

共价有机框架(COFs)在光催化制备过氧化氢(H₂O₂)领域的研究进展

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摘要

过氧化氢(H₂O₂)作为绿色高效氧化剂, 广泛应用于化工合成、环境治理及生物医药等领域, 但传统蒽醌法存在能耗高、污染大的缺陷, 光催化制备过H₂O₂就是利用太阳能和光催化剂驱动O₂还原H₂O氧化生成H₂O₂, 是极具前景的绿色路径。共价有机框架(COFs)因结构可调、比表面积大、共轭稳定, 结构易调控等特性, 成为光催化产H₂O₂的理想材料。本文梳理了COFs的光催化机制, 设计策略、及优化方向, 分析了稳定性、成本等挑战, 并总结了2020~2025年具有代表性的几种COFs用于光催化产H₂O₂的设计策略与不足之处, 对COFs精准设计与实际应用进行展望, 为COFs光催化产H₂O₂领域的发展提供参考。

关键词

共价有机框架, 光催化, 过氧化氢, 太阳能转化

Research Progress of Covalent Organic Frameworks (COFs) in Photocatalytic Preparation of Hydrogen Peroxide (H₂O₂)

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Abstract

Hydrogen peroxide (H₂O₂), as a green and efficient oxidant, is widely used in chemical synthesis, environmental treatment, and biomedicine, etc. However, the traditional anthraquinone method has the drawbacks of high energy consumption and significant pollution. Photocatalytic production

of H₂O₂ utilizes solar energy and photocatalysts to drive the reduction of O₂ and oxidation of water to generate H₂O₂, which is a promising green approach. Covalent organic frameworks (COFs) have become ideal materials for photocatalytic production of H₂O₂ due to their adjustable structures, large specific surface areas, stable conjugation, and easy structural regulation. This paper reviews the photocatalytic mechanism, design strategies, and optimization directions of COFs, analyzes the challenges such as stability and cost, and summarizes several representative design strategies and shortcomings of COFs for photocatalytic production of H₂O₂ from 2020 to 2025. It looks forward to the precise design and practical application of COFs, providing reference for the development of COFs in the field of photocatalytic production of H₂O₂.

Keywords

Covalent Organic Framework, Photocatalysis, Hydrogen Peroxide, Solar Energy Conversion

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1. 引言

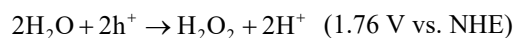
过氧化氢(H₂O₂)是“绿色”化工原料,分解产物仅为水和氧气,在造纸漂白、废水处理、有机合成等领域不可或缺[1]。据《2025 年全球 H₂O₂ 市场报告》,全球需求年增长率达 5.2%,但传统制备方法存在显著瓶颈:蒽醌法依赖化石能源(每生产 1 吨 H₂O₂ 需 0.8 吨标准煤) [2],且产生有机废液;而光催化技术利用半导体材料吸收太阳能并驱动 O₂ 双电子还原(2e⁻ ORR)或通过水双电子氧化(2e⁻ WOR)生成 H₂O₂ [3],为化学合成提供了一种绿色、低能耗的方法,是解决传统渠道生成 H₂O₂ 缺陷的关键路径。传统光催化材料(如 TiO₂、g-C₃N₄) [4] [5]存在光响应范围窄(仅紫外光)、载流子复合率高(>70%)、O₂ 吸附能力弱(吸附能 < -0.2 eV)等问题[6] [7]。COFs 的出现为这一领域带来突破:作为结晶多孔材料,COFs 具备三大核心优势——结构可调性(精准调控孔道尺寸与电子能带)、高比表面积(二维 COFs 比表面积可达 2000 m²·g⁻¹)、共轭稳定性(促进载流子传输) [8] [9]。由此 COF 光催化剂表现出令人印象深刻的催化性能,并且由于其良好的组织框架和定制设计的特性,提高了电荷转移效率和载流子迁移率,已经达到了成熟的发展阶段。此外,由于其可设计的分子框架,COFs 允许对其能带结构和催化位点进行微调,在光催化合成 H₂O₂ 领域展现出巨大潜力[10] [11]。本文基于 2020~2025 年的研究进展,总结了几种代表性 COFs 的创新性设计策略和缺陷。

