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Review

A Review: Metal-Organic Frameworks Electrochemical Biosensors for Bioorganic Materials Detection

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Abstract- Metal-organic frameworks (MOFs) have become a highly promising porous material for the detection of cancer biomarkers due to their special characteristics, such as permanent porosity and tuneable pore size. Such advantages make MOFs well-suited for use in biosensing applications. In this review, a comprehensive overview of the use of MOFs in the electrochemical detection of bioorganic materials has been provided. We begin by discussing the adjustable surface areas and porosity of MOFs, which are crucial for their applicability in biosensing. The ability to control the porosity of MOFs allows for the efficient capture and detection of specific biomarkers. Furthermore, the presence of functional sites on MOF surfaces enhances their sensitivity and selectivity towards target molecules. In the next step, we investigated different biosensors for the detection of cancer biomarkers that have used MOF to improve their performance. These biosensors utilize the unique properties of MOFs to selectively bind and detect specific biomarkers associated with different types of cancer. The high sensitivity and selectivity of these biosensors make them promising tools for early cancer diagnosis and monitoring.

Keywords- Metal-organic frameworks; Electrochemical sensor; Bioorganic materials; Biosensors; Nanomaterial

1. INTRODUCTION

Metal-organic frameworks (MOFs) are a captivating and groundbreaking category of hybrid materials that combine organic and inorganic constituents [1-3]. These substances are distinguished by their crystalline structure and porous characteristics, achieved through the organization of positively charged organic ligands and metal ions. MOFs have garnered considerable attention in recent years due to their distinct attributes and potential applications. One of their key features is their high tunable porosity, which allows for the storage and separation of various gases and chemicals. This porosity is achieved through the precise control of the framework structure and the ability to adjust the shape and size of the pores. In addition to their porosity, MOFs also exhibit a stable framework and a high internal surface area. This large surface area provides ample space for chemical reactions and adsorption processes, making MOFs promising candidates for catalysis and gas storage applications. Another notable feature of MOFs is their atomic-level structural uniformity. This means that each unit within the material has the same composition and arrangement, leading to consistent performance and predictable behavior. Additionally, the topological structure of MOFs can be adjusted, enabling the creation of materials with specific characteristics and capabilities [4]. MOF-based substances are available in a variety of forms, including MOF derivatives, MOFs, and MOF composites pristine. These materials have found numerous applications in different fields. For example, they have been utilized for gas storage and differentiation, fuel cells, solar cells, batteries and supercapacitors, sample preparation, photocatalysis, drug delivery, and sensors [5-8]. Overall, MOFs represent broad capabilities for the development of advanced functional materials with high performance. Their unique combination of tunable porosity, stability, uniformity, and structural versatility has turned them into attractive compounds for use in various applications in science and industry [9-11].

The remarkable characteristics of luminescence, non-toxicity, and biodegradability make MOFs highly attractive for use in sensing and biosensing applications [12,13]. However, two weaknesses of MOFs in aqueous solutions, including limited conductivity and stability, have limited their application in electrochemical sensors and biosensors. To surmount this obstacle, researchers have commenced incorporating highly conductive substances like metal oxide or metal nanoparticles and carbonaceous materials into MOFs, generating nanocomposites that enhance the electrochemical performance and conductivity of MOFs [14]. These materials should exhibit a substantial surface area, elevated sensitivity, and reproducibility, as well as distinct catalytic, electronic, and biocompatible properties. Numerous studies have documented the utilization of functionalized MOFs and their composites for modifying electrode surface chemistry in electrochemical sensing applications. The existence of electroactive species, such as organic ligands and metal ions, within these MOFs and composites, contributes to their exceptional electrocatalytic properties. By altering the surface chemistry of the electrode, these devices demonstrate improved characteristics that significantly enhance their performance

compared to traditional electrodes. This approach holds promise for expanding the range of applications for MOFs in electrochemical biosensing and sensing. Electrochemical devices have become highly sought-after tools in various fields of analytical research due to their reliability, attractiveness, versatility, high sensitivity, and ease of use. Electrochemical sensors, in particular, have gained significant attention and are widely used for a diverse range of applications in analytical chemistry [15-22]. These sensors offer high sensitivity, simplicity, easy fabrication, environment friendly, portability, cost-effectiveness, and the potential for decentralized in-field analysis [23-30]. One of the key advantages of electrochemical sensors is that their performance can be improved by modifying the electrode surface chemistry. Additionally, modified electrodes demonstrate surface anti-fouling properties and prevent oxide formation, further enhancing their effectiveness [31-37]. Given the recognition of these advantages, the scientific community in the field of electrochemistry continually seeks new materials to modify electrode surfaces. These materials should possess a high surface area and reproducibility, as well as unique catalytic, electronic, and biocompatibility properties [38-42].

Nanostructures which possess a high ratio of surface to volume, usually differ from bulk materials [43-52]. and display surprising and exclusive characteristics, resulting in the expansion of the nanostructures' utilization in many fields, including technological, practical, material science, biotechnology, photocatalysts, and energy [53-59]. For example, nanomaterials, such as inorganic nanostructures [60-68], quantum dot [69] and carbons [70,71] can be used in many areas like colorimetric and electrical sensors because of their unique optical and electrical characteristics. Recently, due to the innovative progressions of nanocomposites and countless associated applications in plenty of fields, a wide range of methods, such as sol-gel [72-77], co-precipitation [78-83] solid-state [84,85], and sonochemistry [86-90] have been discovered and applied to fabricate nanocomposites. Because the morphology and size of the nanocomposites play a key role in their functions in numerous applications, Researchers and scientists have attempted to fabricate different nanocomposites with variable morphologies and sizes by altering the underlying conditions that influence nanocomposites' characteristics [91,92]. For instance, the fabricated nanocomposites' morphology and size can be adjusted by alterations in temperature, reactants' concentration, and surfactant utilization [93-96].

