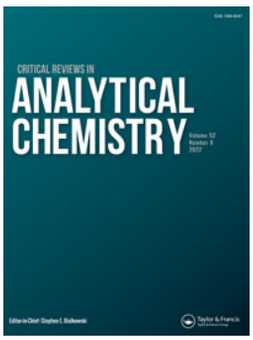

Critical Reviews in Analytical Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/batc20

Electrochemical (Bio)Sensors for the Detection of Organophosphorus Pesticides Based on Nanomaterial-Modified Electrodes: A Review

Rong Ding, Zhaojie Li, Yan Xiong, Wei Wu, Qingli Yang & Xiudan Hou

To cite this article: Rong Ding, Zhaojie Li, Yan Xiong, Wei Wu, Qingli Yang & Xiudan Hou (2022): Electrochemical (Bio)Sensors for the Detection of Organophosphorus Pesticides Based on Nanomaterial-Modified Electrodes: A Review, Critical Reviews in Analytical Chemistry, DOI: 10.1080/10408347.2022.2041391

To link to this article: https://doi.org/10.1080/10408347.2022.2041391

CRITICAL REVIEWS IN ANALYTICAL CHEMISTRY
https://doi.org/10.1080/10408347.2022.2041391

Taylor & Francis
Taylor & Francis Group

REVIEW ARTICLE

Electrochemical (Bio)Sensors for the Detection of Organophosphorus Pesticides Based on Nanomaterial-Modified Electrodes: A Review

Rong Ding[a], Zhaojie Li[a], Yan Xiong[b], Wei Wu[a], Qingli Yang[a], and Xiudan Hou[a]

[a]College of Food Science and Engineering, Qingdao Agricultural University, Qingdao, China; [b]Weihai Customs, Weihai, China

ABSTRACT

Organophosphorus pesticides were easily remained in fruits and vegetables which would be harm to the environmental safety and human health. In recent years, due to the simple preparation process, fast response and high sensitivity, the electrochemical (bio)sensors have received increasing attention, which were extensively used as the sensing platform for the detection of OPPs. The mechanisms for the determination of OPPs mainly included redox of nitrophenyl OPPs, enzyme hydrolysis and inhibition, immunosensor, aptasensor. Nowadays, the mainly explored electrode material has focused on metal-organic frameworks, metal and metal derivatives, carbon materials (carbon nanotube, graphene, g-C_3N_4), MXene, etc. These nanomaterials played important roles in the electrochemical (bio)sensors, which included: (a) as an electrocatalyst to promote the redox reaction, (b) as a carrier to load the enzyme or aptamer, (c) as a recognizer to identify the targets. The nanomaterials-based electrochemical (bio)sensor was a rapid, cost-effective methods to detect OPPs with high sensitivity. Besides, this review compared the analytical performance of different nanomaterials-based electrochemical (bio)sensors, and also identified the key challenges in the future. It would provide new ideas and insights to the further development and application of electrochemical (bio)sensors and the detection of pesticides in real samples.

KEYWORDS

Acetylcholinesterase; aptamer; electrochemical (bio)sensor; nanomaterial; organophosphorus pesticides

Introduction

Pesticides (i.e., insecticides, fungicides, herbicides, etc.), as the main food and environmental pollutants, are widely used in agricultural production, directly acting on the plant surface and soil.[1] However, only a small amount of sprayed pesticides has achieved the desired goal. The accidental spillage of pesticides would be the long-term retention in environmental samples, and cause the environmental pollution problem. Among them, organophosphorus pesticides (OPPs), as a class of compounds containing ester bonds, have been widely used in the agricultural production and greatly improved the effectiveness of agricultural pest control due to the high efficiency and broad spectrum.[2] On the other hand, with the rapid growth of population, the demand for food production is also increasing, which puts pressure on the intensive use of OPPs. However, OPPs have a long half-life and break down when exposed to sunlight in the air. Excessive use and accumulation in environment can lead to the pollution of soil, water and air. In addition, it is estimated that OPPs remains in soil (2.62-129 μg kg^{-1}), water (0.85-16.24 μg L^{-1}), and fruits and vegetables (40 pg g^{-1}) for a period of time and thus can reach human systems through the food chain with little effort, and the residual OPPs pose serious risks to environmental safety and human health. The high toxicity of OPPs are mainly due to the fact that they would combine with cholinesterase to form the stable phosphorylated cholinesterase in vivo, and the activity of cholinesterase is inhibited.[3] Acetylcholinesterase (AChE) can catalyze the hydrolysis of acetylcholine into choline and acetate. When the activity of AChE is inhibited, a large number of acetylcholine would be accumulated to cause the high excitation of cholinergic nerve fibers and further cause the impaired neuromuscular activity of organisms with AChE, even fatal.[4] OPPs also pose a threat to the neuroendocrine, physiological and metabolic systems, leading to complications such as neuritis, neuroteratogenesis and genotoxicity.[5] Upon investigation, The global consumption of OPPs was 5 million tons in 2010 and 6.8 million tons from 2011 to 2015. In view of the widespread use of OPPs, it is believed that OPPs contaminate fruits, vegetables and water resources and adversely affect the health of humans and other animals. Therefore, current and future increases in food production must be better quality and fewer OPPs. Therefore, it is necessary to develop efficient, rapid and sensitive methods to determine OPPs.[6]

Traditional detection and analysis methods for OPPs mainly included gas chromatography, gas chromatography-mass spectrometry, high performance liquid chromatography, high performance liquid chromatography-mass spectrometry, enzyme-linked immunosorbent assay, etc.[7–10] These analytical techniques exhibit high accuracy and feasibility for the detection of pesticides, but they also require

CONTACT Xiudan Hou qdxdhou@qau.edu.cn College of Food Science and Engineering, Qingdao Agricultural University, No. 700 Changcheng Road, Qingdao 266109, China

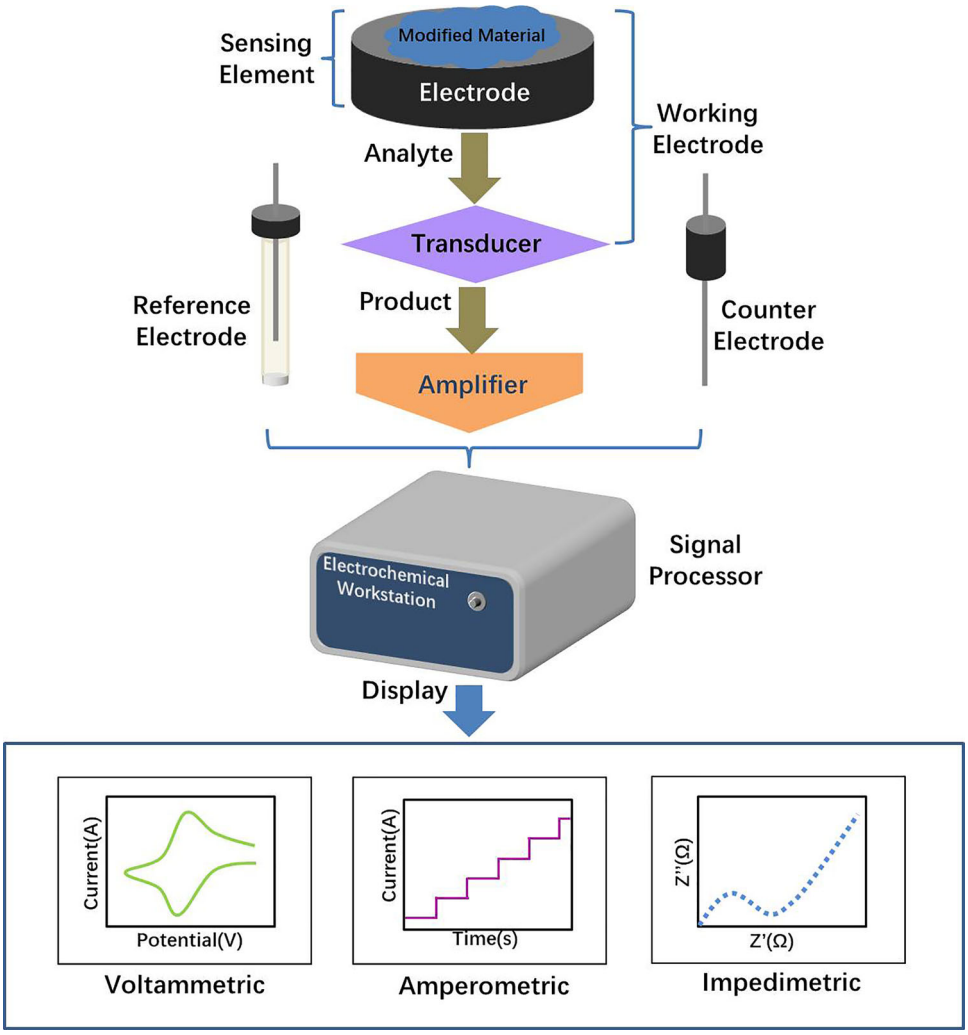

Figure. 1. Schematic diagram of a conventional electrochemical sensor.

extremely complex sample pretreatment, precision instruments and professional technicians and long analysis time, which greatly limit the convenience of their application in real samples.

