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ZIF-8 metal–organic frameworks and their hybrid materials: emerging photocatalysts for energy and environmental applications

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In the face of escalating environmental challenges such as fossil fuel dependence and water pollution, innovative solutions are essential for sustainable development. In this regard, zeolitic imidazolate frameworks (ZIFs), specifically ZIF-8, act as promising photocatalysts for environmental remediation and renewable energy applications. ZIF-8, a subclass of metal–organic frameworks (MOFs), is renowned for its large specific surface area, high porosity, rapid electron transfer ability, abundant functionalities, ease of designing, controllable properties, and remarkable chemical and thermal stability. However, its application as a standalone photocatalyst is limited by issues such as particle aggregation, poor water stability, and insufficient visible light absorption. By integrating ZIF-8 with various photoactive materials to form composite catalysts, these drawbacks can be mitigated, leading to enhanced photocatalytic efficiency. The review discusses the synthesis, properties, and applications of ZIF-8-based photocatalysts in light-driven H_2 evolution, H_2O_2 evolution, CO_2 reduction, and dye and drug degradation. It also highlights the challenges and future research directions in developing cost-effective, scalable, and environmentally friendly ZIF-8 composites for industrial applications. The potential of ZIF-8 composites to contribute to sustainable global energy solutions and environmental cleanup is significant, yet further exploration is required to harness their capabilities thoroughly.

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1. Introduction

The world faces growing challenges related to environmental pollution, particularly water contamination, and the need for sustainable energy solutions. According to recent estimates, over 1.2 billion people lack access to sufficient drinking water, and increasing carbon emissions from fossil fuel use exacerbate global environmental concerns, leading to environmental issues that necessitate the search for an alternative sustainable energy supply.^{1–5} Additionally, agricultural runoff containing harmful chemicals such as pesticides, organic dyes, and industrial waste further pollutes water bodies, causing significant risks to human welfare and ecosystems.^{6–9} In response to these challenges, solar-light-driven photocatalysis has emerged as a promising, eco-friendly technology.⁶ This process utilizes semiconductors to produce reactive oxygen species (ROS) such as superoxide ($O_2^{\cdot-}$), peroxide ($O_2^{\cdot}$), and hydroxyl radicals ($\cdot OH$), which can degrade pollutants, reduce CO_2 into hydrocarbon fuels, and address various environmental issues.^{10–13} These charge carriers facilitate the pro-

duction of ROSs, which are involved in the degradation of inorganic and organic pollutants, and the reduction of CO_2 to hydrocarbon fuels.^{14–16} Research has extensively explored semiconductor-based heterogeneous photocatalysis driven by direct solar energy or other light sources using materials such as $g-C_3N_4$,^{17–19} perovskites,²⁰ quantum dots,²¹ TiO_2 ,²² Bi_2WO_6 ,²³ CuO ,²⁴ ZnO ,²⁵ CdS ,²⁶ ZnS ,²⁷ and Fe_3O_4 .²⁸ However, photocatalytic applications face challenges such as large band-gaps, fast recombination of photogenerated charge carrier pairs, photocorrosion, limited solar energy application, and low recyclability, all of which restrict their photocatalytic performance.^{29–31} Therefore, it is essential to develop innovative photocatalysts with inclusive applications.

Over the last several decades, there has been an extensive surge in attention to MOFs as encouraging photocatalysts attributed to their extensive surface area, elevated porosity, and adjustable structures, and they have emerged as promising microporous crystalline materials within the coordination polymer family.^{32–34} MOFs consist of inorganic metal components linked by organic materials to create one-dimensional, two-dimensional, or three-dimensional micro- or nanoporous systems. With their unique structures and properties, MOFs have found applications across various fields, including photocatalysis, adsorption, clean energy generation, electronics, energy storage, and medical applications.^{35–38} MOF-templated

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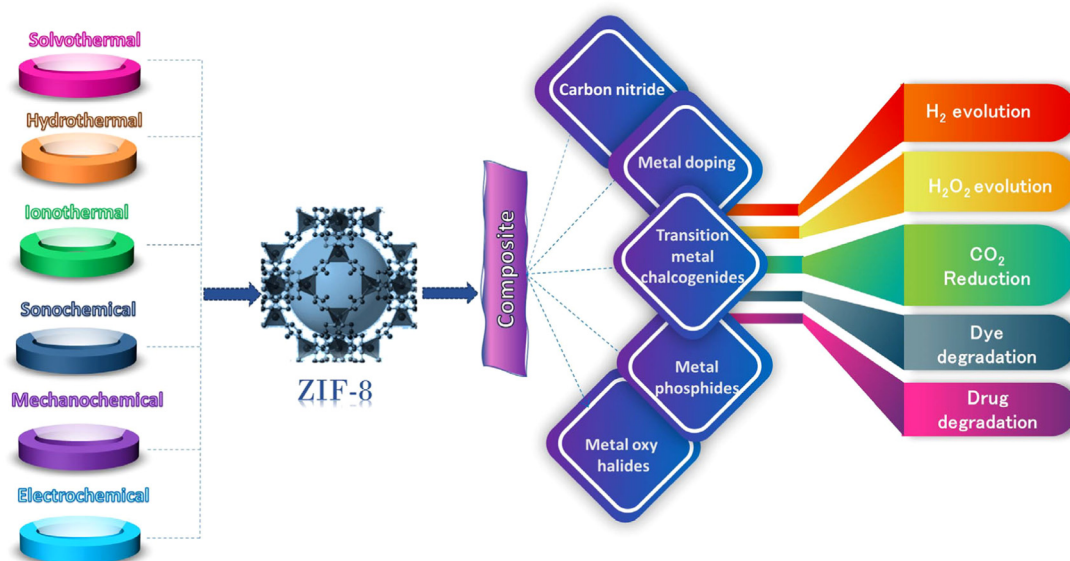


Fig. 1 Schematic representation of the overall contents of the review.

photocatalysts are particularly valued for their high surface area, which enhances active site exposure, mass transfer, and charge carrier transport.^{39–41} Their tunable properties, superior adsorption capacity, flexible frameworks, and multifunctionality make MOFs highly promising as porous photocatalysts.^{42,43} MOFs are characterized by their crystalline nature and exceptional porosity.⁴⁴ With impressive surface areas exceeding 6000 m² g^{−1} and pore diameters ranging from 5 to 25 angstroms, MOFs exhibit nearly 90% of free volumes.⁴⁵ Additionally, their band gaps render them responsive to light, enabling them to utilize solar energy effectively.⁴⁶ Their sizeable specific surface area facilitates an even and extensive dispersion of active species, benefiting the catalyst's performance.⁴⁷ Moreover, MOFs' elevated porosity enhances their ability to adsorb and absorb gases, and the pores can house active species, protecting them from deactivation due to agglomeration.⁴⁸

By modifying synthesis conditions, various functional MOFs can be created due to their highly adaptable structures. ZIFs are attracting considerable attention because of their outstanding chemical and thermal resistance, maximum yield, modifiable micropore shapes and sizes, and flexible design and functionality.^{49,50} One notable example of ZIFs is ZIF-8, renowned for its excellent chemical and thermal stability. ZIF-8 comprises Zn(II) ions and 2-methylimidazole ligands. Based on the Hard and Soft Acids and Bases (HSAB) theory, Zn(II) ions create robust coordination bonds with azolate ligands, resulting in the bond between Zn(II) and 2-methylimidazole being among the most stable coordination interactions.^{51,52} ZIF-8 offers advantages such as an extensive surface area, adjustable pore sizes, active channels, flexible chemical structures, and intense hydrophobicity. ZIF-8's synergistic interaction between the Zn²⁺ metal center and imidazolate linker provides abundant active sites for photocatalysis, surpassing

traditional semiconductors like TiO₂ and ZnO, which rely on fixed material structures.⁵³ The Zn²⁺ center serves as a redox site, facilitating electron transfer, charge stabilization, and reduced recombination, while the organic linker enhances photocatalytic interactions *via* coordination bonds, π – π stacking, and charge transfer. This hybrid system enables broader light absorption, tunable band gaps, and higher reactivity compared with conventional materials. The porous, high-surface-area framework of ZIF-8 supports guest molecule encapsulation, doping, and multifunctional catalysis, enhancing catalytic efficiency. Its structural flexibility and selective interactions make it ideal for targeted photocatalytic applications like CO₂ reduction and pollutant degradation, while its stability under irradiation resists photodegradation, unlike TiO₂ or CdS.⁵⁴ Additionally, ZIF-8 can be prepared at RT with minimal expense. Nonetheless, it has certain limitations: (i) ZIF-8 often clumps together in water, leading to the growth of particle dimensions and resistance to transfer, which diminishes their adsorption capacity; (ii) extracting ZIF-8 nanomaterials from aqueous solutions is demanding, hindering their ability to be regenerated and reused; (iii) ZIF-8 has a limited response to visible light due to its broadband gap, which reduces its effectiveness under solar irradiation. Consequently, the application of ZIF-8 monomers is significantly limited.⁵⁵ To address these issues, photoactive molecules or semiconductors are combined with ZIF-8 to create ZIF-8-based binary or ternary photocatalysts. The formation of these novel multifunctional composites or hybrids is achieved by carefully combining ZIF-8 with functional materials. Unlike single-component photocatalysts, while rapid electron-hole recombination is common, thoughtfully engineered composite photocatalysts can leverage the combined advantages of each individual component while mitigating their drawbacks, leading to enhanced photocatalytic efficiency.⁵⁶ Various ZIF-8-



based composites, including oxides,⁵⁷ sulfides,⁴⁶ C_3N_4 ,⁵⁸ and metals,⁴⁸ have been developed to date. These hybrids have demonstrated outstanding photocatalytic performance compared with pristine ZIF-8.

This review article offers a comprehensive analysis of ZIF-8 and its hybrid materials, highlighting their dual role in energy generation and environmental remediation. Unlike existing studies that often focus on either adsorption or specific photocatalytic applications, this work uniquely integrates insights across both domains. It demonstrates how ZIF-8-based materials can address clean energy needs, such as hydrogen and hydrogen peroxide production, while simultaneously tackling pollutant degradation and wastewater treatment. This dual approach positions ZIF-8 as a versatile platform for sustainable energy solutions and environmental protection. By bridging these critical areas, the review presents a unified framework for designing multifunctional photocatalytic systems that meet global energy and environmental challenges, marking a significant contribution to the field. The urgency of this work is underscored by the increasing need for sustainable solutions to global challenges like energy shortages and water pollution, making this review a timely and valuable contribution to the field. So this review aims to fill these gaps by providing an integrative analysis of the dual functionality of ZIF-8-based materials in energy generation and environmental remediation. It systematically summarizes recent progress in ZIF-8's structural engineering, highlighting strategies such as doping with metals and composite formation with semiconductors to enhance photocatalytic efficiency. The review further delves into the mechanisms driving ZIF-8's photocatalytic activities, offering a holistic understanding of its role in addressing global challenges in sustainability. Here we have outlined various preparation techniques for ZIF-8 and ZIF-8-based hybrid synthesis in photocatalysis, offering theoretical guidance and promoting the development of ZIF-8-based photocatalysts and summarizing recent advances in ZIF-8 and their hybrids for energy and environmental applications, with a focus on synergistic effects that enhance the stability and photocatalytic activity of these materials. Lastly, it discusses the current challenges and future directions. Overall, this review not only establishes a foundational database for ZIF-8 MOFs and their photocatalytic properties but also provides strategic insights for designing and synthesizing ZIF-based MOFs with possible applications within the discipline of photocatalysis (Fig. 1).

2. Overview of ZIF-8 metal–organic framework

ZIFs are a subclass of MOFs that have garnered widespread attention because of their combination of zeolite and MOF properties, such as extensive surface area, crystallinity, microporosity, and notable chemical and thermal stability.^{59,60} They are named for their zeolite-like structure, where the typical tetrahedral aluminum or silicon with bridging oxygen is

replaced by zinc or silicon bridged by imidazolate. Both structures share a bond angle of 145° , as illustrated in Fig. 3a. Numerous ZIFs have been documented, typically featuring metal ions like cobalt or zinc connected through nitrogen to imidazolate linkers, forming adjustable nanopores.⁶¹ These pores are created by a CoN_4 or ZnN_4 tetrahedral complex, which allows guest molecules to enter for applications in catalysis and gas storage and enable molecular-level differentiation for gas separation. Imidazole is part of the heterocyclic compound family, characterized by a 5-membered ring structure. Its chemical formula is $C_3N_2H_4$, consisting of 3 carbon atoms and 2 nitrogen atoms positioned at the 1st and 3rd locations in the ring (Fig. 3b). Due to the hydrogen atom's ability to link with either nitrogen atom, imidazole exists in two tautomeric states.⁶² Also referred to as 1,3-azole, imidazole is a strongly polar compound that dissolves easily in water and displays amphoteric properties, meaning it can act as both an acid and a base.⁶³ In its solid form, imidazole is a white, colorless substance with a boiling point of 267.8°C and a melting point of 88.9°C .⁶⁴

Compared with zeolites, ZIFs possess greater flexibility owing to their inorganic–organic framework and functionalized imidazolate linkers. This flexibility allows easier control over their structures and pore sizes, enabling greater ease in modifying their properties. ZIF-8, one of the most extensively researched ZIFs, consists of zinc tetrahedral clusters linked by 2-methyl imidazolate. It is synthesized using zinc salt and 2-methyl imidazole, forming a sodalite (SOD) type zeolite structure that takes the shape of a truncated octahedron.⁵⁹ These octahedrons interconnect to form a 3D framework, as shown in Fig. 3c. Initially synthesized by Yaghi *et al.* in 2006 through solvothermal methods, ZIF-8 and other ZIFs demonstrate significant chemical resistance in heated organic solvents, water, and alkaline aqueous solutions, a trait not observed in other MOFs (Fig. 3d).^{45,59}

ZIF-8 possesses extremely high surface areas. In Yaghi's initial study, ZIF-8 demonstrated a Brunauer–Emmett–Teller (BET) surface area of $1630\text{ m}^2\text{ g}^{-1}$, significantly exceeding any zeolite, providing abundant active sites that enhance the adsorption of reactant molecules like dyes, drugs, and water, thereby improving photocatalytic efficiency.^{59,65,66}

Its microporous structure, with pore openings of $3.4\text{ \AA}$ and pores with a diameter of $11.6\text{ \AA}$, is attributed to the methyl groups on the imidazolate linkers. As a result, pore sizes are roughly twice those of zeolites, while the apertures are analogous to the minimal molecular sieves, enabling selective adsorption and diffusion of target molecules, facilitating the trapping of reactants and intermediates to boost degradation and energy conversion processes.⁵⁹

ZIF-8 is also thermally and chemically stable, enduring a wide range of temperatures and pH conditions, making it ideal for harsh photocatalytic environments, such as acidic or basic systems used in pollutant degradation.⁶⁷

Although its wide bandgap ($\sim 5.1\text{ eV}$) limits direct photocatalysis under visible light, ZIF-8 serves as an excellent support material for narrow-bandgap semiconductors, for facilitating



charge transfer when doping with metals (Cu, Ag) or combined with other photocatalytic materials like (TiO₂, Cu₂O, g-C₃N₄), improving light absorption and charge separation, and reducing the recombination of charge carriers.^{65,66}

ZIF-8 is stable and insoluble in water and methanol, even in reflux conditions, and resists hydrolysis, which is uncommon among zinc-based MOFs. This exceptional stability is attributed to two factors: the strength of the bond between the imidazolate nitrogen and the metal ion, which is analogous to covalent solids.⁶⁸ The hydrophobic nature of ZIF-8 pores, which deters water molecules and prevents their attack on the MIm₄ (M = Zn) tetrahedral units, which contributes to ZIF-8's exceptional stability, is highly advantageous for various applications, allowing it to withstand harsh chemical and thermal environments.⁶⁹

The structural tunability of ZIF-8, achieved through ligand modification or metal ion substitution, optimizes its electronic properties, surface chemistry, and light-harvesting abilities for targeted applications. Moreover, its metal center (Zn²⁺) facilitates electron transfer, enhancing the generation of ROSs such as hydroxyl radicals and superoxide anions, crucial for photocatalytic oxidation.⁷⁰

Finally, ZIF-8 acts as a stabilizer or protective layer for embedded semiconductors, reducing photocorrosion and ensuring long-term activity, particularly for sensitive materials like Cu₂O. These characteristics collectively make ZIF-8 a versatile and robust platform for photocatalytic applications in energy generation and environmental remediation (Fig. 2).⁷¹

3. Synthesis procedures

The synthesis strategies for creating ZIF-8 structures with desirable and valuable properties are influenced by various synthetic factors. The primary precursors for ZIF-8 fabrication are zinc metal and 2-methylimidazole. Several parameters

need to be fine-tuned during the crystallization procedure, including the concentration of starting materials, temperature, solvent choice, and agitation rate. In this discussion, we explore several methods for synthesizing ZIF-8, including solvothermal, hydrothermal, ionothermal, sonochemical, mechanochemical, and electrochemical synthesis.