This review provides a comprehensive overview of the recent progress in applications of MOFs in electroanalytical advancements in recent years. The graphical abstract highlights several representative approaches for functionalizing MOFs, including post-synthetic MOFs modification, incorporating functional materials into MOFs, and creating electroactive MOFs. These strategies have been extensively studied for designing effective interfaces for electrochemical sensing. The review also explores the diverse applications of MOFs in detecting trace levels of various analytes. The versatility and tunability of MOFs make them highly suitable for sensing applications, as they can be customized to possess specific

properties and functionalities. This enables the sensitive and selective detection of target analytes. Furthermore, the review discusses the current challenges and highlights the potential future research directions in this thriving area. Despite the significant progress made in the field of electroanalytical applications of MOFs, there are still several challenges that need to be addressed. These include improving the stability and reproducibility of MOF-based sensors, as well as enhancing their performance in complex sample matrices.
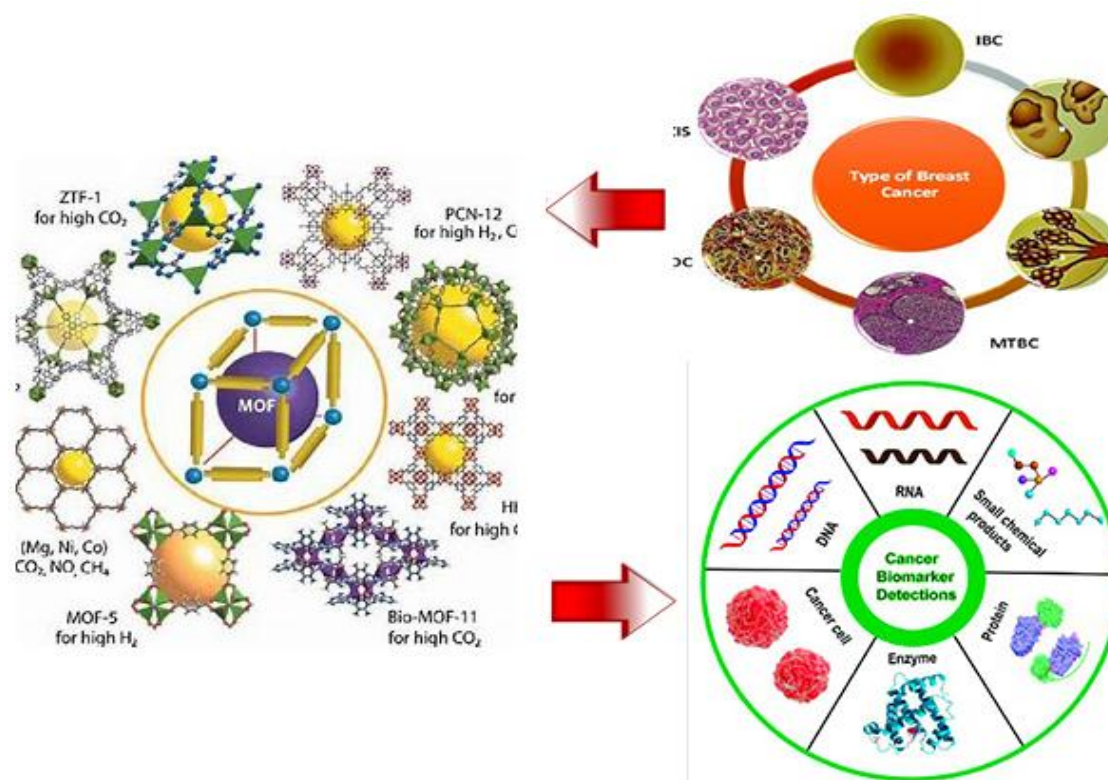

Figure 1. The scheme of metal-organic frameworks electrochemical biosensors for bioorganic materials detection

2. MOFS STRUCTURAL PROPERTIES

MOFs are known for their regular crystalline structures, which possess a range of beneficial properties for various applications. Among the important superiorities of MOFs is their permanent porosity, which allows for the capture and transport of guest molecules. This porosity also plays a crucial role in charge transport and catalysis. In addition to their porosity, MOFs offer easy modulation, thermal stability, and chemical stability. These features make them highly customizable, allowing for the design of structures tailored to specific applications. Furthermore, MOFs exhibit high specific surface areas, which provide ample space for accommodating guest molecules and enhancing electron transfer [97]. The ordered micro-/mesoporous nature of MOFs contributes to their electrochemical sensing capabilities [98,99]. Porosity plays a crucial role in various aspects of MOFs, including charge transport, guest

molecule capturing, and catalysis. Having a large surface area and internal space in MOFs provides the possibility of selectively accommodating specific guest molecules. This high porosity also facilitates electron transfer and leads to improved sensor performance in fast measurements with enhanced selectivity and sensitivity. Furthermore, the improved porosity of MOFs enhances the electrical conductivity and chemical activation process [100,101]. These materials possess uniformly distributed active sites that facilitate efficient sensing of target analytes. The presence of triphenylene- or benzene- derived ligands with S, N, or O donor atoms in MOFs further enhances their electrochemical detection properties. These ligands form π-conjugated structures with enlarged surface areas, promoting electron transport and improving sensitivity [102,103]. Overall, MOFs with highly crystalline structures, enhanced porosity, and expansive surface areas hold immense potential for the advancement of highly sensitive sensing applications. Their unique combination of traits makes them versatile materials for a diverse range of biosensing applications [104] particularly in the realm of electrochemical sensors [105,106].

