

<https://doi.org/10.18321/ectj1683>

Recent Progress in Electrochemical Sensors for Organophosphorus Pesticide Monitoring in Food and Environmental Samples: A Review

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Article info

Received:
23 September 2025

Received in revised form:
28 November 2025

Accepted:
15 January 2026

Keywords:

Organophosphorus pesticide
Electrochemical methods
Electrochemical sensors
Limit of detection
Electrode materials

Abstract

Organophosphorus pesticides (OPP), such as malathion (MTN), methyl parathion (MP), and chlorpyrifos (CHL), are widely used in agriculture to control pests and increase crop yields. However, their persistent residues in vegetables, fruits, and drinking water pose significant threats to human health, including neurotoxic and carcinogenic effects. Therefore, the development of efficient detection methods with high sensitivity, selectivity, and rapid response is of great importance. Among various analytical approaches, electrochemical methods have attracted considerable attention due to their simplicity, low cost, potential for miniaturization, and suitability for field applications. This review presents an overview of recent advances in electrochemical sensors for the detection of common OPP. Various approaches to the surface modification of working electrodes are described, including the use of nanomaterials, polymers, and metal-organic frameworks. The mechanisms of electrochemical oxidation and reduction of pesticides, as well as key analytical parameters of sensors – such as detection limit, linear range, sensitivity, and selectivity – are analyzed. Current problems, including interference from coexisting compounds and long-term sensor stability, are also discussed. In addition, future research directions are outlined, such as integration with portable devices and applications in real-world samples. This review contributes to a deeper understanding of current trends and challenges in the development of advanced electrochemical sensors for OPP monitoring.

1. Introduction

Modern standards of living largely depend on the production and use of thousands of chemicals, many of which are synthetic and toxic. These substances are released into the air, soil, and water through various pathways, contributing to environmental pollution. Environmental contaminants originate from both anthropogenic and natural sources and may pose significant risks to human health. Approximately three million cases of pesticide poisoning are reported annually, with organophosphate compounds being among the most widely used pesticides [1]. Organophosphate pesticides (OPP) are a type of organic compounds containing phospho-

rus. Approximately 2 million tons of OPP are used worldwide each year, accounting for about 40% of total pesticide use globally [2]. The general chemical structure of OPP is shown in Fig. 1 [4], where R_1 and R_2 represent alkoxy groups. Other possible substituents include phenyl, ethyl, amino, substituted amino, and alkylthio groups. X denotes a good leaving group sensitive to hydrolysis, which is displaced during the phosphorylation of acetylcholinesterase by OPP [3, 4].

Due to insufficient data on the required concentration, farmers often use excessive concentrations of OPP on their fields [5]. As a result, it is extremely important to regularly determine and monitor the level of OPP toxicity in agricultural crops in order to facilitate the development of policies that define acceptable pesticide concentration limits and thereby promote safe farming practices. A variety

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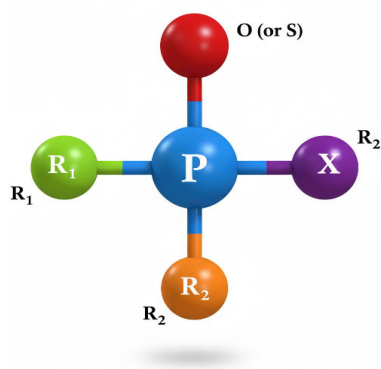


Fig. 1. Schematic illustration of the general structure of organophosphorus compounds. Adapted from [4]. Open access via PubMed Central.

of conventional chromatographic techniques are applied for the analysis of OPPs. Among them are gas chromatography (GC) and its coupled form gas chromatography – mass spectrometry (GC–MS), as well as liquid chromatography and liquid chromatography – mass spectrometry (LC–MS) [6, 7]. In addition, high-performance liquid chromatography (HPLC) in combination with UV detection is also frequently employed [8].

Although chromatographic methods are well established and highly reliable, they are often associated with limitations such as expensive instrumentation and labor-intensive procedures. Moreover, their time-consuming separation processes restrict their applicability for real-time monitoring. To overcome these limitations, alternative approaches for OPP detection have been explored, including fluorescent and colorimetric analyses [9], spectroscopic techniques such as nuclear magnetic resonance (NMR), X-ray, and Fourier transform infrared (FTIR) spectroscopy [10], as well as electrochemical methods [11, 12]. Among these strategies, optical methods such as colorimetric and spectroscopic methods based on the interaction of light and the matrix often suffer from external interference from accompanying compounds and exhibit high background noise levels under unsuitable experimental conditions [9]. Such interference can lead to false positive or negative results, thereby reducing analytical reliability. In comparison, electrochemical methods offer higher accuracy and reproducibility using relatively simple devices such as potentiostats, making them suitable for on-site OPP monitoring [13]. Furthermore, electrochemical sensors have attracted significant attention due to their compatibility with miniaturization and their ability to achieve very low detection limits, even at the nanomolar level [14].

Analytical sensing methods offer notable advantages such as high throughput, rapid response, and ease of use for quantitative determination [15]. In recent years, various sensory analysis strategies have been proposed for the determination of malathion, including colorimetric [16], electroanalytical [17], luminescent [18], and surface-enhanced Raman scattering (SERS) methods [19]. Among these, colorimetric and electrochemical approaches have attracted particular attention. Colorimetric methods enable rapid analyte detection based on visible color changes. Typically, the induced color change can be directly recognized with the naked eye, and quantitative signals can be easily obtained using a spectrophotometer or imaging device [20]. In contrast, electrochemical reactions occur as a result of electron transfer processes at the working electrode, which are less sensitive to external factors such as light, temperature, or humidity. Figure 2 illustrates the principle of electrochemical detection. To combine the advantages of both methods, it is necessary to develop a sensor that provides dual output of colorimetric and electrochemical signals. Such bimodal systems offer improved reliability compared to single-signal methods, as the two outputs can mutually validate the results.

