

亚胺类共价有机框架材料在光催化应用中的最新进展

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摘要

共价有机框架(Covalent Organic Frameworks, COFs)是一类由有机构筑单元通过强共价键精准连接而成的新型多孔有机材料。这类材料兼具可调控的拓扑结构、永久孔隙率、高结晶度、大比表面积及优异的化学与物理稳定性, 为其在多类光催化领域的应用奠定了坚实基础。连接化学是调控COFs合成过程与物化性质的核心要素, 在众多连接方式中, 亚胺键因制备简便、结构与功能兼具丰富的可设计性, 已发展为构筑COFs材料最常用且最重要的连接方式之一。本文系统阐述亚胺连接COFs的设计策略与合成方法, 进而综述其在光催化领域的研究进展, 并深入剖析该类材料在实际应用中面临的挑战。

关键词

亚胺类共价有机框架, 光催化, 合成方法, 应用

Latest Advances in Imine-Based Covalent Organic Frameworks for Photocatalytic Applications

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Abstract

Covalent organic frameworks (COFs) are a novel class of porous organic materials constructed from

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organic building blocks via precise linkage by strong covalent bonds. Featuring tailorable topological structures, permanent porosity, high crystallinity, large specific surface areas, and excellent chemical and physical stability, these materials lay a solid foundation for their applications in various photocatalytic fields. Linkage chemistry serves as the core factor in regulating the synthesis process and physicochemical properties of COFs. Among diverse linkage types, the imine linkage has become one of the most commonly used and crucial linkages for constructing COFs owing to its facile preparation and remarkable designability in both structure and function. This review systematically elaborates the design strategies and synthetic methods of imine-linked COFs, further summarizes the research progress of these materials in photocatalysis, and deeply analyzes the challenges encountered in their practical applications.

Keywords

Imine-Based Covalent Organic Frameworks, Photocatalysis, Synthesis Methods, Applications

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1. 引言

全球能源需求的持续攀升叠加日益严峻的环境问题,进一步推动了可再生能源转化与储能技术的研发进程[1]。太阳能作为一种理想的可持续能源,若能被高效捕获并转化为稳定、可储存的化学能载体,将为实现净零碳排放目标提供极具潜力的解决方案。光催化技术可借助催化剂将太阳能直接转化为化学能,是连接太阳能与清洁能源载体的关键桥梁[2][3]。作为一种新型光催化剂,共价有机框架(COFs)是一类新兴多孔晶态材料,由有机分子基元通过共价键有序连接而成,具有高度规整的孔道结构与优异的结构可调控性,是催化领域应用不可或缺的关键要素。因此,COFs是适用于催化反应的理想材料[4]-[9]。目前,基于动态亚胺化学的亚胺连接COFs成为数量最多的COF。合成反应在有机酸或路易斯酸催化剂存在下,芳香胺和醛的反应可以形成亚胺键,在具有略微可逆缩合反应下进行反应可使产生错误结构的键能够以正确方式重新形成,直到获得周期性且热力学稳定的结构[10][11]。因此亚胺连接的COF表现出优异的水解稳定性,并且在大多数有机溶剂中即使在酸性和碱性条件下也保持稳定,使其成为可持续和高性能光催化应用的理想选择,如氢气生产, H_2O_2 还原和有机物转换等[12]-[14]。

2. 亚胺类 COFs 材料的合成方法

制备兼具高孔隙率与优异结晶度的亚胺COFs需要确立适宜的合成条件(包括反应温度、反应时间、压力及溶剂组合),这对于平衡COFs的框架形成与结晶过程至关重要。自2005年Yaghi课题组首次通过溶剂热条件合成出COFs以来,目前已有多种不同的方法被用于亚胺类COFs的制备[15][16]。

2.1. 溶剂热合成法

溶剂热法是实验室制备亚胺键连接COFs最常用的方法。一般操作如下:将芳香族胺和醛单体加入耐压管,与溶剂和催化剂一起混合均匀,然后进行冷冻-泵-解冻循环中脱气。随后将耐压管密封并加热至指定温度,保持一定反应时间。最后,将获得的沉淀清洗和干燥以获得COFs粉末[17]。

