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MOF-Based Active Packaging Materials for Extending Post-Harvest Shelf-Life of Fruits and Vegetables

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Abstract: Active packaging that can extend the shelf-life of fresh fruits and vegetables after picking can assure food quality and avoid food waste. Such packaging can prevent the growth of microbial and bacterial pathogens or delay the production of ethylene, which accelerates the ripening of fruits and vegetables after harvesting. Proposed technologies include packaging that enables the degradation of ethylene, modified atmosphere packaging, and bioactive packaging. Packaging that can efficiently adsorb/desorb ethylene, and thus control its concentration, is particularly promising. However, there are still large challenges around toxicity, low selectivity, and consumer acceptability. Metal-organic framework (MOF) materials are porous, have a specific surface area, and have excellent gas adsorption/desorption performance. They can encapsulate and release ethylene and are thus good candidates for use in ethylene-adjusting packaging. This review focuses on MOF-based active-packaging materials and their applications in post-harvest fruit and vegetable packaging. The fabrication and characterization of MOF-based materials and the ethylene adsorption/desorption mechanism of MOF-based packaging and its role in fruit and vegetable preservation are described. The design of MOF-based packaging and its applications are reviewed. Finally, the potential future uses of MOF-based active materials in fresh food packaging are considered.

Keywords: metal-organic frameworks; active packaging; ethylene absorption/desorption; post-harvest fruit and vegetable; shelf-life.

Introduction

Fruits and vegetables are necessary for people's wealth and health, and with the continuous development of means of agricultural production, preservation packaging, and logistics technology, the consumption of fruits and vegetables is increasing worldwide. Consumers are increasingly concerned about the quality of food in terms of nutritional content and freshness, and prefer to purchase food based on its color, aroma, texture, and other characteristics. However, the freshness and appearance of fruits and vegetables are strongly affected by the storage time and preservation conditions [1]. Due to their nature, fruits and vegetables are prone to spoilage and deterioration after picking, leading to economic losses and other problems. About 30% of the world's food is wasted every year due to spoilage, microbial attack, and mechanical damage [2,3], and this has aroused wide concern around the world. In December 2020, the Food and Agriculture Organization of the United Nations (FAO) called for innovation and technology to promote healthy and sustainable fruit and vegetable production, reduce losses and waste, guarantee product safety and quality, and extend the shelf-life of fresh produce. Therefore, there is an urgent need to develop safe, environmentally friendly food packaging to extend the shelf-life of fruits and vegetables.

Discussions

The fabrication of innovative packaging is an essential factor in the industrial chain, and adsorption technology for packaging has particular advantages, such as the storage and selective adsorption/desorption of gases. MOF materials are potential gas adsorbents due to their high specific surface area, microporous nature, and pore volume. Hu's group investigated the gas adsorption of UiO-66(Zr) and found that it can undergo reversible CO_2 adsorption and desorption more than 500 times, with good resistance to structural damage. Kapelewski's team fabricated a modified MOF-74 which can store hydrogen through physical adsorption, with a working capacity of 11.0 g • L^{-1} at 25 ° C. Jiao et al. demonstrated selective gas adsorption of HKUST-1, which exhibited better adsorption of xenon (Xe) than krypton (Kr), with an adsorption capacity of more than 60% (mass fraction), which is almost twice that of commercial activated carbon. Therefore, MOF materials as ethylene adsorbents are a crucial development for the packaging industry.

Application of MOF Packaging Materials in Fruit and Vegetable Preservation. In active packaging, an active agent that functions as, for example, a release system, absorption system, or removal system is incorporated in the packaging material to improve the safety and shelf-life of food. Recent studies have highlighted MOFs as potentially active agents in fruit and vegetable preservation because of their excellent gas scavenging, antibacterial activity, and moisture absorption.

