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REVIEW

Non-precious metal-modified sensors for nitrite detection

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Abstract
Nitrite is widely used due to its personal properties. It not only exists in the food processing and chemical industry but also in every corner of the natural world. Nevertheless, excessive use of nitrite can cause serious environmental and human health hazards. Therefore, the efficient and sensitive detection of nitrite content has become a problem that must be faced. Among numerous methods, the electrochemical method has been widely studied for its advantages, such as fast reaction speed, high sensitivity, and miniaturization. The principle of operation of the nitrite electrochemical sensor is as follows. A modified layer located on the electrode surface oxidizes nitrite to nitrate. The sensing signal generated during oxidation can be converted into a measurable electrochemical signal. The electrochemical signal is proportional to nitrite concentration within a certain range, so that nitrite can be quantitatively detected. However, the sensor's performance is affected by the high oxidation potential of the bare electrode in electrochemistry. Therefore, the electrode is often modified to improve the sensor's performance in the study. In this review, the research progress of materials other than precious metals is discussed in the electrochemical detection of nitrite in recent years (2023–2013). The properties of carbon materials, non-noble metals, metal-organic framework compounds, conductive polymers, and their composites in electrochemical sensors are discussed in detail. Besides, it also looks forward to the challenges and prospects of nanomaterials in electrochemical sensor applications.

Keywords Non-precious metal · Composite materials · Nitrite · Electrochemical sensor

Introduction

Nitrite is a nitrogenous compound that is ubiquitous in nature. It is mainly derived from the nitrogen cycle in nature. It is not only present in the environment but also widely used in the food processing and chemical industries [1]. It can be used in dye production in the chemical industry and certain organic synthesis, while it can be used as a food colorant and preservative in food production. However, when nitrite levels are too high, there is a greater risk to human health and aquatic plants. On the one hand, when the nitrite concentration exceeds 0.02 mg/L, it will directly affect the growth and development of aquatic organisms, will induce disease outbreaks, and may even lead to the death of many aquatic organisms [2]. On the other hand, nitrite can form nitrosamines in the human body. Nitrosamines are precursors of carcinogenic compounds, and long-term ingestion can induce the development of cancer [3, 4]. The International Agency for Research on Cancer has classified nitrite as a possible carcinogen to humans (class 2a) [5]. At present, most countries have enacted corresponding laws and regulations to control the content of nitrite, which can reduce the harm of nitrite to humans and the environment to some extent. However, we still need to establish a complete testing program. A complete detection procedure is established when a systematic understanding of the mechanism of action nitrite is available [6].

At present, a variety of methods have been developed for the detection of nitrite content to control the excessive intake of nitrite content. Studies have been reported in the literature, and it has been found that the methods used include spectrophotometry [7, 8], chemiluminescence

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[9, 10], chromatography [11, 12], capillary electrophoresis [13–15], fluorescent probes [16], and electrochemistry [17]. Among the known methods, the electrochemical method has attracted wide attention because of its advantages of high sensitivity, simplicity, and accuracy.

In electrochemical detection, the electrochemical sensor is the most important component. The principle is that nitrite interacts with the material and thus undergoes a specific redox reaction at the electrode surface. The electrochemical active substances are produced during the reaction. And the substances can be converted into a detectable electrochemical signal by the sensor, thus being used for qualitative and quantitative analysis [18, 19]. The electrochemical method can realize direct electrocatalytic oxidation of nitrite on the electrode surface. However, the sensor's performance is hindered by the high oxidation potential of nitrite at the bare electrode [20]. Therefore, the electrode needs to be modified to improve the detection performance of the sensor.

With the development of science and technology, various materials have been developed for modifying electrodes. The modified sensor for nitrite detection not only increases the electrochemical reaction of NO_2^- redox but also plays a great role in expanding the detection range of nitrite and reducing the detection limit [21]. In recent years, nanomaterial sensors have become a powerful analytical tool due to the development and use of various functional nanomaterials [4]. At present, the nanomaterials commonly used to modify electrodes include graphene (GR), carbon nanotubes (CNTs), carbon nanofibers, carbon nanodots, and other carbon materials; metals, metal oxides, and other metal materials; metal-organic framework compounds [22]; conducting polymers [23]; and enzymes [24]. Carbon materials have become the most widely used materials among the above-mentioned nanomaterials due to their large specific surface area and wide range of raw materials. The metal-organic framework is a material that emerged in the later period and has attracted extensive research because of its unique and fascinating structure. Modified electrodes exhibit higher reactivity and faster electron transfer rates for nitrite detection. Although there are many electrodes modified by precious metals in metal oxides, they show good electrocatalytic properties when used for nitrate detection. For example, Salagare et al. doped palladium oxide (PdO) with RGO using an in situ chemical solution technique for nitrite sensing. The peak oxidation current of nitrite showed a linear relationship with its concentration ranging from 10 to 1500 μM, and the LOD was 10.14 μM [25]. Salagare et al. prepared silver nanoparticle-modified zinc oxide nanocomposites by ethylene glycol reduction method for nitrite sensing. The detection range of nitrite was 30~1400 μM, and the detection limit was 14 μM [26]. The application of electrodes modified by precious metals is limited in practical work due to the scarcity of precious metals and the difficulty of polymerization. Therefore, this article does not take precious metal materials as the object of study.

This article reviews the application of nanomaterial-modified electrochemical sensors in nitrite detection in the past decade (2023–2013). Research on nitrate sensors is on the rise overall, and composites tend to outperform single materials. In addition, when summarizing the various detection limits and linear ranges for nitrite, it was found that the sensor has a wide linear range and the detection limits have been down to the micromolar level. In research, nitrite sensors have been used to detect a variety of actual samples, including water, soil, beverages, sausages, and pickles. The purpose of this article is to provide the reader with a systematic understanding of the current state of research on sensors modified with non-precious materials so that more convenient and feasible sensors can be developed.

Nitrite sensor based on carbon

In the electrochemical method, it is not efficient when used directly to detect nitrite due to the high oxidation potential of the bare electrode. Therefore, some functional nanomaterials are commonly used to modify the electrode. Among the functional nanomaterials developed, carbon materials have attracted extensive research because of their large specific surface area and high electrical conductivity [27]. In recent years, researchers have developed a variety of electrochemical sensors modified with carbon materials of different properties. The sensors can be used for the detection of nitrite. These carbon materials include carbon nanotubes [28], graphene [29], and nanoporous carbon (NC) [30]. In this section, the application of carbon nanotubes and graphene materials in electrochemistry is mainly introduced. The properties of these nanocomposites are then summarized in Table 1.

Nitrite sensor based on carbon nanotubes

Since CNTs have been studied, scholars have continuously used them for modifying electrochemical sensors. Carbon nanotubes are rolling graphene sheets with axis symmetry. Based on the different layers of graphene, it can be divided into single-walled nanotubes (SWCNTS) and multi-walled nanotubes (MWCNTS) [87]. Single-walled nanotubes have attracted extensive research because they can be compatible with other substances. For example, Xian et al. applied a covalent modification approach to immobilize single-walled carbon nanotubes with single-stranded deoxyribonucleic acid composites on the surface of glassy carbon electrodes (GCEs) [31]. The modified electrodes not only have a large specific surface area and good electrical conductivity, but the presence of single-walled nanotubes can

Table 1 Electrochemical nitrite sensor based on carbon material

Electrode material	Method	Linear range (μM)	LOD (μM)	Sample	Ref.
SWCNTs/ssDNA/GCE	DPV	0.6–540	0.15	Sausage	[31]
DNA-CNTs/Cu^{2+}/GCE	Amp	0.03–2600	0.03	–	[32]
Poly(1,8-DAN)/f-MWCNT/CPE[a]	Amp	0.3–6.5	0.075	Water	[33]
GC/PEDOT[b]/CNT/Fe_3O_4/GCE	DPV	0.5–150	0.022	Water	[34]
MWCNTs/PPy-C[c]/GCE	LSV[s]	500–10,500	2.3	Water	[35]
Nb_2C@MWCNTs-STAB/GCE	DPV	0.1–2000	0.022	Spinach and milk	[36]
CoPc[d]/MWCNTs/GCE	DPV	10–1,050,000	2.11	–	[37]
CoTLMethPc[e]/MWCNTs/GCE	DPV	0.05–1.05	0.035	Beetroot vegetable	[38]
c-MWCNT/TiN/GCE	Amp	0.006–950	0.04	Water and meat	[39]
PBA[f]/MWCNTs/GCE	DPV	10–400, 400–2100	0.5	Mustard and ham sausage	[29]
GC/SWCNT/3/GCE	DPV	5–200	1.08	Tap and mineral water	[40]
HOOC-MWCNT/GCE	DPV	100–700	0.565	Pond and underground water	[41]
PPy/SDS[g]/f-MWCNTs/GCE	DPV	3–1120	0.11	Tap water	[42]
TiO_2/MWCNT/GCE	DPV	0.02–600	0.011	Dam receiving waste	[28]
Fe_2O_3/MWCNTs/GCE	Amp	10–1000	0.1	Tap water	[43]
Bi_2Se_3@MWNTs-COOH/CE	DPV	0.01–7000	0.002	Tap and moat water	[44]
Stir bar-shaped/N-rGO/GCE	CA[t]	0.2–1200, 1500–7800	0.13	Ham sausage and tap water	[22]
LRGO[h]/PDAC[i]/ION-RGO	DPV	10–400	7.2	–	[45]
Ni/PDDA[j]/rGO/SPCE[k]	CV	6–20, 20–100	1.99	Sausages and pickled vegetable	[46]
N, O co-doped LIG	DPV	5–450	0.8	Tap water and pickle water	[47]
Cu-rGO/ITO	DPV	10–100	1.875	Cheese, sausage, and salami	[48]
GO/copper terephthalate/GCE	SWV	5–625	0.3	Tap, bore well, and sewage water	[49]
rGOIm/GCE	SWV	1–1000	0.28	Tap water	[50]
rGO-MOS_2-PEDOT/GCE	DPV	1–1000	0.059	Water and milk	[51]
rGO/zirconium hexacyanoferrate	SWV	0.00323–0.04198	0.00139	Water and milk	[52]
rGO/ZnO/GCE	LSV	200–4000	1.18	Tap water	[53]
AGCE[l]/ERGO/PBCB[m]	CV	30–500	2.46	Tap water	[54]
Co_3O_4-rGO/CNTs/GCE	Amp	0.1–8000	0.016	Tap water	[55]
CuO/H-C_3N_4/rGO	CV	0.2–110	0.025	–	[56]
Fe_3O_4/GO/COOH/GCE	DPV	1–85, 90–600	0.37	Water	[57]
Polyaniline/RGO/IDE	Amp	400–183,700	0.1	Tap water	[58]
rGO/Pani/AsM[n]/GCE	SWV	25–7500	10.71	Ground and sewage water	[59]
ERHG[o]/GCE	Amp	0.2–10,000	0.054	Tap water and liquid milk	[60]
rGO-MoS_2/GCE	Amp	0.2–4800	0.17	Tap water	[61]
$Ni(OH)_2$/sr-GO/GCE	Amp	0.1–663.6	0.07	Mineral water	[62]
RGO/$MnFe_2O_4$/PANI/GCE	DPV	0.05–12,000	0.015	Water	[63]
CuOx/ERGO/GCE	Amp	0.1–100	0.072	Tap water and meat	[64]
Fe_2O_3/H-C_3N_4/rGO/GCE	DPV	0.025~3000	0.01843	–	[65]
CuO/MWCNTs/SPE	CA	4000–6500	0.039	Tap and mineral water	[66]
$LaAlO_3$@GO/GCE	Amp	0.01–1540.5	0.0041	Drinking water and meat	[67]
Mn-rGO-GCE	DPV	0.1–5.5	0.02	Juice and tap water	[68]
PC_{ST}[p]/GCE	Amp	0.1–100	0.043	Meat	[69]
PHCNs[q]/GCE	Amp	0.037–6950	0.01	Pickle	[70]
CoPx@P,N–RPCs[r]/GCE	DPV	0.01–1184	0.005	Sausage and mineral water	[30]
Si/C/Al/$SiPy^+Cl^-$	Amp	0.2–280	0.01	Meat and water	[71]
CoOx/C/GCE	DPV	0.2–2500	0.05	Sausage	[72]
CC	Amp	0.25–3838.5	0.03	Sausage and mineral water	[73]
PANI@GO/GCE	Amp	2–44,000	0.5	Rain and tap water	[74]
(NiCo-RGO)GCE	DPV	60–860	1.8	Water cucumber juice and milk	[75]
GC/poly-TBO-SWCNT	Amp	1–4000	0.37	Wastewater	[76]

