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Metal-organic frameworks as an alternative smart sensing platform for designing molecularly imprinted electrochemical sensors

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ABSTRACT

Although molecularly imprinted electrochemical sensors (MIECS) have proposed an intriguing potential to compete with other sensor types, they are still subject to limitations such as heterogeneous binding sites, random polymerization, and a rigid and dense network resulting in low sensitivity and specificity. Recently, MOFs as a promising sensory material have been proposed and designed to overcome the limitations mentioned above. In this context, the introduction of MOFs into MIECS shows excellent potential for fabricating a selective layer on an electrochemical sensor resulting in enhanced sensing performance. Herein, we focused our efforts on serving a comprehensive review for the researchers while revealing the cross-section of MOFs and MIECs to develop an alternative approach to improve the sensitivity of the electrochemical sensors by using MOFs-based materials. Moreover, the employment of various materials, including nanoparticles, carbon-based materials, and nanocomposites with specific functions on the performance of MIECS, has been assessed. This review will also cover the recent progress achieved in MOFs-based MIECs adapted for the detection wide range of analytes from small molecules such as amino acids, pharmaceuticals, pesticides to larger molecules, proteins. These make this review very attractive and have a great potential to result in new, further, and innovative approaches for solving challenges in MIPs and opening a new field for electrochemical sensors.

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1. Introduction

Molecular imprinting is an innovative technique that allows synthetic biorecognition cavities, which mimic the native biological derivatives such as antibodies, receptors, enzymes, etc. [1]. The basis of molecular imprinting relies on the polymerization of the functional monomer with excess crosslinking agents in the presence of the target analyte. After removal of the target analyte, the synthetic cavities complementary to the template in the spatial and chemical structure of the template expose out to be responsible for selective rebinding of the template. Herein, the molecular imprinting technique enables bio-mimicking receptors with high specific affinity comparable to natural receptors and superior stability to natural biomolecules [2]. Molecularly imprinted polymers (MIPs) called plastic antibodies and/or plastic enzymes have emerged as effective materials to develop biomimetic electrochemical sensors. Although the formation of MIPs possessing good stability, high temperature, and pressure resistance, and long shelf life, seems relatively easy, some variables such as the use of suitable functional monomer and crosslinker, the optimum ratios between functional monomer, template, and crosslinker should be well discussed to obtain the maximum yield [3]. Besides, the construction of imprinted materials for the macro-structures such as proteins, polypeptides, and enzymes has some inherent limitations considering poor mass transfer and solubility, denaturation, and heterogeneous affinity in binding cavities due to complex structure [4]. Therefore, electrochemical sensors may compete with other sensor types, but the limited sensitivity and stability still remain challenging. Recently, a solution was proposed using metal-organic frameworks (MOFs) to create materials suitable for recognizing and binding targets with high sensitivity and selectivity.

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MOFs, three dimensional crystalline porous hybrid materials possessing inorganic coupling units (metal ions or metal clusters) coordinated by electron-donating organic ligands [5], have also gained increasing attention as functionalized electrode materials in innovative sensing applications [6] using their excellent properties, including stable and ordered crystal structure, large surface area, high porosity, non-toxicity, and availability of various functional groups [7]. The porous structure of MOFs enhances convective diffusion to increase the mass transfer rates as well as adsorption capacity [8]. The unique features like unsaturated metal coordination sites, designed crystal structure, tunable porosity, etc., serve as excellent coating electrode materials for creating novel sensing platforms [9]. Besides the sensing application towards various analytes such as H_2O_2, glucose, dopamine, heavy metals, proteins, etc. [10], MOFs have been revealed great potential in gas storage, catalysis, drug delivery, and batteries [11].

Several different reviews based on MIPs and MOFs have been reported over the years regarding their sensor applications. Yang et al. [12] reported the recent works associated with enhancing the sensitivity of MIECs as well as the challenges and current problems of sensors. Bhogal et al. [13] reported a comprehensive review of core-shell MIPs in optical, electrochemical, and piezoelectric sensors with the challenges and opportunities. In recent years, some reviews revealed fabrication of a MOFs-based sensor has already been available [14–18]. In this context, incorporating MOFs into MIPs shows excellent potential for fabricating selective layers in an electrochemical sensor. This review covers the recent studies specifically about MOFs-based molecularly imprinted electrochemical sensors (MIECs) that can present the more effective and affordable methods to provide highly specific and reliable tests for rapid and reliable detection and identification of compounds within a short time. One of the critical issues in developing the detection system is that simultaneous identification and quantification is a highly complex task because of sensitivity and reusability. This review will be a pioneer to guide the researchers to overcome the limitations mentioned above. Herein, we suggest an alternative review for the researchers to develop an alternative approach to improve the sensitivity of the electrochemical sensors by using MOFs-based materials. These make the review have a great potential to result in new, further, and innovative approaches for solving challenges in MIPs and opening a new field for MOFs.

2. Molecularly imprinted polymers (MIPs): principles, design, and challenges

2.1. Molecular imprinting approaches

The first starting point date back to the research of Polyakov related to synthesizing silica gel and finding out its adsorption features for imprinted dyes [19]. Then, the interaction of natural antibodies and specific antigens as template models was proposed by Pauling in 1940 [20]. Both preliminary developments form the basis of artificial molecular recognition. Wulff and coworkers pioneered MIP synthesis and designing for biomimetic catalytic applications. As a result, the MIP strategy is classified as one of the most promising techniques for recognizing target molecules. This scientific trend forced researchers to synthesize MIPs with various materials. Template, monomer, crosslinker, and initiator are the main keystones for the foundation of MIPs. The template-monomer complex, called the pre-polymerization complex, is polymerized in the presence of a high percentage of crosslinking agents to stabilize 3D-polymer chains under appropriate conditions. After extracting or removing the template molecules from the polymer, the imprinted cavities are exposed as synthetic receptors having a complementary geometrical size and chemical structures (Fig. 1). In other words, the host cavities, which are specific to the target molecules, are tailored in imprinted polymeric matrices. The molecular imprinting approach relies on the well-known “lock-key” biorecognition model [21]. The most attention is focused on developing and applying molecularly imprinted polymer-based structures, which can replace antibodies, receptors, and many other expensive affinity reagents [22]. The substrate molecules are bound to artificial cavities with high selectivity and affinity in diverse metabolic biochemical reactions. Similarly, molecular imprinting is based on two main points: (i) the structure of polymeric matrixes and (ii) the nature of binding interaction between template and polymer. As a result, reversible covalent, non-covalent interactions or hybrid interactions between the template molecule and functional monomer with appropriate binding groups are allowed to form. The functional groups of the polymer are covalently bound to the template in the first examples of traditional imprinting methods [23]. Later on, it was reported that the template-monomer interactions could be possible with non-covalently interactions, including van der Waals forces, hydrogen bonding, and dipolar interactions. This non-covalent binding for imprinting approaches was firstly reported by Klaus Mosbach et al., in 1988 [24].

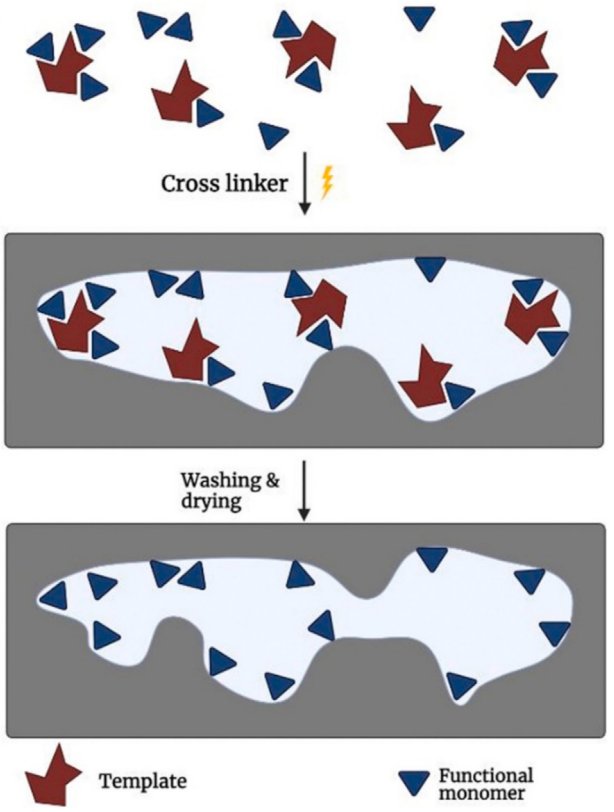


Fig. 1. Schematic representation of polymerization and removal processes resulting in the formation of specific cavities for the template. Reprinted from Ref. [23] with permission from Elsevier.

2.2. Design and synthesis of MIPs as artificial receptors

In order to develop efficient, specific, and selective MIP-based materials, the most important step in MIP fabrication is proper synthesis route and designing well-oriented/accessible cavities. Functional monomers interact with target molecules through covalent or non-covalent interactions and form complex networks in

the solution phase before the polymerization process. Therefore, it is possible, to sum up the interactions utilized in three types depending on the interactions and arrangements of functional monomers around target molecules: covalent, non-covalent, and semi-covalent interactions [25].

2.2.1. Covalent imprinting

The pre-polymerization complexes are synthesized via the covalently bonding of functional monomers to template molecules to form stable polymers. The high bond strength/stability of covalent bonds enables the synthesis of MIPs that are more selective than other synthesis methods. Moreover, the low probability of nonselective binding in covalent imprinting is due to stoichiometric interactions between functional monomers and template molecules [26]. However, the harsh template removal step should be applied to break down those covalent bonds in this approach, and relatively slow adsorption kinetic limited the performance of the MIPs developed due to the re-formation of covalent bonds between functional groups and template molecules.

