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

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19 **Abstract**

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

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

35 *Key Findings and Conclusions:* The MOFs-based films emerge as promising candidate  
36 materials for food packaging applications, as the incorporation of MOFs substantially  
37 enhances the mechanical properties, water resistance, and barrier performance of pure  
38 biopolymer films. However, traditional food packaging methodologies encounter  
39 several challenges, including antibacterial, antioxidant properties, and the effective  
40 removal of active molecules. To overcome these limitations, the incorporation of

41 various MOF nanomaterials to enhance the physical and functional attributes of  
42 packaging films have been persistently investigated. Therefore, MOFs-based  
43 multifunctional film materials could be a viable alternative to develop food packaging.

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

## 46 **1. Introduction**

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

60 Recently, the substitution of biodegradable natural renewable polymers for  
61 petroleum-based compounds has become the focus of research endeavors (Abedi-  
62 Firoozjah et al., 2023; Alizadeh, Khezerlou, Tavassoli, Abedini, & McClements, 2024;  
63 Roy et al., 2023). Natural biopolymers including cellulose (Pang et al., 2024; Zhang et  
64 al., 2023), starch (Sanchez, Pinzon, & Villa, 2022; Zhang et al., 2022), chitosan (Chen  
65 et al., 2023; Nian, Xie, Sun, Wang, & Cao, 2023), gelatin (Khan, Riahi, Kim, & Rhim,  
66 2023; Riahi, Hong, Rhim, Shin, & Kim, 2023), and sodium alginate (SA) (Zhang,  
67 Zhang, Zhang, et al., 2024; Zhang et al., 2023) have been extensively investigated

68 within the food packaging industry. Regrettably, a considerable gap persists between  
69 the current state of biopolymer research and their practical applications in comparison  
70 to traditional packaging materials, attributed to their high production costs, inferior  
71 performance, and limited ductility (Feng et al., 2023). Therefore, it is necessary to  
72 enhance the mechanical and barrier properties of biodegradable packaging materials to  
73 protect food from the external atmosphere containing moisture and mechanical hazards.  
74 Through the implementation of various strategies aimed at augmenting the performance  
75 of biopolymers, including chemical modifications (cross-linking and graft  
76 copolymerization), physical modifications (filler incorporation and laminated  
77 composite formation), the utilization of deep eutectic solvents, irradiation-induced and  
78 biological enzyme treatments to enhance the performance of biopolymers, rendering  
79 them more adept for applications in food packaging, while concurrently preserving their  
80 environmental protection and sustainability attributes (Khajavian, Vatanpour, Castro-  
81 Muñoz, & Boczkaj, 2022).

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

90 [Huerta, & Lieder, 2021](#)). Among them, owing to their high specific surface area, tunable  
91 pore structure, selective adsorption capabilities, excellent chemical stability, low  
92 density, and ease of processing, MOFs have been widely investigated in the domain of  
93 food packaging field. MOFs constitute a category of porous nanomaterials, wherein  
94 organic ligands (such as dicarboxylic acid, tricarboxylic acid, tetracarboxylic acid, and  
95 imidazolate) and metal ions (serving as secondary building units) are interconnected to  
96 create an open crystalline scaffold with consistent porosity ([Alizadeh, Khezerlou,](#)  
97 [Tavassoli, Abedini, & McClements, 2024](#); [Zhang et al., 2024](#)). Moreover, MOFs are  
98 distinguished from other materials and can manifest unique chemical functionalities  
99 and intriguing adsorption characteristics through the concatenation of functional groups.  
100 In particular, due to their enduring porosity and pronounced crystallinity, MOFs can  
101 effectively engage with a diverse array of analytes ([Cheng, Tang, Zhang, Wu, & Yang,](#)  
102 [2021](#)). The inorganic-organic hybrid nature of nano-MOFs enables their facile  
103 integration with polymer matrices, rendering them highly appealing as nanofillers for  
104 the fabrication of high-performance nanocomposites. Different from other food  
105 packaging fillers, the advantages of MOFs are predominantly manifested in their  
106 multifunctionality. For instance, the remarkable benefits of MOFs facilitate their  
107 utilization as reinforcing agents ([Khan et al., 2023](#); [Wei et al., 2023](#)), active components  
108 ([Riahi et al., 2023](#)), luminescent indicators ([Tang et al., 2023](#)), and bioactive carriers  
109 ([Sanchez et al., 2022](#); [Wang et al., 2022](#)), thereby offering a prospective foundation for  
110 the advancement of diverse, targeted MOFs-based packaging films. Currently, some  
111 researches have underscored the potential of multifunctional MOFs-based films for

112 packaging applications (enhanced, active and intelligent), attributable to their superior  
113 physical properties, effective gas control within the packaging, as well as their  
114 antibacterial and antioxidant attributes ([Alizadeh, Khezerlou, & McClements, 2024](#);  
115 [Chen, Wang, Kong, & Wang, 2024](#); [Geng et al., 2023](#); [Sharanyakanth et al., 2020](#)).

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

## 134 2. Synthesis strategies for MOFs-based packaging films

135 MOFs-based packaging films commonly consist of solid MOFs particles  
136 randomly embedding into a three-dimensional network structure and the aqueous phase  
137 medium formed by the hydrogel. Therewith, MOFs and the hydrogel matrix could be  
138 considered as the dispersed phase and the flowing phase, respectively (Wang, Xu, Gao,  
139 Yao, & Zhang, 2019). Moreover, the physical and chemical cross-linking properties of  
140 the polymer materials and the hydrogen bonds between internal molecules can  
141 effectively combine with MOFs. The selection of synthetic strategies affects the final  
142 products, such as the structure of MOFs, the dispersibility of MOFs in hydrogels and  
143 the morphology of materials, thereby playing a crucial role in the performance and  
144 application of composite materials. Currently, the selection of synthesis methodologies  
145 for MOFs that are appropriate for utilization in food packaging is contingent upon the  
146 desired attributes of the MOF nanomaterials and their anticipated applications in the  
147 food industry (Alizadeh, Khezerlou, & McClements, 2024). Synthesis strategies  
148 generally include solvothermal/hydrothermal, ambient temperature stirring,  
149 microwave-assisted, ultrasound-assisted, electrochemical, and electrospinning  
150 approaches (Fig. 1a) (Zhang et al., 2024). Furthermore, the preparation process of  
151 MOFs-based packaging films can roughly be divided into three synthesis schemes (Fig.  
152 1b-d): *in-situ* growth method, direct mixing method and one step method. In the field  
153 of food packaging, these methods can be chosen based on specific process requirements.

### 154 2.1. Preparation of MOFs for food packaging applications

155 The MOFs for food packaging was fabricated via a bottom-up approach, entailing

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

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

176 *Ambient temperature stirring*: the method entails the continuous agitation of metal  
177 precursors, organic ligands, and additional solvents at a consistent temperature,

178 accompanied by stirring for a predetermined duration ([Sultana et al., 2023](#)). Owing to  
179 its absence of necessity for extreme temperature or pressure conditions and the  
180 facilitation of manipulating the reaction process, it holds considerable importance in  
181 the realm of sustainable chemical synthesis. Nevertheless, the principal constraint of  
182 this approach is the inadequate removal of the solvent, which ultimately culminates in  
183 the reduced purity of the resultant product.

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

194 *Ultrasound-assisted:* the operational principle of this method is founded on  
195 acoustic cavitation, encompassing the creation and disintegration of bubbles within the  
196 solution to produce localized hot spots. The morphological attributes of MOFs  
197 fabricated via this method are influenced by ultrasonic frequency, intensity, solvent  
198 volatility, temperature, and the gas content of the solvent. Additionally, ultrasound  
199 facilitates the cleansing of the MOF surface and activates unsaturated active metal ion

200 sites ([Alizadeh, Khezerlou, & McClements, 2024](#)). In comparison to the solvothermal  
201 method, the ultrasonic-assisted technique typically maintains elevated temperatures,  
202 prompting swift chemical reactions and immediate crystallization. However, it is  
203 imperative to cautiously assess the potential hazards associated with the noise generated  
204 by ultrasonic equipment, and large-scale production remains in its nascent stages.

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

216 *Electrospinning*: this method is highly appropriate for integrating MOFs into  
217 various hybrid materials, thereby endowing them with additional functionalities. The  
218 process involves amalgamating a slurry containing MOF with a polymer solution,  
219 followed by electrospinning to produce MOF-polymer composite nanofibers.  
220 Depending on the specific MOFs required, the electrospinning procedure can be fine-  
221 tuned by selecting appropriate solvents and polymers, as well as by adjusting

222 electrospinning parameters. The synthesis of MOFs via electrospinning offers  
223 numerous benefits, such as simplicity, high efficiency, versatility, scalability, and the  
224 capacity to yield products with elevated surface areas (Zhang et al., 2024). It is  
225 noteworthy that the design and development of MOFs-based electrospinning nanofibers  
226 represent an efficacious strategy for their utilization as a superior carrier for  
227 biomolecular encapsulation. Electrospinning nanofibers possess the potential benefits  
228 of enhancing the dispersion of embedded materials, optimizing the efficiency of  
229 controlled release, augmenting stability, and boosting bioavailability in the delivery of  
230 food ingredients (Castro-Muñoz, Kharazmi, & Jafari, 2023). Hence, encapsulating  
231 functional molecules within MOFs-based nanofibers will furnish an appropriate storage  
232 milieu for these molecules, thereby ensuring efficient delivery. However, it is important  
233 to acknowledge that this method encounters challenges in scaling up production and  
234 the potential degradation of the resulting polymer material, necessitating further  
235 advancements.