Table 1 (continued)

Electrode material	Method	Linear range (μM)	LOD (μM)	Sample	Ref.
[PDDA/α_2-$K_7P_2VW_{17}O_{62}$·18H_2O-CNTs]$_{10}$/ITO	CV	0.05–2130	0.0367	Apple, orange, and peach juice, coconut juice, sterilized milk, sausage, and pickled vegetable	[77]
IL–SWCNT	Amp	1–12,000	0.1	Milk	[78]
Hb/IL/MWILE-modified electrode	CV	10–15,000	1.46	Sausage	[79]
MWCNTs/carbon ceramic electrode (CCE)	DPV	15–220	4.74	Spinach	[80]
GR-MWCNTs/FeNPs nanocomposite	Amp	0.1–1680	0.076	River, tap, and rain water	[81]
PDDA-rGO/GCE	Amp	0.5–2000	0.2	Drinking water	[82]
Chitosan/phenylamine-GO/GCE	Amp	5–4650	2	Tap water	[83]
CoNi NPs/ERGO/GCE	Amp	0.1–30, 30–330	0.05	Hot dog sausage, mortadella salami, and feta white cheese	[84]
Cu-NDs/RGO/GCE	Amp	1.25–13,000	0.4	River water	[85]
CTAB-GO/MWNT/GCE	DPV	5–800	1.5	Human urine	[86]

[a] *Carbon paste electrode*
[b] Poly(3,4-ethylene dioxy-thiophene)
[c] Polypyrrole-carbon black
[d] Cobalt (II) phthalocyanine
[e] Tetra L-methionine cobalt (II) phthalocyanine
[f] Prussian blue analogues
[g] Sodium dodecyl sulfate
[h] Light-scribed reduced graphene oxide
[i] Poly(diallyl dimethyl ammonium) hydrochloride
[j] Poly(diallyldimethylammonium chloride)
[k] Screen-printed carbon electrode
[l] Activated glassy carbon electrode
[m] Poly(brilliant cresyl blue)
[n] Polyaniline–arsenomolybdate
[o] Electrochemically reduced holey graphene
[p] Porous carbon derived from sodium tartrate
[q] Porous hollow carbon nanospheres
[r] Phosphorus/nitrogen co-doped reticular porous carbon frameworks
[s] Linear sweep voltammetry
[t] Chronoamperometry

enhance the electron transfer rate so that the sensor has high catalytic performance. Under the optimal experimental conditions, the linear range of the sensor can be gained from 0.6 to 540 μM, and the minimum detection limit is as low as 0.15 μM by differential pulse voltammetry (DPV). In addition, the sensor has good stability and strong anti-interference ability. The good stability of the sensor is mainly attributed to the fact that the nanocomposites are immobilized on the electrode surface by covalent bonds rather than simply physically adsorbed on the electrode surface. Based on this research, the composite material was further optimized. For example, Yang et al. used a one-step electrodeposition method to immobilize DNA-CNTs/Cu^{2+} on the surface of a glassy carbon electrode [32]. Through cyclic voltammetry (CV), it can be found that adding CNTs/Cu^{2+} can enhance charge transfer and reduce the hindrance of DNA film to charge. After optimization of the experimental conditions, the sensor was measured using amperometry (Amp). The results showed that the DNA-CNTs/Cu^{2+}-modified sensor had a linear range of 3×10^{-8}~2.6×10^{-3} M and a detection limit of 3×10^{-8} M (S/N = 3). The reproducibility of the sensor was studied using five identically modified electrodes, and the RSD was measured to be 4.4%. These results indicated that the reproducibility of the sensor was good. In addition, the current response of nitrite was measured every day. It was found that the current response value was maintained at more than 88% of the initial reaction after 30 days. This result indicated that the sensor had strong stability and could be detected in real samples.

Compared with other materials, multi-walled carbon nanotubes have remarkable electrocatalytic activity and a strong current response. However, there is almost no interaction of available ions to detect a particular analyte at low concentrations, and multi-walled nanotubes are less hydrophobic in aqueous solutions. To overcome these problems, multi-walled nanotubes can be modified by adding appropriate functional groups to improve the hydrophobicity and electrocatalytic stability of the nanotubes [21, 88, 89]. For example, Sudha et al. constructed COOH-functionalized multi-walled nanotubes for modifying glassy carbon electrodes [41]. COOH-functionalized multi-walled nanotubes had more graphitic properties than the original MWCNT, so more active sites (C=C and COOH groups of HOOC-MWCNT) can interact with the analyte. The feature can achieve the purpose of low-concentration sensing. In addition, the detection range of the sensor was determined to be 100 µM~0.7 mM, and the detection limit was 565 nM by differential pulse voltammetry. To demonstrate the practicability of the sensor, the samples of ground pond water were tested. The results showed a recovery of 102% for nitrite. To further improve the performance of this composite, it can be compounded with a metal material. For example, Zhu et al. compounded COOH-functionalized multi-walled nanotubes with Bi_2Se_3 [44]. Bi_2Se_3@MWNTs-COOH nanocomposites were synthesized to modify GCE/carbon electrodes (CE) by a one-step hydrothermal method. Five samples were prepared by adding different concentrations of reagents. Among them, Bi_2Se_3@MWNTs-COOH-50% had the lowest charge transfer resistance. The result indicated that the composite has the highest electron transfer rate. By measuring the CV curves of different electrodes, it can be obtained that Bi_2Se_3@MWNTs-COOH had the largest current response value (Fig. 1). The result indicated that Bi_2Se_3@MWNTs-COOH has a larger surface area, which is favorable for nitrite adsorption. The disposable electrochemical sensor has a detection range of 0.01 µM~7.0 mM, and the minimum detection limit is 0.002 µM for the detection of nitrite. In short, the sensor has great potential for the detection of nitrite.

Nitrite sensor based on graphene

Graphene is a two-dimensional carbon nanomaterial composed of sp^2 hybrid orbital carbon atoms. Its structure is a honeycomb hexagonal lattice network and can be extended indefinitely [90]. Graphene has become the most promising material for nitrite detection because of its cheap raw material and good electrical conductivity [60, 91]. Graphene can be divided into graphene oxide (GO) and reduced graphene

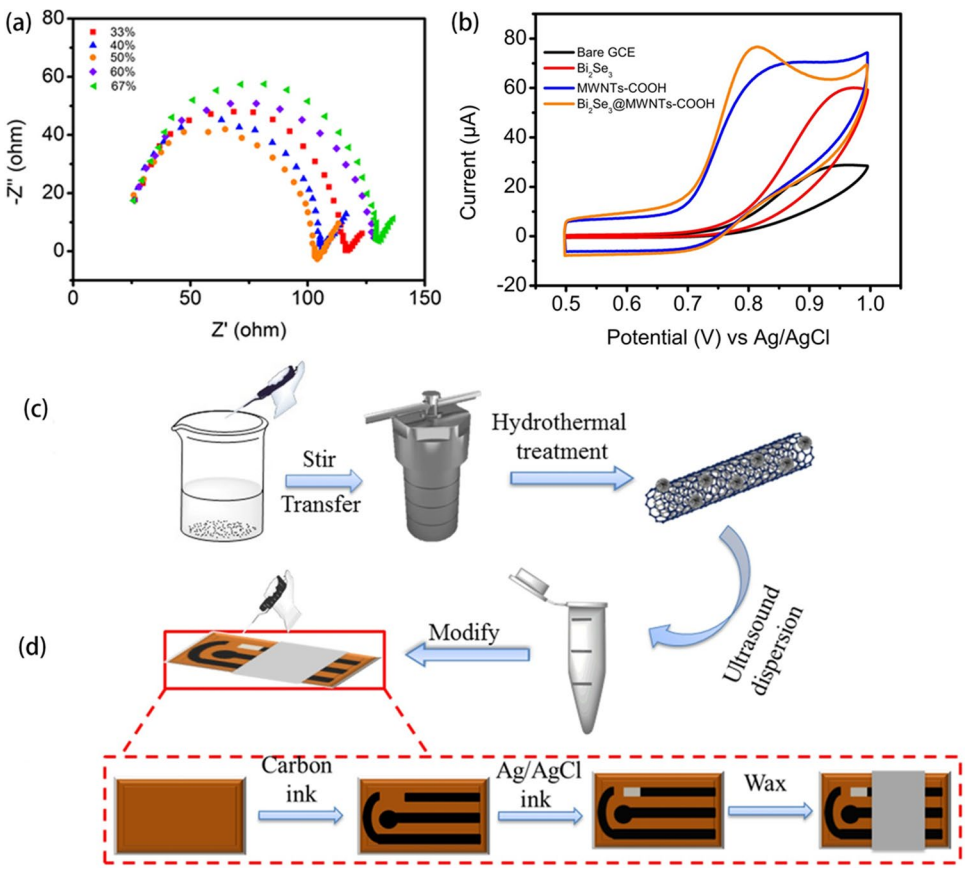


Fig. 1 **a** EIS of Bi_2Se_3@MWNTs-COOH-x electrodes. **b** CV curves of the different electrodes to detect 1.0-mM nitrite in 0.1-M PBS (pH 7.0) at 100 mV s^{-1}. **c** Schematic diagram of the synthesis method of Bi_2Se_3@MWCNTs-COOH/CEs and the preparation process **d** [44]. Copyright 2021, Elsevier

oxide (rGO). Reduced graphene oxide includes chemically reduced graphene oxide (CrGO) and electrochemically reduced graphene oxide (ErGO). rGO has higher electrical conductivity compared to GO. So rGO is more widely used than graphene [6, 21]. However, pure graphene has serious aggregation and homogeneity problems. So electrochemical properties are usually reduced [92].

