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Electrochemical sensors for nitrogen species: A review

Heejeong Ryu[a,*], Dorian Thompson[a], Yuankai Huang[b], Baikun Li[b], Yu Lei[a,*]

[a] Department of Chemical and Biomolecular Engineering, University of Connecticut, CT 06269, United States
[b] Department of Civil and Environmental Engineering, University of Connecticut, CT 06269, United States

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ABSTRACT

This review provides an overview of electrochemical sensors for nitrogen species, especially, ammonium, nitrate, and nitrite. Due to the extensive anthropogenic activities, the concentration of nitrogen species has been dramatically increased in the environment. In particular, fertilizers containing ammonium and nitrate have been extensively used in agriculture whereas nitrite-included additives or preservatives have been used in food industry. Since excessive nitrogen species have an adverse effect to environment and human health such as eutrophication and methemoglobinemia (blue baby syndrome), efforts have been made to develop efficient monitoring methods. On that account, the U.S Environmental Protection Agency (EPA) established the maximum contaminant level (MCL) for nitrate and nitrite to be 10 mg/L nitrate-N and 1 mg/L nitrite-N in drinking water, respectively. Typical analytical methods for nitrogen species are chromatography or spectrometry. However, these methods require expensive instrumentations, skilled operator, and considerable sample pretreatment and analysis time. As an alternative approach, electrochemical sensors have been explored to monitor nitrogen species owing to its simplicity, superior sensitivity, versatility, rapidity, field applicability, and selectivity. In this review, electrochemical based detection methods for nitrogen species especially ammonium, nitrate and nitrite are systematically discussed, including the fundamentals of electrochemical techniques, sensing mechanisms, and the performance of each sensor.

1. Introduction

Nitrogen compounds are one of the most important nutrients in the soil and aquatic ecosystem. However, the excessive amount of nitrogen in the environment has become a severe concern in the world [1]. In general, nitrogen species cycle through the environment in the form of organic and inorganic nitrogen. The source of organic-N are proteins, amino acids, urea, living or dead organisms, and decaying plant materials, while inorganic-N exists in form of gaseous nitrogen, ammonia gas, ammonium ion, nitrate, and nitrite [2]. Due to the extensive anthropogenic activities, the concentration of nitrogen species has been dramatically increased in natural environments. For example, ammonium and nitrate have been widely used as fertilizers in agriculture while nitrite has been extensively used as additives or preservatives in the food industry [3,4]. Because of the adverse effect to environment and human health including eutrophication and methemoglobinemia (blue baby syndrome), monitoring nitrogen species in the environment have become an important topic [5]. In addition, the U.S Environmental Protection Agency (EPA) announced the maximum contaminant level (MCL) for nitrate and nitrite to be 10 mg/L nitrate-N and 1 mg/L nitrite-N in drinking water, respectively [6]. Therefore, developing an accurate, sensitive, low-cost, real-time *in situ* monitoring system has been of a great importance.

Current standard detection methods for nitrogen species are based on chromatography or spectrometry. However, these methods require expensive instrumentations, skilled personnel for operation, and lengthy sample pretreatment and analysis time. To improve the user-friendliness, electrochemical sensor has been emerged as an excellent alternative approach to detect nitrogen species because of its simplicity, superior sensitivity, versatility, rapidity, field applicability, and selectivity. The fundamental of electrochemical sensors is the manipulation of the reaction at the interface of electrode and solution to utilize the electron transfer as an analytical signal. Hence, the surface modification plays an important role in developing an electrochemical sensor with high performance [7]. In the past decades, efforts have been focused on developing innovative functional materials to determine nitrogen species with high sensitivity and selectivity. Moreover, another merit of electrochemical analysis is attributed to the measurement diversity, relying on different techniques such as voltammetry, amperometry, potentiometry, and conductometry. Each aforementioned electrochemical technique has unique advantages and can be tailored for particular analysis of nitrogen species. This review paper focuses on discussing various electrochemical sensors for detection of nitrogen species. The brief

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* Corresponding authors.
E-mail addresses: heejeong.ryu@uconn.edu (H. Ryu), yu.lei@uconn.edu (Y. Lei).

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Table 1
Voltammertric sensors for nitrogen species.

Target Analyte	Electrode	Detection techniques	Medium	Linear range	Sensitivity/response time	Limit of detection	Types of sample	Ref.
Ammonium	Ag-CNT	Differential-pulsed voltammetry (DPV)	0.1 M Na_2SO_4	0.2–1 mM	0.613 mA/mM	1 µM	Groundwater	[11]
Nitrate	PPy-NW electrodes	Pulsed voltammograms	–	10 µM–1 mM	1.17–1.65 mA/mM	4.5 ± 1µM		[12]
Nitrate	Cu Nanowire electrode	Differential-pulsed voltammetry (DPV)	0.1 M Na_2SO_4	8–5860 µM	1.375 mA/mM	1.35 µM	Tap water/River water	[13]
Nitrate/Nitrite	Cu/MWCNT/RGO/GCE	Square wave voltammetry (SWV)	Na_2SO_4/H_2SO_4	0.1–75 µM	–	20 nM/30 nM	Mineral/tap water	[14]
Nitrite	CG/PPy/CS/GCE	Differential pulse voltammetry (DPV)	0.1 M NaAc-HAc buffer (pH 4.0)	0.2–1000 µM	–	0.02 µM	Tap water/Commercial water/Salt water/Soybean milk water	[15]
Nitrite	MnTMPyP/ $NbWO_6$/ GCE	Differential pulse voltammetry (DPV)	PBS (pH 7.0)	0.12- 3.57 mM	–	0.38 µM	–	[16]
Nitrite	α-MnO_2-based electrode	Differential pulse voltammetry (DPV)	0.1 M PBS	10–800 µM	17.1 µA/µM	0.5 µM	–	[17]
Nitrite	GNPs/graphene/ MCE electrode	Differential pulse voltammetry (DPV)	0.1 M Acetate buffer (pH 4.75)	0.3–720 µM	–	0.1 µM	Lake water/River water/Industrial sewage/Food	[18]
Nitrite	α-Fe_2O_3 NPs-ZnO NRs-Ag electrode	Linear square voltammetry (LSV)	0.1 M PBS	1–1250 µM	131.2 µA/ µMcm^2	0.015 µM	Tap water/Mineral water/Pond water	[19]

working principle of each electrochemical technique, the sensing mechanism, and the performance of each nitrogen species sensor are discussed in subsequent sections. The review is closed with the conclusion and discussion of future trends.

2. Voltammertric sensors for nitrogen species

2.1. *Working principles of various voltammetric sensing techniques*

Voltammetry is the most frequently used technique in analytical chemistry. Voltammetry records current over the variance of applying potential to observe the reaction on the electrode. One of the essential voltammetric techniques is cyclic voltammetry, which provides comprehensive understanding of electrochemical properties including stability of the products, intermediates, electron transfer kinetics, and reversibility of reaction. Moreover, in a reversible reaction, the measured current can be directly correlated with concentration of analytes. In the case of cyclic voltammetry, the potential is linearly varied in assigned range and the consequent current change is measured [8]. Another technique which sweeps potential linearly in one direction is a linear sweep voltammetry (LSV). While cyclic voltammetry is more suitable for reversible reactions, linear sweep voltammetry becomes more useful for irreversible reaction. The peak current indicates either the oxidation or reduction of the analytes and the height of limiting current is used to correlate with the concentration of the analytes. Moreover, the sensitivity of the measurement can be improved as the scan rate is increased because more oxidation/reduction of the analyte can occur [8]. The other way to apply potential is to use a pulse: for example, differential pulse voltammetry (DPV) applies potential with a series of pulse with a linear baseline. Prior to the potential change, the current is measured and the difference of the current is recorded over potential change. It can prevent the charging current effect by measuring the current before potential changes which also attributes to improved sensitivity. In reversible reactions, symmetric peaks are observed while asymmetric peaks appear in irreversible reactions. Thus, the peak current can be used to interpret the concentration of analyte in reversible reactions [9]. The other type of pulse voltammetry is square wave voltammetry (SWV) which provides superior sensitivity and rapidity. The waveform of square wave voltammetry is unique because it contains a pulse amplitude and staircase waveform. It measures the forward and reverse current when oxidation and reduction occur at the electrode surface, respectively. This separate measurement prevents the inherent charging current effect and thus enables fast and sensitive analysis. The current difference between forward and reverse is plotted over the potential and the peak current is then used to correlate with analyte concentration [8,10]. In the following section, the application of these voltammetric techniques in the detection of nitrogen species will be discussed and Table 1 summarized the performance of voltammteric sensors for nitrogen species detection.

