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Metal oxide-based electrochemical sensors for pesticide detection in water and food samples: a review

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The increasing need for food and agricultural resources necessitates using pesticides to protect plants, but this approach also poses pesticide poisoning and environmental hazards. Although designing an effective pesticide detection method is challenging, various technologies collaborate to develop an effective electrochemical sensor for detection of various pesticides. This review article examines the various metal oxides, their synthesis techniques, and their applications in electrochemical sensors, particularly for environmental applications, to detect pesticides in a variety of contaminated environmental samples. Metal oxides have unique properties that make them useful for pesticide detection because of their more active sites and electrical, optical, and semiconducting properties. Samarium molybdate-based electrode materials are considered the most promising direction for the development of electrode materials for pesticide sensors due to their economy, chemical stability, multiple valences, low detection limit, high sensitivity, and high electrocatalytic activity performance. In addition, this study investigates the current research trend in the detection of pesticides using metal oxide-based sensors in environmental samples, and researchers should expect new research perspectives and ideas. Overall, the metal oxide-based pesticide detection sensors will surely aid in meeting the growing demands for food and environmental monitoring and protection.

Environmental significance

Pesticides protect agricultural crops from insects, weeds, and illnesses. Despite this, a considerable fraction of these pesticides fail to reach their targets, resulting in unintended consequences such as soil contamination and poisoning of ground and surface water resources. This article comprehensively reviews pesticide monitoring in environmental samples using metal oxide electrocatalysts. Metal oxide-based electrochemical pesticide detection provides sensitive, selective, and rapid detection methodologies with significant environmental implications. This methodology allows for more effective monitoring, risk assessment, and the promotion of sustainable agricultural practices, all of which contribute to protecting and preserving our environment.

1. Introduction

The word "pesticide" is frequently used to describe several groups of fungicides, wood preservers, rodenticides, household disinfectants, and garden chemicals used to kill pests or develop resistance.[1] Pesticides from various functional groups are used to grow crops worldwide. Pesticide residues are frequently found in water, air, and soil due to their ubiquitous use. Most pesticide compounds have been categorized according to their level of hazard, mode of operation, chemical composition, application timing, and application methods. The advent of chemical pesticides has significantly enhanced agricultural crop yields in recent decades.[2–4] Moreover, the uncontrolled and excessive use of pesticides has resulted in food contamination and environmental, aquatic, and agricultural pollution. Vegetables, fruits, processed foods, air, soil, and water are some of the sources of pesticide residues that can enter the food chain.[5] Dietary exposure to agricultural pesticides is a serious public health risk, especially in developing nations, as it can have immediate and long-term consequences on human health. Chemical pesticides can harm human health by being cytotoxic, carcinogenic, and mutagenic.[6,7] The

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consequences of pesticides on the environment and human health are shown in Fig. 1.

Pesticides are classified into two types: inorganic and organic. Inorganic pesticides include inorganic fungicides, arsenic insecticides, fluoride insecticides, and inorganic herbicides, whereas organonitrogen pesticides, organophosphates, and organochlorine pesticides are among the latter.[8–13] Organophosphates are the most common type of plant pesticide and include chlorfenvinphos, fenitrothion, malathion, fonofos, methamidophos, monocrotophos, phosalone, methyl parathion, chlorpyriphos, diazinon, dichlorvos, and demeton-*S*-methyl.[14–25] Organophosphate pesticides control pests in orchards, vegetables, cultivation, and industrial plantations. These pesticides are made up of any organic compound that contains phosphorus. Organophosphate pesticides cause hyperarousal conditions and muscle paralysis.[26] Along with organophosphate pesticides, organonitrogen pesticides, which include carbamates, phenyl urea, triazines, and their derivatives such as propoxur, aminocarb, simazine, carbaryl, propazine, and atrazine, are important pesticides.[27–33] Organonitrogen pesticides are viewed as less ecologically stable than organophosphate pesticides, but when they enter the digestive system, they pose a risk to human health.[34] Various commercial methods have been developed to detect pesticides, such as fluorescence analysis,[35] liquid chromatography,[36] mass spectrophotometry,[37] chromatography,[38] high-performance liquid chromatography,[39] gas chromatography,[40] *etc.* For instance, Sahoo *et al.*[41] demonstrated pesticide nano sensing using zinc oxide quantum dots, employing optical and electrochemical techniques for detecting water samples. Amde *et al.*[42] also introduced a nanofluid containing zinc oxide nanoparticles in an ionic liquid. This allows for single-drop liquid microextraction of fungicides from environmental waters prior to high-performance liquid chromatographic analysis. Despite the high accuracy and sensitivity of these methods, uneconomical and more detection time and advanced instruments are not suitable for rapid and real-time analysis in practical applications. On the other hand, electrochemical sensors have become an alternative method for detecting pesticides due to their low cost, sensitivity, rapid response, and easy miniaturization.[43,44] Umamaheswari *et al.*[45] successfully developed a smartphone-based portable sensor for mesotrione that is appropriate for use in nonlaboratory environments. Future commercialization of this technology would make it possible to use it in real-time monitoring applications. Furthermore, researchers have enhanced these desirable characteristics by introducing suitable electrocatalysts through electrode modification.

As previously stated, the electrocatalyst has a significant effect on electrochemical performance. Hence, researchers are interested in developing a novel material with improved physicochemical properties for various fields. Metal oxides play a key role in electrochemical applications due to their porous nature, which leads to a high surface area, more active sites, and electrical, optical, and semiconducting properties.[46–50] The chemical flexibility and crystal structural properties of metal oxide nanomaterials pave the way for various applications such as energy storage, optoelectronics, sensors, infrared detectors, and other technologies.[51–56] Transition metals have piqued the interest of researchers because they typically have multiple valence states and can easily form a redox cycle between high and low oxidation states.[57,58] Their mixed oxidation states and enriched performances benefit energy storage, photoelectrochemical conversion, and other technologies. For example, George *et al.*[59] developed a review of metal oxide-based electrochemical detection of chemical and biochemical species in biological samples. Hua *et al.*[60] discussed heavy metal removal from wastewater using nanosized metal oxides for review. Thus, the size of the particles also reveals the unique and outstanding properties of metal oxides. According to previous literature, sensors utilizing metal oxide materials have been proposed for detecting heavy metal ions, and chemical and biochemical compounds in environmental and biological samples.[61,62] For instance, some literature studies have reported

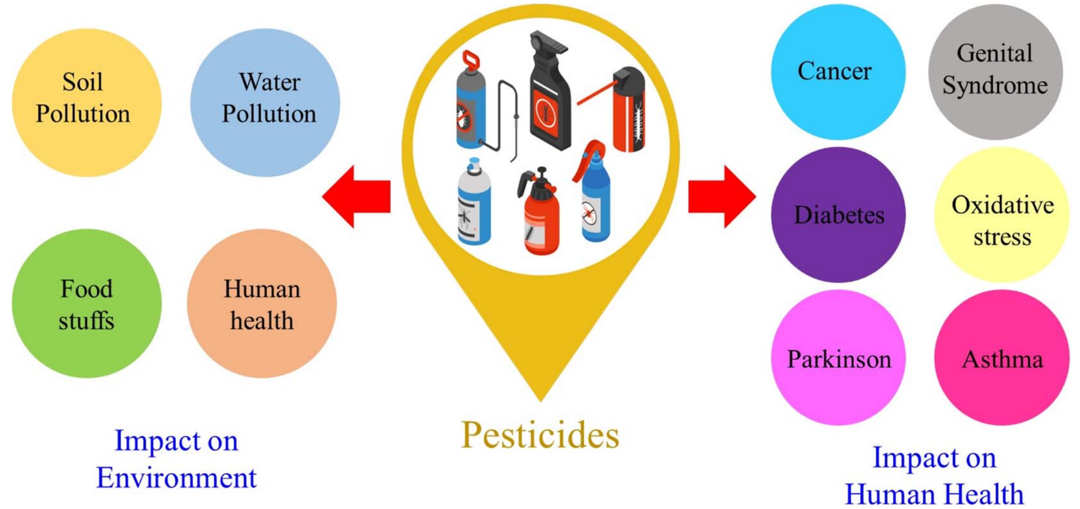


Fig. 1 The schematic diagram of pesticide impacts on the environment and human health.

on detecting pesticides with different metal oxide-modified electrodes, as shown in Table 1. Because of the physiochemical characteristics, the metal oxide-modified electrodes largely boost the sensitivity and reproducibility of the electrochemical sensor. In the realm of electrochemical sensors, metal oxide-based materials can be used. To the best of the authors' knowledge, no review papers have been published on the various metal oxide (neodymium molybdate, samarium molybdate, bismuth vanadate, dysprosium vanadate, lanthanum stannate, iron oxide) based electrochemical detection of pesticides (methyl parathion, carbendazim, paraoxon, fenitrothion, 2,4,6-trichlorophenol, carbofuran) in water and food samples.

This review discusses a variety of electrochemical (bio) sensing analyses for highly sensitive pesticide detection. Different nanomaterials have been used to amplify signals from electrochemical analysis techniques. The current review focuses on using metal oxides to develop various (bio)sensing approaches. Metal oxides produce highly successful results when used in electrochemical sensing because they are biocompatible and can detect biological activity during absorption. The authors define metal oxides, their preparation methods, characteristics, and structures in this review. Finally, this study will discuss various electrode material-based electrochemical sensors for pesticide detection and electrode materials that are most efficient for pesticide detection in water and food samples. Moreover, the potential challenges and prospects for pesticide detection are investigated.