## 236 2.2. Preparation process of MOFs-based film

237 The incorporation of synthesized MOFs or their precursors (metal ions and organic  
238 linkers) into diverse polymer substrates such as casting, coating and nanofiber films,  
239 results in varied properties and application outcomes (Roy et al., 2023). The  
240 predominant attribute of MOFs-based casting films is their superior mechanical  
241 robustness and flexibility, and the integration of rigid MOF components enhances the  
242 overall rigidity or brittleness of film, with the extent of enhancement contingent upon  
243 the quantity of MOF incorporated and its dispersion. While the incorporation of MOF

244 may impact the processability of the casting film, such as melt fluidity and formability,  
245 the endowment of specific functionalities to MOF can provide novel attributes to the  
246 MOFs-based casting film (Sultana et al., 2023). The essential of MOFs-based coating  
247 films lies in their surface characteristics, and the incorporation of MOF can confer  
248 hydrophilic or hydrophobic surface properties to the coating. Furthermore, the addition  
249 of functional fillers into the coating enhances its capability for selective adsorption,  
250 catalysis, or sensing functionalities. And the homogeneity of MOF dispersion within  
251 the coating is critical for its overall performance (Zhang, Ahari, Zhang, & Jafari, 2023).  
252 The customization of pore size and porosity in MOFs-based nanofiber films is  
253 conducive to the selective response and regulation of target gases. Nanofiber films  
254 inherently possess a high specific surface area, and the incorporation of MOFs can  
255 significantly enhance their adsorptive capabilities, which ensures the precision of food  
256 monitoring and prolongs the shelf life of food products (Tavassoli et al., 2024).  
257 Additionally, the MOFs not only integrate with nanofiber membranes to fabricate  
258 multifunctional composite membranes but also contribute to the long-term stability of  
259 these films. All in all, the impact and underlying mechanisms of MOFs on various film  
260 materials vary significantly. It is imperative to select suitable film materials and MOFs  
261 based on the specific application criteria, and subsequently tailor the fabrication process  
262 accordingly.

#### 263 2.2.1. *In-situ* growth method

264 The purpose of the *in-situ* growth method is to directly synthesize MOFs in a  
265 polymer matrix, eliminating the need to acquire MOFs separately. Specifically, this

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

#### 277 2.2.2. Direct mixing method

278 In this method, start by preparing nanoscale MOFs particles, which could require  
279 homogenizing pestle grinding mortar, and mixed with a certain formula with polymer  
280 precursors. After the formation of a three-dimensional network in the hydrogel, the  
281 MOFs particles were successfully adhered to the polymer matrix. The direct mixing  
282 method is extensively utilized in the preparation of MOFs-based packaging films owing  
283 to their simplicity, gentle reaction conditions, and ease of control over the content and  
284 structure of MOFs. Another advantage of the direct mixing protocol is the convenient  
285 combination of water-sensitive MOFs-ligands and hydrogels. Certain functional  
286 molecules that typically cannot directly bind to hydrogels can be incorporated into the  
287 polymer matrix by first combining them with MOFs as primary carriers. What is worthy

288 of our attention is that MOFs can offer multiple binding sites for various small  
289 molecules and biomacromolecules through chemical coupling, encapsulation, and  
290 surface coordination, making them highly versatile (Zhao et al., 2023). Consequently,  
291 the utilization of direct mixing strategies to develop multifunctional platforms for  
292 MOFs-based films holds significant promise.

### 293 2.2.3. One step method

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

### 309 **3. Food packaging applications of MOFs-based films**

310 The three aforementioned methods used for producing MOFs-based films  
311 packaging merge the advantages of MOF materials and hydrogel substrates. As a result,  
312 a variety of composite materials with complementary properties, including adjustable  
313 composition and structure, flexibility, water stability, and pore structure characteristics,  
314 are obtained. Hence, the use of MOFs-based packaging films has been extensively  
315 explored in the fields of wound healing treatment (Zhang, Wang, Xiang, Jiang, & Zhao,  
316 2023), contaminant adsorption (Laddha, Jadhav, Agarwal, & Gupta, 2023), and target  
317 substance detection (Wang et al., 2023). In this section, emphasis will be placed on the  
318 applications of MOF materials in food packaging, especially the physicochemical  
319 modification of packaging films, the control of the packaging inner environment and  
320 food freshness, and the monitoring of food freshness. Furthermore, by drying the  
321 hydrogel based on MOFs to prepare MOFs-based films, the physicochemical properties  
322 of the packaging film can be greatly enhanced, particularly the mechanical capability.  
323 Therefore, in food packaging, MOF-based hydrogels are the preferred material for  
324 freshness indicators due to their ability to enhance coloring efficiency through their  
325 water content. The MOFs-based films are more appropriate for substituting petroleum-  
326 based packaging on the premise of ensuring safety.

#### 327 3.1. MOFs as reinforcers to modify packaging film

##### 328 3.1.1. Enhancement of mechanical properties

329 The assessment of the mechanical properties of packaging films can serve as a  
330 reliable indicator for predicting the performance of materials under various food

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

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

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

371 In summary, the mechanical properties are crucial for optimizing the processing  
372 and application of film materials based on MOFs. Upon external pressure-driven  
373 conditions in food packaging applications, the composite materials must be strong  
374 enough to maintain structure, and protect food from mechanical damage. It has been

375 demonstrated that the inclusion of a particular MOF enhanced the mechanical  
376 properties of the film in comparison to the pure polymer matrix. However, there are  
377 still several challenges in the current research. Although high concentration of MOFs  
378 has superior mechanical properties, excessive MOF content may result in the  
379 dissociation of heavy metal ions, thereby causing safety issues. The mechanical  
380 properties of the film exhibit significant deviations at different positions due to the  
381 uneven distribution of MOF particles.

### 382 3.1.2. Improvement of water resistance

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

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

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

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

### 426 3.1.3. Promotion of barrier performance

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

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

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

#### 475 3.1.4. Others considerations

476 In addition to the aforementioned mechanical properties, water resistance, and  
477 barrier performance, it is necessary to investigate other physical attributes (e.g.,  
478 thickness, thermal and morphological properties) of MOFs-based films. Among them,  
479 the packaging film thickness constitutes a pivotal parameter influencing mechanical,  
480 water absorption capacity, light resistance, and transparency, with the primary  
481 determinant of film thickness being the compositional makeup of the film substrate and  
482 the type and concentration of the filler material ([Abedi-Firoozjah et al., 2023](#)).  
483 According to the findings of [Tavassoli et al. \(2024\)](#), the incorporation of Ag-MOF  
484 substantially augmented the thickness of the pristine methylcellulose film, an effect

485 attributable to the integration of Ag-MOF into the film network and enhancing the solid  
486 content of the film. Nevertheless, certain studies have demonstrated that the  
487 incorporation of MOFs does not significantly affect the film thickness, likely due to  
488 even distribution and minimal concentration of fillers within the film matrix ([Jafarzadeh  
489 et al., 2024](#); [Maroufi et al., 2023](#)).

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

507 thermal degradation of the film.

508       The preparation of MOFs-based films is typically followed by a comprehensive  
509 microstructural analysis (including scanning electron microscopy (SEM), Fourier  
510 transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD)) to elucidate the  
511 morphological modifications of MOFs within the film substrates ([Riahi et al., 2023](#);  
512 [Zhang et al., 2024](#)). Typically, to observe the morphological structures of the film, the  
513 relevant images are obtained and analyzed by means of scanning electron microscopy  
514 (SEM) and field-emission SEM (FE-SEM). The resulting images from these  
515 microscopies afford insights into various morphological attributes, including the  
516 surface smoothness or roughness of the film, the homogeneity of filler dispersion, the  
517 presence of agglomerates, and potential fractures within the film ([Akhila & Badwaik,  
518 2022](#)). The SEM analysis on SA-based hydrogel film revealed that the films without  
519 MOF had a smooth surface but after the addition of fillers the surface showed distinct  
520 protrusions ([Wang et al., 2024](#)). Interestingly, the hydrophobic nature of the organic  
521 ligands facilitates the enhancement of the hydration of SA by the MOF, leading to the  
522 formation of a colloidal solution with a roughened surface. FTIR spectroscopy as a  
523 technique utilized for the analysis of molecular vibrations provides insights into the  
524 nature of chemical bonds and functional groups. When MOFs interact with the polymer  
525 matrix, the nature of the chemical interaction between MOFs and the film matrix can  
526 be elucidated through the analysis of experimental results. The metal centers within  
527 MOFs have the potential to form coordination bonds with the functional groups present  
528 in the matrix, leading to the emergence of new absorption peaks or shifts in the original

529 peak positions in the FTIR spectrum (Feng et al., 2023). Furthermore, the incorporation  
530 of MOFs may induce rearrangements of polymer chains or alterations in the local  
531 chemical environment within the film (Tang et al., 2023). It is noteworthy that MOFs  
532 can adsorb gases or substances on the surface of film, and the resulting FTIR spectrum  
533 may exhibit corresponding adsorption peaks, indicative of adsorption phenomena.  
534 Generally, MOFs tend to engage in hydrogen bonding and electrostatic interactions  
535 within the embedded film matrix (Zhang et al., 2024).