3.1 Solvothermal

In the pioneering work by Yaghi *et al.*, solvothermal synthesis was used to create twelve distinct ZIF crystals, designated as ZIF-1 to ZIF-12, which were successfully synthesized using a range of organic solvents, including methanol, *N,N*-dimethylformamide (DMF), *N*-methyl pyrrolidine (NMP) and *N,N*-diethylformamide (DEF).^{59,72} To aid the formation, organic amines like pyridine and triethylamine (TEA) were introduced as deprotonating agents into the DMF or DEF solvent. The development and architecture of ZIF-8 feature large spherical cages called sodalite cages connected by six-ring windows.⁷³

Methanol's versatility as a solvent in organic synthesis prompted various research groups to explore its use in ZIF synthesis, with additives such as high molecular weight, which was found to enhance ZIF-8 formation.⁷⁴ Chen *et al.* later achieved the synthesis of ZIF-8 (initially referred to as MAF-4) using methanol as the reaction medium. This involved a meticulous layering process where a methanol solution containing 2-methylimidazole was gradually coated onto an aqueous ammonia solution, including Zn(OH)₂, over the course of one month.⁷⁵ Following this, Venna *et al.* introduced an approach for synthesizing ZIF-8 *via* the solvothermal method, with methanol as the solvent. They initiated the process by stirring the mixture for 5 minutes at room temperature before transferring it into a Teflon-lined autoclave. Subsequently, the solution was heated for 5 hours at 150 °C under autogenous pressure. This approach, while still utilizing comparatively elevated temperatures, significantly reduced the time required for syn-

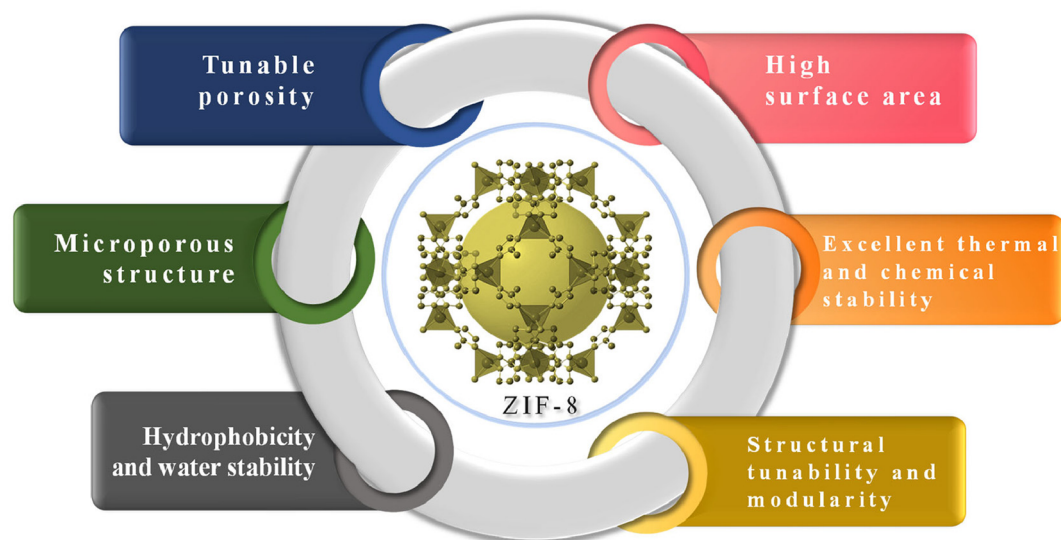


Fig. 2 Schematic representation of various properties of ZIF-8.



thesis and benefited from the cost-effectiveness of methanol as a solvent. The structure of ZIF-8 crystals was also examined. The average crystal size of ZIF-8 was approximately 45 nm, determined using Scherrer's equation from the amplifying of the X-ray diffraction (XRD) peaks shown in Fig. 3e. TEM analysis confirmed the formation of ZIF-8, with diffraction rings matching XRD peaks and indicating a body-centered cubic arrangement with a unit cell dimension measuring 16.48. TEM images revealed sharp, hexagonal crystals around 55 nm, with lattice fringes corresponding to the (222) planes, captured with minimal TEM exposure to prevent crystal amorphization.⁷⁶ Further nanoscale ZIF-8 was synthesized using methanol by combining a solution of methanol containing Zn(NO₃)₂ and 2-methylimidazole under ambient conditions.⁷⁷

To refine the synthesis process, Wiebcke *et al.* introduced sodium 1-methylimidazole/formate and *n*-butylamine as modulating ligands into methanol solutions, allowing for the regulation of ZIF-8 crystal size. This adjustment enabled the tuning of crystal sizes ranging from 10 to 65 nm for nanocrystals or approximately 1 mm for microcrystals. Through the utilization of *ex situ* scanning electron microscopy (SEM) and *in situ* energy dispersive X-ray diffraction (EDXRD), we have demonstrated that the solvothermal crystallization of ZIF-8, modulated by sodium formate, proceeds rapidly, resulting in the formation of large, high-quality single crystals within a brief time-frame (<4 hours).^{83,84} Alternative alcohols like isopropyl alcohol and ethanol also demonstrated effectiveness in this context. However, concerns over the costly, toxic, and flam-

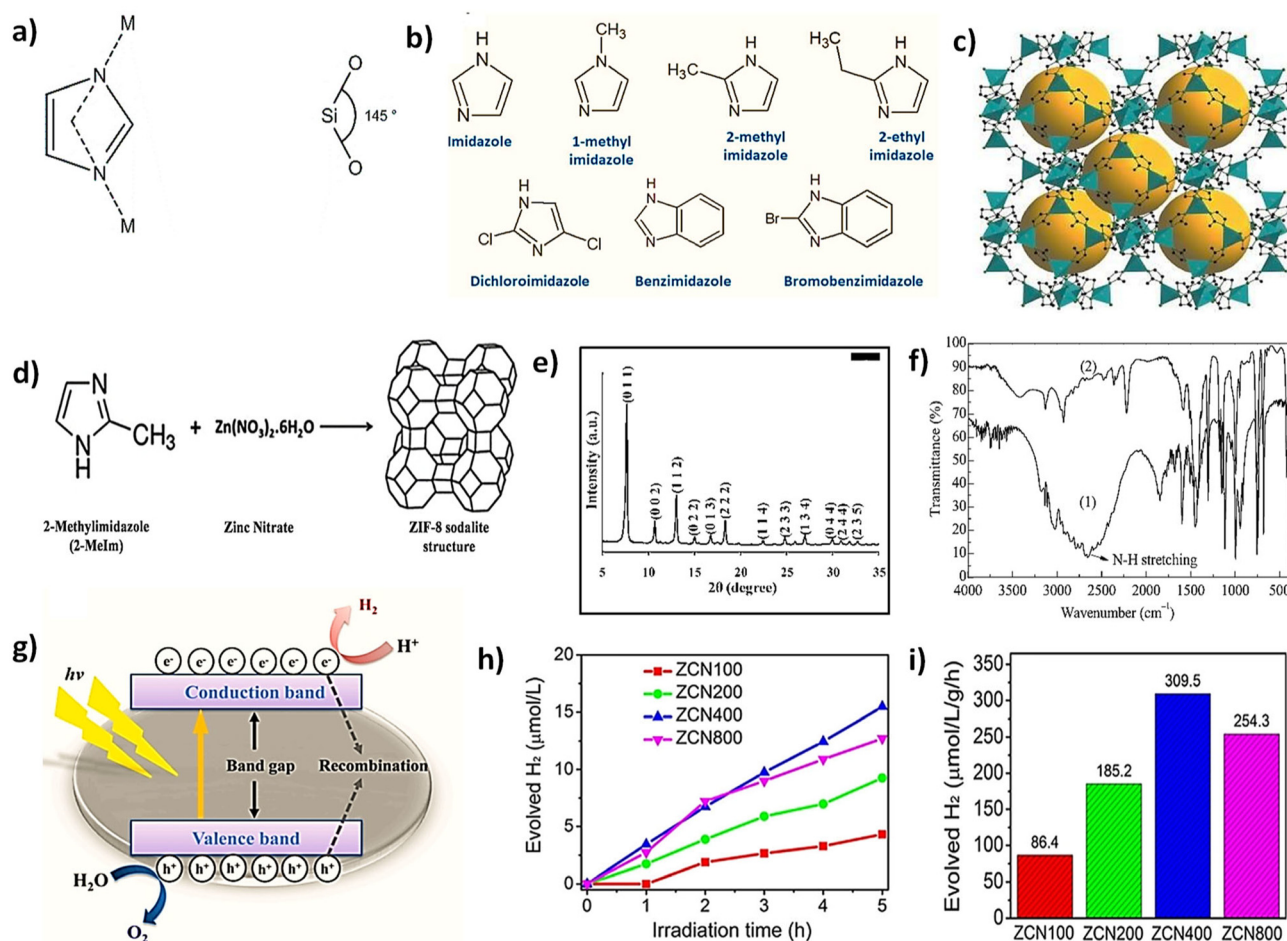


Fig. 3 (a) The bridging angle in both ZIFs and zeolites is 145° [reproduced from ref. 78 with the permission from The University of Liverpool]. (b) Imidazole and certain derivatives of it are utilized as linkers [reproduced from ref. 79 with the permission from Elsevier, copyright 2023]. (c) The structure of ZIF-8, with yellow spheres representing the pore volume [reproduced from ref. 78 with the permission from The University of Liverpool]. (d) Sodalite structure of ZIF-8 formed from zinc metal and 2-methylimidazole [reproduced from ref. 45 with the permission from Elsevier, copyright 2017]. (e) XRD pattern of ZIF-8 crystals used for membrane fabrication [reproduced from ref. 76 with the permission from American Chemical Society, copyright 2010]. (f) FTIR spectra of 2-methylimidazole (1) and ZIF-8 sample (ILs-R1) (2) synthesized via the ionothermal method in [emim]Br [reproduced from ref. 80 with the permission from Elsevier, copyright 2015]. (g) Photocatalytic hydrogen generation through water splitting [reproduced from ref. 81 with the permission from Elsevier, copyright 2020]. (h) Solar-powered photocatalytic hydrogen generation performance, including hydrogen production rates (i), for various ZIF-8/modified g-C₃N₄ nanocomposites ZCN X [reproduced from ref. 82 with the permission from Elsevier copyright 2018].



mable nature of organic solvents prompted a shift towards hydrothermal synthesis methods during this period.⁸⁵

3.2 Hydrothermal

Researchers have opted for water, the most economical solvent available, in their endeavors, wherein a solution of zinc(II) nitrate is immersed in an excess amount of 2-methylimidazole (Hmim/Zn = 70).⁸⁶ This approach aligns with the growing trend of adopting greener and simpler methods, reducing reliance on toxic organic solvents. Additionally, water-based processes for ZIF production have been optimized with additives. Under ambient temperature, ZIF-8 nanoparticles can be synthesized *via* the hydrothermal method, which involves three main stages: (a) dissolving zinc sources in demineralized water, (b) dissolving organic ligands in demineralized water, and (c) combining both the solutions to initiate the reaction and generate ZIF-8 particles.⁸⁷ Ding and his co-workers reported that the hierarchically structured ZIF assembled through the hydrothermal technique exhibited a surface area of 304 m² g⁻¹, with dimensions of several micrometers in length, 1–2 micrometers in width, and around 300 nm in thickness.⁸⁸ Song *et al.* capitalized on the benefits of the hydrothermal process and the unique properties of ZIF-8. The XRD pattern indicates that the product possesses a dense diamond (Zn) structure. As depicted in the SEM image, the product exhibits a characteristic plate-like morphology, with dimensions typically ranging from 3 to 5 μm. It is plausible to infer that an excess of water diminishes the overall solution's basicity, thereby retarding the deprotonation rate of Hmim.⁸⁵

Butova *et al.* (2017) demonstrated a streamlined approach in utilizing triethylamine (TEA) to synthesize a ZIF-8 catalyst in a single phase with remarkable properties: a large specific surface area of 1340 m² g⁻¹, and excellent thermal stability up to 470 °C in N₂ and 400 °C in air, all achieved in water without the need for organic solvents.⁸⁹ In a separate study, Oozeerally *et al.*, in 2019, compared two synthesis methods for ZIF-8: hydrothermal synthesis at 140 °C and room temperature synthesis. The hydrothermal method yielded a compound with an exceptional specific surface area of 1967 m² g⁻¹, rendering it highly applicable.⁹⁰ ZIFs synthesized *via* the hydrothermal method typically exhibit a particle size of about 100 nm, while those made using the solvothermal approach have a particle size closer to 30 nm. Several composites and heterojunctions incorporating ZIF-8, such as Zn₂SnO₄/ZIF-8,⁹¹ ZIF-8/NiFe₂O₄,⁹² and ZIF-8@TiO₂ core-shell micron composites,⁹³ have been effectively fabricated using the hydrothermal process.

3.3 Ionothermal

A novel synthesis approach known as ionothermal synthesis has emerged for the production of ZIF materials.^{94,95} Cooper *et al.* suggested an alternative solvothermal method for preparing ZIFs, utilizing an ionic liquid as the medium.⁹⁶ This novel method, known as the ionothermal technique, is gaining significant interest among researchers working with various ZIFs. In ionothermal synthesis, the ionic liquid acts as a salt capable of melting at temperatures between 150 °C and

200 °C, the range typically used for synthesizing zeolites.⁹⁴ This method utilizes environmentally friendly solvents such as eutectic mixtures and ionic liquids, which offer several advantages and exhibit fascinating properties that make them exceptional solvents. These properties include stability at elevated temperatures, high solubility for both non-polar and polar inorganic and organic compounds, low melting point, and suitable viscosity, along with the advantages of having minimal vapor pressure and being non-flammable. Additionally, a significant advantage of ionic liquids is their ability to be recycled and reused, contributing to sustainable practices.

Morris and his team were the first to recognize the feasibility of employing ionic liquids in the synthesis of ZIFs. They documented the generation of four ZIFs, with structures either known or novel, under ionothermal parameters utilizing the ionic liquid 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide.⁹⁷ Martins and coworkers introduced an ionic liquid synthesis approach utilizing the commercially available IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.⁹⁷ This synthesis methodology has garnered considerable interest among researchers due to its adaptability in an open system.