Electrochemical sensors have attracted more and more attention to be as a sensing platform for the detection of OPPs due to the simple preparation process, fast response and high sensitivity. A chemical signal was generated through the interaction between a sensing membrane (namely a modified electrode material) and the target molecules, and then the chemical signal was converted into a measurable electric signal via a conversion element. The content of unknown analyte was calculated based on the corresponding relationship of between the displayed electrochemical signal and the concentration of standard analyte to be detected. It can be broadly divided into current/potential sensors, electrochemical luminescence sensors, electrochemical impedance sensors and photoelectrochemical sensors. As shown in Figure 1, the traditional electrochemical sensor was composed of a three-electrode system of a working electrode, a reference electrode and an auxiliary electrode. Generally, the electrochemical techniques used for the detection of OPPs can be classified into voltammetry, amperometry and potentiometry. It is noteworthy that voltammetric techniques such as cyclic voltammetry (CV), differential pulse voltammetry (DPV), square wave voltametry (SWV), linear sweep voltametry (LSV) and electrochemical impedance spectroscopy (EIS) are the most familiarly detected strategies.[11–13] In this process, the electrode material plays a vital role to improve electrochemical activity and response.

Nanomaterials-based electrochemical sensor with high sensitivity and specificity is an ideal choice for the detection of OPPs. Therefore, this paper reviewed the recent research progress of electrochemical sensor for detecting OPPs, mainly including the detection mechanism for OPPs, electrode materials and other characteristics of various electrochemical biosensors based on different electrode materials.[14] This review summarized four types of electrochemical sensor for the identification toward OPPs, which included redox of nitrophenyl OPPs, enzyme inhibition, DNA-based electrochemical biosensor, electrochemical immunosensor. Nowadays, the mainly explored electrode materials have focused on metal and metal derivatives, metal-organic frameworks (MOFs), carbon materials, MXene, etc. The construction and integration of the sensor based on these nanomaterials would provide a more realistic and concise vision, and also expand the application of electrochemical sensor in various fields.

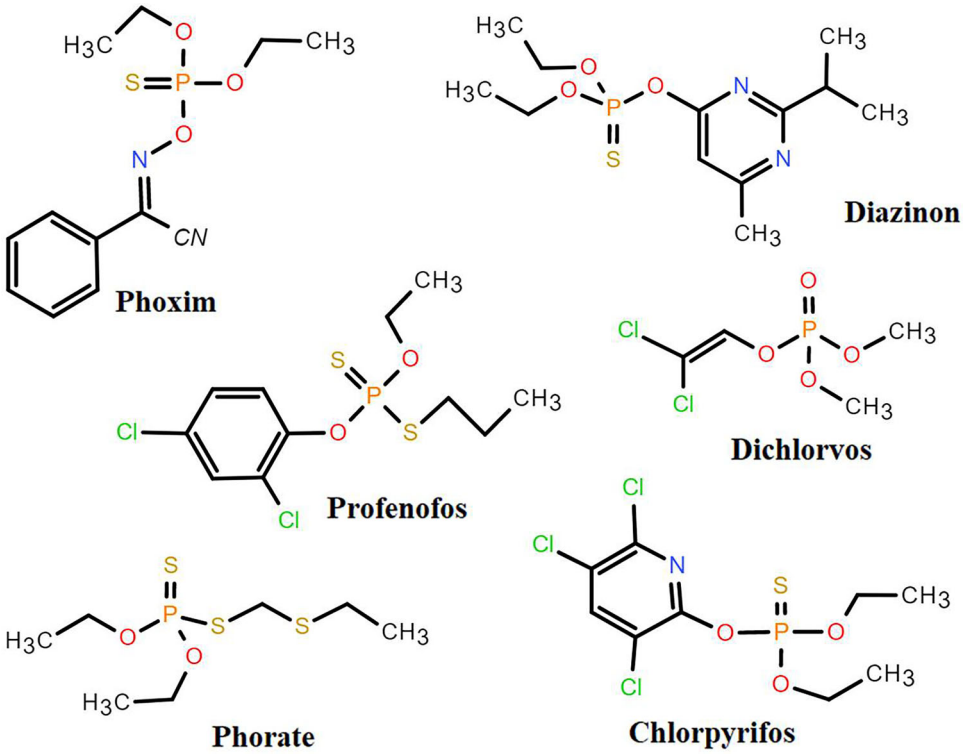

Figure. 2. The chemical structure of representative OPPs.

Electrochemical mechanism

OPPs are essentially esters of phosphoric acid with different combinations of oxygen, nitrogen, carbon and sulfur. All OPPs have a common structural pattern, which contain a phosphorus atom in the center connecting with a double bond to an oxygen or sulfur atom, and alkoxy/thioalkoxy/aryloxy (O-R, O-R') and alkoxy/propyl/other substituents (X) are attached to the phosphorus atom. Different X、R、R' resulted in the various toxicity of OPPs.[15] The representative OPPs (phorate, phoxim, chlorpyrifos, diazinon, profenofos and dichlorvos, etc.) were shown in Figure 2. The advantages and disadvantages of electrochemical (bio)sensors with different electrochemical mechanisms for the detection of OPPs and their applications were shown in Table 1.

Redox of nitrophenyl OPPs

Nitrophenyl OPPs (i.e., paraoxon, parathion, methyl-parathion, etc.) are considered to be highly toxic, and paraoxon is the most toxic among them. Parathion and methyl-parathion (MP) can be decomposed into paraoxon through a series of photolysis and oxidative decomposition.[16] Nitrophenyl OPPs can directly generate an electrochemical response on the electrode surface due to the structural characteristics of nitrophenyl OPPs, and the response is derived from the reduction of nitro group (-NO_2). The reduction potential is relatively negative, and a plurality of substances which can interfere with the reduction potential are more disadvantageous to the detection of nitrophenyl OPPs, so OPPs can be indirectly quantified by detecting a reduction peak of a -NO_2 reduced intermediate product with a relatively low potential.

Electrochemical (bio)sensors based on the reduction of -NO_2 have emerged in recent years. Gannavarapu et al reported a simple and scalable technique for the preparation of ordered nanostructured diatom-zirconia complexes as a highly selective and sensitive non-enzymatic electrochemical sensor for the detection of MP.[17] Figure 3 exhibited the electrochemical sensing pathway. The electrochemical response of this sensor resulted from the conversion of -NO_2 to hydroxylamine group -NHOH with a strong irreversible reduction peak, and the conversion of the formed -NHOH to nitrosophenyl group (-NO) during the anodic scanning, which was a reversible reaction. The voltammograms recorded in the absence of MP yielded no peaks, which indicated that there was no electron transfer occurring in the absence of analyte. Shanmugam et al. prepared N, S co-doped reduced graphene oxide (GO) nanocomposites loaded with SnS_2 nanosheets (SnS_2/NS-RGO) to detect MP through the continuous cyclic voltammetry response.[18] In the first cycle, the irreversible current peak from NO_2-MP to NHOH-MP pair of reversible redox peaks was generated in −0.041 V and −0.066 V resulted from the $2e^-$ and $2H^+$ transfer. Besides, the wide-range concentration addition of MP and the sensitivity at SnS_2/NS-RGO were investigated by using an amperometric (i-t) procedure. Results indicated that the established method possessed high sensitivity (4.033 $\mu A\ \mu M^{-1}\,cm^{-2}$), lower detection limit (0.17 nM), and wider linear range (0.001-176 μM). Through the feasibility analysis of electrochemical detection of MP in river water and black grape samples by SnS_2/NS-RGO, it was found that the added MP had good recovery. However, in this mechanism, the irreversible reduction process would cause huge damage to the electrode to increase the detected cost.

Table 1. Application of electrochemical (bio)sensors with different electrochemical mechanisms for the detection of OPPs.

Electrochemical mechanism	Recognition element	Advantages	Disadvantages
Redox of nitrophenyl OPPs	Nitro(-NO_2)	Simple, fast, high sensitivity	Damage to electrodes, increased cost
Enzyme hydrolysis or inhibition	Enzymes	Wide range of detection, low detection limit	Enzymes are easily inactivated and not easily controlled
Electrochemical immunosensor	Antigen Antibody	High sensitivity and strong specificity	High cost of identifying original
Electrochemical aptasensor	Aptamers	Low synthesis cost and high purity, specific recognition	For OPPs, the screening of small molecular substances needs to be improved
Molecularly imprinted electrochemical sensors	Molecularly imprinted polymer	High selectivity, reliability, improved stability, low cost	Long analysis time, slow diffusion of target molecules on the imprinted membrane, and uneven distribution of binding sites

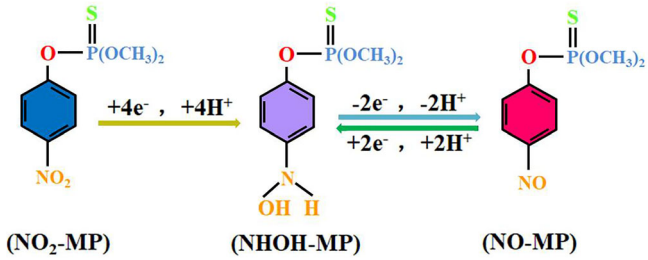

Figure. 3. Mechanism the electrochemical detection of MP.