2.2.2. Non-covalent imprinting

The most common type of interaction utilized in MIP design is non-covalent imprinting, which mainly allows weak intermolecular interactions, including hydrogen bonding, electrostatic interactions, hydrophobic interactions, Pi-Pi stacking, and van der Waals forces between the template and the functional monomers during the formation of the pre-polymerization complex. Furthermore, selecting a suitable solvent and monomer is essential for the pre-polymerization complex to be stable in the polymerization step. However, an excessive amount of functional monomer is requested because of the low binding constant, resulting in undesirable non-selectivity [27].

2.2.3. Semi-covalent imprinting

Apart from covalent and non-covalent imprinting in the synthesis of MIPs, an approach called semi-covalent imprinting is known as a hybrid approach between these two approaches. In this approach, the pre-polymerization complex is formed using covalent bonds, while non-covalent bonds are simultaneously utilized during the interaction of the target molecule with the monomer [28].

The necessary components for synthesizing MIPs include functional monomer(s), crosslinker(s), initiator, and a suitable solvent [25]. Functional monomers, one of the important ingredients in the preparation of MIPs, affect the performance of the synthetic receptor and impart specificity. They also affect the mechanical stability and porosity of the polymer complex formed through covalent or non-covalent interactions. In non-covalent printing, L-phenylalanine, 17β-estradiol, methacrylic acid, 2-hydroxyethyl methacrylate, acetylsalicylic acid, and 4-vinyl pyridine are widely used as functional monomers. In covalent imprinting, 1,3-diols, amines, and boronic acids are often preferred as functional monomers due to reversible covalent bond formation features. In addition, functional monomers are important in the successful synthesis and design of MIP as well as helping to form stable attachment moieties to the polymer matrix [29]. Another important component in the preparation of MIPs is crosslinker. The main role of crosslinkers is to provide a rigid polymerization matrix. It is important to choose it carefully, as it has a significant effect on the morphology of MIPs in terms of both physical and chemical properties.

Furthermore, the crosslinker provides stability of the binding cavity for selective recognition of the template molecule. Crosslinkers such as ethylene glycol dimethacrylate (EDMA or EGDMA), trimethylolpropane trimethacrylate (TRIM), and 1,4-divinyl benzene (DVB) are widely used in molecular imprinting [29,30]. The initiator is also an important component required for the initiation of polymerization reactions. Generally, heat or UV-induced free radical polymerization is used to synthesize MIPs. Azobisnitriles, free radicals, are among the most widely used initiators. In particular, 2,2′-azobis-(isobutyronitrile) (AIBN) and 2,2′-azobis-(2,4-dimethylvaleronitrile) (ADVN) have often found application in the preparation of MIPs. In addition, temperature is classified as an important factor in the polymerization process. It was concluded that a lower initial temperature would be more accurate for the stability of the polymerization complex [29,31]. And finally, another component that plays an important role in molecular imprinting is solvents. Solvents have a significant influence on MIP morphology, such as pore formation with the crosslinker. Because the stability of the pre-polymerization complex is affected by the solvent environment, the choice of solvent has a significant impact on the recognition performance of MIPs. For example, highly polar solvents such as methanol and water adversely affect the bonds between the functional monomer and the template molecule, resulting in the synthesis of MIPs with lower selectivity. Therefore, non-polar solvents such as dichloromethane or acetonitrile may be preferred, unlike polar solvents. In this case, the dielectric constant of non-polar solvents will be important. It was found to have a negative effect on the selectivity of MIP, as increasing dielectric constant affects hydrogen bond interactions. In summary, selectivity was best observed in MIPs synthesized in apolar solvents with low dielectric constant [29,32].

2.3. Challenges and emerging trends of molecularly imprinted polymers

One of the aims of MIP design is to enhance the selectivity, sensitivity, and compatibility of materials against biomolecules in biological samples. The physicochemical properties of the starting materials used in MIPs as well as the resulting polymeric network, should be compatible with the physiological requirements of the analyte biomolecules [21]. The imprinting technology can happen the best performance under appropriate conditions. Imprinted polymers are traditionally made of dense networks that are created during polymerization [19]. One problem is that large templates structure can be entrapped in the network and can not easily diffuse back into the network to find binding sites [33]. These limitations in network diffusion cause a failed recognition mechanism. It is observed a slow leakage in the template which is used for trace substances based MIPs. The solvents should not effectively diffuse into the cavities to destroy interactions between monomer and template. Moreover, there are many problems related to MIP usage in catalysis. The insolubility in various solvents, heterogeneous cavities, slow mass transportation because of high amount crosslinking, imprinting errors in aqueous media can be observed. To address these issues and improve catalytic activity, two main strategies regarding the fabrication, performance, and applications of recent MIP-MOF sensors are proposed as molecularly imprinted MOF films and molecularly imprinted core-shell nanoparticles via utilizing porosity of MOFs to overcome solvent compatibility and substrate solubility problems [34].

3. Metal-organic frameworks (MOFs): general aspects and practical considerations

Metal-organic frameworks (MOFs) are described as coordination polymers formed by the self-assembly of inorganic metallic centers and organic binders as a hybrid structure by coordinated dative bonds [35]. Although MOFs that are porous hybrid polymers have been known since the 1960s, they have started to find many

uses thanks to remarkable research in recent years [33]. In order to obtain MOFs with the direct reaction of inorganic and organic parts, various synthesis techniques, i.e., sonochemical, electrochemical, hydrothermal, solvothermal, microwave, and mechanochemical, etc., are used [35]. MOFs' unique and advantageous characteristics, such as easy and low-cost synthesis methods, large specific surface area, and great porosity, enable their use in sensor studies to improve sensitivity and selectivity besides allowing simultaneous analysis [36]. There are numerous options when choosing metals and organic binders for the MOF synthesis process to obtain perfect MOF crystal structures being shaped in many different ways (cubic, tetragonal, and monoclinic, etc.) [35]. It is also possible to obtain specific MOF structures designed for the targeted analyte by changing the constitution [33]. The most prominent features of MOFs can be listed as follows: excellent porosity, uniform structure, functionalization and adsorption ability, having active catalytic sites, controllable pore size and structure, water, thermal and chemical stability [33,35]. Besides these features, MOFs also have certain disadvantages such as fragility, insolubility in particular solvents, and accumulation during hydrothermal and pyrolysis processes [37].

Metal/metal oxide nanomaterials and polymers are widely used with MOF composites. The frame structure of the MOF is kept with the metal oxide after the calcination technique [38]. The formed moieties with MOF composites have overcome many difficulties because of synergistic properties. The combination of MOF and metal/metal oxide nanomaterials composites displays new potentials to eliminate the low active sites of MOFs, superior stability, the rendering of user-friendly structures, and improvement of electrical properties [39]. The new class of 2D metallically conducting MXenes contributes to the design of biosensors [40]. Recent developments in the formation of a relatively open a new avenue for the design of conducting composites with metallic conductivity and advanced sensing properties.

Hence, many researchers sway forward to study the combination of metal moieties and MOFs composites to enlighten innovative properties of MOF structures.

The electrochemical sensor performance has been improved by integrating Ni-, Co-, Fe-, Zn-, and Cu-metal ions within MOFs (Fig. 2). The researchers widely prefer CoFe-MOFs with 3D-porous nano-cube structures due to their larger surface areas, water compatibility, and electroactive properties. Cu-MOFs serve as an electrochemical probe signal with excellent catalytic activity, high conductivity, and well configuration [41].

The chromium terephthalate-based mesoporous MOF [MIL-101(Cr)] materials have been used as a sorbent to extract the trace analytes from water because of its high surface area, large mesoporous pores, a large number of unsaturated Cr(III) sites, and excellent chemical and solvent stability [38]. The amino-functionalized titanium(IV) based MOFs [NH_2-MIL-125(Ti)] with semiconducting materials have photoluminescence properties and photocatalytic activities that make them an ideal candidate for potential application of photoelectrochemical sensors [42].

Metal sulfides (such as SeS_2, ZnS, CoS) referred as electrode materials have been used in biosensing, supercapacitors, photocatalysis and batteries. Metal sulfides contribute to design the electrochemical sensors in the terms of synthesis of special morphologies, adjustable structures, and multi-functional porous compositions. The metal sulfide composites synthesized with uniform porous distribution and morphology have high electrochemical performance [39,43].

SeS_2 takes place in the chalcogenide group consisting of a chalcogen anion and an electropositive element. SeS_2 is a cathode material used in batteries because of its facile electron transportation, excellent conductivity, and high stability [39]. Moreover, selenium-based cathodic composites have an excellent volumetric energy density, and it shows a higher impact of electrochemical performance on electrode surface area. Recent reports have shown that the bimetallic organic framework composed of ZnS and CoS is widely used for photocatalytic hydrogen evolution [43].

As a subclass of MOFs, zeolite-like compounds are synthesized by metal ions and chelated clusters of organic ligands such as phosphonates and carboxylates. The zeolitic imidazolate frameworks (ZIFs) are based on the nets of aluminosilicate zeolites. ZIF-8 is referred to as a prototype for the imidazole-based MOFs used as the support. This prototype has excellent thermal and chemical stability and a high mass transfer rate and adsorption capacity [44]. For example, Sun et al. synthesized ZIF-67 consisting of Co-ion and imidazole ligand in methanol. ZIF-67 has a high specific surface area and microporosity. Moreover, cobalt ion chelating magnetic beads contribute to increasing the pores in the polymeric matrix. Therefore, the lower target concentration is sensitively detected with MIP based electrochemical sensor [43].

As most importantly, nanomaterials can be integrated with MOFs porosity within matrices. Nanomaterial is widely used for enhancing the conductivity of the electrode in electrochemical sensor platforms. Functionalized nanomaterials and nanoparticles doping play an important role in modifying the electrode surface. Carbon nanomaterials, magnetic (Fe_3O_4) [44], metallic nanoparticles (Au, Ag NPs) [45], and graphene quantum dots (GQDs) [46] are especially preferred for enhancing the electrochemical sensor performance.