单体溶解度、溶剂组合及其比例、催化剂浓度、反应时间和温度是COFs设计和合成中需要考虑的关键问题。催化剂通常是AcOH。而溶剂选择中,均三甲苯/二噁烷/乙酸混合体系是应用最为广泛的适宜

溶剂组合，二噁烷-乙酸水溶液、正丁醇/邻二氯苯/3 mol/L 乙酸等其他混合体系也得到了大量应用。为了提高 COFs 的结晶性，通常需要优化溶剂热合成条件，例如繁琐的溶剂筛选、高反应温度(>120°C)和较长的聚合时间(>3 天)。由此溶剂热合成方法耗时且耗能高，使得 COFs 的大规模生产具有挑战性[18]-[25]。

2.2. 室温合成

与繁琐苛刻的溶剂热合成法相比，室温合成无需高压环境，具有温和的反应条件。通过设计合理的低温或室温合成策略，可实现对缺陷生成及单晶度的良好调控，制备出大尺寸 COF 单晶[26]-[29]。

目前，有研究利用醋酸增强醛单体在水溶液中的反应性，提出了一种简单且绿色环保的合成亚胺连接 COF 的方法。作者通过将起始有机单体在水和醋酸中搅拌，在室温下可以在极短的反应时间(最长 1 分钟)内合成出高度结晶且多孔的 COF。该过程的关键在于利用不溶性醛单体沿生成的分子/水界面与 1,4-二胺苯(DB)反应，成功合成了 16 个不同的 COFs。并且还通过界面聚合和制备独立纳米纸，实现 CNF 表面的 COF 纳米层均匀生长 CNF@COF。值得注意的是，这些独立纳米纸通过膜分离工艺在去除水溶液中微量 OFX 的效率极高。室温合成为绿色合成和加工各种 COFs 铺平了道路，为在多个领域的实际应用铺平了道路[30]。

2.3. 熔融法化学合成

南开大学化学学院的张振杰课题组首次将有机调节剂介导的熔融合成引入 COFs 的合成中。在典型的熔融合成过程中，包括单体和调节剂在内的有机分子作为熔剂，在高温下溶解其他反应物，随着温度升高形成均匀溶液，有助于液相中的传质和成核过程。这种基于熔融聚合原理的熔融(助熔)法合成的 COFs 能够直接成型(块体、多孔海绵、膜)，通常比传统溶剂热方法合成的具有更高的结晶度和规则有序的孔结构，具有广泛的应用前景。基于熔融合成法，该课题组已经实现一系列 COFs 材料的低成本公斤级合成，为 COFs 材料的规模化应用铺平道路[31]-[35]。

2.4. 其他合成策略

Hou 等人提出了一种利用液相介质阻挡放电(DBD)等离子体合成共价有机骨架(COFs)的有效策略。DBD 等离子体属于常压非平衡等离子体，具有能耗低、可在常温常压下运行的优势，能够促进诸多在其他条件下难以发生的化学反应。此外，DBD 等离子体还具备与酸催化剂类似的酸性特征，因此可催化需酸激活的有机反应。实验在不到 1 小时的时间内就实现了亚胺键型 COFs (ILCOF-1、Py-COF)的快速制备。粉末 X 射线衍射(PXRD)图谱显示，反应进行 10 分钟后，即可观察到 ILCOF-1 与 Py-COF 的特征衍射峰，且随着反应时间的延长，最终产物的结晶度逐步提升。等离子体法能够通过介质阻挡放电产生高温，其产生的大量活性自由基与自身的酸性特质，是实现高质量亚胺键型 COFs 快速制备的关键因素。与传统方法不同，该方法具有操作简便、反应快速、无需额外加热、无需惰性气体保护及加压处理等优势[36]。

3. 亚胺类 COFs 材料在光催化中的应用

胺类与醛类反应物的多样性推动了亚胺键型共价有机骨架的新型结构、拓扑构型与功能特性的开发，同时提升了材料的稳定性与适用性。因此，科研人员越来越关注合成具有多样结构的亚胺键连接型 COFs，并将其应用于产氢、H₂O₂ 还原及有机物氧化等光催化应用领域[37]-[40]。

