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Application of Nanocomposites Based on Graphene and Metal Materials in Measurement of Nitrate/Nitrite in Food Samples

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Abstract: Nitrite (NO_2^-) has been broadly applied in industrial and agricultural products; it is often found in various foods, water, environmental systems, and biological samples, though NO_2^- is a toxic inorganic contaminant that is hazardous to the health of humans and other organisms. In recent years several approaches have been recommended for detecting and monitoring NO_2^- that the electrochemical method is of very attention, among them, due to its easy miniaturization, cost-effective, rapidness, straightforward operation. Graphene nanocomposites have a considerable synergistic electrocatalytic effect toward the nitrite redox, magnifying the electrochemical response signals and improving the sensitivity, selectivity, and feasibility of the nitrite detection in various real samples. In this article, we report the recent developments in electrochemical sensors based on graphene**/**metal nanocomposites for the measurement of nitrate/nitrite in the food samples and identifying performances, including limit of detection (LOD), detection ranges, pH, sensitivity, stability, and technology used were determined.

Keywords: electrochemical; graphene; metal; nanocomposite; nitrite; nitrate; food sample.

1. Introduction

Nitrate (NO_3^-) and nitrite (NO_2^-) as inorganic compounds are found in natural and processed foods. These compounds are present in vegetables, specifically green leafy vegetables, such as spinach and lettuce, cabbage, red beet-root, radish, and drinking water, which contributes about 80%-95% of dietary NO_3 intake; however, processed food and animal food products are commonly major sources for dietary NO_2^- intakes [1]. Oral commensal bacteria under the tongue or in the stomach are known to be responsible for changing dietary NO_3^- to NO_2^-. Historically, there are several pieces of evidence showing that NO_2^- intake at high concentrations can be a serious threat for health due to its possible endogenous conversion to nitrosamines and increase in several severe and chronic toxicities such as thyroid disorders, methemoglobinemia, infant central nervous system defect, spontaneous abortion, and gastrointestinal cancers [2]. The methemoglobin leads to blue baby syndrome via decreasing oxygen transferring capacity, and nitrosamine is a factor for carcinogenicity. In return, one of

the recent researches showed that restricted dietary NO_2^- may stimulate numerous favorable effects, particularly on the cardiovascular system and metabolic pathways [3]. Thus, many countries have established strict roles on nitrite dosage. It was reported that the maximum contamination level for NO_2^- in drinking water (WHO, USEPA) is 1.0mg/l. Also, WHO has determined acceptable daily intake (ADI) levels of nitrite (0.07 mg nitrate/ kg body weight per day) and nitrate (3.7 mg nitrate/ kg/day) largely based on drinking water standards [4]. It was estimated that in Iran, the mean dietary intake of NO_3^- and NO_2^- from different food groups and drinking water is 505±160 and 7.7±2.2 mg/d, respectively [1]. Concerning NO_2^- importance in health, accurate estimation of NO_2^- content in food source seems to be a challenging issue and an important barrier for food and nutrition sciences because there is a close relationship between NO_2^- content and food safety. Over the past decade, the various process is proposed for the efficient analysis of nitrite, including ion-chromatography [5], spectrophotometric [6], chemiluminescence [7], capillary electrophoresis [8], and electrochemical method [9]. Most of the mentioned techniques require technical personnel and costly equipment besides being time-consuming. However, the electrochemical method is affordable, simple, and trustable, with high sensitivity, good selectivity, and rapid response. Therefore, it is known as an alternative method with high performance for controlling and strict testing of NO_2^- in foods. In electrochemical methods, the electrocatalytic oxidation of nitrite on the electrode surface occurs by factors such as platinum (Pt), glassy carbon, gold (Au), copper (Cu), and transition metal oxide electrodes. However, the main restriction of this method is that it is susceptible to contaminations, which reduces the accuracy and sensitivity. Therefore, modified electrodes with different nanomaterials (metal, carbon, and polymeric) and their nanocomposites are proposed as alternative strategies to improve the performance of designed electrodes for nitrate detection in food samples. These electrodes electrochemical response to NO_2^- have high redox and increase the detection range and lower detection limit (LOD) for NO_2^- [3]. Furthermore, modified electrodes with nanomaterials and their nanocomposites have high electrical conductivity, good resistance to heat and corrosion, good physicochemical stability, and large specific surface area. In recent years, among modified electrodes, electrochemical sensors based on graphene are of more attention due to their good catalytic ability, large surface area, high conductivity, and [1] and metal nanoparticle have been further developed due to their unique physicochemical characteristics, small size, and the high surface-to-volume ratio [2]. Although, throughout the past decade, several reviews were presented on modified electrochemical sensors. However, our main goal is focusing on the sensors that are exclusively modified using metal and graphene-based nanoparticles, specifically the detection of nitrate and nitrite in food samples. A brief comparison of their electrolyte pH, detection limit, range of detection, sensitivity, and stability is made.

2. Materials and Methods

In this research, we study electrodes modified with metal and graphene nanoparticles and metal/graphene nanocomposites to detect nitrate/nitrite in food samples. For this reason, the Google Scholar, Science Direct, and Pup Med databases and articles of 2000 till 2020 have been searched with keywords “nitrite”, “nitrate”, “modified electrodes”, “graphene”, “metal nanoparticles” and “food sample”, then their electrolyte pH, the limit of detection, range of detection, sensitivity and stability was compared.

