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Development of electrochemical sensors for quick detection of environmental (soil and water) NPK ions

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All over the world, technology is becoming more and more prevalent in agriculture. Different types of instruments are already being used in this sector. For the time being, every farmer is trying to produce more crops on a piece of land. Eventually, soil loses its nutrients; however, to grow more crops, farmers use more fertilizers without knowing the proper conditions of the soil in real time. To overcome this issue, many scientists have recently focused on developing electrochemical sensors to detect macronutrients, *i.e.*, nitrogen (N), phosphorus (P), and potassium (K), in soil or water rapidly. In this review, we focus mainly on the recent developments in electrochemical sensors used for the detection of nutrients (NPK) in different types of samples. As it is outlined, the use of smart and portable electrochemical sensors can be helpful for the reduction of excess fertilizer and can play a vital role in maintaining suitable conditions in soils and water. We are optimistic that this review can guide researchers in the development of a portable and suitable NPK detection system for soil nutrients.

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1. Introduction

Nowadays, advanced technologies are becoming more and more popular, and covering various aspects to improve our daily lives. In agriculture, a variety of technological tools and engineering nanoparticle-based fertilizers[1] have already been developed to facilitate agricultural work and to increase crop yield. Various macronutrients and micronutrients in soil are considered the most important factors for good harvesting. Micronutrients, especially nitrogen (N), phosphorus (P), and potassium (K), play an important roles in the cultivation and production of crops.[2] An adequate amount of NPK in the soil is required for optimal crop production. When NPK deficiency occurs in the root zone, it can lead to different types of syndromes such as yellowing of leaves, spots on leaves, and reduction of flowers and fruits, and details of deficiency are described in the previously reported studies.[3–5]

To reduce this deficiency in plants, farmers use various fertilizers to supply these nutrients without knowing the present condition, *i.e.*, the need for nutrients by the plants. As a result, sometimes they use excess amounts of fertilizers for the fertilization of the plants, results in various negative impacts such as water pollution, eutrophication, soil contamination, and reduction in the population of soil microorganisms.[6,7] To optimize crop production, it is important to know how much NPK is present in the soil and how much NPK should be added at that time.[8,9] Various analytical techniques such as gas chromatography-mass spectroscopy, ion-chromatography, atomic absorption spectroscopy, UV-vis spectroscopy, and field effect transistor have been used for the determination and quantification of different types of chemical elements and compounds; however, these methods are very expensive, need a well-arranged set up, time consuming, require skilled person for data acquisition and interpretation, and the vigilant way for sample preparation though these methods are provided with high accuracy and precision.[10–12]

For these reasons, the development of a simple, economically feasible, and rapid technique for the detection of NPK is crucial. In the last decade, various types of sensors have been developed for the detection of NPK in soil, such as electrochemical sensors, optical sensors, and mass-sensitive biosensors. Among these biosensors, an electrochemical sensor is one of the most sensitive and rapid tools for NPK detection. It is a promising strategy for developing an innovative, cost-effective, and portable NPK testing method for soil. The use of this electrochemical sensor has many advantages; for example, this type of sensor is more sensitive, reproducible, and

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repeatable than other sensors[2] and is sometimes comparable with conventional techniques.

The sensitivity and selectivity of an electrochemical sensor mainly depend on the surface modification of the transducer. Nowadays, researchers are interested in using different types of nanomaterials to modify the transducer. Metal and metal oxide nanoparticles are mainly used to develop transducers for electrochemical sensors for soil testing, environmental analysis, food safety,[13] health management, and clinical diagnostics due to their low cost, easy modification, and availability. Nanomaterials of different sizes and shapes have been used for the development of electrochemical sensors.

In this review article, we will discuss recent developments of different kinds of sensors used for the detection of NPK in different environmental samples with the current state of research and their mechanism of operation. We review several nanomaterial-based electrochemical sensors and summarize various parameters of different NPK sensors that have been previously reported. We also discuss some prospects for electrochemical sensors based on nanomaterials as alternative soil tests.

2. Conventional technique of NPK testing

In the traditional technique of NPK investigation of agricultural fields, soil samples were taken randomly from different locations in the field. The samples were mixed and packed and levelled well. Then, the samples were transported to a laboratory where the samples were chemically processed for various analyses. Then, the processed samples were analyzed in a state-of-the-art laboratory using various expensive instruments. Analytical instruments include atomic mass spectroscopy (AAS), UV-visible spectroscopy, gas chromatography-mass spectroscopy (GCMS), and field effect transistors. These types of test methods sometimes require more than one day for sample processing and analysis and trained personnel for instrument operation and chemical processing.

Actually, nowadays, electrochemical sensing is getting popular as conventional methods are very expensive, need a well-arranged setup, are time-consuming, and require a skilled person for data acquisition and interpretation, a vigilant way for sample preparation though these methods are provided with high accuracy and precision,[10–12] we have mentioned earlier, here the detection range and limit of conventional methods vary from sample to sample; for example, for the atomic adsorption spectroscopy (AAS) the detection limits for most elements (ppm) and absolute detection limits (μg) is 0.01–5, and the details are discussed in these ref. 14–21. Actually, this part should be focused more carefully as there are hardly any review papers providing a summary of the conventional methods. Here, we have mentioned a few of the conventional techniques without providing any detailed explanations.

Smart electrochemical sensors, based on microcontroller potentiostat, *i.e.* very cheap and versatile platform in electrochemistry and instrumentation[35] and wireless communication technology[36,37] have also been widely used for human health monitoring such as blood glucose, blood pressure, heart rate, wrist pulse, and other health-related conditions.[38–43] If we design electrochemical sensors for sensing NPK in soil or soil water samples, a quick, accurate and easy determination is possible, thus introducing a smart sensing system in agriculture. In the schematic figure, we show that by using this kind of electrochemical sensor, designed with a smartphone-based application, it may be possible to determine the desired ion present in the soil sample dispersed in water. Already these kinds of electrochemical sensors have been developed for specific ion detection in urine or in blood samples as described elsewhere in the ref. 16–21. Therefore, we should try to improve this kind of system to detect different macronutrients in soil samples/water solutions.

2.1 Advanced electrochemical sensors for the detection of nitrogen (N)

Nitrogen is one of the most important elements in the environment and occurs in several chemical forms, including nitrate (NO^{3-}), nitrite (NO^{2-}), ammonium (NH^{4+}), nitrous oxide (N_2O), nitrogen oxide (NO), and nitrogen gas (N_2). Recently, farmers have been using fertilizers in an inefficient and uncontrolled manner to meet the demand for surplus food production for the gradually growing population.[44] These increasing amounts of N species have been shown to have a range of negative impacts on terrestrial and aquatic ecosystems.[45,46] To avoid excessive use of fertilizers and to use the fertilizers properly, farmers need to monitor the nitrogen species consumed by crops in a short time. An advanced electrochemical sensor is a highly sensitive, selective, low-cost, and easily measurement *in situ* device that enables fertilizer selection for cultivation in real-time.

2.1.1. Nitrate ion detection. Nitrates are the most oxidized form of nitrogen found in soil and water in the form of highly soluble and mobile mineral salts.[47] Previous studies indicate that the nitrate ion can serve as the basis for the nitrogenous nutrition of plants and soil microorganisms.[48,49] The easily detectable nitrate ions can be detected and quantified by an electrochemical sensor, as summarized in Table 1.

