

Review

Enzymeless Electrochemical Glucose Sensors Based on Metal–Organic Framework Materials: Current Developments and Progresses

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Abstract: Electrochemical glucose sensors play a crucial role in medicine, bioscience, food science, and agricultural science. Metal–organic frameworks possess exceptional properties, such as large specific surface area, high porosity, tunable pore structure, high catalytic activity, open metal active sites, and structural diversity. The catalytic activity of metal–organic frameworks enables electrocatalytic oxidation of glucose without the need for enzymes. Consequently, enzymeless electrochemical glucose sensors based on metal–organic framework materials have gained much attention and have been extensively studied for glucose detection. This mini-review provides an overview of the development and progress of enzymeless electrochemical glucose detection based on metal–organic framework material–modified electrodes, including doping materials, sensitivity, detection limit, and fast response capability. With the advancement of this technology, enzymeless electrochemical glucose sensors can continuously and stably detect glucose and can be utilized in various fields, such as wearable devices.

Keywords: metal–organic frameworks; modified electrodes; electrochemical sensors; electrocatalytic oxidation of glucose; enzymeless glucose biosensors



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1. Introduction

Glucose is a vital energy resource required to maintain the daily activities of human body [1]. Abnormal glucose levels can lead to diabetes and, in severe cases, other complications, such as diabetic nephropathy, diabetic retinopathy, diabetic cardiovascular, and diabetic neuropathy. Therefore, accurate, sensitive, and rapid detection of glucose levels is of utmost importance for diabetic patients [2–4].

Metal–organic frameworks (MOFs) are porous coordinated polymer crystals made of metal ions and organic ligands that possess many advantages, including large specific surface area, high porosity, tunable pore structure, high catalytic activity, open metal active sites, and structural diversities. Thus, MOFs have become one of the hot research topics in the field of electroanalytical chemistry [5–9]. MOFs are mainly classified by organic ligands, such as carboxylic acids, azaheterocycles, and phosphonic acids. Among them, carboxylic acids are the most common ligands, such as terephthalic acid (TPA) and homophthalic tricarboxylic acid (BTC). Carboxylic acid MOFs include Matériaux de l’Institut Lavoisier (MIL) series (Fe, Al, Cr-based) [10–12], isorecticular metal–organic frameworks (IRMOFs) series (M = Zn, Cd, Be, Mg, and Ca) [13,14], and Universitetet i Oslo (UiO) series (Zr-based) [15,16]. Nitrogen heterocyclic MOFs mainly use imidazolipids and bipyridines as organic ligands, with the most typical being the zeolitic imidazolate frameworks (ZIF) series [17,18]. Phosphonic acid MOFs are rare because it is challenging to obtain ideal structures.

Electrochemical sensors use electrodes as signal transducers to measure the electrochemical signal of a target analyte or a product resulting from an associated chemical or biochemical reaction with the target analyte. The electrode surface is often modified with

some special materials or constructs to enhance recognition of the target analyte, catalytic oxidation or reduction, or amplification of the electrochemical signal, thus quantifying the target analyte. Although it is possible to immobilize glucose oxidase and glucose dehydrogenase on the electrode to exploit the highly selective oxidation of glucose, the main challenges of enzymatic glucose sensors lie in the stability, cost, preservation, and lifetime of the sensors caused by the stability of the enzymes.

This review aims to provide a brief review of recent research and progress on enzymeless electrochemical glucose sensors based on MOF-modified electrodes with the potential to aid in the development of future glucose monitoring devices (Figure 1). In general, in alkaline aqueous solution, glucose is catalytically oxidized to gluconolactone with MOFs as the catalyst, while glucose molecules lose electrons at the electrode, generating a current measured for the concentration of glucose (Figure 1). There are two catalytic steps: (1) the lower valent state of MOFs loses the electrons to form higher valent states of MOFs under alkaline conditions; and (2) the higher valent state of MOFs oxidizes glucose to gluconolactone and are reduced back to the lower valent state of MOFs (Figure 1). With the advantages of large specific surface area, high catalytic activity, open metal active sites, and structural diversity of MOFs, they can be used as effective sensing materials for glucose detection. By focusing on MOF-modified electrodes, this review provides insights into the development of enzymeless electrochemical glucose sensors in terms of doping materials, sensitivity, detection limit, linear detection range, and other capabilities (Table 1). With the development of this technology, the resulting enzymeless electrochemical glucose sensors can continuously detect glucose and could be applied in a variety of areas, including wearable devices.

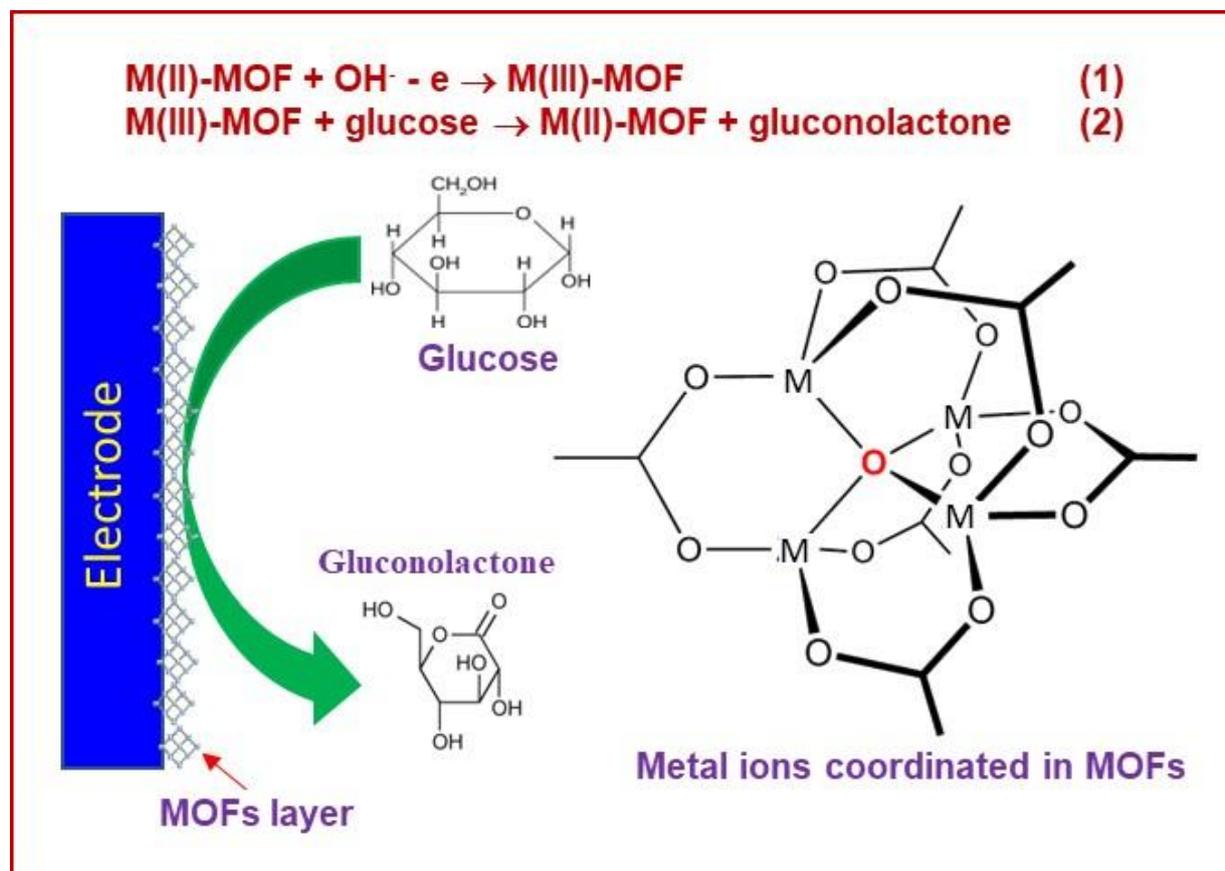


Figure 1. Schematic illustration of principle of enzymeless electrochemical glucose sensing via catalytic oxidation of glucose by MOFs.

