytic yields through reduced recombination. Recent work on hybrid COF systems further highlights ultrafast charge transfer processes resolved at the elementary level, which can guide designs for higher efficiency in sustainable H_2O_2 production [100–102].

By combining these advanced characterization techniques, a holistic understanding of the photocatalytic mechanisms in COF-based systems can be developed. For example, in situ IR spectroscopy can identify the formation of reactive intermediates, while TAS can track how quickly these intermediates are generated and consumed. TDPL can reveal the efficiency of exciton separation, and KPFM can map how separated charges migrate across the COF structure. Together, these techniques provide a multi-dimensional view of the photocatalytic process, enabling the rational design of COF-based materials for efficient and sustainable H_2O_2 production.

3.5. Reactor Design

Types of Reactors for COF-Based Systems

The reactor design plays a critical role in the efficiency and yield of H_2O_2 production in COF-based systems. Different types of reactors can be employed depending on the specific requirements of the catalytic process, including batch reactors and continuous flow systems.

(a) Batch Reactors

Batch reactors are the simplest type of reactors and are widely used in COF-based H_2O_2 generation studies (Figure 18). In this configuration, the COF catalyst is mixed with the reaction solutions in a closed vessel, allowing for controlled conditions such as temperature, concentration, and light exposure [103]. While batch systems are suitable for small-scale production and offer experimental flexibility, they often suffer from limitations related to mass transfer and reaction kinetics, leading to variable H_2O_2 yields depending on the reaction time and conditions. Recent advancements in batch reactor designs, such as the optimization of stirring rates and light intensity, have been shown to enhance mass transfer and improve H_2O_2 yields, demonstrating that careful reactor design can significantly influence performance [104]. These include:

- *Stirred Tank Reactors*: These reactors enhance mass transfer through mechanical stirring, enabling uniform distribution of the COF catalyst and reactants. Studies have indicated that optimizing stirring rates can lead to higher yield outcomes, as observed in COF-103 systems where yields improved by 30% with increased stirring speeds [105].
- *Photoreactors*: Specialized photoreactors designed for batch systems can improve light exposure and reaction efficiency. For instance, using a quartz reactor with integrated UV-Vis light sources allow researchers to monitor real-time reaction conditions effectively, improving the predictability of H_2O_2 yields.

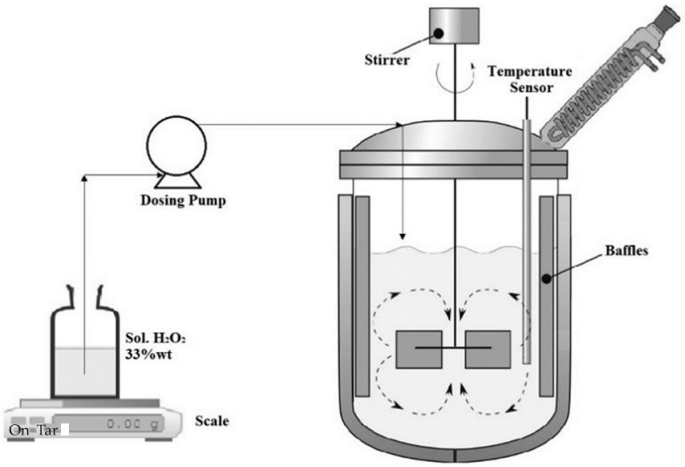


Figure 18. Batch reactor [106].

(b) Continuous Flow Systems

Continuous flow systems represent a more advanced approach for COF-mediated H_2O_2 production (Figure 19), offering several advantages over batch reactors. In these systems, reactants continuously flow through a fixed bed of COF catalyst, allowing for real-time reaction and product collection. Continuous flow reactors enhance mass transfer efficiency and mitigate issues related to concentration gradients, thus promoting higher H_2O_2 yields [107].

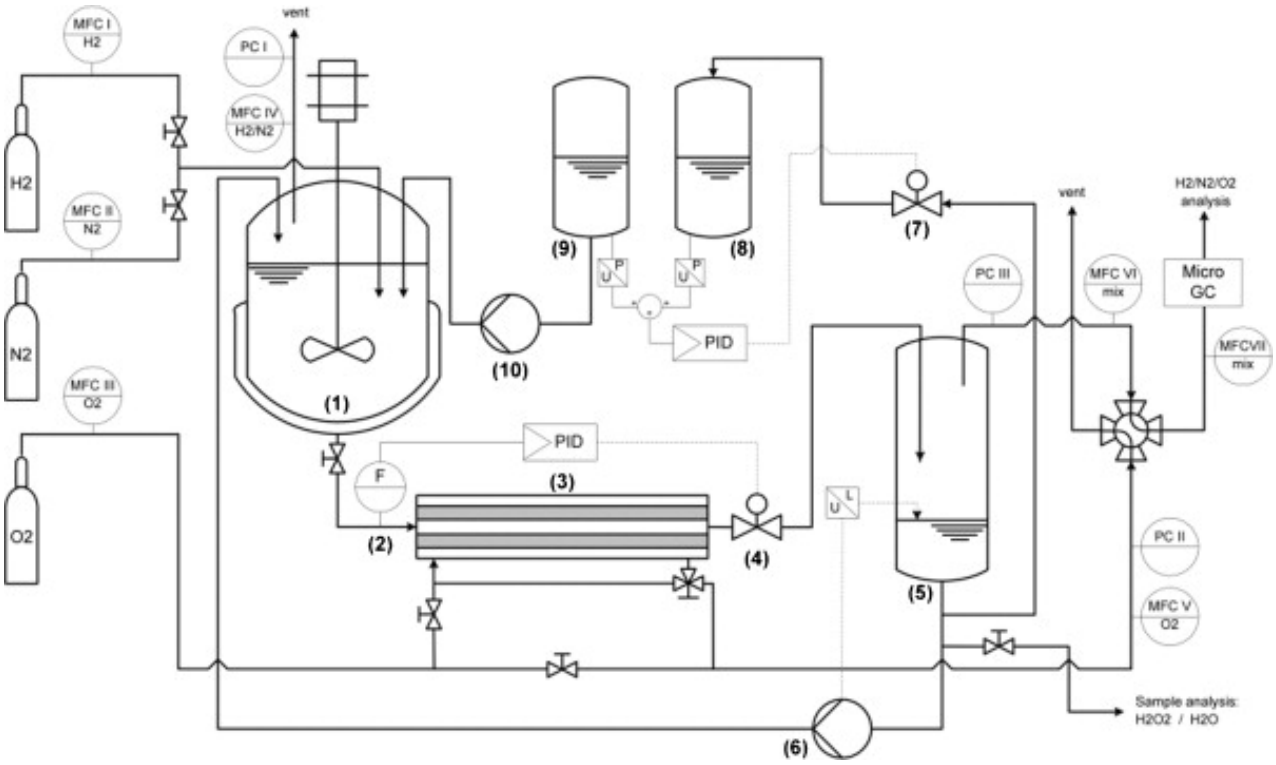


Figure 19. Continuous flow system [108,109].

Moreover, continuous reactors can operate under varying conditions such as temperature, pressure, and light exposure, providing greater control over the reaction environment. This flexibility allows for the optimization of reaction parameters in real time, maximizing the overall efficiency of the H_2O_2 generation process. Recent studies have demonstrated that implementing continuous flow systems can result in H_2O_2 production rates that are

significantly higher than those achieved in batch setups, making them attractive for potential scalability in industrial applications [110]. The adoption of continuous flow systems introduces significant advantages for COF-based H_2O_2 generation, such as;

- *Improved Mass Transfer*: Continuous flow reactors minimize concentration gradients and enhance mass transport, leading to improved reaction rates [111]. Research has demonstrated that utilizing microfluidic continuous flow systems can achieve yields approaching 50 mmol L^{-1} h^{-1}, significantly surpassing batch reactors.
- *Real-time Optimization*: The ability to continuously adjust parameters such as temperature, pressure, or light intensity allows for a more dynamic approach to optimization. For example, continuous photochemical reactors have been employed to achieve varying light intensities and flow rates, enhancing process flexibility and optimizing H_2O_2 yields based on real-time data.
- *Scalability and Industrial Application*: Continuous flow systems are inherently more suitable for scaling compared to batch reactors. Research that successfully scaled COF-based H_2O_2 production to pilot plant operations has shown the potential for integration into industrial processes while maintaining high yields and operational stability.

3.6. Mechanisms Involved in COF-Mediated H_2O_2 Generation

The reaction mechanisms underpinning COF-mediated H_2O_2 generation are complex and involve several critical processes, including charge transfer, photon absorption, and the formation of reaction intermediates.

3.6.1. Charge Transfer Processes

These mechanisms are critical to the efficiency of COF-mediated H_2O_2 generation, and the key processes thereof are:

- *Generation of Electron-Hole Pairs*: Upon light irradiation, COFs generate electron-hole pairs due to the excitation of electrons from the valence band to the conduction band. Efficient charge transfer is crucial for catalytic activity, as the separation of these charge carriers dictates their availability for subsequent reactions. In COF-mediated systems, the incorporation of functional groups or co-catalysts can enhance charge carrier separation and extend their lifetimes, promoting their participation in H_2O_2 generation [112,113].

The following equations represent the electron-hole pair generation and charge transfer process in COFs (Figure 20).

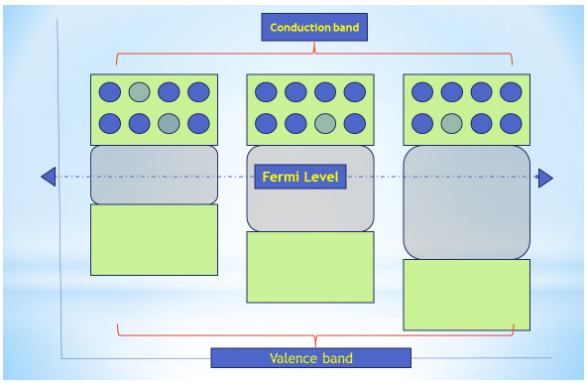


Figure 20. Energy-band diagram showing electron hole formation and electron excitation. The faded areas represent the available holes within the conduction band for accepting electrons.

Photon Absorption:

$$COF + h\nu \rightarrow COF$$

Electron-Hole Pair Generation:

$$COF* \rightarrow e^-_{CB} + h^+_{VB}$$

Charge Separation and Transfer:

$$e^-_{CB} \rightarrow e^-_{surface}, h^+_{VB} \rightarrow h^+_{surface}$$

Redox Reactions:

$$e^-_{surface} + A \rightarrow A^-, h^+_{surface} + D \rightarrow D^+$$

Recombination (Loss Process):

$$e^-_{CB} + h^+_{VB} \rightarrow COF + energy$$

- *Interfacial Charge Transfer*: Charge transfer often occurs at the interface between COFs and absorbates (like oxygen or other reactants). Surface modifications that engineer the electronic landscape can enhance these charge transfer processes. For instance, COFs layered with a thin coating of conductive polymers have been shown to enhance interfacial charge transfer rates, facilitating more efficient H_2O_2 production [114].

3.6.2. Role of Photon Absorption

The mechanism of photon-absorption involves the bandgap optimization. The ability to modulate the bandgap of COFs can be crucial for maximizing light absorption across the solar spectrum (Figure 21). Strategies such as copolymerization or incorporating alternative linkers enable the creation of COFs tailored for optimal light utilization. Research has demonstrated that COFs with narrowing bandgaps can double visible light absorption, resulting in a significant increase in overall photocatalytic efficiency for H_2O_2 production [115,116]. The ability of COFs to absorb photons effectively is paramount to their photocatalytic performance. The bandgap of COFs can be tuned through structural modifications, allowing for optimized light absorption across a broader spectrum. Efficient photon absorption leads to an increased generation of electron-hole pairs, enhancing the overall rate of ORR essential for H_2O_2 production [117–120]. This phenomenon is achieved through exciton dynamics. Excitons, formed upon photon absorption, play a pivotal role in determining catalytic performance. Efficient dissociation of excitons into free charges is essential for photochemical reactions. Techniques such as sensitization with colored dyes have been shown to enhance exciton dissociation, thereby boosting the H_2O_2 generation rates significantly.

3.6.3. Reaction Intermediates

Another key aspect of this fundamental catalytic process is the formation and stability of reaction intermediates, which directly influences the efficiency and selectivity of H_2O_2 production. During ORR, adsorbed O_2 undergo a one-electron reduction to form superoxide radicals (O_2^-). These radicals can further react with protons (H^+) or participate in additional reduction steps to yield H_2O_2. Additionally, hydroperoxy radicals (HOO^-) also play a significant role in this mechanism. Understanding the stabilization of these intermediates is crucial for improving H_2O_2 yields. Research has shown that COF can provide a favorable microenvironment for stabilizing these reactive intermediates, which enhances H_2O_2 production while minimizing side reactions (Wang et al., 2024) [121,122]. Moreover, the reaction pathway can shift based on conditions such as pH and temperature, as well as the specific COF employed. COFs designed with tailored functionalities can

direct the selective production of H_2O_2 over undesired side products, underscoring the importance of COF design in influencing reaction selectivity.

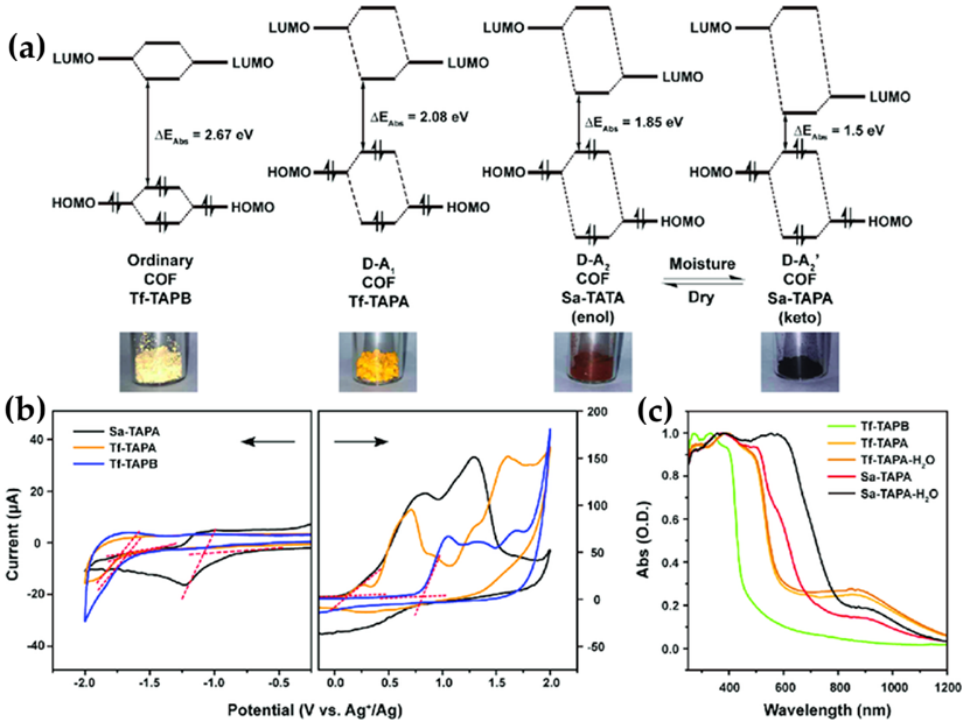


Figure 21. Band gap optimization detailing Band gaps of three COFs. (**a**) Energy level diagrams of Tf-TAPB, Tf-TAPA, and Sa-TAPA (dry and moisture-adsorbed) COFs. (**b**) Cyclic voltammetry of Sa-APA, Tf-TAPA, and Tf-TAPB (**left**: negative scan; **right**: positive scan). (**c**) UV−vis−NIR absorption spectra of Tf-TAPB, Tf-TAPA (dry and wet), and Sa-TAPA (dry and wet) COFs.