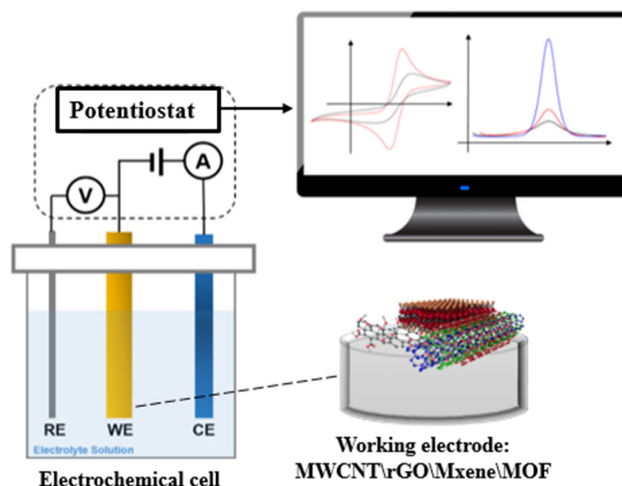


Fig. 2. Scheme of the electrochemical method of analysis.

Electrochemical analysis methods use relatively low-cost and simple equipment and are versatile and powerful approaches that provide accuracy, high sensitivity, and selectivity. Electrochemical sensing is based on the measurement of electrical quantities such as potential, current, or charge that result from the interaction between an electrode and the substance being analyzed. Typically, an

electrochemical cell consists of a counter electrode (CE), a working electrode (WE), and a reference electrode (RE). In voltametric methods, a time-dependent variable voltage (for example, Ag/AgCl) is used on the reference electrode (RE), and the current response between WE and CE is measured, where a redox reaction occurs [21].

2. Methods

An extensive literature was conducted using leading scientific databases, including Scopus, Web of Science, ScienceDirect, Wiley Online Library, and SpringerLink, covering studies published between 2012 and 2024. The review focused on strategies for modifying working electrode surfaces, such as the incorporation of nanomaterials, functional polymers, and metal–organic frameworks. It also addresses the mechanisms of electrochemical oxidation and reduction of pesticides, along with key analytical performance metrics of the developed sensors, including detection limit, linear dynamic range, sensitivity, and selectivity. To ensure a strong thematic alignment, the literature search was guided by carefully selected keywords, including “electrochemical method”, “electrochemical sensor”, “modification materials”, “organophosphorus pesticides”, “pesticide monitoring sensors”, and “enzymatic and non-enzymatic sensors”.

3. Commonly used types of electrochemical sensors

Electrochemical sensors can be broadly classified into enzymatic and non-enzymatic types [22]. Enzymatic sensors utilize biological enzymes to catalyze reactions between the target analyte and the electrode surface, enabling highly selective detection [23]. In contrast, non-enzymatic sensors depend on the direct electrochemical interaction of the analyte with noble metal-based electrodes, offering simpler design but often lower specificity. A typical exam-

ple is the development of wearable sensors based on enzymes, which use organophosphorus hydrolase (OPH) to detect OPPs in food samples [24]. In addition, numerous acetylcholinesterase (AChE)-based sensors have been investigated, exploiting the strong interaction between OPP and the active sites of the enzyme. One development used a glassy carbon electrode (GCE) modified with AChE and a conductive polymer to detect malathion, which showed a linear response range of 9.99–99.01 nM with a detection limit of 4.08 nM [25]. In another study, an enzymatic electrochemical sensor based on reduced graphene oxide (rGO) was developed for the detection of chlorpyrifos, which achieved a limit of detection of 65.7 nM in the range of 0.5–470 ng·mL⁻¹ and showed a wide linear range [26]. Moreover, an rGO-based electrochemical enzyme sensor for diazinon demonstrated an ultra-low detection limit of 0.99 nM [27]. As a result, electrochemical enzyme sensors provide high selectivity, high sensitivity, very low detection limits, and fast response times for OPP monitoring [28].

Enzymatic sensors are highly selective but have a number of limitations. When subjected to increased temperatures, they are not thermally stable and break down in alkaline as well as acidic environments [22, 29, 30]. In addition, they are often unable to detect less dangerous organophosphorus compounds (OPCs), as these substances block AChE only after metabolic activation. This behavior requires the conversion of the P = S bond to P = O in OPC structures to increase their toxicity and ensure detectability [31]. Other disadvantages of enzyme biosensors include high cost, low reproducibility, and gradual loss of enzyme activity over time [32]. Heavy metals contained in the sample can also influence sensor selectivity and may result in erroneous positive detections [32, 33]. A detailed comparison of enzymatic and non-enzymatic sensors with an assessment of key characteristics is presented in Table 1.

Table 1. Overview of key differences between enzymatic and non-enzymatic sensors [33].

Parameter	Enzymatic Sensor	Non-enzymatic Sensor
Special feature	High selectivity to OPP	Selectivity varies from moderate to low
Stability	Unstable at extreme pH and temperature	Stable over broad pH and temperature
Cost	Expensive due to enzyme use	Low-cost, prepared with common materials
Obstacles	Strongly affected by heavy metals	Less influenced by external interference
Requirements for samples	Requires pure and clean samples	Tolerant to sample impurities

4. Materials for electrode modification and their role in the design of electrochemical sensors

The selection of electrode materials remains one of the most important tasks in the manufacture of electrochemical sensors. Although many electrode materials have been noted for their synergistic effect and ability to enhance electrical reactions at relatively low potentials, current methods for depositing nanocomposites and nanoparticles onto electrode surfaces remain inconsistent, uncontrollable, and difficult to standardize. This heterogeneity limits the reproducibility of sensor characteristics. Nevertheless, the use of matrix-assisted rapid nanoparticle growth methods is a promising approach that allows for better control of the integration of different electrode materials and contributes to the development of stable and reproducible electrochemical sensors. In further research, a combination of these materials can be used for electrodes, paying particular attention to those materials that are characterized by high electrical conductivity and sensitivity. Although most electrochemical detection is based on redox reactions occurring on the electrode surface, in certain cases the analyte does not participate in redox reactions. In such cases, sensitivity can be determined by suppressing the current signal resulting from the adsorption of the analyte on the electrode surface. To ensure selective adsorption of specific analytes, an electrode design with molecularly imprinted polymers (MIPs) can be used (Fig. 3).