Liang *et al.* reported a method to determine the concentration of soluble nitrate ions in water. In their study, copper nanowires were annealed at 600 °C to obtain maximum reactive surface area for the reduction of nitrate ions.[50] The schematic diagram of the nanowire-based copper electrode modification is shown in Fig. 1. However, the electrode was also prepared at an annealing temperature of 600 °C. The modified copper electrode showed a dynamic range of 8 to 5860 μM with a detection limit of 1.35 μM for nitrate ions in water. In another research work, a glassy carbon electrode was modified with copper, MWCNT, and RGO to detect nitrite ions by linear voltammetry (LSV).[51] The detection of nitrate ions in tap and mineral water, sausage, salami, and cheese samples showed linearity from 0.1 to 75 μM with a detection limit of 30 nM at pH 3. Moreover, branched Ag nanoparticle electrodeposition was performed in an ammonium sulfate medium and the modified surface was well suited for electro catalytic reduction of nitrate.[52] The ultra-

Table 1 A comparison of electrochemical sensors for the detection of nitrate ions

Analytical method	Linear range	Low level of detection	Sample	Analyte	References
UV-visible spectrometry	1–100 μg mL^{-1}	0.33 μg mL^{-1}	Drinking water	Nitrate	22
UV-visible spectrometry	0.5–13.7 mg L^{-1}	—	Municipal waste water	Nitrate	23
Ultraviolet (UV) light	0.08–4.0 mg L^{-1}	0.04 mg L^{-1}	Natural waters	Nitrate	24
UV-visible spectrometry	0.5–3.0 mg L^{-1}	—	Agricultural soil samples and water samples	Phosphates	25
UV-visible spectrometry	0.5–5.0 μg mL^{-1}	—	Soil/water	Phosphates	26
Ion chromatography	4.30–4.36 mg L^{-1}	0.03 mg L^{-1}	Soil extract	Nitrate	27
Ion chromatography	0.90–0.92 mg L^{-1}	0.02 mg L^{-1}	Soil extract	Phosphates	27
Ion chromatography	0.30 to 5.6 mg L^{-1}	0.10 mg L^{-1}	Natural waters	Potassium	28
Gas chromatography-mass spectrometry	0.02–10 mg L^{-1}	3 μg L^{-1}	Natural waters	Nitrate	29
Gas chromatography-mass spectrometry	0.5–208.5 mg L^{-1}	0.176 mg L^{-1}	Water	Potassium formate	30
Headspace gas chromatography (HS-GC)	—	2.5 mg kg^{-1}	Soil sample	Phosphorus	31
High-performance liquid chromatography with UV detection	0.2–200 ppm 0.2–200 ppm	9.5 mg L^{-1} 1.33 mg L^{-1}	Environmental water samples Environmental water samples	Nitrate Phosphate	32
Graphene-based field-effect transistor	0.001–100 mg L^{-1}	1.1 μg L^{-1}	Water	Nitrates	33
ZnO nanorods field-effect transistors (FETs)	1–5000 μM 2–25 000 μM 2–15 000 μM	1.0 μM 0.1 μM 0.4 μM	Nutrient solution or water	Phosphate Nitrates Potassium	34

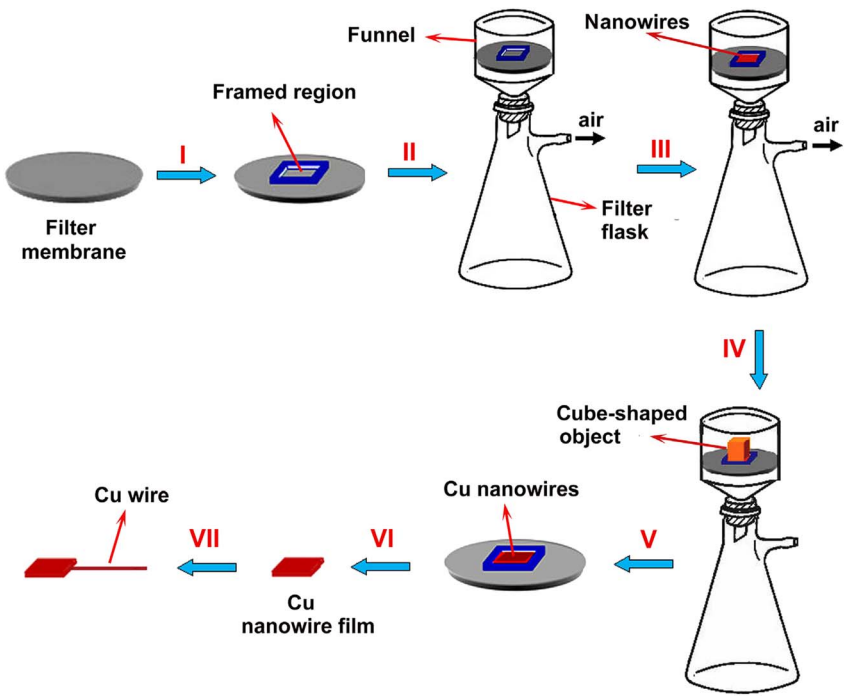

Fig. 1 Thermal annealing preparation of nanowire-based Cu electrode, this figure has been adapted from ref. 50 with permission from Elsevier, copyright September 2016.

microelectrode was able to detect nitrate ion concentration in a wide linear range (4–1000) μM. The modified electrode could be used for up to 100 interrogation cycles and was much more selective for the direct detection of nitrate ions in synthetic aquifer samples without pretreatment and pH adjustment of the solution used in the experiments. In addition, the detection of nitrate ions in agricultural soils has been performed using graphene oxide (GO) nanosheets and poly(3,4-ethylenedioxythiophene) nanofibers.[53] These could detect nitrate ions from soil extracts. The modified surface GO allowed for increasing the charge transfer resistance of the modified electrode and could detect a wide concentration range of

0.44–442 mg L^{-1} in the soil medium. Moreover, graphene foam (GF) was added with titanium dioxide nanofibers and nitrate reductase enzyme molecules.[54] In another work, nitrate reductase was entrapped in the growing PPy and the carboxyl group of CNT was immobilized. The optimal reactions were found in 0.1 M PBS at pH 7.5.[55] This nitrate detection exhibits a linear range of 0.44–1.45 mM. Faisal and Abu have also shown that nitrate reductase can be immobilized on PPy surfaces to detect nitrate ions in wastewater.[56]

Wang *et al.* reported research on self-assembled graphene oxide (GO)-three-dimensional copper oxide nanoparticles. The coupling increased the sensitivity and catalytic activity of copper for the detection of nitrate ions, which was the highest priority.[57] The electrochemical detection was carried out in seawater with a low detection limit of 7.89 μM. Moreover, the Ti nanocomposite electrode modified with graphene oxide nanosheets showed excellent durability for the detection of nitrate ions compared to Ti–Cu and Cu–Zn electrodes.[58] In addition, a carbon fiber micro-disc electrode was coupled with square-wave voltammetry to investigate the effects of aerosols on human health. In this study, the nitrate concentration followed a linear response of 0.003–2 mM with a detection limit of 1.10 μM.[59] Inam and others reported research work on the modification of Ag-working electrodes with electrodeposited copper nanoclusters in 2021. The modified electrode for nitrate ion detection showed a good linear concentration range (0.05 to 5) mM, with a detection limit of 0.207 nM. Another research study reported the detection of nitrate ions by an electrode modified with copper nanoclusters in freshwater.[60] In addition, trace-etched polycarbamate membranes were electrochemically modified with copper nanowires. Detection of nitrate was performed in water samples containing chloride and nitrites.[61] Moreover, the electrode modified with Pt–Cu showed a linear response between 0.12 and 4.75 mM concentration of nitrate ions neutral medium by the differential pulse voltammetry method. They found that Cu(I) and Cu(II) oxides reduced the reduction of nitrate, but this electrode showed excellent sensitivity (2.3782 μA μM^{-1} cm^{-2}).

A new chemical sensor was developed on an ion-printed polymer matrix using copper nanoparticles and a polyaniline nanocomposite to detect nitrate ions. A monomer functionalized with aniline adheres to the copper nanoparticles and the electrode was used to detect nitrate in real water samples.[62] Fu demonstrated the modification of a micro band electrode with a palladium-tin bimetallic composite using a micro-electromechanical system. The double layer was formed by an electrochemical deposition method, which has improved electro catalytic activity.[63] In this observation, they found repeatability and stability for 60 days, and a linear range from 1 mg L^{-1} to 20 mg L^{-1}. In addition, poly(3-octyl-thiophene) and molybdenum disulfide (POT-MoS_2) were applied to a gold electrode. The fabricated POT-MoS_2 layer acted as an ion-to-electron conversion layer. The nanocomposites showed high accuracy over a period of 27 days.[64] The detection of nitrate showed a dynamic linear range of 1–1500 ppm. The working principle of this soil sensor is shown in Fig. 2. Another research work dealt with the reduction of nitrate ions on AuNP surfaces on the surface of carbon paper electrodes functionalized with selenium particles.[65] The modified electrode was successfully used in seawater samples with a detection limit of 8.6 μM.