Table 1. A part of enzymeless electrochemical glucose sensors based on a variety of MOFs.

MOF/Composite Classification	MOFs *	Detection Limit **	Sensitivity	Linear Range	Reference
Monometallic MOFs	Ni-MOF	0.76 μM	2859.95 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	1–1600 μM	[19]
	Ni-BTC	2.5 μM	932.68 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ 273.04 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	5–3000 μM 3500–6000 μM	[20]
	Cu-MOF	0.11 μM	-	5–3910 μM 3910–10,950 μM	[21]
	CPO-27-Ni	1.46 μM	40.95 $\mu\text{A}\cdot\text{mM}^{-1}$	0.04–0.5 mM 1–6 mM	[1]
	ZIF-67 HNPs	0.96 μM	445.7 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ 95.9 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.005–3.3 mM 3.3–42.1 mM	[22]
Bimetallic MOFs	Cu@Ni MOF	0.4 μM	496 $\mu\text{A}\cdot\text{mM}^{-1}$	0–5 mM	[23]
	Co _{0.33} Ni _{0.67} -HLDH	3.1 μM	242.9 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.01–2 mM	[24]
	Ni/Co(HHTP)MOF	100 nM	3250 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.3 μM –2.312 mM	[25]
	Ni@Cu-MOF	1.67 μM	1703.33 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	5–2500 μM	[26]
	Cu/Co-MOF	2 μM	18.68 $\text{mA}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.02–0.8 mM	[2]
MOFs with carbon nanomaterials	Ni-MOF/CNTs	0.82 μM	13.85 $\text{mA}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	1 μM –1.6 mM	[27]
	Ni(TPA)-SWCNT	4.6 μM	-	20 μM –4.4 mM	[3]
	Cu-MOF/MWCNTs	0.4 μM	3878 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.5 μM –11.84 mM	[28]
	Ag@ZIF-67/MWCNTs	0.49 μM	13.014 $\mu\text{A}\cdot\mu\text{M}^{-1}\cdot\text{cm}^{-2}$	33–400 μM	[29]
	Cu-MOF/CNHs	78 nM	-	250 nM–1.2 mM	[4]
	GS@ZIF-67	0.36 μM	1521.1 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	1–805.5 μM	[30]
	Co-MOF/Acb	1.7 μM	0.255 $\mu\text{A}\cdot\mu\text{M}^{-1}\cdot\text{cm}^{-2}$	5–1000 μM	[31]
MOFs with metal nanoparticles	Ni/Co LDH/GNRs	0.6 μM	344 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	5 μM –0.8 mM	[32]
	Ag/ZIF-67	0.66 μM	0.379 $\mu\text{A}\cdot\mu\text{M}^{-1}\cdot\text{cm}^{-2}$	2–1000 μM	[33]
	Au@Ni-BTC	1.5 μM	1447.1 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	5–7400 μM	[34]
	Cu/Ni-MOFs	66.67 nM	17.12 $\text{mA}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.20–2.72 mM	[35]
	Au@NiCo LDH	0.028 μM	864.7 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.005–12 mM	[36]
MOFs with metal oxides	Cu ₂ O@ZIF-67	6.5 μM	307.02 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ 181.34 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.01–10 mM 10–16.3 mM	[37]
	CuO/Ce-MOFs	2 nM	2058.5 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	5 nM–8.6 mM	[38]
	Ni-MOF/Ni/NiO	0.8 μM	367.45 $\text{mA}\cdot\text{M}^{-1}\cdot\text{cm}^{-2}$	4–5664 μM	[39]
	Ag@TiO ₂ @ZIF-67	0.99 μM	0.788 $\mu\text{A}\cdot\mu\text{M}^{-1}\cdot\text{cm}^{-2}$	48 μM –1 mM	[40]
	Mn ₃ O ₄ @ZIF-67	0.24 μM	3421.0 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.8 μM –6.0 mM	[41]
MOFs on metal foams	[Mn ₂ (Ni(C ₂ S ₂ (C ₆ H ₄ COO) ₂) ₂)(H ₂ O) ₂] ₂ ·2DMF	0.1 μM	27.9 $\text{A}\cdot\text{M}^{-1}\cdot\text{cm}^{-2}$	2.0 μM –2.0 mM	[42]
	Cu-MOFs/CF	0.076 μM	30,030 $\text{mA}\cdot\mu\text{M}^{-1}\cdot\text{cm}^{-2}$	0.001–0.95 mM	[43]
	(NiFe) MOFs/NF	0.67 μM	41.95 $\text{mA}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	2–1600 μM	[44]
	Co-MOFs/NF	1.3 nM	10,886 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.001–3 mM	[45]
	CoFe-PBA/Co-ZIF/NF	0.02 μM	5270 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	1.4 μM –1.5 mM	[46]
MOFs pyrolyzed	Co-MOFs	-	254.21 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ 102.80 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.001–2 mM 2–8 mM	[47]
	Cu/Ni-MOFs	0.06 μM	-	0.1 μM –2.2 mM	[48]
	NiCo-MOFs	0.2 μM	265.53 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.5 μM –4.38 mM	[49]
	ZIF-67	3.9 μM	1074.22 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.5–1000 μM	[50]
	ZIF-67-GO	0.34 μM	3172 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.5–10.0 μM	[51]
	ZIF-67-BP	0.2 μM	6427 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.5 μM –1.8 mM	[52]
	ZIF-67/MWCNTs/Au	0.1 μM	1138.4 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.2 μM –1.1 mM	[53]
	ZIF-67	5.69 μM	0.227 $\text{mA}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	0.1–1.1 mM	[54]
	Ni-MOFs	0.92 μM	2918.2 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$	5 μM –4.1 mM	[55]

* Abbreviations: CPO = Coordination polymers of Oslo; HNPs = hollow nanoprisms; HLDH = hollow layered double hydroxide; CNHs = carbon nanohorns; GS = graphene sheets; Acb = acetylene black; LDH = layered double hydroxide; GNRs = graphene nanoribbons; CF = copper foam; NF = nickel foam; ** signal-to-noise ratio (S/N) = 3.

2. Enzymeless Electrochemical Glucose Sensors Based on a Variety of Metal–Organic Framework Materials

2.1. Monometallic MOFs

In general, transition metal ions, such as Cu, Co, Ni, etc., can be used as the metal centers of MOFs because these metals possess various stable valence states that allow for easy electron gain and loss, making them potential catalysts for electrode reactions. The unique electronic properties of these metals facilitate the binding of reactants and make it easier for the products to leave [56,57]. Additionally, the open metal active sites on the MOFs' surface can act as electron-transfer channels, which can significantly enhance the electrocatalytic activity of the electrode [58,59]. By adjusting the electronic properties and chemical structures of the MOFs, the catalytic activity of the electrode can be optimized for glucose detection.

As an example of monometallic MOFs, a Cu-MOF-based enzymeless electrochemical sensing system was constructed for chronoamperometric determination of glucose in alkaline media [21]. The synthesized Cu-MOFs have a high specific surface area and porous structure. The carbon paste (CP)-based sensing electrode has good electrical conductivity. This synergistic effect leads to a good electrocatalytic activity for glucose oxidation (Table 1). The sensor exhibited long-term stability, good selectivity, and anti-interference ability. It was applied to the determination of glucose in serum with satisfactory results [21]. The Cu-MOF-based sensor demonstrates the potential of using MOFs in developing enzymeless electrochemical glucose sensors.