Equation (1) (general equation representing adsorption of O_2 on a catalyst);

$$O_2\ (ads) + e^- \rightarrow O_2{\cdot}^-\ (ads) \quad (1)$$

Equation (2) (alkaline medium);

$$O_2\ (ads) + e^- \rightarrow O_2{\cdot}^-\ (ads) \quad (2)$$

Equation (3) (acidic medium);

$$\begin{gathered} O_2\ (ads) + H^+ + e^- \rightarrow HO_2{\cdot}(ads) \\ O_2\ (ads) + e^- \rightarrow O_2{\cdot}^-\ (ads) \end{gathered} \quad (3)$$

Equation (4) (non-aqueous systems);

$$O_2 + e^- \rightarrow O_2{\cdot}^- \quad (4)$$

3.7. Design of COFs for Sustainable H_2O_2 Generation

3.7.1. Modifications for Enhanced Structure—Activity Relationship

To enhance the photocatalytic performance of COFs, researchers have explored a variety of modification strategies that can be broadly categorized as compositional and structural adjustments. The selection of appropriate ligands, such as porphyrins and triazine derivatives, is crucial for constructing COFs with improved stability, light absorption, and charge carrier mobility [123]. Furthermore, optimizing the COF's topology, particularly

through the creation of three-dimensional (3D) structures, offers advantages such as higher thermal stability, larger specific surface area, and enhanced electron transport properties.

Composite formation with other materials, such as MOFs or g-C_3N_4, has also proven effective. COF-MOF composites, often achieved through post-synthesis modification, leverage covalent bonding to improve charge separation and overall stability. Similarly, combining COFs with g-C_3N_4 enhances visible light absorption and charge carrier transport, leading to improved photocatalytic degradation of pollutants. Incorporating metal semiconductors [30] like TiO_2, ZnO, CdS, and MoS_2 into COFs addresses common issues such as wide band gaps and electron-hole recombination, thereby improving the photocatalytic efficiency and stability of the composite materials. Finally, post-synthesis modification, which involves functionalizing COFs after their initial synthesis, allows for the introduction of new properties or enhancement of existing ones, further optimizing photocatalytic activity through surface grafting or the incorporation of additional functional groups. These collective strategies aim to improve the structural integrity, light harvesting capabilities, charge separation efficiency, and overall photocatalytic performance of COFs for the degradation of organic pollutants.

To optimize COFs for photocatalytic H_2O_2 generation, several modifications can be employed to improve their electronic, optical, and catalytic properties, including:

Donor-Acceptor (D-A) Motifs: Incorporating electron-rich (donor) and electron-deficient (acceptor) units into the COF backbone enhances light absorption, promotes charge separation, and improves redox potential, which are critical for efficient O_2 reduction to H_2O_2. For example, the photocatalytic reduction of O_2 to H_2O_2 can be represented as:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

The *Donor-Acceptor* structure facilitates the generation of electrons (e^-) and holes (H^+) under light irradiation, driving this reaction.

Functional Group Integration: The introduction of functional groups such as hydroxyl (-OH) or amine (-NH_2) facilitates O_2 adsorption and activation (Figure 22), enhancing the overall photocatalytic efficiency [124]. For instance, hydroxyl groups can interact with O_2 as follows:

$$O_2 + \text{-OH} \rightarrow \text{-OOH} \rightarrow H_2O_2$$

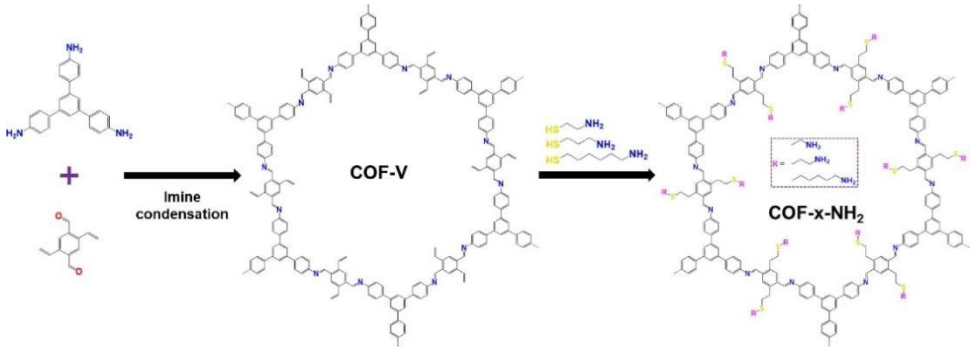


Figure 22. Modification of Pore Surface for COF Functionalization.

Heteroatom Doping: This involves incorporating heteroatoms such as nitrogen (N) or sulfur (S) into the COF structure, in order to tune the electronic properties, improves charge carrier mobility, and reduce recombination losses. For example, nitrogen doping can create active sites for O_2 adsorption and reduction.

$$\text{N-doped COF} + O_2 \rightarrow N - O_2{}^- \rightarrow H_2O_2$$

Co-Catalyst Incorporation: This means embedding co-catalysts, e.g., metal nanoparticles or metal-free species within the COF matrix to further enhance the charge transfer and catalytic activity, leading to higher H_2O_2 yields. For example, a co-catalyst like Pt can accelerate the reduction of O_2 to obtain high yield.

$$O_2 + 2H^+ + 2e^- \rightarrow \text{Pt-}H_2O_2$$

3.7.2. Construction Strategies for Optimal Performance

The construction of COFs with well-defined structures and tailored properties is crucial for achieving high-performance H_2O_2 generation. Precise placement and control of active catalytic sites within the COF ensures accessibility and uniform distribution, resulting in maximized efficiency and promotion of the desired reaction of H_2O_2 generation. It also ensures enhanced stability, improved mass transport, tenability, high surface area and lesser production of by-products.

Crystalline and Porous Frameworks: Designing COFs with high crystallinity and porosity ensures a large surface area, providing abundant active sites and facilitating efficient mass transport of reactants and products. The porous structure allows O_2 to diffuse and react efficiently:

$$O_2 \text{ (adsorbed)} + 2H^+ + 2e^- \rightarrow H_2O_2 \text{ (desorbed)}$$

Tunable Pore Sizes: Precise control over pore sizes allows for optimal O_2 diffusion and H_2O_2 desorption, improving reaction kinetics and selectivity. This ensures that the produced H_2O_2 is efficiently released from the active sites.

Conjugated Backbones: Highly conjugated structures enhance light absorption and charge carrier mobility, which are essential for driving the photocatalytic process. The light absorption generates excitons (electron-hole pairs):

$$\text{COF} + h\nu \rightarrow e^- + H^+$$

These charge carriers then participate in the reduction of O_2 to H_2O_2.

Modular Design: Using pre-designed building blocks with specific functionalities enables the creation of COFs with tailored electronic and structural properties, ensuring a strong structure—activity relationship. For example, a COF with a built-in D-A structure can be represented as:

$$\text{Donor} + \text{Acceptor} \rightarrow \text{D-A-COF}$$

Combining these modification and construction strategies can be engineered towards building COFs that exhibit exceptional photocatalytic performance, making them promising materials for sustainable H_2O_2 generation. Figure 23 shows the various reversible reactions and pathways utilized for COF synthesis.

3.8. Material Modifications for Enhanced Activity in COF-Based Photocatalysts

To optimize COFs for catalytic H_2O_2 production, various material modification strategies can be employed. These modifications aim to enhance light absorption, improve charge carrier dynamics, increase active site exposure, and reduce recombination rates. Below, we discuss the current state of material modifications by incorporating advanced strategies such as crystal morphology engineering, insertion of metal atoms, and the design of spatially separated redox sites.

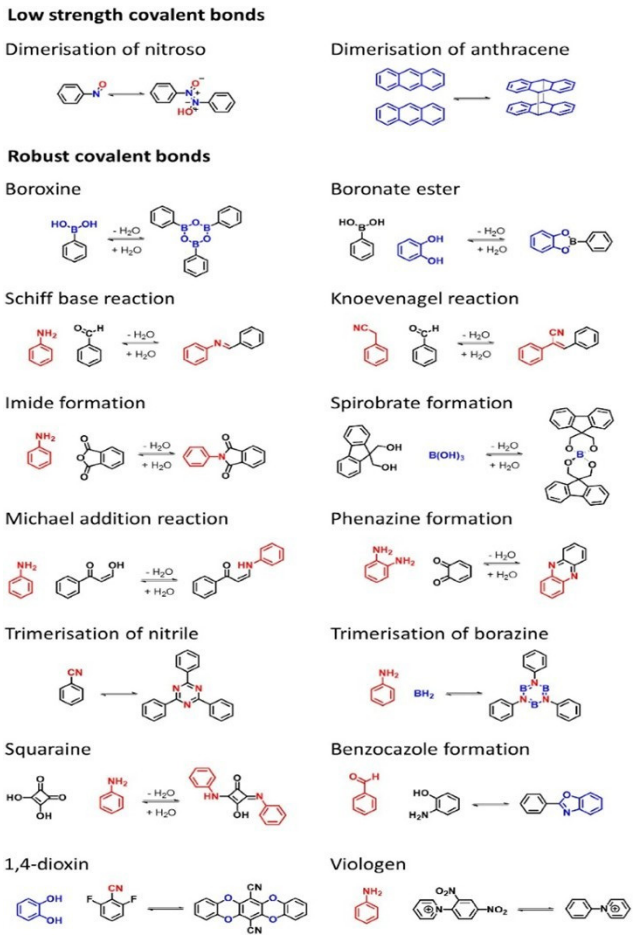


Figure 23. Reversible Reactions for COF Construction indicating formation of covalent bonds for various linkers [125].

3.8.1. Functional Group Integration

The purpose of functional group integration is to tailor the electronic properties and surface chemistry of COF materials, enabling precise control over their catalytic behavior in H_2O_2 generation. Introducing specific functional groups (e.g., -OH, -COOH, -NH_2) into the COF structure can enhance its affinity for reactants like H_2O and O_2, improve light absorption, and facilitate charge transfer. For example, electron-donating groups like -NH_2 can increase the electron density of the COF backbone, promoting the reduction of O_2 to H_2O_2 by lowering the energy barrier for the $2e^-$ ORR pathway, as demonstrated in amine-functionalized COFs achieving yields up to 5000 μmol h^{-1} g^{-1} under visible light. Conversely, electron-withdrawing groups such as -COOH can enhance hole mobility, aiding water oxidation and reducing recombination losses by 20–30%.

The role of functional groups in modulating hydrophobicity prevents H_2O_2 decomposition in aqueous environments, improving selectivity to >90%. Critical analysis shows that over-functionalization can block pores, reducing surface area by 15–25% and impacting mass transport, a trade-off that requires balanced grafting (e.g., 10–15% coverage) for optimal performance. Compared to traditional metal oxide catalysts like TiO_2, which lack such tunability, COF functional integration allows for site-specific catalysis, as seen in -OH-modified COFs that stabilize intermediates like $\cdot O_2^-$, boosting efficiency by 1.5–2 times. Future optimizations could explore combinatorial approaches, such as dual-group integration (e.g., -OH and -NH_2), to synergistically enhance both ORR and WOR pathways.

3.8.2. Heteroatom Doping

Doping with heteroatoms modifies the electronic structure by introducing active sites, allowing for fine-tuned bandgap engineering and improved photocatalytic activity in COF-based H_2O_2 generation. Incorporating heteroatoms such as nitrogen, sulfur, or boron into the COF can alter its bandgap (e.g., reducing from 2.5 eV to 1.8 eV in N-doped COFs), enhance charge carrier separation, and create additional active sites for photocatalytic reactions. For instance, nitrogen doping can introduce mid-gap states that improve visible light absorption (extending response to >500 nm) and provide additional sites for O_2 adsorption and activation, leading to H_2O_2 yields of 4500 μmol h^{-1} g^{-1}, a 40% increase over undoped counterparts.

Sulfur doping enhances sulfur's electron-donating properties, promoting selective $2e^-$ ORR and reducing side reactions like O_2 evolution by 25%. Boron doping, on the other hand, creates Lewis acidic sites that stabilize hydroperoxyl intermediates (HO_2^-), improving selectivity to 92–95%. Critical comparison with heteroatom-doped carbon materials (e.g., N-doped g-C_3N_4) shows COFs offer superior porosity for better reactant diffusion, but doping can introduce defects that lower crystallinity if not controlled, potentially decreasing stability by 10–20%. Co-doping (e.g., N and S) synergistically narrows the bandgap while maintaining framework integrity, as evidenced by dual-doped COFs achieving AQY of 10–12%. To mitigate challenges like dopant aggregation, precise control via post-synthetic methods is recommended, ensuring uniform distribution for long-term performance in sustainable H_2O_2 systems.

3.8.3. Co-Catalyst Incorporation

The introduction of co-catalysts enhances charge separation and provides active sites for specific reactions, making it a key strategy for improving COF performance in H_2O_2 generation. Materials like Pt, CoO_x, or MoS_2 can be integrated into COFs to accelerate specific redox reactions, acting as electron sinks or hole reservoirs that reduce recombination rates by 30–50%. For example, Pt nanoparticles embedded in COFs facilitate the reduction of O_2 to H_2O_2 by lowering the overpotential, achieving faradaic efficiencies (FE) of >95% in electrocatalytic systems. Similarly, CoO_x co-catalysts promote water oxidation, enhancing overall photocatalytic yields to 6000 μmol h^{-1} g^{-1} by improving hole extraction.

