

# MOFs and their derivatives: Functionalization strategy and applications as sensitive electrode materials for environmental EDCs analysis

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## ABSTRACT

Endocrine-disrupting chemicals (EDCs) are a category of exogenous organic pollutants that pose substantial hazards to human health and the environment due to their ability to disrupt the functioning of the endocrine system. However, implementing suitable technology is one of the most effective ways to address EDCs. Electrochemical sensors provide cost-effective and fast solutions to this challenge, using metal-organic framework (MOF) technology. MOFs, as a distinct hierarchical structural class, offer diverse topologies, tunability, reactivity and porosity, but their lower conductivity and instability limit their effectiveness in electrochemical sensor applications. The study focuses on investigating the functionalization strategy of the outer and inner surfaces of MOF crystals, which involves introducing functional groups, replacing components, incorporating guest molecules, defect engineering and hybrid composite construction. We explore the latest advancement in electrochemical sensors based on MOFs, emphasizing their use in the recognition of environmental EDCs. The oxidation mechanisms of EDCs on the electrode surface were also discussed. In this review, we provide clear and straightforward guidance for the structural design of MOFs as well as the improvement of durable, efficient and resilient portable electrochemical sensors for environmental EDCs detection. Furthermore, this work addresses current challenges and highlights the future prospects of MOFs as sensor materials for environmental EDCs analysis.

## 1. Introduction

Endocrine-disrupting chemicals (EDCs) refer to a category of exogenous compounds including plasticizers and some pesticides that disrupt the body's endocrine systems, which control growth, development, metabolism and reproduction [1]. Plasticizers such as bisphenol A (BPA) and phthalates are broadly used chemicals that are extensively utilized in the manufacture of polyvinyl chloride (PVC) and polymer-based plastics, which are present in various products such as household supplies, medical devices and food-contact packages [2,3]. Prolonged exposure to low concentrations of toxic bisphenol A and phthalates can lead to many health issues, such as prostate cancer, breast cancer and metabolic disorders, which have a significant impact on the human reproductive and neuroendocrine systems [4]. Besides, pesticides such as methyl parathion, malathion, glyphosate and chlorpyrifos have the ability to imitate or hinder hormones, resulting in negative impacts on

health [5–8]. The excessive and improper use of pesticides has led to the accumulation of large quantities of harmful residues, which has caused significant public concern over the safety of food, health and the environment. Thus, the accurate and prompt identification of the above EDCs is essential in order to safeguard human well-being, existence and ecological balance.

Until now, various conventional techniques, such as atomic absorption spectrometry, mass spectrometry, high-performance liquid chromatography and fluorescence have been applied for detecting environmental EDCs. However, the majority of the techniques are more sophisticated and may require skilled operators, costly equipment, high detection expenses and lengthy detection durations, making them unsuitable for most laboratories. In addition, accurate detection of the target analyte at a low concentration level continues to pose a significant obstacle. Hence, it is imperative to create a detection device with the ability to identify target analytes at very low concentrations, namely at

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parts per million (ppm) levels. In contrast, electrochemical detection strategies provide advantages compared to conventional approaches, including enhanced sensitivity, the capability to recognize at a low concentration level, quick response time and portable equipment for on-site use [9]. EDCs such as BPA and phthalates, due to their electroactive nature, can be detected directly by adopting suitable electrochemical sensing approaches. For the non-electroactive EDCs such as polychlorinated biphenyls (PCBs) and PFAS, they can be identified after interaction with electro-active substances via electrochemical sandwich assay or by signal variants from impedance measurements [10]. Recent electrochemical sensing systems have also used nanomaterials to enhance the selectivity and sensitivity of the electrochemical systems [11].

Currently, metal-organic frameworks (MOFs) have gained massive attention due to their excellent possessions. MOFs, also known as porous coordination polymers (PCPs), are mixed materials that are made when metal ions or metal ion clusters combine with organic ligands [12,13]. This unique category of multifunctional materials has the benefits of high porosity, structural versatility, substantial pore size and extensive surface area. In addition, the physicochemical characteristics of MOFs can be modified during the fabrication process by the alteration of ligands, temperature and metals. These features of MOFs make them very promising for a diversity of uses, including gas separation and storage, catalysis, adsorption, sensors, energy storage and biomedical applications [14]. Many scientists have conducted investigations into the potential use of MOFs as electrode materials for the improvement of electrochemical sensor [15]. Because of their remarkable responsiveness and seamless integration capabilities, MOFs have already exhibited substantial potential as electrode materials for the identification of environmental EDCs. For instance, Naik et al. synthesized UiO-66-NDC/GO to develop an electrochemical sensor capable of detecting bisphenol A with excellent sensitivity and selectivity. The improved sensor was able to attain a LOD of 0.025  $\mu\text{M}$  with a linear concentration ranging from 10 to 70  $\mu\text{M}$  [16]. However, metal-organic framework face challenges in practical use, including limited specific recognition ability, low number of recognition sites, and slow response speed [17]. Besides, MOFs often exhibit low conductivity and stability, especially in aquatic environments. This is because the metal cores of MOFs have hydrophilic characters and easily attract water molecules. Furthermore, MOFs with weaker coordination bonds and carboxylate linkers are susceptible to hydrolysis in aqueous environments, which can cause structural breakdown or complete disintegration [18–22]. These drawbacks significantly impact sensor performance, making them inadequate for detecting low concentrations of environmental EDCs.

In this case, the functionalization of MOF is crucial to improve the surface area, porosity and recognition sites, as well as the sensor's performance. The sensitivity, selectivity and overall performance of MOFs-based sensors may be greatly enhanced by the introduction of functional groups, metal ion doping, post-synthetic alteration and surface engineering. For instance, the introduction of carboxyl groups to MOFs may improve sensing capability through the coordination chemistry, hydrogen bonding and electrostatic interactions with the analyte. Moreover, it provides reactive sites for the subsequent functionalization of the MOF's surface, which facilitates the incorporation of additional functional molecules onto the MOF, enabling the enhancement of sensor performance [23]. Currently, the most cutting-edge and trending research is the use of metal ion doping techniques on MOFs. Metal ions are crucial for maintaining the structural stability of MOFs through bond formation or coordination with organic ligands. This increased stability ensures that the MOF remains structurally intact and maintains its capacity to detect a variety of environmental pollutants. Hu et al. produced Cr-MOF materials to enhance the electrochemical sensor's capacity to detect P-nitrophenol. The Cr-MOF-based sensor demonstrated exceptional sensitivity, with a LOD of 0.7  $\mu\text{M}$  across a broad range of 2–500  $\mu\text{M}$  [24].

In this work, a comprehensive review of MOF-based electrochemical

sensors for the analysis of environmental EDCs is provided. To date, many reviews have been documented about the preparation process, structural features, and applications of MOF [18,25–30]. Besides, different strategies including postsynthetic methods, surface functionalization, et al. have been reviewed for the functionalization of MOFs to make them become promising candidates for various applications [31–34]. In most of these cases, researchers extensively explored post-synthetic modification (PSM) of MOFs though direct synthesis modification (DSM) is flexible and simple. This review offers a thorough comparison of both PSM and DSM and investigates the synergies, constraints, and complementary aspects of these two functionalization strategies. This balanced perspective enables readers to understand the specific applications that may favor one strategy over another. Still, the discussion and summary of advanced MOF-based electrochemical sensors and their detection capabilities for various EDCs remain absent. Thus, this review provides a comprehensive overview of the MOF-based electrochemical sensors used to study various environmental EDCs monitoring, along with a summary of the enhancements achieved by functionalization. Finally, this review explores the current obstacles and potential opportunities for the utilization of the sensor based on MOF in the field of environmental EDCs analysis.

## 2. Overview of MOFs

Metal-organic frameworks (MOFs) are a novel type of material that has gained attention due to their exceptional properties. In 1995, Omar M. Yaghi and his team successfully synthesized MOF crystalline for the first time, known as MOF-5 [35]. Subsequently, scientists have extensively investigated the process of creating and analyzing MOFs, resulting in the development of a vast collection of MOF materials with varied structures and functions. Over the past two decades, researchers have successfully created more than 100,000 MOF with different structures, characters and dimensionalities. The wide range of structures that may be formed by combining metal ions and organic ligands have enabled several applications in various fields, such as gas storage and separation, catalysis, drug administration, sensing and more [21,36–40].

### 2.1. Traditional synthetic method

Synthesis strategies play a vital role in controlling and enhancing the physical properties of MOFs, such as crystal structure, morphology, dimension, porosity and surface area. However, it is crucial to improve MOFs' sensing performance even more by creating novel synthesis strategies to overcome their shortcomings, which include low stability and electrical conductivity. Some traditional synthetic strategies for MOFs and MOF-based materials are summarized, which include hydrothermal/solvothermal, electrochemical synthesis, microwave-assisted, mechanochemical and ultrasound-assisted method. In this section, these traditional strategies have been discussed in detail.

The hydrothermal/solvothermal process has been considered a highly convenient and straightforward technique due to several advantages, including enhanced solubility of the reactant, simplified purification of the result, reduced corrosiveness to equipment, and the ability to adjust crystal size [41,42]. Over the past decade, the hydrothermal/solvothermal approach has been widely employed for synthesizing high-quality porous materials, such as zeolites, metal oxides and MOFs. In a hydrothermal system, metal salts and organic ligand were mixed with water (dipolar protic solvent), and the mixture was placed into teflon-lined hydrothermal autoclave reactors for chemical reactions. During the reaction, the autoclave maintains a certain pressure, which facilitates the generation of the necessary pressure in the water phase and the formation of crystalline structure. Krisbiantoro et al. reported a hydrothermal strategy to synthesize a BDC-based MOF by employing a novel and effective bis(2-hydroxyethyl) terephthalate linker, as shown in Fig. 1a. The hydrothermal reaction was conducted at a temperature of 130 °C for 12 h [43]. However, chemical reactions

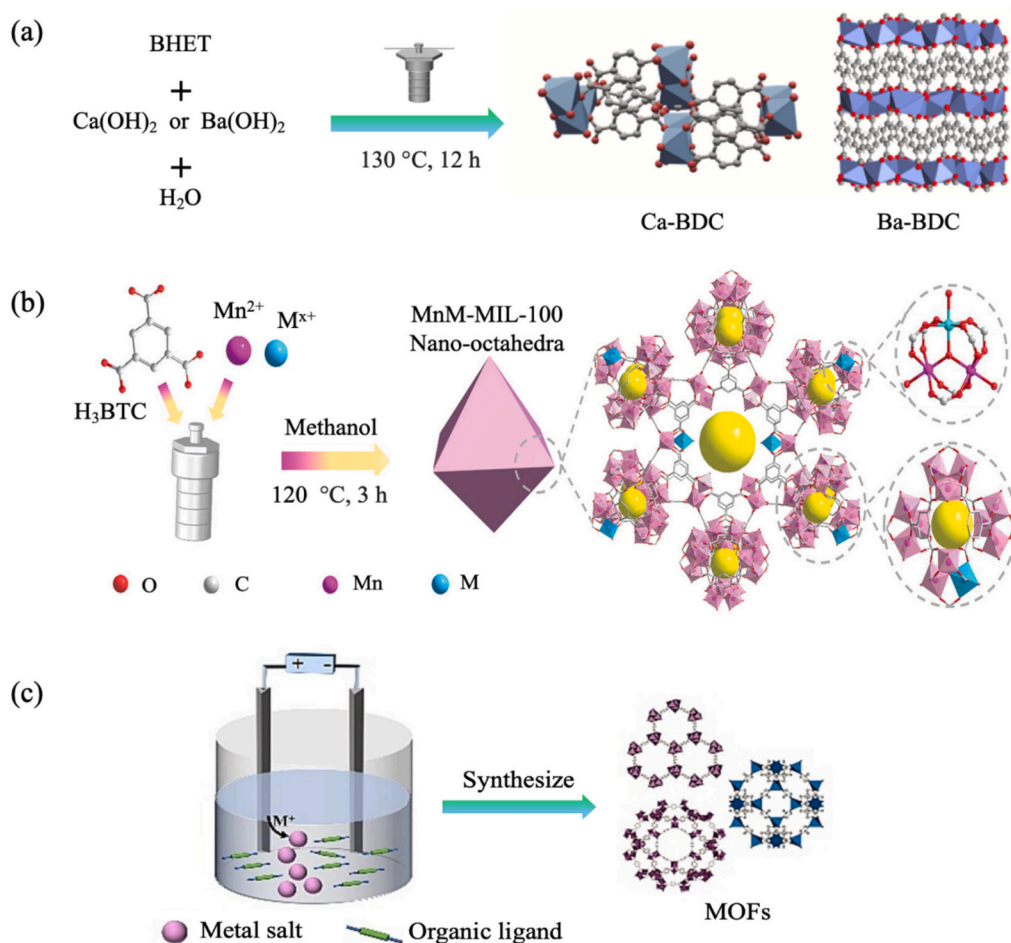


**Fig. 1.** Traditional synthetic strategies for MOFs and MOF composites. (a) Hydrothermal method. Reproduced with permission [43], Copyright 2024, Elsevier. (b) Solvothermal method. Reproduced with permission [45], Copyright 2021, Wiley-VCH. (c) Electrochemical method. Reproduced with permission [50], Copyright 2023, Elsevier.

occur in the presence of organic solvents (protic or aprotic solvents) in the solvothermal process [44]. Li et al. synthesized a series of multi-metallic Mn-based MIL-100 nano-octahedra composites using a facile solvothermal strategy (Fig. 1b). Methanol was employed as an organic solvent that penetrates the pores of MOFs, hence possibly modifying their pore size and surface area, which is crucial for enhancing the characteristics of MOFs [45].

The electrochemical synthesis approach has drawn significant attention from scientists owing to its capacity to precisely manipulate MOF formation, resulting in more uniform and monodisperse MOF particles, which is advantageous for sensing applications [46]. In 2005, Mueller et al. initially reported on the electrochemical synthesis method and constructed the Cu-based framework HKUST-1 by anodic dissolution [47]. Since then, this technique has become a promising methodology for the construction of MOFs due to its scalability, rapidity and environmental friendliness [48,49]. The formation process of MOF through an electrochemical process is shown in Fig. 1c [50]. In this process, an electrode (anode) is submerged in a solution that contains a supporting electrolyte and an organic linker. When an electric voltage is applied, the metal anode undergoes oxidation, resulting in the dissolution of the metal into the electrolyte as positively charged metal ions. Subsequently, these metal ions become available in the solution for interaction with organic linker molecules. The metal ions and organic linkers undergo a coordination reaction, resulting in the creation of the MOF structure on the electrode surface [47,51]. Utilizing an electrochemical synthesis approach, Zhang et al. synthesized Cu-MOF, which demonstrated superior glucose sensing capabilities. The notable

performances can be attributed to the vertically oriented architecture's enhanced ion transport and the high conductivity that came from the entirely electrochemical synthesis [52].

For the synthesis of functional nanomaterials, researchers have proposed some traditional heating techniques, such as electric heating, sand baths, oil baths and jacket heating. However, these methods are time-consuming and require a significant amount of energy. Currently, microwave heating by irradiation of materials is being used as an alternative to traditional heating. The rapid nucleation process of microwave-assisted synthesis makes it advantageous for producing MOFs with a uniform particle size distribution in a short period of time [53]. In microwave process, a mixture of solvents is transferred to a Teflon vessel, which is placed in the microwave device for a specific period of time for heat treatment [54]. Microwave technology enables the creation of localized areas of intense heat and facilitates the quick transport of heat, resulting in a speedy and consistent process of particle production, ultimately leading to more evenly distributed particle sizes [55]. Li et al. employed a microwave-assisted strategy to produce ultrathin trimetallic MOF nanosheets based on NiCoFe as shown in Fig. 2a. The as-synthesized  $\text{Ni}_4\text{Co}_4\text{Fe}_2$ -MOF nanosheets demonstrate good electrochemical stability with excellent OER activity, suggesting a useful method for controlling the electronic structure of metal sites in MOFs [56].

