

Review

Molecularly Imprinted Polymer/Metal Organic Framework Based Chemical Sensors

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Abstract: The present review describes recent advances in the concept of molecular imprinting using metal organic frameworks (MOF) for development of chemical sensors. Two main strategies regarding the fabrication, performance and applications of recent sensors based on molecularly imprinted polymers associated with MOF are presented: molecularly imprinted MOF films and molecularly imprinted core-shell nanoparticles using MOF as core. The associated transduction modes are also discussed. A brief conclusion and future expectations are described herein.

Keywords: molecularly imprinted polymers; metal organic framework; chemical sensors; electrochemical sensors; gravimetric sensors; optical sensors

1. Introduction

The field of chemosensors and biosensors has experienced a constant expansion, with an increasing number of papers published in the last years regarding their development and applications [1]. Increasing attention has been given to the replacement of biological receptors with semisynthetic or synthetic receptors such as engineered proteins, aptamers and molecularly imprinted polymers (MIPs) [2–6], which offer a more stable, robust and cheap alternative for molecular recognition.

MIPs serve as synthetic receptors for a wide variety of molecules and are synthesized using molecular imprinting techniques. Molecular imprinting involves the use of functional monomers, cross-linkers and template molecules to create specific and selective cavities in a three-dimensional polymer network. The polymerization is performed in the presence of template molecules, represented by the analyte of interest, followed by the extraction of the template from the polymer matrix. The resulting cavities are complementary in shape and size with the template (target analyte) and offer interaction points and a coordination sphere around the target [7].

MIPs have been regarded as a promising substitute for their biological counterpart in various research fields such as chromatography [8–10], biotechnology [11], environmental science [12], food safety [13,14], biomedical sciences [15,16] and sensors design [17].

In recent years MIPs have found widespread application in the development of sensing devices, with an interdisciplinary research area occurring from combining sensors and MIPs [18–20]. The increasing interest in integrating MIPs in sensors is due to their unique properties, such as low cost, high stability, high selectivity, long storage time, reusability and tailorability for practically any target analyte.

The choice of appropriate component materials is of paramount importance, because it defines the recognition selectivity and sensitivity. Numerous materials, such as responsive polymers, lanthanide ion complexes [21], sol-gel-derived xerogels [22], carbon nanoparticles [23], silica particles [24], quantum dots [25,26], and metal, can be fused with MIPs in singular or multiple combinations. Metallic silver and gold particles are widely used as the core material due to their electronic properties and scattering/plasma behavior with respect to the light emitted. For example, Chen et al. [27] developed an imprinted recognition element for surface-enhanced Raman spectroscopy (SERS) applications using silver nanoparticles. The hybrid system Ag@MIP showed extremely high SERS activity, detecting with high sensitivity the target molecules (Rhodamine B) and improving the signal-to-noise ratio and repeatability, with the overall SERS intensity being related to the densities of imprinted cavities in the MIP film.

Metal organic frameworks (MOFs) are one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) metal complexes with organic linkers, such as carboxylates or phosphonates. First defined by Yaghi and co-workers in 1995 [28,29], following the pioneering work of Hoskins and Robson, MOFs are crystalline porous hybrid materials that contain coupling units (metal ions or metal-oxo units) coordinated by electron-donating organic ligands. A subgroup of MOFs that consist of pores with dimensions less than 2 nm is microporous metal organic frameworks (MMOFs). While they show similar adsorption properties as other porous materials capable of physisorption, the incorporation of metal centers enables them to interact with adsorbed hydrogen molecules more strongly to enhance hydrogen adsorption. Chen et al. [30] synthesized a MOF (MOF-505) based on the NbO topology, proving that the metal-oxide units and the organic ligands are important features for hydrogen binding. MOFs with aromatic ligands generally have a high specific surface area and large pore volume with a well-defined pore size, which had been proved to be effective through hydrogen and methane adsorption [31,32]. They are mainly used in gas storage, electrode materials for batteries, electrocatalysts for important reactions taking place in fuel cells or electrolyzers or electrode materials for supercapacitors.