Uniform loading (e.g., 1–5 wt.%) prevents aggregation and maintains porosity, while overloading can block pores and reduce efficiency by 15–20%. Critical analysis compares noble-metal co-catalysts (e.g., Pt) with earth-abundant alternatives (e.g., NiS), noting that the latter offer cost-effective stability (e.g., >200 h) but lower activity (FE 80–85%). Additionally, hybrid co-catalysts (e.g., Pt-CoO_x), enable dual-functionality for simultaneous ORR and WOR, boosting solar-to-chemical conversion efficiency to 1–2%. However, Co-catalyst leaching challenge in acidic media can be addressed through covalent anchoring, ensuring long-term durability. This integration not only elevates COF performance but also aligns with green chemistry by minimizing metal usage through single-atom co-catalyst designs.

3.8.4. Crystal Morphology Engineering

This increases active site exposure and promotes faster charge transfer. By Altering the crystal morphology of COFs, such as constructing 2D structures or engineering specific facets, this can significantly enhance their photocatalytic performance. Two-dimensional COFs offer a high surface area and abundant active sites, while facet engineering can expose specific crystal planes that favor certain reactions. For example, exposing (001) facets in a COF can enhance charge separation and provide more active sites for H_2O_2 production.

Nanosheet structures shorten migration paths, reducing losses by 25% compared to bulk COFs. Critical comparison with 3D COFs shows 2D morphologies excel in light

harvesting due to thinner layers (e.g., 5–10 nm), but 3D variants provide better mechanical stability for long-term use (>300 h). Additional points include template-assisted synthesis for hierarchical morphologies (e.g., hollow spheres), which improve mass transport and yield by 1.5 times, and solvothermal control of aspect ratios to balance surface area with stability. Challenges such as scalability in morphology control can be overcome with mechanochemical methods, ensuring uniform facets for industrial H_2O_2 applications.

3.8.5. Insertion of Single-Atom Catalysts (SACs)

In order to enhance charge carrier dynamics and reduce recombination of COFs, SACs can be introduced into the framework. SACs insertion involves the incorporation of isolated metal atoms (e.g., Fe, Co, Ni) into the COF structure. These metal atoms can act as highly active sites for specific reactions, improve charge carrier separation, and reduce recombination rates. For instance, Fe-SACs can enhance the activation of O_2 and promote its reduction to H_2O_2, while also improving the overall stability of the COF.

SACs minimize metal loading (0.5–2 wt.%), reducing costs and environmental impact compared to nanoparticle catalysts. Critical analysis shows Co-SACs excel in WOR by facilitating hole transfer, but Fe-SACs are superior for ORR due to optimal d-band centers. SAC stabilization via coordination with N or O atoms in COFs, prevents aggregation and extends stability, and dual-SAC systems (e.g., Fe-Co) for balanced redox, boosts efficiency. Challenges like SAC migration under high potentials can be addressed through strong anchoring sites, ensuring SAC-COFs outperform traditional catalysts in sustainable H_2O_2 production.

3.8.6. Spatially Separated Redox Sites

Designing COFs with spatially separated redox sites, such as donor-acceptor (D-A) structures, can significantly enhance charge separation and reduce recombination. In D-A structures, electron-rich (donor) and electron-deficient (acceptor) units are arranged in a way that promotes directional charge transfer. This spatial separation ensures that electrons and holes migrate to different regions of the COF, reducing recombination and improving the efficiency of H_2O_2 production.

Further details emphasize the use of alternating D-A motifs (e.g., triazine as acceptor and pyrene as donor), which create built-in electric fields for ultrafast charge migration (92%), and integration with heteroatoms for fine-tuned band alignment, minimizing energy losses. Challenges like mismatched energy levels can be mitigated through DFT simulations, ensuring D-A COFs achieve solar-to-H_2O_2 efficiencies > 1% for scalable applications.

3.8.7. Integration of Modification Strategies

Functional group integration and heteroatom doping can be combined to tailor the electronic properties and surface chemistry of COFs. Crystal morphology engineering can be used to expose specific facets that enhance charge separation, while SACs can be incorporated to provide highly active sites for O_2 reduction. Similarly, spatially separated redox sites can further improve charge separation, ensuring efficient utilization of photogenerated carriers for H_2O_2 production.

It shows the structural and electronic modifications in COFs induced by doping (Figure 24). The central focus is the D-A relationship, indicating alteration in electronic distribution between donor and acceptor sites induced by doping. This modification likely enhances charge transfer and modulates optoelectronic properties, such as bandgap and conductivity, due to changes in the local chemical environment. The strategic introduction of dopants tunes the COF's functionality, relevant for applications in catalysis or energy conversion, aligning with advanced materials science research.

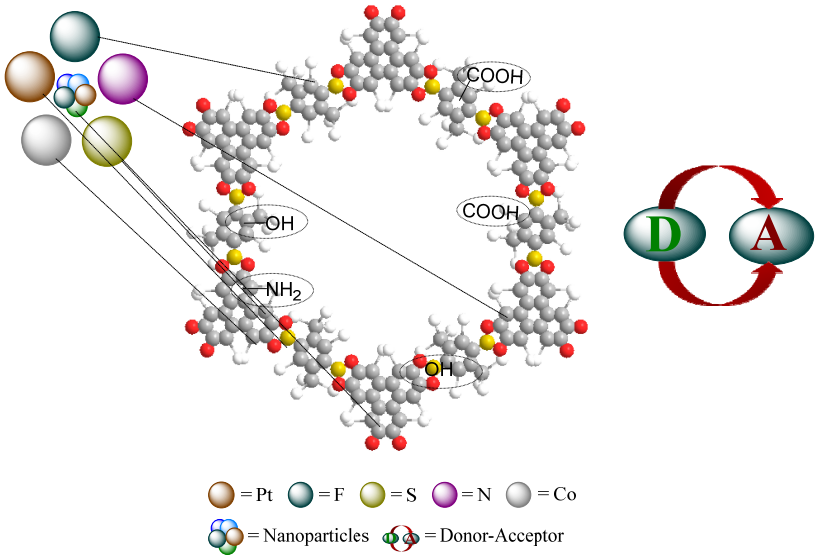


Figure 24. Doping of COFs and influence of dopants on Donor-Acceptor relationship for a S-containing COF sample.

3.9. Band Engineering for H_2O_2 Generation

In semiconductor-based photocatalysis, the band potential plays a critical role in determining the feasibility of redox reactions. COFs as a class of porous and crystalline materials, exhibit tunable band structures, which influence their ability to facilitate the ORR for H_2O_2 generation. The key parameters in this analysis include the conduction band minimum (CBM) and the valence band maximum (VBM), which dictate charge carrier separation and transfer efficiency. In electron transfer for oxygen reduction, the CBM should be lower than the one-electron reduction potential of O_2 (E_0 = +0.695 V_{NHE}), enabling electron transfer to molecular oxygen, facilitating the formation of O_2^- radicals, which subsequently undergo protonation and further reduction to yield H_2O_2. Secondly, in hole-induced oxidation reaction, the VBM must be positioned below the oxidation potential of H_2O ($E_0 \approx$ +1.23 V_{NHE}) to enable hole-mediated oxidation reactions without excessive charge recombination. Similarly, an optimally placed VBM ensures sufficient oxidative driving force to sustain charge separation while preventing undesirable side reactions.

Band engineering in COFs offer structural flexibility that allows for various synthetic strategies such as D-A design, functionalization, and linker and π-conjugation modifications.

Band potential engineering in COFs is a critical design strategy for optimizing H_2O_2 generation. By fine-tuning the CBM and VBM to match the electrochemical requirements of ORR, charge separation can be enhanced, excited-state lifetimes can be prolonged, and the photocatalytic H_2O_2 yield can be ultimately improved. However, future studies should explore real-time electronic structure modulation via external stimuli, such as applied bias or molecular encapsulation, to further optimize performance.

In a 2022 study by Ni and colleagues, the engineering of Flat Bands and Dirac Bands in 2D COFs was studied. The study examined the relationships between molecular orbital symmetry, lattice symmetry, and electronic structure characteristics in COFs. It also provided insights into how band engineering can influence electronic properties [126]. Other studies explored band gap opening from displacive instabilities in layered COF materials, investigating how these phenomena affect band dispersion and band gap energy—crucial for optimizing photocatalytic performance. Similarly, a study on optoelectronic processes in COFs discussed the integration of semiconducting properties in COFs, including band structure tuning for applications in sensors, photocatalysis and energy storage. Methodologies used in band gap engineering in COFs are DFT calculations, development of

tight-binding models to analyze electronic band dispersions in COFs with specific lattice symmetries, crystal orbital overlap population (POOP) analysis to study bonding interactions within materials, and contributory effects of electronic states to charge transfer processes, and optoelectronic characterization, such as UV-Vis and photoluminescence measurements [127–130].

3.10. Electronic System for H_2O_2 Generation: COF-Based Electrodes

The electrochemical two-electron oxygen reduction reaction ($2e^-$ ORR) is a promising sustainable route for on-site H_2O_2 production, offering a green alternative to the energy-intensive anthraquinone process. A critical component of this technology is the design of efficient, selective, and stable electrocatalysts. Covalent organic frameworks (COFs) in this case, have proven to be the next-generation electrode materials for H_2O_2 generation due to their tunable electronic structures, high surface areas, and well-defined porous architectures [131].

3.10.1. Electronic Structure and Catalytic Mechanism

The extended π-conjugated systems facilitate efficient electron transport. The band gap, HOMO-LUMO levels and charge distribution of COFs can be precisely engineered at the molecular level by selecting appropriate building blocks (triazine, porphyrin or phenazine units) and linkage types (imine, B-ketoenamine, olefin) [132]. This tenability enables optimization of the binding energy of oxygen intermediates (•OOH), thereby enhancing selectivity toward the $2e^-$ ORR pathway over the competing $4e^-$ pathway that yields water.

3.10.2. Design Strategies for COF-Based Electrodes

Recent studies have demonstrated that incorporating redox-active moieties such as quinones, metalloporphyrins, or heteroatom-doped sites such as N, B, F into COF backbones can significantly boost H_2O_2 activity [133,134]. For example, imine-linked COFs with built-in quinone groups exhibit excellent selectivity for $2e^-$ ORR by stabilizing the •OOH intermediate through favorable electronic interactions. Additionally, the ordered nanopores of COFs facilitate mass transport of O_2 and electrolyte ions, while also exposing abundant active sites.

To improve electrical conductivity, which is a common limitation of pristine COFs, strategies such as π-extension, D-A architecture design, and integration with conductive substrates (e.g., carbon cloth, graphene, or conductive polymers) have been employed. Some COFs have even demonstrated intrinsic semiconducting or metal-like behavior when properly designed, enabling direct use as freestanding electrodes.

3.10.3. Performance and Stability

COF-based electrodes have shown remarkable H_2O_2 Faradaic efficiencies (often >90%) and production rates in both acidic and neutral media. Their crystalline nature allows for precise structure—activity correlation studies via in situ spectroscopy and computational modeling such as DFT. Moreover, the robust covalent linkages in COFs confer excellent chemical and electrochemical stability under operational conditions, a crucial advantage over molecular catalysts or metal nanoparticles that may leach or degrade.

Despite the promise, scaling up COF synthesis still faces some challenges like ensuring long-term mechanical integrity, and enhancing electronic conductivity without compromising porosity or catalytic site density. Developing hierarchical COF architectures, hybrid COF/composite electrodes, and flow-cell configurations suitable for continuous H_2O_2 production can mitigate the stated challenges. Also, integrating COF electrodes with

renewable energy sources could enable decentralized green energy-driven H_2O_2 synthesis, advancing the vision of a sustainable chemical economy.

4. Application of H_2O_2 and New Light for On-Site Detection

4.1. Applications of H_2O_2

H_2O_2 is a versatile chemical compound widely utilized across various industries due to its strong oxidizing properties. Its applications span from agriculture to pharmaceuticals and textiles, making it an essential substance in both industrial and environmental contexts (Figure 25).

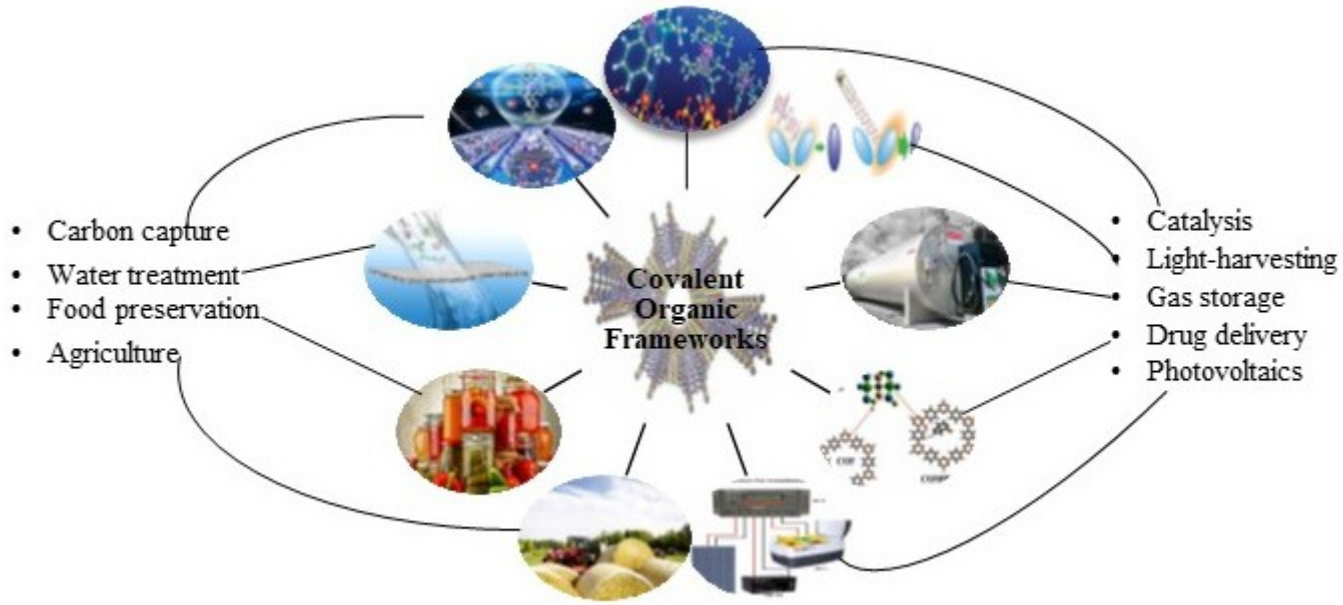


Figure 25. Various applications of COFs in different fields.

(a) Agriculture (Pest Control)

In agriculture, H_2O_2 serves as an effective pest control agent [135]. Its strong oxidizing capability allows it to act as a disinfectant and fungicide, helping to manage plant diseases and pests. According to Zaib et al., the application of H_2O_2 in agricultural settings not only aids in controlling fungal pathogens but also promotes plant growth by enhancing root development and nutrient uptake. This dual functionality makes H_2O_2 a valuable tool for sustainable agricultural practices, reducing the reliance on chemical pesticides and minimizing environmental impact [136].