Nitrate contamination of food and mineral water was also studied using the modified electrode with copper nanostructure. In this study, a hydrodynamic amperometric electrode was used to detect the concentration of nitrate ions, which

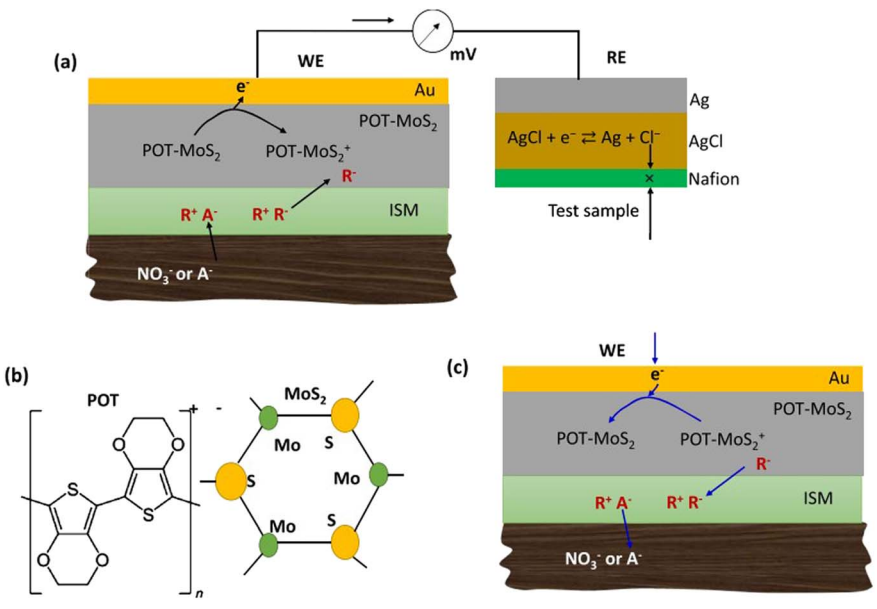

Fig. 2 Graphical representation of the working principle of the soil sensor. (a) Oxidation process for the detection of nitrite ions, (b) molecular structure of POT and MoS_2, and (c) mechanism of the reduction process of the working electrode, this figure has been adapted from ref. 64 with permission from American Chemical Society, copyright Aug 1, 2019.

Table 2 A comparison of the electrochemical sensors for the detection of nitrate ions

Sensing material	Detection range	Detection limit	Method of detection	Detection medium	Types of sample	Ref.
AuNPs/CS/MXene/GCE	0.5–3300 μM	0.069 μM	Amperometry	0.1 M PBS (pH 7)	Water	67
Cu@TiO_2-Nf/PAR/GCE	5–7500 μM	2.1 μM	DPV	PBS (pH 1.7)	Water	68
Cu/SPE (Ag)	0.05–5 mM	0.21 nM	LSV	0.1 M KCl	Water	69
Cu nanowire electrode	8–5860 μM	1.35 μM	DPV	0.1 M Na_2SO_4	Tap water/river water	50
Cu/MWCNT/RGO/GCE	0.1–75 μM	20 nM/30 nM	SWV	Na_2SO_4/H_2SO_4	Mineral/tap water	51
Ppy-NW electrodes	10 μM to 1 mM	4.5 ± 1 μM	Pulsed voltammograms	N/A	N/A	70
AgNS on carbon and Ag UMEs	4–1000 μM	3.2–5.1 μM	Chronoamperometry	0.1 M Na_2SO_4	Synthetic aquifer	52
Ag-doped zeolite expanded graphite epoxy electrode	1–10 mM	0.08 mM/0.004 mM	Multiple pulsed amperometry	0.1 M Na_2SO_4	N/A	71
Cu electrode	0.1–2.5 mM	4.2 μM	Amperometry	0.1 M Na_2SO_4	Mineral water/soft drinks sample	72
Chitosan/bentonite nanocomposite-based ISE	20 mM to 0.8 M	N/A	Potentiometry	N/A	N/A	73
Self-assembly nanobeads-packed (nBP) hetero columns ion-selective microelectrode	0.1 μM to 0.1 M	N/A	Potentiometry	N/A	N/A	74
Ppy-NS ISE	0–200 mg L^{-1}	N/A	Potentiometry	N/A	N/A	75
NiR/PEDOT NWA/AuE	3.22–17.74 μM	N/A	Amperometry	0.1 M KCl	Water	54
NiR/rGO/Ppy/GCE	5 × 10^3–10^4 μM	275 μM	CV	0.1 M KCl	Freshwater	56
NiR/CNTs/Ppy/GCE	440–1450 μM	170 μM	Amperometry	0.1 M PBS	Freshwater	55
NiR/Gr foam/Ti NF	0.16–7128 μM	0.16 μM	Amperometry	N/A	Soil extract	76
NiR/ZnO NRs/AgE	1–3400 μM	1 μM	Amperometry	N/A	Freshwater	77
NiR/GO/PEDOT NF/AuE	7.09–7128 μM	2.17 μM	EIS	N/A	Soil extract	53
Gr/CuE	9–940 μM	10 μM	Amperometry	0.1 M NaOH	Freshwater	78
Gr/Cu NPs/AuE	10–90 μM	7.89 μM	DPV	0.01 M HCl + 0.1 M Na_2SO_4	Freshwater	57
CuNPs/MWCNT-PEI/PPy-PSS/GCE	100–5000 μM	30 μM	Amperometry	0.1 M PBS	Freshwater	79
CuOx/CNTs/GCE	10–700 μM	N/A	DPV	0.1 M Na_2SO_4	Freshwater	80
Cu-modified CF MDE	3–2000 μM	1.1 μM	SWV	0.1 M KCl	PM2.5 particle extraction in water	59
Cu NCs/PtmE	6.25–300, 300–3500 μM	5 μM	LSV	N/A	Freshwater	60
CuNCs/PGE	1–35 μM	0.59 μM	Amperometry	0.01 M H_2SO_4+ 0.05 M K_2SO_4	Food extract/ freshwater	81
Cu NWA/TEPM	10–400 μM	3.0 μM	LSV	1 mM H_2SO_4 + 0.1 M K_2SO_4	Freshwater	61
Cu NW/CuE	8–5860 μM	1.35 μM	DPV	Acidic (pH 2)	Freshwater	50
Cu NPs/PtE	6.25–1000 μM	N/A	LSV	0.1 M Na_2SO_4	Freshwater	82
Macroporous Ag film/ITO	20–5000 μM	N/A	SWV	1 M NaOH	Freshwater	83
Ag networks like film/GCE	80–6520 μM	3.5 μM	Amperometry	0. M PBS	Freshwater	66
3D dendrite Ag NSt/Au mEA	2–1000 μM	2 μM	SWV	0.5 M NaCl	Freshwater	84
AgNPs/AuE	0.39–50	0.39	SWV	NaCl (34.5 g L^{-1})	Seawater	85
AgNPs/AuE	1 × 10^{-3} to 0.01 μM	9 × 10^{-4}	CV	NaCl (34.5 g L^{-1})	Seawater	86
Oxide-deficient Cu–Pt	120–990 μM	0.159 μM	DPV	0.1 M KCl	Freshwater	87
Pd NPs/epoxy-Cu	32–560 μM	N/A	Amperometry	0.1 M PBS	Freshwater	88
Pd–Sn composite/MEA	16–322.6 μM	3.06 μM	LSV	0.01 M $KClO_4$	Freshwater	63
Porous Cu–Ni alloy	20–1000 μM	2 μM	Amperometry	0.5 M K_2SO_4	Freshwater	89
Pd–Au NPs composite	16–242 μM	1.19 μM	LSV	N/A	Freshwater	90

Table 2 (*Contd.*)

