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Review paper

Recent advances in nanomaterials-based electrochemical sensors for herbicide detection

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Abstract

In recent decades, herbicides have been extensively used to preserve the quantity and quality of crops, thereby meeting the growing demand for food production worldwide. Environmental pollution resulting from the excessive utilization of pesticides, particularly the over-application of herbicides to safeguard desirable crops from weeds, poses a significant threat to both human health and the ecological system. It is essential to detect these pollutants at low concentrations, particularly in water and soil samples. While commonly accepted analytical procedures (chromatography and spectroscopy methods) are available, these highly sensitive and time-consuming methods are hindered by their high costs, the requirement for bulky equipment, the need for user training, and the necessity for sample pre-treatment. Electrochemical sensors address the limitations of traditional detection methods and offer significant potential for the efficient, sensitive, and cost-effective detection of herbicides. The development of nanomaterial-based electrochemical sensors for detecting herbicides has attracted considerable attention because of their benefits, including high selectivity, sensitivity, real-time monitoring capabilities, and user-friendliness. This review provides a thorough overview of the recent advancements in nanomaterial-based electrochemical herbicide sensors. The review begins with a general introduction, followed by a discussion on electrochemical sensors and the significance of incorporating nanomaterials into electrochemical sensors. Additionally, the review highlights recent advancements in electrochemical sensors that utilize various nanomaterials, including carbon-based nanomaterials, metal and metal oxide nanoparticles, metal-organic frameworks and transition metal chalcogenides, for the quantitative determination of herbicides. Finally, the review outlines the perspectives associated with the practical application of nanomaterial-based electrochemical herbicide sensors.

Keywords

Carbon-based nanomaterials; metal-organic frameworks; transition metal chalcogenides; modified electrode

Introduction

Maximizing crop yield is a key goal in contemporary agriculture. To safeguard their crops at different stages of growth, farmers use a variety of chemical pesticides designed to eliminate pests and competing plants. Herbicides, especially those formulated to manage weeds before and after they emerge, are the most commonly used type of pesticide. The application of herbicides is beneficial for eliminating unwanted plants that could otherwise impede the healthy growth of the desired crops. Despite their advantages, the residues resulting from the excessive use of herbicides in cultivated crops, water, and soil are regarded as serious environmental hazards [1,2].

Based on their chemical structure, herbicides are classified into several families, including triazines, organochlorines, chlorophenoxy acids, urea, and organophosphates, among others. Herbicides applied to crops can function as plant growth regulators, desiccants, and defoliant agents that help thin fruit or prevent premature fruit drop. The increasing use of herbicides in intensive agriculture over the past few decades has helped sustain both the quantity and quality of crops, leading to a rise in global food production. However, these compounds can enter aquatic ecosystems through surface runoff, spray drift, leaching, deposition, and soil erosion. When these compounds exceed specific concentration thresholds, they can present serious risks to both environmental and human health [3-5].

Elevated levels of pesticide residues have been linked to cancer, neurological disorders, bone marrow abnormalities, infertility, cytotoxic effects, and disruptions in endocrine function. The presence of herbicide residues and their metabolites in soil, water, and food is currently a primary concern in food safety and environmental chemistry [6,7].

Considering this situation, it is essential to continuously monitor these compounds in environmental compartments to safeguard both the ecosystem and human health.

Conventional analytical techniques, including high-performance liquid chromatography [8], capillary electrophoresis [9], atomic absorption spectroscopy [10], and mass spectrometry [11], typically demonstrate high levels of precision and accuracy. Nonetheless, these methods have several operational and economic constraints that hinder their use for extensive field monitoring. These limitations include their complexity, time-consuming processes, the need for sample pretreatment, costly equipment, and the necessity for highly skilled personnel.

Electrochemical sensors are widely favoured over other traditional methods due to their low cost, rapid assay times, and simple procedures. These electrochemical devices are highly versatile, lightweight, easy to manufacture, and amenable to miniaturization. Electrochemical sensors have proven to be effective tools for detecting low concentrations of target analytes in minimal sample volumes. It is also well-suited for in situ analysis, point-of-care testing, and real-time in vivo analysis [12-15].

The sensing electrode plays a crucial role in electrochemical detection, as it affects the electrochemical sensitivity through the redox reaction occurring between the electrode material and the electrolyte. However, overpotential and electrode fouling can result in weak electrochemical signals when directly measuring target analytes using conventional electrodes such as glassy carbon electrodes (GCEs), carbon paste electrodes (CPEs), gold electrodes (GEs), and screen-printed electrodes (SPEs). These limitations of conventional electrodes can be overcome by modifying the working electrode surface with materials that possess enhanced conductivity and sensitivity.

The choice of appropriate working electrode materials, which must possess adequate stability, along with their subsequent surface modification, is crucial for obtaining sensors with high selectivity and remarkable sensitivity. This approach leads to improved sensitivity in analyte detection, even in the presence of interfering substances [16-20].

In the context of electrochemical detection systems, the modification of working electrodes with nano-sized modifiers provides appealing new characteristics. The dimensions of nanomaterials range from 1 to 100 nm, and they are beneficial due to their excellent specific surface area and high surface-to-volume ratio [21-23]. Nanostructured materials can serve as highly tunable and selective catalysts because of their distinctive electronic properties. The excellent surface area of nanostructured electrodes can improve the adsorption kinetics of target analytes, which is particularly beneficial for enhancing the sensing response. Utilizing nanomaterials to modify the working electrode surface enhances its conductivity and sensitivity, leading to improved sensitivity in analyte detection, even in the presence of interfering substances [24-27].

In this review, we have examined various electrochemical-based sensing platforms for the highly sensitive determination of herbicides. We primarily focus on the development of nanomaterial-based electrochemical sensors for herbicides, highlighting the latest advancements in electrochemical sensors that utilize nanomaterials, including carbon-based nanomaterials, noble metal and metal oxide nanoparticles, metal-organic frameworks, and transition metal chalcogenides.

Electrochemical sensors

Key considerations in selecting an appropriate detection strategy and tools for specific applications include sensitivity, cost, rapidity, and reliability. Cost is a primary driving force behind contemporary innovation; however, it is not the sole important criterion. Achieving accurate and reliable measurements within a short timeframe should not be compromised in the pursuit of cost reduction [28].

An electrochemical sensor is an instrument that analyses a target substance either qualitatively or quantitatively. The core principle of an electrochemical sensor lies in the sensing signal produced by the reaction between the measured substance and a specific sensing element. This signal is then converted into a recognizable electrical signal that is proportional to the concentration of the target analyte using a specific transducer [29-31]. A comprehensive electrochemical analysis system comprises electrochemical sensing equipment, an electrochemical detection instrument, and an electrolyte. The electrochemical detection instrument, specifically the electrode device, typically features a three-electrode configuration, which includes a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). The WE is the site where the electrocatalytic reaction takes place and is often modified with various nanomaterials to improve the efficiency of the electrocatalytic process. The CE completes the circuit, facilitating the continuous flow of electrons, while the RE ensures the precise application of a potential to the WE [32,33].

Typically, electrochemical sensors consist of three electrodes: the working (sensing) electrode, the reference electrode, and the counter (auxiliary) electrode, along with electronic instrumentation for data collection. While traditional electronic instrumentation can be large and costly, recent advancements in electronics have made it possible to miniaturize these devices. The adoption of such miniaturized instruments can enhance the use of electrochemical sensors in point-of-care and field-deployable applications [34,35].

Electroanalytical techniques for the electrochemical determination of herbicides encompass voltammetry and amperometry.

Notably, voltammetric methods, including linear sweep voltammetry (LSV), cyclic voltammetry (CV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV), are among the most commonly used sensing strategies for detecting herbicides across a variety of sample matrices. The distinction between these methods is based on their potential applications. The simplest of these methods is LSV, in which the current is measured as the applied potential increases linearly over time. CV is a method that allows for the simultaneous observation of redox peak potential and current, thereby facilitating the study of reversible redox processes. In comparison to LSV and CV, DPV and SWV exhibit greater sensitivity for herbicide analysis due to the use of pulse techniques, making them commonly utilized in the development of electrochemical sensors. Both DPV and SWV are based on a potential staircase; however, DPV differs in that it measures the current just before and after each pulse is applied, rather than calculating the difference between forward and reverse pulse currents as in SWV. The current difference is then plotted versus the applied staircase potential [36-38].

Like voltammetry, amperometric sensors measure the current response at a specific potential; however, in this case, the applied potential is maintained at a constant level. In other words, the amperometric approach involves measuring changes in current at a fixed potential. In amperometric sensors, a constant voltage is applied to the working electrode, inducing a current to flow, which is subsequently recorded as a function of time. By relying on a specific potential for a given analyte, amperometric sensors provide selective and sensitive measurements [39,40].