Doping graphene with various heteroatoms is an effective method to improve the structural and electrochemical properties of graphene. Yuan et al. used a simple laser engraving method to prepare N and O co-doped porous graphene under UV irradiation (Fig. 2) [47]. LIG was detected by DPV. The results showed a good linear relationship between the peak current and the analyte concentration. And the sensor had a detection range of 5~450 μM, and the minimum detection limit was 0.8 μM, which was 55 times lower than the detection limit of 3 mg/L set by the World Health Organization. Surprisingly, the electrode had good reproducibility and strong anti-interference ability. In short, the sensor has broad application prospects in detecting nitrite. Cheng et al. prepared graphene-based nanocomposites sb-ZnO (stir bar-shaped ZnO)/N-rGO for modifying glassy carbon electrodes by combining a novel stir bar-shaped ZnO with N-doped reduced graphene oxide using a hydrothermal method [22]. There is a large active surface area due to extra valence bonds between π-electron and lone pairs of N atoms in graphene oxide. The large active surface can accelerate the electron transfer rate. In addition, ZnO enhances the electron transfer capability and provides a large surface area due to a wide direct band gap and extended excitation binding energy. With the synergistic effect of N-rGO and sb-ZnO, the nanocomposite-modified electrode has a low detection limit of 0.13 μM and a linear range of 0.2 μM~1.2 mM and 1.5~7.8 mM. In addition, the recovery rate of nitrite by this sensor is between 96.0 and 103.0% in practical applications of ham sausage, sauerkraut, and tap water.

Another way to improve the sensitivity is to incorporate various nanomaterials, such as metal oxides and conducting polymers. In recent years, transition metal hydroxides have been confirmed to have high electrocatalytic activity and are promising for various applications in electrochemical sensors. For example, Salagare et al. successfully prepared cobalt-nickel-reduced graphene oxide nanoparticles by complexing transition metal mixed oxides $NiCo_2O_4$ with RGO using urea nitrate complexing agent auto-ignition method [75]. The nanocomposite has a unique porous structure and layered connections. CV and DPV method was used to study the electrocatalytic behavior of the material towards nitrite. The results showed that the composite-modified graphite electrode (NiCo-RGO) had a larger peak anodic current than the bare graphite electrode. The linear range was found to be 60~860 μM with a detection limit of 18.0 μM about the NiCo-RGO/GCE-based sensor for nitrite detection by the DPV method. In addition, the material showed good reproducibility, repeatability, and stability for electrochemical sensing of nitrite. Good recoveries were obtained in real samples of water, cucumber juice, and milk. The sensor has good prospects for commercialization. Yılmaz-Alhan et al. prepared a two-dimensional carbon-metal oxide composite electrode to modify the glassy carbon electrode

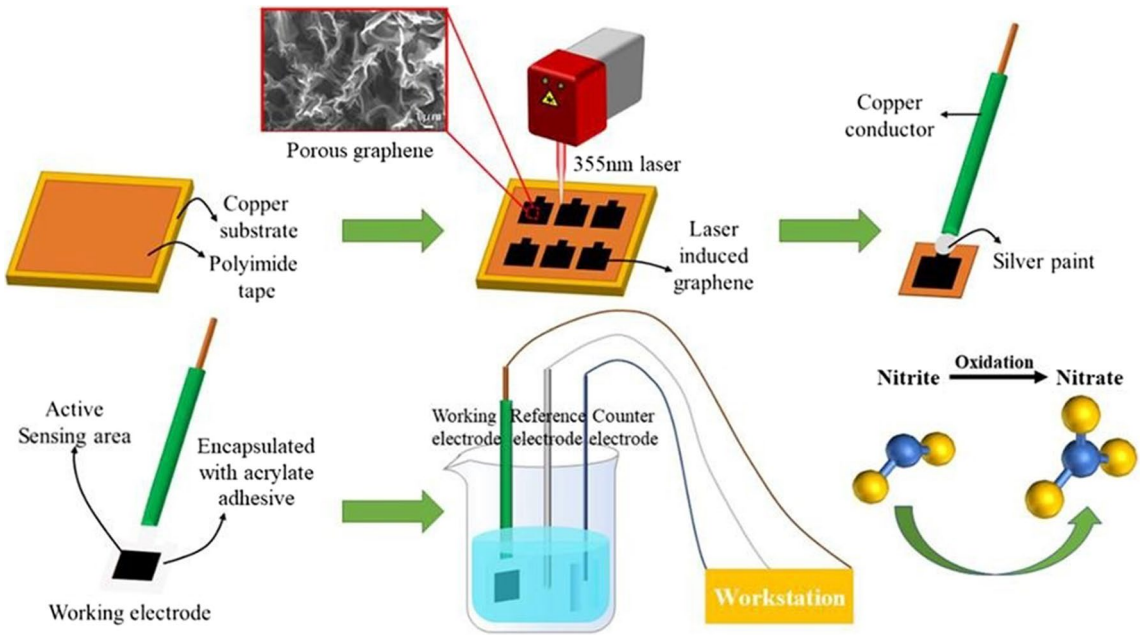
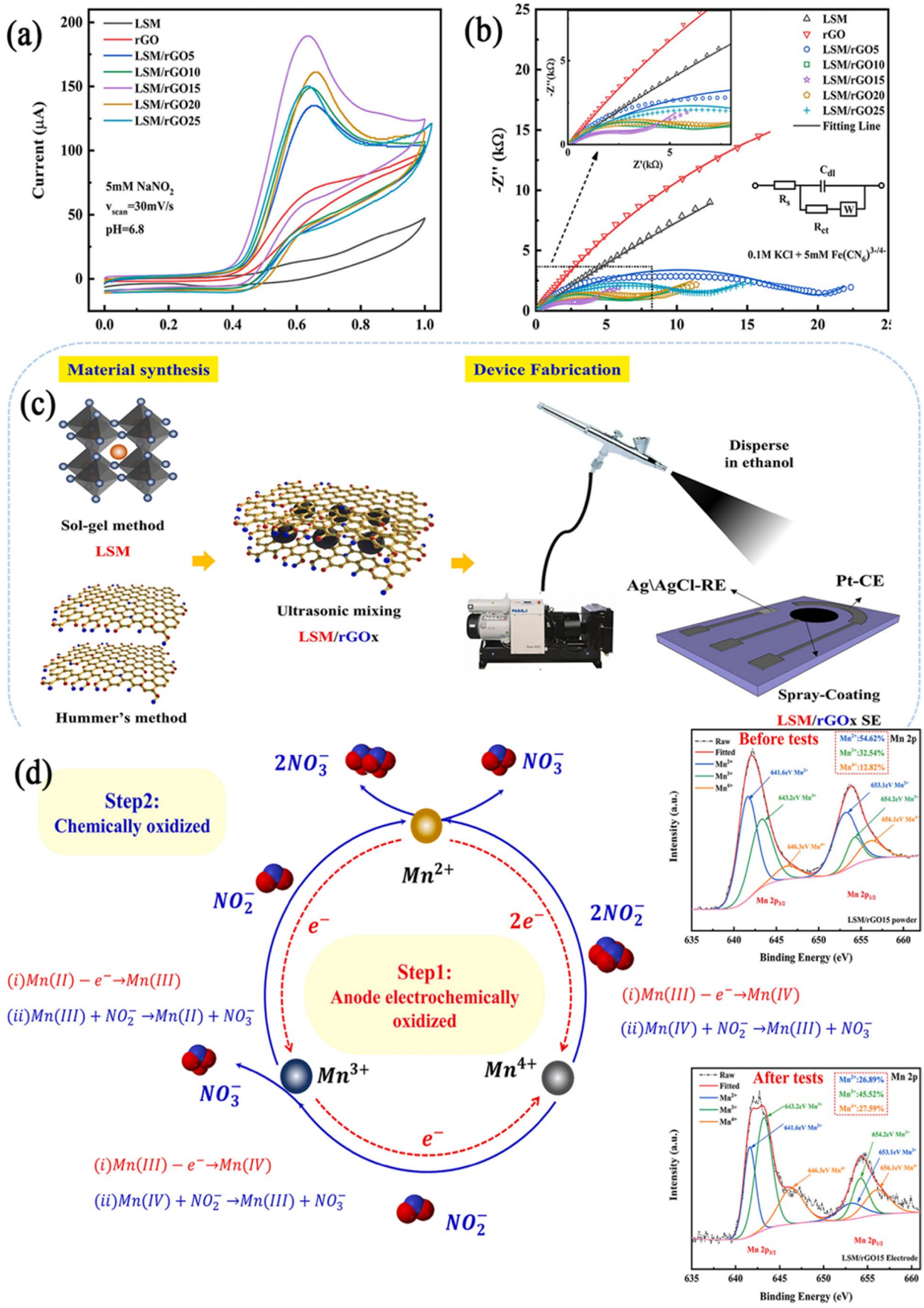


Fig. 2 Fabrication scheme of LIG and electrochemical sensing electrodes [47]. Copyright 2022, Elsevier

[68]. Transition metal manganese oxide was doped with reduced graphene oxide and then combined with a glassy carbon electrode to form MnO_2-rGO/GC electrode. The MnO_2-rGO-based composites have good electrochemical properties due to the high electrical conductivity of the MnO_2-rGO/GC electrode, which enables rapid electron transfer between the redox couple and the electrode surface. The sensor has a detection limit as low as 0.02 μM and a detection range of 0.1~5.5 μM. The MnO_2-reduced graphene oxide composite was used to test fruit juice and tap water with good recovery and high interference resistance. Wang et al. prepared nanocomposites ($Ni(OH)_2$/sr-GO) of nickel hydroxide and reduced graphene oxide by a one-step solvothermal method without reducing agents and bases. They constructed an electrochemical sensor for nitrite detection [62]. In electrochemical tests, the $Ni(OH)_2$/sr-GO nanocomposites showed high electrocatalytic activity. The detection range of the sensor is 0.1~663.6 mM, and the detection limit is 0.07 mM (S/N = 3) by amperometry. In addition, the sensor has good selectivity and stability, and low relative deviation with good recovery can be obtained to detect nitrite in water samples. Cheng et al. prepared perovskite oxides $La_{0.8}Sr_{0.2}MnO_3$ (LSM) and reduced graphene oxide by sol-gel method and Hummer method [93]. Then, the LSM/rGO_x composites were successfully prepared by mixing the two in different proportions by probe ultrasound. At 15 wt% rGO content, LSM particles have the best dispersion on rGO. In addition to this, composites have the largest peak current and the smallest transfer resistance in CV and electrochemical impedance tests. This shows that LSM/$rGO_{1.5}$ composites have the strongest oxidation ability to nitrite and the fastest electron transfer rate. The catalytic mechanism of LSM/rGO_x for nitrite oxidation can be inferred from electrochemical tests. Firstly, Mn(II) or Mn(III) is electrochemically oxidized to Mn(III) and Mn(IV), and secondly, Mn(III) and Mn(IV) chemically oxidize NO_2^- to NO_3^- (Fig. 3). The three-electrode sensor based on LSM/rGOx has an ultra-low detection limit (0.016 μM), good stability, and accuracy for NO_2^- detection in water. And it is expected to be used for the detection of nitrite in real environments. Among the conductive polymers, polyaniline has been widely studied for its good conductivity and stability. For example, Sivakumar et al. prepared polyaniline-@graphene oxide (PANI@GO) nanocomposites and used them to modify GCE [74]. The electrochemical performance of PANI@GO/GCE for nitrite oxidation was evaluated by comparing PANI@GO/GCE with GO/GCE, PANI/GCE, and bare GCE electrodes by CV technique. The results showed that the electrode had the highest oxidation current (about 45.7 μA) and the lowest overpotential (0.83 V). The electrode had a wide linear range (2–44,000 μM), high sensitivity (117.23 μA mM^{-1} cm^{-2}), and low detection limit (0.5 μM). In addition, PANI@GO/GCE electrode had good selectivity, stability, repeatability, and reproducibility in nitrite detection. A good recovery rate (98.07~106.11%) was obtained when the electrode was used in real-time applications of rain water and tap water samples, indicating that the sensor is suitable for real-time applications. Li et al. successfully prepared polyaniline/reduced graphene oxide composites by combining polyaniline with reduced graphene oxide by in situ electrochemical reduction and cyclic voltammetry electrochemical polymerization, which was used to modify the interdigital electrode (IDE) [58]. The electrochemical test on the composite showed that the π-π superposition force between aniline and rGO made electron transfer easier and contributed to the conductivity of IDE compared to bare electrodes. At the same time, the increase in conductivity and the transfer of electrons are conducive to the polymerization of aniline, which can increase the current and reduce the oxidation potential. The property gives the sensor good electrochemical performance. The detection range of the sensor is 0.4~183.7 mM, and the detection limit is 0.1 μM. Reduced graphene oxide is a derivative of graphene, different graphene materials can be obtained depending on the reduction method. Among them, ErGO is widely used because of its easy control and safety in synthesis. For example, Yue et al. prepared CuO_x/ErGO nanohybrids by electrodeposition method [64]. Depending on the pH, CuO_x/ErGO nanohybrids with different morphologies can be synthesized. With the gradual increase of pH, CuO_x/ErGO can take on peony-shaped, honeycomb-shaped, rose-shaped, and purple myrtle-shaped. Among them, the electrochemical sensor prepared from honeycomb CuO_x/ErGO showed the highest electrocatalytic activity for nitrite oxidation. The sensor has a detection limit as low as 0.072 mM and a detection range of 0.1–100 mM. In addition, the recovery rate of the sensor was between 94.29 and 106.21% when detecting drinking water. The method is highly accurate in detecting nitrite and has good prospects for development and application.

