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Molecularly Imprinted Polymer-Based Fluorescent Sensors: A Promising Tool for Food and Environment Analysis

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ABSTRACT

Molecular imprinting technology (MIT), also called as molecular template technology, it is a novel and innovative technology use in material chemistry, polymer chemistry, biochemistry, and other different approaches. Molecularly imprinted fluorescence sensor (MIFs), a technique used to know the unique and selective capability of 3- dimensional cross-linked polymer called the molecularly imprinted polymers (MIPs). The MIPs has wide variety of applicability, correct plasticity, stability, excessive selectivity and their inner recognition sites can be selectively combined with template molecules to obtain selective detection. Molecularly imprinted fluorescence sensor (MIFs) carries fluorescent substance into molecularly imprinted polymer synthesis and transforms the binding sites between target molecules and molecularly imprinted materials into detected or readable fluorescence signals. This sensor shows the advantages of excessive sensitivity and selectively of fluorescence detection. Molecular imprinting materials shows research significance and broad application prospects. This review gives importance on progress in the construction and application of MIFs turned into reviewed with emphasis on the practice principle, detection methods, and molecular recognition mechanism widely used for food analysis.

KEYWORDS: *Molecularly imprinted polymer; fluorescence sensor; food quality and safety*

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INTRODUCTION

Molecular imprinting technology (MIT) is an emerging research tool based on interaction of antigen and antibody as well as enzyme and substrate, the importance of MIT is to synthesize three- dimensional (3-D) cross-linked polymers having unique molecular recognition potential [1]. Molecularly imprinted polymers (MIPs) display several advantages, such as selective adsorption, good affinity, easy preparation, good resistance as well as lower in cost. MIPs reveal huge utility application in several fields such as solid phase extraction, chemical biomimetic sensing technology, chromatographic separation methods and mimic enzymes [2]. Conventional MIPs have good specific recognition performance as a result, they lack signal output ability during analysis and recognition. Consequently, they need to be used in combination with instrumental authentication methods [3]. The fluorescence sensor usually made up of a recognition unit and a signal output unit. Molecularly imprinted fluorescence sensors (MIFs) can be comprises by addition of fluorescent material into the molecularly imprinted polymer synthesis system, which is helpful to understand specific identification and fluorescence detection of the target [4]. MIFs have an emerging novel tool in the field of medicine, environment and food safety analysis. [5]

In ancient times, several food and environment safety incidents have occurred, as a result food safety turning into the focus of global attention [6]. Food safety is relatively close human health, financial growth as well as social stability and is a major issue concern to national wealth and people's living [7]. Now, the food safety detection technology is much important and the validation strategies include gas chromatography, fluid chromatography, capillary electrophoresis, supercritical thin chromatography, fuel chromatography-mass spectrometry [9], and liquid chromatography-mass spectrometry [10]. But, the instrumental techniques having some drawbacks like complicated sample pretreatment procedure, higher in costs, difficult operation, time consuming and costly equipment. This technique is not able of achieve rapid detection, thus requiring proficient operators. In contrast, the fast detection technology this is easy, fast, low-cost, selective, and shows high specificity [11].

MIFs not only exhibit the advantages of definite recognition and definite adsorption of molecular imprinting but also have high sensitivity and selectivity of fluorescent materials. This feature is key in integrating the detection unit and signal output unit proficiently in the quick recognition of food quality as well as safety [12]. This review broadly focuses on the preparation of MIFs, the recognition methods and molecular detection mechanisms. The application of MIFs in the rapid recognition of food quality and safety hazard factors including agricultural and veterinary drug residues, heavy metals, and environmental organic pollutants as well as the research focus on progress trend on the MIFs is discussed.

Preparation of MIPs

MIPs are category of polymeric materials obtained from template molecules and functional monomers by means of covalent or non-covalent bonds to form preassemblies. Under the action of cross-linking agents and initiators, they are afterward entirely matched with the template molecules in shape and structure [13]. The preparation principle of MIPs as shown in **(Fig.1)** and the process is generally divided into three steps [14].