Application of nanomaterials in electrochemical sensors

Due to the diverse biological, chemical, and physical properties of nanomaterials and their nanocomposites, considerable effort has been dedicated to developing synthetic procedures that allow for precise control over shape, surface charge, size, and physicochemical characteristics in recent decades [41,42].

Nanomaterials offer significant advantages in diverse applications, including catalysis, energy storage devices, energy conversion, biotechnology, imaging, and sensor technologies, due to their enhanced properties. Three primary approaches have been utilized for the synthesis of nanomaterials: chemical strategies (including chemical vapor deposition, thermal decomposition, sol-gel processes, and hydrothermal technique), physical strategies (such as laser ablation, and physical vapor deposition), and electrochemical strategies (such as electrodeposition, and anodic oxidation), as well as photochemical strategies (photodeposition) [43].

Recent advancements in nanotechnology and the synthesis of nanomaterials have created opportunities for the evolution of advanced sensing systems. Firstly, it is widely recognized that electrode materials play a crucial role in the development of high-performance electrochemical sensing platforms for detecting target analytes using various analytical principles [44].

The recent emergence of nanomaterials has opened new avenues for designing nanomaterial-based modified electrodes, facilitating effective interactions and electron transfer between the target species and the electrode surface for electrochemical sensing. For example, the unique catalytic and electrical properties, along with the large number of adsorption-active sites and high surface area-to-volume ratio of nanostructures, enable improved catalytic and sensing responses through the quick movement of target analytes in nanomaterial-based sensors [45,46].

The properties of nanomaterials are highly influenced by their shape and size; therefore, the synthetic process that controls their morphology and growth is critical. Additionally, the integration of dimensional, geometric, compositional, and structural properties of nanomaterials is essential for imparting unique functionalities and characteristics to these materials. nanomaterials may

aggregate, leading to an increase in particle size, which in turn affects their catalytic performance. In other words, larger particles typically exhibit lower activity compared to smaller or well-dispersed nanoparticles. Consequently, it is advantageous to minimize aggregation through the functionalization of nanomaterials, which also enhances the stability of nanomaterial dispersions. Surface derivatization of nanostructures can typically be accomplished through several methods, including the deposition of a layer of another inorganic substance (resulting in inorganic core-inorganic shell composites), the attachment of organic capping agents, and the covalent binding of biomolecules (such as antibodies and DNA) at the interface [47-49].

For the catalytic properties of nanomaterials, factors such as composition, geometry, oxidation state, and the physical/chemical environment are crucial in determining their catalytic reactivity and activity, with particle shape and size also being significant considerations. Electrocatalytic activity influences the effectiveness of catalytic reactions, thereby enhancing output signals and improving detection sensitivity [50,51]. Thus, nanomaterials are essential in the development of electrochemical sensing platforms, as they possess the suitable properties needed to enhance overall electrochemical reduction/oxidation, increase sensitivity, and address challenges related to interference issues and selective detection [52].

This review discusses several key types of nanomaterials and their nanocomposites that have been extensively utilized in the design of high-performance electrochemical sensors for herbicide detection.

Nanomaterial-based electrochemical sensors for herbicide detection

Carbon-based nanomaterials

Carbon, being one of the most versatile elements on Earth, has garnered significant attention, particularly because of its ability to form various hybridization states (sp , sp^2 , and sp^3). This versatility allows it to create a diverse array of allotropes, ranging from diamond, the hardest material known, to graphite, the softest [53]. Carbon-based nanomaterials are categorized into 0D, 1D, and 2D materials based on their shape, with representative examples including fullerene (0D), carbon nanotubes (CNTs, 1D), and graphene (Gr, 2D). All carbon-based nanomaterials exhibit several notable inherent properties, including high electrical conductivity, mechanical strength, chemical stability, biocompatibility, and a high surface-to-volume ratio. They can be readily functionalized through non-covalent and covalent modifications with functional groups. Additionally, they can be combined with other materials to create composites that exhibit synergistic effects for the intended applications. Further functionalization with nanoparticles not only significantly enhances their physicochemical properties but also helps prevent agglomeration [54-57].

The unique characteristics of carbon nanomaterials, related to their electrical, mechanical, thermal, and optical properties, have paved the way for a wide range of applications, including bioimaging, cancer therapy, drug delivery, sensors, energy storage and generation, among others. Furthermore, their remarkable electrochemical properties, such as a high surface area, electrocatalytic activity, excellent electrical conductivity, as well as adsorption capacity and high porosity, make them promising candidates for electrochemical applications, particularly in sensing [58-60].

The most used carbon-based materials include CNTs, Gr and its derivatives (reduced graphene oxide (rGO) or graphene oxide (GO)), mesoporous carbon particles. In particular, Gr and CNTs, which possess a high conductivity, large surface area, and good biocompatibility, have become focal points of research. CNTs are categorized into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Due to their unique structure and electrochemical properties, they are

frequently used as additives to load or fill other materials, creating composite materials with specialized properties. Gr is a unique 2D carbon material that exhibits higher thermal and electrical conductivity, as well as a larger surface area compared to CNTs. Gr-based materials have been utilized to fabricate electrodes for electrochemical sensing devices [61-64].

This section provides a comprehensive review of the application of carbon-based nanomaterials in the design of electrochemical sensors for herbicide detection. Tables 1 to 3 summarize the various electrochemical sensors based on various carbon nanomaterials (carbon-based nanomaterials such as CNTs, Gr and its derivatives and other carbon nanomaterials) for the determination of herbicides together with their sensing features, including limit of detection (LOD), linear detection range, and detection method.

Table 1. A summary of the analytical features of CNT-based electrochemical sensors for herbicide detection

Electrochemical sensor	Analytes	Method	LOD, nM	Linear range, μM	Ref.
MWCNT-COOH-MIP/CPE	Diuron	SWV	9.0	0.052 to 1.25	[65]
GCE/MWCNTs	Propham	SWV	759	3 to 38.6	[66]
		SWAdSV	365	2 to 47.8	
SPCE-CNT/Nafion	Paraquat	SI-DPV	170	0.54 to 4.30	[67]
GCE/A-MWCNT-FS	Clopyralid	DPV	0.8	0.005 to 10.0	[68]
MWCNTPEs	Phenmedipham	SWV	6.96*	0.02 to 2.0**	[69]
GCE/MWCNTCOOH	Diuron	DPV	68.8	-	[70]
FePc/MWCNTPE	Fluometuron	DPSV	69.8*	0.4 to 15.0**	[71]
		SWSV	10.0*	0.4 to 7.5**	[71]
MWCNTs-CS@NGQDs/GCE	Diuron	DPV	40.0*	0.08 to 12.0**	[72]
(MWCNT/NiTsPc)n film modified ITO electrode	Diquat	DPV	962	1.3 to 13.0	[73]

* $\mu\text{g L}^{-1}$, ** mg L^{-1}

Table 2. A summary of the analytical features of graphene-based electrochemical sensors for herbicide detection

Electrochemical sensor	Analytes	Method	LOD, nM	Linear range, μM	Ref.
PPY-g-NGE/GCE	Paraquat	DPV	41.0 and 58.0	0.5 to 2.00	[74]
Ppy/GF/PGE	Paraquat	SWV	8.22	0.18 to 1.37	[75]
TRGOPE	Naptalam	SWV	10.0	0.1 to 10.0	[76]
n-GR/GCE	Pendimethalin	DPAdSV	8,690 and 1.05	1.76 to 401 and 0.00196 to 753	[77]
t-LIG	Paraquat	SWV	540	0.5 to 35.0	[78]
MIP/ERGO/GCE	Propachlor	DPV	0.08×10^{-3}	0.001 to 0.1	[79]
GCE/rGO	Diuron	Amperometric	360	5.0 to 50.0	[80]
rGO-modified GCE	Fenuron	DPV	340	0.4 to 12.0 and 20.0 to 50.0	[81]
RGO/SPE	Glyphosate	DPV	0.144	0.001 to 1.0	[82]

Table 3. A summary of the analytical features of other carbon nanomaterial-based electrochemical sensors for herbicide detection

Electrochemical sensor	Analytes	Method	LOD, nM	Linear range, μM	Ref.
N,S-OMC/GCE	Amitrole	DPV	700	3.0-750.0	[85]
PANI/C ₇₀ /GCE	Triclopyr	SWV	9*	10.0 to 100.0*	[86]
g-C ₃ N ₄ /GCE	Aclonifen	SWV	1.28	0.01-1.2	[90]
CB-CTS-ECH/GCE	Bentazon	SWV	1,400	1.99-65.4	[91]
g-C ₃ N ₄ -CTAB/CPE	Linuron	SWV	24.7	0.1 to 300	[92]
	Amino-triazole		64.1	0.3 to 45	[92]
CMK-3/GCE	Paraquat	ASSWV	64.0	60.0 to 450.0	[93]

* ng mL^{-1}

Carbon nanotubes

Wong *et al.* [65] developed a voltammetric sensor based on CPE modified with carboxyl functionalized MWCNTs (MWCNT-COOH) and molecularly imprinted polymer (MWCNT-COOH-MIP/CPE). They utilized the MWCNT-COOH-MIP/CPE sensor for the sensitive and selective detection of diuron in real river water specimens. The adsorptive and catalytic characteristics of MWCNT-COOH, combined with the adsorptive and selective properties of MIP, enhanced the analytical signal of the fabricated sensor, allowing for the satisfactory detection of diuron in water samples. An electrochemical investigation of diuron using an MWCNT-COOH-MIP/CPE sensor was conducted with the SWV method. Good results were achieved with a linear concentration range from 0.052 to 1.25 μM , sensitivity of 0.51 A L mol^{-1} and LOD of 9.0 nM. In recovery investigations, the MWCNT-COOH MIP/CPE sensor demonstrated an RSD of less than 5 %, indicating the suitability of the proposed technique for practical applications.