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

### 546 3.2 MOFs as active agents to control in-package environment and food freshness

547 As numerous studies have demonstrated, MOFs have emerged as highly desirable  
548 components in food industry applications, owing to their characteristic biocompatibility  
549 and inertness towards matrices (Shashikumar et al., 2023). Currently, MOFs are  
550 employed as active agents, especially in active food packaging, demonstrating

551 antibacterial properties and facilitating the removal of active molecules, thereby  
552 extending the shelf life of packaged products. Furthermore, MOF materials have the  
553 potential to selectively desorb and absorb bioactive compounds, and are preferably  
554 integrated into the active packaging of minimally processed foods. Their physical and  
555 chemical properties, essential for a potential packaging material, position MOFs as an  
556 advanced and eco-friendly choice for food packaging ([Sharanyakanth et al., 2020](#)). In  
557 this section, the potential applications of MOFs as active agents in food packaging  
558 materials, focusing on their ability to control the internal environment of packaging and  
559 food freshness are reviewed.

### 560 3.2.1. Antimicrobial properties

561 Food spoilage predominantly results from microbial contamination and oxidation  
562 processes. Consequently, it is crucial to prolong the shelf life and enhance the quality  
563 and safety of food by utilizing antibacterial packaging materials ([Ebrahimzadeh,  
564 Biswas, Roy, & McClements, 2023](#)). Antibacterial agents are typically incorporated  
565 into films to inhibit the spoilage of diverse food products and the proliferation of  
566 pathogenic microorganisms. The antimicrobial efficacy of packaging films and fillers  
567 is contingent upon the concentration of the incorporated antimicrobial agents, the nature  
568 of the polymer matrix, the predominant microbial load, the chemical composition of  
569 the food, pH, moisture content, storage conditions, and the specific type of  
570 microorganism ([Shen et al., 2023](#)). Recent studies have indicated that due to the  
571 effective antibacterial properties of MOFs, primarily involving structural damage to  
572 cell walls and disruption of crucial biochemical pathways, the nanomaterials are

573 considered to be an ideal filler for bioactive compounds in packaging films (Zhang et  
574 al., 2022).

575 For instance, incorporation of 4% Zn-MOF (which has antimicrobial activity) into  
576 gelatin films increased their antimicrobial activity against Gram-positive (*S. aureus* &  
577 *L. monocytogenes*) and Gram-negative (*S. enterica* & *E. coli*) bacteria (Riahi et al.,  
578 2023). The Zn-MOF, with a distinctive dodecahedral shape, was combined into the  
579 gelatin matrix, and the apparent morphology and color of the composite film underwent  
580 a transformation as the quantity of filler was increased. Owing to the innate highly  
581 porous structure of Zn-MOF, the production of reactive oxygen species (ROS), and the  
582 liberation of metal ions into bacterial media, MOFs demonstrated superior antibacterial  
583 efficacy against four bacterial species. Among these, ROS encompassing singlet  
584 oxygen, hydroxyl radicals, and superoxide anions, exert their antibacterial effects by  
585 damaging nucleic acids, inactivating proteins, and inducing lipid peroxidation, thereby  
586 impeding bacterial growth (Riahi, Rhim, Bagheri, Pircheraghi, & Lotfali, 2022).  
587 Moreover, the visual appearance of tomatoes (Day 16) during storage was substantially  
588 enhanced under the coating of MOF-based films (Fig. 2A). In a separate investigation,  
589 it was demonstrated that the integration of Co-MOF-based nanofibers into SA films  
590 effectively inhibited the growth of *E. coli* and *S. aureus* (Wei et al., 2023). Similarly,  
591 the incorporation of Co-MOF-based particles can enhance the antibacterial efficacy of  
592 various pure matrices, such as PVA (Li et al., 2023), CA (Zhang et al., 2023), and  
593 carboxymethyl cellulose (Tang et al., 2023) films. In summary, these studies show that  
594 Co-based MOFs can serve as efficacious additives in films to extend the shelf life of

595 packaged foods and enhance safety. The antibacterial properties of these films are likely  
596 attributable to the active capacity of agents to disrupt bacterial cell membranes, thereby  
597 leading to the efflux of cellular contents and ultimately cell death.

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

### 614 3.2.2. Antioxidant properties

615 Active packaging incorporating antioxidant complexes represents an effective  
616 approach to extending shelf life while maintaining food safety and quality (Roy et al.,

617 [2023](#)). The antioxidant potential of MOFs can be ascribed to their distinctive structural  
618 configuration, including the interconnection of metal nodes through organic ligands,  
619 which confers them with substantial porosity and surface area. Interestingly, certain  
620 MOFs have demonstrated inherent antioxidant characteristics, attributable to the redox  
621 reactivity of their metal centers or organic linkers. On the one hand, MOFs containing  
622 copper or manganese metal centers exhibit potential in catalyzing the  
623 disproportionation of superoxide radicals ([Xiang et al., 2023](#)). On the other hand, the  
624 synthesized MOFs are designed to release antioxidant components in response to  
625 specific stimuli by modifying organic ligands, and the modification strategy ensures  
626 enhanced specificity, minimizes side effects, and has better biocompatibility  
627 ([Jafarzadeh et al., 2024](#)). Commonly, the susceptibility of packaged foods to oxidative  
628 degradation is evaluated through antioxidant assays, including the ferric reducing  
629 antioxidant power (FRAP), 2,2-diphenyl-1-picrylhydrazyl (DPPH), and 2,2'-casino-bis  
630 (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS).

631 The escalating demand for high-quality and safe food products has spurred the  
632 investigation into antioxidant packaging films fabricated from MOF materials. For  
633 example, ZIF-8 has been embedded in gelatin-based films, serving as a favorable  
634 antibacterial component in food packaging ([Riahi et al., 2023](#)). The pure gelatin film  
635 exhibited good antioxidant properties by the ABTS assay, as evidenced by the  
636 interaction between free radicals and the free amino groups of gelatins. The radical  
637 scavenging ability of MOFs is realized through the synergistic effects of hydrogen  
638 donors, electron transfer pathways, and free radical adducts. In addition, the

639 hydrophilicity of the film facilitates the release of active components into the ABTS  
640 aqueous solution, thereby enhancing the interaction between the MOFs and ABTS free  
641 radicals (Riahi et al., 2022). Currently, limited literature is available on the antioxidant  
642 properties of MOF materials in food packaging application. The main research focuses  
643 on the encapsulation of guest molecules with antioxidant capabilities within MOFs or  
644 to graft these molecules onto organic ligands. It is significant to emphasize that the  
645 formulation of MOF within the film matrix should be optimized to the greatest extent  
646 possible to effectively enhance the antioxidant activity of packaging materials.

### 647 3.2.3. Gas controlling performance

648 The presence of oxygen, ethylene, water vapor, and other gases within the internal  
649 environment of food packaging adversely affects the quality and shelf life of food  
650 products. Some specific MOFs have gained significant interest as application  
651 components in the food industry, primarily due to their characteristic hydrophilic outer  
652 surface and hydrophobic inner cavity (Fig. 2B). Hence, MOF materials exhibit  
653 promising potential for gas absorption and storage applications within the domain of  
654 food packaging (Shashikumar et al., 2023): (1) Oxygen scavenging: Oxygen facilitates  
655 the oxidation of lipid-rich food matrices, fosters the proliferation of aerobic  
656 microorganisms and initiates oxidation reactions, thereby diminishing food quality.  
657 Some specific MOF materials possess excellent oxygen adsorption capacity, which  
658 reduces the oxygen concentration within the food packaging. This approach promotes  
659 the extension of the shelf life for perishable food and contributes to the preservation of  
660 their nutritional integrity and sensory qualities (Geng et al., 2023). (2) Moisture

661 absorption: Excessive moisture within food packaging can promote the proliferation of  
662 molds and bacteria, culminating in food spoilage and compromising safety. Owing to  
663 the intrinsic high porosity and large specific surface area of MOFs, these materials  
664 exhibit an outstanding capability for water absorption. The alteration of MOF pore  
665 dimensions, coupled with the strategic selection of linkers and secondary building units  
666 are helpful to adjust its hydrophilic properties and water adsorption characteristics  
667 ([Zhang et al., 2023](#)). (3) Ethylene concentration controlling: Controlling the ripening  
668 process of fresh produce, particularly fruits indigenous to tropical climates, poses a  
669 significant challenge during storage and transportation, and is crucial for preserving the  
670 desired quality attributes ([Sharanyakanth et al., 2020](#)). Ethylene as a phytohormone that  
671 directly determines the ripening and senescence processes of fruits and vegetables  
672 ([Wang et al., 2023](#)). Through the regulation of ethylene levels within the packaging, the  
673 unique properties of MOFs can markedly retard the ripening progression and extend  
674 the shelf life of fresh agricultural products ([Zhang et al., 2023](#)). (4) Other gas controlling  
675 capabilities: Apart from the aforementioned gases, customized MOFs can target other  
676 gases (including various volatile organic compounds (VOCs) and carbon dioxide)  
677 adsorption to improve the internal environment of food packaging. Among them, the  
678 adsorption of carbon dioxide by MOF materials plays an important role in regulating  
679 the pH levels within food packaging, thereby inhibiting the proliferation of spoilage  
680 microorganisms. VOCs, which are the primary contributors to food odor resulting from  
681 the oxidation of the food matrix and microbial activity, can also be adsorbed using MOF,  
682 effectively enhancing the sensory quality of packaged food products ([Alizadeh,](#)

683 [Khezerlou, Tavassoli, Abedini, & McClements, 2024](#)).

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

705 [2021](#)).