Sensing material	Detection range	Detection limit	Method of detection	Detection medium	Types of sample	Ref.
PEG-SH/SePs/Au NPs	16–500 μM	8.6 μM	DPV	0.1 M KCl	Freshwater	65
PNA-SA-modified SiO_2@Fe_3O_4/CPE	101–1453 μM	87 μM	SWV	BR-buffer	Freshwater	91
CuxO-GCS/BPPGE	10–100 μM	1.032 μM	CV	1 mM $HClO_4$ + 1 M $NaClO_4$	Soil extract/food extract	92
PPy/Ag NPs/GCE	$1–10^4$ μM	5 μM	CV	0.1 M K_2SO_4	Freshwater	93
PPy/Pd NCs/GCE	1×10^{-4} to 8×10^{-4}	0.74	DPV	0.1 M PBS	Freshwater	94
PANI/WO_3/Cu Nsh/GCE	40–246 μM	1.2 μM	LSV	0.1 M H_2SO_4	Freshwater	95
PANI/Cu NPs/GCE	$1–10^5$ μM	5 μM	LSV	0.1 M KCl	Freshwater	62
PPy/GCE	0.001–0.006 mM	N/A	SWSV	pH 9	Water	96
PANI/Cu/MWCNT/Au electrode	0.8–30 μM	0.09 μM	DPV	0.1 M PBS (pH 5)	Waste water	97
Chit/ZnO/Pt	0.1–2 μM	0.01 μM	CV	0.1 M Na_2SO_4 (pH 5.5)	Drinking water	98

had a linear dynamic range from 1 to 35 μM. The repeatability was evaluated as 2.3% and the detection limit was 0.59 μM. In addition, a two-layer bimetallic electrode modification was performed using two different salt solutions of copper and silver.[66] The electrodeposited silver film behaves like a porous network-like structure and the average particle size was 200 nm. The linearity of the catalytic current increases from 0.08 to 6.52 mM.

2.1.2. Nitrite ion detection. Nitrite is an essential intermediate in the biological nitrogen cycle. The main source of nitrite in the water environment is the nitrogen fertilizer from agriculture.[48] However, it has a bad effect on the human body (lethal dose 1.1 g), if it is present in drinking water and aquatic life as well.[48,99] A comparison of electrochemical techniques for the detection of nitrite ions is shown in Table 2.

Stepwise modification of the glassy carbon electrode by chitosan (CS), polypyrrole (PPy), and carboxyl graph (CG) showed excellent differential pulse voltammetry (DPV) for the detection of nitrite ions in real water samples.[100] The obtained electrochemical current showed a linear relationship with a wide range from 0.2 to 1000 μM with a detection limit of 0.02 μM. Moreover, the GCE modified with manganese porphyrin and niobium tungstate nano sheets showed an excellent detection limit of 0.380 μM.[101]

A micro-structuring system was developed to fabricate the working electrode. In this study, the reported linearity range was between 10-800 μM and the detection limit was 0.5 μM.[103] In another study, ZnONRs (NR = Nano Rods) were grown on a seeded silver electrode and then dip-coated with Fe_2O_3 NPs. ZnONRs with Fe_2O_3 NPs significantly increase the electrocatalytic activity.[104] The modified electrode showed a linear

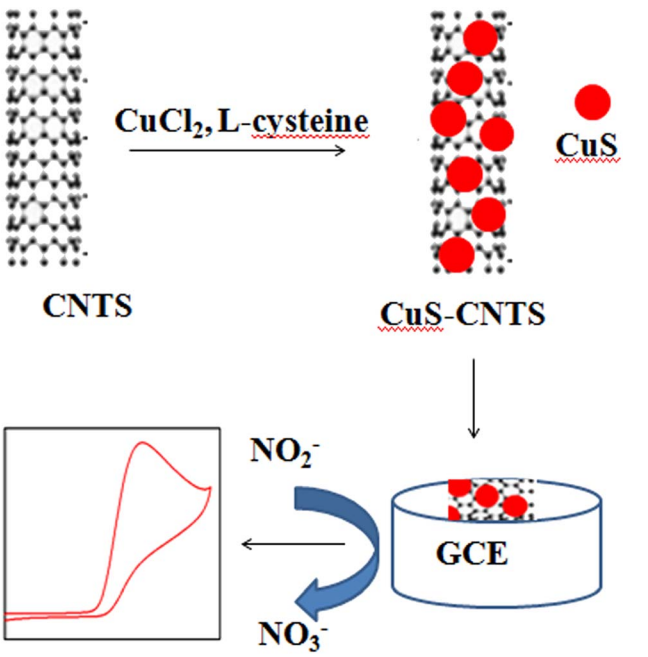

Fig. 3 Schematic of the modification process for CuS-MWCNTs, this figure has been adapted from ref. 102 with permission from Elsevier, copyright 15 May 2016.

response from 1 to 1250 μM. Moreover, copper sulfide (CuS) nanoparticles and multi-walled carbon nanotube (MWCNT) nanocomposites were synthesized to prepare a GCE for the detection of nitrite ions. The composite showed excellent electro catalytic activity in the oxidation of nitrite ions in PBS (pH 7.0). The detection of nitrite ions showed linearity between 1 μM and 8.1 mM with a detection limit of 0.33 μM.[102] The electrode modification process is shown in Fig. 3. In addition, Pt nanoparticles were loaded with $Ni(OH)_2$/MWCNTs by a simple reduction process, which showed remarkable electro catalytic performance in nitrite oxidation.[105] It has a sensitivity of 145 μA mM^{-1}.

A novel electrochemical sensor was fabricated to determine the nitrite ion concentration on a hollo site modified with silver nano rods by a chemical process. Then, a MoS_2 layer was prepared on an Ag/HNT nanocomposite by a hydrothermal process, and the catalytic activity of the finally modified carbon paste electrode was significantly enhanced. It provides good linearity from 2 to 425 μM.[106] Moreover, in the research study, a GCE was fabricated using chitosan@N,S-coded MWCNTs, and gold nanoparticles (AuNPs) to obtain a nitrite sensor with a linear range of 1–5000 μM and a detection limit of 0.2 μM.[107] In another study, a silver and graphene oxide-modified electrode was fabricated using ethanolamine and Ag nanoparticles. In this work, the detection limit and linear response range were reported to be 0.023 μM and 0.05 to 3000 μM, respectively.[108] Wu *et al.* modified an electrode with Cu_2O/CNTs to detect nitrite ions, with a linear concentration range from 0.1 nM to 1 mM.[109] A schematic diagram of the electrode modification for nitrite ion detection is shown in Fig. 4. Huang *et al.* deposited gold nanoparticles on a poly(3-methylthiophene) (P3MT) modified glassy carbon electrode to form nano-Au/P3MT/GCE. Amperometric detection showed that the modified electrode exhibited excellent electrochemical responses for the detection of nitrite ions with a linear concentration range of 10–1000 μM.[110] Moreover, the study on the detection of nitrite ions by amperometric detection in aqueous solution showed a satisfactory detection limit of 0.4 μM.[111] Moreover, the glassy carbon electrode modified with gold nanoparticles showed excellent electro catalytic activity for the oxidation of nitrite ions. This gold-modified electrochemical sensor is comparatively better than the bare GCE and planar gold electrode, which showed a detection limit of 2.4 μM.[112] Another study[113] was carried out using a composite of 5-amino-1,3,4-thiadiazole-2-thiol (p-ATT) on functionalized multiwalled carbon nanotubes (FMWCNTs), and thus modified (FMWCNTs-ATT polymer (p-ATT)) glassy carbon electrode was used to detect ammonium ions amperometrically, and the oxidation peak was observed at 0.84 V. The peak of the modified electrode was larger than that of the bare electrode. This amperometric method showed a linear detection range of 10 to 1000 nM with a detection limit of 0.2 nM for the nitrite ion in the water medium.