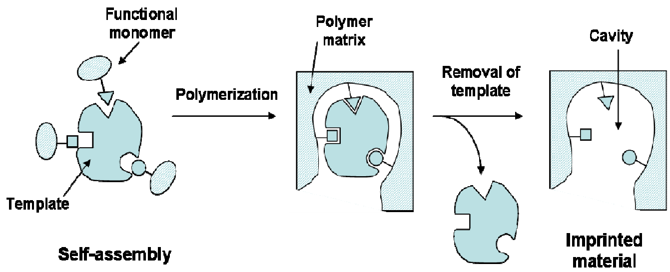

Fig.1: the preparation principle of MIPs

1. Template molecules and functional monomers are assembled in suitable solvents, and the host and guest know each other to form stable supramolecular complexes [15] with several definite detection sites and specific spatial arrangement.
2. A cross linking agent and an initiator are added into the assembled solution, the process of photo polymerization or thermal polymerization is initiated by the initiator, and a highly cross linking polymerization is performed around the template-functional monomer supramolecular complex to form a rigid polymer with a three-dimensional spatial structure [16].
3. Elute the template molecules attach to the polymer with an eluent mostly alkyd or alkali alcoholic solution to obtain a MIP [17] with 3-D holes that can be completely matched to the template molecule. The imprinted cavities can suitably bind to the template molecules again and obtain a specific recognition effect on the template molecules.

Construction of molecularly imprinted fluorescence sensors MIFs

The fluorescence sensors are capable to alter the detection between the molecular recognition unit and target into a fluorescence response signal and detect the concentration of the target by monitoring the fluorescence intensity. The fluorescence sensor do change the cognizance into the molecular consciousness soloist then target of a fluorescence reply sign or notice the concentration over the target with the aid of limit the fluorescence intensity, an MIFs was constructed by introducing fluorescent materials into the MIPs synthesis system. As shown in **(Fig.2)** [18]. MIFs are greatly selective, sensitive, precise, and stable compared to all conventional sensors [19], and have been extensively used to identify many kinds of pollutants which is present in environment [20].

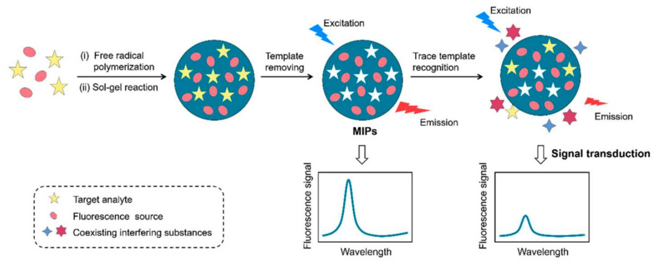

Fig.2. the preparation process of molecularly imprinted fluorescence sensors (MIFs)

Application of MIFs in Food Quality and Safety Detection

Now a day, the determination regarding food quality or safety hazard elements typically includes chromatography techniques, such as high-performance liquid chromatography, gas chromatography, and then high-performance liquid chromatography-mass spectrometry. These strategies display the advantages about high recovery, more reproducibility and less detection limit; however, it hourly require a drag pattern pretreatment process. Moreover, in that place are mean drawbacks, certain so high-priced gear and reagents, long detection time, unsuited for detection over a tremendous number over samples, and lack on portability. Fluorescence sensing analysis demonstrates the character about excessive sensitivity, lower detection limit, quickly reaction speed, helpful selectivity, low cost, then utilization concerning exceedingly easy devices or equipment. In recent years, including the mild progress then aging concerning surface molecular imprinting, nanomolecular imprinting technology, then high-performance fluorescent nanomaterials preparation technology, the selective awareness yet fluorescence detection overall performance on MIFs with respect to hazard factors in complex food matrices have been significantly enhanced [21]. The MIFs has been extensively old within food characteristic or safety analysis. Mostly the research focal point concerning the fluorescence detection regarding arable then veterinary drug residues, drug residues, prohibited additives, heavy metals, environmental natural pollutants and other factors [22].

1. MIFs in Pesticides

A long-term and large-scale use of pesticides leads to environmental air pollution or extended pesticide residues between arable products, thus destroying the ecological balance similarly rising the hazard regarding food safety. The fluorescent MIPs is prepared by molecular imprinting method, a three-dimensional cross linked polymer along unique focus sites, as execute to understand selective recognition, adsorption, and fluorescence discovery regarding pesticide molecules (template molecules). Various discoveries for pesticides detection like Li *et al.* prepared MIPs with specific fluorescence response to cyhalothrin by silylation of FeSe QDs. with the help of surfactant-modified CdTe QDsas carrier and acryl amide as the functional monomer [23]. Similarly Wei *et al.* reported that a specifically recognize cyhalothrin using free radical polymerization for the rapid fluorescence analysis of cyhalothrin residues in River water [24]. Later Wang *et al.* used SiO_2-coated red QDs as a support carrier and reference signal source using the sol-gel method [25]. Liu *et al.* reported that FIPs encapsulated nitrogen-doped graphene QDs, prepared by alkaline self-polymerization of dopamine using dopamine as the functional monomer and cross linking agent. The fluorescent strip was constructed for specific detection of thiamethoxam [26]. Amjadi *et al.* prepared a ratio MIFs by imprinting carbon quantum dot silica spheres and CdTe/CdS QDs in the same polymer using the sol-gel method, in this investigation done a study of diniconazole residues in environmental water and soil samples [27].