The described strategy enables the deposition of a thin film on the electrode, employing the analyte

itself as the matrix. Nevertheless, adsorption-type sensors require electrode preconditioning before every experiment, which remains a limitation. Hence, upcoming research should prioritize the development of easier methods to minimize this drawback and improve sensor applicability. A useful alternative is the development of electrochemical sensors for OPPs or similar toxins, in which antidotes are utilized. These antidotes are specially engineered chemical agents that interact with harmful compounds and counteract their toxicity. Nanomaterials with strong adsorption capacity, high catalytic efficiency, large specific surface area, increased number of active centers due to incomplete coordination of surface atoms, high surface activity, and labeling of specific biomolecules are widely used to enhance biosensor signals [34].

Currently, research data concerning antidote-based electrochemical sensors remain scarce, which underlines the importance of conducting further investigations in this direction. The use of highly conductive electrocatalytic materials possessing a large active surface can improve the generated current signal, such as multi-walled carbon nanotubes (MWCNTs), graphene oxide (GO), rGO, graphene (GR), aptamer and MXene (Fig. 3). The application of nanomatrices makes it possible to detect particular pesticides with high selectivity, despite the coexistence of other organophosphorus compounds in the testing environment. Similarly, the use of carbon nanomaterials in sensor components allows electrodes to be used as signal amplifiers for the quantitative detection of analyzed substances at low concentrations [35, 36].

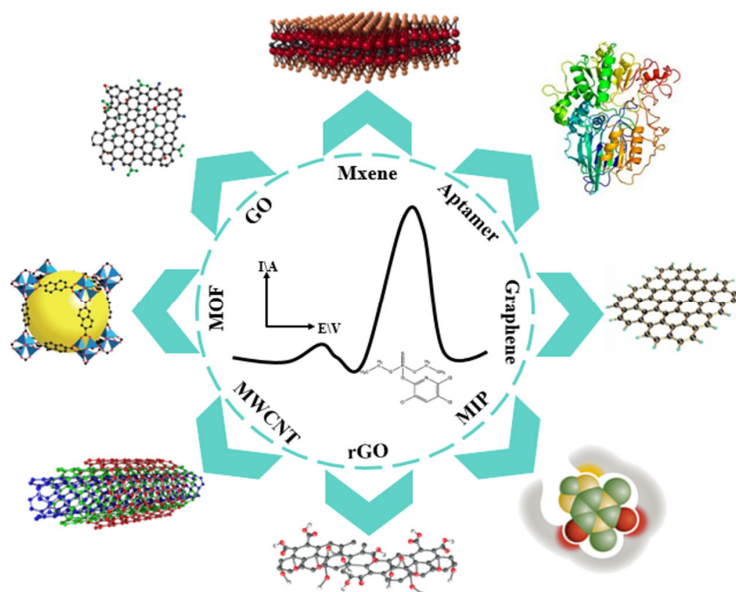


Fig. 3. Advanced electrode materials for next-generation electrochemical sensors.

These studies highlight significant advances in the design and surface engineering of carbon-based materials and metal oxide nanostructures with tunable physicochemical properties and enhanced functional performance. Hydrophobic-modified nanodiamond powders exhibit well-defined structural features, high specific surface area, and excellent stability, which make them attractive for various advanced applications [37]. Zinc oxysulfide nanomaterials synthesized via hydrothermal routes show improved photocatalytic activity, highlighting the potential of mixed-anion metal compounds for energy- and environment-related technologies [38]. Superhydrophobic rGO systems [39] are characterized by high electrical conductivity, chemical robustness, and tailorable surface chemistry, while mechanically robust ZnO-based superhydrophobic materials demonstrate strong durability and long-term stability under practical conditions [40]. Collectively, these studies suggest that combining conductive carbon supports with metal oxide nanostructures can yield hybrid materials with increased surface area, enhanced charge-transfer capabilities, and favorable interfacial properties.

In other studies, Pt@r-GO@MWCNT nanocomposites were obtained using a simple one-time method, which were subsequently used to study the electrochemical activity of chlorogenic acid on various electrodes. Due to the large specific surface area, excellent electrical conductivity, and catalytic properties of Pt@r-GO@MWCNTs, Pt@r-GO@MWCNTs/GCE showed a strong electrochemical response to chlorogenic acid compared to bare GCE [41].

In another study, conductive polymers in the form of nanofibers were integrated with nanomaterials, using polyaniline (PANI) nanofibers combined with single-walled carbon nanotubes (SWCNTs) for the detection of malathion. PANI is an inexpensive, mechanically strong, and easily adaptable conductive polymer, making it a promising material for use in electrochemical sensors [42–44]. Its redox properties further expand its applicability in this field [45]. To improve performance, PANI was modified with dodecylbenzenesulfonic acid (DBSA) and converted into nanofibers via chemical oxidative polymerization, which substantially enhanced its electrochemical activity and detection characteristics [46].

Despite significant advances in electrochemical sensor design, nanostructured sensors remain limited by a critical drawback: their operational lifetime is reduced due to fouling of the active surface caused by chemical interactions with extraneous compounds present in reaction media or wastewater. Various

methods of protection against contamination have been proposed to solve this problem, including in-situ immobilization of nanoparticles [47]. Future investigations focused on reducing surface contamination will contribute to overcoming the limitations of nanostructured electrochemical sensors.

The main challenge in developing electrochemical non-enzymatic sensors remains the selection of an optimal electrode material [48]. Metal alloys containing two or more metals have attracted considerable interest, offering new opportunities for highly efficient electrocatalysis [49–51]. However, metal oxides are particularly promising due to their enhanced electronic properties, exceptional thermal stability (up to 1000 °C), resistance to oxidation, and tolerance to electromagnetic radiation, surpassing both pure metals and their alloys in these aspects [52]. Consequently, recent studies have focused on oxides of iron (Fe), copper (Cu), nickel (Ni), bismuth (Bi), tungsten (W), and titanium (Ti) for electrode modification [53]. Significant advancements in metal oxide research are closely tied to their integration with polymeric and carbon-based nanomaterials, such as carbon nanotubes (CNTs) and graphene. These hybrid systems enable targeted tuning of the electronic properties of the composites [54]. Although several reviews address electrochemical sensors for the detection of OPPs, the rapidly evolving field of non-enzymatic OPP analysis remains insufficiently systematized. In this review, we provide a comprehensive analysis of materials for electrode fabrication, including metals and their nanocomposites, metal oxides with varying degrees of oxidation, and carbon-based hybrid nanostructures. Special attention is given to the correlation between material structure and sensitivity toward various OPPs. The aim of the study is to conduct a comparative assessment of the analytical characteristics of modified electrodes (using both noble and transition metals) in the detection of three widely used OPPs: chlorpyrifos (CPF), malathion (MTN), and methyl parathion (MP).