Wang and colleagues detailed the production of various ZIFs, notably ZIF-8, through the ionothermal method. The XRD spectra for the ZIF-8 and ZIF-67 samples corresponded closely with the simulated patterns derived from the sod-type single-crystal data. The FTIR spectrum of the ZIF-8 sample shows that the vibrational frequency for the N–H bond of 2-MIm at 3335–2500 and 1820 cm⁻¹ has vanished, indicating complete deprotonation of 2-MIm upon coordination with Zn (Fig. 3f). This finding indicates that the samples produced by both rapid and controlled cooling methods were pure-phase sodalite-type ZIFs. The SEM micrographs of ZIF-8 and ZIF-67 samples created through rapid cooling had an aggregated spherical shape with average particle sizes of 0.5 μm and 0.35 μm, respectively. Conversely, samples cooled through programmed cooling displayed truncated rhombic dodecahedral shapes, with dimensions of 50 μm and 5 μm for ZIF-8 and ZIF-67, respectively. These findings underscored that samples cooled *via* programmed methods yielded larger and more uniform structures compared with those cooled rapidly.⁸⁰

3.4 Sonochemical

The sonochemical method involves using ultrasound waves to facilitate chemical reactions, leading to reduced reaction times compared with solvothermal synthesis. It can also be called the sono-crystallization process. This synthesis offers an alternative approach to producing ZIFs, complementing conventional oven heating methods. This method not only facilitates nucleation but also ensures homogeneous dispersion of nucleation.⁹⁸ The sonochemical method involves generating and collapsing bubbles in solutions, known as acoustic cavitation, which generates high pressures, temperatures, and rapid cooling and heating rates.⁹⁹

Research by Seoane *et al.* indicates that under ultrasound radiation at a frequency of 47 kHz and a power of 110 W, pure ZIF-8 frameworks were formed at very low temperatures



(45–60 °C) and briefer durations (6–9 hours) compared with traditional solvothermal synthesis methods. By incorporating a synthetic activator and enhancing the substrate concentration ($\text{Zn}^{2+}:\text{DMF} = 1:9.3$), an 85% yield was achieved. Consequently, the sonochemical method proves more favorable for rapidly synthesizing smaller-sized ZIF-8 particles. SEM images of the ZIFs were prepared through sonocrystallization. By analyzing these SEM images, cumulative crystal size distributions were derived. Moreover, these crystals were observed to be smaller and exhibited a narrower particle size distribution compared with conventionally synthesized materials.¹⁰⁰

Recent work by Cho and his colleagues demonstrated the successful synthesis of abundant amounts of ZIF-8 employing a direct ultrasonic method in dimethylformamide in the midst of NaOH and triethylamine as a modulating agent. It exhibited comparable physiochemical properties, thermal stability, and chemical stability to traditional synthesized ZIF-8 but with a significantly reduced reaction time of 24 hours.¹⁰¹ Furthermore, they achieved scale-up to a 1-liter synthesis of ZIF-8 through this sonochemical synthesis process, showing potential for industrial applications.

3.5 Mechanochemical

Mechanochemistry, as an environmentally friendly and efficient approach, has exhibited remarkable potential, and it involves ball milling for the fabrication of ZIFs.¹⁰² By eliminating the need for solvents and salts during the synthesis method, the mechanochemical synthesis method can significantly decrease environmental pollution and minimize the incorporation of impurities within the crystal lattice. In 2006, the initial step towards obtaining nonporous $\text{Zn}(\text{IM})_2$ was achieved through manual milling of ZnO with a substantial excess of IM.^{103,104} Adams *et al.* demonstrated the generation of nonporous $\text{Zn}(\text{IM})_2$ products through a two-step mechanochemical process initiated from ZnCl_2 .^{104,105}

Recognizing the constraints associated with oxide-based precursors in direct grinding for ZIF synthesis, Friščić *et al.* introduced advanced mechanochemical approaches known as liquid-assisted grinding (LAG) and ion- and liquid-assisted grinding (ILAG). These techniques allowed the formation of ZIFs from a balanced 1:2 molar ratio of ZnO and various ligands, including imidazole, 2-ethylimidazole, and 2-methylimidazole, at ambient temperature.^{106,107} It was observed that adding a small-volume liquid phase enhanced molecular mobility, while salt additives accelerated ZIF formation.¹⁰⁸ Moreover, the topology of the resulting ZIFs could be adjusted by varying the milling liquids (such as ethanol, DMF, and DEF) and salt enhancers (like NH_4NO_3 , $\text{NH}_4\text{CH}_3\text{SO}_3$, and $(\text{NH}_4)_2\text{SO}_4$). Friščić *et al.* also monitored the ball mill grinding process, the synthesis of intermediates, and the transition of ZIF topologies through *in situ* high-energy synchrotron X-ray diffraction.¹⁰⁹

Lately, Tanaka and co-authors showcased a completely solvent-free mechanical transformation of ZnO to ZIF-8 free from any additional substances. They accomplished this by adding nano-sized ZnO powders (averaging 24 nm in particle size) along with MIM into a ball mill operating at 100 rpm.¹¹⁰

It was observed that larger nanoparticles retained untransformed ZnO, whereas smaller nanoparticles did not, indicating that nano-sized ZnO particles were more prone to converting into ZIF-8. The suggested mechanism involves the breaking down of nanoparticle agglomerates into smaller pieces, followed by the formation of complexes *via* the reaction between ZnO and MIM. The resulting ZIF-8 agglomerates into nanoparticles, which subsequently coat the ZnO. Besides crystalline ZIFs, Cheetham and his team demonstrated the synthesis of amorphous ZIFs through ball milling. Through grinding, various amorphous ZIF products can be synthesized.

3.6 Electrochemical

For more than a decade, researchers have employed the electrochemical synthesis method to produce MOFs.¹¹¹ This method is categorized into cathode synthesis and anode synthesis based on the underlying reaction mechanisms. In the solution, anode synthesis involves the dissolution of metals at the anode, forming metal ions that subsequently self-assemble with organic linkers. On the other hand, cathode synthesis utilizes oxoanions such as NO_3^- or ClO_4^- to create an alkaline gradient near the cathode. This gradient aids in the deprotonation of organic linkers, facilitating their self-assembly with incorporated metal ions.¹¹²

Researchers have increasingly turned to electrochemical synthesis methods to produce ZIF-8 crystals, drawn by their numerous advantages: low energy requirements, mild operational conditions, rapid kinetics, significant yields, and simplicity of operation and equipment.¹¹³ Martinez Joaristi and co-authors utilized an anode synthesis method to fabricate ZIF-8 using solvents such as water, ethanol, methanol, and DMF. Notably, ZIF-8 synthesis exhibited flexibility in electrolyte choice (Na_2SO_4 , KCl, or KNO_3) and achieved reduced synthesis durations (<20 min).¹¹⁴

Worrall *et al.* successfully synthesized 5 ZIF coatings using the anodic method, incorporating 2 metals, zinc and cobalt, along with 4 different linkers: imidazole (IM), benzimidazole (bIM), 2-methylimidazole (mIM), and 2-ethylimidazole (eIM). PXRD confirmed the composition of the coatings which verified the synthesis of ZIF-8, that shares the stable SOD structure, when zinc and mIM were used as precursors. SEM was employed to analyze the quality and morphology of the ZIF coatings, and the SEM images suggested tiny crystals with unclear morphology constituting the coating. However, upon in-depth examination, the expected morphology of rhombic dodecahedral characteristic of ZIF-8 crystals became evident.¹¹⁵

The research group of Li proposed a three-electrode setup for an easy and adaptable electrochemical approach to synthesize ZIF-8, ZIF-67, as well as hybrid ZIF-67/ZIF-8 films. These films displayed coherent and consistent properties when deposited on conductive substrates (such as FTO, carbon cloth, and Ni foam) and nanostructured materials in just seconds at standard ambient temperature. An especially significant benefit was the ability to precisely regulate film thickness at the micron scale by adjusting the electrosynthesis time.¹¹⁶



The synthesis of ZIF-8 materials demonstrates the versatility and adaptability of different methods, each offering unique benefits and limitations. From traditional solvothermal and hydrothermal approaches to more novel ionothermal, sonochemical, mechanochemical, and electrochemical methods, advancements have been made to optimize crystal size, morphology, and yield while promoting environmental sustainability and scalability. Each method fine-tunes parameters such as solvents, temperatures, and additives, showcasing the diverse strategies available for ZIF-8 production, making it a promising material across various applications. Table 1 summarizes the advantages and disadvantages of the abovementioned synthetic procedures.^{99,117–123}

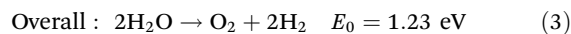
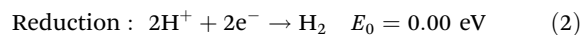
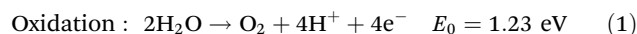
4. Photocatalytic applications

ZIF-8 demonstrates photocatalytic potential due to its extensive surface area, high porosity, and exceptional chemical stability, which enhance the adsorption and interaction of reactant species. Although its direct light-harvesting ability is constrained by a broad bandgap, the incorporation of ZIF-8 with photoactive semiconductors augments its photocatalytic efficacy by promoting superior charge separation, efficient electron transport, and prolonged carrier lifetimes, thus driving enhanced photocatalytic processes.

4.1 H₂ evolution

Photocatalytic H₂ production from water is seen as a prominent solution to the global energy scarcity.^{124,125} This process involves three key stages: (1) photons with energy exceeding the bandgap excite electrons in the valence band (VB) to the conduction band (CB), resulting holes in the VB; (2) the resulting charge carriers separate and emigrate to the material's surface; (3) electrons in the CB reduce adsorbed H⁺ to H₂,

while holes in the VB oxidize water into oxygen. These steps are crucial for the redox reactions required for H₂ production.¹²⁶



For the H₂ evolution reaction (HER) to occur, the CB energy level must be lower than 0 V ($E(\text{H}^+/\text{H}_2)$) under the normal hydrogen electrode (NHE). Additionally, the VB energy level must be higher than 1.23 V ($E(\text{O}_2/\text{H}_2\text{O})$) for the water oxidation reaction to proceed (Fig. 3g).⁸¹

The development of numerous photocatalysts has gradually made photocatalytic hydrogen production an ideal and feasible technology. Among them, g-C₃N₄ has garnered significant attention due to its appropriate energy band (2.8 eV), stable structure, cost-effectiveness, and easy availability. Since 2009, g-C₃N₄ has been extensively utilized in photocatalytic H₂ generation. Thus, Tian and his team effectively incorporated ZIF-8 nanoparticles onto a modified rod-like g-C₃N₄ structure. The ZIF-8 nanoparticles display a sharply defined polyhedral crystal shape around 200 nm in average size, while the modified g-C₃N₄ materials form rod-like structures with irregular surface pores. This ZIF-8/g-C₃N₄ photocatalyst was used for H₂ evolution *via* solar-driven water splitting. Relative to pristine ZIF-8, the ZIF-8/g-C₃N₄ hybrid photocatalysts demonstrated a marked increase in hydrogen generation activity when exposed to light. Additionally, they investigated the impact of varying amounts of g-C₃N₄ on the photocatalytic efficiency of the ZIF-8/g-C₃N₄ hybrid, finding that 400 mg of g-C₃N₄ generated the highest H₂ production rate of 309.5 μmol L⁻¹ g⁻¹ h⁻¹ (Fig. 3h and i). This improved efficiency was supplied to the combined effects of the hybrid, which promoted excellent charge separation and light absorption.⁸²

Table 1 Comparative advantages and disadvantages of various synthesis methods

Methods	Advantages	Disadvantages
Solvothermal	- Readily obtained single crystals - Allows controlled tuning of particle morphology	- Requires soluble precursor reagents - Large amounts of solvent waste generated - Potentially hazardous handling of corrosive/explosive metal salts (chlorides, nitrates) in the presence of organic liquids
Hydrothermal	- Simple, easy and low-cost synthesis method - Production of high quality 1D nanostructures	- The reaction takes a long time for high quality crystals - Produces relatively large particle sizes, limiting surface area
Ionothermal	- The morphology is controlled by synthesis parameters - Eliminates the need for toxic organic solvents by using ionic liquids	High cost of ionic liquids limits large-scale application
Sonochemical	- Rapid synthesis, significantly reducing reaction time - Produces smaller particles with narrow size distributions	- High-energy ultrasound equipment is necessary - Limited scalability for large-scale production
Mechanochemical	- Solvent-free, eco-friendly, and low-cost synthesis - Rapid and energy-efficient process	- Limited control over morphology and size of particles - Not suitable for producing large quantities with uniform characteristics
Electrochemical	- High yield - Less time required, morphology can be controlled through the control of synthesis parameters such as time, temperature <i>etc.</i>	Unsuitable for large-scale production



Nitrogen (N) vacancies on the interface of g-C₃N₄ create strong electronegativity, resulting in hydrogen adsorption and microbubble formation that obstructs reactions. In high-salinity seawater, charged ions occupy these N vacancies, competing with hydrogen protons for photogenerated electrons and further hindering hydrogen generation. For this, Xing *et al.* revealed that incorporating ZIF-8 into g-C₃N₄ eliminated the nitrogen-induced vacancies, enhancing hydrogen generation through photocatalytic seawater splitting. TEM images revealed numerous pores, about 32 nm in diameter, within the sheet structure of ZCNQ40. Nitrogen doping enhanced light absorption in all samples, leading to a decreased band gap. As shown in Fig. 4a, by DRS curves, the band gap of ZCNQ40 reduced from 2.66 eV to 2.58 eV, and the Mott-Schottky arcs of pristine g-C₃N₄ and ZCNQ40 both showed an ascending line, confirming their n-type semiconductor nature. The band alignment potential of ZCNQ40 shifted negatively by 0.09 V, from

−1.33 V for pure g-C₃N₄ to −1.42 V (vs. SCE), indicating a shift to lower energy in the conduction band potential. The composite containing 40 mg of ZIF-8 (ZCNQ40) produced the most H₂ in seawater, reaching 116.95 μmol L^{−1} g^{−1} h^{−1}, and in distilled water, achieving 218.4 μmol L^{−1} g^{−1} h^{−1}, with these rates being 5.6 times and 3.1 times higher, respectively, compared with those achieved with pure g-C₃N₄.¹²⁷ Suda *et al.* (2020)¹²⁸ developed an innovative hybrid Z-scheme photoactive catalyst by integrating copper-doped ZIF-8 with g-C₃N₄ for hydrogen production. The inclusion of g-C₃N₄ notably boosted the H₂ production rate from 32.2 μmol L^{−1} g^{−1} h^{−1} to 213.3 μmol L^{−1} g^{−1} h^{−1}. This enhancement was due to the creation of a Z-scheme charge carrier separation mechanism resulting from the combination of copper-ZIF-8 with g-C₃N₄. Additionally, g-C₃N₄ optimized the absorption in the 480 nm range, which ZIF-8 alone could not capture.¹²⁸ Chang *et al.* developed a nitrogen-doped carbon (C-ZIF) decorated g-C₃N₄ hetero-