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

### 715 3.3 MOFs as indicative factors for monitoring of food freshness

716 Intelligent packaging encompasses the incorporation of internal or external  
717 indicators within the packaging matrix to monitor the dynamic interaction between food  
718 products, packaging materials, and the ambient environment, without usually affecting  
719 the quality and flavor attributes of the food ([Zhang, Sun, Sang, Jia, & Ou, 2022](#)).  
720 Commonly, the intelligent packaging film is composed of pigments sensitive to targeted  
721 gases and biodegradable polymer matrices. It is noteworthy that the selection and  
722 preparation of pigments constitutes a critical aspect in the development of intelligent  
723 films. Recently, some alcohol-soluble dyes such as synthetic pigments (e.g.,  
724 bromocresol green, cresol red, polyaniline and alizarin) and natural extracted colorants  
725 (e.g., anthocyanin, curcumin and betacyanin) have found extensively application as  
726 sensor materials in food packaging ([Zhang, Sun, Sang, Jia, & Ou, 2022](#)). The principle

727 of MOFs-based luminescent films in food packaging relies on the distinctive properties  
728 of MOFs, such as their extensive surface area, adjustable constituent units, modifiable  
729 organic ligands, and tailorable pore sizes (Zhang et al., 2024). The luminescent  
730 attributes of MOF as indicators can be attributed to four primary strategies that facilitate  
731 the interaction between the indicator and the analyte (Fig. S1): (1) The utilization of  
732 lanthanide elements exhibiting luminescent characteristics or other metal salts with  
733 coloration properties. (2) Using organic ligands comprising conjugated or aromatic  
734 moieties that possess luminescent attributes or other ligands modified by specialized  
735 functional groups. (3) Encapsulating fluorescent guest molecules or pigments into non-  
736 luminescent MOFs. (4) Using catalytic emitters for the functionalization of target  
737 molecules to achieve luminescent objectives (Liu, Xie, Cheng, Shao, & Wang, 2019;  
738 Zhang et al., 2024).

739 According to the aforementioned luminescence response strategy, some MOFs-  
740 based luminescent packaging films have developed recently for the detection of diverse  
741 different gas targets. The volatile amines generated by meat products emit a  
742 disagreeable odor and constitute a significant health risk to humans. Xu et al. (2023)  
743 presented on the development of an ammonia-sensitive colorimetric film with Co-BIT  
744 loaded within CA matrix to monitor the spoilage of shrimp (Fig. 3A). The coloration of  
745 Co-BIT microcrystals transitioned from blue to brown after exposure to volatile  
746 ammonia, demonstrate that the synthesized MOF had good ammonia-sensitive  
747 discoloration capability. Additionally, the characteristic absorption peak of the infrared  
748 spectrum of Co-BIT was obviously shifted after contact with volatile amines. This

749 alteration is attributed to the formation of hydrogen bonding interactions between the  
750 MOF and amines, resulting in a modification of the Co element coordination  
751 environment and ultimately leading to a change in the color characteristics of the MOF  
752 (Can, Demirci, Sunol, & Sahiner, 2020). The CA/Co-BIT composite film demonstrates  
753 a substantial color response to ammonia, and its color stability (stored at 30 °C and 53%  
754 relative humidity for 45 days) fulfills the criteria for intelligent packaging applications  
755 ( $\Delta E$  value < 1.0) (Zhang et al., 2023). Furthermore, the utilization of shrimp as a  
756 representative model for meat products was employed to further explore the  
757 applicability of colorimetric composite film as an intelligent packaging material for  
758 meat deterioration. The color change of the composite film is intimately associated with  
759 the accumulation of total volatile basic nitrogen (TVB-N) in shrimp spoilage.  
760 Regrettably, there exists a deficiency in the pertinent assessment of the fitting properties  
761 between color difference parameters and TVB-N levels.

762 In short, the intrinsic color attributes of MOFs broaden the applications of MOFs-  
763 based colorimetric films and provide some advantages for manufacturing intelligent  
764 food packaging materials. The stability of this material can compensate for the  
765 deficiencies of natural colorants which easily decomposes when exposed to heat, light  
766 and enhance the sensitivity of the colorimetric film. However, MOFs-based intelligent  
767 films require the supplementary use of spectrometers for a more accurate demonstration  
768 of the phenomena. In addition, articles on the applications of organic ligand  
769 modification and catalytic coloration of MOFs in intelligent packaging are still lacking.  
770 Consequently, it is imperative to invest more resources towards the direct visualization

771 of substantial color changes and to develop MOFs-based film sensor arrays capable of  
772 detecting multiple targets in future research.

### 773 3.4 MOFs as active compound carriers

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

782 Certain natural active components, such as anthocyanins, curcumin, and catechins,  
783 lack sufficient stability and are prone to degradation upon exposure to light and varying  
784 temperatures ([Fernandes et al., 2020](#)). Substantial progress has been made in enhancing  
785 the stability of these biological compounds without changing the main physical and  
786 chemical properties, including copigmentation, MOFs-loading, and  
787 microencapsulation ([Klisurova et al., 2019](#); [Liu et al., 2023](#); [Yao, Xu, Zhang, Liu, &  
788 Zhang, 2021](#)). Nevertheless, the majority of organic ligands utilized in the synthesis of  
789 MOFs are derived from non-renewable petroleum raw materials, which constrains their  
790 applicability within the food industry owing to the non-biodegradability and inherent  
791 toxicity of MOFs ([Chen et al., 2021](#)). Hence, cyclodextrin (CD)-based MOFs have  
792 attracted special attention due to their common edible properties, biodegradability and

793 excellent biocompatibility. As a non-toxic organic ligand for MOFs, CD is a cyclic  
794 oligosaccharide composed of glucose units, possessing a hydrophobic cavity capable  
795 of encapsulating guest molecules of diverse sizes and geometries (Kang et al., 2023).  
796 The CD-MOFs possess a porous structure with an extensive surface area, rendering  
797 them excellent hosts for the encapsulation and delivery of bioactive compounds.

798 Curcumin is widely used in food packaging as an active ingredient to improve  
799 food quality and safety attributable to its effective antioxidant, anti-inflammatory and  
800 antibacterial properties. However, the limited solubility and bioavailability of curcumin  
801 in aqueous environments, and its instability under various environmental conditions  
802 constrain its application in the realm of food packaging (Sanchez et al., 2022). Kang et  
803 al. (2023) employed  $\gamma$ -CD-MOFs as a slow-release carrier and integrated it with  
804 curcumin to fabricate a multifunctional material denoted as Cur-CD-MOFs. The non-  
805 toxic Cur-CD-MOFs were synthesized through the interaction between the carrier and  
806 the carbonyl group, enolic side ring, and benzene ring of curcumin. Curcumin was not  
807 only uniformly dispersed in the porous structure of  $\gamma$ -CD-MOFs, but also encapsulated  
808 in the hydrophobic cavities of these materials, thereby significantly enhancing the  
809 thermal stability and photochemical stability of curcumin. Subsequently, Cur-CD-  
810 MOFs were incorporated into a binary film composed of pullulan (Pul) and trehalose  
811 (Tre), resulting in the formation of a Cur-CD-MOFs-Pul/Tre food packaging film. The  
812 curcumin released by the MOF within this composite film effectively suppressed the  
813 spoilage and dehydration of Centennial Seedless grapes (CSg). In another study, a CD-  
814 MOFs with structural components entirely sourced from edible constituents,

815 specifically potassium chloride and food-grade  $\gamma$ -CD, has been developed (Su, Su, Xing,  
816 & Tan, 2024). The researchers hypothesize that the principal rationale for the utilization  
817 of MOFs as host materials for anthocyanins is the disparity between the molecular  
818 dimensions of anthocyanins and the pore size of the CD-MOFs, ensuring the possibility  
819 of encapsulation in the pores of CD-MOFs (Fig. 2C). On the other hand, the presence  
820 of diverse functional sites within CD-MOFs facilitates the stabilization of anthocyanins  
821 in these pores, a process mediated by a spectrum of non-covalent interactions between  
822 the skeletal structure of MOF and the anthocyanin molecules (Chen et al., 2021). The  
823 DPPH scavenging efficacy of unencapsulated anthocyanins was significantly  
824 diminished after exposure to heat and ultraviolet radiation. Notably, the degradation of  
825 antioxidant capacity was efficiently mitigated upon the encapsulation of anthocyanins  
826 within CD-MOFs. In the storage experiment of Kyoho grapes, the incorporation of a  
827 film with anthocyanin-MOF composites can remarkably curtail the desiccation of plant  
828 tissues and inhibit the hydrolysis of monosaccharides and the respiration of over-  
829 ripening fruits.

830 In addition to loading some functional factors that prolong the shelf life of food,  
831 MOFs are capable of encapsulating pigments prone to leaching, thereby ensuring food  
832 safety and the precision of indicator responses (Alnoman et al., 2022) (Fig. 3B). The  
833 time-temperature stability and relatively poor selectivity of food freshness indicators  
834 have persistently posed significant challenges, and addressing these challenges is  
835 essential for enhancing the efficacy and dependability of solid-state colorimetric  
836 indicators (Hashemian et al., 2023) (Fig. 3C). At present, MOFs as porous structure and

837 large surface area nanomaterials are suitable for accommodating colorimetric indicators,  
838 resulting in ensuring stable display of the probe. Moreover, the active metal nodes and  
839 organic linkers of MOFs are capable of engaging in a multitude of chemical and  
840 physical interactions, such as hydrogen bonding,  $\pi$ - $\pi$  stacking, and electrostatic  
841 attractions between the functional groups of MOFs and biological ligands, further  
842 enhancing their potential in indicator applications (Cheng et al., 2021).