Chen et al. developed a simple and efficient diffusion control strategy to prepare ZIF-67 hollow nanoprisms (ZIF-67 HNPs) for the preparation of enzymeless glucose sensors [22]. The hollow structure provided a pathway for the rapid diffusion of the guest molecule in the MOF material. The sensor exhibited good electrocatalytic activity for glucose oxidation (Table 1). The enzymeless electrochemical sensor achieved satisfactory results in the analysis of glucose in human serum samples with good reproducibility, selectivity, and long-term storage stability [22]. The use of ZIF-67 HNPs in the construction of enzymeless electrochemical glucose sensors also represents a significant advancement in MOF-based sensing materials.

In 2018, a Ni-based redox-active MOF for a sensitive enzymeless glucose sensing platform was constructed by Lopa et al. [1]. The Ni-MOF was Ni₂(dihydroxyterephthalic acid), which is also known as CPO-27-Ni^{II} and MOF-74-Ni^{II}. CPO-27-Ni^{II} has high purity, crystallinity, and a large surface area, and can exhibit excellent redox activity in the alkaline medium due to the formation of the Ni^{II}/Ni^{III} redox pair. The resulting enzymeless glucose sensor based on the Ni-MOF-catalyzed oxidation of glucose could be used for the point-of-care detection of glucose (Table 1) [1]. Wang et al. prepared Ni-BTC and used it directly for the construction of enzymeless electrochemical glucose sensors (Table 1) [20]. The method showed good selectivity and sensitivity in serum analysis. The high performance of Ni-BTC-based enzymeless glucose detection may be due to the efficient charge transfer during electrocatalytic glucose oxidation [20]. Zeraati et al. reported another Ni-MOF-based electrochemical sensor [19]. The MOF material was synthesized with a surface area as high as 1381 m²/g. The amperometric response from oxidation glucose via Ni-MOFs could reach a steady state within 3 s. The resulting enzyme sensor displayed a lower detection limit and higher sensitivity (Table 1) [19]. Relatively, Ni-MOF-based glucose sensors showed higher sensitivities [19,20] than those sensors based on other monometallic MOFs. This might be attributed to the large surface areas and the more exposed and highly catalytic active sites of Ni-MOFs. The Ni-MOF-based sensors represents a significant advancement in the development of MOF-based glucose sensors.

2.2. Bimetallic MOFs

Kim et al. successfully synthesized Cu@Ni-based bimetallic MOFs with a spherical structure by a two-step hydrothermal reaction [23]. The MOF material was modified on the GCE for enzymeless glucose sensors in alkaline solutions (Figure 2). The bimetallic

MOFs material exhibited better electrocatalytic activity compared to the monometallic MOF material. Electrochemical analysis showed that the sensor has good electrocatalytic activity for glucose oxidation with good selectivity (Table 1). Compared to monometallic MOF material, the Cu@Ni MOF exhibited better electrocatalytic activity, mainly due to the synergistic effect of Cu and Ni in the MOF material [23]. The use of bimetallic MOF materials in enzymeless electrochemical glucose sensors represents a significant advancement in the development of MOF-based sensing materials.

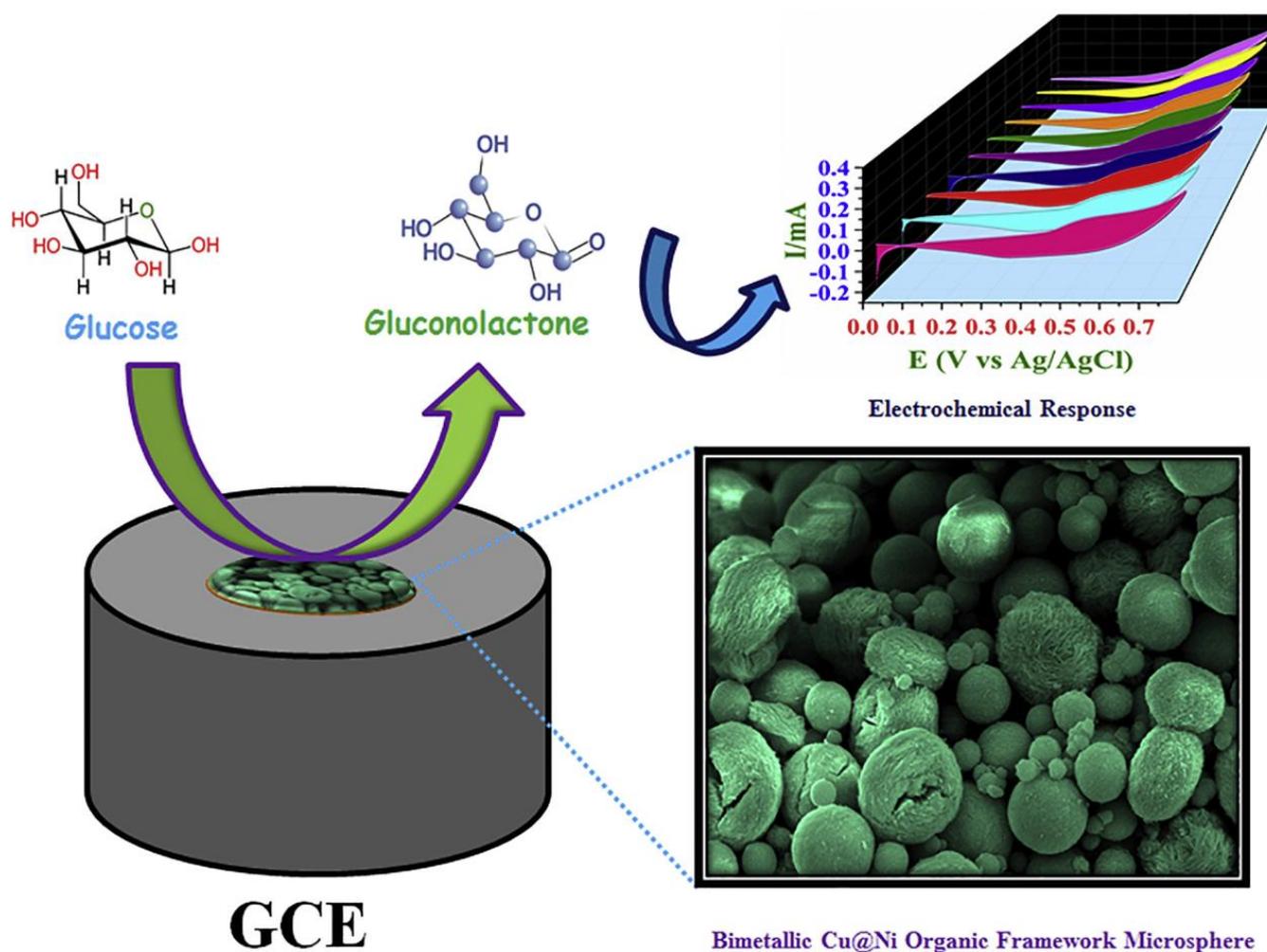


Figure 2. Pictorial representation of bimetallic Cu@Ni organic framework for electrochemical glucose oxidation [23].

Kong et al. obtained a $\text{Co}_x\text{Ni}_{1-x}$ -LDHs (LDH = layered double hydroxide) structure by adjusting the molar ratio of cobalt and nickel, which gradually transformed from a yolk-shell structure to a hollow structure [24]. The resulting electrochemical glucose sensor showed that LDH with a hollow structure has better performance than the yolk-shell structure because the hollow structure has a shorter electron-transfer pathway than the yolk-shell structure. Meanwhile, for the hollow layered double hydroxide (HLDH), $\text{Co}_{0.33}\text{Ni}_{0.67}$ -HLDH has a higher response current than $\text{Co}_{0.21}\text{Ni}_{0.79}$ -HLDH (Table 1), which may be attributed to its fine structure and more reasonable molar ratio of cobalt to nickel [24]. The use of LDH materials with a hollow structure represents a significant advancement in the development of MOF-based sensing materials for glucose detection.