2.2. *Voltammetric sensors for ammonium (NH_4^+) detection*

Compared to potentiometric sensor, voltammetric sensor is not widely used in the application of NH_4^+ detection. In a recent report, a novel detection system was developed to detect ammonium and nitrite simultaneously using silver-based carbon electrode. Two-roll mill procedure was conducted to fabricate carbon nanotubes (CNTs) epoxy composite electrode. Then silver nanoparticle was electrochemically deposited on the surface of CNT electrode. Through this process, unique structure similar to microarray was obtained even though the electrode was macroelectrode. Different kinds of electrochemical techniques including cyclic voltammetry (CV), square wave voltammetry (SWV) and differential pulse voltammetry (DPV) were applied to analyze the electrochemical properties of the electrode as well as determine both ammonium and nitrite concentration. Through cyclic voltammetry analysis, the oxidation process of ammonium and nitrite was investigated in the solution containing 0.1 M Na_2SO_4 as a supporting electrolyte. A notable anodic peak occurred for both ammonium and nitrite at +0.15 V/SCE and +0.7 V/SCE, respectively. The anodic peak current was ascribed to the formation of complex ($Ag\ (NH_3)^{2+}$) for ammonium and formation of nitrate as a result of oxidation of nitrite, respectively. Square wave voltammetry (SWV) and differential pulse voltammetry (DPV) were further used to evaluate the sensing performance of the as-prepared sensing electrode. According to the results, differential pulse voltammetry (DPV) provided enhanced sensitivity and comparable low limit of detection. The sensing results were also validated using other detection method such as spectrophotometry. Overall, this work prepared a novel functional material and utilized advanced voltammetry techniques to realize an effective sensor for ammonium and nitrite detection [11].

2.3. Voltammertric sensors for nitrate (NO_3^-) detection

As nitrate can be reduced electrochemically, voltammetric technique has been widely applied in the detection of nitrate. Aravamudhan et al. presented a microfluidic based sensing platform to monitor nitrate using doped-polypyrrole nanowires (PPy-NWs). Firstly, polypyrrole nanowire was fabricated using electropolymerization method and then exploited as a functional sensing material, owing to its excellent sensitivity and good conductivity. Superior selectivity and rapid reactivity was achieved when nitrate was doped into PPy-NWs. This process endowed PPy-NWs to tailor their structure of host cavity for target analyte such as the size of pores and charge distribution. The as-prepared PPy-NWs were modified on the surface of Pt interdigitated electrode through dielectrophoresis (DEP) technique. Prior to evaluate the sensing performance, the fabricated microfluidic sensor was analyzed by cyclic voltammetry and amperometry. After obtaining the calibration curve, the flow-based analysis was performed through pulse voltammogram. The pulse voltammogram contained a two-step potential process. The former potential was used to pre-oxidize PPy-NWs at $+0.65$ V while the latter potential was applied for nitrate reduction at -0.15 V. As the nitrate concentration was added continuously, the linearly increased peak current response was observed [12].

In another study, Liang et al. presented a Cu nanowire based electrochemical sensor to determine nitrate in water. Motivated by their previous study of Cu nanowire showing great performance for the hydrogenation of cinnamaldehyde with excellent catalytic activity and selectivity, Cu nanowire was explored as a nitrate sensing material because their remarkable properties, including that good conductivity and large active area could provide rapid electron transfer and abundant adsorption sites for nitrate. The Cu nanowire was grown under optimal annealing temperature (600 °C) using a simple and green synthesizing method. The electrochemical properties of the fabricated sensor were studied through cyclic voltammetry (CV) and linear sweep voltammetry (LSV) and the sensing performance toward nitrate was evaluated by differential pulse voltammetry (DPV). Since the nitrate was reduced to ammonium under acidic condition, pH value was optimized to 2 in order to obtain sharpest peak current. As the nitrate was reduced on the surface of electrode, linearly increased peak current was observed. The Cu nanowire-based sensor was capable of detecting nitrate in water with a wide linear range and high sensitivity. However, it revealed that the presence of nitrite also interfered the response and thus further research on how to differentiate nitrate and nitrite needs to be investigated [13].

Bagheri et al. also proposed a copper based electrochemical sensor to detect nitrate and nitrite. Instead of using copper nanowires, Cu metal nanoparticle was fabricated and Cu metal nanoparticles-multiwalled carbon nanotubes-reduced graphene oxide (Cu/MWCNT/rGO) was prepared as the sensing material. Copper has been reported as an excellent material for electro-reduction of nitrate and nitrite, but it suffered from complicated pretreatment and modification process. Moreover, electrochemical activity was facilitated by integrating the nanoparticles with reduced graphene oxide and multiwalled carbon nanotubes because of their intrinsic advantages such as large surface area and superior charge transfer properties. In addition, aggregation and restocking could be prevented. A glassy carbon electrode was used as substrate and the synthesized material was functionalized on the electrode to serve as the working electrode. Through square wave voltammetry, the sensing performance was investigated and it revealed the cathodic peak current was linearly increased with the addition of the nitrate and nitrite [14].

2.4. Voltammertric sensors for nitrite (NO_2^-) detection

Due to the toxicity of nitrite, extensive efforts have also been made to develop nitrite sensors based on the catalytic oxidation of nitrite. Various approaches to fabricate novel functional material have been proposed. Meanwhile, the majority of the reports about voltammetric nitrite sensors rely on differential pulse voltammetry. Recently, Xiao et al. developed an electrochemical sensor for monitoring nitrite in water using carboxyl grapheme (CG)/polypyrrole/chitosan-modified glassy carbon electrode (GCE). The rationale to choose graphene and polypyrrole relies on their large surface area and an abundant of active sites which facilitate charge transfer. In addition, chitosan attracted nitrite through electrostatic interaction owing to the positively charged amine group on the surface. Therefore, this material was expected to possess excellent selectivity and sensitivity for nitrite detection. After synthesizing CG/PPy nanocomposite, it was mixed with CS solution and then the prepared solution was drop cast on the surface of GCE. In order to evaluate the sensing performance of the as-prepared electrode, differential pulse voltammetry was conducted. It showed that DPV peak was linearly increased as the concentration of nitrite increased from 0.2 to 1000 μM. The limit of detection was as low as 0.02 μM [15].

Fan et al. also synthesized a novel nanocomposite for nitrite detection. The functional material was prepared by the electrostatic self-assembly techniques. The $LiNbWO_5$ was used as the host material because it can generate negatively charged nanosheet, niobium tungstate nanosheets $[NbWO_6]^-$, by an acidification and exfoliation process. Then, this host material can attract positively charged material such as manganese porphyrin (MnTMPyP) cation through electrostatic interaction, resulting in a novel functional material for nitrite detection. The sensing performance of manganese porphyrin/niobium tungstate modified glassy carbon electrode was evaluated using differential pulse voltammetry. It showed a linear response as the nitrite concentration change from 0.12 to 3.57 mM. The limit of detection was evaluated as 38 μM [16].

To take the oxidization power of MnO_2, Dai et al. fabricated a tunnel-structured α-MnO_2 nanoparticle for nitrite sensing application. Among various phase structure of MnO_2, α-MnO_2 showed superior electrochemical reactivity toward nitrite over β-MnO_2 and γ-MnO_2, and thus was used as a functional material for nitrite sensor. Instead of using conventional inkjet printer, piezoelectric-based micro-plotter was employed to deposit nanoparticles. Such direct deposition technique provided the great quality of printed pattern, thus improving the reproducibility of the sensor. Differential pulse voltammetry was employed to examine the performance of the as-developed sensor. The concentration of nitrite was varied from 10 to 800 μM and the DPV peak current was linearly increased over the tested concentration range [17]. To make the sensor affordable, Wang et al. developed a new low-cost sensing platform relying on paper-based electrode to monitor nitrite. The paper-based electrode was fabricated by incorporating reduced graphene oxide with mixed cellulose ester (MCE) membrane. Then, gold nanoparticles were electrochemically deposited on the surface of graphene-MCE. The electrochemical oxidation of nitrite was recorded through both cyclic voltammetry and differential pulse voltammetry. The current density was linearly increased with the addition of nitrite in the range of 0.3 to 720 μM and the limit of detection of the sensor was determined to be 0.1 μM [18].