3.1. 光催化析氢

太阳能光催化分解水制氢是转化清洁可再生能源太阳能生产绿色氢能的有效方法，近年来的研究证

实, 多种亚胺键型 COFs 可用作高效的光催化析氢反应(HER)催化剂[41]-[44]。

Thomas 等人研究发现, 亚胺键的质子化作用会使材料的光吸收发生红移, 并影响电荷的分离与传输过程, 进而实现光催化析氢性能的提升。亚胺基团的取向同样对电荷分离调控起到重要作用。Li 等人发现, 具有相反亚胺键取向的同类亚胺 COFs 材料, 表现出截然不同的催化性能。在以抗坏血酸(AA)为牺牲剂的光催化析氢反应中, 体系会发生原位质子化。其中, D-C=N-A 取向的 COFs 同样实现了析氢性能的提升, 这表明正确的亚胺键取向可促进电荷分离, 而反向的亚胺键取向则会抑制电荷分离[45] [46]。

3.2. 光催化产 H₂O₂

过氧化氢(H₂O₂)作为一种绿色氧化剂, 被广泛应用于消毒、漂白、化学合成及航天航空等多个领域, 因具备广泛的工业与环境应用价值而备受关注。亚胺类 COFs 凭借其高孔隙率的共轭骨架结构与优异的结构可设计性, 展现出更为优异的光催化产过氧化氢活性[47]-[49]。

Van Der Voort 团队设计并合成了一种亚胺键型 Py-Da COF, 其中苊与联吡啶单元的协同作用在光催化过程中发挥关键作用。该 COFs 材料由苊基构筑单元 1,3,6,8-四(4-甲酰基苯基)苊(Py-CHO)与 1,4-苯二胺经缩合反应制得, 其 BET 比表面积高达 2448 m²·g⁻¹。将该材料用于光催化产过氧化氢(H₂O₂)时, 无论是在纯水体系还是水/乙醇混合体系中, 反应 1 小时内的产率均可达到 461 μmol·g⁻¹。该材料光催化效率的提升, 可归因于其较大的孔容与较高的比表面积, 这两种特性能够促进氧气与反应物快速扩散至催化活性位点。该过程对于改善材料有限的氧气吸附能力尤为有利[50]。

4. 总结

与其他多孔材料(如无机沸石、金属有机框架、笼状化合物和无定形多孔有机聚合物)不同, COFs 是一类独特的聚合物, 可通过构筑基元的拓扑性质进行结构预设计, 以可逆或不可逆的化学反应驱动并呈现出结晶度和结构完整性。其中, 亚胺键连 COFs 材料因其出色的物理化学特性、高结晶度、大的比表面积和永久孔隙率, 已在吸附、传感、储能、催化和生物应用等领域表现出极大的潜力和应用价值; 然而, 针对亚胺键连 COFs 材料的相关性研究仍局限于通过不同构筑单元及连接方式制备新型材料, 其很大程度被限制在实验室的合成。因此, 除了要开发新的有机配体、合成条件、潜力应用来实现理论与实验的完美结合外, 对功能化 COFs 材料的研究设计将是大势所趋。