Nitrite sensor based on metal-organic frameworks

Among functional nanomaterials, metal-organic frameworks are the later emerging porous materials. Metal-organic frameworks are important porous crystalline coordination polymers that are self-assembled by various metal ions or metal clusters and organic ligands through coordination bonds. It has the advantages of a large specific surface area, high porosity, and adjustable pore size [94–96]. At present, it has been widely used in electrochemical sensing (Fig. 4) [97]. However, the original MOF is chemically less stable because of weak coordination bonds and active groups in the MOF [98]. In addition to this, the original MOF conductivity is lower. This is due to less skeletal overlap between the


(a)
LSM
rGO
LSM/rGO5
LSM/rGO10
LSM/rGO15
LSM/rGO20
LSM/rGO25
5mM NaNO2
vscan=30mV/s
pH=6.8
Current (μA)
(b)
-Z'' (kΩ)
Z'(kΩ)
Fitting Line
Cdl
Rs
W
Rct
0.1M KCl + 5mM Fe(CN6)3-/4-
(c)
Material synthesis
Device Fabrication
Sol-gel method
LSM
Hummer's method
Ultrasonic mixing
LSM/rGOx
Disperse in ethanol
Ag\AgCl-RE
Pt-CE
Spray-Coating
LSM/rGOx SE
(d)
Step2:
Chemically oxidized
2NO3-
NO3-
Mn2+
NO2-
2NO2-
e-
2e-
Step1:
Anode electrochemically oxidized
(i)Mn(II) − e−→Mn(III)
(ii)Mn(III) + NO2- →Mn(II) + NO3-
(i)Mn(III) − e−→Mn(IV)
(ii)Mn(IV) + NO2- →Mn(III) + NO3-
Mn3+
Mn4+
Before tests
After tests
Intensity (a.u.)
Binding Energy (eV)
LSM/rGO15 powder
LSM/rGO15 Electrode

◂**Fig. 3** **a** CV curve of the sensor at a scanning rate of 30 mV s^{-1} in 5-mM $NaNO_2$. **b** Nyquist diagram of the sensor in 0.1-M KCl solution containing 5-mM $[Fe(CN)_6]^{3-/4-}$. **c** Description of making electrochemical sensor based on LSM/rGO_x sensor electrode. **d** Schematic diagram of nitrite oxidation reaction mechanism and XPS results of Mn before and after electrochemistry tests [93]. Copyright 2022, Elsevier

p-orbital of the ligand and the d-orbital of the metal ions. Performance is not ideal when used for inspection [99]. In order to overcome these disadvantages, they are generally modified. One approach is to combine metal-organic frameworks with other functional materials to form composites, and the other is to pyrolyze MOFs to obtain their derivatives [100]. This section mainly introduces the application of MOF composites and their derivatives in electrochemical sensors. The performance of MOFs in electrochemical sensors is shown in Table 2.

Nitrite sensor based on MOF composite

In MOF-based composites, electroactive materials are often used to prepare continuous composites. These materials include metal oxides, carbon-based materials, and conductive polymers. Carbonaceous materials such as graphene, carbon nanofibers, and graphite dots are the preferred substrate materials for the preparation of composite materials. Among many kinds of MOFs, Cu-MOF materials have good electrocatalytic performance due to the REDOX properties of Cu^+/Cu^{2+}. For example, Sivakumar et al. prepared copper nanoporous carbon (Cu@NPC) nanoporous structures using a solvothermal method based on a two-step method (Fig. 5d) [119]. However, its poor electrical conductivity has limited the further development of electrochemical sensing. Adding carbon material to Cu-MOF material can overcome this problem. Due to the characteristics of π-π interaction and hydrogen bond interaction between carbon-based materials and MOFs, the conductivity and electron transfer rate can be accelerated in MOFs. For example, copper-functionalized MOF materials were synthesized by compounding copper ions with UiO-67-BPY and subsequently combined copper-chelated UiO-67-BPY MOF with graphene oxide for modification of electrodes [104]. In electrochemical tests, the current of Cu@MOF/ERG (electrochemically reduced graphene)/GCE is large compared to Cu@MOF/GCE, indicating faster electron transfer. The possible reason is that the π-electron conjugation effect of MOFs is amplified due to the chelation of bipyridyl ligands with copper, thereby enhancing the charge conductivity. In addition, the synergistic effect between ERG and MOFs makes the electrode surface more stable, which is beneficial to increase the specific surface area of the electrode and improve its sensitivity in electrochemical detection. The sensor was investigated through the DPV, and its detection range was 10–6000 μM with the detection limit of 1.2 μM for nitrite. In addition, the electrode had excellent reproducibility and stability and had great potential for future sensor platforms. Ambaye et al. synthesized carbon black (CB)/Cu-MOF nanocomposites via ultrasound and used them to modify SPCE (Fig. 5c) [117]. CB/Cu-MOF/SPCE electrodes were compared with SPCE, Cu-MOF/SPCE, and CB/SPCE electrodes by CV method and LSV in order to study the electrochemical response of electrodes to nitrite detection. The results showed that the CB/Cu-MOF/SPCE electrode had the highest current response and was 5 times higher than that of bare SPCE (Fig. 5a, b). The electrode material had a wide detection range (1.0–200.0 μM) and low detection limit (0.084 μM) when used for nitrite sensing. The electrochemical sensing of nitrite showed good reproducibility, repeatability, and stability. In addition, CB/Cu-MOF/SPCE obtained a satisfactory recovery rate (100.90~103.40%) in the detection of nitrite in wastewater samples. The results showed that the sensor has great potential in the detection of nitrite in aquatic substrates. Salagare et al. successfully synthesized a composite material based on carboxyl-functionalized MWCNTs/Co-MOFs by solvothermal method and successfully built a sensor for nitrite determination [118]. Under optimal experimental conditions, the sensor based on this composite exhibits excellent electrocatalytic performance. It has a wide linear range (80–1160 μM) and a low detection limit (18.8 μM). In addition, the sensor obtained satisfactory recoveries for the determination of nitrite in beverage and water samples, which is promising for application.

In the construction of heterostructures, the hybridization of MOFs and iron-based oxides is more widely used. Compounding MOFs with iron oxides can significantly improve the electrical conductivity and catalytic activity of the materials. For example, Amali et al. constructed an electrochemical sensor platform for nitrite detection using Fe_2O_3 NPs/Cu-BDC (copper(II)-benzene-1,4-dicarboxylate) MOF-modified screen-printed carbon electrode [103]. The composites were characterized, and the results proved to be successfully synthesized. The Rct of the material was significantly reduced due to the addition of Fe_2O_3 NPs. The reason is that the synergistic effect of both reduces the interface electron transfer resistance of the composite, which is conducive to improving the electrocatalytic activity of nitrite oxidation. Under the best experimental conditions, the electrode was studied using amperometry, and the results demonstrated that the sensor has a wide detection range and low detection limit, the detection range is 1~2000 μM, and the detection limit is 0.074 μM (S/N = 3). Among the conductive polymers, polypyrrole is widely used because of its good electrical conductivity, ease of polymerization, and low cost [120, 121]. In recent years, conductive polypyrrole and metal-organic skeleton composites have made great progress in the field of electrochemistry. For example, Xu et al.

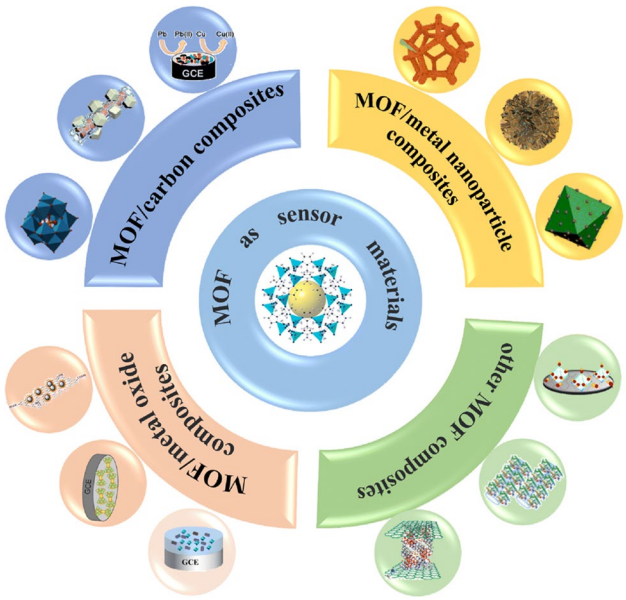


Fig. 4 Application of MOF composites in electrochemical sensors [97]. Copyright 2023, RSC Advances

successfully prepared a new PPy/UiO-66 nanocomposite by compounding PPy with UiO-66 by in situ polymerization [122]. In the electrochemical test, the sensors prepared from PPy/UiO-66 composite not only increased the activity of catalytic nitrite but also increased the conductivity. The enhanced performance of the sensor may be due to the good electrical conductivity of the conductive polypyrrole that promotes electron transfer in the nanocomposite and provides a large specific surface area for the adsorption and reaction of NO_2^-. The large surface area facilitates the catalytic oxidation of analytes. The sensor based on PPy/UiO-6 composite has a detection range of 0.05~1055.5 μM and a detection limit of 0.037 μM. It can be used as a potential nitrite sensing material.