Carbon nanomaterials have been widely used because of their morphological diversity, good chemical stability, large specific surface area, and biocompatibility [38]. Because of the superparamagnetic features of Fe_3O_4 nanoparticles, they are incorporated with MOF to facilitate the sensor construction process [44]. Metallic nanoparticles with good electrical conductivity and biocompatibility were embedded in the MOF surface to facilitate higher electron transfer, large surface-to-volume ratio, simple preparation, and long-term stability [47]. The graphene quantum dots doped with nitrogen atoms can be considered an ideal electron mediate because of its edge effects, unique quantum confinement, high conductivity, low toxicity, electrocatalytic activity, and biocompatibility [46].

4. Metal-organic frameworks based MIECs

Molecularly imprinted electrochemical sensors (MIECs) have gained great attention concerning the selectivity and better control of film thickness, but the limited sensitivity and stability remain challenges to be improved [2]. Therefore, various smart techniques and strategies of the interdisciplinary areas have emerged to cope with these problems by combining MIECs with different materials. MOFs exhibited excellent properties as a functional material within MIPs to improve the sensitivity and selectivity of MIECs, resulting in gained considerable attention in sensor applications as selective recognizing elements [48].

Despite the recognition capability for the targets, MIPs based sensors suffer from heterogeneous binding sites and poor sensitivity that limit the performance of MIPs in sensing applications. Therefore, nanomaterials are introduced to improve the sensitivity of MIPs, as well as the conductivity of the sensing surface. In terms of molecularly imprinted electrochemical sensors, enhancement of the sensitivity, selectivity, response time, stability, and reusability should be comprehensively considered to develop reliable and accurate electrochemical sensors. MOFs are ideal electrode materials, possess controllable and fascinating morphologies (nano, meso, and 2D MOFs), and modifiable surface properties that provide the development of the MIPs containing more homogeneously

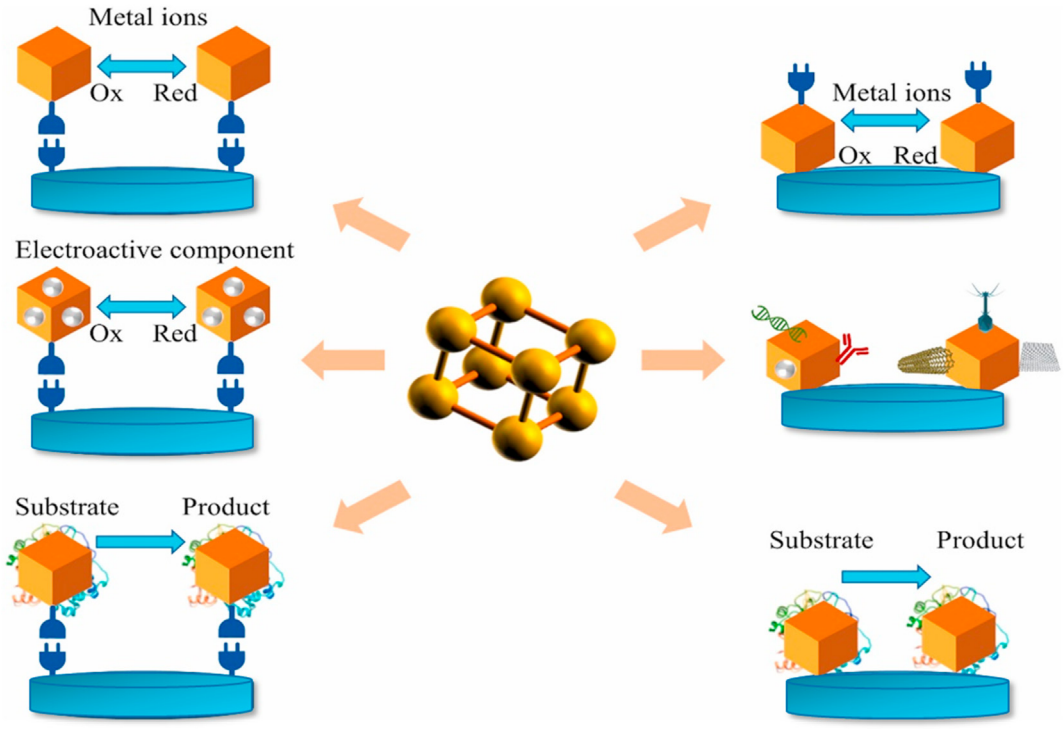


Fig. 2. MOFs-based strategies for designing electrochemical sensors. Reprinted from Ref. [41] with permission from Elsevier.

binding sites with high affinity for the target molecule. Furthermore, MOFs derived materials, and MOFs composites (metal nanoparticles, metal oxides, carbon materials, etc.) have been widely used for improving the performance of sensors with the desired stability and reproducibility. As will be seen below, the design of MOFs with desirable properties and integration with MIP demonstrated outstanding potential for electrochemical applications with further development.

4.1. Construction strategies of MOFs to improve the sensitivity of MIECs

The controllable morphologies and functionalization of pores of MOFs allow them to possess various specific structural motifs with higher apparent surface area and novel porous function. Furthermore, flexible and dynamic structures make MOFs effective coating materials to generate unique structural motifs for constructing high-dimensional frameworks in sensing applications [7]. Despite the highly selective structure of MIPs-based electrochemical sensors, they can suffer from some significant issues such as low sensitivity, heterogeneous binding sites, and template leakage [49]. To overcome these issues, several strategies are preferred. Integrating MOFs with MIPs-based electrochemical sensors is one of the important strategies. MOFs, with their unique properties and structure, enables improved catalytic activity and enhanced conductivity resulting in better sensitivity. The current strategies with rational design and controllable synthesis of MOFs for producing reliable electrochemical sensors are presented.

4.1.1. MOFs with metal nanoparticles

The sophisticated features of transition metal nanoparticles (TMNPs) such as high conductivity, good biocompatibility, and electrocatalytic activity make them potential materials for modifying MOFs in electrochemical applications. Inspired by the properties of nanoparticles, researchers have made an effort to improve the sensitivity of electrochemical sensors by using nanoparticles. For example, Xu et al. [50] incorporated Pt nanoparticles with Zr-based MOF, UiO-66, which was limited because of poor conductivity. Herein, highly ordered heterojunction Pt-doped MOFs and mesoporous molecularly imprinted polymers were successfully synthesized onto the homemade carbon paste microelectrode (CPME) (Fig. 3A) [50]. It seems that MOF-metal nanoparticles composites could overcome the main difficulties of MOFs and improve them to high stability and better electrical properties [51]. For example, Bagheri et al. have reported peroxides-like catalytic activity of MOF- based nanocomposites for sensitive fluorescence detection of patulin based on the Ag nanoparticle/flake-like Zn-based MOF nanomaterials (AgNPs@ZnMOF)MIP. They achieved a sensitive probe for patulin determination with a relative standard deviation (RSD%) values in the range of 0.83–1.95 in complex media without significant interfering effects (Fig. 3B) [51].

4.1.2. MOFs with carbon materials

Numerous types of carbon-based materials, such as mesoporous carbon (MC), graphene, carbon nanotubes, and CDs, have been used in conjunction with MIP for fabricating EC sensors [52]. These materials are highly ordered carbon structures with large surface area, have been used in the field of EC sensors to facilitate the electron transfer rate and improve conductivity. The reported work by Rawool et al. [53] is based on developing a dual template MIP sensor with composite Cu-MOF/MC material for the simultaneous determination of Rifampicin (RIF) and Isoniazid (INZ) (Fig. 4A) [53]. Composite Cu-MOF/MC was synthesized on the surface of MIP/GCE by electropolymerization of polypyrrole and successfully applied in pharmaceutical formulations, blood serum, and urine samples. The CNTs with MOFs (CNTs@MIL-53) have been used to modify an electrode for the determination of 17β-estradiol (E2) on MIP sensors by measuring differential pulse anodic stripping voltammetry. Under optimum conditions, the oxidation peak current displayed a calibration response for the lead over a 1.0–50 nM concentration