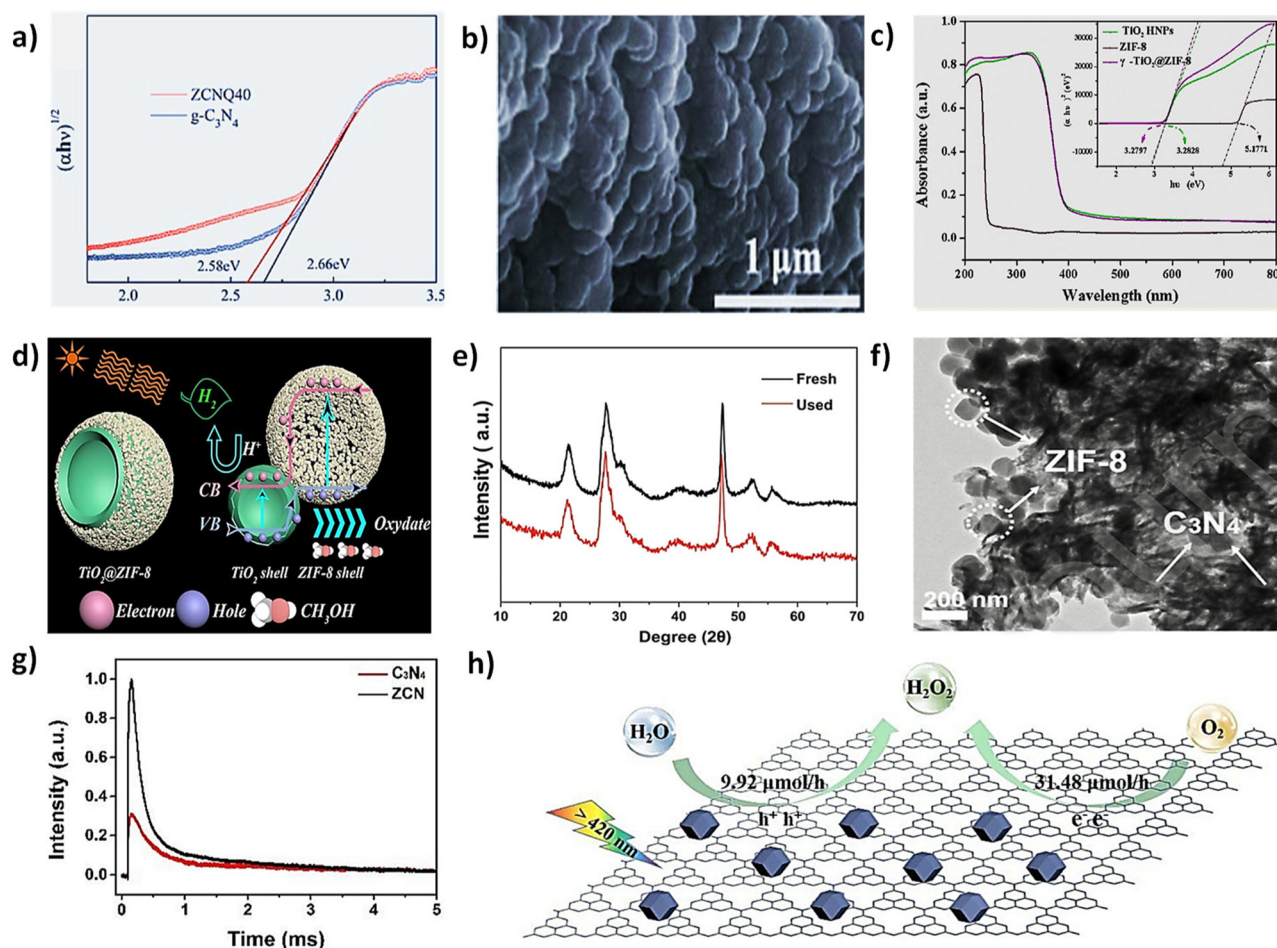


Fig. 4 (a) DRS spectra of g-C₃N₄ and ZCNQx [reproduced from ref. 127 with the permission from Elsevier, copyright 2021]. (b) SEM images of 10-C-ZIF@g-C₃N₄ [reproduced from ref. 129 with the permission from The Royal Society of Chemistry, copyright 2020]. (c) UV-Vis absorption spectra of TiO₂ HNPs, ZIF-8, and γ-TiO₂@ZIF-8; fitted curves of the Tauc plot (inset). (d) The hydrogen evolution reaction mechanism of TiO₂@ZIF-8 under simulated solar light irradiation [reproduced from ref. 130 with the permission of copyright 2015]. (e) XRD patterns of ZnS/ZIS-20 before and after repeated photocatalytic hydrogen production [reproduced from ref. 86 with the permission from The Royal Society of Chemistry, copyright 2020]. (f) TEM morphology of ZCN catalyst. (g) TPV of C₃N₄ (red line) and ZCN (black line). (h) The mechanism diagram for photocatalytic water splitting to produce H₂O₂ using ZCN [reproduced from ref. 131 with the permission from Elsevier copyright 2020].



structure through thermal treatment. This C-ZIF@g-C₃N₄ heterostructure, with an optimal ratio of C-ZIF and g-C₃N₄, displayed outstanding photocatalytic performance in H₂ generation compared with pure g-C₃N₄. The SEM images show that the C-ZIF maintains a rhombic dodecahedral structure with roughened surfaces after annealing and cleaning and is well-integrated with g-C₃N₄, forming a heterostructure with intense interfacial contact (Fig. 4b). The composite demonstrates outstanding H₂ evolution activity, achieving 1238 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is 1.95 times greater than pure g-C₃N₄ and 1.57 times greater than 10-C-ZIF + g-C₃N₄. The increased results were attributed to effective charge transfer at the C-ZIF@g-C₃N₄ interface, which significantly restrained the recombination of photoexcited electron-hole pairs, thereby enhancing photocatalytic efficiency.¹²⁹

Nanomaterials based on carbon, including carbon nanotubes, graphene, and graphitic PAN, can greatly enhance electron-hole separation in g-C₃N₄ through the formation of carbon/g-C₃N₄ composites, thereby boosting photocatalytic activity and serving as efficient HER catalysts. Inspired by this idea, He *et al.* developed C-ZIF-8/g-C₃N₄, derived from ZIF-8 carbon. Their study on photocatalytic H₂ evolution revealed that pure g-C₃N₄ produced hydrogen at a slow rate of 0.9 $\mu\text{mol L}^{-1} \text{g}^{-1} \text{h}^{-1}$, attributed to its inert surface for HER. The composite displays an IV-type isotherm, which suggests the presence of mesopores. As the carbon-ZIF content increases in the C-ZIF/g-C₃N₄ composites, the PL intensity significantly decreases, suggesting enhanced electron-hole separation due to the movement of photoexcited electrons from g-C₃N₄ to C-ZIF, which acts as an efficient electron receptor. Time-resolved fluorescence decay spectroscopy was used to determine the charge carrier lifetimes of g-C₃N₄ and the 1 wt% C-ZIF/g-C₃N₄ composite, both of which exhibited an exponential decay in their charge carrier lifetimes. The short lifetime increases from 1.27 ns in g-C₃N₄ to 2.39 ns in the composite, while the long lifetime extends from 9.33 ns to 13.93 ns. This increase in charge carrier lifetimes, due to the addition of C-ZIF, enhances photocatalytic efficiency. Remarkably, the inclusion of C-ZIF to g-C₃N₄ led to a notable increase in the photocatalytic hydrogen generation performance of the composite, reaching 32.6 $\mu\text{mol L}^{-1} \text{g}^{-1} \text{h}^{-1}$. This rate is 2.8 times greater than that of Pt/g-C₃N₄ and 36.2 times greater than pristine g-C₃N₄, indicating enhanced charge separation.¹³²

Loading a photosensitizer like AgBr enhances the visible light response in materials. Upon decomposition, Ag⁺ ions create a hybrid heterostructure that improves charge transfer and, due to their unique SPR effect, significantly boosts light absorption. Recently, to study this, Dai and colleagues successfully developed a three-component photocatalyst comprising Ag-AgBr/ZIF-8/g-C₃N₄ utilizing an ionic liquid-assisted *in situ* growth method. The HRTEM analysis of A(1.1)/g/Z(13) revealed a lattice spacing of 0.282 nm, associated with the (200) plane of AgBr, and the SAED pattern verified its crystalline structure. This newly formed system demonstrated significantly enhanced photocatalytic efficiency for hydrogen generation compared with ZIF-8, AgBr and g-C₃N₄. The enhancement was

largely due to the role of Ag⁺, which served as a linking bridge, facilitating the creation of multiple electronic transmission pathways. XRD spectra confirmed Ag⁺ within the composite, while AgBr increased the photocurrent density and acted as a photosensitizer. The AgBr/g-C₃N₄ and AgBr/ZIF-8 composites demonstrate higher photocurrent densities compared with their individual components. The A(1.1)/g/Z(6.5) composite achieves the maximum density, highlighting it as the optimal ratio. AgBr enhanced light absorption and formed a p-n heterojunction with g-C₃N₄, suppressing exciton recombination. The composite achieved a H₂ generation rate of 2058 $\mu\text{mol L}^{-1} \text{g}^{-1} \text{h}^{-1}$, which was 49 times more than that of unmodified g-C₃N₄ alone, maintaining 91% efficiency after 5 cycles.¹³³

Transition metal chalcogenides, with their layered structure, direct band gap, and high absorption coefficient, are promising for hydrogen production.¹³⁴ For example, TiO₂ is highly effective in photocatalytic applications owing to its suitable band gap (~3.2 eV), strong oxidative power, high chemical stability, non-toxicity, cost-effectiveness, and photostability, ensuring its widespread use in solar energy applications. In 2019, Zhang and co-authors fabricated TiO₂@ZIF-8 by coordinative incorporation, employing TiO₂ hollow nanospheres (HNPs) coated with ZIF-8 through a sonochemical technique, and significantly enhanced HER under solar irradiation. The process involved a two-step approach: first modifying TiO₂'s surface to increase its area, followed by hybridizing it, the composite achieved a hydrogen production rate 3.5 times greater than pristine TiO₂ HNPs, with a quantum efficiency of up to 50.89% and notable stability. Optoelectronic measurements and photoluminescence indicated that ZIF-8's porous structure and effective charge separation improved the photocatalytic activity. The band gaps for ZIF-8, γ -TiO₂@ZIF-8, and TiO₂ HNPs were 5.18 eV, 3.28 eV, and 3.28 eV, respectively (Fig. 4c). The reduction in the E_g values of the samples contributed to improved photocatalytic efficiency. The conduction band edges were -0.31 eV for TiO₂ and -4.73 eV for ZIF-8. Under artificial sunlight with methanol as the sacrificial reagent, bare ZIF-8 showed no H₂ evolution, while TiO₂ HNPs had an HER of 74.6 $\mu\text{mol g}^{-1} \text{h}^{-1}$, limited by low surface area and fast charge carrier recombination. A physical mixture of ZIF-8 and TiO₂ HNPs displayed a reduced rate of 4.63 $\mu\text{mol g}^{-1} \text{h}^{-1}$. However, the γ -TiO₂@ZIF-8 composite significantly enhanced the HER to 254.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$, 3.4 times greater than the pristine TiO₂ HNPs. The α - and β -TiO₂@ZIF-8 composites also improved the HER, to 186.1 $\mu\text{mol g}^{-1} \text{h}^{-1}$ and 105.0 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. The proposed mechanism for photocatalytic H₂ evolution is presented in Fig. 4d. Five successive photocatalytic tests were conducted under simulated sunlight, and the amount of H₂ produced consistently enhanced with irradiation time during every cycle. The system exhibited excellent stability over a prolonged period of 30 hours, with the hydrogen evolution rate in the fifth cycle.¹³⁰

Bulk MoS₂, with a 1.2 eV band gap, is generally unsuitable as a photocatalyst due to its insufficient oxidation and reduction capabilities. However, exfoliated MoS₂ shows a direct band gap ranging from 1.89 to 3.96 eV as a result of



quantum confinement effects, enhancing its photocatalytic potential. For example, Ren and associates exfoliated MoS₂@ZIF-8 hybrid for the HER through sonication, showing improved absorption of light and hydrogen evolution reaction efficiency in comparison with pristine ZIF-8. The exfoliated photocatalyst revealed an absorption edge at 415 nm, suggesting an appropriate band structure for HER applications. The MoS₂@ZIF-8 composite had a measured band gap of 3.41 eV, which is shorter than the 5.15 eV band gap of pure ZIF-8. This composite structure obtained an H₂ generation rate of 68.4 $\mu\text{mol L}^{-1} \text{g}^{-1} \text{h}^{-1}$. The activity of MZ was analyzed by measuring hydrogen generation under using a Xe lamp. The H₂ generation rate for ZIF-8 was 0.01 $\mu\text{mol h}^{-1} \text{g}^{-1}$, and bulk MoS₂ showed no activity. In contrast, the exfoliated MoS₂ (EM) in the MZ composite significantly enhanced the average H₂ evolution rate to 29.9 $\mu\text{mol h}^{-1} \text{g}^{-1}$.¹³⁵

ZIF-8 has been extensively utilized in the development of core-shell or core-shell-like catalysts. Zeng and co-authors created a novel core-shell structure, with ZIF-8 forming the shell and CdS NPs as the core. Initially, CdS nanoparticles were solidified using PVP and formed ZIF-8 shells on the CdS cores. Despite the limited hydrogen production rate of the resulting samples, the core-shell CdS@ZIF-8 structures exhibited enhanced specificity for hydrogen synthesis compared with pristine CdS NPs. The photocatalytic breakdown of formic acid was carried out to examine the harmonious interaction between CdS and ZIF-8. The photocatalysts used for formic acid decomposition included pristine CdS nanoparticles, MCS, SCS-20, and SCS-40. The photocatalytic kinetic profiles were obtained. In comparison with pure CdS NPs, the MCSs demonstrate greater photocatalytic performance for H₂ production throughout the entire photocatalytic process. However, SCS-20 exhibits enhanced photocatalytic efficiency for H₂ production only during the initial 3.5 hours, and SCS-40 displays improved efficiency only during the first 2.5 hours.¹³⁶

ZnS, a traditional metal sulfide, is widely recognized as a photocatalyst because of its high electron-hole pair generation rate and non-toxic nature. Song *et al.* aimed to develop bimetallic sulfides that integrate ZIF-derived sulfide structures with the capability for visible light absorption and effectively create bimetallic sulfides that integrate the structural benefits of ZIF-derived sulfides. In this study, a series of ZnS/ZnIn₂S₄ hybrid materials derived from ZIF-8 were successfully prepared by changing the amount of ZIF-8 to optimize the ratios of ZnS and ZnIn₂S₄. The hydrogen evolution performance of these materials was tested using TEOA as a hole scavenger. As shown in Fig. 4e, pure ZnS, owing to its wide band gap of 3.55 eV, showed no hydrogen production. Pure ZnIn₂S₄ achieved a H₂ generation rate of 118.4 $\mu\text{mol L}^{-1} \text{g}^{-1} \text{h}^{-1}$, which is significantly lower than the composites, indicating reduced charge transfer efficiency and faster electron-hole recombination. The ZnS/ZIS-*x* composite exhibited improved hydrogen generation rates of 332 $\mu\text{mol L}^{-1} \text{g}^{-1} \text{h}^{-1}$, 453.4 $\mu\text{mol L}^{-1} \text{g}^{-1} \text{h}^{-1}$, and 286.3 $\mu\text{mol L}^{-1} \text{g}^{-1} \text{h}^{-1}$ as *x* varied from 10 to 30, with ZnS/ZIS-20 delivering the

maximum output, demonstrating an optimal ratio maximizing HER performance. The hydrogen generation rates achieved by the ZnS/ZIS composites in this study were considerably greater than those of ZnIn₂S₄-based photocatalysts, highlighting a promising method for developing efficient HER catalysts.⁸⁶

Transition metal phosphides (TMPs) are promising HER catalysts due to their excellent catalytic and electronic properties. Due to phosphorus sharing similar chemical properties with nitrogen, TMPs retain significant characteristics from multi-electron orbitals.^{137,138} For instance, Jin and colleagues formulated a ternary novel photocatalyst comprising WO₃/NiP₂/ZIF-8, utilizing eosin-Y (EY) as a sensitizer, and 30% TEOA was used as a sacrificial agent. XRD, SEM, and TEM characterization revealed that WO₃ forms nanowires and ZIF-8 exhibits a well-defined dodecahedron morphology with good crystallinity. XPS confirmed the valence states of the elements, and UV-Vis DRS data indicated that the modified catalyst has a broader visible light absorption range than pure WO₃. The hybrid catalysts showed improved electron transfer, better charge separation, and longer lifetimes than the individual catalysts, enhancing H₂ production. The photocatalytic HER achieved an emission rate of 341.2 $\mu\text{mol L}^{-1} \text{g}^{-1} \text{h}^{-1}$ over 5 hours, which was 11.3 times higher than the pure WO₃. This improvement was attributed to the increased active sites and surface area presented by the NiP₂ co-catalyst in conjunction with ZIF-8. Additionally, NiP₂ aided in capturing photogenerated electrons, which then reacted with protons in the solution to produce hydrogen.¹³⁹

ZIF-8-based nanomaterials have demonstrated significant potential in enhancing H₂ generation when integrated with materials like g-C₃N₄, carbon nanostructures, and other semiconductors. These hybrid systems improve charge separation, light absorption, and stability, leading to higher hydrogen evolution rates compared with pristine materials. By optimizing band gaps and enhancing interfacial interactions, these composites achieve impressive photocatalytic efficiency under light irradiation, highlighting their potential for sustainable hydrogen production. Table 2 summarizes the photocatalytic activity of ZIF-8 MOF-based nanocomposites in H₂ and H₂O₂ evolution.

