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Recent advances in multifaceted applications of MOF-based hydrogels

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Abstract

Metal-organic frameworks (MOFs) have recently garnered attention due to their intriguing physiochemical properties; however, their instability and unsatisfactory processability have limited them from achieving a wide range of applications. Therefore, structural new MOFs and MOF-based hydrogels have been developed to address associated drawbacks (such as inherent brittleness and instability in the crystalline state). The development of MOF-based hydrogels has been the focus of some recent attempts. Compared to the original MOFs, they have several better properties (such as improved mechanical strengths). This review will provide the latest overviews of current research developments on MOF-based hydrogels. We primarily focus on the classification of these hydrogels and their associated synergistic effects. We also emphasize microscale composite design, macroscale performance, and extended applications in catalysis, water treatment and biomedicine. Further, we anticipate that this review will be valuable for individuals seeking insights into the applications of MOFs-based hydrogels.

Keywords: Metal-organic frameworks, hydrogel, water remediation, targeted delivery

INTRODUCTION

The design and development of porous materials has demonstrated vast applications in various fields. A primary characteristic of these materials is their low density, which results from a significant amount of void space. This property can be leveraged to develop a wide range of functionalities, depending on the intended applications. Porous materials such as metal-organic frameworks (MOFs)/covalent organic frameworks (COFs)/hydrogen-bonded organic frameworks (HOFs) play significant roles due to their distinctive characteristics[1].

In this regard, MOFs, recognized as porous coordination polymers, have witnessed considerable advancements in recent years. They represent a distinct category of porous crystalline materials created through the coordination bond interactions between organic ligands and metal-containing nodes[2,3]. The current landscape features thousands of MOFs with a wide range of molecular compositions, topological structures, crystal forms, and pore architectures[4]. Moreover, the physical properties, topological structures, ligands, and metal nodes in MOFs can be tailored to enhance their characteristics and practical performance through interweaving motifs, mixed ligand strategies, and functionalization[5]. Nonetheless, the practical applications of MOFs (such as in water treatment) are constrained by the processability challenges associated with their inherently fragile and powdered crystalline forms. In response to this impediment, MOF composite materials have emerged as a focal point in research, leveraging their adaptability and unique microporous structure. However, challenges such as material compatibility, MOF matrix decomposition, and other factors continue to impede the effective application of MOF composite materials[6-9].

MOFs have highly controllable pore structures, large specific surface areas, and diverse functionalities, making them extensively utilized in gas adsorption, separation, storage, and other areas. Compared to conventional materials used for gas adsorption, MOFs offer tunable pore sizes, high surface areas, and a variety of functional groups, enhancing their ability to adsorb and store gas molecules. By altering the composition and structure of metal ions and organic ligands, it is possible to optimize gas adsorption and energy storage performance[10-12].

COFs are another type of porous material formed by covalent bonding of conjugated organic molecules. They typically feature a two- (2D) or three-dimensional (3D) arrangement structure, excellent conductivity and chemical stability, making them suitable for applications in electronic devices, sensors, catalysis, and other fields. Their structures and properties can be regulated through synthesis methods and the design of organic molecular structures, offering high customizability and application potential. In the field of electronic devices and sensors, traditional materials include organic semiconductor materials, metal oxides, 2D materials, *etc.* In contrast, COFs exhibit excellent chemical stability and can withstand varying environmental conditions, ensuring their suitability for the long-term reliable operation of these devices and sensors[13].

Another class of porous materials, HOFs, is formed by non-covalent interactions between supramolecular assembly units. HOFs typically have a molecular-level pore structure and affinity, rendering them appropriate for applications such as molecular recognition, catalysis, and separation. Their structure and properties can be regulated through intra- or intermolecular interactions, with unique characteristics. HOFs can recognize specific molecules, enabling their use in molecular separation and detection[14]. Additionally, the synthesis of HOFs is typically straightforward and environmentally sustainable, requiring no extreme temperatures or pressures, thereby promoting green synthesis methods.

Hydrogels, due to their crosslinked 3D polymer networks, superior water contents, swelling, and responsiveness, demonstrate characteristics of elastic solids, including deformability and softness[15-17]. The integration of MOFs with hydrogel matrices in the form of MOFs-based hydrogel composites/systems emerges as a strategic solution to counteract the brittleness and limited processability commonly encountered in MOFs[18]. This synergistic combination with the unique properties of both MOFs and hydrogels provides new possibilities for diverse applications. The 3D network characteristic of hydrogels plays a pivotal role in addressing the challenges posed by MOFs. Firstly, it ensures the uniform dispersion of MOF materials within the hydrogel matrix, mitigating issues related to agglomeration and facilitating a more homogenous distribution of MOFs throughout the composite structure. This uniform dispersion contributes to enhanced mechanical integrity and stability, addressing one of the primary limitations of MOFs. Furthermore, the integration of MOFs within the hydrogel matrix imparts an additional layer of functionalities. The inherent versatility of MOFs allows for the modulation and alteration of the properties and functions of the hydrogel matrix. The synergistic integration of MOFs and hydrogels presents a unique opportunity to customize composite materials for specific needs, including adjustable porosity, controlled release of substances, and improved mechanical properties. These advancements have significant implications for various practical applications in drug delivery, sensing technologies, tissue engineering, and environmental remediation. The combination of MOFs and hydrogels offers a sophisticated and efficient strategy to leverage the respective strengths of these materials. The 3D structure of hydrogels not only overcomes the limitations of MOFs but also serves as a versatile platform for the design of advanced materials with tailored characteristics[19].

Overall, when compared with COF and HOF materials, MOFs present several real-time challenges and are the most anticipated materials in diverse applications. So, it is important to focus on and tackle the limitations involved in current MOF research. This paper offers a thorough overview of hydrogel and MOF materials, outlining their classifications, synthesis methods, and distinctive structural and chemical compositions. It also explores the preparation methods and applications of MOFs-based hydrogels. By directing attention not only to traditional MOFs but also to MOFs-based hydrogels and other derivatives, this review aims to offer valuable information and inspiration to researchers unfamiliar with MOFs, hydrogels, MOFs-based hydrogels, and other MOFs derivative composites. The emphasis is on reviewing the latest developments in MOFs-based hydrogels and their applications. This review seeks to help readers, including those with limited understanding of MOFs-based hydrogels or even chemistry, grasp the concepts of MOFs-based hydrogels and acquire the knowledge they seek. The integration of MOF and hydrogels opens new avenues for research and development, offering innovative solutions to long-standing challenges in materials science and paving the way for novel applications across various disciplines.

DESIGNING PRINCIPLES

What is MOFs

MOFs are compounds defined by their 3D network structures composed of transition metal ions and organic ligands connected through coordination bonds. These porous coordination polymers are formed by linking inorganic metal ions or clusters with organic ligands[20-23]. Figure 1 illustrates this unique structural arrangement, which gives MOFs a hybrid nature, combining characteristics of both organic and inorganic materials[24]. The coordination bonding between metal ions and organic ligands generates a highly porous framework, contributing to the distinctive properties MOFs exhibit. This structure forms a stable crystalline material with a high density of pores and voids, making it suitable for gas adsorption, molecular storage, catalytic reactions, and more.

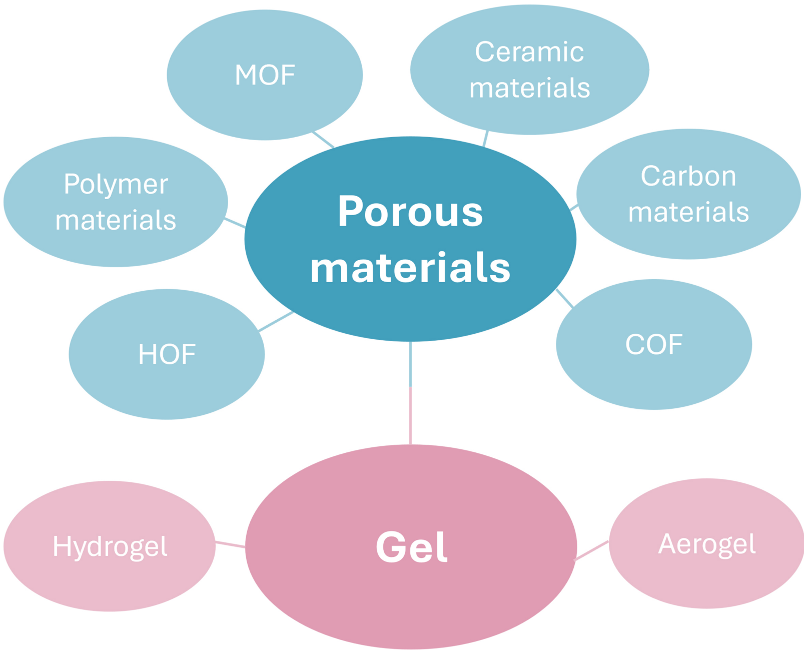

Figure 1. Schematic showing the classification of porous materials and gel materials.

MOFs are typically named based on specific types or structural frameworks. For example, the zeolitic imidazolate frameworks (ZIFs) series MOFs follow this convention. Other classifications of MOFs include inorganic metal organic framework 9IRMOF), coordination pillared layer (CPL), materials of institute Lavoisier (MIL), porous coordination network (PCN), and University of Oslo (UiO). Due to their porous structure and inherent stability, MOFs have garnered significant attention, leading to extensive research and applications across various scientific fields, including atmospheric water harvesting, oil-water separation, gas storage/separation, energy storage, drug delivery, sensing, and catalysis[25-30]. The porous nature of MOFs allows for effective adsorption and storage of gases and other substances, making them vital in gas separation technologies and as carriers for controlled drug delivery. Additionally, their stability positions MOFs as excellent candidates for catalytic applications and sensing materials. Despite their versatile and promising features, the practical application of MOFs has been limited by several challenges. One significant issue is their intrinsic brittleness, leading to fragmentation and difficulty in handling and processing. This rigidity restricts their usability in real-world applications[31-34]. To overcome these limitations, innovative strategies have been developed, such as creating MOF-based composites with materials such as hydrogels to improve their mechanical properties and expand their applicability. For example, Hu *et al.* synthesized enzyme-embedded MOFs with biological activity approximately one order of magnitude higher than traditionally synthesized MOF complexes[35]. Their study also demonstrated that microfluidic synthesis is a viable method for producing MOFs with enhanced properties[36]. Similarly, Fu *et al.* developed a fiber platform based on ZIF-8, which exhibits superior protein adsorption capacity compared to other platforms[36].

In summary, MOFs represent a versatile class of materials with broad applications due to their unique structure and stability. However, addressing the challenges of rigidity and brittleness is essential for unlocking their full potential in practical applications.