Mechanochemical synthesis is known as the combination of mechanical and chemical processes to produce nanomaterials. Pichon et al. reported the first study on the mechanochemical method for making porous MOF [57]. In mechanochemical processes, an external force is

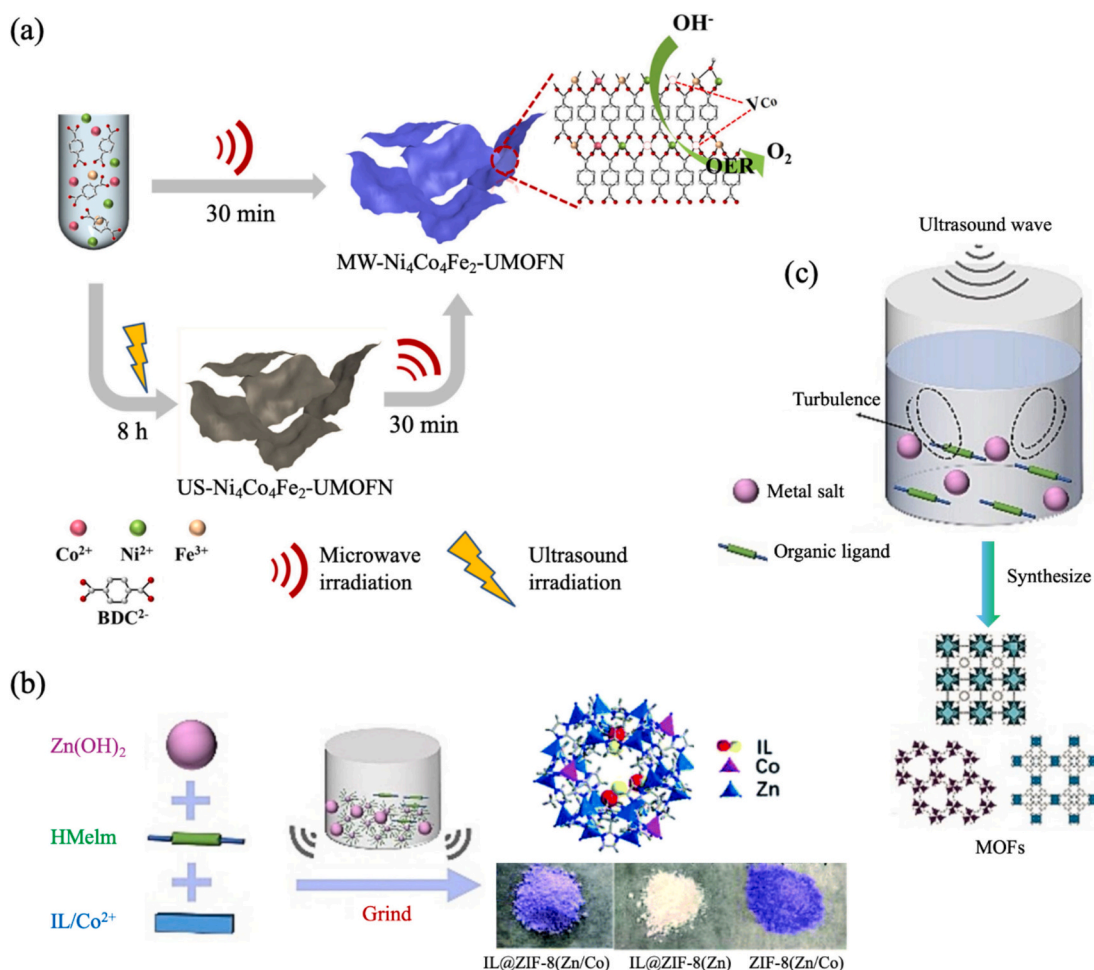


**Fig. 2.** Traditional synthetic strategies for MOFs and MOF composites. (a) Microwave-assisted synthesis. Reproduced with permission [56], Copyright 2021, Elsevier. (b) Mechanochemical synthesis. Reproduced with permission [62], Copyright 2020, The Royal Society of Chemistry. (c) Ultrasound-assisted method. Reproduced with permission [50], Copyright 2023, Elsevier.

responsible for both chemical transformation and the mechanical breakdown of intramolecular bonds [58]. Recently, several grinding technologies in mechanochemical processes, such as neat grinding (no solvent), liquid-assisted grinding (LAG), and ion- and liquid-assisted grinding (ILAG) for MOFs synthesized, have been widely applied [59–61]. Sun et al. reported a solvent-free mechanochemical system for the synthesis of multifunctional MOFs, including  $\text{ZIF-8(Zn/Co)}$ ,  $\text{IL@ZIF-8(Zn)}$ , and  $\text{IL@ZIF-8(Zn/Co)}$  as shown in Fig. 2b. This technique enables precise control of the stoichiometry and shape of the MOFs, leading to heightened thermal stability, increased adsorption capacities, and enhanced catalytic activity [62]. Mechanochemical synthesis is generally a solvent-free process that has benefits in terms of clean synthesis, energy, response time and conversion efficiency [60].

For the rapid creation of MOF, ultrasound-assisted method has gained significant attention. In this process, the reactants are placed in a sonication vessel, which is designed for sonication, and subjected to high-frequency ultrasound (20 to 10,000 kHz). During the synthesis of MOFs, ultrasonic waves create cavities in a combination of metal ions and organic linkers. Cavitation creates very reactive substances that help metal ions and organic ligands work together to make MOF precursors [63]. These initial substances undergo further condensation processes in the presence of sound waves, resulting in the creation of well-defined MOF structures. Increased mass transfer and localized heating from cavitation facilitate the fast formation and development of MOF crystals. The schematic diagram of ultrasound technique is displayed in Fig. 2c [50]. The ultrasound-assisted system ensures consistently high

temperatures, leading to swift chemical reactions and quick crystal growth with uniformly dispersed nucleation centers, thereby reducing both the crystallization time and the crystal size [64]. Zarekarizi et al. used an ultrasonic-assisted strategy for synthesizing 2D  $\text{Co(II)}$  MOF (TMU-69) in 15 min, whereas a solvothermal process requires 3 days to form the framework. The use of ultrasonic irradiation also improved control over the size and morphology of the materials. Under ideal circumstances, new TMU-69 nanoplates demonstrated more robust adsorption kinetics for Congo red [65].

## 2.2. Functionalization strategies of MOFs

The functionalization strategies of MOFs are essential for customizing their features to fulfill unique application demands. At present, direct synthesis modification (DSM) and post-synthetic modification (PSM) processes are widely used for the functionalization of MOFs. These methodologies offer meticulous manipulation of characteristics including porosity, surface area, chemical reactivity and selectivity, allowing MOFs to tackle intricate obstacles in many sectors. This section will provide a full discussion of the functionalization strategies of MOFs. The recent development of DSM and PSM of MOF has been highlighted, and their remarkable properties have also been covered. This discussion will provide new pathways for future MOF research by enabling the precise control of MOF structures and properties.

### 2.2.1. Direct synthesis modification (DSM)

Direct synthesis modification (DSM) of MOFs is a flexible method that entails integrating desired functionalities directly into the MOF structure during its initial synthesis. During the direct synthesis modification of MOFs, various additives and chemicals can be incorporated with the original mixtures to achieve specific functionalities. For instance, Abid et al. used ammonium hydroxide as an additive in the direct synthesis of UiO-66 to increase its structural characteristics. It was found that the addition of ammonium hydroxide decreased the crystal size of Zr-MOFs and increased both pore size and pore volume, indicating the application of additives for the enhancement of MOF properties [66]. Another study found that the presence of monocarboxylic acids, specifically p-toluylic acid (p-TA) [67], has a significant effect on crystal dimension because it influences both nucleation and crystal growth rates. Fig. 3 shows the effects of p-TA on NH<sub>2</sub>-MIL-125. p-toluylic acid (p-TA) can partially serve as an organic linker, promoting the nucleation rate and leading to the creation of additional nuclei. These nuclei then proceed to develop into small crystals. Simultaneously, p-TA functions as a blocking agent, inhibiting crystal growth. The high concentration of p-TA inhibits nucleation, resulting in the creation of a limited number of nuclei that experience gradual growth and finally develop into large crystals [68–70].

In the direct synthesis process, solvent acts as a coordinating agent for metal ions as well as a structure-directing agent and a reaction medium. The presence of co-solvents can significantly impact the morphological characteristics of MOFs by affecting the rate of nucleation and crystal formation during the synthesis process. MOF crystal dimension, shape and dispersion can be accurately manipulated by adjusting the composition and properties of the co-solvent mixture [71–73]. Jiang et al. produced Cu-MOF-74 materials by employing different cosolvents for analyzing their morphological characteristics [74]. The Cu-MOF-74 samples prepared at 80 °C using isopropyl alcohol as a cosolvent exhibit a rod-like morphology (Fig. 4a), whereas ethanol leads to the formation of unidirectional and bidirectional bouquet-like morphology (Fig. 4b and c) at 65 and 80 °C, respectively. The Cu-MOF-74-iso-80 material has the high specific surface area, measuring 1025.0 m<sup>2</sup>g<sup>−1</sup>. Furthermore, its capacity to adsorb NO is higher than that of the other samples (Fig. 4d). Therefore, the meticulous choice and adjustment of the co-solvent are crucial, as they might enhance the desirable properties of the MOF.

MOF structures have the ability to incorporate different metal ions through direct synthetic ion exchange and the alteration of metal ions can easily improve the characteristics of the framework. For instance, Zhang et al. constructed MOFs with improved characteristics by introducing second-transition metal ions (Ti, Mn, Zn, and Cu) into Fe-MOF and the fabrication procedure is shown in Fig. 5a. From the morphological analysis it can be seen that Fe-M-T100 (M = Ti, Mn or Zn) possesses a stacked and spherical form structure, whereas Fe-Cu-T100 has a rhombic hexahedral structure. Notably, Fe-Ti-T100 has the most robust correlation among them. The variation in metal bond angles is responsible for the difference in morphology and adsorption capacity. The existence of these metallic species within the MOF metal cluster nodes has a substantial influence on the effectiveness of CO<sub>2</sub> conversion [75]. Similarly, Dong et al. employed various metal ions, such as Fe<sup>3+</sup>, Zr<sup>4+</sup> and La<sup>3+</sup>, to form connections with 2-aminoterephthalate (H<sub>2</sub>ATA) in order to produce three different MOFs, and the fabrication process is shown in Fig. 5b. The SEM study reveals that three MOFs, namely Fe-MOF-NH<sub>2</sub>, Zr-MOF-NH<sub>2</sub>, and La-MOF-NH<sub>2</sub>, exhibit distinct morphologies, including a flat spindle structure, a wafer accumulation structure, and a wool-ball-like structure, respectively. Among them, La-MOF-NH<sub>2</sub> exhibits the most superior electrochemical performance. This may be primarily due to the presence of many active species and the strong structure of the wool-ball-like formation, which is produced by the intertwining of numerous streaky-shaped particles [76].

In the DSM system, the construction of mixed-linker metal-organic frameworks (MIXMOFs) is a highly effective approach for manipulating the physical-chemical characteristics of MOFs. Taddei et al. constructed UiO-66 framework based on amino- and bromo-functionalized MIXMOFs (MIXUiO-66) in order to enhance its characteristics, and the results have proven to be effective [77]. Another functionalization strategy is to incorporate functional groups into the MOF. These functional groups possess the capacity to increase the properties of MOFs. Huang et al. controlled the coordination manner of aliphatic amine groups present in MOFs via a crystal-engineering strategy. With and without free aliphatic amines, two isomeric MOFs were synthesized under appropriate synthetic conditions using Zn (II) ions and dicarboxylate ligands with a secondary amine bridging, resulting in improved MOF's properties. This work indicates that by introduction of metal ions and organic ligands, the coordination behaviors of amine groups in MOFs can be regulated [78]. A possible reason is the amine group's

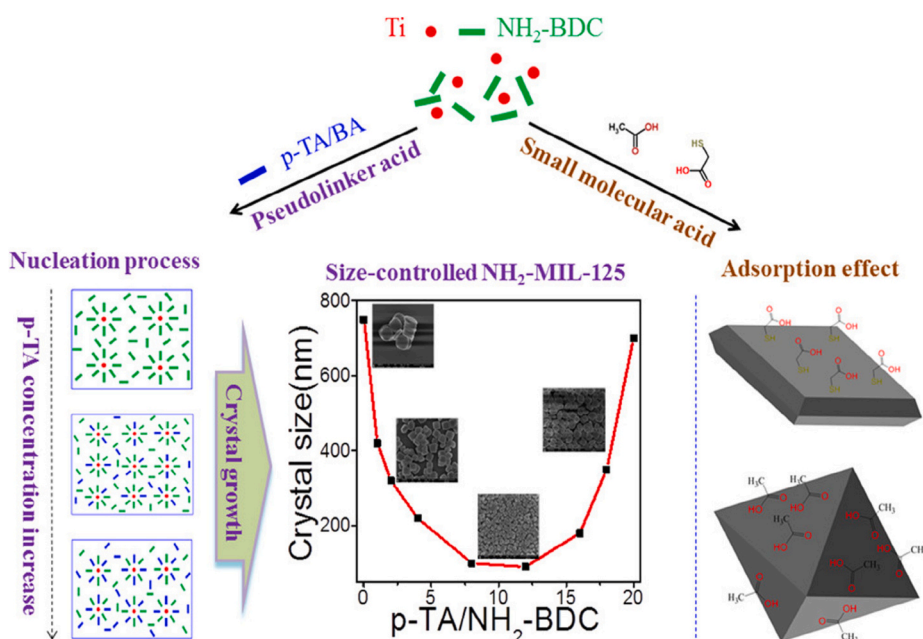


Fig. 3. Effects of monocarboxylic acids on NH<sub>2</sub>-MIL-125. Reproduced with permission [67], Copyright 2017, American Chemical Society.

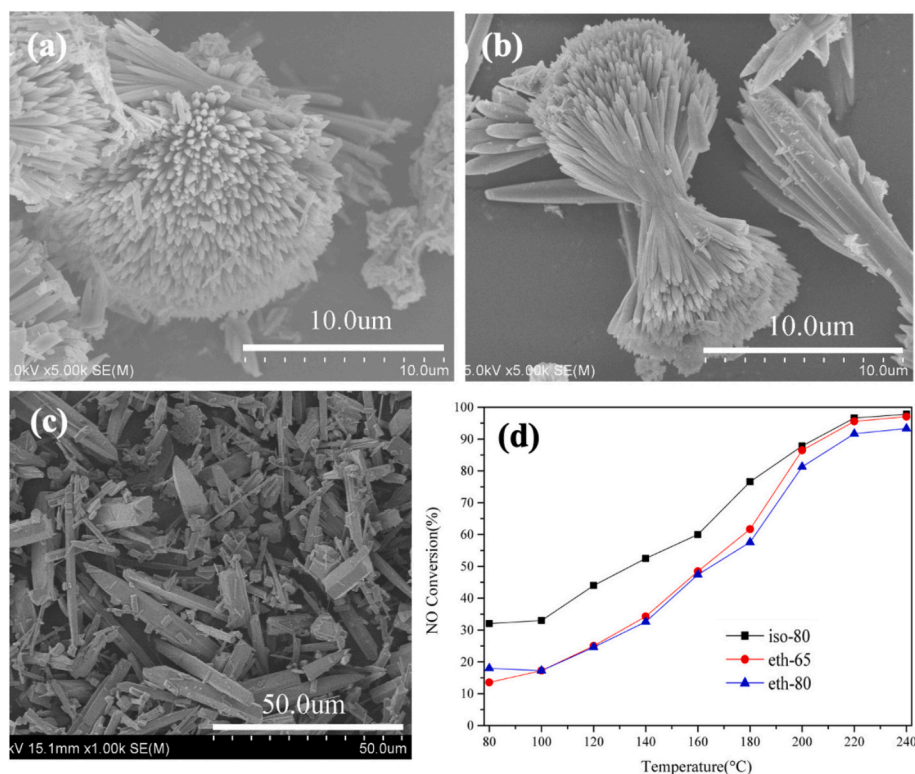


**Fig. 4.** SEM images of Cu-MOF-74 materials: (a) ethanol –65, (b) ethanol –80 and (c) isopropyl alcohol –80, (d) Low-temperature selective catalytic reduction properties. Reproduced with permission [74], Copyright 2017, American Chemical Society.

ability to participate in hydrogen bonding and electrostatic interactions, which ultimately enhance the characteristics of MOF.