2. 光催化生产 H₂O₂ 的机理

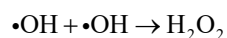
光催化 H₂O₂ 生产的过程大致可以分为三个连续的部分。首先,光催化剂被光照射后吸收光子。当入射光子能量超过光催化剂的带隙(E_g)时,电子从价带(VB)激发到导带(CB) [12]。其次,被激发的电子和由此产生的空穴在光催化剂内部迁移或重新组合[13]。激发后,电子和空穴将扩散到光催化界面,促进同时进行的还原和氧化过程[14]。生成 H₂O₂ 的反应主要包括水氧化反应(WOR)和氧还原反应(ORR)两种途径 [15],并且这两种反应同时发生生成过氧化氢。相关的反应步骤如下:

WOR:

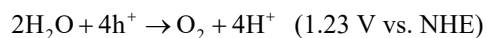
2e⁻直接途径:



2e⁻间接途径:

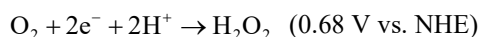


4e⁻途径:

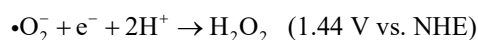
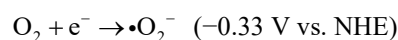


ORR:

2e⁻直接途径:



2e⁻间接途径:



4e⁻途径:

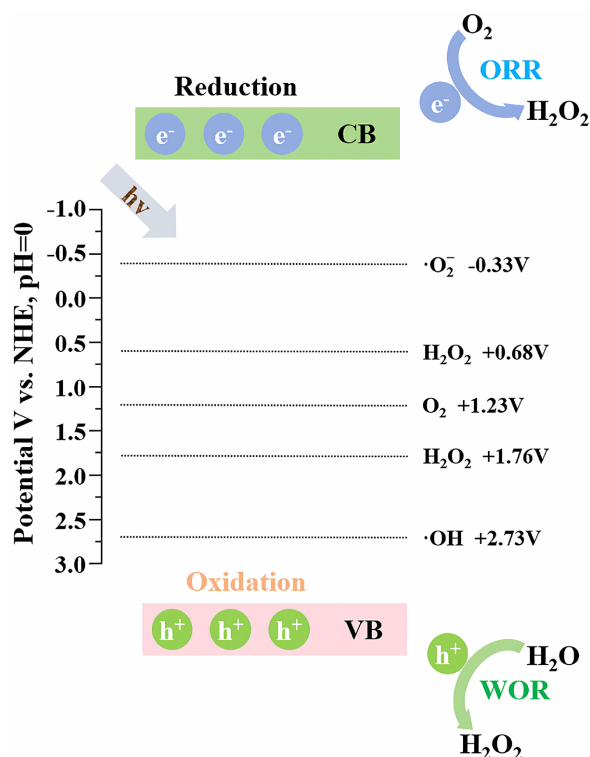


Figure 1. Reaction potentials corresponding to ORR and WOR during H₂O₂ production

图 1. 生产 H₂O₂ 时 ORR 和 WOR 对应的反应势

H₂O₂ 生成过程中所涉及的 ORR 和 WOR 对应电位如图 1 所示。根据中间产物的存在与否，2e⁻ ORR 可分为直接和间接两类途径。为了通过 2e⁻ ORR 途径直接获得 H₂O₂，光催化剂的导带(CB)电位必须控制