Another voltammetry technique that has been widely used in nitrite detection is linear square voltammetry. Ahmad et al. proposed an innovative electrode preparation method in the development of a nitrite sensor. Instead of using conventional drop cast or pasting methods for electrode modification, Fe_2O_3 nanoparticle-coated ZnO nanorods (ZnO NRs) was directly grown on the surface of Ag electrode which improved stability and reproducibility. In brief, glass slide was first coated with Ag using radio frequency (RF) sputtering. Then, hydrothermal method was applied to grow ZnO NRs on Ag film electrode. Lastly, dip coating was used to produce Fe_2O_3-modified ZnO NRs/Ag electrode. Prior to

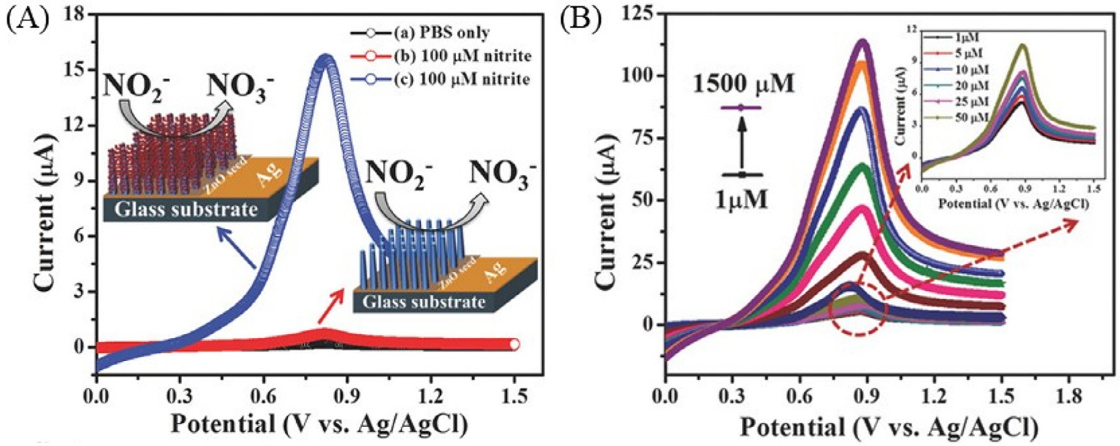

Fig. 1. (A) LSVs in the absence (a) and presence of 100×10^{-6} M nitrite at ZnO NRs/Ag (b), and Fe_2O_3 modified ZnO NRs/Ag (c) electrode in 0.1 m PBS at a scan rate of 100 mV s^{-1}. Insets show the nitrite detection scheme using Fe_2O_3 modified ZnO NRs/Ag and bare ZnO NRs/Ag electrodes. (B) LSVs in the presence different concentration of nitrite $(1 - 1500 \times 10^{-6}$ M) at Fe_2O_3 modified ZnO NRs/Ag electrode in 0.1 m PBS at a scan rate of 100 mV s^{-1}. Reproduced with permission from ref. [19].

examine its sensing performance, the quality of the surface modification was investigated through electrochemical impedance spectroscopy (EIS). Finally, linear square voltammetry was performed to detect various concentration of nitrite (Fig. 1). Linear current response was observed over a wide range of nitrite concentration. Therefore, this work offered a new electrode modification method to fabricate nitrite sensor with enhanced reproducibility, stability, sensitivity, and selectivity [19].

3. Amperometric sensors for nitrogen species

3.1. *Working principle of amperometric sensing technique*

In general, amperometry is deemed as a more sensitive technique than voltammetry because the background charging current from varying potential is prohibited. It measures current when constant potential is applied to a working electrode. The applied voltage results in a reduction or oxidation reaction at the electrode surface and the corresponding cathodic or anodic current is recorded and correlated with the target concentration. It is a prerequisite to perform cyclic voltammetry in order to obtain the reduction or oxidation potential of the analytes. The charge transfer at the interface is used to quantify the analyte of interest [7,8]. Among various type of applications, chronoamperometry has been utilized as an excellent sensing technique, as it measures the current at the electrode as a function of time when stepped potential is applied in the working electrode. The corresponding current change is used to understand a relationship with analyte concentration. This technique is very sensitive and useful to monitor diffusion-controlled process [8]. In the following section, various approaches to utilize amperometry for nitrate and nitrite determination will be reviewed.

3.2. *Amperometric sensors for nitrate (NO_3^-) detection*

Zhad et al. explored two different silver based electrochemical sensors for nitrate detection. The authors compared Ag-modified carbon (Ag/CE) and Ag-modified Ag (Ag/AgE) ultramicroelectrodes (UMEs) to evaluate their electrocatalytic activity toward nitrate reduction. Pulse amperometry was used to deposit AgNS while ammonia was used as complexation agent to resolve deposition problem. Microelectrode and macroelectrode exhibited different shapes during cyclic voltammetry analysis. Sigmoidal shaped curve occurred for microelectrodes while conventional peak shaped curve was observed for macroelectrode. A comparison of the results indicated that Ag/AgE was more promising than Ag/CE to achieve higher sensitivity and lower limit of detection. The merit of the developed method was the applicability at neutral pH which is necessary for nitrate analysis in real environmental samples. This research demonstrated a potential application of the Ag-modified UMEs on microfluidic based sensor for real-time monitoring nitrate in the environment [20].

Another silver-based material was also explored to detect both nitrate and nitrite simultaneously in aqueous solution. Manea et al. proposed an Ag-doped, zeolite-expanded graphite-epoxy composite electrode (AgZEGE) as a novel material for the fabrication of nitrate and nitrite sensor. In general, zeolite supported electrocatalysts were usually considered to reduce the overpotential and enhance the electrical signals, thus improving sensitivity. The electrode was simply fabricated by mixing components comprising of epoxy resin, conductive-expanded graphite filler powder, and silver-doped zeolite. Different analytical techniques including cyclic voltammetry (CV), chronoamperometry (CA) and multiple pulse amperometry (MPA) were applied to understand the electrochemical behaviors and sensing performance of the as-prepared electrode. The cyclic voltammetry experiments shed light on oxidation and reduction peak potential value for further CA and MAP analysis. While CA was based on constant potential amperometry, the MPA was based on altering potential between the two obtained values. For example, −1.35 V (vs. SCE) was applied for 150 ms to reduce nitrate to nitrite and +0.9 V (vs. SCE) was maintained for 150 ms for nitrite oxidation. As a result of applying CA and MPA, it revealed that the MPA was the most suitable technique due to its superior sensitivity. This study indicates that the developed sensing strategy could be an alternative method to detect nitrite and nitrate simultaneously in the environment [21]. Among several approaches to develop nitrate sensors, efforts have also been made to improve conventional batch mode-based detection system through exploring flow-based detection platform. By integrating amperometry with flow-based detection system, Gamboa et al. proposed an innovative sensing platform using amperometric flow detector to monitor nitrate in both mineral water and soft drinks. Maintaining certain quality of the electrode surface is also important aspect for sensor development, so the author employed a new approach to activate the copper electrode using a renewable process. Hence, flow injection analysis (FIA) configuration with sustainable copper surface was developed for nitrate sensing. The copper electrode surface was activated through a two-step potential process. The electrode was first polarized at +0.05 V to induce dissolution of copper. Afterward, the dissolved copper was redeposited on the surface of electrode at −0.25 V. In order to maintain good stability, an activation step was required before injecting 3 samples. As the nitrate reduction occurred on the copper electrode, corresponding peak current was monitored. The linear amperometric responses over continuous addition of nitrate and improved limit of detection demonstrated the applicability of this