(b) Pharmaceuticals

In the pharmaceutical industry, H_2O_2 is employed as a disinfectant and antiseptic agent [137]. It is commonly used for sterilizing surgical instruments, cleaning wounds, and as a preservative in certain formulations. Lee et al. highlighted that H_2O_2′ ability to release reactive oxygen species (ROS) makes it effective in killing bacteria [138] and viruses [139], thus ensuring a sterile environment in healthcare settings. Furthermore, its role in oxidative stress studies provides insights into various disease mechanisms, making it a compound of interest in pharmaceutical research.

(c) Bleaching Agent in the Textile Industry

H_2O_2 is extensively used as a bleaching agent in the textile industry due to its effectiveness and environmentally friendly profile compared to traditional chlorine-based bleaches. Its application in bleaching processes helps achieve brighter and whiter fabrics without the

harmful byproducts associated with chlorine bleaching. Lima et al. reported that H_2O_2 is particularly advantageous in cotton and other cellulose-based textiles, as it does not damage the fibers while providing excellent bleaching efficiency. This characteristic aligns with the growing demand for sustainable practices in the textile industry, making H_2O_2 a preferred choice for manufacturers [140].

(d) Water Treatment

H_2O_2 is increasingly utilized in water treatment processes due to its strong oxidizing properties. It can effectively degrade organic pollutants, disinfect water, and reduce odor and color. Several studies highlighted the use of H_2O_2 in advanced oxidation processes (AOPs) for treating wastewater, where it works in combination with UV light or catalysts to generate hydroxyl radicals that break down harmful contaminants. This application not only enhances water quality but also supports regulatory compliance in wastewater management [141–144].

(e) Food Preservation

H_2O_2 is also applied in the food industry as a sanitizing agent to ensure food safety and extend shelf life. Its antimicrobial properties make it effective against a wide range of pathogens, including bacteria, yeasts, and molds. H_2O_2 was shown to be effective in reducing microbial load on fresh produce, thus improving food safety and minimizing spoilage during transportation and storage. This application is crucial in maintaining public health and minimizing foodborne illnesses [145–147].

(f) Sterilization and Disinfection

H_2O_2 is a powerful oxidizing agent widely used for sterilization and disinfection in medical environments, food processing, and water treatment. COF-based photocatalytic systems can generate H_2O_2 on-site, providing a sustainable and cost-effective alternative to traditional H_2O_2 production methods. in medical environments, COF-based systems can be integrated into air or surface sterilization devices in hospitals to continuously produce H_2O_2, reducing the risk of infections. Similarly in water treatment, COF-based membranes or reactors can be used to generate H_2O_2 for disinfection, eliminating harmful pathogens without the need for chemical storage of transportation. COF-based systems can also be used in food industries for food processing facilities for sterilization and packaging, ensuring food safety and shelf-life extension.

(g) Pollution Remediation

H_2O_2 is a key reagent in AOPs for degrading organic pollutants in water and air. COF-based photocatalysts can produce in situ H_2O_2, enabling efficient degradation of pollutants such as dyes, pharmaceuticals, and pesticides. For example, COF-based systems can be used to degrade organic dyes like Rhodamine B in textile wastewater. The in situ production of H_2O_2, combined with visible light irradiation, generates hydroxyl radicals (•OH) that break down the dye molecules into non-toxic byproducts. Secondly, COF-based photocatalysts can degrade pharmaceutical residues in water, addressing the growing concern of pharmaceutical pollution in aquatic ecosystems. In air purification, COF-based systems can be integrated into air purifiers to generate H_2O_2 for degrading volatile organic compounds (VOCs) and other airborne pollutants.

4.2. On-Site Detection Technologies

The ability to detect H_2O_2 concentrations in real-time is crucial for various applications, including environmental monitoring and clinical diagnostics. Emerging technologies, particularly those utilizing COFs, offer promising strategies for on-site detection. Real-time monitoring of H_2O_2 concentrations is crucial for optimizing photocatalytic systems and

ensuring safe and efficient operation. The mentioned advanced detection techniques are as follows:

Fluorescence Quenching: Fluorescence-based sensors can detect H_2O_2 by measuring changes in fluorescence intensity. For example, H_2O_2 can quench the fluorescence of certain dyes or quantum dots, providing a sensitive and selective detection method.

Electrochemical Sensors: Electrochemical sensors measure H_2O_2 concentrations by detecting the current generated during its redox reaction at an electrode surface. These sensors are highly sensitive, portable, and suitable for integration with COF-based systems.

Colorimetric Detection: Colorimetric sensors use color-changing reagents (e.g., titanium oxysulfate) to detect H_2O_2. The intensity of the color change can be quantified using a spectrophotometer or even a smartphone camera, enabling simple and cost-effective on-site detection.

4.2.1. Integration of COF-Based Systems with Detection Technologies

Combining COF-based photocatalytic systems with advanced detection techniques enables real-time monitoring and control of H_2O_2 production. For example:

Flow Reactors: COF-based photocatalytic flow reactors can be equipped with electrochemical sensors to continuously monitor H_2O_2 concentrations and adjust reaction conditions for optimal performance.

Portable Devices: COF-based systems integrated with fluorescence or colorimetric sensors can be used in portable devices for on-site H_2O_2 production and detection in remote or resource-limited settings.

Smart Systems: COF-based photocatalytic systems can be connected to IoT-enabled sensors for real-time data collection and analysis, facilitating automated control and optimization.

4.2.2. Specific Examples of Practical Applications

COF-based systems with specific characters enable wide practical applications (Figure 25). Additionally, COFs have shown promise in various environmental applications, including sterilization, water treatment, and dye degradation (Figure 26). These materials leverage their porous structure to achieve high efficiency.

Medical Sterilization: A COF-based photocatalytic device integrated into a hospital HVAC system continuously produces H_2O_2 for air sterilization, reducing the spread of airborne pathogens.

Textile Wastewater Treatment: A COF-based reactor treats textile wastewater by generating H_2O_2 in situ, degrading Rhodamine B and other dyes into harmless byproducts.

Portable Water Purification: A portable COF-based device equipped with a colorimetric sensor produces and monitors H_2O_2 for disinfecting drinking water in remote areas.

4.2.3. Emerging Strategies for Real-Time Monitoring

Recent advancements in sensor technologies have led to the development of COF-based sensors capable of detecting H_2O_2 with high sensitivity and selectivity. COFs, known for their tunable porosity and functionalization possibilities, provide an ideal platform for sensing applications. Yue et al. demonstrated a COF-based sensor that utilizes fluorescence quenching to detect H_2O_2 concentrations in real-time. The sensor exhibited a rapid response time and a wide detection range, making it suitable for various applications, from industrial monitoring to food safety [148].

Additional studies have illustrated innovative sensor designs, such as the electrochemical sensors [149] developed by Zhao et al., which show excellent sensitivity and selectivity towards H_2O_2 even in the presence of interferents. These innovative strategies enable accurate real-time monitoring in both environmental settings and industrial processes. The

work by Park et al. also introduced a piezoelectric sensor that offers high portability and low detection limits, making H_2O_2 detection feasible for on-site applications [150].

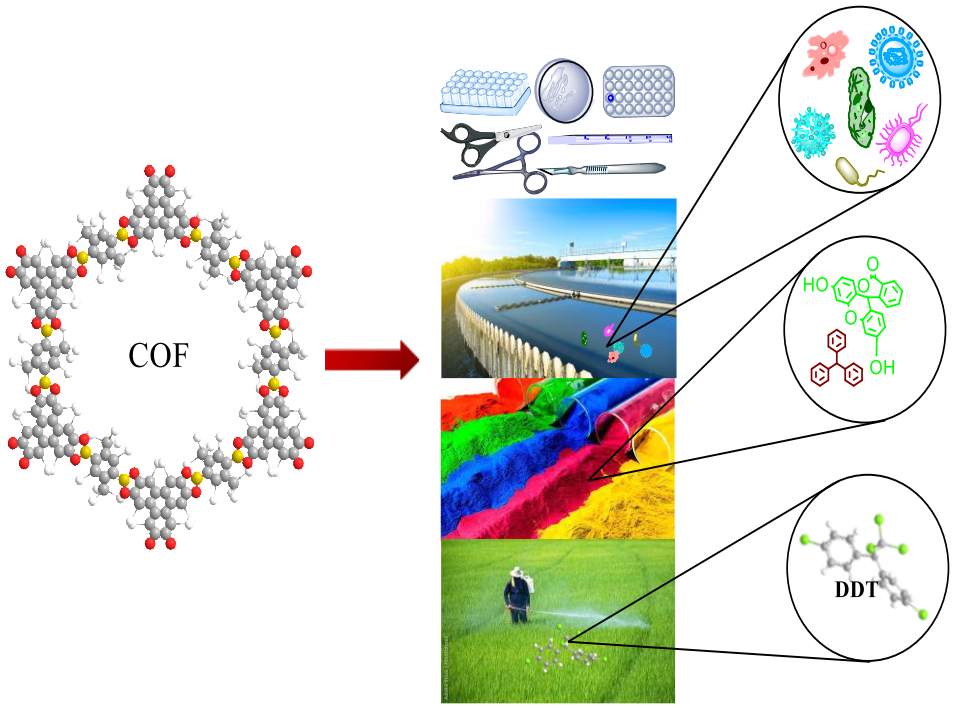


Figure 26. Various applications of COFs in sterilization, water treatment and dye degradation.

4.2.4. Benefits of COFs in Detecting H_2O_2

COFs offer several advantages in the detection of H_2O_2, particularly in environmental monitoring and clinical diagnostics.

Environmental Monitoring: COF-based sensors can detect trace amounts of H_2O_2 in environmental samples, such as water and air, helping to assess pollution levels and oxidative stress in ecosystems. Notable literatures highlighted COFs' capability to selectively capture H_2O_2 from complex matrices, enhancing the accuracy of environmental assessments. This feature is crucial for ensuring compliance with environmental regulations and protecting public health [151–156].

Clinical Diagnostics: In clinical settings, accurate detection of H_2O_2 is essential for monitoring oxidative stress and related diseases. COF-based sensors can provide rapid and sensitive detection of H_2O_2 levels in biological samples, aiding in the diagnosis and management of conditions such as diabetes and cardiovascular diseases. Wang et al. reported on a COF sensor that demonstrated high selectivity for H_2O_2 in serum samples, showcasing its potential for point-of-care diagnostics [154–156].

Sustainability: The use of COF-based sensors can contribute to more sustainable practices by utilizing less hazardous materials and generating less waste than traditional detection methods. The development of COFs often prioritizes environmentally friendly synthesis routes, enhancing the overall sustainability of sensing technologies.

Cost-Effectiveness: COFs are derived from inexpensive organic building blocks, making them a cost-effective option for high-performance sensors. Their ease of synthesis and functionalization allows for mass production, reducing the overall cost of detection devices. These attributes make COF-based sensors accessible for various applications, from industrial monitoring to everyday consumer products.

The applications of H_2O_2 span diverse industries, including agriculture, pharmaceuticals, textiles, water treatment, and food preservation, highlighting its versatility and importance. Advances in on-site detection technologies, particularly through COF-based

sensors, provide innovative solutions for real-time monitoring of H_2O_2 concentrations. These developments not only enhance our understanding of H_2O_2′ role in various contexts but also pave the way for improved environmental and clinical assessments.

4.3. Perspective

4.3.1. Direct Generation from Electronic or Organic Methods

The generation of H_2O_2 through innovative electronic or organic methods has garnered significant attention in recent years. This perspective highlights the advancements in electrocatalysis and organic photoredox reactions as promising pathways for sustainable and efficient H_2O_2 production. As the demand for H_2O_2 continues to rise across various applications, the need to overcome challenges associated with traditional production methods becomes increasingly crucial.

4.3.2. Novel Pathways for H_2O_2 Generation

(a) Electrocatalysis

Electrocatalysis represents a cutting-edge approach for the direct generation of H_2O_2. This method involves the electrochemical reduction of O_2 to produce H_2O_2, typically at ambient conditions, as described in (Figure 27). Recent studies have focused on optimizing electrocatalysts to enhance the efficiency and selectivity of this process. For example, Lee et al. reported the use of transition metal high-entropy based catalysts [157] that exhibit high catalytic activity and stability for the electrochemical synthesis of H_2O_2, achieving significant improvements in yield and reduction potential. The scalability of this process presents a significant advantage over traditional production methods, such as the anthraquinone process, which is energy-intensive and environmentally detrimental.

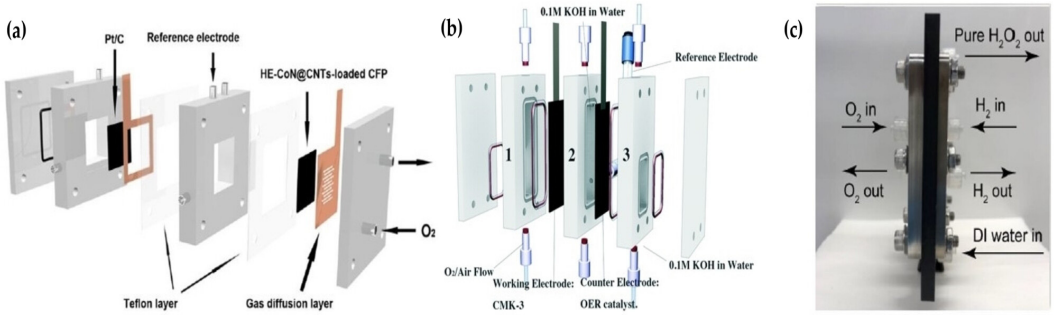


Figure 27. Various H_2O_2 Generation Devices Schematic diagram for different types of hydrogen peroxide production devices. (**a**) A device with two electrolyte compartments, a single FFP, no membrane, and a fixed electrolyte. (**b**) A two-compartment device developed into flow type for modular-scale and low-cost H_2O_2 electrosynthesis. (**c**) An advanced device with double membranes and solid electrolyte maximally strengthened the mass transfer between the important ions (H^+, HO_2^-, OH^-) and catalysts [158].

(b) Organic Photoredox Reactions

Organic photoredox reactions are another promising method for synthesizing H_2O_2, utilizing visible light to drive the formation of H_2O_2 from organic substrates [159]. This method leverages photocatalysts to facilitate the unthermodynamic synthesis of H_2O_2 in a more sustainable manner. Some studies demonstrated that using tailored organic photocatalysts can significantly enhance the selectivity and yield of H_2O_2 from various organic precursors, enabling the use of abundant solar energy for its generation [160–162]. This pathway not only minimizes reliance on fossil fuels but also opens the door to cleaner, renewable methods for H_2O_2 production.