Xu et al. prepared an enzymeless electrochemical glucose sensor based on Ni/Co(HHTP)MOFs/CC (HHTP = triphenyl-2,3,6,7,10,11-hexanol) by a simple hydrothermal synthesis method with direct growth of conductive Ni/Co bimetallic MOFs on carbon

cloth (CC) [25]. Due to the excellent conductivity between Ni/Co(HHTP)MOFs and CC, the resulting sensor had good performance with a response time of 2 s under optimized conditions (Table 1). In addition, the Ni/Co(HHTP) MOF/CC sensor was successfully applied to the detection of glucose in real serum and beverages [25]. Xue et al. constructed a two-dimensional nanosheet Ni@Cu-MOFs to prepare a modified electrode for catalytic glucose oxidation. The Ni@Cu-MOF/GCE sensor also had a good performance with good selectivity and reproducibility (Table 1). The sensor was used for the detection of human serum samples, and it was found that the general substances in human serum basically did not interfere with the detection of glucose, indicating that the Ni@Cu-MOF/GCE glucose sensor has good prospects for practical applications [26].

2.3. Composites of MOFs with Carbon Nanomaterials

Due to the poor electrical conductivity of MOFs [60], carbon materials are often used to enhance the conductivity of MOFs. When carbon nanotubes, graphenes, and other carbon nanomaterials with large surface area are incorporated, the overall surface area of the composite materials of MOFs with carbon nanomaterials could be increased compared to MOFs alone. Therefore, carbon-based nanomaterials have a favorable effect on the catalytic oxidation of glucose by MOFs.

In the study by Wang et al., layered three-dimensional Ni(TPA)-MOFs were synthesized by a solvothermal method [3]. Then, single-walled carbon nanotubes (SWCNTs) were mixed with Ni(TPA)-MOFs by ultrasonication. The Ni(TPA)-SWCNT-modified GCE was prepared as an electrochemical glucose sensor. The results showed that the oxidation reaction and electrocatalytic activity of the nanocomposite with SWCNT for glucose were significantly improved compared to the single component Ni(TPA)-MOFs, while SWCNTs could enhance the conductivity and adsorption capacity of MOFs for the catalytic process [61]. The electrochemical glucose sensor has excellent selectivity and is capable of fast response (<5 s) for glucose detection (Table 1). For the glucose assay with actual serum samples, the sensor had results in good agreement with the automated biochemical analyzer. These results demonstrate the high accuracy and promising applications of the sensor in rapid glucose analysis [3].

Zheng et al. prepared composites of Cu-MOFs and carbon nanohorns (CNHs) with electrocatalytic activity of Cu-MOFs on glucose oxidation [4]. The effective glucose biosensing interface was constructed via the synergistic effect of Cu-MOFs and carbon nanohorns nanocomposites. The resulting sensor displayed a wide linear detection range and a low detection limit for glucose analysis (Table 1). The results were comparable to those based on the clinical method (hexokinase method). The determination of glucose in commercial pear juice also demonstrated the reliability and accuracy of the sensor [4]. Zhang et al. developed a composite material of Ni-MOFs and carbon nanotubes (Ni-MOFs/CNTs) by in situ self-assembly in carbon nanotube suspensions [27]. The resulting Ni-MOFs has a porous structure, facilitating close contact between glucose and the active center of Ni-MOFs for efficient electrocatalytic oxidation of glucose. The chronoamperometric study showed that the resulting glucose sensor exhibited good reproducibility, repeatability, long-time stability, and high selectivity (Table 1) [27].

Wu et al. successfully prepared composites of Cu-MOFs/multi-walled carbon nanotubes (MWCNTs) (Cu-MOFs/MWCNTs) [28]. A high-performance enzymeless glucose sensor was constructed based on the Cu-MOFs/MWCNT-modified GCE using a layer-by-layer electrodeposition method [28]. The multilayer composite membrane on the electrode could effectively increase the exposure of active sites, as well as the reaction contact surface area for catalytic oxidation of glucose (Table 1) [28]. Chen et al. prepared graphene nanosheet (GS)@ZIF-67 composites with ordered layered nanostructures by loading polyhedral ZIF-67, in situ, on both sides of the physically exfoliated graphene nanosheets at room temperature (Figure 3) [30]. The synthesized GS@ZIF-67 complexes exhibited higher catalytic activity for glucose oxidation compared to individual components. The resulting sensor exhibited a good performance with good stability and selectivity for glucose anal-

ysis (Table 1). The glucose sensor was also successfully applied to the glucose detection in human serum with satisfactory results [30]. The ordered layered nanostructures of the GS@ZIF-67 composites provided a large specific surface area and abundant active sites, which contributed to the excellent electrocatalytic performance of the sensor for glucose oxidation.

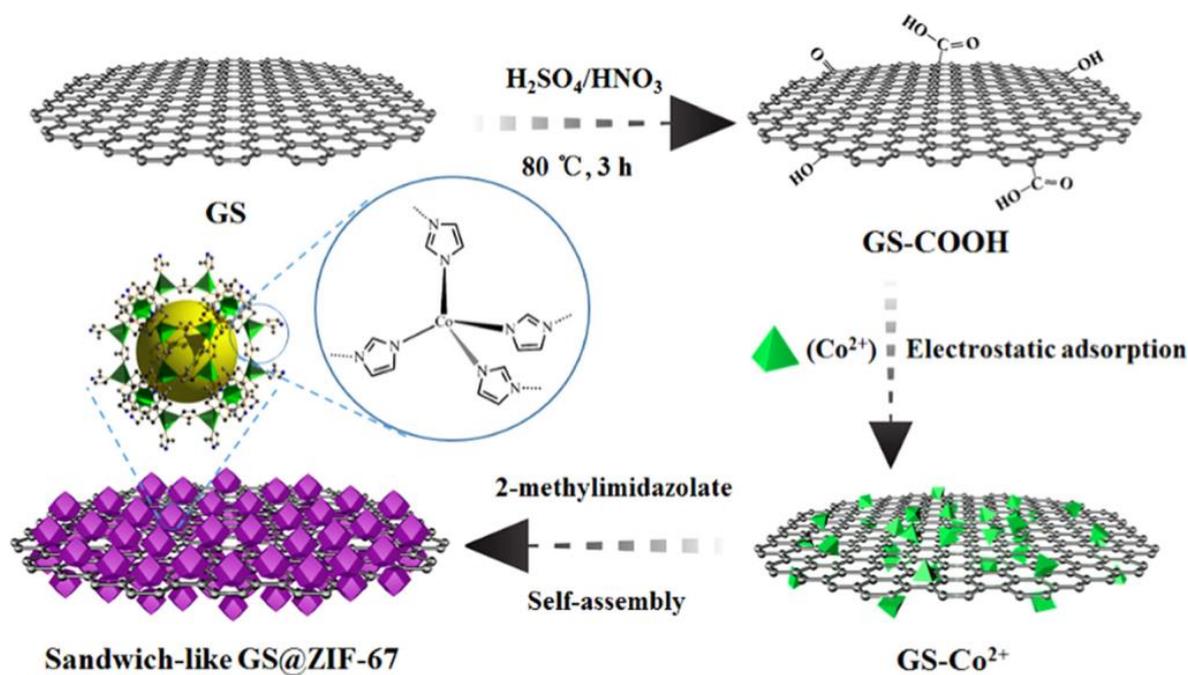


Figure 3. Illustration of the fabrication of sandwich-like GS@ZIF-67 hybrids [30].