Enzyme hydrolysis or inhibition

Enzyme-based biosensors exhibit excellent performance in the monitoring of pesticides, which are considered to be the most promising alternative approach. AChE-based optical and electrochemical sensors, whether inhibitory or non-inhibitory biosensor systems, all possessed great prospect of applications. In the case of amperometricresponse, OPPs was measured through the electrochemically active products with various immobilization strategies. Generally, the electrochemical biosensor mainly included cholinesterase-based biosensor (cholinesterase inhibitor/indirect method) and phosphohydrolase (OPH)-based biosensors (direct method), and due to the sensitivity of enzyme to multiple analytes, the former was more common and less selective for OPPs.[19]

OPH can directly catalyze the hydrolysis of phosphorus-oxygen, phosphorus-sulfur bond, phosphoru-fluorine and phosphorus-cyanogen bonds. OPH exhibits strong hydrolysis toward parathion and paraoxon, and their hydrolysis products are usually electroactive substances. For example, OPH can catalyze the hydrolysis of paraoxon to generate p-nitrophenol, and then p-nitrophenol can produce oxidation-reduction reaction on the surface of electrode to produce the current signal, which is proportional to the concentration of paraoxon to realize the quantitative analysis. Stoytcheva et al. developed an electrochemical organophosphorus hydrolase sensor for the direct determination of paraoxon.[20] Firstly, the chitosan (CS), carbon nanotubes, hydroxyapatite and organophosphorus hydrolase were immobilized on the surface of glassy carbon electrode by one-step electrodeposition method, and experimental conditions were optimized via CV and chronoamperometry methods. A good linear relationship between the current and the concentration of paraoxon was found in the range of 5-80 μM L^{-1}. The sensitivity and detection limit were 5.1 nAL μM^{-1} and 0.1 μM L^{-1}, respectively. Recoveries of paraoxon in tap water were between 98.4% and 101.2%, and the established sensor showed good anti-interference ability to atrazine and trichlorfon. Besides, the sensor had good repeatability and relative standard deviation was less than 3%. Therefore, the electrochemical biosensor based on OPH can directly detect OPPs quantitatively using OPPs as enzyme substrate, but many studies have shown that the sensitivity is low. Therefore, the current research focuses on improving the sensitivity of the electrochemical biosensor based on OPH to detect OPPs.

Compared with the OPH-based electrochemical biosensor, the AChE-based electrochemical biosensor possessed higher sensitivity and lower detection limit, However, it was indirect determination and the sensor response was irreversible. Based on the inhibition of OPPs for the AChE activity, AChE can catalyze the hydrolysis of acetylthiocholine to generate acetic acid and thiocholine, and thiocholine as an electroactive substance, can generate redox current under a certain voltage. OPPs being structurally similar to acetylcholine, is a natural substrate of AChE, so OPPs have higher specific bonding interaction with AChE. They can be combined with hydroxyl of serine in the active center of AChE to form stable phosphorylated or carbamylated enzyme, thereby inhibiting the activity of enzyme, reducing the yield of thiocholine, correspondingly, reducing the oxidation current of thiocholine, and establishing a quantitative relationship between the inhibition rate of enzyme activity and the concentration of pesticides through the change of current.[21,22] Therefore, the detection and quantitative analysis of OPPs were realized. The detection process of AChE toward OPPs based electrochemical biosensors was shown in Figure 4. He et al reported a electrochemical biosensor for the rapid determination method of malathion based on the adsorption/desorption process of AChE, in which AChE was anchored on the acicular polyaniline-coated carbon hollow sphere core-shell (HCS@PANI) nanostructure composite.[23] It was found that the developed electrochemical biosensor had practicability, accuracy and applicability for the detection of malathion in food and environment samples (tap water, apple, tomato and cucumber). The proposed method with HCS@PANI nanocomposite as the sensitive layer for the immobilization and catalysis of AChE had potential application in the highly sensitive detection of pesticides. Zhao and his colleagues have developed a disposable and portable enzyme-based biosensor using two-dimensional

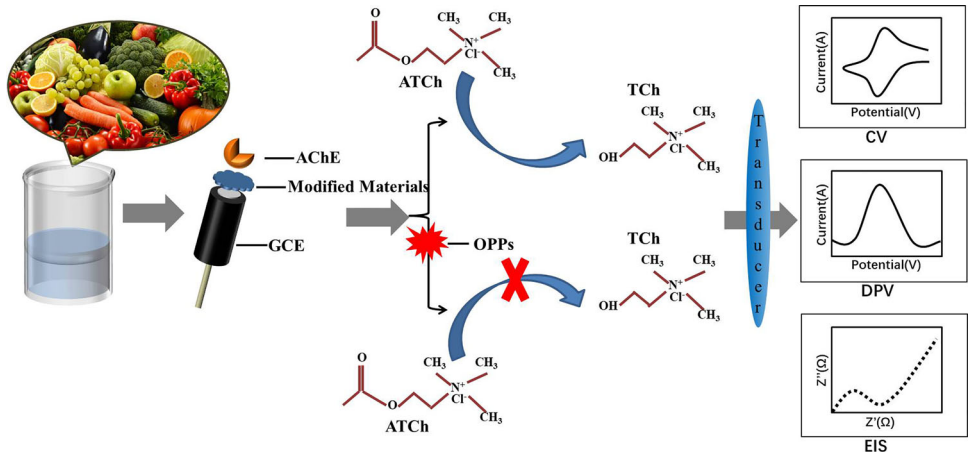

Figure. 4. The detection process of AChE based electrochemical biosensors toward OPPs.

transition metal dihalides.[24] The screen-printed electrode (SPE) was used as the electrode substrate to improve the sensing performance on the basis of the modification of MoS_2 nanosheets and gold nanoparticles, and the immobilization of AChE via glutaraldehyde as the crosslinking agent. Under the optimized conditions, the electrochemical biosensor showed a good linear relationship with the concentration of paraoxon in the range of 1.0-1000 μg L^{-1}, and a detection limit of 0.013 μg L^{-1}. The biosensor was successfully applied to detect paraoxon in apple and pakchoi, and exhibited a good response. The low-cost, rapid and reliable determination of OPPs in agricultural products was realized, which provided a reliable method for the rapid detection of OPPs in agricultural product.

He et al. reported a co-reactant free electro-chemiluminescence (ECL) enzyme-based biosensor using polymer nanoparticles (PFBT PNPs) as a luminophore for the detection of OPPs.[25] In the absence of OPPs, H_2O_2 from the enzymatic reaction inhibited the ECL signal of PFBT PNPs, resulting in an ECL off state, whereas in the presence of OPPs, the ECL signal was significantly enhanced. The linear range of detection was from 1.0×10^{-12}-1.0×10^{-7} M and the detection limit was as low as 1.5×10^{-13} M. Lettuce, cabbage, and pakchoi purchased from the local supermarket after the preliminary treatment was used as samples to study the effectiveness of the biosensor, indicating that this method has the potential for rapid and sensitive detection of OPPs in food analysis. This non-co-reactant strategy avoided the addition of exogenous species or dissolved oxygen as a co-reactant, and more importantly, H_2O_2 was released by many oxidase-induced reactions, which opened up a promising avenue in the field of enzymatic biosensor. Considering the cost of AChE, Bao et al reported a cost-effective plant esterase (PLaE) enzyme being alternative to AChE.[26] The high-purity PLaE extracted from many plants such as wheat, soybean, rice and sorghum at low cost, which had the same inhibition mechanism with AChE. This method exhibited a good response recovery in the real samples (carrots and apples) contaminated by OPPs. PLaE was easy to obtain, so the simple, sensitive and reliable PLaE-CS/AuNPs-GNs composite biosensor had great potential in the detection of OPPs in food and environmental safety. PLaE, a good substitute for AChE, was expected to be one of the research hotspots of AChE-based biosensor.

Electrochemical immunosensor

Electrochemical immunosensor, which combined the traditional immunoassay and biosensing technology, was based on the specific immunoreaction between antigen and antibody (Ab) to convert into the measurable electric signal. The immunosensor had high sensitivity and strong specificity.[27,28] In recent years, electrochemical immunosensors for the detection of pesticide residues have gained more attention and application.[29,30] A novel amperometric immunosensor for the determination of chlorpyrifos residue was developed by Sun et al, which used multi-walled carbon nanotubes-thionine-chitosan (MWCNTs-THI-CHIT) nanocomposite film as electrode the modified material.[31] Then the anti-chlorpyrifos monoclonal Ab was covalently immobilized on the surface of MWCNTs-THI-CHIT/GCE at the aid of glutaraldehyde. The modification process was characterized by CV and EIS. The high stability of the MWCNTs-THI-CHIT modified GCE made it easier to immobilize antibodies on the proposed immunosensor, to ensure effective activity retention of the loaded immunoreactants, which could improve the sensitivity and accuracy of the immunosensor. Besides, because CHIT and THI could protonate NH_2 groups, the immunosensor was easily regenerated and reused. Under the optimized conditions, the relative change of peak current of DPV was linear with the logarithm of chlorpyrifos concentration in the range of 0.1-1.0 $\times 10^5$ ng mL^{-1}, and the limit of detection was 0.046 ng mL^{-1}. The proposed immunosensor exhibited high repeatability, stability, good selectivity and reproducibility, which made it a potential alternative tool for the ultrasensitive detection of chlorpyrifos residues in vegetables and fruits (cabbage, lettuce and Chinese chives).