4.3.3. Scalability

Scaling up COF-based photocatalytic systems for industrial H_2O_2 production presents significant challenges, including maintaining structural integrity, ensuring uniform light distribution, and achieving cost-effective synthesis. Key barriers include low-yield synthesis (gram-scale vs. ton-scale), mechanical fragility in large reactors, and high costs (~$10–100/g for lab-scale COFs). No pilot-scale demonstrations for COF H_2O_2 have been reported; however, general TEA for photocatalytic H_2O_2 suggests LCOH ~$3–6/kg, competitive with anthraquinone ($2–3.5/kg) if scaled. Critically, solvent-free mechanochemistry could reduce costs by 50%, but stability in flow reactors remains untested [41,163].

Potential Solutions

Modular Reactor Designs: Developing modular photocatalytic reactors can facilitate scalability by allowing incremental expansion. These reactors can be designed to optimize light absorption, mass transfer, and reaction kinetics, ensuring efficient H_2O_2 production at larger scales.

Continuous Flow Systems: Implementing continuous flow reactors instead of batch systems can improve scalability and productivity. Flow systems enable consistent reaction conditions and easier separation of products, making them suitable for industrial applications.

Scalable Synthesis Methods: Developing cost-effective and scalable synthesis methods for COFs, such as mechanochemical or solvent-free approaches, can reduce production costs and enable large-scale manufacturing.

4.3.4. Integration with Renewable Energy

Integrating COF-based photocatalytic systems with renewable energy sources can enhance sustainability and reduce reliance on fossil fuels. The Potential Strategies for integration are outlined below.

Solar Energy Integration: COF-based systems can be directly coupled with solar panels to harness sunlight for photocatalytic H_2O_2 production. This approach aligns with the goal of sustainable and green chemistry.

Wind Energy Utilization: In regions with abundant wind resources, wind turbines can provide the electrical energy needed to power photocatalytic reactors, especially for processes requiring additional energy inputs (e.g., UV light sources).

Hybrid Energy Systems: Combining multiple renewable energy sources (e.g., solar and wind) with energy storage systems (e.g., batteries) can ensure a stable and continuous energy supply for COF-based photocatalytic systems.

4.3.5. Life Cycle and Techno-Economic Analysis

Conducting life cycle assessments (LCA) and techno-economic analyses (TEA) is essential to evaluate the environmental impact, cost-effectiveness, and practical viability of COF-based H_2O_2 production systems. Key considerations for life cycle assessment and techno-economic analysis are outlined below.

(a) Life Cycle Assessment (LCA):

Raw Material Sourcing: Assess the environmental impact of sourcing raw materials for COF synthesis, including the energy and resources required.

Manufacturing Process: Evaluate the energy consumption, waste generation, and emissions associated with COF synthesis and reactor fabrication.

End-of-Life Disposal: Analyze the recyclability and environmental impact of decommissioned COF-based systems.

(b) Techno-Economic Analysis (TEA):

Capital and Operating Costs: Estimate the costs of building and operating COF-based photocatalytic systems, including materials, energy, and maintenance.

Production Efficiency: Compare the cost-effectiveness of COF-based systems with conventional H_2O_2 production methods, such as the anthraquinone process.

Market Viability: Assess the potential market demand for COF-based H_2O_2 production systems and identify niche applications where they can offer competitive advantages.

4.4. Sustainable and Efficient Systems for H_2O_2 Production

The potential for creating sustainable and efficient systems for H_2O_2 production lies in addressing the limitations associated with traditional methods.

Environmental Benefits: Conventional H_2O_2 production methods often involve the use of toxic solvents, high energy input, and the generation of hazardous waste. In contrast, the new electronic and organic pathways emphasize the use of water and air as feedstocks, aligning with the principles of green chemistry. The move toward cleaner processes significantly reduces the environmental impact and increases safety in industrial applications.

Efficiency and Economic Viability: The advances in electrocatalytic and photoredox systems hold promise for improving the overall efficiency of H_2O_2 production [164,165]. By minimizing energy consumption and maximizing yield, these methods can potentially lower production costs. For example, Lin et al. indicated that integrating renewable energy sources, such as solar and wind [166,167], with electrocatalytic systems can optimize energy input and reduce operating costs further, making H_2O_2 production economically viable on a larger scale [168].

Scalability and Industrial Integration: As the technology matures, scalability remains a crucial consideration for industrial application. Research into modular setups for electrocatalysis and photoredox reactions can provide flexible and adaptable solutions for H_2O_2 production within existing chemical manufacturing infrastructures. This adaptability could facilitate the transition toward more sustainable production practices that can seamlessly integrate with current operations.

Overcoming Traditional Challenges: The challenges faced in traditional H_2O_2 production, such as safety risks associated with concentrated H_2O_2 and logistics of transportation, can be mitigated through these new methods. By generating H_2O_2 on-site and under milder conditions, industries can enhance safety and reduce the complexities of storage and transport.

4.5. Emerging Opportunities and Research Directions

Machine Learning and Computational Design: Leveraging machine learning and computational modeling can accelerate the discovery of new COF structures with optimized photocatalytic properties, reducing the time and cost of experimental screening.

Multifunctional COFs: Developing multifunctional COFs that can simultaneously perform multiple tasks (e.g., H_2O_2 production, pollutant degradation, and CO_2 reduction) can enhance their utility and economic viability.

Self-Healing Materials: Incorporating self-healing properties into COFs can improve their durability and longevity, reducing the need for frequent replacement and maintenance.

Similarly, integrating COFs with high-entropy alloys (HEAs) could create a promising avenue for advancing hydrogen and H_2O_2 generation technologies. By leveraging the multi-metallic composition and tunable electronic properties of HEAs with the high surface area, porosity, and chemical stability of COFs, HEA-doped COF materials can offer enhanced catalytic activity and durability for electrochemical and photocatalytic H_2

and H_2O_2 evolution reactions (HER) and other small-to-large scale material needs. The synergy between HEAs, known for their excellent conductive properties and resistance to degradation, and COFs, known for their design flexibility and active site accessibility, can lead to efficient, cost-effective, and scalable catalysts. Future research should focus on optimizing HEA—COF interfaces, exploring green synthesis methods, and evaluating performance under industrial conditions, paving the way for sustainable hydrogen and hydrogen peroxide production systems.

5. Conclusions

H_2O_2 is a versatile and environmentally friendly oxidizing agent with widespread applications across industries, including agriculture, pharmaceuticals, textiles, water treatment, and food preservation. However, traditional methods of H_2O_2 production, such as the anthraquinone process, are energy-intensive, generate harmful by-products, and pose significant environmental and economic challenges. This has spurred the development of sustainable and efficient alternatives, particularly through the use of COFs in photocatalytic and electrocatalytic H_2O_2 generation.

COFs, with their tunable porosity, high surface area, and functionalization capabilities, have emerged as promising materials for H_2O_2 production. Their structural versatility allows for the incorporation of active sites tailored for specific reactions, enhancing both selectivity and efficiency. Recent advancements in COF-based systems have demonstrated significant improvements in H_2O_2 yields, driven by optimized charge transfer, photon absorption, and stabilization of reaction intermediates. These developments highlight the potential of COFs to revolutionize H_2O_2 production by enabling milder reaction conditions, reduced environmental impact, and scalable processes.

Photocatalytic and electrocatalytic methods leveraging COFs have shown particular promise. Photocatalysis harnesses solar energy to drive H_2O_2 generation, while electrocatalysis utilizes electrochemical reduction of oxygen. Both approaches benefit from the structural and electronic properties of COFs, which enhance mass transport, reaction kinetics, and overall catalytic performance. Furthermore, the integration of COFs into flexible and scalable electrode architectures has opened new avenues for practical applications, including on-site H_2O_2 generation and real-time monitoring using COF-based sensors. However, despite these advancements, challenges remain in achieving high catalytic efficiency, long-term stability, and industrial scalability of COF-based systems. Future research should focus on optimizing COF synthesis, enhancing mechanical and thermal stability, and integrating COFs with renewable energy sources to further improve sustainability. Additionally, life cycle assessments and techno-economic analyses will be critical for evaluating the practical viability of these systems in industrial settings.

The development of COF-based materials for H_2O_2 generation represents a significant step toward sustainable chemical production. By addressing the limitations of traditional methods and leveraging the unique properties of COFs, researchers are paving the way for greener, more efficient, and cost-effective H_2O_2 production processes. Continued innovation in this field holds the potential to transform H_2O_2 into a cornerstone of sustainable industrial practices, benefiting both the environment and the economy.

Author Contributions: P.Z. conceptualized the study and supervised the project; A.A.A. performed the literature review and wrote the original draft; R.C., Y.L., X.W. and L.L. analyzed the data. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (12375344), and the program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning (TP2019040).

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Kielman, J. How To Use (and Not Use) Hydrogen Peroxide as A Disinfectant. Hunker. 2020. Available online: https://www.hunker.com/13725927/hydrogen-peroxide-disinfectant-advice-how-to-use/ (accessed on 4 February 2025).
2. Tofani, G.; Cornet, I.; Tavernier, S. Estimation of hydrogen peroxide effectivity during bleaching using the Kappa number. *Chem. Pap.* **2021**, *75*, 5749–5758. [CrossRef]
3. Yin, R.; Anderson, C.E.; Zhao, J.; Boehm, A.B.; Mitch, W.A. Controlling contaminants using a far-UVC-based advanced oxidation process for potable reuse. *Nat. Water* **2023**, *1*, 555–562. [CrossRef]
4. Côté, A.P.; El-Kaderi, H.M.; Furukawa, H.; Hunt, J.R.; Yaghi, O.M. Reticular Synthesis of Microporous and Mesoporous 2D Covalent Organic Frameworks. *ACS Publ.* **2007**, *129*, 12914–12915. [CrossRef]
5. Deng, L.; Zhang, J.; Gao, Y. Synthesis, Properties, and Their Potential Application of Covalent Organic Frameworks (COFs). In *Mesoporous Materials—Properties and Applications*; IntechOpen: London, UK, 2018. [CrossRef]
6. He, N.; Zou, Y.; Chen, C.; Tan, M.; Zhang, Y.; Li, X.; Jia, Z.; Zhang, J.; Long, H.; Peng, H.; et al. Constructing ordered and tunable extrinsic porosity in covalent organic frameworks via water-mediated soft-template strategy. *Nat. Commun.* **2024**, *15*, 3896. [CrossRef]
7. Tan, D.; Fan, X. COF-Based Photocatalysts for Enhanced Synthesis of Hydrogen Peroxide. *Polymers* **2024**, *16*, 659. [CrossRef]
8. Different Processes in Producing Hydrogen Peroxide Supply. Available online: https://www.slchemtech.com/news/different-processes-in-producing-hydrogen-peroxide.html (accessed on 1 February 2025).
9. Guo, Y.; Dong, Y.; Li, C.; Lei, Z. Reaction Mechanism of Anthraquinone Hydrogenation over Pd Based Monometallic and Bimetallic Catalyst. *Catal. Lett.* **2022**, *152*, 1050–1063. [CrossRef]
10. Fink, A.G.; Delima, R.S.; Rousseau, A.R.; Hunt, C.; LeSage, N.E.; Huang, A.; Stolar, M.; Berlinguette, C.P. Indirect H_2O_2 synthesis without H_2. *Nat. Commun.* **2024**, *15*, 766. [CrossRef]
11. National Academies of Sciences, Engineering, and Medicine; Division on Earth and Life Studies; Board on Chemical Sciences and Technology; Committee on a Research Agenda for a New Era in Separation Science. *A Research Agenda for Transforming Separation Science*; The National Academies Press: Washington, DC, USA, 2019. [CrossRef]
12. Kim, H.; Choi, Y.; Hu, S.; Choi, W.; Kim, J.-H. Photocatalytic hydrogen peroxide production by anthraquinone-augmented polymeric carbon nitride. *Appl. Catal. B Environ.* **2018**, *229*, 121–129. [CrossRef]
13. Guo, Z.; Tian, Y.; He, J.; Song, H. Photocatalytic Water Splitting for H_2 Production via Two-electron Pathway. *ChemCatChem* **2024**, *16*, e202301595. [CrossRef]
14. Wang, Z.; Liu, X.; Zhang, X.; Zhang, H.; Zhao, Y.; Li, Y.; Yu, H.; He, G. Realizing one-step two-electron transfer of naphthalene diimides via a regional charge buffering strategy for aqueous organic redox flow batteries. *Mater. Horiz.* **2024**, *11*, 1283–1293. [CrossRef] [PubMed]
15. Costentin, C. Electrochemical approach to the mechanistic study of proton-coupled electron transfer. *Chem. Rev.* **2008**, *108*, 2145–2179. [CrossRef]
16. Jiang, Y.; Ni, P.; Chen, C.; Lu, Y.; Yang, P.; Kong, B.; Fisher, A.; Wang, X. Selective electrochemical H_2O_2 production through two-electron oxygen electrochemistry. *Adv. Energy Mater.* **2018**, *8*, 1801909. [CrossRef]
17. Geng, K.; He, T.; Liu, R.; Dalapati, S.; Tan, K.T.; Li, Z.; Tao, S.; Gong, Y.; Jiang, Q.; Jiang, D. Covalent Organic Frameworks: Design, Synthesis, and Functions. *Chem. Rev.* **2020**, *120*, 8814–8933. [CrossRef]
18. Diercks, C.S.; Yaghi, O.M. The atom, the molecule, and the covalent organic framework. *Science* **2017**, *355*, eaal1585. [CrossRef]
19. Uribe-Romo, F.J.; Doonan, C.J.; Furukawa, H.; Oisaki, K.; Yaghi, O.M. Crystalline Covalent Organic Frameworks with Hydrazone Linkages. *J. Am. Chem. Soc.* **2011**, *133*, 11478–11481. [CrossRef]
20. Biswal, B.P.; Chandra, S.; Kandambeth, S.; Lukose, B.; Heine, T.; Banerjee, R. Mechanochemical Synthesis of Chemically Stable Isoreticular Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2013**, *135*, 5328–5331. [CrossRef]
21. Dalapati, S.; Jin, E.; Addicoat, M.; Heine, T.; Jiang, D. Highly Emissive Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138*, 5797–5800. [CrossRef]
22. Guan, X.; Li, H.; Ma, Y.; Xue, M.; Fang, Q.; Yan, Y.; Valtchev, V.; Qiu, S. Chemically stable polyarylether-based covalent organic frameworks. *Nat. Chem.* **2019**, *11*, 587–594. [CrossRef]
23. Traxler, M.; Dichtel, W.R. Continuous flow synthesis and post-synthetic conversion of single-crystalline covalent organic frameworks. *Chem. Sci.* **2024**, *15*, 7545–7551. [CrossRef]
24. Lohse, M.S.; Bein, T. Covalent Organic Frameworks: Structures, Synthesis, and Applications. *Adv. Funct. Mater.* **2018**, *28*, 1705553. [CrossRef]