One of the reasons for the great attention paid to MOFs in recent years is their ability to combine organic ligands and metal ions in different ways, which provides scientists with a wide range of compounds with adjustable properties. These materials offer intrinsic functionalities such as customizable pore size, ease of functionalization, diversity, and high surface area, as measured by the Brunauer-Emmett-Teller (BET)/Langmuir method [107]. The porosity size and surface area of MOFs are crucial factors that impact various aspects of their performance. For instance, these characteristics play a vital role in biodistribution, affecting how MOFs are distributed throughout the body. Additionally, the circulatory lifetime of MOFs in vivo, their ability to target specific tissues or cells, and their surface charge are all influenced by surface area and the porosity size. An example of the impact of porosity size and surface area on MOF properties can be seen in the case of HTMU-55. This MOF exhibited different morphologies, including micro and nanorods as well as nanospheres, due to the presence of hydrophobic fluoro groups. These unique structural features make HTMU-55 an excellent candidate for applications as a heterogeneous catalyst, as it possesses significant catalytic activity and a large surface area [108]. In summary, MOFs have emerged as an exotic class of materials with infinite combinations of metal ions and organic ligands. Their intrinsic functionalities, such as diversity, ease of functionalization, rational aperture design, and high surface area make them highly versatile materials. The porosity size and surface area of MOFs greatly influence their biodistribution, surface charge circulatory lifetime in vivo and targeting abilities. The example of HTMU-55 demonstrates how these characteristics can result in unique morphologies and significant catalytic activity.

One example of a microporous MOF is the $[Bi_2O(H_2O)_2(C_{14}H_2O_8).nH_2O$ (SU-101)] MOF, which was fabricated using polyphenols known for their excellent chemical stability in in laboratory tests. This MOF demonstrated greater stability in comparison to carboxylate-based

MOFs and Ellagic acid. The MOF's characterization proved its high specific surface area (S_{BET}) of 412 m^2/g, as well as its colloidal stability and biocompatibility [109]. In the modular synthesis approach, a strong linkage is formed in ditopic ligands through the imine bond of NU-401-Q (ZrMOF) when cycloaddition occurs with phenylacetylene, enhancing the chemical stability of the MOF [110]. On the other hand, it is possible to synthesize different MOF structures with the same topology by changing the building blocks. Biomolecules such as nucleobases, peptides/proteins, amino acids, and carbohydrates can serve as ideal building blocks for this purpose. This opens up possibilities for designing MOFs with diverse structures and properties by incorporating these biomolecules [111]. Polycarboxylate cuboctahedral Rh(II) is a type of metal-organic polyhedral supermolecule that has been widely used in the creation of linking bimetallic MOFs, specifically secondary building units (SBU) [112]. These supermolecules have shown great promise in the field of cancer biomarker detection particularly through various electrochemical techniques.

Among the electrochemical methods that have been employed in the measurement of different cancer biomarkers include impedance spectroscopy (EIS) [113], differential pulse voltammograms/polarography (DPV/DPP), square wave voltammetry (SWV), linear sweep voltammetry (LSV), cyclic voltammetry (CV), and chronoamperometry (CA). These techniques involve the measurement of electrical potentials under controlled currents [114-117]. One advantage of these electrochemical techniques is that they overcome the shortcoming of old methods by minimizing the influence of capacitive charging. This allows for more accurate and reliable detection of biomarkers. MOF electrochemical sensors can compress the detected signals into current, resistance, voltage and capacitance, which can then be used to monitor biomarkers. This provides a convenient and efficient way to track the presence and levels of cancer biomarkers [118].

Usually, in electrochemical techniques for measuring biomarkers using MOF-based sensors, electricity, capacitance, voltage and resistance are used as detection mechanisms. These mechanisms rely on the variations in conductive paths caused by the presence of biomarkers. The role of electric dipole moments is also crucial for electron and energy transfer in these sensors [119,120]. In recent years, various types of porous nanomaterials have been evolved for biosensing applications. However, certain materials like metal and carbon-based nanostructures have drawbacks such as higher energy loss, toxicity, and non-reusability. Porous silica materials may also cause hemolysis when they interact with phospholipids in red blood cells during the analysis of real samples. On the other hand, MOFs have gained significant attention due to their high applicability. Their porosity and tunable surface properties make them ideal for biomarker detection. These properties allow for efficient capture and release of biomolecules, making MOFs promising candidates for biosensing applications [121]. However, MOFs exhibit distinct characteristics in terms of their stability, reversibility-irreversibility behavior, and binding characteristics in comparison to other porous materials

such as COFs and HOFs [122,123]. These unique features make MOFs particularly favorable for the cancer biomarkers detection both onsite and offsite [124]. High porosity and crystalline nature are among the most important advantages of MOFs, which contribute to their exceptional electrochemical activities. Furthermore, the presence of metal centers within their frameworks further enhances their electrochemical performance [125,126]. However, despite these advantages, there are still limitations in the synthesis and design of MOFs that hinder their widespread application in sensor technology for real analysis. For instance, MOF morphology collapse at high temperatures restricts their use in thermal approaches [127,128]. Therefore, further research and development efforts are needed to overcome these drawbacks to fully utilize the potential of MOFs in sensor applications. The transformation and structure of linkers affect factors such as manufacturing expenses, manipulation, and time requirements. It is important to handle precursors with caution due to their sensitivity to heat and solvents. Additionally, when designing MOFs for the identification of cancer biomarkers, it is important to consider aspects like reusability or restoration for practical and industrial purposes [124]. Consequently, there is a necessity to explore the potential of MOFs in creating medical devices for cancer biomarker detection while addressing these limitations. In light of this examination, MOFs can be categorized as advanced porous materials due to the incorporation of metallic ions within their frameworks [129]. The existence of metallic ions generates an electrostatic and electronic environment that enhances signal amplification.