参考文献

- [1] Shu, A., Qin, C., Li, M., Zhao, L., Shangguan, Z., Shu, Z., *et al.* (2024) Electric Effects Reinforce Charge Carrier Behaviour for Photocatalysis. *Energy & Environmental Science*, **17**, 4907-4928. <https://doi.org/10.1039/d4ee01379d>
- [2] Li, X., Chen, Y., Tao, Y., Shen, L., Xu, Z., Bian, Z., *et al.* (2022) Challenges of Photocatalysis and Their Coping Strategies. *Chem Catalysis*, **2**, 1315-1345. <https://doi.org/10.1016/j.checat.2022.04.007>
- [3] Buzzetti, L., Crisenza, G.E.M. and Melchiorre, P. (2019) Mechanistic Studies in Photocatalysis. *Angewandte Chemie International Edition*, **58**, 3730-3747. <https://doi.org/10.1002/anie.201809984>
- [4] Côté, A.P., Benin, A.I., Ockwig, N.W., O'Keeffe, M., Matzger, A.J. and Yaghi, O.M. (2005) Porous, Crystalline, Covalent Organic Frameworks. *Science*, **310**, 1166-1170. <https://doi.org/10.1126/science.1120411>
- [5] Ding, S., Gao, J., Wang, Q., Zhang, Y., Song, W., Su, C., *et al.* (2011) Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki-Miyaura Coupling Reaction. *Journal of the American Chemical Society*, **133**, 19816-19822. <https://doi.org/10.1021/ja206846p>
- [6] Lohse, M.S. and Bein, T. (2018) Covalent Organic Frameworks: Structures, Synthesis, and Applications. *Advanced Functional Materials*, **28**, Article 1705553. <https://doi.org/10.1002/adfm.201705553>
- [7] Gao, C., Li, J., Yin, S., Sun, J. and Wang, C. (2020) Redox-Triggered Switching in Three-Dimensional Covalent Organic Frameworks. *Nature Communications*, **11**, Article No. 4919. <https://doi.org/10.1038/s41467-020-18588-1>
- [8] Xiang, Z.H. and Cao, D.P. (2013) Porous Covalent-Organic Materials: Synthesis, Clean Energy Application and Design.

Journal of Materials Chemistry A, **1**, 2691-2718.