To boost the sensing ability of MOF, several metal centres, such as Cu and Fe can be incorporated into the framework through direct synthesis modification. For instance, Yang et al. constructed Cu/Fe-BTC composites for the sensitive detection of triflumuron. Cu/Fe-BTC materials have significant reactivity towards triflumuron as a result of the inclusion of Cu and Fe metal centres, which operate as active catalytic sites, promoting redox reactions. The BTC (benzene-1,3,5-tricarboxylate) framework increases the surface area and porosity, making it easier for triflumuron molecules to reach the active areas [79]. Liao et al. fabricated a porous composite of  $\text{Ni}_3\text{ZnCo}_0.7/\text{Ni}$  as sensitive electrode materials, and Fig. 6a displays the preparation diagram of  $\text{Ni}_3\text{ZnCo}_0.7/\text{Ni}/\text{GCE}$ . The  $\text{Ni}_3\text{ZnCo}_0.7/\text{Ni}$  composite modified electrode significantly enhances the electrocatalytic activity towards hydroquinone and catechol compared to the NiC and ZnC modified electrodes. The superior activity may be attributed to the improvement of the active surface area of the modified electrode. Additionally, the Ni atom exhibits exceptional electrocatalytic efficiency towards dihydroxybenzene [80]. In another study, Cu-MOF/N-doped GO nanocomposites have been used to detect 4-nitrophenol. The Cu-MOF/NGO/SPCE exhibited a higher current response to 4-nitrophenol compared to bare-SPCE, Cu-MOF/SPCE, and NGO/SPCE (Fig. 6b). The sensor demonstrated a LOD of  $0.035 \mu\text{M}$  and a LOQ of  $0.116 \mu\text{M}$ , within a concentration range of  $0.5\text{--}100 \mu\text{M}$  [81].

### 2.2.2. Post-synthetic modification (PSM)

Post-synthetic Modification (PSM) is a process that modifies a material chemically after its initial synthesis. In the early 2000s, post-synthetic modification of MOFs became a prominent field of research due to the need to accurately regulate the characteristics of MOFs to suit certain applications. PSM was initially documented by Lee et al. [82] and Kim et al. [83] in 1999 and 2000, respectively. Up to date, numerous investigations have been conducted to increase the characteristics of MOFs with the use of PSM. There are two distinct parts to the PSM

approach: covalent PSM and coordinative PSM. Covalent PSM refers to the process of modifying MOFs by incorporating new functional groups through the creation of covalent bonds. Conversely, coordinative PSM refers to the alteration of MOFs by coordinating extra metal ions or molecules to the metal nodes of the framework.

PSM allows certain functional groups to be incorporated onto the MOF's surface or inside its pores [84]. These functional groups have the ability to provide the appropriate chemical reactivity, allowing MOFs to selectively trap or catalyze certain molecules. Besides, chemical functionalities can be attached to unsaturated metal sites or organic ligands, which enhance the ability to attract and bind molecules while also inhibiting the diffusion of unintended molecules. For instance, Gaikwad et al. produced a modified version of MOF-177 by introducing amine groups to enhance the adsorption of  $\text{CO}_2$  at low pressure. The uptake values achieved were 4.8 times higher than the surface-unmodified MOF [85]. Cao et al. synthesized MOF called UiO-66- $\text{NH}_2$  using 4-carboxy-phenylboronic (4-CPBA). Fig. 7 illustrates the synthesis procedure. Amine groups have a crucial function in interacting with carboxyl groups and offering additional active sites. The UiO-CPBA fluorescence sensor demonstrated a highly effective sensing response, with a linear range of  $1\text{--}100 \mu\text{M}$  and a LOD of  $0.15 \mu\text{M}$  for the measurement of sialic acid [86].

Component replacement is another effective post-synthetic modification process. This method entails the replacement of metal ions or clusters, as well as the substitution of organic ligands [87]. The replacement of metal ions can increase the attraction for adsorption, whereas the replacement of organic ligands significantly affects the size of the pores in the MOF [88]. Ban et al. used a metal substitution approach to convert a meta-stable ZIF-108 framework into a range of more stable MOFs at a relatively low transformation temperature of  $60^\circ\text{C}$ . The partial metal-substituted ZIF crystals, produced with  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  ions, displayed notable differences in their crystalline structures, surface areas, and affinities for  $\text{CO}_2$  adsorption. Specifically, the bi-metallic  $\text{Ni}_{0.07}\text{Zn}_{0.93}$ -ZIF-108 exhibited an outstanding selectivity for

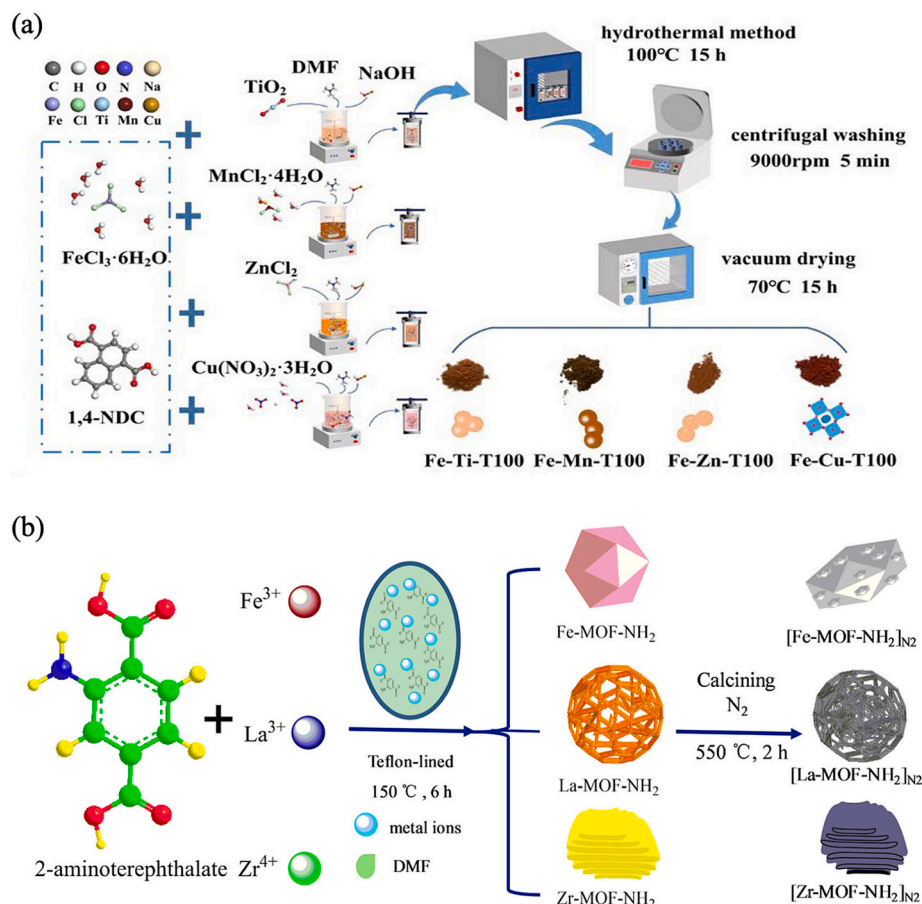


Fig. 5. (a) The synthesis process of Fe-M-T100 (M = Ti, Mn, Zn, or Cu). Reproduced with permission [75], Copyright 2024, Elsevier. (b) Preparation strategy of Fe-MOF-NH<sub>2</sub>, Zr-MOF-NH<sub>2</sub>, and La-MOF-NH<sub>2</sub>. Reproduced with permission [76], Copyright 2018, American Chemical Society.

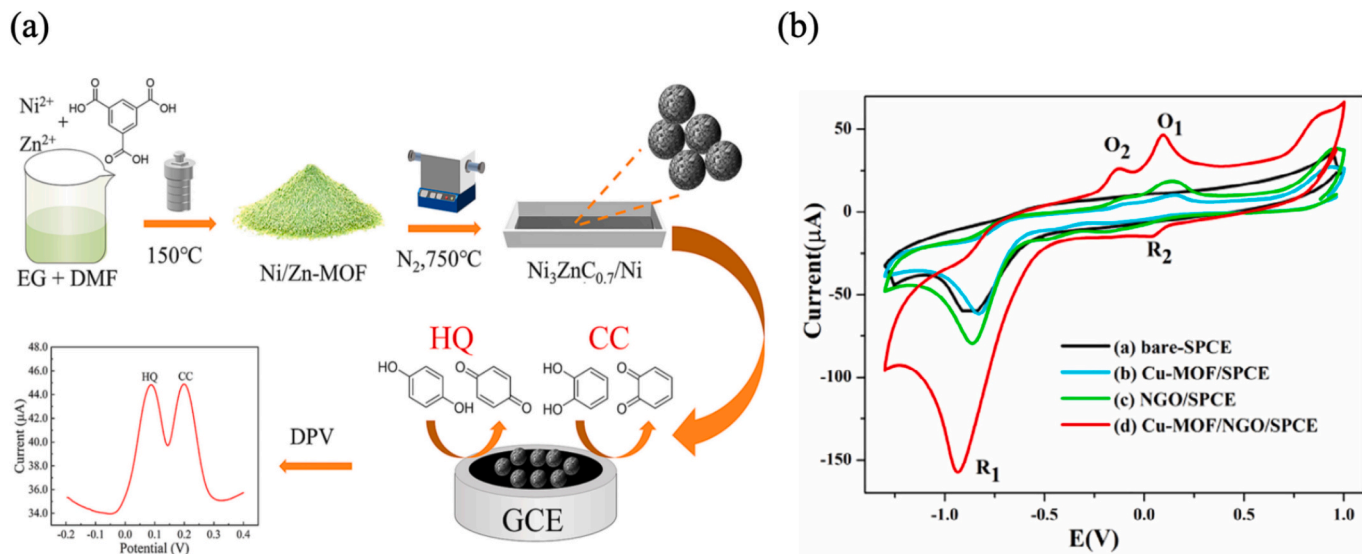


Fig. 6. (a) Fabrication and sensing mechanism diagram of  $\text{Ni}_3\text{ZnCo}_{0.7}/\text{Ni}/\text{GCE}$ . Reproduced with permission [80], Copyright 2024, Elsevier. (b) CV curves of the prepared samples at 0.1 mmol/L 4-nitrophenol in 0.1 M PBS. Reproduced with permission [81], Copyright 2022, Elsevier.

$\text{CO}_2/\text{N}_2$  adsorption, with a value of 227. The mixed matrix membranes, which include metal-substituted ZIF particles as fillers, have consistently demonstrated improved property in applications involving the separation of  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$  [89]. Ligand substitution has been employed to alter the size of the membrane pore in MOF, either

increasing or decreasing it, with the aim of improving the effectiveness of electrochemical applications [90]. The exchange of organic ligands has a comparable impact on MOF properties, including pore diameters, chemical functionalities, adsorption capacities, crystal sizes and structures, which are important to control for sensor effectiveness. Raissa

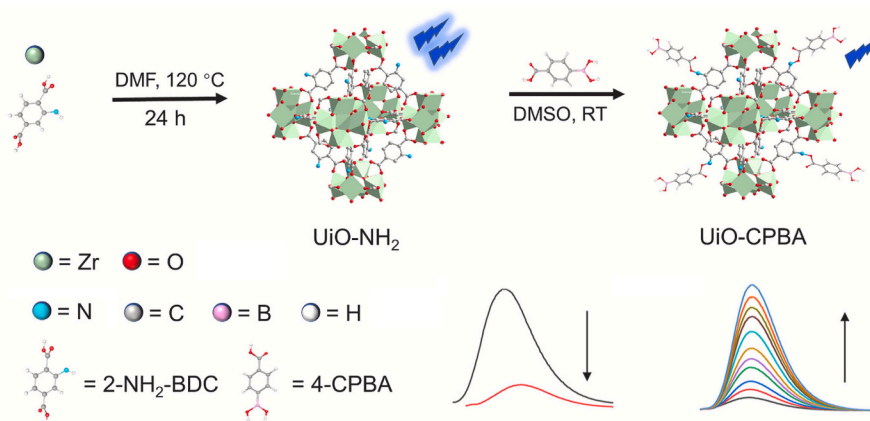


Fig. 7. Fabrication strategy of UiO-CPBA. Reproduced with permission [86], Copyright 2022, Elsevier.

et al. studied the effect of ligand exchange on the efficiency of bimetallic NiCo-MOF in order to maximize its sensor performance and the ligand exchange process is shown in Fig. 8a. The XRD study indicates a noticeable difference in the pattern of  $\text{KNiCoPO}_4$  in comparison to NiCo-M (10:1), indicating that a ligand substitution has occurred. The findings demonstrate that substituting a ligand with a phosphate group results in further changes in both abundance and surface area, enhancing the electrochemical efficacy of NiCo-MOF. The ligand exchange process in NiCo-MOF with a Ni/Co ratio of 10:1 leads to enhanced the supercapacitor's performance with a higher capacity of  $522 \text{ C g}^{-1}$  at  $0.5 \text{ A g}^{-1}$  [91].

The incorporation of guest molecules into MOFs offers a flexible method to customize their characteristics for a diverse array of uses. Guest molecules have the ability to inhabit the pores and channels present in the MOF structure, which in turn affects the MOF's adsorption and reactive capabilities. Ploskonka et al. conducted research on the impact of guest molecules on the adsorption and reactivity of the MOF in both the gaseous and liquid phases. It was found that the presence of the guest molecule such as isopropanol, dimethylformamide, triethylamine,

acetone,

benzene and pentane have a substantial effect on improving the characteristics of MOFs [92]. Wang et al. utilized a post-synthetic approach for incorporating  $\text{NH}_3$  molecules into MOF-74 (Co), which led to the formation of  $\text{NH}_3\text{@MOF-74}(\text{Co})$ . The AC impedance measurements demonstrated that the  $\text{NH}_3$ -modified  $\text{NH}_3\text{@MOF-74}(\text{Co})$  exhibits a remarkable proton conductivity of  $6.8 \times 10^{-3} \text{ S/cm}$ , which is 10,000 times higher than that of the pristine MOF-74(Co) at 98 % relative humidity (RH) and  $50^\circ \text{C}$  (Fig. 8b and c) [93]. In addition, guest molecules can function as either proton carriers or proton-conducting media by participating in potential hydrogen bonding networks, hence enhancing the characteristics of MOFs [94–97].

In recent years, defect engineering has received significant interest to enhance the activities of MOFs. The intentional elimination of certain linkers or metal ion nodes would result in a wide range of material variations, including modifications to the pore structure, electronic characteristics, catalytic properties and adsorption capabilities [98–100]. Fan et al. successfully achieved uniform implantation of Ag nanoparticles on MOF using PSM, resulting in the development of UIO-

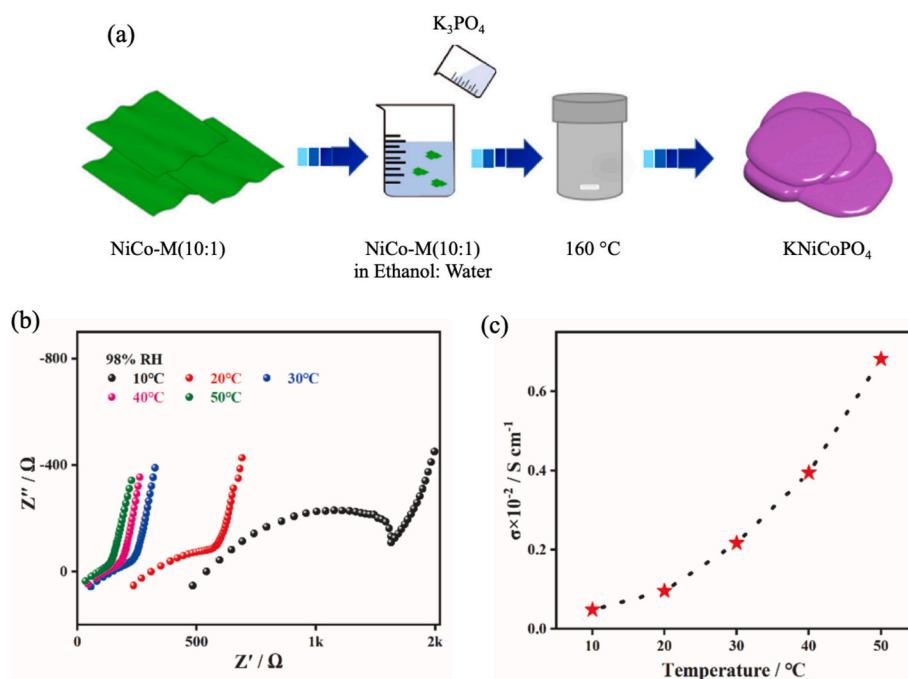


Fig. 8. (a) Structural transformation of  $\text{KNiCoPO}_4$  from NiCo-M. Reproduced with permission [91], Copyright 2024, Elsevier. (b) EIS curves and (c) Proton conductivity of  $\text{NH}_3\text{@MOF-74}(\text{Co})$  at different temperatures. Reproduced with permission [93], Copyright 2024, Elsevier.