2. MIFs in Veterinary Drugs/Drug Residues.

In recent years, illegal use of forbidden additives, incorrect use of veterinary drugs moreover overuse of drugs in production, use of livestock, poultry, aquatic products have becomes some of the important factors affecting food safety. For example, tetracycline is mostly used in livestock and poultry production as a broad-spectrum bacteriostatic agent. Owing to high dosage, longer time as well as abuse of drug, it will produce major residues in animal muscle, milk, liver, thus endangering food safety. Due to higher selectivity as well as proper stability, FIPs can proficiently recognize and detect veterinary drug molecule in complex sample i.e. meat products, blood, urine and feces to handle with a variety of unfavorable factors. Thus the veterinary drug residue analysis method based on MIFs demonstrate higher sensitivity and more selectivity

3. MIFs in Heavy Metals

A rapid growth of industrial economy, the liberation of heavy metal sewage is becoming ever more severe and poses a major amount of hazard to the environment and creature health. Heavy metals are extremely poisonous, toxic, not easily degradable, bioaccumulative, and easily transfer in the food chain. Heavy metals contaminate the agricultural products as well as food to causing severe harm. In view of the heavy metal contamination, the development of a simple, rapid, and precise MIF is of huge impact to protect the environment of agricultural products, food quality as well as safety. Various application of MIFs was in heavy metals detection like, Luo *et al.* reported a direct introduction CdTe QDs on the surface of sulfhydryl-modified magnetic silica spheres for quantitative analysis of Cd^{2+} but also for magnetic adsorption and removal of Cd^{2+} [29]. Similarly Tan *et al.* prepared Zn^{2+} and Cd^{2+} ion imprinting by sol-gel blotting [30].

4. MIFs in environmental Organic Pollutants

Environmental organic pollutants such as aromatic hydrocarbons, phenols, dyes etc contain teratogenic carcinogenic and hazards element, which are major threats to human health. In earlier research, the high-performance liquid chromatography (HPLC) and mass spectrometry (MS) were frequently to measure the content concerning urinary albumin. While the sensitivity as well as specificity of mass spectroscopy was high, the equipment was expensive and detection cost was high. MIFs have been mostly employed for speedy detection of organic pollutants in the environment. Environmental organic pollutants were studied by Li *et al.* prepared FIPs by encapsulating $YVO_4:Eu^{3+}$ rare earth nanoparticles and carbon quantum dots use for the rapid determination of p-nitrophenol in environmental water and urine [31]. Similarly, Zhou *et al.* done hydrothermally treated APTES-grapheme oxide to obtain silylated graphene quantum dots, which were introduced into the FIPs of p-nitrophenol by sol-gel method [32]. Wu *et al.* reported the preparation of FIPs using AuCNs for the first time and effectively applied these FIPs in the fluorescence analysis of bisphenol in seawater [33]. Organic pollutant analysis based on Molecular imprinted fluorescence frequently suffered from the complex matrix interference and which will result in false positive and false negative results. It will be essential to develop a novel approach to construct anti-interference FIPs and MIFs for determination of traces of environmental organic pollutants in food and environment samples. Relatively combining a prompt pretreatment procedure with MIFs is another useful solution to keep away from matrix interference.

Conclusions

Molecularly imprinted fluorescence sensor combine the high selectivity of Molecular imprinting technology with the more sensitive response of fluorescent matter and convert the molecular recognition into understandable fluorescence signal. The MIFs improve the performance of molecular imprinting and diverse range of applications, MIFs promoting high-efficiency and high-sensitivity determination of trace substances in complex matter. MIFs is compared to all traditional analytical techniques it reveal the characteristics of high sensitivity as well as high selectivity and thus display major potential and superior application with respect to the rapid detection of food and environment safety. Preparations of MIFs with better selectivity, higher sensitivity, and the combination of tablet computers, and cloud databases to construct an innovative intellectual fluorescence rapid finding platform are of huge significance in promoting the advance of rapid detection technology for food and environment safety.