3. Results and Discussion

3.1. Modify the electrode with graphene-based nanoparticles.

Using graphene as a matrix for electrochemical biosensors has attracted remarkable interest. Graphene sheets used to modify the sensors have some advantages, such as increasing the surface area of sensors, immobilizing a major amount of enzymes, antibodies, cells, or probe ssDNAs, and enhancing the received electrochemical response [10]. Graphene is formed of monolayers of carbon atoms that are arranged in a hexagonal configuration, the basic building block of graphite [11]. Graphene is known for its large surface area, controllable properties, and high electrical and thermal conductivity. It is considered a suitable material for designing electrochemical sensors [12]. Also, this material can be used in various fields. Figure 1.

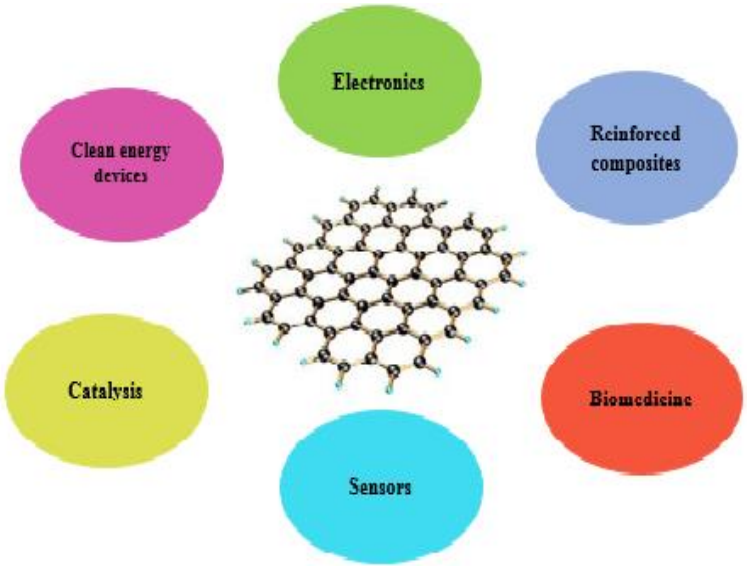

Figure 1. Graphene applications in various fields.

One remarkable advantage of graphene over fullerenes and carbon nanotubes is that graphene can be synthesized readily at a low cost in chemical laboratories [13]. On the other hand, the graphene particles' electron transferring ability is almost 60 times more than single-walled carbon nanotubes. The conductance conductivity property of graphene is different according to treatment methods, preparation, and graphene particles' morphology. There are various methods for graphene synthesis such as; exfoliation and cleavage of natural graphite, chemical vapor deposition, plasma-enhanced chemical vapor deposition, electric arc discharge, micromechanical exfoliation of graphite epitaxial growth on electrically insulating surfaces, like opening carbon nanotube, silicon carbide, and solution-based reduction of graphene oxide [10]. Modified electrodes by graphene or nanocomposites based on graphene have many applications due to their high surface to volume ratio, high conductivity, and well catalytic ability [14]. Among the graphene family, graphene oxide (GO) and reduced graphene oxide (rGO) are extensively used as modifier substances in nitrite sensors. Mani *et al*. could fabricate nitrite sensors by chemically reduced graphene oxide with a sensitivity of 0.0267 A M^{-1}, the linear range of 8.9–167μM and LOD of 1 μM [15]. In electrochemical reduced holey graphene (ERHG), the number of exposed edge planes, defect density, and the electron-transfer rate was increased remarkably. Jing Zhang *et al*. fabricated an electrode by ERHG to detect nitrite. Results showed that the electrode has LOD of 0.054 μM and excellent stability [16]. Graphene nanoribbons (GNs) have reactive edges that can enhance the electrocatalytic properties and

adsorption of molecules used in the electrode. Mehmeti *et al*. used graphene nanoparticles (GN/GCE) for nitrite detection in water samples. The proposed electrode had LOD of 0.22µM, detection range from 0.5 to 105 µM, and well stability [14]. Doping of graphene with heteroatoms such as S, N, K, and P is a way to develop its structural and electrochemical performances. Moreover, the electronic properties, chemical activities, and optical properties of graphene increase by chemical doping with heteroatoms like nitrogen (NrGO). Chen *et al*. used metal-free nitrogen-doped reduced graphene oxide (NrGO) for nitrite detection in food; the results showed that the designed electrode has a detection limit of 0.2 µM, detection range of 0.5 –5000 µM, good sensitivity, and good stability [17]. The electrochemically activated graphite (EAG) had more surface area and high-energy adsorption sites that act as reservoirs for the rapid diffusion of the target molecule on the electrode surface. Selvakumar Palanisamy *et al*., used EAG to detect nitrite; this electrode had LOD of 38nM, sensitivity 0.126 µAµM^{-1} cm^{-2}, wider detection range, and excellent stability [18]. Table 1 shows the stability, sensitivity, and limitation in detecting electrodes modified with graphene nanoparticles for sensing of nitrate and nitrite in food samples.

3.2. Modify the electrode by the metal nanoparticle.

Metal nanoparticles have been extensively used for designing biosensors due to their unique catalysis properties and biocompatibility. For example, sensors based on gold nanoparticles to determine biological materials have received much attention due to their good stability—figure 2 [19].