843 The overall quality of beef decreased gradually during storage, with nutrients  
844 being subject to degradation by microbial and enzymatic activity, resulting in the  
845 production of volatile biogenic amines (Han et al., 2023). To effectively monitor the  
846 freshness of beef, Zhang et al. developed a photothermally stable pigment through the  
847 incorporation of the phytochemical alizarin (AL) into the microporous framework of  
848 ZIF-8, utilizing physical adsorption and hydrogen bonding mechanisms (Zhang, Zhang,  
849 Zhang, et al., 2024). It is worth noting that the structural characteristics and crosslinking  
850 level increase the difficulty of ammonia diffusion after the integration of the AL@ZIF-  
851 8 composite into the polymer matrix to create an intelligent film, which ultimately  
852 affects the color intensity and distribution in the film. Generally, compared with natural  
853 colorants, traditional synthetic dyes can induce pronounced color transitions  
854 characterized by high saturation and contrast within an abbreviated timeframe, and are  
855 more resistant to light and thermal (Silva, Mastrantonio, Costa, & Morais, 2019).  
856 Nevertheless, the formation of hydrogen bonds between water vapor molecules in high-  
857 humidity environments can result in pigment migration, and potentially posing risks to  
858 food safety in packaging and ultimately affecting human health. In addressing the above

859 issue, this fascinating report showcased the amination of the organic ligand within  
860 MOFs and the subsequent grafting of bromothymol blue (BTB) pigment by amide  
861 coupling reactions (Wang et al., 2022). The majority of BTB molecules are integrated  
862 into the framework through intermolecular interactions, preserving the structural  
863 integrity of the MOF, resulting in the modified pigment (MOF-BTB) grafting results  
864 are considerable. Furthermore, through assessing the adsorption capacity of Co-MOF  
865 for the synthetic chemical pigments phenol red (PR) and bromothymol blue (BTB),  
866 Zhang et al. integrated PR or BTB into Co-MOF to construct color nanohybrids for  
867 monitoring the freshness of fresh-cut fruits (Zhang, Zhang, Wang, et al., 2024). Owing  
868 to the adsorption efficacy of Co-MOF, the pigment migration characteristics in the  
869 sodium carboxymethyl cellulose (CMC-Na) film were enhanced, thereby offering  
870 significant insights into the modulation of pigment migration via MOFs.

871 In conclusion, MOFs offer a proficient platform for encapsulating multifunctional  
872 natural extracts or colorants, enabling them to exert targeted effects, thereby endowing  
873 the extension of shelf life and monitoring functions of food packaging. The  
874 development of an efficient industrial-scale production method for MOFs is essential  
875 to facilitate their potential application as carriers in food packaging field. Additionally,  
876 the cavity dimensions within the porous nanoparticle MOF must be appropriately  
877 matched to the guest molecule size. A cavity that is too small may not accommodate  
878 the embedding of the guest molecule, while a cavity that is too large may not provide  
879 sufficient adsorption or grafting strength to effectively retain the guest molecule. The  
880 MOFs composed of heavy metals have non-biodegradable properties and intrinsic

881 toxicity, necessitating a thorough evaluation of their safety for use in food packaging.  
882 The domain of natural material transport and targeted gas capture utilizing the emerging  
883 edible CD-MOF remains in its infancy, requiring further investigation (Rajkumar,  
884 Kukkar, Kim, Sohn, & Deep, 2019). In particular, the modulation of their pore size and  
885 morphology can significantly influence the loading capacity and release kinetics of  
886 active compounds. In subsequent investigations, it would be beneficial for researchers  
887 to explore the integration of novel food constituents into MOFs-based film materials  
888 for delivery applications. For instance, the incorporation of *Zingiber officinale* into  
889 active packaging systems can augment the nutritional profile of food formulations  
890 (Garza-Cadena et al., 2023); carminic acid, characterized by its multifaceted properties  
891 including coloring, sensory enhancement, and health promotion, incorporated into  
892 packaging materials can enhance the functionalization of intelligent packaging systems  
893 (Ferreira-Suarez, Paredes-Vargas, Jafari, García-Depraect, & Castro-Muñoz, 2024);  
894 and the Capsaicin, renowned for its therapeutic effects in the prevention and treatment  
895 of gastric disorders and thermoregulation, presents itself as a promising candidate for  
896 such integration (Castro-Muñoz, Gontarek-Castro, & Jafari, 2022). Finally, Table 3  
897 summarizes the utilization of representative MOFs as loaders within the context of food  
898 packaging over the past few years.

#### 899 **4. Toxicity of MOFs-based films**

900 The application scenarios of MOFs-based packaging films are frequently in direct  
901 or indirect contact with food. The retention of hazardous solvents employed in the  
902 synthesis process and the raw materials for the synthesis of MOFs (namely organic

903 ligand functional groups and metal ions) are the primary contributors to the toxic effects  
904 associated with MOFs. Hence, the assessment of the toxicity of MOFs and their  
905 migration behavior within polymer matrices are imperative for ensuring human health  
906 and environmental safety (Ettlenger et al., 2022). This section discusses safety concerns  
907 pertaining to MOFs-based fillers in packaging films, encompassing potential risks and  
908 strategies for their mitigation.

909 The primary consideration must be the potential risks posed by the toxicity of  
910 metal ions that constitute MOFs in the realm of food packaging. Accordingly, it is  
911 imperative to ascertain the minimal acceptable human tolerance limits for such metals,  
912 particularly when employing bioincompatible heavy metal ions. Furthermore, the  
913 migration of MOFs after their incorporation into the polymer matrix should also be  
914 evaluated to prevent direct contact between the MOF and foodstuffs. The intrinsic  
915 nanoscale particle size of MOFs renders them susceptible to invasion, with their pores  
916 being laden with volatile organic solvents after preliminary synthesis or washing  
917 procedures. The activation of MOFs facilitates the evacuation of residual solvents from  
918 the pores and the removal of guest molecules from the framework pores by vacuum  
919 treatment, heat treatment, solvent exchange, and other methodologies (Chang et al.,  
920 2023). Additionally, to ensure the material functions without adverse effects on  
921 organisms, it is necessary to consider factors such as inflammation and immune  
922 response, and to conduct in vitro and in vivo studies on cells is essential to assess the  
923 biocompatibility and toxicity of MOFs with various cell types and tissues (Ettlenger et  
924 al., 2022).

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

## 943 **5. Conclusion and future perspectives**

944 Food packaging is mainly designed for food safety and long-term preservation.  
945 The recent advancements in packaging technology have introduced enhanced, active  
946 and intelligent packaging materials. Empirical evidence has demonstrated the

947 advantages of MOFs in the domain of food packaging, ensuring the quality and safety  
948 of food products. The multifunctional properties of MOFs can be utilized to enhance  
949 the food supply chain across various stages of progression.

950 MOFs as a kind of reinforcer can modify the comprehensive physical performance  
951 (e.g., mechanical properties, water resistance, barrier performance and thermal  
952 properties) of packaging films by increasing novel factors such as tortuosity within the  
953 film structure. These attributes render the polymer matrix more diverse, facilitating the  
954 development of advanced packaging innovations. Numerous MOFs-based film  
955 materials exhibit UV-blocking capabilities, enhanced oxygen barrier properties,  
956 reduced water vapor permeability, superior thermal stability, and increased mechanical  
957 robustness. These functionalities are typically challenging to attain in pristine polymer  
958 matrices. Characteristics of nanocomposites have the potential to transform the  
959 biopolymer sector, mitigating its limitations and serving as a viable alternative to  
960 petrochemical-based packaging materials. Some studies on nanocomposite films have  
961 reported the development of antibacterial and antioxidant attributes of MOFs  
962 incorporated within composite films, as well as the improvement in modified  
963 atmosphere engineering properties, enabling packaging to remove or inhibit substances  
964 capable of causing food spoilage. Among them, the cavity structure of MOFs can  
965 selectively adsorb and desorb gases such as oxygen, carbon dioxide, and ethylene. This  
966 capability allows MOF nanoparticles to regulate the gas composition within packaging  
967 environments, thereby prolonging the shelf life of food products. In addition, by  
968 diminishing the oxygen concentration in the packaging atmosphere, MOFs-based

969 packaging systems can decelerate oxidation reactions, thereby retarding spoilage  
970 processes. MOFs can also serve as indicative factors for monitoring food freshness in  
971 intelligent packaging materials, as they can be engineered to respond to alterations in  
972 pH, temperature, humidity, or gas concentrations. For instance, when exposed to  
973 specific target gases or as food starts to spoil, MOFs will undergo a color change. Such  
974 colorimetric films can assist consumers in assessing the freshness of products, thereby  
975 contributing to the reduction of food waste. Additionally, MOFs can function as carriers  
976 for the encapsulation, protection, and controlled release of bioactive compounds, which  
977 further expands their utility in packaging applications.

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

989         In summary, MOFs and their composite materials as functional coatings in food  
990 packaging have garnered significant interest, particularly for their potential in the

991 controlled release of preservatives and ensuring product safety. Therefore, it is  
992 necessary to develop multifunctional MOFs with exceptional sensing, stability, and  
993 adsorptive properties for integration into intelligent packaging systems. Nevertheless,  
994 several challenges must be overcome before their widespread adoption. Currently, the  
995 cost associated with large-scale production of MOFs is prohibitively high. Another  
996 concern is the potential migration of MOFs from packaging materials into food  
997 products. Lastly, a comprehensive assessment of the metabolic pathways is necessary  
998 to guarantee that any unintentional ingestion of MOFs does not adversely affect human  
999 health in the long term.