MOFs have attracted increasing interest in recent years as highly sensitive platforms for the development of sensors [33,34]. The use of MOFs is extensive, due to their numerous architecture properties: stable framework, ultra-high porosity, large internal surface area, pore volume, wide range of thermal and chemical stability, non-toxic nature, luminescent nature and chemical functionality. Selectivity of recognition has been obtained through covalent grafting of a specific receptor molecule on the MOF skeleton for the selective luminescent detection of parathion [35].

MOF-based sensors including a molecularly imprinted structure are a new, emerging research field. Currently only a few papers have been reported in the literature leading to promising results and opening paths for the development of a new generation of sensors. Thus, the review herein focuses on promising recent advances in MIP sensors using MOFs. Two main strategies regarding the fabrication, performance and applications of recent MIP-MOF sensors are presented: molecularly imprinted MOF films and molecularly imprinted core-shell nanoparticles using a MOF as core.

2. Sensors Based on Molecularly Imprinted MOF Thin Films

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation as well as the experimental conclusions that can be drawn.

2.1. Fabrication of Molecularly Imprinted MOF Thin Films

An important step for the fabrication of MIP sensors is the selection of the most appropriate functional monomer to yield interactions with the template molecules. The monomer:template ratio should be carefully optimized to eliminate the heterogeneity in the distribution of the imprinted cavities and to improve the quality of the signal. Bis-aniline-crosslinked gold nanoparticles (AuNPs) as a general MOF have received increased attention recently [36]. The generic protocol consisted of the synthesis of AuNPs functionalized with p-aminothiophenol, followed by electropolymerization of p-aminothiophenol-functionalized AuNPs in the presence of a template molecule. The template was then extracted from the polymer matrix, resulting in selective recognition sites for the analyte of interest. Several template molecules have been investigated such as estradiol [37], aflatoxin B1 [38], 1,3,5-trinitrotoluene [39], gemcitabine [40], glyphosate [41] and tetracycline [42]. These studies followed several steps for the fabrication of selective recognition cavities for the analytes of interest, which are summarized below: computational design, polymerization and removal of the template molecules.

In order to select an appropriate functional monomer, theoretical calculations were used to assess conformational and chemical complementarities between the template and functional monomers in different ratios. It was found that π -donor-acceptor interactions naturally play a significant role in facilitating complex formations and in achieving high stability. For example, one property of nitroaromatics, such as 1,3,5-trinitrotoluene, which may be exploited in detection schemes is their electron-accepting capability [43]. Substitution of the electron-withdrawing nitro groups on the aromatic ring lowers the energy of the empty orbitals, thereby making these compounds good electron acceptors. Conjugated polymers such as p-aminothiophenol are promising candidates for redox sensing because they are electron donors [44].

The polymerization of MIP-MOF has been achieved by electrochemical deposition. MIP-based sensors may sometimes deliver poor signal quality, due to the variation in the distance of the imprinted cavities from the surface of sensor. In order to avoid this problem and to enhance the signal, researchers have focused on developing ultra-thin polymeric films on the sensor surface by electrodeposition. Electrodeposition enables the formation of polymers directly onto electrode surfaces and has turned out to be promising and versatile in controlling film thickness, forming firmly adhered films, and tuning film electrochemical properties [39]. Thus, in order to obtain thin polymeric films, cyclic voltammetry was employed. The electropolymerization was carried out in a solution of 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in PBS (pH 7.2) containing 0.1 mg/mL p-aminothiophenol-functionalized AuNPs and 0.1 mg/mL template solution, by cycling the potential from -0.35 V to $+0.80$ V vs. SCE (Saturated Calomel Electrode), at a scan rate of 100 mV/s, for 10 cycles [27,35–38]. In the case of estradiol, the electropolymerization was carried out from -0.35 to 0.60 V, in order to avoid the oxidation of estradiol which occurs at 0.60 V [35]. The porogen solvent plays an important role in designing MIPs; thus, different organic solvents (e.g., acetone, ethanol) were added to the electropolymerization solution to assure the solubility of the template and to reduce the surface tension since most MIPs are hydrophobic. The modified electrodes were then washed with appropriate extraction solvents for 20 to 60 min in order to remove the imprinted molecules and adsorbates on the surface of the film, triggering the formation of selective recognition cavities in the MIP film. Selecting an appropriate organic solvent in molecular imprinting is not guided only by the solubility of the template, but mainly by the stability of the pre-polymerization complex and the target porosity of the MIP, which is why this solvent used is also called a porogen.