Application of MOFs in Ethylene Adsorption/Desorption of Fruit and Vegetable Packaging. Ethylene affects the shelf-life and maturity of fresh agricultural produce and causes spoilage of fruits and vegetables. In food packaging, it is always necessary to avoid ethylene coming into direct contact with the food surface due to safety concerns. Zhang et al. developed MOFs that can be used to encapsulate ethylene and then release it in a controlled manner at the desired stage. It has been proved that ethylene gas can be adsorbed by copper terephthalate MOFs (CuTPA) that have a porosity of 0.39 cm^3g^{-1} and can adsorb and release up to 654 pL of ethylene. Not only can it create an ethylene-rich space to facilitate the ripening of fruit, but it can also inhibit the spoilage of post-harvest fruits and vegetables and thus extend their shelf-life. Selective adsorption and desorption of chemicals responsible for fruit and vegetable ripening can be achieved with MOFs because of their unique porous structures. In another study, alginate shells combined with MOFs containing aluminum and tricarboxylic acid 1,3,5-benzenetricarboxylic acid ligands demonstrated an uptake capacity of 41 cm^3g^{-1} for ethylene, while 0.41-0.455 mgL^{-1} of ethylene was released within 3 h. Recently, Zhang et al. evaluated MOF's potential to be embedded in packaging films as an ethylene adsorber; this study indicates that MgF-embedded LDPE packages could effectively delay banana ripening and extended their shelf life. Significantly, MgF has promising potential as an ethylene adsorber, justifying further work to investigate its application for fresh produce shelf-life extension; this study verified its feasibility under simulated in-transit condition.

However, although MOFs have been proved to be promising candidates for the selective adsorption of ethylene, their dependence on the humidity level for adsorption to occur can, in some cases, limit their application. Awalgonkar's team found that MOFs have excellent adsorption capacity even under a low relative humidity, which is significantly higher than that of traditional oxidizing agents such as potassium permanganate (KMnO4). Moreover, the hydrophilicity of MOFs under conditions of high relative humidity can contribute to the interaction between the MOF and ethylene and increase ethylene adsorption. Chopra's group investigated the desorption of ethylene and ethylene inhibitor 1-methyl cyclopropane (1-MCP) by Basolite C300 and Basolite A520, and showed that Basolite C300 had a good ripening effect on agricultural products when the package had a high water content.

Combination of Different Materials in MOFs. MOFs for food packaging applications can be combined with other materials that are used to extend the shelf-life of post-harvest fruit and vegetable products in different ways (Table 1). Guan et al. developed an alginate shell containing

MOF cores as a packaging system. The MOF cores were charged with ethylene and encapsulated in compact beads formed in the alginate-Fe(III) matrix. Degradation of the alginate-Fe (III) matrix when it was exposed to aqueous sodium citrate solution triggered the release of ethylene. Zhang's team developed a solid porous MOF to encapsulate ethylene gas for subsequent release. Synthesized copper terephthalate (CuTPA) MOF was loaded with ethylene in sealed containers containing bananas and avocados. The results showed that the CuTPA MOF, which had a highly porous structure, released up to 654 pL/L of ethylene for use with post-harvest agricultural products. In another study, Li et al. developed a CD-based MOF material (a-CD-MOF-Na and a-CD-MOF-K), which not only enhanced the adsorption capacity of ethylene but also the storage stability. The encapsulation capacity of the synthetic material was much higher than that of a single material. In addition to the adsorption of ethylene gas, MOFs can also adsorb other organic volatile gases. Kathuria et al. prepared an MOF material containing bio-based CD and alkali metal ionic groups, which can be used to encapsulate ethanol as a non-toxic adsorbent material. The highest content of CD-MOF adsorbed ethanol was 20 g per 100 g.