66-NH<sub>2</sub>@Ag composites. The UiO-66-NH<sub>2</sub>@Ag composites, which were developed using defects engineering, displayed a significant improvement in CV detection signals compared to Ag NPs or UiO-66, UiO-66-SH substrates [101]. Currently, missing-linker defects and missing-cluster/metal ion defects have extensively been reported. The removal of metal ions from the MOF's structure leads to missing-metal defects, while the absence or replacement of organic ligands causes missing-linker defects. Taddei et al. constructed Zr-MOFs with missing linkers or missing cluster defects using the post-synthetic ligand exchange (PSE) manner. During PSE on defective Zr-MOFs, a competitive exchange can occur between framework linkers and defect-compensating groups. The exact consequences of this exchange depend on the nature of the defects. In the matter of missing linkers, PSE (Fig. 9a) would compete with replacing two monocarboxylic modulators that are linked to adjacent clusters with the incoming linker. In the case of missing clusters, the PSE (Fig. 9b) would compete with substituting one monocarboxylic modulator by coordinating the incoming linker through only one of its carboxylic groups [102]. Similar, Koutsianos et al. used post-synthetic defect exchange as an alternate method to include amino functions at missing cluster defective sites in formic acid-regulated UiO-66. It has been shown that adding amino groups to Zr-MOFs enhances their attraction to CO<sub>2</sub> [103]. Tu et al. studied the formation of metal vacancies and linker vacancies inside a cubic MOF composed of Zn (II) and pyrazolecarboxylic acid by eliminating 25 % of the metal ions and 50 % of the linkers. The MOF with ordered vacancies has an increased pore size, allowing large dye molecules to fit inside the pores. Then, the vacancies were filled with new linkers and metal ions without compromising the structural integrity of the MOF (Fig. 9c) [104].

MOFs frequently experience instability when exposed to extreme circumstances, such as high levels of humidity or acidic environments, resulting in the deterioration of their framework. Polymer coatings serve as a barrier, protecting the MOF particles and enhancing their long-term

stability. Yang et al. produced a series of MOF composites by applying thin layers of polydopamine to the MOF surface, and the results have demonstrated notable stability [105]. To enhance catalytic activity, researchers conducted a study to create a nylon-MOF polymer composite. The covalent hybrid material exhibited more catalytic activity in the degradation of a chemical warfare simulant (CWS) compared to MOFs that are physically confined in nylon without covalent bonding [106]. In addition, a nanocomposite membrane was produced by applying a coating of CuBDC-NH<sub>2</sub>/PU onto a porous nylon sheet. The nanocomposites have exceptional catalytic activity, with a 93.0 % removal rate for dyes such as methylene blue, rhodamine B, and eosin Y [107].

### 3. The characteristics of EDCs

EDCs, are a class of chemicals that have the significant ability to affect the human health as well as animals. They can possibly result in detrimental impacts on reproduction, development, brain health and immunological function, even when present at low concentrations. Humans and animals consume EDCs through ingestion, inhalation, direct skin contact, food and water. Several endocrine-disrupting chemicals exhibit structural similarities to hormones that can easily disrupt the endocrine system. The World Health Organization has identified over 800 substances globally as endocrine-disrupting chemicals owing to their ability to disrupt the endocrine system [108]. Among them, the most widely used EDCs, such as BPA, phthalates, methyl parathion, malathion, glyphosate, and chlorpyrifos, and their detrimental effects on human health have been discussed in detail. Fig. 10 provides a schematic overview of diseases caused by EDCs.

One of the most concerning consequences of EDCs is their impact on development and reproduction. These substances have been associated with some developmental difficulties, such as birth deformities and

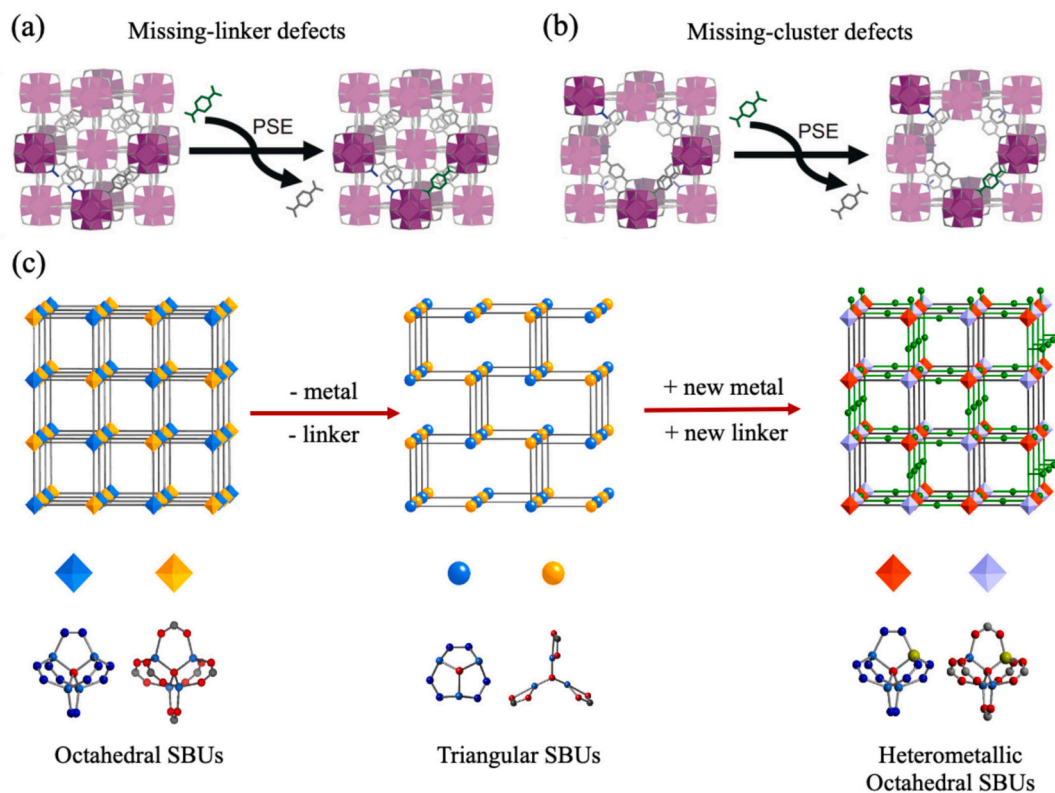


**Fig. 9.** Expected results from exchange reactions involving a BDC analogue (green) on defects containing UiO-66: (a) UiO-66 containing missing-linker defects can either undergo PSE. (b) UiO-66 containing missing-cluster defects can either undergo PSE. Reproduced with permission [102], Copyright 2018, Wiley-VCH. (c) The removal of metal and linker, followed by the insertion of other metals and ligands, produces defects. Reproduced with permission [104], Copyright 2014, American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

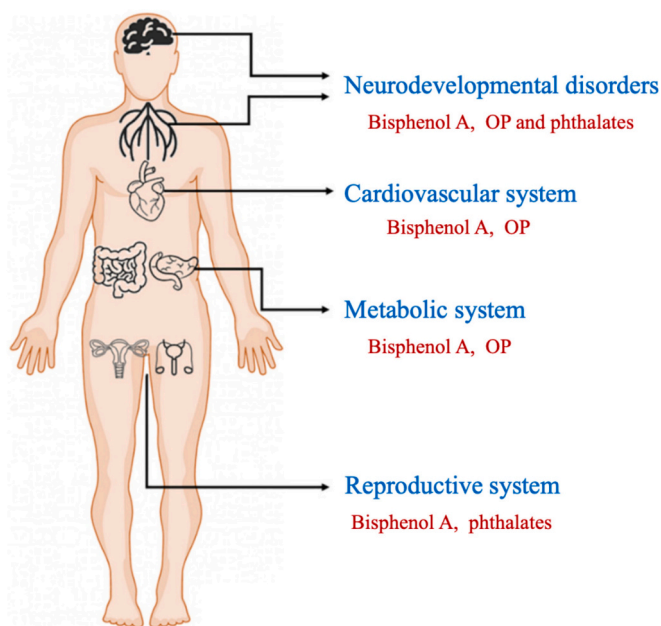


**Fig. 10.** The diagram illustrates the various endpoints of diseases caused by EDCs. Reproduced with permission [122], Copyright 2023, MDPI.

altered reproductive organ development, which may result in long-term fertility troubles [109]. Endocrine-disrupting chemicals with estrogenic characteristics, such as bisphenol A and phthalates, have the potential to trigger the early onset of puberty [110]. Besides, clinical research suggests that exposure to BPA and phthalates causes notable declines in sperm quality due to the effects of estrogen signaling at the genetic and non-genetic levels [111,112]. Furthermore, EDCs link to neurological problems such as behavioral abnormalities, cognitive impairments, and neurodevelopmental disorders. This is so that any interference might induce major neurological alterations since the developing brain is extremely sensitive to hormone signals [113]. Thyroid hormones are critical for proper developmental progression. Children's neurodevelopment suffers due to minor variations in maternal or fetal hormones [114]. EDCs have various impacts on thyroid function, such as affecting the production, transportation, metabolism, and activation of hormones and thyroid receptors (TR) [115].

An uninterrupted maturation of the immune system is essential for its optimal performance in subsequent stages of life. EDCs can impact the immune system, which may raise a person's vulnerability to infections, illnesses, and autoimmune conditions. Hormones are essential for controlling immune responses; any interference can cause autoimmune illnesses by reducing the body's capacity to fight off infections or discriminate between self and non-self [116]. Exogenous substances have the potential to effect both the development and subsequent functioning of the immune system. Recent studies have shown that some endocrine-disrupting chemicals can affect the growth and effectiveness of both the innate and adaptive immune systems [117,118]. EDCs may have transgenerational effects, meaning that exposure may have an impact on generations after the directly exposed individual. This occurs due to the potential for offspring to inherit the epigenetic or genetic modifications caused by EDCs. This transgenerational effect highlights the long-term dangers of exposure to EDCs and the possibility that these chemicals might influence population health beyond several generations [119].

Homeostasis of the endocrine system is crucial for proper growth. Specifically, steroid hormones, such as E2 and progesterone (P4), affect the calcium signaling of the heart muscle during the initial stages of embryonic development [120]. Estradiol and P4 are naturally occurring steroid hormones that have crucial roles in the body, such as controlling

the menstrual cycle, supporting pregnancy, and facilitating embryonic development. Progesterone plays an essential role in the cardiac repolarization process [121]. The contact with OP and BPA resulted in the suppression of calcium signaling throughout the process of developing heart muscle cells. Lee et al. found that OP and BPA possessed structures that are similar to steroid hormones, such as progesterone and estrogen. Besides, OP and BPA have progesterone-like characteristics by inhibiting and interfering with the process of cardiomyocyte development in mouse embryonic stem cells (mESCs) [120].

Exposure to EDCs is common because of the widespread presence of EDCs in many items. They are present in industrial chemicals like polychlorinated biphenyls (PCBs); polymers like bisphenol A; insecticides like DDT; and personal care items like phthalates. Due to their pervasiveness, these substances are always present in humans and wildlife and can be ingested, inhaled, or absorbed via the skin [123]. The effects of EDCs can differ greatly between species, making it more difficult to extrapolate findings from research on animals to people. Because various species have distinct hormonal systems, an EDC that is toxic to one species may not be to another. Understanding these features is essential to evaluating the hazards associated with EDCs and implementing efficient regulatory measures. Safer product formulations, constant research to better understand the mechanisms of action and long-term impacts of EDCs, monitoring and limiting their release, and minimizing exposure are all necessary components of an all-encompassing strategy to protect human health and the environment.

#### 4. MOF-based electrochemical sensor for EDCs analysis

Many review papers have been written on MOFs and their derivatives, which also describe strategies for altering MOFs to boost their properties in several applications [18,20,22,124,125]. However, to the best of our knowledge, there is a lack of comprehensive reviews on the utilization of MOF-based electrochemical sensors for environmental EDCs analysis. This section provides a comprehensive discussion and summary of electrochemical sensors based on MOFs for detecting various environmental EDCs, such as plasticizers and pesticides.

##### 4.1. Plasticizers

Plasticizers like BPA and phthalates are currently a major global issue due to their ability to impact the endocrine system. Researchers have conducted several studies to identify plasticizers. However, there is a lack of comprehensive reviews of electrochemical sensors that use MOFs and their derivatives to detect plasticizers. Therefore, this section delves deeply into the application of MOFs and their derivatives in electrochemical sensors designed to detect plasticizers. Table 1 presents a summary of the electrochemical characteristics of newly published sensors used to detect the aforementioned plasticizers.

Bisphenol A (BPA), also known as 2,2'-bis(4-hydroxyphenyl) propane, is a widely used plasticizer for the manufacturing of polycarbonate and epoxy resins [126] hence released into the environment by both home and industrial waste. It has the potential to cause many detrimental effects on the human body as well as other living organisms. Even minimal exposure to a low concentration of BPA can be harmful to the human body, causing disruptions to both the neurological system and the endocrine system [127,128]. Hence, it is imperative to identify BPA using appropriate, precise and easy analytical techniques for risk evaluation. For BPA detection, several chromatographic systems have been employed for their high sensitivity and efficiency. However, these approaches have certain limitations, such as their reduced efficacy in directly detecting BPA in aqueous samples and their inability to yield quantitative data without additional equipment. In this case, the electrochemical sensor has garnered significant interest due to its rapid and precise response utilizing simple equipment [129].