3. APPLICATIONS OF MOF BASED COMPOSITES IN ELECTROCHEMICAL SENSORS

3.1. Sensing of amino acids and drugs

One of the important functions of amino acids is their key role in the production of valuable substances that are necessary for the proper functioning of the body. They act as the basic biochemical substances and building blocks for this production process. These low molecular weight compounds are involved in vital bodily functions [130]. The concentration of amino acids in plasma is in the micromolar range under normal conditions. However, the balance of amino acids in the body may be disturbed by certain inherited metabolic disorders, include phenylketonuria and tyrosinemia. This can lead to abnormal levels of amino acids. Abnormally high levels of total plasma amino acids have been linked to conditions like fructose intolerance renal failure, and ketoacidosis. Therefore, monitoring amino acid levels can serve as a valuable tool in diagnosing and managing various metabolic disorders. In summary, amino acids act as important biomarkers for a range of metabolic disorders. By assessing their levels in the body, healthcare professionals can gain valuable insights into the functioning of various bodily processes and identify any potential abnormalities or imbalances that may require medical attention [131]. This can result in abnormal levels of amino acids. Unusually elevated levels of overall blood amino acids have been associated with conditions like kidney failure,

ketoacidosis, and fructose intolerance. Chen and colleagues [132] reported the development of a novel electrochemical sensing strategy for the detection of tyrosine (Tyr) utilizing a dual-signal molecularly imprinted polymer (MIP)/pTH/Au@ZIF-67 composite. They used a simple wet chemical reduction procedure for preparation of Au@ZIF-67 composite, which served as a framework to increase electron-transfer performance of the sensor and the surface area. Subsequently, the coating of bare electrode with Au@ZIF-67 was performed, and finally, then pTH was placed on the modified surface through electropolymerization. Finally, the MIP was formed using CV technique. The resulting sensor exhibited excellent selectivity towards Tyr due to the specific π–π stacking interactions and hydrogen bonding between the MIP and Tyr molecules. The pTH, acting as a built-in probe, provided a signal response to further enhance the sensing capabilities of the sensor. Remarkably, the developed sensor demonstrated a remarkable detection limit (DL) of 79 nM and the response is linear in the range of 0.1 nM to 4 μM, indicating its high sensitivity and wide detection range for Tyr. This innovative sensing strategy holds great potential for diverse applications in biosensing and clinical diagnostics, where accurate and sensitive detection of Tyr is crucial. Further research and optimization of this dual-signal MIP/pTH/Au@ZIF-67 composite sensor could lead to advancements in the development of reliable and efficient sensing platforms for other analytes as well. Feng et al. [133] reported the synthesize of a composite material consisting of carbon fiber and ZIF-67 and the impact of the carbon fiber on the catalytic activity of ZIF-67 was investigated. It was found that the presence of carbon fiber inhibited the aggregation and growth of ZIF-67 nanocrystals, resulting in a composite material with enhanced properties. The ZIF-67/PCF composite exhibited a higher number of active sites, improved conductance, and increased transport channels compared to pure ZIF-67. These enhancements contributed to the composite's superior electrocatalytic response in the detection of L-cysteine. The composite demonstrated good performance within the concentration range of 5–160 μM and 160–1580 μM, with a DL as low as 0.5 μM. Overall, the synthesis of the carbon fiber/ZIF-67 composite and the subsequent characterization of its catalytic activity revealed the potential for this material in electrochemical sensing applications, particularly in the determination of L-cysteine. In a study conducted by Peng et al. [134] they utilized AgNPs-modified MIL-101(Fe) for the determination of tryptophan (Trp). The AgNPs/MIL-101/GCE sensor they constructed exhibited a favorable response towards the oxidation of Trp, with a low DL of 0.14 μM. Another recent study by Wu et al. [135] they conducted research on the creation of an electrochemical biosensor using Cu-MOF for the detection of L-tyrosine in simulated biological conditions. The Cu-1 material, which is a MOF, was utilized in this biosensor due to its ability to provide active sites and well-structured frameworks that can selectively identify the small biomolecule L-tyrosine. This Cu-MOF electrochemical biosensor exhibited excellent sensitivity and user-friendliness for detecting L-Tyr in concentrations ranging from 0.01 to 0.09 mM, with a DL of 5.822 μM.