Wen et al. developed a glucose sensor by preparing composites of Co-MOFs and acetylene black (Acb) [31]. The Co-MOF/Acb composites were obtained by mixing Co-MOFs with Acb, and the Co-MOF-modified glassy carbon electrode (GCE) with different Acb loading densities was investigated for glucose detection. The results showed that 2% Acb exhibited the best sensing performance (Table 1). Notably, the linear range of Co-MOF/Acb/GCE was extended more than ten times compared to Co-MOF/GCE without Acb addition [31]. This study demonstrates that the addition of Acb in the Co-MOF composites can significantly improve the sensitivity and linear range of the resulting glucose sensor, making it a promising candidate for practical applications.

Asadian et al. developed an enzymeless glucose detection platform based on the Ni/Co layered double hydroxide (LDH) nanosheets/graphene nanoribbons (GNRs)-modified GCE [32]. Firstly, ZIF-67 nanocrystals were used as a template to grow nanoflake Ni/Co LDH nanosheets. Secondly, the prepared nanosheets were mixed with graphene nanoribbons. Graphene nanoribbons, as an effective binder, increased the mechanical stability of the composite film and thereby improved the electrical conductivity of the modified electrode. The resulting electrochemical sensor had good performance for glucose analysis (Table 1). In addition, the electrode had long-term stability and good selectivity for glucose in the presence of common interfering substances (e.g., AA, DA, and UA) [32].

2.4. Composites of MOFs with Metal Nanoparticles

Meng et al. synthesized Ag@ZIF-67 nanocomposites by continuous deposition reduction [33]. The glucose catalysis was investigated with different Ag loading densities (Figure 4). The results demonstrate that increasing Ag loading density from 0% to 0.5% shortened the response time of the modified electrode by more than 2-fold and increased the sensitivity by 2.5-fold. Ag-0.5%@ZIF-67/GCE showed good electrocatalytic performance

with good selectivity and stability (Table 1) [33]. Chen et al. prepared Au@Ni-BTC by microwave-assisted synthesis [34]. The results showed that Au nanoparticles were uniformly deposited on Ni-BTC microspheres. The resulting electrochemical glucose sensor displayed good performance with high selectivity (Table 1). It was successfully applied for serum sample analysis. The improved glucose sensing performance may be due to the synergistic effect of Au nanoparticles and Ni-BTC, which promoted faster charge transfer at the electrode [34].

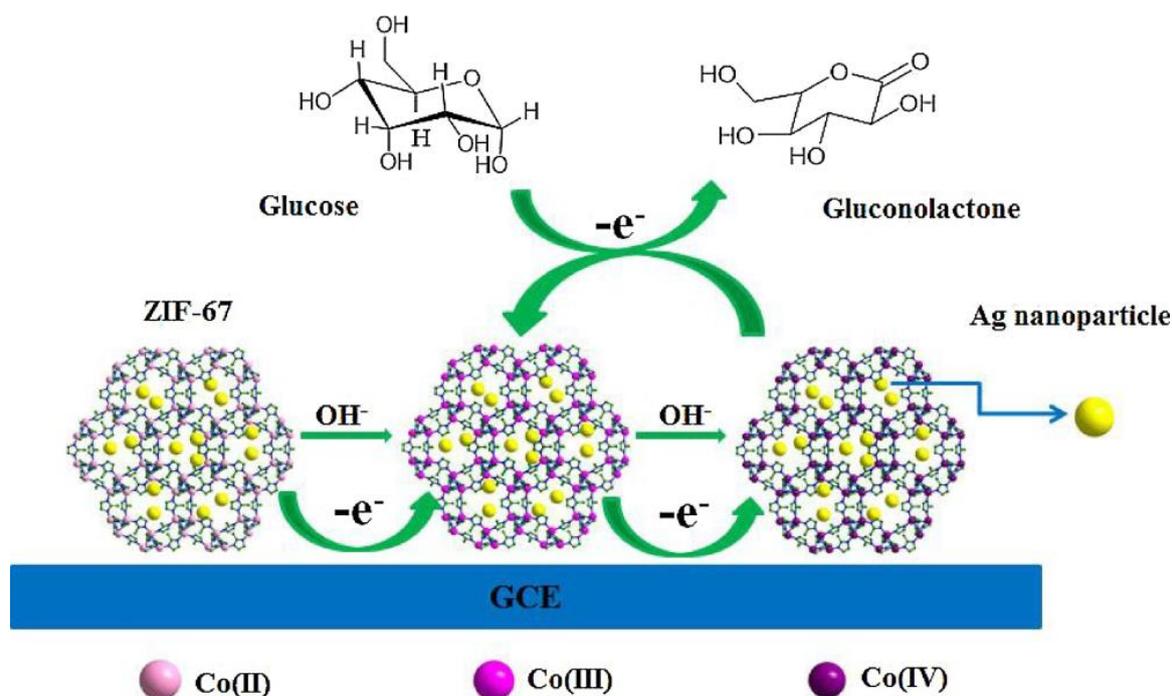


Figure 4. Schematic illustration of the electro-oxidation of glucose to gluconolactone by Ag nanoparticle doped ZIF-67 in NaOH solution [33].

Zhang et al. developed a self-supported Cu/Ni-MOF-modified electrode as an enzymeless glucose sensor by electrodepositing Cu nanoparticles on Ni-MOF derivatives [35]. The porous structure and carbon support of Ni-MOFs ensured fast electron-transfer kinetics for electrocatalytic oxidation of glucose at the electrode. The Cu nanoparticles influenced the array structure of the Ni-MOF-derived membrane, thereby improving its electrochemical performance in glucose detection (Table 1). The electrochemical glucose sensor exhibited good reusability, reproducibility, and stability. The sensor performance was compared to that using the glucose-6-phosphate dehydrogenase for the determination of glucose concentrations in human serum samples. The experimental results further demonstrated the practical feasibility of the modified electrode with Cu/Ni-MOFs [35].

Wang et al. synthesized a rattler-shaped Au@NiCo layered double hydroxide (LDH) hollow-core-shell nanostructure for use in an electrochemical glucose sensor [36]. In a hydrothermal process, ZIF-67 was etched into hollow polyhedra and transformed into NiCo LDH nanosheets by the Kirkendall effect in the presence of Ni salts. Meanwhile, gold nanoparticles were formed in the hollow cavities, and Au@NiCo LDH was obtained with Au nanoparticles as the core and NiCo LDH nanosheets as the shell. The Au@NiCo LDH-based electrochemical sensor exhibited superior electrocatalytic performance for glucose oxidation with excellent anti-interference ability (Table 1). The results suggest that the rattler-type Au@NiCo LDH hollow-core-shell nanostructures would be a promising electrode material for enzymeless electrochemical glucose sensors [36].

It is important to note that the compounding of MOFs with metal nanoparticles, such as Au, Ag, Pt, etc., can effectively improve the conductivity of MOFs; however, sometimes,

the specific surface area, the porosity, and the active sites of the composite materials decrease because the metal nanoparticles encroach on the pore channels of MOFs, leading to reduced amounts of accommodated glucose. This would have a negative impact on the catalytic performance of MOFs. Therefore, the optimization of the synthesis process and the precise control of the doping ratio and loading density of metal nanoparticles are crucial for achieving high-performance MOF nanoparticle-composite electrochemical glucose sensors.

2.5. Composites of MOFs with Metal Oxides

For the enhancement of the catalytic performance of MOFs, metal oxides such as CuO, NiO, Fe₃O₄, TiO₂, Co₃O₄, Mn₃O₄, etc., can also be utilized. The introduction of such metal oxides has a remarkable effect on catalytic glucose oxidation by MOFs. However, the disadvantages of metal oxides lie in that they may also encroach on the pore channels of MOFs, making the number of accommodated reactants inevitably reduced, thus affecting the catalytic performance of MOFs adversely. Therefore, the doping ratio of metal oxides with MOFs needs to be well controlled for the enhanced catalytic performance.