MOFs have gained significant attention as electrode materials for BPA detection because of their large surface areas, customizable pore

**Table 1**  
MOFs-based sensors for the detection of Plasticizers.

| Modified electrodes                                                                      | Techniques   | Electrolyte                     | Plasticizers                | Linear range ( $\mu\text{M}$ )          | LOD ( $\mu\text{M}$ ) | Ref   |
|------------------------------------------------------------------------------------------|--------------|---------------------------------|-----------------------------|-----------------------------------------|-----------------------|-------|
| MOF-508a                                                                                 | DPV          | PBS                             | BPA                         | 0.1–700.0                               | 0.03                  | [130] |
| Cu-MOF/Pd                                                                                | DPV          | PBS                             | BPA                         | 1–150                                   | 0.06                  | [131] |
| Fe-MOF                                                                                   | DPV          | PBS                             | BPA                         | 0.1–15                                  | 0.1                   | [132] |
| Ce-Zn-MOF                                                                                | DPV          | PBS                             | BPA                         | 0.1–100                                 | $7.2 \times 10^{-3}$  | [133] |
| Ce-MOF-ERGO                                                                              | DPV          | PBS                             | BPA                         | $3 \times 10^{-3}$ –10                  | $1.9 \times 10^{-3}$  | [134] |
| UiO-66-NDC/GO                                                                            | DPV          | PBS                             | BPA                         | 10–70                                   | 0.025                 | [16]  |
| CeO <sub>2</sub> /<br>Co <sub>3</sub> O <sub>4</sub> -Fe <sub>2</sub> O <sub>3</sub> @CC | DPV          | PBS                             | BPA                         | 0.5–10<br>10–30                         | $8.7 \times 10^{-3}$  | [135] |
| CMOF-MIPIL/GCE                                                                           | DPV          | PBS                             | BPA                         | $5 \times 10^{-3}$ –5                   | $4 \times 10^{-3}$    | [136] |
| CTAB/Ce-MOF/GCE                                                                          | DPV          | PBS                             | BPA                         | $5 \times 10^{-3}$ –50                  | $2 \times 10^{-3}$    | [137] |
| Cu-BTC                                                                                   | DPV          | PBS                             | BPA                         | $5 \times 10^{-3}$ –2                   | $7.2 \times 10^{-4}$  | [151] |
| Zn-L-IPA                                                                                 | DPV          | PBS                             | BPA                         | 0.01–0.5 0.5–8.5                        | $3.46 \times 10^{-3}$ | [152] |
| 3D Ni-MOF@CNTs                                                                           | DPV          | PBS                             | BPA                         | $1 \times 10^{-3}$ –1                   | $3.5 \times 10^{-4}$  | [153] |
| HCF/Copper-TMA                                                                           | DPV          | PBS                             | BPA                         | 0.05–60                                 | $2 \times 10^{-3}$    | [154] |
| Ce-Ni-MOF/MWCNTs                                                                         | DPV          | PBS                             | BPA                         | 0.1–100                                 | $7.8 \times 10^{-3}$  | [155] |
| Fe-Cu-BTC/AuNPs                                                                          | DPV          | PBS                             | BPA                         | 0.1–1.0                                 | 0.018                 | [156] |
| NH <sub>2</sub> -MIL-88(Fe)/Apt1-Hg <sup>2+</sup> -Apt2/MXene                            | SWV          | PBS                             | Phthalate acid esters       | 0.0422–7.68                             | 22.9                  | [142] |
| DEHP/MCH/Apt/AuNPs                                                                       | SWV          | PBS                             | di(2-ethylhexyl) phthalate  | $2.56 \times 10^{-4}$ –256              | $7.68 \times 10^{-5}$ | [143] |
| /CuMof/PANI-MWCNTs                                                                       |              |                                 |                             |                                         |                       |       |
| MOF/COF heterostructure hybrid composite                                                 | Photocurrent | PBS                             | Dibutyl phthalate           | $1.0 \times 10^{-4}$ –100               | $3.0 \times 10^{-5}$  | [144] |
| Cu <sub>3</sub> (BTC) <sub>2</sub> /Cu <sub>2</sub> O/ITO                                | Photocurrent | Na <sub>2</sub> SO <sub>4</sub> | dibutyl phthalate           | $1 \times 10^{-7}$ – $1 \times 10^{-3}$ | $3.5 \times 10^{-8}$  | [147] |
| NH <sub>2</sub> -Zr-MOF /GDY                                                             | ECL          | PBS                             | di-(2-ethylhexyl) phthalate | $2.56 \times 10^{-6}$ –0.256            | $6.22 \times 10^{-7}$ | [149] |
| Cu <sub>3</sub> (BTC) <sub>2</sub> @Cu <sub>2</sub> O                                    | Photocurrent | PBS                             | dioctyl phthalate           | $2.5 \times 10^{-5}$ –0.1               | $9.15 \times 10^{-6}$ | [150] |

sizes, and modifiable internal surface characteristics. Jahani et al. used MOF-508a as a sensing material to precisely identify bisphenol A using the electrochemical method. MOF-508a exhibited an exceptionally high specific surface area, resulting in a significant improvement of the sensor's performance. The sensor has exceptional sensitivity ( $0.0564 \mu\text{A} \mu\text{M}^{-1}$ ) and a LOD of  $0.03 \mu\text{M}$ , with a broad linear range ( $0.1$ – $700.0 \mu\text{M}$ ) [130]. Metal ions have the ability to increase MOFs' electrical conductivity, which improves their suitability for electrochemical sensing applications. Transition metals, like copper, can act as electron transfer channels, improving sensors' ability to transmit signals. For example, Saravanakumar et al. reported an electrochemical sensor for BPA

recognition using Cu-MOF/Pd-modified GCE. From Fig. 11a and b, it is clearly seen that the oxidation peak current increases progressively as the BPA content rises from 1 to  $150 \mu\text{M}$ . The developed sensor has outstanding sensitivity and a LOD of  $0.06 \mu\text{M}$ , with a linear range of  $1$ – $150 \mu\text{M}$ . Besides, the sensor showed remarkable repeatability, stability and anti-interference properties [131]. Incorporating Fe and Zn into the MOF enhances its structure, surface area and porosity, leading to the creation of novel active sites that might potentially interact with the BPA [132,133]. As a consequence, the sensor's ability to detect low concentrations of BPA is significantly improved. Furthermore, another strategy is to develop MOFs based composites to enhance the sensing

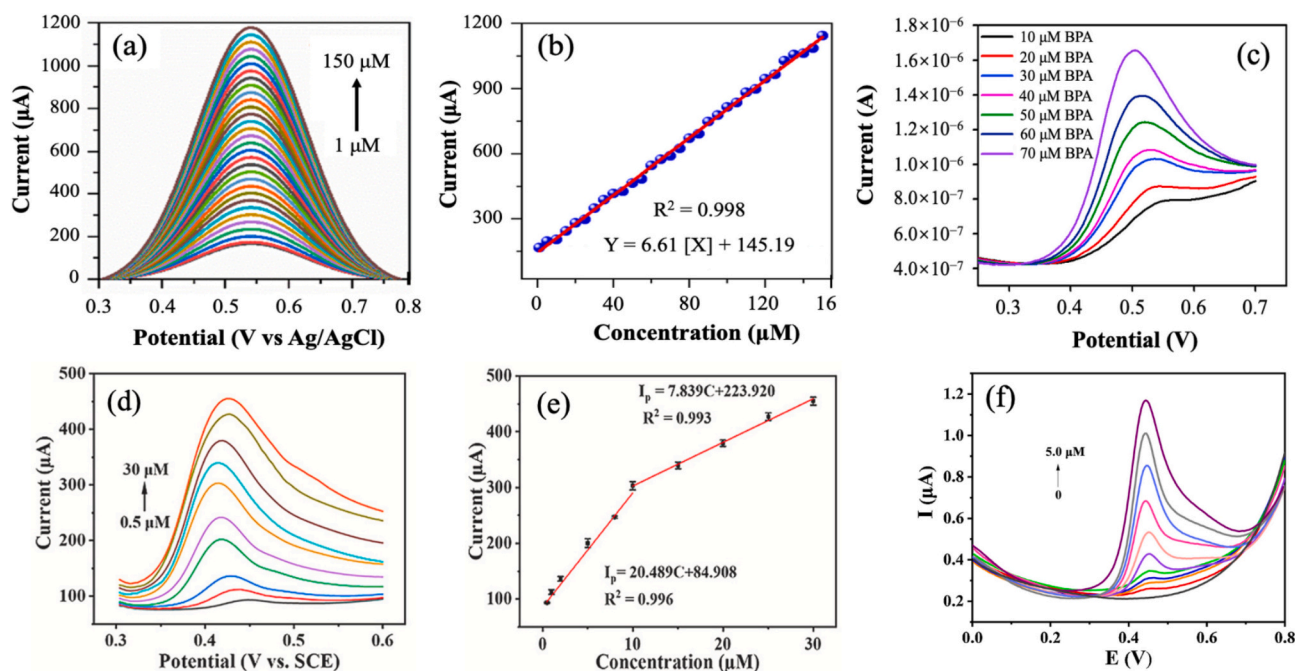


**Fig. 11.** (a) DPV curves of Cu-MOF/Pd-500 at different concentration of BPA. (b) Calibration curve of current vs. concentration. Reproduced with permission [131], Copyright 2023, Elsevier. (c) DPV curves of UiO-66-NDC/GO at different concentrations of BPA. Reproduced with permission [16], Copyright 2023, Elsevier. (d) DPVs of CeO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub>@CC with various concentration of BPA. (e) Calibration curve of BPA. Reproduced with permission [135], Copyright 2023, Elsevier. (f) DPV curves of CMOF-MIPIL at different concentrations of BPA. Reproduced with permission [136], Copyright 2021, Elsevier.

performance. Wang et al. synthesized Ce-MOF-ERGO composites to develop an electrochemical BPA sensor. The Ce-MOF-ERGO/GCE displayed an impressive BPA oxidation reaction compared to bare GCE and Ce-MOF/GCE. The findings were ascribed to the enhanced conductivity, expansive surface area, and abundant active sites of the improved hybrid composite. The experimental results demonstrated high sensitivity and a LOD of  $1.9 \times 10^{-3} \mu\text{M}$ , with a wide linear range of  $3 \times 10^{-3} \mu\text{M}$  to  $10 \mu\text{M}$  [134]. Similarly, Naik et al. synthesized UiO-66-NDC/GO composites to improve BPA recognition capabilities. According to DPV analysis, as presented in Fig. 11c, the oxidation peak current consistently increased as the concentration of BPA increased. The sensor demonstrated remarkable results in detecting BPA, showing both outstanding sensitivity and selectivity. The modified sensor reached a LOD of  $0.025 \mu\text{M}$ , with a linear concentration range of  $10\text{--}70 \mu\text{M}$  [16]. MOF-derived  $\text{CeO}_2/\text{Co}_3\text{O}_4\text{-Fe}_2\text{O}_3$  composites were synthesized via a hydrothermal process, and Fe was added to enhance the material's BPA sensing capabilities. The  $\text{CeO}_2/\text{Co}_3\text{O}_4$ @CC electrode exhibits a specific electrochemical reaction to BPA. The electrochemical response of  $\text{CeO}_2/\text{Co}_3\text{O}_4\text{-Fe}_2\text{O}_3$ @CC was greatly enhanced after being modified by Fe, suggesting that Fe modification played a crucial role in increasing the redox activity of the electrodes. Fig. 11d and e illustrate the BPA sensing characteristics, showing a progressively rising peak current of DPV as the BPA content increased [135]. For the sensitive identification of bisphenol A, a unique composite of conductive MOF and molecularly imprinted poly (ionic liquid) (CMOFMIPIL) was constructed. The DPV analysis shows that the peak current rose gradually as the BPA content increased, and the peak currents from  $5 \times 10^{-3}$  to  $5.0 \mu\text{M}$  showed a strong linear dependency on BPA concentrations (Fig. 11f) [136].

Surfactants have been extensively utilized in electroanalytical chemistry to modify the electrode surface, with the aim of improving the adsorption of analytes and the rate of electron transfer. Zhang et al. reported a highly sensitive sensor for detecting BPA by modifying a hierarchical Ce-MOF with CTAB. The designed sensor has excellent sensitivity with a LOD of  $2 \times 10^{-3} \mu\text{M}$ . The BPA sensing mechanism was studied to understand the electrode surface's adsorption and oxidation processes (Fig. 12) [137]. The electro-oxidation of BPA involves a two-electron and two-proton process, which is consistent with previous reported works [138–140]. The process starts with BPA molecules adsorbing onto the MOF-modified electrode. When an appropriate voltage is supplied, BPA oxidized electrochemically. During the oxidation process, BPA loses two electrons and two protons, resulting in the formation of an oxidized product. The reverse reaction restores the oxidized BPA to its initial state by gaining two electrons and two protons. The transfer of electrons during the oxidation and reduction reactions produces an electric signal, which can be analyzed and correlated with concentration of BPA.

Plasticizers such as phthalates are a class of chemicals that consist of dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid. Phthalates have a high propensity to migrate from the final product and contaminate the surrounding environment, giving rise to substantial health and ecological apprehensions [141]. Exposure of humans to phthalates has been linked to several ailments, particularly reproductive abnormalities, developmental malformations and cancer [3]. Therefore, it is significant to develop a device to precise detection of phthalates.

MOFs provide a flexible and efficient platform for detecting phthalates due to their adjustable structure and reactive sites. Using MOFs as carriers for aptamers could greatly improve the efficiency of electrochemical sensors in detecting phthalates. Aptamers are concise, individual strands of DNA or RNA that possess the ability to selectively attach to certain targets, such as phthalates, with a strong attraction. Liu et al. developed a sensitive sensor for phthalate recognition using MOFs as a carrier for the aptamer. The impact of introducing phthalate acid esters (PAEs) into the  $\text{NH}_2\text{-MIL-88(Fe)/Apt1-Hg}^{2+}\text{-Apt2}$  solution on its electrochemical property was investigated (Fig. 13a). After adding PAEs to the solution, the results show a significant decrease in current response and there is a good linear relationship between the current and PAEs concentration, indicating the sensor's excellent sensitivity and reliability [142]. In another study, DEHP/MCH/Apt/AuNPs/CuMoF/PANI-MWCNTs were used as electrode materials to detect di(2-ethylhexyl) phthalate (DEHP). The sensor displayed notable stability and exceptional repeatability, with a broad linear range ( $2.56 \times 10^{-4}\text{--}256 \mu\text{M}$ ) and a low detection limit ( $7.68 \times 10^{-5} \mu\text{M}$ ) [143]. MOF-based heterostructures have remarkable sensing capabilities due to their unique combination of massive surface area, tunable porosity and functional diversity. Furthermore, the heterostructure's development allows for synergistic interactions between various components, increases stability, and improves charge transfer. Inspired by this, Yang et al. fabricated a new heterostructure hybrid composite ( $\text{NH}_2\text{-UiO-66/TpPa-1-COF}$ ) that combines MOF and covalent frameworks (COF) for the highly sensitive and selective measurement of dibutyl phthalate. Under ideal circumstances, the sensor's detection range was a broad from  $1.0 \times 10^{-4}$  to  $100 \mu\text{M}$ , with a LOD of  $3.0 \times 10^{-5} \mu\text{M}$  [144]. Currently, the molecular imprinting strategy is being extensively utilized to improve the sensor's performance. Molecularly imprinted polymer (MIP) has significant benefits, such as exceptional selectivity, strong stability, simple production and environmental compatibility, making it an excellent choice for identifying target chemicals [145,146]. Considering the above advantages, Yu et al. reported a sensor using molecularly imprinted polymer (MIP)-aptamer [DBP]/ $\text{Cu}_3(\text{BTC})_2/\text{Cu}_2\text{O/ITO}$  to detect dibutyl phthalate. Higher concentrations of DBP resulted in a reduction in the photocurrent (Fig. 13b). This suggests that a large number of DBP molecules were captured by MIP-Aptamer[DBP]/

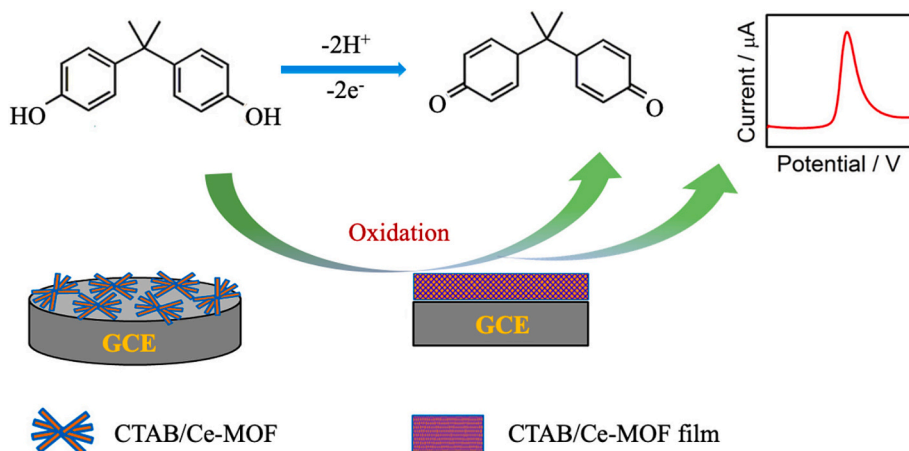


Fig. 12. BPA sensing mechanism. Reproduced with permission [137], Copyright 2018, Elsevier.