Leniart *et al.* [66] studied the electrochemical oxidation of the protham (Pro) herbicide on MWCNT-modified GCE (GCE/MWCNTs) using SWV and square wave adsorptive stripping voltammetry (SWAdSV). The GCE/MWCNTs sensor allows the detection of Pro in the linear concentration range of 3.00 to 38.6 μM with LOD of 0.759 μM (LOQ = 22.8 μM) for the SWV technique and linear concentration range of 2.00 to 47.8 μM for the SWAdSV technique with LOD of 0.365 μM (LOQ = 1.09 μM). Thus, a simple, sensitive, rapid strategy was successfully utilized for the detection of Pro herbicide in River water specimens.

Chuntib *et al.* [67] modified a screen-printed carbon electrode (SPCE) with CNT dispersed in Nafion (SPCE-CNT/Nafion) for the detection of paraquat using Sequential injection-DPV (SI-DPV). The SI system facilitates the straightforward handling of different solutions and promotes greater automation, resulting in benefits such as quick and easy method operation, increased sample throughput, and reduced reagent usage. Under the experimental optimized condition, a linear calibration diagram in the concentration range from 0.54 to 4.30 μM with an acceptable regression coefficient (R^2) of 0.9955 and a LOD of 0.17 μM was achieved. Also, the relative standard deviation (RSD) for 11 replicate measurements using the same electrode was 4.2 %. The reproducibility of the fabrication of seven modified electrodes (SPCE-CNT/Nafion) was 2.3 % RSD. Finally, the SPCE-CNT/Nafion sensor is effective for detecting paraquat contamination in real water specimens.

Ozcan *et al.* [68] designed a sensor by using the modification of GCE with a nanocomposite containing fumed silica (FS) and acid-activated MWCNT (GCE/A-MWCNT-FS). The GC/A-MWCNT-FS sensor demonstrated very high performance in the voltammetric detection of clopyralid (CLD). The reduction current responses of the CLP exhibited a linear increase with CLP concentrations ranging from 0.005 to 10.0 μM . The GCE/A-MWCNT-FS sensor demonstrated high sensitivity to CLP, successfully detecting very low concentrations as low as 0.8 nM. The fabricated GCE/A-MWCNT-FS exhibited very acceptable performance in the detection of CLP in real specimens, including river water, urine, wheat, sugar beet, and herbicide formulations.

Demir and İnam reported a voltammetric sensor for the detection of phenmedipham based on MWCNT-paste electrodes (MWCNTPEs) [69]. SWV measurements documented for phenmedipham indicated that the reduction peak current response boosted linearly from 0.02 to 2.0 mg L^{-1} with an $R^2 = 0.9989$, and the LOQ and LOD were estimated as 23.2 and 6.96 $\mu\text{g L}^{-1}$, respectively. The procedure was also utilized for the determination of phenmedipham in saturated tea sugar, prepared as a spiked natural sample. A concentration of 1.0 g L^{-1} phenmedipham in the sugar solution was successfully measured, yielding a relative error of -5.0 % and an RSD of 3.16 %.

Moritaa *et al.* [70] developed a voltammetric approach involving the direct modification of a GCE through the deposition of consecutive aliquots of diluted dispersions of functionalized CNT

(GCE/MWCNTCOOH) in ethanol. This method aimed to determine diuron in seawater specimens using DPV as the electrochemical method. The GCE/MWCNTCOOH sensor exhibited a sensitivity of $2.20 \mu\text{A } \mu\text{M}^{-1}$, approximately ten times higher than that of the bare GCE ($0.192 \mu\text{A } \mu\text{M}^{-1}$). The LOD and limit of quantification (LOQ) were 68.8 and 229 nM for the GCE/ MWCNT-COOH sensor, while for bare GCE were 0.787 and $2.62 \mu\text{M}$, respectively. The applicability of the GCE/MWCNTCOOH sensor was evaluated using detectable amounts of diuron in seawater specimens, with recovery rates ranging from 76 to 119 %.

Demir *et al.* [71] fabricated a voltammetric sensor based on the iron(III) phthalocyanine/MWCNT paste electrode (FePc/MWCNTPE) to determine fluometuron herbicide. Calibration graphs for fluometuron were created by using the standard addition technique with square wave stripping voltammetry (SWSV) and differential pulse stripping voltammetry (DPSV) under experimental optimal conditions. The working range was established as 0.4 to 15.0 mg L^{-1} in a pH 6.0 Britton-Robinson buffer solution using the FePc/MWCNTPE sensor with DPSV, while the working range was found to be 0.4 to 7.5 mg L^{-1} for SWSV. Additionally, the LOD and LOQ values were found to be 69.8 and $233.0 \mu\text{g L}^{-1}$, respectively, using DPSV. On the other hand, the validation values for the LOD and LOQ were 101 and $337 \mu\text{g L}^{-1}$, respectively, when using SWSV. Finally, the detection of fluometuron utilizing the DPSV strategy at the FePc/MWCNTPE sensor was successfully carried out in real specimens, including tap water and its agricultural drug formulation.

Zhu *et al.* [72] created a DPV sensor to determine diuron by using a GCE modified with chitosan-encapsulated MWCNTs combined with nitrogen-doped graphene quantum dots (MWCNTs-CS@NGQDs/GCE). As illustrated in Figure 1A, NGQDs were initially prepared by pyrolyzing ammonium citrate at elevated temperatures. Subsequently, the MWCNTs-CS@NGQDs composite was synthesized employing a straightforward one-step ultrasonic self-assembly strategy, which relied on the electrostatic interaction between NGQDs and MWCNTs-CS. The WCNTs-CS@NGQDs composite materials were further modified on the GCE surface to create a DPV sensor for the sensitive detection of the diuron (as shown in Figure 1B). Furthermore, the incorporation of NGQDs significantly improved the detection sensitivity of the developed sensor. The MWCNTs-CS@NGQDs/ GCE sensor showed a broad linear concentration range ($0.08\text{--}12 \mu\text{g mL}^{-1}$), a low LOD = $0.04 \mu\text{g mL}^{-1}$ and heightened sensitivity ($31.62 \mu\text{A } (\mu\text{g mL}^{-1})^{-1} \text{ cm}^{-2}$) for the detection of diuron. Also, the created sensor displayed acceptable anti-interference, stability, and reproducibility. Finally, the practical feasibility of the MWCNTs-CS@NGQDs/GCE sensor was assessed by measuring diuron in soil and river water specimens.

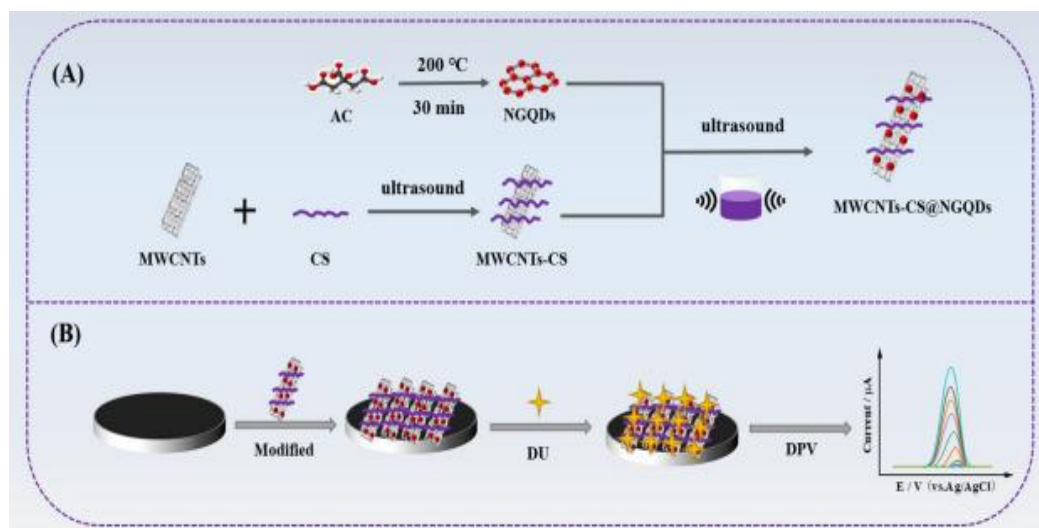


Figure 1. The synthetic procedure for the MWCNTs-CS@NGQDs composite and (B) the detection strategy of diuron using the MWCNTs-CS@NGQDs/GCE sensor [72], originally published under a CC BY 4.0 license

Zattim *et al.* [73] examined the preparation of self-assembled films employing MWCNT and nickel tetrasulphonated phthalocyanine (NiTsPc) as a voltammetric sensor for determining diquat (DQ) herbicide.