4.2 H₂O₂ generation

Hydrogen peroxide (H₂O₂) is a clean oxidant and reductant commonly used in industrial chemistry and is also a promising high-energy fuel for fuel cells.¹⁴⁶ H₂O₂ can be produced through either a two-step single-electron reduction or a one-step two-electron reduction. In photocatalytic systems, holes in the VB oxidize H₂O to O₂ and H⁺, while e⁻ in the CB reduce adsorbed O₂ to H₂O₂. The one-step, two-electron reduction is considered more efficient for producing H₂O₂ from a photoelectrochemical standpoint.¹⁴⁷⁻¹⁴⁹

The two-step single-electron pathway mechanism involves the reactions discussed in eqn (4)–(8). Alternatively, the one-step, two-electron pathway mechanism involves the direct reaction of O₂ with two H⁺ to produce H₂O₂ (eqn (9)). The overall



Table 2 Summary of various ZIF-8 MOF-based nanocomposites and their performance in photocatalytic H₂ and H₂O₂ evolution

Sl. no.	Photocatalytic application	Composite	Sacrificial agent	Light source	Activity	Quantum yield (%)	Ref.
1	H ₂ evolution	TiO ₂ @ZIF-8	Methanol	300 W Xe lamp	254.2 μmol g ⁻¹ h ⁻¹	50.89	130
2		CdS/ZIF-8	Na ₂ S and Na ₂ SO ₃	300 W Xe lamp	2.10 mmol g ⁻¹ h ⁻¹	—	136
3		MoS ₂ @ZIF-8	Methanol	—	29.9 μmol h ⁻¹ g ⁻¹	—	135
4		ZIF-8 derived ZnCdS	Na ₂ S and Na ₂ SO ₃	300 W Xe lamp	5680 μmol g ⁻¹ h ⁻¹	—	140
5		ZIF-8 derived ZnS	TEOA	300 W Xe lamp	3709.23 μmol g ⁻¹ h ⁻¹	0.014	141
6		CdS–ZnNi–ZIF-8	Na ₂ S and Na ₂ SO ₃	300 W Xe lamp	45.6 mmol g ⁻¹ h ⁻¹	—	142
7		Ag–AgBr/g–C ₃ N ₄ /ZIF-8	TEOA	300 W Xe lamp	2058 μmol g ⁻¹ h ⁻¹	7.91	133
8		ZIF-8 derived Co ₃ O ₄ /ZnO	Glycerol	500 W Xe lamp	2241 μmol g ⁻¹ h ⁻¹	—	143
9		ZIF-8 derived ZnS/ZnIn ₂ S ₄	TEOA	300 W Xe lamp	453.4 μmol g ⁻¹ h ⁻¹	—	86
10		Co@ZIF-8/TiO ₂	Methanol	—	13 mmol g ⁻¹ h ⁻¹	—	144
11		C–ZIF@g–C ₃ N ₄	TEOA	300 W Xe lamp	1238 μmol g ⁻¹ h ⁻¹	—	129
12		WO ₃ /NiP ₂ @ZIF-8	TEOA	300 W Xe lamp	295.7 μmol g ⁻¹ h ⁻¹	50.8	139
13		ZIF-8/modified g–C ₃ N ₄	TEOA	300 W Xe-lamp	309.5 μmol L ⁻¹ g ⁻¹ h ⁻¹	—	82
14	H ₂ O ₂ evolution	BiOBr/ZIF-8/ZnO	—	LED light	116 mmol L ⁻¹ g ⁻¹	—	145
15		ZIF-8/C ₃ N ₄	—	Visible light (λ ≥ 420 nm)	2641 μmol h ⁻¹ g ⁻¹	19.54	131

photocatalytic reaction can be summarized as follows (eqn (10)):



The photocatalytic production of H₂O₂ from H₂O and O₂ is an uphill reaction with a standard Gibbs free energy change (ΔG₀) of 117 kJ mol⁻¹.

Zhao *et al.* showed that ZIF-8/C₃N₄ composite is a highly effective photocatalyst for producing H₂O₂ by a two-channel pathway, *i.e.*, both oxygen reduction and water oxidation reaction. The SEM image of C₃N₄ displays a sheet-like structure, while the ZIF-8 (Fig. 4f) display a rhombic dodecahedral shape with an approximate size of 100 nm. ZIF-8 exhibits significant nitrogen adsorption at minimal relative pressures, suggesting the existence of numerous micropores, which is further supported by the pore size distribution analysis. Transient photovoltage (TPV) measurements provide insight into the photocatalytic water-splitting mechanism for H₂O₂ production using the ZIF-8/C₃N₄ composite. Fig. 4g illustrates that the ZCN sample (black line) exhibits a notably higher photocurrent response, signifying an increased accumulation of photo-induced charges on the surface. This implies improved electron–hole separation efficiency in ZCN. Under an O₂ atmosphere, ZCN's photocurrent decreases more than under H₂, indicating rapid oxygen reduction and water oxidation as the rate-determining step. The composite facilitates H₂O₂ production through simultaneous O₂ reduction and H₂O oxi-

dation. The proposed reaction mechanism suggests that in the ZCN composite, visible light excites C₃N₄ to separate electron–hole pairs, where ZIF-8 enhances visible light absorption, and facilitates O₂ adsorption for efficient H₂O₂ production, and its porous structure aids in mass transfer and prevents catalyst poisoning (Fig. 4h). Unlike ZIF-8 alone, which shows no activity, and C₃N₄, which produces only 67.50 μmol h⁻¹ g⁻¹, the composite significantly enhances efficiency by achieving 2461 μmol h⁻¹ g⁻¹. It demonstrates excellent stability, with reusability for at least five cycles under visible light, with only a slight performance decline due to catalyst loss, and the composite maintains good morphological stability throughout the cycles.¹³¹

Bismuth-based materials are commonly employed in photocatalytic studies due to their open structural framework and favorable band gap. Among them, BiOBr is considered an excellent catalyst support because of its strong stability, affordability, responsiveness to visible light, and diverse microstructural properties. To address issues like the agglomeration of ZIF-8, Yang *et al.*¹⁵⁰ employed ZnO/ZIF-8 hybrid photocatalyst under UV light irradiation, which can decompose 98.17% RhB in 12 min. Building on this approach, Han *et al.* synthesized BiOBr/ZIF-8/ZnO ternary composite and demonstrated effective H₂O₂ generation under LED lamp irradiation, reducing ZIF-8 aggregation and enhancing charge carrier separation. The DRS spectra reveal the UV light responsiveness of BiOBr, ZIF-8, ZZ-110, and BZ-9, with the latter showing a red-shift in absorption edges. BZ-9's edge extended to ~500 nm, indicating a broader light response and visible light interaction. Tauc plot analysis calculated the band gaps as 2.70 eV for BiOBr and 2.91 eV for ZZ-110. Electrochemical tests (Fig. 5a) showed that BZ-9 produced an enhanced photocurrent compared with the other catalysts, suggesting better optical absorption and enhanced electron–hole separation efficiency. The LSV curve demonstrated that BZ-9 had the lowest potential, implying a reduced electron–hole recombination rate (Fig. 5b). Mott–Schottky analysis showed flat band potentials of –0.117 for BiOBr and –1.007 for ZZ-110. BiOBr





Fig. 5 (a) H_2O_2 production capacity, (b) the band gaps and (c) Nyquist plots of BiOBr, ZIF-8, ZZ-110, and BZ-9. (d) The photocatalytic mechanisms of BiOBr and ZZ-110 involve two distinct heterojunction types: type II heterojunction and an S-scheme heterojunction [reproduced from ref. 145 with the permission from MDPI, copyright 2023]. (e) The total pathways for production of the main products of photocatalysis of CO_2 [reproduced from ref. 151 with the permission from Elsevier, copyright 2016]. (f) Time-yield plots of CO and H_2 over $\text{TiO}_2/\text{ZIF-8-G2}$ composites [reproduced from ref. 152 with the permission from The Royal Society of Chemistry, copyright 2021]. (g) TGA of ZIF-8, $\text{TiO}_2@/\text{ZIF-8}$ and TiO_2 NPs in air [reproduced from ref. 153 with the permission from Elsevier, copyright 2015]. (h) The synthetic procedure of $\text{ZnO}/\text{ZIF-8}$ hybrid photocatalysts [reproduced from ref. 154 with the permission from Elsevier, copyright 2016].

and the composites generated significant amounts of H_2O_2 , with BZ-9 exhibiting the greatest production of $116 \text{ mmol L}^{-1} \text{ g}^{-1}$ within two hours, 1.4 times greater than pristine BiOBr (Fig. 5c). The photocatalytic mechanism proposed that BiOBr and ZZ-110 establish a conventional type II heterojunction, as illustrated in Fig. 5d. After four cycles, the H_2O_2 evolution of BZ-9 decreased to $109 \text{ mmol L}^{-1} \text{ g}^{-1}$, representing good stability. HCOOH influenced H_2O_2 generation by capturing holes, oxidizing to $\text{HCOO}^\bullet$, which further reacted to form $^\bullet\text{OH}$ and H_2O_2 , with CB electrons at ZZ-110 to reduce O_2 to H_2O_2 .¹⁴⁵

By integrating ZIF-8 with materials like C_3N_4 , BiOBr, and ZnO, the overall photocatalytic performance is greatly enhanced compared with the individual components, showcasing excellent stability, reusability, and scalability for practical applications. These findings underscore the importance of material design in optimizing photocatalytic processes for energy and environmental applications.

4.3 CO_2 reduction

CO_2 is a highly stable molecule ($\Delta G^\circ = -400 \text{ kJ mol}^{-1}$) with a linear structure comprising two double bonds between oxygen and carbon atoms. This stability and its large LUMO–HOMO energy gap of 13.7 eV and high electron affinity of $-0.6 \pm 0.2 \text{ eV}$ make it difficult to convert CO_2 into valuable chemicals without catalysts and energy input. The conversion process is hindered by thermodynamic and kinetic limitations.^{155,156} However, when CO_2 adsorbs onto a photocatalyst surface, its linear structure bends, lowering the energy barrier and increasing reactivity by reducing the LUMO level. This adsorption initiates sequential reactions through one-electron transfers involving electron or proton transfers that break C–O bonds and form new C–H bonds. A reducing agent, such as H_2O , H_2 , CH_4 , or CH_3OH , is needed to supply hydrogen for producing hydrocarbons through photocatalysis. The pathways for photo-

catalytic CO₂ reduction depend on the reductant used. Carbon-free reductants like H₂O and H₂ typically yield C1 products, whereas carbon-containing reductants like CH₄ and CH₃OH can produce C2 and C3 products. Common products from CO₂ photoreduction include CO, HCOOH, HCHO, CH₃OH, CH₄, and C₂H₅OH.^{157–159} Fig. 5e illustrates the electrons, oxidizing holes, and protons (H⁺) required for forming these main products.¹⁵¹

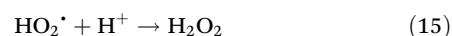
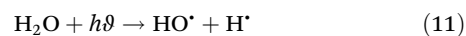
As TiO₂ has strong oxidative power, high chemical stability, and non-toxicity, Yan *et al.* synthesized a composite using ZIF-8 and TiO₂ through grinding and solid-synthesis methods. These composites were employed for the photocatalytic reduction of CO₂. XPS confirmed the appearance of Zn 2p, N 1s, C 1s, Ti 2p, and O 1s in TiO₂/ZIF-8-G2. Peaks at 458.6 eV and 464.3 eV correspond to Ti⁴⁺ (Ti 2p_{3/2} and Ti 2p_{1/2}), while peaks at 1022.1 eV and 1045.1 eV are allotted to Zn 2p_{3/2} and Zn 2p_{1/2}. The CO₂ photoreduction efficiency is attributed to TiO₂/ZIF-8-G2, with its photocatalytic efficiency at specific time intervals reaching 5.04, 13.38, 31.85, and 43.49 mmol g⁻¹, as depicted in Fig. 5f. The UV-DRS spectra indicate that TiO₂/ZIF-8-G2 exhibits a broader absorption band and an extended absorption edge near 400 nm, suggesting enhanced light absorption. The EIS results reveal that TiO₂/ZIF-8-G2 has the shortest radius within the TiO₂/ZIF-8-GX photocatalysts, indicating superior conductivity and more efficient photogenerated electron transfer. This aligns with the photocurrent and CO₂ photoreduction performance. Consequently, a CO production rate of 21.74 mmol g⁻¹ h⁻¹ with a remarkable 99% selectivity was attained in the solid-gas system without the use of sacrificial agents or photosensitizers. The group's previous highest CO generation rate was 10.67 mmol g⁻¹ h⁻¹, achieving 90% selectivity.¹⁵²

SnO₂, known for its high oxidation potential and electron-hole capture, has been widely used in various fields. Wang *et al.* synthesized T-ZIF-8/SnO₂ spherical photocatalysts *via* the sol-gel method for CO₂ reduction, forming type-II heterojunctions. HRTEM showed that T-ZIF-8 retained its framework with spherical deformation, while SnO₂ appeared as ~9 μm particles, covered by T-ZIF-8. The materials exhibited type-IV isotherms with H3 hysteresis loops, indicating slit pores from nanoparticle aggregation. A reduced PL intensity in T-ZIF-8/SnO₂ compared with T-ZIF-8 indicated slower electron-hole recombination, attributed to the heterojunction's multiple charge transfer pathways. This enhanced charge separation, reduced recombination, and improved charge carrier transport, increasing active sites and reducing the bandgap. Under simulated sunlight, T-ZIF-8/SnO₂ demonstrates exceptional photocatalytic performance, achieving a CO₂ generation rate of 16.6 μmol g⁻¹ h⁻¹, which is 1.4 and 4.9 times greater than the pristine SnO₂ and T-ZIF-8, respectively. Furthermore, it attains a CH₄ generation rate of 14.7 μmol g⁻¹ h⁻¹, which is 1.9 and 6.1 times higher than that of pure SnO₂ and T-ZIF-8. These findings verify that the heterojunction significantly enhances both photocatalytic CO₂ reduction efficiency and CH₄ selectivity.¹⁶⁰

CO₂ reduction using ZIF-8-based photocatalysts highlights significant advancements in overcoming the inherent stability of CO₂ and promoting its conversion into valuable chemicals. The formation of heterojunctions in these composites plays a major role in increasing photocatalytic activity by facilitating charge transfer and enhancing the overall conversion of CO₂ into useful products such as CO and CH₄ without the need for sacrificial agents. The photocatalytic performance of ZIF-8 MOF-based nanocomposites in CO₂ reduction and dye and drug degradation has been summarized in Table 3.

