MOFs-based Electrochemical Sensors and Biosensors for the Analysis of Food Contaminants

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Abstract. Nowadays, with the rapid increase of people's living standards, they paid more attention to food safety. a new method to detect food additives and bacteria is urgently needed. MOFs are a great material to be used to make a chemosensory of their high stability and porous structure. Compared to the MOFs sensor with any other sensors, it is more convenient, fast and sensitive. It shows excellent potential for the detection of food safety issues in the future. In this article, the important research significance of MOF in the field of food containers was introduced. Various methods of preparing MOFs, including the hydrothermal method, diffusion method and solvent-free method are introduced. Then present the influencing factors of MOFs materials from their fluorescence properties and heavy metals. Finally, the detection of coffeic acid, nitrite and carbendazim by MOF electrochemical sensor in the food safety field has been extended and evaluated. Aiming to connect the MOFs-based chemical sensors with the field of food safety.

Keywords: Metal-organic framework; chemical sensor; biosensors

1. Introduction

Food safety issues have attracted extensive attention in recent years. Natural harmful substances, environmental contaminants, food additive abuse, substances produced during food processing, storage, transportation, and cooking, as well as contaminants in tools and utensils, such as high-temperature processed foods with a high starch content, which may produce acrylamide, a potential carcinogen, are categories of food contaminants. These food additives pose a risk to human health, as evidenced by the Guangdong toxic rice incident in December 2000 and the Nanjing Guan Shengyuan "black heart" moon cake incident on November 8, 2001. Consequently, the development of effective, sensitive, and precise sensors to monitor the food chain and control the risk of noxious compounds in food is crucial. Chemical sensors are sensitive equipment that converts the amounts of various chemical compounds into electrical impulses [1]. Chemical sensors are comparable to human olfactory and gustatory sense organs (as shown in Figure 1). To identify food, it typically employs portable microbiological detectors, visible spectrophotometers, and gas chromatographs. Although these traditional sensors can identify dangerous elements in food, the analysis of food is a problem due to their lack of high sensitivity and precision. They typically require complex apparatus, trained person operation, and time-consuming procedures, which severely restricts their application in food contamination detection [1]. Due to the complexity of food matrices, it is difficult to identify many trace food pollutants. Traditional approaches can no longer provide the demand for rapid and effective analysis of food contamination [1]. MOFs, or metal-organic frameworks, are composed of materials with ultra-high specific surface area, ultra-high porosity, and natural linkers. As chemical sensors, MOFs are optimized in terms of sensitivity, selectivity, response time, and material stability. Reliability for chemical sensor applications [1,2], MOFs, a unique porous material, have fixed gas detection sensitivity because they can efficiently concentrate analyte molecules.

In addition, the possibility of post-synthetic alteration of MOFs adds a new dimension to the diversity of synthesis, which is a nice surprise. Some researchers have recently begun to investigate the potential of MOFs as chemical chemosensors [1]. Despite the absence of practical applications, Nevertheless, chemical sensors/biosensors based on MOFs offer superior sensitivity, selectivity, response time, and detection range in comparison to sensors based on other nanomaterials [1]. This gives MOFs significant benefits over other prospective chemosensory materials, such as MOFs-1011 and MOFs-177 [1,2].

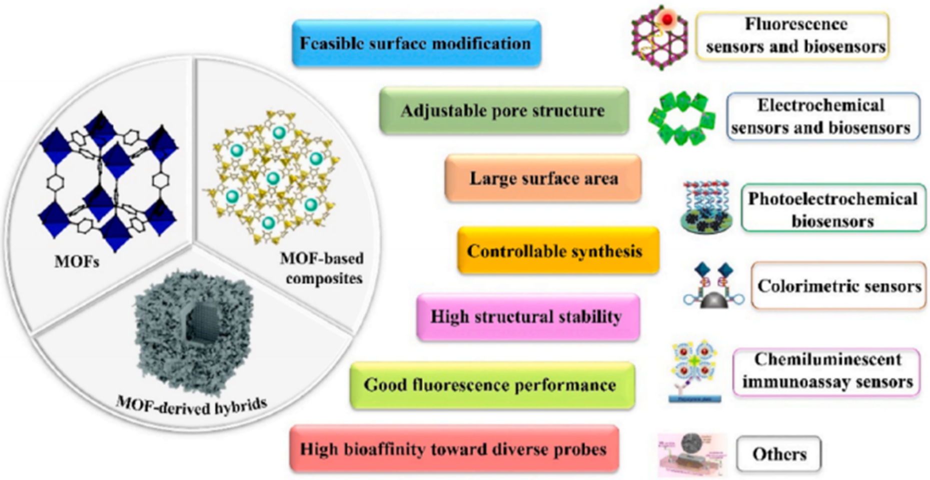

Fig.1 Schematic illustration of the chemosensors and biosensors based on MOFs, MOFs-based composites, and MOFs-derived hybrids for the analysis of food contaminants [1].