2. Metal oxides

Metal oxides can be categorized into three classes based on their chemical properties and structural characteristics. These three main categories are acidic, basic, and amphoteric oxides.[63] Metal oxides are compounds consisting of metal-bound oxygen atoms exhibiting admirable physicochemical properties. The metal oxides can be prepared in various sizes from micro to nanometers.[64] A metal oxide is considered a conventional model due to its excellent nature, such as abundant active sites, larger specific surface area, various electronic states, excellent electronic conductivity, enhanced electrochemical behavior, and thermal properties.[62,65] The metal cation and the oxygen anion coordination located in the metal oxide surface leads to the formation of the relative acidity and basicity of the atom. The metal oxide's acidity and basicity sites significantly impact its catalytic properties. Infrared spectroscopy, calorimetry, and other methods were used to identify the acidic and basic sites of metal oxides.[66,67]

Metal oxide nanoparticles or materials modified or coated with functional groups, ligands, polymers, or other molecules to impart specific characteristics or functions are referred to as functionalized metal oxides.[68] The purpose of these modifications is frequently to improve the material's performance in a variety of applications, such as biomedical, sensing, and catalysis.[69] This functionalization adds novel performance, improves electrocatalytic characteristics, and allows for more specific interactions with pesticide analytes, resulting in increased sensitivity, selectivity, and overall performance.[70] For example, Krishna *et al.*[71] developed metal oxides with surface modification for highly sensitive electrochemical detection of heavy metals, organophosphates, and nutrients in water samples. The detecting agents ZrO_2, MnO_2, and MgO, incorporated into the ink, exhibit specific affinities for lead, fenitrothion, and nitrite, respectively. Metal oxides are immobilized on a GCE that has been modified with nitrogen–sulfur co-doped activated carbon-coated carbon nanotubes. The resulting proposed sensor demonstrates excellent electrocatalytic properties for fenitrothion detection with a detection limit of 1.69 nM, showing reliability in water samples.

Metal oxides are used as food additives to improve the visual appeal, texture, and nutritional content of numerous food products.[72] Metal oxide nanoparticles (NPs), such as titanium dioxide (TiO_2), silicon dioxide (SiO_2), zinc oxide (ZnO), and iron oxide (Fe_2O_3) are used as food additives in a variety of ways. These metal oxides are used for various functions, including food coloring, anti-caking, antimicrobial, and micronutrient supplements.[73] TiO_2 is a common white pigment,[74] SiO_2 is utilized as an anti-caking agent and thickener,[75] ZnO is used as a nutrient supplement,[76] and Fe_2O_3 nanoparticles are used as natural food coloring agents in the food industry.[77] For example, Garcia *et al.*[78] previously discussed the metal oxide-based food additives in food packaging, applications, migration, and regulations. In nanotechnology, advancements can result in the development of novel metal oxide formulations that offer improved bioavailability and targeted nutrition delivery.

Table 1 Some literature studies reported on the detection of pesticides with different nanomaterial-modified electrodes

Materials	Methods	Linear range (μM)	LOD (μM)	Pesticides	Reference
$MnCo_2O_4$	DPV	0.015–435	0.002	Paraoxon-ethyl	174
$PrCoO_3$	DPV	0.001–84	0.002	Carbendazim	175
Graphene oxide	*i*–*t*	1–47	1.2	Fenuron	176
$AgWO_4$	DPV	1–1108	0.066	Crisquat	177
$SrTiO_3$	DPV	0.01–434	0.003	Trichlorophenol	155
rGO/Cu/CuO	DPV	0.05–20	0.005	Carbaryl	178
CuO	CV	0.01–30	0.003	Fenamiphos	178
TiO_2	DPV	5–150	0.02	2,4-Dichlorophenol	179
Fe_3O_4	CV	0.05–100	0.02	Chlorpyrifos	180
$Bi_2Sn_2O_7$	CV	0.05–500	0.014	Omethoate	181
$Pr_2(WO_4)_3$	*i*–*t*	0.01–313	0.005	Fenitrothion	182

Metal oxides can also undergo photo-assisted adsorption and deportation to control their semiconductor properties.[79] The reactivity towards electromagnetic radiation, multiple valences, and the oxidation state of metal oxides make them more promising materials for catalytic reactions such as electrochemical redox reactions, isotopic exchange, photocatalysis, and various other applications currently under investigation by researchers.[80] Sivalingam *et al.*[81] demonstrated that the Co_3O_4 material possesses a redox activity characteristic that can be used for energy storage and sensing applications. The outstanding properties of metal oxides make them excellent candidates in several fields like electrochemical and biosensors, electrocatalysis, energy storage, optoelectronics, photoelectrochemical conversion, and surface-enhanced Raman spectroscopy.[51,54,82–84] Therefore, metal oxides are considered one of the crucial materials in the field of electrochemical sensors.

2.1. Synthesis techniques of metal oxides

Metal oxides that have received the most attention for electrochemical detection of pesticides in aqueous systems are titanium iron, copper, manganese, and zinc oxides.[85–87] They can be found in a variety of forms, including particles, rods, cubes, tubes, and others. Metal oxides' shape and size both have an impact on their electrocatalytic performance. Over the last decade, researchers have focused on developing efficient synthetic methods for producing highly stable, shape-controlled, and monodispersed metal oxide nanomaterials.[60] In general, synthesis procedures can be divided into two types: (1) physical methods such as high-energy ball milling, severe plastic deformation, ultrasound shot peening, inert gas condensation, and (2) chemical methods such as controlled chemical coprecipitation, pulse electrode position, chemical vapor condensation, liquid flame spray, microemulsion, gas-phase reduction, liquid-phase reduction, *etc.*[88] Hydrothermal, thermal decomposition and coprecipitation synthesis procedures are widely used because of their high yields and scalability, making them simple to execute.[89] Metal oxide characterization research focused on crystal structure, size, morphology, and specific surface area properties. Moreover, several electrochemical sensor-based modified electrodes were introduced to determine pesticides in environmental samples. Balamurugan *et al.*[90] synthesized the dysprosium stannate electrode material using a simple coprecipitation method for electrochemical detection of carbofuran. Ganesan *et al.*[91] developed neodymium molybdate by a hydrothermal approach and used it to construct an electrochemical sensor for methyl parathion detection. Kokulnathan *et al.*[92] synthesized samarium molybdate using a sonochemical method for electrochemical detection of carbendazim. Compared to all other synthesis methods, coprecipitation, hydrothermal, and sonochemical methods are the most efficient and beneficial due to low cost, environmental friendliness, high yield, mild conditions, less pollution, and effective reaction. The most commonly used metal oxide synthesis methods for pesticide detection are summarized in Table 2.

2.2. Important properties of metal oxides in developing electrochemical sensing

Metal oxides are economical, easily synthesized, biocompatible, and loaded with a catalyst.[93] Thus, they are potential materials for altering electrodes. Furthermore, metal oxides have tuneable properties due to their flexible structure. The remarkable characteristic of metal oxides is their capacity to immobilize the electrocatalyst, which improves a sensor's selectivity and sensitivity against environmental contaminants by loading the electrocatalyst in a metal oxide.[59] For example, cerium oxide electrode materials have exhibited outstanding electrocatalytic activity because of their mixed-valence oxidation state conversion between Ce(III) and Ce(IV), which helped with fast electron transport.[94] Furthermore, Fe_3O_4 electrode materials have unique properties such as high mobility of oxygen ions, superparamagnetic, low toxicity, biocompatibility, small sizes, and extraordinary catalytic activities in oxidative processes, which lead to increased sensitivity and stability of pesticide detection.[95,96] Spinel-type oxides demonstrate exceptional structural durability. They also possess a distinctive pore volume and offer a greater number of electrochemically active sites. These properties arise from the synergistic effect of diverse metal ion configurations, allowing for the utilization of bimetallic catalysts in electrochemical pesticide sensors.[97] Metal oxides, such as TiO_2, ZnO, and SnO_2, exhibit high sensitivity to various pesticides due to their semiconducting nature.[98–100] Bao *et al.*[101] developed a TiO_2 material that demonstrated excellent electrocatalytic performance due to its textural properties, pore dimension, pore volume, distribution, and specific surface area.

Table 2 A summary of used metal oxide synthesis methods for pesticide detection

Materials	Synthesis method	Morphology	Pesticides	Reference
Fe_3O_4	Hydrothermal	Quasi-spherical	Malathion	183
TiO_2	Sonochemical	Long tube	Paraquat	184
$Dy_2Sn_2O_7$	Coprecipitation	Nanoplatelet	Carbofuran	90
CeO_2	Sonochemical	Spherical	Hydrazine	185
$AgWO_4$	Hydrothermal	Nanoparticle	Crisquat	177
$NiCo_2O_4$	Hydrothermal	Microsphere	Paraoxon ethyl	186
$PrCoO_3$	Hydrothermal	Nanoflake	Carbendazim	175
$SrTiO_3$	Hydrothermal	Micro-pebble	2,4,6-Trichlorophenol	155
Fe_3O_4	Coprecipitation	Nanoparticle	Triazine	187

For these reasons, metal oxides have been used to create a variety of electrochemical sensors that can be utilized in various environmental monitoring applications.[93,102] Electrode modification with metal oxide materials has numerous applications in sensing heavy metals, phenolics, pesticides, and other harmful inorganic compounds.[103–106] These types of metal oxide electrodes, compared to other unique modified electrodes, have a promising future for detecting environmental toxins.