4.4 Dye degradation

The elimination of dyes from industrial wastewater is essential due to their harmful effects on aquatic life and their potential carcinogenic risks to humans. Traditional dye removal methods often fail to achieve complete degradation and produce significant amounts of suspended solids. Therefore, an efficient process that can fully degrade dyes with minimal waste is critically needed. Photocatalysis is a promising approach for degrading various toxic and organic pollutants in wastewater. The detailed mechanism of photocatalysis is explained in the following reactions.^{184–186}



Finally, the dye reacts with an HO[•] radical to form intermediate products and end products:



TiO₂ is commonly implemented as a photocatalyst because of its excellent activity and robust chemical and photochemical stability.¹⁵⁰ Chandra *et al.* embedded TiO₂ nanotubes within ZIF-8 to fabricate a TiO₂@ZIF-8 for the degradation of RhB and MB dyes. FESEM and HRTEM images show that the composite retains the hexagonal morphology of ZIF-8, where TiO₂ nanoparticles appear as dark spots within the ZIF-8 cages. According to the UV-DRS spectral analysis, the composite exhibited a flat band structure, identical to what is seen with TiO₂ nanoparticles, with a slight reduction in the band gap from about 3.35 eV to 3.25 eV, due to changes in the microenvironment within the ZIF-8 framework, and amplified the photocatalytic performance of the TiO₂ NPs encapsulated within the ZIF-8 framework. Surface analysis using BET adsorption measurement revealed a decrease in surface area ranges from 1432.91 m² g⁻¹ to 253.882 m² g⁻¹ when comparing the isotherms of the



Table 3 Summary of various ZIF-8 MOF-based nanocomposites and their performance on photocatalytic CO₂ reduction, dye, and drug degradation

	Photocatalytic application	Composite	Band gap (eV)	Light source	Activity	Ref.
1	CO ₂ reduction	TiO ₂ /ZIF-8	1.97	LED lamp, 40 W	CO = 21.74 $\mu\text{mol g}^{-1} \text{h}^{-1}$	161
2		ZnO/ZIF-8	3.23	Hg lamp, 125 W	CH ₃ OH = 6843.12 $\mu\text{mol g}^{-1}$	162
3		Pt/ZIF-8	4.21	Hg lamp, 125 W	CH ₃ OH = 5365.01 $\mu\text{mol g}^{-1}$	162
4		Cu/ZIF-8	2.09	Hg lamp, 125 W	CH ₃ OH = 426.02 $\mu\text{mol g}^{-1}$	162
5		Au/ZIF-8	1.69	Hg lamp, 125 W	CH ₃ OH = 232.20 $\mu\text{mol g}^{-1}$	162
6		Cu-TiO ₂ /ZIF-8	—	UV lamp, 320–480 nm	CH ₃ OH = 4.88 $\mu\text{mol g}^{-1}$	163
7		TiO ₂ /ZIF-8	—	UV lamp, 8 W	CO = 0.53 $\text{mmol g}^{-1} \text{h}^{-1}$, CH ₄ = 0.18 $\text{mmol g}^{-1} \text{h}^{-1}$	164
8		CdS/ZIF-8	2.41	Xe lamp, 300 W	CO = 32.13 $\mu\text{mol h}^{-1}$	161
9		CdSe QD@ZIF-8	—	Xe lamp, 300 W	CO = 3.526 $\mu\text{mol g}^{-1} \text{h}^{-1}$, CH ₄ = 0.102 $\mu\text{mol g}^{-1} \text{h}^{-1}$	165
10	Drug degradation	ZIF-8/TiO ₂	2.98	300 W Xe lamp	TC = 90% in 40 min	93
11		ZIF-8/Cu ₂ O	4.31	Solar light	TC = 84.1% in 120 min	166
12		ZIF-8 derived CuO/ZnO	—	300 W Xe lamp	TC = 87% in 60 min	167
13		ZIF-8/MoS ₂	1.05	300 W Xe lamp	Ciprofloxacin = 93.2% in 180 min	168
14		ZIF-8/g-C ₃ N ₄	2.73	—	TC = 87.6% in 40 min	143
15	Dye degradation	Ag/AgCl@ZIF-8/g-C ₃ N ₄	—	Visible light	Levofloxacin = 94.5% in 60 min	169
16		CuONPs/ZIF-8	4.93	Sunlight	Rh6G = 96.5% in 105 min	57
17		MnO ₂ @ZIF-8	5.46	300 W xenon lamp	RhB > 96.0%	170
18		ZIF-8/NiFe ₂ O ₄	—	500 W halogen lamp	MB = 94% in 120 min	92
19		ZIF-8/Fe ₂ O ₃	—	500 W Xe lamp	Reactive red = 94%	171
20		ZnO@ZIF8	3.31	Metal halide lamp/575 W	MB = 97.65% in 45 min	154
21		ZIF-8 derived ZnO	—	UV lamp/18 W	MB = 76% in 60 min	172
22		RGO/black TiO ₂ /2D-ZIF-8	—	Visible light	MB = 0.0232 min, DH = 0.0118 min	173
23		MoO ₃ @ZIF-8	—	PL-XQ 350 W xenon	MB = 95% in 300 min	174
24		CuO-ZnO/ZIF-8	1.96	Solar light	AO7 = 98.1% in 100 min	175
25		ZIF-8/g-C ₃ N ₄	2.80	Xe lamp/300 W	RhB = 99.8% in 60 min	58
26		Ag-doped ZIF-8	3.2	Visible LED light	MO = 100%, RhB = 93% in 30 min	176
27		ZIF-8@AgNPS	5.13	UV-vis light	CR = 100%	177
28		Ag/AgCl@ZIF-8	3.3	Hg lamp/175 W	MB = 100% in 90 min	178
29		AgCl/Ag@ZIF-8	—	Xe lamp/210 W	RhB = 86% in 60 min	179
30		ZIF-8/Ag ₂ S	3.24	100 W Xe and 100 W LED	RhB = 100% in 75 min	180
31		CdSNPs@ZIF-8	2.95	UV-visible	MB = 83.2% in 120 min	181
32		ZIF-8/Zn-Al LDH	—	UV light/70 W	MB = 58% in 180 min	182
33		ZIF-8@CQD	4.95	300 W Xe lamp	MB = 91%	183
34		TiO ₂ @ZIF-8	3.25	Solar light	MB = 87.5%, RhB = 64.85%. 120 min	153

ZIF-8 framework and the composite. This observation confirmed the coating of TiO₂ NPs within the framework pores, resulting in reduced void space accessible to N₂ gas molecules. Thermal gravimetric analysis indicated high stability of both ZIF-8 and TiO₂@ZIF-8 up to 236 °C and 254 °C, respectively, in atmospheric air and up to 240 °C and 270 °C under an inert N₂ atmosphere. Beyond these temperatures, the frameworks gradually decomposed, with a gradual decline observed until approximately 670 °C (Fig. 5g). After 2 hours of catalysis, complete elimination of dye color was achieved, and the removal rate of RhB and MB by TiO₂@ZIF-8 was 64.85% and 87.5%, respectively. In comparison, TiO₂ and ZIF-8 alone exhibited lower degradation rates, with methylene blue degradation at 29% and 86.25% and rhodamine-B degradation at 53.6% and 50%, respectively. Notably, TiO₂@ZIF-8 maintained a high recycling rate, demonstrating almost the same efficiency even in the fifth catalytic cycle. In contrast, TiO₂ nanotubes exhibited significantly reduced catalytic efficiency after just the second degradation cycle.¹⁵³

TiO₂ thin films doped with Fe, Cu, Ce, or Zn were designed to enhance the photocatalytic efficiency of the nano-

composite.¹⁸⁷ Considering this, Yurtsever *et al.* examined the effects of crystallization time and the amount of ZIF-8 on the photocatalytic performance of Cu-TiO₂/ZIF-8. These films exhibited superior light absorption compared with other ZIF-8-coated TiO₂ films and bare ZIF-8. This enhanced light absorption likely boosts photocatalytic activity, suggesting that using undoped or doped TiO₂ thin films as supports can enhance the photocatalytic efficiency of ZIF-8. They observed that decreasing the ZIF-8 loading and shortening the development time led to enhanced photocatalytic performance. Specifically, nanocomposites with 5% ZIF-8 loading and a growth time of 15 minutes exhibited the greatest photocatalytic efficiency, with a first-order rate constant 4 times and 1.4 times greater than that of pristine ZIF-8 and Cu-TiO₂, respectively. However, increasing the ZIF-8 content to 46% led to aggregate clumping, which decreased the photocatalytic efficiency. The ZIF-8/TiO₂ nanocomposite thin films, which were synthesized using 1% copper or 1% cerium-doped TiO₂ as substrates, displayed the highest activity for MB degradation. Both films removed 19% of the dye under 254 nm LED light in 1 hour and achieved 36% and 29% dye removal, respectively, under 365 nm LED light in the same time frame.¹⁸⁸



He *et al.* developed a ternary system comprising RGO/black TiO₂/2D-ZIF-8 for the degradation of MB. The integration of 2D-ZIF-8 into the system enhanced the capacity of dye adsorption and facilitated *in situ* accumulation. The three-component composite exhibited dual diverse interfaces, which were crucial for the movement and segregation of charge carriers. The rate constant for MB photocatalytic decomposition was found to be 0.0232 min⁻¹, which is 3.3 times higher than black TiO₂ alone. The ternary GO/B-TiO₂/2D-ZIF-8 composites showed the smallest semicircle diameter, indicating that RGO/B-TiO₂/2D-ZIF-8 has the maximum charge carrier mobility. The photocatalytic degradation mechanism explains that photogenerated electrons on black TiO₂ surfaces struggle to react with O₂ to form O₂^{•-}, as the redox potential of the O₂/O₂^{•-} couple (−0.33 eV) is lower than the CB energy of black TiO₂ (−0.27 eV). Furthermore, the redox potential of the H₂O/OH[•] couple (2.53 eV) exceeds the VB energy of ZIF-8 (0.34 eV), making it inefficient for photogenerated holes to convert H₂O into OH[•]. Consequently, the holes directly interact with MB during the photodegradation process. The excellent electrical conductivity of RGO also contributes to the efficient separation of electron-hole pairs and lowers the recombination rate, which in turn improves the photodegradation of MB.¹⁷³

Recently, ZnO photocatalysts have attracted significant attention owing to their non-toxicity, stability, cost-effectiveness, and efficient photocatalytic activity. Yang *et al.* introduced an innovative method for producing ZIF-8/ZnO composite photocatalysts *via* a micro-catalysis approach, utilizing ZIF-8 as the reactant and AgNO₃ as the catalyst, varying the concentration of AgNO₃ (Fig. 5h). The treatment with a 25 mM AgNO₃ solution resulted in the edges of the ZIF-8 surface becoming spherical, leading to a reduction in particle size. Increasing the AgNO₃ concentration to 50 mM further decreased the particle size to approximately 200 nm, with a more pronounced spherical morphology. The composite synthesized with a 50 mM AgNO₃ solution (designated as ZIF-8/ZnO (50)) achieved supreme decomposition performance at approximately 98.17% compared with its counterparts synthesized with 100 mM and 25 mM of AgNO₃. Additionally, the composite demonstrated robust photostability, retaining a photocatalytic activity of 95.54% after reuse for four cycles as ZnO/ZIF-8(50) showcased high photocatalytic stability, with only a 2.63% reduction in activity after four cycles, attributed primarily to inevitable catalyst loss. Consequently, ZnO/ZIF-8 (50) demonstrates commendable preparation and reusability properties.¹⁵⁴

ZnO, an n-type semiconductor possessing conductivity between 10⁻⁷ and 10⁻³ S cm⁻¹ and a binding energy of 60 meV, pairs effectively with CuO, a p-type semiconductor possessing a narrow band gap and conductivity around 10⁻⁴ S cm⁻¹. Saravanan *et al.* synthesized CuO/ZnO nanocomposites, followed by Abdollahi and collaborators, used a precipitation method to create a CuO–ZnO/ZIF-8 photocatalyst, which was tested for the photocatalytic decomposition of methylene blue, malachite green and Acid Orange 7. The sample with 20 wt% ZIF-8 was found to have a reduced band gap energy of 1.96 eV,

compared with the band gap energies of ZIF-8 and CuO–ZnO, as determined by DRS analysis. Additionally, incorporating ZIF-8 into the CuO–ZnO heterojunction increased the specific surface area from 12.3 m² g⁻¹ to 22.2 m² g⁻¹. This increase allowed the photocatalyst to adsorb a larger amount of dye, which was then decomposed under visible light, and the study found that increasing photocatalyst loading from 0.5 to 1 g L⁻¹ improved the photodecomposition rate, attributed to the increased number of active sites. The CuO–ZnO/ZIF-8-20 photocatalyst demonstrated a photocatalytic activity of 51%, 98.1%, and 59% for removing malachite green, Acid Orange 7, and Methylene blue at pH 7.¹⁷⁵

Cao *et al.* effectively coated MnO₂ onto ZIF-8 through a reaction process. The incorporation of MnO₂ NPs onto ZIF-8 ensured their even dispersion, enhancing the active surface area (Fig. 6a). The MnO₂@ZIF-8 nanoparticles display a notable size enlargement as compared with the original ZIF-8. The sizes of the MnO₂@ZIF-8 NPs are 605 ± 60 nm, 410 ± 45 nm, and 205 ± 30 nm at I₀R₄ concentrations of 0.1 mM, 0.5 mM, and 1.0 mM, respectively (Fig. 6b). ZIF-8 and the composite analyzed *via* N₂ adsorption/desorption exhibited type I nitrogen isotherms, indicating micropores at low pressures and mesopores at relative pressures above 0.9. Consequently, the synthesis of the ZIF-8@MnO₂ heterojunction facilitated optimized charge carrier separation, leading to the generation of abundant free radicals like OH[•]. Additionally, the MnO₂@ZIF-8 NPs have a zeta potential (ζ) value of 15–23 mV, which is noticeably lower than that of the ZIF-8 crystals. In a Fenton-like process, the resulting ZIF-8@MnO₂ hybrid served as a photocatalyst for the decomposition of RhB and reached over 96.0% within 120 minutes, significantly outperforming the 63% degradation rate achieved with pristine ZIF-8. The recyclability of MnO₂@ZIF-8 nanoparticles in the photocatalytic degradation of RhB indicates that the ratio remained above 80% after five cycles, demonstrating excellent recycling stability and reusability. These promising outcomes stemmed from the porous structure of ZIF-8s, facilitating the adsorption of more RhB molecules.¹⁷⁰

Faraji and associates harnessed the magnetic characteristics of NiFe₂O₄ to develop a ZIF-8/NiFe₂O₄ composite, which allows for convenient separation from the reaction mixture. This composite photocatalyst was scrutinized for its efficacy in decomposing MB under a 500 W halogen lamp, with visible light (≥400 nm) as the irradiation source. The magnetic performance of NiFe₂O₄ and the Z/NFO-30 composite was analyzed under an external magnetic field of ±1.5T at ambient temperature. Pure NiFe₂O₄ nanoparticles exhibited superparamagnetic behavior with a saturation magnetization (M_s) of approximately 38.54 emu g⁻¹. In contrast, the composite, which includes ZIF-8 integrated with NiFe₂O₄, showed a lower M_s of about 10 emu g⁻¹, as shown in Fig. 6c. This reduction in M_s is attributed to the integrating of ZIF-8 into the NiFe₂O₄ matrix, affecting the total mass and magnetic properties. Among the samples, Z/NFO-30 displayed the weakest emission peak intensity, indicating a reduced recombination rate of photoexcited charge carriers. Their research revealed that the





Fig. 6 (a) Fabrication of MnO₂@ZIF-8 core-shell nanocomposites. (b) Size (hydrodiameter) distribution of the ZIF-8 crystals and the MnO₂@ZIF-8 nanocomposites prepared at varied peptide concentrations [reproduced from ref. 170 with the permission from Elsevier, copyright 2021]. (c) Magnetic hysteresis curve of NiFe₂O₄ nanoparticles and Z/NFO-30 composite [reproduced from ref. 92 with the permission from Elsevier, copyright 2020]. (d) FE-SEM of ZIF-8/Ag₂S. (e) Optical bandgap for ZIF-8, Ag₂S, and ZIF-8/Ag₂S by using Tauc plots. (f) S-scheme mechanism of ZIF-8/Ag₂S photocatalyst under vis-light irradiation [reproduced from ref. 180 with the permission from Elsevier, copyright 2016]. (g) TG and DTG curves of MoS₂/ZIF-8 composite (a and a'); MZ-5@Carboxyl cotton (b and b'); pristine cotton fabric (c and c'). (h) EIS plots of MZ-5@Carboxyl cotton, MoS₂ and ZIF-8 (i) transient photocurrent responses of MoS₂, ZIF-8 and MZ-5@Carboxyl cotton [reproduced from ref. 189 with the permission from Elsevier, copyright 2016].

photocatalyst, formulated with 30 wt% NiFe₂O₄, exhibited the most robust photocatalytic activity, achieving a degradation efficiency of 94% within 120 minutes. Additionally, its magnetic nature enabled the composite to be renewed and reutilized for four cycles while maintaining a degradation efficiency of 90%.⁹²