3.2. Sensing of glucose

Insulin deficiency and some other metabolic disorders include cardiovascular diseases endocrine syndrome, diabetes, and hypoglycemia are common complications of abnormal blood glucose levels [136]. Therefore, it is crucial to monitor and manage glucose levels accurately in the human body. The first enzymatic glucose biosensor was reported by Lyons and Clark in 1962, and after that enzymatic biosensors have been widely studied [137]. Considering the problems that enzymes have, including their high price, researchers became interested in the development of non-enzymatic glucose measurement methods, and many reports have been published on this issue in recent years. One promising candidate in this field is MOFs due to their outstanding structure, tunable pore volume, and large surface area. These properties make MOFs highly attractive for non-enzymatic electrochemical sensing applications. MOFs have gained recognition for their unique structural properties, such as periodic topology structure, tunable structure and pore size, and variable organic linker and metal node. These characteristics make MOFs ideal precursors for synthesizing porous metal complexes [138,139]. A notable example is the development of a 3D Ni2P/G composite through the phosphorization of Ni-MOF-74/G. In this process, Ni-MOF-74 serves as the precursor [140]. The combination of graphene and Ni_2P particles in the Ni_2P/G results in a synergistic effect, leading to increased electrocatalytic activity and excellent conductivity. The composite demonstrates great potential for sensitive electrochemical detection of glucose, with a DL of 0.44 μM and a broad linearity within the range of 5 μM to 1.4 mM. To validate its applicability for glucose detection, the Ni_2P/G composite was tested in human serum. It is important to highlight that chemically exfoliated graphene (CEG) and physically exfoliated graphene (PEG) materials exhibit significant differences. These variations arise from differences in methods of fabrication, graphitization degree, electron transfer ability, morphological structure, content of oxygen, and the capacitance of electric double layer. These distinctions contribute to the unique properties and performance of each type of graphene material [141-143]. On the other hand, it has been suggested that constructing hybrids with a well-ordered structure between polyethylene glycol (PEG) and MOFs could offer even greater advantages in enhancing sensing activity. This is because PEG has the ability to generate a lower capacitance of the electric double layer, resulting in lower background currents. In a recent study by Wu and colleagues [144] they introduced a novel sandwich-like hetero-structured material consisting of ZIF67 polyhedron loaded with PEG nanosheets (referred to as GS@ZIF-67) for the purpose of detecting glucose. This innovative approach holds promise for improving the sensitivity and accuracy of glucose detection.

3.3. Sensing of neurotransmitters

Neurotransmitters (NTs) are naturally occurring chemical messengers that carrying chemical signals to stimulate neurons, muscle cells, or gland cells and they play a vital task in

the functioning of the human nervous system. While there are over 100 identified NTs, only a few are considered to be the most important. These NTs can be classified into different groups based on their chemical function or structure. Abnormal neurotransmission in the central nervous system (CNS) has been associated with various physical disorders and mental, including Parkinson's disease, Huntington's disease, Alzheimer's disease, arrhythmias, schizophrenia, and congestive heart failure. Therefore, it is of utmost importance to accurately and promptly measure NT levels in various biological samples using reliable methods. This measurement can provide valuable insights into health diagnosis, disease pathology, and potential treatment options [145]. In recent years, significant efforts have been dedicated to developing techniques for detecting NTs. These endeavors aim to enhance our understanding of the role of NTs in various physiological and pathological processes. By precisely measuring NT levels, researchers and healthcare professionals can obtain invaluable information that can assist in diagnosing and treating neurological and psychiatric disorders [146]. In recent studies, researchers have been exploring the use of different MOFs combined with conductive nanomaterials for electrochemical detection of nanotubes (NTs). One subclass of MOFs that has gained attention is zeolitic imidazolate frameworks (ZIFs), which share a similar structure to zeolites. ZIFs offer several advantages, including flexibility in structure, ease of synthesis, the ability to be functionalized on the surface, and stability in both chemical and hydrothermal environments when compared to other MOFs [147-149].

Graphene, a highly conductive nanomaterial, has also shown promise for detection using electrochemical methods due to its fascinating electrochemical characteristics. The high rate of electron transfers at the surface of the edge plane and defects in composites of MOFs and graphene have sparked renewed interest in this field [150]. Recently, three different research groups have reported the use of ZIFs combined with graphene for electrochemical detection of dopamine (DA). These composites, namely GO/ZIF-67, Graphene/ZIF-8 [151], and RGO/ZIF-8 ([152,153]) were fabricated by growing ZIFs on graphene or its derivatives in situ. The incorporation of ZIFs into these composites has proven beneficial as it prevents the aggregation of graphene nanosheets, leading in a huge expand in the accessible surface area of the ZIF composites. This enhanced surface area improves the sensitivity and efficiency of the electrochemical sensing process. Overall, these findings highlight the potential of MOF-graphene composites, specifically those incorporating ZIFs, for effective electrochemical detection of NTs. The ZIF composites achieved in this study demonstrate remarkable stability and exhibit excellent conductivity and electron transfer at the electrode surface. The electrochemical performance of DA is significantly enhanced by the combination of graphene or its derivatives with ZIF materials. Interestingly, even though all the MOFs used in this study have the same structure, the limit of detection for DA varies. For instance, Graphene/ZIF-8 has a limit of detection of 1.0 µM, while RGO/ZIF-8 has a limit of detection of 30 nM, and GO/ZIF-67 has a limit of detection of 50 nM. These results highlight the importance of both graphene