Nitrite sensor based on MOF derivatives

The preparation of MOF derivatives can not only retain the structural properties of parent MOFs but also enhance the electrical conductivity and catalytic activity of the parent body. There is great potential for electrochemical analysis [88]. In recent years, two-dimensional (2D) ZIF derivatives have attracted much attention due to their low diffusion resistance and easily available active centers and have been successfully applied to energy storage and antibiotic removal. Yang et al. first synthesized Co-ZIF-L in rod form and then carbonized it under an Ar atmosphere to obtain CoN-CRs (Fig. 6g) [109]. CoN-CSs were obtained by pyrolysis of the flakes of Co-ZIF-L. The prepared materials were

Table 2 MOF-based electrochemical nitrite sensor

Electrode material	Method	Linear range (μM)	LOD (μM)	Sample	Ref.
MIL-53(Fe)/GCE	Amp	0.4–7000	0.36	Disinfection and tap water	[101]
Zn–TCPP(BP)/FTO[u]	Amp	1–2000	0.26	Tap and lake water	[102]
Fe_2O_3 NPs/Cu-BDC[v]MOF/SPCE	Amp	1–2000	0.074	Tap and mineral water	[103]
Cu@MOF/ERG/GCE	DPV	10–6000	1.2	Tap and river water	[104]
Nickel phthalocyanine-MOF	DPV	10–11,500,000	2300	–	[105]
Cu-MOF−GO/GCE	Amp	0.1–100	0.00147	Water	[106]
MWCNTs/Zr-aminoterephthalate	SWV	2–440	0.22	Root nodule	[107]
Cu@C@ZIF-8/GCE	DPV	0.1–300	0.033	Sausage	[108]
CoN-CRs/MGCE	Amp	0.5–4000, 4000–8000	0.17	Sausage and tap water	[109]
Ni/Co, N-CP/GCE	CA	1–500	0.094	Milk and tap water	[110]
a-Fe_2O_3/CNT hybrids/GCE	Amp	0.5–4000	0.15	Pond and tap water	[111]
Cu-Ni-BTC-CPE	Amp	1.0–1536, 1536–3636	0.4	Waste water	[112]
ZIF-67C@rGO/NiNPs/GCE	Amp	0.2–123, 123–473	0.086	Sausage	[113]
Cu-MOF/rGO hybrid/GCE	CA	3–40,000	0.033	Pond water	[89]
CuNps/CNTs/mGCE	Amp	5–705	0.18	Tap water	[114]
C-A Zn/Co-Fe PNSs@CC	Amp	1.25–701.25	0.44	Sausage and pure water	[115]
CNFs-Bi-MOF/GCE	Amp	0.02–2000	0.000184	Water	[116]
CB/Cu-MOF/SPCE	LSV	1–200	0.084	Wastewater	[117]
a-Fe_2O_3-CNTs/GCE	CV	0.5–4000	0.15	Tap and pond water	[111]
Carboxyl-functionalized MWCNTs/Co-MOFs	DPV	80–1160	18.78	Water and beverage	[118]

[u]4,4,4,4-(Porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) fluorine-doped SnO_2 transparent conductive glass (FTO)

[v]copper(II)-benzene-1,4-dicarboxylate (Cu-BDC)

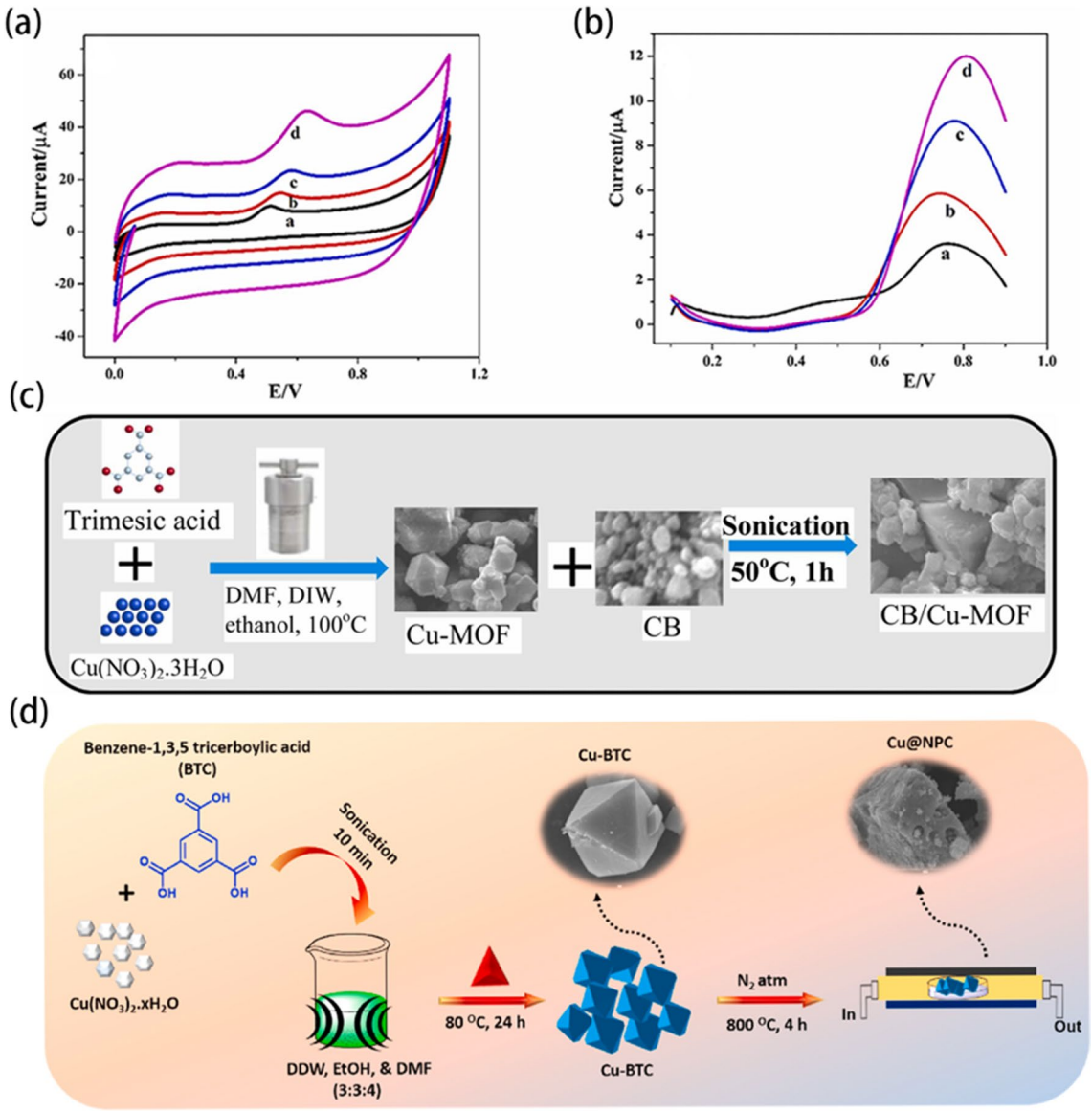
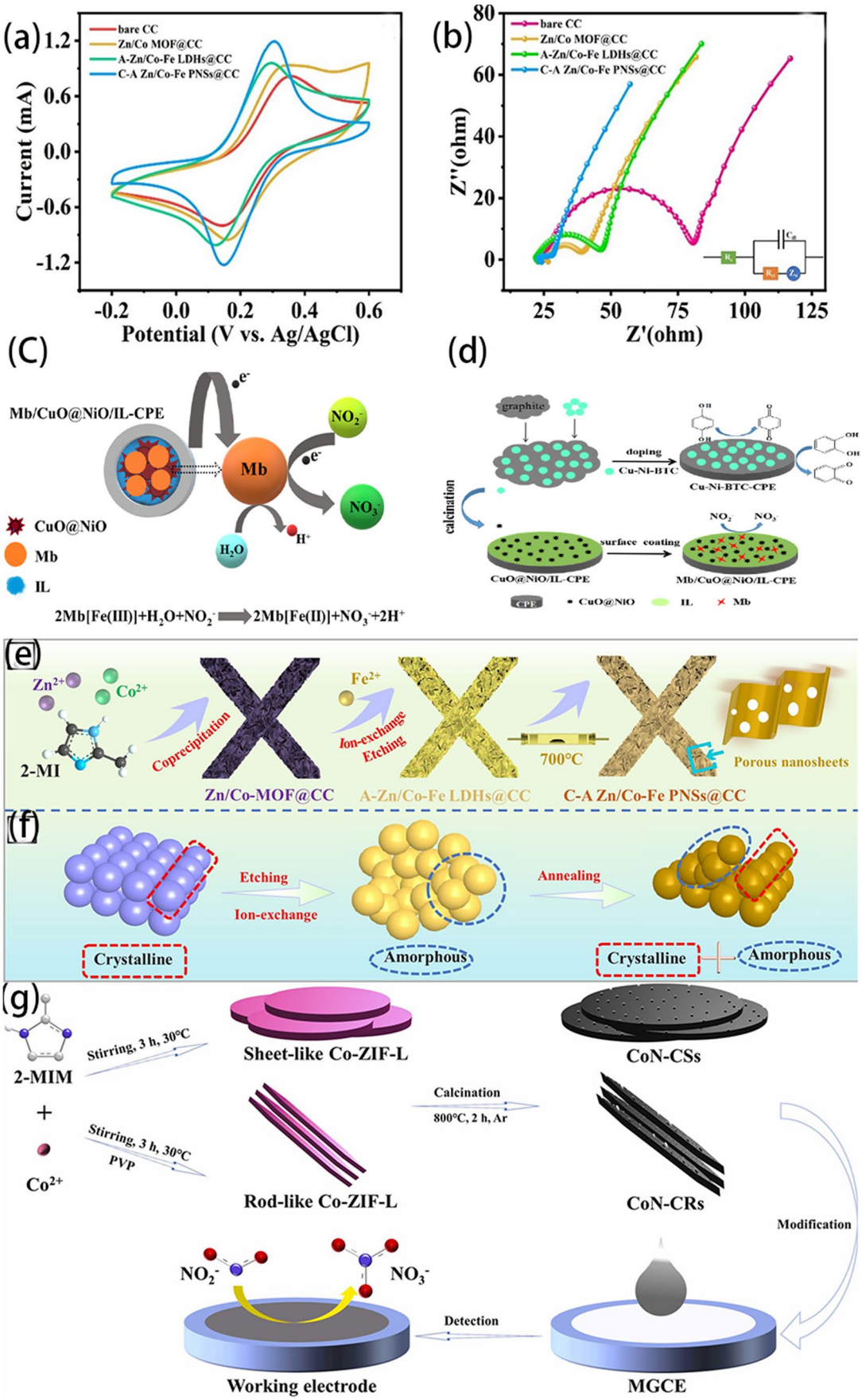