What is hydrogel

Hydrogel is a kind of hydrophilic gel with 3D network structure. In water, it expands rapidly and absorbs a large amount of water while maintaining its structure and stability without dissolving. However, if the water-absorbed hydrogel is exposed to air, its volume will gradually shrink with the water evaporation. The material substrates used determine the grid structure of hydrogels, resulting in varying swelling properties, durability and stability among different hydrogels. In general, the higher the degree of crosslinking, the better the durability and stability of the hydrogel, but its water absorption capacity will be reduced[37]. As shown in Figure 2, this exceptional water-retention capability positions hydrogels as pivotal materials in various scientific and technological applications[38-51]. Park *et al.* developed a hydrogel with a specific response to nitric oxide[52]. The hydrogel responds only to nitric oxide and then expands and has proved to have great potential in the direction of drug delivery. Yao *et al.* developed a hydrogel coating, which has a wide range of applications. The hydrogel coating can significantly reduce friction and performs well in durability tests. Meanwhile, it has a stimulus-responsive structure[53].

Based on the classification of synthetic materials, hydrogels can be categorized into natural polymer hydrogels, synthetic polymer hydrogels, and hybrid hydrogels. Natural polymers offer superior compatibility, but their stability is poor and they are prone to degradation. Synthetic polymer hydrogels have good stability, but most of the crosslinking agents used to synthesize polymer hydrogels are toxic to humans. With the development of research, the hybrid hydrogel with good biocompatibility and stability has been paid growing attention. The aggregated state of a hydrogel is a nuanced equilibrium between solid and liquid phases, endowing it with dynamic and versatile behaviors. In its swollen state, a hydrogel retains a specific shape, behaving akin to a solid material, yet simultaneously, it exhibits fluidic properties as solutes can diffuse within its matrix, manifesting liquid-like characteristics[54]. This dual nature of hydrogels makes them inherently adaptable and well-suited for applications in fields ranging from biomedical engineering to environmental science. The ability of hydrogels to maintain their structural integrity while absorbing and retaining water renders them invaluable for applications where controlled water release, drug delivery, or tissue engineering are essential[26,55-63]. Moreover, the unique dual-phase behavior of hydrogels provides a platform for tailored designs in responsive materials, where environmental stimuli can trigger changes in the structure and properties of hydrogels. Hydrogels with various functionalities possess significant promise for advancing technologies in drug delivery systems, wound healing, and biosensing applications, among others[64,65].

What are MOF-hydrogel composites and the synthesis of MOFs-based hydrogel

Adding fillers to enhance the mechanical strength or performance (such as flexibility and conductivity) of hydrogels is a common material design strategy[66]. The mechanical strength and other performance are difficult to balance. The addition of MOFs makes the mechanical strength and performance (such as catalytic performance and heavy metal ions adsorption performance) of hydrogels even better[10]. This unique marriage of MOFs and hydrogels imparts enhanced mechanical strength to the resulting composites compared to standalone hydrogels. The hierarchical structure and interconnected channels within MOF-hydrogel composites not only accommodate the hydrogel matrix but also offer an extended surface area, providing ample space for functionalization and the incorporation of active species.

In the synthetic process of MOF-hydrogel composites, two primary methods have gained prominence. The first entails the direct integration of pre-synthesized MOFs into a hydrogel matrix, preserving the unique properties of both components. The second involves the *in-situ* growth of MOFs within an already-formed hydrogel, facilitating a more intimate integration of the two materials. These methods offer versatile approaches to tailor the composition, structure, and properties of MOF-hydrogel composites, allowing for the optimization of their performance in specific applications [Table 1].

Table 1. Two preparation methods of MOFs-based hydrogels and their advantages and disadvantages

Synthetic method	Advantages	Limitations
Direct mixing	- Simple and easy to execute, no complex synthesis steps required - Rapid sample preparation	- Poor interfacial viscosity between MOFs and hydrogels may affect material properties - Difficult to control uniform distribution of MOFs in hydrogels - May weaken interactions between MOFs and hydrogels, impacting performance
In-situ growth	- Achieves strong integration of MOFs and hydrogels, enhancing stability - Enables control over distribution and morphology of MOFs - Material properties can be tuned during preparation	- Requires more complex synthesis steps and conditions - May involve toxic reagents or catalysts - Difficult to achieve specific structures or morphologies in MOF-based hydrogels

MOFs: Metal-organic frameworks.

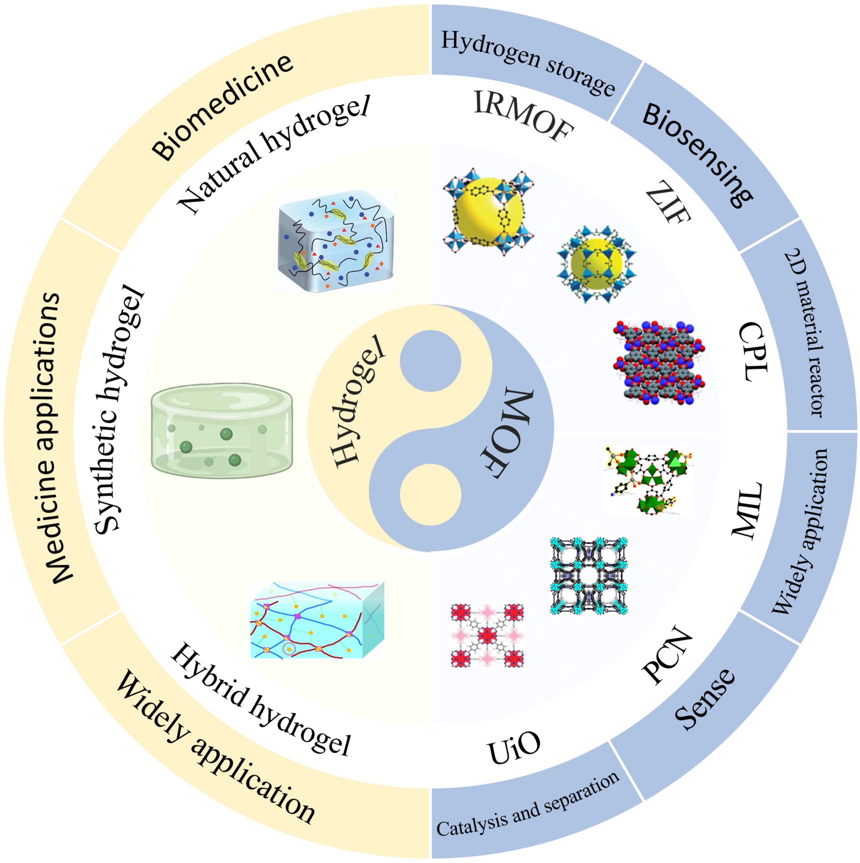

Figure 2. The illustration of classification and function of MOF and hydrogel materials. Reproduced with permission from ref[44]. Copyright 2019 American Chemical Society. Reproduced with permission from ref[45]. Copyright 2006 Slovensko Kemijsko Drustvo. Reproduced with permission from ref[46]. Copyright 2018 Royal Society of Chemistry. Reproduced with permission from ref[47]. Copyright 2020 Royal Society of Chemistry. Reproduced with permission from ref[48]. Copyright 2017 Royal Society of Chemistry. Reproduced with permission from ref[49]. Copyright 2008 American Chemical Society. Reproduced with permission from ref[50]. Copyright 2022 Elsevier. Reproduced with permission from ref[51]. Copyright 2021 Elsevier. MOF: Metal-organic framework.

Direct incorporation of pre-synthesized MOFs into a hydrogel matrix

Directly incorporating pre-synthesized MOFs into a hydrogel matrix provides a flexible strategy for creating advanced composite materials with customized properties. As shown in Figure 3, in one modality of this method, prior to the initiation of gelation, MOF crystals are carefully synthesized and added to the

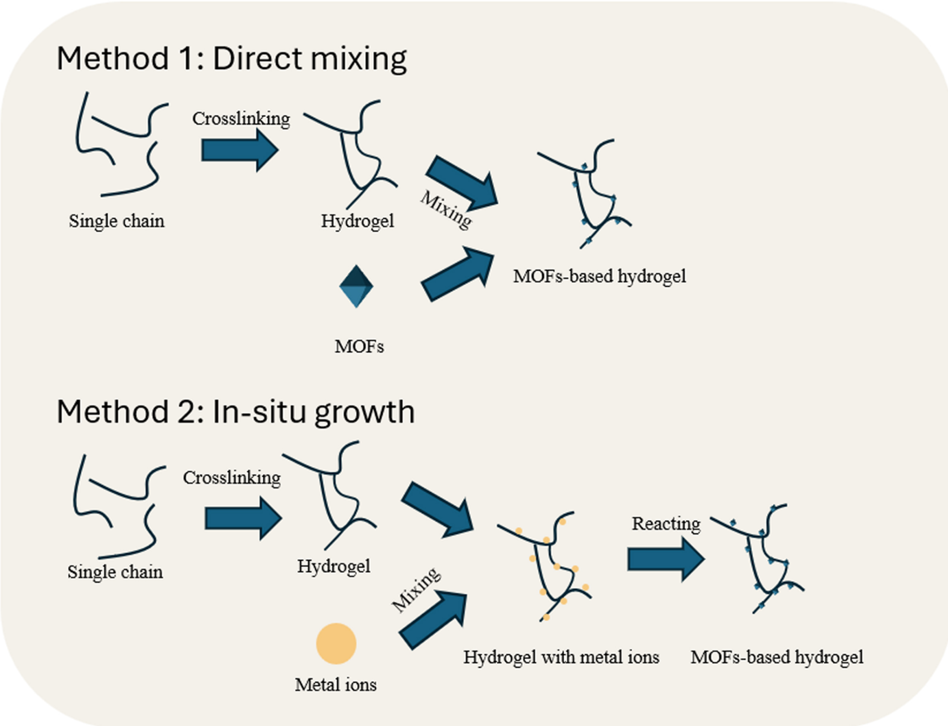

Figure 3. The illustrations of the fabrication procedure of MOFs-based hydrogel by direct mixture and *in-situ* growth. MOFs: Metal-organic frameworks.

hydrogel's liquid precursor or solution[11]. During the subsequent gelation process, the hydrogel matrix encapsulates and enwraps the pre-existing MOF crystals, resulting in the creation of MOF-hydrogel composites. This approach guarantees a uniform distribution of MOFs throughout the hydrogel matrix, offering control over the dispersion and interaction of MOF particles[35].

An alternate strategy in this synthesis approach involves the addition of MOF crystals to the hydrogel system after the introduction of a gelation trigger and the formation of the pre-polymerized sol. In this dynamic process, MOF crystals are incorporated into the evolving hydrogel network post-gelation initiation[12]. The stepwise addition of MOF crystals enables temporally controlled integration, affecting the structural and mechanical properties of the resulting MOF-hydrogel composites. This approach facilitates precise adjustments, improving the flexibility and functionality of the composite materials for targeted applications.

In situ growth of MOF on hydrogel

The *in-situ* growth method has become a novel and dynamic technique for preparing MOF-hydrogel composites, gaining attention in recent years due to its distinctive advantages. Distinguishing itself from traditional methodologies, this technique utilizes chemical or physical methods to connect, polymerize, and deposit materials, capitalizing on the synergistic advantages of combining two distinct matrices[11]. This approach, commonly used in the synthesis of composite materials, utilizes the intrinsic properties of the matrix material along with external conditions such as high temperature and pressure to create growth centers on the matrix. In the case of MOF-hydrogel composites, the *in-situ* growth method harnesses nano effects or external conditions to trigger the growth of MOFs within the pores of the hydrogels. The MOF precursors are integrated into the hydrogel matrix, supplying the essential components for *in situ* growth.