For the simultaneous detection of nitrite ions with nitrate ions, Ag particle-doped zeolite with graphite epoxy electrode (AgZEGE) was used using multiple pulse amperometry (MPA). MPA improved the electrochemical response over other conventional methods.[71] The studied electrochemical sensor was successfully used for the analysis of tap water samples spiked with nitrite ions and showed a linear response at 0.1–1 mM nitrite concentration. Another sensor for the simultaneous detection of superoxide anions and nitrite ions was fabricated stepwise on a Pt electrode. First, a CNT/PPy

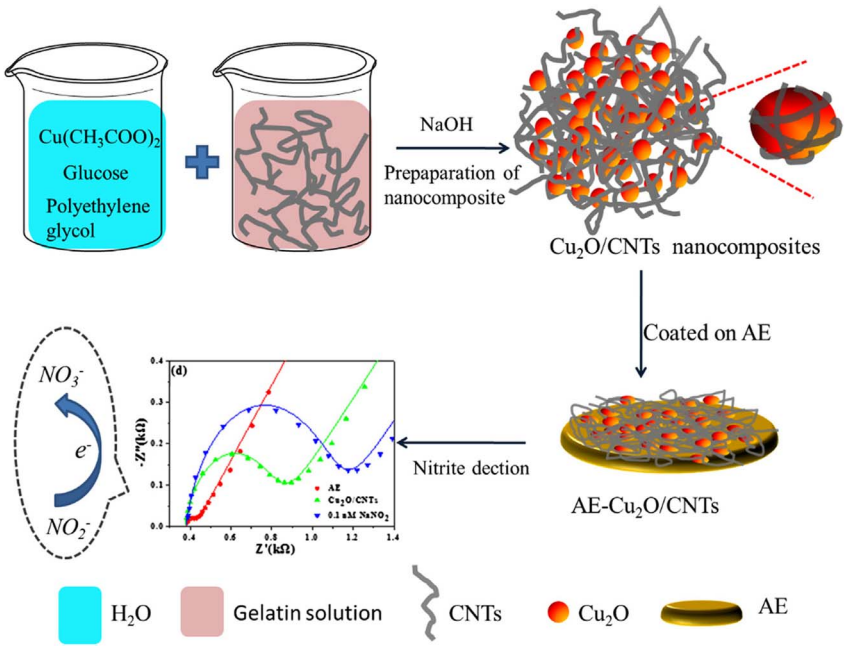

Fig. 4 Schematic representation of the fabrication of Cu_2O/CNTs composite-based sensor, (i) preparation of Cu_2O/CNTs composite, (ii) Au electrode modification with Cu_2O/CNTs composite and (iii) nitrite ion detection; this figure has been adapted from ref. 109 with permission from Elsevier, copyright November 2018.

Table 3 Comparison of the electrochemical sensors developed for the detection of nitrite ions

Sensing material	Detection range	Detection limit	Method of detection	Detection medium	Types of sample	Ref.
Poly(1,8-DAN)/f-MWCNT	0.3–6.5 μM	0.075 μM	Amperometry	0.1 M PBS + 0.1 M KCl	N/A	121
GO-CS-AuNPs/GCE	0.9–18.9 μM	0.3 μM	Amperometry	0.1 M PBS	N/A	122
Cu/MWCNT/RGO/GCE	0.1–75 μM	N/A	SWV	Na_2SO_4/H_2SO_4, pH 3	Water	51
MnTMPyP/$NbWO_6$/GCE	0.12–3.57 mM	0.38 μM	DPV	PBS (pH 7)	N/A	101
CG/PPy/CS/GCE	0.2–1000 μM	0.02 μM	DPV	0.1 M NaAc-HAc buffer (pH 4)	Tap/commercial/salt/ soybean milk water	100
α-MnO_2- based electrode	10–800 μM	0.5 μM	DPV	0.1 M PBS	N/A	123
GNPs/graphene/MCE electrode	0.3–720 μM	0.1 μM	DPV	0.1 M acetate buffer	Lake/river/industrial water/ food	124
α-Fe_2O_3 NPs-ZnO NRs-Ag electrode	1–1250 μM	0.015 μM	LSV	0.1 M PBS	Tap/mineral/pond water	104
Cu-MOF/rGO/GCE	3 μM to 40 mM	33 nM	Chronoamperometry	0.1 M PBS	N/A	125
CuS-MWCNT/GCE	1 μM to 8.1 mM	0.33 μM	Amperometry	0.1 M PBS	Tap water	102
Pt/$Ni(OH)_2$/MWCNTs/GCE	0.4 μM to 5.67 mM	0.13 μM	Amperometry	0.1 M PBS	Milk sample	126
Pt NWNs/GCE	1 μM to 24 mM/24–132 mM	0.14 μM	Chronoamperometry	0.1 M PBS	N/A	127
Ag/HNTs/MoS_2/CPE	2–425 μM	0.7 μM	Amperometry	0.1 M PBS	Tap water/aqueduct water	106
AuNPs/CS@N,S co-doped MWCNTs/GCE	1–7000 μM	0.2 μM	Amperometry	M PBS (pH 7.4)	Food	107
Pd/Fe_3O_4/poly DOPA/RGO	2.5–6470 μM	0.5 μM	Amperometry	0.1 M PBS	River water/food	128
Ag-AEfG100/GCE	0.05–3000 μM	0.023 μM	Amperometry	PBS (pH 7.4)	Tap water	108
Cu_2O-CNTs/Au electrode	0.1 nM to 1 mM	0.0188 nM	EIS	5 mM $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ in PBS (pH 7.4)	Tap water	109
Nano-Au/P3MT/GCE	10–1000 μM	2.3 μM	Amperometry	PBS (pH 4.0)	Iodized salt	110
Bare GCE	N/A	0.4 μM	Amperometry	N/A	Aqueous	111
Au/GCE	10–5000 μM	2.4 μM	CV	0.2 M acetate buffer	Water	112
Cyt c/l-Cys/P3MT/MWCNT/GCE	10–100 μM	0.5 μM	Amperometry	0.1 M PBS	Aqueous	129
P-NiTAPc film-modified electrode	0.5–8000 μM	0.1 μM	Amperometry	H_2SO_4–Na_2SO_4 solution (pH 2.0)	Water	130
Ag-NEEs	10–300 μM	N/A	CV	0.1 M PBS	N/A	131
MC/GCE	0.5–100 μM	0.1 μM	DPV	BR-buffer (pH 3.5)	Water	132
Boron-doped diamond electrode	2–1000 μM	0.05 μM	CV	N/A	Aqueous	133
p-ATT/GCE	0.05–100	340 pM	Amperometry	0.2 M PBS	Water	134
VO(SB)-modified CPE	3.9–40 μM	0.613 μM	CV	0.1 M TBAP	N/A	135
AgZEGE	100–1000 μM	10 μM	Amperometry, CV	0.1 M Na_2SO_4	Water	71
Pt/poly(1,8-DAN)Pt/CA	0.5–100 μM	0.1 μM	Amperometry	Acetate buffer (pH 4)	Water/food/soil	115
CoPc modified electrode	N/A	0.005 μA	CV	PBS (pH 7.3)	N/A	116
CuNPs/CNTs/CS/GCE	0.1–2500 μM	0.024 μM	Amperometry	0.05 M PBS	N/A	136
CoL/MNSs/CPE	0.2–30 μM	0.015 μM	DPV	BR-buffer	Water	137
Cu/Ag/MWCNTs/GCE	1 μM to 1 mM	0.2 μM	Amperometry	PBS (pH 7)	Lake/drinking/sea water	138
AuNPs-PEI/CSPE	0.01–4 μM	0.0025 μM	DPV	PBS (pH 6.5)	Tap/cannel water	139
Snsubmicroparticles/GCE	5–1000 μM	0.5 μM	DPV	0.1 M PBS	N/A	140
Snsubmicroparticles/GCE	150–900 μM	10 μM	Amperometry	0.1 M PBS	N/A	140
Snsubmicroparticles/GCE	100–500 μM	50 μM	Impedance	0.1 M PBS	N/A	140

composite was deposited on a Pt electrode and then Cu and ZnSOD were deposited on it, which increased the electro catalytic response for the detection of nitrite ions.[114] Micaela Badea modified the Pt electrode with a poly (1,8 diaminonapthelene) film for amperometric detection of nitrites in the water bath and flow injection analysis.[115] This analysis was also applied to food, soil, vegetable, and fertilizer samples. Another research work on the determination of nitrite ions was carried out on the surface of a carbon electrode modified with cobalt-pathalocyanine.[116] Also, a poly (pyrrole viologen) nitrite reductase biosensor modified with GCE was developed for the detection of nitrite ions. The linear range and detection limit of the modified electrode were 5.4–43.4 μM and 5.4 μM, respectively.[117]

In another research demonstration, the working electrode was modified with nano-diamond powder, which has catalytic activity for the oxidation of nitrite ions. Here, the electrochemical response increases with increasing nitrite ion concentration in the water medium.[118] In addition, the detection of nitrite ions was also carried out by modifying the GCE electrode with Pt and Fe(III) nanoparticles.[119] Abdollah Salimi, modified cobalt oxide (CoO) nanoparticles and flavin adenine dinucleotide (FAD) composite modified GCE using cyclic voltammetry, which showed excellent catalytic efficiency to reduce the over potential. In amperometric detection of nitrite ions, the modified electrode shows a linear dynamic range of 1–30 μM and a detection limit of 0.20 μM.[120]

2.1.3. Ammonium ion detection. In agricultural ecosystems, ammonium ions are important for plant growth when external inputs are low. In contrast, it causes toxicity when the amount is in the millimolar range. Root and shoot growth is affected due to the toxicity of ammonium ions. There are multiple conventional methods to determine ammonium ion concentration and electrochemical sensing research work is listed in Table 3.