2.3. Classification of metal oxides on the basis of their importance for different pesticides

Metal oxides have significance in a variety of applications, including pesticides. Metal oxides can be classified according to their importance for various pesticides based on their distinct properties and functions. Antifungal metal oxides: copper oxides (CuO and Cu_2O) are known for their antifungal properties. Fungicides containing them are used to control several fungal diseases in crops. Copper-based pesticides are efficient against a wide range of fungi.[107] Herbicide metal oxides: aluminium oxide (Al_2O_3) nanoparticles have also shown promise in herbicide formulations. They can improve the adhesion and penetration of herbicides on plant surfaces. Iron oxide (Fe_2O_3) nanoparticles have been investigated for use in herbicides. They can be utilized as herbicidal substance carriers, enhancing their transport and effectiveness. Titanium dioxide (TiO_2) is used as a pesticide carrier and can enhance the adhesion of the active ingredient to the target surface.[108,109] Insecticide metal oxides: some insecticides contain zinc oxide (ZnO). It can act as a carrier for other active substances and is used in pest control formulations. Magnesium oxide (MgO) can improve the efficacy of insecticides by serving as a transporter or synergist. Silicon dioxide (SiO_2) is frequently used as an enhancer or transport in pesticide formulations. It can improve active component stability, dispersibility, and effectiveness.[110,111]

2.4. Diverse tuning approaches for enhancing metal oxide electrochemical sensing

Metal oxides are versatile materials with specific electrochemical properties that allow them to be used in a wide range of sensing applications. Researchers use several tuning approaches to improve their performance. These approaches are aimed at modifying the structure, composition, and surface properties of metal oxides. In this section, we look at various tuning strategies for improving the electrochemical sensing capabilities of metal oxides. Scheme 1 shows the schematic diagram of several tuning approaches for improving metal oxide electrochemical sensing applications.

(1) Nanostructure engineering: the surface area and active sites are improved using nanostructure engineering to increase electrochemical reactivity. Techniques like sol–gel synthesis, hydrothermal methods, or template-assisted processes are used. Nanostructured metal oxides have higher sensitivity and faster response times because of their increased surface area and improved charge transfer kinetics.[112,113]

(2) Surface functionalization: the surface is modified with specific functional groups to improve selectivity. Organic molecules, polymers, or biomolecules are attached to the surface of the metal oxide. Functionalization enhances the affinity of metal oxides towards target analytes, improving selectivity and reducing interference from other species.[114,115]

(3) Mesoporous structures: mesoporous metal oxides can improve mass transport and accessibility of analytes to the electrode surface. Mesoporous metal oxide structures are prepared using sacrificial or template techniques. The mesoporous structure improves sensor performance by accelerating the diffusion of target species to the electrode surface.[116,117]

(4) Size control: the size of metal oxide particles is modified to enhance their electrochemical performance. The particle size is precisely controlled during synthesis through variations in reaction conditions. The tunable features of size-controlled metal oxides enhance the electrochemical sensors' sensitivity, selectivity, and response times.[118,119]

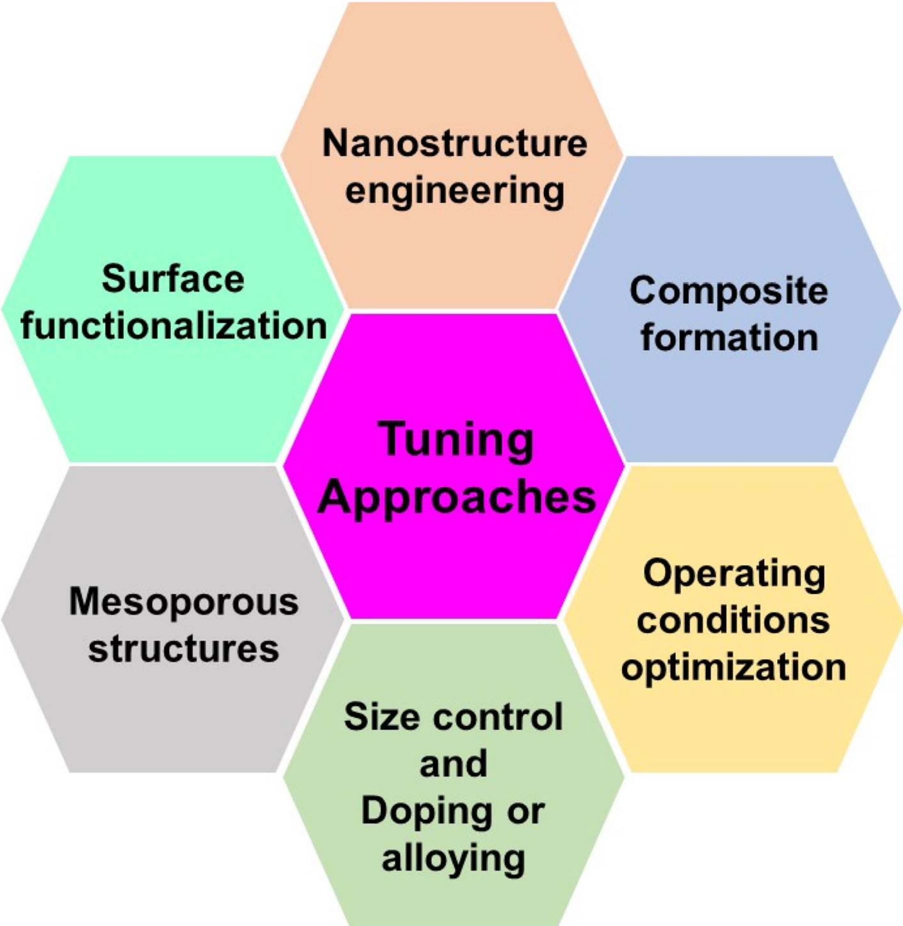
(5) Doping or alloying: the electronic and chemical properties are modified to optimize sensor performance. This is done by introducing doping elements or forming alloys with metal oxides during synthesis. The range of applications for metal oxide sensors can be increased by doping with elements like transition metals, enhancing selectivity, conductivity, and catalytic activity.[120–122]

(6) Operating condition optimization: the experimental parameters such as pH, temperature, and applied potential are adjusted. The operational conditions are investigated and optimized methodically for the best sensor efficiency. It is ensured that the sensor operates under ideal conditions, which enhances the signal-to-noise ratio and overall performance.[123–125]

(7) Composite formation: the advantages of different materials are combined to achieve a synergistic effect. Metal oxides are integrated with other materials, such as incorporate polymers, carbon materials, or conductive nanomaterials. Composite metal oxides enhance conductivity, stability, and sensitivity, offering improved overall performance compared to individual components.[126–128]

3. Metal oxide-based electrochemical sensors for pesticide detection

Electrochemical sensors have been developed regularly with the advancement of electrical devices and metal oxides, notably in pesticide monitoring.[129] However, due to the lower electroactivity of electrochemical sensors, the electrochemical detection of pesticides without a modified electrode is challenging. Because of this, modified electrodes are needed for signal measurability in pesticide detection. Metal oxides are being used as electrode materials due to their enhanced electrocatalytic activity, portability, and accuracy.[130–132] Thus, various reviews have thoroughly clarified the preparation, mechanism, and applications of metal oxide-based enhanced electrochemical detection.[59,61,112,133,134] This section mainly discusses the various pesticide monitoring-based electrochemical sensors created in the area using a range of metal oxides. Metal oxides are being presented as an appealing choice for designing and



Scheme 1 The schematic diagram of several tuning approaches for improving metal oxides–electrochemical sensing applications.

fabricating effective electrochemical sensors due to their superior physical and chemical properties.

3.1. Methyl parathion sensor

Methyl parathion (MPN) is an organophosphorus pesticide widely used as a fungicide and insecticide in industry and agriculture because of its high toxicity and effectiveness.[135] MPN has a substantial impact on agricultural product harvesting. The significant toxicity of MPN residue can readily pose severe safety threats to food safety and the ecological system.[136] Therefore, developing an effective, easy, economical, and highly sensitive detection MPN monitoring technology is critical. Ganesan *et al.*[91] synthesized a porous 3D flower-like neodymium molybdate (pf-$Nd_2Mo_3O_9$) by a hydrothermal approach to construct an electrochemical sensor for MPN detection. The structure and shape of the pf-$Nd_2Mo_3O_9$ material were confirmed by X-ray diffraction (JCPDS no. 33-936) and TEM investigation (Fig. 2A). A cyclic voltammetry (CV) sensor for MPN organophosphate pesticide detection was developed using the pf-$Nd_2Mo_3O_9$ electrode material. This procedure used differential pulse voltammetry (DPV) with a glassy carbon electrode (GCE). The electrochemical sensor for detecting MPN was developed by immersing an electrode in an electrolytic solution containing the required pesticides. Fig. 2B depicts the variation in the current as a function of the amount of the pf-$Nd_2Mo_3O_9$ modified GCE. The peak current response was higher after modifying the pf-$Nd_2Mo_3O_9$/GCE, compared to the unmodified GCE because of its high surface area (0.18 cm^2), superior charge transit, and more active sites. These results show that modifying pf-$Nd_2Mo_3O_9$/GCE can provide superior electrocatalytic performance for MPN detection. According to the linearity study, the electrochemical detection of MPN has a concentration range of 0.5 to 300 μM. The electrochemical detection mechanism of MPN reveals that the cathodic peak (R_1) is attributed to the direct reduction of MPN by hydroxylamine ($4e^-$ & $4H^+$ transfer process), while the redox couple (O_1 & R_2) results from the reversible behavior of hydroxylamine to nitroso derivatives ($2e^-$ & $4H^+$ transfer process)[91,137] (Fig. 2D). Fig. 2C depicts the DPV cure of pf-$Nd_2Mo_3O_9$/GCE for different MPN concentrations *vs.* obtained current response. According to the DPV studies, the calculated sensitivity and limit of detection values were 1.88 $\mu A\ \mu M^{-1}\ cm^{-2}$ and 5.7 nM. The investigated technique was used to measure the amount of MPN in water and food samples. These results demonstrate that the technique produces accurate results when used to monitor MPN in a variety of contaminated food and water samples.

