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Development of multifunctional metal-organic frameworks (MOFs)-based nanofiller materials in food packaging: A comprehensive review

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Abstract

Background: Food packaging plays an indispensable role in reducing food postharvest losses and enhancing sustainable development. Metal-organic frameworks (MOFs)-based film materials showed potential in the field of food packaging. Among various nanofillers, MOFs stand out as multifunctional materials characterized by their convenient integration with polymer matrix to develop enhanced, active and intelligent food packaging materials.

Scope and approach: This review initially provided a concise overview of the several synthesis strategies of MOFs and three primary methods for the fabrication of MOFs-based films. Furthermore, the multifaceted functions of MOFs as reinforcers, active agents, and indicative factors in the context of food packaging have also been systematically reviewed. Especially, the functional MOFs-based films for the encapsulation of diverse bioactive compounds applied to delay food spoilage and real-time monitoring of food freshness were discussed. Finally, the toxicological impacts of MOF fillers in food packaging applications were highlighted, encompassing an evaluation of potential risks and the exploration of mitigation strategies.

Key Findings and Conclusions: The MOFs-based films emerge as promising candidate materials for food packaging applications, as the incorporation of MOFs substantially enhances the mechanical properties, water resistance, and barrier performance of pure biopolymer films. However, traditional food packaging methodologies encounter several challenges, including antibacterial, antioxidant properties, and the effective removal of active molecules. To overcome these limitations, the incorporation of various MOF nanomaterials to enhance the physical and functional attributes of packaging films have been persistently investigated. Therefore, MOFs-based multifunctional film materials could be a viable alternative to develop food packaging.

Keywords: Metal-organic framework; Food packaging; Reinforcer; Antimicrobial; Antioxidant; Carrier

1. Introduction

Food packaging is crucial for safeguarding against chemical, physical, and biological hazards that can compromise food integrity and safety. Synthetic polymers are characterized by self-efficiency and simplicity, fulfilling the fundamental requirements for protection, sealing, and containment of products (Siddiqui et al., 2024). Among them, plastics are extensively employed in packaging due to their convenience, low-cost, robust chemical stability, excellent mechanical and barrier properties. However, the lack of sustainability and biodegradability of plastics poses a substantial challenge, adversely affecting human health and the environmental ecosystem (Zhang, Ahari, Zhang, & Jafari, 2023). Hence, investigations into food packaging must solve the environmental problems caused by the uncontrolled applications and inappropriate disposal of non-biodegradable materials, and it is imperative to innovate and develop alternative materials for decreasing environmental impact (Flórez, Guerra-Rodríguez, Cazón, & Vázquez, 2022; Zhang et al., 2023).

Recently, the substitution of biodegradable natural renewable polymers for petroleum-based compounds has become the focus of research endeavors (Abedi-Firoozjah et al., 2023; Alizadeh, Khezerlou, Tavassoli, Abedini, & McClements, 2024; Roy et al., 2023). Natural biopolymers including cellulose (Pang et al., 2024; Zhang et al., 2023), starch (Sanchez, Pinzon, & Villa, 2022; Zhang et al., 2022), chitosan (Chen et al., 2023; Nian, Xie, Sun, Wang, & Cao, 2023), gelatin (Khan, Riahi, Kim, & Rhim, 2023; Riahi, Hong, Rhim, Shin, & Kim, 2023), and sodium alginate (SA) (Zhang, Zhang, Zhang, et al., 2024; Zhang et al., 2023) have been extensively investigated within the food packaging industry. Regrettably, a considerable gap persists between the current state of biopolymer research and their practical applications in comparison to traditional packaging materials, attributed to their high production costs, inferior performance, and limited ductility (Feng et al., 2023). Therefore, it is necessary to enhance the mechanical and barrier properties of biodegradable packaging materials to protect food from the external atmosphere containing moisture and mechanical hazards. Through the implementation of various strategies aimed at augmenting the performance of biopolymers, including chemical modifications (cross-linking and graft copolymerization), physical modifications (filler incorporation and laminated composite formation), the utilization of deep eutectic solvents, irradiation-induced and biological enzyme treatments to enhance the performance of biopolymers, rendering them more adept for applications in food packaging, while concurrently preserving their environmental protection and sustainability attributes (Khajavian, Vatanpour, Castro-Muñoz, & Boczkaj, 2022).

The advent of inorganic nanomaterials (specially MOFs and two-dimensional (2D) materials) has introduced innovative approaches to augment the physical and chemical attributes of the polymer matrix in food packaging. These enhancements encompass the following aspects: augmentation of mechanical properties (Castro-Muñoz et al., 2019), enhancement of barrier properties (Vatanpour et al., 2023), improvement in water vapor transmission (Castro-Munoz, 2023), augmentation of chemical resistance (Castro-Munoz, Ahmad, Malankowska, & Coronas, 2022), and enhancement of antimicrobial attributes (Gontarek-Castro, Rybarczyk, Castro-Muñoz, Morales-Jiménez, Barragán-

Huerta, & Lieder, 2021). Among them, owing to their high specific surface area, tunable pore structure, selective adsorption capabilities, excellent chemical stability, low density, and ease of processing, MOFs have been widely investigated in the domain of food packaging field. MOFs constitute a category of porous nanomaterials, wherein organic ligands (such as dicarboxylic acid, tricarboxylic acid, tetracarboxylic acid, and imidazolate) and metal ions (serving as secondary building units) are interconnected to create an open crystalline scaffold with consistent porosity (Alizadeh, Khezerlou, Tavassoli, Abedini, & McClements, 2024; Zhang et al., 2024). Moreover, MOFs are distinguished from other materials and can manifest unique chemical functionalities and intriguing adsorption characteristics through the concatenation of functional groups. In particular, due to their enduring porosity and pronounced crystallinity, MOFs can effectively engage with a diverse array of analytes (Cheng, Tang, Zhang, Wu, & Yang, 2021). The inorganic-organic hybrid nature of nano-MOFs enables their facile integration with polymer matrices, rendering them highly appealing as nanofillers for the fabrication of high-performance nanocomposites. Different from other food packaging fillers, the advantages of MOFs are predominantly manifested in their multifunctionality. For instance, the remarkable benefits of MOFs facilitate their utilization as reinforcing agents (Khan et al., 2023; Wei et al., 2023), active components (Riahi et al., 2023), luminescent indicators (Tang et al., 2023), and bioactive carriers (Sanchez et al., 2022; Wang et al., 2022), thereby offering a prospective foundation for the advancement of diverse, targeted MOFs-based packaging films. Currently, some researches have underscored the potential of multifunctional MOFs-based films for packaging applications (enhanced, active and intelligent), attributable to their superior physical properties, effective gas control within the packaging, as well as their antibacterial and antioxidant attributes (Alizadeh, Khezerlou, & McClements, 2024; Chen, Wang, Kong, & Wang, 2024; Geng et al., 2023; Sharanyakanth et al., 2020).

Therefore, this review provides a comprehensive overview of the recent advancements in MOFs nanomaterials within the realm of food packaging, and discusses the mechanical properties, water resistance, barrier performance, thermal stability, as well as the antibacterial and antioxidant characteristics of MOFs-based food packaging films. It also accentuates the latest research findings pertaining to the utilization of MOFs as indicator functional factors and carriers in food packaging, alongside the practical deployment of MOFs-based films in active and intelligent food packaging applications (Scheme 1). Lastly, the toxic effects of MOFs materials in packaging applications are emphasized, and offers a comprehensive evaluation along with strategies for mitigating potential risks. Previously published review on MOFs-based food packaging films (Sharanyakanth et al., 2020), focuses on the synthesis of MOFs and its application in food packaging, however, lacks an exposition on the utilization of MOFs as reinforcers to improve the physical properties of packaging materials and MOFs as indicative factors for monitoring food freshness. Hence, this review aims to present the most recent insights into the characteristics and applications of MOF nanomaterials in enhanced, active, and intelligent food packaging systems. Additionally, this study is anticipated to furnish comprehensive details on the effect of MOF fillers in biopolymer-based sustainable and functional food packaging materials.

2. Synthesis strategies for MOFs-based packaging films

MOFs-based packaging films commonly consist of solid MOFs particles randomly embedding into a three-dimensional network structure and the aqueous phase medium formed by the hydrogel. Therewith, MOFs and the hydrogel matrix could be considered as the dispersed phase and the flowing phase, respectively (Wang, Xu, Gao, Yao, & Zhang, 2019). Moreover, the physical and chemical cross-linking properties of the polymer materials and the hydrogen bonds between internal molecules can effectively combine with MOFs. The selection of synthetic strategies affects the final products, such as the structure of MOFs, the dispersibility of MOFs in hydrogels and the morphology of materials, thereby playing a crucial role in the performance and application of composite materials. Currently, the selection of synthesis methodologies for MOFs that are appropriate for utilization in food packaging is contingent upon the desired attributes of the MOF nanomaterials and their anticipated applications in the food industry (Alizadeh, Khezerlou, & McClements, 2024). Synthesis strategies generally include solvothermal/hydrothermal, ambient temperature stirring, microwave-assisted, ultrasound-assisted, electrochemical, and electrospinning approaches (Fig. 1a) (Zhang et al., 2024). Furthermore, the preparation process of MOFs-based packaging films can roughly be divided into three synthesis schemes (Fig. 1b-d): *in-situ* growth method, direct mixing method and one step method. In the field of food packaging, these methods can be chosen based on specific process requirements.

2.1. Preparation of MOFs for food packaging applications

The MOFs for food packaging was fabricated via a bottom-up approach, entailing the direct synthesis of non-layered MOF nanosheets comprising metal nodes and organic ligands. This method predominantly employs small molecule compounds, surfactants, or confined spaces to restrain the vertical growth of MOF nanosheets (Zhang et al., 2024). These synthetic strategies facilitate the precise control of the size, shape, and composition of the MOFs fabricated, enabling their customization for specific applications. Additionally, the synthetic method can be expanded to incorporate defects or dope MOFs, thereby generating hybrid materials with enhanced performance characteristics (Sharanyakanth & Radhakrishnan, 2020). Hence, there is an imperative need for diverse MOF synthesis methods to augment and fulfill the multifunctional attributes of MOF-based films.

Solvothermal/hydrothermal: this method remains the most prevalent approach for the synthesis of MOFs to date. The process involves the dissolution of metal ion precursors and organic ligands within the same system, which is then sealed within a stainless-steel chamber lined with polytetrafluoroethylene (PTFE) under specific temperature, pressure, and time conditions (Tang et al., 2023). Moreover, the pH level can be modulated by incorporating suitable acids and bases, thereby achieving the desired morphology and characteristics of the MOF. Nonetheless, the primary drawbacks of this method include the extended reaction duration and the necessity for organic solvents, which constrain its scalability and diminish the sustainability of the manufacturing process.

Ambient temperature stirring: the method entails the continuous agitation of metal precursors, organic ligands, and additional solvents at a consistent temperature, accompanied by stirring for a predetermined duration (Sultana et al., 2023). Owing to its absence of necessity for extreme temperature or pressure conditions and the facilitation of manipulating the reaction process, it holds considerable importance in the realm of sustainable chemical synthesis. Nevertheless, the principal constraint of this approach is the inadequate removal of the solvent, which ultimately culminates in the reduced purity of the resultant product.

Microwave-assisted: this approach is grounded in the interaction between moving charges in polar solvents and microwave radiation, which facilitates the synthesis of MOFs. The crystal growth can be modulated by altering pivotal parameters such as reactant concentrations, reaction duration, solvent nature, and energy input (Zhang et al., 2024). In contrast to conventional heating methods, this approach offers a unique reaction milieu for the system, expediting the synthesis of smaller crystals. Beyond enhancing yield and diminishing reaction time, the microwave-assisted synthesis also boasts the advantage of generating minimal or negligible by-products. Nonetheless, attaining consistent outcomes in MOF synthesis across diverse microwave apparatuses poses a significant challenge.

Ultrasound-assisted: the operational principle of this method is founded on acoustic cavitation, encompassing the creation and disintegration of bubbles within the solution to produce localized hot spots. The morphological attributes of MOFs fabricated via this method are influenced by ultrasonic frequency, intensity, solvent volatility, temperature, and the gas content of the solvent. Additionally, ultrasound facilitates the cleansing of the MOF surface and activates unsaturated active metal ion sites (Alizadeh, Khezerlou, & McClements, 2024). In comparison to the solvothermal method, the ultrasonic-assisted technique typically maintains elevated temperatures, prompting swift chemical reactions and immediate crystallization. However, it is imperative to cautiously assess the potential hazards associated with the noise generated by ultrasonic equipment, and large-scale production remains in its nascent stages.

Electrochemical: this approach involves submerging the electrodes (anode and cathode) into an electrolyte solution that contains a metal salt precursor and an organic ligand. The continual dissolution of metal salts at the anode ensures a steady supply of metal ions, which subsequently react with the conductive salts and organic linker molecules present within the electrochemical environment (Zhang et al., 2024). The electrochemical synthesis approach boasts advantages such as abbreviated reaction times, simplified processing, controllable operation, and adherence to safety and environmental conservation under ambient temperature and pressure conditions. Nevertheless, the cathodic reactions in this method have yet to reach full maturity, a situation that may stem from the nascent nature of the electrochemical synthesis pathway for MOFs, warranting further investigation.