5. Detection methods for widely utilized organophosphorus pesticides

5.1 Malathion detection

Strategic modifications of the electrode surface can substantially enhance the sensitivity, selectivity, stability, and cost-effectiveness of electrochemical sensors for malathion detection. A key requirement for these modifications is the use of electrically conductive materials that are compatible with electrochemical analysis.

In electrochemical analysis, nanomaterials such as nanofibers, carbon derivatives, and metallic nanoparticles are widely employed, each offering distinct advantages [55, 56]. Conductive polymers are equally important because they enhance sensor response and sensitivity. Studies have shown that such polymers can exhibit electrocatalytic effects, maintain stable mechanical and chemical structures, display functional flexibility, and detect minor variations effectively. Reference [57] describes a sensor constructed from a polyamide 6/polypyrrole polymer matrix combined with rGO. The polyamide 6 base was doped with polypyrrole and processed into nanofibers by electrospinning, which increased the surface area and porosity of the resulting 3D nanostructure. The addition of rGO further improved sensitivity. rGO, a low-cost, carbon-based nanomaterial, is valued for its conductivity, catalytic properties, and adsorption efficiency. The study also compared chemical and electrochemical reduction methods for rGO, concluding that chemically rGO provided better sensor performance. The sensor achieved an LOD of 0.8 ng/mL with a recovery rate between 99% and 105% in water samples.

Table 2 shows the results of recent research on the detection of malathion using electrochemical methods with electrodes of various compositions. Within these methods, nanomaterials together with conductive polymers are considered essential for advancing sensor technologies. Their large surface-to-volume ratio and numerous active centers make nanomaterials particularly valuable for customizing electrode interfaces.

A recent review highlighted several electrochemical sensors built on SiC/CuO-NPs platforms. Particular attention was paid to the highly selective detection of MTN at concentrations down to 0.01 nM using a SiC/CuO-NPs nanocomposite, where the detection principle was based on the suppression of the redox process (Fig. 4). Under optimized experimental conditions, the inhibition rate showed a strong linear correlation with the concentration of MTN in the range of 0.03–3.0 nM, reaching a detection limit of 0.01 nM (S/N = 3). In addition, the sensor demonstrated excellent selectivity, reproducibility, and stability and was effectively applied to real water samples, yielding a recovery rate of 99.33% to 106.6%, confirming its reliability [65].

Table 2. Comparative overview of immobilization matrices for MTN electrochemical sensing.

Methods	Improving components	LOD	Samples	Ref.
CV EIS SWV	Ionic liquid Chitosan Gold nanoparticles	0.68 nM	Apple Tomato	[55]
CV EIS	Polyamide 6 Polypyrrole Reduced graphene oxide	2.4 nM	Tap water River water	[56]
CV EIS DPV	Acrylamide-based molecularly imprinted polymer (MIP)	1.8×10^{-4} nM	Olive oils	[57]
LSV	H ₂ SO ₄ doped NH ₂ – Al MOF	5.05×10^3 nM	–	[58]
CV EIS	Peptide nanotube Molecularly imprinted polydopamine	4.2×10^{-3} nM	Lettuce Tomato	[59]
CV	Carbon black Pillar (5) arene	15 nM	Grapes Wines Peanuts	[60]
CV	Peptide nanotubes, Horseradish peroxidase Nafion	0.25 nM	Vapour gas	[61]
CV	Magnetic iron nanoparticles	2.9×10^3 nM	Tomato Pond water	[62]
CV DPV	Covalent organic framework material (COF) Multiwalled CNTs	5.0×10^2 nM	Water Spinach	[63]
DPV CV EIS	PEDOT (conducting polymer) Ionic liquid Reduced form of graphene oxide	0.35 nM	Apple juice	[64]

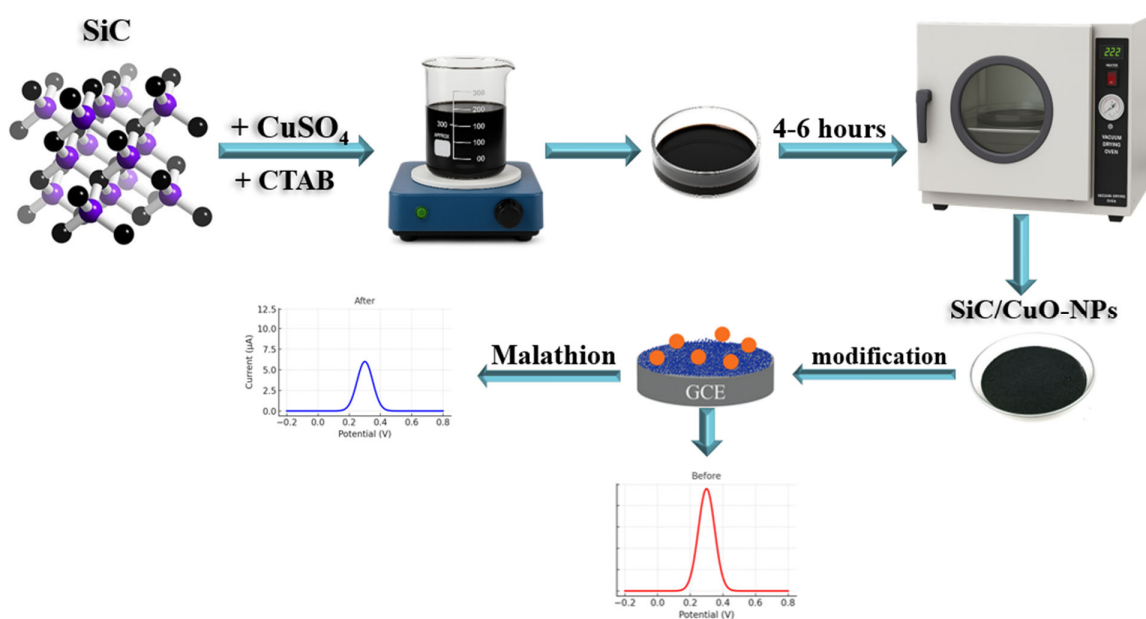


Fig. 4. Design and modification of a glassy carbon electrode with SiC/CuO-NPs for malathion sensing. Adapted from Ref. [65] with permission from Wiley-VCH, Copyright 2021.

