# Photocatalytic MOF Membranes for Advanced Seawater Purification: From Material Design to Sustainable Water Treatment

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**Abstract:** Seawater pollution remains a pressing global challenge, intensified by industrial discharges, agricultural runoff, and maritime activities. Conventional water treatment methods are often limited by high energy costs, insufficient selectivity, and the risk of secondary pollution. Metal-organic frameworks (MOFs), recognized for their tunable porosity and high surface areas, are emerging as promising materials for advanced water purification. The integration of photocatalytic properties into MOF membranes offers a significant advantage: the addition of self-cleaning functionality to the inherent separation process, paving the way for more energy-efficient purification. This review explores recent progress in photocatalytic MOF membranes for treating seawater, addressing the critical issues of water scarcity and marine pollution. It examines how these materials can be enhanced through strategies like ligand functionalization, heterostructure engineering, and metal ion doping to boost their performance against organic pollutants, heavy metals, and pathogens. The synthesis of MOFs is discussed, alongside the critical need to optimize their stability, light absorption, and charge separation efficiency. Key challenges such as membrane fouling, salt scaling, and long-term durability are analyzed, along with potential solutions through material design and process engineering. Recent advances confirm the potential of these membranes for revolutionary improvements in water technology, especially when combined with renewable energy sources, highlighting their role in promoting sustainable water management and providing innovative directions for the field.

**Keywords:** Photocatalytic MOF membranes, Seawater purification, Heterostructure engineering, Anti-fouling and salt-scaling resistance, Sustainable water treatment.

## 1. INTRODUCTION

### 1. 1. Global Challenges of Seawater Pollution and Scarcity

With the rapid development of industrialization and the rapid growth of population. Seawater pollution and the escalating global water scarcity crisis have emerged as pressing challenges, not only that, precious resources such as fresh water, only 2. 5% of the world's water is freshwater, and less than 1% of this is accessible for use, and the rest is almost seawater [1], so it is really important to improve seawater purification technology, which demand immediate and innovative solutions. Ghanimeh S *et al*. underscores the severe threats posed by the contamination of seawater with organic pollutants, heavy metals, and pathogenic microorganisms, which not onlyjeopardize marine ecosystems and human health, but also exacerbate the scarcity of clean water resources worldwide [2]. Complementing this perspective, Angelakis A N *et al*. highlight the inherent limitations of conventional water treatment technologies, such as high energy consumption , poor efficiency and insufficient selectivity, thereby emphasizing the urgent need for advanced materials and novel purification strategies [3]. However, the traditional separation membranes are usually very expensive and easy polluting the environment. Therefore, how to prepare high-efficiency separation membrane from low-cost, green renewable materials remains a huge challenge [4]. Within this context, metal-organic frameworks (MOFs) have garnered considerable attention due to their highly tunable porosity and versatile chemical functionalities, which facilitate efficient adsorption and catalytic degradation of a broad spectrum of contaminants [5]. On the whole, these studies illuminate the multifaceted nature of seawater pollution challenges and underscore the transformative potential of MOF-based materials in addressing the urgent global need for clean and sustainable water resources.

### 1. 2. Metal Organic Skeletons (MOFs) as Emerging Materials in Water Treatment

With the rapid development of membrane science, membrane technology has achieved tremendous development in field concerning chemicals, petroleum, energy, aerospace, food, and environmental protection. According to the material of the membrane, membranes can be roughly divided into two categories: organic membranes and inorganic membranes. Organic membranes mainly include polyethersulfone and polyvinylidene fluoride membranes, with shortcomings that include a relatively short service life, poor thermal stability, and low selectivity, which limit the application of polymer membranes in the field of membrane separation [6]. Meanwhile, inorganic membranes mainly include ceramic membranes and molecular sieve membranes, which are not easy to prepare and are fragile [8]. Therefore, new membrane materials need to be developed to meet higher demands regarding separation performance.

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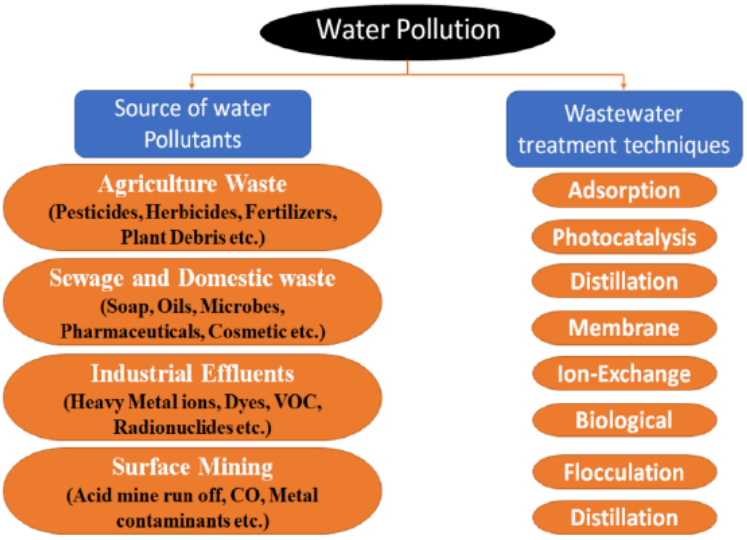


**Figure 1:** Different sources and treatment techniques of wastewater (from [6]).

Metal-organic frameworks (MOFs) are crystalline porous materials formed through the coordination-driven self-assembly of metal ions or secondary building units with organic ligands. This modular architecture allows for precise control over pore size, surface chemistry, and structural stability, endowing MOFs with exceptional potential in molecular separation, adsorption, and catalysis. Lu W *et al*. highlighted that certain MOFs possess extraordinarily high specific surface areas exceeding 7000 $m^2/g$, providing abundant active sites for efficient adsorption and catalytic reactions [5]. Since MOFs have the advantages of high specific surface area and large porosity, they are suitable for various applications, such as gas adsorption and energy storage. So MOF membranes prepared from MOFs exhibit more excellent performance than conventional membranes in the field of adsorption and separation due to their unique advantages of high selectivity and permeability[9]. The pioneering work by Li *et al*. in synthesizing the robust MOF-5 framework catalyzed extensive research into unexplored MOF families, novel synthetic pathways, and diverse applications. Subsequent efforts, fueled by the immense combinatorial possibilities of metal clusters and organic linkers, have yielded an astonishing library of over 84, 000 distinct MOFs in the last twenty years. This has led to the extensive development and application of several hallmark MOF series, such as Isoreticular MOFs (IRMOFs), Zeolitic Imidazolate Frameworks (ZIFs), Materials of Institute Lavoisier (MIL), University of Oslo (UiO), and Porous Coordination Networks (PCNs)[10]. Li H *et al*. (2021) used the secondary growth MOF synthesis method to use titanium dioxide to induce the UIO-66 seed layer to make a highly stable and highly selective UIO-66 film, with a salination rate of 99. 9% and a water flux of 37. 4 L • m−2 • h−1. The membrane not only has good performance in high-salt and low-salt solutions, but also has good stability under extreme conditions. Researchers has found that MOF materials have excellent dsorption performance for heavy metals, which make them a potential heavy metal adsorbent [11]. Wu F *et al*. (2025) has found utilization of MOF materials for the adsorptive removal of heavy metals, Pb and Cd, from aqueous environments. One previous study confirmed that a MOF membrane (UIO-66-S), which was prepared using $ZrCl_4$, DMF, and other reagents, could effectively adsorb mercury in wastewater [12]. The membrane presented excellent mercury removal efficiency and could remove more than 80% of mercury in wastewater within 20 min. In addition, the membrane solved the problems of unstable MOF materials and difficult membrane regeneration during the purification process, so that the MOFs could present excellent stability and durability. After multiple purifications of wastewater, the mercury removal rate of the membrane could be maintained above 98% [13]. It can be seen that MOF membranes could effectively purify wastewater. Collectively, these studies establish MOFs as a highly versatile and emerging class of materials with tunable structural features and multifunctionality, making them ideal candidates for innov Photocatalysis has risen to prominence as a powerful technique for addressing environmental challenges, particularly in the realm of seawater purification. This innovative strategy is distinguished by its ability to confront a broad spectrum of pollutants simultaneously, encompassing salts, heavy metals, organic contaminants, and pathogens that are omnipresent in seawater. ative water purification applications.

### 1. 3. Photocatalysis : The Principle and Advantages of Environmental Restoration

Photocatalysis is an advanced oxidation process that absorbs photon energy through catalysts (usually

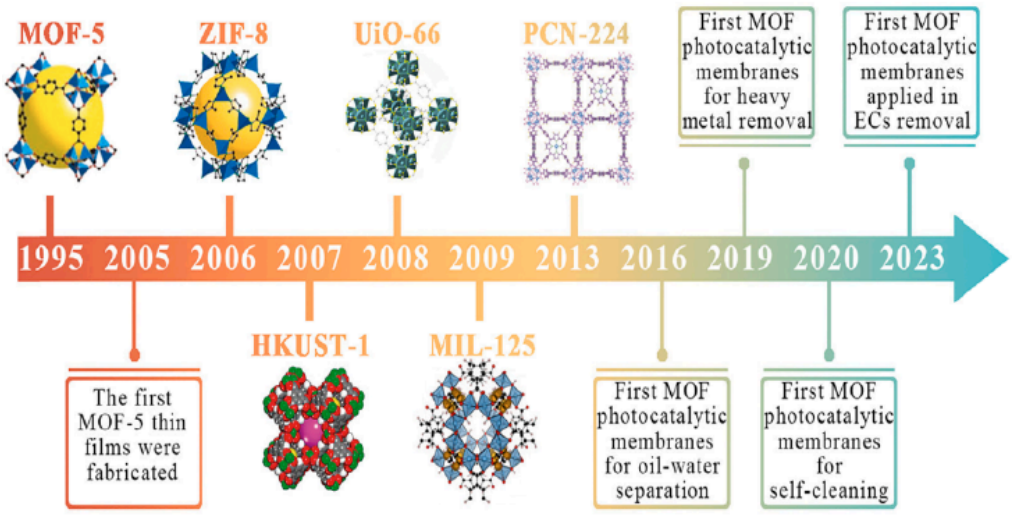


**Figure 2:** The development process of MOF. (from [10]).

semiconductor materials) under light irradiation, induces the generation and separation of electron-hole pairs, and then drives a series of redox reactions' Advanced Oxidation Process [14]. It has several important core characteristics, one is strong oxidation ability: means the OH oxidation potential produced in the reaction is extremely high, which can efficiently decompose organic pollutants. The final products are mostly $CO_2$ and $H_2O$, which achieves deep mineralization and avoids secondary pollution [15], the second is broad spectrum: it shows good degradation effect on a variety of pollutants like dyes, phrnols, pesticides, drugs and personal care products, etc. It also has antibacterial, oill removal and other abilities [16]. The third is the sustainability of energy sources: using sunlight as the main energy input, which is in line with the concept of green and sustainable development. In addition, there is also catalyst stability and reusability: the ideal semiconductor photocatalyst (such as $TiO_2$) is chemically stable, not easy to dissolve or inactivate, and can be designed for fixed system recycling [16]. Because of these, Photocatalysis has risen to prominence as a powerful technique for addressing environmental challenges, especially in the realm of seawater purification. This innovative strategy is distinguished by its ability to confront a broad spectrum of pollutants simultaneously, encompassing salts, heavy metals, organic contaminants, and pathogens that are omnipresent in seawater. Photocatalysis has been widely used in the field of seawater treatment. 1. Degrading organic pollutants: treating oil pollution and non-degradable organic matter caused by offshore oil leakage, industrial wastewater discharge, ship discharge, etc. [18]. 2. Sterilization: Inactivate pathogenic bacteria, viruses and other microorganisms in seawater, and provide the possibility of pretreatment of seawater desalination or direct preparation of sanitary water [19]. 3. Auxiliary desalination pretreatment: degrade natural organic matter (NOM) in seawater to alleviate the membrane pollution and scaling problems of subsequent reverse osmosis (RO) or distillation processes [20]. 4. Resource utilization (hydrogen production and chemical production): use photocatalytic decomposition of seawater to produce $H_2$ or high value-added chemicals (such as $H_2O_2$), and realize the synchronous recovery of energy and resources [16]. Collectively, these studies demonstrate the multifaceted advantages of photocatalytic technology in seawater treatment, especially their ability to synergistically remove diverse pollutants, effectively addressing the complex challenges posed by seawater composition. As a green and efficient advanced oxidation technology, photocatalysis technology has shown great application potential in the field of seawater purification and resource utilization. Through continuous interdisciplinary collaborative innovation, photocatalysis technology is expected to provide more economical and environmentally friendly solutions to the global water crisis and energy challenges.

### 1. 4. The Purpose of Exploring Photocatalytic MOF Membrranes for Seawater Purification

Because of the promising ability of MOF to overcome the inherent limitations of traditional treatment technologies. The pursuit of photocatalytic MOF membranes for seawater purification has attracted considerable interest, Karakaş *et al*. (2025) illustrated that embedding MOFs within graphene sponges significantly enhances solar-driven desalination efficiency by synergistically combining MOF porosity with photothermal conversion, thereby facilitating effective contaminant removal and accelerated water evaporation [21]. In a

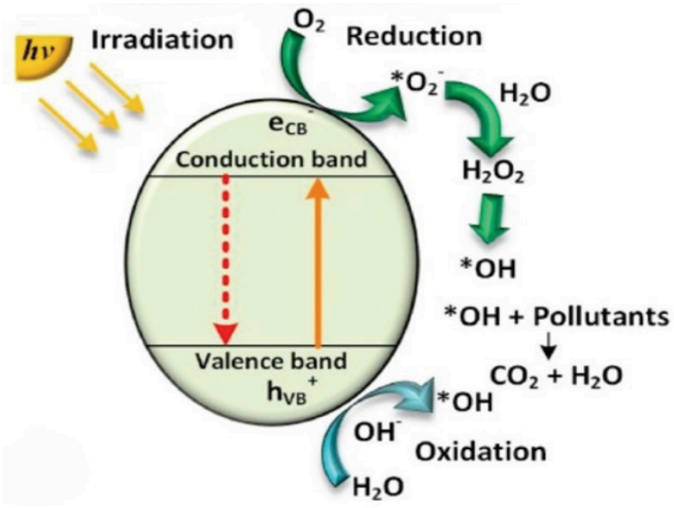


**Figure 3:** Photocatalytic mechanism.

complementary approach, Ma *et al*. innovatively repurposed facial tissue waste to construct flexible, hierarchical MOF-based photothermal materials that reduce evaporation enthalpy, markedly improving the energy efficiency of seawater desalination and wastewater treatment processes [22]. Addressing membrane fouling—a critical challenge in seawater treatment—Wang *et al*. employed graphene oxide to assist the dispersion and assembly of photocatalytic MOF membranes, resulting in enhanced self-cleaning properties and superior pollutant degradation performance [23]. Additionally, Gan *et al*. developed vertically oriented MOF films supported on organic–inorganic hybrid substrates, achieving remarkable efficacy in purifying complex wastewater mixtures, which closely parallels the multifaceted contaminant profile of seawater [24]. Together, these investigations highlight the central objective of harnessing photocatalytic MOF membranes to realize efficient, sustainable, and scalable seawater purification. By exploiting their tunable structural features and photocatalytic capabilities, these membranes offer a transformative pathway toward addressing global water scarcity and pollution challenges with renewable energy integration and improved operational stability.