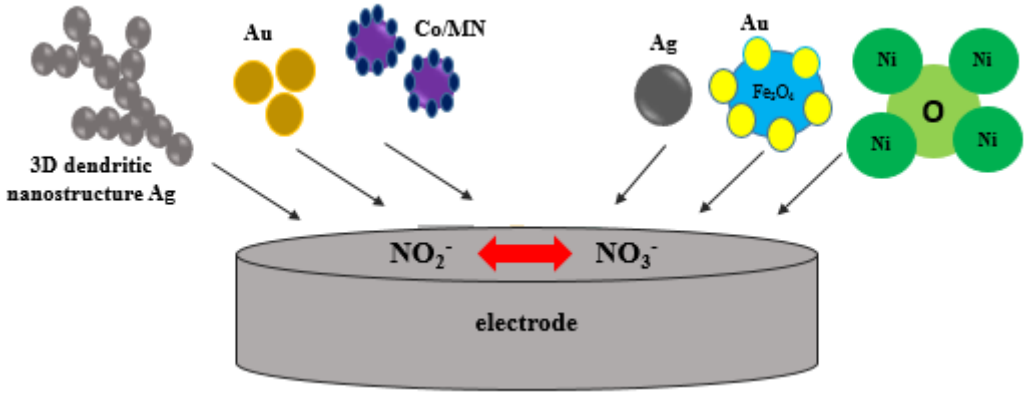

Figure 2. Modify the electrode by the metal nanoparticle.

Chen *et al*. used Au nanoparticles for nitrite detection. Modified electrodes had LOD of 82 nM, detection range from 0.1 –4000 and 4000 – 10000 µM, high sensitivity, and good stability [20]. Wan *et al*. designed electrodes with Au nanoparticles on a carbon paper electrode and investigated their electrochemical behaviors. Results showed LOD of 0.093µM and higher sensitivity for the designed electrode [21], also Wang *et al*. produced Au nanoparticles on choline chloride. It was shown that the modified electrode has LOD of 1.0×10^{-7} M, a sensitivity of 0.354µAµM$^{-1,}$ and a linear range of 4.0×10^{-7} to 7.5×10^{-4}M [22]. Yu *et al*. used Au-Fe_3O_4 nanoparticles as a modified electrode with a linear range of 3.6×10^{-6} to 1.0×10^{-2} M, and LOD of 8.2×10^{-7}M; also, this electrode has good stability and selectivity [23]. Huang *et al*. modified an electrode with Au-copper nanochain on glassy carbon electrode with LOD of 0.2 µM, the linear range of 0.01 to 4.0 mM, the sensitivity of 17.55 µA mM−1, and excellent stability [24]. Shen Liu *et al*. designed a sensor for detection of nitrite by Au–Fe (III) nanoparticles and

differential pulse voltammetry (DPV) with LOD of 2.0 × 10^{-7} M, and amperometric results showed LOD of 1.0×10^{-7} M [25]. Comparison of electrodes modified with Au nanoparticles showed that the electrode modified with Au nanoparticles on the surface of choline chloride had the lowest detection limit. The most stable was the Au /copper modified electrode. Magnetic nanoparticles have been used as supports and carriers in biosensors for food safety assessment due to wide surface area and well biocompatibility [26]. Parsaei *et al*. used cobalt (II)-Schiff base complex and magnetite nanospheres to detect nitrite in water samples. The designed sensor had LOD of 1.5 × 10^{-2} µmol L^{-1}, detection range from 0.2 to 30.0 µmol L^{-1}, good sensitivity, and stability [27]. Dhanya *et al*. synthesized silver nanoparticles and used them to detect nitrite; the sensor was shown to have LOD of 1.5×10^{-15} mol dm^{-3} and high sensitivity [28]. Guadagnini *et al*. modified carbon electrodes with silver nanoparticles to determine nitrite and nitrate; the designed electrode had LOD of 3.7 × 10^{-6} M and 4.0 × 10^{-6} M, respectively, and low stability and sensitivity [29]. Hu and coworkers designed a nitrite sensor by 3D dendritic nanostructure of silver, which had LOD of 2µ M, the sensitivity of 28.2 $mAmM^{-1,}$ and short-term stability [30]. Shivakumar *et al*. designed an electrochemical sensor to detect nitrite in water and sausage by silver nanoparticles with LOD 0.031µM, the sensitivity of 580 mA $mM^{-1}cm^{-2,}$ and long-term stability [9]. In general, we can say that electrodes modified with Ag nanospheres by green synthesis had the highest LOD. Investigations showed that electrode modification with other metal or metal oxide nanoparticles such as NiO [31], copper, and CuO [32] had almost similar LOD, and Copper–Cobalt nanoparticles had the highest LOD for nitrite oxidation; also CuO nano chains showed the highest stability**.** Table 2 shows the stability, sensitivity, and LOD of electrodes modified with metal nanoparticles for nitrate and nitrite detection in food samples.

3.3. Modify electrode by metal nanoparticle/graphene-based nanocomposites.

Nanocomposites are a combination of two or more different nanoparticles that can strengthen the weak points of an electrode and improve the electrode properties, including physical, chemical, thermodynamic, magnetic, electrochemical, and stability properties [34]. There are many studies about applying graphene/metal nanocomposites in biosensors' design to determine nitrite in food samples. In these biosensors, graphene sheets act as a substrate with high specificity to accommodate final biomolecules. Also, they facilitate transferring the electrons between the electrode and the analyte. Figure 3 [39]. Here we refer to electrodes that are modified using metal and graphene composites.