5.2 Application of enzymes in malathion sensing

Enzyme-based biosensors are among the most widely studied types of biosensors, with electrochemical transducers frequently employed in their design. These systems are highly effective for monitoring catalytic reaction rates associated with biological processes [58]. Enzymatic measurements can be performed through various modes: by determining the rate at which an analyte is metabolized by the enzyme, by assessing the degree of enzyme activation or inhibition caused by the analyte, or by evaluating changes in enzyme activity resulting from analyte interaction.

Although enzymes exhibit specificity toward organophosphorus pesticides (OPP), they do not directly and selectively bind to malathion, requiring the addition of an auxiliary reagent to facilitate detection [61]. The need for this complementary substrate means that enzyme-based sensors cannot be considered truly label-free. Moreover, the inherent sensitivity of biological macromolecules and the high cost of enzyme production restrict their use. Extreme pH or elevated temperatures can easily affect the active sites of enzymes, leading to denaturation and irreversible loss of activity [66].

In the context of OPP detection, the primary mechanism relies on the inhibition of specific enzymes by the OP itself, acting as the target analyte. The reduction of enzymatic functionality is observed as a weakened catalytic interaction with the corresponding substrate, since the active center of the

enzyme is occupied by the organophosphate. This inhibition disrupts the normal hydrolysis of a specific substrate, leading to the formation of an electroactive product. The oxidation current generated by this product can then be measured [60]. By comparing current values before and after enzyme inhibition, researchers can determine the presence and level of the OPP.

Article [61] reports a reversible reaction-based biosensing strategy using butyrylcholinesterase (BChE) for the detection of organophosphorus compounds (OPCs) on screen-printed electrodes (SPEs) with reduced working surface areas compared to earlier single-use platforms. Building on previous studies involving acetylcholinesterase (AChE) encapsulated in peptide nanotubes (PNTs) and signal amplification via horseradish peroxidase (HRP), this work introduces design modifications to enhance sensitivity, stability, and reusability [61]. In the proposed architecture, BChE was immobilized within a composite matrix consisting of PNTs, HRP, and Nafion, which collectively increased the effective reactive surface area, enhanced electron-transfer efficiency, and preserved enzyme activity. Biosensor performance was evaluated using cyclic voltammetry (CV) for the detection of malathion in the gas phase. The inhibition-based response exhibited a linear relationship with malathion concentration in the range of 6–25 ppbv ($R^2 = 0.941$), demonstrating reliable quantitative performance. Notably, the BChE-based biosensor maintained excellent operational stability, retaining functionality for up to six weeks without cold

storage. In addition, the sensor electrodes were reusable over multiple measurement cycles, highlighting their practicality and cost-effectiveness. Overall, this study underscores the potential of BChE-based reversible inhibition biosensors as robust, low-cost platforms for sensitive OPC detection, particularly in gas-phase applications where long-term stability and reusability are critical.

For malathion detection, three enzymes have been primarily employed: acetylcholinesterase, butyrylcholinesterase [61, 67], and lipase [68]. Table 3 summarizes these enzymes along with the complementary substrates used in the respective studies.

To overcome these limitations, enzyme-based sensors are often used in combination with nanomaterials, which have advantageous physicochemical properties such as a large surface-to-volume ratio, increased catalytic activity, and excellent compatibility. They are responsible for improving the durability of the sensing platform while supporting its sensitivity. Recent studies have investigated the use of various nanomaterials, including silver nanoparticles (AgNPs), gold nanoparticles (AuNPs), GO, and rGO, in combination with enzymes for the detection of malathion. Table 4 shows the results of these studies and the corresponding approaches.

Table 3. Combinations of enzymes and substrates used in malathion detection

Enzyme employed	Substrate	Process	Ref.
Acetylcholinesterase (AChE)	Acetylthiocholine chloride	Acetylthiocholine hydrolyzed into thiocholine and acetic acid	[60]
Butyrylcholinesterase (BChE)	S-butyrylthiocholine chloride	Hydrolysis of butyrylthiocholine generates thiocholine and butyric acid, followed by the enzymatic decomposition of hydrogen peroxide into water catalyzed by peroxidase	[61]
Butyrylcholinesterase (BChE)	S-butyrylthiocholine (DTNB)	Malathion inhibits BChE resulting in decreased thiol generation; activity quantified colorimetrically reagent (5,5'-dithiobis(2-nitrobenzoic acid) to TNB)	[67]
Lipase	p-Nitrophenyl acetate	Hydrolysis of p-nitrophenyl acetate results in the formation of p-nitrophenol and acetic acid	[68]

Table 4. Methods and materials applied in enzyme-based malathion detection

Components	Dynamic range	LOD	Method	Ref.
AgNPs, AChE	2×10^{-6} to 1×10^{-4} nM	5.56×10^{-7} nM	Fluorescence spectroscopy	[69]
rGO, Tetraethylenepentamine Copper nanowires, AChE	3×10^{-3} nM to 60 nM	1.2×10^{-4} nM	Electrochemical	[70]
AgNPs, GO, AChE	1×10^{-5} to 1 nM	1×10^{-5} nM	Surface plasmon resonance	[71]
AuNPs, Nitrogen doped rGO AChE	3 nM to 3×10^{-6} nM	3×10^{-7} nM	Electrochemical	[72]

5.3 Monitoring of methyl parathion residues

Methyl Parathion (MP) is a highly toxic organophosphate pesticide that requires strict safety measures and must be used exclusively by trained professionals. Minimal contact with MP, through any route of exposure, is capable of causing significant central nervous system impairment. The acceptable daily intake (ADI) defined by the FAO for this pesticide is limited to 0.003 mg/kg body weight [73]. As per IUPAC standards, its chemical name is O,O-dimethyl O-p-nitrophenyl phosphorothioate.