The assembly of the (MWCNT/NiTsPc) film was investigated, along with its morphological and structural characteristics (Figure 2). The (MWCNT/NiTsPc)_n film modified ITO electrode displayed good electrocatalytic properties for DQ compared to the bare ITO, confirming that the fabricated sensor is highly sensitive for determining DQ. The achieved LOD was 9.62×10^{-7} M. Also, the (MWCNT/NiTsPc)_n film modified ITO electrode was tested on real specimens, showing a good recovery rate (98.5 %) in organic apples.



Figure 2. The self-assembly of the (MWCNT/NiTsPc)_n film in 4 states and the photograph for the desired structuration of the MWCNT and NiTsPc molecules distributed on the ITO substrate [73], originally published under a BY NC ND 4.0 license

Graphene and its derivatives

Li *et al.* [74] reported a procedure for the fabrication of polypyrrole-grafted nitrogen-doped graphene (PPY-g-NGE) as a sensory platform for paraquat detection. They developed the PPY-g-NGE modified GCE (PPY-g-NGE/GCE) to examine its electrochemical behaviour and enable sensitive detection of paraquat using CV and DPV. The PPY-g-NGE/GCE sensor demonstrated outstanding electrochemical activity and electro-catalytic performance for the redox reactions of paraquat, attributed to the synergistic effects between NGE and PPY. The two reduction peaks of paraquat in DPV at -0.60 and -1.00 V were significantly amplified at the PPY-g-NGE/GCE sensor. Under optimum experimental conditions, the reduction peak currents of paraquat at the PPY-g-NGE/GCE exhibited a linear relationship over the concentration range of 0.05 to 2.00 μ M, with LODs of 41.0 nM for Peak 1 and 58.0 nM for Peak 2, respectively.

Ebrahimiasl *et al.* [75] modified a pencil graphite electrode (PGE) with a polypyrrole/nano-graphene nanocomposite (Ppy/GF/PGE), which was utilized for the determination of paraquat in agricultural water. Chronoamperometry, CV, and SWV techniques were employed for determination and detection. A linear concentration response was detected within the range of 0.18 to 1.37 M, exhibiting an R^2 of 0.999 and a LOD of 8.22 nM.

Brycht *et al.* [76] synthesized thermally reduced graphene oxide (TRGO) from graphite through graphite oxide using a modified Hummers approach, followed by additional thermal reduction of GO

in an argon atmosphere. They utilized the TRGO to create a TRGO paste electrode (TRGOPE), which demonstrated outstanding conductivity and rapid electron transfer kinetics. The TRGOPE was employed for the determination of the naptalam using the SWV mode. It was observed that the SWV response of naptalam at TRGOPE was linear across two ranges: 0.1 to 1.0 μM and 1.0 to 10.0 μM . Acceptable repeatability of the SWV responses was attained, along with a very low LOD in the 10 nM concentration range in an acidic medium. The results indicated that the TRGOPE sensor can be effectively used for the quantification of naptalam in river water specimens.

Koçak and Çelikkan [77] studied the electrochemical behaviour of pendimethalin at a Nafion-graphene-modified GCE (n-GR/GCE). Studies conducted with n-GR/GCE revealed that it performs more effectively for the detection of pendimethalin. The determination of pendimethalin using the differential pulse adsorptive stripping voltammetry (DPAdSV) technique with n-GR/GCE resulted in a broader working range, as well as a lower LOD. For the first peak current of pendimethalin, the calibration curve established using the DPAdSV strategy with n-GR/GCE sensor showed a working range of 1.76 to 401 μM , with a LOD value of 8.69 μM . For the second peak current of pendimethalin, the calibration curve obtained using the DPAdSV method with n-GR/GCE sensor exhibited a working range of 1.96 nM to 753 μM , with a calculated LOD value of 1.05 nM.

Sain *et al.* [78] created a flexible laser-induced graphene (LIG)-based electrode for the determination of Paraquat by the SWV procedure. LIG is a three-dimensional porous material created by using CO_2 laser irradiation to pattern polyimide (PI) films. It possesses a range of remarkable properties, including high conductivity, significant porosity, and biocompatibility. LIG was subsequently treated in a phosphate buffer to produce treated LIG (t-LIG). Electrochemical characterization was performed using CV, which indicated a strong current response and greater surface activation of t-LIG compared to LIG. The detection of Paraquat using t-LIG through the SWV approach demonstrated a wide linear concentration range of 0.5 to 35.0 μM , with a sensitivity of 46.6 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ and a LOD of 0.54 μM . t-LIG demonstrated an excellent average recovery rate of 96.6 % for Paraquat when tested with spiked real water specimens.

Elshafey and Radi [79] designed an electrochemical sensor based on MIP and electrochemically reduced graphene oxide (ERGO) to determine propachlor. The modified electrode (MIP/ERGO/GCE) was characterized using scanning electron microscopy and various electrochemical techniques. The MIP/ERGO/GCE sensor sensitivity is attributed to the heightened surface area of the ERGO, while its selectivity is derived from the MIP film. The proposed sensor demonstrated a broad linear range for log propachlor concentration (0.1 pM to 0.1 μM) with a low LOD of 0.08 pM. The results showed that the MIP/ERGO/GCE sensor displayed strong repeatability in the electrochemical detection of propachlor. Ultimately, the practical application of the fabricated sensor was demonstrated using samples from tap and lake water.

Alves *et al.* [80] developed a novel analytical procedure utilizing batch injection analysis and amperometric detection, employing a reduced graphene oxide-modified GCE (GCE/rGO) for the effective and sensitive determination of diuron herbicide in tap water and food beverages, including orange juice and whole grape specimens. The proposed sensor (GCE/rGO) exhibited a 7.6-fold increase in the oxidation current of diuron compared to the un-modified GCE, leading to a method characterized by detectability and high sensitivity. The developed sensor offered significant analytical features for the quantification of diuron, including a LOD of 0.36 μM , a linear concentration range of 5.0 to 50.0 μM , acceptable precision (RSD < 3.7 %), and accuracy, with recovery levels ranging from 80.8 to 105.5 %.

Borges *et al.* [81] proposed a voltammetric sensor based on a reduced graphene oxide (rGO)-modified GCE (rGO-modified GCE) for the determination of fenuron in water specimens. Spectroscopic and morphological analyses indicated that the rGO-modified GCE exhibits superior properties, including enhanced electrical conductivity and faster electron transfer rates, in comparison to GCE and GO used as control materials [81]. DPV was conducted using optimal parameters, yielding two linear ranges: 0.4 to 12.0 μM and 20.0 to 50.0 μM . The method demonstrated high sensitivities of 6.83 and 1.9 $\mu\text{A } \mu\text{M}^{-1}$, respectively, along with a low LOD of 0.34 μM . Interference, reproducibility, and Stability tests demonstrated that rGO-modified GCE is sufficiently reliable for use as a voltammetric sensor for fenuron detection in real water specimens.

Janjani *et al.* [82] synthesized reduced graphene oxide (RGO) through the reduction of suspended GO and subsequently utilized it to create a modified SPE (RGO/SPE). The detection of glyphosate was then carried out by using this sensor (RGO/SPE). RGO/SPE sensor serves as a platform for the adsorption of glyphosate and enhances the rate of electron transfer compared to bare SPE. DPV was used to quantify glyphosate, achieving a LOD of 0.144 nM over a broad concentration range of 1.0 to 1000.0 nM. Finally, the applicability of the RGO/SPE sensor was evaluated by the detection of glyphosate in garden soil and tap water samples.

Other carbon nanomaterial

Mesoporous carbon materials have garnered significant interest from both industry and academia due to their outstanding properties, including a large pore volume, high surface area, suitable thermal stability, and enhanced mass transport. A variety of synthesis methods enable the fabrication of mesoporous carbon materials with tunable pore sizes and architectures. Moreover, these porous structures enable the integration of functional organic or inorganic components into the channels or onto the walls, resulting in significant improvements in properties and application performance. Consequently, they are ideal materials for applications in energy storage, electrocatalysis, sensing, adsorption/separation, and biomedicine [83,84].