Zhang et al. developed CuO nanoparticle-modified multilayer Ce-MOFs composites (CuO/Ce-MOFs) by in situ precipitation [38]. Ce-MOFs and CuO/Ce-MOFs were characterized by electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and thermogravimetric analysis. CuO nanoparticles were found to be uniformly distributed on the surface of Ce-MOFs. The SEM and TEM images of CuO/Ce-MOF exhibit a composite structure where CuO nanoparticles were well distributed on the Ce-MOF surface [38]. The XRD peaks indicated that CuO nanoparticles were successfully synthesized on Ce-MOF surface. The XPS results confirmed the presence of a mixed valence state (Ce³⁺/Ce⁴⁺) in the Ce-MOF, while the Cu 2p peaks were found in the survey spectrum of CuONPs/Ce-MOF. The thermogravimetric analysis displayed two stages of weight loss of Ce-MOF. After modification with CuO nanoparticles onto Ce-MOF, the thermal weight loss of Ce-MOF was decreased by 20%, indicating the successful synthesis of CuO/Ce-MOF [38]. The CuO/Ce-MOF-modified electrodes showed good electrocatalytic activity for glucose in 0.1 M NaOH. Furthermore, the enzymeless glucose sensor was constructed using the modified electrode. The sensor exhibited excellent performance with good repeatability, reproducibility, stability, and selectivity (Table 1). The results of glucose detection in human serum were satisfactory [38]. Shu et al. synthesized Ni-MOF/Ni/NiO/C nanocomposites by an efficient one-step calcination method and constructed an enzymeless electrochemical glucose sensor by immobilizing the composites on the GCE with Nafion membranes [39]. The glucose sensor exhibited decent performance with good reproducibility, long-term stability, and good selectivity (Table 1). In addition, the constructed high-performance sensor was used to monitor glucose levels in human serum and satisfactory results were obtained [39]. The study suggests that Ni-MOF/Ni/NiO/C nanocomposites can be a promising material for the development of high-performance enzymeless glucose sensors.

Arif et al. synthesized ZIF-67-encapsulated Ag@TiO₂ complexes using a solvothermal method and modified them on the GCE [40]. The porosity of ZIF-67 facilitated the diffusion and encapsulation of glucose, and its cavity could be used as a reaction vessel. The electrochemical behavior of Ag@TiO₂@ZIF-67 shows enhanced activity for glucose oxidation compared to Ag@TiO₂ and ZIF-67. The glucose sensor based on Ag@TiO₂@ZIF-67 had a good performance for glucose analysis (Table 1) [40]. These results suggest that the ZIF-67-encapsulated Ag@TiO₂ complex can serve as a promising electrode material for enzymeless electrochemical glucose sensors with excellent performance. Dong et al. reported the successful synthesis of a Mn₃O₄@ZIF-67 composite on carbon cloth (Mn₃O₄@ZIF-67/CC) by a one-step hydrothermal method [41]. The enzymeless glucose sensor was constructed based on Mn₃O₄@ZIF-67/CC. The resulting sensor exhibited a good performance with high stability, reproducibility, and selectivity for glucose sensing (Table 1). The practical feasibility of the sensor was confirmed by the detection of glucose concentration in human serum samples, and the detection results were consistent with those of commercial glucose meters [41].

2.6. MOFs on Metal Foams

It is important to note that the performance of MOF-based glucose sensors can be influenced by factors such as the morphology, pore size, specific surface area, and composition of MOFs, as well as the preparation methods used to modify the electrodes. Zhou et al. synthesized $[\text{Mn}_2(\text{Ni}(\text{C}_2\text{S}_2(\text{C}_6\text{H}_4\text{COO})_2)_2)(\text{H}_2\text{O})_2] \cdot 2\text{DMF}$ on copper foam (Cu foam, CF) by a one-step hydrothermal method [42]. Because the $[\text{NiS}_4]$ nucleus has multiple redox states, the $[\text{NiS}_4]$ center in the highly oxidized state could oxidize glucose to gluconolactone. Thus, the enzymeless electrochemical glucose sensor was constructed based on the resulting modified electrode to catalyze the enzymeless oxidation of glucose. The enzymeless glucose sensor displayed excellent performance with satisfactory stability and reproducibility (Table 1) [42].

Zhang et al. have successfully prepared MIL-53 (NiFe) MOFs on nickel foam (Ni foam, NF) for use as a self-supporting electrode for enzymeless glucose detection [44]. The sensor has high sensitivity and a low detection limit due to the abundant active sites in MIL-53 (NiFe) MOFs and its good stability in alkaline solutions (Table 1). In addition, the molecular sieve effect of MIL-53 (NiFe) MOFs showed significant anti-interference ability, even at interfering concentrations as high as 20% glucose concentration. In addition, thermal treatment was performed to remove residual TPA from the MOF channel, which increased the linear range of the assay to 2–1600 μM [44]. Overall, this study demonstrates the potential of MIL-53 (NiFe) MOFs as a promising candidate for enzymeless glucose detection. Chen et al. successfully prepared Prussian blue analogues (PBA)/ZIF nanocomposites on NF [46]. The electrochemically active PBA particles and NF substrate can effectively reduce the transfer resistance and greatly improve electron transfer and mass transfer efficiency. The resulting electrode based on CoFe-PBA/Co-ZIF/NF were used for the highly selective and sensitive detection of glucose (Table 1). The sensor was successfully used for the detection of glucose in human serum [46].

The direct in situ growth of MOFs on Cu and Ni foams can improve the electrical conductivity of MOFs and thus enhance its catalytic activity. This method can effectively retain the intact pore channels of MOFs without encroachment. However, the reproducibility and stability of the electrodes prepared by this method need to be improved because it is difficult to control in situ growth uniformity. Further improvement in stability and reproducibility is needed to meet the commercialization needs for sensor construction.

2.7. Pyrolyzed MOFs

Pyrolysis of MOFs has been shown to transform crystalline MOFs into amorphous derivatives with a similar chemical composition. Amorphous materials obtained from the pyrolysis of MOFs have attracted a lot of attention in the field of catalysis due to their rich catalytic active sites and enhanced catalytic activities. The amorphous structure of these materials provides a higher degree of disorder and a greater number of defects, which leads to the exposure of more active sites and improved catalytic properties. Additionally, the high surface area and unique morphology of the resulting amorphous materials allow for better mass transfer, facilitating access to the active sites [62,63]. These amorphous derivatives can be used as promising catalysts for various chemical reactions, including glucose oxidation for enzymeless glucose sensors.

Han et al. developed a novel method to prepare a high-performance Co_3O_4 -based glucose sensor for the first time by rational design of a novel Co-MOF precursor [47]. The Co-MOF precursor exhibits a one-dimensional chain in the molecular structure and is further extended by hydrogen bonding to form a three-dimensional framework. The Co-MOF crystals were further stacked into microfloral clusters and then transformed into curved sheet-like Co_3O_4 after heat treatment at 450 $^\circ\text{C}$ in an air atmosphere. The curved Co_3O_4 -modified GCE ($\text{Co}_3\text{O}_4/\text{GCE}$) was used to prepare the enzymeless glucose sensor. The resulting sensor worked well at low and high concentrations with sensitivities of 254.21 $\mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$ and 102.80 $\mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$, respectively (Table 1). The electrochemical glucose sensor has good anti-interference ability, reproducibility, and stability [47].

Zhou et al. investigated the heat treatment of ZIF-67 hollow spheres at various temperatures to obtain amorphous derivatives that have high catalytic activity as electrocatalysts for oxygen evolution reaction and enzymeless glucose sensing [50]. The ZIF-67 hollow spheres were heat-treated at 260 °C for 3 h, and intermediate products with amorphous structures were formed during the transformation of ZIF-67 to Co₃O₄ nanocrystals. The chemical composition of the amorphous derivatives was similar to that of ZIF-67, but their carbon and nitrogen contents were significantly higher than those of the crystalline samples at 270 °C and above. The catalytic activity of the amorphous Co₃O₄ derivative was significantly higher than that of the crystalline Co₃O₄ as an electrocatalyst for the oxygen evolution reaction and enzymeless glucose sensing (Table 1) [50]. Overall, the amorphous Co₃O₄ derivatives obtained by heat treatment of ZIF-67 hollow spheres could be a promising candidate for the development of efficient electrocatalysts and glucose sensors.