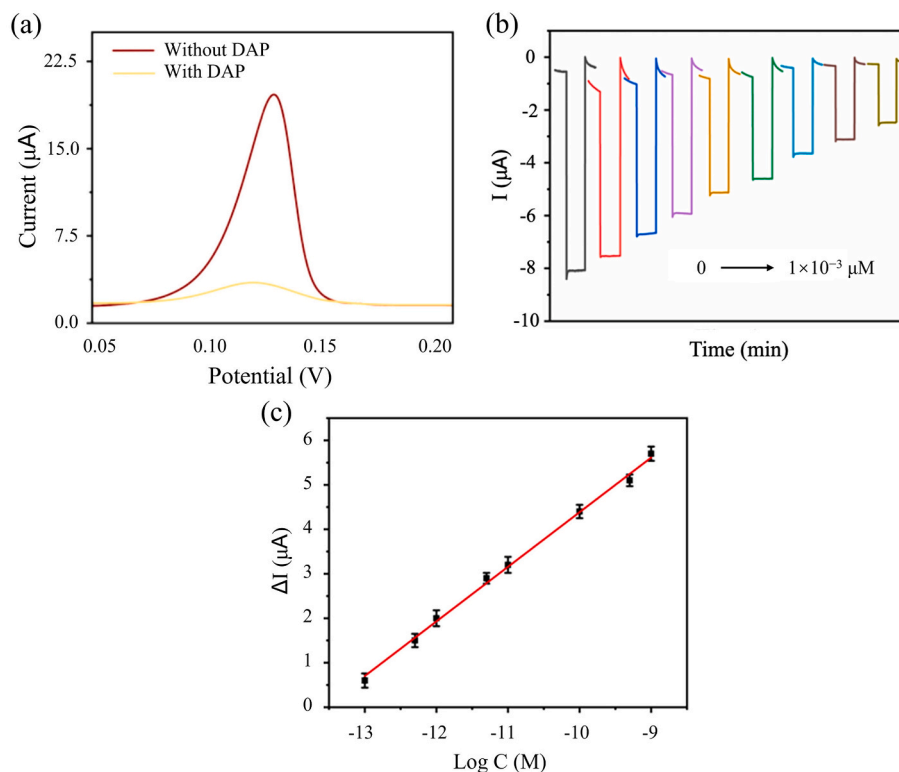


**Fig. 13.** (a) DPV current response with and without addition of DAP. Reproduced with permission [142], Copyright 2024, Elsevier. (b) Photocurrent responses of as-prepared sample with various concentrations of DBP. (c) The calibration curve between the current vs. concentration of DBP. Reproduced with permission [147], Copyright 2023, Elsevier.

Cu<sub>3</sub>(BTC)<sub>2</sub>/Cu<sub>2</sub>O/ITO, hence impeding the transfer of charges. The calibration curve demonstrates a strong linear correlation between current and concentration (Fig. 13c). The constructed sensor

demonstrated a linear range from 1 × 10<sup>-7</sup> to 1 × 10<sup>-3</sup> μM, with an exceptionally LOD of 3.5 × 10<sup>-8</sup> μM [147]. The phthalate oxidation process involves the transfer of electrons from the phthalate molecules,

**Table 2**

MOFs-based electrochemical sensors for the detection of pesticides.

| Modified electrodes                                                            | Methods     | Electrolyte | Pesticides       | Linear range (μM)                                | LOD (μM)                 | Ref   |
|--------------------------------------------------------------------------------|-------------|-------------|------------------|--------------------------------------------------|--------------------------|-------|
| Zr-BDC-rGO                                                                     | SWV         | PBS         | Methyl parathion | 3.8 × 10 <sup>-3</sup> –11.4                     | 1.9 × 10 <sup>-3</sup>   | [163] |
| CCM/UiO-66                                                                     | DPV         | PBS         | Methyl parathion | 7.6 × 10 <sup>-2</sup> –76                       | 3.72 × 10 <sup>-3</sup>  | [164] |
| UiO-66/KB-CNTs                                                                 | DPV         | PBS         | Methyl parathion | 5 × 10 <sup>-3</sup> –12                         | 1.53 × 10 <sup>-3</sup>  | [168] |
| Fe <sub>3</sub> O <sub>4</sub> /C-dots@Ag-MOFs                                 | DPV         | PBS         | Methyl parathion | 5 × 10 <sup>-5</sup> –0.02                       | 1.16 × 10 <sup>-5</sup>  | [170] |
| ACHe/NF-Ni-doped Co/CoO/NC-CPE                                                 | DPV         | PBS         | Methyl parathion | 1.9 × 10 <sup>-5</sup> –0.19                     | 6.84 × 10 <sup>-6</sup>  | [171] |
| UiO-66/NPC/ERGO                                                                | SWV         | PBS         | Methyl parathion | 7.6 × 10 <sup>-3</sup> –15.2                     | 1.5 × 10 <sup>-3</sup>   | [172] |
| Pt NPs/UiO-66-NH <sub>2</sub> /MWCNTs                                          | DPV         | PBS         | Methyl parathion | 0.11–227.95                                      | 0.026                    | [173] |
| CRL@MAC-ZIF-8/CS                                                               | CV          | PBS         | Methyl parathion | 0.5–114                                          | 0.06                     | [174] |
| CdS-Sm-BDC-g-C <sub>3</sub> N <sub>4</sub>                                     | DPV         | PBS         | Malathion        | 0.03–0.15                                        | 7.4 × 10 <sup>-3</sup>   | [177] |
| Cu-Co MOGs                                                                     | DPV         | PBS         | Malathion        | 5 × 10 <sup>-7</sup> –5                          | 3 × 10 <sup>-7</sup>     | [178] |
| BTCA-P-Cu-CP/CPE                                                               | Amperometry | PBS         | Malathion        | 6 × 10 <sup>-4</sup> –0.024                      | 1.7 × 10 <sup>-4</sup>   | [179] |
| MIL-88B(Fe)/SPCE                                                               | SWV         | PBS         | Malathion        | 1 × 10 <sup>-6</sup> –1                          | 7.9 × 10 <sup>-7</sup>   | [180] |
| ZrO <sub>2</sub> @Fe <sub>2</sub> O <sub>3</sub> -C                            | DPV         | PBS         | Malathion        | 3.07 × 10 <sup>-8</sup> –3.07 × 10 <sup>-2</sup> | 3.9 × 10 <sup>-9</sup>   | [182] |
| Cu <sub>2</sub> O@mC                                                           | DPV         | PBS         | Glyphosate       | 10 <sup>-9</sup> –0.1                            | 7.69 × 10 <sup>-10</sup> | [187] |
| Cu-BTC MOF                                                                     | DPV         | PBS         | Glyphosate       | 1.0 × 10 <sup>-6</sup> –1.0 × 10 <sup>-3</sup>   | 1.4 × 10 <sup>-7</sup>   | [188] |
| Co-H <sub>2</sub> ABDC                                                         | DPV         | PBS         | Glyphosate       | 1 × 10 <sup>-3</sup> –100                        | 2.3 × 10 <sup>-4</sup>   | [189] |
| Au-MOF-MIP                                                                     | LSV         | PBS         | Glyphosate       | 5.92 × 10 <sup>-9</sup> –5.92 × 10 <sup>-3</sup> | 4.73 × 10 <sup>-9</sup>  | [190] |
| Ti <sub>3</sub> C <sub>2</sub> Tx/Cu-BTC                                       | DPV         | PBS         | Glyphosate       | 10 <sup>-7</sup> –1                              | 2.6 × 10 <sup>-8</sup>   | [191] |
| CuCo <sub>2</sub> O <sub>4</sub> /H-gC <sub>3</sub> N <sub>4</sub> /3D-rGO/FTO | SWV         | PBS         | Glyphosate       | 1 × 10 <sup>-5</sup> –1.2 × 10 <sup>4</sup>      | 6.3 × 10 <sup>-7</sup>   | [192] |
| Cu-TCPP/Au NPs/CP                                                              | DPV         | PBS         | Glyphosate       | 0.2–120                                          | 0.03                     | [193] |
| Fe-PyDA/CNF                                                                    | DPV         | PBS         | Chlorpyrifos     | 1–150                                            | 0.0151                   | [196] |
| ACHe/MOF/μE                                                                    | DPV         | PBS         | Chlorpyrifos     | 2.85 × 10 <sup>-5</sup> –2.85 × 10 <sup>-4</sup> | 1.71 × 10 <sup>-5</sup>  | [197] |
| ACHe/Z1200/EμPAD                                                               | EIS         | PBS         | Chlorpyrifos     | 2.85 × 10 <sup>-5</sup> –2.85 × 10 <sup>-3</sup> | 8.56 × 10 <sup>-6</sup>  | [198] |
| MnFe-MOF/SPE                                                                   | SWV         | PBS         | Chlorpyrifos     | 1 × 10 <sup>-3</sup> –0.1                        | 8.52 × 10 <sup>-4</sup>  | [199] |
| TGO@UiO-66/GCE                                                                 | SWV         | BRB         | Chlorpyrifos     | 5 × 10 <sup>-3</sup> –0.3                        | 1 × 10 <sup>-3</sup>     | [200] |
| HKUST-1@MIP/GEC                                                                | DPV         | PBS         | Chlorpyrifos     | 0.01–1                                           | 3 × 10 <sup>-3</sup>     | [201] |

which is facilitated by the applied voltage. The procedure involves the adsorption of phthalate molecules onto the electrode surface, followed by their oxidation. For instance, di(2-ethylhexyl) phthalate (DEHP) undergoes oxidation, resulting in the loss of electrons and the formation of  $\text{DEHP}^+$ . MOF, or molecularly imprinted polymer-modified electrode increases the connection between the phthalate molecules and the electrode, hence enhancing the accuracy and specificity of the detection [142,148]. Further research has been carried out to detect phthalate, employing several MOF-based materials such as  $\text{NH}_2\text{-Zr-MOF/GDY}$  [149],  $\text{Cu}_3(\text{BTC})_2/\text{Cu}_2\text{O}$  [150]. These materials have demonstrated their efficacy during phthalate detection.

#### 4.2. Pesticides

Several modified electrochemical sensors have been reported for the identification of pesticides [19,157–161]. However, the accurate detection of pesticides remains a significant difficulty due to the limited surface area, low conductivity and poor selectivity of modified electrochemical sensors. Recently, MOFs have been using extensively due to their exceptional sensing capabilities in pesticide identification. This section broadly investigates the electrochemical sensor based on MOF for the recognition of pesticides. Table 2 provides a brief summary of the electrochemical characteristics of recently published sensors based on MOF used for detecting several pesticides.

Methyl parathion (MP) is a common organophosphorus pesticide (OPP), and even at low concentrations, it has high toxicity, bio-accumulates, and harms the environment and health over time. Methyl parathion damages the seminiferous tubules, which lowers the concentration of sperm [162]. For these reasons, quantitative MP detection

is crucial. A nanocomposite consisting of a zirconium-based MOF material with terephthalic acid as a ligand (Zr-BDC) and reduced graphene oxide (rGO) was suggested to be used for the detection of MP. This nanocomposite, referred to as Zr-BDC-rGO, has a high sensitivity to MP. The Zr-OH groups in the Zr-BDC-rGO nanocomposite have a strong affinity for phosphate groups, allowing the ability to selectively recognize MP and have a greater adsorption capability. With the presence of methyl parathion, the sensor displayed a broad linear range of  $3.8 \times 10^{-3}$ – $11.4 \mu\text{M}$  and a LOD of  $1.9 \times 10^{-3} \mu\text{M}$  [163]. Zirconium boosts the properties of MOFs by increasing the surface area and active sites, hence improving sensitivity for MP detection. By taking advantage of zirconium and terephthalic acid ( $\text{H}_2\text{BDC}$ ), CCM/UiO-66 materials were developed for MP detection. Fig. 14a displayed distinct DPV responses, and the peak currents exhibited an upward trend as the volume of MP rose. Within the concentration range of  $7.6 \times 10^{-2}$ – $76 \mu\text{M}$ , a clear linear correlation was observed between the peak current and the concentration of MP (Fig. 14b). The results exhibited excellent sensitivity and a LOD of  $3.72 \times 10^{-3} \mu\text{M}$ , with a broad linear range of  $7.6 \times 10^{-2}$  to  $76 \mu\text{M}$ . The sensing mechanism of MP was studied (Fig. 14c) to understand the electrode surface oxidation reaction [164]. During the first reduction scan, the irreversible reduction of the nitro group to the hydroxylamine group ( $-\text{NHOH}$ ) was observed. Then the hydroxylamine group was oxidizing to produce the nitroso group ( $-\text{NO}$ ). The parent hydroxylamine group was obtained by converting the nitroso group during the second scan. The lowering of the nitro group was also responsible for a rapid decline in signal intensity. The decrease in active surface area of the electrode resulting from the adsorption of MP molecule. This is due to the MP molecule's ability to either cover or block the active sites in the electrode's surface area [165–167]. Furthermore, MOF's chemical bonds

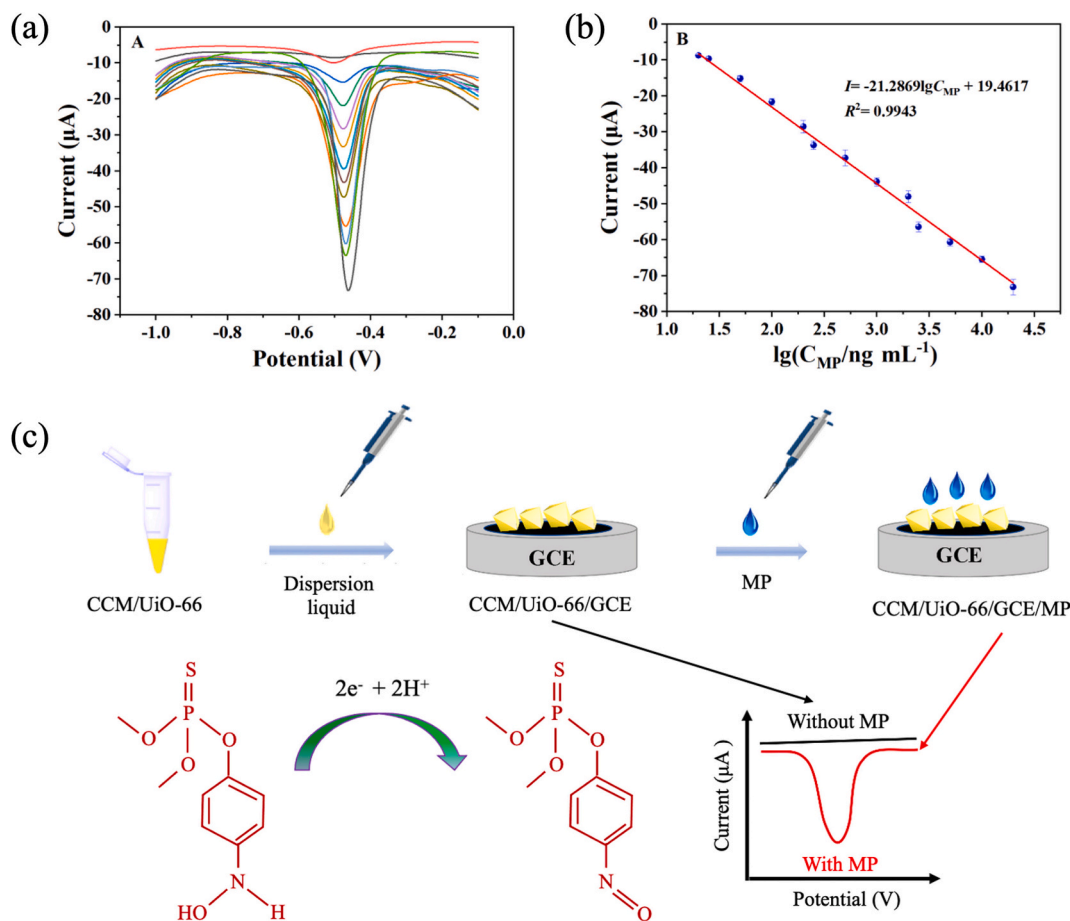


**Fig. 14.** (a) DPV curves of CCM/UiO-66 at different concentrations of MP. (b) Calibration curve between the current and the MP concentrations. (c) Schematic illustration of MP sensing mechanism. Reproduced with permission [164], Copyright 2023, Elsevier.

demonstrated a robust interaction with MP [168]. The MOF's large surface areas and regular channels allow for better and more selective MP adsorption while also facilitating the diffusion and transport of PM molecules [169].