2. Preparation of MOFs

MOFs are usually obtained by solvothermal reaction of organic ligands and metal salts at relatively low temperatures (below 300 °C). Among them, organic ligands play a crucial role in the formation of frameworks, and the structure of metal ions also affects the structure of MOFs [3]. With the continuous in-depth research on MOFs materials, MOFs materials have gradually become more abundant in synthesis methods, among which the more widely used methods include a hydrothermal (solvothermal) method, diffusion method and solvent-free synthesis method [4].

2.1 Hydrothermal Method

The hydrothermal synthesis method is to heat the metal ions and organic ligands in a closed reaction system to carry out the synthesis reaction. This method has the advantages of strong stability and high heating temperature. For example, $Zn(NO_3)_2{\cdot}6H_2O$ is weighed and dissolved in N,N-dimethylformamide with ophthalmic acid (the ratio of the two raw materials is 2:1), after cooling and washing, it is dried in the drying box to obtain a white solid powder, namely MOF-5 [5]. Through thermogravimetric analysis and optical microscope observation, the crystal particle size of MOFs prepared by the hydrothermal method is larger than that of MOFs synthesized at room temperature [6]. For example, it was found that the MOF-5 crystals synthesized by the hydrothermal method showed a regular cubic crystal structure, the particle surface was smooth, and the crystal particles were complete, while the MOF-5 crystals synthesized at room temperature were much smaller, and the crystal structure was irregular, and agglomeration occurred.

2.2 Diffusion Method

The diffusion method is a method for preparing coordination polymers. For example, the preparation method of water vapor diffusion is to coordinate the organic ligand with metal ions through a carboxylic acid expulsion reaction to generate the required coordination polymer. The interfacial diffusion method is used to prepare liquid reactants, which separates samples by slowly evaporating the target metal salt solution and the organic ligand to make the solution reach the natural saturation state. The gel diffusion method is used to prepare solid-compatible polymers. Through natural sedimentation and osmotic diffusion, the two groups on the gel and gel surface react at the interface to obtain the desired products [7]. This method does not have high requirements for high temperature and high-pressure environments, and the naturally formed crystal structure is neat, but due to the shortcomings of long reaction time, the requirements for good solubility of the reactants themselves are relatively high. During the experiment, the two standpipes should be connected through A horizontal pipe with sand core, and the reaction solution A and B should be placed in the standpipes on the left and right sides of tube H respectively. After adding the reaction solution, the pipe mouth should be closed and left to stand, so that the solutions on both sides of tube H could spread and react with each other through the sand core.

2.3 Solvent-Free Method

The solvent-free synthesis method is to grind the solid reactants, and under the action of external force, the two start to react, and after the external force is withdrawn, the reaction continues for some time to obtain the product. The synthesis method is considered feasible and can realize the preparation of high-quality membranes, and has the advantages of green environmental protection and large-scale production[8]. Orita et al. found through experiments that the solvent-free synthesis method can accelerate the self-assembly process of the reactants [9]. Pichon et al. reported a method for preparing a coordination polymer [Cu(INA)2]. The reactants were ground copper acetate and isonicotinic acid for 10 min by grinding, and the reaction was obtained in polymer crystal. The operation process is simple, the reaction process time is short, only about 10-20 min and the environmental pollution is small. This method responds to the concept of green environmental protection and is the key direction for researchers to develop and utilize in the next step.

3. Construction of A Chemical Sensor/Biosensor Based on MOFs

The floor response is the determining factor for MOFs substances as chemical sensors. Since chemical sensing properties are generally impacted by surface reactions, MOFs are regarded as some of the most ideal sensing compounds. Rapidly emerging recently is the application of MOFs in chemiresistive sensors that convert electrical signals from floor reactions.

3.1 Fluorescence Characteristics

MOFs can recognize a variety of sensors, such as FL chemosensors/biosensors with sensing methods such as FL excitation, FL burst, enzyme catalysis, and biosensing [1,3], as shown in Figure 2.