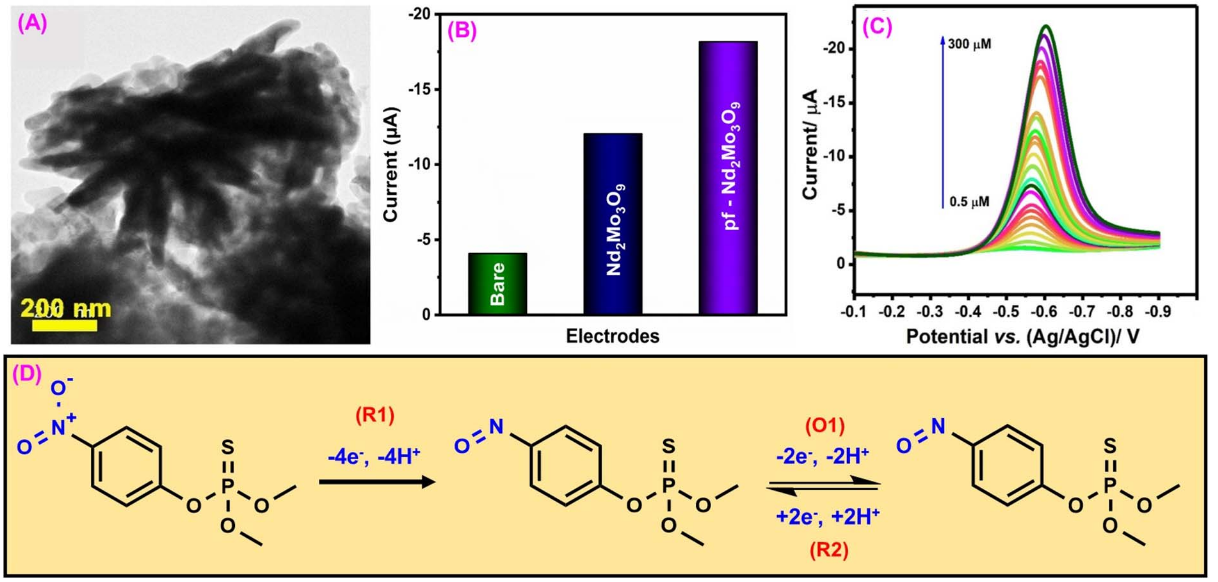


Fig. 2 (A) TEM image of pf-$Nd_2Mo_3O_9$. (B) CV investigation of the bare GCE (green), $Nd_2Mo_3O_9$ (blue), and pf-$Nd_2Mo_3O_9$ (purple). (C) DPV signal of pf-$Nd_2Mo_3O_9$ for MPN detection. (D) Electrochemical detection mechanism of MPN[103] (modified). ((A and C) License number: 5542351439158).

3.2. Carbendazim sensor

Carbendazim (CRM) is a benzimidazole fungicide whose benzimidazole ring is tough to break, leading to environmental harm.[138] CRM is employed in agriculture during pre and post-harvest for pathogen protection, which will harm fruits and crops.[139] The CRM residue can cause eye irritation, contact with derma, liver disease, skin inflammation, and chromosome changes in organisms which results in adversative environmental impact.[140] CRM is a carcinogen for human health due to its toxicity even though it has agricultural and economic benefits. Compared to other techniques, the electrochemical approach has proven to be reliable for CRM detection. Kokulnathan *et al.*[92] effectively synthesized a samarium molybdate ($Sm_3(MoO_4)_3$) electrocatalyst for sensitive electrochemical CRM detection in real-world environmental samples (Fig. 3A). A simple sonochemical approach for producing a $Sm_3(MoO_4)_3$ nanomaterial that is more stable, anti-interference and sensitive for CRM detection by an electrochemical sensor has been developed.[92] The structure and shape of the $Sm_3(MoO_4)_3$ material were confirmed by X-ray diffraction (JCPDS no. 34-0512), and FE-SEM (2D nanosheets) investigation (Fig. 3B and C). The $Sm_3(MoO_4)_3$ modified screen-printed electrode (SPCE) current response (6.6 μA) was two fold higher than that of the unmodified SPCE due to extraordinary properties of $Sm_3(MoO_4)_3$, such as chemical stability, abundant reserves, and multiple valences. Joseph & Santhoshkumar *et al.*[141,142] discussed the electro-oxidation mechanism of CRM. They found that the process is quasi-irreversible and involves the transfer of two electrons and two protons. This transfer leads to the formation of the benzimidazole radical and methyl carbamate. The benzimidazole radical undergoes dimerization, and the resulting dimer undergoes reduction, eventually producing alcohol. Therefore, in CRM, the imidazole-2-yl-carbamate component passes through oxidation, and a two-electron and two-proton reaction produces the imidazole carbonyl derivative (Fig. 4). Fig. 3D reveals the DPV results of $Sm_3(MoO_4)_3$/SPCE for different CRM concentrations *vs.* obtained current response and linearity studies (R^2 = 0.9902). According to the DPV studies, the calculated sensitivity and limit of detection values are 13.34 μA μM^{-1} cm^{-2} and 1 nM. The performance of the proposed sensor suggests that $Sm_3(MoO_4)_3$ has a promising future for determining CRM in environmentally hazardous samples.

3.3. Paraoxon sensor

Paraoxon is an organophosphate pesticide commonly used in agriculture to control insects/pests and produce a huge amount of crops while harming environmental and biological systems.[143] This insecticide, mainly sprayed on beans, wheat, cotton and fruits, can affect the neurological systems of all living things, including watersheds, humans, and animals.[144] Gopi *et al.*[145] constructed an effective electrochemical sensor based on $BiVO_4$ as an electrocatalyst for detecting hazardous paraoxon pesticide. The material characterization revealed that the synthesized $BiVO_4$ had superior conductivity, sufficient oxygen vacancies, and good chemical stability. Fig. 5A shows the crystal structure of the synthesized $BiVO_4$ material.[146] TEM image confirmed the open walnut-like structure branched dendrites of $BiVO_4$ (Fig. 5B).[147] In this process, DPV with a SPCE was used. The electro-reduction current response of paraoxon towards $BiVO_4$/SPCE and the bare SPCE was investigated using the CV technique (Fig. 5C). This study showed that, compared to the bare SPCE, the modified $BiVO_4$ material had a high current response and minimum potential window, indicating that the $BiVO_4$ material had excellent electroconductivity for paraoxon detection. The possible electrochemical redox process of

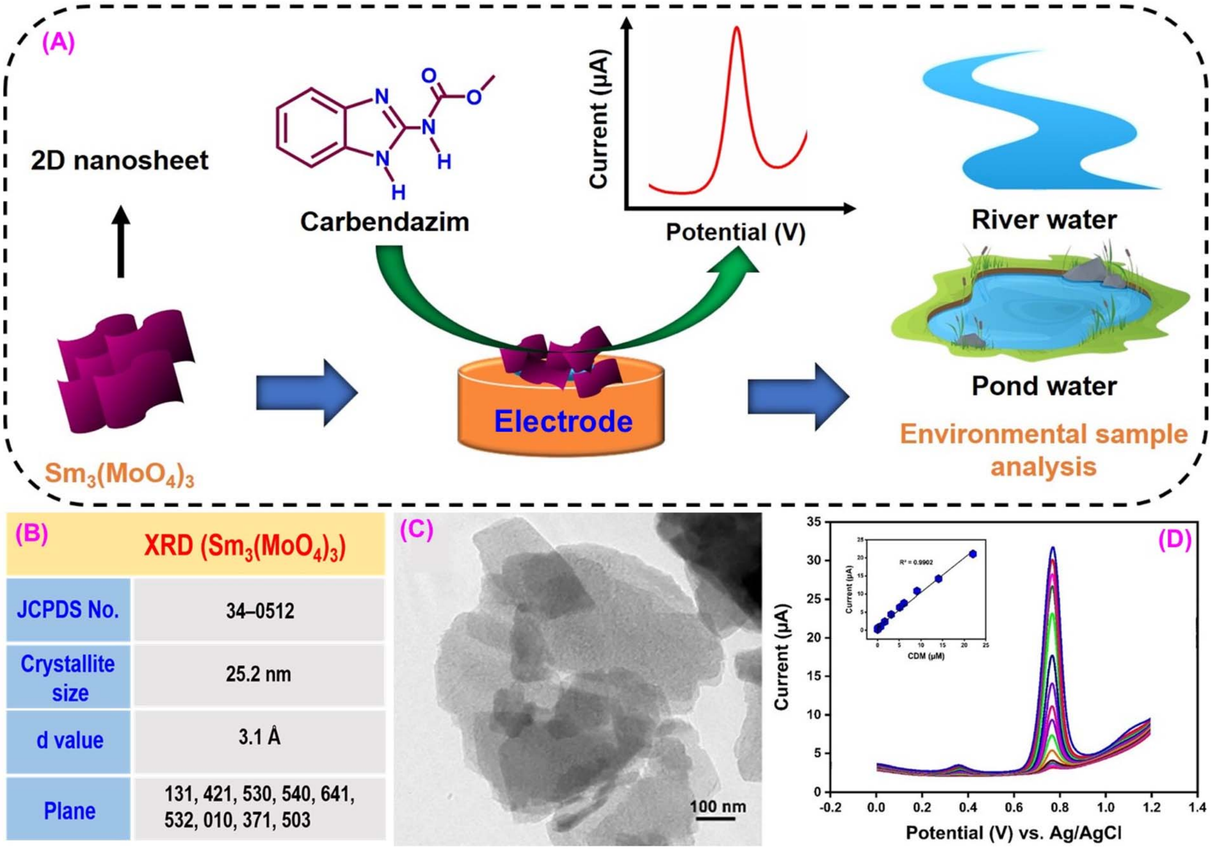


Fig. 3 (A) Graphical illustration of $Sm_3(MoO_4)_3$ as an electrode material for a CRM sensor. (B) Crystal structure studies of $Sm_3(MoO_4)_3$. (C) Morphological studies of $Sm_3(MoO_4)_3$. (D) DPV curves of $Sm_3(MoO_4)_3$ for CRM detection[79] (modified). ((C and D) License number: 5547980179571).