### 1. 5. Significance of Research

Photocatalytic water treatment is anadvanced oxidation, unlike traditional separation techniques such as filtration and sedimentation, it aims to eliminate pollutants completely, through harnessing semiconductors or hybrid materials to generate electron-hole pairs under light irradiation, it triggers redox reactions that effectively degrade organic pollutants and inactivate pathogenic microorganisms. Chen *et al*. demonstrated that photocatalytic processes enable thorough mineralization of contaminants via oxidation by photogenerated free radicals, significantly enhancing purification efficiency [29]. Furthermore, photocatalysis disrupts microbial cell membranes and biofilms, markedly improving the antifouling properties of membrane materials. Bao *et al*. (2024) reported that heterostructured MOFs used in seawater oxidation exhibit enhanced membrane durability due to this effect [26].

Integrating photocatalytic functions into MOF membranes creates a synergistic mechanism that combines physical sieving with chemical degradation. Yuan *et al*. highlighted that incorporating photoactive metals such as Ti, Fe, or Cd into MOFs extends their light absorption into the visible spectrum, thereby boosting photocatalytic activity [27]. Constructing heterojunctions by coupling MOFs with semiconductors like graphene or graphitic carbon nitride further broadens light absorption and promotes efficient charge separation, which is essential for high photocatalytic performance, as discussed by Zhou *et al*. [28]. Additionally, surface nanostructuring enhances photocatalytic efficiency by increasing light capture and photothermal effects, a strategy supported by Dai *et al*. , who investigated MOF-induced crystallization mechanisms that improve surface morphology and catalytic sites [25].

Collectively, these studies underscore that advancing MOF-based photocatalytic technology for water treatment depends on optimizing light absorption, charge carrier dynamics, and surface architecture. Such improvements maximize pollutant degradation and membrane antifouling capabilities, positioning photocatalytic MOF membranes as a promising, sustainable solution for seawater purification.

With the rapid development, the pursuit of sustainable and efficient seawater purification has

become more and more important, and traditional seawater treatment still has many disadvantages, not only high energy consumption and high cost, but also certain chemical pollution and ecological impact on the environment. In a comprehensive review, Abounahia *et al*. delve into the potential of polyacrylonitrile-based membranes for forward osmosis processes. These membranes are lauded for their low energy requirements and robust resistance to fouling, making them crucial for advancing sustainable water treatment technologies [34]. Parallel to this development, Xu *et al*. [33] highlight the innovative S-scheme heterojunctions, notably WO/SnInS, that exhibit enhanced photocatalytic activity. These heterojunctions facilitate effective charge separation, expediting the degradation of persistent pollutants in seawater. This breakthrough significantly contributes to the removal of contaminants that pose threats to marine ecosystems and human health. Moreover, Yin *et al*. explore multifunctional indium-based metal-organic frameworks (MOFs), which integrate multiple functionalities—fluorescence detection, physical adsorption, and photocatalytic redox reactions—into a single material. Their study underscores the versatility and environmental compatibility of MOFs for comprehensive pollutant removal from seawater. This multifaceted approach offers a promising pathway for addressing the intricate challenges associated with seawater contamination [31]. In another pivotal study, Jinhong *et al*. demonstrate the exceptional photocatalytic efficiency of MOF-derived InO microrods decorated on MgInS nanosheets. These materials form Z-scheme heterojunctions, effectively degrading antibiotics such as tetracycline. This innovation tackles complex contaminant challenges in seawater, ensuring the removal of even the most resistant pollutants [30]. These research endeavors emphasize the critical role of advanced materials and membrane technologies in achieving sustainable and energy-efficient.

## 2. THE DEVELOPMENT AND PERFORMANCE OF MOF MEMBANE

The structural characteristics and diversified customization of metal-organic frameworks (MOFs) are fundamental to their effectiveness as membrane materials. Therefore, we can regulate MOF based on the needs of photocatalyst and purified seawater.

### 2.1. Ligand Functionalization

Ligand functionalization refers to the introduction of specific functional groups or functional molecules on organic ligands by chemical methods, such as -NH2, -OH, -COOH, -NO2, -SH, etc. before or after the synthesis of MOF. These functional groups are like installing on the walls of the "building" of MOF. Different "tools" or "switches", so as to accurately regulate the physical and chemical properties of MOF. Therefore, ligand functionalization can be regarded as a "molecular-level engineering", which allows researchers to accurately regulate the functional group, topological structure, specific surface area, pore volume and spatial resistance effect in the structure of MOF by selecting the type of lind, so we can use the selection of ligands and control the metal center to improve the photocatalytic activity. For this, the

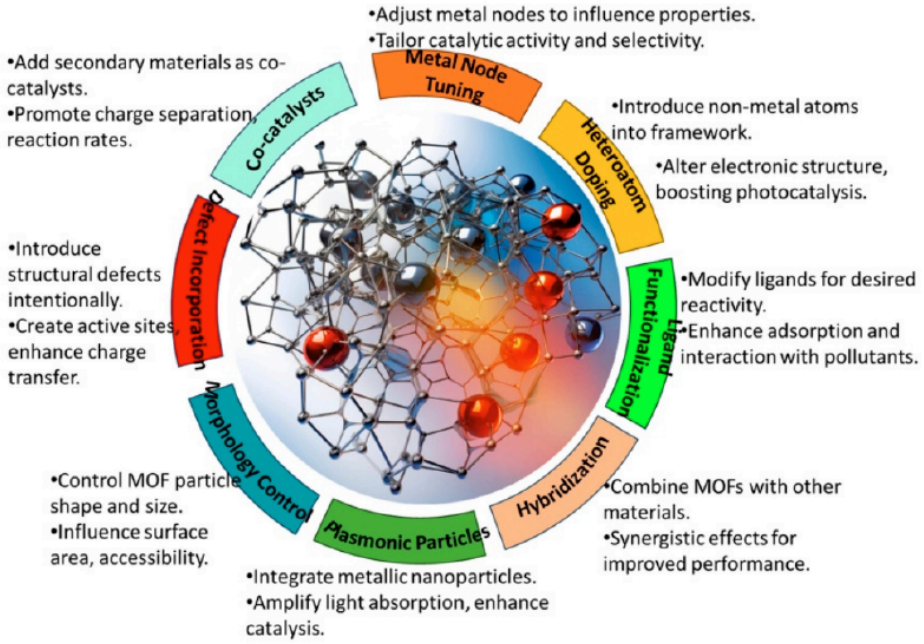


**Figure 4:** Various strategies adopted when designing base photocatalysis MOF. (from[31] ).

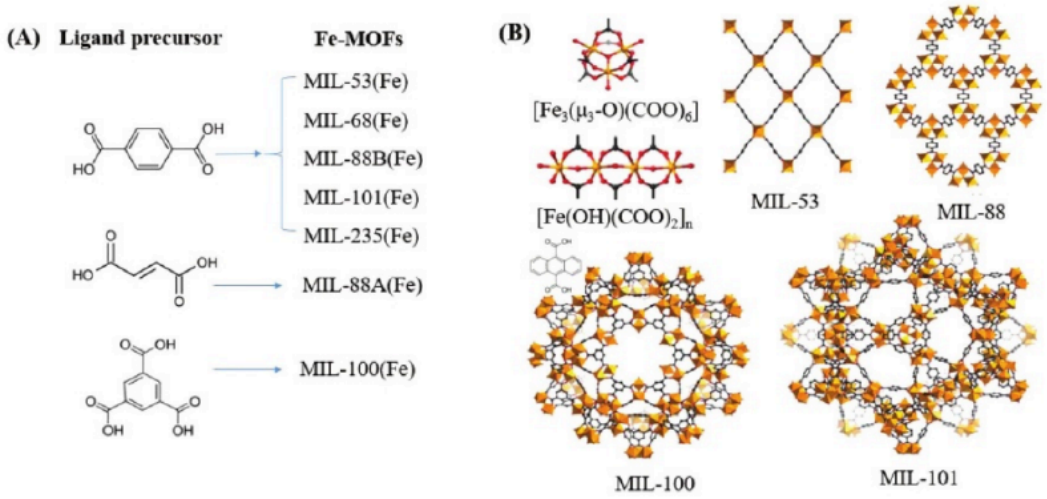


**Figure 5:** (**A**) Fe-MOFs prepared with different ligand precursors; (**B**) structures of metal clusters and representative MIL series of Fe-MOFs. (from [39]).

researchers have adopted many different methods. The most commonly used method is to introduce covalent modification of functional groups. This method can achieve diverse chemical functionalization while maintaining structural stability, but it is also a challenge to maintain the stability of functional groups when directly synthesizing MOF. Not only that, the existence of competitive ligands at the coordination site also has a great impact on the formation of MOFs. They can form nucleation at specific points in the process of synthesis, thus changing the crystal morphology, and can regulate the specific crystal surface and its required surface reacticity. The pioneering experimental work systematically investigating the impacts of ligand types on the photocatalytic activity of MOFs was first conducted by Mu *et al*. in 2018 [35]. By employing Zr-O clusters and various terephthalate linkers, they obtained five different amorphous UiO-66-X (X=H, $NH_2$, Br, $(OH)_2$, $(SH)_2$) MOFs. The light absorption capabilities of these MOFs were determined using UV–Vis diffuse reflectance spectra (UV–Vis DRS). This study revealed that while the absorption band edge of pristine UiO-66 was located at 330 nm within the UV spectrum, the band edges of UiO-66 functionalized with SH and OH groups redshifted into the visible light region. This phenomenon was attributed to the conjugated π-electron transition between the chromophores and the Zr centers. Among them, UiO-66-$(SH)_2$ exhibited the most superior effectiveness in degrading rhodamine B (RhB) under visible light irradiation. This exceptional performance was ascribed to its efficient separation of photogenerated electrons and holes, as validated by photocurrent measurements.

Subsequently, to systematically probe the effects of mixed linker ratios on the activity of MOF-based photocatalysts, Chen *et al*. [36] prepared two types of UiO-66-Zr composites via direct synthesis and post-oxidation techniques, namely UiO-66-$(SCH_3)_{2-x}$h and UiO-66-$(SOCH_3)_x(SCH_3)_{2-x}$, respectively. They found that these mixed-linker MOFs demonstrated a reduced band gap, enhanced photo-responsiveness, and improved catalytic performance compared to their counterparts, UiO-66-$(SCH_3)_2$ and UiO-66-$(SOCH_3)_2$, which are composed of single, neat linkers. The n-π*and π-π* transitions arising from photoexcitation of aromatic groups in organic ligands play a crucial role in enhancing the overall light absorption and photogenerated charge density in MOFs. Consequently, the optoelectronic properties of MOFs can be modulated by extending the conjugated aromatic systems or modifying functional groups within the organic ligands [37]. For instance, (Fan *et al*. , 2021) tuning functional groups in Zr-based MOFs enables adjustable $CO_2$ adsorption and separation functions [38].

Fe-MOFs have garnered significant interest due to their visible-light-responsive Fe–O clusters, which enable efficient solar energy utilization, and the natural abundance of iron, which lowers cost. As shown in Figure **5A**, various Fe-MOFs (*e. g*. , MIL-53, MIL-88, MIL-100, MIL-101) can be synthesized from iron precursors like $Fe(NO_3)_3$ or $FeCl_3$ and organic ligands such as $H_2BDC$, $H_2FUM$, or $H_3BTC$. The photocatalytic reduction of Cr(VI) or U(VI) has been achieved on MIL-53(Fe) using $(NH_4)_2C_2O_4$or HCOOH as hole scavengers. Among them, MIL-100(Fe) with tricarboxylate linkers exhibits superior stability over dicarboxylate-based Fe-MOFs (*e. g*. , MIL-53, MIL-88, MIL-101). Both possess 3D frameworks Figure **5B,** but MIL-100(Fe) shows remarkable thermal and aqueous stability, whereas MIL-101(Fe) can transform into MIL-53 or MIL-88 in strongly polar solvents. Photocatalytic performance is strongly influenced by

surface properties, where a larger specific surface area is generally beneficial. The observed differences among Fe-MOFs are primarily attributed to their band gaps and adsorption capacities. Future research should focus on enhancing their photocatalytic activity and hydrothermal stability under harsh conditions [39].

Ligand engineering also facilitates the construction of heterojunction systems. Tong *et al*. employed BDC ligands within an $Ag_3PO_4$-decorated MOF-5 framework, where the conjugated structure of BDC reduced photocorrosion and promoted well-defined heterojunction formation, increasing photocatalytic activity by 4. 3 times compared to pure $Ag_3PO_4$ [40]. In another study, Mao *et al*. fabricated a SCu-CZS30 nanocomposite by doping CdS/ZnS QDs into Cu-decorated, thiol-functionalized UiO-66. This composite exhibited hydrogen evolution rates 202. 6, 10. 2, and 3. 3 times higher than pristine CdS, ZnS, and $Cd_{0.5}Zn_{0.5}S$, respectively, with thiol groups critically bridging $Cu^{2+}$ ions and enhancing photocatalytic performance [41].