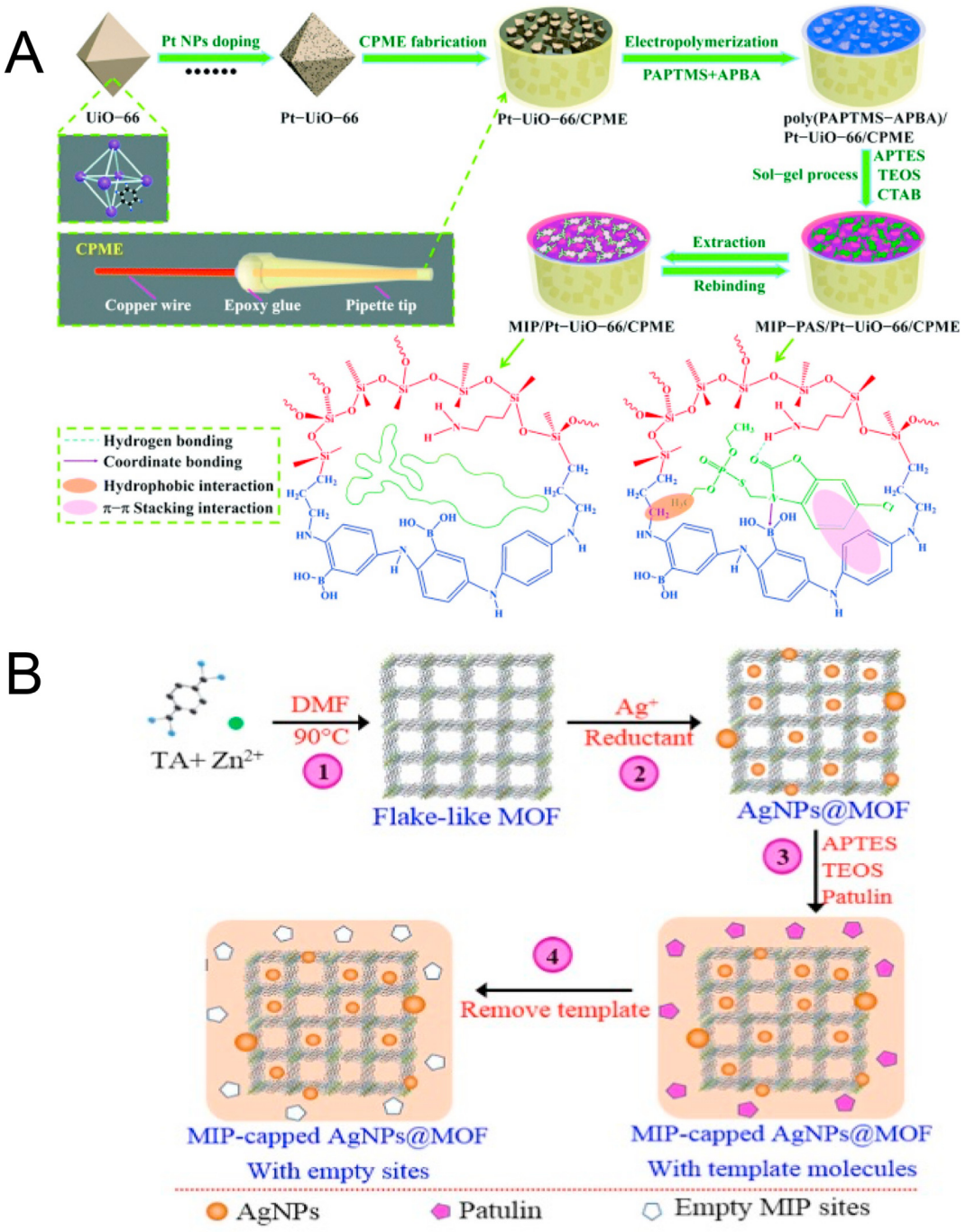


Fig. 3. Schematic presentation for the fabrication of MIP films on Pt-UiO-66/CPME (A); and MIP-capped AgNPs@ZnMOF (B). Reproduced from Ref. [50] with permission from the Royal Society of Chemistry. Reproduced from Ref. [51] with permission from Elsevier.

range with an excellent LOD of 0.79 nM. For example, Han et al. [54] developed cMWCNT/MOF-199 based MIECs on the GCE to detect 3-chloro-1,2-propanediol (3-MCPD). The electrochemical sensor was prepared by the electropolymerization of *o*-phenylenediamine (o-pD) that showed a high sensitivity for the 3-MCPD molecules in the range of 1.0×10^{-9} to 1.0×10^{-5} mol L^{-1} with a LOD of 4.3×10^{-10} mol L^{-1} (Fig. 4B) [54].

Furthermore, graphene oxide effectively can improve thermal and electrical conductivity performance due to the two-dimensional honeycomb lattice that allows fast electro-displacement of electroactive species in electrochemical sensors. El Jouhari et al. [55] developed ultrasensitive and highly selective MIP sensors and successfully applied them for simultaneous determination of rutin (Fig. 4C) [55]. The MIP was fabricated on the zeolitic imidazolate framework (ZIF-8) and reduced graphene oxide (rGO) by the electropolymerization of pyrrole.

4.1.3. MOFs with nanocomposites

With recent advances in nanoscience and nanotechnology, nanocomposite modified MOFs show great application in electrochemical sensing. For example, Hatamluyi et al. [56], are fabricated MIEC sensors based on 3D-framework UiO-66-NH_2 on the surface

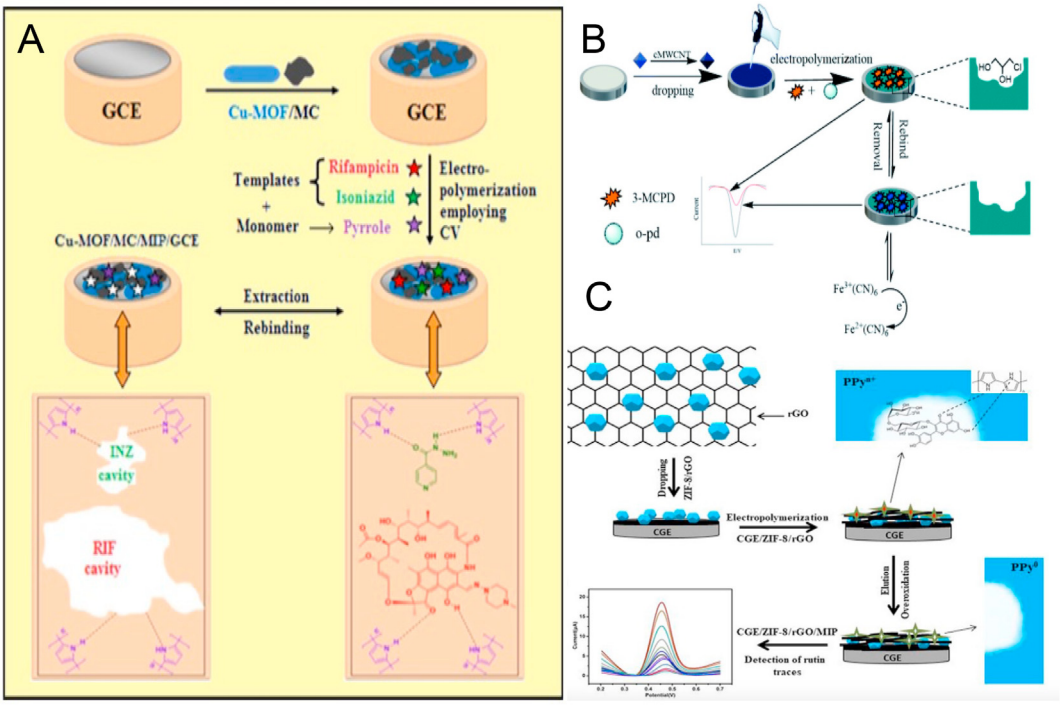


Fig. 4. Schematic presentation for the fabrication of Cu-MOF/MC/MIP/GCE based MIECs (A); MIP/cMWCNT/MOF-199/GCE based MIECs (B); and GCE/ZIF-8/rGO based MIECs (C). Reproduced from Refs. [53,55] with permission from Elsevier. Reproduced from Ref. [54] with permission from the Royal Society of Chemistry.

of a glassy carbon electrode by incorporation of hexagonal boron nitride nanosheets (HBNNS) with carbon-quantum dots (CQDs) (Fig. 5A) [45]. They combined the superior catalytic activity of HBNNS and CQDs with high selectivity properties of MIP for ultraselective detection of trace levels of an anticancer drug, Oxaliplatin (OXA). This study presented the great potential of MOFs for EC sensors that displayed two dynamic linear ranges from 1.0 to 20.0 nM and 20.0–250.0 nM with a detection limit of 0.37 nM, as well as showed highly selective detection of OXA in aqueous/real samples with extraordinary imprinting factor as 15.49. Furthermore, the nanocomposites of the CNTs, Prussian blue nanoparticles and MOFs (PB-MIL-53/CNTs) have been integrated to modify an electrode for the high selectivity of 17β-estradiol (E2) on MIP by electropolymerization of pyrrole (Fig. 5B) [57] The CNTs and PB play an important role in improving the conductivity of the sensor and accelerating the electron transmission due to the outstanding properties such as electrocatalytic and redox properties under optimum conditions, MIECS displayed a calibration response for EP over a concentration range 10^{-14} to 10^{-9} mol L^{-1} and an estimated with an excellent LOD of 6.19×10^{-15}.

4.2. Applications of MOF-based MIECs

As highlighted above, composite MOF structures with functional materials such as metal nanoparticles, carbon-based materials, and nanocomposites could effectively improve MOFs' conductivity and catalytic performance. The composite materials incorporating these materials with MOFs can display excellent advantages and improve selectivity to achieve sensitive detection/monitoring of multiple analytes. Moreover, the unique strategies of MOFs-based MIECs have been adapted to detect analytes from small molecules such as amino acids, pharmaceuticals, pesticide residue, etc., to larger molecules such as proteins, and so on [58]. In recent years, several exciting research articles have highlighted the combination of MOFs with MIECs to show their potential for diverse sensing applications in medical, pharmaceuticals, food, and environmental fields (Table 1).

The increased production and consumption of pharmaceuticals has led to their emergence as rapidly growing environmental pollutants even at very low ($ng.L^{-1}$-$\mu g.L^{-1}$) concentrations. Therefore, MOFs-based MIECs have been widely used for sensing active molecules and pharmaceuticals due to their selective recognition capability. Wang et al. [59] proposed to modify the electrode with C_3N_4 nanosheets and ZIF-8 (MOF) combined with MIP for the fast and ultrasensitive electrochemical sensing of furosemide, which has been employed as an effective medicine for chronic renal failure. The constructed electrochemical sensors exhibited selective determination of furosemide in the linear range of 0.08–100 μM with LOD of 8.0 nM. The developed sensor showed the satisfactory determination of the furosemide in tablet form with good recovery of 100.36%.

Enantiomeric recognition and chiral separation have also gained significant attention in drug analysis and bioanalysis. β-CD has been used in the field of chiral separation due to its truncated cone structure with a hydrophobic cavity. Therefore, the advantage of β-CD was combined with the metal-organic framework and molecular imprinting sensor for the first time in order to develop enantiomeric recognition of L-phenylalanine (L-Phe) [60]. The developed sensor showed good sensing performance and selectivity for L-Phe, with an enantioselectivity coefficient of 2.12 over D-Phe.