1000

#### 1001 **Declaration of competing interest**

1002 The authors declare that they have no known competing financial interests or  
1003 personal relationships that could have appeared to influence the work reported in this  
1004 paper.

1005

#### 1006 **Data availability**

1007 Data will be made available on request.

1008

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## Figure Captions

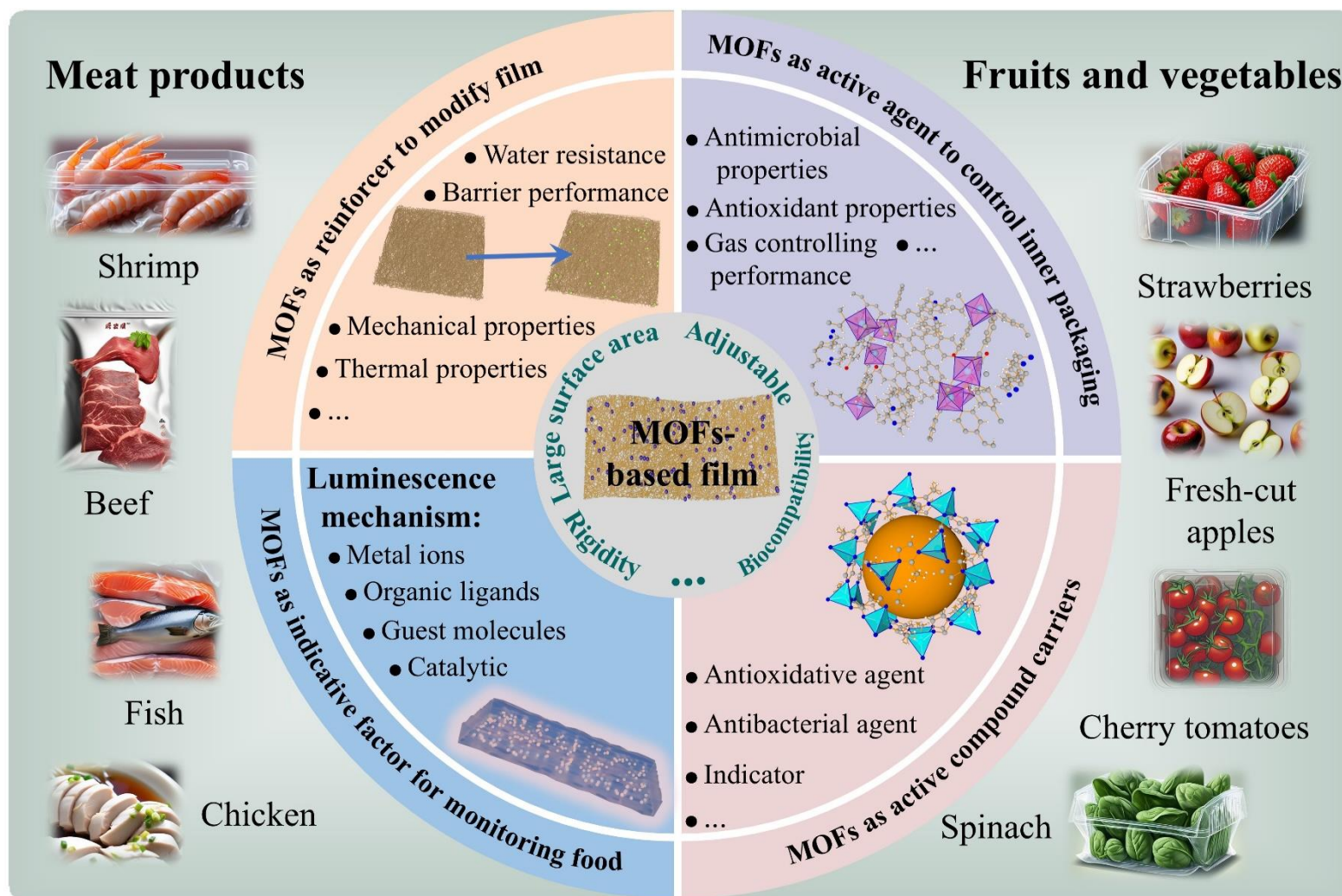
**Scheme 1.** Schematic representation of MOFs-based film for food packaging application.

**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.

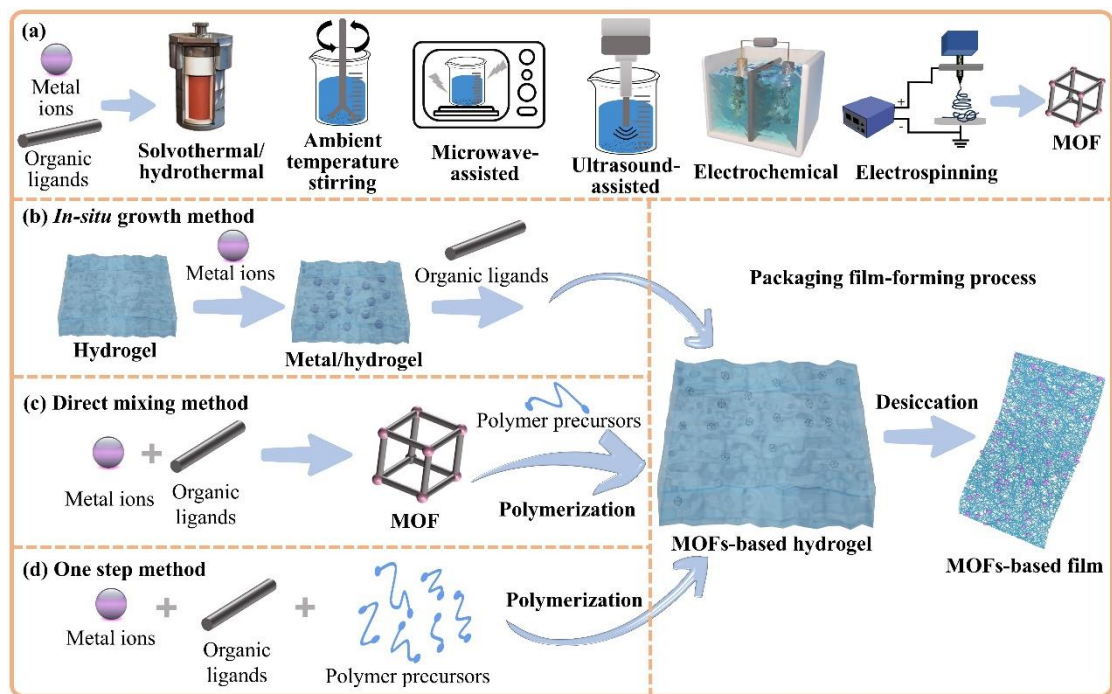
**Fig. 2.** A. (a) Microscopic morphology of Zn-MOF; (b) Actual view, surface and cross-sectional of gelatin-based composite films; (c) The visual characteristics of tomatoes with neat gelatin film and gelatin/Zn-MOF3% composite film (Riahi et al., 2023). B. (a) Schematic diagram for curcumin release 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  $\gamma$ -CD,  $\gamma$ -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