Electrospinning: this method is highly appropriate for integrating MOFs into various hybrid materials, thereby endowing them with additional functionalities. The process involves amalgamating a slurry containing MOF with a polymer solution, followed by electrospinning to produce MOF-polymer composite nanofibers. Depending on the specific MOFs required, the electrospinning procedure can be fine-tuned by selecting appropriate solvents and polymers, as well as by adjusting electrospinning parameters. The synthesis of MOFs via electrospinning offers numerous benefits, such as simplicity, high efficiency, versatility, scalability, and the capacity to yield products with elevated surface areas (Zhang et al., 2024). It is noteworthy that the design and development of MOFs-based electrospinning nanofibers represent an efficacious strategy for their utilization as a superior carrier for biomolecular encapsulation. Electrospinning nanofibers possess the potential benefits of enhancing the dispersion of embedded materials, optimizing the efficiency of controlled release, augmenting stability, and boosting bioavailability in the delivery of food ingredients (Castro-Muñoz, Kharazmi, & Jafari, 2023). Hence, encapsulating functional molecules within MOFs-based nanofibers will furnish an appropriate storage milieu for these molecules, thereby ensuring efficient delivery. However, it is important to acknowledge that this method encounters challenges in scaling up production and the potential degradation of the resulting polymer material, necessitating further advancements.

2.2. Preparation process of MOFs-based film

The incorporation of synthesized MOFs or their precursors (metal ions and organic linkers) into diverse polymer substrates such as casting, coating and nanofiber films, results in varied properties and application outcomes (Roy et al., 2023). The predominant attribute of MOFs-based casting films is their superior mechanical robustness and flexibility, and the integration of rigid MOF components enhances the overall rigidity or brittleness of film, with the extent of enhancement contingent upon the quantity of MOF incorporated and its dispersion. While the incorporation of MOF may impact the processability of the casting film, such as melt fluidity and formability, the endowment of specific functionalities to MOF can provide novel attributes to the MOFs-based casting film (Sultana et al., 2023). The essential of MOFs-based coating films lies in their surface characteristics, and the incorporation of MOF can confer hydrophilic or hydrophobic surface properties to the coating. Furthermore, the addition of functional fillers into the coating enhances its capability for selective adsorption, catalysis, or sensing functionalities. And the homogeneity of MOF dispersion within the coating is critical for its overall performance (Zhang, Ahari, Zhang, & Jafari, 2023). The customization of pore size and porosity in MOFs-based nanofiber films is conducive to the selective response and regulation of target gases. Nanofiber films inherently possess a high specific surface area, and the incorporation of MOFs can significantly enhance their adsorptive capabilities, which ensures the precision of food monitoring and prolongs the shelf life of food products (Tavassoli et al., 2024). Additionally, the MOFs not only integrate with nanofiber membranes to fabricate multifunctional composite membranes but also contribute to the long-term stability of these films. All in all, the impact and underlying mechanisms of MOFs on various film materials vary significantly. It is imperative to select suitable film materials and MOFs based on the specific application criteria, and subsequently tailor the fabrication process accordingly.

2.2.1. *In-situ* growth method

The purpose of the *in-situ* growth method is to directly synthesize MOFs in a polymer matrix, eliminating the need to acquire MOFs separately. Specifically, this method involves preparing the hydrogel substrate, followed by adding soluble metal salts in a water solution, and allowing the metal ions to fully disperse and attach to the hydrogel network through physical or chemical effects. Then, organic ligands are introduced to bind with the metal ions, ultimately resulting in the formation of the desired MOFs-based film material (Shao et al., 2022). Typically, the composite material synthesized using the *in-situ* method exhibits excellent flexibility and moldability, while also ensures the uniform dispersion of MOF crystals within the polymer network. In addition, the *in-situ* method has a certain universality, and the obtained MOFs-based film materials possess remarkable properties, including abundant pores, good biocompatibility, and enhanced adsorption efficiency, meanwhile maintaining the original porous structure of MOF materials (Wang et al., 2022).

2.2.2. Direct mixing method

In this method, start by preparing nanoscale MOFs particles, which could require homogenizing pestle grinding mortar, and mixed with a certain formula with polymer precursors. After the formation of a three-dimensional network in the hydrogel, the MOFs particles were successfully adhered to the polymer matrix. The direct mixing method is extensively utilized in the preparation of MOFs-based packaging films owing to their simplicity, gentle reaction conditions, and ease of control over the content and structure of MOFs. Another advantage of the direct mixing protocol is the convenient combination of water-sensitive MOFs-ligands and hydrogels. Certain functional molecules that typically cannot directly bind to hydrogels can be incorporated into the polymer matrix by first combining them with MOFs as primary carriers. What is worthy of our attention is that MOFs can offer multiple binding sites for various small molecules and biomacromolecules through chemical coupling, encapsulation, and surface coordination, making them highly versatile (Zhao et al., 2023). Consequently, the utilization of direct mixing strategies to develop multifunctional platforms for MOFs-based films holds significant promise.

2.2.3. One step method

To form MOFs-based packaging films by the one step method, the addition of a precursor of polymer, metal salts, and organic ligands into the reaction system can simultaneously form the structure of MOFs and hydrogels crosslinking, also known as simultaneous formation of MOF and hydrogel method. At this moment, with the assistance of organic ligands, the chelation process facilitates the uniform dispersion of MOF particles within the gel network, ultimately leading to the formation of MOF-based hydrogels (Wang, Xu, Gao, Yao, & Zhang, 2019). Nevertheless, the most normally used method for synthesizing MOFs is solvothermal synthesis, wherein high-temperature heating is employed, which could pose challenges in promoting hydrogels formation. Therefore, it is worthwhile to explore alternative MOF synthesis methods that do not necessitate high temperature, such as electrospinning, mechanochemical reactions, and ambient temperature stirring. Moreover, some studies have shown that zeolitic imidazolate frameworks (ZIFs) type of MOFs possess excellent chemical stability when exposed to solvents, and can be easily synthesized in aqueous solutions at room temperature (Rauf et al., 2022).

3. Food packaging applications of MOFs-based films

The three aforementioned methods used for producing MOFs-based films packaging merge the advantages of MOF materials and hydrogel substrates. As a result, a variety of composite materials with complementary properties, including adjustable composition and structure, flexibility, water stability, and pore structure characteristics, are obtained. Hence, the use of MOFs-based packaging films has been extensively explored in the fields of wound healing treatment (Zhang, Wang, Xiang, Jiang, & Zhao, 2023), contaminant adsorption (Laddha, Jadhav, Agarwal, & Gupta, 2023), and target substance detection (Wang et al., 2023). In this section, emphasis will be placed on the applications of MOF materials in food packaging, especially the physicochemical modification of packaging films, the control of the packaging inner environment and food freshness, and the monitoring of food freshness. Furthermore, by drying the hydrogel based on MOFs to prepare MOFs-based films, the physicochemical properties of the packaging film can be greatly enhanced, particularly the mechanical capability. Therefore, in food packaging, MOF-based hydrogels are the preferred material for freshness indicators due to their ability to enhance coloring efficiency through their water content. The MOFs-based films are more appropriate for substituting petroleum-based packaging on the premise of ensuring safety.

3.1. MOFs as reinforcers to modify packaging film

3.1.1. Enhancement of mechanical properties

The assessment of the mechanical properties of packaging films can serve as a reliable indicator for predicting the performance of materials under various food processing and treatment conditions. Currently, the most commonly analyzed and reported mechanical properties in the literature are tensile strength (TS) and elongation at break (EB). These properties represent the maximum tension that the film can withstand before fracturing and the maximum elongation of the film before rupture is expressed as a percentage, respectively (Flórez et al., 2022). The mechanical properties of packaging films can be altered by a multitude of factors, including the characteristics of the polymer (such as molecular weight, degree of etherification or acylation), the method employed in film formation, moisture content, storage time, conditions during measurement and throughout testing, as well as the type of polymer solvent utilized. Furthermore, it is important to consider that the mechanical strength of film is influenced by the composition of the composite polymer, which includes intermolecular forces, crystallinity, and microstructure of the film network (Qu et al., 2022). Among them, MOF materials are anticipated to be an excellent means of improving the mechanical properties of polymers due to their unique rigidity. Therefore, an integration was made between the TS and EB of pure polymer packaging films and MOF crystal-polymer films, as presented in Table 1.

Research has demonstrated that the mechanical properties of natural polymer-based films are significantly impacted by the type and content of MOF fillers (Alizadeh, Khezerlou, Tavassoli, Abedini, & McClements, 2024). More precisely, the physical properties of MOFs-based films depend on the metal salts and organic ligands that constitute the MOF material, the concentration of the polymer solution, and the specific interaction between the polymer matrix and the MOF. For instance, Zhang et al. (2023)

integrated the nano ZIF67 (Co^{2+} and 2-Methylimidazole) into a cellulose acetate (CA) matrix to develop a strong and tough packaging film. By increasing the MOF content in the polymer, the confinement of ZIF67 nanofiller enhanced the rigidity of the CA film, resulting in a significant improvement in its mechanical properties. In general, the dispersion and interaction of nanofillers with the polymer matrix is a crucial factor for maximizing the reinforcing effect. Accordingly, the enhancement effect of nanocrystals is attributed to the strong hydrogen bond interaction between the well-dispersed filler and the matrix, which inhibits phase separation and promotes effective stress transfer at the interface. Similarly, another work by Chen et al. (2021) investigated the mechanical properties of CA films with flower-like Cu-MOF nanoparticles. The neat CA films exhibited the minimum TS and EB, whereas the film with 7 wt% Cu-MOF showed the maximum mechanical parameters. The blooming-shape MOF could be utilized as an efficient reinforcing agent for polymer matrix due to the high surface area and unique surface structure, which is beneficial for the absorption and dispersion of impact energy. Interestingly, the enhancement effect of Cu-MOF on the mechanical properties of CA film is comparable to that of graphene (Liu et al., 2014). Therefore, MOFs are expected to be an alternative material to graphene, resulting in higher economic benefits for enhancing the physical properties of packaging.

In summary, the mechanical properties are crucial for optimizing the processing and application of film materials based on MOFs. Upon external pressure-driven conditions in food packaging applications, the composite materials must be strong enough to maintain structure, and protect food from mechanical damage. It has been demonstrated that the inclusion of a particular MOF enhanced the mechanical properties of the film in comparison to the pure polymer matrix. However, there are still several challenges in the current research. Although high concentration of MOFs has superior mechanical properties, excessive MOF content may result in the dissociation of heavy metal ions, thereby causing safety issues. The mechanical properties of the film exhibit significant deviations at different positions due to the uneven distribution of MOF particles.

3.1.2. Improvement of water resistance

The primary purpose of food packaging film is to shield food from the external environment and prevent water transfer. Generally, the stability of the polymer structure could be directly affected by carrying high-moisture food and high humid external environment. Hence, the strategy of improving the water resistance of packaging films has always been universally applicability (Zhang et al., 2024). At present, there are several pathways to measure the water resistance of film materials (Abedi-Firoozjah et al., 2023; Zhang et al., 2023): (1) Moisture content (MC): the conventional factor that indicates the compactness and hydrophobicity of polymers. (2) Water solubility (WS): this physical parameter is indicative of the sensitivity of the packaging film to high moisture foods or water immersion. (3) Water absorption (WA): the crucial attribute reflects the capacity of the film to absorb water during the storage and distribution of packaged products, which has a significant impact on the efficiency of color response. (4) Water contact angle (WCA): the important characteristic to evaluate the hydrophilic/hydrophobic properties of the packaging film surface.

Some research has been revealed that a reliable method for improving the water resistance of packaging films was the mixing of hydrophobic MOF fillers (Khezerlou et al., 2023; Dey, Hou, Sillanpää, & Pramanik, 2023). Zhang et al. (2022) developed a bilayer composite film that the Ag-MOF-loaded p-coumaric acid modified chitosan (P-CS/Ag@MOF) and chitosan nanoparticles (P-CSNPs/Ag@MOF) were combined with a polyvinyl alcohol/starch (PVA/ST) matrix as the upper and lower films, respectively. The WC of film decreased sequentially with increasing concentrations of the internal loading substance. This can be explained that the hydrophobic nature of MOF resulted in a strong interaction between the hydrophobic group and the amino group of chitosan, preventing the water molecule from connecting with the amino group on the chitosan chain. In another work, Tavassoli et al. (Tavassoli et al., 2024) fabricated a composite biopolymer film comprising methylcellulose and chitosan nanofibers, with lactoferrin (LAC)-loaded Ag-MOF nanoparticles incorporated within its structure. The WA of the neat composite film was significantly greater than that of the film containing LAC-loaded Ag-MOF. This phenomenon could be attributed to the interaction between Ag-MOFs and biopolymer molecules in the film matrix, which enhanced its swelling resistance. Furthermore, these particles acted as hydrophobic fillers to inhibit the absorption of water by the film, thereby reducing its tendency to expand (Sani, Tavassoli, Hamishehkar, & McClements, 2021).