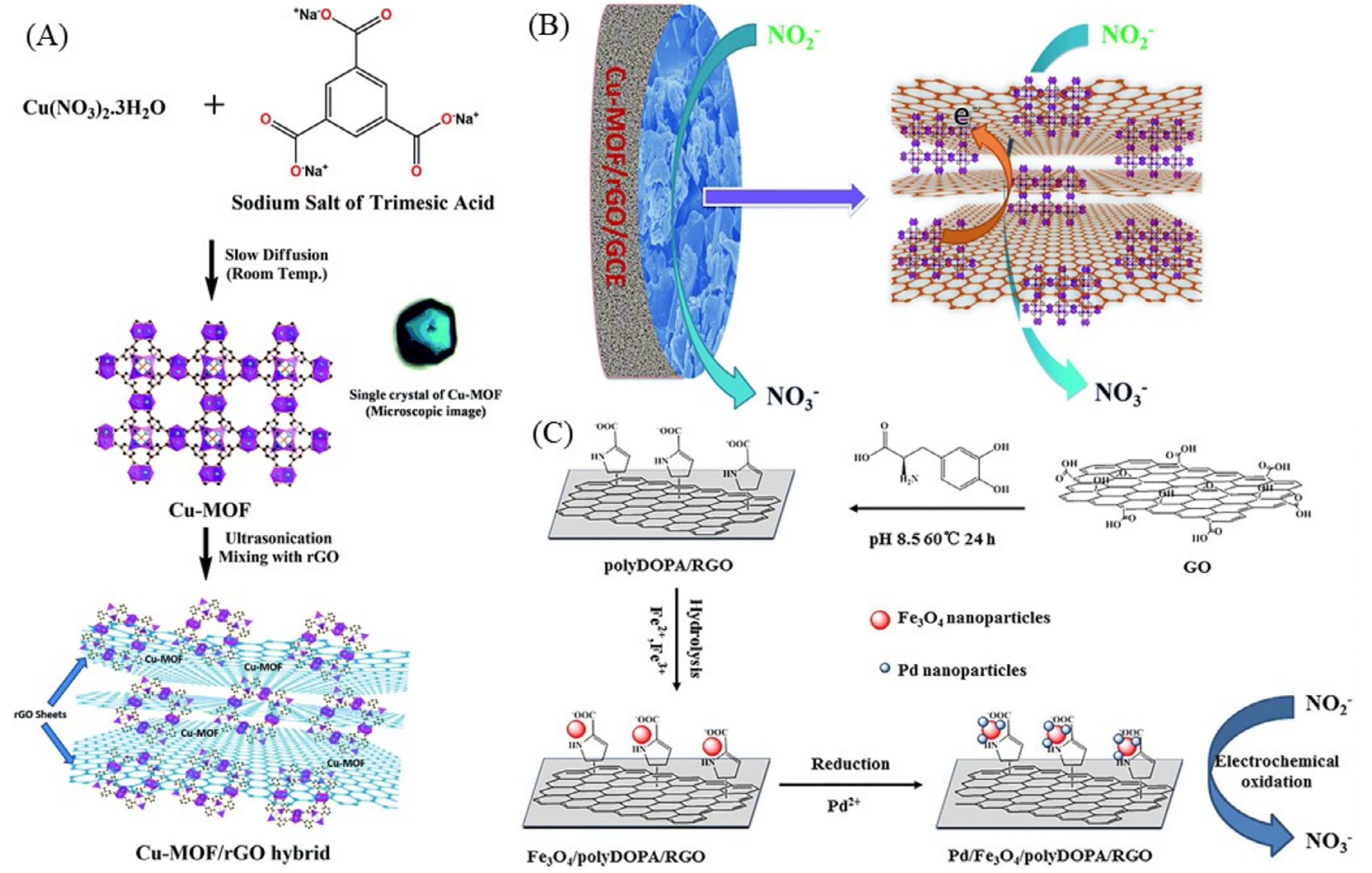

Fig. 2. (A) Schematic synthesis of the Cu-MOF. (B) Schematic of the nitrite sensor. Reproduced with permission from ref. [23]. (C) The synthesis scheme of Pd/Fe_3O_4/polyDOPA/RGO composite for electrochemical oxidation of nitrite. Reproduced with permission from ref. [29].

approach. Moreover, this approach was more advantageous than other conventional batch-mode detection systems in terms of frequency of analysis and the requirement of a smaller volume of sample [22].

3.3. Amperometric sensors for nitrite (NO_2^-) detection

Amperometric technique has been widely applied in nitrite detection. Saraf et al. fabricated an excellent hybrid material using copper metal organic frameworks and reduced graphene oxide (Cu-MOF/rGO) to develop supercapacitor and nitrite sensor. Instead of using solvothermal or hydrothermal techniques, a more mild approach based on solvent diffusion technique was employed to synthesize Cu-MOF. Then ultrasonication-assisted technique was applied to hybridize with rGO (Fig. 2A). In general, metal organic frameworks have been used in many applications but their conductivity is insufficient for sensing application. Therefore, the combination of Cu-MOF with rGO which shows high electrical conductivity was proposed as a solution. After preparing the material, it was used to modify the surface of glassy carbon electrodes (GCEs) (Fig. 2B). Then, cyclic voltammetry (CV) was conducted to interpret the electrochemical properties of the as-prepared electrode. It revealed that the modified electrode surface allowed nitrite to be oxidized into the nitrate and donates an electron. Under chronoamperometry detection, a linear amperometric response was obtained over a wide range of nitrite concentration with high sensitivity and low limit of detection as listed in Table 2 [23].

Recently, Zheng's group reported CuS-multiwalled carbon nanotubes (MWCNTs) nanocomposites-based sensor to determine nitrite. The hydrothermal method was selected to deposit CuS on the surface of MWCNT, which was used to modify the surface of glassy carbon electrode for direct oxidation of nitrite. In order to investigate electrochemical properties of the as-prepared electrode, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed. As a result, the electron transfer efficiency on the modified electrode was confirmed and the reaction was revealed as a diffusion-controlled reaction based on the CVs at different scan rates. Furthermore, amperometric response was also recorded by adding nitrite. It showed a linear relationship between ampermetric current and nitrite concentration from 1 μM to 8.1 mM [24]. Later on, the same group developed a new material for nitrite detection, which relied on Pt nanoparticles on Ni $(OH)_2$/MWCNT nanocomposites. The sensing material was prepared by dispersing Ni $(OH)_2$ into MWCNTs, followed by loading Pt nanoparticles under a mild reduction reaction. The GCE modified with Pt/Ni $(OH)_2$/MWCNTs was used as the working electrode. Cyclic voltammetry study indicates that an obvious oxidation peak was observed on the as-prepared Pt/Ni $(OH)_2$/MWCNTs electrode, which was attributed to the Pt nanoparticle's superior electrocatalytic property. In addition, the reaction kinetics was studied by varying the scan rate. Since the anodic peak current was proportional to square root of scan rate, the reaction followed a diffusion-controlled process. Finally, amperometry was performed to evaluate the sensor's detection capability [25].

Chen et al. also proposed a new sensing material for nitrite detection using simple and ecofriendly synthesizing method. The authors synthesized the free-standing Pt nanowire networks (Pt NWNs) by utilizing hydrogen bubble template. The synthesis was simply achieved by mixing H_2PtCl_6 solution with $NaBH_4$ solution. Then the fabricated Pt NWNs was drop-cast on the surface of glassy carbon electrode. Firstly, electrochemical behavior of the as-prepared electrode was analyzed using cyclic voltammetry. Meanwhile, differential pulse voltammetry and chronoamperometry were employed in detection. Differential pulse

Table 2
Amperometric sensors for nitrogen species.

Target Analyte	Electrode	Detection techniques	Medium	Linear range	Sensitivity/ response time	Limit of detection	Types of sample	Ref.
Nitrate	AgNS on carbon and Ag UMEs	Chronoamperometry	0.1 M Na_2SO_4	4–1000 μM	0.08 mA/mM/ 0.07 mA/mM	3.2–5.1 μM	Synthetic aquifer sample	[20]
Nitrate/ Nitrite	Ag-doped zeolite-expanded graphite-epoxy electrode	Multiple pulsed amperometry (MPA)	0.1 M Na_2SO_4	1–10 mM	0.025 mA/mM/ 0.057 mA/mM	0.08 mM/0.004 mM	–	[21]
Nitrate	Cu electrode	Amperometry	0.1 M Na_2SO_4 (pH 2.0)	0.1–2.5 mM	–	4.2 μM	Mineral water/Soft drinks sample	[22]
Nitrite	Cu-MOF/rGO/GCEs	Chronoamperometry	0.1 M PBS	3 μM–40 mM	43.736 μA/μMcm^2	33 nM	–	[23]
Nitrite	CuS-MWCNT/GCEs	Amperometry	0.1 M PBS (pH 7.0)	1 μM–8.1 mM	131.2 μA/ μMcm^2	0.33 μM	Tap Water	[24]
Nitrite	Pt/ Ni $(OH)_2$/MWCNTs/ GCE	Amperometry	0.1 M PBS (pH 7.4)	0.4 μM–5.67 mM	145 μA/μMcm^2	0.13 μM	Milk sample	[25]
Nitrite	Pt NWNs/GCE	Chronoamperometry	0.1 M PBS (pH 4.0)	1 μM–24 mM/ 24–132 mM	16.94/4.34 μA/mM	0.14 μM	–	[26]
Nitrite	Ag/HNTs/MoS_2 /CPE	Amperometry	0.1 M PB (pH 4.0)	2–425 μM	0.0899 μA/μM	0.7 μM	Tap water /Aqueduct water	[27]
Nitrite	AuNPs/CS@N, S co-doped MWCNTS/GCE	Amperometry	PBS (pH 7.4)	1–7000 μM	0.7595 μA/μMcm^2	0.2 μM	Food	[28]
Nitrite	Pd/Fe_3O_4/poly DOPA/ RGO	Amperometry	0.1 M PBS (pH 7.4)	2.5–6470 μM	0.01537 mA /mM	0.5 μM	River water/Food	[29]
Nitrite	Ag-AEfG100/GCE	Amperometry	PBS (pH 7.4)	0.05–3000 μM	200 μA/ μMcm^2	0.023 μM	Tap water	[30]