As a result, MOF crystals develop within the pores of the hydrogel, leading to the formation of MOFs-based hydrogel composites[67]. This synthesis strategy presents a distinctive opportunity to customize the structure and properties of the composite material, enabling improved functionality and performance in targeted applications such as drug delivery and catalysis. The *in-situ* growth method represents an innovative strategy for designing and synthesizing advanced materials with exceptional properties.

APPLICATION

The MOFs-based hydrogels show their multifaceted utility across various domains, including five key areas of application: electrocatalysis, water treatment, detection and sensors, biomedical applications with a focus on antibacterial properties, wound healing, and drug delivery, and finally, miscellaneous applications that highlight the adaptability and innovation potential of MOFs-based hydrogels [Figure 4]. Each section unfolds a distinct facet of the functionality of hydrogels, demonstrating their capacity to address complex challenges and contribute to advancements in fields ranging from environmental remediation to healthcare[68].

Catalysis

The porous architecture of MOF-based hydrogels offers numerous surfaces and channels, facilitating efficient adsorption of reactants onto catalytic sites[69]. The metal ions in MOFs provide electrons and actively participate in reactions, with metal centers typically showing catalytic activity for specific reactions. Studies have demonstrated that both pyridinic and graphitic nitrogen serve as highly effective active sites. Wang *et al.* utilized carrageenan/NiCo-MOF hydrogels as precursors to synthesize porous carbon aerogels (Ni_3S_2-Co_9S_8/NCAs) as electrocatalysts for the oxygen evolution reaction (OER)[70]. Electrochemical tests [Figure 5A], revealed outstanding catalytic performance, surpassing most transition metal sulfide catalysts, with an overpotential of just 337 mV. This high performance can be attributed to the large surface area, the interfacial synergy between Ni_3S_2 and Co_9S_8, and the unique 3D porous structure, which offers numerous active sites and enhances mass transport and electron mobility after freeze-drying. Sikdar *et al.* developed a scalable method based on "hydrogel-organic interfacial diffusion" for the direct growth of MOF nanocrystals on porous graphene hydrogels, enabling precise control over structure[71]. Molecular dynamics simulations indicated that the two-stage diffusion process plays a critical role in the tunable formation of MOF-based hydrogels. The resulting hydrogel-derived aerogels exhibited excellent performance in the OER, with high operational stability, a low overpotential, and a small Tafel slope, reflecting a fast OER rate. These studies emphasize the importance of tailored synthetic approaches, unique nanoscale structural designs, and the interplay of materials in improving catalytic performance. From the well-distributed Fe elements in mesoporous carbon sheets to the core-shell structure of N-doped carbon nanotubes and the hierarchical porous structure with interfacial synergy in carrageenan/NiCo-MOF hydrogels, each contribution provides valuable insights. Collectively, these advancements underscore the versatility and promise of MOF-based hydrogels in advancing the field of electrocatalysis.

Ma *et al.* developed MOF-based hydrogels capable of rapidly degrading organophosphorus chemicals under ambient conditions, introducing a range of hydrogels with diverse functions and topologies[24]. Among these, MOF-808 exhibited the highest efficiency in hydrolyzing organophosphorus compounds. Hydrogels incorporating MOF-808 were able to rapidly degrade both simulated and real nerve agents, with the shortest degradation half-life reported among MOF-based hydrogels. This study provides a significant breakthrough in the design of protective devices for rapid detoxification. In a related development, Weng *et al.* synthesized novel MOF-hydrogel microspheres, demonstrating a synergistic effect between the hydrogel and the MOF layer [Figure 5B][72]. The porous hydrogel matrix created a biocompatible environment for encapsulated enzymes, preventing undesirable restrictions and chemical interactions, allowing the enzymes

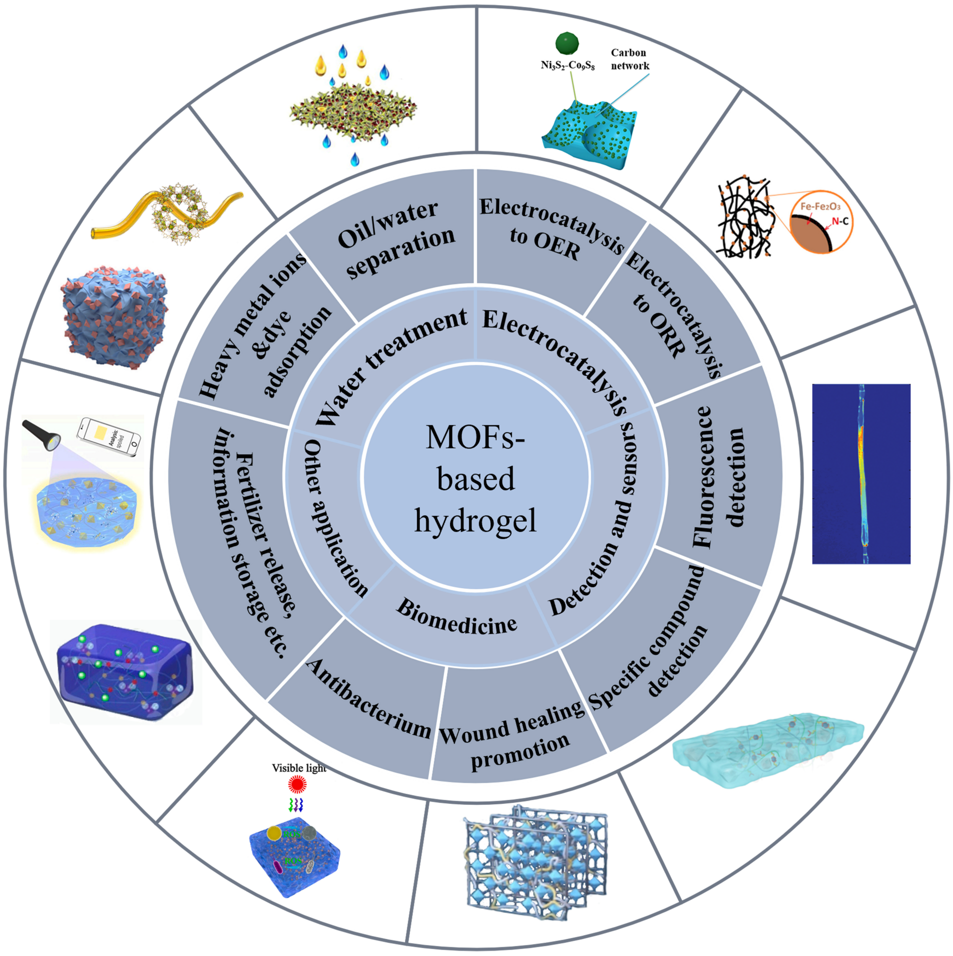

Figure 4. The illustration of the application classification of MOFs-based hydrogel. Reproduced with permission from ref[70]. Copyright 2022 American Chemical Society. Reproduced with permission from ref[72]. Copyright 2021 Elsevier. Reproduced with permission from ref[92]. Copyright 2018 Royal Society of Chemistry. Reproduced with permission from ref[94]. Copyright 2022 American Chemical Society. Reproduced with permission from ref[109]. Copyright 2023 Elsevier. Reproduced with permission from ref[98]. Copyright 2023 Elsevier. Reproduced with permission from ref[119]. Copyright 2023 Elsevier. Reproduced with permission from ref[127]. Copyright 2022 Elsevier. Reproduced with permission from ref[85]. Copyright 2023 Elsevier. Reproduced with permission from ref[76]. Copyright 2022 Elsevier. Reproduced with permission from ref[73]. Copyright 2020 Elsevier. MOFs: Metal-organic frameworks.

to maintain high natural activity. Simultaneously, the MOF layer protected the enzymes from harsh environments, providing the hybrid reactor with strong stability. Notably, this system exhibited high enzyme tolerance to polar organic solvents. Together, these studies highlight the versatility of MOF-based hydrogels in diverse catalytic and protective applications.

Water treatment

Over the several years, MOFs have been extensively applied in water treatment. The functional groups in the hydrogel can form hydrogen bonds with ions to enhance adsorption. Under appropriate pH conditions, the surface of MOFs-based hydrogels may be positively or negatively charged, thus interacting with ions with opposite charges through electrostatic attractions. In some cases, MOFs-based hydrogels may react with ions to form precipitation or other compounds, further enhancing the removal performances[73]. For oil-water separation, adjusting the surface chemical properties of MOFs-based hydrogels allows for the modulation of their hydrophilicity and hydrophobicity, enabling selective adsorption of either oil or water. Some MOFs-based hydrogels can be tailored to possess lipophilic characteristics, effectively adsorbing the