- [9] Dogrua, M. and Bein, T. (2014) On the Road Towards Electroactive Covalent Organic Frameworks. *Chemical Communications*, **50**, 5531-5546. <https://doi.org/10.1039/c3cc46767h>
- [10] Huang, T.H., Zhang, W.F., Yang, S., Wang, L.P. and Yu, G. (2024) Imine-Linked Covalent Organic Frameworks: Recent Advances in Design, Synthesis, and Application. *Smart Materials*, **5**, Article 6.
- [11] Segura, J.L., Mancheño, M.J. and Zamora, F. (2016) Covalent Organic Frameworks Based on Schiff-Base Chemistry: Synthesis, Properties and Potential Applications. *Chemical Society Reviews*, **45**, 5635-5671. <https://doi.org/10.1039/c5cs00878f>
- [12] Chen, Y., Liu, R., Guo, Y., Wu, G., Sum, T.C., Yang, S.W., *et al.* (2024) Hierarchical Assembly of Donor-Acceptor Covalent Organic Frameworks for Photosynthesis of Hydrogen Peroxide from Water and Air. *Nature Synthesis*, **3**, 998-1010. <https://doi.org/10.1038/s44160-024-00542-4>
- [13] Ren, J.Y., Ji, C.Q., Du, B.W., Liu, Q.X., Yu, K.X., Ahn, D., *et al.* (2024) A Fully Saturated Covalent Organic Framework. *Journal of the American Chemical Society*, **146**, 30784-30789. <https://doi.org/10.1021/jacs.4c13256>
- [14] Chakraborty, A., Alam, A., Pal, U., Sinha, A., Das, S., Saha-Dasgupta, T., *et al.* (2025) Enhancing Photocatalytic Hydrogen Peroxide Generation by Tuning Hydrazone Linkage Density in Covalent Organic Frameworks. *Nature Communications*, **16**, Article No. 503. <https://doi.org/10.1038/s41467-025-55894-y>
- [15] Yuan, Z.L., Xie, L.X., Liu, R.L., Li, Z.F. and Li, G. (2026) Latest Advances in Fabrication Strategies and Applications of Single-Crystalline Covalent Organic Frameworks. *Coordination Chemistry Reviews*, **552**, Article 217510. <https://doi.org/10.1016/j.ccr.2025.217510>
- [16] Kim, S. and Choi, H.C. (2019) Light-Promoted Synthesis of Highly-Conjugated Crystalline Covalent Organic Framework. *Communications Chemistry*, **2**, Article No. 60. <https://doi.org/10.1038/s42004-019-0162-z>
- [17] Uribe-Romo, F.J., Hunt, J.R., Furukawa, H., Klöck, C., O’Keeffe, M. and Yaghi, O.M. (2009) A Crystalline Imine-Linked 3-D Porous Covalent Organic Framework. *Journal of the American Chemical Society*, **131**, 4570-4571. <https://doi.org/10.1021/ja8096256>
- [18] Xiao, A.K., Zhang, Z., Shi, X.S. and Wang, Y. (2019) Enabling Covalent Organic Framework Nanofilms for Molecular Separation: Perforated Polymer-Assisted Transfer. *ACS Applied Materials & Interfaces*, **11**, 44783-44791. <https://doi.org/10.1021/acsami.9b18062>
- [19] Liao, Q.B., Ke, C., Huang, X., Zhang, G.Y., Zhang, Q., Zhang, Z.W., *et al.* (2019) Catalyst-Free and Efficient Fabrication of Highly Crystalline Fluorinated Covalent Organic Frameworks for Selective Guest Adsorption. *Journal of Materials Chemistry A*, **7**, 18959-18970. <https://doi.org/10.1039/c9ta06214a>
- [20] Su, Y.J., Qin, M.L., Kong, J.L., Zhai, Q.G., Yuan, D.Q., Liu, Z.S., *et al.* (2024) Solvothermal Shaping of Imine-Linked Covalent Organic Frameworks by a Two-Step Solvent Feeding Process. *Advanced Functional Materials*, **34**, Article 2400433. <https://doi.org/10.1002/adfm.202400433>
- [21] Han, X.H., Chu, J.Q., Wang, W.Z., Qi, Q.Y. and Zhao, X. (2022) A Two-Step Solvothermal Procedure to Improve Crystallinity of Covalent Organic Frameworks and Achieve Scale-Up Preparation. *Chinese Chemical Letters*, **33**, 2464-2468. <https://doi.org/10.1016/j.ccl.2021.11.066>
- [22] Tan, J., Namuangruk, S., Kong, W., Kungwan, N., Guo, J. and Wang, C. (2016) Manipulation of Amorphous-to-Crystalline Transformation: Towards the Construction of Covalent Organic Framework Hybrid Microspheres with NIR Photothermal Conversion Ability. *Angewandte Chemie International Edition*, **55**, 13979-13984. <https://doi.org/10.1002/anie.201606155>
- [23] Laemont, A., Matthys, G., Lavendomme, R. and Van Der Voort, P. (2024) Mild and Scalable Conditions for the Solvothermal Synthesis of Imine-Linked Covalent Organic Frameworks. *Angewandte Chemie International Edition*, **63**, e202412420. <https://doi.org/10.1002/anie.202412420>
- [24] Xu, H., Luo, Y., Li, X., See, P.Z., Chen, Z., Ma, T., *et al.* (2020) Single Crystal of a One-Dimensional Metallo-Covalent Organic Framework. *Nature Communications*, **11**, Article No. 1434. <https://doi.org/10.1038/s41467-020-15281-1>
- [25] Liu, W.B., Li, X.K., Wang, C.M., Pan, H.H., Liu, W.P., Wang, K., *et al.* (2019) A Scalable General Synthetic Approach toward Ultrathin Imine-Linked Two-Dimensional Covalent Organic Framework Nanosheets for Photocatalytic CO₂ Reduction. *Journal of the American Chemical Society*, **141**, 17431-17440. <https://doi.org/10.1021/jacs.9b09502>
- [26] Chen, Y.C., Shi, Z.L., Wei, L., Zhou, B.B., Tan, J., Zhou, H.L., *et al.* (2019) Guest-Dependent Dynamics in a 3D Covalent Organic Framework. *Journal of the American Chemical Society*, **141**, 3298-3303. <https://doi.org/10.1021/jacs.8b13691>
- [27] Liu, F., Qian, H.L., Yang, C. and Yan, X.P. (2020) Room-Temperature Preparation of a Chiral Covalent Organic Framework for the Selective Adsorption of Amino Acid Enantiomers. *RSC Advances*, **10**, 15383-15386. <https://doi.org/10.1039/d0ra02647f>
- [28] Matsumoto, M., Dasari, R.R., Ji, W., Feriante, C.H., Parker, T.C., Marder, S.R., *et al.* (2017) Rapid, Low Temperature