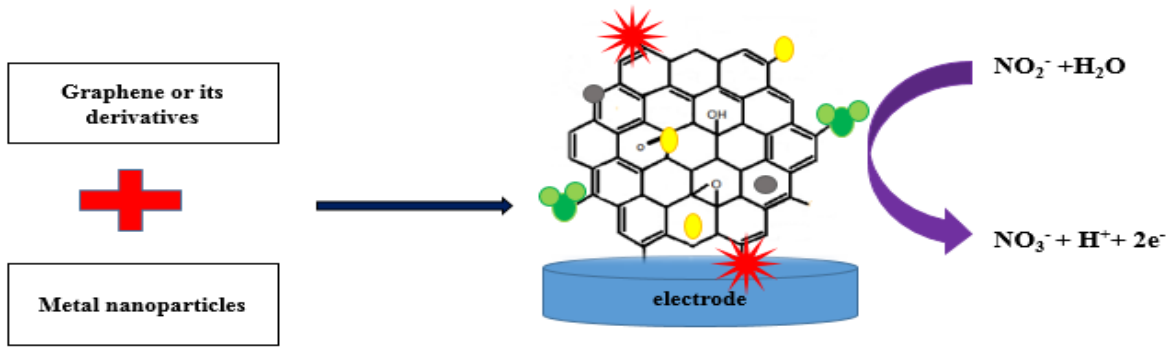

Figure 3. Modify electrode by metal nanoparticle/ Graphene-based nanocomposites.

3.3.1. Au nanoparticle/graphene-based nanocomposites.

Research has shown that Au NPs/Gr nanocomposites have been the most favored candidates for nitrite sensing. Therefore several nanocomposites of Au have been developed to detect nitrite such as AuNPs/Gr/GCE [40], ERGO/Au NPs /SPCE [41], Au/f-GE/GCE [42], w-GN/Au/GCE [43], Au-HNTs-GO/GCE [44], Au_2Pt_1NPs/PyTSNG/GCE [45] and AuPd/rGO/GCE [46]. Electrochemically reduced graphene oxide sheets provide a three-dimensional structure for AuNPs attachment and nitrite absorption and catalyze its oxidation. For example, ERGO/AuNPs /SPCE modified electrode has a low LOD of 0.13µM, a wide linear range, high sensitivity, and good stability. Therefore, it was a useful tool for detecting nitrite in various real food samples [41]. ZON *et al*. have shown that the spherical Au nanoparticles/3D flower-like network of graphene represents a great electrochemical ability in the oxidation of nitrite in pickled pork samples, with LOD of 0.01 µM, detection range of 0.125 to 20375.98 µM, and excellent stability [42]. Wavy graphene(W-GN) has a disordered structure with side and dangling bonds, which creates a high electrochemical catalytic activity. The electrode surface modification using w-GN/Au/GCE showed that the current reaction of nitrite is better than bare electrode, so the electrode has LOD of 6.0×10^{-8} molL $^{-1}$, good selectivity, powerful catalytic activity, wide linear range, and almost good stability [43]. Halloysite nanotubes (HNTs) are considered as a novel kind of natural nanotubes because of their low price and high length-to-diameter (L/D) ratio, and they have been attracted by researcher's attention for electrodes' designing. Also, there are hydroxyl groups on the HNTs surface that metal nanoparticles can grow directly on its surface. Zhang *et al*. synthesized Au-HNT-GO nanocomposites for fabricating an electrochemical sensor for nitrite detection in tap water. The results indicated that the sensor has excellent performance, LOD of 0.03 µM, the sensitivity of 0.0231 to 0.0865, good reproducibility, and long-term stability [44]. Li *et al*. decorated Au-Pt bimetallic nanoparticles (Au-PtNPs) on the surface of NG with 1, 3, 6, 8-pyrene tetra sulfonic acid sodium salt. The sensor had a linear range of 0.5–1621 µM and LOD of 0.19 µM to detect nitrite in ham sausage samples. The current response is also decreased 5.7% of its original response after two weeks [45]. Li *et al*. synthesized Au–Pd nanoparticles to design Au–Pd/rGO/GCE electrodes for nitrite detection in tap water. This electrode had LOD of 0.02µ M, good reproducibility, a linear range of 0.05-1000.0 M, and good stability [46]. Results showed that the electrode of Au nanoparticles/3D flower-like network graphene represents the lowest LOD, and ERGO/AuNPs /SPCE electrode has the highest stability among the designed sensors nitrite [41].

3.3.2. Pt nanoparticle/graphene-based nanocomposites.

Researches showed that platinum (Pt) morphology has a remarkable impact on nitrite detection [47]. On the other hand, platinum/graphene composite had more impact on nitrite oxidation due to its high catalytic sites. PtNPs prevent graphene agglomeration and have a synergistic effect on the oxidation of nitrite. Therefore, different platinum composites have been used to detect nitrite in food samples, such as Pt-RGO/GCE [48], Pt-ErGO/GCE [49], Ni-Pt/Gr/GCE [50], Co-Pt/Gr/GCE [51], Cu-Pt/Gr/GCE [52]. Yang *et al*. deposited platinum nanoparticles on a reduced graphene surface. The amperometry results showed that the Pt–RGO modified electrode has LOD of 0.1 µM, detection range of 0.25−90 µM, and sensitivity of 0.4964 µA mM^{-1}. Also oxidation current response remained 95.2% after 15 days [48]. As metal nanoparticles can improve the conductivity and catalytic potential of ErGO, Vijayaraj *et*