The integration of microporous MOFs in MIP materials has proven to be a highly sensitive and selective platform for TNT detection in different water samples, as shown by Guo et al. [61], where the use of f p-amino thiophenol (PATP) and PATP functionalized-AuNPs. The hybrid molecularly imprinting MMOFs was prepared in situ on the surface of PATP functionalized gold electrodes via electropolymerization by utilizing the unique properties of gold nanoparticles.

Toxins have a significant impact on feed and food, resulting in adverse health effects for humans. Therefore, the development of

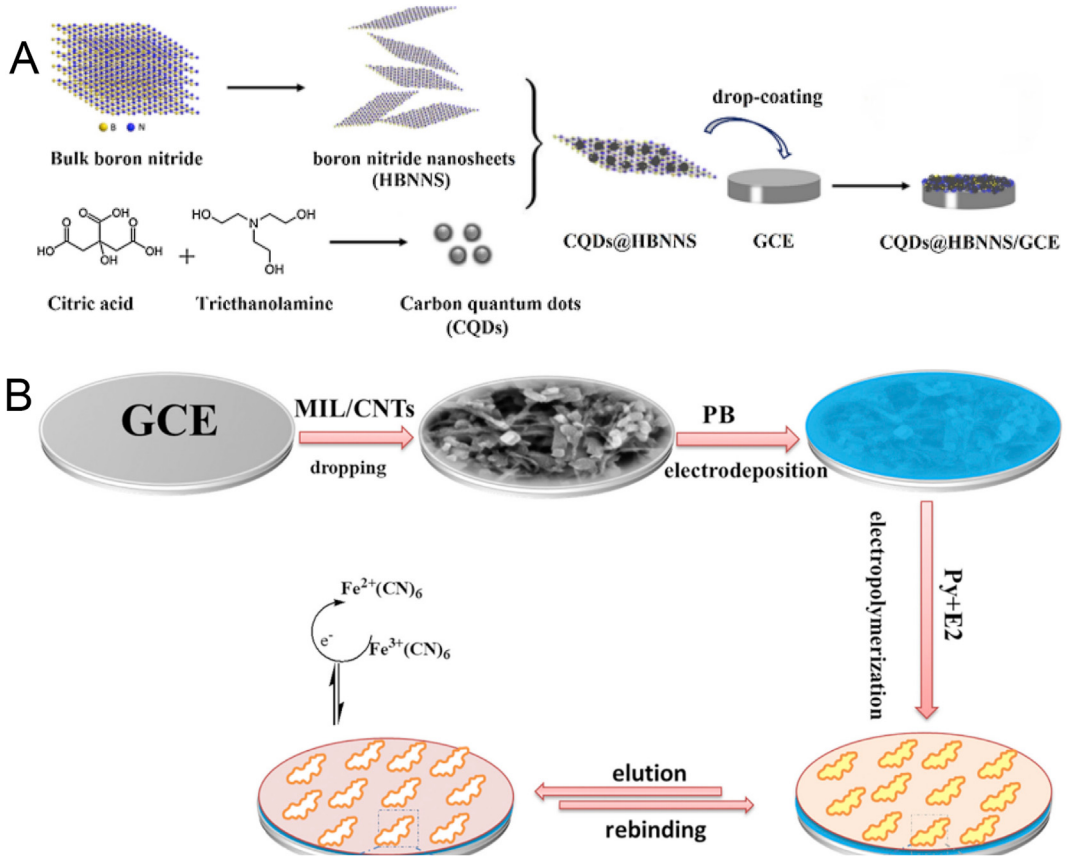


Fig. 5. Schematic presentation for the fabrication of CQDs@HBNNS/UiO-66-NH_2/MIP/GCE sensor (A); and MIP-PB-MIL-CNTs/GCE sensor (B). Reproduced from Refs. [45,57] with permission from Elsevier.

rapid and sensitive detection methods is essential to detect toxins in different matrices. For example, the incorporation of Ni-based MOFs in MIP materials have been proposed as sensing materials due to their excellent conductivity and recognition sites, as shown by Lei et al. [62], where three different Ni-based organic ligands of $Ni_3(HITP)_2$, $Ni_3(HHTP)_2$ and $Ni_3(HIB)_2$ were prepared with high conductivity and large effective surface area for the detection of bisphenol A (BSA) with excellent selectivity from 8.6 to 98.2% for analogs (PN, ET, 2-NP, 4-NP, HQ, and HBPA).

Jiang et al. [63] developed and synthesized MIP-MOF for the sensing and rapid detection of aflatoxin B1 (AFB1). In their study, p-amino thiophenol-functionalized gold nanoparticles were used as the ligand to synthesize MOFs in the presence of AFB1. It was noted that the first MIP-MOF electrochemical sensor was reported for the selective detection of aflatoxin B1 in food samples.

Furthermore, metal sulfides such as ZnS and CoS are applied in photocatalysis, biosensing, lithium batteries, and supercapacitors due to their low cost, high electrochemical stability, and high catalytic performance [43]. Duan et al. reported that MOF modified ZnS/CoS composite materials and MIPs was fabricated on GCE in the presence of chloroneb as template molecule by electropolymerization of pyrrole. This study is the first report using multimetal compound composite materials and MOFs-based MIPs for the detection of organochlorine pesticide chloroneb. The sensor was verified to determine the chloroneb in agricultural products and environmental samples with high accuracy.

MOFs-based MIECs have been proposed as a sensing platform to detect biomacromolecules due to their extremely large surface area and good biocompatibility. Bovine serum albumin (BSA) imprinted on 3D porous electrocatalytic framework materials was reported [64] where AuNPs supported amino-functionalized Ti-benzenedicarboxylate porous metal-organic frameworks (Au/NH2-MIL-125(Ti)) was prepared. Besides, this study showed a wide linear concentration range of $10-^{18}$ g mL^{-1} to 10^{-12} g mL^{-1} of BSA with an extremely low detection limit of 4.147×10^{-12} g mL^{-1}. While NH_2-MIL-125(Ti) was chosen to improve the catalytic activity and sensitivity of MIECS for detecting BSA, AuNPs were used to interact with functional monomers L-Cys via Au—S bonds which provide the electrostatic and hydrogen bonding between L-Cys and BSA molecules.

4.3. Performance of MOF-based MIECs coatings versus conventional MIECs

Despite having unique properties such as high selectivity for template molecules, the applications of MIECs are still subject to some limitations due to rigid and dense network, poor site accessibility, incomplete template removal, and reorganization resulting in low sensitivity in the sensor system. MIECs also suffer from the difficulties of imprinting biomacromolecules and removing the template molecule. Therefore, various strategies, including multifunctional monomers and porous MIPs, have been proposed to utilize these issues and improve the sensitivity of electrochemical sensors [65]. MOFs are received significant attention in the fabrication of electrochemical sensors due to their attractive properties such as a large surface area, exposed active sites, ultrahigh and tunable pores [48]. MOF@MIP-based electrochemical sensors (MOF@MIECs) are in their infancy; however, they offer better advantages over conventional electrochemical sensors. MOFs-based materials have been shown highly sensitive platforms to design

Table 1
Recent advances for electrochemical applications of MIP-based MOFs.

Analyte	Transducer	Method	LOD	Linearity Range	Application Samples	Recovery	Reference
Clenbuterol hydrochloride Ractopamine	N@Fe-MOF@C-DTMIP/GCE	CV	0.303 pM	8 nM-1 pM	Human urine	97.4–101.2	[67]
Melamine	MIP-MIL-53(Fe)/GCE	DPV	8.21 pM	1 μM-10 pM	Milk	93.4–103.4	[65]
Squamous cell carcinoma antigen	Fe (III)-MIL-88B $-NH_2$@ZnSeQDs/Ab/GCE	CV	31 fg mL^{-1}	0.0001–100 ng mL^{-1}	Human serum	96.0–104.0	[68]
Cysteine enantiomers	MIP-PB-*PC*-CNTs/GCE	DPV	6.0 fM	0.1 μM-0.1 pM	Human serum	96.0–104.1	[69]
Tyrosine	MIP/pTH/AuNPs@ZIF-67/GCE	DPV	0.79 nM	4 μM-10 nM	Human serum	95.8–118.0	[70]
Imidacloprid	UMV-Ce-MOF/MIPs/GCE	DPV/EIS	0.34 nM	2–120 nM	Apples Bananas Tomatoes	90.0–102.3 9 6.0–107.2 88.5–114.3	[71]
Buprenorphine	Zn/La^{3+}/MOF/MIP/GCE	DPV	1.08 ng mL^{-1}	4–50 ng mL^{-1}	Human blood	99.1–100.2	[47]
Ciprofloxacin	Co-MOF/MIP/GCE	DPV	17 nM	0.15 mM-0.5 μM	Pills	99.05–102.0	[72]
Diclofenac	Zr-MOF/MIP/GCE	DPV	0.043 μM	1.5 mM-6.5 μM	Tablet	101.3–102.2	[73]
Flutamide	ZnO–Co_3O_4@C_3N_4 NC	DPV	0.00373 μM	0.01–98.6 μM	Human urine Human serum	98.9–99.0 98.3–99.5	[74]
Dioctyl phthalate	MIP/$Cu_3(BTC)_2$@Cu_2O/ITO	EIS	9.15 pM	25 pM-0.1 μM	Bottled water	95.7–101.3	[75]
Gallic acid	MIP/Fe_3O_4@ZIF-67/AuE	DPV	0.297 pM	0.6 nM-6 pM	Water	89.5–118.4	[76]
Nitrofurazone	BC/Cr_2O_3/Cr-MIL-101 AgNPs/MIP/GCE	DPV	0.003 μM	0.005–10 μM	Human urine Human blood	98.2–102.84 98.86–103.04	[38]
Patulin mycotoxin	MIP/Au@PANI/SeS_2@Co MOF/SPE	DPV	0.66 pM	0.001–100 nM	Apple juice	94.5–106.4	[39]
Norfloxacin	MIP/CoFe-MOFs/AuNPs/GCE	DPV	0.131 pM	6 nM-5 pM	Milk	97.04–110.2	[45]
Patulin	MIP/Au@Cu-MOF/N-GQDs/GCE	DPV	0.0007 ng mL^{-1}	0.01–70 ng mL^{-1}	Apple juice	97.6–99.4	[46]
Hemoglobin	Ag- MOF@MC-MIP/AuE	DPV	0.09 pM	1 μM-0.2 pM	Human blood	95.65–104.2	[77]
Histamine	MIP-Au@Fe-BDC/N, S-GQDs/GCE	DPV	0.026 nM	0.078–250 nM	Human serum Canned tuna fish	96.8–102.0 95.9–103.0	[78]
2,4- Dichlorophenol	Cu–BTC/ErGO/GCE	DPV	0.083 μM	1.5–24 μM	Lake water	97.17–104.15	[79]
Nitrobenzene	JUC-62@pOMC/GCE	DPV	18 μM	0.05–420 μM	Tap water Lake water	96.60–101.54 102.40 –103.57	[80]