25. Nagai, A.; Guo, Z.; Feng, X.; Jin, S.; Chen, X.; Ding, X.; Jiang, D. Pore surface engineering in covalent organic frameworks. *Nat. Commun.* **2011**, *2*, 536. [CrossRef] [PubMed]
26. Li, X.; Geng, K.; Fu, S.; Jin, E. Molecular engineering toward large pore-sized covalent organic frameworks. *Chem. Synth.* **2024**, *4*, 15. [CrossRef]
27. Fan, H.; Mundstock, A.; Feldhoff, A.; Knebel, A.; Gu, J.; Meng, H.; Caro, J. Covalent Organic Framework–Covalent Organic Framework Bilayer Membranes for Highly Selective Gas Separation. *J. Am. Chem. Soc.* **2018**, *140*, 10094–10098. [CrossRef]
28. Prabu, M.; Ketpang, K.; Shanmugam, S. Hierarchical nanostructured $NiCo_2O_4$ as an efficient bifunctional non-precious metal catalyst for rechargeable zinc–air batteries. *Nanoscale* **2014**, *6*, 3173. [CrossRef]
29. Guo, L.; Jia, S.; Diercks, C.S.; Yang, X.; Alshmimri, S.A.; Yaghi, O.M. Amidation, Esterification, and Thioesterification of a Carboxyl-Functionalized Covalent Organic Framework. *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 2023–2027. [CrossRef]
30. Wang, G.-B.; Xie, K.-H.; Xu, H.-P.; Wang, Y.-J.; Zhao, F.; Geng, Y.; Dong, Y.-B. Covalent organic frameworks and their composites as multifunctional photocatalysts for efficient visible-light induced organic transformations. *Coord. Chem. Rev.* **2022**, *472*, 214774. [CrossRef]
31. Li, X.; Cai, S.; Sun, B.; Yang, C.; Zhang, J.; Liu, Y. Chemically Robust Covalent Organic Frameworks: Progress and Perspective. *Matter* **2020**, *3*, 1507–1540. [CrossRef]
32. Xu, X.; Wu, X.; Xu, K.; Xu, H.; Chen, H.; Huang, N. Pore partition in two-dimensional covalent organic frameworks. *Nat. Commun.* **2023**, *14*, 3360. [CrossRef]
33. Yang, J.; Kang, F.; Wang, X.; Zhang, Q. Design strategies for improving the crystallinity of covalent organic frameworks and conjugated polymers: A review. *Mater. Horiz.* **2022**, *9*, 121–146. [CrossRef]
34. Ma, T.; Kapustin, E.A.; Yin, S.X.; Liang, L.; Zhou, Z.; Niu, J.; Li, L.-H.; Wang, Y.; Su, J.; Li, J.; et al. Single-crystal x-ray diffraction structures of covalent organic frameworks. *Science* **2018**, *361*, 48–52. [CrossRef] [PubMed]
35. Ji, C.; Kang, C.; Patra, B.C.; Zhao, D. Flexible Covalent Organic Frameworks: Design, Synthesis, and Applications. *CCS Chem.* **2024**, *6*, 856–881. [CrossRef]
36. Nikkhoo, E.; Mallakpour, S.; Hussain, C.M. Design, synthesis, and application of covalent organic frameworks as catalysts. *N. J. Chem.* **2024**, *47*, 6765–6788. [CrossRef]
37. Wang, Z.; Zhang, S.; Chen, Y.; Zhang, Z.; Ma, S. Covalent organic frameworks for separation applications. *Chem. Soc. Rev.* **2020**, *49*, 708–735. [CrossRef]
38. Younas, R.; Jubeen, F.; Bano, N.; Andreescu, S.; Zhang, H.; Hayat, A. Covalent organic frameworks (COFs) as carrier for improved drug delivery and biosensing applications. *Biotechnol. Bioeng.* **2024**, *121*, 2017–2049. [CrossRef]
39. Evans, A.M.; Ryder, M.R.; Ji, W.; Strauss, M.J.; Corcos, A.R.; Vitaku, E.; Flanders, N.C.; Bisbey, R.P.; Dichtel, W.R. Trends in the thermal stability of two-dimensional covalent organic frameworks. *Faraday Discuss.* **2021**, *225*, 226–240. [CrossRef]
40. Rogge, S.M.J.; Bavykina, A.; Hajek, J.; Garcia, H.; Olivos-Suarez, A.I.; Sepúlveda-Escribano, A.; Vimont, A.; Clet, G.; Bazin, P.; Kapteijn, F.; et al. Metal–organic and covalent organic frameworks as single-site catalysts. *Chem. Soc. Rev.* **2017**, *46*, 3134–3184. [CrossRef]
41. Zhang, X.; Yan, M.; Chen, P.; Li, J.; Li, Y.; Li, H.; Liu, X.; Chen, Z.; Yang, H.; Wang, S.; et al. Emerging MOFs, COFs, and their derivatives for energy and environmental applications. *Innovation* **2025**, *6*, 100778. [CrossRef]
42. Maleki, B.; Esmaeili, H.; Venkatesh, Y.K.; Yusuf, M. A critical review on MOFs and COFs-based heterogeneous catalysts in biodiesel generation: Synthesis methods, structural features, mechanisms, kinetic, economic/environmental evaluation, and their performance. *Process Saf. Environ. Prot.* **2024**, *187*, 903–925. [CrossRef]
43. Xiao, Y.; Wei, S.; Wu, X.; Lu, C. Two-Dimensional Covalent Organic Frameworks with Carbazole-Embedded Frameworks Facilitate Photocatalytic and Electrocatalytic Processes. *Molecules* **2024**, *29*, 5071. [CrossRef]
44. Guo, L.; Gong, J.; Song, C.; Zhao, Y.; Tan, B.; Zhao, Q.; Jin, S. Donor–Acceptor Charge Migration System of Superhydrophilic Covalent Triazine Framework and Carbon Nanotube toward High Performance Solar Thermal Conversion. *ACS Energy Lett.* **2020**, *5*, 1300–1306. [CrossRef]
45. Gu, H.; Liu, X.; Wang, S.; Chen, Z.; Yang, H.; Hu, B.; Shen, C.; Wang, X. COF-Based Composites: Extraordinary Removal Performance for Heavy Metals and Radionuclides from Aqueous Solutions. *Rev. Environ. Contam. Toxicol.* **2022**, *260*, 23. [CrossRef]
46. Lin, C.-Y.; Zhang, D.; Zhao, Z.; Xia, Z. Covalent Organic Framework Electrocatalysts for Clean Energy Conversion. *Adv. Mater.* **2018**, *30*, 1703646. [CrossRef] [PubMed]
47. Gatou, M.-A.; Bika, P.; Stergiopoulos, T.; Dallas, P.; Pavlatou, E.A. Recent advances in covalent organic frameworks for heavy metal removal applications. *Energies* **2021**, *14*, 3197. [CrossRef]
48. Hooriabad Saboor, F.; Shahsavari, S.; Zandjou, M.; Asgari, M. From Structure to Catalysis: Advances in Metal-Organic Frameworks-Based Shape-Selective Reactions. *ChemNanoMat* **2024**, *10*, e202400049. [CrossRef]

49. Zhu, D.; Zhu, Y.; Chen, Y.; Yan, Q.; Wu, H.; Liu, C.-Y.; Wang, X.; Alemany, L.B.; Gao, G.; Senftle, T.P.; et al. Three-dimensional covalent organic frameworks with pto and mhq-z topologies based on Tri- and tetratopic linkers. *Nat. Commun.* **2023**, *14*, 2865. [CrossRef] [PubMed]
50. Li, X.; Ji, X.; Zhang, X.; Chen, X.; Li, H.; Zhang, S.; Huo, F.; Zhang, W. Construction of functional covalent organic framework films by modulator and solvent induced polymerization. *Nat. Commun.* **2025**, *16*, 1223. [CrossRef]
51. Yu, B.; Tao, Y.; Yao, X.; Jin, Y.; Liu, S.; Xu, T.; Wang, H.; Wu, H.; Zhou, W.; Zhou, X.; et al. Single-Crystalline 3D Covalent Organic Frameworks with Exceptionally High Specific Surface Areas and Gas Storage Capacities. *J. Am. Chem. Soc.* **2024**, *146*, 28932–28940. [CrossRef]
52. Yin, Y.; Zhang, Y.; Zhou, X.; Gui, B.; Wang, W.; Jiang, W.; Zhang, Y.-B.; Sun, J.; Wang, C. Ultrahigh–surface area covalent organic frameworks for methane adsorption. *Science* **2024**, *386*, 693–696. [CrossRef]
53. Jiang, S.-Y.; Zhou, Z.-B.; Gan, S.-X.; Lu, Y.; Liu, C.; Qi, Q.-Y.; Yao, J.; Zhao, X. Creating amphiphilic porosity in two-dimensional covalent organic frameworks via steric-hindrance-mediated precision hydrophilic-hydrophobic microphase separation. *Nat. Commun.* **2024**, *15*, 698. [CrossRef] [PubMed]
54. Lu, J.; Han, Y.; Wang, K.; Zhang, Y.; Li, J.; Xu, Y.; Sun, L.; Yang, J.; Li, G. Functionalization of Covalent Organic Frameworks with Peptides by Polymer-Assisted Surface Modification and the Application for Protein Detection. *Anal. Chem.* **2022**, *94*, 15139–15145. [CrossRef]
55. Song, X.; Wang, R.; Wang, X.; Han, H.; Qiao, Z.; Sun, X.; Ji, W. An amine-functionalized olefin-linked covalent organic framework used for the solid-phase microextraction of legacy and emerging per- and polyfluoroalkyl substances in fish. *J. Hazard. Mater.* **2022**, *423*, 127226. [CrossRef]
56. Wang, J.; Zhu, W.; Meng, F.; Bai, G.; Zhang, Q.; Lan, X. Integrating dual-metal sites into covalent organic frameworks for enhanced photocatalytic CO_2 reduction. *ACS Catal.* **2023**, *13*, 4316–4329. [CrossRef]
57. Liu, P.; Cai, K.; Tao, D.-J.; Zhao, T. The mega-merger strategy: M@ COF core-shell hybrid materials for facilitating CO_2 capture and conversion to monocyclic and polycyclic carbonates. *Appl. Catal. B Environ.* **2024**, *341*, 123317. [CrossRef]
58. Zhang, S.; Wang, X.; He, H.; Yang, X.; Li, Q.; Yuan, Y. Green and Large-Scale Synthesis of Covalent Organic Frameworks for Practical Applications. *Adv. Funct. Mater.* **2025**, 2510196. [CrossRef]
59. Yang, Y.; Zhao, W.; Niu, H.; Cai, Y. Mechanochemical Construction 2D/2D Covalent Organic Nanosheets Heterojunctions Based on Substoichiometric Covalent Organic Frameworks. ACS Appl. *Mater. Interfaces* **2021**, *13*, 42035–42043. [CrossRef] [PubMed]
60. Shinde, D.B.; Aiyappa, H.B.; Bhadra, M.; Biswal, B.P.; Wadge, P.; Kandambeth, S.; Garai, B.; Kundu, T.; Kurungot, S.; Banerjee, R. A mechanochemically synthesized covalent organic framework as a proton-conducting solid electrolyte. *J. Mater. Chem. A* **2016**, *4*, 2682–2690. [CrossRef]
61. Asokan, K.; Patil, M.K.; Mukherjee, S.P.; Sukumaran, S.B.; Nandakumar, T. Scalable Mechanochemical Synthesis of β-Ketoenamine-linked Covalent Organic Frameworks for Methane Storage. *Chem.-Asian J.* **2022**, *17*, e202201012. [CrossRef]
62. Lv, H.; Zhao, X.; Niu, H.; He, S.; Tang, Z.; Wu, F.; Giesy, J.P. Ball milling synthesis of covalent organic framework as a highly active photocatalyst for degradation of organic contaminants. *J. Hazard. Mater.* **2019**, *369*, 494–502. [CrossRef]
63. Shirokura, T.; Hirohata, T.; Sato, K.; Villani, E.; Sekiya, K.; Chien, Y.-A.; Kurioka, T.; Hifumi, R.; Hattori, Y.; Sone, M.; et al. Site-Selective Synthesis and Concurrent Immobilization of Imine-Based Covalent Organic Frameworks on Electrodes Using an Electrogenerated Acid. *Angew. Chem. Int. Ed.* **2023**, *62*, e202307343. [CrossRef]
64. Qing, Q.; Luo, J.; Liu, S.; Wang, J.; Wang, Z.; Xiong, X.-G.; Chen, J.; Lu, Y. General synthesis of covalent organic frameworks under ambient condition within minutes via microplasma electrochemistry approach. *Nat. Commun.* **2025**, *16*, 2571. [CrossRef]
65. de Lasa, H.; Serrano, B.; Salaices, M. (Eds.) Photocatalysts, Radiation Sources and Auxiliary Equipment for Photocatalysis. In *Photocatalytic Reaction Engineering*; Springer: Boston, MA, USA, 2005; pp. 49–62.
66. Hernández-Ramírez, A.; Medina-Ramírez, I. (Eds.) *Photocatalytic Semiconductors: Synthesis, Characterization, and Environmental Applications*; Springer: Cham, Switzerland, 2015. [CrossRef]
67. Ma, W.; Yu, L.; Kang, P.; Chu, Z.; Li, Y. Modifications and Applications of Metal-Organic-Framework-Based Materials for Photocatalysis. *Molecules* **2024**, *29*, 5834. [CrossRef] [PubMed]
68. Geletii, Y.V.; Hill, C.L.; Atalla, R.H.; Weinstock, I.A. Reduction of O_2 to Superoxide Anion (O_2•-) in Water by Heteropolytungstate Cluster-Anions. *J. Am. Chem. Soc.* **2006**, *128*, 17033–17042. [CrossRef]
69. Tang, Y.; Wang, W.; Ran, J.; Peng, C.; Xu, Z.; Chu, W. The evolution of photocatalytic H_2O_2 generation: From pure water to natural systems and beyond. *Energy Environ. Sci.* **2024**, *17*, 6482–6498. [CrossRef]
70. Wang, H.; Wang, H.; Wang, Z.; Tang, L.; Zeng, G.; Xu, P.; Chen, M.; Xiong, T.; Zhou, C.; Li, X.; et al. Covalent organic framework photocatalysts: Structures and applications. *Chem. Soc. Rev.* **2020**, *49*, 4135–4165. [CrossRef]
71. Liu, Y.; Zhou, W.; Teo, W.L.; Wang, K.; Zhang, L.; Zeng, Y.; Zhao, Y. Covalent-Organic-Framework-Based Composite Materials. *Chem* **2020**, *6*, 3172–3202. [CrossRef]
72. Diesen, V.; Jonsson, M. Formation of H_2O_2 in TiO_2 Photocatalysis of Oxygenated and Deoxygenated Aqueous Systems: A Probe for Photocatalytically Produced Hydroxyl Radicals. *J. Phys. Chem. C* **2014**, *118*, 10083–10087. [CrossRef]

