Applications and Outlooks for MOFs in Food Engineering

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Abstract. Food detection and food packaging play critical roles in the realm of food engineering in maintaining food safety and quality. Because of the specific large surface area (SSA) and customizable topologies, metal-organic frameworks (MOFs) have become recognized as promising materials with distinctive features. Examples of MOFs employed as photochemical and electrochemical sensors for food detection are provided in this research. These MOF-based sensors have great selectivity and sensitivity, making it possible to quickly and accurately identify pollutants or signs of food rotting in samples. Additionally, the use of MOFs in food packaging has advantages including a longer shelf life and antibacterial qualities. Food is protected from outside influences by being enclosed within MOF structures, which delays deterioration and rotting. Additionally, MOFs with antibacterial qualities can successfully stop the growth of microbes, ensuring the safety of food. MOFs have the potential to be used in new application areas, such as the controlled release of dietary supplements and flavor enhancers, in addition to food detection and packaging. To guarantee the stability and effectiveness of MOFs in various applications, additional study is necessary. The relevance of food detection and packaging in food engineering is highlighted in this paper's conclusion, which also explores the potential of MOFs as adaptable tools in both fields. The examples shown show how important MOFs are as sensors and packaging materials, but further study is needed to fully utilize their potential and address any issues that might arise.

Keywords: Metal-organic frameworks, electrochemical sensing, optical sensing, food analysis, food packaging.

1. Introduction

The world over, food safety is a critical and worrying issue. Ensuring the safety and quality of food supply has become a significant concern due to the rise of the population and worldwide trade. Accurate and dependable detection of potentially dangerous compounds in food, such as pesticides and histamine, is one of the most important parts of food safety. However, there are several restrictions with the present detection techniques for these dangerous compounds, which make monitoring and control less efficient.

Additionally, packaging is essential for maintaining the quality and freshness of food. The packaging sector does, however, confront difficulties, especially when it comes to perishable goods like fruits and vegetables. The shelf life and nutritional content of these fresh products are frequently not maintained by the present packaging forms and materials. In order to effectively address these problems and improve the general quality and safety of food products, there is an increasing demand for creative packaging solutions.

As a result of overcoming these difficulties, MOFs have become a promising technology with numerous uses in packaging and food safety. MOFs are extremely porous structures created when metal nodes and organic linkers work together. They are the perfect choice for a variety of applications thanks to their special qualities, which include a substantial area of surface, adjustable porosity, and exceptional chemical stability.

MOFs offer great potential in food safety by providing new avenues for the detection of harmful substances. Analyte redox reactions in electrochemical systems are affected by the analyte's absorbance and the way electrochemical sensors are used. It might affect the luminescence intensity of MOFs [1]. Furthermore, MOFs have so far attested to their versatility. They were created for food packaging, the removal of foreign substances from food, and the detection and supervision of such substances in food items. MOFs have become a crucial component of food packaging due to their strong biocompatibility and lack of host reaction during testing [2].

In summary, the existing limitations in the detection methods for harmful substances in food and the need for improved packaging solutions highlight the significance of exploring new technologies. The remarkable characteristics of MOFs make them attractive for addressing these challenges in food safety and packaging. The following sections will present the fundamentals of MOFs and their applications in food analysis and packaging.

2. Definition, Synthetic Methods and Features of MOFs

MOFs are a series of crystalline organic-inorganic hybrid materials which are composed of metal ions or clusters connected via organic ligands. Compares to previous materials such as zeolites as well as activated carbon, MOFs equip a more significant internal surface area. Similar to isoreticular substances, MOFs include network linkages and pore topologies, but they also contain metallic ions or a range of ligands. This hybrid material which is composed of inorganic and organic items is made by adding a super possibility, resulting in a one to three-dimensional framework with metal ions acting as binding sites and ligands acting as support. The different specific features such as chemical properties or adsorption capacities of MOFs can be controlled by the category of inorganic section and the type of construction of MOFs.