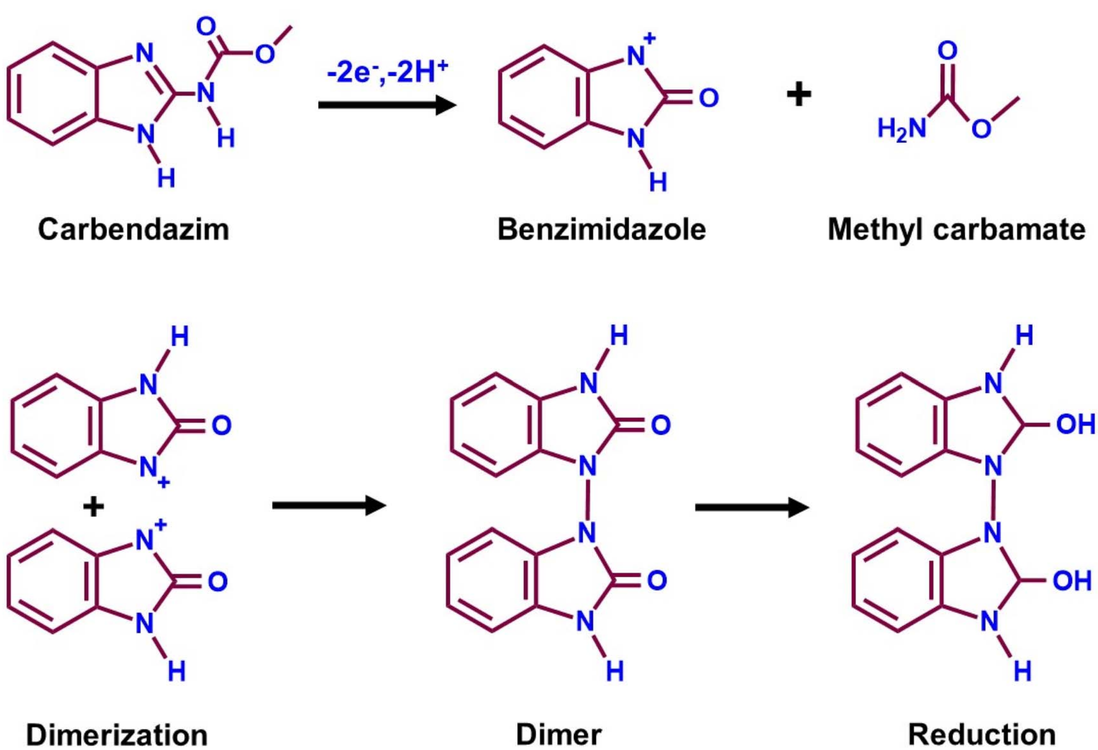


Fig. 4 The possible electrochemical detection mechanism of CRM.

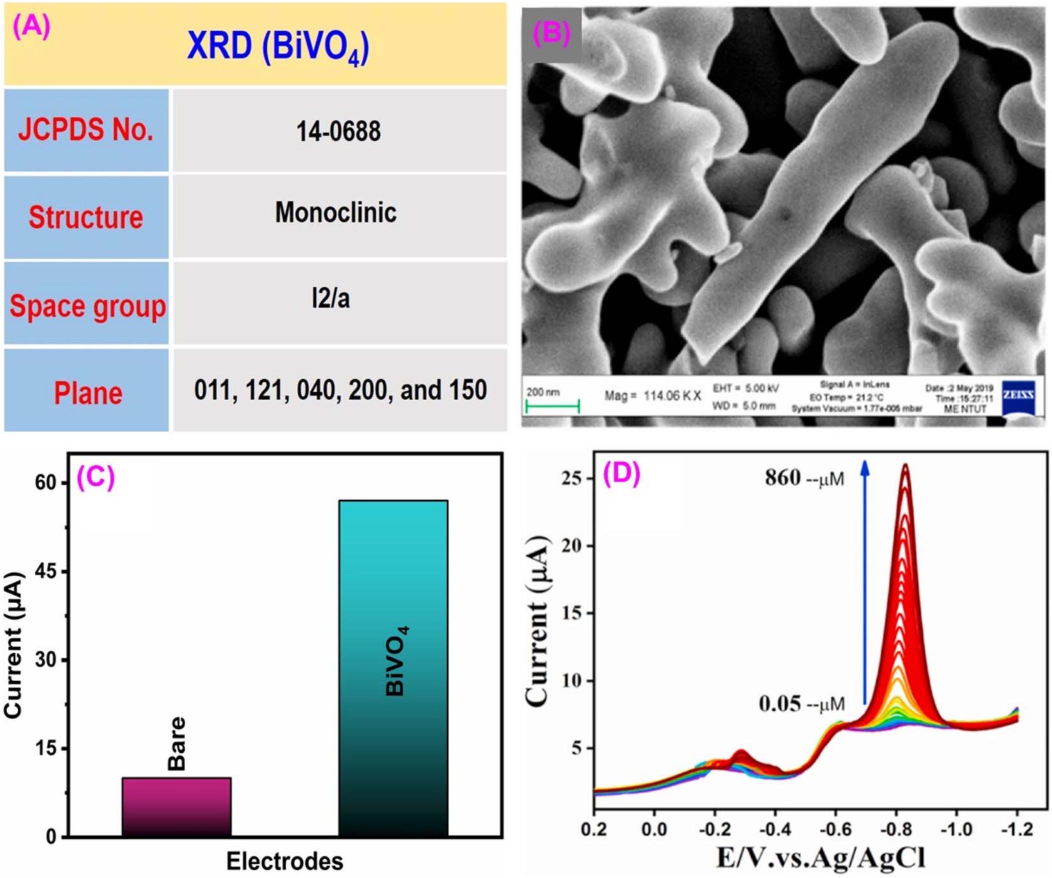


Fig. 5 (A) XRD data of $BiVO_4$. (B) TEM data of $BiVO_4$. (C) CV signal of the bare SPCE and $BiVO_4$/SPCE towards paraoxon detection. (D) DPV signal of $BiVO_4$/SPCE for detection of various concentrations of paraoxon[112] (modified). ((B and D) License number: 5542341491022).

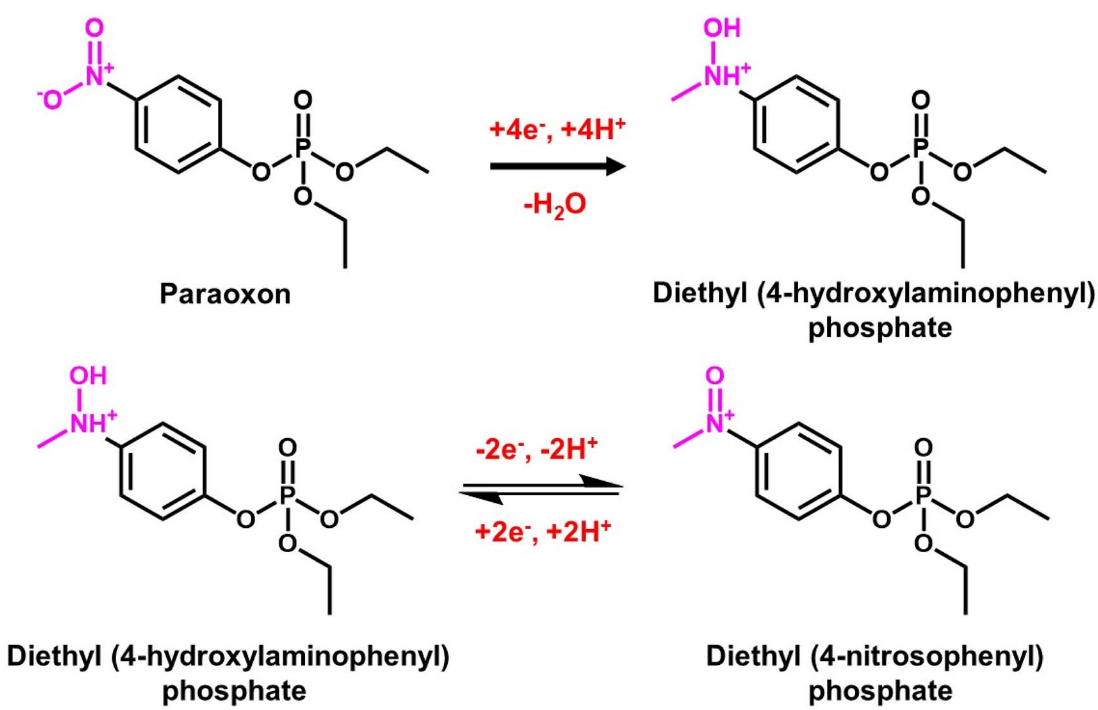


Fig. 6 The electrochemical oxidation mechanism of the paraoxon sensor.

paraoxon is depicted in Fig. 6, and is more similar to previously described literature.[148] Fig. 5D shows the DPV signals for paraoxon concentrations using $BiVO_4$/SPCE. The limit of detection and sensitivity for paraoxon were calculated to be 0.034 μM and 0.0345 μA μM^{-1} cm^{-2}. Compared to conventional detection materials, the $BiVO_4$/SPCE sensor performs admirably.