73. Baran, T.; Wojtyła, S.; Minguzzi, A.; Rondinini, S.; Vertova, A. Achieving efficient H_2O_2 production by a visible-light absorbing, highly stable photosensitized TiO_2. *Appl. Catal. B Environ.* **2019**, *244*, 303–312. [CrossRef]
74. Yuhaneka, G.; Rozafia, A.I.; Utomo, W.P.; Iryani, A.; Hartanto, D. Synthesis of Porous g-C_3N_4 and Its Application as Photocatalyst for Methylene Blue Degradation. *Malays. J. Fundam. Appl. Sci.* **2022**, *18*, 463–472. [CrossRef]
75. Kistan, A.; Narmatha, S.; Chitra, M.; Mayavan, L. A novel mesoporous Bi2MoO6/g-C_3N_4 nanocomposite as an effective photocatalyst against toxic organic pollutants. *Diam. Relat. Mater.* **2025**, *151*, 111841. [CrossRef]
76. Cao, H.; Chen, G.; Yan, Y.; Wang, D. Advances in Two-Electron Water Oxidation Reaction for Hydrogen Peroxide Production: Catalyst Design and Interface Engineering. *ChemSusChem* **2025**, *18*, e202401100. [CrossRef]
77. Sun, Y.; Sinev, I.; Ju, W.; Bergmann, A.; Dresp, S.; Kühl, S.; Spöri, C.; Schmies, H.; Wang, H.; Bernsmeier, D.; et al. Efficient Electrochemical Hydrogen Peroxide Production from Molecular Oxygen on Nitrogen-Doped Mesoporous Carbon Catalysts. *ACS Catal.* **2018**, *8*, 2844–2856. [CrossRef]
78. McCrory, C.C.L.; Jung, S.; Peters, J.C.; Jaramillo, T.F. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **2013**, *135*, 16977–16987. [CrossRef]
79. Chanussot, L.; Das, A.; Goyal, S.; Lavril, T.; Shuaibi, M.; Riviere, M.; Tran, K.; Heras-Domingo, J.; Ho, C.; Hu, W.; et al. Open Catalyst 2020 (OC20) Dataset and Community Challenges. *ACS Catal.* **2021**, *11*, 6059–6072. [CrossRef]
80. Yusran, Y.; Guan, X.; Li, H.; Fang, Q.; Qiu, S. Postsynthetic functionalization of covalent organic frameworks. *Natl. Sci. Rev.* **2020**, *7*, 170–190. [CrossRef] [PubMed]
81. Akinnawo, S.O. Covalent organic frameworks: Design, synthesis, characterization, and applications. *ChemPhysMater* **2024**, *3*, 36–63. [CrossRef]
82. de Jong, M.H.J.; Ganesan, A.; Cupertino, A.; Gröblacher, S.; Norte, R.A. Mechanical overtone frequency combs. *Nat. Commun.* **2023**, *14*, 1458. [CrossRef]
83. Liu, Y.; Li, L.; Sang, Z.; Tan, H.; Ye, N.; Sun, C.; Sun, Z.; Luo, M.; Guo, S. Enhanced hydrogen peroxide photosynthesis in covalent organic frameworks through induced asymmetric electron distribution. *Nat. Synth.* **2025**, *4*, 134–141. [CrossRef]
84. Bao, C.-H.; Li, L.; Wang, X.-F.; Xia, S.-S.; Wang, X.; Jin, C.-C.; Chen, Z. Bringing Porous Framework Materials toward Photocatalytic H_2O_2 Production. *Nano Lett.* **2025**, *25*, 4115–4136. [CrossRef]
85. Guo, J.; Xu, Y.; Jin, S.; Chen, L.; Kaji, T.; Honsho, Y.; Addicoat, M.A.; Kim, J.; Saeki, A.; Ihee, H.; et al. Conjugated organic framework with three-dimensionally ordered stable structure and delocalized π clouds. *Nat. Commun.* **2013**, *4*, 2736. [CrossRef]
86. Zahan, M.; Podder, J. Structural, optical and electrical properties of Cu:MnO_2 nanostructured thin films for glucose sensitivity measurements. *SN Appl. Sci.* **2020**, *2*, 385. [CrossRef]
87. Yang, S.-T.; Kim, J.; Cho, H.-Y.; Kim, S.; Ahn, W.-S. Facile synthesis of covalent organic frameworks COF-1 and COF-5 by sonochemical method. *RSC Adv.* **2012**, *2*, 10179. [CrossRef]
88. Li, Z.; Zhi, Y.; Feng, X.; Ding, X.; Zou, Y.; Liu, X.; Mu, Y. An azine-linked covalent organic framework: Synthesis, characterization and efficient gas storage. *Chem.-A Eur. J.* **2015**, *21*, 12079–12084. [CrossRef]
89. Fan, H.; Gu, J.; Meng, H.; Knebel, A.; Caro, J. High-flux membranes based on the covalent organic framework COF-LZU1 for selective dye separation by nanofiltration. *Angew. Chem. Int. Ed.* **2018**, *57*, 4083–4087. [CrossRef]
90. Lyle, S.J.; Osborn Popp, T.M.; Waller, P.J.; Pei, X.; Reimer, J.A.; Yaghi, O.M. Multistep Solid-State Organic Synthesis of Carbamate-Linked Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2019**, *141*, 11253–11258. [CrossRef]
91. Wang, Z.; Yu, S.; Chen, G.; Zhang, Y.; Chen, S.; Niu, J.; Liang, L.; Feng, J.; Khan, M.A.; Lucier, B.E.G.; et al. De Novo Structure Determination of Covalent Organic Frameworks by NMR Crystallography. *J. Am. Chem. Soc.* **2025**, *147*, 32085–32095. [CrossRef] [PubMed]
92. Zhu, D.; Zaffalon, M.L.; Pinchetti, V.; Brescia, R.; Moro, F.; Fasoli, M.; Fanciulli, M.; Tang, A.; Infante, I.; De Trizio, L.; et al. Bright Blue Emitting Cu-Doped Cs_2ZnCl_4 Colloidal Nanocrystals. *Chem. Mater.* **2020**, *32*, 5897–5903. [CrossRef]
93. Zhang, Y.; Zhang, D.; Zhao, Y.; Yuan, X.; Liu, H.; Wang, J.; Sun, B. An ionic liquid-assisted quantum dot-grafted covalent organic framework-based multi-dimensional sensing array for discrimination of insecticides using principal component analysis and clustered heat map. *Microchim. Acta* **2021**, *188*, 298. [CrossRef]
94. Yue, H.-B.; Guo, J.W.; Fu, S.Q.; Li, X.; Wen, W.Q.; Jiang, W.Z.; Tong, R.; Haranczyk, M. Structural design, preparation and characterization of light, isotropic and robust statically determined organic frameworks as reusable adsorbents. *Chem. Eng. J.* **2018**, *335*, 887–895. [CrossRef]
95. Son, D.; Cho, S.; Nam, J.; Lee, H.; Kim, M. X-ray-Based Spectroscopic Techniques for Characterization of Polymer Nanocomposite Materials at a Molecular Level. *Polymers* **2020**, *12*, 1053. [CrossRef] [PubMed]
96. Shi, R.; Liu, L.; Lu, Y.; Wang, C.; Li, Y.; Li, L.; Yan, Z.; Chen, J. Nitrogen-rich covalent organic frameworks with multiple carbonyls for high-performance sodium batteries. *Nat. Commun.* **2020**, *11*, 178. [CrossRef] [PubMed]
97. Krishna, D.N.G.; Philip, J. Review on surface-characterization applications of X-ray photoelectron spectroscopy (XPS): Recent developments and challenges. *Appl. Surf. Sci. Adv.* **2022**, *12*, 100332. [CrossRef]

98. Roztocki, K.; Rauche, M.; Bon, V.; Kaskel, S.; Brunner, E.; Matoga, D. Combining In Situ Techniques (XRD, IR, and 13C NMR) and Gas Adsorption Measurements Reveals CO_2-Induced Structural Transitions and High CO_2/CH_4 Selectivity for a Flexible Metal–Organic Framework JUK-8. *ACS Appl. Mater. Interfaces* **2021**, *13*, 28503–28513. [CrossRef]
99. Lin, C.; Sun, L.; Meng, X.; Yuan, X.; Cui, C.; Qiao, H.; Chen, P.; Cui, S.; Zhai, L.; Mi, L. Covalent Organic Frameworks with Tailored Functionalities for Modulating Surface Potentials in Triboelectric Nanogenerators. *Angew. Chem.* **2022**, *134*, e202211601. [CrossRef]
100. Jin, S.; Ding, X.; Feng, X.; Supur, M.; Furukawa, K.; Takahashi, S.; Addicoat, M.; El-Khouly, M.E.; Nakamura, T.; Irle, S.; et al. Charge Dynamics in A Donor–Acceptor Covalent Organic Framework with Periodically Ordered Bicontinuous Heterojunctions. *Angew. Chem. Int. Ed.* **2013**, *52*, 2017–2021. [CrossRef]
101. Jakowetz, A.C.; Hinrichsen, T.F.; Ascherl, L.; Sick, T.; Calik, M.; Auras, F.; Medina, D.D.; Friend, R.H.; Rao, A.; Bein, T. Excited-State Dynamics in Fully Conjugated 2D Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2019**, *141*, 11565–11571. [CrossRef] [PubMed]
102. Pan, Q.; Abdellah, M.; Cao, Y.; Lin, W.; Liu, Y.; Meng, J.; Zhou, Q.; Zhao, Q.; Yan, X.; Li, Z.; et al. Ultrafast charge transfer dynamics in 2D covalent organic frameworks/Re-complex hybrid photocatalyst. *Nat. Commun.* **2022**, *13*, 845. [CrossRef]
103. Zheng, L.; Zhang, Z.; Lai, Z.; Yin, S.; Xian, W.; Meng, Q.-W.; Dai, Z.; Xiong, Y.; Meng, X.; Ma, S.; et al. Covalent organic framework membrane reactor for boosting catalytic performance. *Nat. Commun.* **2024**, *15*, 6837. [CrossRef]
104. Liu, S.; Wang, M.; He, Y.; Cheng, Q.; Qian, T.; Yan, C. Covalent organic frameworks towards photocatalytic applications: Design principles, achievements, and opportunities. *Coord. Chem. Rev.* **2023**, *475*, 214882. [CrossRef]
105. Xie, M.; Xia, J.; Zhou, Z.; Chu, J.; Zhuang, Y.; Zhang, S. Flow pattern, mixing, gas hold-up and mass transfer coefficient of triple-impeller configurations in stirred tank bioreactors. *Ind. Eng. Chem. Res.* **2014**, *53*, 5941–5953. [CrossRef]
106. Kamo, T.; Takaoka, K.; Otomo, J.; Takahashi, H. Production of hydrogen by steam gasification of dehydrochlorinated poly(vinyl chloride) or activated carbon in the presence of various alkali compounds. *J. Mater. Cycles Waste Manag.* **2006**, *8*, 109–115. [CrossRef]
107. Peng, Y.; Wong, W.K.; Hu, Z.; Cheng, Y.; Yuan, D.; Khan, S.A.; Zhao, D. Room Temperature Batch and Continuous Flow Synthesis of Water-Stable Covalent Organic Frameworks (COFs). *Chem. Mater.* **2016**, *28*, 5095–5101. [CrossRef]
108. Razu, M.H.; Hossain, F.; Khan, M. Advancement of Bio-hydrogen Production from Microalgae. In *Microalgae Biotechnology for Development of Biofuel and Wastewater Treatment*; Alam, M.A., Wang, Z., Eds.; Springer: Singapore, 2019; pp. 423–462.
109. Lichtarowicz, M. Chemical Reactors. Available online: https://www.essentialchemicalindustry.org/processes/chemical-reactors.html (accessed on 11 September 2025).
110. Khalil, S.; Alazmi, A.; Gao, G.; Martínez-Jiménez, C.; Saxena, R.; Chen, Y.; Jiang, S.-Y.; Li, J.; Alhashim, S.; Senftle, T.P.; et al. Continuous Synthesis and Processing of Covalent Organic Frameworks in a Flow Reactor. *ACS Appl. Mater. Interfaces* **2024**, *16*, 55206–55217. [CrossRef]
111. Klement, W.J.N.; Savino, E.; Rooijmans, S.; Mulder, P.P.M.F.A.; Lynn, N.S., Jr.; Browne, W.R.; Verpoorte, E. Electrochemical Flow Reactors: Mass Transport, iR Drop, and Membrane-Free Performance with In-Line Analysis. *ACS Electrochem.* **2025**, *1*, 504–515. [CrossRef]
112. Li, X.; Gao, M.-L.; Wang, S.-S.; Hu, Y.; Hou, D.; Liu, P.-N.; Xiang, H. Nanoscale covalent organic framework-mediated pyroelectrocatalytic activation of immunogenic cell death for potent immunotherapy. *Sci. Adv.* **2024**, *10*, eadr5145. [CrossRef]
113. Song, Y.; Sun, Q.; Aguila, B.; Ma, S. Opportunities of Covalent Organic Frameworks for Advanced Applications. *Adv. Sci.* **2018**, *6*, 1801410. [CrossRef]
114. Irie, T.; Das, S.; Fang, Q.; Negishi, Y. The Importance and Discovery of Highly Connected Covalent Organic Framework Net Topologies. *J. Am. Chem. Soc.* **2025**, *147*, 1367–1380. [CrossRef]
115. Singh, N.; Yadav, D.; Mulay, S.V.; Kim, J.Y.; Park, N.-J.; Baeg, J.-O. Band gap engineering in solvochromic 2D covalent organic framework photocatalysts for visible light-driven enhanced solar fuel production from carbon dioxide. *ACS Appl. Mater. Interfaces* **2021**, *13*, 14122–14131. [CrossRef] [PubMed]
116. Khojastegi, A.; Khosropour, A.; Amirjalayer, S.; Mosleh, I.; Abbaspourrad, A. Modulating Narrow Bandgap in a Diacetylene Functionalized Woven Covalent Organic Framework as a Visible Light Responsive Photocatalyst. *Adv. Funct. Mater.* **2024**, *34*, 2309367. [CrossRef] [PubMed]
117. Wei, S.; Chang, S.; Li, H.; Fang, Z.; Zhu, L.; Xu, Y. Polymer photocatalysts for photocatalytic hydrogen peroxide production. *Green Chem.* **2024**, *26*, 6382–6403. [CrossRef]
118. Chang, Q.; Zhang, P.; Mostaghimi, A.H.B.; Zhao, X.; Denny, S.R.; Lee, J.H.; Gao, H.; Zhang, Y.; Xin, H.L.; Siahrostami, S. Promoting H_2O_2 production via 2-electron oxygen reduction by coordinating partially oxidized Pd with defect carbon. *Nat. Commun.* **2020**, *11*, 2178. [CrossRef]
119. Sun, X.; Yang, J.; Zeng, X.; Guo, L.; Bie, C.; Wang, Z.; Sun, K.; Sahu, A.K.; Tebyetekerwa, M.; Rufford, T.E. Pairing Oxygen Reduction and Water Oxidation for Dual-Pathway H_2O_2 Production. *Angew. Chem. Int. Ed.* **2024**, *63*, e202414417. [CrossRef]