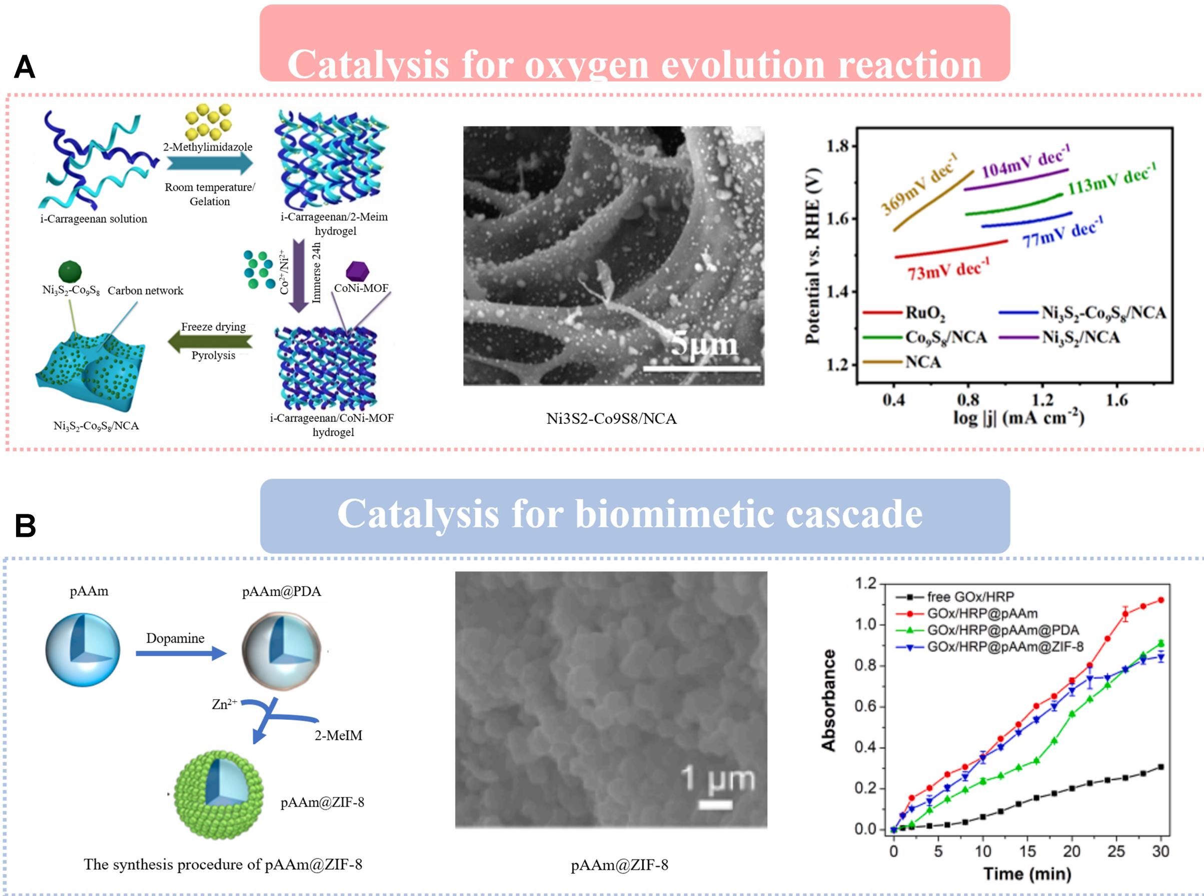

Figure 5. The illustration of preparation, characterization, and the electrocatalyst performance of the MOFs-based hydrogel. (A) The illustration of the fabrication procedure and the SEM images (5 μm) of Ni_3S_2-Co_9S_8/NCA, and the Tafel plots of the Ni_3S_2-Co_9S_8/NCA, Co_9S_8/NCA, Ni_3S_2/NCA, NCA, and RuO_2. Reprinted (adapted) with permission from ref[70]. Copyright 2022 American Chemical Society; (B) The illustration of the fabrication procedure. The XRD image (1 μm) of pAAm@ZIF-8. Time-dependent absorbance of $ABTS^{•+}$ catalyzed by free GOx/HRP system, GOx/HRP@pAAm, GOx/HRP@pAAm@PDA, and GOx/HRP@pAAm@ZIF-8, respectively. Reproduced with permission from ref[72]. Copyright 2021 Elsevier. MOFs: Metal-organic frameworks; SEM: scanning eletron microscope; XRD: X-ray diffraction; ZIF: zeolitic imidazolate framework.

oil phase while repelling water. Additionally, these hydrogels can enhance separation efficiency through interactions with oil and water molecules via hydrogen bonding, van der Waals forces, and electrostatic interactions. In response to the urgent global challenge of water treatment, researchers are increasingly exploring innovative materials to develop efficient and sustainable solutions. Among these, MOFs-based hydrogels have surfaced as promising candidates for a variety of applications. This section highlights the diverse functionalities and applications of these hydrogels in water treatment, from seawater desalination to the removal of radioactive uranium. Seawater desalination is crucial for addressing freshwater shortages, and solar vapor generation offers a low-cost, safe, and efficient solution. Guo *et al.* developed a hybrid hydrogel evaporator with a high vapor-generation rate and anti-salt-pollution capabilities[74]. The incorporation of konjac glucomannan (KGM) enhances water transport, improves hydration, and reduces evaporation enthalpy. Its numerous hydroxyl groups aid in contaminant removal while its biomass-based nature keeps costs low. The evaporator, featuring magnetically responsive MOF-derived photothermal nanoparticles, benefits from optimized solar absorber distribution via magnet-assisted fabrication. Additionally, the hydroxyl groups capture heavy metal ions and organic dyes, making the device suitable for use in underdeveloped regions due to its low cost and self-cleaning properties. Building on this, Fu *et al.*

addressed the challenges of composite membranes in water treatment by creating a polyvinyl alcohol/ polydopamine (PVA/PDA) hybrid layer combined with ZIF-8[75]. This PVA/PDA@ZIF-8 forward osmosis membrane overcomes the low permeability and fouling issues seen in traditional systems. Its porous structure provides additional channels for water transport while reducing salt diffusion. With fewer surface-charged groups, it minimizes interactions with contaminants, enhancing both water flux and selectivity. Dynamic fouling tests confirmed the membrane's excellent antifouling properties and recovery performance. Wang *et al.* took a different approach, reporting a MOF-based hydrogel with high mechanical strength, achieved by leveraging the reaction between alginate and metal ions to form MOF nuclei, preventing the growth of large particles[76]. This strengthens the polymer chains within or on the surface of the MOFs [Figure 6A]. The resulting stretchable MOF-based hydrogel tube demonstrated superior dye removal from water, particularly effective in wastewater treatment and oil-water separation. The hydrophilic membrane formed on the composite's surface not only prevents oil penetration but also improves the durability of the nano-photocatalyst powders. Addressing common challenges such as mechanical instability and low water flux in oil-water separation, Gao *et al.* synthesized a superhydrophobic MOF-based hydrogel by immersing 2D Ni-Fe MOF-halloysite nanotube (HNT) composites into PVA hydrogels[77]. The resulting material exhibits underwater super-oleophobicity, allowing efficient oil-water separation even after ten cycles [Figure 6B]. The nanosheets on the outer nanotubes enhance the composite's pore structure and mechanical strength, ensuring long-term performance.

Addressing the need for selective absorption, Biswas *et al.* fabricated MOF-gelatin nanocomposite materials by integrating UiO-66 or MOF-801 with gelatin and hydrogels[78]. Due to high physicochemical compatibility, MOF particles distribute uniformly within the gelatin matrix without affecting the material's porosity. Under appropriate humidity, these composites selectively absorb acetic acid, with an absorption ratio of 260 $\mu g \cdot dm^{-3}$, making them potentially useful for protecting cultural heritage artifacts. The overuse of antibiotics poses a significant threat to human health, and MOFs, known for their large surface area and tunable pore structures, are effective adsorbents for these pollutants. Luo *et al.* designed aluminum-based MOF hydrogel microspheres as adsorbents for bisphenol A. By adding chitosan (CS), they increased the porosity, resulting in microspheres with higher specific surface area and total pore volume[79]. Batch experiments confirmed enhanced adsorption performance, with results following the pseudo-second-order kinetic model and the Freundlich isotherm. Notably, these microbeads can be easily regenerated with methanol, maintaining over 96% adsorption efficiency even after five cycles. Chai *et al.* developed ZIF-8/ hydrogel composite beads for the adsorption and detection of fluoroquinolone antibiotics using an *in-situ* one-pot method[80]. This approach avoids common issues such as particle agglomeration and particle-polymer interaction. The composite beads achieved a pollutant adsorption capacity of up to 2,887 $mg \cdot g^{-1}$, demonstrating excellent mechanical stability after seven days in water and retaining high performance after three cycles. This study highlights the potential of MOF-based hydrogels for addressing pharmaceutical industry pollutants. To enhance the stability and durability of MOFs, the 3D interconnected reduced graphene oxide framework has gained popularity for its multifunctional properties and mechanical support. In pursuit of effective water purification, Mao *et al.* introduced a one-step self-assembly process for ZIF-8-based hydrogels, which transform into aerogels upon drying[81]. These ZIF-8 hybrid aerogels exhibit high porosity, superhydrophobicity, and superior absorption properties, along with photocatalytic dye degradation capabilities. This makes them effective in removing harmful dyes, heavy metal ions, and benzene pollutants from water. The synthetic strategy has also shown potential for fabricating other functional hydro/aerogels.

Dye wastewater, which always appears around paper, textile, and plastic factories, is expanding the impact on the ecosystem. Chen *et al.* developed polyethyleneimine-modified MOF-based hydrogels via an *ex-situ*

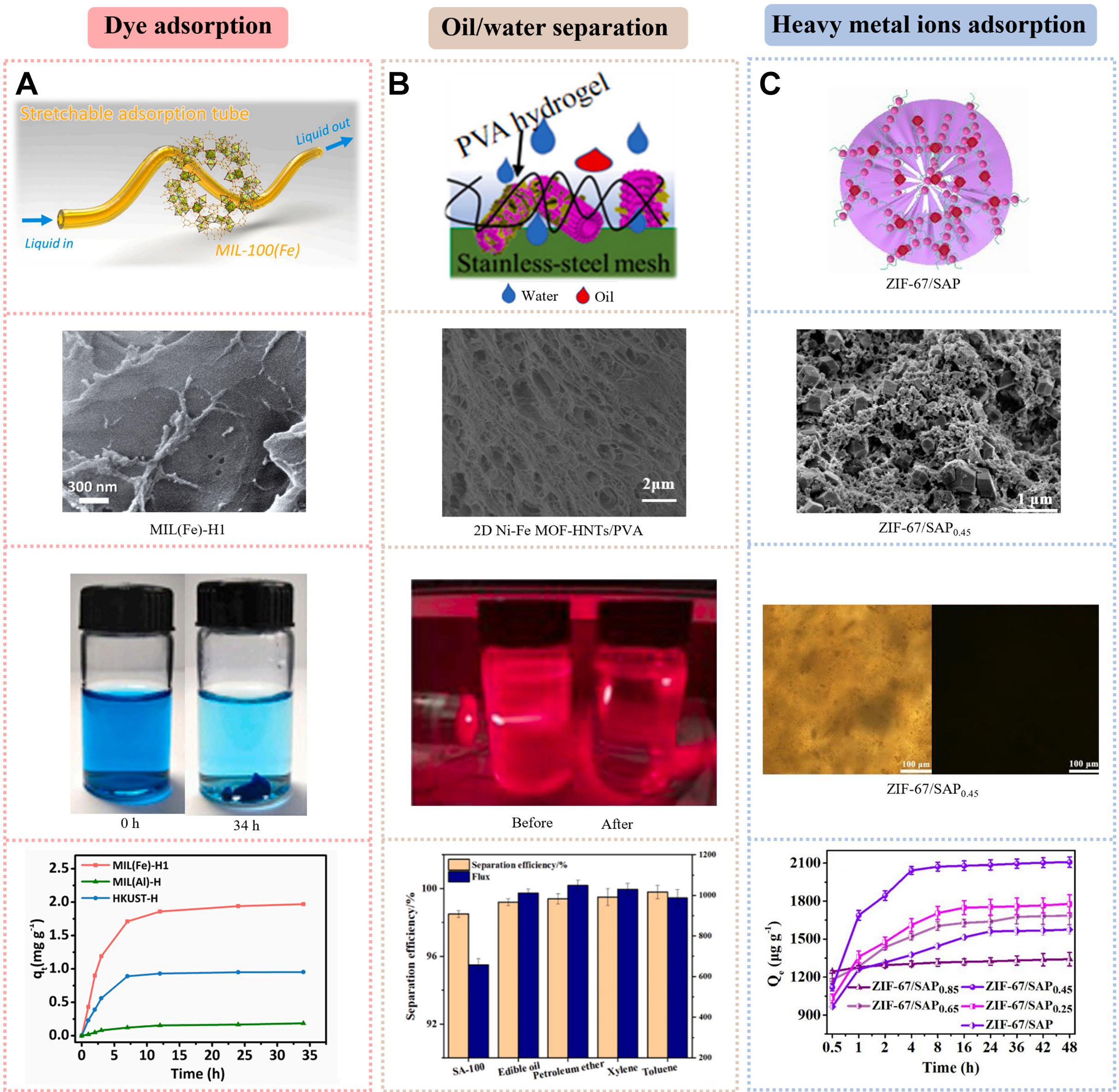

Figure 6. Schematic illustration, characterization, and the performance of water treatment of the MOFs-based hydrogels. (A) The illustration of the working principle of MOF(Fe)-H1. The SEM image (300 nm) of MOF(Fe)-H1. The photo of the MB solution exposed to MOF(Fe)-H1 before and after 3 h. And the time-dependent adsorption curves of MB on MIL(Fe)-H1, MIL(Al)-H, and HKUST-H. Reproduced with permission from ref[76]. Copyright 2022 Elsevier; (B) The illustration of the 2D Ni-Fe MOF-HNTs/PVA hydrogel-coated meshes. The SEM image of 2D Ni-Fe MOF-HNTs/PVA (2 μm). Oil-in-water emulsion separation and oil/water separation ability on 2D Ni-Fe MOF-HNTs/PVA decorated stainless steel mesh. Reproduced with permission from ref[77]. Copyright 2022 Elsevier; (C) The illustration of the internal structure of the ZIF-67/SAP composite hydrogel. The SEM image (1 μm) of ZIF-67/$SAP_{0.45}$. The optical images and fluorescence images of the uranium uptake effect on ZIF-67/$SAP_{0.45}$. The uranium uptake curves on different ZIF-67/SAP_x in 1 mg·L^{-1} uranium-containing seawater (x = 0, 0.25, 0.45, 0.65, 0.85). Reprinted (adapted) with permission from ref[84]. Copyright 2020 American Chemical Society. MOFs: Metal-organic frameworks; SEM: scanning eletron microscope; 2D: two dimensional; HNTs: halloysite nanotubes; PVA: polyvinyl alcohol; ZIF: zeolitic imidazolate framework; SAP: sodium alginate (SA) and polyethyleneimine (PEI).