So far, most of the immunosensors used to detect multiple pesticide residues have based on the superposition of single detection. For more OPPs, it is far from meeting the detected needs of actual samples. Therefore, a broad-spectrum Ab for detecting OPPs has been gradually reported, and the Ab can effectively recognize most OPPs. It is

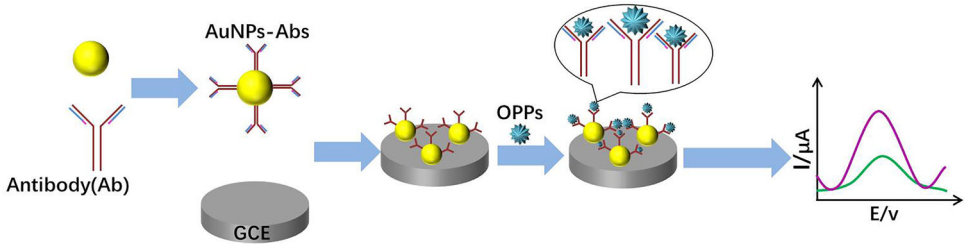

Figure. 5. Detection principle of the electrochemical immunosensor.

necessary to develop immunosensors based on a broad spectrum of Abs to detect all OPPs.

Dong et al. used a broad-spectrum Abs against OPPs as a sensitive recognition element, and attempted to couple the broad spectrum Abs with gold nanoparticles (AuNPs) to form AuNP-Abs.[32] The method can not only reduce the waste of Abs, but also enhance the combination of Abs and nanomaterials. Prussian blue (PB) with good redox properties was immobilized on the electrode surface by electrochemical deposition method, which can improve the anti-interference ability and stability of electrochemical immunosensor. Under the optimal experimental conditions, the electrochemical behavior of OPPs on the electrode surface was determination, which demonstrated that the constructed electrochemical immunosensor could be effectively applied to the quantitative determination of OPPs concentration in vegetable samples (cabbage and spinach). The detection range of the electrochemical immunosensor reached 1.82×10^{-3}-3.29×10^{4} ng mL^{-1}, and the sensitivity was higher.

More importantly, the electrochemical immunosensor is easy to prepare and coupled with other metal materials (such as AuNPs) to form the capture probe, which are modified on the electrode surface to anchor more Abs and further improve the conductivity. The detection principle of the immunosensor was shown in Figure 5. OPPs were captured and connected to the electrode surface through the specific recognition of Ab with target OPPs. This method had advantages of rapid detection speed, high sensitivity and excellent reproducibility, which exhibited extensive developing potential in the field of immunosensor. It was unsatisfactory that the Ab is immobilized on the surface of the electrode, because the ability to captured the target is limited, and the signal presented in the actual detection process decreases with the increase of the concentration of target, and finally reaches the closed state. Therefore, the research of signal amplification of immunosensor was particularly important. The Ab was correctly and effectively fixed on the surface of the electrode to further improve the anti-interference ability and the stability of the immunosensor.

Electrochemical aptasensor

Aptamers are short single-stranded nucleic acid with the specific sequence (DNA or RNA molecule) introduced in 1990, and have high affinity and selectivity toward the target.[33,34] Many screening methods have been developed, including electrophoresis (Systematic Evolution of Ligands by Exponential Enrichment, SELEX), cell SELEX, magnetic bead-based SELEX, and other SELEX methods.[35] Aptamers could specifically recognize various targets on the basis of functional interactions (i.e., aromatic rings, electrostatic, hydrogen bonding, vander Waals forces, etc.). Nowadays, aptamers have been synthesized with low cost and high purity, greatly increasing the reproducibility of detection methods. Numerous electrochemical aptasensors based on different transduction strategies have been designed and fabricated to detect OPPs. However, due to the limited number of aptamers being available for various OPPs, aptamers for other OPPs still needed to be screened urgently to expand their application.

Selvolini et al. fabricated an electrochemical DNA nucleic acidaptamer sensor for the detection of profenofos, which was based on the competitive format and disposable graphite SPE.[36] The thiol-bound DNA capture probe was immobilized on a AuNPs/polyaniline composite film modified electrode, and the capture probe was complementary to the selected aptamer sequence. Different solutions of profenofos with certain amounts of biotinylated aptamers were dropped onto the established DNA sensor. Hybridization reactions were measured using streptavidin-alkaline phosphatase enzyme conjugates, which would catalyze the hydrolysis of naphthyl-1-phosphate. The enzyme product was detected by DPV. Dose-response curves were obtained between 0.10 μM and 10 μM with a detection limit of 0.27 μM. As shown in Figure 6, Yang et al. A dual signal amplification strategy based on AChE and DNA probes was developed to detect OPPs.[37] Firstly, AChE and a hairpin auxiliary DNA probe containing Hg^{2+} were immobilized on the electrode. In the electrolyte solution, AChE would catalyze acetylthiocholine chloride to generate thiocholines, which could interact with Hg^{2+} in the stem of the hairpin auxiliary DNA probe and further convert the DNA conformation to single-stranded DNA. This single stranded DNA in turn triggered a hybridization chain reaction between the two hairpin probe DNAs and produced a long double stranded DNA which could capture many methylene blue molecules and produce a significant current signal by DPV. OPPs could inhibit the activity of AChE, so that the hydrolysis product was reduced, thereby reducing the yield of long-chain double-stranded DNA, further reducing the current signal of methylene blue to realize the sensitive quantitative detection of OPPs. A good linear relationship between the current and the concentration of aldicarb was obtained in the range of 20-4000 μg L^{-1}, with a detection limit of 10 μg L^{-1}. Besides, in order to explore the potential application of the sensor

Table 2. Applications of nanomaterials-based electrochemical biosensors.