al. modified ErGO surface by platinum nanocomposites film for nitrite detection in tap water. The electrochemical results indicated that the modified electrode has LOD of 0.22µM. Linear ranges of 5-100 mM and 100-1000 mM and oxidation current response remained 99.8% after 6 days and 90.02% after 12 days [49]. One of the reasons for using double metal composite, except the synergistic effect of metals on the catalyst activity, was to overcome the cost of using one expensive metal. The electrochemical results show that the electrode modified with Ni-Pt/Gr/GCE had better catalytic performance than Pt/Gr. Hameed *et al*. used Ni-Pt/Gr/GCE, Co-Pt/Gr/GCE, and Cu-Pt/Gr/GCE to detect nitrate in tap and river water samples. The electrochemical results showed LOD of 0.49, 0.145, and 0.035µM, the sensitivity of 0.08518, 0.04596- 0.09771, and 0.2103-0.6269, the detection range of 10−15000, 1−2000; 2000−15000 and 1−1000, and 1000−15000 µM, respectively and excellent stability for the electrodes. Results showed that Cu-Pt/Gr/GCE electrode has the lowest LOD and Co-Pt/Gr/GCE electrode has the highest stability.

3.3.3. Pd nanoparticle/ Graphene-based nanocomposites.

Palladium (Pd) nanoparticles are widely used due to their excellent conductivity, relatively low price, well electrocatalytic performance, and high chemical inertness [53]. Fu *et al*. designed nanoparticles of Pd and reduced graphene oxide (RGO) electrode for nitrite detection. The results showed that Pd and graphene nanoparticles have a synergistic effect on nitrite oxidation. This electrode had a detection range of 1−1000 µM, and LOD of 0.23 µM, also oxidation current response remained 94% after one hour [54]. Zhao *et al*., a modified electrode with Pd/Fe3O4/polyDOPA/RGO to detect nitrite in river water and sausage. The amperometric response showed LOD of 0.5µM, and a detection range of 2.5−6470 µM, also oxidation current response remained 90% after 9 days [55]. Results showed that Pd/rGO/GCE electrode has the lowest LOD, and Pd/Fe3O4/polyDOPA/RGO/GCE electrode has the highest stability.

3.3.4. Ag nanoparticle/graphene-based nanocomposites.

Silver nanoparticles have been widely used to prepare electrochemical sensors due to their biocompatibility, wide specific surface, and catalytic activity [56]. Ikhsan *et al*. designed a sensor with GO and Ag nanoparticles for nitrite detection in water, using LSV (Linear Sweep Voltammetry) and amperometric techniques. LOD values were 2.1 and 0.037 µM, and the detection ranges were 10−180, and 1−1000 µM, respectively. The result showed that 95% of the electrode's stability has remained after one week [57]. Ahmad *et al*. synthesized silver and reduced graphene nanoparticles to modify the electrode's surface. The electrochemical results indicated a detection range of 0.1−120 µM, LOD of 0.012 µM, and sensitivity of 18.4. Also, 94.5% of the electrode's stability remained after 5 weeks [58]. TiO_2 is widely used to prepare electrochemical sensors because it is cost-effective and has high conductivity and good biocompatibility. Zhang *et al*. used Ag/TiO_2/r-GO/GCE electrode for detection of nitrite in tap and rainwater; electrochemical results indicated that the modified electrode showed well electrocatalytic efficiency for the nitrite oxidation, the sensor had a LOD of 0.4 µM, the sensitivity of 0.112, linear range 1-1100 µM and the oxidation response retained 90 % after three weeks [56]. Results showed that Ag-rGO/GCE electrode has the lowest LOD and the highest stability.

3.3.5. Cu nanoparticle/ Graphene-based nanocomposite.

Wang *et al*., were designed an electrode with copper nanoparticles and graphene pallets for the determination of nitrate in river water and tap water samples. The amperometric results showed that the designed electrode has a detection range of 0.15−10500 μM, and LOD of 0.06 μM. Also, the oxidation response remained 95.9% after 15 days [59]. Majidi *et al*. fabricated a nitrite sensor by Cu nanoporous film supported by the electrode of graphene nanosheets. The amperometric results confirmed the following results: The LOD was equal to 0.0887, detection range 0.1−100 μM, sensitivity 3.1, and good stability [60]. Results showed that the modified Cu/f-RGO/GCE electrode shows high electrocatalytic activity towards Cu/RGO/GCE and Cu/GCE. In addition to the facile preparation process, non-noble metal present in the electrode could decrease the preparation costs; this electrode had the lowest LOD and highest stability.

3.4. Modify electrode by metal oxide nanoparticle/Graphene-based on nanocomposite.

Crystal structure metal oxide nanoparticles have possessed high catalytic activity due to their high surface ratio to volume. On the other hand, hybridization of them with graphene could present higher electrocatalytic activity, larger specific surface area, and superior biocompatibility. As a result, they are used for designing electrochemical sensors to detect nitrite [61]

3.4.1. Fe_2O_3 nanoparticle/Graphene-based nanocomposite.

Fe_2O_3 nanoparticles have been used for electrochemical sensors' designing because of their low cost, well biocompatibility, excellent bandgap, and high catalytic activity [62], Fe_2O_3/rGO nanocomposite can inhibit the aggregation of rGO sheets by introducing Fe_2O_3 NPs on the surface of rGO nanosheets. In this way, it can expend the surface area of composite in compare to rGO nanosheets alone. Also, Bharath *et al*. synthesized rGO-Fe_3O_4 nanocomposites for detecting nitrite in the rain, tap, and river water. The modified sensor indicated good electrocatalytic activity and good stability, with a sensitivity of 0.2025 and low LOD [63].