Zhou *et al.* [85] synthesized the nitrogen and sulphur-doped ordered mesoporous carbon (N,S-OMC) using a methylene blue dye as both N and S precursor and mesoporous silica SBA-15 as a hard template. Then, they investigated amitrole electro-oxidation at the N,S-OMC modified GCE (N,S-OMC/GCE) by electrochemical methods. The N,S-OMC/GCE displayed enhanced electrochemical performance for the amitrole oxidation, which can be attributed to the open mesoporous structures of N,S-OMC, and the presence of abundant electroactive defect sites on the carbon framework. Furthermore, N,S-OMC/GCE sensor was developed for the detection of amitrole in river water specimens, demonstrating acceptable selectivity and a broad linear concentration range of 3.0 to 750.0 μM .

Pandey *et al.* [86] studied the voltammetric behaviour of triclopyr at C_{70} decorated polyaniline modified GCE (PANI/ C_{70} /GCE). The PANI/ C_{70} /GCE sensor displayed a calibration curve for triclopyr over a linear concentration range of 10.0 to 100.0 ng mL^{-1} with an LOD of 1.9 ng mL^{-1} . The PANI/ C_{70} /GCE sensor demonstrated suitable conductivity for the voltammetric reduction of triclopyr, exhibiting improved reproducibility and sensitivity under optimal conditions. The voltammetric strategy was successfully applied to the analysis of real samples (water and tomato specimens), demonstrating good selectivity and high sensitivity.

As a metal-free 2D material, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) possesses a layered structure with extensive π -conjugation. $\text{g-C}_3\text{N}_4$ is a promising and fascinating material, primarily due to its structural analogy to graphite. Key differences include its sturdy C-N covalent bonds (as opposed to C-C bonds in graphite) and its layered sheets, which are connected by van der Waals forces.

Incorporating heteroatoms like nitrogen into carbon-based materials enhances their properties. Nitrogen atoms act as strong electron-donating sites, enhancing catalytic conductivity due to their inherent chemical nature. Owing to its tri-s-triazine ring structure and high degree of condensation, g-C₃N₄ is a medium-bandgap polymer and an indirect semiconductor. These properties have led to its application in diverse fields, including energy storage, sorbents, electrocatalysis, photocatalysis, and sensing [87-89].

Shetti *et al.* [90] conducted a voltammetric analysis of the aclonifen herbicide in soil and water specimens. They developed a sensing platform for determining aclonifen by coating a GCE with graphitic carbon nitride (g-C₃N₄/GCE). An enhanced cathodic peak was observed at a pH of 8.0 on the modified GCE, likely attributed to the electro-catalytic effect of g-C₃N₄. The SWV approach was utilized to determine aclonifen at trace-level concentrations. The linearity of concentrations was observed in the range of 0.01 to 1.2 μM , with a LOD of 1.28 nM for the aclonifen. The g-C₃N₄/GCE sensor was utilized for the detection of aclonifen in spiked soil and water samples, and the results indicate that the procedure is convenient and practical for use in environmental settings.

Vaz *et al.* [91] reported the fabrication of an electrochemical platform employing a GCE modified with a carbon nanosphere (CB)-based cross-linked chitosan (CTS) film for the detection of bentazon in water specimens. The incorporation of CTS, CB, and epichlorohydrin (ECH) as the cross-linking agent enhanced both the electrochemical signal and the chemical stability and electron transfer properties of the electrode. The CB-CTS-ECH/GCE sensor showed a linear concentration range of 1.99 to 65.4 μM , and a LOD of 1.4 μM . Also, the proposed sensor demonstrated a sensitivity of 6.22 A mol⁻¹ L cm⁻² for bentazon. The suggested technique demonstrated acceptable intra- and inter-day repeatability, demonstrating a high level of stability. Finally, the CB-CTS-ECH/GCE sensor was utilized to determine bentazon in natural water specimens.

In agricultural areas, linuron and aminotriazole are widely used herbicides to protect crops, but their widespread use pollutes the environment, especially when they are mixed with water or soil. To tackle these environmental concerns and detect trace amounts of herbicides, Ilager *et al.* [92] developed an electrochemical sensor utilizing a g-C₃N₄ and cetyltrimethylammonium bromide (CTAB) modified CPE (g-C₃N₄-CTAB/CPE) for the determination of linuron and aminotriazole. The influence of pH on oxidation revealed that the maximum current response occurred at a pH of 6.0 for linuron and at a pH 4.2 for aminotriazole. Further experiments were conducted for the detection of aminotriazole and linuron utilizing the SWV technique. The g-C₃N₄-CTAB/CPE sensor demonstrated the ability to detect linuron and aminotriazole over a wide range of concentrations, exhibiting clear linear relationships within the ranges of 0.12 M to 300 μM for linuron and 0.30 to 45 μM for aminotriazole. The LODs were determined to be 24.7 and 64.1 nM for linuron and aminotriazole, respectively. Ultimately, the created sensor was evaluated by quantifying linuron and aminotriazole in soil and water specimens.

Rajaram *et al.* [93] synthesized ordered mesoporous carbon, referred to as CMK-3, using the nano-casting strategy and characterized it by diverse electroanalytical and physicochemical techniques. Using CV measurements on a CMK-3 modified GCE (CMK-3/GCE) with the standard redox couple ([Fe(CN)₆]^{3-/4-}), the electrochemical surface area was determined to be 0.081 cm². The CMK-3/GCE sensor was employed as an electro-catalyst for the determination of the herbicide paraquat. The concentration studies revealed a linear relationship in sensitivity within the linear concentration range of 60.0 to 450.0 μM . Anodic stripping SWV (ASSWV) demonstrated a sensitivity of 9.51 $\mu\text{A } \mu\text{M}^{-1}$ and a LOD of 64.0 nM. The real-time applicability of the sensor was assessed using fruit and vegetable extracts, and the analysis indicated that the recovery values ranged from 102 to 105 %.

Metals and metal oxide nanoparticles

A category of nanomaterials includes metal nanoparticles (NPs) such as gold, platinum, and silver, which have been extensively used in the production of electrochemical sensors. Metal nanoparticles possess distinctive properties, including nonreactiveness, high reduction potential, biocompatibility, low cytotoxicity, ease of surface functionalization, and size-dependent electrical characteristics. These attributes make them a practical option for surface modification materials in electrodes. Additionally, metallic NPs can enhance the mass transport rate and facilitate rapid electron transfer, both of which contribute to increased sensitivity of the electrodes used. Furthermore, metal oxide NPs (such as Fe_2O_3 , MnO , CuO , TiO_2 , ZnO , *etc.*) with various morphologies are commonly employed in the development of electrochemical sensors because of their outstanding electrical and photochemical properties, excellent stability, and large surface area [94-97].

Therefore, this section aims to highlight the application of metallic and metal oxide nanoparticles for detecting herbicides. Table 4 summarizes the various electrochemical sensors based on metallic and metal oxide NPs for the determination of herbicides, together with their sensing features, including LOD, linear detection range, and detection method.

Farahi *et al.* [98] developed the CPE modified with silver particles (Ag-CPE) as an interesting device for the analysis of paraquat by the SWV method. Metallic silver particle deposits were successfully acquired through electrochemical deposition in acidic media using CV. The results indicate that, under optimal conditions, the increase in the two cathodic peak currents was linear with the increase in the concentration of the paraquat, ranging from 100 nM to 1 mM. The LOD for Peak 1 was determined to be 20.1 nM. The methodology was successfully applied for detecting paraquat in citrus fruit cultures.

Sun *et al.* [99] reported the synthesis of core-shell structured $\text{SiO}_2@\text{Au}$ nanoparticles with uniform morphology and developed a non-enzymatic sensor for the sensitive detection of diuron in the presence of indole-3-acetic acid, utilizing a $\text{SiO}_2@\text{AuNPs}$ film-modified GCE ($\text{SiO}_2@\text{AuNPs}/\text{GCE}$). The $\text{SiO}_2@\text{AuNP}$ nanocomposite, characterized by a high surface area, a high number of uniform reactive sites, and significant catalytic activity, demonstrated an improved voltammetric response for diuron. Furthermore, DPV revealed a linear relationship for diuron concentrations ranging from 0.20 to 55.0 μM , with an LOD of 51.9 nM. In conclusion, this sensor was employed for the detection of diuron in vegetable specimens.