blend method, which efficiently adsorb anionic dyes[82]. Characterization revealed uniform particle distribution on the hydrogel surface, promoting adsorption. In methyl orange experiments, these hydrogels exhibited an adsorption capacity of 900.5 ± 19.09 mg·g^{-1}. Similarly, Zhu *et al.* introduced a rapid growth model to create MOF-alginate composites for dye removal, maintaining the shape of the original hydrogels and allowing control over macroscopic forms[83]. This simple synthesis method facilitates the use of MOF materials in various practical applications. In addition to dyes, heavy metal ions released by industries cause significant environmental harm, but they also hold potential for recycling. Bai *et al.* fabricated ZIF-67/SAP0.45 MOF-based hydrogels with positively charged polyethyleneimine and negatively charged sodium alginate chains, providing porosity, anti-biofouling properties, and mechanical strength [Figure 6C][84]. These hydrogels demonstrated high uranium uptake capacity and retained efficiency after five adsorption-desorption cycles in real seawater. Song *et al.* further developed MOF-based hydrogels capable of selectively adsorbing U(VI) from seawater[85]. By incorporating MOFs into the hydrogel network via coordination bonds, they achieved excellent mechanical strength and U(VI) adsorption capacity of up to 159.56 $mg \cdot g^{-1}$, with continuous uranium uptake at 0.21 $mg \cdot g^{-1} \cdot day^{-1}$ in natural seawater. For the detection of uranium ions, Cui *et al.* designed a sensor/adsorbent composite using terbium(III) as a crosslinker to hybridize a luminescent MOF with sodium alginate gel[86]. This MOF-based hydrogel features multiple luminescence centers and binding sites, offering ultra-high sensitivity, a wide quantification range, and excellent anti-interference capabilities. The composite performs well without requiring complex sample preparation and shows high accuracy in detecting uranium contamination in drinking water. While copper ions are not radioactive, overexposure can damage the liver and kidneys. To develop effective copper adsorbents, Zhang *et al.* reported a ZIF-8-alginate hybrid hydrogel (PVS/SA@ZIF-8) with amine functional groups that enhance heavy metal ion adsorption through chelation[87]. This hybrid exhibits excellent adsorption capacity for Cu(II) (165.17 $mg \cdot g^{-1}$), with improved mechanical properties and recyclability. Additionally, Mahmoud *et al.* synthesized a pectin hydrogel-MOFs (PHM) composite material from citrus peel by-products using calcium chloride as a crosslinker[88]. Adsorption studies confirmed that the material follows a pseudo-second-order kinetic model and the Langmuir isotherm, effectively removing heavy metal ions from tap water, seawater, and wastewater.

In summary, from oily water treatment to adsorption of anionic dyes and heavy metal ions, MOFs-based hydrogels exhibit exceptional capabilities in addressing critical environmental challenges. The incorporation of MOFs into hydrogel matrices not only enhances mechanical strength but also introduces unique functionalities, such as superhydrophobicity, superoleophobicity, and excellent adsorption properties. The ability to selectively remove pollutants, resist fouling, and withstand harsh conditions makes these composites highly promising for widespread use, especially in underdeveloped areas. The demonstrated effectiveness in uranium removal, dye adsorption, and separation of oil and water highlights the versatility and practicality of MOFs-based hydrogels in tackling diverse water treatment scenarios. As researchers continue to explore innovative synthesis methods and tailor these materials for specific applications, the future holds great potential for the development of even more sustainable water treatment technologies.

Detection and sensors

In the field of chemical sensing, the pursuit of specific and efficient detection methods has spurred significant research. MOFs have emerged as promising materials for biosensing due to their exceptional properties. Lian *et al.* demonstrated a MOF-based hybrid hydrogel for the detection of β-lactamase, a marker for penicillin allergy[89]. By crosslinking the MOF matrix with alginate hydrogels [Figure 7A], they achieved a selective and efficient detection mechanism for β-lactamase. Chemotherapy drugs such as daunorubicin, adriamycin, and mitoxantrone are essential for cancer treatment but often cause adverse effects. Mitoxantrone, in particular, has significant cardiotoxic effects and reduces platelet levels, making dose detection crucial for managing side effects. Yu *et al.* developed a lanthanide MOF with high selectivity for detecting ofloxacin, achieving a detection limit of 1.1×10^{-9} M and a rapid response time of six seconds[90]. This study highlights the potential of MOF materials and MOF-based membranes in applications such as detection and anti-counterfeiting.

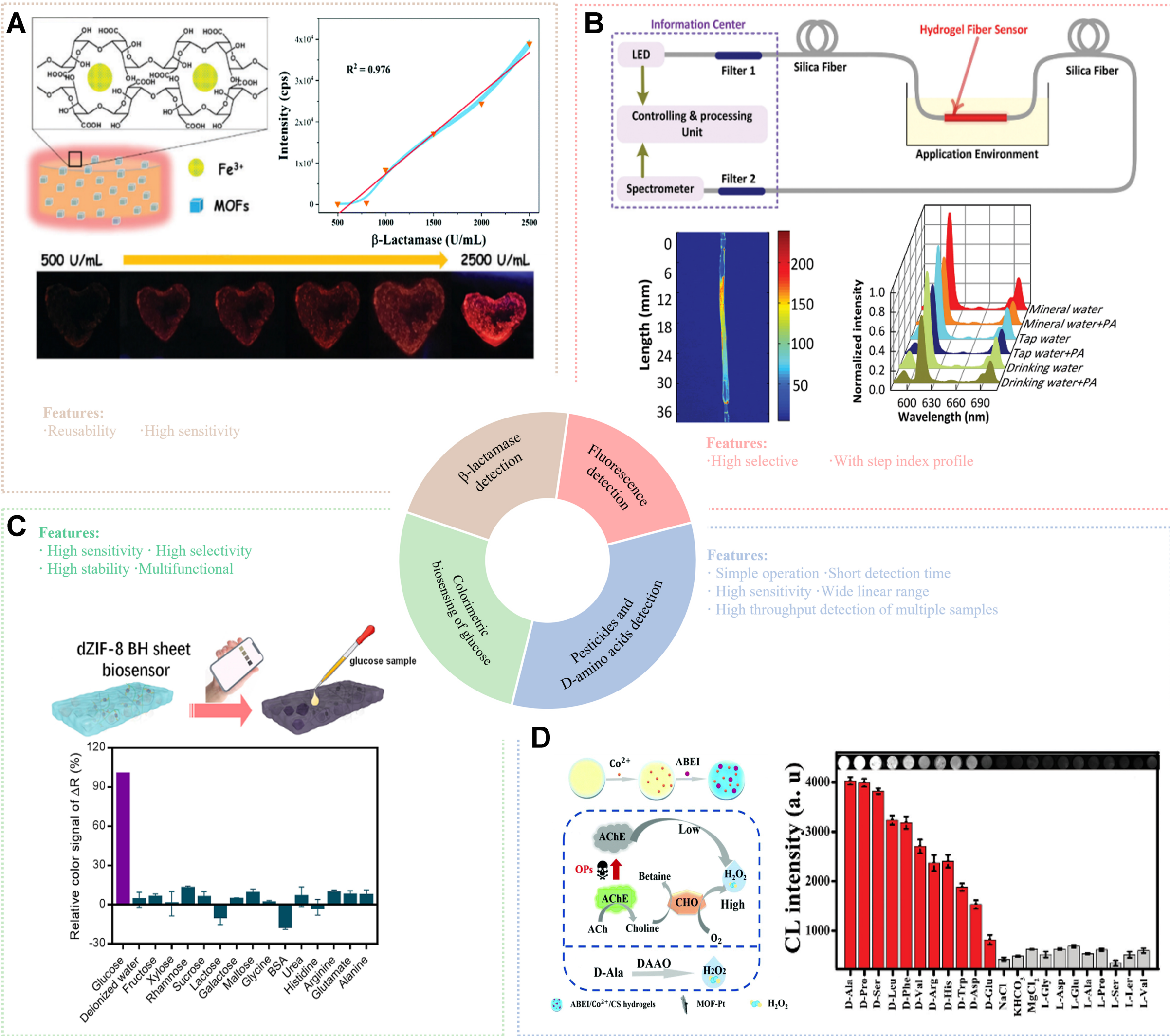

Figure 7. The illustration and the image of the preparation, application, and detection performance of the MOFs-based hydrogel. (A) The illustration of the composite hydrogels **1**@SA. The linear curve between intensities of **1**@SA and the β-lactamase concentrations with error bars. And the photographs of the **1**@SA hydrogels toward the various concentrations of β-lactamase serum solutions. Reproduced with permission from ref[89]. Copyright 2018 Royal Society of Chemistry; (B) The illustration of the detection platform. The pseudo-color image of the scattered light intensity along the hydrogel optical fiber axis. Fluorescence responses to practical water samples including mineral water, tap water, and drinking water. Reproduced with permission from ref[92]. Copyright 2018 Royal Society of Chemistry; (C) Schematic illustration of the dZIF-8 BH portable biosensor for glucose detection. And the selectivity of the biosensor toward glucose. Reprinted (adapted) with permission from ref[94]. Copyright 2020 American Chemical Society (Condition: 1 mM glucose; 10 mM interferents; incubation for 15 min); (D) The schematic illustration of the fabrication of ABEI/Co^{2+}/CS hydrogel and the detection principle of the hydrogel towards OPs. The comparison between $_D$-AAs and $_L$-AAs, and insets show the corresponding CL imaging measured at an exposure time of 3 min. Reproduced with permission from ref[13]. Copyright 2018 Royal Society of Chemistry. MOFs: Metal-organic frameworks; CS: chitosan; OPs: organophosphorus pesticides; CL: chemiluminescence.