It is worth noting that the incorporation method of MOFs into a film may affect the WS of the final product, contingent on the composition of the MOF, the type of polymer, and whether the carrier is amplified or weakened within the film network

(Etxabide, Mate, & Kilmartin, 2021). All in all, certain biopolymers are constrained in their applicability to food packaging due to their hydrophilicity, and the film modification strategy of hydrophobic MOF can effectively make up their shortcomings. However, it is important to consider the cost of the noble metal series of MOFs. Therefore, the optimal ratio of the amount of MOF to the water resistance of the film has been subject to ongoing research. Finally, Table 1 concludes the integration of water resistance parameters between pure film and MOFs-based composite film.

3.1.3. Promotion of barrier performance

Absorption, diffusion and desorption are the important factors influencing the external barrier properties. Moreover, surface hydrophobicity and molecular diffusion significantly affect the permeability of the film (Roy et al., 2023). One of the primary functions of food packaging is to create a separatable barrier between the foods and the surrounding environment, and delay the spoilage of the food. Among the various properties of packaging material, three key parameters are most frequently studied to evaluate their barrier effectiveness against liquids, gases, and light (Zhang et al., 2023): (1) Water vapor permeability (WVP): This parameter represents the ability to prevent moisture interaction interior and exterior the packaging, which is also an effective factor in maintaining food quality. (2) Oxygen permeability (OP): The conventional factor indicates the oxygen permeation rate of internal and external food packaging, and directly affects the change of oxygen content in the packaging, which in turn results in food spoilage. (3) UV-vis-shielding: the crucial attribute reflects the rate of nutrient oxidation induced by light-food interactions, ultimately affects the food freshness.

For enhancing the barrier properties of the film to extend the shelf life of food, one of the key strategies in the design and manufacture of packaging films with high barrier properties is the incorporation of effective fillers (Alizadeh, Khezerlou, Tavassoli, Abedini, & McClements, 2024). As an example, the ceramide was loaded in the Cu-BTC MOF to obtain a modified MOF (Cer@MHKUST-1), and then the composite was encapsulated into a binary matrix composed of chitosan and gelatin (Nian et al., 2023). The incorporation of Cu-MOF-based composites into the matrix results in enhanced cross-linking between the internal chains, accompanied by a reduction in the mobility of the chains due to the filling of the free space in the polymer, ultimately leads to the modified film exhibiting a good water vapor barrier. Another potential explanation is the formation of hydrogen bonds between the filler and the matrix decreasing the number of free hydrophilic groups, thereby reducing the diffusion rate of water vapor through the film (Amjadi et al., 2019). For similar reasons as mentioned above, the MOFs-based films had a dense surface, which contributed to improve gas barrier performance. Moreover, the ceramide, and carboxyl and amino groups in the organic ligands of MOF have the capacity to absorb ultraviolet light, and enhancing the light barrier and opacity. Consequently, the incorporation of Cer@MHKUST-1 could safeguard packaged foods from mild oxidation and deterioration. It is noteworthy that MOFs with a colored appearance frequently exhibit strong ability to scatter or absorb ultraviolet light, which consequently enhances the UV blocking efficiency of the film (Tang et al., 2023). This provides a significant potential for manufacturing multifunctional colored MOFs for food packaging applications in the future.

In short, research results indicates that the barrier properties of specific MOFs-incorporated films could be influenced by a number of factors, including the integrity of the film substrate, the crystal structure and composition of the MOF, the ratio of MOF to polymer, and the hydrophobic properties of the film components. The selection of the appropriate MOF nanomaterials for the assembly of barrier packaging materials represents a pivotal aspect of the successful application. Nevertheless, the utilization of food packaging materials necessitates the consideration of the MOF-related economic efficiency and the recyclability of fillers, in addition to the potential for film additives to migrate to food. Hence, the barrier performance of the film material is enhanced after adding the MOF, and it must still undergo rigorous safety testing and certification. A summary of parameters assessing barrier performance of pure polymer and MOFs-based films is given in Table 1.

3.1.4. Others considerations

In addition to the aforementioned mechanical properties, water resistance, and barrier performance, it is necessary to investigate other physical attributes (e.g., thickness, thermal and morphological properties) of MOFs-based films. Among them, the packaging film thickness constitutes a pivotal parameter influencing mechanical, water absorption capacity, light resistance, and transparency, with the primary determinant of film thickness being the compositional makeup of the film substrate and the type and concentration of the filler material (Abedi-Firoozjah et al., 2023). According to the findings of Tavassoli et al. (2024), the incorporation of Ag-MOF substantially augmented the thickness of the pristine methylcellulose film, an effect attributable to the integration of Ag-MOF into the film network and enhancing the solid content of the film. Nevertheless, certain studies have demonstrated that the incorporation of MOFs does not significantly affect the film thickness, likely due to even distribution and minimal concentration of fillers within the film matrix (Jafarzadeh et al., 2024; Maroufi et al., 2023).

Currently, the thermal properties of packaging films are evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass transition temperature (T_g) and melting temperature (T_m) in the DSC results represent the stability (thermal, mechanical and dimensional) and processability of the film under high-temperature conditions, respectively (Roy et al., 2023). Additionally, TGA quantified the internal structural collapse of the film in response to elevated temperatures, which eventually resulted in thermal degradation and decomposition. The thermal stability property of the MIL-53 (Fe) microparticles-added polylactic acid (PLA) films were characterized by Qi et al. (2023). The elevation in the decomposition temperature of the composite film is ascribed to the augmented interfacial adhesion between the particles and the PLA within the film matrix. It can be concluded that due to the high thermal stability of MOF, the incorporation of nanofillers significantly intensifies the thermal stability of PLA films. Another study reported that the addition of nano cobalt-based MOF (Co-MOF) to the CA matrix improved the thermal stability (Zhang et al., 2023). The onset of decomposition temperature and the peak decomposition temperature of the CA film are markedly elevated through the integration of MOFs, demonstrating the heat barrier effect of MOF in hindering the thermal degradation of the film.

The preparation of MOFs-based films is typically followed by a comprehensive microstructural analysis (including scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD)) to elucidate the morphological modifications of MOFs within the film substrates (Riahi et al., 2023; Zhang et al., 2024). Typically, to observe the morphological structures of the film, the relevant images are obtained and analyzed by means of scanning electron microscopy (SEM) and field-emission SEM (FE-SEM). The resulting images from these microscopies afford insights into various morphological attributes, including the surface smoothness or roughness of the film, the homogeneity of filler dispersion, the presence of agglomerates, and potential fractures within the film (Akhila & Badwaik, 2022). The SEM analysis on SA-based hydrogel film revealed that the films without MOF had a smooth surface but after the addition of fillers the surface showed distinct protrusions (Wang et al., 2024). Interestingly, the hydrophobic nature of the organic ligands facilitates the enhancement of the hydration of SA by the MOF, leading to the formation of a colloidal solution with a roughened surface. FTIR spectroscopy as a technique utilized for the analysis of molecular vibrations provides insights into the nature of chemical bonds and functional groups. When MOFs interact with the polymer matrix, the nature of the chemical interaction between MOFs and the film matrix can be elucidated through the analysis of experimental results. The metal centers within MOFs have the potential to form coordination bonds with the functional groups present in the matrix, leading to the emergence of new absorption peaks or shifts in the original peak positions in the FTIR spectrum (Feng et al., 2023). Furthermore, the incorporation of MOFs may induce rearrangements of polymer chains or alterations in the local chemical environment within the film (Tang et al., 2023). It is noteworthy that MOFs can adsorb gases or substances on the surface of film, and the resulting FTIR spectrum may exhibit corresponding adsorption peaks, indicative of adsorption phenomena. Generally, MOFs tend to engage in hydrogen bonding and electrostatic interactions within the embedded film matrix (Zhang et al., 2024).

The mechanical robustness, barrier efficacy, moisture resistance, and thermal stability of packaging films are predominantly determined by the composition of the internal matrix. Although the incorporation of MOFs as a modification strategy can enhance the multifaceted properties of the film, challenges pertaining to its shedding rate and heterogeneity remain to be addressed. In addition, the concurrent addition of substances in conjunction with MOFs exerts a synergistic influence, modulating the interfacial compatibility and hydrophobic character of the system, thereby affecting the barrier properties of the film. In instances of diminished interfacial compatibility, the cohesion of the film within the material is reduced, resulting in enlarged voids and consequently, an augmented gas permeation rate.

3.2 MOFs as active agents to control in-package environment and food freshness

As numerous studies have demonstrated, MOFs have emerged as highly desirable components in food industry applications, owing to their characteristic biocompatibility and inertness towards matrices (Shashikumar et al., 2023). Currently, MOFs are employed as active agents, especially in active food packaging, demonstrating antibacterial properties and facilitating the removal of active molecules, thereby extending the shelf life of packaged products. Furthermore, MOF materials have the potential to selectively desorb and absorb bioactive compounds, and are preferably integrated into the active packaging of minimally processed foods. Their physical and chemical properties, essential for a potential packaging material, position MOFs as an advanced and eco-friendly choice for food packaging (Sharanyakanth et al., 2020). In this section, the potential applications of MOFs as active agents in food packaging materials, focusing on their ability to control the internal environment of packaging and food freshness are reviewed.

3.2.1. Antimicrobial properties

Food spoilage predominantly results from microbial contamination and oxidation processes. Consequently, it is crucial to prolong the shelf life and enhance the quality and safety of food by utilizing antibacterial packaging materials (Ebrahimzadeh, Biswas, Roy, & McClements, 2023). Antibacterial agents are typically incorporated into films to inhibit the spoilage of diverse food products and the proliferation of pathogenic microorganisms. The antimicrobial efficacy of packaging films and fillers is contingent upon the concentration of the incorporated antimicrobial agents, the nature of the polymer matrix, the predominant microbial load, the chemical composition of the food, pH, moisture content, storage conditions, and the specific type of microorganism (Shen et al., 2023). Recent studies have indicated that due to the effective antibacterial properties of MOFs, primarily involving structural damage to cell walls and disruption of crucial biochemical pathways, the nanomaterials are considered to be an ideal filler for bioactive compounds in packaging films (Zhang et al., 2022).

For instance, incorporation of 4% Zn-MOF (which has antimicrobial activity) into gelatin films increased their antimicrobial activity against Gram-positive (*S. aureus & L. monocytogenes*) and Gram-negative (*S. enterica & E. coli*) bacteria (Riahi et al., 2023). The Zn-MOF, with a distinctive dodecahedral shape, was combined into the gelatin matrix, and the apparent morphology and color of the composite film underwent a transformation as the quantity of filler was increased. Owing to the innate highly porous structure of Zn-MOF, the production of reactive oxygen species (ROS), and the liberation of metal ions into bacterial media, MOFs demonstrated superior antibacterial efficacy against four bacterial species. Among these, ROS encompassing singlet oxygen, hydroxyl radicals, and superoxide anions, exert their antibacterial effects by damaging nucleic acids, inactivating proteins, and inducing lipid peroxidation, thereby impeding bacterial growth (Riahi, Rhim, Bagheri, Pircheraghi, & Lotfali, 2022). Moreover, the visual appearance of tomatoes (Day 16) during storage was substantially enhanced under the coating of MOF-based films (Fig. 2A). In a separate investigation, it was demonstrated that the integration of Co-MOF-based nanofibers into SA films effectively inhibited the growth of *E. coli* and *S. aureus* (Wei et al., 2023). Similarly, the incorporation of Co-MOF-based particles can enhance the antibacterial efficacy of various pure matrices, such as PVA (Li et al., 2023), CA (Zhang et al., 2023), and carboxymethyl cellulose (Tang et al., 2023) films. In summary, these studies show that Co-based MOFs can serve as efficacious additives in films to extend the shelf life of packaged foods and enhance safety. The antibacterial properties of these films are likely attributable to the active capacity of agents to disrupt bacterial cell membranes, thereby leading to the efflux of cellular contents and ultimately cell death.

Although MOFs are versatile exhibiting antibacterial attributes, selecting appropriate metal ions and organic ligands is essential when prioritizing antibacterial properties. The primary function of food packaging materials is to hinder the proliferation of pathogens and eliminate their toxins. Hence, the incorporation of antibacterial properties is crucial for prolonging the shelf life of food products and ensuring food safety. Unravelling the primary mechanism by which metal nanoparticles exert bactericidal effects is significant. The liberation of dissociated ions, which engage with the negative charge of the bacterial cell wall, constitutes a pivotal factor in the process of cell death (Siddiqui et al., 2024). Additionally, the spreading of antibacterial agents through packaging materials is also a critical factor influencing the effectiveness of their antibacterial functions, which is contingent upon physical and chemical factors, and it may also be influenced by interactions with the packaging polymers. At present, complete preservative efficacy cannot be universally applied to all food types, necessitating a case-by-case evaluation of the effectiveness of preservatives in packaging. Finally, Table 2 summarizes the applications of representative MOFs-based packaging films in bacteriostasis over the past few years.