Shetti *et al.* [100] studied the voltammetric determination of molinate at zinc oxide nanoparticles modified CPE (ZnO-CPE) by the SWV technique. The voltammetric response at the ZnO-CPE in pH 3.0 was significantly better than that of the nascent electrode. The ZnO-CPE demonstrated an outstanding ability to meet the desired analytical requirements. The lowest LOD of 10 nM was attained within the concentration range of 0.002 to 0.25 mM for molinate.

Demir prepared the modified CPE with carbon powder, $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, and mineral oil ($\alpha\text{-Fe}_2\text{O}_3\text{-CPE}$) for the voltammetric determination of desmedipham [101]. Additionally, the oxidation of desmedipham produced two distinct peaks at $\alpha\text{-Fe}_2\text{O}_3\text{-CPE}$, demonstrating its strong electrocatalytic properties. Under optimal experimental conditions, the voltammetric behaviour of desmedipham exhibited two linear concentration ranges: 0.15 to 1.20 mg L^{-1} and 1.20 to 4.50 mg L^{-1} . As a result, the developed square wave stripping voltammetry (SWSV) was effectively used to assess desmedipham in spiked commercial samples (strawberry juices), achieving recoveries between 96.00 and 104.00 % with an acceptable RSD.

Raja *et al.* [102] fabricated a voltammetric sensor to determine diuron based on a pencil graphite electrode modified with bismuth oxide ($\text{Bi}_2\text{O}_3/\text{PGE}$). The $\text{Bi}_2\text{O}_3/\text{PGE}$ sensor demonstrated good

selectivity, a broad linear concentration range (5.0 to 160.0 ng), an excellent sensitivity of 2.83 ng, superior stability and reproducibility. The fabricated sensor demonstrated higher sensitivity for determining diuron in tomato specimens, achieving a recovery rate of 99.9 %.

De Matos Morawski *et al.* [103] synthesized platinum nanoparticles (PtNPs) through a one-stage reaction using chitosan (CS) as a stabilizing agent. The synthesized nanocomposite was utilized in the fabrication of a modified GCE (PtNPs/CS/GCE) for the simultaneous and selective detection of isoproturon and diuron in river water samples. The PtNPs/CS/GCE sensor exhibited outstanding repeatability for the target analytes (isoproturon and diuron), along with excellent sensitivity and selectivity. Under differential pulse adsorptive stripping voltammetry (DPAdSV) optimal conditions, the LOD was calculated as 20.0 $\mu\text{g L}^{-1}$ for diuron and 7.0 $\mu\text{g L}^{-1}$ for isoproturon. The proposed strategy successfully determined both analytes (isoproturon and diuron) in river water specimens at three concentrations, yielding a recovery range of 90-110%.

Fathi *et al.* [104] proposed an electrochemical strategy to determine 2,4-dichlorophenoxyacetic acid. They modified the GCE with manganese oxide, silver nanoparticles, and alizarin yellow R polymer (Ag-MnOxNPs/PAYR/GCE). Ag-MnOx/PAYR/GCE was utilized for the detection of the 2,4-dichlorophenoxyacetic acid herbicide in water specimens. The authors propose that the combination of metal nanoparticles with conductive polymer will result in a novel nanocomposite with synergistic properties. The linear concentration range (22.0 to 11,752 μM) and LOD (7.33 μM) were evaluated for the oxidation peak at 0.8 V using the CV method. Additionally, the linear concentration range (6.0 μM to 14.308 mM) and LOD (2.0 μM) were achieved using the DPV method. This fabricated sensor was utilized for the quantification of 2,4-dichlorophenoxyacetic acid in water specimens, yielding satisfactory results.

Malode *et al.* [105] developed a voltammetric sensor based on CPE modified with cetyltrimethylammonium bromide and titanium-dioxide nanoparticles (TiO_2 /CTAB-CPE) for aminotriazole detection. The SWV procedure was used to investigate the aminotriazole herbicide in both water and soil specimens. The developed TiO_2 /CTAB-CPE sensor demonstrated a low LOD of 2.53 nM for aminotriazole. The TiO_2 /CTAB-CPE sensor exhibited the ability to detect aminotriazole in both water and soil specimens, featuring advantages such as high electrical conductivity, electrocatalytic properties, rapid response, as well as repeatability, sensitivity, and reproducibility, all supported by CV and SWV techniques.

Thimoonnee *et al.* [106] presented a voltammetric sensor for the simultaneous detection of paraquat and glyphosate. This sensor utilizes a graphite screen-printed electrode that has been modified with a dual-MIP, which is coated on a mesoporous silica-platinum core (MSN-PtNPs@d-MIP/GSPE). They first synthesized Amino-mesoporous silica nanoparticles (MSN-NH₂) via a co-condensation strategy. Platinum nanoparticles (PtNPs) were subsequently deposited onto the MSN-NH₂ surface through a chemical reduction process. Ultimately, the dual-MIP was applied to the MSN-PtNP core. Quantitative analysis was conducted using DPV, revealing an oxidation current at -0.95 V for paraquat and +0.97 V for glyphosate. The MSN-PtNPs@d-MIP/GSPE sensor demonstrates strong linear calibration curves for both analytes within the range of 0.025 to 500.0 μM , with LODs of 3.1 nM for paraquat and 4.0 nM for glyphosate. The proposed sensor was effectively utilized to simultaneously detect concentrations of paraquat and glyphosate in water.

Ouedraogo *et al.* [107] designed a voltammetric sensor based on CPE modified with Zinc oxide nanoparticles (ZnONPs-CPE) for the determination of toxic diuron herbicide. The ZnONPs-CPE sensor displayed a remarkably improved sensitivity in the diuron oxidation current response compared to the unmodified CPE. Under experimental conditions, linear responses for diuron were observed in the ranges of 1.3 to 7.7 and 8.6 to 30.0 μM . The LOD and LOQ were determined to be

0.22 μM and 0.84 μM , respectively. Finally, the ZnONPs-CPE sensor, constructed with eco-friendly materials, is both selective and sensitive, and it was effectively utilized to determine diuron in water and soil specimens, achieving recovery rates ranging from 98 % to 101.5 %.

Table 4. A summary of the analytical features of metal and metal oxide nanoparticle-based electrochemical sensors for herbicide detection

Electrochemical sensor	Analytes	Method	LOD, nM	Linear range, μM	Ref.
Ag-CPE	Paraquat	SWV	20.1	10 to 1000	[98]
$\text{SiO}_2\text{@AuNPs/GCE}$	Diuron	DPV	51.9	0.20 to 55.0 μM	[99]
ZnO-CPE	Molinate	SWV	10	2 to 250	[100]
$\alpha\text{-Fe}_2\text{O}_3\text{-CPE}$	Desmedipham	SWSV	41.00* and 50.00	0.15 to 1.20** and 1.20 to 4.50**	[101]
$\text{Bi}_2\text{O}_3\text{/PGE}$	Diuron	CV	2.83*	5.0 to 160.0***	[102]
PtNPs/CS/GCE	Isoproturon	DPAdSV	7.0*	-	[103]
	Diuron		20.0*		
Ag-MnOx/PAYR/GCE	2,4-Dichlorophen-oxyacetic acid	DPV	2,000	6.0-14,308	[104]
		CV	7,330	22.0-11,752	
$\text{TiO}_2\text{/CTAB-CPE}$	Aminotriazole	SWV	2.53	0.01 - 0.65	[105]
MSN-PtNPs@d-MIP/GSPE	Paraquat	DPV	3.1	0.025-500.0	[106]
	Glyphosate		4.0		
ZnONPs-CPE	Diuron	SWV	220	1.3 to 7.7 and 8.6 to 30.0	[107]
$\text{MnO}_2\text{-NiO-modified electrode}$	Atrazine	Ampero-metric	400	0.8 to 120.0	[108]
$\text{TiO}_2\text{-xNT/Cu}_x\text{O sensor}$	Glyphosate	DPV	0.70 pM	0.55-1000.00 pM	[109]

* $\mu\text{g L}^{-1}$; ** mg L^{-1} ; ***ng

Udayan reported a straightforward procedure for the fabrication of a MnO_2 nanotube decorated with NiO nanoparticles ($\text{MnO}_2\text{-NiO}$) through a hydrothermal method, accompanied by a calcination step [108]. The $\text{MnO}_2\text{-NiO}$ nanocomposite was subsequently investigated as an electrochemical sensing material for the determination of atrazine. They obtained a LOD of 400 nM, with a linear concentration range for atrazine spanning from 0.8 to 120.0 μM by the amperometric method. The applicability of the $\text{MnO}_2\text{-NiO-modified electrode}$ was also revealed in waste and tap water specimens, highlighting its feasibility for amperometric sensing applications.