3.4. Fenitrothion sensor

Fenitrothion (FN) is an organophosphate compound that is widely used as an insecticide in current agricultural practices. However, prolonged exposure to FN poses significant risks to human health and can lead to pollution of food, water, and land sources. It serves an effective solution for controlling flies, cockroaches, and mosquitoes in agricultural contexts and public health initiatives when applied as a residual contact spray.[149–151] Given these concerns, Ganesan *et al.*[152] proposed a green approach for developing dysprosium vanadate ($DyVO_4$) for FN insecticide detection. The crystal structure of the $DyVO_4$ electrode material has been verified using the JCPDS no. 074-0775 reference (Fig. 7A). They developed a $DyVO_4$ electrode material through a hydrothermal approach, which attained a 3D hierarchical micro flower-like morphology (Fig. 7B). Morphological characterization is more critical in the electrochemical sensor since both their shape and size have an impact on their electrocatalytic performance. The $DyVO_4$ modified GCE current response (−52 μA) was four-fold higher than that of the unmodified GCE due to extraordinary properties of $DyVO_4$, such as excellent stability, multilayer architectures, variety of active states, presence of oxygen sites, and higher energy density (Fig. 7C). The R_1 reduction peak results from the transfer of four electrons ($+4e^-$) and four protons ($+4H^+$) from FN's nitro group (NO_2–FN) to the hydroxylamine group (NHOH–FN). Additionally, the reverse scan revealed the presence of the redox peaks O_1 and R_2, which are associated with the conversion of nitroso–FN (NO–FN) from NHOH–FN ($-2e^-$, $-2H^+$) and its subsequent reduction back to NHOH–FN ($+2e^-$, $+2H^+$).[152] According to the DPV studies, the calculated sensitivity and limit of detection values are 14.2 μA μM^{-1} cm^{-2} and 1.4 nM (Fig. 7D). The results of this sensor demonstrate that $DyVO_4$ is a promising tool for monitoring FN in environmental pollutant samples.

3.5. 2,4,6-Trichlorophenol sensor

2,4,6-Trichlorophenol (TCL) is a chlorinated organic compound that has been identified as one of the most hazardous organic

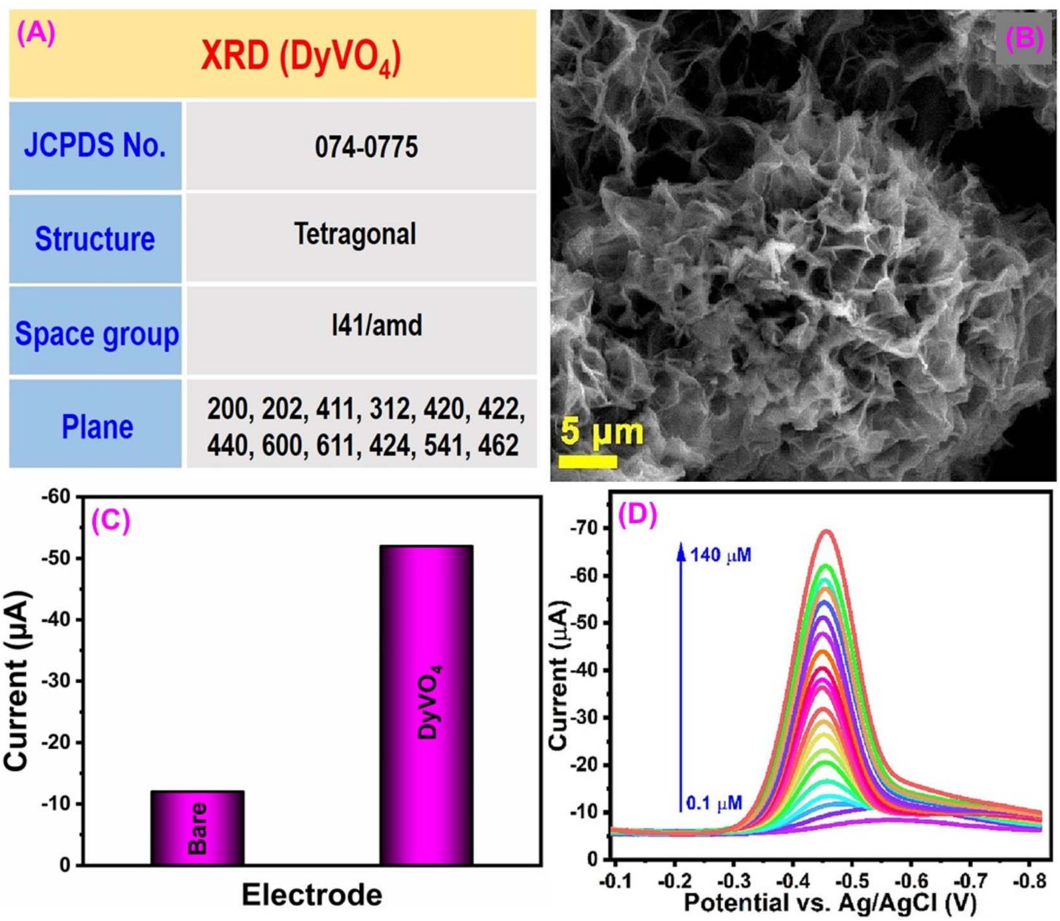


Fig. 7 (A) Crystal structure analysis of $DyVO_4$. (B) Morphological studies of $DyVO_4$. (C) CV response of the bare GCE and $DyVO_4$/SPCE towards FN detection. (D) DPV response of $DyVO_4$/GCE for detection of various concentrations of FN[119] (modified). ((B and D) License number: 5550950069266).

pollutants due to its extensive development and use in industrial and agricultural operations.[153,154] TCL is widely utilized in a variety of sectors, including medicines, disinfectants, insecticides, fungicides, pesticides, and intermediates in the manufacturing of various dyes, as well as wood preservatives.[155] The untreated discharge of TCL-contaminated water into the aquatic environment can harm drinking water and human health.[155,156] Ramadhass *et al.*[157] created a sensor containing lanthanum stannate ($Ln_2Sn_2O_7$) that was synthesized using a simple coprecipitation method and evaluated its electrochemical properties to detect TCL (Fig. 8A). Furthermore, the morphological investigation using FE-SEM determined the structure of the $Ln_2Sn_2O_7$ material (hexagonal nanosheets). On the other hand, the crystal structure (cubic and *hkl* planes) investigation with XRD was used to analyze the physicochemical properties of $Ln_2Sn_2O_7$.[158] An increase in the oxidation current response as compared to bare shows that $Ln_2Sn_2O_7$ has catalytic activity for the electrochemical oxidation of TCL (Fig. 8B). It is possible that TCL behaves similarly to the 4-nitrophenol oxidation mechanism.[157,159] The proposed $Ln_2Sn_2O_7$ electrode-based TCL sensor exhibits a wide linear range (0.1–650 μM), a low-level limit of detection (0.074 μM), and excellent sensitivity (1.5 μA μM^{-1} cm^{-2}) (Fig. 8C). This sensor attained higher levels of storage stability, reproducibility, and repeatability than the diagnostic techniques that have been previously reported,[160–162] and it offers substantial technological breakthroughs. The proposed $Ln_2Sn_2O_7$ electrode-based TCL sensors are the best option for environmental sample monitoring based on the reasonable results of the real sample determination.

3.6. Carbofuran sensor

Carbofuran (CBF), often known as furadan, is one of the most significant carbamate pesticides. It can shorten the growth time of crops and boost agricultural yields.[163,164] Because of their high insecticidal mobility, relatively low ecological persistence, and great efficacy in eradicating insects and pests, carbamate compounds are a wide range of pesticides used extensively around the world.[165] CBF is mainly used to control insects in pumpkins, tomatoes, bananas, mangoes, maize, soybeans, rice, potatoes, corn, and brinjals. It can overstimulate the neurological