This approach is particularly valuable in solvothermal synthesis, as it overcomes limitations associated with precursors bearing certain functional groups while harnessing the potential of organic transformations in ligands to functionalize both the interior and exterior surfaces of MOFs [42]. Beyond these advantages, recent advances have introduced novel techniques such as post-synthetic metal exchange (PSME), post-synthetic elimination and installation (PSE&I), and tandem PSM [43].

PSM of MOF ligands is also effective in regulating the photocatalytic activity of MOF-based photocatalysts. For instance, Zeama *et al*. [44] conducted PSME between $Ti^{4+}$ and $Zr^{4+}$ in an amine-functionalized UiO-66 derivative [$(Zr_{0.87}Ti_{0.13})$/UiO-66-$NH_2$]. This exchange induced pore size tuning through altered electron density, which polarized $CO_2$ and enhanced both the selectivity and performance of photocatalytic $CO_2$ reduction. Moreover, the metal exchange process facilitated a shift from LLCT (ligand-to-ligand charge transfer) to LMCT (ligand-to-metal charge transfer). In another study, Fu *et al*. (2021) [45] achieved partial PSM in MR/$NH_2$-MIL-125(Ti) by replacing some amino groups with MR chromophores. This modification boosted the rate constant for Cr(VI) removal by 9 times compared to the parent $NH_2$-MIL-125(Ti).

Hu *et al*. [46] reported an ethylenediamine (EDA) functionalized ZIF-8 for the photocatalytic reduction of Cr(VI) under visible light irradiation. They identified the $–CH_3$ site on the 2-methylimidazole chains of ZIF-8 as the grafting site for the amine groups. The increased electron density induced by the grafted amines led to enhanced visible light absorption and higher photocatalytic activity in the modified ZIF-8 compared to its unmodified counterpart. In conclusion, ligand functionalization and post-synthetic modification (PSM) of MOFs serves as an effective strategy for tuning their physical and chemical properties, thereby boosting their photocatalytic performance. However, there remains a need to develop more efficient modification methods and to gain a deeper understanding of how the modification process influences the MOF's structure and properties. Further exploration in these areas will undoubtedly contribute to the advancement and optimization of MOF-based photocatalysts.

### 2.2. Heterostructure Constructing

Constructing heterojunctions in MOFs is recognized as an effective strategy for tuning their photocatalytic performance, primarily through band engineering. When the energy bands of two distinct semiconductors come into contact, an internal electric field is generated, driving the spatial separation of photogenerated carriers due to the band potential difference, thereby significantly suppressing electron-hole recombination and enhancing photocatalytic efficiency [47][48]. The bandgap of MOFs, ranging from 1. 0 to 5. 5 eV and tunable by metal clusters, organic linkers, and guest molecules, provides a foundation for diverse heterojunction designs. [49]Common MOF-based

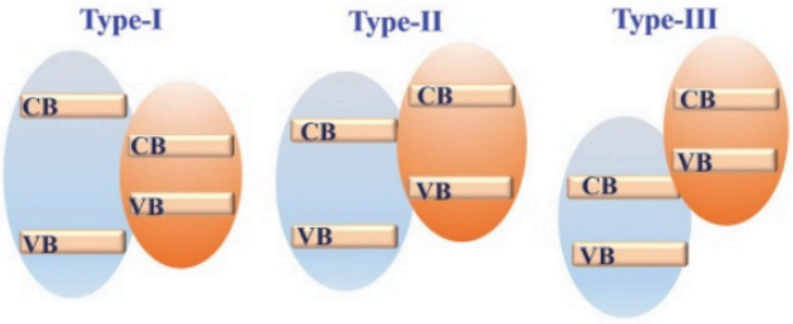


**Figure 6:** Schematic diagram of three heterogeneous junctions (from [39]).

heterostructures include Schottky junctions, Type-I, Type-II, and Z-scheme heterojunctions [47] Figure **6**. Among these, MOF-based Schottky junctions, formed by combining metals (or precious metals) with MOFs, facilitate electron transfer from the MOF's conduction band (CB) to the metal, enabling efficient carrier separation. [50] In Type-I (straddling gap) heterojunctions, both the valence band maximum (VBM) and conduction band minimum (CBM) of one semiconductor are higher than those of the other, leading to the spatial accumulation of both photogenerated electrons and holes in the same semiconductor component. While this increases the local carrier concentration, it also makes them more prone to recombination [41, 51]. In contrast, Type-II (staggered gap) heterojunctions overcome this limitation by enabling electrons and holes to migrate to different semiconductor components through a staggered band alignment, thereby significantly improving carrier separation efficiency [52-54]. For instance, g-$C_3N_4$, with its favorable energy levels and excellent light absorption, is often employed to construct efficient Type-II heterojunctions: Huang *et al*. [111] demonstrated enhanced charge separation and photocatalytic performance in g-$C_3N_4$/MIL-53(Fe) prepared via a one-pot method, while Zhang *et al*. [112] reported similar benefits in UiO-66/g-$C_3N_4$ synthesized through a facile annealing approach. Beyond g-$C_3N_4$, semiconductors such as CdS, $TiO_2$, and $Bi_2WO_6$ are also suitable for forming heterojunctions with MOFs. [56, 57] Li *et al*. [58] developed a Type-II PCN-222-PW12/$TiO_2$ heterojunction via a solvothermal method, which exhibited superior visible-light activity due to improved carrier separation; Wu *et al*. [59] synthesized a core-shell $Cu_2O$@HKUST-1 heterostructure with optimal Type-II band alignment, achieving enhanced tetracycline hydrochloride removal through synergistic interfacial contact and carrier dynamics.

However, Type-II heterojunctions only utilize the lower VB and higher CB of the heterojunction components, limiting the full potential of redox capabilities. To address this, Z-scheme heterojunctions have been proposed. In the direct Z-scheme mechanism, electrons in the higher-reduction-potential CB and holes in the higher-oxidation-potential VB recombine directly, thereby spatially separating and retaining the other carriers with strong redox abilities in the respective components, thus maximizing photocatalytic efficiency. For example, Liang *et al*. designed a ternary Z-scheme BiOI@UIO-66($NH_2$)@g-$C_3N_4$ heterojunction that efficiently degraded organic pollutants via enhanced charge separation; Cui *et al*. [62] reported a MIL-53(Fe)/α-$Bi_2O_3$/g-$C_3N_4$ composite and Sepehrmansourie *et al*. proposed a double Z-scheme UiO-66/$NH_2$-MIL-125/g-$C_3N_4$ heterojunction, both leveraging a direct dual Z-scheme mechanism for effective carrier separation and reactive species generation [60, 61]. Furthermore, MOF-on-MOF heterojunctions (*e. g*. , the core-shell x-$NH_2$-MIL-125@NTU-9 developed by Yu *et al*. [63]) and QDs/MOF composites (*e. g*. , $CsPbBr_3$ QDs/UiO-66($NH_2$) reported by Wan *et al*. [64]) demonstrate exceptional performance in $CO_2$ reduction and pollutant degradation by optimizing interfacial band alignment and charge transfer [62, 65, 66]. It is noteworthy that while heterojunction engineering significantly enhances the optoelectronic properties and catalytic activity of MOFs, practical applications must address long-term stability, the impact of synthesis processes on MOF structure, and potential metal ion leaching.

### 2.3. Doping Metal Ions and Introducing Co-Catalysts

Metal ion doping and the introduction of co-catalysts represent two well-established and effective strategies for enhancing the performance of MOF-based photocatalysts. By incorporating metal ions into the MOF framework, the surface electronic properties can be effectively regulated, where these ions serve as electron traps to facilitate electron-hole separation while creating additional active sites [67-69]. Doping, often achieved via convenient one-pot synthesis, effectively tunes the electrical and optical properties of MOFs. For instance, Yin *et al*. [70] prepared Cu-doped UiO-66, where the incorporated Cu ions and concomitant oxygen vacancies (OVs) acted synergistically as electron traps and mediators, effectively suppressing electron-hole recombination and enhancing charge separation efficiency. Typically, introducing transition metal ions (*e. g*. , $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$) or rare-earth metal ions (*e. g*. , $Er^{3+}$, $Ce^{3+}$, $La^{3+}$) can create impurity levels within the MOF's band gap, which not only extends the spectral absorption range but also serves as electron acceptors to facilitate the separation of photogenerated charge carriers [67-69]. This approach can be extended to multi-metal systems; Bhattacharyya *et al*. [71] demonstrated that a Zr/Ce/Ti trimetallic MOF exhibited nearly double the photocatalytic degradation efficiency for Nile blue compared to its monometallic counterpart, attributed to improved orbital overlap between metal clusters and organic linkers favoring charge transfer.

On the other hand, encapsulating co-catalysts within MOF cavities, leveraging their tunable porous nature, provides a viable pathway to boost catalytic performance. Primary methods for co-catalyst incorporation include the "ship-in-a-bottle" (*e. g*. ,

dual-solvent method) and "ship-around-a-bottle" approaches [72, 73]. Noble metal co-catalysts (*e. g.* , Pd) are highly regarded for their ability to form Schottky barriers with MOFs and potentially exhibit surface plasmon resonance (SPR). Liang *et al*. [74] synthesized Pd@MIL-100(Fe) via a simple alcohol reduction method, which efficiently removed theophylline under visible light irradiation, benefiting from the SPR of Pd nanoparticles and their capacity to capture electrons. However, the cost and scarcity of noble metals have driven the exploration of alternatives, such as non-noble metal co-catalysts (*e. g.* , the $Co(dmgH)_2$ used by Luo *et al*. [75]), quantum dots (QDs), and polyoxometalates (POMs), all showing great promise. For example, Wu *et al*. [76] encapsulated $MAPbI_3$ perovskite QDs within PCN-221 via the ship-in-a-bottle method, achieving a 38-fold enhancement in $CO_2$ reduction efficiency compared to bare QDs. Dutta *et al*. [77] encapsulated Cu-POM within MIL-101(Fe) to create a POMOF membrane, where the high electronegativity of Cu-POM facilitated the capture of photogenerated electrons and imparted a negative surface charge for efficient contaminant sieving via electrostatic interactions.

The efficacy of these strategies is further corroborated by numerous studies: incorporating N-doped carbon quantum dots (N-CQDs) derived from coconut shells into MOF-5 enhanced photocatalytic Cr(VI) reduction efficiency by 2. 5 times [78]; coupling black phosphorus (BP) with a platinum co-catalyst in reduced Ti-based MOFs boosted photocatalytic hydrogen production by 10. 3 times, due to the strong interaction between BP and Ti that reduced $Ti^{4+}$ on the surface of black phosphorus [79]; and Zhu *et al*. demonstrated that using $Ni_3(HITP)_2$ MOF nanosheets as a co-catalyst in a hybrid system with a photosensitizer and an electron donor dramatically increased the photocatalytic $CO_2$ reduction rate to 3. 45 × $10^4$ μmol $g^{-1}$ $h^{-1}$ with 97% selectivity [80]. In summary, both metal ion doping and co-catalyst encapsulation share the core advantages of effectively promoting photogenerated charge separation, providing additional active sites, and potentially synergistically broadening the light response, ultimately significantly enhancing the photocatalytic performance of MOFs.

### 2.4. Confined Catalysis and Metal Nanoparticle Modification

The confined catalysis effect of metal-organic frameworks (MOFs), combined with their unique advantages as host matrices for metal nanoparticles (MNPs), collectively underpin the enhancement of catalytic performance in composite materials. The high specific surface area and tunable pores of MOFs not only effectively encapsulate functional molecules and nanoparticles, preventing their aggregation and growth, but also regulate the electronic structure of the guests through the formed stable confined space, thereby significantly boosting catalytic activity and stability [81, 82]. Particularly when the guests are MNPs, their intrinsic localized surface plasmon resonance (LSPR) effect and lower Fermi energy levels make them exceptional electron acceptors and mediators, greatly enhancing the composite's absorption of visible and even infrared light [83, 72]. Numerous successful examples exist: for instance, Sun and Li [84] encapsulated Pd nanoclusters within $NH_2$-Uio-66, where the formed electron-rich Pd sites significantly improved the efficiency of the Suzuki coupling reaction; whereas Shen *et al*. [85] developed Pd@UiO-66($NH_2$) nanocomposites, which, due to the highly dispersed Pd nanoparticles, exhibited excellent visible-light photocatalytic activity in Cr(VI) reduction. Similarly, the superior performance of catalysts like Cu/Cu@UiO-66, constructed via strategies such as the double-solvent method, is attributed to a synergy enabled by the MOF's confinement effect, namely the combined action of the Schottky junction formed by encapsulated Cu quantum dots and the plasmonic effect of Cu nanoparticles, which optimizes charge separation and utilization. [86] Research shows that this synergy extends beyond single metals; in composite systems like Pt/MIL-125(Ti)/Ag, the metal-MOF double interfaces successfully integrate Schottky junction charge trapping with the surface plasmon resonance effect, further optimizing the separation and utilization of photogenerated charge carriers [87]. Therefore, MOF-based confined catalysis provides a highly promising platform for designing and constructing efficient, stable, and multifunctional catalytic materials.

### 2.5. Morphology Regulation

Research has shown that the morphological structure of photocatalytic membranes is significantly influenced by the morphology, dosage, and functional group properties of MOFs [88, 89]. MOF morphologies are primarily categorized into two-dimensional (2D) nanosheets and three-dimensional (3D) nanoparticles. With their high specific surface area and fully exposed active sites, 2D MOFs can stack in an ordered manner to form layered structures with interlayer channels, making them excellent building blocks for high-performance membranes that integrate efficient separation and photocatalytic degradation [90]. For instance, Wang *et al*. [95]fabricated a 2D heterostructure membrane by alternately arranging 2D MOF-2 and g-$C_3N_4$ nanosheets, which exhibited a smooth surface and well-defined layered structure. The tightly stacked layers created uniform nanochannels

that stabilized permeation flux at 23. 6 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ over a wide pH range and achieved approximately 60% removal of atrazine by membrane filtration alone. It is important to emphasize that excessively large or small interlayer spacing may impede charge transfer or reduce permeation and retention, respectively, underscoring the importance of precise interlayer control and balanced photocatalytic-separation performance in developing 2D MOF-based membranes.