- Formation of Imine-Linked Covalent Organic Frameworks Catalyzed by Metal Triflates. *Journal of the American Chemical Society*, **139**, 4999-5002. <https://doi.org/10.1021/jacs.7b01240>
- [29] Zhang, J., Cheng, C., Guan, L., Jiang, H. and Jin, S. (2023) Rapid Synthesis of Covalent Organic Frameworks with a Controlled Morphology: An Emulsion Polymerization Approach via the Phase Transfer Catalysis Mechanism. *Journal of the American Chemical Society*, **145**, 21974-21982. <https://doi.org/10.1021/jacs.3c06764>
- [30] Kong, X.Y., Wu, Z.Q., Strømme, M. and Xu, C. (2023) Ambient Aqueous Synthesis of Imine-Linked Covalent Organic Frameworks (COFs) and Fabrication of Freestanding Cellulose Nanofiber@COF Nanopapers. *Journal of the American Chemical Society*, **146**, 742-751.
- [31] Wang, Z.F., Yang, Y., Zhao, Z.F., Zhang, P.H., Zhang, Y.S., Liu, J.J., *et al.* (2021) Green Synthesis of Olefin-Linked Covalent Organic Frameworks for Hydrogen Fuel Cell Applications. *Nature Communications*, **12**, Article No. 1982. <https://doi.org/10.1038/s41467-021-22288-9>
- [32] Zhang, Y.S., Mao, T.H., Hao, L.Q., Sun, T.K., Wang, T.H., Cheng, P., *et al.* (2023) Solvent-Free Synthesis of C=N Linked Two-Dimensional Covalent Organic Frameworks. *Macromolecular Rapid Communications*, **44**, Article 2200722. <https://doi.org/10.1002/marc.202200722>
- [33] Zhang, P.H., Wang, Z.F., Yang, Y., Wang, S., Wang, T., Liu, J.J., *et al.* (2022) Melt Polymerization Synthesis of a Class of Robust Self-Shaped Olefin-Linked COF Foams as High-Efficiency Separators. *Science China Chemistry*, **65**, 1173-1184. <https://doi.org/10.1007/s11426-022-1224-3>
- [34] Wang, Z.F., Zhang, Y.S., Wang, T., Hao, L.Q., Lin, E., Chen, Y., *et al.* (2023) Organic Flux Synthesis of Covalent Organic Frameworks. *Chem*, **9**, 2178-2193. <https://doi.org/10.1016/j.chempr.2023.03.026>
- [35] Wang, Z.F., Zhang, Y.S., Liu, J.J., Chen, Y., Cheng, P. and Zhang, Z.J. (2024) Flux Synthesis of Two-Dimensional Covalent Organic Frameworks. *Nature Protocols*, **19**, 3489-3519. <https://doi.org/10.1038/s41596-024-01028-5>
- [36] He, J., Jiang, X., Xu, F., Li, C., Long, Z., Chen, H., *et al.* (2021) Low Power, Low Temperature and Atmospheric Pressure Plasma-Induced Polymerization: Facile Synthesis and Crystal Regulation of Covalent Organic Frameworks. *Angewandte Chemie International Edition*, **60**, 9984-9989. <https://doi.org/10.1002/anie.202102051>
- [37] Zhang, W.W., Chen, L.J., Dai, S., Zhao, C.X., Ma, C., Wei, L., *et al.* (2022) Reconstructed Covalent Organic Frameworks. *Nature*, **604**, 72-79. <https://doi.org/10.1038/s41586-022-04443-4>
- [38] Li, W.Q., Huang, X.F., Zeng, T.W., Liu, Y.A., Hu, W.B., Yang, H., *et al.* (2021) Thiazolo[5,4-d]thiazole-Based Donor-acceptor Covalent Organic Framework for Sunlight-Driven Hydrogen Evolution. *Angewandte Chemie International Edition*, **60**, 1869-1874. <https://doi.org/10.1002/anie.202014408>
- [39] Ran, L., Li, Z.W., Ran, B., Cao, J.Q., Zhao, Y., Shao, T., *et al.* (2022) Engineering Single-Atom Active Sites on Covalent Organic Frameworks for Boosting CO₂ Photoreduction. *Journal of the American Chemical Society*, **144**, 17097-17109. <https://doi.org/10.1021/jacs.2c06920>