or its derivatives and ZIFs in achieving high-sensitivity sensors for electrochemical detection. The practical applicability of these electrochemical sensors was confirmed by successfully testing them on real samples, with satisfactory recovery rates. In a recent investigation conducted by Tang et al. [154] they presented the development of a composite material called Ag-ZIF-67, which consists of silver nanoparticles embedded within ZIF-67 nanopinnas. The synthesis process involved the use of ultrasonication and reduction in the presence of ZIF-67 and of $AgNO_3$, resulting in the formation of the Ag-ZIF-67 composite. The researchers discovered that this composite exhibited excellent performance in electrochemical detection of DA and acetaminophen (AP). Ultrasonic irradiation was found to increase the specific surface area of ZIF-67 and enhance the filling of Ag nanoparticles, leading to improved electrochemical sensing capabilities. The combination of ZIF-67 and Ag nanoparticles had a synergistic catalytic effect, which greatly contributed to the enhanced performance, as depicted. The sensor that was fabricated using this method demonstrated a low DL of 0.05 μM for DA and 0.2 μM for AP. Real sample testing demonstrated outstanding recovery rates ranging from 96.5% to 100.8% for DA and from 96.3% to 103.4% for AP. In another study by Wang et al., sonication method was used for fabrication of a Cu(tpa)-graphene oxide nanocomposite [14]. The interaction between Cu(tpa) and graphene oxide (GO) was found to be due to hydrogen bonding, Cu-O coordination, and π-π stacking interactions. This hybrid composite sensor, which combines the unique properties of Cu(tpa) and graphene oxide, was used to detect DA and ascorbic acid (AP). The presence of both components in the sensor resulted in an improved electrochemical redox peak profile for the two analytes. The high conductivity of EGRO and electron transfer action of Cu(tpa) resulted in a synergistic effect, leading to the successful detection of DA and adrenaline (AP) with a detection limit of 0.21 μM and 0.36 μM, respectively. The effectiveness of this nanocomposite sensor in detecting DA and AP was further confirmed in some real sample including serum and urine. The utilization of MOFs has revolutionized the field of electrochemical sensing of NTs by enabling the development of MOF-based composites with conducting materials. Previous studies have primarily focused on DA detection, with limited research on other NTs. However, these studies have demonstrated excellent stability, reproducibility, selectivity through anti-interference tests, and potential applications in real samples. The sensing of DNA, miRNA, and ATP is of great significance in biological development and maintaining life functions. Any abnormal changes in the DNA bases concentration can lead to various diseases, for examples tumors and hereditary abnormalities. Therefore, it is crucial for pathologists and biologist to recognize DNA bases accurately, as early detection of diseases can greatly benefit patients by increasing their chances of recovery. In this regard, MOFs play a vital role in the electrochemical sensing of DNA. These materials are highly valued due to their ease of production and unique structural characteristics. By utilizing MOFs, researchers can develop efficient and sensitive methods to detect DNA, miRNA, and ATP, which are essential molecules involved in numerous biological

processes. The detection of DNA is particularly important as it serves as the blueprint for life and plays a fundamental role in genetic inheritance. By accurately sensing DNA, scientists can gain insights into various genetic abnormalities and diseases, enabling early intervention and personalized treatment strategies. Furthermore, the detection of miRNA, small non-coding RNA molecules, allows for the identification of specific gene expression patterns associated with different diseases. This knowledge can aid in the development of targeted therapies and precision medicine. Additionally, the sensing of ATP, a molecule responsible for energy transfer within cells, is crucial for understanding cellular metabolism and overall physiological functions. Abnormal ATP levels can indicate cellular dysfunction and contribute to the development of various diseases. Overall, the ability to sense DNA, miRNA, and ATP using MOFs provides researchers with valuable tools to investigate biological processes and detect diseases at an early stage. This advancement in sensing technology holds great promise for improving patient outcomes and advancing our understanding of complex biological systems. Copper-based MOFs have shown promise as materials for constructing sensing interfaces. These MOFs have customizable pore voids and functional pore walls, making them ideal for mimetic catalysis. Interestingly, certain iron porphyrin derivatives can be easily modified to serve as building blocks for MOFs. These derivatives also possess peroxidase activity comparable to heme proteins. In a study conducted by Ling et al. [155] an electrochemical label-free sensing approach for DNA was developed. This strategy relied on the mimetic MOFs catalytic activity and the allosteric switch of hairpin DNA. The researchers used a one-pot reaction to synthesis a signal probes by incorporating iron (III) meso-5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin chloride (FeTCPP) within HKUST-1 MOF. Streptavidin (SA) was then conjugated with these probes to serve as the recognition component. Overall, the utilization of MOFs in sensing interfaces and mimetic catalysis opens up exciting possibilities for the development of advanced sensing technologies and catalytic systems. The capacity to modify the pore configuration and functional characteristics of MOFs enables the creation of tailored materials that exhibit improved efficacy across diverse applications. The combination of FeTCPP@MOF composites has displayed promising abilities in catalyzing the oxidation of o-phenylenediamine (o-PD) to 2,2'-diaminoazobenzene. This catalytic function is achieved through a mimicking process. Initially, the SA aptamer sequence is inaccessible within a hairpin DNA structure due to its loop topology. However, when target DNA is added, the loop of the hairpin DNA attaches to the target sequence, causing the stem of the hairpin DNA to unfold. This unfolding results in the formation of a structure that includes the combined SA aptamer. The activated hairpin DNA structure can selectively bind to FeTCPP@MOF-SA through the affinity between the SA aptamer and SA. This binding event allows the activated hairpin DNA to act as a mimetic catalyst, significantly enhancing the peroxidase activity for the oxidation of o-PD in the presence of H_2O_2. Consequently, this oxidation process generates a measurable electrochemical signal through the production of the oxidized product (o-PDox).

In summary, the FeTCPP@MOF composites exhibit mimicking catalytic behavior in the oxidation of o-PD to 2,2'-diaminoazobenzene. The activation of a hairpin DNA structure enables selective binding to FeTCPP@MOF-SA, leading to enhanced peroxidase activity. This catalytic process produces a detectable electrochemical signal through the formation of o-PDox (oxidized product). The DL for the electrochemical sensing of DNA was determined to be 0.48 fM. MicroRNA (miRNA) is a short RNA molecule which serves as a crucial biomarker, as abnormal expression of miRNA has been associated with various diseases, for example cancer [156]. Therefore, development of sensitive miRNA biosensing strategies to enable early disease detection is essential. In a study by Li et al. [157] a non-enzymatic electrochemical biosensing approach was reported. This strategy utilized a combination of target catalyzed hairpin amplification and nanohybrid composites for signal amplification. The researchers created PdNPs@Fe-MOFs by combining palladium nanoparticles (PdNPs) with amino-functionalized iron-based MOFs (Fe-MIL-88NH2 MOFs). These nanohybrid composites had a large surface area as well as numerous active sites, making them ideal for immobilizing biotin-labeled signal probes (H_2) and tracer indicators. These nanocarriers facilitated the quick catalysis of the oxidation reaction of 3,3′,5,5′-tetramethylbenzidine in the presence of H_2O_2. This innovative biosensing strategy shows promise for sensitive detection of miRNA, enabling early identification of various diseases.