In terms of morphological regulation, 2D MOF nanosheets have attracted extensive attention due to their unique structural features and physicochemical properties [96]. Compared to bulk MOFs, ultrathin 2D MOFs with high aspect ratios offer shortened carrier migration distances, abundant surface reaction sites, tunable band gaps, and enhanced light-harvesting capacity [97, 98]. Their high surface area also facilitates substrate diffusion and integration with co-catalysts [99]. Ding *et al*. synthesized [100] vertically aligned 2D Ni-MOF nanosheet arrays on nickel foam via an in situ solvothermal method, achieving 86. 6% mineralization efficiency in ethyl acetate degradation, which was attributed to abundant active sites, improved light absorption, and efficient mass/electron transfer.

Two primary strategies—top-down and bottom-up—are employed for synthesizing 2D MOF nanosheets. Top-down methods, including ultrasonic, chemical, or mechanical exfoliation, disrupt weak interlayer interactions such as van der Waals forces or hydrogen bonds [101]. In contrast, bottom-up approaches such as template-assisted, solvothermal, or surfactant-mediated synthesis enable direct growth of 2D nanostructures [102, 103]. For example, Zuo *et al*. [104] used a surfactant-stabilized coordination method to prepare ultrathin porphyrin-based MOF nanosheets coordinated with Pt single atoms (thickness: 2. 4±0. 9 nm), which exhibited exceptional photocatalytic activity. It is worth noting that although liquid-phase and chemical exfoliation allow mild-condition synthesis, ultrasound-induced shear forces may introduce surface defects [105]. Bottom-up strategies, by suppressing vertical growth and promoting interfacial expansion, offer greater potential for preparing well-crystallized and highly photoactive 2D MOF nanosheets.

On the other hand, 3D MOF nanoparticles are widely used in photocatalytic membranes due to their tunable pores and open channels, which enhance membrane surface roughness and influence pore structure and filtration performance [88]. The membrane support typically exhibits finger-like and spongy pores, with the latter providing higher mechanical strength to resist compaction during filtration [106]. The incorporation of hydrophilic MOFs notably affects membrane formation. Zhou *et al*. [107] demonstrated that MIL-125(Ti) increased PVDF solution viscosity and slowed solvent-nonsolvent exchange. As the MIL-125(Ti) content increased from 2. 5% to 10%, dense interconnected sponge-like microstructures formed, boosting pure water flux from 2. 3 to 64. 3 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$. However, further increasing the content to 20% induced nonsolvent nucleation during phase inversion, causing interfacial defects.

Notably, MOF addition does not always enhance membrane flux. Wu *et al*. [108] observed that MIL-53(Fe) suppressed macropore formation, increased pore tortuosity, and reduced flux in composite membranes (45 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) compared to pristine membranes (48 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$), although tetracycline rejection reached 87%. Moreover, hydrophilic functional groups impact membrane microstructure: Choe *et al*. [89] reported that increasing the content of $NH_2$-MIL-125 (enriched with $–NH_2$ groups) from 0% to 0. 5% slightly enlarged spongy and finger-like pore sizes in ultrafiltration membranes, elevating flux from 405. 65 to 841. 05 $L \cdot m^{-2} \cdot h^{-1}$.

In summary, precise control over MOF morphology, surface properties, optimal dosage, and hydrophilic functionalization is essential for optimizing the morphological structure of MOF-based photocatalytic membranes.

### 2.6. Other Adjustment Strategies

Mingjie *et al*. demonstrated that porphyrin-based Bi-MOFs, enriched with surface active sites, significantly enhance photocatalytic performance, highlighting how precise surface engineering can tailor MOF properties for targeted pollutant degradation [197]. In a related study, Veetil *et al*. developed mixed matrix membranes incorporating PEG-modified UiO-66 MOF, showing that polymer modification improves membrane compatibility and gas separation efficiency, underscoring the critical role of functionalization in membrane design[201] . Moaness *et al*. investigated GO/MOF composite coatings on alumina nanoporous membranes, achieving enhanced antifouling properties, which addresses a major challenge in membrane longevity and performance through composite engineering [200]. Tursi *et al*. reported that decorating multi-walled carbon nanotubes (MWCNTs) with $TiO^2$as fillers in nanocomposite membranes markedly improved photocatalytic degradation efficiency, exemplifying how biomimetic composite structures can elevate membrane functionality [202]. Additionally, Yutian *et al*. provided an extensive review on engineering MOF-based membranes for gas and liquid separation, emphasizing the importance of pore size

tuning and surface chemistry modification—principles aligned with biomimetic design and composite material engineering—to optimize separation performance [203]. In general, these studies illustrate that integrating functional groups, composite materials, and biomimetic structural designs constitutes a powerful strategy to enhance MOF membranes, advancing their application in efficient separation and photocatalytic processes.

## 3. PREPARATION OF MOF-BASED PHOTOCATALYTIC MEMBRANES

The fabrication of photocatalytic metal-organic framework (MOF) membranes remains a challenging yet critically important area of research, as it directly governs their efficiency and practical application. Long *et al*. emphasized the importance of forming continuous, defect-free films through in situ growth, a process in which MOF crystals are directly synthesized on a substrate, thereby enhancing the structural integrity and photocatalytic performance of the membrane. Conversely, Ejaz *et al*. (2021) highlighted the secondary growth method, which utilizes seed crystals to precisely control membrane thickness and morphology, thereby optimizing light absorption and charge transfer within the MOF layer [90]. Electrochemical deposition, as reviewed by the Membrane Science and Technology Research Group (2019), provides a versatile approach to control MOF nucleation and growth on conductive substrates, improving membrane homogeneity and the distribution of photocatalytic active sites [91]. However, challenges such as particle agglomeration and achieving uniform dispersion persist [92]. Furthermore, Bin *et al*. (2023) demonstrated that enhancing the interfacial compatibility between MOF particles and the polymer matrix is essential for membrane stability and photocatalytic efficiency, particularly under harsh seawater conditions that are prone to fouling and scaling. In summary, these studies collectively suggest that the selection of an appropriate fabrication method—whether in situ growth, secondary growth, or electrochemical deposition—requires a balanced consideration of structural integrity, photocatalytic activity, and operational durability [93]. Resolving these challenges is pivotal to advancing the practical application of photocatalytic MOF membranes for seawater purification. Several common preparation methods will now be discussed.

### 3.1. Selection and Challenges of Substrate Materials

Conventional powdered MOFs alone are increasingly inadequate to meet the demands of advanced applications, whereas MOF membranes have effectively filled this gap. Since Hermes *et al*. [110] first successfully synthesized MOF films with innovative structures on solid substrates, such membranes have progressively expanded the application scope of MOFs. For instance, MOF films have been used in photocatalytic dye degradation with stable performance [111], and Zhao *et al*. [112] fabricated MOF-based films via electrodeposition that achieved efficient photocatalytic hydrogen production and good reusability. In addition, a range of mixed-matrix MOF membranes have been widely applied in various wastewater treatment scenarios [113, 107]. Nevertheless, the removal efficiency of MOF-based photocatalytic membranes for aquatic pollutants remains a major challenge. More suitable preparation methods are needed to improve the

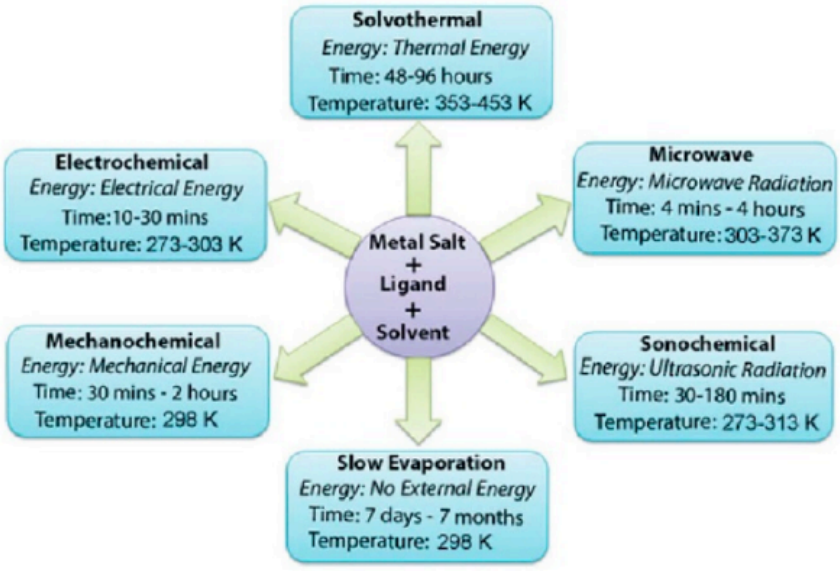


**Figure 7:** Commonly used methods and synthesis conditions for MOF preparation (from [109]).

compatibility between membrane materials and MOF photocatalysts and achieve efficient and stable performance in water treatment.

The choice of membrane substrate is critical in the design of MOF-based photocatalytic membranes. Organic polymers and inorganic ceramics are the two main types of substrates used. Polymer membranes are widely adopted due to their low cost and ease of processing, but they often exhibit limited stability under photocatalytic conditions, especially against ROS attack and harsh reaction environments. Among them, polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF), which contain high dissociation energy C–F bonds, demonstrate notable photostability [114]. In a comparative study by Raota *et al*. [115], $TiO_2$-PVDF, $TiO_2$-polyethersulphone (PES), and porphyrin-PVDF membranes were subjected to intense UV irradiation (2223 W $m^{-2}$) and methylene blue degradation. After 250 hours of UV aging, $TiO_2$-PVDF maintained its initial removal efficiency, whereas the photocatalytic activity of $TiO_2$-PES and porphyrin-PVFF declined significantly, indicating the superior stability of PVDF substrates and inorganic catalysts. It should be noted, however, that fluorinated polymers may pose environmental risks and require careful consideration before use as membrane substrates [116].

In contrast, inorganic ceramic membranes exhibit excellent physicochemical stability, mechanical strength, and fouling resistance, which contribute to their enhanced durability during photocatalytic reactions and membrane cleaning. Their high specific surface area and porous structure also provide abundant active sites for photocatalyst immobilization, making them more suitable for MOF-based photocatalytic applications. However, the high preparation cost has historically restricted their widespread use. In recent years, the use of low-cost natural materials such as kaolin, diabase, and dolomite has significantly reduced the cost of ceramic membranes [117]. Combined with low operating expenses and long service life, the lifecycle cost of ceramic membranes has become competitive with that of polymer membranes [118]. Future efforts should focus on synergistic development of low-cost ceramic substrates and novel MOF photocatalytic membranes to advance the performance and applicability of these composite materials.

### 3.2. Crystallization Growth Methods

The crystallization growth method, encompassing in-situ and secondary growth, offers a straightforward approach for fabricating MOF-based photocatalytic membranes by promoting nucleation and crystallization on substrate surfaces. In-situ growth involves immersing the substrate directly into a reaction solution containing metal ions and organic ligands, facilitating MOF membrane formation through nucleation [119]. This method maximizes MOF exposure and enhances light utilization, as seen in Qian *et al*. 's work where UiO-66-NH2 nanoparticles were grown on carbon fiber cloth (CFC) via solvothermal treatment [120]. However, challenges such as weak bonding between the MOF layer and substrate often lead to agglomeration and detachment, compromising uniformity and stability. To address this, chemical modification of the substrate—for instance, using polydopamine (PDA) as an adhesive layer—can introduce abundant nucleation sites and strengthen interactions, as demonstrated by Li *et al*. in the growth of ZIF-67 on polypropylene membranes [121]. Alternatively, secondary growth separates nucleation and crystal growth into distinct steps: seed crystals are first deposited on the substrate to form a nucleation layer, followed by immersion in an MOF reaction solution for controlled crystallization [122]. This approach, exemplified by Du *et al*. in preparing UiO-66-NH2(Zr/Hf) membranes on α-Al2O3 supports, improves nucleation efficiency, reduces defects, and enhances membrane quality and longevity [113]. Other studies, such as Wang *et al*. 's fabrication of MAF-4/MAF-7 on PES membranes[123], Zhu *et al*. 's development of hydrophilic SSM/UiO-66-NH2/CMn meshes [124], and Lee *et al*. 's growth of MIL-100(Fe) on PAN nanofibers [125], further illustrate the versatility of in-situ growth. Despite its directness and effectiveness, in-situ growth faces scalability issues due to slow kinetics and demanding synthesis conditions, whereas secondary growth provides superior control over microstructure and adhesion. Overall, while crystallization growth methods are widely applicable, they typically involve time-consuming processes, necessitating optimizations like substrate modifications to balance simplicity and performance in photocatalytic applications [126-128].

### 3.3. Electrochemical Method

Compared with other methods, electrochemical synthesis can be performed at room temperature with low energy consumption, short reaction time, and simple equipment, making it a green synthesis approach [129]. This method primarily includes anodic and cathodic synthesis [130]. In anodic precipitation, a positive voltage is applied to dissolve the anode metal electrochemically, and the released metal ions react with organic ligands in the electrolyte to form MOF membranes on the anode [131]. However, the preparation of MOF membranes containing high-valent metal cations often requires elevated reaction temperatures. To address this, a novel high-temperature and high-pressure electrochemical

cell was developed, enabling the effective synthesis of such MOFs in an environmentally friendly and non-corrosive solution [132]. For cathodic deposition, metal salts are typically added to the electrolyte as the metal source, but this may introduce impurities or hinder MOF film formation. A proposed solution involves using hydrogen peroxide, which is reduced to superoxide ions during the reaction, deprotonating the organic ligands and effectively suppressing metal hydroxide co-precipitation, thereby yielding high-purity MOF membranes [133]. Moreover, since conventional electrochemical methods often employ organic solvents that cause environmental concern, researchers have developed a cathodic precipitation method using water as the sole solvent. This approach requires no supporting electrolyte and can produce a ZIF-8 membrane with low defect density within one hour, presenting a simple and pollution-free route [134]. The fundamental distinction between the two methods lies in the metal ion source: in cathodic synthesis, metal ions are supplied from salts in the electrolyte rather than from electrode dissolution. Meanwhile, the $OH^-$ generated at the cathode deprotonates the ligands, facilitating their self-assembly with metal ions on the electrode surface to form MOFs. Typically, anodically deposited membranes form more readily on substrates, while cathodically deposited ones favor electrode surfaces [135]. In principle, electrochemical synthesis utilizes anodic dissolution via oxidation or cathodic deposition through base generation to produce metal ions, which then coordinate with organic ligands in the electrolyte. This strategy allows for the direct use of metal substrates instead of metal salts and minimizes anionic impurities in the final product [136]. For instance, Cai *et al*. employed cathodic electrodeposition to synthesize dandelion-like bimetallic Bi/Mo-MOFs (Figure **3e**). By immersing two graphene plate anodes and a Ni foam cathode into an aqueous electrolyte containing trimesic acid (BTC), $Bi(NO_3)_3$, a Mo source (*e. g.* , $MoO_4^{2-}$ or its precursor), and $NaNO_3$, they successfully deposited MOFs on the Ni foam at room temperature by applying a current density of 20 mA $cm^{-2}$ for 10 minutes [137].