Ohse *et al.* [109] developed a voltammetric sensor using nanostructured TiO_2 films modified with Ti^{3+} ions and copper oxides for the detection of glyphosate in water specimens. The TiO_2 nanotubular structure, fabricated through potentiostatic anodization, was further modified by the cathodic reduction of Ti^{4+} to Ti^{3+} ions and the electrodeposition of copper to create a $\text{TiO}_2\text{-xNT/Cu}_x\text{O}$ sensor. Under optimal conditions, the $\text{TiO}_2\text{-xNT/Cu}_x\text{O}$ sensor demonstrated a significant capability to detect trace levels of glyphosate by inhibiting the peak current in DPV. It achieved a low LOD of 0.34 pM and limits of quantification (LOQ) of 0.70 pM within a linear concentration range of 0.55 to 1000.00 pM. The sensor exhibited strong stability and good precision (both intermediate precision and repeatability), with no significant variations in electrochemical response, and achieved recovery rates ranging from 91.06 to 99.38 %.

Metal-organic frameworks

Metal-organic frameworks (MOFs) are highly ordered crystalline materials created by combining organic linkers and metal nodes. MOFs are an ideal option for electrochemical applications due to their remarkable physical and chemical properties, which include extremely high porosity, adjustable

structures, a large surface area, and excellent chemical and thermal stability, along with simple synthesis methods. Thanks to the unique interactions between flexible organic linkers and rigid metal centres, MOF films, characterized by high densities and accessible electrochemically active sites, have shown promise as modifiers for electrode surfaces [110–113]. This section examines the latest advancements in MOF-based electrochemical sensors designed for detecting herbicides. Table 5 summarizes the various electrochemical sensors based on MOFs for the determination of herbicides together with their sensing features, including LOD, linear detection range, and detection method.

Table 5. A summary of the analytical features of MOF-based electrochemical sensors for herbicide detection

Electrochemical sensor	Analytes	Method	LOD, pM	Linear range, pM	Ref.
MIP-MOF	Glyphosate	LSV	0.8*	1.0 to 1.0×10^6 *	[114]
Cu-BTC/ITO	Glyphosate	DPV	0.14	1.0 to 1.0×10^7	[115]
cMOF-modified GCE	Paraquat	DPV	4.1×10^5	0.2×10^6 to 5.0×10^6	[116]
Cu-TCPP/AuNPs/CP	Glyphosate	DPV	30	0.2×10^6 to 120.0×10^6	[117]
Ti ₃ C ₂ T _x /Cu-BTC/GCE	Glyphosate	DPV	0.02	0.1 to 1.0×10^6	[118]
Zr-CuBTC MOFs/GCE	Glyphosate	DPV	0.9	-	[119]
Cu-PZDA#CNF/GCE	Glyphosate	DPV	0.00312	0.01×10^6 to 200×10^6	[120]
ZIF-67/MCPE	Atrazine	DPV	3.7×10^6	4.0×10^6 to 44.0×10^6	[121]

*pg L⁻¹

Do *et al.* [114] constructed the molecularly imprinted MOF films on gold electrode surfaces *via* electropolymerisation of p-aminothiophenol-AuNPs in the presence of the glyphosate (template molecule). The performance of the MIP-MOF electrochemical sensor for determining glyphosate was evaluated using LSV with a hexacyanoferrate/hexacyanoferrite solution (as the redox probe). The electron transfer rate increased with the glyphosate concentration, attributed to a p-doping effect. The MIP-MOF electrochemical sensor, featuring specific recognition cavities, was capable of binding glyphosate within a concentration range of 1 pg L⁻¹ to 1 µg L⁻¹, with a LOD of 0.8 pg L⁻¹. The created sensor demonstrated high selectivity and the capability to detect glyphosate in tap water specimens.

Cao *et al.* [115] synthesized the porous Cu MOF with 1,3,5-benzenetricarboxylic acid as an organic ligand (Cu-BTC), and applied it as a modifier to prepare a DPV sensor (Cu-BTC/ITO) for glyphosate detection. Utilizing Cu-BTC MOF as a detection matrix enhances the electrode active sites due to the material's high surface area, thereby further improving the sensing performance. Furthermore, under optimal conditions, the LOD of the Cu-BTC/ITO sensor for glyphosate is 0.14 pM. The relative change in current response is linearly proportional to the logarithm of glyphosate concentration over the ranges of 1.0 pM to 1.0 nM and 1.0 nM to 10.0 mM. Additionally, the created sensor can also be used for detecting glyphosate in soybean specimens.

Zhao *et al.* [116] constructed the 2D conductive MOF (cMOF) based on copper ions and 2,3,7,8,12,13-hexahydroxyl truxene through an energy-efficient interfacial reaction. They served the cMOF-modified GCE as a voltammetric sensor for detecting paraquat. The cMOF-modified GCE demonstrated a low LOD (41 nM), an acceptable linear concentration range (0.2 to 5.0 µM) for the detection of paraquat.

Jiang *et al.* [117] developed a sensing platform based on copper porphyrin MOF and AuNPs-modified carbon paper (Cu-TCPP/AuNPs/CP) for the selective detection of glyphosate via DPV. The Cu-TCPP exhibits an extensive surface area and exceptional catalytic activity, which enhances the availability of copper sites for binding with glyphosate, thereby enabling selective detection and improving the sensitivity of the voltammetric sensor. Under optimized experimental conditions, the Cu-TCPP/AuNPs/CP sensor demonstrated a linear detection range of 0.2 to 120.0 µM, with a LOD of

0.03 μM . The fabricated sensor was used to detect glyphosate in water, wheat, soybeans, and carrots, achieving recoveries ranging from 97.5 % to 110.7 %.

Wang *et al.* [118] synthesized 2D $\text{Ti}_3\text{C}_2\text{T}_x$ material through a chemical etching process, followed by the *in situ* growth of Cu-BTC using $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets as a template, which resulted in the fabrication of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{Cu-BTC}$ nanocomposite. Finally, the $\text{Ti}_3\text{C}_2\text{T}_x/\text{Cu-BTC}$ nanocomposite was modified onto a GCE ($\text{Ti}_3\text{C}_2\text{T}_x/\text{Cu-BTC}/\text{GCE}$) using the adsorption method. The $\text{Ti}_3\text{C}_2\text{T}_x/\text{Cu-BTC}/\text{GCE}$ sensor was applied for the electrochemical sensing of glyphosate. The voltammetric sensor utilizing $\text{Ti}_3\text{C}_2\text{T}_x/\text{Cu-BTC}$ leverages the benefits of distinctive electrocatalytic activity and high electrical conductivity, resulting in excellent sensing performance for glyphosate. This includes a low LOD of 0.026 pM and a broad linear response range from 0.1 pM to 1.0 μM . In addition, the $\text{Ti}_3\text{C}_2\text{T}_x/\text{Cu-BTC}/\text{GCE}$ sensor demonstrates outstanding selectivity, good stability, and reproducibility.

Nguyen *et al.* [119] synthesized the Zr-Cu MOF combined with 1,3,5-benzenetricarboxylic acid (Zr-CuBTC MOFs) by a hydrothermal strategy. Then, they employed the Zr-CuBTC MOFs as a modifier on the GCE (Zr-CuBTC MOFs/GCE) for detecting glyphosate. The results indicated that the Zr-CuBTC MOF is the most promising material for the detection of glyphosate. Under optimized conditions, the Zr-CuBTC MOFs/GCE sensor can determine glyphosate in a water environment, achieving a LOD as low as 0.9 pM. The fabricated sensor was utilized to detect glyphosate in surface water specimens. The results demonstrated acceptable recoveries, ranging from 94.6 - 107.1 %.

Dey *et al.* [120] developed a voltammetric sensor utilizing a copper-organic framework/carbon matrix, which was prepared using 3,5-pyrazoledicarboxylic acid (PZDA, as the organic ligand) through a solvothermal procedure in the presence of a carbon nanofiber matrix (Cu-PZDA#CNF). The Cu-PZDA#CNF was employed as a modifier on GCE (Cu-PZDA#CNF/GCE) for the voltammetric detection of glyphosate. The Cu-PZDA#CNF/GCE sensor has fundamental characteristics including numerous reactive sites, a large surface area, a broad detection range (0.01 to 200.0 μM), a low LOD (3.12 nM), and an excellent sensitivity (173.88 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$) for glyphosate detection. Additionally, to evaluate its real-time applicability and practicality, the Cu-PZDA#CNF/GCE sensor was employed to detect glyphosate in vegetable specimens.

Singh *et al.* [121] fabricated cobalt(II) imidazolate framework (ZIF-67) and applied it as a catalyst for the voltammetric determination of the atrazine herbicide. ZIF-67 was subsequently integrated onto the CPE surface to create a ZIF-67 modified CPE (ZIF-67/MCPE). DPV and CV techniques were employed to analyse atrazine at the ZIF-67/MCPE sensor. The sensor exhibited outstanding sensitivity and proved effective in detecting atrazine. The ZIF-67/MCPE sensor showed a low LOD of 3.7 μM within a linear detection range from 4.0 to 44.0 μM . Furthermore, the practical application of the sensor was assessed by testing it on fresh liquid milk and sewage water. The sensor exhibited an outstanding capability to detect atrazine, achieving a recovery rate between 96 and 99 %.