In a separate study, Lian *et al.* developed a MOF-based hydrogel in the form of a sandwiched mixed matrix membrane [Eu@MIL-116(Ga)@Alg] for the detection of mitoxantrone[91]. This membrane demonstrated remarkable sensitivity, selectivity, and detection capabilities in serum, utilizing a novel detection principle based on Förster resonance energy transfer (FRET). While many luminescent MOFs have been discovered as potential detectors and sensors, the complexity of their detection processes often limits on-site applications. To address this, Zhao *et al.* introduced a novel and rapid sensing platform by integrating MOFs into hydrogels on an optical fiber[92]. This core-clad structure enhanced light delivery and luminescence collection while protecting the MOFs from harsh environments. At the same time, it allowed for analyte penetration and interaction. The platform showed highly selective detection of explosive picric acid using water- and thermally stable europium(Eu), 1,4-naphthalenedicarboxylic acid (H2NDC) (EuNDC) as the fluorescent material, as demonstrated in a representative experiment [Figure 7B].

Organophosphorus pesticides, widely used for their high efficiency, are highly toxic and harmful to humans. Overuse disrupts ecosystems and threatens human health. To address this, Jia *et al.* developed MOF-on-MOF hydrogels capable of detecting pesticides and degrading them after use[93]. They fabricated a composite material (ZIF-8-on-Zn_2@SA) by using MOF(Zn_2) as the core and wrapping it with ZIF-8. The porous structure of ZIF-8 exposes nitrogen sites, enabling high chemical activity and strong fluorescent emission. This composite can detect thiophanate-methyl (TM) visually, offering a broad linear range, low detection limit, and high recovery rates, making it promising for agricultural applications. Enzyme-based biosensing can be selective and efficient, but enzymes often lose activity. To overcome this, Zhong *et al.* created a hybrid sensor by co-encapsulating enzymes in ZIF-8 and double-crosslinked alginate [Figure 7C][94]. These enzymes convert glucose into a blue-violet product, facilitating colorimetric glucose biosensing with smartphone integration. The enzymes remained stable and active for 30 days at room temperature. Further advances were made by Shen *et al.*, who grafted UiO-66-NH_2 and PAMAM onto sodium alginate to create hydrogels (SA@UiO-66-NH_2@PAMAM) that independently degrade organophosphorus derivatives[95]. Building on this, Chen *et al.* developed a MOF-based hydrogel that visualizes nerve agent hydrolysis via a yellow color change[94]. This hydrogel can be easily shaped into cotton and used as a multifunctional sensor with smartphone integration. Sun *et al.* designed a colorimetric sensor by combining porphyrin-based MOFs with polyacrylamide-DNA hydrogel, achieving strong peroxidase-like activity and stability[96]. The sensor demonstrated excellent selectivity, a wide linear range, and low detection limits, making it both user-friendly and effective for chemical sensing. In another approach, Lu *et al.* developed a chemiluminescence sensor for detecting organophosphorus pesticides and D-amino acids[13]. Using N-(4-aminobutyl)-N-ethylisoluminol/Co^{2+}/CS hydrogels as the matrix, catalyzed by MOFs [Figure 7D], they enhanced sensor sensitivity. The system detects up to 17 types of organophosphates by inhibiting acetylcholinesterase (AChE) activity, which reduces H_2O_2 production and affects the chemiluminescence system. It can also detect other reactants that produce H_2O_2.

The collective endeavors of various research teams showcase the remarkable progress in developing MOFs-based hydrogels for advanced and selective chemical sensing applications. Furthermore, the innovative applications extend to addressing environmental concerns, such as the detection of organophosphorus pesticides and the development of multifunctional hydrogels for agriculture. These advancements highlight the potential of MOFs-based hydrogels as crucial contributors to the future of detection and sensor technologies, providing solutions to pressing challenges across various fields, including healthcare and environmental protection.

Biomedical application

Antibacterial

MOFs-based hydrogels have emerged as a cutting-edge approach to address the challenges associated with bacterial infections and delayed healing. Bacterial adhesion and colonization hinder wound healing. According to the three reported MOFs, Gwon *et al.* fabricated three bioactive MOFs-based hydrogels with diacrylated polyethylene glycol, 4-arm thiolated polyethylene glycol (PEG), and MOFs[97]. The release test of MOFs-based hydrogels showed high-performance antibacterial activities and stability. Moreover, one of them exhibited an excellent 99.9% antibacterial effect without cytotoxicity in human dermal fibroblasts.

Photocatalysis can promote skin wound healing by facilitating certain reactions. Deng *et al.* introduced injectable double-network MOF-based hydrogels (Au@ZIF-8) that generate reactive oxygen species (ROS) under light irradiation[98]. Compared to traditional ZIF-8, the composite hydrogels exhibit enhanced light absorption and improved charge carrier separation, leading to more efficient ROS generation. These hydrogels demonstrate bactericidal activity, remain stable and safe, and promote wound healing [Figure 8A], highlighting their potential as wound dressing materials. Han *et al.* developed photo-responsive hydrogels strengthened with Prussian blue nanoparticles (PBNPs)[99]. These hydrogels capture bacteria via electrostatic adsorption, disrupting the bacterial membrane surface potential and respiration. Combined with their photothermal properties, the hydrogels effectively eliminate bacteria. Additionally, they exhibit excellent mechanical strength, biocompatibility *in vitro*, and antibacterial properties *in vivo*. Despite the development of many wound dressings, achieving effective bacterial prevention, efficient release of bactericidal agents, and avoiding overhydration remains challenging. Yao *et al.* addressed these challenges by loading ZIF-8 into a porous PVA hydrogel membrane[100]. This composite hydrogel exhibits antibacterial and anti-inflammatory properties while maintaining a large contact angle (120°) for physiological fluids, preventing the absorption of unwanted liquids. The MOFs release Zn(II) ions slowly, while the PVA membrane protects the MOFs from degradation in physiological fluids. For diabetic patients, delayed wound healing often leads to diabetic foot ulcers, affecting about 15% of patients. Huang *et al.* developed a curcumin-based MOF hydrogel coated with quaternary ammonium salt CS to enhance diabetic wound healing[101]. The inclusion of Zn(II) ions and vancomycin strengthens the hydrogel's antibacterial properties, rapidly killing captured bacteria. Anti-inflammatory properties of curcumin and photothermal performance of the hydrogel create an immune microenvironment that accelerates healing. Li *et al.* created an injectable hydrogel with antibacterial and antioxidant properties by incorporating α-lipoic acid, which helps reverse oxidative stress-induced cell damage and promotes cell proliferation and migration[102]. Zhang *et al.* designed a zinc MOF-based hydrogel with alginate and poly(propylene glycol) to integrate photodynamic therapy, enhancing the antibacterial effect by disrupting bacterial membranes and increasing ROS production[103]. Qiu *et al.* developed a Zn-MOF-based hydrogel with high ROS scavenging capacity and sustained antibacterial activity, making it suitable for regulating ROS-dominated inflammatory environments[104].

Collectively, these studies showcase the remarkable progress in developing MOF-based hydrogels as versatile and effective materials for antibacterial applications in wound healing. These hydrogels hold great promise for enhancing therapeutic outcomes and addressing challenges in wound care.

Wound healing and drug delivery

There are other ways to promote the healing of diabetic foot ulcers. Copper ions are reported to be active for wound healing, but the copper ions concentration in the healing is proven as toxic level. Xiao *et al.* synthesized a Cu-based MOF with polymer hydrogels and fabricated a MOF-hydrogel system that can release copper ions in an appropriate concentration[105]. Through the reference experiment, the pure MOF nanoparticles which will degrade in the protein solution are protected well from degradation by the hydrogels. The copper ions are released but the concentration is kept at a safe level, and the wound healing is accelerated. Yang *et al.* reported a MOFs-based hydrogel hybrid system that can continuously release hydrochloride, curcumin, and Cu(II) ions, while also maintaining a moist microenvironment that promotes wound healing in diabetic mice[106]. Via the experiment to the two call lines (HaCat and HSF cells), the cytotoxicity and healing effects of MOFs-based hydrogels are demonstrated, with *in vivo* local treatment showing excellent therapeutic efficacy in enhancing the healing of diabetic wounds. Via a simple solvothermal reaction, Wang *et al.* fabricated donut-like MOFs and furthermore fabricated a light-responsive hydrogel[107]. The tough surface of the CuNA facilitates the loading and release of basic fibroblast

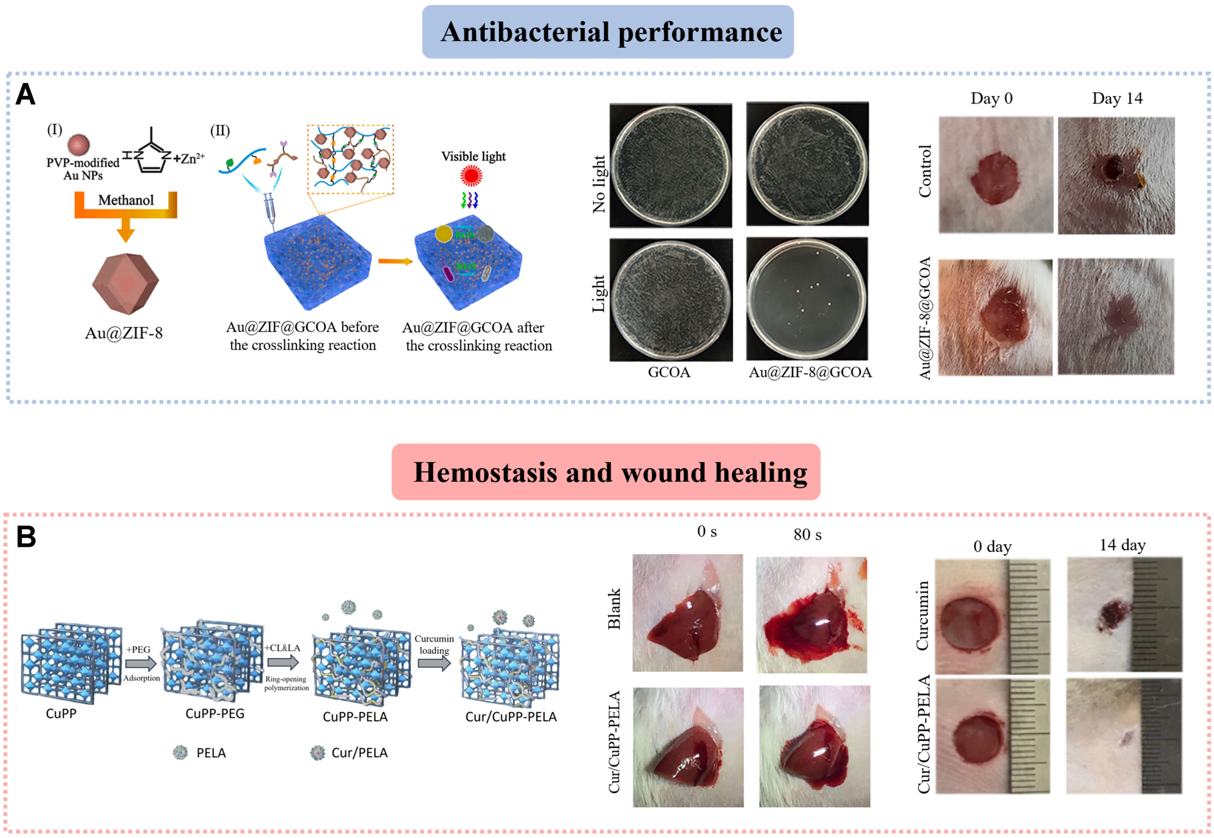

Figure 8. The illustration of preparation and the performance about biomedicine of the MOFs-based hydrogel. (A) The illustration of fabrication procedure of the Au@ZIF-8 and Au@ZIF@GCOA, and the antibacterial principle of the Au@ZIF@GCOA. The photograph of visible colony units of *E. coli* on Luria - Bertani agar plate. And representative photos of wounds on the backs of mice with different treatments at different periods. Reproduced with permission from ref[98]. Copyright 2021 Elsevier; (B) The illustration of the fabrication procedure of the Cur/CuPP-PELA hydrogel. *In vivo* hemostatic capacity evaluation of Cur/CuPP-PELA. And wound healing photographs at designed times with different treatments; each scale is 1 mm. Reproduced with permission from ref[99]. Copyright 2022 Elsevier. MOFs: Metal-organic frameworks; ZIF: zeolitic imidazolate framework.