For the groundwater used as drinking water, ammonium ion concentration was measured with a new silver-decorated carbon nanotube-epoxy composite using the differential pulse voltammetry technique.[141] The newly modified electrode has very good sensitivity and excellent electroactivity for the direct oxidation of nitrite ions. Another technique for the detection of ammonium ions was developed on a lab-on-a-chip (LOC), which works for *in situ* and real samples by potentiometric measurements. The fabricated device consists of poly(dimethylsiloxane) and an integrated sensor platform that includes four working microelectrodes, two reference microelectrodes, and one counter microelectrode.[142] It can measure fast and reliable data in real time when immersed in a laminar flow of ambient water. In addition, an ion-selective electrode (ISE) with solid contact was developed by modifying it with graphite paste, polypyrrole, and ionophore-immobilized polyvinyl chloride materials.[143] In this process, the ISEs possess a short reaction time. In addition, a wireless real-time ion-selective solid-state membrane was developed for the detection of ammonium ions in wastewater.[144] It saves 25% of power under normal operating conditions. In another research work, a zeolite-based conductometric micro sensor was successfully used for the detection of ammonium ions in real media.[145] The modified electrode exhibited high

Table 4 Comparison of the electrochemical sensors for the detection of ammonium ions

Sensing material	Detection range	Detection limit	Method of detection	Detection medium	Types of sample	Ref.
PMB@GLDH/AuNPs/SPEC	0.65–300 μM	N/A	Amperometry	PBS (pH 9.5)	Water	148
Ag-CNT	0.2–1 mM	1 μM	DPV	0.1 M Na_2SO_4	Groundwater	141
Ppy COSANE-Au microelectrode	1 μM to 40 mM	0.04 mM	Potentiometric	Buffer Tris-HCl/Tris	Tap/sewage water	142
NH^{4+} selective ASS electrode	1 μM to 0.1 M	<1 μM	Potentiometric	N/A	Tap/well water	143
Solid state ISM	1–64 mg N/L	$1 \times 10^{-6.5}$ M	Potentiometric	N/A	Wastewater	144
Natural zeolite clinoptilolite-Au interdigitated microelectrode (IDμE)	0.01 μM to 1 mM	0.01 μM	Conductometric	5 mM KH_2PO_4/ Na_2HPO_4 (pH 6.2)	N/A	145
25,27-Di-(5-thio-octyloxy)calix[4] arene-crown-6-Au interdigitated electrode (IDE)	0.01–1 mM	0.01 mM	Conductometric	5 mM KH_2PO_4/ Na_2HPO_4 (pH 6.2)	River water	146
Alanine dehydrogenase/SPE	10–100 mM	0.18 mM	Amperometric	PBS (pH 7)	N/A	150
PET microporous membrane	4.2–66 μM	0.12 μM	CV, DPV, SWV	Water/1,6-dichlorohexane	Water	149

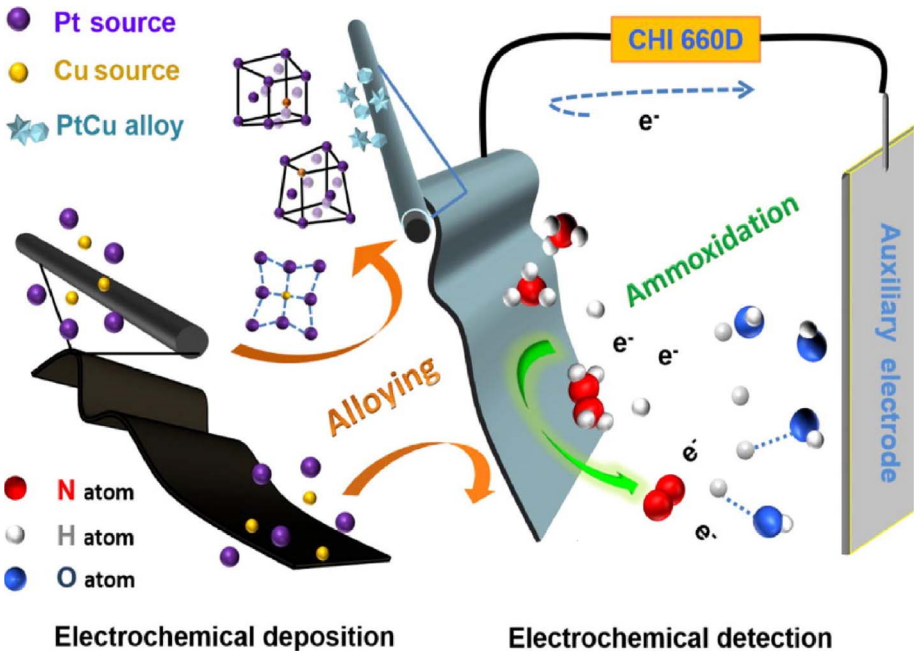

Fig. 5 Schematic representation for the preparation of Pt_7Cu1-CC electrode and its application for ammonia detection; this figure has been adapted from ref. 147 with permission from Elsevier, copyright 1 October 2022.

operational and storage stability and has a detection limit of 100 μM. Saiapina *et al.* reported a conductometric sensor based on 25,27-di-(5-thio-octyloxy) calyx [4]aren-crown-6 for the measurement of monovalent, divalent, and trivalent cations. The developed sensor has satisfactory sensitivity and high signal repeatability, as well as a linear range of 0.01 to 1.5 mM and a detection limit of 10 μM.[146] The carbon fabric electrode was modified by electrodeposition of a PtCu alloy, which reduced the crystal lattice spacing of Pt to oxidize ammonium ions. The first developed electrode modified with PtCu alloy showed a linear response of 0.5–250 μM and a detection limit of 8.6 nM.[147] The schematic is shown in Fig. 4.

Electrodeposition and electro polymerization techniques were used to prepare the SPEC/AuNPs/PMB electrode, and then a thin layer of glutamate dehydrogenase was applied to prepare an enzymatic membrane.[148] In the study, the ammonium ion concentration was indirectly measured in the ammonium solution containing nicotinamide adenine di-nucleotide hydrogen phosphate (NADH). Another research work was carried out in the medium of water/1,6-dichlorohexane with amperometric detection.[149] Here, the detection limit was 0.12 μM and the linear range was between 4.2 and 66 μM. Moreover, a group of chemicals was added to the NH^{4+} ion medium, namely alanine dehydrogenase enzyme, pyruvate substrate, and nicotinamide adenine dinucleotide (NADH).[150] Finally, the oxidation of NADH was carried out at 0.55 V, which is proportional to the ammonium ion concentration in the river water samples (Table 4 and Fig. 5).

3. Potassium (K) detection

As a macronutrient, potassium (K) is regularly required by plants during their life cycle for the movement of water, nutrients and carbohydrates. It is related to all kinds of metabolic activities of plant growth and fruiting. Therefore, the role of potassium is essential for efficient plant production.

The detection of potassium ions is very important due to its significance in agriculture and proper fertilization of the cropland. A versatile electrochemical detection of potassium was performed using various modified electrode surfaces, which are summarized in Table 5. There are several types of potassium ion receptor compounds and probes whose main performance is also listed.