Using DPV analysis, the electrochemical behavior of MP on the HCP5@AuNPs-ERGO/GCE electrode was evaluated. The nitro substituent (NO_2) within the MP structure exhibited an irreversible four-electron transfer process, generating a hydroxylamine group (NHOH/NO^-). This intermediate could further undergo a reversible two-electron exchange between the hydroxylamine and nitroso states (Fig. 5) [74]. The reduction signal attributed to this transformation provided the basis for the quantitative measurement of methyl parathion.

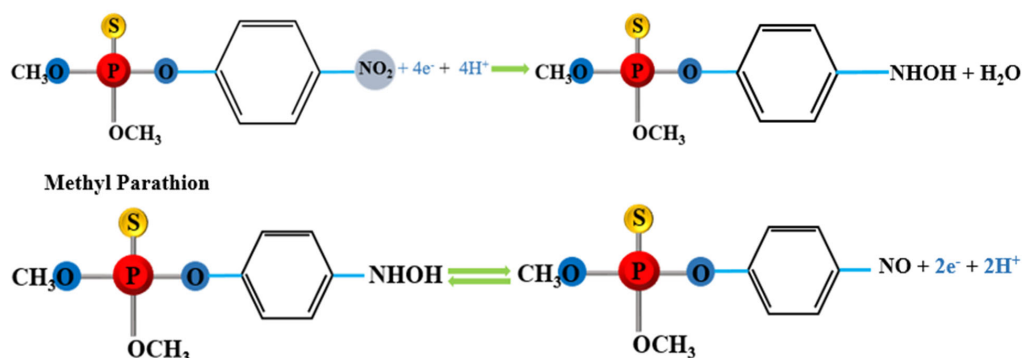


Fig. 5. Schematic representation of MP electrochemical reactions at HCP5@AuNPs-ERGO/GC electrode. Adapted with permission from Ref. [74]. Copyright 2019, Royal Society of Chemistry.

Recent advances in electrochemical sensing have highlighted the exceptional properties of carbon-based nanomaterials, including graphene, carbon nanotubes (CNTs), and their derivatives. These materials have become indispensable in sensor design due to their high electrical conductivity, large surface area, and rapid electron transfer kinetics. Graphene oxide possesses an exceptionally large surface area, which enables strong redox responses and high adsorption capacity [75]. Its reduced derivative, enriched with multiple functional moieties, facilitates the immobilization of diverse electrode materials. In addition, porous graphene oxide doped with Cu^{2+} and Ni^{2+} ions been engineered for the monitoring of OPPs in vapor-phase samples [76]. CNTs a well-known class of one-dimensional carbon nanostructures, have been widely investigated due to their superior electrical conductivity, remarkable chemical robustness, and large specific surface area, making them attractive for electrochemical sensing applications. To detect MP, spinosad, chlorpyrifos, and deltamethrin, an electrochemical sensor with remarkable selectivity and sensitivity ($1846.9 \mu\text{A} \mu\text{M}^{-1}$) was constructed by combining Zn(II) phthalocyanines (ZnPc), boron dipyrromethene (BODIPY), and single-walled carbon nanotubes (SWCNTs). When tested with DPV, the ZnPc-BODIPY-SWCNT/GCE platform demonstrated a pronounced preference for MP detection.

The sensing performance of the roll-to-roll fabricated non-enzymatic sensor for MP detection is primarily governed by the synergistic contribution of electrocatalytic activity and adsorption-controlled interfacial processes arising from the hybrid GNPs/ ZrO_2 -modified electrode architecture [77]. The integration of a two-dimensional carbon material with a metal oxide coating creates a multifunctional sensing interface that effectively addresses the intrinsic electrochemical inertness of many organophospho-

rus pesticides (Fig. 6). From an electrocatalytic standpoint, graphene nanoplatelets provide a highly conductive network with a large density of edge-plane defects and π -conjugated domains, which facilitate rapid electron transport and enhance charge-transfer kinetics at the electrode–electrolyte interface. This conductive scaffold ensures efficient signal transduction during the electrochemical reduction of nitroaromatic moieties present in MP. The incorporation of ZrO_2 further improves electrocatalytic performance by stabilizing intermediate redox species and lowering the activation energy associated with electron-transfer processes. Although ZrO_2 itself is not a classical redox-active oxide, its strong Lewis acidic nature promotes favorable interfacial interactions that indirectly enhance electrochemical response.

Equally critical is the role of adsorption-driven processes, which dominate the recognition mechanism for nitroaromatic OPPs. ZrO_2 exhibits a pronounced affinity toward phosphoryl (P=O) groups through strong Lewis acid–base interactions, enabling selective adsorption and preconcentration of MP molecules at the electrode surface. Simultaneously, π – π stacking interactions between the nitroaromatic ring of MP and the graphene basal planes further reinforce analyte accumulation at the sensing interface. This dual adsorption mechanism significantly increases the local concentration of MP near the electrode surface, thereby amplifying the electrochemical signal. The adsorption-controlled preconcentration, combined with enhanced electron-transfer efficiency, enables sensitive detection of MP via square-wave voltammetry (SWV) without the need for enzymatic recognition elements. The rapid response time (~ 10 min) reflects the efficient mass transport and fast surface binding kinetics associated with the nanostructured hybrid interface. Although the reported limit of detection 1×10^3 nM,