MOFs are frequently prepared through sol-gel and other techniques, for instance, the electrochemical technique, which is primary for the production of continuous and fast microcrystalline MOFs; hydro/solvothermal technique, which is for producing high-quality MOF crystals; slow solvent evaporation technique; mechatronics approach (environmentally friendly, cost-effective, quick reaction, no creation of pollutants or poisonous substances, and solvent-free) and the sonoche method. These processes are all similarly sensitive to variations in solvent type, reagent concentration, starting material volumetric ratio, reaction pH, counter ions, temperature, pressure, timeframe, and ambient [3].

MOFs are more economical for manufacturing than receptors because of their huge SSA, enormous pore volume, ease of modification, and accessibility. There are omnifarious aspects in applications for MOFs including adsorption, gas storage, separation, drug delivery, catalysis and sensing detection.

3. Food Analysis: Types and Instances of MOF-Based Sensing Platforms

To date, there are various detection methods widely applied in food analysis such as the chromatography method including the HPLC and GLC, as well as the nuclear magnetic resonance spectroscopy, and enzyme-binding immunoadsorption assays. Nevertheless, there are drawbacks when applying these methods, such as complex instrument operation, relatively inefficient processes, and excessive costs for purchasing and maintaining instruments [4]. Hence, due to the high adsorption ability, sensitivity, and strong specificity of MOFs, it is considered that they can be used as sensors in food detection.

For instance, MOFs have shown considerable potential as chemical and optical sensors owing to their unique architectures and reaction processes.

There are two categories of MOF-based sensors: chemical sensors and optical sensors.

Chemical sensors rely on changes in the adsorption or desorption of target molecules in the MOF's pores, resulting in quantifiable changes in a physical property such as electrical conductivity or impedance. The capacity of a MOF to selectively adsorb or desorb certain compounds depends on the MOF's chemical composition, pore size, and pore geometry. For example, a MOF having polar functional groups may preferentially adsorb polar molecules over nonpolar ones.

Optical sensors rely on changes in the optical characteristics of the MOF upon interaction with target molecules. These include changes in fluorescence intensity, hue, or luminescence lifespan.

MOFs suited for use in optical sensors frequently contain chromophores or fluorophores that interact with target molecules by chemical or physical mechanisms such as π-π interactions, hydrogen bonding, or charge transfer. The interactions between the MOF and the target molecule might lead to changes in the chromophore or fluorophore, leading to modifications in the optical signal.

3.1. MOF-Based Electrochemical Sensing

The basic idea behind the use of MOFs as electrochemical sensors is the incorporation of MOFs as a thin film or coating onto the electrode surface. The target analyte interacts with their functional groups, changing the resulting electrochemical signal, which is the basis for the detection method. On the MOF surface, this contact may take the form of charge transfer, adsorption, or chemical reactions. The type of metal ion MOFs can be embellished to make the sensors suitable for various areas of food analysis, such as the detection of pesticides, the detection of foodborne pathogens or toxins produced by them, and the detection of heavy metals.

3.1.1. Pesticide Detection

The development of pesticide detection relies heavily on MOF as a sensing element since the issue of pesticide residues and environmental contamination is becoming increasingly critical. Several pertinent studies have been conducted up to this point, some of which are reviewed below.

Organophosphorus Pesticides (OPPs) are a type of chemical molecule that is extensively employed in agriculture as insecticides, herbicides, and fungicides. They work by blocking the action of cholinesterase, an enzyme that is essential for the proper functioning of both insects' and mammals' neurological systems.

Gao et al. introduced an inorganic substances pesticide sensor using a nanocomposite called Zr-BDC-rGO for methyl parathion (MP) detection, a typical organic phosphate pesticide, to solve the issue of the existence of OPP residues. Constructed from graphene oxide, the sensor had undergone electrical reduction and a zirconium-MOF compound known as Zr-BDC that used the acid terephthalic as a ligand. This sensor's linear range was improved to 0.001-3.0 LG mL^{-1} after tuning, and the sensitivity of it is 0.0005 mg/L which is high for samples of Chinese cabbage and a low limit of detection (LOD) of 0.0005 mg/L [5].