3.4. Electrochemical MOF sensors for detection of cancer

Biomarkers in the form of MOFs have garnered considerable attention as electrochemical sensors. This is primarily because MOFs possess redox and catalytic active sites, making them ideal for detecting and analyzing biomolecules. The ligands, active metal ions, and linkers present in MOFs contribute to their electrochemical sensing capabilities [158]. In particular, the use of electrochemical techniques has the potential to address the growing need for accurate cancer diagnosis at an early stage. To achieve this, researchers have focused on fabricating and immobilizing MOFs through various synthetic methods. By modifying the synthesis process, MOFs can be tailored to exhibit high sensitivity and improved recognition potential for cancer biomarkers. Overall, the utilization of MOFs as electrochemical sensors holds promise in advancing the field of cancer diagnosis, enabling early detection and potentially improving patient outcomes [159].

An interesting application involves incorporating PtCu nanoparticles (NPs) into a Cu-MOF, which not only provides active centers for detecting hydrogen peroxide (H_2O_2), but also serves as an electroconductive support for a nonenzymatic electrochemical sensor. The integration of MOFs and NPs in this manner leads to improved sensor activity, particularly in the detection of H_2O_2 within living tumor cells [160]. This research was conducted by Chen et al. in 2018. In a similar vein, Singh and his colleagues recently developed a novel Co-MOF that is linked by benzene-1,3,5-tricarboxylate. This particular MOF was designed specifically

for recognizing vascular endothelial growth factor 165 (VEGF165), which is a crucial biomarker in various types of cancers. By utilizing this Co-MOF, the researchers aimed to enhance the detection and understanding of VEGF165 in cancer research and diagnosis. The presence of $[Fe(CN)_6]^{3-/4-}$ can cause changes in redox potentials, which can be observed when VEGF165 interacts with MOF. This interaction is believed to be influenced by charge interactions between the two molecules. The limit of detection for this interaction is 5.23 pM, and it occurs under pH 7 conditions. The change in electrochemical signals is attributed to the reduction process, which is likely due to the non-conducting nature of the antigen [161]. In recent research by Dai et al. a novel approach to generating electrochemical signals for the detection of cancer biomarkers was proposed. The study focused on utilizing the various oxidation states of electron-rich deficient functionalities of biomarkers and metals to create redox processes. This approach has the potential to greatly enhance the sensitivity and accuracy of detection methods [162].

One specific application of this approach involved the development of an electrochemical immunosensor (sandwich-type Co-MOF) for the detection of prostate-specific antigen (PSA), a commonly used biomarker for prostate cancer. The Co-MOF was fabricated using Pd NPs (palladium nanoparticles) and amino-zeolitic imidazolate framework-67 (Pd/NH2-ZIF-67). This unique combination acted as a redox mediator, enabling the detection of PSA in a broad range of concentrations, from 100 fg/mL to 50 ng/mL [162]. The sensitivity of this electrochemical immunosensor was further highlighted by its limit of detection (LOD) of 0.03 pg/mL. This means that even extremely low concentrations of PSA can be accurately detected using this method. Overall, the development of this electrochemical immunosensor represents a significant advancement in the field of cancer biomarker detection. By harnessing the power of redox processes and utilizing the unique properties of metal-organic frameworks, researchers are paving the way for more sensitive and accurate diagnostic tools for cancer detection. In another example, Hatami and colleagues developed a specialized electrochemical aptasensor using a nanocomposite of graphene oxide on Cu(II)-MOF. This aptasensor was designed to selectively detect MUC1, in the presence of different proteins and amino acids. They proposed a mechanism for the Metal organic framework biosensor, suggesting that the formation of the MUC1-aptamer complex leads to a decrease in the redox peak $[Cu^{2+}-Cu^{+}]$ in the MOF [163]. In another work, Qiu and his team fabricated a composite material by linking tetrachloroauric acid and inserting gold nanoparticles into a Cu(II)-based MOF. This nanocomposite served as a sensitive electrochemical radiometric sensor for detecting DA. The addition of Ay nanoparticles and poly(xanthurenic acid) to the Cu-tetrakis(4-carboxyphenyl)porphyrin enhanced the electrocatalytic performance of the Cu-MOF, allowing for the detection of cancer biomarkers through DA oxidation on the MOF surface [164]. These two studies demonstrate the potential of Cu(II)-MOF-based materials in electrochemical sensors for detecting specific biomolecules, such as MUC1 and DA. The incorporation of

graphene oxide nanocomposites and gold nanoparticles further enhances the sensitivity and performance of these sensors, enabling their application in various fields, including cancer diagnostics and monitoring. In a recent study, Sun and colleagues have developed a novel hybrid platform for the detection of cancer biomarkers in exosomes. This platform combines ferrocene-doped MOFs and black phosphorus nanosheets on *InSnO₂* (indium tin oxide) slices, along with methylene blue-labeled single-strand DNA aptamers on the *InSnO₂* slice. The researchers found that the presence of MB on the platform led to a reduction in redox current and electron transfer (ET), which significantly enhanced the signal transduction for exosomes detection. The limit of detection (LOD) achieved with this platform was 100 particles per milliliter, making it highly sensitive for detecting exosomes. This innovative hybrid platform holds great promise for the early detection of cancer biomarkers in exosomes. By utilizing the unique properties of ferrocene-doped MOFs, black phosphorus nanosheets, and MB-labeled DNA aptamers, this platform offers a highly sensitive and efficient method for exosomes detection. The ability to detect exosomes at such low concentrations could potentially revolutionize cancer diagnosis and treatment. Further research and validation are needed to explore the full potential of this hybrid platform in clinical settings [165].