The schematic principle of the fabrication of this molecularly imprinted MOF sensor for template molecule detection is presented in Figure 1.

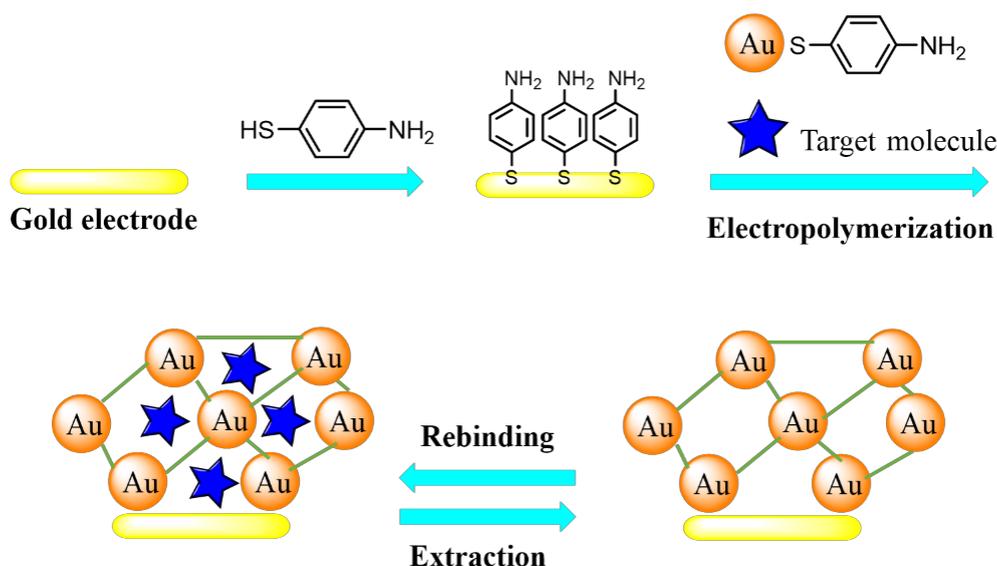


Figure 1. Schematic principle of the fabrication of this molecularly imprinted MOF sensor for template molecule detection.

As seen above, the protocol for developing electrochemical sensors by direct electropolymerization of the monomer on the transducer is simpler and faster, avoiding the need for lengthy and complex synthesis steps. Moreover, the imprinted film thickness is easily controlled through the chosen electrochemical parameters: potential range, scan rate, number of cycles.

2.2. Electrochemical Sensors Based on Molecularly Imprinted MOF Thin Films

Once the template has been entrapped during electropolymerization, as shown in Figure 1, the conditions for extraction should be optimized in terms of solvent composition and time of contact. After extraction of the template, the prepared MIP-modified electrodes were kept in solutions of different concentrations of target analytes, in order to investigate the uptake process for variable concentrations of analytes. Analytes are all electron acceptors due to their oxidizing properties. The electropolymerized polythioaniline, a conjugated polymer, is an electron donor. Its conductivity is increased when the template doping rate increases, leading to a p-doping of the conjugated polymer, due to charge delocalization.