Hou et al. deposited homogeneous ZIF-67 crystals on buckypaper (BP) and then prepared CoP/Co-BP by pyrolysis treatment and phosphorylation in an argon atmosphere. ⁵²CoP/Co-BP was then modified onto BP with a sponge-like nanostructure for improved performance of enzymeless glucose sensing (Table 1). The optimal operating voltage of the sensor was 0.45 V (vs. SCE) at pH = 13. The synergistic effect between the highly active CoP nanostructure and BP resulted in good electrical conductivity. The uniform distribution of CoP nanoparticles on BP prevented the formation of dense structures and facilitated the electron transfer. The sensor had good selectivity and long-term stability. The method was applied to the determination of glucose in spiked human serum, and the results were satisfactory [52].

Yang et al. developed a novel electrochemical glucose sensor based on Co₃O₄/MWCNTs/Au nanocomposites [53]. MWCNTs were incorporated into ZIF-67 precursors. Then, ZIF-67/MWCNTs with Au³⁺ were calcined at high temperature. Eventually, MWCNTs were embedded into the Co₃O₄ porous material and gold nanoparticles were successfully decorated on Co₃O₄/MWCNTs, allowing the nanocomposites to form a three-dimensional interconnected conductive network. The electrochemical results showed that the presence of MWCNTs and gold nanoparticles significantly improved the electron-transfer rate and the electrocatalytic activity of Co₃O₄ for the oxidation of glucose. Thus, the Co₃O₄/MWCNTs/Au-based sensor was able to detect glucose in a wide linear range with high sensitivity and a low detection limit (Table 1) [53]. The nanocomposites provided good selectivity, reproducibility, and long-term stability for glucose sensing.

Shi et al. prepared cobalt nanoparticle-porous carbon composites (ZIF-N₂) by pyrolysis of ZIF-67 in a N₂ atmosphere, which were successfully used for enzymeless glucose detection in alkaline media [54]. Similarly, in an air atmosphere at the same temperature, ZIF-67 was calcined to obtain ZIF-Air. Through a series of physicochemical and electrochemical characterizations, the results show that different atmospheres and temperatures for pyrolysis had a significant effect on the properties of the resulting materials. Compared with ZIF-Air, ZIF-N₂ has superior electrical conductivity, catalytic activity, and electrochemical effective surface area. The sensitivity of the sensor based on ZIF-N₂ exhibited good performance for glucose analysis (Table 1). The resulting sensor had good selectivity, long-term stability, and reproducibility [54].

2.8. Other MOFs

The catalytic oxidation of glucose can be enhanced by compounding MOFs with MOFs. The development of new core-shell MOFs for glucose sensing has a broad research prospect. Lu et al. prepared a core-shell electrochemical sensor based on MOF@MOF composites for enzymeless sensing of glucose in alkaline media (Figure 5) [64]. The UiO-67@Ni-MOFs core-shell composite was synthesized by growing Ni-MOFs on UiO-67 cores under the modulation of polyvinylpyrrolidone (PVP). In the sensor system, UiO-67 with large specific surface area and good conductivity was used to accelerate the electron-transfer rate of UiO-67@Ni-MOFs. The UiO-67@Ni-MOF composite exhibited higher electrocatalytic activity

for glucose oxidation compared to UiO-67 and Ni-MOF alone. The resulting sensor was 5–550 μM and 550 μM –3.9 mM with a response time within 5 s and a detection limit of 0.98 μM . The sensor exhibited satisfactory reliability and accuracy for glucose level detection in human serum samples [64].

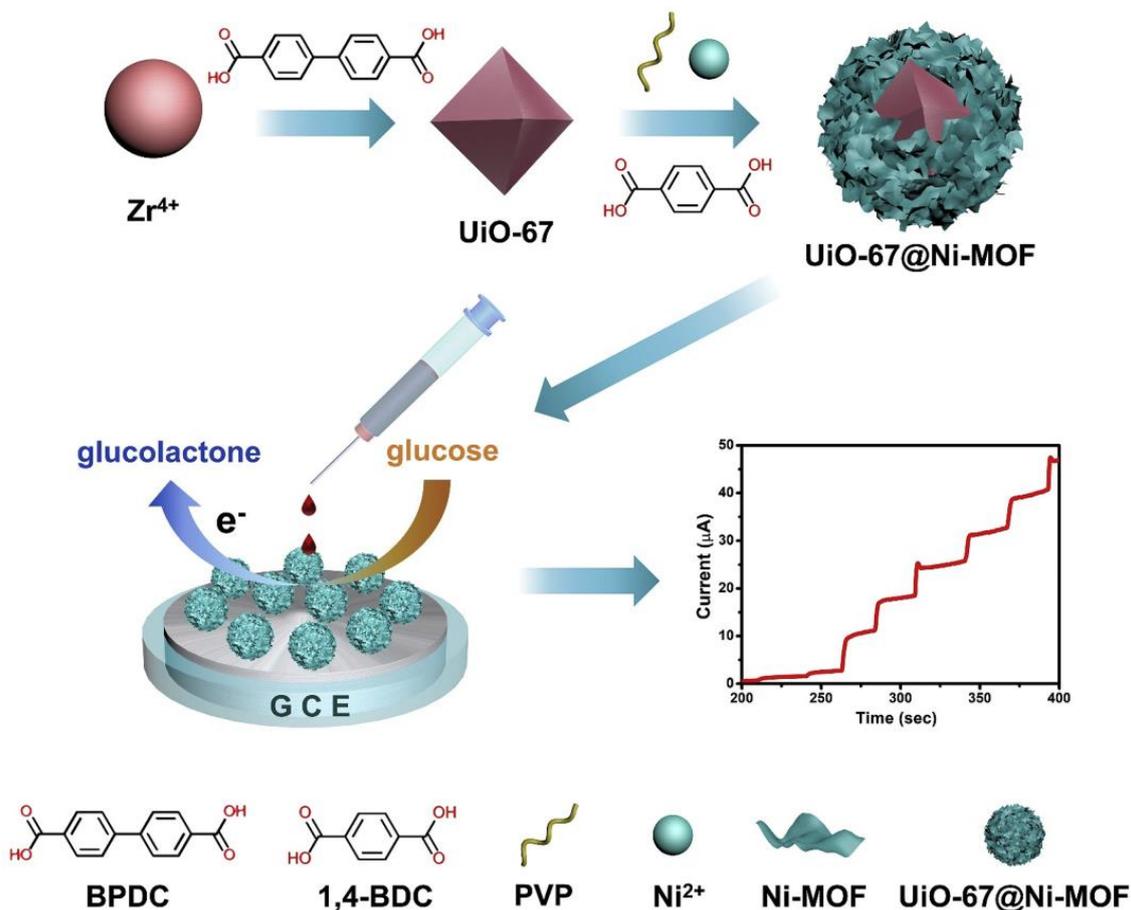


Figure 5. Schematic illustration of the synthesis of core-shell UiO-67@Ni-MOF composites and enzymeless electrochemical glucose sensing via catalytic oxidation of glucose by UiO-67@Ni-MOF [64].