在 0.68 V 以下。 $2e^-$ ORR 的间接路径通常涉及中间体的生成和转化。在间接路径中, O_2 首先被还原为 $\bullet O_2^-$ 中间体, 然后这个中间体经过质子化和进一步的反应最终生成 H_2O_2 。为了实现这一过程, 光催化剂的 CB 电位通常需要低于 -0.33 V, 以驱动 O_2 单电子还原为 $\bullet O_2^-$ 。相较于两电子直接途径, 虽然间接途径在中间体调控上具有较大的灵活性, 但也对材料的表面性能提出了更高的要求。相应的, $2e^-$ WOR 也可分为直接途径和间接途径。通过 $2e^-$ 直接 WOR 生产 H_2O_2 所需的光催化剂的价带(VB)电势理论上必须超过 1.76 V。相比之下, 通过 $2e^-$ 间接 WOR 生产 H_2O_2 所需的 VB 电势理论上必须超过 2.73 V [16]。同时, 与间接途径相比, $2e^-$ 直接 WOR 和 ORR 更具热力学优势, 但缺乏动力学优势[17]。作为光催化 H_2O_2 产中不希望发生的反应, $4e^-$ WOR 将直接影响 H_2O_2 的生产效率和稳定性。这种情况可归因于它与反应底物的 $2e^-$ ORR 竞争。光催化生产 H_2O_2 依赖于 O_2 作为原料。 $4e^-$ WOR 消耗 H_2O 生成 O_2 , 导致 O_2 的循环消耗, 降低了 $2e^-$ ORR 可用的 O_2 浓度。同时, $4e^-$ WOR 会消耗大量的 H_2O , 这会影响质子供应, 间接抑制 $2e^-$ ORR 的进展。此外, $4e^-$ WOR 产生的 O_2 可能通过歧化反应催化 H_2O_2 的分解。因此, 为了保证 H_2O_2 的高产率, 提高 $2e^-$ 途径的选择性也是相关研究的重要课题。

3. 光催化产 H_2O_2 的 COFs 材料设计策略

COFs 的结构设计是实现高效光催化产 H_2O_2 的核心, 从广义上讲, 提高 H_2O_2 产率的策略包括分子工程、基于 COF 的异质结构的构建和晶体结构的调节[18]。国内团队通过“精准调控配体与构筑单元”, 如混合配体策略; 引入功能单元; 增强键合能力; 设计共轭体系等开发了多类功能化 COFs, 针对性解决 O_2 吸附、载流子传输及稳定性问题。

3.1. 混合配体策略优化电子与孔道结构

Tang 等团队[19]采用混合配体共聚合策略, 将两种醛类单体, 即对苯二甲酸(TA)和 2,5-二(噻吩-2-基)对苯二甲酸(DTTA)与 2,4,6-三甲基-1,3,5-三嗪(TMT)以精确控制的比例共聚合, 形成交替排列的二维框架 TA/DTTA-2-TMT。该设计优化了孔道尺寸(1.5 nm, 适合 O_2 扩散), 比表面积提升至 $1800\text{ m}^2\cdot\text{g}^{-1}$; 同时, 噻吩单元的引入有效地促进了电荷载流子的分离, 配体间电子耦合抑制了光生载流子复合[20] [21], 载流子寿命从 2.1 ns 延长至 4.3 ns, 有助于更多的电子参与反应, 最终实现 H_2O_2 生成速率 $3451\text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ 。

虽然混合配体策略能有效优化电子与孔道结构, 但该设计策略面临 COFs 的稳定性与功能性的冲突: 混合配体策略需平衡“亲水性”与“结晶性”的难题, TA 的引入虽然增强了水亲和力, 但会破坏 DTTA 的共轭结构, 导致框架结晶度下降[22]; 长期光催化过程中, 这种结构无序会进一步加剧, 引发活性位点失活。同时其材料性能依赖 TA 与 DTTA 的精确摩尔比, 在工业级合成中难以实现分子层面的精确调控; 配体比例的微小偏差会导致孔道尺寸波动较大[23], 将直接影响 O_2 的扩散效应, 导致其催化性能下降。