Modified material	Recognition element	Electrode	Methods	Analytes	Samples	Linear range	LOD	Ref.
Metal organic frameworks								
CP-MOF-ferrocene/MCH/ Aptamer/gold	Aptamer	GCE	DPV	Malathion	Cucumbers Beans	25-850 ng L^{-1}	17.18 ng L^{-1}	[44]
MIP/Co_3O_4@MOF-74/cycle4	Molecularly imprinted polymer	GCE	CV	Fenamiphos	Orange juice	1.0×10^{-11}–1.0×10^{-9} M	3.0×10^{-12} M	[45]
Cu-BTC MOF material	Cu^{2+}	ITO	DPV	Glyphosate	Soybean	1.0×10^{-12}–1.0×10^{-9} M 1.0×10^{-9}–1.0×10^{-5} M	1.4×10^{-13} M	[46]
Pt@UiO66-NH_2	Enzyme	GCE	DPV	Malathion	Cabbage Apple	1×10^{-14}–1×10^{-9} M	4.9×10^{-15} M	[47]
ZIF-8/ Methylene blue	Enzyme	ITO	DPV	Paraoxon	Apples Eggplants	——	1.7 ng/mL	[48]
CdTe Quantum dots@ Fe-based metal-organic framework	Aptamer	GCE	ECL	Malathion	Water	1.0×10^{-6}–1.0 μg L^{-1}	0.3 pg L^{-1}	[49]
Burkholderia cepacia lipase @MOF nanofibers/chitosan	Enzyme	GCE	DPV	Methyl parathion	Lettuce Cabbage	0.1-38 μM	0.067 μM	[50]
EμAD	Enzyme	μE	DPV	chlorpyrifos	Cucumber Capsicum Brinjal	10-100 ng L^{-1}	6 ng L^{-1}	[49]
Metal nanoparticles								
Nanogold/ mercaptomethamidophos	Enzyme	GCE	DPV	Chlorpyrifos Dichlorvos etc.	Apple Cabbage	0.1–1500 ng·mL^{-1}	0.019-0.077 ng·mL^{-1}	[51]
AChE-Chitosan /Pd@Au nanowires network	Enzyme	GCE	DPV	Malathion	Tap water	0.1 pM-100 nM	0.037 pM	[52]
Au-Pt@BSA-Graphene nanoribbons	Redox reactions in the diazinon	GCE	SWV	Diazinon	Soil Apple	0.01–10.0 μM 10.0-170 μM	0.002 μM	[53]
Au-ZrO_2-GNs	Nitro redox reaction	GCE	SWV	Methyl parathion	Cabbage	1–100 ng mL^{-1} 100-2400 ng mL^{-1}	1 ng mL^{-1}	[54]
PFBT PNPs	OH^-	GCE	ECL	OPPs	Lettuce, Cabbage pakchoi	1.0×10^{-12}–1.0×10^{-7} M	1.5×10^{-13} M	[25]
AuNP–Abs–PB	Antibody	SPCE	CV	OPPs	Baby cabbages Spinaches	1.82×10^{-3}-3.29×10^{4} ng mL^{-1}	0.003 ng mL^{-1}	[32]
AuNPs/PANI	Aptamer	GSPE	DPV	Profenofos	Pear juice	0.10 μM-10 μM	0.27 μM	[36]
HP probe modified gold electrode	Enzyme	Gold electrode	DPV	Aldicarb	Ginger	——	10 μM	[37]
Metal oxides								
AChE/CS@TiO_2-CS/rGO	Enzyme	GCE	DPV	Dichlorvos	Cabbage juice	0.036–22.6 μM	29 nM	[55]
CuO-CeO_2	Cu^{2+}	GCE	DPV	Malathion	Lake water Garlic Apple	10 fM–100 nM	3.3 fM	[56]
CuOx@mC	Cu^{2+}	GCE	DPV	Glyphosate	Apple	1.0×10^{-15}–1.0×10^{-4} M	7.69×10^{-16} M	[57]
CuO-TiO_2	Cu^{2+}	GCE	DPV	Methyl parathion	Ground water	0–2000 ppb	1.21 ppb	[58]
Si-ZrO_2	Nitro redox reaction	GCE	DPV	Methyl parathion	Sewage water	3.4×10^{-9}–8.7×10^{-6} M	59.3×10^{-12} M	[17]
HCS@PANI nanocomposite	Enzyme	GCE	CV SWV	Malathion	Tap water, Apple, Tomato Cucumber	1.0–10 μg·mL^{-1}	0.16 ng·mL^{-1}	[23]
Metal-based other materials								
AuNPs/MoS_2/GA/AChE-BSA	Enzyme	SPE	Amperometry	Paraoxon	Apple Pakchoi	1.0–1000 μg L^{-1}	0.013 μg L^{-1}	[24]
TMDs	Enzyme	GCE	Voltammetry	Fenitrothion	Apples	1–1000 nM	2.86 nM	[59]
NF/AChE/NF-$NiCo_2S_4$	Enzyme	CPE	DPV	Methyl Parathion Paraoxon	——	1.0×10^{-12}–10^{-8} g·mL^{-1} 1.0×10^{-13}–10^{-10} g·mL^{-1}	4.2×10^{-13} g·mL^{-1} 3.5×10^{-14} g·mL^{-1}	[60]
Carbon nanotubes								

(*continued*)

Table 2. Continued.

Modified material	Recognition element	Electrode	Methods	Analytes	Samples	Linear range	LOD	Ref.
Au/CNTs	Reduction of parathion	GCE	LSV	Parathion	Water Celery, Lettuce Cabbage	6.0×10^{-5}–5.0×10^{-7} M	1.0×10^{-7} M	[61]
CuO NFs-c-SWCNTs	Aptamer	GCE	DPV	Chlorpyrifos	Apple Celery Cabbage	0.1–150 ng mL^{-1}	70 pg mL^{-1}	[62]
h-CNT-μPs/Nafion	Nitro redox reaction	GCE	CV	Methyl parathion	Tomato Cabbage	0.3–20.0 μM 20.0–150.0 μM	0.092 μM	[63]
CS-cMWCNT-HA	Enzyme	GCE	CV	Paraoxon	Tap water	5.0–80.0 μM	0.1 μM	[20]
MWCNTs-THI-CHIT	Antibody	GCE	DPV	Chlorpyrifos	Cabbage, Lettuce Chinese chives	0.1–1.0 $\times 10^5$ ng mL^{-1}	0.046 ng mL^{-1}	[31]
Hal-MWCNTs	Nitro redox reaction	GCE	CV	Methyl parathion	Romaine Kiwifruit juices	0.5–11 μM	0.034 μM	[64]
Graphene								
N-HG	Nitrogen-doped holey graphene	GCE	DPV	Methyl parathion	River water Grapes Apples Cucumbers	1 ng ml^{-1}–150 $\mu g \cdot ml^{-1}$	3.5 pg·ml^{-1}	[65]
BSA/Aptamer/rGO-CuNPs	Aptamer	SPCE	DPV	Profenofos Phorate Isocarbophos Omethoate	Rape Spinach	0.01–100 nM 1–1000 nM 0.1–1000 nM 1–500 nM	0.003 nM 0.3 nM 0.03 nM 0.3 nM	[38]
ERGO-CS/Hb	Hb	FTO	DPV	Methyl parathion	Vegetable	0.076–0.988 μM	79.77 nM	[66]
VS_2QDs-GNP/CMWCNTs/DZBA/BSA	Aptamer	GCE	DPV EIS	Diazinon	Humanserum River water Soil Apple Lettuce	50 fM–10 nM 10 fM–10 nM	11 fM 2 fM	[67]
SnS_2/NS-RGO	Nitro redox reaction	GCE	CV	Methyl Parathion	River water Black grapes	0.001–176 μM	0.17 nM	[18]
PLaE-CS/AuNPs-GNs	Enzyme	GCE	DPV	Methyl Parathion Malathion	Carrot Apple	1.5–1513.5 nM	1.51 nM	[26]
Graphitic carbon nitride								
AChE/CS/Pd WLNCs/g-C_3N_4	Enzyme	GCE	CV	OPPs	Cabbage	3.89–20800 nM	1.30 nM	[68]
WO_3/g-C_3N_4 nanocomposite	Enzyme	PGE	CV	Phosmet	Wheat flour	0–125 nM	3.6 nM	[69]
Quantum dots								
GQDs/PAM	PAM probe	GCE	DPV	Fenthion	Water Soil	1.0×10^{-11}–5.0×10^{-7} M	6.8×10^{-12} M	[70]
MXene								
MXene/Au-Pd nanocomposites	Enzyme	SPE	Amperometry	Paraoxon	Pear Cucumber	0.1-1000 μg L^{-1}	1.75 ng L^{-1}	[71]
AChE/Ag@$Ti_3C_2T_x$	Enzyme	GCE	DPV	Malathion	Tap water	10^{-14}–10^{-8} M	3.27×10^{-15} M	[72]
AChE-Chit/MXene/Au NPs/MnO_2/Mn_3O_4	Enzyme	GCE	DPV	Methamidophos	Orange	10^{-12}–10^{-6} M	1.34×10^{-13} M	[73]
AChE/$Ti_3C_2T_x$-CS/GR	Enzyme	GCE	CV	DDVP	Urban tap water	11.31 μM–22.6 nM	14.45 nM	[74]

Abbreviations: CP, complementary probe; MOF, metal organic framework; MIP, molecularly imprinted polymer; GCE, glassy carbon electrodes; DPV, differential pulse stripping voltammetry; CV, cyclic voltammetry; ITO, indium tin oxide electrode; ZIF-8, zeolitic imidazolate framework-8; ECL, electrochemiluminescence; EμAD, electrochemical micro Analytical Device; μE, gold microelectrode; BSA, bovine serum albumin; SWV, square wave voltammograms; GNs, graphene nanosheets; PFBT PNPs, poly polymer nanoparticles; Abs, antibodys; PB, Prussian blue; SPCE, screen-printed carbon electrode; PANI, polyaniline; CS, chitosan; HCS, hollow sphere core-shell; GA, glutaraldehyde; TMD, transition metal disulfide; NF, Moreover, nafion; LSV, linear scan voltammetry; c-SWCNTs, carboxyl-functionalized single walled carbon nanotubes; h-CNT-μPs, honeycomb CNT-microparticles; ERGO, reduced graphene oxide; Hb, hemoglobin; FTO, Fluorine-tin oxide glass substrates. VS_2QDs, vanadium disulfide quantum dots; GNP/CMWCNTs, grapheme nanoplatelets/carboxylated multiwalled carbon nanotubes; DZBA, diazinon binding aptamer; EIS, electrochemical impedance spectroscopy; PLaE, plant esterase; PGE, pencil graphite electrode.

strategy in the analysis of actual food samples, fresh ginger was selected to detect aldicarb residues, and the sensor showed good accuracy in the detection of aldicarb, with a recovery of 98.3-105.3%.

Aptamers have outstanding characteristics, including easy synthesis and modification, good chemical stability and high affinity, which makes the electrochemical aptasensor exhibits the advantages of economy, simplicity, sensitivity. However, with the development of electrochemical aptasensor, it has been found that the effective immobilization of aptamer on the electrode is a great challenge. For the first time, Fu et al proposed to immobilize the aptamer on the sensing interface by one-step co-electrodeposition, and applied it to detect four kinds of OPPs (phorate, profenofos, omethoate and isocarbophos).[38] Specifically, GO was used to link NH_2-modified aptamers during the preparation of the electrodeposition solution, which provided a basis for the immobilization of aptamers. Secondly, the introduction of copper nanoparticles (CuNPs) into the aptamer-GO mixed solution can improve the conductivity of the electrodeposited film, thus exhibiting the excellent electrochemical performance and avoiding the complex modification steps in the preparation process of aptasensor. Under the optimal conditions, the detection limits of profenofos, phorate, isocarbophos and omethoate were 0.003 nM, 0.3 nM and 0.03 nM, respectively. The aptasensor was also successfully applied to the analysis of phorate in vegetables. It was confirmed that this strategy had opened up a new way for the effective fixation of aptamer, and developed a new type of aptasensor for detecting OPPs, which would have broad application prospects in other fields.