Additionally, Luo et al. published research on the utilization of the Mn/Fe-MIL (53)-MOF composite to detect two common pesticides, chlorpyrifos (CPF) and a particular class of common OPPs, in actual samples including tap water, bottled water, and the cabbage. Compared to pure FeMIL, Mn/Fe-MIL (53)-MOF demonstrated a higher electron transfer rate. Additionally, the material was made particularly choline-destructive by the manganese addition, which prompted the invention of an easy-to-use, precise, and sensitive colorimetric method for OPPs detection. The suggested colorimetric approach quantitatively identified MP concentration of 0.01-0.12 mol/L and CPF of 0.005-0.05 mol/L with LODs of 2.8×10^{3} mol/L and 0.95×10^{-3} mol/L(3S/N), respectively [6].

3.1.2. Mycotoxins Detection

Mycotoxins are poisonous compounds that some fungi make that can contaminate food and animal feed. A wide variety of agricultural items, such as cereals, nuts, spices, and dried fruits, contain these naturally occurring poisons. Mycotoxins come in over 400 distinct varieties, but the most prevalent ones include zearalenone, patulin, aflatoxins, and ochratoxins. Fungal species like Aspergillus, Penicillium, Fusarium, and others create these poisons.

Potential health hazards from eating mycotoxin-contaminated food and feed include kidney and liver damage, immune system suppression, and possibly cancer. In addition, mycotoxins are challenging to get rid of since they remain stable even after heating or processing. Finding a good electrochemical sensor to detect mycotoxins is therefore crucial.

Numerous studies provide insight into the electrochemical senses' abilities for detection and eradication. Regarding it, Lu et al. proposed an aptasensor (AuNPs/FeMOF-PEI-GO) to detect patulin in apple juice. This sensor had a LOD of 2.17×10^{-10} mg/L, providing an idea of precise analysis of trace mycin in food safety [7]. Wen et al. altered an electrochemical aptasensor utilizing Cu-N-MOF in a different research project. This sensor could analyze deoxynivalenol, a typical mycotoxin in contaminated wheat samples, with a LOD of 8.0 106 mg/L and a linear range of 2.0×10^{-5} - 0.02 mg/L ($R^2 = 0.994$) [8].

3.2. MOF-Based Optical Sensing

As a form of optical sensor, MOFs are capable of detecting a variety of analytes, including gases, ions, and tiny molecules. This is accomplished by utilizing fluorescent or luminescent MOFs, which produce light in response to modifications in their structure or composition brought on by analytes. The MOF's architecture can be adjusted to improve the sensor's sensitivity and selectivity for particular analytes.

Wang et al. create a ratiometric fluorescent probe using MOF materials with good biogenic amines (BAs), for visually detecting BAs in food through covalent interactions of fluorescein 5-isothiocyanate (5-FITC) with EuMOF. Experimental evidence supports the sensing mechanism of analyte-induced energy transfer, pH-responsive structural changes of FITC, as well as interactions between EuMOF and FITC. At the concentration of 2.78 - 41.67 mg/L, the fluorescence intensity ratio was linearly related to the histamine concentration. The LOD was 1.11 mg/L (S/N = 3) [9].

4. Multiple Uses of MOFs in Food Packaging

MOFs have attracted much attention in food packaging because of their potential of enhancing food safety and extending shelf life. The unique structural features of MOFs make them suitable for adsorbing or desorbing functional substances which can be used in food packaging.

For many industrial uses, including food packaging, MOFs have become a promising class of materials. MOFs have a number of distinctive qualities that make them desirable for applications involving food safety and shelf life. The ability of MOFs to efficiently adsorb and desorb food components helps to mitigate negative impacts on food quality. For instance, MOFs can be used to remove volatile molecules that give packaged goods aromas and off flavors or to absorb ethylene, which is naturally produced by fruits and vegetables and speeds up the ripening and decay of those foods. This is made possible by their high porosity and surface area. Utilize MOFs' capacity to encapsulate compounds to incorporate active components, such as antibacterial agents, into the polymer matrix of food packaging materials. This approach not only reduces waste but also provides an alternative to antimicrobials and conventional preservatives that might be harmful to people's health.