Metal sulfides are highly effective photocatalysts because of their strong charge carrier migration capabilities, excellent light absorption properties, suitable band structure, and abundance of exposed active sites. Jabbar and co-authors examined the photocatalytic degradation of RhB using a ZIF-8/Ag₂S nanocomposite photocatalyst, where Ag₂S nanoparticles were effectively dispersed on the ZIF-8 surface, creating a high-efficiency heterogeneous catalyst through the co-precipitation method. The morphology of the composite, as shown in Fig. 6d, revealed semicubic particles with a slight shape change from pure ZIF-8, indicating successful Ag₂S nano-

particle precipitation. UV-vis absorption spectra demonstrated improved visible light absorption in the ZIF-8/Ag₂S composite due to its reduced band gap, as further confirmed by the band gap values of 5.58 eV for ZIF-8, 0.93 eV for Ag₂S, and 3.24 eV for the composite (Fig. 6e). This narrowed band gap is attributed to the effective dispersion of Ag₂S within the ZIF-8 structure. In RhB degradation tests, the ZIF-8/Ag₂S nanocomposite achieved complete photodegradation within 75 minutes in an airlift reactor, compared with 120 minutes in a batch reactor, with enhanced performance due to improved mixing and increased dissolved oxygen. The study also explored the impact of catalyst dosage, with the composite showing 100% degradation efficiency at optimal loading compared with 51.6% for ZIF-8 and 39.7% for Ag₂S alone, and it follows an S-scheme heterojunction photocatalytic mechanism (Fig. 6f). Finally, the composite demonstrated excellent stability and reusability, maintaining high photodegradation efficiency over five cycles,

due to the dispersion of Ag_2S aggregates on the ZIF-8 surface.¹⁸⁰

MoS_2 , with its low band gap and reactive edge, features a “sandwich” S–Mo–S structure that enhances the visible light response, making it effective for boosting the photocatalytic efficiency of ZIF-8.¹⁹⁰ Chen and his team effectively fabricated ZIF-8 on carboxylated cotton cloth and then grew MoS_2 on the ZIF-8 surface, creating an $\text{MoS}_2/\text{ZIF-8}/\text{carboxyl cotton}$ composite. Fig. 6g shows TG and DTG curves, where $\text{MoS}_2/\text{ZIF-8}$ powder and MZ-5@Carboxyl cotton display distinct weight losses due to decomposition, leaving final residues of $\sim 76.5\%$ and $\sim 34.1\%$, respectively. XPS analysis revealed that S, Mo, Zn, C, O, and N are the key elements in MZ-5@Carboxyl cotton, with strong peaks indicating the presence of S 2p, Mo 3d, and Zn 2p, confirming that MoS_2 is closely integrated with the ZIF-8 surface. The EIS spectra for the composite (Fig. 6h) dis-

played a smaller arc radius, indicating enhanced light-induced charge transfer due to $\text{MoS}_2/\text{ZIF-8}$ heterostructures. This was supported by the highest electron–hole separation efficiency observed in the photocurrent response (Fig. 6i) and confirmed by Mott–Schottky analysis (Fig. 7a), identifying MZ-5@Carboxyl cotton as an n-type semiconductor. This composite efficiently degraded methylene blue (MB), achieving approximately 99.8% degradation of the aqueous solution after 21 minutes of visible-light exposure. The fabric with five layers of ZIF-8 demonstrated the highest MB degradation efficiency and retained approximately 94.8% of its photocatalytic activity after six recycling cycles.¹⁸⁹

Doping MOFs with active agents enhances photocatalytic efficiency. The challenge lies in developing cost-effective, stable doped nanomaterials with precisely-controlled properties for efficient visible light absorption. In light of this,



Fig. 7 (a) Mott–Schottky plots of MZ-5@Carboxyl cotton [reproduced from ref. 189 with the permission from Elsevier, copyright 2016]. (b) FTIR spectra of the prepared samples (Ag@ZIF-8 denotes 15% Ag^+ doped ZIF-8). (c) TEM images of Ag-15%@ZIF-8 crystals. (d) Photodegradation performance of pure ZIF-8 and different amounts of Ag-doped ZIF-8 for eliminating RhB. (e) The proposed dye degradation mechanism of Ag@ZIF-8 photo-catalyst under visible-light irradiation [reproduced from ref. 176 with the permission from Elsevier, copyright 2020]. (f) Photodegradation first order rate constant of dyes by different samples in visible LED light: (1) without catalyst (only LED), (2) LED/ H_2O_2 , (3) pristine ZIF-8, (4) physical mixture of prior AgNO_3 and ZIF-8, (5) Ag-10%@ZIF-8, and (6) Ag-15%@ZIF-8 [reproduced from ref. 176 with the permission from Elsevier, copyright 2020]. (g) SEAD pattern of S22 [reproduced from ref. 177 with the permission from Elsevier, copyright 2020]. (h) LSV curves of ZIF-8, AgBr, and 40 wt% AgBr/ZIF-8 photocatalysts in 0.5 M Na_2SO_4 electrolyte [reproduced from ref. 191 with the permission from Elsevier, copyright 2019]. (i) PL spectra of ZIF-8, Ag_3PO_4 , and $\text{Ag}_3\text{PO}_4/\text{ZIF-8}$ nanocomposite [reproduced from ref. 192 with the permission from Elsevier, copyright 2023].



Thanh *et al.* synthesized Fe-doped ZIF-8 with varying molar ratios of Zn/Fe and evaluated the photoinduced photocatalytic activity of the resulting materials for decomposing Remazol deep black B (RDB). The XRD analysis of Fe-doped ZIF-8 displayed the typical peaks of ZIF-8, with no detectable peaks for iron oxide. Nonetheless, the intensity of these peaks diminished as the iron content was increased. The peaks for Fe 2p_{3/2} were observed at 710 and 709 eV, suggesting the presence of Fe (II) and Fe(III). The N₂ adsorption/desorption isotherms for ZIF-8 and Fe-ZIF-8, both exhibiting type IV with H4 hysteresis, are typical of mesoporous materials. The Fe-ZIF-8 (1:9) sample displayed a slightly altered shape at high relative pressure, indicating structural distortion due to iron oxide incorporation. ZIF-8 had a specific surface area of 1484 m² g⁻¹, which decreased with iron addition to 1469, 1104, and 735 m² g⁻¹ for Fe-ZIF-8 (1:9), (2:8), and (3:7), respectively, confirming that iron oxide encapsulation reduced the accessible void space. To assess the sustainability of Fe-ZIF-8 for RDB removal, the used Fe-ZIF-8 was renewed by drying at 100 °C and then used again for photocatalytic decomposition of the RDB dye. After three cycles, the decolorization efficiency of Fe-ZIF-8 catalysts was 90–95% of that observed with the fresh catalysts.¹⁹³

Jafar Abdi and team synthesized a porous Ag-doped ZIF-8 photocatalyst at ambient temperature using a facile and rapid synthesis. This catalyst was employed for the degradation of both MO and RhB dyes. The FTIR spectrum of Ag@ZIF-8 confirms that the ZIF-8 framework remains intact, with key absorption bands preserved. The broad band at 3400 cm⁻¹ and the band at 1633 cm⁻¹ correspond to the O–H stretching and bending vibrations, respectively. These hydroxyl groups, linked to adsorbed water, are essential for photocatalytic activity (Fig. 7b). ZIF-8 crystals possess a rhombic dodecahedron shape with a mesoporous structure. Fig. 7c demonstrates that Ag nanoparticles are well-dispersed throughout the ZIF-8 framework with little aggregation. The XRD spectrum of Ag@ZIF-8 shows preserved ZIF-8 peaks with no contaminants, while decreased intensity indicates Ag NP integration. EIS experiments revealed that the Ag-15%@ZIF-8 exhibited a narrower Nyquist plot arc radius compared with pure ZIF-8, reflecting enhanced light-induced charge migration and better exciton separation. This sample also illustrates the maximum photocatalytic efficiency, with first-order kinetic rate constants of 0.1016 min⁻¹ for RhB and 0.2102 min⁻¹ for MO. Photodegradation data (Fig. 7d) indicated that Ag NP enhanced dye removal. Increasing Ag content to 20 wt% improved performance, but higher doping did not yield further benefits. The rate constant (k) for decolorization was calculated using a first-order kinetic model (Fig. 7e). The Ag-15%@ZIF-8 photocatalyst mineralized over 93% of the dyes after 4 cycles (Fig. 7f). The photocatalytic efficiency of Ag-doped ZIF-8 was superior to that of a physical mixture of pure ZIF-8 and AgNO₃, because of the enhanced performance of the heterojunction formed between them.¹⁷⁶

Silver (Ag) has garnered significant attention as a coupling material. Silver nanoparticles and compounds, including Ag₃VO₄, Ag₂O, Ag₂S, Ag₃PO₄, Ag₂CO₃, and particularly silver

halides (AgX, where X = I, Br, and Cl), are extensively used for purifying organically contaminated wastewater through photocatalytic degradation.^{194–198} The combination of elemental silver with silver halides enhances their activity in the visible light spectrum. Chandra *et al.* introduced a novel composite, ZIF8/AgNPs, designed for the photocatalytic degradation of MB. With its remarkable surface area of 1370.91 m² g⁻¹ and distinctive synergistic properties, the composites, labeled as SZ, SZ1, SZ2, and SZ3, varied in silver content. The size of the encapsulated silver NPs increased proportionally with their dosing amount. The crystalline nature of AgNPs, SZ2, and SZ composites was verified through the SEAD pattern depicted in Fig. 7g, respectively. Using the Tauc method, the band gap in all composites has been determined to be 5.27 eV and 5.13 eV, respectively, attributed to ZIF-8. However, the SZ composite, which contains a significant amount of Ag NPs, shows a broad band at 2.16 eV and 1.62 eV. This is because of the Ag and the imidazole ring interactions. Notably, SZ2, synthesized using a 300 mL suspension of Ag NPs, exhibited exceptional photocatalytic efficiency, achieving a 97.25% degradation rate for MB and complete degradation for CR at pH ≥ 7, while SZ, SZ1, SZ3, and ZIF-8 can decompose off 85.56, 90.56, 86.43 and 84.18% MB and 98.09, 96.18, 97.7 and 95.80% CR. This clearly illustrates the greatly improved photocatalytic performance of SZ2 and the superior activity of SZ1 compared with ZIF-8.¹⁷⁷

Silver halide photocatalysts, recognized for their strong visible light response and exceptional photoactivity, have attracted considerable interest from researchers. AgX (X = Cl, Br, I) has been confirmed as an effective co-catalyst. In this context, He and colleagues described the synthesis of a ZIF-8/AgBr composite through the solvothermal method, utilized for the light-activated degradation of MB under light exposure. The SEM image of 40 wt% AgBr/ZIF-8 reveals AgBr particles randomly distributed on the ZIF-8 surface, a finding confirmed by EDS analysis. Optical analysis demonstrated enhanced light absorption capacity due to the combination of ZIF-8 and AgBr. Moreover, a bathochromic shift in the spectral absorption band was observed with higher AgBr content. The LSV curves in 0.5 M Na₂SO₄ show that AgBr exhibits a greater electrical density than ZIF-8, aligning with the PC results. The 40 wt% of the composite further enhances the electrical density, highlighting the synergistic impact of AgBr and ZIF-8 on electron transfer (Fig. 7h). The improved efficiency in charge separation stemmed from the synergistic impact of ZIF-8 and AgBr coupling. The recorded rate of MB degradation was 0.0273 min⁻¹, and the degradation performance achieved 99.5% under visible light exposure for 60 minutes. Stability and recyclability tests revealed that the 40 wt% of AgBr/ZIF-8 photocatalyst demonstrated reliable photocatalytic performance, maintaining its effectiveness through six repeated cycles.¹⁹¹

A study by Liu and his group demonstrated that the effect of incorporating ZIF-8 on the photocatalytic activity of Ag/AgCl was discussed. Initially, Ag/AgCl NPs were incorporated on the ZIF-8 surface with a 50 wt% loading, resulting in the synthesis of a (50%) Ag/AgCl/ZIF-8 composite. This hybrid displayed significant absorption of 420–800 nm in the wavelength range



due to the SPR phenomenon of Ag particles generated *in situ* on the surface of AgCl nanoparticles. In comparison with Ag/AgCl alone, the composite demonstrated excellent photocatalytic performance, attributed to the bifunctional activity of ZIF-8: adsorption of RhB and production of superoxide species, contributing to RhB mineralization. The photocatalytic efficiency of the hybrid in degrading MB was calculated without catalyst, with ZIF-8 alone, and with Ag/AgCl@ZIF-8 under UV light. Without a catalyst, MB degradation reached 67.31% over 90 min, while ZIF-8 alone exhibited limited improvement, achieving 51.53% degradation after 60 min of UV irradiation. In contrast, Ag/AgCl@ZIF-8 showed remarkable performance, achieving nearly 100% degradation within 20 min of UV exposure, despite minimal removal (9.25%) in the dark. The study concluded that while ZIF-8 alone had marginal effects, Ag/AgCl@ZIF-8 significantly increased photocatalytic performance, primarily attributed to improved photocatalysis.¹⁷⁸

Guan *et al.* prepared a composite material composed of Ag/AgCl/ZIF-8/TiO₂/C on cotton fabric using a straightforward method. The Ag/AgCl/ZIF-8/TiO₂/C photocatalyst achieved a methylene blue degradation activity of 98.5% in 1 h 45 minutes under visible light, exhibiting a first-order kinetic rate constant of 0.0332 min⁻¹. Additionally, the photocatalyst maintained an 85% degradation efficiency of MB after three cycles, indicating its excellent stability. They demonstrated that the ZIF-8 in the composite promoted oxygen molecules throughout the photocatalytic decomposition, and photogenerated holes in the photocatalyst's VB oxidized water molecules to OH[•], resulting in the formation of hydroxyl OH[•] and O₂^{•-}, which were the active species liable for the photodegradation of MB during this process.¹⁹⁹

Silver orthophosphate (Ag₃PO₄), a p-type semiconductor, has garnered significant attention in organic pollutant remediation through impressive visible light capture.²⁰⁰ Considering this, Motora *et al.* synthesized a novel Ag₃PO₄@ZIF-8 p-n heterojunction using the chemical precipitation method at ambient temperature. The photocatalytic efficiency of this new photocatalyst was assessed for organic pollutants, including Congo Red, Crystal violet, and rhodamine B. The Ag₃PO₄@ZIF-8 heterojunction displayed distinct peaks for both Ag₃PO₄ and ZIF-8, with no extra peaks detected, verifying that the heterojunction was successfully synthesized without any impurities. The PL spectra in Fig. 7i demonstrated that the Ag₃PO₄@ZIF-8 heterojunction had lower PL intensity, indicating reduced charge carrier recombination. Furthermore, the photoinduced current demonstrated that the Ag₃PO₄@ZIF-8 heterojunction revealed the greatest photocurrent among ZIF-8 and Ag₃PO₄, indicating superior light absorption. This suggests remarkable electron-hole separation and reduced electron-hole recombination, which improves the photocatalytic activity of the heterojunction. Furthermore, the EIS semicircle radius for the Ag₃PO₄@ZIF-8 heterojunction was lower than Ag₃PO₄ and ZIF-8, reflecting enhanced current-carrying capacity, which is critical for effective photocatalysis. The developed photocatalyst showed exceptional photocatalytic

activity, degrading 90.7% of CV, 94.7% of CR, and 99.0% of RhB within 2 hours. The reusability of the photocatalyst, which is crucial for its practical application, was also examined. The Ag₃PO₄@ZIF-8-5% heterojunction demonstrated superior cyclic stability over five cycles, verifying its strong potential for real-world wastewater treatment applications.¹⁹²

CQDs are fluorescent nanomaterials with a carbon framework and nanocrystals sized 2–10 nm. They are valued for low toxicity, high biocompatibility, tunable luminescence, and easy modification, making them a promising candidate for photocatalysis due to their fluorescence emission across the near-infrared to blue spectrum. Taking these aspects, Si *et al.* employed an impregnation method in which ZIF-8 structures were modified with carbon quantum dots and evaluated for their ability to remove methylene blue from water. The ultra-high resolution confocal laser scanning microscope (CLSM) image reveals the external morphology of CQDs@ZIF-8. CQDs emit fluorescence between 450 and 470 nm. It shows their distribution within ZIF-8, confirming the successful construction of the core-shell structure. The ZIF-8@CQD hybrid demonstrated a higher absorption capacity and improved responsiveness to visible light due to its core-shell structure, achieving a 91% removal activity for MB and a rate constant that was six times higher than that of ZIF-8 alone. Furthermore, the ZIF-8@CQD photocatalyst maintained excellent structural stability and catalytic activity over three reuse cycles without any loss of performance.¹⁸³

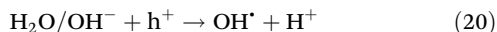
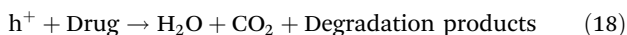
Studies indicate that combining ZIF-8 with materials such as graphitic carbon nitride, and zinc oxide not only boosts the degradation rates but also enhances the reusability and durability of the photocatalysts. Investigating the underlying mechanisms of charge transfer and degradation pathways in these composites could also provide deeper insights and lead to the improvement of more efficient and versatile photocatalytic systems for various environmental applications.