Selective Adsorption/Desorption Mechanism of Ethylene in Packaging. Typically, the environment of agricultural products in packaging materials consists of multiple gases such as ethylene, water, and others. Importantly, ethylene biosynthesis affects the growth cycle and respiration rate of plants, which can alter their physical and chemical stability. Because of the complicated gas environment, the selective adsorption and capacity of ethylene is vital for the packaging materials to be effective. Different types of fruits and vegetables have different sensitivities to ethylene and, therefore, ethylene has a different effect on their bioreactions. Fresh fruits can be divided into leapfrog and non-leapfrog types according on their ripening mechanism and ripening behavior [6]. Leapfrog fruits and vegetables such as apples, peaches, and avocados usually have a high rate of ethylene production and are highly sensitive to ethylene gas, whereas non¬leapfrog vegetables (broccoli, cauliflower) and fruits (cherries, grapes) maintain ethylene emission concentrations at basal concentrations because their respiration rate does not change significantly. All changes in leapfrog fruits, such as color, hardness, taste, and flavor, are regulated by ethylene, which acts continuously in the metabolic process because fruits are active organisms, and product deterioration can be influenced by intrinsic characteristics of the fruit and the storage environment. Most importantly, the sensitivity of plant tissues to ethylene is inextricably linked to the time of contact with the atmosphere and temperature. Therefore, the selectivity of ethylene of MOF packaging materials is a critical factor.

Discussion of Selective Adsorption/Desorption Mechanism. MOFs can selectivity adsorb different gases depending on the pore size and chemical properties of the MOF. A gas can be selectively adsorbed by a metal-organic framework in three ways: adsorbent-adsorbent interaction, molecular sieve effect, and stimulated response gate opening.

- Adsorbent-absorbent interactions. The sorbent-adsorbent interaction is an affinity between the inner surface and the sorbent in the MOF. This affinity may be due to the interacting van der Waals forces. As a MOF has different adsorption sites, the distribution of the charge and electron cloud can change. Some research, showed computationally that chemical bonds form through the van der Waals force interaction of the aldehyde "tail" with the MOF junction. The different geometries of the metal sites and the pores of the MOFs they studied provided different contributions of the bonds to the adsorption energetics.
- Molecular sieve effect. Since MOFs are composed of nano-scale pores, there is a possibility of a molecular sieve effect, which means that MOFs can selectively adsorb specific gas molecules. The performance depends on the pore size or channel size. A study has shown that, due to their pore structure, MOFs can selectively adsorb nitrogen from mixtures containing ethylene.
- Stimulus Response Gate. When a stimulus such as temperature, pressure, or light triggers the MOF response gate, the gate is opened and gas molecules enter the pores of the MOF. In a

study of the photosensitive properties of an MOF, the diaryl ethylene-azobenzene metal-organic backbone showed different adsorption properties at different sites.

Although the mechanism of the scavenging of ethylene by MOFs is not well understood, many researchers suggest that it is mainly due to electrostatic interactions between positively charged metal ions and the pelectrons of the ethylene molecules. Li's team reported the use of $Fe_2(O_2)$(dobdc), an MOF material containing Fe-peroxy sites, to separate ethane/ethylene mixtures. They found that the Fe-peroxy sites in this MOF have a strong interaction with ethane, leading directly to a polymer grade 99.99% pure ethylene product from the ethane/ethylene mixture. In the absence of Fe-peroxy sites, the Fe_2 (dobdc) MOF becomes biased to adsorb more ethylene by opening the iron sites. Lin et al. reported the synthesis via calcium nitrate and square acids of ultramicroporous MOFs ($Ca(C_4O_4)(H_2O)$) (also known as UTSA-280) with rigid one-dimensional channels. The size of the ultra micropores is similar to ethylene molecules, and so these MOFs can act as molecular sieves to allow the passage of ethylene while preventing the passage of ethane molecules. To evaluate the feasibility of using UTSA-280 for gas separation, Li et al. performed gas penetration experiments using a quaternary methane/ethylene/ethane/propane mixture. They found that there was specific enrichment of ethylene in the quaternary gas mixture due to the sieving effect. They also demonstrated the ability of this MOF material to selectively enrich ethylene in complex cracking streams. This research progress has paved the way for advancing the use of MOFs with selective adsorption in agricultural food packaging.