voltammetry was used to measure the response over different concentration of nitrite. It showed a linear response with the concentration. The sensitivity was calculated for both low and high concentration range which were 386.1 μA/mM and 32.8 μA/mM, respectively. Chronoamperometry was further performed to measure current change by adding the nitrite solution gradually. It showed a linear relationship between the current and nitrite concentration in the range of 1 μM to 24 mM and 24 to 132 mM, respectively. The corresponding sensitivities for both concentration ranges were calculated to be 16.94 and 4.34 μA/mM, respectively [26].

A silver/halloysite nanotube/molybdenum disulfide nanocomposite (Ag/HNT/MoS_2) was also applied in the construction of an electrochemical nitrite sensor. As a first step of material synthesis, silver nanorod was grown inside the lumen of halloysite nanotube by a chemical process. Next, a MoS_2 layer was hydrothermally generated on the Ag/HNT nanocomposite. The as-prepared functional material was used to modify carbon paste electrode (CPE). The catalytic performance of the as-prepared sensor was investigated through amperometry. As the nitrite concentration changed from 2 to 425 μM, the oxidation peak current was linearly increased [27].

Recently, Rao et al. also presented a novel sensing material, consisting of gold nanoparticle (AuNPs)/chitosan@N,S Co-doped MWCNTs, for nitrite detection. The integration of the merits and unique properties of those components improved electrical properties, mechanical strength, biocompatibility, large active area, and chemical stability. As a first step in material synthesis, MWCNTs were co-doped with N and S through reflux condensation and calcination. Under a facile reflux reaction, the surface of N,S Co-doped MWCNTs were modified with chitosan. Then,the CS@N,S Co-doped MWCNTSs was drop-cast on the glassy carbon electrode, followed by electrochemical deposition of AuNPs. Thus, AuNPs/CS@N,S Co-doped MWCNTs, which possessed highly porous and large active surface area with excellent electrochemical capability, was employed to determine nitrite concentration. Amperometry was performed to investigate the sensing performance of the as-prepared electrode toward different concentration of nitrite. Under the optimal applied potential of +0.90 V, the electrode exhibited rapid and sensitive response to the addition of nitrite. Therefore, the developed nitrite sensor demonstrated remarkable sensitivity, rapidness, low limit of detection, as well as great selectivity and stability [28].

Zhao et al. also reported an ecofriendly approach to develop Pd/Fe_3O_4/polyDOPA/RGO based electrochemical sensor to detect nitrite in river water and cured food. The basic concept of the proposed material was to construct the most desirable support material for Pd nanoparticles (Pd NPs) where nitrite oxidation occurs. It revealed that Fe_3O_4 combined with graphene could be a great support material because it promotes distribution, catalytic activity and stability of Pd NPs. Instead of employing conventional strategy to combine graphene with nanocomposite, the graphene was coated with 3,4-Dihydroxy-l-phenylalanine (DOPA) through a polymerization process to provide a surface adherent layer for growing Pd and Fe_3O_4 nanoparticles. In addition, this coating layer prevented aggregation and precipitation of nanocomposites. The polyDOPA/RGO composite was further modified with Pd and Fe_3O_4 nanoparticles through *in situ* nucleation. Afterward, the synthesized material was drop cast on the surface of glassy carbon electrode and denoted as Pd/Fe_3O_4/polyDOPA/RGO/GCE (Fig. 2C). The electrocatalytic behavior was systematically interpreted through various techniques including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). According to the kinetic analysis, the nitrite oxidation was determined as an irreversible and diffusion-controlled process. For sensing performance evaluation, amperometry was performed at a working potential of +0.82 V. The anodic peak current was linearly increased as the concentration of nitrite increased. Moreover, the selectivity, stability and applicability of the as-developed nitrite sensor for real samples were investigated and this study offered a promising approach using environment-friendly synthesis to effectively detect nitrite in real samples [29].

In another research, Ma et al. designed an advanced sensing material by co-functionalizing ethanolamine (AE) and silver nanoparticles (AgNPs) on graphene oxide (Ag-AEfG) for nitrite detection. In order to achieve well-disturbed AgNPs on graphene oxide, AE-functionalized surface was required as it could prevent agglomeration of nanoparticles and distortion of the GO structure. A simple one-step hydrothermal method was used to produce GO co-functionalized with AE and AgNPs. Electrochemical characterization revealed that an irreversible and diffusion-controlled reaction occurred on the prepared electrode. Finally, amperometry was applied to evaluate its sensing performance for nitrite quantification. The results demonstrated that the designed sensor was capable of detecting nitrite with high sensitivity, selectivity, and stability as illustrated in Table 2 [30].

Table 3
Potentiometric sensors for nitrogen species.

Target Analyte	Electrode	Detection techniques	Medium	Linear range	Sensitivity/ response time	Limit of detection	Types of sample	Ref.
Ammonium	Polymeric membrane-PpyCO-SANE-modified Au microelectrode	Potentiometry	Buffer tris-HCl/tris	1 μM–40 mM	–/10 and 12 s	0.04 mM	tap water/ sewage	[32]
Ammonium/ Nitrate	NH_4^+ -selective ASS electrode	Potentiometry	–	1 μM–0.1 M/ 10 μM–0.1 M	>52 mV/decade/ >–52 mv/decade/ <25/<25	<1 μM/<–10 μM	tap water/ well water	[33]
Ammonium/ Nitrate	Solid state ISM	Potentiometry	–	1–64 mg N/L	–/~10 s	$1 \times 10^{-6.5}$ M (~ 7.9 μg N/L)/ $1 \times 10^{-5.3}$ M (~ 55.7 μg N/L)	Wastewater	[34]
Nitrate	Chitosan/bentonite nanocomposite-based ISE	Potentiometry	–	20 mM–0.8 M	–54.6 mV/decade		–	[36]
Nitrate	Self-assembly nanobeads- packed (nBP) hetero columns Ion selective microelectrode	Potentiometry	–	0.1 μM–0.1 M	–61.369 mV/decade	–	–	[37]
Nitrate	PPy-NS ISE	Potentiometry	–	0–200 mg/L	–(55.0 ± 1.1) mV/decade	$10^{-4.8}$ M	Soil	[38]

4. Potentiometric sensors for nitrogen species

4.1. Working principle of potentiometric sensing technique

Potentiometric sensors are composed of an ion-selective membrane (ISM) coated working electrode and an inner reference electrode submerged in liquid electrolyte, and typically possess high selectivity to the target ion. It measures the open-circuit potential (OCP) between the working and reference electrodes in the absence of current flow using a high impedance voltmeter. Since the ion-selective membrane is usually modified with functional groups, only target ions can transport through the membrane. The amount of target analyte can be quantified by the potential difference [31]. In particular, potentiometric sensors have been employed in wastewater treatment plant and onsite monitoring for nitrogen species. The next section will discuss potentiometric sensors for ammonium and nitrate detection and the performance of each sensors are summarized in Table 3.