Fig. 5 **a** CV and **b** LSV responses of 100-μmol L^{-1} nitrite at (a) bare-SPCE, (b) Cu-MOF/SPCE, (c) CB/SPCE, and (d) CB-Cu-/SPCE. **c** Schematic description of the preparation procedures of the CB/Cu-MOF [117]. Copyright 2023, Elsevier. **d** Schematic representation of Cu-BTC and Cu@NPC [119]. Copyright 2023, Elsevier

analyzed by a series of techniques, and the results showed that CoN-CRs had stronger nitrite detection performance than CoN-CSs. The possible reason is that CoN-CRs have better surface area and more accessible active sites. Under optimal experimental conditions, the CoN-CRs-based sensors have a wider linear range of 0.5–8000 μM and a detection limit of 0.17 μM. The sensor has been successfully applied to the detection of nitrite in sausage and tap water with satisfactory recoveries. In conclusion, CoN-CRs are a promising sensing material for nitrite detection. Most of the current studies have focused on two-dimensional compounds of MOFs, and fewer studies have been conducted on three-dimensional compounds. Therefore, it is of great significance to study the MOFs of ternary composite systems. Gao et al. prepared the core-shell heterostructures of Cu@C@ZIF-8 composites by lysing Cu-MOFs@ZIF-8 under an Ar atmosphere as an electrochemical sensing platform for nitrite detection [108]. Due to the large specific surface area and high catalytic activity of the Cu@C, ZIF-8 had excellent electrocatalytic activity for nitrite detection. In the electrochemical test, the sensor has a linear response range of 0.1~300.0 μM and a lower detection limit of 0.033 μM. Besides, the sensor has good stability and reproducibility. In addition, the sensor's good selectivity is mainly attributed to the ZIF-8's narrow penetration channel. The sensor has been applied to the detection of nitrite in sausages


(a)
bare CC
Zn/Co MOF@CC
A-Zn/Co-Fe LDHs@CC
C-A Zn/Co-Fe PNSs@CC
Current (mA)
Potential (V vs. Ag/AgCl)
(b)
Z''(ohm)
Z'(ohm)
(C)
Mb/CuO@NiO/IL-CPE
Mb
CuO@NiO
IL
2Mb[Fe(III)]+H2O+NO2- → 2Mb[Fe(II)]+NO3-+2H+
(d)
graphite
doping
Cu-Ni-BTC
Cu-Ni-BTC-CPE
calcination
surface coating
CuO@NiO/IL-CPE
Mb/CuO@NiO/IL-CPE
(e)
2-MI
Coprecipitation
Ion-exchange Etching
700°C
Porous nanosheets
Zn/Co-MOF@CC
A-Zn/Co-Fe LDHs@CC
C-A Zn/Co-Fe PNSs@CC
(f)
Etching
Ion-exchange
Annealing
Crystalline
Amorphous
(g)
2-MIM
Stirring, 3 h, 30°C
Sheet-like Co-ZIF-L
CoN-CSs
Calcination
800°C, 2 h, Ar
Stirring, 3 h, 30°C
PVP
Rod-like Co-ZIF-L
CoN-CRs
Modification
Detection
Working electrode
MGCE

◂**Fig. 6** **a** CV results of 0.1-M KCl at different electrodes in 5.0-mM $[Fe(CN)_6]^{3-/4-}$ solution [115]. Copyright 2023, Elsevier. **b** EIS results at different electrodes in 5.0-mM $[Fe(CN)_6]^{3-/4-}$ solution and 0.1-M KCl [115]. **c** The mechanism of nitrite sensing [112]. Copyright 2020, Elsevier. **d** Schematic diagram of C-A Zn/Co-Fe synthesis PNSs@CC [115]. **e** Schematic diagram of synthesis mechanism [115]. **f** Schematic diagram of the synthesis method of Mb/CuO@NiO/IL-CPE and the preparation process [112]. **g** Description of the construction of CoN-CSs and CoN-CRs for nitrite detection [109]. Copyright 2022, Elsevier

with satisfactory results. In addition, Zhe et al. successfully constructed crystalline-amorphous zinc/cobalt iron porous nanosheets (C-A Zn/Co-Fe PNSs) on carbon cloth (CC) using a multi-step heterogeneous synthesis strategy [115]. By characterizing the composites, the results show that it is composed of interlaced carbon fibers and uniformly distributed hybrid nanosheet. And the special hybrid structure of the nanosheets is conducive to local enrichment of nitrite. Among the prepared materials, C-A Zn/Co-Fe PNSs@CC have the largest oxidation peak current and the lowest charge transfer resistance (Fig. 6a, b, d, e). These advantages show that C-A Zn/Co-Fe PNSs@CC has fast electron transfer ability and more significant conductivity. In addition, sensors based on C-A Zn/Co-Fe PNSs@CC have the advantages of wide linear range (1.25~4001.25 μM), low detection limit (0.44 μM), and high sensitivity (1297.13 μA/(mM cm^2)). This study provides a new way for the development of catalysts with excellent electrocatalytic activity and has great application prospects in nitrite detection. Dong et al. prepared Ni-MOF by microwave radiation and converted Cu^{2+} and Ni^{2+} ions into Cu/Ni organic skeletons to form Cu-Ni-BTC (1,3,5-benzenetricarboxylic acid, H3BTC) [112]. Then, the Cu-Ni-BTC is calcined to obtain a derivative CuO@NiO. Finally, myoglobin (Mb) is fixed on a sensing interface based on a CuO@NiO and ionic liquid (IL) composite membrane (Fig. 6f). Electrochemical tests showed that Mb maintained biological activity on the surface of CuO@NiO/IL composite membrane. Mb/CuO@NiO/IL has good electrocatalytic activity for nitrite. The nitrite sensing mechanism is shown in (Fig. 6c). Mb/CuO@NiO/IL-CPE (carbon paste electrode)-based sensors have linear ranges of 1.0~1536 μM and 1536~3636 μM for NO_2^-, with detection limits as low as 0.4 μM.

Nitrite sensor based on metal materials (excludes non-precious metals)

In recent years, electrochemical sensors based on different chemically modified electrodes have been manufactured. Among them, metal material is a commonly used electrode-modified material. Its surface size is adjustable, and it has good electrocatalytic activity and can be used as a sensor for long-term stability and selectivity at relatively low temperatures [123, 124]. This section focuses on the application of non-precious metal materials as well as composite materials in nitrite sensors. The properties of such nanomaterials are summarized in Table 3.

Nitrite sensor based on metal oxides (excludes non-precious metals)

In recent years, metal oxides prepared by suitable methods have the advantages of a larger specific area, good electrical conductivity, low price, and better stability. Due to these advantages, metal oxides are widely used in the research of nitrite sensors [8, 125]. Puspalak et al. successfully synthesized cobalt oxide nanoparticles for modification of CPE electrodes by precipitation and calcination method using green synthesis method with sugarcane juice as capping agent [154]. The CV method shows that the electrode has a certain response value for different concentrations of nitrite. In Amp detection, sensors based on this electrode have a wide detection range (50–800 μM) and a low detection limit (0.3 μM) in the detection of nitrite. What is more, the sensor can be used to detect nitrite in farmland soil samples, which can alleviate soil pollution to a certain extent and has a greater application prospect. As a kind of multi-purpose metal oxide, TiO_2 has been applied in the field of electrochemical sensing because of its advantages of good biocompatibility, high conductivity, and low cost. Salagare et al. successfully prepared TiO_2-RGO nanocomposites by compositing TiO_2 with RGO and used them to modify a glassy carbon electrode to construct a nitrite sensing platform [155]. The composite material has larger surface area, higher electrical conductivity, and excellent nitrite electrocatalytic activity. By CV and LSV methods, it was found that the oxidation peak of the TiO_2-RGO electrode to nitrite was higher than that of other electrodes, and the electrode based on the composite material had a high sensitivity (4.853 μA/μM cm^2), a wide linear range (10~2000 μM), and a low detection limit (0.006 μM). In addition, the sensor has obtained a good recovery rate in the determination of NO_2^- in water and buttermilk samples and has a good application prospect. Among many metal oxide-based nanomaterials, ZnO is recognized as the best nanostructure due to its wide band gap and strong binding energy [159, 160]. However, most of the ZnO-based nanomaterials prepared have the disadvantages of high detection limit and low sensitivity at present. It is well known that the topography of nanomaterials has a great influence on the performance of the sensor, and the large specific surface area can accelerate the electron transfer during the sensing process [161]. Therefore, it is possible to start by changing the morphology of ZnO. For example, Cheng et al. synthesized a unique approximately nearly spherical ZnO nanostructure by solvothermal method [127].

Table 3 Non-precious metal-based electrochemical nitrite sensor

Electrode material	Method	Linear range (μM)	LOD (μM)	Sample	Ref.
Sn-CeO_2/GCE	CA	10–600	0.016	Pond water	[125]
Carbon black/$NiCo_2S_4$@CeO_2/GCE	Amp	0.2–7400	0.03	Tap and mineral water	[126]
Near-spherical ZnO/GCE	CA	0.6–220, 460–5500	0.39	Ham sausage, pickle, tap water	[127]
MnO_2/PANI/GCE	CA	19.98–732.17	1.08	Water	[128]
CuO/NiO/FTO	Amp	1–1800	0.013	Tap water	[129]
MoO_3/Co_3O_4/CC	Amp	0.3125–4514	0.075	Water and sausage	[130]
$NiCo_2O_4$/GCE	Amp	10–300	1.04	Tap water and river water	[131]
FeSeNR/CC	Amp	0.625–6775.5	0.07	Pickled vegetables	[132]
TiO_2–Ti_3C_2TX/CTAB/CS/GCE	DPV	3–250, 250–1250	0.85	Tap and sea water and milk	[133]
NiP/NF	Amp	0.1–4000	0.01	Drinking water	[134]
APJCP-SP-FTO[w]	Amp	2.5–1300	0.437	Tap water	[135]
MnO_2	DPV	10–800	0.5	–	[136]
a-MnO_2-MoS_2/GCE	Amp	100–800	16	Drinking water	[137]
$MoSe_2MoO_3$/GCE	CV	2.5–80	0.1	Potable and tap water	[138]
CuO NPs/GCE	LSV	10–50	1.1	–	[124]
Cu/CBSA NFNs[x]/GCE	DPV	0.5–500	0.1	Mineral water	[139]
$NiFe_2O_4$-CPE	Amp	0.1–1000	0.1236	Tap water	[140]
NiFe-LDH NSAs/CC	Amp	5−1000	0.02	Tap and Dongpu reservoir water	[141]
CFO/SPCE	Amp	0.016–1921	6.6	Tap water and mineral water	[142]
Co_3O_4-DCS/GCE	Amp	6.6–300, 300–13,840	0.22	Tap water and milk	[143]
CeO_2-CuO/GCE	CA	10–5000	10	–	[144]
CuO/NiO/GC	Amp	1–5000	0.5	Urine	[145]
MnO_2/GO-SPE	CV	0.1–1, 1–1000	0.09	Tap and packaged water	[146]
$NiCo_2CO_3(OH)_2$/GCE	Amp	5–4000	0.002	–	[147]
Fe_2O_3@MoS_2/GCE	Amp	2–6730	1	Drinking water and river water	[148]
Fe_3O_4/RGO/GCE	DPV	10–2882	0.1	Tap, rain, and river water	[149]
$PrFeO_3$-MoS_2/CS/GCE	Amp	5–3000	1.67	Tap water	[150]
Fe_3O_4/MoS_2/GCE	Amp	0.5–328	0.2	–	[151]
TOSC-MoS_2/GCE	Amp	6–3140, 3140–4200	2	Drinking and river water	[152]
PANI-MoS_2/GCE	Amp	4.0–4834	1.5	Drinking and river water	[153]
CoO@CPE	Amp	50–800	0.3	Soil	[154]
TiO_2-RGO/GE	LSV	10–2000	0.006	Tap and ground water, buttermilk	[155]
NP-Fe_2O_3–CoO/GCE	Amp	200–16,200	0.1	Sausage	[156]
SiO_2/C/Mn(II) phthalocyanine	CV	0.79–15.74	0.2	Water and sausage meat	[157]
TiO_2/carbon ionic liquid electrode	LSV	0.5–1500	0.2	Sausage	[158]