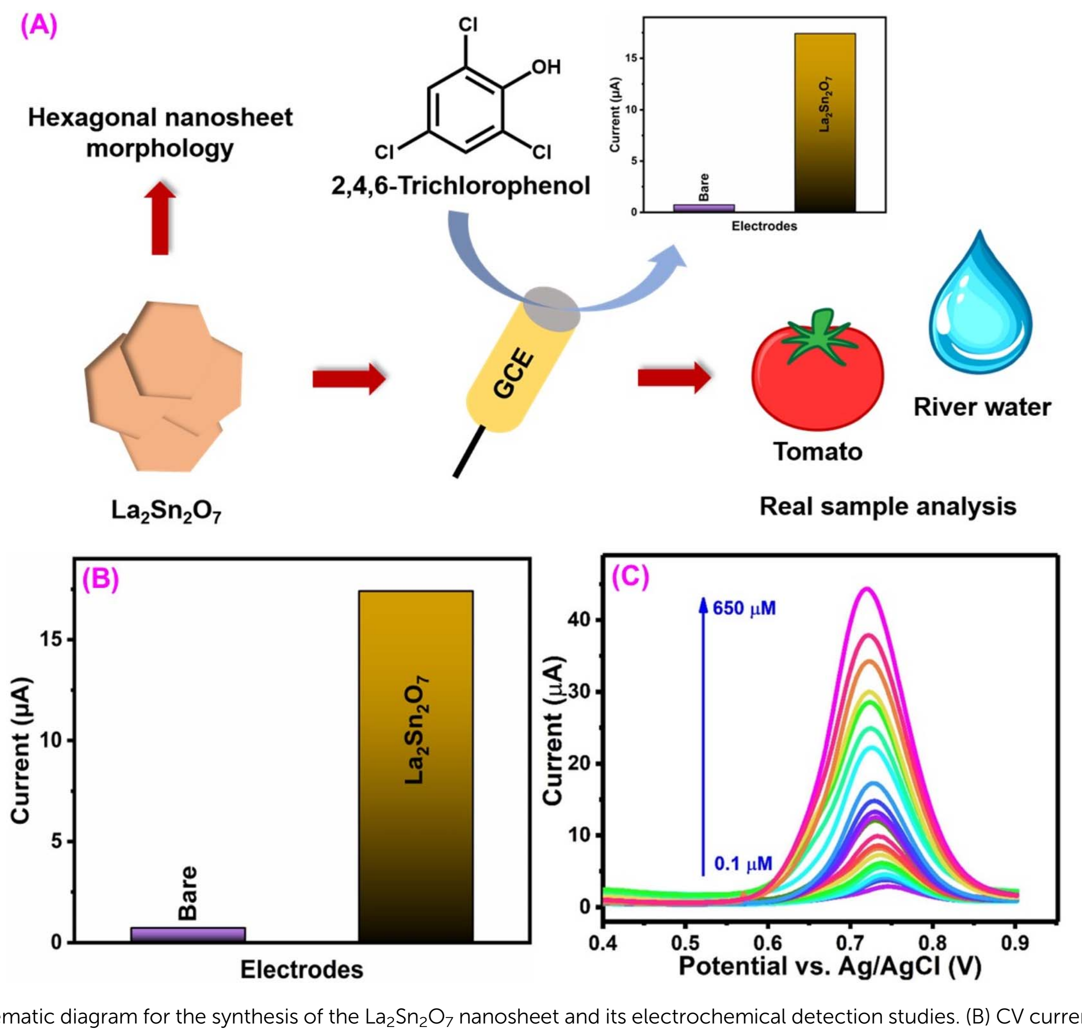


Fig. 8 (A) Schematic diagram for the synthesis of the $La_2Sn_2O_7$ nanosheet and its electrochemical detection studies. (B) CV current response of the bare GCE and $La_2Sn_2O_7$/GCE towards TCL detection. (C) DPV response of $La_2Sn_2O_7$/GCE for detection of various concentrations of TCL[124] (modified). ((C) License number: 5570091012633).

system, leading to death, respiratory paralysis, disorientation, dizziness, and drowsiness.[166] Rajiv *et al.*[167] designed a biogenic iron oxide/magnetic glassy carbon electrode (Fe_3O_4/MGCE) for electrochemical detection of CBF in various vegetable samples. *Artocarpus heterophyllus* seed extract was used to prepare Fe_3O_4 nanoparticles. They attempted a green chemical synthesis of Fe_3O_4 nanoparticles without the use of any surfactant or other reducing reagent. Furthermore, the synthesized Fe_3O_4 was characterized and validated using several analytical techniques.[167] The electrochemical catalytic activity of the Fe_3O_4 on the modified electrode surface must boost the electron transfer process, leading to CBF oxidation (Fig. 9A). Fig. 9C depicts the detailed electrochemical oxidation detection mechanism of CBF.[166] The Fe_3O_4-based CBF sensor has attained excellent sensitivity (6.53 ± 0.084 μA μM^{-1} cm^{-2}), a wide linear range (0.3 to 38.5 μM), and a low limit of detection (0.01 μM) (Fig. 9B). The benefits of the suggested sensor, such as high sensitivity, reproducibility, storage stability, and selectivity have resulted in a significant result for real-world detection of CBF in various food samples. After reviewing the existing literature, it is summarized that the metal oxide-based electrode material is suitable for the electrochemical detection of pesticides in water and food samples (Table 4). Overall, compared to other electrode materials in this study, the $Sm_3(MoO_4)_3$-based electrode materials are more attractive due to their economy, low limit of detection, high sensitivity, and high electrocatalytic activity performance.

4. Environmental sample analysis

Examining the practical applicability is crucial for electrochemical pesticide detection. The electrochemical techniques were also used to detect pesticides in real-world samples. The proposed approach was used to determine pesticides in water and food samples to ensure their applicability in real-world

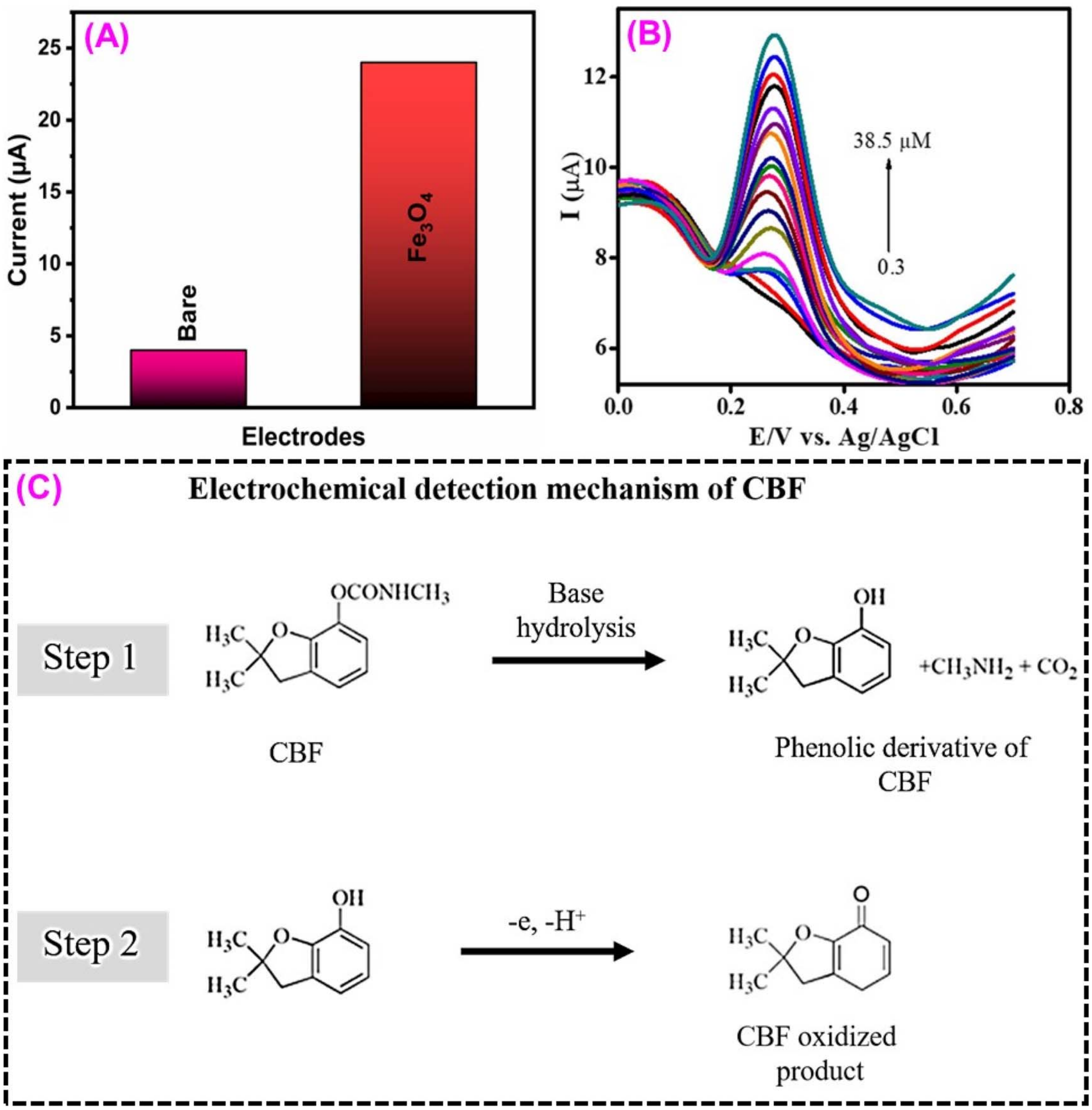


Fig. 9 (A) CV current signal of Fe_3O_4/MGCE and Fe_3O_4/MGCE towards CBF detection. (B) DPV signal of Fe_3O_4/MGCE for the CBF concentrations from 0.3–38.5 μM. (C) Possible electrochemical detection mechanism of CBF[134] (modified). ((B) License number: 5570091331923).

analyses. Zeng *et al.*[168] used the spiking method to evaluate the practical use of the developed sensor in detecting simazine in various water samples. This investigation showed that tap, river, and pond water samples had a high recovery rate.[169] Prabhu *et al.*[170] reported a synthesis of ZnO@Cu nanoparticles with the CTAB surfactant for electrochemical detection of 2,4-dichlorophenol in environmental samples. This study used square wave voltammetry (SWV) with a carbon paste electrode (CPE). The real-time application of the suggested ZnO@Cu/CPE towards 2,4-dichlorophenol was tested using environmental samples such as water, vegetables, and fruits. Furthermore, a one-step co-electrodeposition method was developed for fabricating ZrO_2-decorated graphene-based electrochemical sensors for methyl parathion detection in vegetable samples. This sensor demonstrated excellent stability, reproducibility, and a new and promising approach for pesticide analysis.[171] Moghaddam *et al.*[172] created a Pt/$NiCo_2O_4$ electrode material with distinct structural properties using a hydrothermal approach and subsequently used it as a new platform for carbendazim detection. DPV and liquid chromatography-mass spectrometry (LC-MS) with a SPCE were used for this practical study. This sensor was used to determine pesticides in tomato and lettuce samples to ensure its applicability in real-world analyses. Then, Narayanan *et al.*[173] developed a hybrid nanomaterial CuO/Nd_2O_3 using a one-step coprecipitation approach and investigated a novel platform for non-enzymatic malathion pesticide detection. This sensor electrode material exhibits intriguing electrochemical properties due to its nano-size, stability, and high surface area. The vegetable & fruit extract samples were tested using the DPV technique at varied concentrations of malathion pesticide. The proposed sensor results indicate that the approach is highly accurate in real-world applications. The electrochemical detection of pesticides in environmental samples using metal oxide electrode materials is presented in Table 3.