4.2. Potentiometric sensors for ammonium (NH_4^+) detection

In order to ease detection of ions in a flowing system, an intricate microfluidic platform has been created. Gallardo-Gonzalez et al. designed a microfluidic, two-part Lab-on-a-chip (LOC) for real-time potentiometric readings for ammonium detection in flowing sewage water. The first part of the LOC was a poly (dimethylsiloxane) (PDMS) microfluidic structure with microfilters and a detection chamber, fabricated by soft lithography with a silicon mold. Since the LOC would mostly be utilized in a sewage system, the PDMS structure helped reduce the amount of harmful materials diffusing into the detection chamber, as well as mitigate clogging. Inside the detection chamber was the second part of the LOC, including a sensing platform consisting of four Au working electrodes, two Ag/AgCl reference electrodes, and a Pt auxiliary electrode. The Au electrodes were functionalized with polypyrrole through cyclic voltammetry and then with an ammonium ionophore solution in order for the system to be selective to ammonium. In this study, parameters of the LOC were recorded, and the robustness of the chip was compared to a commercial sensor using different water samples. Considering good reproducibility, this specialized detection platform could be a viable option to monitor ammonium concentration in sewage [32].

Schwarz et al. also developed an all solid-state ion selective electrode to detect ammonium and nitrate. In this novel electrode, graphite paste was used to complete the electrical connection to a wire and was in solid contact with a polypyrrole layer, which acted as a mediator between the graphite paste and an ion-selective membrane. After the polypyrrole layer was electrodeposited onto the graphite layer, a nitrate or ammonium-selective membrane comprising of ion conducting polyvinylchloride (PVC) and species-selective ionophore was deposited onto the electrode through a simple drop-cast method. In this study, tridodecylmethylammonium nitrate (TDMA-NO_3) and nonactin were used as a nitrate and ammonium ionophore, respectively. These as-prepared ISEs were tested in different concentrations of ammonium and nitrates with good sensitivity, limit of detection, and coefficient of selectivity. Furthermore, the comparison of the detection results between the developed ion-selective electrodes (ISEs) and ion chromatography indicated that this sensor can be an alternative detection method for ammonium and nitrate [33].

To integrate wireless data acquisition into solid state ion-selective membrane sensor, Huang et al. developed an innovative sensing platform to monitor ammonium and nitrate in wastewater. The miniatured sensor was fabricated on test strips. Moreover, wireless remote data acquisition system provided real-time monitoring of sudden change in concentration or shock which can be further used to control the system thoroughly. The ionophore polymer cocktails containing commercial ammonium and nitrate ionophore, plasticizer, and PVC were used to modify the electrode by a simple drop-cast method. Temperature compensation was achieved by adding resistor-type temperature senor to monitor the environmental temperature simultaneously. Instead of using Ag/AgCl as the reference electrode, screen-printed carbon electrode was used as reference electrode to avoid interference by chloride (Fig. 3A). Once the analytes diffused into the membrane, it resulted in the change of its charge state. Accordingly, a potential change occurred and was recorded and correlated with the nitrogen species concentration change (Fig. 3B). This work provided an effective way for remote sensing of ammonium and nitrate [34].

Cuartero et al. also proposed a new analysis method to detect multiple ions including ammonium in a solution, with the use of a single ISE. In this process, the dynamic potentiometric signals from ions were analyzed using Principal Component Analysis (PCA), in order to gather useful quantitative and qualitative information on the ions. A polymeric membrane consisting of the ionophore 18-crown-6 was incorporated into the working electrode, which was filled with a high KCl concentration saturated with AgCl. When the ISE was used in a flow cell, the passage of ions in the sample resulted in co-extraction and cation exchange between the cations and the potassium in the electrode, thus generating transient potentiometric signals. The readings of these signals were proven to depend on a multitude of variables, so PCA was applied to accurately model the signal response. The effects of using PCA to determine ion species and concentration, in both individual and binary mixtures, are studied in this work. Multivariant calibration curves are

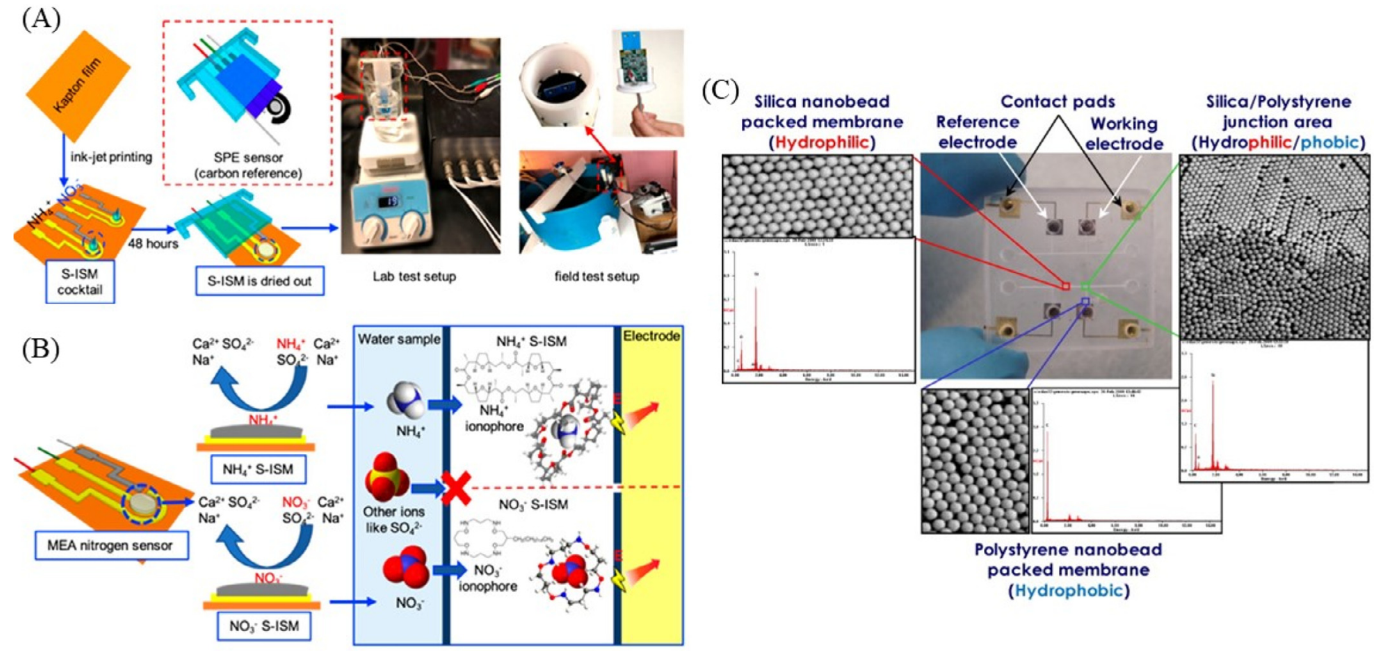

Fig. 3. (A) Diagram of the nitrogen S-ISM sensors for lab tests and field tests. Fabrication process and test setup of S-ISM sensors. (B) Structure and mechanism of the nitrogen S-ISM sensors. Selectivity of the S-ISM and the dynamic steps of NH_4^+ and NO_3^- ions moving from bulk water solution into S-ISM. Reproduced with permission from ref. [34]. (C) Photograph of the dual ion-selective lab chip and the ESEM images with EDS data of the self-assembly nBP columns. Reproduced with permission from ref. [37].

generated from regression of the principal components, which was confirmed to deliver an acceptable overall accuracy, while greatly simplifying the handling of the transient potentiometric signals. This work provides a novel method for accomplishing multiple ions detection using one ISE [35].

4.3. Potentiometric sensors for nitrate (NO_3^-) detection

Ionophore-enabled potentiometric sensors are also popular in the detection of nitrate. Mendoza et al. investigated a chitosan/bentonite nanocomposite-based ion selective electrode for nitrate detection in water. The chitosan/bentonite nanocomposite was synthesized through ionic exchange reaction. The driving force of this composite formation was electrostatic attraction between positively charged amine group in the chitosan and negatively charged bentonite surface. Graphite-epoxy electrode was then modified with the synthesized material via solvent cast method. The potentiometric response was recorded at difference concentration of nitrate and it showed a linear relationship with a Nernstian slope of −54.6 mV/decade. This study suggested a simple and low-cost approach to develop ISE sensor for monitoring nitrate in water [36].

Jang et al. developed a polymer lab-on-a-chip sensor to monitor not only nitrate but also pH and Cd (Ⅱ) in water. For nitrate detection, the ion-selective sensor was fabricated by utilizing self-assembled nanobeads-packed (nBP) hetero-columns. The hydrophobic polystyrene nanobeads was used to help both liquid ion exchange (LIX) membrane and Ag/AgCl reference microelectrode to have sufficient ion selectivity and stability by holding internal KCl solution. The hydrophilic silica nanobeads constructed a pathway to load samples. The prepared planar microelectrode on microsensor chip was attached to the designed microfluidic chip (Fig. 3C). The assembled device was used to evaluate its sensing performance toward different concentration of nitrate. As a result of potentiometric measurements, the developed detection system demonstrated a feasibility as a miniatured environmental sensor for nitrate detection in water with high sensitivity and selectivity [37].