3.2. 功能单元增强 O_2 吸附与活化

Chi 等团队[24]针对 O_2 吸附不足的瓶颈, 设计了含嘧啶单元的 BTT-MD-COF: 以 1,3,5-三(4-氨基苯基)三嗪(BTT)为连接体, 与含嘧啶环的 2,5-二羟基对苯二甲酸(MD)通过亚胺键聚合。嘧啶环作为强电子受体, 通过 π - π 相互作用增强 O_2 吸附(吸附能 -0.5 eV , 远高于不含嘧啶的 COFs), 并将 O_2 还原能垒从 0.8 eV 降至 0.3 eV; 均一孔道(1.2 nm)为 O_2 扩散与 H_2O_2 脱附提供高效通道, 最终 H_2O_2 生成速率达 $5691.2\text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ 。

该研究通过“嘧啶单元增强 O_2 吸附”实现了高选择性一步 $2e^-$ ORR, 但该设计方案存在策略局限性与长期稳定性隐患: 嘧啶环作为强电子受体, 通过 π - π 作用增强了 O_2 吸附, 但过度吸附会导致 O_2 分子“卡死”在活性位点上——过量 O_2 占据嘧啶环的电子轨道后, 会抑制光生电子向 O_2 的转移[25], 同时阻

碍反应中间体 $\bullet\text{OOH}$ 的形成,反而降低催化速率;框架的“刚性-柔性的平衡”是保证长期性能的关键,设计中采用了高刚性的亚胺键连接来增强 O_2 吸附,但长期 O_2 吸附-脱附循环会引发“框架微裂纹”(如晶面间距从0.34 nm扩大至0.38 nm),材料结晶度会逐渐下降,活性位点嘧啶环也会流失,导致 H_2O_2 产率逐渐下降。

3.3. 稳定键合提升极端环境耐受性

Wang等[26]团队开发了偶氮键($-\text{N}=\text{N}-$)连接的COF-TPT-Azo:以4,4'-二氨基偶氮苯为配体,与2,4,6-三(4-甲醛苯基)-1,3,5-三嗪(TPT)通过偶氮键聚合。偶氮键(键能 $210\text{ kJ}\cdot\text{mol}^{-1}$)远高于亚胺键($160\text{ kJ}\cdot\text{mol}^{-1}$) [27],使COF-TPT-Azo在 $\text{pH}=10$ 的碱性溶液中连续运行72 h后,结晶度仍保持85%, H_2O_2 生成速率仅下降10%;偶氮键的光响应特性(顺反异构)可动态调整电子结构,对电子-空穴对的重组具有更强的抑制作用,进一步提升载流子迁移速率[28]。

该研究通过偶氮键替代亚胺键提升了框架稳定性,但存在光响应稳定性隐患和催化选择性为验证问题:偶氮键的顺反异构特性虽然增强了光吸收范围,但长期强光照下(如夏季户外光照),顺式偶氮键会不可逆的转化为反式[29],导致框架共轭结构破坏,这将抑制光生载流子的分离,载流子寿命将缩短,最终导致 H_2O_2 产率下降;研究中仅测试了“无牺牲剂碱性条件”下的性能($1498\text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$),未评估复杂体系中的选择性——比如在含还原性有机物(如苯酚)的废水中,偶氮键的强氧化性可能优先氧化有机物[30],而非还原 O_2 生成 H_2O_2 ,目标产物选择性将大幅下降。