3.2.2. Antioxidant properties

Active packaging incorporating antioxidant complexes represents an effective approach to extending shelf life while maintaining food safety and quality (Roy et al., 2023). The antioxidant potential of MOFs can be ascribed to their distinctive structural configuration, including the interconnection of metal nodes through organic ligands, which confers them with substantial porosity and surface area. Interestingly, certain MOFs have demonstrated inherent antioxidant characteristics, attributable to the redox reactivity of their metal centers or organic linkers. On the one hand, MOFs containing copper or manganese metal centers exhibit potential in catalyzing the disproportionation of superoxide radicals (Xiang et al., 2023). On the other hand, the synthesized MOFs are designed to release antioxidant components in response to specific stimuli by modifying organic ligands, and the modification strategy ensures enhanced specificity, minimizes side effects, and has better biocompatibility (Jafarzadeh et al., 2024). Commonly, the susceptibility of packaged foods to oxidative degradation is evaluated through antioxidant assays, including the ferric reducing antioxidant power (FRAP), 2,2-diphenyl-1-picrylhydrazyl (DPPH), and 2,2′-casino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS).

The escalating demand for high-quality and safe food products has spurred the investigation into antioxidant packaging films fabricated from MOF materials. For example, ZIF-8 has been embedded in gelatin-based films, serving as a favorable antibacterial component in food packaging (Riahi et al., 2023). The pure gelatin film exhibited good antioxidant properties by the ABTS assay, as evidenced by the interaction between free radicals and the free amino groups of gelatins. The radical scavenging ability of MOFs is realized through the synergistic effects of hydrogen donors, electron transfer pathways, and free radical adducts. In addition, the hydrophilicity of the film facilitates the release of active components into the ABTS aqueous solution, thereby enhancing the interaction between the MOFs and ABTS free radicals (Riahi et al., 2022). Currently, limited literature is available on the antioxidant properties of MOF materials in food packaging application. The main research focuses on the encapsulation of guest molecules with antioxidant capabilities within MOFs or to graft these molecules onto organic ligands. It is significant to emphasize that the formulation of MOF within the film matrix should be optimized to the greatest extent possible to effectively enhance the antioxidant activity of packaging materials.

3.2.3. Gas controlling performance

The presence of oxygen, ethylene, water vapor, and other gases within the internal environment of food packaging adversely affects the quality and shelf life of food products. Some specific MOFs have gained significant interest as application components in the food industry, primarily due to their characteristic hydrophilic outer surface and hydrophobic inner cavity (Fig. 2B). Hence, MOF materials exhibit promising potential for gas absorption and storage applications within the domain of food packaging (Shashikumar et al., 2023): (1) Oxygen scavenging: Oxygen facilitates the oxidation of lipid-rich food matrices, fosters the proliferation of aerobic microorganisms and initiates oxidation reactions, thereby diminishing food quality. Some specific MOF materials possess excellent oxygen adsorption capacity, which reduces the oxygen concentration within the food packaging. This approach promotes the extension of the shelf life for perishable food and contributes to the preservation of their nutritional integrity and sensory qualities (Geng et al., 2023). (2) Moisture absorption: Excessive moisture within food packaging can promote the proliferation of molds and bacteria, culminating in food spoilage and compromising safety. Owing to the intrinsic high porosity and large specific surface area of MOFs, these materials exhibit an outstanding capability for water absorption. The alteration of MOF pore dimensions, coupled with the strategic selection of linkers and secondary building units are helpful to adjust its hydrophilic properties and water adsorption characteristics (Zhang et al., 2023). (3) Ethylene concentration controlling: Controlling the ripening process of fresh produce, particularly fruits indigenous to tropical climates, poses a significant challenge during storage and transportation, and is crucial for preserving the desired quality attributes (Sharanyakanth et al., 2020). Ethylene as a phytohormone that directly determines the ripening and senescence processes of fruits and vegetables (Wang et al., 2023). Through the regulation of ethylene levels within the packaging, the unique properties of MOFs can markedly retard the ripening progression and extend the shelf life of fresh agricultural products (Zhang et al., 2023). (4) Other gas controlling capabilities: Apart from the aforementioned gases, customized MOFs can target other gases (including various volatile organic compounds (VOCs) and carbon dioxide) adsorption to improve the internal environment of food packaging. Among them, the adsorption of carbon dioxide by MOF materials plays an important role in regulating the pH levels within food packaging, thereby inhibiting the proliferation of spoilage microorganisms. VOCs, which are the primary contributors to food odor resulting from the oxidation of the food matrix and microbial activity, can also be adsorbed using MOF, effectively enhancing the sensory quality of packaged food products (Alizadeh, Khezerlou, Tavassoli, Abedini, & McClements, 2024).

At present, the potential of MOFs as targeted gas adsorbents can be investigated at two distinct levels. On the one hand, MOFs with sufficient ethylene adsorption capabilities were chosen as the packing fillers, and the adsorption efficiency of these MOFs remains uncompromised by the moisture emanating from the respiration of fresh agricultural produces. On the other hand, it is imperative to investigate methodologies for encapsulating MOFs within the film matrix to cater to the diverse requirements of various applications (Zhang et al., 2023). In previous research, various ethylene scavengers have been explored for the development of active packaging, including activated carbon, halloysite nanotubes, zeolites, potassium permanganate, and 1-methylcyclopropane. However, their high cost, potential risks to human safety, and limitations in film-forming ability pose significant challenges to the commercialization of ethylene scavenging packaging. Relevant studies have demonstrated that MOF composites composed of ZIF-8 and zeolite exhibit a notable adsorption capacity for ethylene, which can regulate the ethylene atmosphere of product packaging, thereby effectively preserving the food freshness (Sultana, Siddiqui, & Gaikwad, 2022). Sultana et al. (2023) utilized lignocellulosic nanofibers derived from bagasse and guar gum to fabricate films by the solvent casting method, and integrating double ethylene adsorption factors (ZIF-8/zeolite composites) into the films. The incorporation of MOFs rendered the resultant multifunctional biodegradable films capable of exhibiting effective ethylene scavenging activity. Furthermore, the inclusion of zeolite in lignocellulosic paper also demonstrated ethylene scavenging capabilities (Dai et al., 2021).

In summary, the gas controlling performance of MOFs holds considerable promise for a variety of food packaging applications according to the current research status. Owing to the distinctive crystal lattice of MOF and the high surface area as solid adsorbents, it can effectively eliminate the residual water and oxygen molecules within the headspace of food packaging. Moreover, MOFs exhibit stability in aqueous environments, retaining their structural integrity and adsorption capacity following desorption/adsorption cycles, and are easily regenerated by the surrounding environment. However, the literature reporting on the control of gases other than ethylene using MOFs is still limited.

3.3 MOFs as indicative factors for monitoring of food freshness

Intelligent packaging encompasses the incorporation of internal or external indicators within the packaging matrix to monitor the dynamic interaction between food products, packaging materials, and the ambient environment, without usually affecting the quality and flavor attributes of the food (Zhang, Sun, Sang, Jia, & Ou, 2022). Commonly, the intelligent packaging film is composed of pigments sensitive to targeted gases and biodegradable polymer matrices. It is noteworthy that the selection and preparation of pigments constitutes a critical aspect in the development of intelligent films. Recently, some alcohol-soluble dyes such as synthetic pigments (e.g., bromocresol green, cresol red, polyaniline and alizarin) and natural extracted colorants (e.g., anthocyanin, curcumin and betacyanin) have found extensively application as sensor materials in food packaging (Zhang, Sun, Sang, Jia, & Ou, 2022). The principle of MOFs-based luminescent films in food packaging relies on the distinctive properties of MOFs, such as their extensive surface area, adjustable constituent units, modifiable organic ligands, and tailorable pore sizes (Zhang et al., 2024). The luminescent attributes of MOF as indicators can be attributed to four primary strategies that facilitate the interaction between the indicator and the analyte (Fig. S1): (1) The utilization of lanthanide elements exhibiting luminescent characteristics or other metal salts with coloration properties. (2) Using organic ligands comprising conjugated or aromatic moieties that possess luminescent attributes or other ligands modified by specialized functional groups. (3) Encapsulating fluorescent guest molecules or pigments into non-luminescent MOFs. (4) Using catalytic emitters for the functionalization of target molecules to achieve luminescent objectives (Liu, Xie, Cheng, Shao, & Wang, 2019; Zhang et al., 2024).

According to the aforementioned luminescence response strategy, some MOFs-based luminescent packaging films have developed recently for the detection of diverse different gas targets. The volatile amines generated by meat products emit a disagreeable odor and constitute a significant health risk to humans. Xu et al. (2023) presented on the development of an ammonia-sensitive colorimetric film with Co-BIT loaded within CA matrix to monitor the spoilage of shrimp (Fig. 3A). The coloration of Co-BIT microcrystals transitioned from blue to brown after exposure to volatile ammonia, demonstrate that the synthesized MOF had good ammonia-sensitive discoloration capability. Additionally, the characteristic absorption peak of the infrared spectrum of Co-BIT was obviously shifted after contact with volatile amines. This alteration is attributed to the formation of hydrogen bonding interactions between the MOF and amines, resulting in a modification of the Co element coordination environment and ultimately leading to a change in the color characteristics of the MOF (Can, Demirci, Sunol, & Sahiner, 2020). The CA/Co-BIT composite film demonstrates a substantial color response to ammonia, and its color stability (stored at 30 ℃ and 53% relative humidity for 45 days) fulfills the criteria for intelligent packaging applications (ΔE value<1.0) (Zhang et al., 2023). Furthermore, the utilization of shrimp as a representative model for meat products was employed to further explore the applicability of colorimetric composite film as an intelligent packaging material for meat deterioration. The color change of the composite film is intimately associated with the accumulation of total volatile basic nitrogen (TVB-N) in shrimp spoilage. Regrettably, there exists a deficiency in the pertinent assessment of the fitting properties between color difference parameters and TVB-N levels.

In short, the intrinsic color attributes of MOFs broaden the applications of MOFs-based colorimetric films and provide some advantages for manufacturing intelligent food packaging materials. The stability of this material can compensate for the deficiencies of natural colorants which easily decomposes when exposed to heat, light and enhance the sensitivity of the colorimetric film. However, MOFs-based intelligent films require the supplementary use of spectrometers for a more accurate demonstration of the phenomena. In addition, articles on the applications of organic ligand modification and catalytic coloration of MOFs in intelligent packaging are still lacking. Consequently, it is imperative to invest more resources towards the direct visualization of substantial color changes and to develop MOFs-based film sensor arrays capable of detecting multiple targets in future research.

3.4 MOFs as active compound carriers

MOFs as appealing and multifunctional nanocarriers can be utilized for the encapsulation of active compounds, their high-water stability, exceptionally large pores, robust thermal stability, extensive surface area, and numerous unsaturated sites, fulfilling the requirements for an effective carrier material (Khezerlou, Tavassoli, Khalilzadeh, Ehsani, & Kazemian, 2023). Currently, the applications of MOFs-based carriers in food packaging involves the encapsulation of substances (e.g., antioxidative, antibacterial activity and indicative characteristics) within the MOF cavity to achieve the desired results.

Certain natural active components, such as anthocyanins, curcumin, and catechins, lack sufficient stability and are prone to degradation upon exposure to light and varying temperatures (Fernandes et al., 2020). Substantial progress has been made in enhancing the stability of these biological compounds without changing the main physical and chemical properties, including copigmentation, MOFs-loading, and microencapsulation (Klisurova et al., 2019; Liu et al., 2023; Yao, Xu, Zhang, Liu, & Zhang, 2021). Nevertheless, the majority of organic ligands utilized in the synthesis of MOFs are derived from non-renewable petroleum raw materials, which constrains their applicability within the food industry owing to the non-biodegradability and inherent toxicity of MOFs (Chen et al., 2021). Hence, cyclodextrin (CD)-based MOFs have attracted special attention due to their common edible properties, biodegradability and excellent biocompatibility. As a non-toxic organic ligand for MOFs, CD is a cyclic oligosaccharide composed of glucose units, possessing a hydrophobic cavity capable of encapsulating guest molecules of diverse sizes and geometries (Kang et al., 2023). The CD-MOFs possess a porous structure with an extensive surface area, rendering them excellent hosts for the encapsulation and delivery of bioactive compounds.