- [40] Chen, W.B., Wang, L., Mo, D.Z., He, F., *et al.* (2020) Modulating Benzothiadiazole-Based Covalent Organic Frameworks via Halogenation for Enhanced Photocatalytic Water Splitting. *Angewandte Chemie International Edition*, **59**, 16902-16909. <https://doi.org/10.1002/anie.202006925>
- [41] Yang, J., Acharjya, A., Ye, M., Rabeah, J., Li, S., Kochovski, Z., *et al.* (2021) Protonated Imine-Linked Covalent Organic Frameworks for Photocatalytic Hydrogen Evolution. *Angewandte Chemie International Edition*, **60**, 19797-19803. <https://doi.org/10.1002/anie.202104870>
- [42] Zhou, T., Wang, L., Huang, X., Unruangsri, J., Zhang, H., Wang, R., *et al.* (2021) PEG-Stabilized Coaxial Stacking of Two-Dimensional Covalent Organic Frameworks for Enhanced Photocatalytic Hydrogen Evolution. *Nature Communications*, **12**, Article No. 3934. <https://doi.org/10.1038/s41467-021-24179-5>
- [43] Li, Y., Yang, L., He, H., Sun, L., Wang, H., Fang, X., *et al.* (2022) In Situ Photodeposition of Platinum Clusters on a Covalent Organic Framework for Photocatalytic Hydrogen Production. *Nature Communications*, **13**, Article No. 1355. <https://doi.org/10.1038/s41467-022-29076-z>
- [44] Li, Z., Liu, C.C., Deng, Q.W. and Deng, W.Q. (2024) Rational Design of Covalent Organic Frameworks as Photocatalysts for Water Splitting. *Advanced Functional Materials*, **34**, Article 41. <https://doi.org/10.1002/adfm.202402676>
- [45] Yang, J., Ghosh, S., Roeser, J., Acharjya, A., Penschke, C., Tsutsui, Y., *et al.* (2022) Constitutional Isomerism of the Linkages in Donor-Acceptor Covalent Organic Frameworks and Its Impact on Photocatalysis. *Nature Communications*, **13**, Article No. 6317. <https://doi.org/10.1038/s41467-022-33875-9>
- [46] Dong, W.B., Qin, Z.Y., Wang, K.X., Xiao, Y.Y., Liu, X.Y., Ren, S.J., *et al.* (2023) Isomeric Oligo(Phenylenevinylene)-Based Covalent Organic Frameworks with Different Orientation of Imine Bonds and Distinct Photocatalytic Activities. *Angewandte Chemie International Edition*, **62**, Article 202216073. <https://doi.org/10.1002/anie.202216073>
- [47] Chakraborty, A., Chakraborty, P. and Pachfule, P. (2025) Covalent Organic Framework for Photocatalytic Hydrogen Peroxide Production: A Green Pathway. *Chemistry of Materials*, **37**, 9614-9632. <https://doi.org/10.1021/acs.chemmater.5c02292>

- [48] Zou, X.Y., Shi, Q.K., Cheng, M., Huang, D.L., *et al.* (2025) Metal-Organic Framework-Based Materials for Photocatalytic Hydrogen Peroxide Production: Insights into Mechanism, Modification Strategies, and Environmental Applications. *Advanced Energy Materials*, **15**, Article 2501424.
- [49] Krishnaraj, C., Sekhar Jena, H., Bourda, L., Laemont, A., Pachfule, P., Roeser, J., *et al.* (2020) Strongly Reducing (Diarylamino)benzene-Based Covalent Organic Framework for Metal-Free Visible Light Photocatalytic H₂O₂ Generation. *Journal of the American Chemical Society*, **142**, 20107-20116. <https://doi.org/10.1021/jacs.0c09684>
- [50] Liu, L.J., Gao, M.Y., Yang, H.F., Wang, X.Y., Li, X.B. and Cooper, A.I. (2021) Linear Conjugated Polymers for Solar-Driven Hydrogen Peroxide Production: The Importance of Catalyst Stability. *Journal of the American Chemical Society*, **143**, 19287-19293. <https://doi.org/10.1021/jacs.1c09979>