surfaces in the construction of electrochemical sensors to solve imprinting problems. The highly porous and extended 3D structure of MOFs@MIP materials provided an ideal platform for MIECs, which could be used to promote protein imprinting and facilitate the template removal from the polymeric network [64]. Therefore, integrating MOFs with MIPs is currently receiving the most interest in designing rapid, sensitive, and effective MIECs. Moreover, owing to MOFs feasibility of external surface modifications, it is allowed by introducing nanomaterials such as nanoparticles, carbon-based materials, and nanocomposites having high conductivity which offer great advantages to improve the stability and performance followed by increasing the sensitivity of sensors [66].

5. Conclusion and future prospects

As mentioned above, electrochemical MIP sensing is intensively used to determine amino acids, proteins, pesticides, biomarkers, pharmaceuticals, and so on. The MIP technology has advantages besides its disadvantages. To overcome the disadvantages of the MIP technique, successful correlations might be established with the MOF. These properties belonging MOF, such as large active area, excellent porosity, controllable pore size and uniform structure, and functionalization, contribute to enhancing the MOFs-based MIECs performance. Furthermore, the integration of Ni-, Co-, Fe-, Zn-, and Cu-metal ions within MOFs are applied due to their robust porosity, resistance to thermal changes, and chemical stability. At the same time, the effects of nanomaterials on MOFs-based MIECs cannot be ignored. Nanomaterials consisting of nanocomposites, carbon nanomaterials, and metal nanoparticles integrated with MOFs-based MIECs show highly sensitive, stable, high conductivity, and rapid platforms. As seen in Table 1, the researchers have been widely utilized the DPV technique while using MOFs-based MIECs. It is an electrochemical method with high sensitivity to detect at pM-fM levels. In conclusion, the literature survey compiled in this review figured out the intriguing potential of MOFs-based MIECs due to fact that MOFs could be classified as promising ingredients to overcome the challenges of MIPs as well as opening new application field to develop the efficient coating materials for selective, specific, robust, cost-, and user-friendly determination of analyte molecules.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] J. Pan, W. Chen, Y. Ma, G. Pan, Molecularly imprinted polymers as receptor mimics for selective cell recognition, Chem. Soc. Rev. 47 (2018) 5574–5587. https://doi.org/10.1039/c7cs00854f.

[2] L. Uzun, A.P.F. Turner, Molecularly-imprinted polymer sensors: realising their potential, Biosens. Bioelectron. 76 (2016) 131–144. https://doi.org/10.1016/j.bios.2015.07.013.

[3] K. Graniczkowska, M. Pütz, F.M. Hauser, S. De Saeger, N.V. Beloglazova, Capacitive sensing of N-formylamphetamine based on immobilized molecular imprinted polymers, Biosens. Bioelectron. 92 (2017) 741–747. https://doi.org/10.1016/j.bios.2016.09.083.

[4] A. Maziz, E. Özgür, C. Bergaud, L. Uzun, Progress in conducting polymers for biointerfacing and biorecognition applications, Sensors and Actuators Reports 3 (2021) 100035. https://doi.org/10.1016/j.snr.2021.100035.

[5] Y. Xue, S. Zheng, H. Xue, H. Pang, Metal-organic framework composites and their electrochemical applications, J. Mater. Chem. A. 7 (2019) 7301–7327. https://doi.org/10.1039/C8TA12178H.

[6] Y. Zhao, D. Li, Lanthanide-functionalized metal-organic frameworks as ratiometric luminescent sensors, J. Mater. Chem. C. 8 (2020) 12739–12754. https://doi.org/10.1039/d0tc03430d.

[7] P. Kumar, A. Deep, K.H. Kim, Metal organic frameworks for sensing applications, TrAC Trends Anal. Chem. 73 (2015) 39–53. https://doi.org/10.1016/j.trac.2015.04.009.

[8] Q. Du, P. Wu, F. Hu, G. Li, J. Shi, H. He, Novel molecularly imprinted polymers on metal-organic frameworks as sensors for the highly selective detection of zearalenone in wheat, New J. Chem. 43 (2019) 7044–7050. https://doi.org/10.1039/c9nj00589g.

[9] X. Jiang, Z. Chengjun, C. Zhong, J. Li, The electrochemical sensors based on MOF and their applications, Prog. Chem. 29 (2017) 1206–1214. https://doi.org/10.7536/PC170619.

[10] Z. Wang, M. Gui, M. Asif, Y. Yu, S. Dong, H. Wang, W. Wang, F. Wang, F. Xiao, H. Liu, A facile modular approach to the 2D oriented assembly MOF electrode for non-enzymatic sweat biosensors, Nanoscale 10 (2018) 6629–6638. https://doi.org/10.1039/c8nr00798e.

[11] F. Amiripour, S. Ghasemi, S.N. Azizi, Design of turn-on luminescent sensor based on nanostructured molecularly imprinted polymer-coated zirconium metal–organic framework for selective detection of chloramphenicol residues in milk and honey, Food Chem. 347 (2021) 129034. https://doi.org/10.1016/j.foodchem.2021.129034.

[12] B. Yang, C. Fu, J. Li, G. Xu, Frontiers in highly sensitive molecularly imprinted electrochemical sensors: challenges and strategies, TrAC Trends Anal. Chem. 105 (2018) 52–67. https://doi.org/10.1016/j.trac.2018.04.011.

[13] S. Bhogal, K. Kaur, A.K. Malik, C. Sonne, S.S. Lee, K.H. Kim, Core-shell structured molecularly imprinted materials for sensing applications, TrAC Trends Anal. Chem. 133 (2020) 116043. https://doi.org/10.1016/j.trac.2020.116043.

[14] P.L. Wang, L.H. Xie, E.A. Joseph, J.R. Li, X.O. Su, H.C. Zhou, Metal-organic frameworks for food safety, Chem. Rev. 119 (2019) 10638–10690. https://doi.org/10.1021/ACS.CHEMREV.9B00257/SUPPL_FILE/CR9B00257_SI_001.PDF.

[15] Ü. Anik, S. Timur, Z. Dursun, Metal organic frameworks in electrochemical and optical sensing platforms: a review, Microchim. Acta 186 (2019) 18–24. https://doi.org/10.1007/s00604-019-3321-0.

[16] L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp, Metal–organic framework materials as chemical sensors, Chem. Rev. 112 (2011) 1105–1125. https://doi.org/10.1021/CR200324T.

[17] C. Sen Liu, J. Li, H. Pang, Metal-organic framework-based materials as an emerging platform for advanced electrochemical sensing, Coord. Chem. Rev. 410 (2020) 213222. https://doi.org/10.1016/j.ccr.2020.213222.

[18] I. Stassen, N. Burtch, A. Talin, P. Falcaro, M. Allendorf, R. Ameloot, An updated roadmap for the integration of metal-organic frameworks with electronic devices and chemical sensors, Chem. Soc. Rev. 46 (2017) 3185–3241. https://doi.org/10.1039/c7cs00122c.

[19] C. Alexander, H.S. Andersson, L.I. Andersson, R.J. Ansell, N. Kirsch, I.A. Nicholls, J. O'Mahony, M.J. Whitcombe, Molecular imprinting science and technology: a survey of the literature for the years up to and including 2003, J. Mol. Recogn. 19 (2006) 106–180. https://doi.org/10.1002/jmr.760.

[20] L. Pauling, A theory of the formation of antibodies, J. Am. Chem. Soc. 372 (1940) 2643–2657. https://pubs.acs.org/sharingguidelines.

[21] D.R. Kryscio, N.A. Peppas, Critical review and perspective of macromolecularly imprinted polymers, Acta Biomater. 8 (2012) 461–473. https://doi.org/10.1016/j.actbio.2011.11.005.

[22] S. Ramanavicius, A. Jagminas, A. Ramanavicius, Advances in molecularly imprinted polymers based affinity sensors (review), Polymers (Basel) 13 (2021). https://doi.org/10.3390/polym13060974.

[23] A.M. Mostafa, S.J. Barton, S.P. Wren, J. Barker, Review on molecularly imprinted polymers with a focus on their application to the analysis of protein biomarkers, TrAC Trends Anal. Chem. 144 (2021) 116431. https://doi.org/10.1016/j.trac.2021.116431.

[24] B. Sellergren, M. Lepistö, K. Mosbach, Highly enantioselective and substrate-selective polymers obtained by molecular imprinting utilizing noncovalent interactions. NMR and chromatographic studies on the nature of recognition, J. Am. Chem. Soc. 110 (1988) 5853–5860. https://doi.org/10.1021/ja00225a041.