Curcumin is widely used in food packaging as an active ingredient to improve food quality and safety attributable to its effective antioxidant, anti-inflammatory and antibacterial properties. However, the limited solubility and bioavailability of curcumin in aqueous environments, and its instability under various environmental conditions constrain its application in the realm of food packaging (Sanchez et al., 2022). Kang et al. (2023) employed γ-CD-MOFs as a slow-release carrier and integrated it with curcumin to fabricate a multifunctional material denoted as Cur-CD-MOFs. The non-toxic Cur-CD-MOFs were synthesized through the interaction between the carrier and the carbonyl group, enolic side ring, and benzene ring of curcumin. Curcumin was not only uniformly dispersed in the porous structure of γ-CD-MOFs, but also encapsulated in the hydrophobic cavities of these materials, thereby significantly enhancing the thermal stability and photochemical stability of curcumin. Subsequently, Cur-CD-MOFs were incorporated into a binary film composed of pullulan (Pul) and trehalose (Tre), resulting in the formation of a Cur-CD-MOFs-Pul/Tre food packaging film. The curcumin released by the MOF within this composite film effectively suppressed the spoilage and dehydration of Centennial Seedless grapes (CSg). In another study, a CD-MOFs with structural components entirely sourced from edible constituents, specifically potassium chloride and food-grade γ-CD, has been developed (Su, Su, Xing, & Tan, 2024). The researchers hypothesize that the principal rationale for the utilization of MOFs as host materials for anthocyanins is the disparity between the molecular dimensions of anthocyanins and the pore size of the CD-MOFs, ensuring the possibility of encapsulation in the pores of CD-MOFs (Fig. 2C). On the other hand, the presence of diverse functional sites within CD-MOFs facilitates the stabilization of anthocyanins in these pores, a process mediated by a spectrum of non-covalent interactions between the skeletal structure of MOF and the anthocyanin molecules (Chen et al., 2021). The DPPH scavenging efficacy of unencapsulated anthocyanins was significantly diminished after exposure to heat and ultraviolet radiation. Notably, the degradation of antioxidant capacity was efficiently mitigated upon the encapsulation of anthocyanins within CD-MOFs. In the storage experiment of Kyoho grapes, the incorporation of a film with anthocyanin-MOF composites can remarkably curtail the desiccation of plant tissues and inhibit the hydrolysis of monosaccharides and the respiration of over-ripening fruits.

In addition to loading some functional factors that prolong the shelf life of food, MOFs are capable of encapsulating pigments prone to leaching, thereby ensuring food safety and the precision of indicator responses (Alnoman et al., 2022) (Fig. 3B). The time-temperature stability and relatively poor selectivity of food freshness indicators have persistently posed significant challenges, and addressing these challenges is essential for enhancing the efficacy and dependability of solid-state colorimetric indicators (Hashemian et al., 2023) (Fig. 3C). At present, MOFs as porous structure and large surface area nanomaterials are suitable for accommodating colorimetric indicators, resulting in ensuring stable display of the probe. Moreover, the active metal nodes and organic linkers of MOFs are capable of engaging in a multitude of chemical and physical interactions, such as hydrogen bonding, π-π stacking, and electrostatic attractions between the functional groups of MOFs and biological ligands, further enhancing their potential in indicator applications (Cheng et al., 2021).

The overall quality of beef decreased gradually during storage, with nutrients being subject to degradation by microbial and enzymatic activity, resulting in the production of volatile biogenic amines (Han et al., 2023). To effectively monitor the freshness of beef, Zhang et al. developed a photothermally stable pigment through the incorporation of the phytochemical alizarin (AL) into the microporous framework of ZIF-8, utilizing physical adsorption and hydrogen bonding mechanisms (Zhang, Zhang, Zhang, et al., 2024). It is worth noting that the structural characteristics and crosslinking level increase the difficulty of ammonia diffusion after the integration of the AL@ZIF-8 composite into the polymer matrix to create an intelligent film, which ultimately affects the color intensity and distribution in the film. Generally, compared with natural colorants, traditional synthetic dyes can induce pronounced color transitions characterized by high saturation and contrast within an abbreviated timeframe, and are more resistant to light and thermal (Silva, Mastrantonio, Costa, & Morais, 2019). Nevertheless, the formation of hydrogen bonds between water vapor molecules in high-humidity environments can result in pigment migration, and potentially posing risks to food safety in packaging and ultimately affecting human health. In addressing the above issue, this fascinating report showcased the amination of the organic ligand within MOFs and the subsequent grafting of bromothymol blue (BTB) pigment by amide coupling reactions (Wang et al., 2022). The majority of BTB molecules are integrated into the framework through intermolecular interactions, preserving the structural integrity of the MOF, resulting in the modified pigment (MOF-BTB) grafting results are considerable. Furthermore, through assessing the adsorption capacity of Co-MOF for the synthetic chemical pigments phenol red (PR) and bromothymol blue (BTB), Zhang et al. integrated PR or BTB into Co-MOF to construct color nanohybrids for monitoring the freshness of fresh-cut fruits (Zhang, Zhang, Wang, et al., 2024). Owing to the adsorption efficacy of Co-MOF, the pigment migration characteristics in the sodium carboxymethyl cellulose (CMC-Na) film were enhanced, thereby offering significant insights into the modulation of pigment migration via MOFs.

In conclusion, MOFs offer a proficient platform for encapsulating multifunctional natural extracts or colorants, enabling them to exert targeted effects, thereby endowing the extension of shelf life and monitoring functions of food packaging. The development of an efficient industrial-scale production method for MOFs is essential to facilitate their potential application as carriers in food packaging field. Additionally, the cavity dimensions within the porous nanoparticle MOF must be appropriately matched to the guest molecule size. A cavity that is too small may not accommodate the embedding of the guest molecule, while a cavity that is too large may not provide sufficient adsorption or grafting strength to effectively retain the guest molecule. The MOFs composed of heavy metals have non-biodegradable properties and intrinsic toxicity, necessitating a thorough evaluation of their safety for use in food packaging. The domain of natural material transport and targeted gas capture utilizing the emerging edible CD-MOF remains in its infancy, requiring further investigation (Rajkumar, Kukkar, Kim, Sohn, & Deep, 2019). In particular, the modulation of their pore size and morphology can significantly influence the loading capacity and release kinetics of active compounds. In subsequent investigations, it would be beneficial for researchers to explore the integration of novel food constituents into MOFs-based film materials for delivery applications. For instance, the incorporation of *Zingiber officinale* into active packaging systems can augment the nutritional profile of food formulations (Garza-Cadena et al., 2023); carminic acid, characterized by its multifaceted properties including coloring, sensory enhancement, and health promotion, incorporated into packaging materials can enhance the functionalization of intelligent packaging systems (Ferreyra-Suarez, Paredes-Vargas, Jafari, García-Depraect, & Castro-Muñoz, 2024); and the Capsaicin, renowned for its therapeutic effects in the prevention and treatment of gastric disorders and thermoregulation, presents itself as a promising candidate for such integration (Castro-Muñoz, Gontarek-Castro, & Jafari, 2022). Finally, Table 3 summarizes the utilization of representative MOFs as loaders within the context of food packaging over the past few years.

4. Toxicity of MOFs-based films

The application scenarios of MOFs-based packaging films are frequently in direct or indirect contact with food. The retention of hazardous solvents employed in the synthesis process and the raw materials for the synthesis of MOFs (namely organic ligand functional groups and metal ions) are the primary contributors to the toxic effects associated with MOFs. Hence, the assessment of the toxicity of MOFs and their migration behavior within polymer matrices are imperative for ensuring human health and environmental safety (Ettlinger et al., 2022). This section discusses safety concerns pertaining to MOFs-based fillers in packaging films, encompassing potential risks and strategies for their mitigation.

The primary consideration must be the potential risks posed by the toxicity of metal ions that constitute MOFs in the realm of food packaging. Accordingly, it is imperative to ascertain the minimal acceptable human tolerance limits for such metals, particularly when employing bioincompatible heavy metal ions. Furthermore, the migration of MOFs after their incorporation into the polymer matrix should also be evaluated to prevent direct contact between the MOF and foodstuffs. The intrinsic nanoscale particle size of MOFs renders them susceptible to invasion, with their pores being laden with volatile organic solvents after preliminary synthesis or washing procedures. The activation of MOFs facilitates the evacuation of residual solvents from the pores and the removal of guest molecules from the framework pores by vacuum treatment, heat treatment, solvent exchange, and other methodologies (Chang et al., 2023). Additionally, to ensure the material functions without adverse effects on organisms, it is necessary to consider factors such as inflammation and immune response, and to conduct in vitro and in vivo studies on cells is essential to assess the biocompatibility and toxicity of MOFs with various cell types and tissues (Ettlinger et al., 2022).

Generally, the synthesis of MOF involves energy-intensive processes and the use of organic solvents, which may lead to environmental pollution and greenhouse gas emissions. Consequently, it is imperative to devise sustainable and eco-friendly synthesis methods to optimize energy conservation and preclude the utilization of deleterious solvents. Researches should also pay more attention to enhance the stability of MOFs within packaging films and thoroughly assessing their potential environmental and food-related hazards. Furthermore, the utilization of biocompatible metal ions within a biologically acceptable range, including potassium, calcium, and titanium with peptides, carbohydrates, amino acids, and cyclodextrin derivatives as organic ligand linkers can foster the eco-friendly production of MOFs (Sharanyakanth et al., 2020). Moreover, the surface modification of MOFs, involving processes such as coating or the grafting of materials with excellent biocompatibility, is undertaken to diminish the likelihood of metal ion release. Concurrently, MOFs undergo post-treatment with non-toxic capping agents or ligands to stabilize the metal nodes and inhibit their dissolution. Ultimately, in order to avoid resource wastage, it is crucial to monitor the number of cycles for MOFs-based intelligent or active films, and the alteration in the efficacy of the guest molecules released upon repeated utilization should also be carefully evaluated.

5. Conclusion and future perspectives

Food packaging is mainly designed for food safety and long-term preservation. The recent advancements in packaging technology have introduced enhanced, active and intelligent packaging materials. Empirical evidence has demonstrated the advantages of MOFs in the domain of food packaging, ensuring the quality and safety of food products. The multifunctional properties of MOFs can be utilized to enhance the food supply chain across various stages of progression.

MOFs as a kind of reinforcer can modify the comprehensive physical performance (e.g., mechanical properties, water resistance, barrier performance and thermal properties) of packaging films by increasing novel factors such as tortuosity within the film structure. These attributes render the polymer matrix more diverse, facilitating the development of advanced packaging innovations. Numerous MOFs-based film materials exhibit UV-blocking capabilities, enhanced oxygen barrier properties, reduced water vapor permeability, superior thermal stability, and increased mechanical robustness. These functionalities are typically challenging to attain in pristine polymer matrices. Characteristics of nanocomposites have the potential to transform the biopolymer sector, mitigating its limitations and serving as a viable alternative to petrochemical-based packaging materials. Some studies on nanocomposite films have reported the development of antibacterial and antioxidant attributes of MOFs incorporated within composite films, as well as the improvement in modified atmosphere engineering properties, enabling packaging to remove or inhibit substances capable of causing food spoilage. Among them, the cavity structure of MOFs can selectively adsorb and desorb gases such as oxygen, carbon dioxide, and ethylene. This capability allows MOF nanoparticles to regulate the gas composition within packaging environments, thereby prolonging the shelf life of food products. In addition, by diminishing the oxygen concentration in the packaging atmosphere, MOFs-based packaging systems can decelerate oxidation reactions, thereby retarding spoilage processes. MOFs can also serve as indicative factors for monitoring food freshness in intelligent packaging materials, as they can be engineered to respond to alterations in pH, temperature, humidity, or gas concentrations. For instance, when exposed to specific target gases or as food starts to spoil, MOFs will undergo a color change. Such colorimetric films can assist consumers in assessing the freshness of products, thereby contributing to the reduction of food waste. Additionally, MOFs can function as carriers for the encapsulation, protection, and controlled release of bioactive compounds, which further expands their utility in packaging applications.

At present, MOFs-based packaging films have increasingly garnered attention as a research focal point, owing to the multitude of potential benefits associated with the application of MOF nanomaterials in food packaging. On the one hand, the inherently porous nature of MOFs allows for the manipulation of their porosity and surface chemical attributes, enabling the customization of MOFs for specific applications based on varying characteristics. To render MOFs suitable for food packaging applications, MOFs can also be engineered to exhibit robust physical and chemical stability under diverse conditions, including high humidity and elevated temperatures. In addition, MOFs are typically incorporated into the polymer matrix via physical adsorption, thereby avoiding chemical reactions with the original film to cause food safety problems.