Recently, molecularly imprinted polymer (MIP) coatings on the surface of MOF have gained significant attention for detecting MP. For example, using methyl parathion (MP) as a template molecule, a MIP was applied to the surface of the  $\text{Fe}_3\text{O}_4/\text{C-dots}@ \text{Ag-MOFs}$ , significantly enhancing the chip's MP selectivity [170]. The integration of MOFs with other materials to create hybrid composites has emerged as a prominent field of study. This approach aims to increase the surface area and active sites, thereby promoting the interaction with MP and leading to enhanced sensitivity. Thus, researchers have fabricated several MOF-based hybrid composites, including AChE/NF-Ni-doped Co/CoO/NC-CPE [171], UiO-66/KB-CNTs [168], UiO-66/NPC/ERGO [172], Pt NPs/UiO-66- $\text{NH}_2$ /MWCNTs [173] and CRL@MAC-ZIF-8/CS [174]. These composites have substantial sensing capability for methyl parathion as compared to single-phase GCE.

An organophosphate pesticide named malathion is frequently applied in agricultural sectors. Malathion is quickly and efficiently absorbed by humans through a number of pathways, including the gastrointestinal system, skin, lungs and mucous membranes. Malathion, a neurotoxic substance, inhibits acetylcholinesterase function, causing symptoms associated with cholinergic syndrome. Malathion exposure also results in a variety of symptoms, including headaches, nausea, tightness in the chest, and unconsciousness [175,176]. Therefore, it is crucial to functionalize MOF for improving sensing capability in order to detect malathion residue rapidly and accurately. Advanced functional materials, such as g- $\text{C}_3\text{N}_4$  and semiconductor CdS metal-based MOF were constructed for the recognition of malathion. Compared to other materials, the CdS-SmBDC-CN5 composite had a smaller Nyquist radius (Fig. 15a), indicating that the material promotes effective charge transfer, which is important for detecting malathion. The sensor

demonstrated outstanding sensitivity of  $25 \mu\text{A}\mu\text{M}^{-1}$  and a low detection limit of  $7.4 \times 10^{-3} \mu\text{M}$ . MOF, have demonstrated remarkable sensing performance towards malathion [177]. The thio-compounds have a strong affinity for Cu or Cu-containing substances; thus, the thio-compounds may inhibit the redox processes of the copper or copper-containing compounds, offering an effective strategy for the identification of malathion. Inspired by this, He et al. constructed phytic acid-based Cu-Co metal-organic composite for the development of new malathion electrochemical sensor. Besides, they studied the morphological effect on the sensing performance. The as-prepared PA-Co, PA-Cu and PA-Cu-Co materials possess irregular particles, a crosslinked nanoporous network structure and a cross-network structure with a rough surface and multiple channels, respectively as shown in Fig. 15(b-d). The presence of multiple channels and rough surfaces facilitates the dispersion of the electrolyte solution, as well as the subsequent interaction between the PA-Cu-Co composite and malathion. This is due to the increased contact area, which significantly enhances the effectiveness of malathion detection. From the DPV analysis (Fig. 15e), when the malathion concentration increases in the PBS solution, then the current response decreases, suggesting that malathion has the capacity to be adsorbed onto PA-Cu-Co composites, hence impeding the electron transfer capability between PA-Cu-Co composites and the electrode [178]. As reported, several MOF-based composite, such as BTCA-P-Cu-CP/CPE [179], MIL-88B(Fe)/SPCE [180],  $\text{H}_2\text{SO}_4$ -doped  $\text{NH}_2$ -Al-MOF [181] and  $\text{ZrO}_2@ \text{Fe}_2\text{O}_3\text{-C}$  [182] have proven to be efficient for the electrochemical identification of malathion. MOF-based electrochemical sensors can identify malathion through oxidation, hydrolysis and adsorption processes. Initially, the modified electrode adsorbs malathion molecules. After that, malathion hydrolyzes to produce a more electrochemically active compound called malaoxon [183,184]. Malaoxon oxidation produces a current that reflects the levels of malathion, and the current is proportional to its concentration. Furthermore, the MOF improves conductivity to speed up electron transmission,

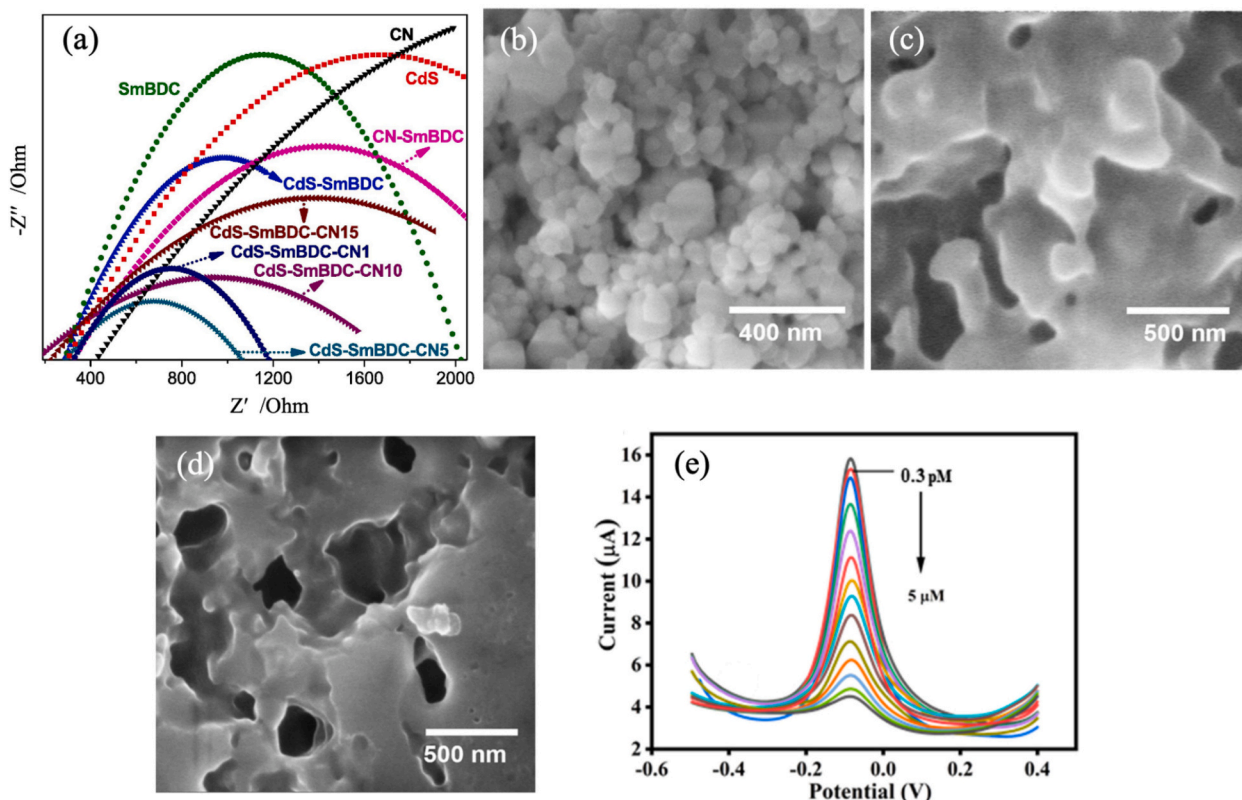


**Fig. 15.** (a) EIS curves of as-prepared samples. Reproduced with permission [177], Copyright 2024, Elsevier. SEM images of (b) PA-Co. (c) PA-Cu. (d) PA-Cu-Co composite. (e) DPV curves of PA-Cu-Co at different malathion concentrations. Reproduced with permission [178], Copyright 2023, Elsevier.

which provides a strong oxidation reaction towards malathion and makes the sensor extremely sensitive [182,185].

Glyphosate, a nonselective herbicide, has the potential to cause loss of mitochondrial transmembrane potential and oxidative stress in the liver and brain, which can lead to neurodegenerative illnesses like Parkinson's disease [186]. Consequently, it is essential to analysis the amount of glyphosate in food and biological samples. Due to the non-electroactive properties of glyphosate, it is challenging to identify it at a low concentration level. Researchers have conducted several studies to create an electrochemical sensor based on MOFs for accurate glyphosate identification. Gu et al. fabricated a CuOx@mC composite using benzene-1,3,5-tricarboxylic acid as an organic ligand to construct an electrochemical glyphosate sensor. Fig. 16a illustrates the formation of CuOx@mC composites and their glyphosate sensing mechanism. They observed an interesting phenomenon that the Cu-glyphosate combination prevents electron transport because copper ions can coordinate with glyphosate, which lowers peak current. The electrochemical response signal is recorded using the DPV technique, and when the concentration of glyphosate increases in the PBS solution, the peak current decreases gradually (Fig. 16b). The CuOx@mC composite exhibited superior electrochemical sensitivity and a LOD ( $7.69 \times 10^{-10}$   $\mu$ M) towards glyphosate compared to HKUST-1, perhaps due to its mesoporous structure and enhanced conductivity [187]. Cao et al. constructed an electrochemical sensor using Cu-BTC MOF to identify non-electroactive glyphosate. Strong oxidation-reduction reactions were seen by the Cu-BTC/GCE during the glyphosate detection process. It may be the reason of the glyphosate's great affinity for  $\text{Cu}^{2+}$  exhibited by its

carboxyl and amino groups upon combination, allowing the glyphosate to be adsorbed on the metal core of Cu-BTC frameworks. By taking advantages of Cu-BTC MOF such as large surface area, increased reactive site, and enhanced adsorption capabilities, the sensor shows excellent sensitivity and an ultralow detection limit ( $1.4 \times 10^{-7}$   $\mu$ M), with a wide linear range ( $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-3}$   $\mu$ M and  $1.0 \times 10^{-3}$  to  $10$   $\mu$ M) [188]. In another study, a cobalt metal organic framework (Co-H<sub>2</sub>ABDC MOF) was prepared using 2-aminoterephthalic acid (2-ABDC) as an organic ligand for the construction of electrochemical glyphosate sensor. According to the SEM examination, the fabricated Co-H<sub>2</sub>ABDC MOF has thick rods and hexagonal-like structured flakes with prismatic edges (Fig. 16c). The sensor demonstrated excellent glyphosate detection capabilities in a wide range ( $1 \times 10^{-3}$  to  $100$   $\mu$ M) with a LOD of  $2.3 \times 10^{-4}$   $\mu$ M (Fig. 16d and e) [189]. Researchers have conducted several studies using MOF-based electrodes to increase the efficacy of glyphosate sensing [190–193]. During the glyphosate oxidation process, the oxidation-reduction reaction of MOF generates a responsive current. Phosphonate, amino and carboxylate groups in glyphosate exhibit significant attraction for  $\text{Cu}^{2+}$  ions in the Cu-BTC when glyphosate is introduced. The Cu-BTC MOF's metal center readily adsorbed the glyphosate, forming a glyphosate  $\text{Cu}^{2+}$  complex that prevents electron transfer and decreases the response current [188,189,191]. The difference in response current before and after the reaction is used to calculate the glyphosate concentration.

Chlorpyrifos is a widely used pesticide that has been linked to serious health hazards for people. Exposure can cause neurotoxicity, cognitive impairments and developmental delays, especially in youngsters

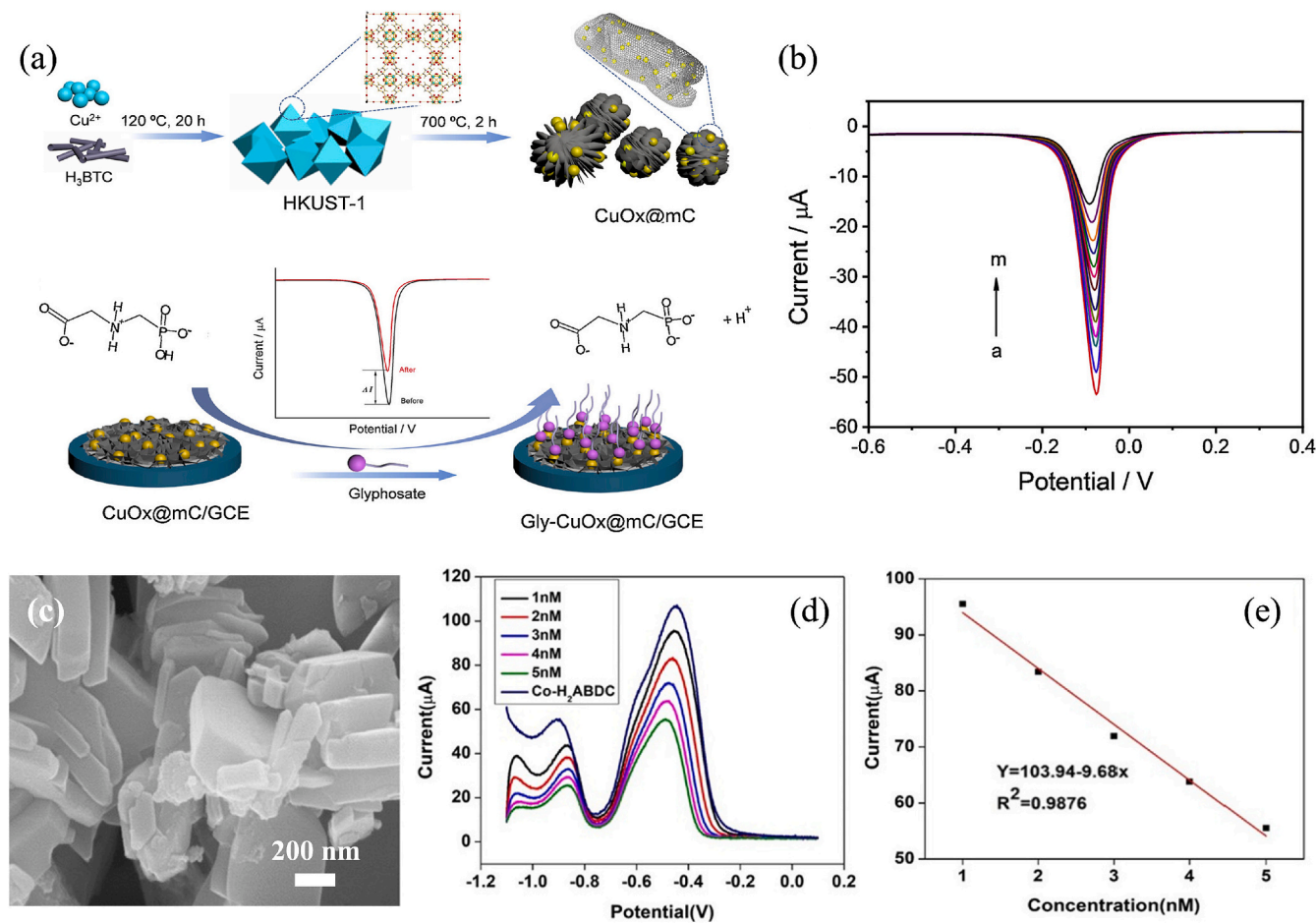


**Fig. 16.** (a) Illustration of the growth of CuOx@mC and the sensing mechanism of glyphosate. (b) DPV curves of CuOx@mC composite at different concentrations glyphosate. Reproduced with permission [187], Copyright 2020, Elsevier. (c) SEM image of Co-H<sub>2</sub>ABDC MOF. (d) DPV curves of Co-H<sub>2</sub>ABDC at different concentration of glyphosate. (e) Linear calibration curve between the current and the concentration. Reproduced with permission [189], Copyright 2022, Elsevier.