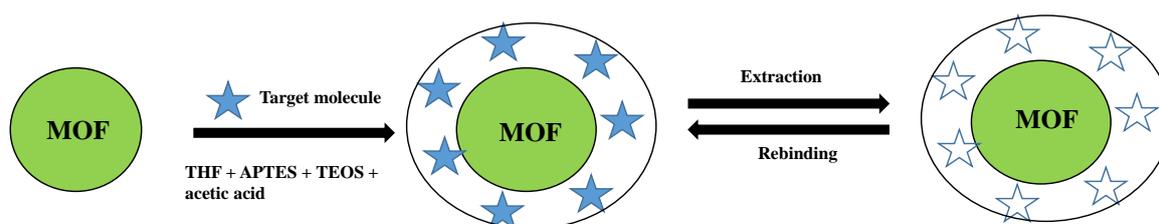
Linear sweep voltammetry measurements in the presence of a redox probe (ferro/ferricyanide) show an increase in the current peak and a shift of the peak potentials to a more positive value potential with the increase of the concentration of the template, related to the binding of the analyte in the specific cavities. As the concentrations of template molecules in the imprinted film increases, the electron transfer rate increases. The shift of potentials to more positive values shows that the charge transfer process takes place more easily when template molecules are embedded in the film. The fabricated sensors were firstly applied for the detection of various concentrations of target analytes in buffered solutions. A linear relationship between the signal-blank/signal ratio and the logarithmic concentration of the analytes was obtained in each case. A linear range from fM to nM and a low limit of detection in the fM range was obtained for the MIP sensors. Compared to the MIP, the response currents of the NIP (Not Imprinted Polymer) did not change significantly with the concentration change, demonstrating the successful formation of imprinting cavities in MIP films. The selectivity of the MIP sensors was also investigated towards the binding of structurally related compounds, proving excellent selectivity [37–42]. The observed sensitivities of detection can be classified as: 1,3,5-trinitrotoluene > estradiol > gemcitabine > aflatoxin B1 > tetracyclin > glyphosate; these different sensitivities are due to the different rates of doping, concerning the number of imprinted cavities and the charge transfer rate. Analytical performances are reported in Table 1.

Table 1. Analytical performances of MIP-MOF-based chemical sensors.

Target	Transduction Type						Reference
	Electrochemistry		Quartz Microbalance		Fluorescence		
	Detection Limit	Dynamic Range	Detection Limit	Dynamic Range	Detection Limit	Dynamic Range	
estradiol	0.3 pg/L	1 pg/L to 1 µg/L					[37]
aflatoxin	0.9 pg/L	1 pg/L to 1 mg/L					[38]
1,3,5-trinitrotoluene	0.9 pg/L	1 pg/L to 1 µg/L					[39]
gemcitabine	0.9 pg/L	1.1 pg/L to 11.4 µg/L					[40]
glyphosate	0.8 pg/L	1 pg/L to 1 µg/L					[41]
tetracycline	44.4 pg/L	9 pg/L to 10 µg/L					[42]
metallocarb			0.069 mg/L	0.1–0.9 mg/L			[45]
hemoglobine					0.062 mg/mL	0–0.6 mg/mL	[46]

3. Sensors Based on Molecularly Imprinted Core-Shell Nanoparticles Using MOF as a Core

Molecularly imprinted core-shell nanoparticles using a MOF as core have been successfully integrated in mass sensors. Qian et al. [45] reported a quartz microbalance (QCM) MIP sensor employing a type of MOF for the sensitive detection of metalcarb. The MOF MIL-101 was used as a support for synthesizing MIP via a sol-gel process. Firstly, MIL-101 was chemically synthesized from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and terephthalic acid and used to synthesize MIL@MIP nanoparticles. MIL@MIP was synthesized by thermal polymerization in a solution of tetrahydrofuran containing MIL-101, the monomer (3-aminopropyl)triethoxysilane, the cross-linker tetraethyl orthosilicate, the template metalcarb and acetic acid as a catalyst. The structure of the molecularly imprinted core-shell nanoparticles using a MOF as core is presented in Figure 2.