growth factor. The composite hydrogel demonstrates strong mechanical strength, excellent biocompatibility, antibacterial properties, and bioactivity.

Bacterial infections in wounds represent a major threat to public health. Wang *et al.* recently presented an innovative approach to address this concern by introducing a photothermal zirconium-ferrocene MOF nanosheets functionalized with carrageenan-based hydrogels incorporating polyethylene glycol dicarboxylic acid[108]. The MOFs-based hydrogels were designed to capture bacteria through the generation of ROS, leading to bacterial destruction. Additionally, the hydrogels exhibited bactericidal activity by degrading H_2O_2 into toxic hydroxyl radicals. These composite hydrogels demonstrated superior bactericidal efficacy and low biological toxicity, with the added benefit of enhanced sterilization through their photothermal performance. In another study by Nie *et al.*, composite hydrogels were engineered for the treatment of chronic wounds without causing additional inflammation. This was achieved by incorporating a curcumin-loaded MOF[109]. In *in vivo* conditions, the composite hydrogels transformed into hydrogels, tightly adhering to and completely sealing the wound, thereby promoting wound healing. Notably, the hydrogels effectively trapped bacteria and fluid dressing, inhibiting the further dispersal of pathogenic microorganisms. Figure 8B illustrates the high photothermal effect, immune-modulatory properties, hemostasis, and temperature-sensitive sol–gel transition capacity exhibited by these composite hydrogels.

Osteoarthritis affects millions of people worldwide. Synergistic therapy provides long-term joint lubrication without shear thinning and mitigates systemic toxicity associated with oral administration. Wu *et al.* developed a core-shell MOFs-based hydrogel[110]. The poly(N-isopropylacrylamide) (pNIPAm) can be programmatically grown on the surface of the MOFs. The reversible swelling and collapsing behavior of the composites can be controlled by temperature, allowing for thermal-responsive drug release. When utilized as water lubrication additives, the composites significantly reduce the coefficient and wear volume. In cell culture studies with HeLa and BEAS-2B cells, the composites demonstrated excellent biocompatibility. Additionally, cobalt (Co) ions are known to promote angiogenesis and bone regeneration. Sun *et al.* fabricated 2-ethylimidazole (eIm)-doped ZIF-67 and furtherly create nanocomposite hydrogels[111]. By changing the linker composition, the releasing of the Co ions from the nanocomposite hydrogels can be controlled, and hybrid hydrogels can release Co ions for up to 21 days. The *in vitro* study demonstrates that the nanocomposite hydrogels can promote bone regeneration and show their neovascularization abilities and good biocompatibility.

The challenges in tumor treatment, such as incomplete tumor removal and systemic toxicity, limit its effectiveness. Kaur *et al.* fabricated plasmonically active hydrogels that can controllably release drugs[112]. The plasmonic hydrogels showed viscoelastic and self-healing properties due to the interaction between ZIF-8 and carboxymethyl CS. Benefiting from the size of ultrasmall gold nanoparticles, the nanoparticles can be checked in the urine, which proves the PHG can be degraded. Light is used wildly on the treatment of the tumor including photothermal therapy and photodynamic therapy. Li *et al.* encapsulated liquid metal [eutectic gallium indium (EGaIn)] nanoparticles in the MOFs (ZIF-8) and fabricated nanoparticle composite materials [liquid metal supraparticles (LMSPs)][113]. The nanoparticles possess the performance of stable photothermal and controllable Zn(II) ions releasing. Furthermore, they combined LMSPs with alginate-based hydrogels to fabricate injectable hybrid hydrogels. The hybrid composite hydrogels performed at the capacity of safety, stability and biodegradation. Zhang *et al.* reported MOFs-based hydrogels as intelligent nanobots [$FeSe_2$–Ce6/MOF@Aichi hemagglutinin/polyethyleneimine/CpG@hexahydrophthalic anhydride nanoparticles (FSMH)] that can the intracellular redox balance and trigger the immune response in cancer cells[114]. The FSMH can convert hydrogen peroxide into hydroxyl radicals, thereby reducing intracellular oxidative stress. The negative charges on the hydrogel ensure the system remains highly stable in blood circulation. Unlike traditional MOF materials, beta-cyclodextrin-based MOFs offer brilliant properties compared to conventional MOFs. Shao *et al.* integrated beta-cyclodextrin-based MOFs with polymers to fabricate two complexes with distinct morphologies and structures[115]. By employing the hydrophobic molecule curcumin, the hybrid materials are proven to possess the ability to stabilize the included drug and controll the drug releasing[116].

Other application

The application of MOF-based hydrogels has expanded beyond the above uses, demonstrating versatility in various fields. This section highlights several innovative developments in MOF-based hydrogels for different applications.

One notable example is the use of 3D printing technology. Liu *et al.* developed stretchable and tough MOF-based hydrogels by combining hydrogels with MOF ligands to create 3D printing ink. They characterized the ink and optimized parameters to adjust the modulus, strength, and toughness of the printed structures[117]. Similarly, Zhang *et al.* created MOF-802@PVA hydrogel composites that exhibit excellent proton conductivity and stability, making them promising for energy-related applications, although conductivity decreases at higher temperatures[118].

MOF-based hydrogels have also been used in smart materials. Cui *et al.* designed self-bleaching photochromic hydrogels by integrating zinc-based MOFs and tungsten oxide. These hydrogels respond rapidly to ultraviolet (UV) light, enabling "writing" and "erasing" abilities [Figure 9A][119]. Furthermore, Nie *et al.* fabricated composite paper with ZIF-8 and cellulose pulp, which demonstrated exceptional performance in adsorption, filtration, and sterilization, including a high PM2.5 removal efficiency of 99.68%[120].

In biomedical applications, Wang *et al.* synthesized hydrogel-metal-organic-framework nanoparticle composites (HMOFNCs), which immobilized enzymes and biomolecules, protecting their activity and allowing control over biomacromolecule performance[121]. Tang *et al.* advanced this field by producing a double-network hydrogel with strong mechanical properties and multi-color fluorescence, suitable for applications such as QR codes and information storage [Figure 9B][122].

MOF-based hydrogels also demonstrate significant potential in proton-conducting materials. Kong *et al.* developed MeSA@MOF-303-PVA hydrogels with tunable proton conductivity by doping MOF-303 nanocrystals with methanesulfonic acid (MeSA)[123]. In agriculture, Lin *et al.* created dual-sensitive MOF-based hydrogels that enhance fertilizer release, combining temperature- and pH-sensitive units with MIL-100(Fe) to improve water retention and slow-release performance [Figure 9C][124].

In the realm of mechanical and structural applications, Xu *et al.* developed nanocomposite hydrogels that are highly stretchable and compressible, able to recover quickly from strains of up to 500%[125]. de Lima *et al.* demonstrated that the crystal size of UiO-66 MOFs impacts water absorption and mechanical strength, making these hydrogels valuable for biocompatible applications[126]. Jia *et al.* further expanded the use of MOF-based hydrogels for visual detection, developing Ru@UiO-OH hydrogels that detect volatile trimethylamine (TMA) vapor through fluorescence changes [Figure 9D][127].

MOF-based hydrogels are also being explored in energy and electronic applications. Kim *et al.* developed a hydrogel coupled with a MOF film that exhibits robust thermoelectric harvesting capabilities, showing high thermal voltage and current output[128]. Khan *et al.* proposed Zn-MOF-based hydrogels with excellent tensile properties and electrical conductivity, making them suitable for wearable strain sensors and electronic skin[129]. Finally, Xiao *et al.* synthesized pH-sensitive fluorescent hydrogel microneedle tips that can be integrated with smartphones for wound pH visualization, applying machine learning algorithms for enhanced accuracy[130].

In conclusion, the diverse applications of MOF-based hydrogels, ranging from biomedical sensing to energy harvesting and smart materials, highlight their versatility and growing importance across multiple fields. As ongoing research continues to expand their capabilities, these hydrogels are poised to play a critical role in future technological advancements.

CONCLUSION AND OUTLOOK

Conclusion

Recent years have witnessed an increase in literature regarding the use of MOF materials, reflecting growing interest within the research community. Among these, MOFs-based hydrogels have gained attention. This review summarizes the recent developments of MOFs-based hydrogels by highlighting the quantity of reported research. Due to their impressive flexibility and physical and chemical stability, these hydrogels have been studied and widely applied. They have been shown to offer higher performance on processability and handling than normal MOF powders [Figure 10].