In summary, MOFs and their composite materials as functional coatings in food packaging have garnered significant interest, particularly for their potential in the controlled release of preservatives and ensuring product safety. Therefore, it is necessary to develop multifunctional MOFs with exceptional sensing, stability, and adsorptive properties for integration into intelligent packaging systems. Nevertheless, several challenges must be overcome before their widespread adoption. Currently, the cost associated with large-scale production of MOFs is prohibitively high. Another concern is the potential migration of MOFs from packaging materials into food products. Lastly, a comprehensive assessment of the metabolic pathways is necessary to guarantee that any unintentional ingestion of MOFs does not adversely affect human health in the long term.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Figure Captions

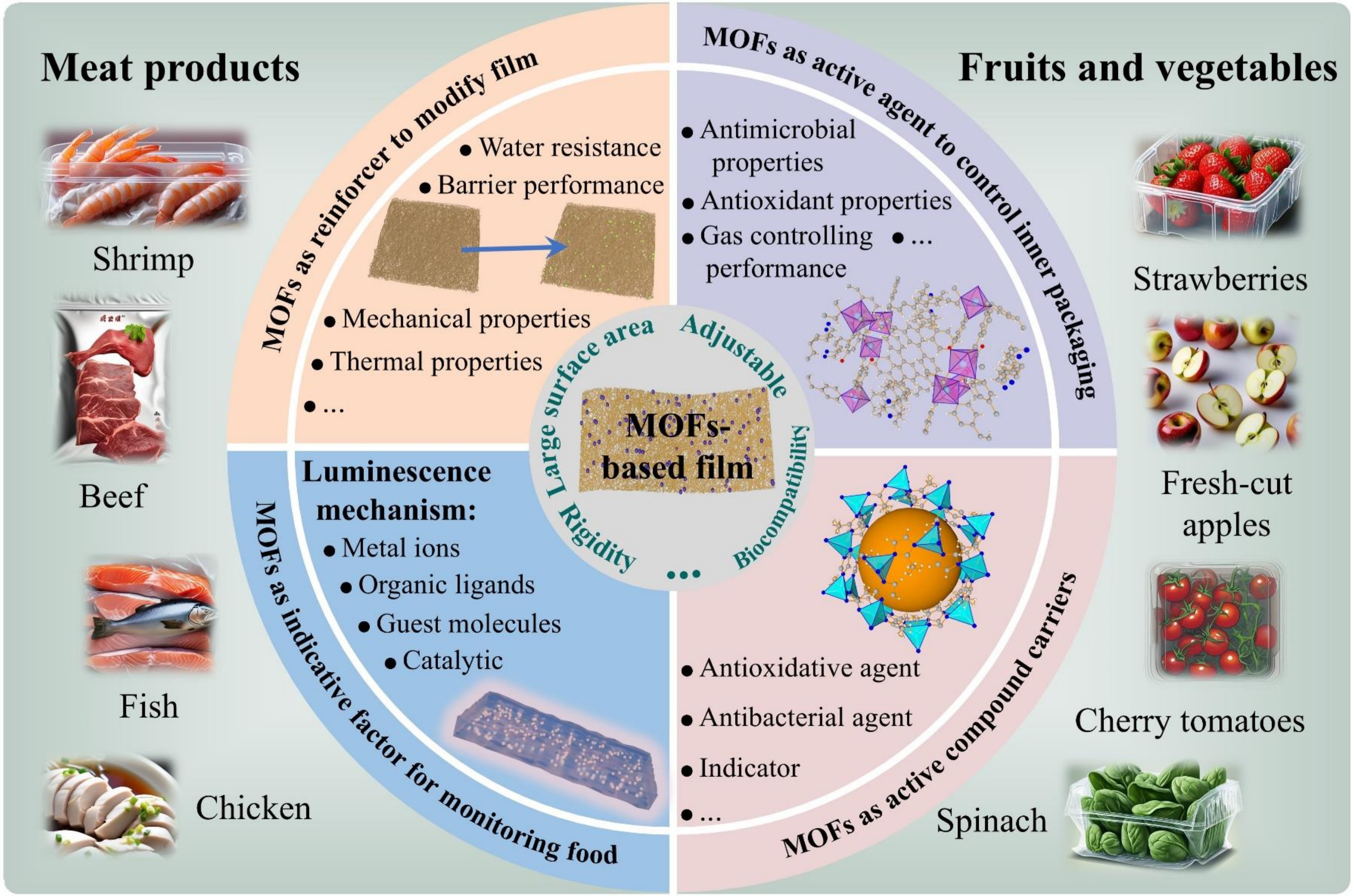
Scheme 1. Schematic representation of MOFs-based film for food packaging application.

Fig. 1. Summary of the several synthesis strategies of MOFs (e.g., solvothermal/hydrothermal, ambient temperature stirring, microwave-assisted, ultrasound-assisted, electrochemical, and electrospinning approaches) and the three synthesis methods of MOFs-based film, including in-situ growth method, direct mixing method and one step method.

Fig. 2. A. (a) Microscopic morphology of Zn-MOF; (b) Actual view, surface and cross-sectional of gelatin-based composite films; (c) The visual characteristics of tomatoes with neat gelatin film and gelatin/Zn-MOF3% composite film (Riahi et al., 2023). B. (a) Schematic diagram for curcumin release from Cur-HKUST-1@carboxymethyl starch (CMS)/PVA; (b) SEM images of the curcumin-loaded HKUST-1@CMS/PVA; (c) Antimicrobial activities of composites (CMS/PVA, HKUST-1@CMS/PVA, and Cur-HKUST-1@CMS/PVA); (d) Storage results for fruit at different times for various treatments (i-control, ii-PE films, iii-HKUST-1@CMS/PVA, and iv-Cur-HKUST-1@CMS/PVA, avocado: left, pitaya: right) (Liang et al., 2022). C. (a) Schematic diagram of Cur-CD-MOFs-Pul/Tre coating on CSg surface; (b) SEM images of γ-CD, γ-CD-MOFs, and Cur-CD-MOFs; (c) the loading capacity (LC, %) and encapsulation efficiency (EE, %) of curcumin, and schematic diagram of Cur-CD and Cur-CD-MOFs; (d) Morphology photographs of fruits of control, Pul/Tre-packed, and Cur-CD-MOFs-Pul/Tre-packed CSg at 0-10 d (Su, Su, Xing, & Tan, 2024).

Fig. 3. A. (a) The color change and (b) FTIR spectra for Co-BIT before and after

exposing to ammonia gas; (c) the variation in coordination environments for Co-BIT after exposing to ammonia gas; (d) the color change for CA/Co-BIT films after exposure to volatile ammonia; (e) photographs of CA/Co-BIT films for monitoring shrimp freshness (Xu et al., 2023). B. (a) SEM images of CD-MOF and PM (PSPAs@CD-MOF, the PSPAs are purple sweet potato anthocyanins); (b) colorimetric response and reversibility of the CA/PSPAs, CA/PM10, CA/PM15 and CA/PM15/EUG (eugenol) films; (c) CA/PM15/EUG10 for pork freshness monitoring and shelf-life extension (Pang et al., 2024). C. (a) Schematic illustration of the steps for the preparation of CA-based colorimetric sensor; (b) Digital photographs of colorimetric solid-state sensors and their corresponding differential map were taken while varying the concentrations of NH_3. The calibration curve was generated to showcase the relationship between the sensor response and NH_3 concentration (on the left side). Furthermore, interday and intraday digital photographs of the colorimetric solid-state sensor were captured before and after exposure to 1.0 ppm NH_3; (c) digital photograph of the colorimetric solid-state sensor before and after exposure to veal chicken and fish samples (Hashemian et al., 2023).



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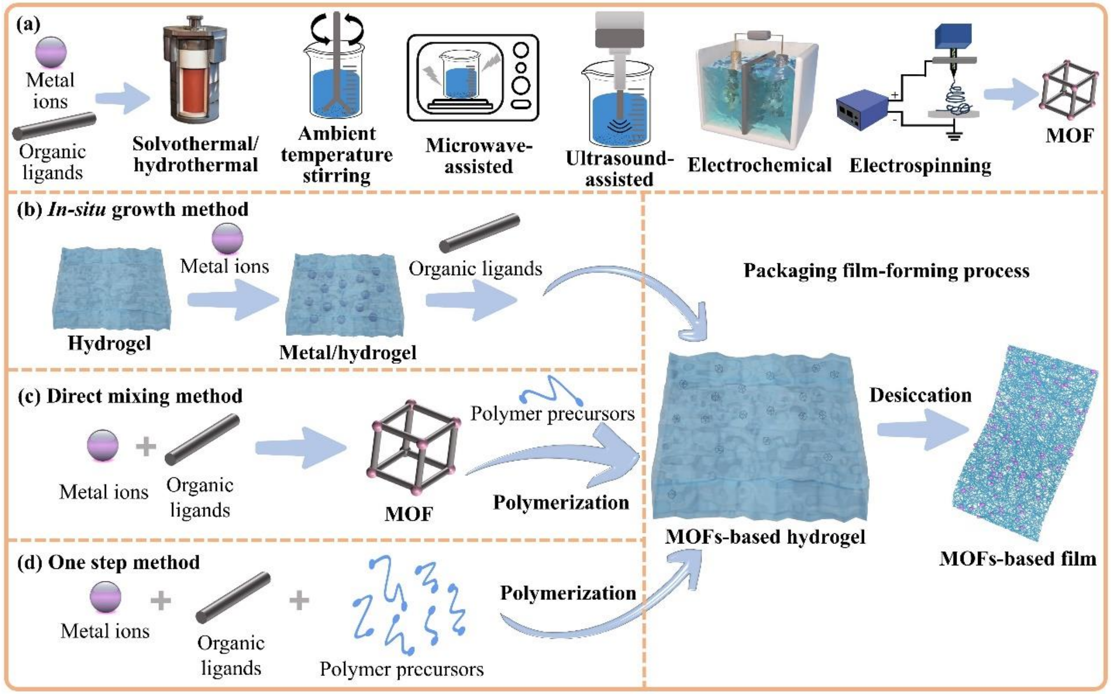

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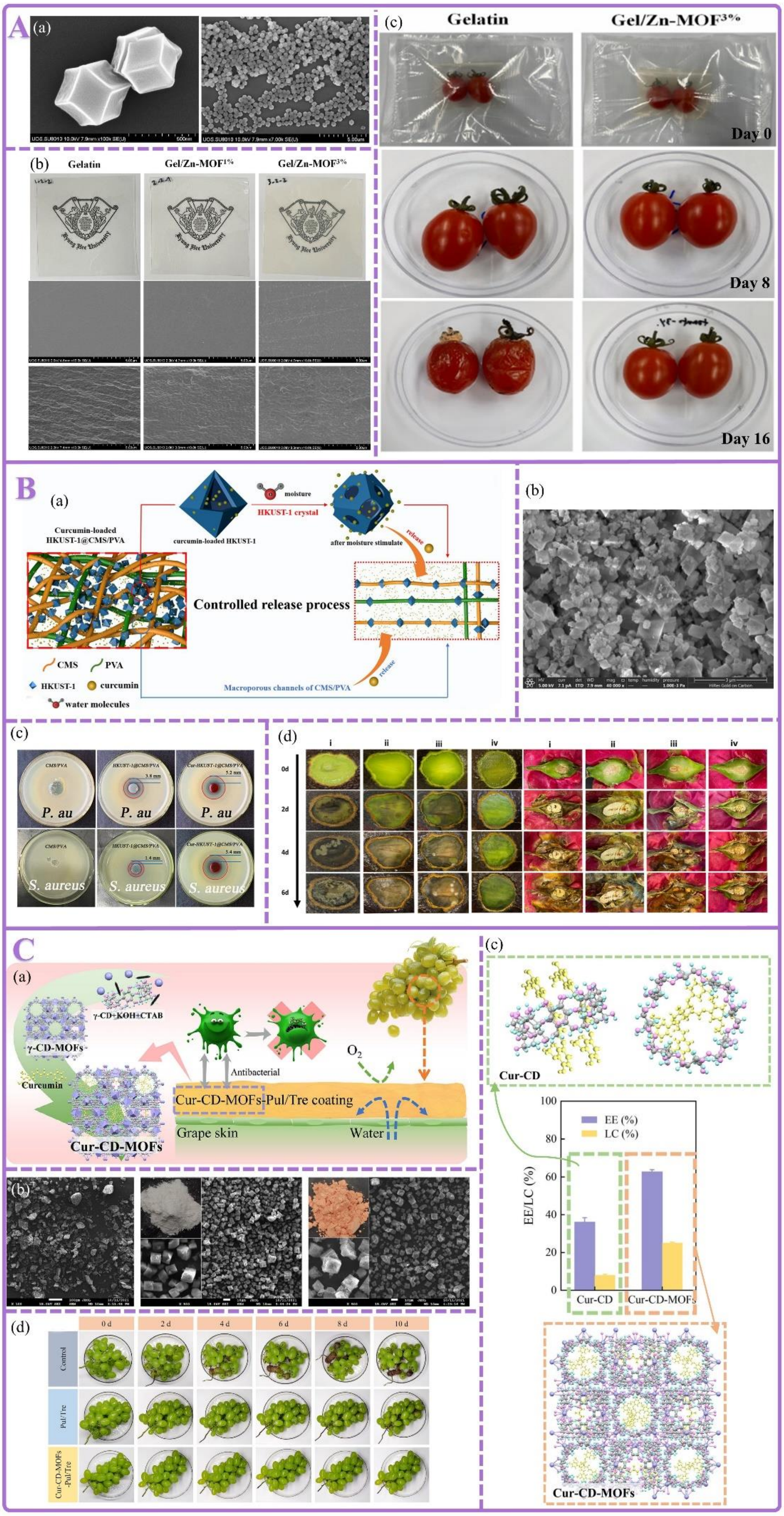
A
(a)
(b)
Gelatin
Gel/Zn-MOF1%
Gel/Zn-MOF3%
(c)
Gelatin
Gel/Zn-MOF3%
Day 0
Day 8
Day 16
B
(a)
Curcumin-loaded HKUST-1@CMS/PVA
curcumin-loaded HKUST-1
moisture
HKUST-1 crystal
after moisture stimulate
release
Controlled release process
CMS
PVA
HKUST-1
curcumin
water molecules
Macroporous channels of CMS/PVA
(b)
(c)
CMS/PVA
HKUST-1@CMS/PVA
Cur-HKUST-1@CMS/PVA
3.8 mm
5.2 mm
1.4 mm
5.4 mm
P. au
S. aureus
(d)
i
ii
iii
iv
0d
2d
4d
6d
C
(a)
γ-CD+KOH+CTAB
γ-CD-MOFs
Curcumin
Cur-CD-MOFs
Antibacterial
O2
Cur-CD-MOFs-Pul/Tre coating
Grape skin
Water
(b)
(c)
Cur-CD
EE (%)
LC (%)
EE/LC (%)
100
80
60
40
20
0
Cur-CD
Cur-CD-MOFs
(d)
0 d
2 d
4 d
6 d
8 d
10 d
Control
Pul/Tre
Cur-CD-MOFs-Pul/Tre