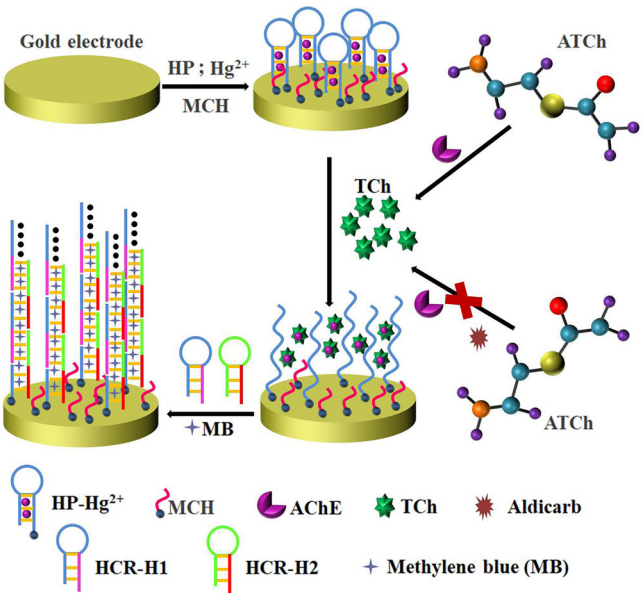

Figure. 6. Principle of the electrochemical aptasensor strategy for the detection of pesticide.(modified from [37]).

Molecularly imprinted electrochemical sensors

Molecularly imprinted polymers (MIPs) was a kind of biomimetic receptor polymers by creating specific binding pores on the surface. These structures, as well as the various binding sites formed internally, provide high selectivity for MIP-based electrochemical (bio)sensors.[39,40] Generally, biologically excited MIPs are excellent sensing materials. They can be prepared in batches, or thin layers on the electrode surface with high sensitivity selectivity. In fact, the binding efficiency of MIPs depends on the rational selection of functional monomers, cross-linking agents and porogens. It is formed in the presence of cross-linked template substances (organic substances, metal ions, microorganisms). After the solvent is removed, a mark is left in the polymer network. These fingerprints constitute the acceptor site, which will identify the template with excellent selectivity during the recombination step.[41,42]

Electrochemical (bio)sensors based on MIPs are increasingly used in various fields. Although its selectivity has been improved, there are still limitations including long analysis time, slow diffusion of target molecules on the entire printing film, and uneven distribution of active sites. Therefore, continuous in-depth research on new materials can achieve better sensitivity. Motaharian et al. developed an electrochemical sensor based on MIP nanoparticles for the highly

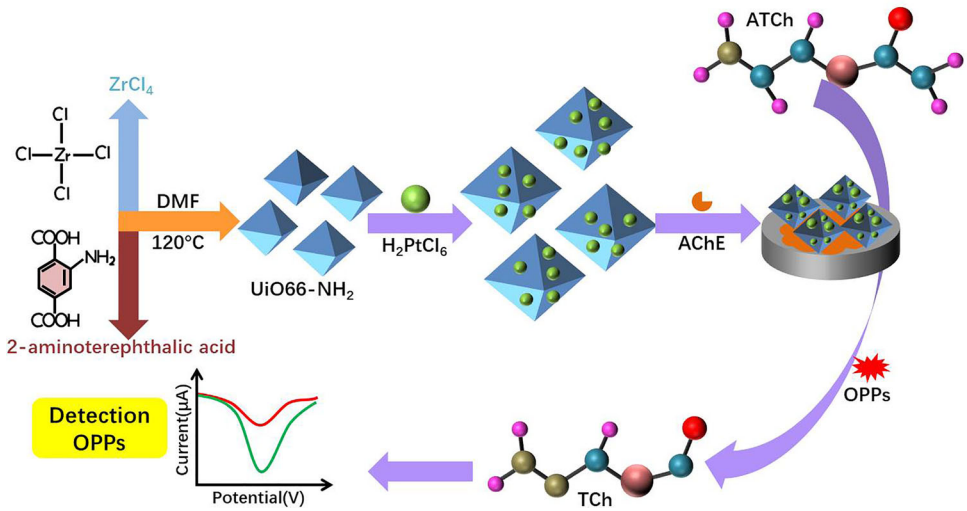

Figure 7. The synthetic process of Pt@UiO66-NH_2 and the detecting process toward OPPs.

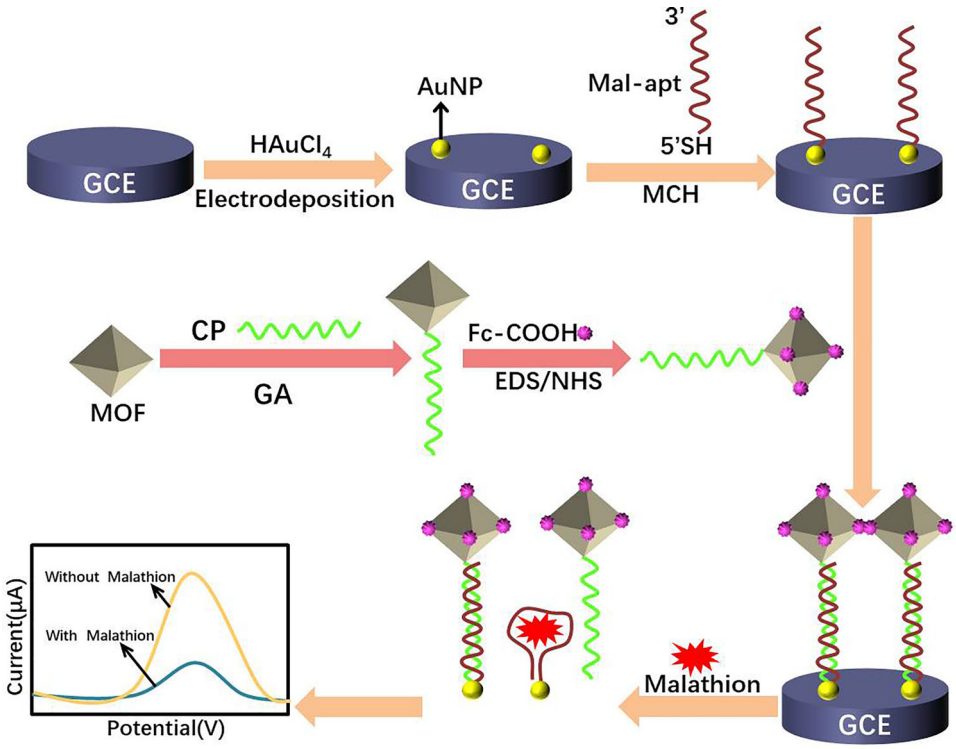

Figure 8. Schematic illustration of the ultrasensitive aptamer sensor for malathion assay based on UiO-66-NH_2 and Fc.

selective and ultrasensitive determination of diazinon(DZN).[43] In this study, DZN-imprinted polymer nanoparticles were synthesized by the suspension polymerization, and then modified on the surface of carbon paste electrodes (CPE) The adsorption capacity of MIP nanoparticles modified CPE toward diazinon was much higher than that of CPE-based non-imprinted polymer nanoparticles. Under optimized extraction and analysis conditions, the proposed sensor showed excellent sensitivity (95.08 μA L μmol^{-1}) toward DZN with two linear ranges of 2.5×10^{-9} – 1.0×10^{-7} M and 1.0×10^{-7} – 2.0×10^{-6} M and the detection limit of 7.9×10^{-10} M.

Nanomaterials-based OPPs electrochemical biosensors

In the application of electrochemical sensors, the modification of the electrode surface with different nanomaterials is crucial, which greatly improves the response of the electrical signal and increases the sensitivity and stability of OPPs detection. With the in-depth study of nanomaterials, in recent years, nanomaterials commonly used for electrode surface modification mainly include metal-organic frameworks (MOFs), metals and metal derivatives, carbon materials (carbon nanotubes (CNTs), graphene, graphitic carbon nitride (g-C_3N_4), quantum dots(QDs)), MXene and so on. These materials are widely used in enzyme or aptamer electrochemical sensors for the detection of OPPs. The use of nanomaterials can further catalyze the substrate to produce optical or electrical signals and increase the sensor response. Table 2 compared the detection performance of these nanomaterial-based biosensors for OPPs, including recognition element, detection method, analytes, sample type, linear range, detection limit, etc.