### 3.4. Vacuum Filtration

Vacuum filtration, also referred to as vacuum-assisted self-assembly, is a predominant and widely adopted technique for fabricating metal-organic framework (MOF)-based photocatalytic membranes, owing to its operational convenience and reliability. This method employs a vacuum force to drive a solution containing MOFs and other materials through a porous substrate, leading to the deposition of MOFs onto the membrane surface and thereby endowing it with photocatalytic functionality. For instance, Zhou *et al*. [138] utilized cross-linking agents such as polyvinyl alcohol (PVA) and glutaraldehyde (GA) to prepare stable CuTz-1/graphene oxide (GO) composite membranes for dye/salt separation and anti-fouling applications, while Wang *et al*. [139] successfully constructed a two-dimensional heterostructured MOF-2/g-$C_3N_4$ membrane via vacuum-assisted assembly. However, the relatively weak hydrogen bonding between the nano-coating and the substrate can lead to particle exfoliation, making it necessary to incorporate cross-linkers like PVA, GA, or polyacrylic acid (PAA) to enhance the interfacial adhesion and stability. Zhu *et al*. [140] modified $NH_2$-MIL-125 with PAA to fabricate an efficient oil-water separation membrane, in which the cross-linking promoted uniform nanoparticle distribution and maintained a separation efficiency of 99% even after 10 testing cycles. Similarly, Gao *et al*. [141] developed PAA@NM88B/GO composites, where the carboxyl groups in PAA formed hydrogen bonds and electrostatic interactions with the amino groups in $NH_2$-MIL-88B (NM88B), significantly improving membrane stability. Furthermore, vacuum filtration can be employed to create MOF-based intermediate layers for thin-film nanocomposite (TFN) membranes. As examples, Zhao *et al*. and Xu *et al*. [142, 143] incorporated Zr-porphyrin MOFs or Zn-TCPP laminates via interfacial polymerization, producing TFN membranes that exhibited enhanced water permeability, excellent photocatalytic self-cleaning capability, and stable rejection performance. Despite its simplicity and the facile control it offers over the loading amount of MOF photocatalysts, excessive nanoparticle loading may cause pore blockage and reduced water flux. More critically, the adhesion of the MOF layer to the substrate prepared by vacuum filtration is often inadequate, posing a risk of coating detachment and consequently compromising the long-term stability of the membranes. Thus, introducing 2D MOF nanosheets, additional 2D materials, or cross-linking agents during the preparation process is a recommended strategy to reinforce the interactions among the structural components within the membrane.

### 3.5. Microwave-Assisted Synthesis

Microwave-assisted synthesis employs microwave radiation (300 MHz to 300 GHz) as an energy source, a method prevalent in organic chemistry but also extensively adopted for the rapid preparation of nanoporous materials like metal-organic frameworks (MOFs). This technique offers benefits such as accelerated crystallization, phase selectivity [145], narrow particle size distribution, and morphological control, along with energy-efficient production of

multidimensional MOFs[146][147]. However, it may induce atomic disorientation, potentially leading to crystal defects or lattice alterations. Numerous MOFs incorporating $Fe^{3+}$, $Al^{3+}$, $Cr^{3+}$, $V^{3+}$, and $Ce^{3+}$ have been synthesized via this approach; for example, Cr-MIL-100 was the first MOF produced using microwave methods [148]. Typically, MOF formation under microwave irradiation occurs at temperatures above 100°C, but the process proceeds more rapidly than with conventional heating. Noteworthy cases include IRMOF-1, which exhibits superior crystal quality and enhanced $CO_2$ adsorption when synthesized via the microwave-assisted route , and HKUST-1, obtained with high purity and a substantial microporous volume of 0. 79 $cm^3\ g^{-1}$ in just 30 minutes [149, 150]. Additionally, Vakili *et al*. fabricated well-defined octahedral UiO-67 crystals by optimizing modulators like HCl and benzoic acid in microwave-assisted synthesis, which boosted specific surface area and pore volume through enhanced linker deficiency and nucleation, reducing synthesis time to under 2. 5 hours while improving morphological control [151].

### 3.6. Sonochemical Method and Mechanochemical Methods

The sonochemical route is a rapid and eco-friendly method for synthesizing metal-organic frameworks (MOFs) by employing high-frequency sound waves (20 kHz–10 MHz). This technique utilizes acoustic cavitation to generate localized high-energy zones, promoting homogeneous nucleation and accelerated crystallization. As a result, it significantly reduces crystallization time and yields much smaller particles compared to conventional solvothermal methods. Cavitation—the formation, growth, and collapse of bubbles under alternating pressure—creates extreme local conditions (≈5000 K and ≈1000 bar), providing the necessary energy for reactions[152]. In solid-liquid systems, cavitation-induced microjets clean, erode, or activate surfaces while dispersing agglomerated particles, enabling phase and crystal size selectivity along with improved crystallization rate and product yield. For instance, Qiu *et al*. first reported the sonochemical synthesis of $[Zn_3(BTC)_2]$ in ethanol, which exhibits selective sensing toward organoamines [153]. Similarly, Guo *et al*. synthesized ZIF-67 via ultrasonication in anhydrous methanol, noting that using water instead led to boat-shaped Co-MOF sheets [154]. It is also observed that reaction time influences particle size, though prolonged sonication time may cause partial crystal decomposition, as demonstrated in HKUST-1 synthesis [155]. Mechanochemical synthesis utilizes mechanical energy to break intramolecular bonds and facilitate chemical transformation reactions, typically employing techniques such as solvent-free grinding, liquid-assisted grinding (LAG), and ion-liquid-assisted grinding (ILAG) for MOF preparation [156]. This method can be conducted at room temperature under solvent-free conditions, avoiding organic solvents and achieving quantitative yields of small MOF particles within short reaction times, generally ranging from 10 to 60 minutes [157]. Metal oxides are often preferred over metal salts as starting materials since water is the only byproduct. However, shape-controlled synthesis remains challenging, and the approach is limited to specific MOF types. To optimize morphology and porosity, Chen *et al*. adjusted the ball milling time (1–5 min at 40 Hz), enhancing the crystallinity of pillar-layered $Zn_2(5\text{-aip})_2(bpy)$ MOFs, as evidenced by smoother surfaces in SEM images and better-defined XRD peaks [158]. The critical role of moisture in synthesizing pillared MOFs was recently highlighted by the Kitagawa group [159]. The addition of small solvent amounts in LAG increases reactant mobility at the molecular level, accelerating reactions and serving as a structure-directing agent, while ILAG has proven highly effective for selectively constructing pillared-layered MOFs [160-162]. For instance, solvent-free mechanochemical synthesis of HKUST-1 yielded a BET surface area of 1, 084 $m^2/g$, which increased to 1, 364 $m^2/g$ with LAG (100 μL MeOH), accompanied by sharper X-ray powder diffraction (XRPD) patterns[168]. In ZIF synthesis, ILAG accelerates formation and directs phase selection; *e.g*., ZIF-8 formed within 30 min using ZnO and HMeIm with $NH_4NO_3$, while grinding duration and additive type influenced topological evolution (*e. g*. , rho-ana-qtz sequence) [161].

### 3.7. New Progress in Prepartion Technology

Recent advancements in the fabrication of MOF-based membranes have focused on enhancing uniformity, stability, and photocatalytic efficiency to meet the demands of seawater purification. Feng *et al*. proposed a facile method involving the direct seeding of MOF-polymer hybrid nanoparticles, enabling the formation of defect-free membranes with improved mechanical robustness and photocatalytic activity [162]. This technique effectively overcomes adhesion issues between MOF crystals and polymer substrates, which often undermine membrane durability. Complementing this, Cheng *et al*. provided a comprehensive review of fabrication strategies, highlighting the critical role of controlled nucleation and growth in tuning membrane porosity and thickness. Such control optimizes light penetration and accessibility of active sites, thereby enhancing photocatalytic performance [163]. Carmen *et al*. further demonstrated the integration of

photocatalytic $TiO_2$ components within tubular membranes, significantly boosting the degradation efficiency of organic pollutants under light irradiation [164]. Expanding material horizons, Yue *et al*. explored covalent organic frameworks (COFs) as promising alternatives to MOFs, showcasing their effective photocatalytic activity in both freshwater and seawater environments, which opens new pathways for membrane material innovation [165]. Additionally, Jigar *et al*. investigated PVDF membranes embedded with inorganic nanoparticles, emphasizing that uniform nanoparticle dispersion and optimized membrane morphology are crucial for achieving superior photocatalytic wastewater treatment [166]. Collectively, these studies underscore that precise control over synthesis parameters—including material composition, structural integrity, and morphology—is essential to maximize the photocatalytic efficiency and long-term stability of MOF-based membranes in seawater purification applications.

## 4. APPLICATION OF PHOTOCATALYTIC MOF MEMBRANES IN WATER TREATMENT

In recent years, photocatalytic metal-organic framework (MOF) membranes have garnered significant attention for applications in water treatment. Their effectiveness stems from the generation of redox-active species, such as electrons ($e^-$), holes ($h^+$), superoxide radicals ($\bullet O_2^-$), and hydroxyl radicals (•OH) [170] , coupled with their inherent ability to reject pollutants via size exclusion. As a result, MOF-based photocatalytic membranes demonstrate robust removal capabilities for various wastewater contaminants, including organic pollutants, heavy metal ions, and pathogenic bacteria. Strategies like ligand functionalization, heterostructure construction, morphology control, and metal ion doping can further enhance the photocatalytic performance of MOFs, thereby improving their water purification efficiency. This section provides a concise summary and discussion of recent advances in the photocatalytic removal of harmful substances (*e. g.* , organic pollutants, heavy metal ions, and pathogens) using MOF-based photocatalysts under visible light irradiation.

### 4.1. Removal of Organic Pollutants

Recent progress in photocatalytic MOF membranes highlights their considerable potential for water purification, particularly in removing organic contaminants. Persistent organic pollutants in water bodies, such as dyes, pharmaceuticals and personal care products (PPCPs), and bisphenol A (BPA), continue to pose challenges for water treatment. Although various methods exist, achieving efficient removal remains a critical issue in public health [171]. The growing dye industry generates substantial dye wastewater from printing, pharmaceuticals, and cosmetics. Li *et al*. fabricated a ternary MOF-based composite catalyst, PCN-222-$PW_{12}/TiO_2$, by integrating $TiO_2$ and the Brønsted acid $H_3PW_{12}O_{40}$ with the Mn-based MOF PCN-222 via a solvothermal method. In subsequent visible-light degradation experiments with Rhodamine B (RhB), the composite containing 5% PCN-222 exhibited the highest photocatalytic activity, achieving a 98. 5% degradation rate. The primary

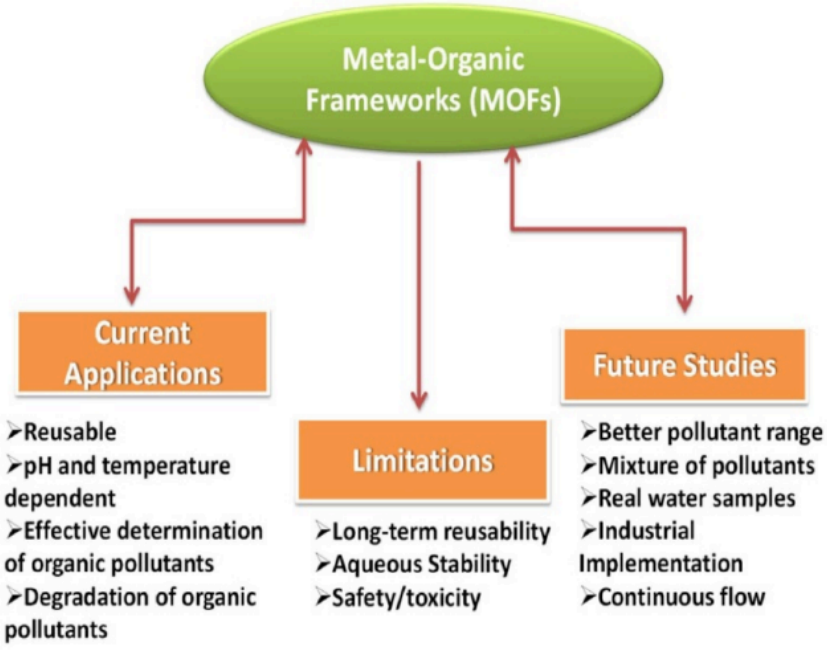


**Figure 8:** The present and future of MOF (from [6]).

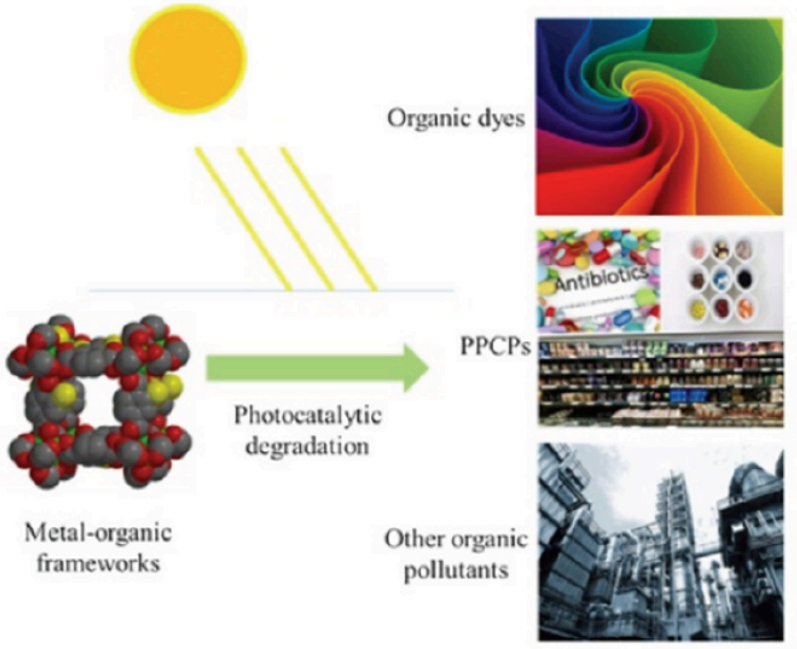


**Figure 9:** Application of MOFs-based photocatalyst for degradation of organic. Pollutants (from [168]).

reactive species responsible for organic dye degradation were identified as $H^+$, $\bullet O_2^-$, and •OH, offering valuable insights for MOF applications under visible light [58].