Xiao et al. developed a novel electrochemical glucose sensor based on $\text{Ni}_3(\text{PO}_4)_2@ZIF-67$ composites by an ion-exchange method using ZIF-67 as a carrier [65]. The electrocatalytic activity of $\text{Ni}_3(\text{PO}_4)_2@ZIF-67/\text{GCE}$ for the oxidation of glucose was significantly improved compared to the GCE, $\text{Ni}_3(\text{PO}_4)_2/\text{GCE}$, and ZIF-67/GCE. The significant improvement in glucose oxidation was mainly attributed to the unique structure of $\text{Ni}_3(\text{PO}_4)_2@ZIF-67$, the mutual promotion of the redox reaction at the Ni(III)/Ni(II) and Co(IV)/Co(III) interfaces, and the increase in surface area. The sensitivity of the resulting sensor was $2783 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$, the linear range was 1.0 μM –4.0 mM, and the detection limit was 0.7 μM (S/N = 3). In addition, $\text{Ni}_3(\text{PO}_4)_2@ZIF-67/\text{GCE}$ was successfully applied to human serum glucose detection with a good recovery rate (92–109%) [65].

Sun et al. synthesized heterohybrid materials of ZIF-67@graphene nanosheets (GSs) (ZIF-67@GS) with a layered morphology by an in situ synthesis method [66]. The high electrical conductivity of graphene nanosheets could effectively enhance the electrochemical activity of ZIF-67. Subsequently, by chemical etching phytic acid (PA), PA-functionalized ZIF-67@GS (PA-ZIF-67@GS) was formed with a unique core-shell structure. The metal active sites, the electrochemically active surface area, and the electron-transfer kinetics of chemically etched ZIF-67@GS were further significantly improved. The prepared PA-ZIF-67@GS hybrids exhibited excellent electrocatalytic activity for the oxidation of glucose, resulting in an ultra-sensitive enzymeless electrochemical sensing platform [66].

3. Discussion

We have reviewed recent developments in enzymeless electrochemical glucose sensors based on MOFs and their composites. These sensors have attracted increasing attention due to their high sensitivity, selectivity, and stability. The MOFs are a class of hybrid materials consisting of metal ions or clusters coordinated by organic ligands, which can form a variety of structures with high surface area, porosity, and functionality. The unique properties of MOFs make them attractive for many applications in biomedical and environmental fields.

In recent years, MOFs have been widely used as electrode modification materials for enzymeless electrochemical glucose sensors. The rational design and engineering of MOFs and their composites have led to the development of various new sensing strategies and detection mechanisms. The combination of MOFs with other materials, such as graphene, carbon nanotubes, and metal nanoparticles, can further enhance the electrocatalytic activity, stability, and selectivity of the resulting sensors. The integration of MOFs with different functional materials has been also explored to enhance their catalytic performance for glucose oxidation, including the use of transition metals, carbon nanomaterials, metal oxides, metal nanoparticles, and in situ growth on metal foams. The catalytic activity of MOFs can also be improved by transforming crystallites to amorphous materials through pyrolysis.

For instance, Shi et al. synthesized cobalt nanoparticle-porous carbon composites (ZIF-N₂) by pyrolysis of ZIF-67 under a N₂ atmosphere, which exhibited excellent electrocatalytic activity for glucose detection in alkaline media [54]. Lu et al. prepared a core-shell electrochemical sensor based on MOF@MOF composites for enzymeless sensing of glucose in alkaline media, which showed high sensitivity and selectivity [64]. The core-shell structure of MOFs and their composites have been shown to improve the stability and sensitivity of the sensors. Xiao et al. developed Ni₃(PO₄)₂@ZIF-67 composites through the ion-exchange method using ZIF-67 as a carrier, which showed high sensitivity and selectivity for glucose detection [65]. Hou et al. prepared CoP/Co-BP by pyrolysis treatment and phosphorylation under an argon atmosphere, which was modified onto BP with a sponge-like nanostructure for improved performance of enzymeless glucose sensing [52]. In fact, among the various MOFs and their composites reported in this review, ZIF-67-based materials have been commonly studied due to their good stability and high catalytic activity for glucose oxidation. The incorporation of other metals, such as Ni and Cu into ZIF-67, has also shown improved sensing performance.

Furthermore, the development of MOF-based sensors has also been driven by the demand for more accurate, reliable, and rapid detection of glucose in complex matrices, such as human serum, saliva, and urine. Many of the MOF-based sensors have demonstrated excellent performance in terms of sensitivity, selectivity, and stability in such matrices, and have been validated with clinical samples.

Despite the significant progress achieved in MOF-based electrochemical glucose sensing, there are still several challenges and limitations that need to be addressed: (1) Although some MOFs are stable in alkaline aqueous solution, for example, the result of XRD examination shows that Ag@ZIF-67 and Cu-MOF still retained their framework structure after being emerged in alkaline solution for a long time [21,33], some MOFs may not be stable in alkaline aqueous solutions [67]. The instability of MOFs could be attributed to the break of the metal–ligand bond [68]. In practice, the composite materials of MOFs could be more stable in alkaline conditions [67,68]. When selecting MOFs as the catalyst for glucose oxidation, special attention needs to be paid to the stability of MOFs in alkaline conditions; (2) Most MOFs are actually not electrically conductive [60]. When some conductive materials are incorporated with MOFs, the overall conductivity of the resulting composites can be improved [69]. The efficiency and selectivity of MOFs as electrocatalysts are commonly attributed to their structures [60]. The high specific surface area of MOFs can expose abundant catalytic active sites to the surface. Their pores of predetermined size/geometry allow rapid mass transport of selected substrates to the active sites and the isolated metal nodes (typically, ions and clusters) of MOFs can serve as the active

sites [59,60,70]. The potential pathways for conducting electrons in these MOFs include redox hopping, pi-pi conjugation, or donor-acceptor charge transfer [60]. (3) There is the need for better understanding and control of the properties and behaviors of MOFs and their composites, such as stability, reproducibility, and toxicity. The effect of various parameters, such as the synthesis method, composition, morphology, and surface chemistry on the performance of the sensors, needs to be systematically investigated. For example, the doping ratio of metal oxides and metal nanoparticles needs to be optimized to maintain the porosity of MOFs without compromising their catalytic activity. The in situ growth of MOFs on metal foams also requires more precise control over the growth process to achieve uniform and reproducible electrode materials; (4) There is a need for the standardization and validation of MOF-based sensors for clinical and industrial applications. The accuracy, precision, and reproducibility of the sensors need to be rigorously tested and compared with established methods and standards. The effect of interference from other analytes in biological samples, matrix effects, and storage conditions also needs to be evaluated.

4. Conclusions and Outlook

In conclusion, MOF-based electrochemical glucose sensors have shown great potential for various applications due to their unique properties and functionalities. The development of MOFs and their composites has opened up new possibilities for designing and engineering highly sensitive, selective, and stable sensors for glucose detection. The use of MOFs as the electrocatalytic material in glucose sensors has shown great potential due to their unique properties, such as high surface area, tunable pore size, and the ability to incorporate different metal ions. Additionally, the use of MOF composites with graphene and carbon nanotubes has further enhanced the electrocatalytic activity and electron-transfer kinetics of the sensing platform. The combination of MOFs with other materials, such as graphene, carbon nanotubes, and metal nanoparticles, has resulted in enhanced sensing performance, including higher sensitivity, a wider linear range, and a lower detection limit. The sensors have also been successfully applied for glucose detection in human serum with good recovery rates. Therefore, MOF-based enzymeless electrochemical glucose sensors have great potential for practical applications in clinical diagnosis and glucose monitoring for diabetes patients.

Further research is needed to address the challenges and limitations of MOF-based sensors and to explore new avenues for their applications. We believe that further studies are needed to better understand the fundamental mechanisms of glucose oxidation on MOF-based electrodes. Additionally, the development of more efficient and stable MOF-based electrode materials for glucose sensing may require exploration of new synthetic strategies and the discovery of novel MOFs with enhanced catalytic properties. Overall, MOF-based electrochemical glucose sensors have great potential for application in clinical diagnosis and personal healthcare, and we anticipate that this field will continue to attract significant attention and efforts from researchers in the coming years.

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