Metal organic frameworks

MOF is a three-dimensional framework materials with metal ions as nodes and organic ligands as linker.[75,76] MOFs possess the advantages of high porosity, adjustable pore diameter, large specific surface area, exposed active sites and more anchor sites provide loading other nanomaterials with high catalytic performance. The pore size of MOFs can also be controlled to achieved the selection of specific analytes, which greatly increases the selectivity of sensor. These advantages make MOF widely used in the fields of catalysis, energy storage and separation.[77–80] Vikrant et al. also summarized the widely applications of MOFs for the biosensor detection of various pesticides (e.g., OPPs and non-OPPs).[81] MOF could identify the target via the tunable pore size directly and also as a carrier to load the recognizer. Cao et al. fabricated a hierarchically Cu-BTC MOF based electrochemical sensor for the detection of glyphosate.[46] The Cu-BTC framework as a directly detection matrix, possessed large specific surface area to increased the reaction site of electrode and further enhance the detection performance. Under optimized conditions, the MOF-based sensor displayed wide detection range of 1.0×10^{-12}-1.0×10^{-9} M and 1.0×10^{-9}-1.0×10^{-5} M, and the lower detection of limit was 1.4×10^{-13} M. Besides, the electrochemical sensor had good reproducibility, stability, and good selectivity for aminomethylphosphonic acid which was the main metabolite of glyphosate. The electrochemical sensor can be used for the detection of glyphosate in soybean in food samples. It

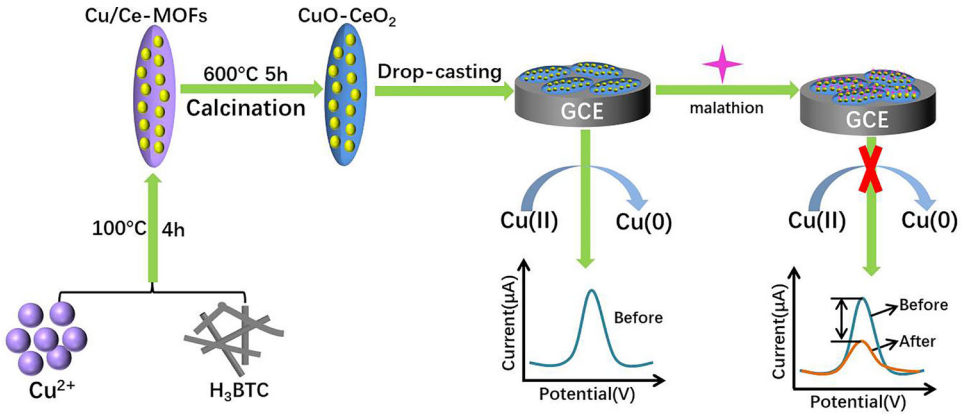

Figure 9. Schematic illustration for the fabrication of CuO-CeO_2/GCE and the electrochemical detection of malathion.

was worth mentioning that the high efficiency sensor based on Cu-BTC had great potential application value in the detection of OPPs in real samples.

Although MOFs are potential materials for electrochemical sensors, they still have some shortcomings such as poor conductivity and unstable structure, which limit their application in the field of electrochemical sensors. Combination of MOFs and other components including metal ions, biopolymers, nanoparticles and proteins have been developed to enhance electrochemical properties and stability. Besides, MOF derivatives, mainly including MOFs-derived carbon and metal oxide nanomaterials, are also developed to improve the stability.[82–85]

As shown in Figure 7, Ma et al. synthesized a zirconium-based MOF nanocomposite anchored by Pt nanoparticles (Pt@UiO66-NH_2) with large specific surface area and high dispersion to fabricate a new AChE-based electrochemical biosensor platform for the detection of malathion.[47] Immobilization of Pt nanoparticles onto the porous MOF to form Pt@UiO66-NH_2 was an advantageous way to enhance the inherent characteristics of MOF, which endowed it new functions and minimize the use of precious metals. Pt@UiO66-NH_2 with good electronic conduction channels provided the ultrahigh surface area and many adsorption sites for the immobilization of AChE. This sensor exhibited high sensitivity for the detection of malathion, with a detection linearity was in the range of 1.0×10^{-14}-1.0×10^{-9} M, and the limit of detection was 4.9×10^{-15} M. The electrochemical biosensor constructed by Pt@UiO66-NH_2/GCE was used to detect OPPs in cabbage and apple samples, which showed the great potential of metal nanoparticles/MOF composites in improving the electrochemical performance of electrochemical biosensors.

The large specific surface area and porous structure of MOFs provide more interfaces and active sites for the interaction between materials and analytes, making MOFs easy to functionalize with various molecules and materials.[86] Various biomolecules (enzymes, nucleic acids, antibodies) have been incorporated into MOFs to further improve the sensitivity and selectivity of electrochemical sensors.[49,87] For example, Li et al. developed a simple immobilization-free homogeneous electrochemical sensing strategy to synthesize pH-responsive zeolite imidazolate framework-8/methyl blue (ZIF-8/MB) composites through a simple one-pot self-assembly method, using AChE as the recognition component.[48] ZIF-8 was used as a biodegradable carrier to encapsulate MB, and the dissolution of ZIF-8/MB composite under acidic conditions would release a large number of MB molecules to generate a strong diffusion current. Thus, OPPs which was an AChE inhibitors would be monitored through the decreased electrochemical signal. Benefiting from the large number of MB molecules trapped in the ZIF-8 framework, the sensing platform had achieved high analytical performance for the detection of paraoxon, with a detection limit of 1.7 ng mL^{-1}. Moreover, the strategy was universal for other OPPs, and worked well in real samples, which indicated that the strategy provided a method for the sensitivity assessment of pesticides in food and environmental samples.

To further improve the selectivity of MOF-based electrochemical sensors for the detection of OPPs, many people have made efforts. As shown in Figure 8, Xu et al. constructed an electrochemical aptamer sensor platform toward detection of malathion, which was coupled with complementary probe and carboxy-ferrocene via the covalent bond to from the MOF-based nanocomposite probe.[44] Ferrocene was immobilized on the MOF to amply its current signal. The complex probe could hybridize with the malathion aptamer immobilized on the electrode through a complementary base pairing reaction. The strong affinity of malathion and its aptamer would cause the MOF-ferrocene probe to be released into the buffer solution, further reducing the DPV signal of ferrocene. The fabricated sensor showed a linear range of 25-850 ng L^{-1} toward malathion with a detection limit of 17.18 ng L^{-1}. Due to the specific recognition of aptamers, more and more aptamer-based electrochemical aptamers have been designed. Chen et al. developed an ultrasensitive electrochemiluminescence (ECL) aptamer sensor for the detection of malathion, using iron-based MOF NH_2-MIL-88 (Fe) as the nano-carrier and signal enhancement of CdTe quantum dots (QDs).[49] NH_2-MIL-88 (Fe) could fix abundant CdTe-QDs. A mechanism for the rapid increased of the ECL intensity of CdTe-QDs had been established. Fe (II) of NH_2-MIL-88 (Fe) was used as a signal enhancer to generated Fe(III) through reduction reaction to realized cyclic reaction. The novel ECL conformal sensor

derived from CdTe-QDs@NH_2-MIL-88 (Fe) for the detection of malathion showed excellent sensitivity with a detection limit of 0.3 pg L^{-1} over the detection range of 1.0×10^{-6}-1.0 mg L^{-1}. Importantly, NH_2-MIL-88 (Fe) as a nanocarrier and signal enhancer provided a direction for ultrasensitive target analysis. In addition to the electrochemical (bio)sensors of the conventional three-electrode system, Nagabooshanam et al. developed an electrochemical microanalytical device (EμAD) for the sensitive detection of chlorpyrifos in the food chain.[88] The gold microelectrode modified with MOF (MOF-Basolite Z1200) and AChE were excellent electroanalytical sensors for the detection of chlorpyrifos. This method only required 2 μL of analyte and was tested over a linear range of 10-100 ng L^{-1}. The detection limit and sensitivity of the developed EμAD were 6 ng L^{-1} and 0.598 μA ng L mm^{-2}, respectively. The applicability of the device for detecting chlorpyrifos from actual vegetable samples was also tested within the prescribed limits. The sensor had good stability and the lifetime was 20 days. The response time of EμAD was 50 seconds, including incubation time of 20 seconds. The developed EμAD also used bluetooth to integrate with a commercial low-cost handheld potentiostat (k-Stat), enabling it to collect real-time data results of field samples with minimum scientific skill, which was comparable to standard electrochemical workstation. These advantages made the new EμAD platform an attractive candidate for field analysis.