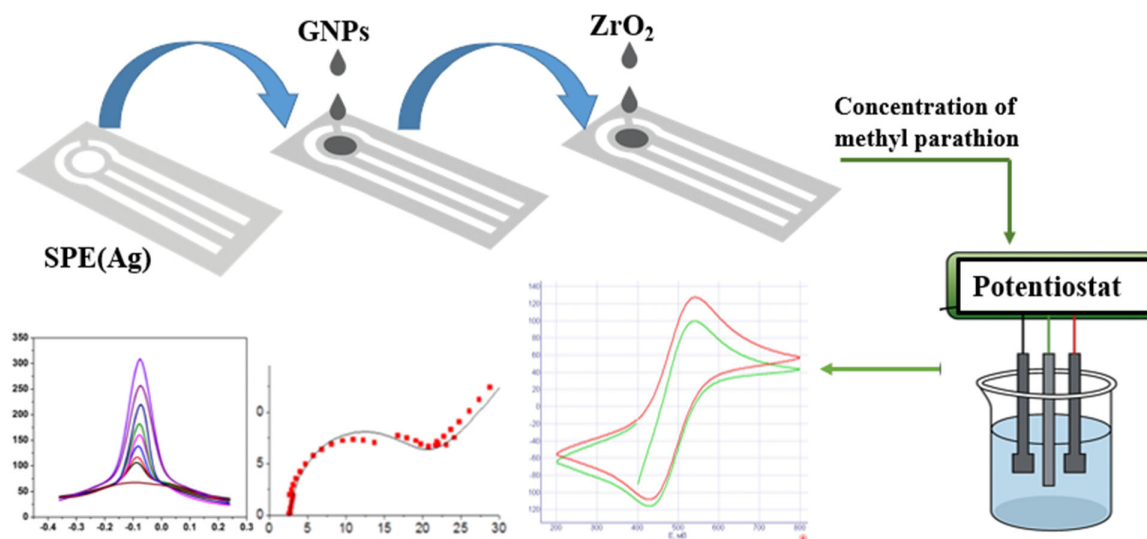


Fig. 6. Diagrammatic representation of roll-to-roll production of the MP sensing device. Adapted with permission from Ref. [77]. Copyright 2021, American Chemical Society.

(0.2 ppm) is higher than those of some enzyme-based systems, the non-enzymatic design offers clear advantages in terms of robustness, scalability, and suitability for continuous roll-to-roll manufacturing.

Overall, this work demonstrates that rational coupling of electrocatalytic signal enhancement with adsorption-driven molecular recognition provides an effective strategy for non-enzymatic electrochemical detection of nitroaromatic organophosphorus pesticides. Such hybrid architectures are particularly attractive for large-scale, low-cost sensor production and highlight the importance of surface chemistry and interfacial design in next-generation pesticide sensing platforms.

5.4 Determination of chlorpyrifos (CPF)

Chlorpyrifos (CPF) is a widely used OPP with the chemical name O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate [78]. Since CPF does not undergo spontaneous oxidation, most detection methods for this compound are based on an electrochemical signal suppression approach, where the presence of CPF inhibits the oxidation of a redox probe.

In one report [79], a novel approach was described for constructing an electrochemical sensor utilizing a screen-printed electrode (SPE) modified with a bimetallic $\text{Mn}^{2+}/\text{Fe}^{3+}$ metal-organic framework (MnFe-MOF) for the direct detection of chlorpyrifos. Square wave voltammetry was applied as the electroanalytical method, achieving a detection limit as low as 0.85 nM (0.29 ppb) within a broad linear range of 1.0 to 100 nM. The sensor was noted for its strong repeatability and excellent resistance to

interferences. The MnFe-MOF material was synthesized through a simple one-pot solvothermal process using terephthalic acid as the organic linker, and its successful formation was verified by multiple characterization techniques. The bimetallic framework displayed remarkable adsorption capacity and electrocatalytic performance toward chlorpyrifos, which was attributed to the synergistic effect between Mn^{2+} and Fe^{3+} ions. As a result, the material was employed as the electrode modifier for non-enzymatic electrochemical determination of CPF. Furthermore, the proposed device achieved satisfactory recovery levels for spiked pesticides in real-sample matrices, confirming its potential for practical applications.

The sensing platform reported by Tunesi et al. [80] exhibits enhanced analytical performance as a result of the synergistic interplay between electrocatalytic activity and adsorption-controlled surface processes enabled by the CuO nanostructured interface. Copper oxide, a p-type semiconductor with well-documented redox activity and favorable charge-transfer characteristics, plays a dual role by amplifying the electrochemical response and facilitating analyte preconcentration at the electrode surface (Fig. 7).

From an electrocatalytic perspective, the in situ growth of CuO nanostructures on the ITO electrode significantly accelerates interfacial electron-transfer kinetics between the electroactive PAM-Cl layer and the underlying electrode. The high density of catalytically active sites and shortened electron diffusion pathways provided by the CuO architecture enhance the electro-oxidation signal of PAM-Cl, which is essential for inhibition-based sensing.

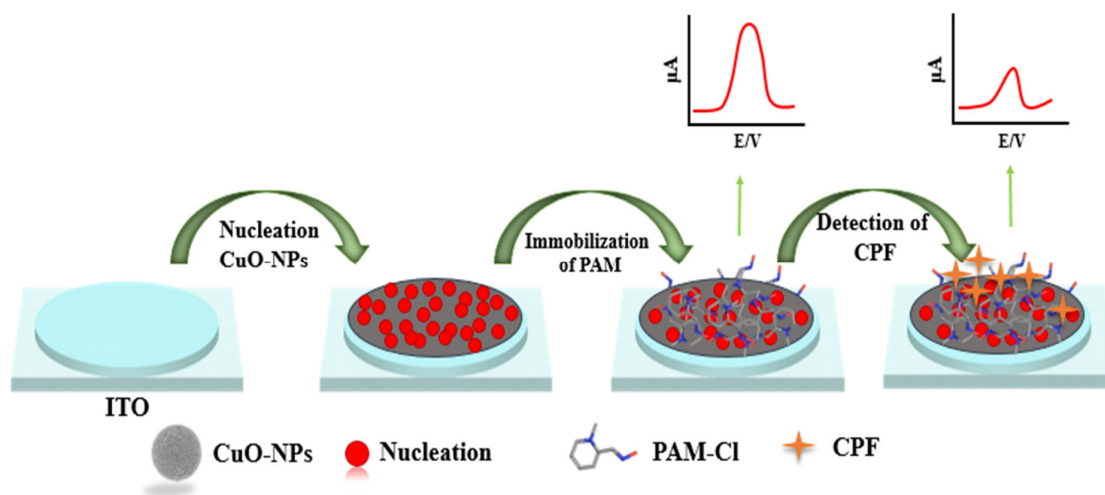


Fig. 7. Diagram showing the template-guided synthesis of a PAM-Cl based electrochemical sensor for chlorpyrifos detection. Adapted with permission from Ref. [80]. Copyright 2018, Elsevier.