**Figure 2.** Structure of the molecularly imprinted core-shell nanoparticles using a MOF as core.

The suspension of MIL@MIP was then dropped onto the QCM surface and dried. The resulting core-shell nanoparticles exhibited an octahedral shape and were uniformly distributed in the polymer film. MIL-101 confers several advantages such as high chemical stability, high stability in water and high surface area.

The QCM sensor based on MIL-101@MIP was applied for the detection of metalcarb in pear juice. For this purpose adsorption studies were performed, showing that the frequency change was linear with the concentration of metalcarb in the range from 0.1 to 0.9 mg/L, with a detection limit of 0.0689 mg/L [45]. The analytical performance is reported in Table 1.

Molecularly imprinted core-shell nanoparticles using a MOF as core were also used in the development of optical sensors, improving their performance through the high surface area of the sensing surface. A fluorescence-based sensor was developed by Guo et al. [46] for the detection

of hemoglobin using bovine hemoglobin as the template molecule, N-isopropyl acrylamide as the temperature-sensitive functional monomer and N,N-methylene bisacrylamide as the cross-linker. $\text{Cu}_3(\text{BTC})_2$ was used as a representative of the MOF and upconversion nanoparticles were used as fluorescence materials. The upconversion nanoparticles were synthesized by a solvothermal reaction and functionalized with polyacrylic acid. The MOF composite was prepared by the solvothermal reaction of copper nitrate, H3BTC and polyacrylamide-modified upconversion nanoparticles in ethanol. The MOF composite was added in the polymerization mixture containing the template hemoglobin, monomer and cross-linker and the polymerization was carried out at 25 °C for 5 h. The template was then extracted by washing with TRIS buffer, the complete extraction being investigated by UV-vis spectrometry. The rebinding of the template was investigated by fluorescence spectrometry, and fluorescence quenching was being observed upon the binding of the template.

The MOF@MIP optical sensor developed by Guo et al. [46] was applied for the detection of hemoglobin. The recognition capability of the imprinted MOF@MIP material was evaluated through the change of the fluorescence signal of the hybrid material at various concentrations of hemoglobin ranging from 0 to 0.6 mg/mL, with a detection limit of 0.062 mg/mL. Specificity studies of the binding of other proteins have also been performed and the sensor exhibited good selectivity for the recognition of hemoglobin. The analytical performance is reported in Table 1.

4. Conclusions

MOF-based molecularly imprinted sensors have attracted increasing attention in recent years. Few MIP/MOF sensors have been developed in the last couple of years and applied for the detection of various analytes of biomedical or environmental interest. Novel porous hybrid MIP/MOF materials have been coupled with electrochemical, optical and mass transducers, resulting in sensors with high sensitivity and selectivity for the analyte of interest. The developed MIP/MOF sensors featured improved thermal stability, improved water compatibility and stability and a high adsorption rate through their high surface area. Among these sensors, electrochemical MIP/MOF sensors prepared by electropolymerization on conductive substrates exhibit high sensitivity and excellent selectivity in complex matrices. Moreover, the imprinted film thickness is easily controlled through the chosen electrochemical parameters: potential range, scan rate, number of cycles. Molecularly imprinted core-shell nanoparticles using a MOF as core were used for mass and optical transduction. The obtained specific surface area is very large, leading to a very large dynamic range.

Although intensive research in the field of MOF-MIP sensors is still needed, the promising results obtained in the field so far open doors for developing cheap and sensitive on-site sensors. In the future, developing MIP biosensors based on MOFs with high stability and long shelf-life is surely an attractive route for designing sensitive, low-cost sensors for many practical applications. They offer many advantages such as high adsorption ability and high transfer rate through their increased surface area due to the MOFs, high selectivity, high chemical and thermal stability, long shelf-life and reusability through MIP, coupled with the high sensitivity of electrochemical, optical and gravimetric methods.

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