120. Yang, X.; Zeng, Y.; Alnoush, W.; Hou, Y.; Higgins, D.; Wu, G. Tuning two-electron oxygen-reduction pathways for H_2O_2 electrosynthesis via engineering atomically dispersed single metal site catalysts. *Adv. Mater.* **2022**, *34*, 2107954. [CrossRef] [PubMed]
121. Meng, J.; Huang, Y.; Wang, X.; Liao, Y.; Zhang, H.; Dai, W. Photocatalytic Production of Hydrogen Peroxide from Covalent-Organic-Framework-Based Materials: A Mini-Review. *Catalysts* **2024**, *14*, 429. [CrossRef]
122. Bu, Y.; Ma, R.; Wang, Y.; Zhao, Y.; Li, F.; Han, G.-F.; Baek, J.-B. Metal-Based Oxygen Reduction Electrocatalysts for Efficient Hydrogen Peroxide Production. *Adv. Mater.* **2024**, *36*, 2412670. [CrossRef]
123. Hu, S.-Y.; Sun, Y.-N.; Feng, Z.-W.; Wang, F.-O.; Lv, Y. Design and construction strategies to improve covalent organic frameworks photocatalyst's performance for degradation of organic pollutants. *Chemosphere* **2022**, *286*, 131646. [CrossRef]
124. Tan, D.; Zhuang, R.; Chen, R.; Ban, M.; Feng, W.; Xu, F.; Chen, X.; Wang, Q. Covalent Organic Frameworks Enable Sustainable Solar to Hydrogen Peroxide. *Adv. Funct. Mater.* **2024**, *34*, 2311655. [CrossRef]
125. Ding, S.-Y.; Wang, W. Covalent organic frameworks (COFs): From design to applications. *Chem. Soc. Rev.* **2012**, *42*, 548–568. [CrossRef] [PubMed]
126. Ni, X.; Li, H.; Liu, F.; Brédas, J.-L. Engineering of flat bands and Dirac bands in two-dimensional covalent organic frameworks (COFs): Relationships among molecular orbital symmetry, lattice symmetry, and electronic-structure characteristics. *Mater. Horiz.* **2022**, *9*, 88–98. [CrossRef]
127. Huang, J.; Golomb, M.J.; Kavanagh, S.R.; Tolborg, K.; Ganose, A.M.; Walsh, A. Band gap opening from displacive instabilities in layered covalent-organic frameworks. *J. Mater. Chem. A* **2022**, *10*, 13500–13507. [CrossRef]
128. Chen, Y.; Jiang, D. Photocatalysis with Covalent Organic Frameworks. *Acc. Chem. Res.* **2024**, *57*, 3182–3193. [CrossRef]
129. Keller, N.; Bein, T. Optoelectronic processes in covalent organic frameworks. *Chem. Soc. Rev.* **2021**, *50*, 1813–1845. [CrossRef]
130. Partho, A.T.; Tahir, M.; Tahir, B. Recent advances in covalent organic framework (COF) nanotextures with band engineering for stimulating solar hydrogen production: A comprehensive review. *Int. J. Hydrogen Energy* **2022**, *47*, 34323–34375. [CrossRef]
131. Hu, X.; Tan, B. Covalent Organic Frameworks as Photocatalysts for Sustainable Solar-to-Hydrogen Peroxide Conversion. *Chem.-A Eur. J.* **2025**, *31*, e202501902. [CrossRef] [PubMed]
132. Chen, C.; Joshi, T.; Li, H.; Chavez, A.D.; Pedramrazi, Z.; Liu, P.-N.; Li, H.; Dichtel, W.R.; Bredas, J.-L.; Crommie, M.F. Local Electronic Structure of a Single-Layer Porphyrin-Containing Covalent Organic Framework. *ACS Nano* **2018**, *12*, 385–391. [CrossRef]
133. N'Diaye, J.; Bagchi, R.; Howe, J.Y.; Lian, K. Redox Active Organic-Carbon Composites for Capacitive Electrodes: A Review. *Sustain. Chem.* **2021**, *2*, 407–440. [CrossRef]
134. Mondal, S.; Ray, J.; Sarma, D. Metallogels as Functional Catalysts: Bridging Soft Materials with Sustainable Transformations. *ChemCatChem* **2025**, *17*, e00640. [CrossRef]
135. Ahmad, I.; Basra, S.M.A.; Wahid, A. Exogenous application of ascorbic acid, salicylic acid and hydrogen peroxide improves the productivity of hybrid maize at low temperature stress. *Int. J. Agric. Biol.* **2014**, *16*, 825–830.
136. Zaib, M.; Sandhu, M.; Zar, M.; Ghani, U.; Rehman, A.; Musharraf, M.; Zubair, M.; Abbas, R.; Raza, I. A Brief Review on Plant Growth Promoting Rhizobacteria (PGPR): A Key Role in Plant Growth. *Int. Res. J. Educ. Technol.* **2023**, *5*, 104–126.
137. Azizi, E.; Fazlzadeh, M.; Ghayebzadeh, M.; Hemati, L.; Beikmohammadi, M.; Ghaffari, H.R.; Zakeri, H.R.; Sharafi, K. Application of advanced oxidation process (H_2O_2/UV) for removal of organic materials from pharmaceutical industry effluent. *Environ. Prot. Eng.* **2017**, *43*, 183–191. [CrossRef]
138. Lee, Y.; Choi, K.-H.; Park, K.M.; Lee, J.-M.; Park, B.J.; Park, K.D. In situ forming and H_2O_2-releasing hydrogels for treatment of drug-resistant bacterial infections. ACS Appl. *Mater. Interfaces* **2017**, *9*, 16890–16899. [CrossRef]
139. Ishida, T. Antiviral activities of Cu_2+ ions in viral prevention, replication, RNA degradation, and for antiviral efficacies of lytic virus, ROS-mediated virus, copper chelation. *World Sci. News* **2018**, *99*, 148–168.
140. Lima, A.F.; Lessa, F.C.R.; Mancini, M.N.G.; Hebling, J.; de Souza Costa, C.A.; Marchi, G.M. Transdentinal protective role of sodium ascorbate against the cytopathic effects of H_2O_2 released from bleaching agents. *Oral Surg. Oral Med. Oral Pathol. Oral Radiol. Endod.* **2010**, *109*, e70–e76. [CrossRef]
141. Sánchez-Montes, I.; Santos, G.O.; Silva, T.O.; Colombo, R.; Lanza, M.R. An innovative approach to the application of electrochemical processes based on the in-situ generation of H_2O_2 for water treatment. *J. Clean. Prod.* **2023**, *392*, 136242. [CrossRef]
142. Wang, F.; van Halem, D.; Liu, G.; Lekkerkerker-Teunissen, K.; van der Hoek, J.P. Effect of residual H_2O_2 from advanced oxidation processes on subsequent biological water treatment: A laboratory batch study. *Chemosphere* **2017**, *185*, 637–646. [CrossRef] [PubMed]
143. Schick, R.; Strasser, I.; Stabel, H.-H. Fluorometric determination of low concentrations of H_2O_2 in water: Comparison with two other methods and application to environmental samples and drinking-water treatment. *Water Res.* **1997**, *31*, 1371–1378. [CrossRef]
144. Raj, C.C.; Quen, H.L. Advanced oxidation processes for wastewater treatment: Optimization of UV/H_2O_2 process through a statistical technique. *Chem. Eng. Sci.* **2005**, *60*, 5305–5311.

145. Amanatidou, A. *High Oxygen as an Additional Factor in Food Preservation*; Wageningen University and Research: Wageningen, The Netherlands, 2001.
146. Arefin, S.; Sarker, M.A.H.; Islam, M.A.; Harun-ur-Rashid, M.; Islam, M.N. Use of Hydrogen Peroxide (H_2O_2) in raw cow's milk preservation. *J. Adv. Vet. Anim. Res.* **2017**, *4*, 371–377. [CrossRef]
147. Zhan, D.; Yu, Q.; Li, M.; Gu, Z.; Sun, S.; Li, Y.; Li, A.; Zhu, R.; Mo, Z.; Ma, R. H_2O_2-enhanced alkaline pretreatment and separation of tobacco stems for biocellulose composite films with potential application in food preservation. *J. Environ. Chem. Eng.* **2024**, *12*, 111751. [CrossRef]
148. Yue, Y.; Ji, D.; Liu, Y.; Wei, D. Chemical sensors based on covalent organic frameworks. *Chem. Eur. J.* **2024**, *30*, e202302474. [CrossRef]
149. Xue, R.; Liu, Y.-S.; Huang, S.-L.; Yang, G.-Y. Recent progress of covalent organic frameworks applied in electrochemical sensors. *ACS Sens.* **2023**, *8*, 2124–2148. [CrossRef]
150. Park, J.; Seo, B.; Jeong, Y.; Park, I. A Review of Recent Advancements in Sensor-Integrated Medical Tools. *Adv. Sci.* **2024**, *11*, 2307427. [CrossRef]
151. Zuo, Z.; Zhang, H.; Gao, S.; Wang, C.; Chen, W.-T.; Hu, G. Recent progress in porous organic frameworks for electrochemical sensing of environmental pollutants. *J. Environ. Chem. Eng.* **2024**, *12*, 113263. [CrossRef]
152. La, D.D.; Khong, H.T.; Nguyen, X.Q.; Dang, T.D.; Bui, X.T.; Nguyen, M.K.; Ngo, H.H.; Nguyen, D.D. A review on advances in graphene and porphyrin-based electrochemical sensors for pollutant detection. *Sustain. Chem. One World* **2024**, *3*, 100017. [CrossRef]
153. Freund, R.; Zaremba, O.; Arnauts, G.; Ameloot, R.; Skorupskii, G.; Dincă, M.; Bavykina, A.; Gascon, J.; Ejsmont, A.; Goscianska, J. The current status of MOF and COF applications. *Angew. Chem. Int. Ed.* **2021**, *60*, 23975–24001. [CrossRef]
154. Wang, A.; Liu, X.; Feng, S.; Wang, Y.; Song, Y.; Gao, Y. Synthesis and Biomedical Applications of Covalent Organic Frameworks for Disease Diagnosis and Therapy. *ChemBioChem* **2024**, *26*, e202400807. [CrossRef]
155. Niu, X.; Yang, Y.; Duan, B.; Li, C.; Zhang, Y.; Zhang, X. A versatile photoelectrochemical biosensor based on in-situ grown 2D COFs film for sensitive detection of Hg2+ and aflatoxin B1. *Chem. Eng. J.* **2024**, *493*, 152628. [CrossRef]
156. Cheng, J.; Wu, Y.; Zhu, L.; Lin, S.; Liu, Y.; Huang, K.; Xu, W. Uric acid biosensors based on molecular recognition: Classifications, Advances, and Prospects. *TrAC Trends Anal. Chem.* **2024**, *179*, 117887. [CrossRef]
157. Lee, J.; Seo, J.H.; Gao, B.; Jang, H.W. Transition Metal-Based High-Entropy Materials for Catalysis. *MetalMat* **2025**, *2*, e31. [CrossRef]
158. Jaramillo Group. Available online: https://jaramillogroup.stanford.edu/device.html (accessed on 4 September 2025).
159. Su, B.J.; Foo, J.J.; Ling, G.Z.S.; Ong, W.-J. Synergistic redox reactions toward co-production of H_2O_2 and value-added chemicals: Dual-functional photocatalysis to achieving sustainability. *SusMat* **2024**, *4*, e192. [CrossRef]
160. Munir, S.; Dionysiou, D.D.; Khan, S.B.; Shah, S.M.; Adhikari, B.; Shah, A. Development of photocatalysts for selective and efficient organic transformations. *J. Photochem. Photobiol. B* **2015**, *148*, 209–222. [CrossRef]
161. Han, C.; Kundu, B.K.; Liang, Y.; Sun, Y. Near-Infrared Light-Driven Photocatalysis with an Emphasis on Two-Photon Excitation: Concepts, Materials, and Applications. *Adv. Mater.* **2024**, *36*, 2307759.
162. Chen, Y.-Z.; Li, W.-H.; Li, L.; Wang, L.-N. Progress in organic photocatalysts. *Rare Met.* **2018**, *37*, 1–12. [CrossRef]
163. Leu, S.-Y.; Tsang, D.C.W.; Lam, J.C.-H.; Zhao, J.; Yuan, Z.; Xu, C.; Lin, C.S.K. Key techno-economic barriers in the valorization of organic solid wastes for chemical production. *One Earth* **2024**, *7*, 742–746. [CrossRef]
164. Ren, P. Novel Heterogeneous Photocatalysts for the Generation of H_2O_2 and CO_2-Reductions. Ph.D. Thesis, University of Antwerp, Antwerpen, Belgium, 2024.
165. Yang, Y.; Tang, Y.; Jiang, H.; Chen, Y.; Wan, P.; Fan, M.; Zhang, R.; Ullah, S.; Pan, L.; Zou, J.-J. 2020 Roadmap on gas-involved photo-and electro-catalysis. *Chin. Chem. Lett.* **2019**, *30*, 2089–2109. [CrossRef]
166. Dehghani, F.; Shafiyi, M.A. Integration of hybrid renewable energy sources with the power system considering their economic complementarity. *IET Renew. Power Gener.* **2023**, *17*, 3638–3650. [CrossRef]
167. Kandpal, V.; Jaswal, A.; Santibanez Gonzalez, E.D.R.; Agarwal, N. (Eds.) Energy Efficiency and Renewable Energy Technologies. In *Sustainable Energy Transition*; Springer Nature: Cham, Switzerland, 2024; pp. 89–123.
168. Lin, Y.-C.; Wyżga, P.; Macyk, J.; Macyk, W.; Guzik, M.N. Solar-driven (photo) electrochemical devices for green hydrogen production and storage: Working principles and design. *J. Energy Storage* **2024**, *82*, 110484. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.