3.4.2. Ce nanoparticle/Graphene-based nanocomposite.

Nanostructures of cobalt oxide are cheap and environment friendly also; they have well conductivity [64]. Co_3O_4 is extensively used to design electrochemical nitrite sensors due to its high surface area and well chemical stability. By considering the exceptional and unique properties of graphene and Co_3O_4, a combination of them might yield enhanced performance. The composite electrode showed high sensitivity, which detected a broad range of nitrite concentrations from 1 to 380 M and had the lowest LOD (0.14 M) [65]. M.Stanković *et al*. compared the ability of cerium, titanium, and selenium dioxide nanoparticles for detecting nitrite in tap water. The suggested sensor acquires acceptable selectivity and sensitivity with a low LOD (0.18 μM) and a broad linear range of 0.7 to 385 μM, under optimized operational circumstances [66]. Also, Luo *et al*. made a nitrite sensor with graphene oxide and cobalt hexacyanoferrate nanoparticles. The results obtained from DPV showed that the designed sensor has low LOD equal to 0.27 μM and a linear range of 1 to 100 μM [67].

Table 1. Application of electrochemical sensors based on graphene nanomaterial's in detection nitrite/nitrate.

Formulation	Technique	Food sample	pH	Detection range	LM	Sensitivity	Stability	R
GNs/GCE	Am	Tap Water	3	0.5-105 µM	0.22 µM	-	5d	[14]
ERHG	Am	Tap water, Liquid milk	7.4	0.2-10,000 µM	0.054 µM	0.311 µA $\mu M^{-1}cm^{-2}$	95 % remained after 3 w	[16]
NrGO	DPV	Pickled garlic, river water	7	0.5-5000 µM	0.2 µM	0.229 µA $\mu M^{-1}cm^{-2}$	93.8% remained after 30 d	[17]
CR-GO/GCE	Am	Water	5	8.9–167 µM	1 µM	0.0267 A M^{-1}	decrease in the response after 4 d	[15]
EAG	Am	Water	-	0.1 µM to 16.4 mM	38nM	0.126 µA μM^{-1} $cm^{-2.}$	96.4% remained after 24 d	[18]

GCE: glassy carbon electrode/ CR-GO: chemically reduced graphene oxide, Am: Amperometry, DPV: Differential pulse voltammetry, LM: Limit of detection, d: day, w: week.

Table 2. Modification of electrodes using metal for detection nitrite/nitrate in a food sample.

Formulation	Technique	Food sample	pH	Detection range	LM	Sensitivity	Stability	R
Ag	SWV	Water	4.5	10^{-14} to 10^{-6} (mol dm−3)	10^{-15} (mol dm^{-3})	high sensitivity	-	[28]
Au–Fe(III)	DPV, Am	Water	5	DPV:3.0 ×10^{-7}–1.5 × 10^{-4} M Am: 2.0 × 10^{-7}–1.5 ×10^{-4} M	DPV:2.0 ×10^{-7} M Am: 1.0 ×10^{-7} M	-	92% retained after 30 d	[25]
Ag	NO_2^-: DPV NO_3^-:CV	Water	6.7	NO_2^-: 5.0 × 10^{-6}–1.1 × 10^{-3} NO_3^-:: 1.0 × 10^{-5}–5.0 × 10^{-3}	NO_2^-: 3.7 × 10^{-6}M NO_3^-::4.0 × 10^{-6}	NO_2^-: 790, NO_3^-: 3400 (AM^{-1} m^{-2})	1 d	[29]
Au	DPV	Water, Sausage	4	4.0×10^{-7} to 7.5×10^{-4}M	1.0×10^{-7} M.	0.354µAμM^{-1}	81% retained after 60 d	[22]
Ag	SWV	Water	7	2–1000µ M	2µ M	28.2 $mAmM^{-1}$	The short-term stability	[30]
Au	Am	Water	7	0.1 –4000 and 4000 – 10000 µM,	82 nM.	252 µA mM^{-1} cm^{-2}	88 % retained after 28 d	[20]
Ag	Am	Water, Sausage	7	0.1^{-8}µM	0.031µM	580 mAmM $^{-1}$ cm^{-2}	long-term stability	[9]
NiO	SWV	Sausage, Pickled	7	0.8–1100 µM.	0.3 µM	Good	93% retained after 20 d	[31]
CoL/MNSs	SWV	water	4.5	0.2–30.0 µmol L^{-1}	1.5×10^{-2} µmol L^{-1}	3.054 µAL µmol^{-1}	85% retained after 90d	[27]
Gd/TiO_2	CV	sausage	7	5.0×10^{-7}mol l^{-1}	8.0×10^{-7} to 4.0×10^{-4} mol l^{-1}	-	94% retained after 14 d	[33]
Au	Ca	water	7	1-100 µM	0.093 µM.	0.08138 mA mM^{-1} & 0.0476 mA mM^{-1}	28 d	[21]
Fe_3O_4@Pt	DPV, Am	Water, orange juice	4	3.3 × 10^{-7} to 1.3 × 10^{-2}M	1.09 × 10^{-7}M	-	93% retained after 21 d	[34]
Alumina	Am, DPV	Sausage	5	5.0×10^{-8}–1.1×10^{-3}mol L^{-1},	1.0×10^{-8}mol L^{-1}	-	14 d	[35]
Au@Fe_3O_4	DPV	Sausage	4	3.6×10^{-6} to 1.0×10^{-2} M	8.2×10^{-7}M	-	95% remained after 15d	[23]
CuO	CV	picked vegetables	7.5	0.004–3.7 mM	0.3 µM	177.9µAmg^{-1} dL^{-1} cm^{-2}	98.5% remained after 30d	[32]
Au-Coper	DPV	Water	7	0.01 ~ 4.0 mM.	0.2 µM	0.0176 µA μM^{-1}	98.60 % remained after 35d	[24]
Pd–Fe	Am	Water	4	6×10^{-6}–5×10^{-3} M.	2×10^{-6}M	-	-	[36]
TO	LSV, CV	Sausage	6	5 × 10^{-7}–1.5 ×10^{-3} M,	2 × 10^{-7} M	-	97.1% remained after 14 d	[37]
Copper–cobalt	Am	Sausages	7.4	0.5 to 430 µM	60 nM	-	96% remained after 30 d	[38]