4.1. Extending Shelf-Life of Fruits and Vegetables

To ensure that the product is in the best possible condition when it reaches the market, it is crucial to control the maturity of fruits and vegetables, especially climacteric fruits, in storage and transportation. The concentration of ethylene is the primary influencing factor of fruit and vegetable maturity. To postpone ethylene production at the moment, the industry mostly relies on early picking, low-temperature storage, and O2/CO2 environment regulation, or controlled adsorption/desorption of ethylene when necessary.

In order to enclose ethylene and discharge it in a controllable manner at the necessary stage, Zhang et al. developed MOFs. It has been shown that ethylene gas may be absorbed and released by using copper terephthalate MOFs (CuTPA), which had a porosity of 0.39 cm3g-1. It can promote fruit ripening by creating an ethylene-rich environment within the packaging, but it can also keep fruits and vegetables from going bad after harvest and extend their shelf life [10].

4.2. As Antibacterial Agents in Food Packaging Materials

As an inorganic-organic hybrid polymer, MOFs have a number of benefits over organic bactericides. They consist of a broad spectrum of antibacterial activity, high efficacy, long-lasting effects, adjustable structures, and thermal stability.

The remarkable antibacterial qualities of MOFs have received increasing attention in recent years, and more research is being done in this field. For instance, Liu et al. discovered that Ag-based MOFs can exhibit strong antibacterial activity in the flora by releasing silver ions as a result of superior antibacterial capability of Ag^+ and the controllable release ability of MOFs to Ag ions [11]. Colinas et al. also assessed the bactericidal efficacy of two varieties of Zn-MOF against Escherichia coli and Staphylococcus epidermidis at the same time. Because Zn-MOF can enter bacteria and cause cell harm by interacting with lipophilic acid or hydroxyl groups on cell membranes. These two Zn-MOFs, therefore, showed better anti-bacterial performances than Zn [12].

5. Conclusion

The adoption of MOFs in food analysis (using electrochemical as well as photochemical sensors) and food packaging has been thoroughly discussed in this paper. The structure, characteristics, and synthesis techniques of MOFs were covered in the paper's opening section, which also highlighted how adaptable these materials may be for many applications. The third section was primarily concerned with the use of MOFs in electrochemical and photochemical sensors for food detection. These sensors show outstanding sensitivity, selectivity, and responsiveness to a range of analytes, opening up interesting opportunities for food safety monitoring. Furthermore, the utilization of MOFs in food packaging was explored, with an emphasis on their ability to extend the shelf-life of perishable foods and provide antimicrobial properties. The incorporation of MOFs into packaging materials could effectively control the release of active compounds, inhibit microbial growth, and prevent food spoilage.

The development and use of MOFs in food engineering for both food detection and food packaging have yielded encouraging results. However, it is critical to recognize several restrictions that require attention in follow-up studies.

MOFs have a lot of potential for sensitivity and selectivity in food detection systems. The stability and repeatability of the MOF-based sensors continue to face problems, though. For them to become more long-term stable and reliable, additional testing and optimization are needed.

While it has been shown that using MOFs in food packaging can effectively extend the shelf life of food products, there are worries about the possibility of MOF particles migrating into the food matrix. To ensure consumer safety, a detailed assessment of the safety aspects and long-term impacts of MOFs used in food packaging is necessary.

For its practical application in food engineering, MOF synthesis' monetary and scaleability-effectiveness must also be taken into account. The broad use of MOFs in the food sector may be hampered by their high present costs and challenging synthesis processes.

Looking ahead, future research should concentrate on designing and fabricating MOFs-based sensors with enhanced performance and reliability. Additionally, further investigations are necessary to study the long-term stability and biocompatibility of MOFs in food packaging applications. Moreover, exploring new applications of MOFs, such as controlled-release systems for nutraceuticals and flavor enhancers, could offer innovative solutions to enhance food quality and safety.

In conclusion, this paper highlights the immense potential of MOFs in food detection and packaging. Continued research and development in this area would undoubtedly lead to significant advancements in ensuring the safety, quality, and longevity of food products.

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