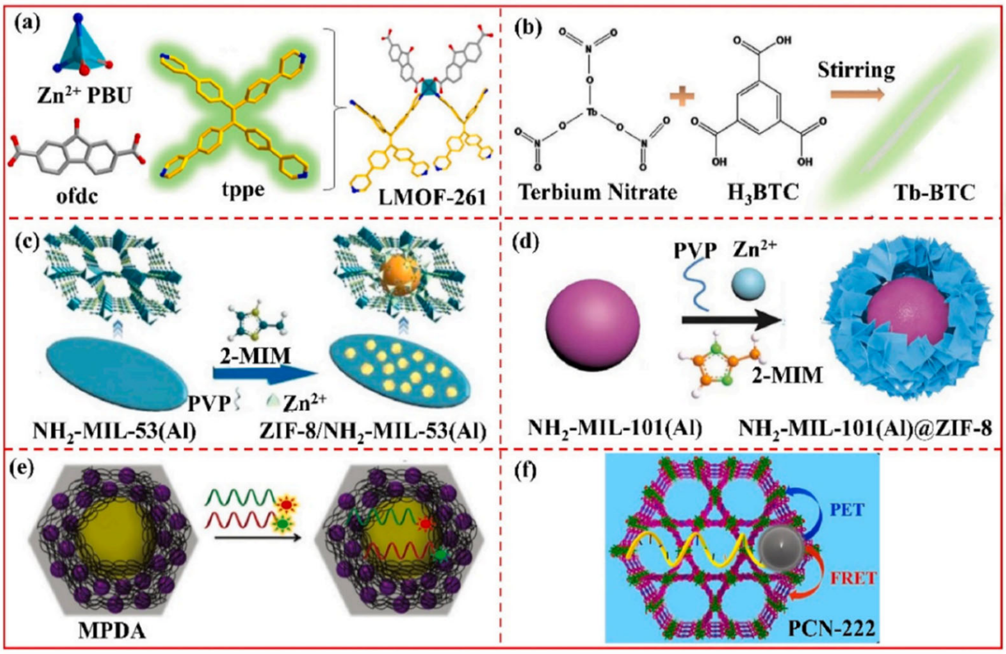

Fig. 2 Metal-organic framework as chemical sensor [1].

MOFs can be used to build a variety of FL chemosensors/biosensors based on sensing processes such as FL excitation, FL burst, enzyme catalysis, and specific recognition (Figure 2) [1]. The sensing characteristics of FL rely on ligands and metal nodes as control centers, a move that can reasonably modulate the sensor inhomogeneity problem. Due to the requirement of organic ligands for the FL capability of MOFs, they can be employed as recognition sites for sexual detection analytes [1]. Therefore, the alteration of organic units to functionalize MOFs can significantly improve FL performance by minimizing non-radiative relaxation or boosting ligand-metal charge transfer effects [1]. In addition, functionalization of hydrophilic groups (such as $-NH_2$ or -OH) on ligands not only increases the water stability of FMOFs [1], but also provides selective binding sites and accelerates electron transmission to the analyte. Various FMOFs, such as A-MOFS [1,3], Zn-MOFs and FL Zr-MOFs have been studied [4].

3.2 Heavy Metals

Rare metal ions serve as coordination centers [1] and certain MOFs, thanks to their remarkable luminescence properties, can be used as FL emitters for the detection of a wide variety of targets [1,4,12]. In the case of such FMOFs, the binding force that exists between the target and the MOF is necessary for producing a detectable sensing signal. This is because the binding force influences the energy transfer. Tb-MOFs made from wood-conjugated organic junctions, for example, have a very high FL [1], which makes it easier for electrons to go from the lower ion to the ligand ion. In conclusion, the sensor can evaluate contaminants as a result of the greater emission that Tb-MOF produces [1].

4. The Applications of MOF Electrochemical Sensor in the food Safety Field

The electrochemical analysis is used widely in the detecting field because of its simple, fast and high selectivity. And compared with other porous materials, MOFs are of high porosity and large surface area. So MOFs are a desirable substance to make the chemosensor. But MOFs have poor electrical conductivity and stability. Combining the MOFs with other electrical conductive substances can supply this gap and lead to an increase in its stability and catalytic activity.

4.1 Detect Coffeic Acid by using GR/CuO@Cu-MOFs Sensor

Graphene improves the stability and electrical conductivity of the sensor [10]. The composites of MOFs and graphene have unique structural characteristics, high specific surface area, good electrical conductivity and other advantages, and show superior electrocatalytic activity for caffeic acid oxidation. Under optimized conditions, the linear range of the sensor for caffeic acid detection is 0.020-10.0μmol/L, and the detection limit is 7.0 nmol/L. In addition, the sensor was successfully applied to the detection of coffeic acid in red wine samples. The red wine sample was diluted 25 times with 0.1mol/L PBS, pH=4. Then coffeic acid was added. Use Differential pulse voltammetry(DPV) to detect the samples, and record the answered current with 0.45 V. The finding is that recovery is 95.89% to 104.59%. The relative standard deviation is 2.27% to 4.40%. This result shows that the sensor has excellent potential.