In another example, Hu and colleagues conducted a study where they created a unique type of metal-organic framework (MOF) using 2-aminoterephthalic acid, gold nanoparticles, and mercaptosuccinic acid. This MOF exhibited both hydrophilic and magnetic properties, making it an ideal candidate for sensing glycopeptide, a breast cancer biomarker. The researchers found that the fabricated MOF had a remarkable sensitivity of 0.5 fmol/μL, allowing it to detect even very low concentrations of the biomarker from standard protein digests [166]. This research opens up new possibilities for the development of advanced sensing technologies in the field of cancer diagnosis and treatment. In a recent study conducted by Zhou and colleagues, they developed novel bimetallic metal-organic framework (MOF) architectures for the detection of the cancer marker protein tyrosine kinase-7 (PTK7). These MOFs, namely Zr-MOF on-Zn-MOF and Zn-MOF on Zr-MOF hybrids, exhibited unique nanosheet and foliace structures, respectively. The researchers conducted electrochemical studies to investigate the performance of the synthesized hybrid MOFs. They found that the Zr-MOF facilitated the binding of the aptamer, which is a short single-stranded DNA molecule that can specifically recognize and bind to target molecules. On the other hand, the Zn-MOF stabilized the formation of a G-quadruplex structure formed by the aptamer strands and PTK7. The detection sensitivity of the aptasensor was evaluated, and it was found that the Zr-MOF on-Zn-MOF hybrid had a limit of detection (LOD) of 0.66 pg/mL, while the Zn-MOF on Zr-MOF hybrid had a LOD of 0.84 pg/mL. This indicates that both hybrid MOFs showed excellent sensitivity in detecting PTK7. Overall, the designed bimetallic MOF architectures provided a promising scaffold for the development of aptasensors for cancer marker detection. The unique structures of these hybrid MOFs allowed for enhanced binding of the aptamer and stabilization of the G-quadruplex

structure, resulting in highly sensitive detection of PTK7. This research holds great potential for the development of effective diagnostic tools for cancer detection and monitoring [167].

In a recent study, Wang and colleagues demonstrated the successful design of two bimetallic TbFe-MOFs by combining different MOFs. These hybrid MOFs were found to be highly effective as electrochemical sensors for detecting the carbohydrate antigen 125 (CA125), which is a biomarker associated with tumors. The researchers observed that the Tb-MOF-on-Fe-MOF exhibited superior properties in terms of its ability to interact with the G-quadruplex structure formed between the aptamer and CA125. This enhanced interaction was attributed to the better immobilization behavior of the hybrid MOF. Impressively, the limit of detection (LOD) for CA125 was found to be an extremely low value of 58 µU/mL, indicating the potential of this sensor for early diagnosis of tumors [168]. In another development, the researchers explored the incorporation of amino-rich functionalities into produced MOFs to enhance their electrochemical detection capabilities. They successfully enriched CDs@ZrHfMOF with carbon dots and amino functionalities, creating a potential sensor for detecting living HER2-overexpressed MCF-7 cells and receptor-2 (HER2). The insertion of carbon dots into the cavities of the ZrHf-MOF resulted in a significant increase in electrochemical activity, enabling the detection of HER2 with a LOD of 19 fg/mL. This sensor also demonstrated the ability to detect living HER2-overexpressed MCF-7 cells, with a LOD of 23 cells/mL. The concentration ranges for HER2 detection were found to be 0.001–10 ng/mL, while the cell concentration range was 1×10^2–1×10^5 cells/mL. sesOverall, these findings highlight the potential of bimetallic MOFs and amino-functionalized MOFs as promising tools for electrochemical sensing applications, particularly in the early diagnosis of tumors and detection of specific biomarkers. In a study by Gu et al. [169] it was proposed that the mechanism for detection could involve the formation of G-quadruplex structures between the aptamer strands and the analyte. Another approach was taken by Duan et al. [170] who developed cobalt phthalocyanine (CoPc) nanoparticle-induced MOFs as electrochemical sensors for detecting colorectal cancer cells (CT26).

The development of two-dimensional MOFs (*2D-MOFs*) and Prussian blue analogues (PBAs) has led to the creation of advanced materials that address the limitations of poor electronic conductivity and slow diffusion in MOFs for electrochemical applications. These materials have shown promising results in reducing transfer resistance and improving mass-transfer and electron efficiency. In fact, the protected electrodes have demonstrated multifunctional capabilities, particularly in their high sensitivity for detecting H_2O_2 and glucose. Moreover, the protected MOF has proven its potential in clinical diagnosis by successfully detecting glucose in human serum. This breakthrough opens up a range of possibilities for its application in various clinical settings [171].

4. CONCLUSION

Strategies to enhance the stability and longevity of MOFs in biological environments are being explored. The translation of MOF-based biosensors from the laboratory to clinical settings requires the development of user-friendly and cost-effective devices. Additionally, the scalability of MOF synthesis and functionalization processes needs to be considered for large-scale production. Looking ahead, future research in this field should focus on addressing these challenges and exploring new directions for MOF-based biosensors. The advancement of novel MOF materials with enhanced stability and improved sensing abilities, along with their integration into multiplexed biosensing platforms for simultaneous detection of numerous cancer biomarkers, is a crucial area of development. The potential of MOFs in electrochemical detection of cancer biomarkers is highly promising. With further progress in this domain, MOF-based biosensors have the capability to transform cancer diagnosis and monitoring, ultimately resulting in better patient outcomes.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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