[w]Screen-printed fluorine-doped tin oxide electrode with activated jute carbon paste

[x]Copper ion–crosslinked bovine serum albumin nanoflower networks

The mixed solvents were synthesized by using polyethylene glycol 400 with water in a volume ratio of 12:1. Unlike other reported transition metal oxide nanoparticles, this approximately spherical ZnO nanostructure had higher uniformity and better dispersion, and no self-aggregation occurs when the particles are small (Fig. 7a, b, c). Comparison of sensing performance of bare GCE and near-spherical ZnO/GCE by CV and CA techniques. The results showed that the current response values of the modified electrodes were significantly higher than those of the bare electrodes. In addition, ZnO-based sensors had a wide linear range, low detection limits, and strong immunity to interference. Moreover, they showed a satisfactory recovery rate in the detection of actual samples. In conclusion, nearly spherical ZnO nanomaterials have a wide range of promising applications for detection and analysis. Besides, nanostructured CeO_2 is also widely used in various fields due to its good chemical and physical properties, superior reusability, and stability [162, 163]. However, the nanostructure CeO_2 has a wide band gap and relatively low conductivity. Therefore, it needs to be modified when used as a sensing material [164]. For example, Manibalan et al. successfully doped Sn with CeO_2 using a

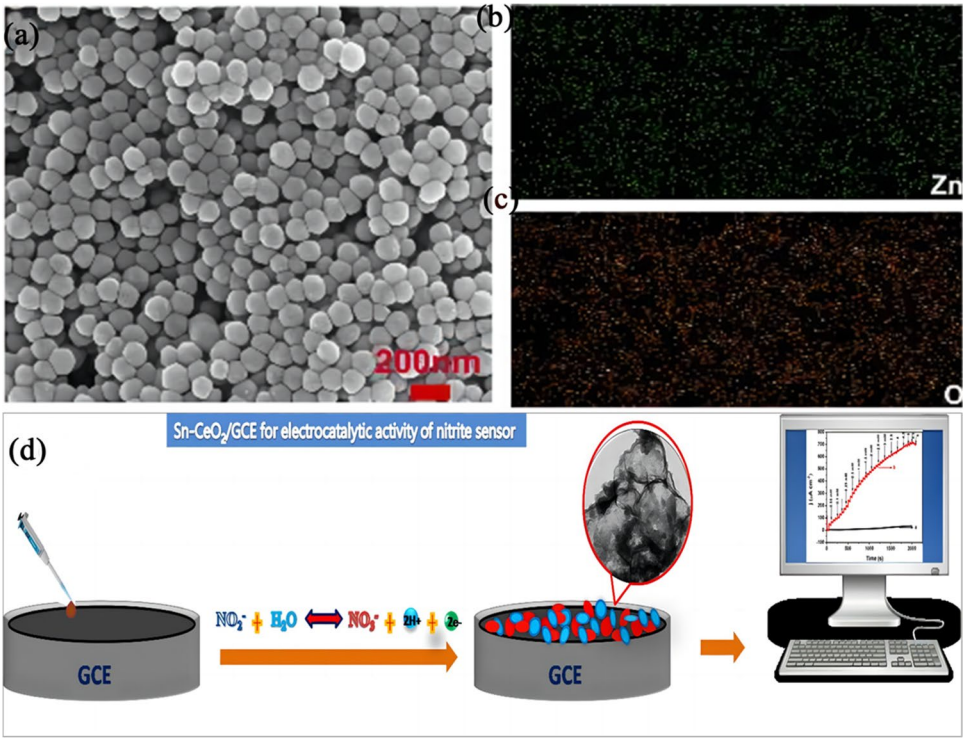


Fig. 7 **a** SEM image of highly dispersed near-spherical zinc oxide. Mapping of **b** element zinc and **c** element oxygen prepared in an optimal solvent (PEG 400 to water volume ratio of 12:1) [127]. Copyright 2022, Elsevier. **d** Schematic diagram of modified electrode preparation [125]. Copyright 2022, Elsevier

simple precipitation synthesis method (Fig. 7d) [125]. The doping of Sn improves charge transfer as well as exposes the CeO_2 metal oxide active region, which can improve the electrical conductivity of CeO_2 and make CeO_2 nanoparticles have better surface properties. Characterized by XRD, FTIR, and TEM techniques, the results showed that the morphology of the catalyst was spherical nanoparticle clumps with a particle size of 8.5 nm. The catalytic performance of Sn-CeO_2/GCE was studied by the amperometry method for nitrite. The results showed that the sensor had a detection range of 10×10^{-6}~6×10^{-3} M and a detection limit of 16 nM. In short, the sensors have good prospects for application and development.

Nitrite sensor based on metal oxide composite (excludes non-precious metals)

The performance of single metal oxides is inferior to that of metal oxide composites when used as catalysts. Metal oxides can be compounded with carbon materials, conductive polymers, metal-organic frameworks, and other substances. The composite nanomaterials of reduced graphene oxide and Fe_3O_4 have excellent catalytic and electrical properties and exhibit excellent electrocatalytic activity in electrochemical sensors. Bharath et al. used mechanochemical ball milling to prepare high-quality graphene nanosheets from graphite in the presence of $KMnO_4$ and aspartic acid [149]. After that, Fe_3O_4/RGO composites were successfully prepared by loading Fe_3O_4 nanoparticles onto graphene using a simple hydrothermal method. The Fe_3O_4-RGO nanocomposites were characterized using HRTEM images, and the results demonstrated that good Fe_3O_4 nanoparticles were distributed on the surface of reduced graphene oxide sheets, with an average particle size of 90 nm. The Fe_3O_4-RGO nanocomposites were loaded into GCE, and the prepared sensor exhibited good electrocatalytic activity, wide detection range, and low detection limit for nitrite. Radhakrishnan et al. prepared Fe_2O_3/rGO composites by one-step hydrothermal method [165], since Fe_2O_3 nanoparticles are well dispersed on the rGO surface and Fe_2O_3 nanoparticles on both sides of rGO can limit the aggregation of rGO. Therefore, the composite has high specific surface area, good electrical conductivity, and good catalytic performance for the oxidation of nitrite (Fig. 8a–f). Sensor based on Fe_2O_3/rGO composites has a wide detection range (0.05–780 μM) and a low detection limit (0.015 μM). The sensor can be applied to the environment, food, and other fields. In addition, conductive polymers have excellent electrical conductivity and tunable organic functional groups for intermolecular interactions with different target analytes. To improve the long-term stability of the conductive polymer, inorganic materials can be added and compounded with the conductive polymer. For example, the synergistic effect of conductive polymers and metal oxides can also show greater electrochemical sensing capabilities. Qiu and Qu combined polyaniline with MnO_2 (Fig. 8g) [128]. The transition metal oxide manganese dioxide has a unique oxidation behavior at different electrochemical potentials when used as an electrochemical

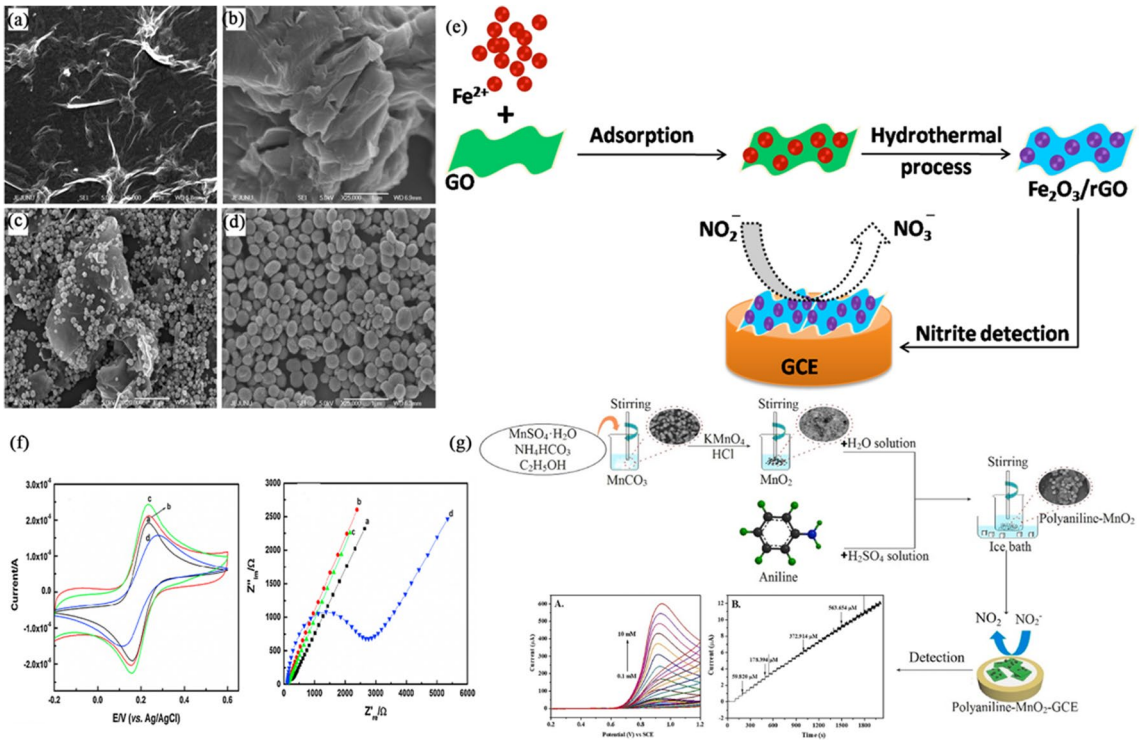


Fig. 8 FE-SEM micrographs of **a** GO, **b** rGO, **c** Fe_2O_3/rGO, and **d** Fe_2O_3. **e** Nitrite detection scheme using Fe_2O_3/rGO-modified glassy carbon electrode. **f** CV behavior of the modified GC electrode in the presence of 1-mM $[Fe(CN)_6]^{3-/4-}$ in 0.1-M KCl with a scan rate of 50 mV s^{-1} and EIS behavior of the modified GC electrode by impedance measurement in the frequency range 100 KHz to 0.1 Hz at a DC potential of 200 mV and an AC potential of ±10 mV in the presence of 1-mM $[Fe(CN)_6]^{3-/4-}$ in 0.1-M KCl (curve a, bare GC; curve b, rGO; curve c, Fe_2O_3/rGO; curve d, Fe_2O_3-modified electrode) [165]. Copyright 2014, Elsevier. **g** Preparation of polyaniline-manganese dioxide organic-inorganic nanocomposites for nitrite electrochemical sensing [128]. Copyright 2022, Elsevier

sensing material. And the amine and imine groups in polyaniline contribute to the adsorption of nitrite on the nanocomposites. The morphology of $MnCO_3$, MnO_2, polyaniline, and polyaniline-MnO_2 nanocomposites was characterized by scanning electron microscopy. The results showed that manganese carbonate was slightly spherical and manganese dioxide was also spherical and larger in size. And in the image of the composite material, block polyaniline can be seen and spherical manganese dioxide was wrapped around the polyaniline. Composite materials were used to modify GCEs to prepare nitrite sensors. The sensor has a low detection limit (CV of 4.38 μM, CA of 1.08 μM) and a wide linear range (CV of 0.1~10 mM, CA of 19.98~732.17 μM). In addition, the organic-inorganic nanocomposite exhibited excellent sensing performance in actual sample analysis.