PPCPs, an emerging class of aquatic contaminants of increasing concern, include antibiotics, anti-inflammatory drugs, and sunscreen agents. Their continuous environmental release, resistance to complete removal by conventional wastewater treatment processes (*e. g.* , activated sludge), and potential ecotoxicity classify them as typical "pseudo-persistent" pollutants. They may promote the spread of antibiotic resistance genes, threatening ecosystems and human health [172].

Among PPCPs, antibiotics are a major focus of photocatalytic degradation research. Askari *et al*. prepared a ZIF-67-based ternary heterojunction photocatalyst, $CuWO_4/Bi_2S_3$/ZIF-67, via a hydrothermal method. They systematically investigated its performance in degrading cephalexin and metronidazole in a continuous-flow system, optimizing reaction parameters using central composite design. Under optimal conditions, degradation rates reached 90. 1% and 95. 6% for the two antibiotics under visible light, with total organic carbon (TOC) removal rates of 74% and 83. 2%, respectively. This material's reaction rate was 9 and 4 times higher than those of pure $Bi_2S_3$ and the binary $CuWO_4/Bi_2S_3$, respectively. This enhancement was primarily attributed to the high specific surface area and improved photogenerated charge carrier separation efficiency resulting from the double Z-scheme heterojunction [173].

In another study, Lv *et al*. synthesized a benzothiazole-functionalized Co-doped $NH_2$-MIL-53(Fe) material (Co-MIL-53-$NH_2$-BT) via a stepwise assembly strategy. This catalyst achieved 99. 8% degradation of ofloxacin within 120 minutes under visible light, primarily due to the effective promotion of electron-hole pair separation and migration by the electron-deficient benzothiazole unit. TOC analysis and six consecutive cycling tests confirmed both efficient pollutant mineralization (to $CO_2$ and $H_2O$) and excellent stability (degradation rate maintained above 90%) [174].

Additionally, Tang *et al*. successfully prepared a $TiO_2$@MIL-101(Cr) photocatalyst by compositing $TiO_2$ with MIL-101(Cr) using a solvothermal method. Characterization confirmed that incorporating $TiO_2$ effectively facilitated electron-hole pair separation and reduced the band gap. After 240 minutes of UV irradiation, the composite achieved 99. 4% BPA degradation, significantly outperforming single-component catalysts [175].

### 4.2. Degradation of Viruses and Bacteria

Significant research progress has been made recently in using MOF-based photocatalytic composites to inactivate bacteria and viruses. The general mechanism involves reactive oxygen species (ROS) generated by the composites attacking microorganisms, leading to their inactivation. The specific inactivation mechanisms can be summarized as follows: (1) ROS attack coenzyme A on the cell membrane, inhibiting respiratory activity and causing

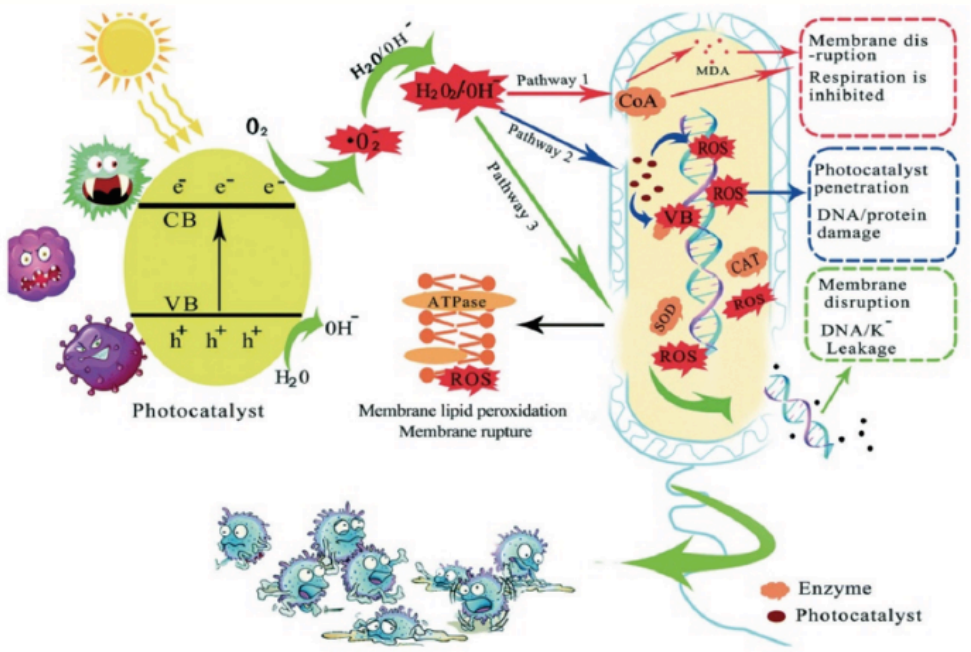


**Figure 10:** Photocatalytic antibacterial mechanism (from [176]).

cell death; (2) ROS compromise the cell membrane, increasing its permeability, allowing ROS to enter the cell and oxidize vital macromolecules like nucleic acids and proteins, ultimately leading to cell death; (3) ROS oxidize the cell membrane, disrupting the cell wall and membrane integrity, resulting in the leakage of intracellular macromolecules and cations (*e. g.* , $K^+$), and consequently, cell death [176] Figure **10**.

Waterborne pathogens pose a serious threat to human health, necessitating the development of rapid and efficient disinfection technologies. Visible-light-driven photocatalysis, as an emerging and advanced approach, shows great promise for bacterial inactivation due to its cost-effectiveness and environmental compatibility [177, 178]. For example, Liang *et al*. developed $MnO_2$/ZIF-8 nanorods that inactivated E. coli under visible light via generation of $h^+$, $\bullet O_2^-$, and •OH [179]. Our previous work utilized a MIL-88B@COF-200@10%PANI ternary composite for efficient inactivation of E. coli and S. aureus, with SEM images confirming damage to bacterial surface structures [180]. Liu *et al*. reported the antibacterial activity of porphyrin-based Zr-MOFs through photodynamic ROS generation [181]. However, research on the bactericidal properties of MOF-based photocatalysts is still nascent; their mechanisms are not fully understood, and the separation of catalysts from bacteria post-treatment remains a significant challenge.

In municipal wastewater treatment, domestic wastewater typically contains substantial suspended solids, soluble organic matter (measured as BOD/COD), and microbial pollutants [182] . Photocatalysis is widely applied here for organic pollutant degradation and pathogen inactivation. Sacco *et al*. used immobilized N-doped $TiO_2$ to achieve approximately 85% organic pollutant degradation and 93% E. coli inactivation under visible light [183]. Lydakis-Simantiris *et al*. employed P25 $TiO_2$ to disinfect secondary effluent, achieving 97% and 89% inactivation of coliforms and enterococci, respectively [184]. Furthermore, Szymański *et al*. combined photocatalysis with ultrafiltration in a UV/$H_2O_2$ system, attaining 65% TOC removal and 65% $TiO_2$ recovery, though residual $H_2O_2$ and by-products could increase effluent ecotoxicity [185]. Pidou *et al*. emphasized that the efficiency of coupled photocatalytic-membrane systems heavily relies on optimal UV light utilization by $TiO_2$, necessitating reactor design optimization for enhanced performance[186].

Beyond water treatment, MOF-based photocatalysis has been explored for air purification. LiPing *et al*. identified ZIF-8 (a zinc-imidazolate MOF, Zeolitic Imidazolate Framework-8) as the most effective bactericide among five water-stable MOFs. They further developed it into a "MOFilter", which demonstrated excellent performance for comprehensive air pollution control and personal protection. This filter medium achieved 97% particulate matter (PM) capture efficiency at 0. 7 m $s^{-1}$ and 99. 99% bactericidal efficiency via photo-induced contact killing within 30 minutes. This study underscores the potential of MOFs in environmental photocatalysis and

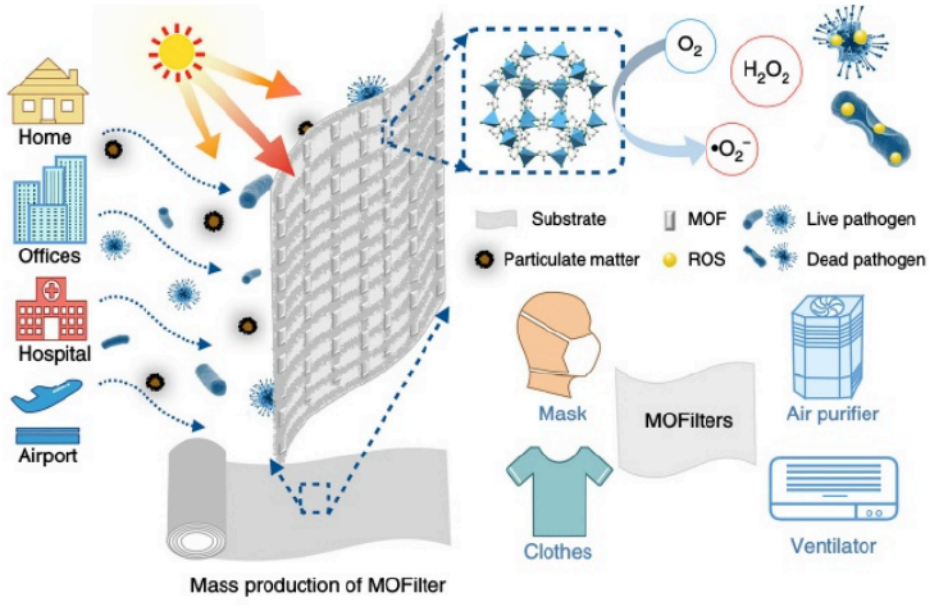


**Figure 11:** Schematic of metal-organic framework (MOF)-based filter. Schematic representation of MOF-based filter (MOFilter) for integrated air cleaning. From [187].

may inspire the design of novel porous photo-biocidal materials [187].

### 4.3. Photocatalytic Reduction of Metal Ions

Heavy metal pollution in aquatic systems is a major global environmental concern. Photocatalysis using MOFs has emerged as a promising strategy for heavy metal reduction, as it can facilitate the complete degradation of pollutants through redox reactions driven by photogenerated charge carriers. This approach utilizes solar energy to convert heavy metal pollutants into less toxic forms, offering a sustainable and effective solution. In photocatalytic metal ion

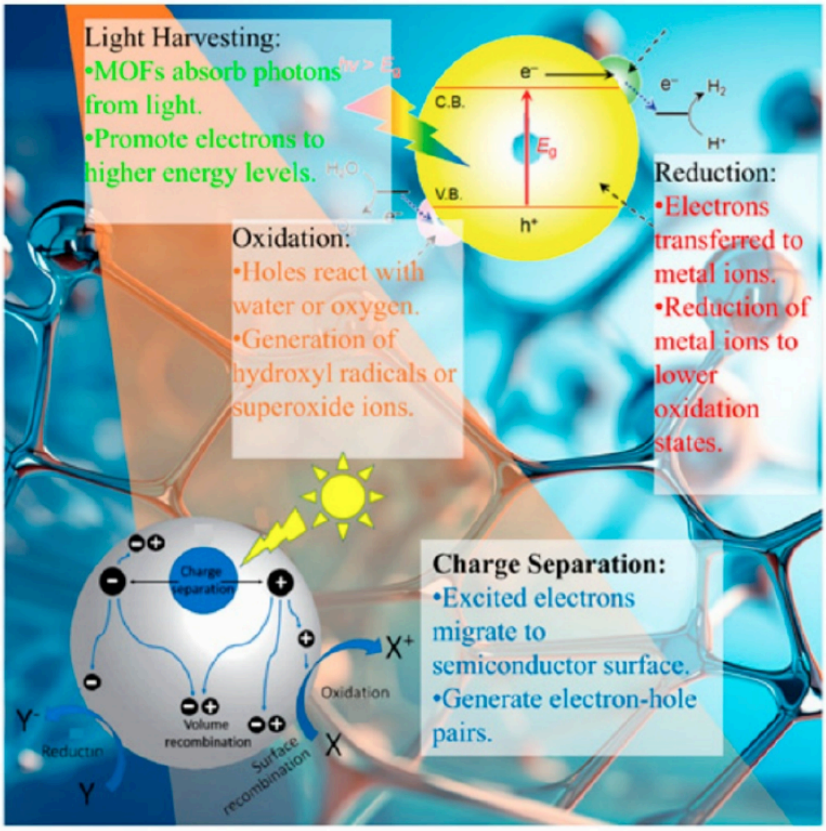


**Figure 12:** Mechanisms involved in the MOF-based photocatalytic removal of heavy metals. (from [31]).

reduction, species like $Au^{3+}$, $Hg^{2+}$, $Pb^{2+}$, $Ag^{+}$, $Cu^{2+}$, and $Cu^{+}$ are readily reduced to their zero-valent metallic states, while $Cr^{6+}$ and $Fe^{3+}$ are typically converted to $Cr^{3+}$ and $Fe^{2+}$, respectively. In contrast, ions like $Cr^{3+}$, $Fe^{2+}$, $Cd^{2+}$, $Ni^{2+}$, and $Mn^{2+}$ are difficult to reduce photocatalytically due to their highly negative reduction potentials [188]. A brief table of MOFs remove heavy metal mechanisms by means of photocatalytic processes, as shown in Figure **12**.