4.5 Drug degradation

The photocatalytic degradation of drugs involves three key steps: photon absorption, excitation, and reaction. Photogenerated carriers separate and migrate to the photocatalyst surface, where they trigger secondary reactions with adsorbed substances. Photogenerated holes can directly degrade drugs. There are two primary degradation pathways: a reductive pathway, which occurs if the conduction band (CB) potential is negative relative to the O₂/O₂^{•-} redox potential (−0.13 eV vs. RHE), and in this pathway, photoexcited electrons react with O₂ to produce superoxide radicals (O₂^{•-}); and an oxidative pathway, where holes on the photocatalyst surface generate hydroxyl radicals (•OH) from H₂O/OH⁻, depending on the pH of the medium. Hydrogen ions can recombine with electrons, producing heat and decreasing photodegradation efficiency. The photocatalyst's redox potential needs to be greater than •OH/OH⁻ (+1.99 eV vs. RHE). Reactive radicals (•OH and O₂^{•-}) can mineralize antibiotics and their intermediates into carbon dioxide and water under extended UV exposure. Both pathways work together to prevent electron



accumulation in the CB and reduce electron-hole recombination more effectively than direct interaction pathways.^{201–204}



Metal oxides are widely used in photocatalysis due to their metal content. TiO_2 is considered an excellent photocatalyst for its non-toxic nature, cost-effectiveness, and high efficiency. Li *et al.* synthesized ZIF-8@ TiO_2 microcomposites *via* a hydrothermal method. The composite retains a dodecahedron shape with textured surfaces. Vibrational peaks at 565 cm^{-1} and 486 cm^{-1} correspond to N–Ti–O and Ti–O–Ti bonds, indicating TiO_2 deposition on ZIF-8 through chemical bonding rather than physical mixing (Fig. 8a). XPS confirms Ti^{4+} binding with ZIF-8's imidazole groups to form N–Ti–O bonds, while EDX mapping shows Ti and O elements dispersed on

ZIF-8@ TiO_2 . Under 40 minutes of irradiation, ZIF-8@ TiO_2 achieves a TC degradation rate of $\sim 90\%$, surpassing TiO_2 and ZIF-8 ($< 70\%$). Trapping experiments revealed $\text{O}_2^{\cdot-}$ as the key reactive species, with benzoquinone (BQ) reducing degradation from 95% to 59%. Other species, such as $\text{OH}^\cdot$ and e^- , played minor roles. The effectiveness order was: no scavenger $>$ IPA $>$ CCl_4 $>$ AO $>$ BQ, confirming $\text{O}_2^{\cdot-}$ as the most crucial active species. The reusability and stability of the ZIF-8@ TiO_2 composite across five degradation cycles, the TC removal rate decreased slightly from 95% to 86%, likely due to the loss of photocatalyst during recovery. This outcome shows that the ZIF-8@ TiO_2 composite exhibits strong stability and reusability, with its internal interactions ensuring sustained high efficiency.⁹³

Cu_2O , with a bandgap of 1.8–2.2 eV, is affordable, eco-friendly, and effective under visible light. Zhou *et al.* developed $\text{Cu}_2\text{O}/\text{ZIF-8}$ (C/Z) *via* an *in situ* growth method. XRD confirmed the synthesis of Cu_2O and ZIF-8, while XPS identified key elements: N 1s (398.7 eV) confirmed the N–C bond, with Cu^+ peaks at 951.8 eV and 932 eV, and Zn 2p peaks at 1021.5 eV and 1044.7 eV (Fig. 8b). The C/Z composite demonstrated improved photocatalytic performance for tetracycline (TC) degradation because of the narrow bandgap of Cu_2O and the increased surface area of ZIF-8, which is 3.3 times greater than Cu_2O alone, offering increased adsorption sites. This led to a



Fig. 8 (a) FTIR spectra of ZIF-8@ TiO_2 [reproduced from ref. 93 with the permission from Elsevier, copyright 2020]. (b) XPS survey spectra of C0.7/Z0.3 sample. (c) ESR spectra of $\text{DMPO}\cdot\text{O}_2^{\cdot-}$ of the Cu_2O , ZIF-8 and C0.7/Z0.3 [reproduced from ref. 166 with the permission from Elsevier, copyright 2021]. (d) N_2 adsorption-desorption isotherm of ZIF-8, g- C_3N_4 , ZIF-8 and 10%-AZCN samples [reproduced from ref. 169 with the permission from Elsevier, copyright 2019].



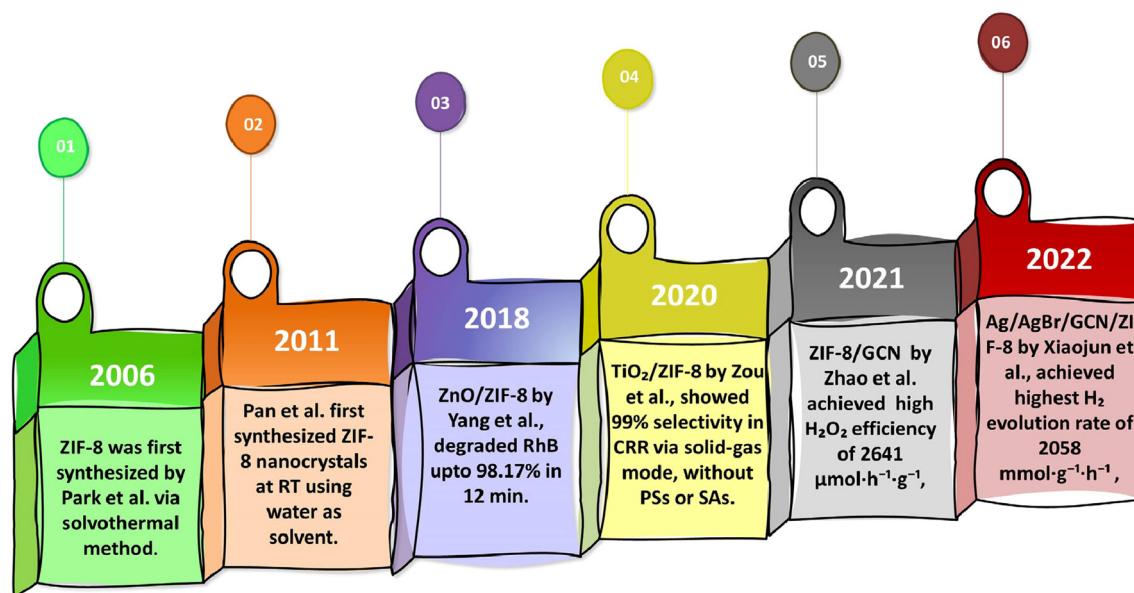


Fig. 9 Development history of ZIF-8 MOFs and their nanocomposites as photocatalysts.

higher response to visible light and greater charge carrier density compared with individual components. The composite also showed superior photocurrent density and charge transfer efficiency, as indicated by a smaller semicircle diameter in the Nyquist plot. ESR analysis confirmed the generation of free radicals during photocatalysis, with $O_2^{\cdot-}$ being the primary radical, supported by weaker $\cdot OH$ signals (Fig. 8c). The C/Z composite achieved over 84.1% TC degradation under visible light within 2 hours, with efficiency slightly decreasing to 75.4% after four cycles. Additionally, the removal rates of TC, oxytetracycline, and tetracycline hydrochloride under visible light were 84.1%, 52.2%, and 73.5%, respectively.¹⁶⁶

Graphitic carbon nitride, having a band gap of 2.7 eV, enhanced the reactive sites and the performance of carrier separation in the photocatalyst. The combination of Ag/AgCl@ZIF-8 with g-C₃N₄ successfully addressed both the extensive band gap of ZIF-8 and the limited surface area of g-C₃N₄. As previously mentioned, Fan *et al.* prepared an Ag/AgCl@ZIF-8 composite that demonstrated superb photocatalytic performance.¹⁷⁸ Furthermore, Zhou *et al.* modified this composite by loading g-C₃N₄ (AZCN) onto its surface to remove levofloxacin (LVFX) by using the facile stirring method. The homogeneous distribution of Ag, Zn, C, N, and Cl validates the successful synthesis of the composite by TEM EDX mapping. The optical characteristics of the photocatalysts were evaluated by UV-vis DRS (Fig. 8d), where g-C₃N₄ shows an absorption edge around 440 nm in the visible region, while ZIF-8's absorption edge is at 246 nm. The Ag/AgCl@ZIF-8 sample exhibits an absorption range from 300 to 800 nm. The PL spectra, where the 10%-AZCN sample exhibits the smallest peak intensity, indicate that the optimal ratio of Ag/AgCl@ZIF-8 to g-C₃N₄ enhances photoelectron transfer effectiveness and maximizes photocatalytic activity. LC-MS

measurement revealed that the AZCN composite, in conjunction with PMS, effectively breaks down LVFX into smaller molecules by sequentially eliminating diverse functional groups, ultimately oxidizing it to CO₂ and H₂O. In addition to photocatalysis, advanced oxidation processes (AOPs) were used in drug wastewater purification. Peroxymonosulfate (PMS) can produce $SO_4^{\cdot-}$ radicals when activated by other reactive species. These radicals oxidize most contaminants and assist other reactive species in the synergistic degradation of LVFX. Without PMS, AZCN achieved only a 53.6% degradation rate for LVFX.¹⁶⁹

The photocatalytic degradation of drugs using ZIF-8-based composites reveals their potential through effective photon absorption and reactive radical generation. Integrating ZIF-8 with various materials enhances photocatalytic performance by improving charge carrier dynamics and radical production, leading to higher degradation rates for various drugs, such as tetracycline and levofloxacin. Future work should focus on refining these composites and exploring new materials to address diverse drug contaminants and improve practical applications in wastewater treatment.

5. Conclusion

Despite their relatively brief development history, ZIFs have garnered significant attention, leading to numerous achievements in recent years. ZIF-8-based materials are increasingly utilized in energy generation and wastewater treatment due to their catalytic activity and high porosity. This review provides in-depth overviews and analysis of the synthesis and applications of ZIF-8-based photocatalysts and their composites in light-mediated H₂ evolution, H₂O₂ evolution, CO₂ reduction, and pollutant removal. ZIF-8 has unique potential for develop-



ing alternative photocatalysts due to their exceptional properties, including effective charge separation, abundant active sites, and persistent porosity. Constructing catalyst composites from ZIF-8 and other functional materials offers several advantages for photocatalytic implementations over traditional single catalyst methods. Photoactive semiconductors or molecules in the composite enhance ZIF-8 solar light utilization. ZIF-8-based composites, with their high surface areas, provide active sites, prevent nanoparticle aggregation, and act as electron acceptors for charge carrier separation. Strong interfacial connections between ZIF-8 and semiconductors harvest visible light enhance electron transfer. As a result, ZIF-8-based composites typically demonstrate much greater photocatalytic efficiency compared with catalysts that consist of only one component. Currently, there is substantial interest in developing ZIF-8-based photocatalysts for environmental remediation and energy production that remain stable in the complex while being cost-effective and environmentally friendly. Although this field has made significant progress, much work remains before these photocatalysts can be widely applied (Fig. 9). However, more research is necessary to make ZIF-8 composite components viable for extensive photocatalytic application, as they are currently expensive, and we believe that current studies only scratch the surface of their potential. Our reasoning is based on the following points:

I. Most ZIF-based materials are microporous, with pore diameters less than 2 nm. This can limit their effectiveness, particularly when dealing with larger pollutant molecules due to steric hindrance. Therefore, it is beneficial to synthesize hierarchically porous materials from ZIFs that incorporate a range of pore sizes, including mesopores, macropores, and micropores.

II. Numerous synthetic techniques have been developed for both research and large-scale production of ZIF-8, yet achieving controlled synthesis with high crystallinity and uniform size remains difficult. Uniform size and crystallinity are crucial for application performance, especially in small-scale devices and electron conduction applications.

III. ZIF-8 has relatively low water stability due to the susceptibility of its coordination bonds to water. Enhancing the long-term water stability of ZIF-8 in a cost-effective manner continues to be a significant challenge.

IV. The chemical and thermal stability of ZIF-8-based composites must be carefully addressed for industrial implementations. Additionally, the catalytic sites and porosity should be managed skilfully.

V. Solar-active ZIF-8-based composites for hydrogen evolution could significantly contribute to renewable global energy solutions. However, ZIF-8 has a broadband gap, restricting its potential for solar energy utilization. Therefore, an adjustment approach to enhance sensitivity to visible light in both pristine ZIF-8 and its composites is crucial. Incorporating plasmonic materials can be advantageous, but it is essential to keep the cost-effectiveness in check.

VI. Multiple reaction parameters, such as temperature, ionic strength, and pH, are analyzed to assess their impact on

pollutant degradation performance. Exploring the relationship between these variables and the effectiveness of ZIF-8 composites is essential to provide valuable references for the most effective synthesis and reaction parameters. This is crucial for the rational fabrication of adsorbents and photocatalysts. Furthermore, ZIF-8 composites must maintain long-term stability in various environmental conditions and be produced cost-effectively for industrial applications. Research should aim to improve solar light absorption efficiency, lower the rate of electron-hole pair recombination, and consider the recyclability of these materials as also important for practical applications.

VII. Photodegradation of organic contaminants using ZIF-8 and its composites is a highly emerging technology for pollution control owing to its low cost and eco-friendly nature. Currently, most research focuses on dye degradation, like RB, MB, and MO. However, there is a need to broaden the scope to include a wider range of organic impurities, such as perfluorinated organic chemicals (PFCs), along with pharmaceutical and personal care products (PPCPs) to better evaluate the photocatalytic decomposition capabilities of these components. It has been recommended to use actual polluted water rather than simulated wastewater and to measure the degradation efficiency by assessing the total organic carbon (TOC) removal percentage along with the highest absorbance of the targeted pollutant. Additionally, to advance toward industrial applications, extensive research is needed to understand the factors influencing photocatalytic efficiency, including co-existing ions, dissolved organic matter, and pH levels.

VIII. Numerous questions concerning the underlying mechanisms still require thorough clarification. In particular, the photocatalytic processes, including the separation of charge carriers generated by light and charge migration within multi-constituent systems, remain insufficiently understood for certain synthesized materials. Gaining a deeper insight into these catalytic mechanisms is crucial for developing next-generation photocatalysts with superior photocatalytic performance. To achieve this, integrating *in situ* characterization methods combined with theoretical simulations might be essential to clarify these mechanisms.

IX. The reclaimability of photocatalysts from aqueous solutions is vital for practical applications. Most ZIF-8/ZIF-8-based composite photocatalysts are solid powders that, despite being stable in aqueous solutions, have a diffusive nature that makes them challenging to separate from the reaction solution for recycling. It is significant to enhance novel ZIF-8/ZIF-8-based composite materials that can be more easily separated from solutions, such as forming films/membranes or shaping them into pellets/monoliths. Additionally, toxicity analyses have not yet been undertaken, which is vital for their resilient use.

X. A wide range of ZIF-8 composites have been developed, and even small variations in synthesis conditions can lead to significantly different properties. Despite continuous advancements in characterization technologies, examining the interface between ZIF-8 and the incorporated materials remains essential. *In situ* techniques like SEM, TEM, FTIR, and XPS are commonly employed to study the formation of ZIF-8 compo-





Fig. 10 Schematic representation of challenges and future research directions toward ZIF-8-based nanomaterials for photocatalytic applications.

sites. Future research should, therefore, aim to explore the synergistic mechanisms of these composites using advanced analytical methods.

XI. Lastly, eco-friendly ZIF-8-based materials are essential for widespread practical applications in energy production and water treatment. The environmentally friendly properties are crucial from a pragmatic standpoint. Therefore, greater emphasis should be placed on achieving a low production-cost ratio while using biocompatible constituents (Fig. 10).

Author contributions

Diptirani Behera: conceptualization, writing – original draft, visualization. Priyanka Priyadarshini: conceptualization, writing – original draft editing and review. Kulamani Parida: conceptualization, visualization, supervision.

Data availability

The submitted review article synthesizes and discusses data that have already been published and are publicly available from the sources cited in the manuscript. No new data were generated during the preparation time frame of this review.

Conflicts of interest

There are no conflicts to declare.

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