The subsequent immobilization of CuNPs further improves electrical conductivity and promotes efficient electron shuttling, resulting in increased current response and improved signal stability. The electrochemical behavior of the PAM-Cl/CuO/CuNP-modified electrode was characterized using cyclic voltammetry in the potential range of 0–1.2 V at a scan rate of 50 mV s^{-1} , confirming the electrocatalytic enhancement of the sensing interface. For quantitative analysis, differential pulse voltammetry (DPV) was employed to determine CPF concentrations, exploiting the high sensitivity of DPV toward electro-oxidative signal inhibition induced by pesticide binding. In parallel, adsorption-driven processes play a critical role in governing sensor performance. Pimelic acid functions as a structure-directing agent by electrostatically interacting with the positively charged pyridine nitrogen centers of PAM-Cl, ensuring controlled molecular orientation and dense surface immobilization. Moreover, the hierarchical morphology and high surface area of the CuO nanostructures promote efficient adsorption of organophosphorus pesticides, increasing the local concentration of CPF at the sensing interface and strengthening the inhibition effect.

As a consequence of this combined electrocatalytic amplification and adsorption-controlled preconcentration, the sensor demonstrated the capability to detect multiple organophosphorus pesticides, including FEN and MP. Notably, the lowest limit of detection was achieved for CPF (LOD = 1.6 nM), highlighting the strong affinity of CPF toward the organized PAM-Cl/CuO interface and underscoring the effectiveness of the nanostructured electrocatalytic design.

In one study, a non-biological sensor with high sensitivity and selectivity was developed. The focus was placed on fabricating a modified electrode functionalized with molecularly imprinted thiophene polymers covalently anchored onto multi-walled carbon nanotubes (ICP@MWCNT) for the selective determination of CPF. To enable the attachment of the thiophene polymer onto the MWCNT surface, a thiophene linker (TAA) was employed. The ICP@MWCNT composite was synthesized through in-situ chemical oxidative polymerization using FeCl_3 as a catalyst, involving thiophene-linked MWCNTs, a pre-polymerization mixture, and the thiophene cross-linker 3,4-ethylenedioxythiophene (EDOT). The resulting electrochemical sensor exhibited high sensitivity toward the detection of CPF in vegetable samples, achieving a detection limit as low as $4 \times 10^{-3} \text{ nM}$. Due to its excellent reproducibility and reusability, this approach is considered promising for the monitoring of pesticide residues in food products [81].

As described in the literature [82], a biosensor was constructed using dicyclohexyl phthalate (DCHP) together with MWCNTs to modify a screen-printed electrode (SPE) for CPF determination. It was noted that, compared with conventional electrodes, SPEs provide certain advantages and can be applied for in situ analysis. The DCHP/MWCNT-based nanocomposite facilitated faster electron transfer at lower potentials and efficiently promoted the electrochemical oxidation of acetylthiocholine. AChE was immobilized on the nanocomposite film, thereby producing an AChE biosensor for pesticide residue monitoring. This device was successfully utilized to measure trace levels of pesticides in real vegetable samples. Based on the inhibition effect of CPF on

AChE activity, the sensor exhibited a broad linear detection range (1.43×10^{-1} – 2.85×10^5 nM), a low detection limit of 1.43×10^{-1} nM, as well as good reproducibility and acceptable stability.

Despite numerous in vitro studies in this field, there is a growing demand for flexible, wearable, and portable OPP sensors that enable real-time monitoring. Most existing inhibition-based sensors are based on OPP adsorption, which has a significant drawback: toxic OPP residues remain bound to the sensor surface after use. To date, there are few studies investigating reusable sensor designs or sustainable disposal methods. Future development of next-generation OPP-based sensors should emphasize the principles of sustainability, including toxicity reduction, biodegradability, recyclability, reusability, and recyclability. In addition, zero-waste operation and overall environmental sustainability should be key factors in development. These considerations are important for improving human life by addressing health problems while minimizing environmental impact.

6. Conclusion

Electrochemical sensing of organophosphate residues in food matrices has emerged as a critical research direction aimed at protecting public health and reinforcing food safety standards. This review provides a systematic overview of a broad range of electrode materials, emphasizing their unique analytical characteristics and mechanistic contributions to organophosphorus pesticide (OPP) detection. With particular attention to three commonly encountered OPPs—MLT, MP, and CPF—the article summarizes recent developments in electrochemical sensor architectures designed to achieve high detection sensitivity. Significant advancements have been realized in the fabrication of sensing platforms that combine rapid response, cost-effectiveness, and operational simplicity. To further improve analytical performance, various strategies have been implemented, including enhanced immobilization and stabilization of recognition elements on electrode surfaces, integration of nanostructured materials to increase the effective electrode–analyte contact area, and the use of catalytic or electrocatalytic systems to amplify the measurable signal.

Despite these achievements, several problems remain. One of the key problems in this area is related to the redox inactivity of most OPPs, which makes their electrochemical analysis difficult. Receptor immobilization can lead to a decrease in their activity

over time; electrodes modified with nanomaterials often face limitations in terms of long-term reuse; and signal amplification strategies require careful selection of stable and soluble signal carriers. To overcome this limitation, the use of carbon nanomaterials and nanomaterials has been proposed as a promising strategy. The main challenge is to increase sensitivity and reproducibility without compromising sensor stability. Innovations related to new nanostructures, advanced immobilization methods, or more reliable amplification strategies are expected to contribute significantly to overcoming these limitations. In addition, there is a growing need for portable electrochemical sensors capable of performing analysis at the sampling site. Such tools will be valuable not only for farmers and consumers seeking rapid quality verification, but also for large food producers and distributors involved in quality control and inventory management. For widespread commercial adoption, future developments must consider manufacturing efficiency, cost-effectiveness, and field applicability. To address this limitation, the incorporation of carbon nanomaterials and nanoarrays has emerged as a promising strategy. The proposed solutions are expected to contribute to the development of electrode materials consistent with the principles of the Sustainable Development Goals.

Acknowledgment

This research was funded by the Abai Kazakh National Pedagogical University (Contract №05-04/250 dated 03.04.2025 “Development of an electrochemical sensor for the detection of organophosphorus pesticides using CuO nanostructures”).

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