4.2 Detect Nitrite by using Cu@C@ZIF-8 Sensor

For the Cu@C@ZIF-8 sensing system [11], ZIF-8 has a suitable size of the pore, which allows nitrite to pass the ZIF-8 shell but not the macromolecule, thus ensuring high sensor selectivity. On the other side, Cu@C acts as an electrocatalyst to promote nitrite oxidation, thus making the sensor highly sensitive. Under optimized conditions, the linear range of the sensor for nitrite detection was 0.1 μmol/L-300 μmol/L, and the lower limit of detection was 0.033 μmol/L. It can detect the nitrite content of sausage. Nitrite was added to different sausage samples. Then use DPV method to detect the content of nitrite. The result shows that the recovery is 95.44% to 105.03%. The relative standard deviation is about 3.51% to 4.49%. It shows that the sensor has great practicability.

4.3 Detect Carbendazim by using MXene/CNH/β-CD-MOFs Sensor

The property of β-CD combined with the porous structure, high porosity and pore volume of MOFs makes β-CD-MOFs have a high adsorption capacity for CBZ [12]. The large surface area, a large number of active sites and high electrical conductivity of MXene/CNH can provide more mass transfer channels. Under optimized conditions, the sensor can detect carbendazim in a linear range (3.0 nmol/ l-10.0 μmol/L) with a detection limit of 1.0 nmol/L. In addition, the sensor can be used to detect carbendazim in tomato samples. Different concentration of carbendazim was added to tomato juice. Then use the sensor to detect. The experiments showed that the recovery is about 97.81%~101.99%. The relative standard deviation is around 2.69%~4.09%.

5. The Applications of MOFs Biosensors in the Food Safety Field

MOF-based composites with MOF-derived heterocycles offer unique FL characteristics, a strong adsorption to a variety of probes (aptamers, antibodies, or DNA), a large specific surface area, rich functionality, and high porosity. [1] Additionally, these composites have a large specific surface area. As was discussed in the preceding paragraph, MOF sensors offer a number of distinct advantages when it comes to the detection of various substances such as caffeic acid, red wine, and nitrite. For the detection of nitrite levels in sausage, for instance, the recovery of MOFs as sensors ranged from 95.44 percent to 105.03 percent, with a relative standard deviation of roughly 3.51 percent to 4.49 percent [12]. When compared to the results from conventional sensors, this value obtained using MOFs is both more precise and efficient. because of the one-of-a-kind structural qualities that MOFs and graphene composites share. MOFs-based composites and heterocyclic compounds have remarkable electrical activity [1], outstanding catalytic capabilities [1,14], and excellent photochemical properties, which expands the applicability of MOFs in the sensing and biosensing areas [1]. [Citation needed] Food additives and fungal toxins were also incorporated into the study in order to facilitate sensitive analytical detection of heavy metal ions.

5.1 Benefits Offered by MOF Biosensors

Food pollutants that can be detected by MOFs include antibiotics, fungal toxins, foodborne pathogens, heavy ions, pesticide residues, and aromatic hydrocarbons [1]. Composite polymers produced from MOFs have been used to create sensors of the fl-type, the ec-type, and the pecs-type [1,14,]. Materials that are either less porous or nonporous, including metal oxides and polymers, are the types of materials that are typically utilized in conventional chemical sensors [1]. In order to increase the sensitivity of these sensors, it is typically necessary to employ a pre-concentration technique that makes use of porous adsorbents as analyte concentrators [14]. As a result of the porous and scalable structure of MOFs, they are capable of efficiently avoiding this process when used as chemical sensing materials. Analyte molecules can be concentrated into highly ordered porous materials by using MOFs since their backbones are porous. As electrochemical sensors, MOFs have a number of advantages, and this is one of them [1].

5.2 Heavy Metal Detection with MOF Biosensors

When ZIF-8 was used for the simultaneous electrochemical detection of Hg^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+} [13], the large surface area and good adsorption capacity of the MOFs enabled a more accurate and sensitive analysis of heavy metal ions. Polypyrrole and Al-MOFs were created for the detection of Pb^2 and Cu^{2+} [12], and the sensor achieved extremely vulnerable and selective spotting of P^{2+} and Cu^{2+} [12].

6. Summary

As a potential chemical sensor, MOFs have garnered a growing amount of interest in the field of food safety. In this article, a scientific investigation into the possibility of using MOFs as chemical sensors for the monitoring of food contaminants is presented. The subsequent step is the preparation of MOFs for use as chemical sensors. The technique of preparation can be broken down into three categories: the hydrothermal method, the diffusion method, and the solvent-free method. Then there is the utilization of MOFs in the detecting process as chemical sensors. MOFs will prove to be more efficient than the more standard types of chemical sensors. This research is essential for the industry that deals with food safety. Last but not least, the widespread application of materials made of MOFs continues to be a hurdle because it is difficult to create MOFs on a big scale.

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