Zhang et al. also reported a new approach to monitor nitrate on soil using a solid-state ion selective electrode. Monolayer and bilayer S-ISEs were fabricated and tested for nitrate detection. Nitrate doped polypyrrole ($PPy(NO_3^-)$) was commonly used for nitrate S-ISE. However, the monolayer S-ISE was infeasible for continuous detection due to the formation of thin water film under the membrane. In order to overcome this challenge, carbon material was introduced between membrane and substrate, thus having a bilayer structure. Therefore, two nitrate S-ISEs, PPy (NO_3^-) and TDDA-graphene, were designed to investigate possibility as a nitrate sensor. TDDA was chosen for ionophore and *o*-Nitrophenyloctylether (*o*-NPOE) was used as plasticizer, while high molecular weight PVC was used to form a membrane. The TDDA was first mixed with PVC and NPOE in THF solution. The $PPy(NO_3^-)$ ISM was synthesized using electro-polymerization. The graphene film was drop-cast on the surface of the electrode to provide solid contact between GCE and solvent polymeric ISM. Different concentration of nitrate including 0, 5, 25, 50, 100, and 200 mg/L was tested and the potentiometric sensor showed quasi-Nernstian response with a slope greater than 50 mV/decade. Moreover, PPy NS ISE exhibited the lowest limit of detection of $10^{-4.8}$ M among other ISEs [38].

5. Conductometric sensors for nitrogen species

5.1. Working principle of conductometric sensing technique

Conductometry is a decent technique to determine target ion concentration by measuring conductivity of the solution. It applies a small amplitude AC signal in a wide range of frequencies to perturb the surface of electrode and measures the corresponding electrical response, which is usually impedance. Impedance measurement provides information such as capacitance, inductance or mass diffusion which is further used to understand electron charge transfer, electrolyte resistance, adsorption of electroactive compounds, and mass transfer of analytes. Conductometry is especially beneficial to monitor an adsorption of target analyte on the surface of electrode. Some analytes are not able to generate electrochemical reaction and thus impedance measurement can be an

Table 4
Conductometric sensors for nitrogen species.

Target Analyte	Electrode	Detection techniques	Medium	Linear range	Sensitivity/response time	Limit of detection	Types of sample	Ref.
Ammonium	Natural Zeolite Clinoptilolite–Au interdigitated microelectrode (IDμE)	Conductometric	5 mM KH_2PO_4/ Na_2HPO_4 (pH 6.2)	0.01 μM–1 mM	2.5 mS/mM/10 ± 2 s	0.01 μM	–	[40]
Ammonium	25,27-di-(5-thio-octyloxy) calix [4] arene-crown-6-Au interdigitated electrode (IDE)	Conductometric	5 mM KH_2PO_4/ Na_2HPO_4 (pH 6.2)	0.01–1 mM	8.22 *μ*s/mM/5–10 s	0.01 mM	River water sample	[41]
Nitrite	Cu_2O-CNTs/Au electrode	Electrochemical Impedance Spectroscopy (EIS)	5 mM $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ in PBS (pH 7.4)	0.1 nM–1 mM	–	0.0188 nM	Tap water	[42]

alternative way because the blocked electrode surface by target analyte alters impedance. The measurement can also be used to analyze surface properties and obtain a signal-concentration correlation at different concentration of analytes [31,39]. The following section will review the detection system based on conductometry for quantifying ammonium and nitrite. The performance of each sensor is summarized in Table 4.

5.2. Conductometric sensors for ammonium (NH_4^+) detection

In an earlier work, Saiapina et al. confirmed the possibility of using zeolite-modified electrodes for ammonium detection. Zeolites improve the conductometric signals from their special ability to change electroanalytical characteristics due to their porous structure, which caused the ion exchange capacity to be different between different zeolite structures (Fig. 4A). Clinoptilolite is the zeolite used to cover the working electrode, as it was widely used because of its high exchange capacity and affinity for ammonium ions through ion replacement with sodium ions in its structure. Characterization of the electrical properties of zeolite electrodes indicated that kinetics played a large factor in the process. The analytical attributes of the assay were studied in different types of neutral and ionic buffer solutions. When compared to the performance of bare electrodes in complex buffer, the zeolite electrodes prevailed as the more effective method. Use of these clinoptilolite electrodes was concluded to be a valid option for detecting the concentration of ammonium ions in a system [40].

To assist with on-site ammonium detection in aqueous solution, Saiapina et al. developed a conductometric sensor based on a hybrid of calixarene and the ionophore 18-crown-6, labeled 25,27-di-(5-thio-octyloxy) calix [4] arene-crown-6. Calixarenes have a unique ability to capture ions from "host-guest" chemistry with their aromatic rings, while 18-crown-6 is known for recognizing ammonium by forming a "host-guest" complex. The fusion of these compounds' fragments into one molecule allowed ammonium cations to be detected with high selectivity and efficiency. While the upper section of the novel molecule was capable of complexation of ammonium from benzene rings, the lower section consisted of disulfide groups to help the compound bind to the gold working electrode. The analytical characteristics of this modified electrode, including the electrode's stability, selectivity to ammonium, and performance in different buffers, were analyzed. While more studies are demanded in order to optimize the solution parameters for the assay, the modified electrode was concluded as a promising tool for ammonium detection. Comparison with other electrochemical analytical methods, such as potentiometry and amperometry, further verified the conclusion [41].

5.3. Conductometric sensor for nitrite (NO_2^-) detection

To employ conductometry for nitrite detection, Wu et al. established an outstanding detection system for nitrite in water by fabricating a Cu_2O/CNT based sensor. Taking into account that direct oxidation of

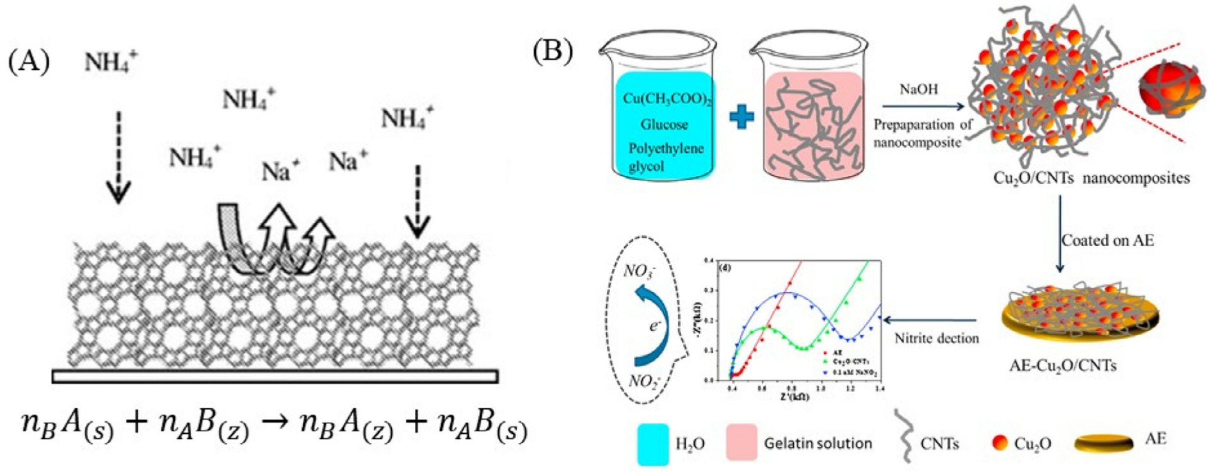

Fig. 4. (A) Ion exchange mechanism in the zeolitic layer: A and B are the evictor ion (i.e.,) and resident ion (i.e., Na^+), respectively, in zeolite and solution phases; nB and nA represent the charge of ion B and ion A, respectively. Reproduced with permission from ref. [40]. (B) Schematic diagram of the fabrication of Cu_2O/CNTs composite-based electrochemical sensor for detecting nitrite detection, including the preparation of Cu_2O/CNTs composite, the modification of the bare Au electrode (AE) with Cu_2O/CNTs composite, and the detection of nitrite ions. Reproduced with permission from ref. [42].

nitrite on bare electrode necessitates over potential, a tailored nanomaterial was prepared to modify the gold electrode. The CNT was selected owing to its unique property including high surface to volume ratio, excellent conductivity and adsorption capacity. In order to improve sensitivity, cuprous oxide (Cu_2O) was integrated with the CNT by employing a simple hydrothermal method. Electrochemical impedance spectroscopy (EIS) was used for measurement because the detection mechanism was based on the observation of electron transfer change on the electrode as a response of adding nitrite. The difference of charge transfer resistance before and after exposure to nitrite (ΔR_{ct}) was recorded. According to the results, the ΔR_{ct} was consistently increased by adding the nitrite (Fig. 4B). The proposed sensor was capable of detecting a wide concentration range of nitrite with high sensitivity [42].