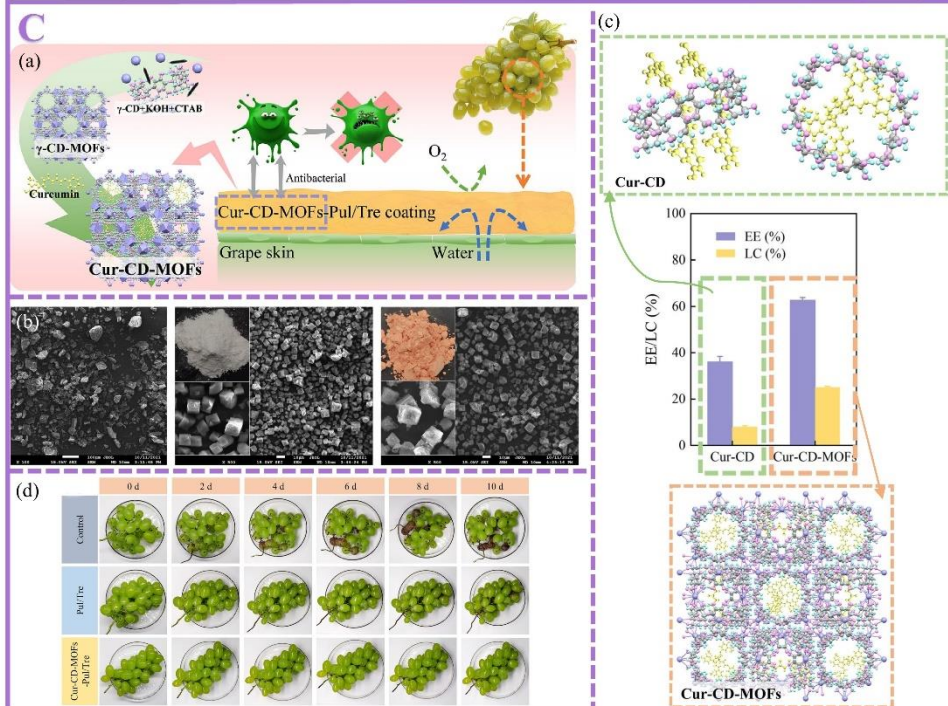
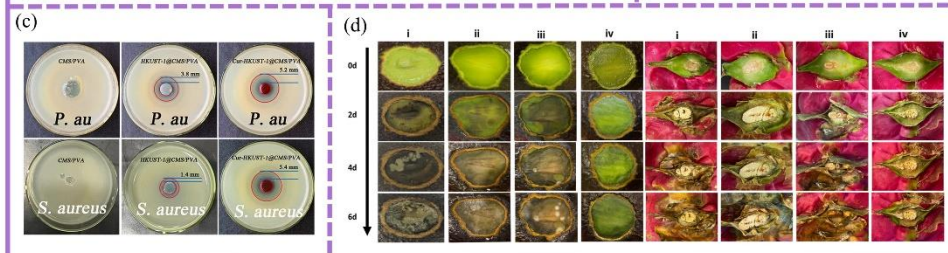
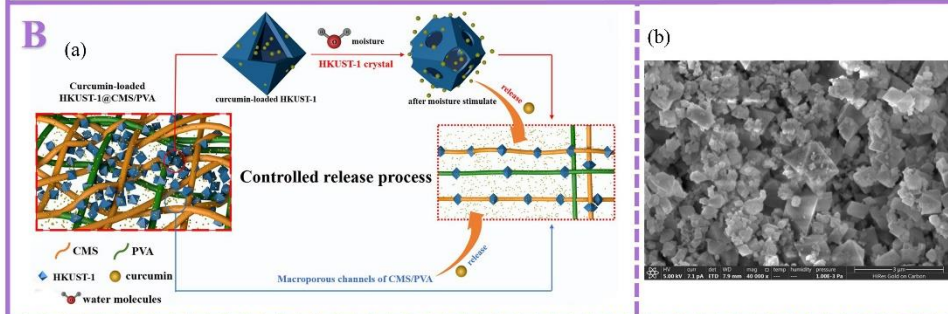
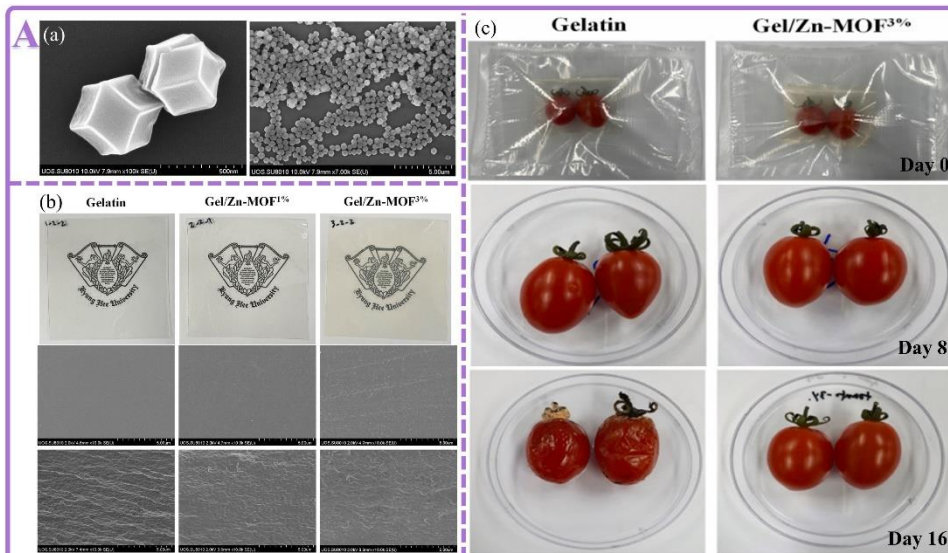
exposing to ammonia gas; (c) the variation in coordination environments for Co-BIT after exposing to ammonia gas; (d) the color change for CA/Co-BIT films after exposure to volatile ammonia; (e) photographs of CA/Co-BIT films for monitoring shrimp freshness (Xu et al., 2023). B. (a) SEM images of CD-MOF 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  $\text{NH}_3$ . The calibration curve was generated to showcase the relationship between the sensor response and  $\text{NH}_3$  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  $\text{NH}_3$ ; (c) digital photograph of the colorimetric solid-state sensor before and after exposure to veal chicken and fish samples (Hashemian et al., 2023).



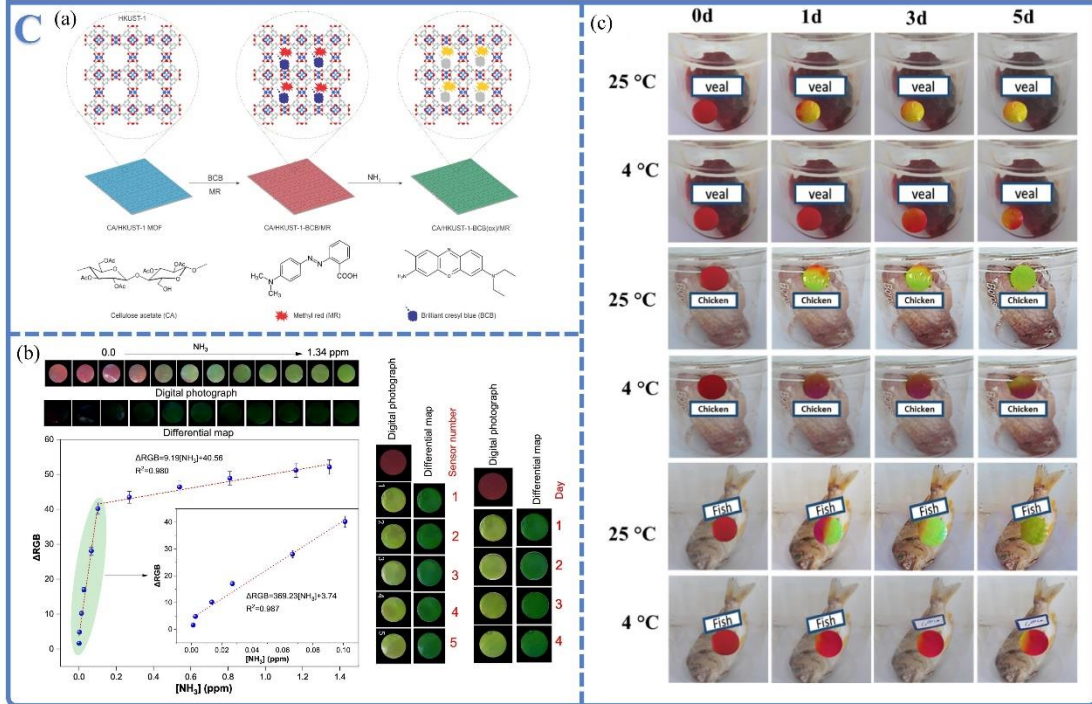
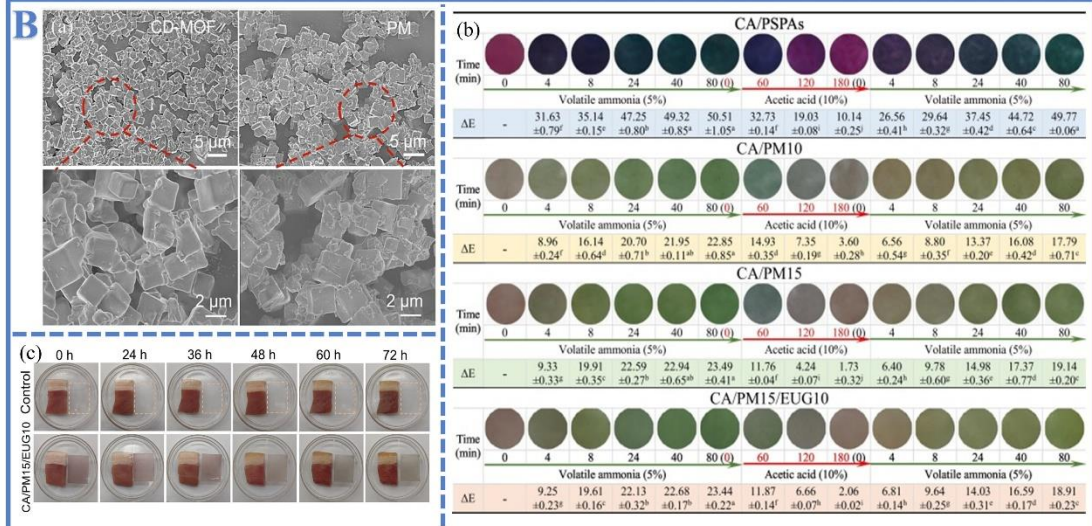
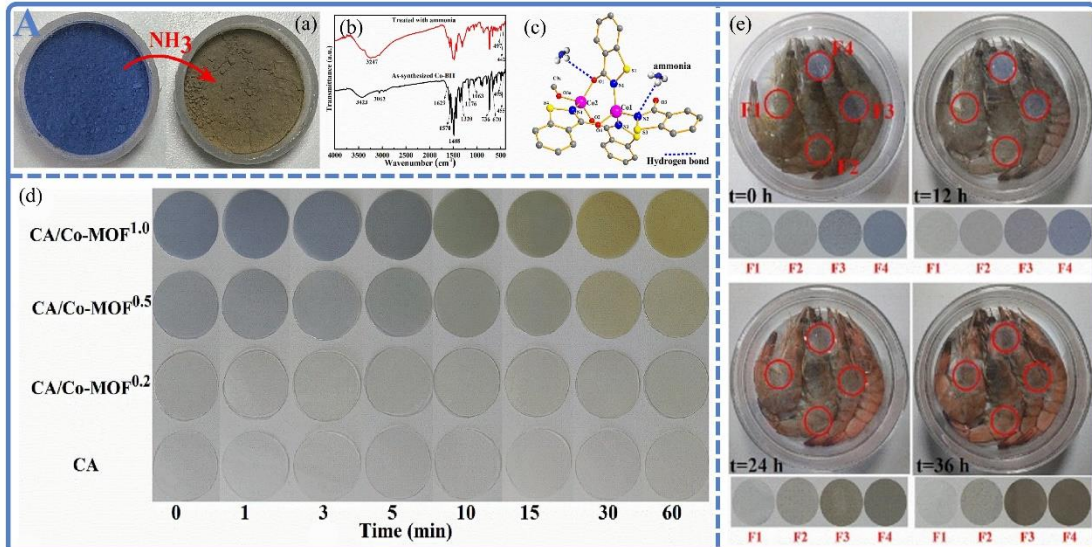
**Scheme 1.** Schematic representation of MOFs-based film for food packaging application.