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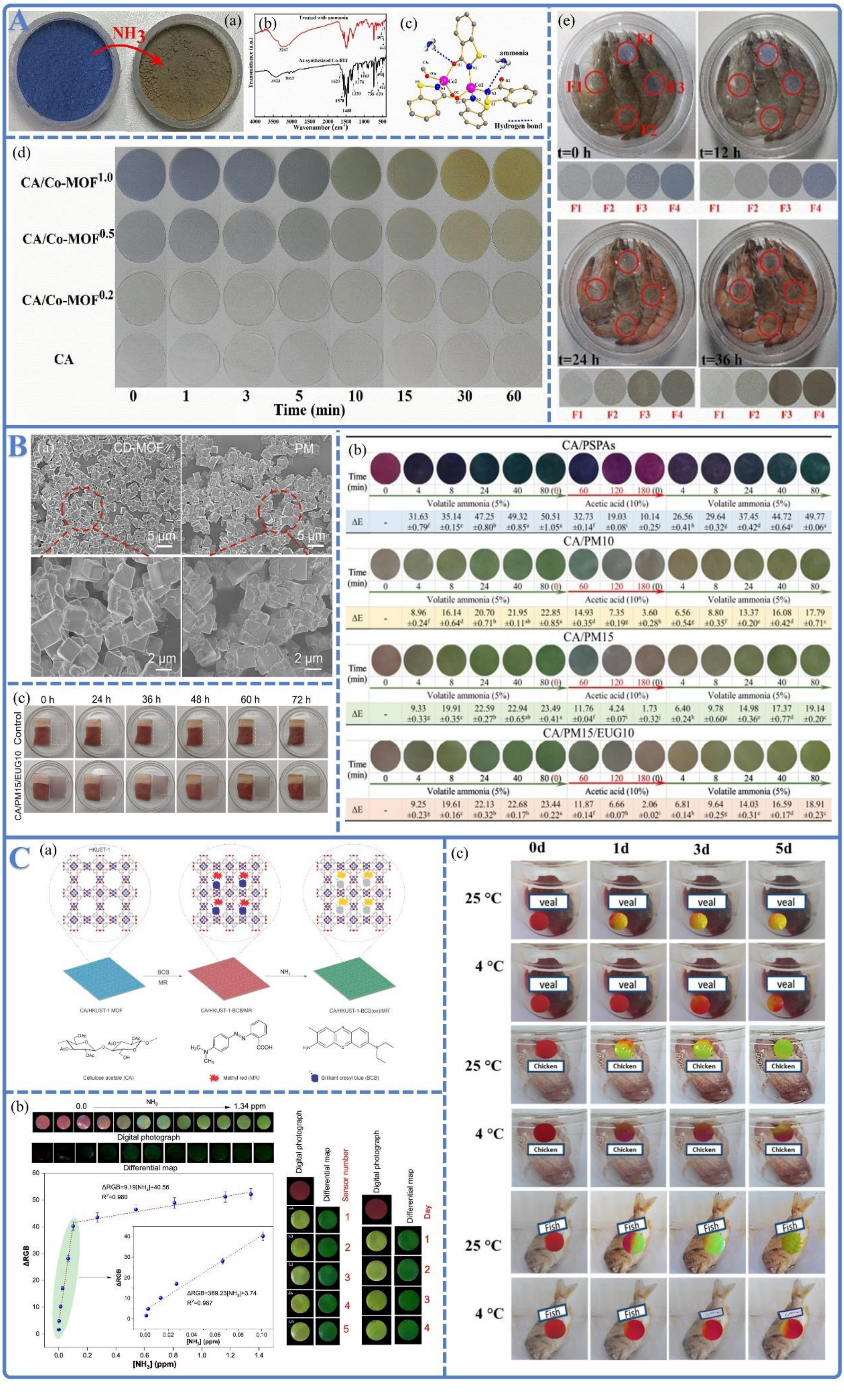

A
(a)
NH3
(b)
Treated with ammonia
As-synthesized Co-BH
Transmittance (a.u.)
Wavenumber (cm-1)
(c)
ammonia
Hydrogen bond
Co1
Co2
(d)
CA/Co-MOF1.0
CA/Co-MOF0.5
CA/Co-MOF0.2
CA
0
1
3
5
10
15
30
60
Time (min)
(e)
F1
F2
F3
F4
t=0 h
t=12 h
t=24 h
t=36 h
B
(a)
CD-MOF
PM
5 μm
2 μm
(b)
CA/PSPAs
Time (min)
0 4 8 24 40 80 (0) 60 120 180 (0) 4 8 24 40 80
Volatile ammonia (5%)
Acetic acid (10%)
Volatile ammonia (5%)
ΔE - 31.63±0.79f 35.14±0.15e 47.25±0.80b 49.32±0.85a 50.51±1.05a 32.73±0.14f 19.03±0.08i 10.14±0.25j 26.56±0.41h 29.64±0.32g 37.45±0.42d 44.72±0.64c 49.77±0.06a
CA/PM10
ΔE - 8.96±0.24f 16.14±0.64d 20.70±0.71b 21.95±0.11ab 22.85±0.85a 14.93±0.35d 7.35±0.19g 3.60±0.28h 6.56±0.54g 8.80±0.35f 13.37±0.20e 16.08±0.42d 17.79±0.71c
CA/PM15
ΔE - 9.33±0.33g 19.91±0.35c 22.59±0.27b 22.94±0.65ab 23.49±0.41a 11.76±0.04f 4.24±0.07i 1.73±0.32j 6.40±0.24h 9.78±0.60g 14.98±0.36e 17.37±0.77d 19.14±0.20c
CA/PM15/EUG10
ΔE - 9.25±0.23g 19.61±0.16c 22.13±0.32b 22.68±0.17b 23.44±0.22a 11.87±0.14f 6.66±0.07h 2.06±0.02i 6.81±0.14h 9.64±0.25g 14.03±0.31e 16.59±0.17d 18.91±0.23c
(c)
0 h
24 h
36 h
48 h
60 h
72 h
Control
CA/PM15/EUG10
C
(a)
HKUST-1
BCB
MR
NH3
CA/HKUST-1 MOF
CA/HKUST-1-BCB/MR
CA/HKUST-1-BCB(ox)/MR
Cellulose acetate (CA)
Methyl red (MR)
Brilliant cresyl blue (BCB)
(b)
0.0
NH3
1.34 ppm
Digital photograph
Differential map
ΔRGB=9.19[NH3]+40.56
R2=0.980
ΔRGB=389.23[NH3]+3.74
R2=0.987
ΔRGB
[NH3] (ppm)
Sensor number
Day
1
2
3
4
5
(c)
0d
1d
3d
5d
25 °C
4 °C
veal
Chicken
Fish

Fig. 3. A. (a) The color change and (b) FTIR spectra for Co-BIT before and after exposing to ammonia gas; (c) the variation in coordination environments for Co-BIT after exposing to ammonia gas; (d) the color change for CA/Co-BIT films after exposure to volatile ammonia; (e) photographs of CA/Co-BIT films for monitoring shrimp freshness (Xu et al., 2023). B. (a) SEM images of CD-MOF and PM (PSPAs@CD-MOF, the PSPAs are purple sweet potato anthocyanins); (b) colorimetric response and reversibility of the CA/PSPAs, CA/PM10, CA/PM15 and CA/PM15/EUG (eugenol) films; (c) CA/PM15/EUG10 for pork freshness monitoring and shelf-life extension (Pang et al., 2024). C. (a) Schematic illustration of the steps for the preparation of CA-based colorimetric sensor; (b) Digital photographs of colorimetric solid-state sensors and their corresponding differential map were taken while varying the concentrations of NH_3. The calibration curve was generated to showcase the relationship between the sensor response and NH_3 concentration (on the left side). Furthermore, interday and intraday digital photographs of the colorimetric solid-state sensor were captured before and after exposure to 1.0 ppm NH_3; (c) digital photograph of the colorimetric solid-state sensor before and after exposure to veal chicken and fish samples (Hashemian et al., 2023).

Table Captions

Table 1

Mechanical properties, water resistance and barrier performance of MOFs-based packaging films.

Table 2

Antibacterial properties of MOFs-based packaging films.

Table 3

Application of MOFs as loaders for food intelligent/active packaging systems.

Table 1

Mechanical properties, water resistance and barrier performance of MOFs-based packaging films.

MOFs	Substrate	Proportion	Synthesis method	Mechanical properties	Water resistance	Barrier performance	Food types	Ref.
Co-MOF	SA	9 wt%	Direct mixing method	TS: 82.5 MPa → 96.4 MPa EB: 10.2 % → 8.5 %	WA: 14.3 % → 10.2 %	UV-vis-shielding: 34.9 % → 5.3 % (T_{250}); 85.2 % → 82.2 % (T_{650}) WVP: 1.45×10^{-6} g/m·h·Pa → 1.26×10^{-6} g/m·h·Pa	Shrimp	(Feng et al., 2023)
Ag-MOF	PVA and ST	2.5 wt%	Direct mixing method	TS: 16.26 MPa → 27.67 MPa	MC: 11.21 % → 9.53 % WS: 48.35 % → 24.98 %	UV-vis-shielding: 4.06 % → 0.18 % ($T_{200-280}$); 26.81 % → 23.89 % (T_{600}) WVP: 0.525 gm·mm^{-2}·h^{-1}·kPa^{-1} → 0.342 gm·mm^{-2}·h^{-1}·kPa^{-1}	/	(Zhang et al., 2022)
Cu-MOF	Gelatin and carrageenan	3 wt%	Direct mixing method	/	/	UV-vis-shielding: 43.7 % → 0.09 %	Shrimp	(Khan et al., 2023)

						(T_{280}); 86.7 % → 47.9 % (T_{660})		
Co-MOF	Carboxymethyl cellulose	5 wt%	Direct mixing method	TS: 45.3 MPa → 85.0 MPa EB: 3.5 % → 11.7 %	WA: 28.3 % → 22.8 %	UV-vis-shielding: 63.5 % → 0.1 % (T_{250}); 89.4 % → 86.7 % (T_{700}) WVP: 3.4×10^{-7} g/m·h·Pa → 2.3×10^{-7} g/m·h·Pa	Shrimp	(Tang et al., 2023)
ZIF-8	Lignocellulosic and guar gum	80 wt%	Direct mixing method	TS: 1.21 MPa → 1.19 MPa	WS: 75.67 % → 46.52 % WCA: 25.35° → 49.47°	UV-vis-shielding: 42.57 % → 5.06 % ($T_{280-400}$) WVP: 0.32 g/m^2/day → 0.31 g/m^2/day	Banana	(Sultana, Kumar, & Gaikwad, 2023)
Cr-MOF	Gelatin and κ-carrageenan	4 wt%	Direct mixing method	TS: 41.8 MPa → 59.7 MPa EB: 27.82 % → 18.2 %	MC: 16.5 % → 11.6 % WS: 61.13 % → 48.28 %	UV-vis-shielding: 7.15 % → 2.6 % (T_{280}); 88.3 % → 73.5 % (T_{600}) WVP: 2.46×10^{-11}	Strawberry	(Khezerlou, et al., 2023)