[25] M. Gao, Y. Gao, G. Chen, X. Huang, X. Xu, J. Lv, J. Wang, D. Xu, G. Liu, Recent advances and future trends in the detection of contaminants by molecularly imprinted polymers in food samples, Front. Chem. 8 (2020) 1–20. https://doi.org/10.3389/fchem.2020.616326.

[26] G. Wulff, Enzyme-like catalysis by molecularly imprinted polymers, Chem. Rev. 102 (2002) 1–27. https://doi.org/10.1021/cr980039a.

[27] J. Ashley, M.A. Shahbazi, K. Kant, V.A. Chidambara, A. Wolff, D.D. Bang, Y. Sun, Molecularly imprinted polymers for sample preparation and biosensing in food analysis: progress and perspectives, Biosens. Bioelectron. 91 (2017) 606–615. https://doi.org/10.1016/j.bios.2017.01.018.

[28] S. Ansari, Combination of molecularly imprinted polymers and carbon nanomaterials as a versatile biosensing tool in sample analysis: recent applications and challenges, TrAC Trends Anal. Chem. (Reference Ed.) 93 (2017) 134–151. https://doi.org/10.1016/j.trac.2017.05.015.

[29] A.E. Rachkov, S.H. Cheong, A.V. El'skaya, K. Yano, I. Karube, Molecularly imprinted polymers as artificial steroid receptors, Polym. Adv. Technol. 9 (1998) 511–519. https://doi.org/10.1002/(SICI)1099-1581(199808)9:8<511::AID-PAT790>3.0.CO;2-H.

[30] E. Yilmaz, K. Mosbach, K. Haupt, Influence of functional and cross-linking monomers and the amount of template on the performance of molecularly imprinted polymers in binding assays, Anal. Commun. 36 (1999) 167–170. https://doi.org/10.1039/a901339c.

[31] D.J. O'Shannessy, B. Ekberg, K. Mosbach, Molecular imprinting of amino acid derivatives at low temperature (0°C) using photolytic homolysis of azobisnitriles, Anal. Biochem. 177 (1989) 144–149. https://doi.org/10.1016/0003-2697(89)90029-8.

[32] A.H. Johnstone, CRC handbook of Chemistry and physics, in: Chief R.C. Weast (Editor), 69th Edition, CRC Press, Boca Raton, Florida, 1988, p. 2400. https://doi.org/10.1002/jctb.280500215. price £57.50. ISBN 0-8493-0369-5, J. Chem. Technol. Biotechnol. 50 (2007) 294–295.

[33] H. Manjunatha, S. Janardan, A. Ratnamala, K.V. Ratnam, L.V. Rao, S. Ramesh, K.C.B. Naidu, N.S. Kumar, A. Khan, A.M. Asiri, Electrochemical Aspects of Metal-Organic Frameworks, INC, 2021. https://doi.org/10.1016/b978-0-12-822099-3.00004-6.

[34] Z. Pinar Gumus, M. Soylak, Metal organic frameworks as nanomaterials for analysis of toxic metals in food and environmental applications, TrAC Trends Anal. Chem. 143 (2021) 116417. https://doi.org/10.1016/j.trac.2021.116417.

[35] W. Cheng, X. Tang, Y. Zhang, D. Wu, W. Yang, Applications of metal-organic framework (MOF)-based sensors for food safety: enhancing mechanisms and recent advances, Trends Food Sci. Technol. 112 (2021) 268–282. https://doi.org/10.1016/j.tifs.2021.04.004.

[36] B. Hassan Pour, N. Haghnazari, F. Keshavarzi, E. Ahmadi, B. Rahimian Zarif, High sensitive electrochemical sensor for imatinib based on metal-organic frameworks and multiwall carbon nanotubes nanocomposite, Microchem. J. 165 (2021) 106147. https://doi.org/10.1016/j.microc.2021.106147.

[37] X. Shi, Y. Shan, M. Du, H. Pang, Synthesis and application of metal-organic framework films, Coord. Chem. Rev. 444 (2021) 214060. https://doi.org/10.1016/j.ccr.2021.214060.

[38] J. Cheng, Y. Li, J. Zhong, Z. Lu, G. Wang, M. Sun, Y. Jiang, P. Zou, X. Wang, Q. Zhao, Y. Wang, H. Rao, Molecularly imprinted electrochemical sensor based on biomass carbon decorated with MOF-derived Cr2O3 and silver nanoparticles for selective and sensitive detection of nitrofurazone, Chem. Eng. J. 398 (2020) 125664. https://doi.org/10.1016/j.cej.2020.125664.

[39] S.P. Selvam, A.N. Kadam, K.R. Maiyelvaganan, M. Prakash, S. Cho, Novel SeS2-loaded Co MOF with Au@PANI comprised electroanalytical molecularly imprinted polymer-based disposable sensor for patulin mycotoxin, Biosens. Bioelectron. 187 (2021) 113302. https://doi.org/10.1016/j.bios.2021.113302.

[40] S. Ramanavicius, A. Ramanavicius, Progress and insights in the application of mxenes as new 2d nano-materials suitable for biosensors and biofuel cell design, Int. J. Mol. Sci. 21 (2020) 1–17. https://doi.org/10.3390/ijms21239224.

[41] Z. Yang, W. Zhang, Y. Yin, W. Fang, H. Xue, Metal-organic framework-based sensors for the detection of toxins and foodborne pathogens, Food Control 133 (2021) 108684. https://doi.org/10.1016/j.foodcont.2021.108684.

[42] Y. Yang, W. Yan, X. Wang, L. Yu, J. Zhang, B. Bai, C. Guo, S. Fan, Development of a molecularly imprinted photoelectrochemical sensing platform based on NH2-MIL-125(Ti)–TiO2 composite for the sensitive and selective determination of oxtetracycline, Biosens. Bioelectron. 177 (2021) 113000. https://doi.org/10.1016/j.bios.2021.113000.

[43] D. Duan, J. Ye, X. Cai, K. Li, Cobalt(II)-ion-exchanged Zn-bio-MOF-1 derived CoS/ZnS composites modified electrochemical sensor for chloroneb detection by differential pulse voltammetry, Microchim. Acta 188 (2021) 1–10. https://doi.org/10.1007/s00604-021-04759-4.

[44] P. Tang, Y. Wang, F. He, Electrochemical sensor based on super-magnetic metal–organic framework@molecularly imprinted polymer for Sarcosine detection in urine, J. Saudi Chem. Soc. 24 (2020) 620–630. https://doi.org/10.1016/j.jscs.2020.06.004.

[45] C. Ye, X. Chen, D. Zhang, J. Xu, H. Xi, T. Wu, D. Deng, C. Xiong, J. Zhang, G. Huang, Study on the properties and reaction mechanism of polypyrrole@norfloxacin molecularly imprinted electrochemical sensor based on three-dimensional CoFe-MOFs/AuNPs, Electrochim. Acta 379 (2021) 138174. https://doi.org/10.1016/j.electacta.2021.138174.

[46] B. Hatamluyi, M. Rezayi, H.R. Beheshti, M.T. Boroushaki, Ultra-sensitive molecularly imprinted electrochemical sensor for patulin detection based on a novel assembling strategy using Au@Cu-MOF/N-GQDs, Sensor. Actuator. B Chem. 318 (2020) 128219. https://doi.org/10.1016/j.snb.2020.128219.

[47] M. Yahyapour, M. Ranjbar, A. Mohadesi, M. Rejaeinegad, Determination of buprenorphine (BUP) with molecularly imprinted polymer Zn/La3+ metal organic framework on modified glassy carbon electrode (GCE), Electroanalysis (2021) 1–10. https://doi.org/10.1002/elan.202100266.

[48] Z. Guo, A. Florea, M. Jiang, Y. Mei, W. Zhang, A. Zhang, R. Săndulescu, N. Jaffrezic-Renault, Molecularly imprinted polymer/metal organic framework