**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.



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## **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 <sub>250</sub> ); 85.2 % → 82.2 % (T <sub>650</sub> ) WVP: 1.45×10 <sup>-6</sup> g/m·h·Pa → 1.26×10 <sup>-6</sup> 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 <sub>200-280</sub> ); 26.81 % → 23.89 % (T <sub>600</sub> ) WVP: 0.525 gm·mm <sup>-2</sup> ·h <sup>-1</sup> ·kPa <sup>-1</sup> → 0.342 gm·mm <sup>-2</sup> ·h <sup>-1</sup> ·kPa <sup>-1</sup>	/	(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 <sub>280</sub> ); 86.7 % → 47.9 % (T <sub>660</sub> )		
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 <sub>250</sub> ); 89.4 % → 86.7 % (T <sub>700</sub> ) WVP: 3.4×10 <sup>-7</sup> g/m·h·Pa → 2.3×10 <sup>-7</sup> 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 <sub>280-400</sub> ) WVP: 0.32 g/m <sup>2</sup> /day → 0.31 g/m <sup>2</sup> /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 <sub>280</sub> ); 88.3 % → 73.5 % (T <sub>600</sub> ) WVP: 2.46×10 <sup>-11</sup>	Strawberry	(Khezerlou, et al., 2023)

						gm/m <sup>2</sup> ·s·Pa → 2.34×10 <sup>-11</sup> gm/m <sup>2</sup> ·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 <sup>-10</sup> gm/m <sup>2</sup> ·s·Pa → 7.9×10 <sup>-10</sup> gm/m <sup>2</sup> ·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 <sub>280</sub> ); 87.4 % → 67.2 % (T <sub>660</sub> ) WVP: 6.7×10 <sup>-10</sup> gm/m <sup>2</sup> ·s·Pa → 6.2×10 <sup>-10</sup> gm/m <sup>2</sup> ·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 <sup>-7</sup> g/m·s·Pa → 4.85×10 <sup>-7</sup> g/m·s·Pa OP: 3.93×10 <sup>-3</sup> g/m <sup>2</sup> ·s → 3.14×10 <sup>-3</sup> g/m <sup>2</sup> ·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 <sub>275</sub> ); 89.5 % → 42.9 % (T <sub>750</sub> ) WVP: 1.67×10 <sup>-7</sup> g/m·s·Pa → 2.56×10 <sup>-7</sup> 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 <sub>280</sub> ); 38.5 % → 16.6 % (T <sub>700</sub> ) OP: 2.73×10 <sup>-3</sup> g/m <sup>2</sup> ·s → 2.58×10 <sup>-3</sup> g/m <sup>2</sup> ·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 <sup>-7</sup> g/m·h·Pa → 5.61×10 <sup>-7</sup> g/m·h·Pa OP: 8.97×10 <sup>-5</sup> g/m <sup>2</sup> ·s → 8.13×10 <sup>-5</sup> g/m <sup>2</sup> ·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 <sup>-11</sup> g/m·s·Pa → 1.9×10 <sup>-11</sup> g/m·s·Pa OP: 2.6×10 <sup>-3</sup> g/m <sup>2</sup> ·s → 2.2×10 <sup>-3</sup> g/m <sup>2</sup> ·s	Apple	(Tavassoli et al., 2024)

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**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 %	<i>E. coli</i> and <i>S. aureus</i>	Fresh-cut apples	<p>0% 3% 5% 10%</p> <p><i>E. coli</i></p> <p><i>S. aureus</i></p>	(Zhao et al., 2023)
SA	Co-MOF	3 %, 6 % and 9 %	<i>E. coli</i> and <i>S. aureus</i>	Shrimp	<p>Control SA0 SA3 SA6 SA9</p> <p><i>E. coli</i></p> <p><i>S. aureus</i></p>	(Feng et al., 2023)
Chitosan	Ag-MOF	0.5 wt%, 1.0 wt% and 2.5 wt%	<i>E. coli</i> and <i>S. aureus</i>	/	<p>(a) (b) (c)</p> <p>(d) (e) (f)</p>	(Zhang et al., 2022)
Gelatin and carrageenan	Cu-MOF	3 wt%	<i>E. coli</i> , <i>S. enterica</i> , <i>S. aureus</i> and <i>L. monocytogenes</i>	Shrimp	<p><i>E. coli</i> <i>S. enterica</i> <i>L. monocytogenes</i> <i>S. aureus</i></p>	(Khan et al., 2023)

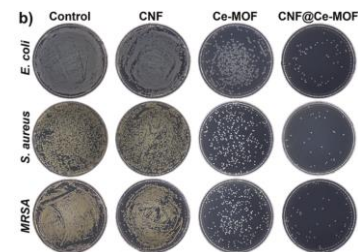
Cellulose nanofibers

Ce-UiO-66

9.23 %

*E. coli*, *S. aureus* and *MRSA* bacteria

Banana and mango



(Huang, Sun, Pu, Zhang, & Zhang, 2023)

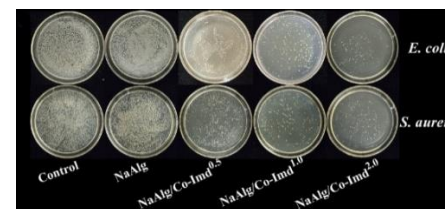
SA

Co-MOF

0.5 wt%, 1.0 wt% and 2.0 wt%

*E. coli* and *S. aureus*

Shrimp



(Wei et al., 2023)

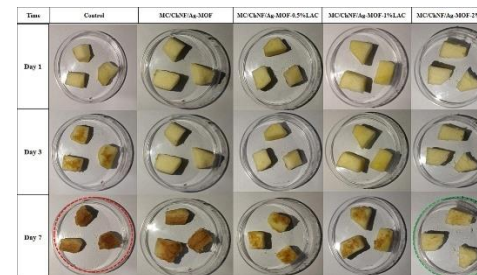
Methylcellulose and chitosan nanofibers

Ag-MOF

0.5 wt%, 1.0 wt% and 2.0 wt%

*E. coli* and *S. aureus*

Apple



(Tavassoli et al., 2024)

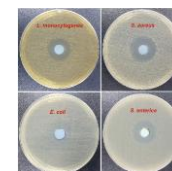
Gelatin/poly(vinyl alcohol)

Cu-MOF

1.0 % and 3.0 %

*L. monocytogenes*, *S. aureus*, *E. coli* and *S. enterica*

Shrimp



(Riahi et al., 2023)

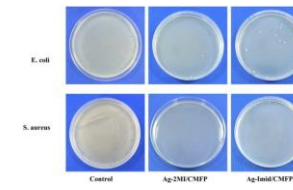
Carboxymethyl  
filter paper

Ag-MOF

/

*E. coli* and *S. aureus*

Cherry  
tomatoes and  
peaches



(Chen et al.,  
2024)

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**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					
$\gamma$ -CD-MOF	KOH	$\gamma$ -CD	Curcumin	Antibacterial	Centennial Seedless grapes	Curcumin-based CD-MOF packaging demonstrates an exceptional efficacy in preserving postharvest produce.	(Kang et al., 2023)
$\beta$ -CD-MOF	KOH	$\beta$ -CD	Catechin	Antioxidant and antibacterial	/	Zein-based films effectively control the release dynamics of catechins.	(Jiang, Liu, Wang, Zhang, & Kang, 2022)
UiO-66	ZrCl <sub>4</sub>	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)
$\gamma$ -CD-	KOH	$\gamma$ -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 <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	2-NH <sub>2</sub> -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 <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	2-NH <sub>2</sub> -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)

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HKUST-1	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{H}_3\text{BTC}$	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	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{H}_3\text{BTC}$	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	$\text{AgNO}_3$	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	$\text{AgNO}_3$	$\text{NH}_2\text{-BDC}$	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)

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$\gamma$ -CD-MOF	KOH	$\gamma$ -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	$\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$	$\text{H}_3\text{BTC}$	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	$\text{Cr}(\text{NH}_3)_9 \cdot \text{H}_2\text{O}$	$\text{H}_2\text{BDC}$	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	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	$\text{H}_3\text{BTC}$	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	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2-methylimidazole	AL	Indicating	Beef	Due to the protective nature of MOFs, the stability of AL is enhanced and the	(Zhang et al., 2024)

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						sensitivity of the indicator is increased.	
Cu-MOF	$\text{Cu}(\text{CO}_2\text{CH}_3)_2$	$\text{H}_2\text{BDC}$	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	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	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)

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