Conflict of interest

The authors declare that they have no conflict of interest

Reference

[1] Pan J, Chen W, Ma Y, Pan G. Molecularly imprinted polymers as receptor mimics for selective cell recognition. Chem. Soc. Rev. 2018; 47(15):5574-87.

[2] Gui R, Jin H, Guo H, Wang Z. Recent advances and future prospects in molecularly imprinted polymers-based electrochemical biosensors. Biosens. Bioelectron. 2018 Feb 15; 100:56-70.

[3] Bagheri AR, Arabi M, Ghaedi M, Ostovan A, Wang X, Li J, Chen L. Dummy molecularly imprinted polymers based on a green synthesis strategy for magnetic solid-phase extraction of acrylamide in food samples. Talanta. 2019 Apr 1; 195:390-400.

[4] Wagner, S.; Bell, J.; Biyikal, M.; Gawlitza, K.; Rurack, K. Integrating fluorescent molecularly imprinted polymer (MIP) sensor particles with a modular micro fluidic platform for nanomolar small-molecule detection directly in aqueous samples. Biosens. Bioelectron. 2018, *99*, 244–250.

[5] Wang J, Dai J, Xu Y, Dai X, Zhang Y, Shi W, Sellergren B, Pan G. Molecularly imprinted fluorescent test strip for direct, rapid, and visual dopamine detection in tiny amount of biofluid. Small. 2019 Jan; 15(1):1803913.

[6] Ovca A, Jevšnik M, Kavčič M, Raspor P. Food safety knowledge and attitudes among future professional food handlers. Food Control. 2018 Feb 1; 84:345-53.

[7] Carvalho FP. Pesticides, environment, and food safety. *Food Energy* Secur. 2017 May; 6(2):48-60.

[8] Chen Y, Lopez S, Hayward DG, Park HY, Wong JW, Kim SS, Wan J, Reddy RM, Quinn DJ, Steiniger D.

Determination of multiresidue pesticides in botanical dietary supplements using gas chromatography–triple-quadrupole mass spectrometry (GC-MS/MS). J. Agric. Food Chem. 2016 Aug 10; 64(31):6125-32.

[9] Liu G, Yang X, Li T, Yu H, Du X, She Y, Wang J, Wang S, Jin F, Jin M, Shao H. Spectrophotometric and visual detection of the herbicide atrazine by exploiting hydrogen bond-induced aggregation of melamine-modified gold nanoparticles. Microchim Acta. 2015 Aug 1; 182(11-12):1983-9.

[10] Rotariu L, Lagarde F, Jaffrezic-Renault N, Bala C. Electrochemical biosensors for fast detection of food contaminants–trends and perspective. TrAC Trends Anal. Chem. 2016 May 1; 79:80-7.

[11] Sun A, Chai J, Xiao T, Shi X, Li X, Zhao Q, Li D, Chen J. Development of a selective fluorescence nanosensor based on molecularly imprinted-quantum dot optosensing materials for saxitoxin detection in shellfish samples. Sens. Actuators B Chem. 2018 Apr 1; 258:408-14.

[12] Wang QH, Fang GZ, Liu YY, Zhang DD, Liu JM, Wang S. Fluorescent sensing probe for the sensitive detection of histamine based on molecular imprinting ionic liquid-modified quantum dots. Food Anal. Methods. 2017 Jul 1; 10(7):2585-92.

[13] Ayankojo AG, Reut J, Öpik A, Furchner A, Syritski V. Hybrid molecularly imprinted polymer for amoxicillin detection. Biosens. Bioelectron. 2018 Oct 30; 118:102-7.

[14] Culver HR, Peppas NA. Protein-imprinted polymers: The shape of things to come?. Chem. Mater. 2017 Jul 25; 29(14):5753-61.

[15] Boulanouar S, Mezzache S, Combès A, Pichon V. Molecularly imprinted polymers for the determination of organophosphorus pesticides in complex samples. Talanta. 2018 Jan 1; 176:465-78.

[16] Dabrowski M, Lach P, Cieplak M, Kutner W. Nanostructured molecularly imprinted polymers for protein chemosensing. Biosens. Bioelectron. 2018 Apr 15; 102:17-26.

[17] BelBruno JJ. Molecularly imprinted polymers. Chemical reviews. 2018 Sep 24; 119(1):94-119.

[18] Yang Q, Li J, Wang X, Peng H, Xiong H, Chen L. Strategies of molecular imprinting-based fluorescence sensors for chemical and biological analysis. Biosens. Bioelectron. 2018 Jul 30; 112:54-71.