based chemical sensors, Coatings 6 (2016) 42. https://doi.org/10.3390/coatings6040042.
[49] S. Bhakta, P. Mishra, Molecularly imprinted polymer-based sensors for cancer biomarker detection, Sensors and Actuators Reports 3 (2021) 100061. https://doi.org/10.1016/j.snr.2021.100061.
[50] L. Xu, J. Li, J. Zhang, J. Sun, T. Gan, Y. Liu, A disposable molecularly imprinted electrochemical sensor for the ultra-trace detection of the organophosphorus insecticide phosalone employing monodisperse Pt-doped UiO-66 for signal amplification, Analyst 145 (2020) 3245–3256. https://doi.org/10.1039/d0an00278j.
[51] N. Bagheri, A. Khataee, B. Habibi, J. Hassanzadeh, Mimetic Ag nanoparticle/Zn-based MOF nanocomposite (AgNPs@ZnMOF) capped with molecularly imprinted polymer for the selective detection of patulin, Talanta 179 (2018) 710–718. https://doi.org/10.1016/j.talanta.2017.12.009.
[52] W. Liu, X.B. Yin, Metal-organic frameworks for electrochemical applications, TrAC Trends Anal. Chem. 75 (2016) 86–96. https://doi.org/10.1016/j.trac.2015.07.011.
[53] C.R. Rawool, A.K. Srivastava, A dual template imprinted polymer modified electrochemical sensor based on Cu metal organic framework/mesoporous carbon for highly sensitive and selective recognition of rifampicin and isoniazid, Sensor. Actuator. B Chem. 288 (2019) 493–506. https://doi.org/10.1016/j.snb.2019.03.032.
[54] S. Han, Y. Ding, F. Teng, A. Yao, Q. Leng, Determination of chloropropanol with an imprinted electrochemical sensor based on multi-walled carbon nanotubes/metal-organic framework composites, RSC Adv. 11 (2021) 18468–18475. https://doi.org/10.1039/d1ra02731j.
[55] A. El Jaouhari, L. Yan, J. Zhu, D. Zhao, M. Zaved Hossain Khan, X. Liu, Enhanced molecular imprinted electrochemical sensor based on zeolitic imidazolate framework/reduced graphene oxide for highly recognition of rutin, Anal. Chim. Acta 1106 (2020) 103–114. https://doi.org/10.1016/j.aca.2020.01.039.
[56] B. Hatamluyi, A. Hashemzadeh, M. Darroudi, A novel molecularly imprinted polymer decorated by CQDs@HBNNS nanocomposite and UiO-66-NH2 for ultra-selective electrochemical sensing of Oxaliplatin in biological samples, Sensor. Actuator. B Chem. 307 (2020) 127614. https://doi.org/10.1016/j.snb.2019.127614.
[57] D. Duan, X. Si, Y. Ding, L. Li, G. Ma, L. Zhang, B. Jian, A novel molecularly imprinted electrochemical sensor based on double sensitization by MOF/CNTs and Prussian blue for detection of 17β-estradiol, Bioelectrochemistry 129 (2019) 211–217. https://doi.org/10.1016/j.bioelechem.2019.04.014.
[58] J. Lei, R. Qian, P. Ling, L. Cui, H. Ju, Design and sensing applications of metal-organic framework composites, TrAC Trends Anal. Chem. 58 (2014) 71–78. https://doi.org/10.1016/j.trac.2014.02.012.
[59] Y. Wang, J. Cheng, X. Liu, F. Ding, P. Zou, X. Wang, Q. Zhao, H. Rao, C3N4 nanosheets/metal-organic framework wrapped with molecularly imprinted polymer sensor: fabrication, characterization, and electrochemical detection of furosemide, ACS Sustain. Chem. Eng. 6 (2018) 16847–16858. https://doi.org/10.1021/acssuschemeng.8b04179.
[60] T. Wu, X. Wei, X. Ma, J. Li, Amperometric sensing of L-phenylalanine using a gold electrode modified with a metal organic framework, a molecularly imprinted polymer, and β-cyclodextrin-functionalized gold nanoparticles, Microchim. Acta 184 (2017) 2901–2907. https://doi.org/10.1007/s00604-017-2281-5.
[61] Z.Z. Guo, A. Florea, C. Cristea, F. Bessueille, F. Vocanson, F. Goutaland, A.D. Zhang, R. Săndulescu, F. Lagarde, N. Jaffrezic-Renault, 1,3,5-Trinitrotoluene detection by a molecularly imprinted polymer sensor based on electropolymerization of a microporous-metal-organic framework, Sensor. Actuator. B Chem. 207 (2015) 960–966. https://doi.org/10.1016/j.snb.2014.06.137.
[62] X. Lei, Z. Deng, Y. Zeng, S. Huang, Y. Yang, H. Wang, L. Guo, L. Li, A novel composite of conductive metal organic framework and molecularly imprinted poly (ionic liquid) for highly sensitive electrochemical detection of bisphenol A, Sensor. Actuator. B Chem. 339 (2021) 129885. https://doi.org/10.1016/j.snb.2021.129885.
[63] M. Jiang, M. Braiek, A. Florea, A. Chrouda, C. Farre, A. Bonhomme, F. Bessueille, F. Vocanson, A. Zhang, N. Jaffrezic-Renault, Aflatoxin B1 detection using a highly-sensitive molecularly-imprinted electrochemical sensor based on an electropolymerized metal organic framework, Toxins 7 (2015) 3540–3553. https://doi.org/10.3390/toxins7093540.
[64] D. Duan, H. Yang, Y. Ding, D. Ye, L. Li, G. Ma, Three-dimensional molecularly imprinted electrochemical sensor based on Au NPs@Ti-based metal-organic frameworks for ultra-trace detection of bovine serum albumin, Electrochim. Acta 261 (2018) 160–166. https://doi.org/10.1016/j.electacta.2017.12.146.
[65] J. An, L. Li, Y. Ding, W. Hu, D. Duan, H. Lu, D. Ye, X. Zhu, H. Chen, A novel molecularly imprinted electrochemical sensor based on Prussian blue analogue generated by iron metal organic frameworks for highly sensitive detection of melamine, Electrochim. Acta 326 (2019). https://doi.org/10.1016/j.electacta.2019.134946.
[66] B. Li, T. Suo, S. Xie, A. Xia, Y. jie Ma, H. Huang, X. Zhang, Q. Hu, Rational design, synthesis, and applications of carbon dots@metal–organic frameworks (CD@MOF) based sensors, TrAC Trends Anal. Chem. 135 (2021) 116163. https://doi.org/10.1016/j.trac.2020.116163.
[67] X. Li, Y. Li, P. Yu, Y. Tong, B.C. Ye, A high sensitivity electrochemical sensor based on a dual-template molecularly imprinted polymer for simultaneous determination of clenbuterol hydrochloride and ractopamine, Analyst 146 (2021) 6323–6332. https://doi.org/10.1039/d1an01413g.
[68] G. Mo, D. Qin, X. Jiang, X. Zheng, W. Mo, B. Deng, A sensitive electrochemiluminescence biosensor based on metal-organic framework and imprinted polymer for squamous cell carcinoma antigen detection, Sensor. Actuator. B Chem. 310 (2020) 127852. https://doi.org/10.1016/j.snb.2020.127852.
[69] D. Duan, H. Yang, Y. Ding, L. Li, G. Ma, A three-dimensional conductive molecularly imprinted electrochemical sensor based on MOF derived porous carbon/carbon nanotubes composites and prussian blue nanocubes mediated amplification for chiral analysis of cysteine enantiomers, Electrochim. Acta 302 (2019) 137–144. https://doi.org/10.1016/j.electacta.2019.02.028.
[70] B. Chen, Y. Zhang, L. Lin, H. Chen, M. Zhao, Au nanoparticles @metal organic framework/polythionine loaded with molecularly imprinted polymer sensor: preparation, characterization, and electrochemical detection of tyrosine, J. Electroanal. Chem. 863 (2020) 114052. https://doi.org/10.1016/j.jelechem.2020.114052.
[71] X. Ma, C. Pang, S. Li, J. Li, M. Wang, Y. Xiong, L. Su, J. Luo, Z. Xu, L. Lin, Biomimetic synthesis of ultrafine mixed-valence metal-organic framework nanowires and their application in electrochemiluminescence sensing, ACS Appl. Mater. Interfaces 13 (2021) 41987–41996. https://doi.org/10.1021/acsami.1c10074.
[72] M. Yahyapour, M. Ranjbar, A. Mohadesi, Determination of ciprofloxacin drug with molecularly imprinted polymer/co- metal organic framework nanofiber on modified glassy carbon electrode (GCE), J. Mater. Sci. Mater. Electron. 32 (2021) 3180–3190. https://doi.org/10.1007/s10854-020-05066-z.
[73] M. Malekzadeh, A. Mohadesi, M.A. Karimi, M. Ranjbar, Development of a new electrochemical sensor based on Zr-MOF/MIP for sensitive diclofenac determination, Anal. Bioanal. Electrochem. 12 (2020) 402–414.
[74] N.M. Umesh, J. Antolin Jesila, S.F. Wang, M. Govindasamy, R.A. Alshgari, M. Ouladsmane, I.V. Asharani, Fabrication of highly sensitive anticancer drug sensor based on heterostructured ZnO-Co3O4 capped on carbon nitride nanomaterials, Microchem. J. 167 (2021) 106244. https://doi.org/10.1016/j.microc.2021.106244.
[75] P.W. Gao, Y.Z. Shen, C. Ma, Q. Xu, X.Y. Hu, High-sensitivity photoelectrochemical heterostructure of the cuprous oxide-metal organic framework for a dioctyl phthalate molecularly imprinted sensor, Analyst 146 (2021) 6178–6186. https://doi.org/10.1039/d1an01348c.
[76] C. Ye, X. Chen, J. Xu, H. Xi, T. Wu, D. Deng, J. Zhang, G. Huang, Highly sensitive detection to gallic acid by polypyrrole-based MIES supported by MOFs-Co2+@Fe3O4, J. Electroanal. Chem. 859 (2020) 113839. https://doi.org/10.1016/j.jelechem.2020.113839.
[77] S. Mandani, B. Rezaei, A.A. Ensafi, P. Rezaei, Ultrasensitive electrochemical molecularly imprinted sensor based on AuE/Ag-MOF@MC for determination of hemoglobin using response surface methodology, Anal. Bioanal. Chem. 413 (2021) 4895–4906. https://doi.org/10.1007/s00216-021-03453-x.
[78] M.H. Mahnashi, A.M. Mahmoud, K. Alhazzani, A. AZ, M.M. Algahtani, A.M. Alaseem, Y.S.A. Alqahtani, M.M. El-Wekil, Enhanced molecular imprinted electrochemical sensing of histamine based on signal reporting nanohybrid, Microchem. J. 168 (2021) 106439. https://doi.org/10.1016/j.microc.2021.106439.
[79] M.B. Nguyen, V.T. Hong Nhung, V.T. Thu, D.T. Ngoc Nga, T.N. Pham Truong, H.T. Giang, P.T. Hai Yen, P.H. Phong, T.A. Vu, V.T. Thu Ha, An electrochemical sensor based on copper-based metal-organic framework-reduced graphene oxide composites for determination of 2,4-dichlorophenol in water, RSC Adv. 10 (2020) 42212–42220. https://doi.org/10.1039/d0ra06700h.
[80] C. Liu, X. Bo, L. Guo, A novel electrochemical sensing platform of JUC-62 metal-organic framework/platelet ordered mesoporous carbon for high selective detection of nitro-aromatic compounds, Sensor. Actuator. B Chem. 297 (2019) 126741. https://doi.org/10.1016/j.snb.2019.126741.