5. Future perspectives and challenges

Pesticides have been utilized to boost agricultural yields worldwide throughout the past century. However, their environmental residues are extremely toxic to nontarget species such as humans and mammals. Thus, reliable technologies for precisely determining these pesticides are reported in the literature. Electrochemical methods, such as voltammetry, DPV, SWV, and amperometry, are the most widely used technology for detecting electroactive chemicals such as pesticides. The creation of metal oxide-based sensors with improved selectivity, sensitivity, and durability by overcoming the drawbacks of enzyme-based sensors has recently sparked increased interest in developing enzyme-free sensors. The rapid advances in environmental technology may be seen in two areas: expanding worldwide awareness of the effects on the environment and public health and commercialization and large-scale production techniques for creating electrochemical sensors. As efforts are undertaken to address environmental concerns and enhance public health outcomes, these sectors are making substantial progress. The usage of a smartphone-based sensor enables the technology's possible commercialization. This means that the sensor might be manufactured on a bigger scale, sold, and used by individuals or organizations to monitor pesticides in real time. This commercialization potential suggests that the technology may become more accessible and widespread in the future. Various methods for constructing electrochemical detection using new metal oxide electrode materials without supporting other materials have been proposed over the last few decades. These sensors, which incorporate greater stability and sensitivity, were designed using several materials' remarkable chemical, physical, and electrical features. Furthermore, using metal oxide electrode materials can potentially satisfy multi-detection requirements in real-world applications. Combining optical and electrochemical sensors into a dual-sensor system results in enhancing applicability and minimizing false positive signals possible. While only a limited number of preliminary studies have explored using metal oxide-based sensors for rapidly detecting pesticides in food, agriculture, health, and other domains, such platforms are essential for addressing future human health challenges and promoting a better quality of life.

There are several challenges associated with this approach. The characterization of these electrodes can be tedious and time-consuming. Additionally, there is uncertainty surrounding the mechanism of the electrode process, and the stability and toxicity of metal oxides pose further concerns. Incorporating metal oxides into molecularly imprinted polymer-based sensors

Table 3 A summary of metal oxide electrode material-based electrochemical detection of pesticides in water and food samples

Materials	Pesticides	Real samples	Recovery (%)	RSD	Reference
GeO_2@Pd	Simazine	Water	92–111	0.42 to 1.58	169
ZnO@Cu	2,4-Dichlorophenol	Water	98.03–99.85	0.218–0.946	170
		Vegetables & fruits	97.08–105.52	0.786–2.810	
ZrO_2	Methyl parathion	Vegetables	96.5–104.4	1.0–4.2	171
CuO NFs	Chlorpyrifos	Fruits and vegetables	95.98–106.72	2.25–4.82	188
Pt/$NiCo_2O_4$	Carbendazim	Vegetables	97.3–103	1.9–2.8	172
CuO–Nd_2O_3	Malathion	Vegetables & fruit extract	94.0–101	1.41–9.26	173
CuO/TiO_2	Methyl parathion	Ground water	98.80–106.72	2.13–3.45	85
TiO_2/CTAB	Aminotriazole	Water	96.23–99.56	0.17–1.26	189
Cu/RGO	Carbendazim	Pond water	99.7–102.2	—	190
SiO_2–MnO_2	Paraoxon	Water	97.9–104.4	2.1–8.8	191
Fe_3O_4@SiO_2	Imidacloprid	Water, fruits & vegetables	94.80–109.40	1.22–10.39	192
Ag/ZnO	Phoxim	Water & vegetables	94.3–105.7	4.08–4.97	193

Table 4 Important findings and summary of the present results

Metal oxide	Important finding	Ref.
Neodymium molybdate	The hydrothermal method was utilized to create 3D flower-like neodymium molybdate (pf-$Nd_2Mo_3O_9$), which was then used to build an electrochemical sensor for methyl parathion (MPN) detection As a result of their large surface area (0.18 cm^2), superior charge transit, and more active sites, the peak current response was greater after modifying pf-$Nd_2Mo_3O_9$/GCE compared to the unmodified glassy carbon electrode (GCE)	91
Samarium molybdate	Samarium molybdate ($Sm_3(MoO_4)_3$) with a significant level of active sites used for electrochemical detection of carbendazim (CRM) in environmental samples Due to a variety of extraordinary features of $Sm_3(MoO_4)_3$, such as chemical stability, abundant reserves, and multivalence, the $Sm_3(MoO_4)_3$ modified screen-printed electrode (SPCE) current response (6.6 μA) was two-fold greater than that of the unmodified SPCE	92
Bismuth vanadate	$BiVO_4$ as an electrocatalyst in a high-performance electrochemical sensor for the detection of hazardous paraoxon pesticide The synthesized $BiVO_4$ exhibited higher conductivity, enough oxygen vacancies, and chemical stability The modified $BiVO_4$ material displays a strong current response and a small potential window when compared to bare SPCE, showing that the $BiVO_4$ material has superior electroconductivity for paraoxon detection	145
Dysprosium vanadate	Due to $DyVO_4$'s extraordinary features, such as superior stability, multilayer structures, a diversity of active states, the presence of oxygen sites, and increased energy density, the current responsiveness of the $DyVO_4$ modified GCE (−52 μA) was four times that of the unmodified GCE	152
Lanthanum stannate	The $La_2Sn_2O_7$ sensor exhibits a lower charge transfer resistance compared to the unmodified electrode, leading to an increased anodic current response TCL's high sensitivity, excellent selectivity and a wide linear range allows for a low detection limit	157
Iron oxide	This sensor utilizes Fe_3O_4 nanoparticles that are synthesized using an eco-friendly and sustainable approach, employing a seed extract derived from *Artocarpus heterophyllus* The electrochemical catalytic activity of Fe_3O_4 on the modified electrode surface must boost the electron transfer process leading to CBF oxidation	167

can enhance the sensing of analyte molecules through guest–host interactions, but it may also introduce instability in some instances. Moreover, the preparation of electrodes can be costly and time-consuming, which can affect consistency. Synthetic routes for metal oxides often require special conditions, impacting their size, shape, stability, and, ultimately, the reproducibility of the sensor. Other parameters, such as electrolyte, temperature, and humidity, also influence the sensing abilities of pesticides. The stability and function of the sensor can be impacted by temperature and moisture, lowering its sensitivity and reaction time. The electrolyte can influence the target pesticide's chemical reactivity and solubility, which will affect the sensor response. Nevertheless, despite these challenges, the development of such sensing devices plays a vital role in improving various aspects of our lives. These devices significantly impact addressing issues related to environmentally hazardous materials, ensuring food safety, enhancing pharmaceutical and clinical diagnostics, and enabling effective security surveillance. Looking ahead, it is hoped that future research will yield promising results in producing cheaper and more environmentally friendly electrode materials, further advancing electrochemical sensing applications.

6. Conclusions

Accurate and direct pollution detection is a constant concern in environmental monitoring, health, life, and food safety. Rapid identification of pollutants in the environment is difficult, due to a lack of convenient and reliable detection methods. Electrochemical sensors are potential tools for detecting a wide range of biochemical targets, heavy metal ions, and environmental contaminants. This has a wide range of applications in environmental monitoring and other domains. The less expensive technology that benefits the public, particularly for agricultural uses, should be employed to put this research to good use. Metal oxides also have a bright technical future because they are economical and simple to prepare, and have various composition and preparation variables that can be used. The review article provides a comprehensive summary of recent advancements in metal oxide synthesis methods, properties, mechanisms, and the use of metal oxide-based electrochemical sensors for detecting pesticides in environmental samples. Furthermore, the study focuses on discussing various metal oxides (including neodymium molybdate, samarium molybdate, bismuth vanadate, dysprosium vanadate, lanthanum stannate, and iron oxide) employed in the electrochemical detection of pesticides (such as methyl parathion, carbendazim, paraoxon, fenitrothion, 2,4,6-trichlorophenol, and carbofuran) in water and food samples. Based on this study's findings, the $Sm_3(MoO_4)_3$-based electrode material outshines other metal oxide electrode materials due to their economy, low detection limit, high sensitivity, and high electrocatalytic activity performance. Furthermore, developing an electrochemical sensor based on new metal oxides is a promising topic for improving sensitivity and selectivity. Using metal oxide-based portable sensors is likely to change commercial sensor technology in the future.

Conflicts of interest

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

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