TO: Titanium Dioxide, Co/MNS: cobalt (II)/Magnetite nanospheres, Ca: Chronoamperometry, SWV: Squarewave voltammetry, LSV: Linear Sweep Voltammetry

Table 3. Modification of electrodes using metal/graphene for detection nitrite/nitrate in a food sample.

Formulation	Technique	Food Sample	pH	Detection range	LM	Sensitivity	Stability	R
Au NPs/Gr/GCE	Am	Sausage, packaged	3	5×10^{-5} to 5.1×10^{-3}M	0.016mM	-	93% after 2d/85% after 60 d	[40]
ERGO/Au NPs /SPCE	DPV	Water, Shrimps, Fish, Sausages	2	1−6000µM	0.13 µM	0.3048 µA $\mu M^{-1}cm^{-2}$	93% after 60 d	[41]
Au/f-GE/GCE	DPV	Pickled pork	7	0.125−20375.98 µM	0.01µM	-	96.03% after 100 d	[42]
w-GN/Au/GCE	DPV	Tap Water, Sausage	7.2	1×10^{-7} to 5×10^{-3} mol L^{-1}	6×10^{-8} mol L^{-1}	-	97% after 2day-95% after 7 d	[43]
Au-HNTs-GO/GCE	Am	Tap water	6	0.1−6330; 330−61900mM	0.03 µM	0.023; .0865 µA m	93% after 7 d	[44]
Au_2Pt_1NPs/PyTSNG/GCE	Am	Ham sausage	-	0.5−1621 µM	0.19 µM	0.0276 µA μM^{-1}	94.3% after 14 days	[45]
Au–Pd/rGO/GCE	Am	Tap water	7	0.05−1000 µM	0.02 µM	-	85% after 5 d -75% after 10 d	[46]
Pt-RGO/GCE	Am	Beverage	7	0.25−90 µM	0.1 µM	0.4964 µA μM^{-1}	95.2% After 15 d	[48]
Pt-ErGO/GCE	Am	Tap Water	5	5−100; 100−1000 µM	0.22 µM	-	99.8% after 6 d 90.02% after 12 d	[49]
Ni@Pt/Gr/GCE	Am	Tap and river water	4	10µM-15mM	0.49 µM	85.18 µA $\mu M^{-1}cm^{-2}$	90.23% after 21 d	[50]
Co@Pt/Gr/GCE	Am	Tap and river water	6	2-15mM	0.145 µM	97.71 µA $\mu M^{-1}cm^{-2}$	87.12% after 30 d	[51]
Cu@Pt/Gr/GCE	Am	Tap and river water	4	1 µM $^{-1}$mM; 1mM^{-15}mM	0.035 µM	0.21; 0.6269 µA $\mu M^{-1}cm^{-2}$	86.87% after 30 d	[52]
Pd/rGO/GCE	DPV	-	7	1−1000 µM	0.23 µM	-	94% after one hour	[54]
Pd/Fe_3O_4/polyDOPA/ RGO/GCE	Am	Yellow River water, sausage	7.4	2.5−6470 µM	0.5 µM	-	90% after 9 d	[55]
GO–Ag/GCE	LSV, Am	Lake water	7.2		37 µM	-	95% after 7 d	[57]
Ag-rGO/GCE	DPV	water	7.4	0.1−120 µM	0.012 µM	18.4 µA $\mu M^{-1}cm^{-2}$	94.5% after 35 d	[58]
Ag/TiO_2/r-GO/GCE	Am	Tap Water, Rain Water	7.1	1 µM −1.1mM	0.4 µM	112.0 µA $\mu M^{-1}cm^{-2}$	90% after 21 d	[56]
Cu/f-RGO/GCE	Am	river water and tap water	2	0.15−10500 µ mol L^{-1}	0.06 µ mol L^{-1}	-	95.9% after 15 d	[59]
NPCu/GNs/GCE	Am	tap, river water, sausage		1×10^{-7}-1×10^{-4} mol L^{-1}	8.87×10^{-8} mol L^{-1}	3.1 AL/mol cm^2	No significant	[60]
Fe_3O_4/RGO/GCE	Am		4	0.5−780 µM	0.015 µM	0.204 µA/µM	92.36% after 25 d	[63]
Co_3O_4/RGO/GCE	Am	Tap water	-	1–380 µM	29.5 µM	0.14 µA $\mu M^{-1}cm^{-2}$	high stability	[65]
CeO/rGO/GCE	Am	Tap water		0.7−385 µM	0.18 µM	-	-	[66]
CoHCF-rGO/GCE	DPV	Tap and river water	6.5	1−100 µM	0.27 µM	-	-	[67]
MnO2/GO-SPE	DPV	Tap water , Packaged water	7.4	0.1−1000 µM	0.09 µM	-	No significant after 3-4 m	[70]
GO/Mn_3O_4 MC/SPE	Am	Beef & drinking water	7	0.1-1300 µM	0.02 µM	2.37; 1.23 µA $\mu M^{-1}cm^{-2}$	97.8% after 30 d	[71]
Fe-ZnO@rFGO/GCE	Am	River, Lake, Sea, Tap water	7.2	10−5000 µM	33 µM	-	no significant	
Ag-AEfG	Am	tap water	7.4	0.05–3000 µM	0.023 µM	200 µA $\mu M^{-1}cm^{-2}$	98.7%	[74]
Au/GO-CS/GCE	Am	water	5	0.9–18.9 µM	0.3 µM	-	-	[75]
Fe3O4 /GO/COOH/GCE	DPV	water	4	1–85 90–600 µM	0.37 µM	0.192 µAμM^{-1}	-	[76]
Au/Cu-TDPAT/ERGO/GCE	DPV	food	7	0.001–1000 µM	0.006 µM	-	95% after 6 d	[77]
Fe2O3 /H-C3N4 /RGO	Am	-	7.4	0.025–3000	0.0186 µM	0.0487 µAμM^{-1}	98% after 15 d	[78]
CuOx/ERGO	Am	Food	4	0.1–100	0.072 µM	-	-	[79]
TiO2 /RGO	DPV	water	7	1–1000 µM	0.21 µM	-	-	[80]
Ni(OH)2 /RGO	Am	water	7	0.1–663.6 µM	0.07 µM	21.93 µAμM^{-1}	90% after 10 d	[81]
RGO/MnFe2O4/PANI	DPV	water	7	0.05- 12000 µM	0.015 µM	-	93% after 30 d	[82]
rGO/ZnO/GCE	LSV/Am	water	7.1	200-4000/ 20-520 µM	1.18/ 1.36 µM	0.3156/ 0.2754 mAmM^{-1} cm^{-2} 1522.5 µA mM^{-1} cm^{-2}	97.55%	[83]
Cu-MOF−GO/GCE	Am	water	7.2	1×10^{-8} to 1×10^{-4} M	470.001 µM		98.2% after 10 C	[84]