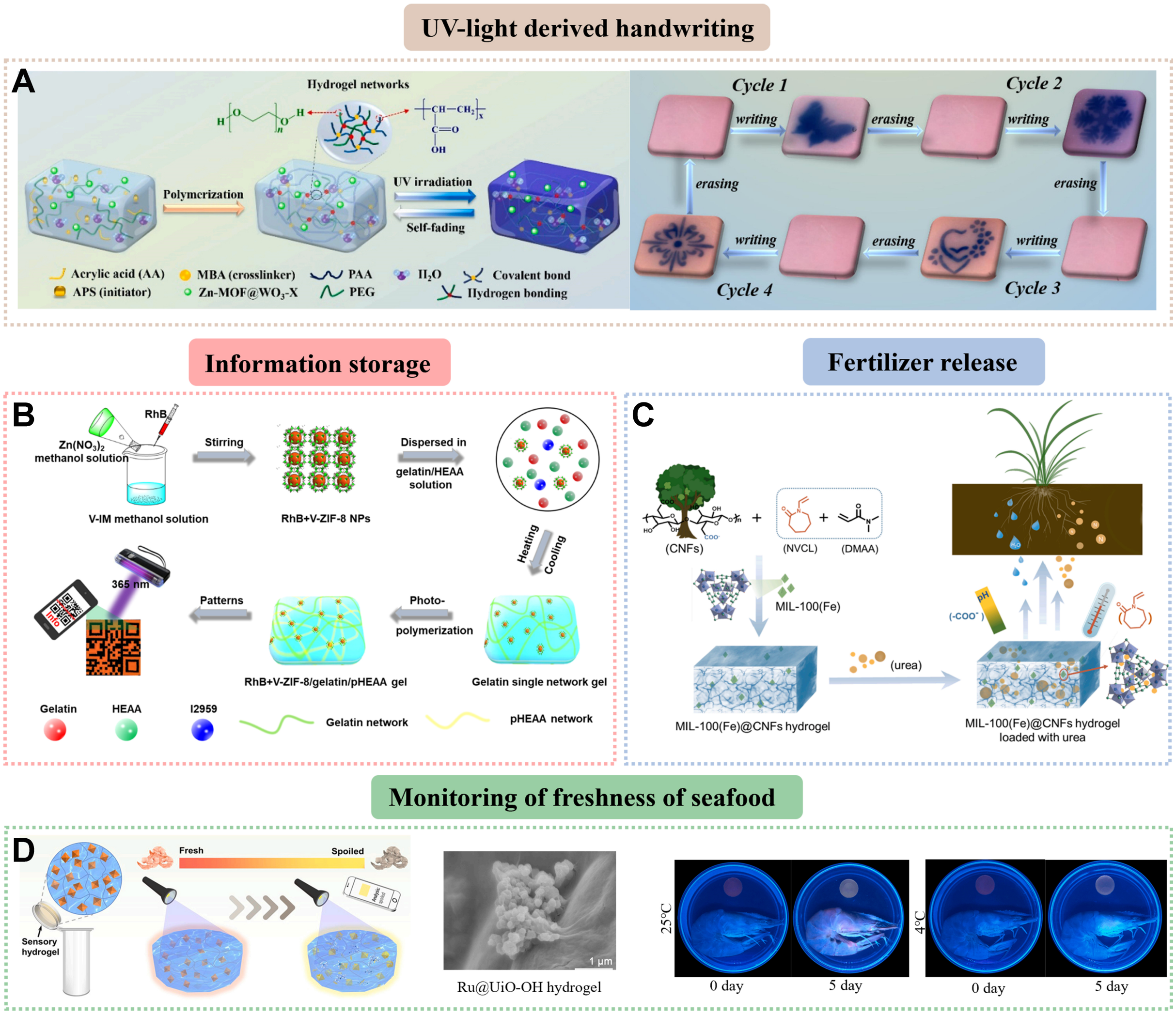

Figure 9. The illustration of the preparation and different applications of MOFs-based hydrogel. (A) The illustration of the fabrication procedure of the P(AA/PEG)-Zn-MOF@WO_3-3. And illustration of the patterning process of P(AA/PEG)-Zn-MOF@WO_3-3 hydrogel by irradiation with UV light through a mask. Reproduced with permission from ref[119]. Copyright 2023 Elsever; (B) The illustration of the fabrication procedure and the information storage of the OFM + NMOF/gelatin/pHEAA hydrogel. Reprinted (adapted) with permission from ref[122]. Copyright 2022 American Chemical Society; (C) The illustration of the fabrication procedure and the fertilizer release of MOF MIL-100(Fe)@CNFs hydrogel. Reproduced with permission from ref[124]. Copyright 2021 Elsevier; (D) The illustration of the internal structure and application of the Ru@UiO-OH. The SEM image (1 μm) of Ru@UiO-OH hydrogel. And sensory hydrogel images for monitoring the freshness of shrimp stored under different conditions in different periods. Reproduced with permission from ref[127]. Copyright 2023 Elsevier. MOFs: Metal-organic frameworks; UV: ultraviolet; OFM: organic fluorescent molecular; NMOF: nano metal–organic frameworks; SEM: scanning eletron microscope.

This article introduces MOFs, hydrogels, and MOF-hydrogel composites, and summarizes the application of MOF-hydrogel composites on water treatment, drug delivery and wound healing, sensors, catalysts, and other fields. Among the large numbers of MOFs, the MIL-101, ZIF-8, MOF-801, and MOF-808 are the most frequently selected, and PVA, pAAm, carrageenan, sodium alginate are commonly used as hydrogel matrices. These materials are successfully employed to fabricate various kinds of MOFs-based hydrogels, promoting advancements in synthesis strategies and widening the scope for rational optimization. Additionally, the stabilization, accessibility, ease of handling, and flexibility of the MOFs are improved, expanding their potential applications. However, current synthesis strategies for MOF-based hydrogels are limited by the variety of matrix materials. Therefore, further exploration of environmentally friendly

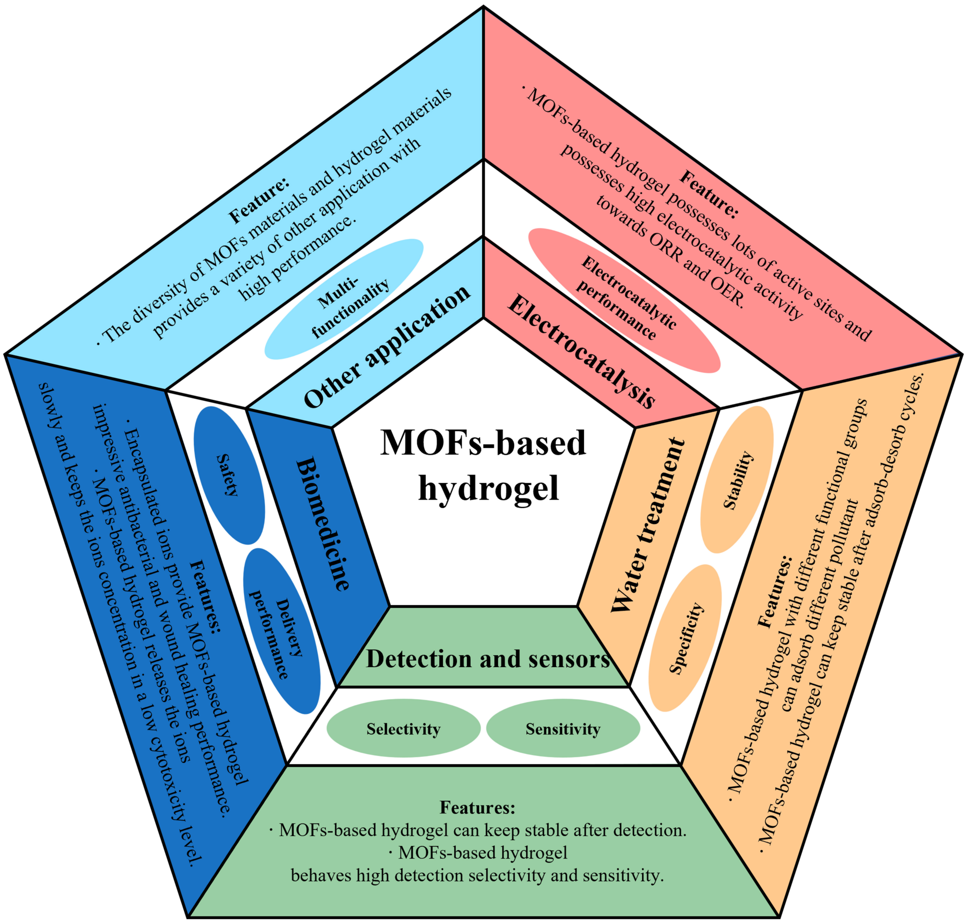

Figure 10. The illustration of the application and features of the MOFs-based hydrogel. MOFs: Metal-organic frameworks.

matrices and advanced pure MOF hydrogel materials is essential.

Challenge

Although numerous studies of MOFs-based hydrogel have been conducted, their application remains far away from reaching a mature stage. Maintaining the structural integrity and activity of the MOF crystals is crucial for fabricating MOFs-based hydrogel. However, under current fabrication conditions, the stability of MOF crystals cannot be guaranteed. As a result, confirming the stability requires characterization using X-ray diffraction and nitrogen isothermal adsorption measurements after the combination of the MOF crystals with the hydrogel matrix.

The synthesis of the MOFs-based hydrogel by direct mixing is limited by particle aggregation and poor matrix interaction, which affects the performance of the composite material. On the other hand, *in situ* MOF growth is a promising method to overcome these limits, but there is little research on it. MOF synthesis typically produces brittle and powdery samples. Due to the inherent fragility and poor processability of MOF powder, many MOF polymer composites still have obvious drawbacks. Polymer MOF composites formed by blending usually lead to poor MOF aggregation, and the compatibility between the polymer and MOF is low, which affects the performance of the material. Meanwhile, most of the preparation process of MOF particles involves toxic reagents, resulting in poor biocompatibility of the MOF powder, which limits the large-scale and long-term application of MOF composite materials in water treatment and biomedicine. So, it is important to highlight the challenges related to the industrial-scale production of MOFs (such as using eco-friendly approaches and improving expiration date).

Outlook

Despite the numerous challenges, MOFs continue to be favored candidates due to their significant advantages. The large-scale and commercial fabrication procedure of MOFs-based hydrogels with stability indicates their outstanding potential for industrial manufacture. However, there is a need to develop sustainable development methods for synthesizing the matrices of MOFs-based hydrogels that ensure consistent quality. Once economical MOFs-based hydrogels are applied in large quantities at an industrial scale, it will represent a meaningful milestone in the development of MOF materials.

We hope this review encourages researchers to generate innovative ideas. The variety of MOFs and matrices within these hydrogels provides endless opportunities for adjusting their functional properties, making them very promising for a wider range of applications in the future.

Future directions

The future development of MOF-based hydrogels offers many exciting possibilities across various scientific fields. One critical area for advancement lies in the careful selection of ligands and metal ions. Optimizing these components can enhance the binding strength between inorganic clusters and coordinating groups, leading to better stability and performance of hydrogels. This is particularly important in applications that demand long-term stability or controlled release properties, such as drug delivery or catalysis. Another promising direction is further research into the structure-performance relationship of MOF-based hydrogels. Combining this with *in situ* characterization techniques or other innovative approaches will provide deeper insights into how structural changes affect the material's functionality. Understanding these mechanisms can guide the design of more efficient hydrogels, especially for applications in environmental remediation, energy storage, or biomedical fields[131-134]. While MOFs such as IRMOF and CPL-MOF have been underexplored in hydrogel systems, future research could expand their use by developing new green hydrogel matrices. These could offer more sustainable and environmentally friendly options for industries looking to reduce their ecological footprint[135]. In the biomedical realm, there is a shift from purely *in vitro* experiments toward *in vivo* applications. Research is increasingly focusing on understanding the mechanisms of MOF-based hydrogels in living organisms. This transition is crucial for developing effective clinical therapies, particularly in wound healing, cancer treatment, and drug delivery systems.

DECLARATIONS

Authors' contributions

Project administration, conceptualization, investigation, writing - review and editing: Wang B
Investigation, writing - review & editing: Fu H, Shen J, Zhang Y, He J
Writing - original draft: He R

Availability of data and materials

Not applicable.

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Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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