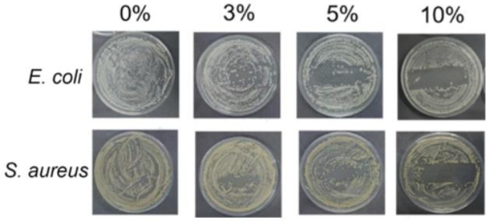
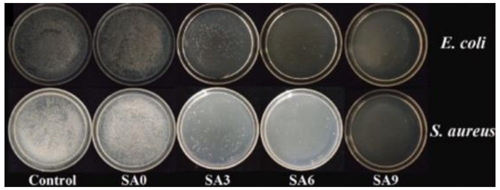
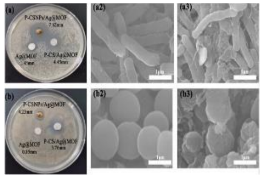
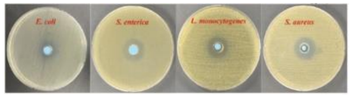
						gm/m^2·s·Pa → 2.34×10^{-11} gm/m^2·s·Pa		
MOF-545	Polycaprolactone (PCL)	10 wt%	Direct mixing method	TS: 13.1 MPa → 18.5 MPa EB: 12.3 % → 2.7 %	WCA: 107.4° → 73.0°	/	Fresh-cut apples	(Zhao, Shi, Liu, & Chen, 2023)
Ce-MOF	Cassava starch	4 wt%	Direct mixing method	/	WCA: 62.2° → 91.8° WS: 8.47 % → 5.0 % MC: 30.22 % → 22.28 %	/	/	(Jafarzadeh et al., 2024)
Zn-MOF	Gelatin	1 wt%	Direct mixing method	TS: 83.5 MPa → 88.0 MPa EB: 8.8 % → 6.8 %	WCA: 62.8° → 65.1°	WVP: 8.8×10^{-10} gm/m^2·s·Pa → 7.9×10^{-10} gm/m^2·s·Pa	Tomato	(Riahi et al., 2023)
Cu-MOF	Gelatin and PVA	3 wt%	Direct mixing method	TS: 65.7 MPa → 82.5 MPa	WCA: 63.2° → 67.6°	UV-vis-shielding: 20.2 % → 0.03 %	Shrimp	(Riahi, Khan, Rhim, Shin,

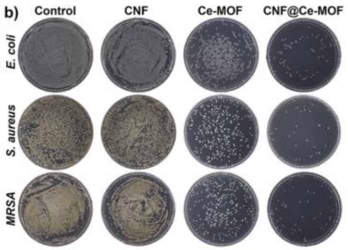
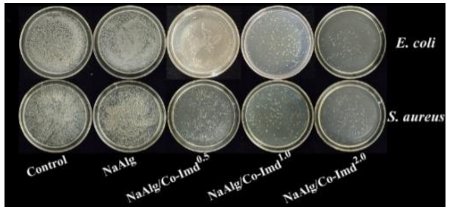
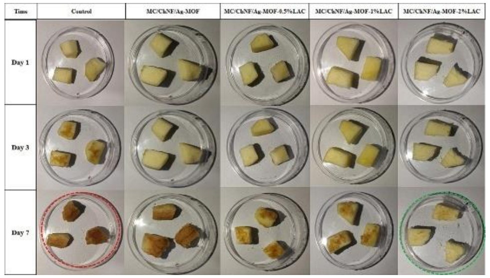
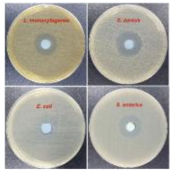
				EB: 6.7 % → 5.3 %		(T_{280}); 87.4 % → 67.2 % (T_{660}) WVP: 6.7×10^{-10} gm/m^2·s·Pa → 6.2×10^{-10} gm/m^2·s·Pa		& Kim, 2023)
Co-MOF	SA	2 wt%	Direct mixing method	TS: 48.56 MPa → 63.81 MPa EB: 11.89 % → 17.84 %	WA: 32.89 % → 26.87 %	WVP: 6.98×10^{-7} g/m·s·Pa → 4.85×10^{-7} g/m·s·Pa OP: 3.93×10^{-3} g/m^2·s → 3.14×10^{-3} g/m^2·s	Shrimp	(Wei et al., 2023)
Co-MOF	PVA	12 wt%	Direct mixing method	TS: 54.66 MPa → 41.77 MPa EB: 181.0 % → 245.3 %	WA: 3.70 % → 5.30 %	UV-vis-shielding: 76.8 % → 5.2 % (T_{275}); 89.5 % → 42.9 % (T_{750}) WVP: 1.67×10^{-7} g/m·s·Pa → 2.56×10^{-7} g/m·s·Pa	Shrimp	(Li et al., 2023)
ZIF67	CA	2 wt%	Direct mixing method	TS: 34.0 MPa → 36.9 MPa	WCA: 39.8° → 59.8°	UV-vis-shielding: 25.2 % → 0.7 %	Shrimp	(Zhang et al., 2023)

				EB: 5.0 % → 2.6 %		(T$_{280}$); 38.5 % → 16.6 % (T$_{700}$) OP: 2.73×10^{-3} g/m^2·s → 2.58×10^{-3} g/m^2·s		
γ-cyclodextrin (CD-MOF)	CA	15 wt%	Direct mixing method	TS: 26.22 MPa → 29.51 MPa EB: 4.33 % → 3.18 %	WCA: 42.06° → 39.36°	WVP: 6.39×10^{-7} g/m·h·Pa → 5.61×10^{-7} g/m·h·Pa OP: 8.97×10^{-5} g/m^2·s → 8.13×10^{-5} g/m^2·s	Pork	(Pang et al., 2024)
Ag-MOF	Methylcellulose and chitosan nanofibers	2 wt%	Direct mixing method	TS: 47.8 MPa → 56.1 MPa EB: 10.1 % → 6.5 %	WS: 46.1 % → 34.86 % WA: 109.0 % → 76.8 %	WVP: 2.13×10^{-11} g/m·s·Pa → 1.9×10^{-11} g/m·s·Pa OP: 2.6×10^{-3} g/m^2·s → 2.2×10^{-3} g/m^2·s	Apple	(Tavassoli et al., 2024)

Table 2

Antibacterial properties of MOFs-based packaging films.

Biopolymer	MOF	Proportion	Bacteria	Food types	Illustration of bacteriostatic effect	Ref.
PCL	MOF-545	3 %, 5 % and 10 %	*E. coli* and *S. aureus*	Fresh-cut apples		(Zhao et al., 2023)
SA	Co-MOF	3 %, 6 % and 9 %	*E. coli* and *S. aureus*	Shrimp		(Feng et al., 2023)
Chitosan	Ag-MOF	0.5 wt%, 1.0 wt% and 2.5 wt%	*E. coli* and *S. aureus*	/		(Zhang et al., 2022)
Gelatin and carrageenan	Cu-MOF	3 wt%	*E. coli*, *S. enterica*, *S. aureus* and *L. monocytogenes*	Shrimp		(Khan et al., 2023)

Cellulose nanofibers	Ce-UiO-66	9.23 %	*E. coli*, *S. aureus* and *MRSA* bacteria	Banana and mango		(Huang, Sun, Pu, Zhang, & Zhang, 2023)
SA	Co-MOF	0.5 wt%, 1.0 wt% and 2.0 wt%	*E. coli* and *S. aureus*	Shrimp		(Wei et al., 2023)
Methylcellulose and chitosan nanofibers	Ag-MOF	0.5 wt%, 1.0 wt% and 2.0 wt%	*E. coli* and *S. aureus*	Apple		(Tavassoli et al., 2024)
Gelatin/poly (vinyl alcohol)	Cu-MOF	1.0 % and 3.0 %	*L. monocytogenes*, *S. aureus*, *E. coli* and *S. enterica*	Shrimp		(Riahi et al., 2023)

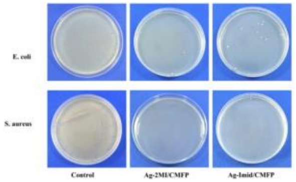
Carboxymethyl filter paper	Ag-MOF	/	*E. coli* and *S. aureus*	Cherry tomatoes and peaches		(Chen et al., 2024)

Table 3

Application of MOFs as loaders for food intelligent/active packaging systems.

MOFs	Precursors		Guest molecule	Functions	Applications	Characteristics	Ref.
	Metal salt	**Organic ligand**					
γ-CD-MOF	KOH	γ-CD	Curcumin	Antibacterial	Centennial Seedless grapes	Curcumin-based CD-MOF packaging demonstrates an exceptional efficacy in preserving postharvest produce.	(Kang et al., 2023)
β-CD-MOF	KOH	β-CD	Catechin	Antioxidant and antibacterial	/	Zein-based films effectively control the release dynamics of catechins.	(Jiang, Liu, Wang, Zhang, & Kang, 2022)
UiO-66	$ZrCl_4$	Terephthalic acid	Melatonin	Antioxidant	Spinach	The MOF-Melatonin composite film demonstrates superior efficacy in extending the shelf life of spinach compared to the application of melatonin through spraying alone.	(Wang et al., 2024)
γ-CD-	KOH	γ-CD	Purple sweet	Antioxidant,	Pork	The colorimetric response of the target	(Pang et al.,

MOF			potato anthocyanins	antibacterial and indicating		film enables the monitoring of pork freshness, and effectively extending its shelf life by up to 100% at a temperature of 25 °C.	2024)
Cr-MOF	$Cr(NO_3)_3\cdot 9H_2O$	2-NH_2-BDC	Lactoferrin	Antibacterial	Strawberries	The gelatin-κ-carrageenan/ lactoferrin-functionalized Cr-MOFs film inhibited the proliferation of spoilage molds on the fruit surface.	(Khezerlou, Tavassoli, Alizadeh-Sani, et al., 2023)
IRMOF-3	$Zn(NO_3)_2\cdot 6H_2O$	2-NH_2-BDC	Eugenol	Antioxidant and antibacterial	Strawberries	The chitosan/IRMOF-3- eugenol complex film exhibits exceptional resistance to oxidation and the capacity for sustained release of antibacterial agents.	(Chen et al., 2023)
γ-CD-MOF	KOH	γ-CD	Anthocyanins	Antioxidant	Kyoho grapes	The light and thermal stability of anthocyanins is enhanced by at least two-fold under the protection of CD-MOFs.	(Su et al., 2024)

HKUST-1	$Cu(NO_3)_2\cdot 6H_2O$	H_3BTC	Curcumin	Antioxidant and antibacterial	Avocado and pitaya	The Cur-HKUST-1-functionalized carboxymethyl starch/PVA composite film exhibited precise moisture-responsive release behavior and notably enhanced the shelf life of a variety of fruits.	(Liang et al., 2022)
Cu-MOF	$Cu(NO_3)_2\cdot 6H_2O$	H_3BTC	Cinnamon essential oil (CEO)	Antioxidant and antibacterial	Beef	The CEO@MOF integrated film exhibited 98.16% ABTS free radical scavenging activity and 99.9% inhibition of bacterial growth.	(Hong, Riahi, Shin, & Kim, 2024)
Ag-MOF	$AgNO_3$	Pyridine-3, 5-dicarboxylic acid	p-coumaric acid	Antioxidant and antibacterial	/	Double-layer composite film represents a promising material for oily food packaging.	(Zhang et al., 2022)
Ag-MOF	$AgNO_3$	NH_2-BDC	LAC	Antioxidant and antibacterial	Apple	The antibacterial agent in the composite film is released gradually, thus preserving the fresh appearance of the apple for an extended duration exceeding seven days.	(Tavassoli et al., 2024)

γ-CD-MOF	KOH	γ-CD	Limonene	Antibacterial	Fresh-cut apple	Molecular docking simulations indicate a propensity for limonene molecules to occupy the cavity of the CD monomer and the internal cavity of the MOF.	(Qin et al., 2024)
HKUST-1	$Cu(NO_3)_2\cdot 5H_2O$	H_3BTC	Methyl red and brilliant cresyl blue	Indicating	Veal, chicken and fish	The sensing platform enables real-time monitoring and data analysis utilizing online signals transmitted based on a smartphone.	(Hashemian et al., 2023)
Cr-MIL-101	$Cr(NH_3)\cdot 9H_2O$	H_2BDC	BTB	Indicating	Grass carp	The pigment mobility within the MOF-BTB labeling system decreases, resulting in a more pronounced and stable color transition.	(Wang et al., 2022)
Cu-MOF	$Cu(NO_3)_2\cdot 3H_2O$	H_3BTC	Red cabbage anthocyanin	Antioxidant, antibacterial and indicating	Shrimp	The extension of shelf life and the detection of shrimp sample deterioration validated the multifunctional capabilities of the packaging film.	(Riahi et al., 2023)
ZIF-8	$Zn(NO_3)_2\cdot 6H_2O$	2-methylimidazole	AL	Indicating	Beef	Due to the protective nature of MOFs, the stability of AL is enhanced and the	(Zhang et al., 2024)

						sensitivity of the indicator is increased.	
Cu-MOF	$Cu(CO_2CH_3)_2$	H_2BDC	Red cabbage anthocyanin	Antioxidant, antibacterial and indicating	Shrimp	The gelatin/carrageenan-MOF film exhibits remarkable efficacy in preventing shrimp spoilage, concurrently facilitating on-site monitoring of its freshness.	(Khan et al., 2023)
ZIF-L	$Zn(NO_3)_2\cdot 6H_2O$	2-methylimidazole	Grape anthocyanins	Indicating	Shrimp and minced beef	The freshness indicator distinctly delineates the steps of freshness and deterioration for shrimp and minced beef.	(Molaei, Moradi, Kahyaoğlu, & Forough, 2022)