Nitrite sensor based on conductive polymer composite

Conductive polymers have been widely used since their inception in 1977 and are of particular importance in materials science [166, 167]. Conducting polymers are increasingly used in the detection of analytes by voltammetry or amperometry due to their selectivity, sensitivity, and strong adhesion to electrode surfaces [168]. They are an excellent choice for developing and modifying highly sensitive electrochemical sensors. A review of the literature from 2015 to 2020 (Science Direct and Wiley websites) shows that the number of papers on conductive polymer-based sensors has been increasing over the past few years [166]. This section focuses on the application of conductive polymer composites in nitrite sensors, and some of the properties exhibited by the material in modified electrodes are summarized in Table 4.

Among the conducting polymers, polyaniline, polypyrrole, polyacetylene, and their derivatives have received great attention. Li et al. prepared a polythiophene derivative membrane-modified GCE by a one-step electropolymerization method to establish a nitrite sensor [177]. DTT is a molten bicyclic heterocyclic compound with a rigid planar frame and an extended π-conjugated electronic structure. The effect of PolyDTTF on the electrochemical oxidation of nitrite was studied. The results showed that PolyDTTF had good electrical conductivity and enhanced electrocatalytic activity, which can greatly improve the electron transfer kinetics and

Table 4 Electrochemical nitrite sensor based on conductive polymer

Electrode material	Method	Linear range (μM)	LOD (μM)	Sample	Ref.
PEDOT/NU-902/FTO	Amp	Up to 1600	1.71	–	[169]
PPy/UiO-66/GCE	Amp	0.05–1055.5	0.037	–	[122]
Poly(3ABA)/GCE	DPV	10–140	0.15	Human serum, orange juice	[170]
PolyNiCo_GCE	Amp	2.49−1700	0.45	Tap water	[171]
CQD_PEDOT/GCE	Amp	0.50–1110	0.088	–	[172]
CG/PPy/CS/GCE	DPV	0.2–1000	0.02	Water	[173]
PDAP-NiHCF/GCE	Amp	0.1–130	0.0151	Water and ham sausage	[174]
PPy-Cunano/GCE	Amp	0.1–0.7, 0.7–1040.7	0.03	Well and lake water	[175]
CuNPs/3D-PANIH/GCE	Amp	0.2–4300	0.07	Lake water and milk	[176]
PolyDTTF/GCE	Amp	0.0055–35	0.002	Ham, sauce beef, and pickle	[177]
Co/PPy/GCE	Amp	2–3318	0.35	Pickled Chinese cabbage	[23]

facilitate the oxidation of nitrite. In addition to this, sensors based on this material had significant detection limits and good detection ranges. The reason may be that PolyDTTF has high electron affinity and synergistic effect, which enables rapid adsorption of analytes to the electrode surface. In conclusion, the preparation method is simple, the film thickness can be controlled, and the sensor can be used for detection in real samples. The sensor offers the possibility of application in the food industry and environmental analysis. Since it is challenging to synthesize a single polymer to meet multiple requirements in the practical application of nitrite detection. Therefore, composites are often used to modify the electrodes. Generally, conducting polymers are often compounded with metal nanoparticles, carbon-based nanomaterials, metal-organic framework chemicals, and other substances. For example, Lu et al. successfully synthesized Co/PPy nanocone composites by compounding metallic cobalt with conductive polymer PPy by electrodeposition technique [23]. Polypyrrole has excellent electrochemical stability and high electrical conductivity compared to other conductive polymers. It can be used as an attachment substrate for various metal nanomaterials. Due to the synergistic effect of nanocomposite components, the composite material has the advantages of high sensitivity, high capacitance, and controllable conductivity. Because its three-dimensional structure provides more active sites for nitrite detection, the composite exhibits good nitrite determination performance in electrochemical studies. Carboxyl graphene is a two-dimensional crystalline carbon material that has received great attention in practice due to its excellent properties. Xiao et al. prepared composites of CG (carboxyl graphene), PPy, and CS (chitosan) nanocomposites [173]. For CS is rich in amino groups, it can attract negatively charged nitrite. The recombination of PPy and CG provides a large specific surface area and numerous active sites. In conclusion, the composite material can improve the selectivity and sensitivity of nitrite determination. In addition, DPV is used for electrochemical performance testing. The results showed that the detection range of the composite-modified sensor was 0.2~1000 μM, and the detection limit was 0.02 μM. The sensor has a promising application in the practical detection of nitrite. Saho et al. synthesized fibrous nanocomposites of reduced graphene oxide, manganese ferrite, and polyaniline (RGO/$MnFe_2O_4$/polyaniline) in a two-step process [63]. The introduction of RGO not only prevents the agglomeration of $MnFe_2O_4$ nanoparticles and increases the specific surface area but also helps to accelerate the electron transfer process from reduced graphene oxide flakes to $MnFe_2O_4$ nanoparticles. In addition, the strong interaction between graphene and polyaniline allows for uninterrupted charge flow during nitrite oxidation (Fig. 9). The electrode modified based on this composite has a wide linear range (0.05~12,000 μM) and a low detection limit (0.015 μM), which can be used for the detection of nitrite in rain water samples.

Conclusion and outlook

This paper reviews the research progress and application status of nitrite electrochemical sensors based on four nanomaterials. The characteristics and advantages of carbon nanomaterials (graphene, carbon nanotubes), metal-organic frameworks, non-precious metals, and conducting polymers are systematically introduced in nitrite electrochemical sensors. These materials have been extensively studied for their unique and fascinating properties (e.g., graphene has large specific surface area and inexpensive and readily available raw materials, metal-organic frameworks with high porosity and tunable pore size). However, individual materials also have some disadvantages, which leads to the performance in nitrite detection often inferior to that of composite materials. Many studies have shown that the synergistic effect of composites not only improves stability and accelerates the electron transfer rate but also provides more active sites in the detection of nitrite. Although the field has achieved great results over the course of decades of development.

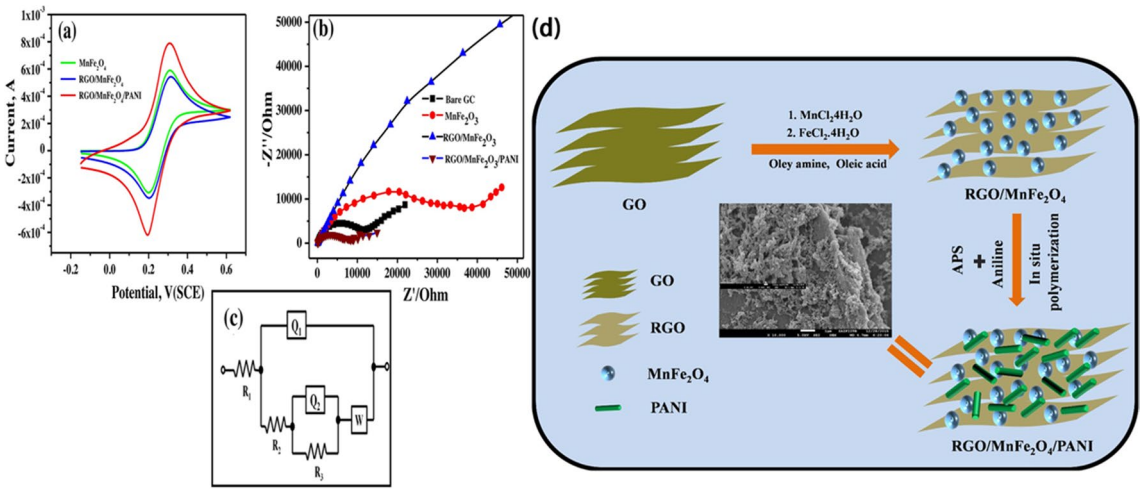


Fig. 9 **a** Ferrocyanide cyclic voltammetry of electrodes modified with different modifiers in a 0.1-M phosphate buffer at pH 7. **b** Nyquist diagram recorded by modifying the electrode with different modifiers at an excitation potential of 0.3 V in a 0.1-M phosphate buffer at pH 7. **c** Equivalent circuit used for the fitting of the impedance plot. **d** The synthesis procedure adopted to synthesize the nanocomposite material [63]. Copyright 2020, Elsevier

However, further research on electrochemical nitrite sensors still faces many challenges. The morphology, purity, and dispersion of carbon nanomaterials have great influence on the electrocatalytic performance. It is necessary to seek new synthesis methods or consider three-dimensional structures. In addition, the carbon nanomaterials will peel off the electrode surface, which will affect the stability of the sensor and limit its further development in the long-term detection of nitrite. Therefore, it is necessary to study more robust fixing methods. Due to the poor structural stability and conductivity of MOF materials, the sensor is not ideal for nitrite detection. Developing functional MOF composites remains a challenge. In addition, the synthesis process of MOF composites that has been studied is too complex to achieve large-scale production, so it is still necessary to explore new synthesis paths. As far as metal materials are concerned, the electrocatalytic performance of precious metals is better than that of non-precious metals, so it is still a difficult problem to find non-precious metals that can replace precious metals. At present, there are few electrochemical methods on the combination of conductive polymers with carbon nanomaterials and metal materials. So it can be considered to combine conductive polymers with other materials to further improve the electrocatalytic performance. In general, the first is the preparation method; the preparation of nanomaterials involves precise and targeted control of the shape and size of the nanomaterials in most cases. Different preparation methods often affect the performance of the catalyst size. In addition to this, most sensors are manufactured on rigid substrates, resulting in a lack of flexibility in the sensors. Second, when designing a catalyst with excellent performance, it is necessary to explain the reaction process and mechanism on the catalyst. In principle, the catalytic performance of a catalyst is determined by its electronic structure, while the true catalytic active site and the exact reaction mechanism of some materials are still unclear. Finally, in most cases, nitrite electrochemical sensors have the disadvantages of high cost of large-scale preparation, time-consuming synthesis process, and threats to humans and the environment of nanomaterials. These disadvantages limit the practical application of the sensor.

For future research on nitrite electrochemical sensors, the following aspects can be considered. First, research should focus on new synthetic methods to change the structure and composition of catalysts in order to adjust their electronic structure. And new nanomaterials can be combined with good conductive polymers. In addition to this, low-cost, biocompatible materials and more environmentally friendly synthesis methods and equipment should be used. Second, the reaction mechanism of nitrite sensors is further explored, and the true catalytic active sites of various materials are clarified. This results in higher sensitivity and better selectivity of nitrite electrochemical sensors. Finally, technologies such as screen printing, ARM microcontrollers, and mobile intelligence can be combined to build portable NO_2^- electrochemical sensors to achieve remote real-time measurement of nitrite content. And existing nitrite sensors can be integrated into nutrient management programs in agroecosystems to facilitate rapid and accurate detection of spatial and temporal changes in nitrite levels in soil.

Availability of data and materials This declaration is "not applicable."

Author contributions Jie Zhang: had the idea for the article, critically revised. Jing-He Yang: had the idea for the article, critically revised.

Tingting Zhang: critically revised. Yu-Xi Yang: performed the literature search and data analysis, write a first draft.

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Declarations

Ethical approval This declaration is "not applicable."

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