Toxic heavy metals are prevalent aquatic pollutants, largely due to their extensive industrial use. Chromium, widely employed in alloy production and tanning, is a prime example, constituting a major heavy metal contaminant. Hexavalent chromium (Cr(VI)) is of particular concern due to its higher solubility and toxicity compared to Cr(III), leading to mutagenic and carcinogenic effects [189]. Consequently, research has intensely focused on reducing highly toxic Cr(VI) [190] . For instance, Zhou *et al*. developed a Z-scheme UiO-66-$NH_2$/$Ag_2CO_3$ heterostructure whose conduction band position (–1. 09 eV vs. NHE) is favorable for reducing $Cr^{6+}$/$Cr^{3+}$ (+1. 05 eV vs. NHE), achieving over 99% Cr(VI) reduction efficiency[190] . Zhao *et al*. constructed a pillared-layer MOF (NNU-36) that also exhibited excellent visible-light Cr(VI) reduction performance due to its suitable band structure [192]. Strategies like decorating with metal nanoparticles (*e. g*. , Pt@MIL-100) or constructing heterojunctions (*e. g*. , g-$C_3N_4$/MIL-53(Fe), rGO/UiO-66-$NH_2$) have been employed to enhance charge separation and migration, thereby boosting photocatalytic efficiency [193-195].

Notably, MOF-based photocatalytic membranes also show great promise for heavy metal remediation. Du *et al*. developed UiO-66-$NH_2$(Zr/Hf) membranes that achieved over 94% Cr(VI) reduction under natural sunlight with excellent cycling stability [196]. Ji *et al*. synthesized a nylon-6@UiO-66-$NH_2$ fiber membrane that adsorbed Cr(VI) via strong electrostatic and chelating interactions, exhibiting a photocatalytic capacity of 27. 1 $mg \cdot g^{-1}$, far exceeding that of pure MOF powder [127]. Furthermore, functionalized MOF membranes (*e. g*. , thiol-modified Zn-MOF) can selectively reduce $Cr_2O_7^{2-}$ or adsorb anions like $MnO_4^{-}$, broadening their application in treating complex heavy metal pollution[190].

Despite notable achievements in Cr(VI) reduction using MOFs, research on the photocatalytic reduction of other heavy metal ions remains relatively limited. Future work should expand the scope of reducible targets through bandgap engineering and structural design, while also addressing the challenge of separating spent MOFs from metal products to facilitate practical application.

## 5. PROBLEMS AND RESEARCH DIRECTIONS IN PRACTICE

### 5.1. Anti-fouling Properties of Photocatalytic MOF Systems

In conventional membrane separation processes, various foulants—including particulate matter, organic contaminants, and microorganisms—are adsorbed and accumulate on the membrane surface or within its pores during mass transfer. This accumulation results in a significant decline in both permeate flux and membrane service life [197]. Membrane fouling can be categorized into reversible and irreversible types. Reversible fouling generally results from cake layer formation or concentration polarization on the membrane surface and can usually be mitigated through physical cleaning. In contrast, irreversible fouling involves the chemical adsorption of contaminants onto the membrane pores or surface, necessitating chemical cleaning for regeneration. Conventional cleaning protocols, which rely on physical and chemical methods, are often energy- and cost-intensive. In this context, photocatalytic technology, recognized for its environmental friendliness and cost-effectiveness, has emerged as a promising approach for mitigating membrane fouling. Studies have also indicated that incorporating MOF nanoparticles into functionalized membranes can effectively enhance their antifouling and self-cleaning properties [198].

Similarly, improving photocatalytic efficiency is beneficial to self-cleaning performance. The photocatalytic efficiency of metal–organic frameworks (MOFs) fundamentally depends on their ability to absorb light and effectively separate photogenerated charge carriers. Assadi highlighted the development of luminescent textiles embedded with photocatalytic materials, which exhibit enhanced light absorption—offering valuable insights for the design of MOF-based systems intended for real-world water purification [209]. Building on this, Jie *et al*. emphasized the importance of interfacial engineering in hybrid membranes. They demonstrated that integrating layered double hydroxides with PVDF-based super-wetting catalytic membranes promotes efficient charge separation through the formation of heterojunctions that suppress electron–hole recombination [210]. Such a charge separation mechanism is also crucial in MOFs, where the deliberate spatial arrangement of metal nodes and organic linkers can be tailored to optimize the separation of photogenerated electrons and holes, thereby enhancing the generation of reactive species.

Song *et al*. reviewed recent advances in solar-driven desalination and highlighted that the photophysical properties of composite materials—including MOFs—play a key role in maximizing light harvesting and facilitating the charge carrier dynamics necessary for driving photocatalytic reactions [211]. Furthermore, Muhammad *et al*. investigated the thermal stability of graphene nanoplatelet–MOF membranes, noting that maintaining structural integrity at elevated temperatures is essential for sustaining effective charge separation and prolonged photocatalytic activity in practical applications [212]. These studies collectively suggest that enhancing the light absorption and charge separation in MOFs requires an integrated strategy encompassing material composition, interfacial design, and operational stability—key factors for advancing photocatalytic technologies in seawater purification.

In addition, the antifouling performance of a membrane is largely governed by its surface characteristics, including hydrophilicity and surface roughness. The incorporation of hydrophilic MOFs into composite membranes introduces numerous hydrophilic sites on the surface. This reduction in foulant-membrane interaction facilitates the permeation of water molecules. A representative example is the reduction of the water contact angle from around 67° for unmodified polysulfone (PSF) membranes to only 34° for $NH_2$-MIL-101(Fe) MOF-integrated membranes, indicating significantly improved hydrophilicity [207]. Consequently, the resulting MOF-composite membranes exhibit excellent antifouling performance, achieving a flux recovery rate as high as 97%.

### 5.2. Performance Indicators and Limitations under Actual Conditions

Recent research endeavors have delved deeply into understanding the practical implications and inherent constraints of photocatalytic Metal-Organic Framework (MOF) membranes in real-world applications. A key area of focus has been their resilience under various operational challenges, including hydrothermal stability, photochemical durability, and mechanical robustness. Jie *et al*., in their 2023 study, illuminated a compelling aspect: two-dimensional Zn-MOF-NH/Cu heterojunctions exhibit exceptional photocatalytic activity. However, they found that prolonged exposure to hydrothermal conditions gradually weakened the structural integrity of these membranes, leading to a decline in their efficiency over time. This highlights a significant hurdle in maintaining the effectiveness of such membranes in long-term applications [213] . In a parallel study conducted by He *et al*. in 2024, another challenge emerged. Membranes integrated with molecular gatekeepers for selective gas separation showed promise in seawater purification systems but suffered from photochemical degradation when continuously exposed to light irradiation. This susceptibility poses a considerable barrier to their sustained deployment in real-world scenarios [214]. Guo *et al*. , in their 2024 research, demonstrated that embedding ZIF-8@CsPbBr nanocrystals within bimetallic MOFs significantly enhanced the

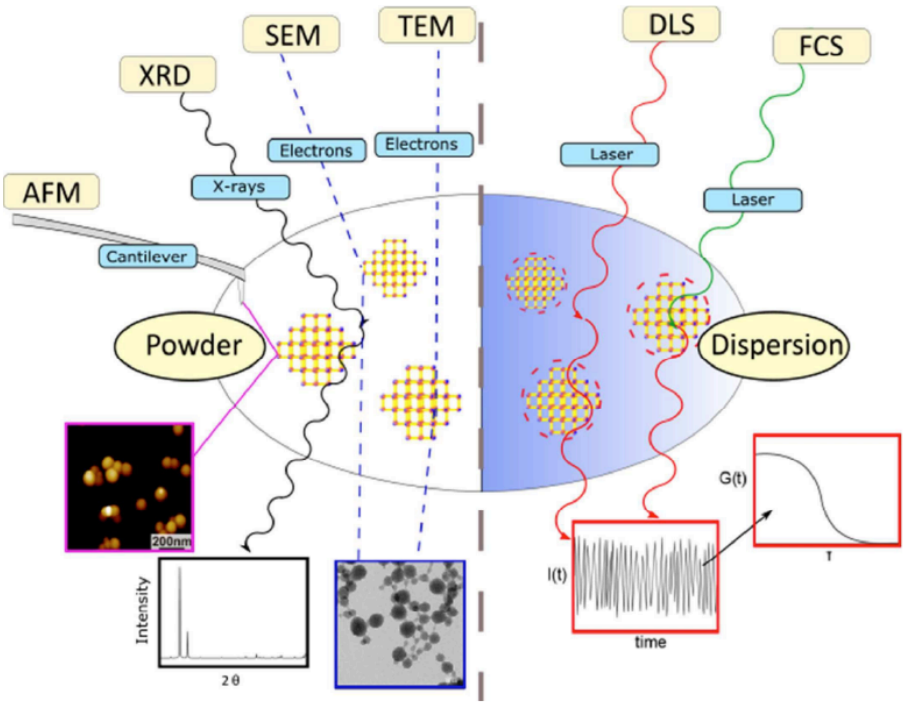


**Figure 13:** Overview of the characterization methods of mof (from [223]).

photocatalytic reduction of CO. Despite this impressive performance boost, these composite membranes fell short in mechanical strength, making them susceptible to damage under dynamic operational stresses [215]. Adding to this body of knowledge, YongLi *et al*. investigated the impact of ligand defects in Ni-MOF-74 on photocatalytic efficiency. They identified that these defects acted as active sites, improving efficiency. Unfortunately, they also served as points of initiation for structural degradation, undermining membrane durability in harsh aqueous environments [216]. Collectively, these findings underscore the delicate balance required between optimizing photocatalytic performance and ensuring material stability and mechanical resilience. Addressing these multifaceted challenges is imperative for advancing the practical application of MOF-based photocatalytic membranes. By doing so, we can pave the way for more sustainable and efficient seawater treatment processes, ultimately contributing to broader environmental and industrial advancements.

### 5.3. Research Methods for Evaluating Membrane Morphology and Photocatalytic Activity

Evaluating membrane morphology and photocatalytic activity is a essential step before optimizing the performance of photocatalytic MOF membranes in seawater purification. Huang *et al*. demonstrated that advanced imaging techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are indispensable for revealing the microstructural features and nanoparticle distribution within MOF-derived composite membranes, which directly impact photocatalytic efficiency [222]. Taking zirconium-fumarate (Zr-fum) MOF nanoparticles as an example, a suite of characterization techniques was employed, Figure **13** including X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and dispersion-based methods such as dynamic light scattering (DLS) and fluorescence

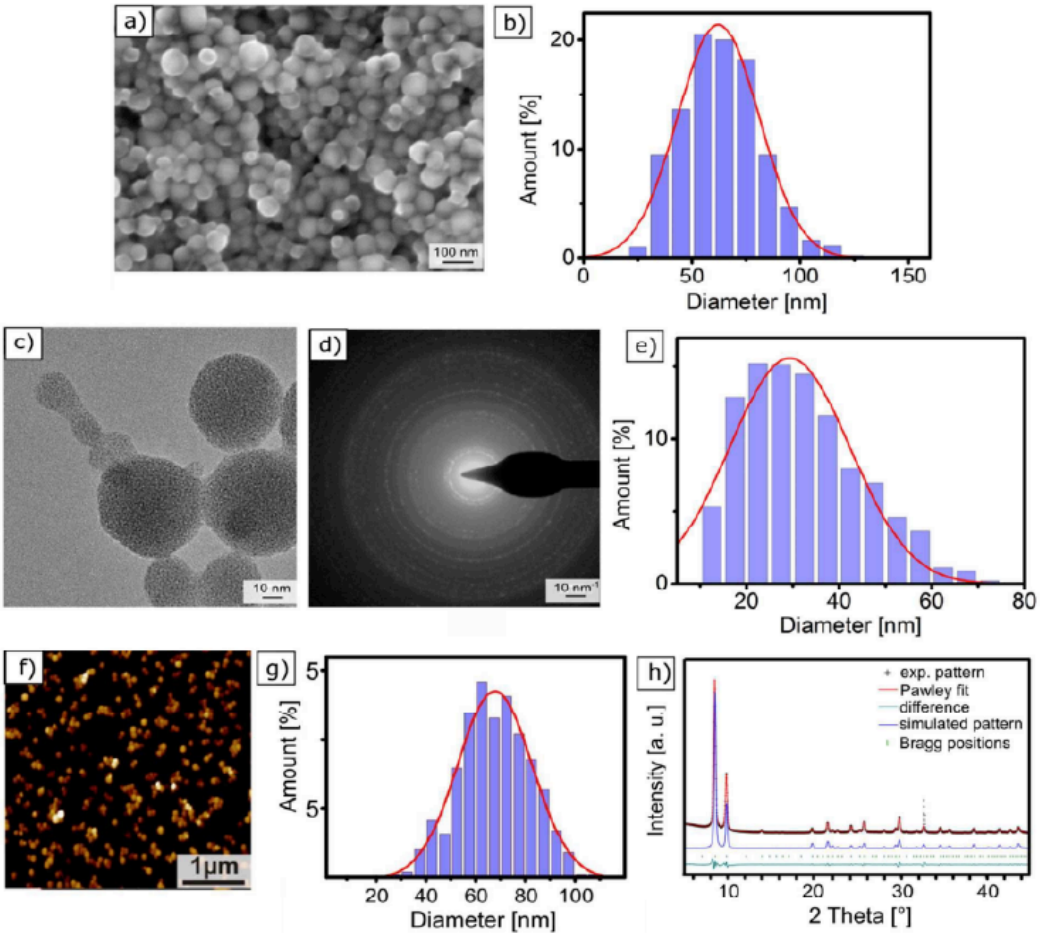


**Figure 14:** Characterisation of Zr-fum MOF NPs with different methods: (**a**) SEM micrograph; (**b**) particle size distribution of Zr-fum MOF NPs from SEM images (Figure S4); (**c**) TEM micrograph; (**d**) electron diffraction pattern of Zr-fum MOF NPs; (**e**) particle size distribution of Zr-fum MOF NPs from TEM images; (**f**) AFM micrograph; (**g**) particle size distribution of Zr-fum MOF NPs from AFM images; (**h**) Experimental PXRD pattern of the Zrfum-3 MOF NPs (black symbols), Pawley fit (red), Bragg positions (green symbols) and the difference between the Pawley fit and experimental data (dark green). The observed reflection intensities are in very good agreement with the simulated PXRD pattern (blue) based on the Pn-3 symmetric of the Zr-fum MOF structure model. (From [223]).

correlation spectroscopy (FCS), to comprehensively characterize and determine the properties of the Zr–fum MOF NPs [223]. Complementing morphological characterization, Sumei *et al*. underscored the significance of spectroscopic methods, particularly UV-Vis diffuse reflectance spectroscopy (DRS), to determine light absorption properties and bandgap energies of Ni-MOF@BiOBr composites, thereby linking optical behavior with degradation rates of organic pollutants [224]. Moreover, Yingzhang *et al*. highlighted photoluminescence (PL) spectroscopy as a powerful tool to probe charge carrier recombination dynamics; a reduced PL intensity signifies enhanced charge separation and improved photocatalytic activity in Pt/NiMg-MOF-74 nanosheets [225]. Kuate *et al*. introduced photothermal-assisted photocatalytic degradation experiments under simulated solar irradiation, effectively quantifying the synergistic effects of thermal and photocatalytic processes on pollutant removal in seawater environments, thus offering a practical approach to activity evaluation [226]. Finally, Xuesong *et al*. advocated for integrating permeability and antifouling performance assessments alongside photocatalytic activity measurements to provide a comprehensive evaluation of membrane functionality, emphasizing that sustainable water purification demands membranes capable of maintaining high flux while resisting fouling during extended operation [227]. These studies establish a robust, multifaceted analytical framework—combining morphological, optical, and functional evaluations—that is crucial for advancing the design and application of photocatalytic MOF membranes in seawater treatment.