4-Aminobenzo-18-crown-6-ether (crown ether) and the K^+ cation can form a complex on the electrochemical surface, which produces an electrochemically measurable signal. This type of work was reported to detect K^+ ions by the DPV technique in the 0.1 M tetra-butyl ammonium bromide (TBAB) medium.[151] In this study, the detection range is 1 μM to 10 mM. Another research work was conducted on ether-modified graphene surfaces in the methylene blue (MB) medium.[152] In addition, K^+ ions form G-quadruplexes with aptamer-modified electrodes. Here, hemin also helps to form this complex on the modified surface.[153] In addition, a dibromaza[7]helicene ionophore was developed and doped with polyvinyl chloride (PVC) on the surface of an Al–Cu/Si-p/SiO_2/Si_3N_4 transducer. The modified electrode also showed a linear response of 1 μM to 10^{-1} M and also has excellent sensitivity in other cationic media.[154] A gold electrode modified with DNA aptamers was also developed for the quantification of K^+ ions in MB, AQMS, and $Na_4Fe(CN)_6$ medium. In this work, a linear response of 10^{-8} to 10^{-5} M and a detection limit of 2.31×10^{-9} M were observed.[155] The aptamers-based biosensor is shown in Fig. 6.

Table 5 Comparison of the electrochemical sensors for the detection of potassium ions

Sensing material	Detection range	LOD	Method of detection	Detection medium	Types of sample	Ref.
AuE/11-MUA/4-AB-18-C-6	1 μM to 10 mM	N/A	DPV	0.1 TBAB	N/A	151
GCE/GO-crown	0.1–10^{-7} μM	1 pM	EIS	1.5 mM MB	N/A	152
AuE/G-quadruplex/hemin	0.1 nM to 0.1 μM	0.1 nM	DPV	100 mM Tris–HCl buffer (pH 6.2)	N/A	153
Al–Cu/Si-p/SiO_2/Si_3N_4/PVC-membrane	1 μM to 10^{-1} M	N/A	EIS	0.1 M Tris–HCl buffer (pH 7)	N/A	154
AuE/K^+ ssDNA	10^{-8} to 10^{-5} M	2.31×10^{-9} M	CV	MB, AQMS, $Na_4Fe(CN)_6$	N/A	153
AuE/p-ATP/AuNPs/DNA	0.1–1 mM 1–30 mM	0.1 mM	SWV	0.1 M Tris–HCl buffer (pH 7.41)	N/A	157
GCE/P(Py-co-PAA)/G-aptamer	20 fM to 1 mM	14.7 fM	EIS	20 mM Tris–HCl buffer (pH 7.4)	N/A	158
SPC/Nafion/4-AB-18-C-6	1–500 ppm	N/A	DPV	3 mMRu(NH^3)$^{6+}$/0.1 TBAB	N/A	159
SCE/CPE/hollandite-MnO_2	4.97×10^{-5} to 9.05×10^{-4} M	N/A	Amperometry	Tris–buffer (pH 8)	N/A	160
GCE/MnO_2 nanorods	2–90 μM	0.05 μM	CV	Tris–buffer (pH 7.4)	Tap and DI water	161
CPEM/$KSr_2Nb_2O_{15}$	1.26×10^{-5} to 1.62×10^{-3} M	7.27 × 10–5 M	Amperometry	0.1 M Tris–buffer (pH 8.3)	N/A	168
AuE/ssDNS-G rich	0.1 nM to 50 nM	0.1 nM	SWV	20 mM Tris–HCl buffer (pH 7.41)	Human serum	164
Carbon SPE/PANI/valinomycin	10^{-5} to 1 M	$10^{-5.8}$ M	Potentiometric	N/A	Artificial serum	75
Al/F-MWCNTs/ZnO/valinomycin	5–25 mM	N/A	EIS	N/A	Soil	166
PET/graphene- valinomycuin	1–20 000 μM	N/A	FET	Tris–HCl buffer	N/A	169
PET/Gel/valinomycin	5–100 μM	N/A	N/A	N/A	Serum	170
3DPE sensors	1–10 000 ppm	1.35 ppm	CV	pH 1.44	Soil pore water samples	167
Valinomycin supported ZnO/rGO nanocomposites on GCE	—	0.956 mM	CV	N/A	Soil sample	171
F-MWCNT/ZnO/valinomycin composites	5–25 mM	—	Impedance	N/A	Soil sample	172
Prussian blue nanotube sensor	5.0×10^{-8} to 7.0×10^{-4} M	2.0×10^{-8} M	CV	N/A	Water	173

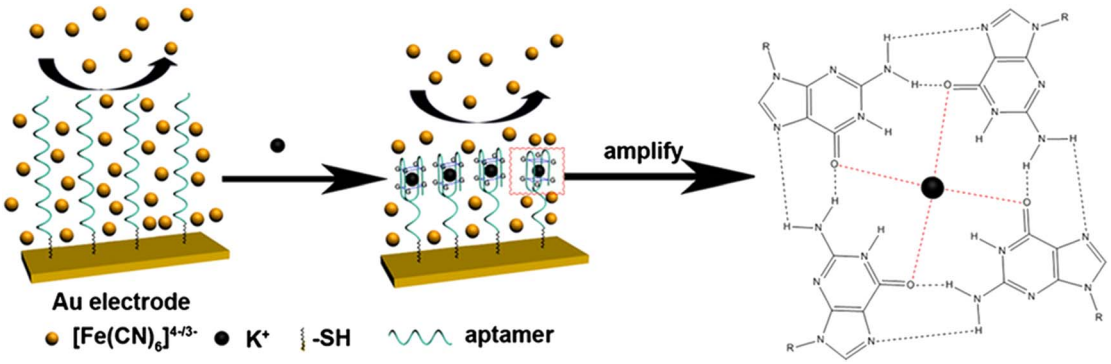

Fig. 6 ssDNA and K^+ reaction mechanism on the modified electrode surface, this figure has been adapted from ref. 156 with permission from Elsevier, copyright 15 October 2013.

Another research was conducted using AuNPs and G-rich ssDNA-modified electrodes to detect potassium ions in the linear range of 0.1–1 mM and 1–30 mM.[157] To improve the conductivity of the electrode modified with G-rich ssDNA, a poly-pyrrole modification was also used as an anchor for the probe and transducer.[158] In addition, a carbon-based sensor was modified with crown ether and Nafion to detect potassium ions using the DPV technique.[159]

Lima *et al.* demonstrated a research work on the modification of working electrodes using hollandite-type manganese oxide to detect potassium ions. In this study, K^+ ion detection was performed by amperometric technique in Tris buffer pH 8.[160] In addition, zinc oxide nanotubes (ZnONRs) were synthesized by a hydrothermal sol–gel method to produce GCE. The synthesized GCEs modified with ZnONRs were used to detect potassium ions in drinking water samples.[161] Furthermore, a single-layer ssDNA electrode modified with graphene and guanine was used to detect K^+ ions, which is suitable for health monitoring and other applications.[162] In addition, the ssDNA probe was attached to AuE by thiol binding and the guanine-rich part captured the K^+ ions. The K^+ ion detection is included in this post[128,163] the electrode modification process and K^+ detection are shown in Fig. 6.

Valinomycin surface coating with an active layer containing the modified electrode for detection of K^+ ions on the polyaniline layer of GCE has been reported.[165] In this study, they reported, a detection range of 10^{-5} to 1 M with a detection limit of $10^{-5.8}$ M. Another research group reported an F-MWCNTs/ZnO/valinomycin electrode surface for the detection of potassium ions in soil extracts. This showed a linear detection range of 5–25 mM.[166] In a recent report, a low-cost on-site detection method but accurate method has been proposed by Denis McCrudden and his group[167] for monitoring soil nutrients. This sensing system consists of a microcontroller with novel 3D printed ion selective electrodes, which can be used for the simultaneous determination of potassium and pH. This electrode showed linearity for potassium ions in the range of 1–10 000 ppm electrodes with LOD of 1.10 ppm and 1.35 ppm at pH values of 1.44 and 3.05, respectively (details in Table 5).

4. Phosphorus (P) ion detection

As we have already discussed, nitrogen, phosphorus and potassium, commonly known as NPK, are the main macronutrients of soil and each of these nutrients has its own role in plant nutrition.[174,175] In this part, we will discuss the existing sensors for the detection of phosphorus, as it is a component of nucleic acids and membrane lipids in plant formation. Including phosphorus, all three mentioned nutrients should be available in the soil. On the other hand, soil erosion and agricultural fertilization may increase toxic substances in water. Phosphate (PO_4^{3-}) can cause eutrophication of water bodies due to its excessive presence.[176] Not only the vital biomolecules of our human body, but also the growth of plants is highly dependent on the presence of an adequate amount of these phosphate ions in the soil, and therefore it plays a crucial role in both the agricultural sector and biomedical applications.