[194,195]. Several studies have been carried out to accurately detect chlorpyrifos at low concentration levels. For example, a reliable chlorpyrifos detection method was developed using an electrochemical sensor utilizing iron MOFs. The Fe-PyDA/CNF hybrid composite has a very porous structure and a large surface area that facilitates the movement of analyte molecules and enhances the interaction with the MOF matrix's redox-active metal sites, thereby improving the oxidation reaction. The Fe-PyDA/CNF demonstrated a wide linear range from 1 to 150  $\mu\text{M}$ , as well as a low limit of detection of 0.0151  $\mu\text{M}$  [196]. The enzyme and MOF combination creates a unique functional material that serves as a reliable substrate for both qualitative and quantitative pesticide measurement. Inspired by this, Nagabooshanam et al. designed a sensitive sensor for the recognition of chlorpyrifos, utilizing acetylcholinesterase (AChE) enzyme and MOF as a functional material. The AChE/MOF microelectrode exhibited excellent sensitivity ( $0.598 \mu\text{A}/\text{ng L}^{-1}/\text{mm}^2$ ) and a low detection limit ( $1.71 \times 10^{-5} \mu\text{M}$ ), with a linear range of  $2.85 \times 10^{-5}$ – $2.85 \times 10^{-4} \mu\text{M}$  [197]. Similarly, they developed the electrochemical micro paper analytical device (E $\mu$ PAD), which was made with conductive carbon ink and basic screen-printing techniques. MOFs offer superior sensitivity when detecting chlorpyrifos, whereas the AChE enzyme offers selectivity [198]. A bimetallic MnFe-MOF was designed by Janjani et al. by incorporating  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  metal centers into the MOF structure for the improvement of electrochemical chlorpyrifos sensor. The SEM image reveals that the as-prepared materials have an irregular shape with a rough surface due to the mismatched coordination with the ligand (Fig. 17a). From the XRD pattern as presented in Fig. 17b, no other impurity peaks were detected, indicating the high purity of MnFe-MOF. The irregular and porous structure of MnFe-MOF might offer a larger surface area for adsorption, which could be

beneficial in electroanalysis due to its abundance of active sites. Besides, the Mn(II) and Fe(III) ion pairs exhibit extraordinary synergism that promotes electron transport, which resulted in high activity for redox catalytic processes and the subsequent identification of chlorpyrifos. When the chlorpyrifos concentration increases in PBS solution, the current response increases gradually, and there is a good relationship between the current and concentration (Fig. 17c and d). The proposed sensor has a broad linear range of  $1 \times 10^{-3}$ – $0.1 \mu\text{M}$  and a LOD of  $8.52 \times 10^{-4} \mu\text{M}$  with high sensitivity and selectivity [199]. For further enhancement of the sensor's performance, MOF-based composites with conducting substrates like graphene oxide (GO) have been investigated. To simultaneously detect paraoxon and chlorpyrifos, a high sensitivity electrochemical sensor based on  $\text{TiO}_2$ -functionalized graphene oxide@UiO-66 (TGO@UiO-66) was designed. The sensor displayed low detection limits of  $1 \times 10^{-3} \mu\text{M}$  for chlorpyrifos, with the linear ranges of  $5 \times 10^{-3}$ – $0.3 \mu\text{M}$  [200]. In order to boost MOF's selectivity, Beig-moradi et al. used MOF as a substrate for the growth of MIPs on it. With a linear range of 0.01 to 1.00  $\mu\text{M}$  and a LOD of  $3 \times 10^{-3} \mu\text{M}$ , the HKUST-1@MIP/GEC electrode demonstrated good performance [201]. The MOF-modified electrode's large surface area and porous structure facilitate the initial adsorption of chlorpyrifos. Hydrolysis of chlorpyrifos results in the conversion of the P=S bond (thiono group) into a P=O bond (oxon form). This reaction results in the formation of 3,5,6-trichloro-2-pyridinol (TCP). Then the TCP is oxidized to a radical form, which may be identified electrochemically as shown in Fig. 17e [199]. The sensing mechanism for detecting chlorpyrifos was further studied in several literatures [202,203].

From Tables 1 and 2, it's notable that PBS electrolyte has been broadly applied for the detection of EDCs. The possible reason is that

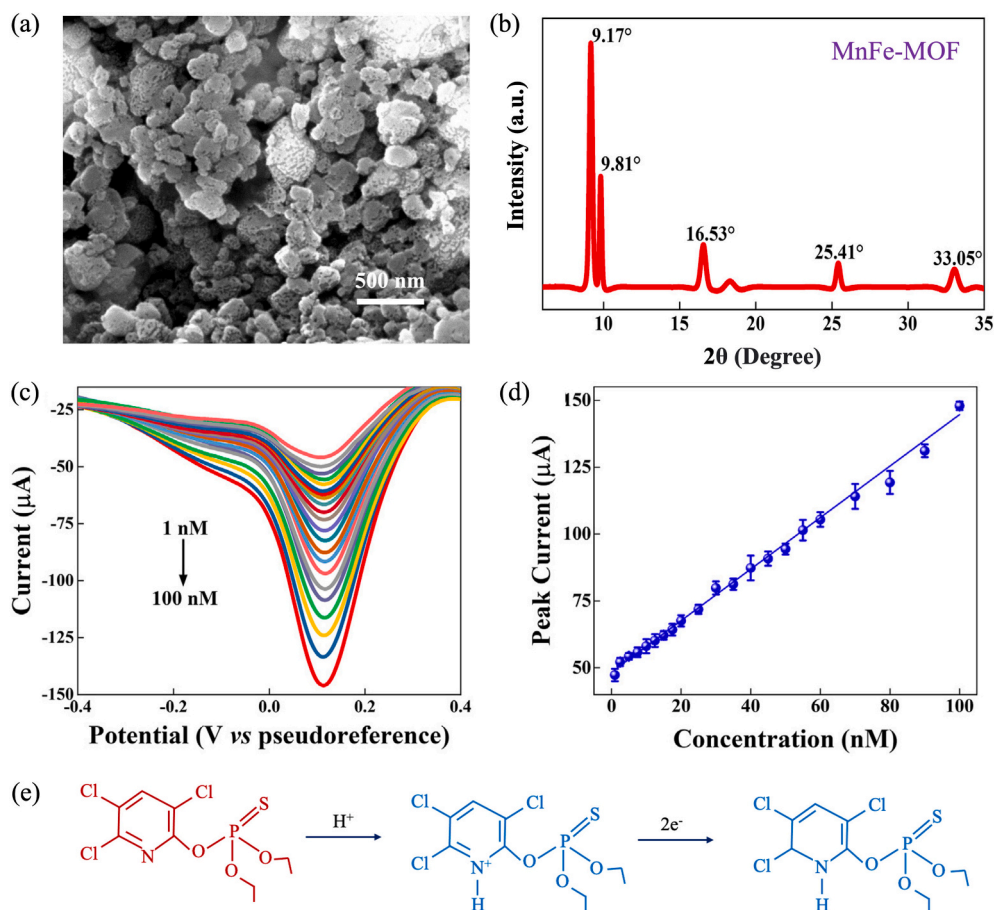


**Fig. 17.** (a) SEM image of MnFe-MOF. (b) XRD pattern of MnFe-MOF. (c) SWV curves of MnFe-MOF at different concentration of chlorpyrifos. (d) Linear calibration curve for chlorpyrifos. Reproduced with permission [199], Copyright 2022, Elsevier. (e) Mechanism for the electroreduction of chlorpyrifos.

PBS has the ability to simulate physiological and ecological environments and ensure steady pH and ionic conditions. However, several MOFs have stability and conductivity issues in PBS electrolyte. For example, the conductivity of Zr-based MOFs, specifically UiO-66 and UiO-66-NH<sub>2</sub>, in PBS is a matter of attention. These MOFs have poor conductivity in PBS due to their intrinsic structural and chemical properties [204,205]. Besides, cobalt-based MOFs exhibit poor electronic conductivity or redox activity due to their simple organic linkers [206]. Similarly, HKUST-1 exhibits low electrical conductivity attributable to its inherent structural and electronic characteristics [207]. The coordination between copper ions and organic linkers is extremely confined, limiting delocalized electron transport throughout the framework. In aqueous conditions, the framework's partial hydrolysis can weaken the structure, further impeding charge mobility. The absence of inherent charge carriers (free electrons or ions) in MOFs also leads to limited electrical conductivity. The absence of redox-active centers in aqueous solutions of PBS further impedes electron transport in the course of electrochemical processes. The crystalline nature of these MOFs and their dense structure hinder charge transport, while the polar environment of PBS does not interact sufficiently to improve conductivity. Most of the articles described that MOFs were utilized. However, some of them may be degraded in buffer solutions due to the susceptibility of their metal-ligand coordination bonds to hydrolysis and competitive interactions [204,205]. The actual active material may not be MOF but rather MOF-derived compounds. Comprehensive analyses need to be conducted to investigate the structure of the materials after the detection process. To increase the conductivity in PBS electrolyte, hybridization with conductive materials such as rGO, CNTs, or metal nanoparticles and hydrophobic surface treatment can be utilized [17,208].

The morphological evolution of MOFs during electrochemical analysis has attracted considerable interest in recent research owing to the associated redox processes [209]. Redox processes can modify the oxidation states of metal centers, resulting in either structural distortions or alterations in the coordination environment [210]. Likewise, organic linkers may experience oxidative or reductive degradation, impacting the stability of the framework. Research indicates that MOFs containing transition metal nodes, such as cobalt or copper, may display redox activity that can either improve or impair their efficacy, contingent upon the electrolyte conditions and the applied potential [211]. Furthermore, interactions with analytes or electrolytes may provoke ligand exchange or framework disintegration. Advanced characterization methods, such as in situ XRD, Raman spectroscopy, and cyclic voltammetry, have been employed to observe these alterations, providing insights into the dynamic behavior of MOFs under electrochemical circumstances. Comprehending these transitions is essential for the design of MOFs with enhanced stability and utility [212].

The electrochemical analysis of EDCs relies on the interaction between the analyte and an electroactive surface, often facilitated by electron transfer processes [140]. This method employs the redox activity of EDCs or their ability to modify the properties of the electrode surface. When an appropriate voltage is applied, the electroactive species experience oxidation or reduction, producing a current that correlates with their concentration. Principal detection techniques encompass cyclic voltammetry (CV), differential pulse voltammetry (DPV), and amperometry, each providing distinct benefits in sensitivity, resolution, and ease of operation. The method's efficacy is attributed to its capacity to identify trace concentrations of EDCs in intricate matrices.

## 5. Conclusions

In this review, we have summarized and illustrated the functionalization strategy of MOF as well as the recent advancements in MOF-based electrochemical sensors for environmental EDCs analysis. Recently, endocrine-disrupting chemicals (EDCs) have become a global concern due to their serious and extensive impacts on the health of both wildlife

and humans. To ensure environmental safety as well as public health, extensive research is significant to develop suitable materials, effective procedures, and precise sensors for the detection of EDCs. MOFs provide considerable advantages as electrodes material for the analysis of EDCs owing to their distinctive structural and chemical characteristics. Their extensive surface area and adjustable porosity provide effective adsorption and pre-concentration of EDCs, hence improving detection sensitivity [137,213]. Due to its unique structural properties, MOF can be functionalized to increase BPA sensing capabilities by incorporating functional groups, guest molecules, and component replacement using direct or post-synthetic modification [156]. Despite significant advancements in utilizing MOFs for electrochemical applications, there are some unresolved concerns and obstacles when it comes to employing MOFs for electrochemical detection of environmental EDCs. These concerns and obstacles are as follows:

- (1) Despite the advancement of various synthesis and modification procedures for MOFs, attaining precise control over morphology and uniformity of particle size for specific applications remains a challenge.
- (2) The majority of MOFs are insulators or semiconductors. Thus, the conductivity and reactivity of MOFs have become major challenges for the construction of high-performance electrochemical sensors.
- (3) Low chemical stability is a major concern since MOFs are prone to degrade upon exposure to water or aqueous electrolytes, resulting in the deterioration or dissociation of metal-ligand interactions. Poor stability leads to structural collapse, reduced porosity, and a less active surface area, thereby restricting the capacity to adsorb target analytes.
- (4) The low selectivity and insufficient anti-interference properties of some MOFs limit their use in the identification of real samples.
- (5) Many MOFs contain dangerous metals such as Pb, Co, and Cd, along with toxic ligands like pyrazole, which could potentially cause environmental safety issues.
- (6) Comprehending the sensing mechanisms of EDCs via MOFs is challenging because of their intricate interactions and structural heterogeneity.
- (7) The pore sizes of some MOFs, such as ZIF-8 (approx. 1.16 nm) and ZIF-67 (approx. 0.34 nm) [214,215], are often smaller than those in many EDC molecules (Ex. BPA and phthalate), potentially restricting the analytes' access to their interior porosity. This restriction renders the interior surface area ineffectual for the sensing system.
- (8) There is an insufficiency in the proper management of complex target analysis or modalities. The real sample may exhibit multiple EDCs, necessitating the fabrication of new MOF-based sensor with extensive sensing capabilities to identify multiple targets effectively.

Future research should focus on exploiting the beneficial properties of MOFs as well as addressing their limitations. The subsequent aspects may be addressed to improve the analytical effectiveness of MOFs in developing high-performance electrochemical sensors: (1) The porous structure and large surface area of MOFs are essential for sensing applications. Further research is needed for the advancement of synthetic techniques to generate regulated MOFs with desired structures, pore sizes and properties. To enable precise customization of MOF properties, several methodologies such as isoreticular expansion, topology-guided design, post-synthetic deprotection, and reverse microemulsion necessitate further exploration [216]. (2) The electrical conductivity of MOFs can be enhanced by including electroactive guest species that promote electron transport. The incorporation of metal ions and/or metal nanoparticles, carbon nanostructures, polymers, and other conductive materials may establish a channel for electron transport, hence enhancing conductivity [217]. Conjugated organic linkers, including

tetrathiafulvalene (TTF) and quinones, are essential for the delocalization of  $\pi$ -electrons and the enhancement of MOF's conductivity. 2D MOFs often exhibit superior conductivity compared to 3D MOFs, owing to their morphological and electrical properties, rendering them useful for sensing applications. Therefore, the selection of metals capable of forming 2D coordination networks is essential [208]. (3) The stability of MOF in water systems can be improved by increasing hydrophobic properties. The hydrophobic properties of MOFs can be increased by attaching hydrophobic groups to the linkers or by forming them around the metal nodes. The hydrophobic functional groups around the metal clusters are capable of protecting the weak coordination bonds against water molecule intrusion and improving the stability of the MOF in aqueous environments [17]. Furthermore, the chemical stability of MOFs can be enhanced by applying a polymer coating to their surface [218]. (4) The integration of functional groups into MOF structures can improve the selectivity and interference properties of the sensors [219]. Thus, the selection of functional groups is essential for attaining the required properties for analyte detection. Post-synthetic modification, which involves adding different functional groups to the MOF's frameworks, can produce MOF materials that exhibit precise molecule recognition when they correctly include the relevant functional groups. This strategy has expanded the application range of MOFs. (5) The eco-friendly synthesis of MOFs can be enhanced by using low-toxicity materials. The bioactive chemicals, as ligands and core metal ions such as Zn, Fe, Zr, Ti, and Ca, exhibit good biocompatibility and comparatively low toxicity as metal nodes. (6) A thorough understanding of the reaction mechanism between MOFs and analytes is critical for designing MOFs and their derivatives. This entails clarifying the sensing mechanisms, such as adsorption and oxidation processes, as well as adjusting the microstructure or morphology through material synthesis and functionalization. (7) To increase the pore size, several strategies may be employed: utilizing longer organic linkers to enhance the distance between metal nodes, thereby generating larger pores; modifying synthetic factors, including temperature, pH, and solvents, to optimize framework topology; implementing defect engineering; and conducting post-synthetic modifications [220]. Moreover, linker labilization is an effective strategy to improve the porosity and pore size of microporous MOFs [221]. (8) Research may focus on the development of electrode arrays with specialized functionalized regions or channels, each designed for a specific analyte, enabling the concurrent detection of multiple targets within a single device. The electrochemical sensor may integrate with machine learning technology to evaluate intricate samples and distinguish signals from multiple targets in continuously. Besides, the integration of the Internet of Things (IoT) and artificial intelligence (AI) into MOF-based electrochemical sensors might substantially improve their efficacy in the real-time monitoring of EDCs. Portable and visual luminescence sensing using MOFs has demonstrated impressive efficacy in detecting diverse analytes [222–224]. Therefore, smartphone-based electrochemical detection platforms could potentially enhance the detection capabilities of EDCs.

Overall, as a new class of porous crystalline materials, MOFs and their derivatives have gained considerable attention for the construction of advanced electrochemical sensors. However, the electrochemical EDC sensor based on MOFs is in its early stages of development and requires additional advancement to become a reliable and stable technology for cost-effective practical use in the future. The review is anticipated to yield valuable insights for the future advancement and extensive application of MOF-based sensors for EDC detection as well as several research disciplines.

## 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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## Data availability

Data will be made available on request.

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