Table 1. Metal-organic frameworks for food packaging application.

Metal-Organic Frameworks	Active Compound	Synthesis Method	Food	Outcomes
Cyclodextrin-based MOF	Hexanal	Vapor diffusion method	Mango	Shelf-life was extended to 15 days
Single-walled nickel-organic framework	Hexanal	—	Banana	Banana placed in a 1-L MOF jar showed no sign of spoilage until day 30; in the control a dark spot was observed on day 9 of storage
MIL-101@CMFP and UIO-66@CMFP	Curcumin	—	Pitaya	Curcumin-loaded nano-metal-organic framework extended the shelf-life of pitaya to 6 days; the control showed signs of spoilage on day 2 of storage
Electrospun pullulan/polyvinyl alcohol nanofibers incorporated in a porphyrin MOF	Thymol	—	Fresh grapes and strawberries	Grapes wrapped in the MOF showed no spoilage for 7 days; control showed rot on day 7 Strawberries remained fresh for 7 days when wrapped in the MOF; control showed mold growths
Silver-based MOF	Chitosan	One-pot synthesis method	Pitaya	Spraying metal-organic framework solution on pitaya maintained its freshness for 14 days; control showed mold growth on day 7
Copper terephthalate MOF	Chitosan	Solvothermal	Bananas and avocados	The shelf-life of bananas and avocados was extended

Although ethylene is known as the fruit-ripening hormone, other chemicals such as acetylene are also effective fruit ripening molecules. Obtained materials to boost the molecular sieving¬based separation of CO2 /C2H2 and realized the overwhelming adsorption of CO2 over C2H2. This study demonstrated that acetylene adsorption/desorption is also accomplished through molecular sieving. There is little research on MOF materials in the field of fruit and vegetable packaging for the adsorption/desorption of acetylene and ethephon, so the research focus can be placed on the fruit and vegetable ripening molecules in the future.

Conclusions

MOFs have been proven to be an efficient component of food packaging due to the possibility of tailoring their structural space through the selection of the metal ions and the organic linker ligands, and their strong ethylene adsorption capacity. However, there are still big challenges in scaling up their use in large-scale food packaging application: the selectivity of separating similar gas molecules through MOFs is limited; the fabrication of MOF-based packaging materials is difficult to integrate into large-scale industry methods; and metal ions and organic ligand functional groups are toxic, which requires more safety characterization for direct application in food packaging.

To solve these problems, the design of MOF-based packaging should be improved, and the mechanism of their action should be thoroughly investigated. For example, by using natural biomolecules as ligands and environmentally friendly transition metals or non-toxic metal ions, the toxicity of such packaging can be avoided and the materials can be made to be recyclable. Continuous advances in the field of microporous and mesoporous MOF materials can facilitate the development of food packaging that can more accurately differentiate between similar gas molecules. Further modification and design of such materials can help to improve performance; for example, the synthesis of MOFs can be achieved by choosing safer and less costly materials and production methods with lower energy consumption.

Overall, the use of MOF materials has strong potential for ensuring food safety and quality, and to extend the shelf-life of fruits and vegetables. In this review, the synthetic pathways for producing MOFs and the effects of ethylene on the ripening of fruits and vegetables have been outlined. Furthermore, the capability of MOF-based packaging to control ethylene adsorption/desorption has been discussed. The biocompatibility and nonreactivity of MOFs have increased the demand for these materials in the food packaging field. Although there are remaining drawbacks to this technology, such as precisely controlling the volume and pore size of MOFs following their modification for food packaging, MOFs and their composites still have promising applications as functional coatings for intelligent food packaging. Therefore, the development of multifunctional MOF materials with excellent sensing, stability, adsorption, and selectivity will assist in the formulation of advanced food packaging to aid the preservation of agriculture foods.

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