SPCE:screen-printed carbon electrode, f-GE: flower-like grapheme, HNTs:halloysite nanotubes, PyTSNG: 1, 3, 6, 8-pyrene tetra sulfonic acid sodium salt, polyDOPA: poly 3,4-Dihydroxy-l-phenylalanine, CoHCF:cobalt hexacyanoferrate, SPE: screen-printed electrodes, MC:microcubes, rFGO:reduced functionalized graphene oxide, CS:Chitosan, TDPAT:tunable electrocatalytic oxidation activity towards, PANI: polyaniline fibrous nanocomposite supported, MOF:Metal–Organic Framework, C: cycle

3.4.3. MnO nanoparticle/Graphene-based nanocomposite.

Among numerous metal oxides, manganese dioxide has achieved much attention for electrode designing because of its low price, high electrocatalytic properties, easy access, and non-toxicity in comparison to Co and Ni [68, 69] Jaiswal *et al*., used modified MnO_2 which was decorated with GO nanocomposite, and screen-printed electrodes for nitrite detection in tap and packaged water. Amperometric results showed a detection range of 0.1mM-1000 mM for nitrite, with LOD of 0.09 µM. No significant decrease in response was observed after 20 cycles [70] Muthumariappan *et al*. used manganese oxide and graphene oxide nanosheets in electrode designing for detection of nitrite *in* beef and drinking water, and the electrochemical results were promising. The detection range was 0.1−420; 490−1318 µM, LOD was 0.02, and the oxidation response remained 97.8% after four weeks [71].

3.4.4. ZnO nanoparticle/Graphene-based nanocomposite.

Recently nanostructured zinc oxide has gained attention due to its great optical and electrical properties. On the other hand, the compilation of ZnO nanostructures into graphene provides new electrical, optical, and catalytic properties [72, 73]. Pandikumar *et al*. modified glassy carbon electrode with reduced graphene oxide and flower-like ZnO, the results were equal to the detection range of 10−5000, LOD of 33µM and excellent stability [74]. Table 3 shows the stability, sensitivity, and limit of detecting electrodes modified with metal/graphene nanoparticles to detect nitrate and nitrite in the a food sample.

4. Conclusions and Future Perspectives

The electrochemical sensors are inexpensive and easy to be miniaturized, which are why their vast usage in food processing, distribution, and storage, particularly in areas and countries that are economically underdeveloped. In recent years, due to graphene and metal nanoparticles' exclusive physical and chemical properties, they have been used to manufacture electrochemical sensors. In this article, we mainly focused on electrodes modified by graphene, metal nanoparticles, and composites. We compared them in terms of detection range, detection limit, sensitivity, and stability. The results showed that the application of metal/graphene nanocomposite in electrode modification could be a promising tool for nitrate/nitrite detection in foods. It can be a good alternative to the present methods.

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Conflicts of Interest

The authors declare no conflict of interest.

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