3.4. 共轭框架促进载流子传输

Wang等人[31]开发并合成了两种高共轭的三嗪基COFs,即TBP-COF和TTP-COF,并检测了它们在 H_2O_2 生产中的光催化效率。TBP-COF ($1882\text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)和TTP-COF ($4244\text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)在纯水中,10 W LED ($\lambda=420\text{ nm}$)可见光照射下的性能差异证明了富氮结构和共轭效应增强了光吸收[32],促进了 O_2 吸附,提高了氧化还原能力,有利于光生载体的高效分离和转移。Tan等人[33]开发了三嗪-噻吩融合COFs:通过以共面三嗪环为连接剂,以平面熔融苯并三噻吩(BTT)和噻吩[3,2-b](TT)为构建块的缩聚方法,成功合成了两种高度共面融合的共价三嗪骨架CTF-BTT和CTF-TT。其光响应范围拓宽至600 nm(覆盖可见光区),噻吩单元将电导率从传统COFs的 $10^{-5}\text{ S}\cdot\text{cm}^{-1}$ 提升至 $1.2\times 10^{-3}\text{ S}\cdot\text{cm}^{-1}$,显著促进了光生电子传输[34]。

Wang, Tan团队通过利用三嗪基的共面性,构筑了高共轭的COFs,证实了共轭效应有利于促进光生载流子的传输,增加了光生电子的有效利用率[35]。虽然该设计策略简单有效,但仍然存在大规模应用的难题:三嗪基COFs的光吸收范围有限,窄带隙要求难以满足,对光生电子-空穴对的分离效率有待进一步提高,另外还必须解决三嗪环在合成过程中溶解度有限的问题[36],减低生产成本,才有望大规模应用。

3.5. 调节分子内极性促进激子解离和形成

Liu等人[37]通过引入适量的苯基作为电子给体,优化COFs的分子内极性,促进激子在COFs中的形成和解离。以苯基($n=0, 1, 2$)含量不同的三嗪核三胺为前驱体,制备了一类具有不同分子内极性的三嗪基COFs。在这三种COFs中,八极共轭结构中具有中等分子内极性的COF-N32在光照射下可以为 H_2O_2 光合作用产生最多的电子。在不需要牺牲剂的情况下,COF-N32在可见光照射12小时, H_2O_2 产率达到 $605\text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ 。此外,COF-N32可以在更多可用的真实水样(包括自来水、河水和海水)中有效地产生 H_2O_2 ,还能够自然阳光照射下有效地产生 H_2O_2 。

该研究通过“三嗪环的 N_{2p} 态和 C_{2p} 调控”实现了 O_2 还原 - 水氧化双路径,但其方案存在双路径机制的平衡难题:双路径效率依赖“分子内极性”与“光生电荷分离的协同”,弱极性(如未优化的 COF-N33)会导致载流子复合率高,无法启动双路径;强极性(如 COF-N31)又会抑制光激子解离(激子寿命延长),导致电荷利用率下降[38],即使优化后的 COF-N32,其双路径协同效率也仅达到 60%,不能突破“极性 - 电荷分离”的平衡性质。

4. 应用挑战与展望

尽管对于 COFs 用于光催化产 H_2O_2 的研究取得显著进展,但 COFs 光催化产 H_2O_2 仍面临四大挑战: 1. 稳定性不足:传统亚胺键 COFs 在酸碱条件下易水解,限制了废水处理等场景的应用[39]; 2. 成本高:COFs 合成需昂贵芳香配体(如三嗪配体 500 元/g),规模化成本约 20 万元/kg,远高于 TiO_2 (500 元/kg) [40]; 3. 自然光利用效率低:现有 COFs 对近红外光(占太阳能 50%)的利用率 < 10% [41]; 4. 产物自分解:COFs 孔道易导致 H_2O_2 积累,引发自分解[42]。由此我们未来的目标有: 1. 开发自稳定 COFs:引入碳 - 碳键、硼氧键等稳定键合方式,提升极端环境耐受性[43]; 2. 低成本规模化合成:利用工业级配体(如石油副产品)或水相合成法[44],降低成本; 3. 近红外响应设计:引入卟啉、酞菁等单元[45],扩展光响应至近红外区; 4. 智能孔道调控:通过动态共价键(如席夫碱键)设计“可切换”孔道[46],减少 H_2O_2 自分解; 5. 实际应用验证:开发固定床反应器[47],用于饮用水消毒或工业废水处理中的 H_2O_2 现场制备。

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