### 5.4. Improving the Stability and Reusability of Photocatalytic MOF Membranes

Enhancing the stability and reusability of photocatalytic MOF membranes is paramount for their effective deployment in seawater purification. For example, Xianqi *et al*. highlighted the pivotal role of modulating the conduction band of MOFs by embedding $TiO_2$ nanoparticles, which not only elevates photocatalytic efficiency but also reinforces the structural integrity of the membranes under sustained light exposure [228]. This strategic incorporation promotes efficient charge separation, thereby mitigating photocorrosion and extending membrane lifespan. In parallel, Angela *et al*. explored composite membranes composed of silver nanoparticles and caffeic acid, revealing that these hybrids possess intrinsic self-cleaning capabilities through the generation of reactive oxygen species. This mechanism effectively curbs membrane fouling and preserves photocatalytic activity across multiple operational cycles [229]. Complementing these insights, Leila *et al*. engineered porphyrin-based MOFs with finely tuned electronic properties that facilitate stable photocatalytic $CO^2$ reduction, underscoring the critical importance of molecular-level design in achieving both high catalytic performance and durability [230]. Moreover, Lan *et al*. demonstrated that the in situ growth of $Cs^3Bi^2Br^9$quantum dots on Bi-MOF nanosheets significantly enhances photocatalytic stability by promoting efficient charge transfer and suppressing electron-hole recombination, enabling repeated use without notable performance degradation [231]. These studies illuminate that advancing self-cleaning and anti-fouling functionalities through deliberate material design and functionalization , which is essential to bolster the longevity and recyclability of photocatalytic MOF membranes. All these efforts are paving the way for their sustainable application in seawater treatment.

### 5.5. Solution to the Problem of Scaling and Scalability in Seawater Treatment

Overcoming the intricate challenges associated with scaling and scalability in seawater treatment is crucial for advancing the real-world application of photocatalytic Metal-Organic Framework (MOF) membranes. Recent research has shone light on innovative solutions to these challenges, providing promising avenues for the sustainable purification of seawater. Faheeda *et al*. have developed a groundbreaking approach by fabricating ultrathin graphene oxide-based nanocomposite membranes [235]. These membranes exhibit exceptional antifouling properties, which are essential for mitigating the scaling issues that frequently plague MOF membranes operating in saline environments. The incorporation of graphene oxide not only enhances the mechanical stability of the membranes but also effectively repels foulants, thereby extending their operational lifespan and efficiency. In a parallel effort, Zhu *et al*. have demonstrated the significant impact of interfacial engineering on the performance of MOF membranes [233]. By modulating Ti–S bonds within S-scheme MOF/CTF nanosheet heterojunctions, they have achieved remarkable improvements in charge separation efficiency and photocatalytic stability. This interface engineering approach not only bolsters the durability of the membranes under harsh seawater conditions but also enhances their overall performance, making them more suitable for large-scale applications. Furthermore, Lin *et al*. have reported a 2D Co(II)-imidazole MOF that exhibits outstanding visible-light photocatalytic efficiency [232]. This material has the potential to drastically reduce the energy consumption barriers associated with large-scale pollutant degradation applications, thereby making seawater treatment more economically viable. Zhang *et al*. (2024) have taken a different route by

exploring Bi-doping in CeO derived from Ce-MOFs [234]. Their research has revealed that Bi-doping not only improves the photocatalytic degradation performance but also enhances the material's robustness. This increased resistance to salt-induced scaling further underscores the potential of this approach in addressing the long-term durability challenges faced by MOF membranes in seawater treatment. Complementing these findings, Hanhua *et al*. have investigated a stable triphenylamine-based Zn(II)-MOF that demonstrates capabilities in photocatalytic hydrogen evolution and photooxidative reactions [236]. The structural stability and multifunctionality of this material emphasize the critical role played by these attributes in addressing the operational challenges associated with seawater purification. Collectively, these studies illustrate that addressing scaling and scalability issues in seawater treatment using MOF membranes requires a multifaceted approach. Advanced material design, interface engineering, and energy-efficient photocatalytic mechanisms must be integrated to enable the sustainable and practical deployment of these membranes. By leveraging these innovative solutions, researchers can pave the way for the widespread adoption of MOF membranes in seawater treatment, thereby contributing to the global effort towards water sustainability.

## 6. CHALLENGES AND FUTURE PROSPECTS

### 6.1. Integration of MOF Membranes with Renewable Energy Sources

The integration of MOF membranes with renewable energy sources has emerged as a promising strategy for sustainable seawater purification. Vevers *et al*. (2024) demonstrated that embedding photocatalytic zinc oxide nanoparticles into ultrafiltration membranes not only enhances antibacterial activity but also effectively controls biofouling under solar irradiation, but also showcase the potential of solar-driven membrane technologies for prolonged and efficient operation [237]. In a complementary study, Valverde *et al*. examined the multiscale architecture of PVDF-HFP@MOF membranes, revealing that optimizing membrane morphology significantly improves light absorption and charge transport—key factors for seamless integration with photovoltaic or solar thermal systems [238]. Marida *et al*. employed the Turbiscan Stability Index to assess the stability of alumina-based photocatalytic membranes under dynamic conditions, addressed a critical challenge for membranes operating alongside variable renewable energy inputs [239]. Additionally, XiaoYu *et al*. investigated the facet-dependent photocatalytic properties of Fe-soc-MOFs for $CO_2$ reduction, highlighting how precise control over MOF crystal facets can substantially boost photocatalytic efficiency, a principle that can be extended to sunlight-driven seawater purification [240]. Finally, Hong Bin *et al*. developed MOF-polymer mixed matrix membranes capable of chemical detoxification, he also demonstrate the versatility of MOF membranes in targeting diverse contaminants when powered by renewable energy-driven photocatalysis [245]. These studies emphasize the critical role of advanced material design and strategic system integration in harnessing renewable energy effectively, thereby advancing scalable, energy-efficient, and environmentally friendly seawater treatment technologies.

### 6.2. The Potential and Challenges of Commercialization

Photocatalytic MOF membrane technology has shown great commercial potential in the field of seawater purification. Its market drivers mainly include: the aggravation of global water shortage, the high energy consumption cost of traditional technology, the abundance of solar energy resources, and the support of environmental protection policies. The following analyzes its commercial application prospects from multiple angles.

The municipal field is the largest application market for seawater desalination, accounting for about 70% of the market share of global seawater desalination applications. With the acceleration of global urbanization and the intensification of surface water pollution, the demand for safe drinking water from municipal water supply continues to grow. Photocatalytic MOF membrane technology is particularly suitable for providing drinking water solutions for coastal cities, which often face the problem of freshwater shortage but abundant seawater resources.

The PSP-MIL-53 photosensitive MOF material developed by Monach University in Australia and Chinese scientists can reduce the total dissolved solid (TDS) in seawater from 2, 233 ppm to less than 500 ppm in 30 minutes, which is lower than the drinking water standard recommended by the World Health Organization (WHO). Accurate (600 ppm). 1 kilogram of this material can produce 139. 5 liters of fresh water per day, and it is easy to clean and reusable. It only needs to be placed in the sun for 4 minutes to regenerate. This high-efficiency performance makes it highly competitive in the field of municipal water supply [241]. Another noteworthy material is Cu-Catecholate MOF-based photothermal film (Cu-CATM), which has a three-dimensional nanowafer array structure, which not

only provides a large number of water transmission channels, but also achieves 92% solar-steam conversion efficiency, and shows lasting evaporation rate and salt-free accumulation characteristics in seawater desalination [245].

Although we have made many achievements in this field, the commercialization of photocatalytic MOF membranes faces many water challenges:

1. Material cost and large-scale production

At present, the production cost of high-performance MOF materials is still high. First of all, the complexity of synthesis and purification requirements limit their large-scale application. For example, the synthesis of PSP-MIL-53 requires multi-step reaction and precise control, which increases the production cost [241]. Although MOF materials have extremely high specific surface area and excellent properties, large-scale production above the kilogram level still faces challenges such as reaction condition control, yield and batch consistency.

To solve this problem, researchers have developed a new preparation process. For example, the MOF assisted pyrolysis-electric replacement method proposed by Wei Dun's team of Central South University successfully prepared a 3D ordered porous carbon composite (3D Ag@NC) anchored with ultra-fine silver nanoparticles through three-dimensional template construction and carbonization process, which provides new ideas for the design of high-performance electrode materials and is expected to reduce production costs [243].

2. Long-term stability and durability

The chemical stability and mechanical stability of MOF materials in the water environment is another major challenge facing commercialization. Some MOF materials are prone to hydrolysis or structural degradation in aqueous solution, resulting in performance degradation. In addition, the reactive oxygen species produced in the photocatalysis process may accelerate the aging of the MOF structure and affect the service life of the membrane [91].

In response to the stability problem, researchers have improved the durability of MOF membranes through a variety of methods such as surface modification, composite carriers and cross-linking strategies. Research shows that appropriate heat treatment or chemical cross-linking can significantly enhance the water stability of MOF materials, enabling them to adapt to the actual application environment [244].

3. System integration and engineering applications

Integrating photocatalytic MOF membranes into large-scale water treatment systems has challenges in engineering design, operation and maintenance management. Specifically, it includes: the optimization design of the lighting system (to ensure the uniformity of the membrane surface lighting), membrane pollution control, energy recovery and automation control [244].

In actual seawater purification applications, complex components of seawater (such as organic matter, particulate matter, microorganisms, etc. ) may affect the performance and service life of the membrane, requiring pretreatment of incoming water, which increases the complexity and cost of the system. In addition, day and night changes and seasonal fluctuations in lighting conditions also pose challenges to the stable operation of the system, requiring energy storage or backup systems to ensure continuous operation [241, 92].

## CONCLUSION

MOF-based photocatalytic membranes possess an extremely high specific surface area, exceptional selectivity, and highly tunable pore structures. These properties allow them to effectively integrate both photocatalytic and photothermal conversion mechanisms. This combination offers a novel material solution and technological pathway to address global challenges in seawater desalination and complex water pollution. Both experimental and theoretical studies demonstrate that these membranes can effectively utilize solar energy to achieve low-energy, high-flux purification of multiple pollutants, while also exhibiting self-cleaning and regenerative capabilities. They are capable not only of efficient desalination and removal of antibiotics and microbial contaminants, but can also be integrated with emerging processes such as antifouling strategies, heavy metal recovery, and solar-driven desalination, demonstrating significant potential for environmental and engineering applications.

However, scaling up these membranes for practical application remains challenging. There are several key issues must be addressed, one of them is developing fabrication methods suitable for industrial-scale production, and ensuring their environmental compatibility and safety throughout the entire life cycle. Secondly, improving their long-term stability in water, we need to develop high-stability MOF materials, give priority to thermodynamically stable metal-ligand bonding, or hydrophobic treatment of MOF to improve its water resistance, acid and alkali resistance. It is also necessary to optimize the membrane structure design,

adopt the mixed matrix membrane strategy, and disperse MOF as a filler in the polymer matrix, which can combine the advantages of the two to improve the mechanical strength and preparation feasibility. There is also an exploration of MOF membrane supported by flexible substrates (such as carbon cloth), or design a multi-layer composite structure, with mechanical support provided by the substrate, and the functional layer is responsible for separation and catalysis, etc, future research needs to focus on innovating MOF materials in a systematic way. This includes optimizing their microstructural design, enhancing functional modulation, deepening the understanding of underlying mechanisms, and improving adaptability to diverse scenarios. Thirdly, it is necessary to strengthen the anti-pollution design of the membrane surface, build a super hydrophilic or even underwater super-oleophobic surface, and reduce the adhesion of organic pollutants and oil stains. Optimize membrane components and hydraulic conditions, design reasonable flow channel structures, and use fluid shear force to slow down pollutant deposition. Explore the cooperative operation mode of photocatalysis and membrane separation processes (such as intermittent lighting, regular reverse flushing). Besides, improving the efficiency of photocatalysis and sunlight utilization is also a problem, when designing MOF, we need to screen and design new ligands and metal clusters, accurately regulate the band gap width and energy band position of MOF, enhance visible light absorption, and develop more heterogeneous junctions of Z-type mechanism or heterogeneous junctions of S-type mechanism (such as MOF semiconductor, MOF carbon material, MOF precious metal nanoparticles), optimize the separation and migration efficiency of photogenic carriers, and retain high redox ability. We can also try to use the isother mulent effect and photothermal conversion to develop the isolaron resonance effect of nanoparticles or develop photothermal MOF materials to convert more light energy into heat energy into heat energy or local electric field enhancement.

Except for the above, I think the use of artificial intelligence and big data can accelerate the development and modular optimization of these materials. Such approaches will help promote the commercialization of MOF photocatalytic membranes and intelligent water treatment systems.

In summary, there are still some challenges in the development of photocatalytic MOF-based membrane technology, but there is no doubt that it holds promise as a sustainable, safe, and efficient solution for water purification systems. It is expected to provide a solid scientific and engineering foundation and play a critical role in addressing global water security challenges and advancing green, low-carbon development.

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