Since most farmers apply fertilizers blindly into the soil and it is necessary to reduce the negative impact of the fertilizer on the environment without reducing the crop yield, therefore, the proper management of this fertilizer is very important. Maria Khaydukova and her group have developed a potentiometric multisensory system for the simultaneous detection of N, P, and K in the aqueous soil extracts of the soils of the desired fields.[177] The sensors they developed can be used to analyze pH and conductivity as well as all three macronutrients in soil samples, and good correlation coefficients of 0.69 to 0.96 were obtained between the target parameters and sensor responses. Quantification of P was possible with a root mean square error (RMSE) of 79 mg kg^{-1} in the range of 35–574 mg kg^{-1}.

Talarico *et al.*[178] reported a screen-printed electrode modified with carbon black nanoparticles (CB) using an amperometric method *via* electrochemical reduction of a molybdophosphate complex. Here, the CB nanoparticles help quantify the molybdophosphate complex at a lower applied potential. This CB-SPE shows a linear range of 0.5–100 μM with a detection limit of 0.1 μM. The system was tested in various water samples such as drinking, river, aquarium and wastewater and showed satisfactory recoveries.

Kabir and his group reported a novel screen-printed electrode (SPE) modified with ammonium molybdate tetrahydrate (AMT) and silver nanowires (AgNWs) for phosphate detection.[179] Since AgNWs are highly conductive, they were added to AMT, which contributes to faster electron transport between AMT and SPE. As a result, the sensor they developed showed a wide detection range of 5 μM to 1 mM and LOD of 3 μM with a high sensitivity of 0.71 μA μM^{-1} and they suggested that this AMT/AgNWs/SPE is promising for simple, low-cost, portable phosphate ion detection and for monitoring the health of water systems and field soils.

Catalytic hydrogen waves (CHW) occur due to a classical reaction in which certain substances in solution catalyze the hydrogen evolution reaction and thus can reduce the overpotential for the hydrogen ion reduction,[180] are based on this idea, and a novel sensor was developed by Zhang *et al.*[181] In this method, a wave corresponding to catalytic hydrogen evolution was observed on the electrode surface modified with molybdenum phosphide (MoP) in the presence of phosphate. The interaction between molybdenum oxides on the surface of MoP microparticles and phosphate results in a structure (change in catalytic properties) similar to phosphomolybdic acid (MoPO), allowing quantitative detection of phosphate in the human blood. Differential pulse voltammetry (DPV) shows a linear range from 0.10 to 20.0 mmol L^{-1} with LOD of 0.030 mmol L^{-1}.

Since natural enzymes lead to denaturation under environmental conditions, they are sometimes not used in measuring instruments. Recently, free-standing cobalt oxide in the form of nano-needle arrays on flexible carbon fabric (CC) serving as a substrate has been developed to detect phosphate ions in human urine,[182] and according to their reports, it is inexpensive and shows scalability, good stability, and high sensitivity. The sensors they developed show a wide linear range of 0.1–1.0 mM and 1.0–30.0 mM with a detection limit of about 10 μM for the phosphate anion.

It is well known that the use of large amounts of chemical fertilizers causes contamination of agricultural wastewater, although they are treated like macronutrients NPK in soil. To determine their presence in watercourses, Jagannathan and coworkers[183] developed a method based on electrochemical impedance spectroscopy measurements involving the detection of urea (N), orthophosphate (PO_4^{3-}) (P), and potassium K^+ (K) in agricultural watercourses, using stainless steel as working and counter electrodes and Ag/AgCl as a reference (details in Table 6).

Although electrochemical sensors might be a good replacement for the conventional existing technique, still there are a few problems, such as sample preparation, and interference of different kinds of ions present in the soil sample solution. We need to focus on these issues. Different kinds of ionophores have already been reported for the selective determination of ion-like, 4-AB-18-C-6 ether that can bind potassium ions in its structure. We need to search more ionophores for different kinds of soil constituents so that we perform an analysis of soil or water samples accurately. When we are able to analyze the soil/water samples accurately, it will be easier for any farmer to measure how much fertilizer is required by the plant at that time, even which types of fertilizer should be applied might be

Table 6 Comparison of electrochemical sensors for the detection of phosphate ions[a]

Electrode material	Method	LOD	Range	Sample	Ref.
PyO/nano-CP/GCE	Amperometric	0.3 μM	1.0–100 μM	Human serum	184
GLA/PyO/CoPC-SPCE	Amperometric	2 μM	2.5–130 μM	Pond water	185
Rotating gold disk electrode	Amperometric	0.11 μM	0.59–3.49 μM	Seawater	186
CB-SPE	Amperometric	0.1 μM	0.5–100 μM	Water samples	178
Screen-printed graphite macroelectrodes	Cyclic voltammetry	0.3 μg L^{-1}	0.5 to 20 μg L^{-1}	Canal water	187
AMT/AgNWs/SPE	Cyclic voltammetry	3 μM	5 μM to 1 mM	Field soil	179
MoP/GCE	DPV	0.030 mmol L^{-1}	0.10 to 20.0 mmol L^{-1}	Human blood	181
Co_3O_4/CC	Amperometric	10.0 μM	0.1–30.0 mM	Human urine	182
Stainless steel	Electrochemical impedance spectroscopy	—	7 to 50 ppm	Simulated agricultural run of water	183
CNT/CNC/Ag@ pANI@AMT microneedle	Voltammetry	0.007 mM	0–0.6 mM	Standard sample and coffee	188
GQDs-Ce^{4+} probe	Fluorescent probe	0.06 μM	0.1 to 20.0 μM	Sodium phosphate	176

[a] Pyruvate oxidase (PyO), poly-5,2′:5′,2″-terthiophene-3′-carboxylic acid, glassy carbon electrode (GCE), poly-TTCA (nano-CP), carbon nanotube-CNT, cellulose nano crystal – CNC, polyaniline – pANI, ammonium molybdenum tetrahydrate – AMT, molybdenum phosphide (MoP).

estimated as they are able to send their data to the local agricultural specialist. It is assumed that, may be initially it will be difficult but gradually it will bring revolution when more farmers in an area are brought under these facilities.

5. Conclusions

The conventional techniques are well-established methods and by using them it is possible to measure specific ions with high accuracy, while the electrochemical sensor is less expensive, easy to use, can perform measurements in a short time, sometimes not requiring much more pretreatment of the samples, and has a low detection limit and accuracy also comparable to the conventional technique. Although all of the work is very impressive, considering linearity regarding the concentration of different analytes, such as for nitrate ions, Cu/MWCNT/RGO/GCE (20 nM-30 nM)[51] and NiR/Gr foam/TiNF (0.16–7128 μM),[76] for nitrite ions, CG/PPy/CS/GCE (0.2–1000 μM)[100] and Cu_2O-CNTs/Au electrode (0.1 nM to 1 mM),[109] for ammonium ions, PMB@GLDH/AuNPs/SPEC (0.65–300 μM)[148] and natural zeolite clinoptilolite-Au interdigitated microelectrode (IDμE) (0.01 μM to 1 mM),[145] for potassium ions, GCE/P(Py-*co*-PAA)/G-aptamer (20 fM to 1 mM),[158] AuE/ssDNS-G rich (0.1 nM to 50 nM),[164] and AuE/G-quadruplex/Hemin,[153] for phosphate analysis, GQDs-Ce^{4+} probe (0.1 to 20.0 μM)[176] and CB-SPE (0.5–100 μM)[178] are very impressive works. However, there are still many opportunities, such as the development of single short measurements, that is, a single measurement will measure different soil/water nutrients with high accuracy, and the development of smartphone-based apps (including artificial intelligence) is in high demand for real-time monitoring of agricultural systems that suggest fertilizer management to farmers. Finally, it will be easier for farmers to optimize production costs and minimize fertilizer use, which will help control pollution. If we assume that a large number of people will use this kind of smartphone-based app, it will be easier to support them (as they will be able to send their soil reports to the specialist) from a local agricultural research center or from any other agricultural specialist; thus, electrochemical sensors might be able to boost smart agriculture and bring a revolution.

Conflicts of interest

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

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