[19] Ahmad OS, Bedwell TS, Esen C, Garcia-Cruz A, Piletsky SA. Molecularly imprinted polymers in electrochemical and optical sensors. Trends Biotechnol. 2019 Mar 1; 37(3):294-309.

[20] Qi J, Li B, Wang X, Fu L, Luo L, Chen L. Rotational paper-based microfluidic-chip device for multiplexed and simultaneous fluorescence detection of phenolic pollutants based on a molecular-imprinting technique. *Anal. Chem.* 2018 Aug 23; 90(20):11827-34.

[21] Yang Y, Niu H, Zhang H. Direct and highly selective drug optosensing in real, undiluted biological samples with quantum-dot-labeled hydrophilic molecularly imprinted polymer micro particles. ACS Appl. Mater. Interfaces. 2016 Jun 22; 8(24):15741-9.

[22] DU XW, ZHANG YX, SHE YX, LIU GY, ZHAO FN, Jing WA, WANG SS, Fen JI, Hua SH, JIN MJ, ZHENG LF. Fluorescent competitive assay for melamine using dummy molecularly imprinted polymers as antibody mimics. J. Integr. Agric. 2016 May 1; 15(5):1166-77.

[23] Li X, Jiao HF, Shi XZ, Sun A, Wang X, Chai J, Li DX, Chen J. Development and application of a novel fluorescent nanosensor based on FeSe quantum dots embedded silica molecularly imprinted polymer for the rapid optosensing of cyfluthrin. Biosens. Bioelectron. 2018 Jan 15; 99:268-73.

[24] Wei X, Hao T, Xu Y, Lu K, Li H, Yan Y, Zhou Z. Facile polymerizable surfactant inspired synthesis of fluorescent molecularly imprinted composite sensor via aqueous CdTe quantum dots for highly selective detection of λ-cyhalothrin. Sens. Actuators B Chem. 2016 Mar 1; 224:315-24.

[25] Wang X, Yu J, Wu X, Fu J, Kang Q, Shen D, Li J, Chen L. A molecular imprinting-based turn-on ratiometric fluorescence sensor for highly selective and sensitive detection of 2, 4-dichlorophenoxyacetic acid (2, 4-D). Biosens. Bioelectron 2016 Jul 15; 81:438-44.

[26] Liu Y, Cao N, Gui W, Ma Q. Nitrogen-doped graphene quantum dots-based fluorescence molecularly imprinted sensor for thiacloprid detection. Talanta. 2018 Jun 1; 183:339-44.

[27] Amjadi M, Jalili R. Molecularly imprinted mesoporous silica embedded with carbon dots and semiconductor quantum dots as a ratiometric fluorescent sensor for diniconazole. Biosens. Bioelectron 2017 Oct 15; 96:121-6.

[28] Sun C, Su R, Bie J, Sun H, Qiao S, Ma X, Sun R, Zhang T. Label-free fluorescent sensor based on aptamer and thiazole orange for the detection of tetracycline. Dye. Pigment.2018 Feb 1; 149:867-75.

[29] Luo X, Guo B, Wang L, Deng F, Qi R, Luo S, Au C. Synthesis of magnetic ion-imprinted fluorescent CdTe quantum dots by chemical etching and their visualization application for selective removal of Cd (II) from water. Colloids Surf. A Physicochem. Eng. Asp. 2014 Nov 20; 462:186-93.

[30] Tan J, Wang HF, Yan XP. A fluorescent sensor array based on ion imprinted mesoporous silica. Biosens. Bioelectron. 2009 Jul 15; 24(11):3316-21.

[31] Li W, Zhang H, Chen S, Liu Y, Zhuang J, Lei B. Synthesis of molecularly imprinted carbon dot grafted YVO4: Eu3+ for the ratiometric fluorescent determination of paranitrophenol. Biosens. Bioelectron. 2016 Dec 15; 86:706-13.

[32] Zhou Y, Qu ZB, Zeng Y, Zhou T, Shi G. A novel composite of graphene quantum dots and molecularly imprinted polymer for fluorescent detection of paranitrophenol. Biosens. Bioelectron. 2014 Feb 15; 52:317-23.

[33] Wu X, Zhang Z, Li J, You H, Li Y, Chen L. Molecularly imprinted polymers-coated gold nanoclusters for fluorescent detection of bisphenol A. Sens. Actuators B Chem. 2015 May 1; 211:507-14.