Transition metal chalcogenides

The advancement of transition-metal dichalcogenides (TMDs) has been a prominent area of research in recent decades. TMDs are compounds of the MX_2 type that feature layered structures, characterized by strong covalent bonds within the layers and weak interactions between the layers. Typically, TMDs are represented as MX_2 , where M denotes the central transition metal atom (from groups 4-7) and X signifies the chalcogen atom (such as S, Te or Se). Depending on their chemical composition and structural arrangement, these materials display a wide range of properties, including semiconducting, semimetallic, metallic, and even superconducting characteristics. TMDs possess remarkable properties, including metallic and semiconducting electrical characteristics,

mechanical strength, a large surface area, and the ability to adapt to intercalate morphologies. The material properties and characteristics of TMDs have attracted research interest across diverse fields, including catalysis, electronics, and energy storage. Leveraging their unique electronic and crystal structures, TMDs have demonstrated significant potential in the field of sensors [122-125].

Table 6 summarizes the various electrochemical sensors based on TMDs for the determination of herbicides, together with their sensing features, including LOD, linear detection range, and detection method.

Table 6. A summary of the analytical features of TMD-based electrochemical sensors for herbicide detection

Electrochemical sensor	Analytes	Method	LOD, nM	Linear range, μM	Ref.
$\text{FeS}_2/\text{Ag NL}/\text{SPCE}$	Acifluorfen	DPV	2.5	0.05 to 1126.45	[126]
GCE/ $\text{MoS}_2/\text{CB}[8]\text{-DNPs}$	Methyl viologen	DPV	0.02	0.73 to 8.0	[127]
$\text{SrS}/\text{Bi}_2\text{S}_3/\text{SPC}$ electrode	Maleic hydrazide	DPV	1.8	0.01 to 814.0	[128]
$\text{Sr}/\text{La}_2\text{S}_3/\text{RDE}$	Mesotrione	Amperometric	2.4	0.01 to 307.01	[129]

Chen *et al.* [126] fabricated a nanocomposite based on silver nano-leaves decorated iron pyrite flowers ($\text{FeS}_2/\text{Ag NL}$) via the sonochemical method. They developed a $\text{FeS}_2/\text{Ag NL}$ nanocomposite-modified SPCE for detecting acifluorfen. The excellent sensitivity of the $\text{FeS}_2/\text{Ag NL}/\text{SPCE}$ sensor is attributed to the electrical conductivity arising from the synergistic effect of the Ag NL and FeS_2 flower. Under optimized conditions for DPV, a linear relationship between concentration and current was established for acifluorfen in the range of 0.05 to 1126.45 μM . The LOD was found to be 0.0025 μM .

Blanco *et al.* [127] designed a voltammetric sensor by using MoS_2 and diamond nanoparticles (DNPs) stabilized with cucurbit[8]uril ($\text{MoS}_2/\text{CB}[8]\text{-DNPs}$). GCEs are modified by drop-casting of suspensions of MoS_2 , followed by a CB [8]-DNPs ($\text{GCE}/\text{MoS}_2/\text{CB}[8]\text{-DNPs}$) and used to determine methyl viologen. The $\text{GCE}/\text{MoS}_2/\text{CB}[8]\text{-DNPs}$ sensor responds linearly to methyl viologen from 0.73 to 8.0 μM with a LOD of 0.22 μM . Furthermore, the sensor's ability to detect methyl viologen in real river specimens has been demonstrated, achieving good recoveries for fortified specimens.

Akilarasan *et al.* [128] fabricated a nanocomposite based on bimetallic strontium sulphide and bismuth sulfide ($\text{SrS}/\text{Bi}_2\text{S}_3$). The synthesized $\text{SrS}/\text{Bi}_2\text{S}_3$ nanocomposites were applied to detect maleic hydrazide herbicide in water and food samples. Additionally, the analytical performance of the $\text{SrS}/\text{Bi}_2\text{S}_3$ modified screen-printed carbon electrode ($\text{SrS}/\text{Bi}_2\text{S}_3/\text{SPC}$ electrode) yielded excellent results, demonstrating a wide concentration range of 0.01 to 104.0 μM and 104.0 to 814.0 μM , along with a LOD of 1.8 nM for maleic hydrazide detection. In conclusion, the real specimen's analysis of the $\text{SrS}/\text{Bi}_2\text{S}_3/\text{SPC}$ electrode was conducted on river water and potato specimens, yielding recoveries of 97.2 to 98.2 % and 97 to 98.9 %, respectively.

Rajaji *et al.* [129] synthesized the strontium-doped La_2S_3 ($\text{Sr}/\text{La}_2\text{S}_3$) by facile sonochemical reaction. The $\text{Sr}/\text{La}_2\text{S}_3$ modifier coated rotating disk electrode ($\text{Sr}/\text{La}_2\text{S}_3/\text{RDE}$) demonstrated an improved electrochemical sensing performance for the determination of the mesotrione herbicide. The electrochemical performance of the $\text{Sr}/\text{La}_2\text{S}_3/\text{RDE}$ is superior to that of La_2S_3 and bare RDE for the determination of mesotrione. The $\text{Sr}/\text{La}_2\text{S}_3/\text{RDE}$ demonstrated excellent sensitivity for mesotrione detection, exhibiting a concentration range of 0.01 to 307.01 μM and a LOD of 2.4 nM.

Conclusions and perspectives

Herbicides are widely used in agriculture to enhance crop yields by managing or removing weeds. The increased use of herbicides has led to higher levels of exposure, causing acute poisoning in both human and environmental health. To significantly mitigate the harmful effects, it is essential to carefully investigate detection and mitigation strategies for these substances. Electrochemical sensors have become a prominent solution due to their high sensitivity, rapid testing capabilities, cost-effectiveness, and environmental friendliness. With the progress of nanotechnology, a variety of nanostructured materials have been incorporated into electrochemical sensors, thanks to their inherent advantages related to electrochemical properties, including effective catalytic activity, a large surface area, high electrical conductivity, and outstanding biocompatibility. The creation of advanced electrochemical sensors based on nanomaterials for detecting herbicide compounds has attracted significant interest because of their benefits, including high selectivity and sensitivity, real-time monitoring capabilities, and user-friendliness.

This review initially explores the fundamental principles of electrochemical sensors and the primary sensing mechanisms involved. The electroanalytical efficiency of sensors is heavily dependent on the choice of nanomaterials used in the quantification process. This is followed by a discussion on the importance of integrating nanomaterials into electrochemical sensors. Finally, this review summarizes the recent trends in the application of various widely used nanomaterials, such as carbon-based nanomaterials, noble metal and metal oxide nanoparticles, MOFs, and TMDs, to enhance the analytical efficiency of electrochemical sensors for the quantitative detection of herbicides. A summary of various nanomaterial-based electrochemical sensing platforms for herbicide detection discussed in this review is presented in Tables 1-6.

Despite the significant advancements made in the electrochemical detection of herbicides, the application of electrochemical sensors in real-world scenarios is still in its early stages. The quantities of targeted herbicides in water specimens are well understood in laboratory settings, but this knowledge is lacking in field analyses. As a result, the findings obtained in the laboratory are challenging to validate against results from real samples due to varying environmental conditions. There is still a considerable distance to cover in advancing the practical detection of herbicides.

Ensuring the reproducibility and stability of electrochemical herbicide sensors in complex real matrices is a major challenge. Furthermore, utilizing composite nanomaterials rather than single nanomaterials is highly effective in attaining long-term stability.

Surface fouling is another limitation of current herbicide sensors, leading to reduced stability, sensitivity, and reproducibility. Consequently, future trends will largely rely on electrode fabrication techniques that minimize the need for frequent cleaning and calibration due to surface fouling.

While the integration of nanomaterials into electrochemical herbicide sensors has demonstrated significant advancements, there are still some shortcomings that must be addressed before these techniques can be applied in real-world scenarios. Most herbicide sensors utilizing nanomaterials have faced limitations due to their time-consuming synthesis processes, high costs associated with mass production, and the toxicity of various classes of nanomaterials to the environment and humans. Therefore, it remains a challenge to introduce nanomaterials that offer good analytical performance while replacing traditional synthesis methods with greener, scalable, more affordable, and less time-consuming procedures.

Additionally, future research can focus on the development of electrochemical sensors utilizing advanced technologies for the multi-residue detection of herbicides in different environments.

Ultimately, further research should focus on developing more robust and reliable devices to expedite herbicide analysis in both laboratory and field settings.

Conflict of interest: None

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