6. Conclusion and future research direction

As the nitrogen species are omnipresent inorganic pollutants in the environment, numerous approaches have been investigated to develop effective monitoring methods. Among various analytical methods, electrochemical based sensors have gathered attention from researchers because it is simple, fast, resilient, suitable for field monitoring, selective, and most importantly, sensitive. Therefore, this review provided an overview of numerous electrochemical based approaches to detect nitrogen species. In particular, ammonium, nitrate and nitrite were selected as target analytes. In case of ammonium sensor, nonactin was mainly used as an ionophore and potentiometry was dominant as a detection technique. Voltammetry was also used to measure the anodic peak current by the formation of complex between the silver electrode surface and ammonium ($Ag\ (NH_3)^{2+}$). However, the electrodes showing either direct or indirect oxidation of ammonium are very limited. Thus, potentiometry seems like the most suitable technique for ammonium detection. For nitrate determination, all popular electrochemical techniques were utilized except conductometry. The merit of nitrate sensor was versatility because it can integrate diverse detection techniques with numerous sensing materials. Moreover, flow-based detection system was also explored to monitor nitrate concentration. For nitrite detection, amperometry was mainly used for measurement owing to the direct oxidation of nitrite on the electrode surface. However, it required relatively high overpotential which was prone to interference from other ions. Hence, most researches aimed to synthesize novel functional materials for improved selectivity. Although various nitrogen sensors were developed, surface fouling, poor stability, and requirement of frequent re-calibration/maintenance are limitations of existing nitrogen sensors. Therefore, a future trend heavily relies on the success of using anti-fouling layer, engineering stable solid-state sensing membranes, and designing a unique sensing configuration suitable for long-term detection.

The electrochemical detection of nitrogen species in aqueous samples has witnessed the initial success. However, the extension of current electrochemical nitrogen species sensors for monitoring nitrogen species in the soil analysis is still challenging due to the lack of aqueous electrolyte in soil. An effective approach to improve the use efficiency of fertilizers and alleviate environmental pollution is through precision farming practices guided by real-time monitoring and near-term forecast of fertilization needs. Such initiative is hampered by the lack of reliable sensing technologies to quantify the spatiotemporal variability of soil nitrogen species concentration. The current state-of-the-art is to collect soil core samples at field sites and then transport off site to the laboratory for measurements, which is prone to errors caused by sample transfer and is unable to track the transient variation of nitrogen concentration in a timely manner. Last two decades have witnessed various nitrogen sensors developed for *in situ* measurement, with the most promising ones being made from ion selective membrane (ISM, ionophores), but only limited for detection in aqueous solution. It still remains an unmet challenge to *in-situ* detect nitrogen signals in soil due to the lack of continuous aqueous phase, which is a pre-requisite for the proper function of ISM-based nitrogen sensor. The introduction of water-containing hydrogel layer on the electrochemical nitrogen species sensors may provide the required environment for diffusion and detection of nitrogen species. In addition, most of ISE sensor studies are limited in lab-scale using clean water solution in short period (e.g. couples of hours). To expand application and prolong lifespan of ISE sensors in real-world environment (e.g., wastewater, soil) characterized with various impurities and interfering ions, solid-state ISE sensors (S-ISE) consisting of ionophore, polymer (PVC, PMMA), plasticizer, and ion-exchanger (lipophilic salt) have been developed [43]. By incorporating ionophores in a thin polymer membrane on an electrode, S-ISE nitrogen sensors showed excellent sensing performance such as accuracy, sensitivity, and selectivity in lab-scale tests with test duration of several hours to several days [44,45]. S-ISE sensors could last 14 days in clean water solution under a static condition in lab tests [46]. However, nitrate S-ISE sensor suffered from diminishing accuracy (errors higher than 5 mg N/L) after 3 days in the real wastewater in a complete stirring tank with continuous flow, attributing to the S-ISE membrane peeling off and sensor surface fouling [34].

Since the response of S-ISE nitrogen sensors depends on the activity of ions between the solution and membrane surface [47], any changes (physical, chemical, or biological) in the S-ISE membrane can influence the sensors' long-term performance. There are three main reasons deteriorating sensor response characteristics. First, the debris and suspended particles in wastewater attach onto the sensor surface, and physically damage sensor surface [48]. The additional diffusion layer made of bacteria and particles forms during biofouling, interferes the diffusion of target ions across the membrane matrix, results in sensor reading drift, and severely shortens the lifespan of sensors [49]. Second, the water layer forms between the S-ISE membrane and the electrode surface, weakens the bonding of the S-ISE membrane and the electrode, acts as an electrolyte reservoir re-equilibrating every concentration change in the water solution [50], and finally leads to sensor reading drift. Third, the lipophilic ion-exchanger in the S-ISE membrane matrix slowly leaches to the bulk solutions overtime, shortening the lifespan of S-ISE nitrogen sensors. Leaching is also a key factor impairing the detection limit of S-ISE nitrogen sensors [51].

Various approaches have been developed to enhance S-ISE sensor’s long-term performance. Joon et al. applied a pure silicone rubber (SR) outer layer onto the traditional PVC based potassium S-ISE sensor to prevent the sensors from physical damage [52]. The reproducibility of the modified sensors was significantly improved from $E0 \pm 35.3$ mV to $E0 \pm 3.5$ mV. Moreover, the adsorption of bovine serum albumin (BSA) was also greatly reduced when SR was applied on the surface, showing the potential of SR to reduce the biofouling on S-ISE surface. Sutter et al. substituted traditional PVC-based ISEs to more hydrophobic co-polymer (PMMA/PDMA) to mitigate the water layer formation problem [53]. Moreover, extremely hydrophobic solid contacts, such as poly(3,4-ethylenedioxythiophene) (PEDOT) [54], polypyrrole (PPy) [55], carbon nanotubes (CNTs) [56], and metal organic frameworks (MOFs) [57] have also been applied in between the S-ISE membrane and the electrode layer to act as an ion-to-electron transducer as well as mitigate the water layer formation. The leaching of the lipophilic ion-exchanger can be determined by differential pulse cathodic stripping voltammetry (DP CSV) and EIS [58], but it is difficult to be prevented due to the small size (<0.5 nm) of the ions. Because the leaching is dependent on the structure of the ion-exchanger, and the stability of the ion-ionophore complexes, future study could focus on the new type of ion-exchanger development (high viscosity, larger ion size, etc.) or ion-exchanger free S-ISE sensors. Another future direction to improve the long-term sensing performance of nitrogen sensors is the fundamental study of the anti-biofouling property of the S-ISE sensors. Zwitterionic polymers could be a promising antifouling candidate for S-ISE sensors, since it has been used in ion-exchanger membranes for decades and showed excellent anti-biofouling properties due to its outstanding resistance against protein and cell adsorption in numerous biological systems [59].

Another strategy coupling with S-ISE sensor material development for long-term accuracy in real-world environment is the integration of mathematical algorithms capable of predicting and eliminating sensor reading drift into sensing data analysis. Curve fitting and regression is a simple but efficient way to extract sensor reading patterns and exceptions [60], but suffering significant errors when processing non-linear and drifting data. Machine learning is a fashionable powerful tool, but requires huge amount of training and testing data to establish reliable models [61], which is nearly impossible for *in situ* monitoring. In contrast, denoising data processing algorithm (DDPA) is a promising approach to compensate the sensor reading drifting problem caused by the impact factors (e.g., physical damage, water layer, leaching, and biofouling). It enables mathematical separation of background noise and electrochemical signals so as to eliminate the noise and amplify the signals with digital filter [62]. It is also capable of detecting unobvious mixing signal in complex water environment with density-based methods [63]. We strongly believe that with the progress of science and technology, more reliable and user-friendly nitrogen species sensors with longer life-time and less maintenance will be developed and commercialized in the near future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this review.

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