Metals and metal derivatives

Metal nanoparticles

Noble metal nanomaterials such as Au, silver (Ag), platinum (Pt), palladium (Pd) and their bimetallic alloys with core-shell structures have unique sizes and shapes, remarkable physical, chemical and electrochemical properties. They play a variety of roles in the design and fabrication of electrochemical sensors and biosensor platforms, including simple synthesis, easy surface functionalization, catalysis of the electrochemical reaction, and enhancement of the electron transfer process, making them attractive for many applications.[89,90] In addition, the shortcomings of fine tunable the optical properties, high specific surface area and strong surface modification ability endowed them with the potential application for the detection of OPPs.[91,92] Recently, metal nanoparticles had shown great potential for improving the sensitivity and selectivity of electrochemical biosensors through the synergistic signal amplification of biofunctionalized metal nanoparticles and effective nanocomposites. The ability to integrating sensor arrays with microfluidic devices offers the possibility for laboratory technology to detect multiple analytes in a high-throughput manner.[93–95]

Based on the successful synthesis of phosphoryl thioglycolate, Zhao and his colleagues designed and prepared a novel Au/phosphoryl thioglycolate multi-residue electrochemical biosensor by combining the nanoscale effect, the strong Au-S bond and the interaction between AChE and phosphoryl thioformamide.[51] Indirect competition method was used to detect eleven OPPs and total OPPs. The electrochemical behavior of the modified electrode was characterized by DPV and EIS. The biosensor exhibited excellent electrochemical performance with a wider linear range of 0.1-1500 ng mL^{-1} and a detection limit of 0.019-0.077 ng mL^{-1}. It had good stability and repeatability, so it could detect the number of OPPs at the same time, instead of one OPP, to achieved rapid detection of the total amount of OPPs. Two OPPs (trichlorfon, dichlorvos) were detected in apples and cabbages, and satisfactory results were obtained. Except for Au NPs, other metal nanoparticles also have their own surface chemical energy, with high specific surface area, good biocompatibility and strong affinity. Bimetallic nanoparticle catalysts have attracted considerable attention due to their unique chemical and physical properties. Among them, Pd NPs exhibit high electrocatalytic activity for various analytes, which made Pd NPs a cheaper alternative in the design of electrochemical sensing platform.[96,97]

In recent years, the research on bimetal synergistic amplification of signal had been increasing. Lu et al. a network structure composed of bimetallic Pd@Au nanowires with high aspect ratio had been developed.[52] The nanowire network structure not only provided a plurality of electronic channels, but also had a large acceptable electroactive surface area for immobilizing enzymes due to the self-interconnection of nanowires with better conductivity. Besides, the stability of enzyme-based electrode was further improved by adopting CS to immobilize enzyme resulting from good film forming property, biocompatibility and innocuity of CS. It was proved that Pd@Au nanomaterials had more advantages than the corresponding monometallic materials due to the synergistic effect. The biosensor based on Pd@Au nanowire network could detect malathion in the range of 0.1 pM-100 nM, with a detection limit of 0.037 pM. Ag NPs and Pt NPs as electrode materials could also be prepared by chemical reduction, metal vapor phase synthesis, electrochemical and photochemical deposition methods. The prepared method was also the key to the development of various nanoparticles on the surface of many electrodes, and required excellent chemical inertness, good stability, low background current, high catalytic and sensing performance.[98–102] Pajooheshpour et al. reported that a novel sensing layer composed of bovine serum albumin (BSA) template Au-Pt bimetallic nanoclusters (Au-Pt@BSA/GCE) and graphene nanoribbons was used as an enzyme-free electrochemical sensor for rapid, selective and sensitive determination of diazinon.[53] The combination of Pt nanoclusters and Au nanoclusters improved the adsorption capacity, stability, sensitivity, electron transfer rate and conductivity. The BSA coating layer facilitated post-synthesis surface modifications with functional materials. Results showed that Au-Pt@BSA/GCE could significantly catalyze the oxidation and reduction of diazinon. The linear range of diazinon was 0.01-10.0 μM and 10.0-170 μM with a detection limit of 0.002 μM. The selectivity, stability and reproducibility of Au-Pt@BSA/GCE were also investigated, which indicated that the sensor had great potential to replaced the enzyme inhibition-based biosensors for the determination of diazinon. The constructed electrode was used for the

determination of diazinon in soil, various waters, fruits and vegetables. Compared with the standard method, the method had excellent ability for diazinon in actual samples.

As metal nanoparticles played a variety of key roles in the design of electrochemical sensor platforms, more and more people had been studying them. Metal nanoparticles have the characteristics of simple synthesis, easy surface functionalization, strong electrochemical catalytic ability and electron transfer ability. However, due to the poor sensitivity and selectivity of single metal nanoparticles, it could only be improved by the synthesis of nanocomposites integrating with other nanomaterials, which provided a strong potential for the development of metal nanoparticle-based electrochemical sensor platform, and promotes the development of other bio-functional nanoparticles and effective nanocomposites. Applications and studies of electrochemical sensors and biosensors promote the development of advanced analytical methods for environmental monitoring and food safety applications.

Metal oxides

Metal oxide-based nanomaterials with various morphologies and sizes have been explored as sensing materials. The synthesis of nanostructured metal oxides mainly focused on the chemical reduction and the controlled separation of formed metal atoms from the bulk solution. They are very useful for preparing uniform nanoparticles such as nanorods, nanofibers, nanobelts, nanoclusters and nanotubes, such as ZrO_2 NPs, SnO_2 NPs, TiO_2 nanotubes and TiO_2 nanofilm.[103–105] They possess large specific surface area, high adsorption capacity, unique electrochemical activity, and long-term stability, so they are of great significance to the design of electrochemical biosensor platform.[106]

Cui et al. have developed a highly stable electrochemical biosensor based on the adsorption of AChE on the CS-TiO_2 sol-gel film and the reduced GO multilayer immobilized substrate.[55] TiO_2 porous sol-gel membrane, as a protein immobilization matrix has attracted a large number of researchers because of its large specific surface area, nontoxic, low cost and excellent biocompatibility. However, it also has the disadvantages of low adhesion and high brittleness, resulted in poor stability of the prepared sensor. In order to solve these problems, some nanomaterials are mixed to form nanocomposite materials to enhance the mechanical strength of each component. The electrochemical biosensor was prepared with the help of good immobilized matrix CS and carbon nanomaterials GO. The linear detection range of dichlorvos was 0.036-22.6 μM with the detection limit of 29 nM. The total detection time was about 25 minutes. The biosensor had good reproducibility and stability in the process of detection and storage, which could accurately detect the content of dichlorvos in cabbage juice.

Transition metal oxides derived from MOFs exhibit good electrical conductivity and keep the same structure as the original MOFs, i.e., large surface area. As shown in Figure 9, Xie et al. prepared a nanostructured CuO-CeO_2 composite from the calcination of a Cu/Ce-MOF to be dropped onto the surface of glass carbon electrode (GCE) for the detection of malathion.[56] The CuO-CeO_2 hybrids provided numerous active sites for the identification of more malathion molecules. The detected principle was based on the fact that the redox signal of CuO was inhibited by malathion due to the coordination interaction between the sulfur groups of malathion and CuO. The excellent analytical performance was attributed to the unique microstructure and the synergistic effect of CuO and CeO_2. The established method provided a linear range of 10 fM $-$ 100 nM and a detection limit of 3.3 fM for malathion. Similarly, Gu and other researchers proposed a non-enzymatic electrochemical sensor for pesticides based on HKUST-1 derived copper oxide@mesoporous carbon (CuOx@mC) composites.[57] The CuOx@mC was formed by the direct pyrolysis of HKUST-1. A plurality of characterization technologies proved that the conductivity of the porous structure of the CuOx@mC was obviously increased after the heat treatment compared with the porous structure of the HKUST-1, and the electrochemical sensing performance of the CuOx@mC composite material to glyphosate was also superior. The detection limit was 7.69×10^{-16} M and the linear range was 1.0×10^{-15}-1.0×10^{-4} M. The constructed electrochemical sensor showed good reproducibility, stability and anti-interference ability. The sensor was applied to the determination of glyphosate in real fruit samples with satisfactory results and good recovery.

Besides, there were many reports concerning metal oxides-based composites for the detection of OPPs. The CuO-TiO_2 hybrid nanocomposite was prepared by Tian and his associates through a simple method, and was modified and immobilized on a GCE, which was used as a non-enzymatic electrochemical sensor for sensitive and selective detection of parathion-methyl.[58] The electrochemical performance of the modified electrode was studied by UV-vis, CV and DPV, Under the optimal conditions, DPV was used to evaluate the detection ability of the modified electrode, and it was found that the modified electrode could sensitively detect methyl parathion in a wide dynamic detection range of 0 $-$ 2000 ppb, and the detection limit was 1.21 ppb. The modified electrode was also used to detect methyl parathion in actual groundwater samples. The results showed that the sensor has high sensitivity, which provided a new idea for the detection of other OPPs in groundwater.

Through the previous studies, it can be found that metal oxide nanomaterials have large specific surface area, high adsorption capacity, unique electrochemical activity and stability, which are important materials for designing electrochemical sensor platform. In order to further improve the sensitivity and detection limit of metal oxide nanomaterials in electrochemical sensors, people continue to explore the synthesis based on nanostructured metal oxides, and adjust their corresponding analytical performance by adjusting the morphology, particle size, surface area and surface function. On the other hand, adding metal oxides to synthesize nanocomposite materials for sensing is a more common method, which can provide a better reference for food and environmental monitoring.

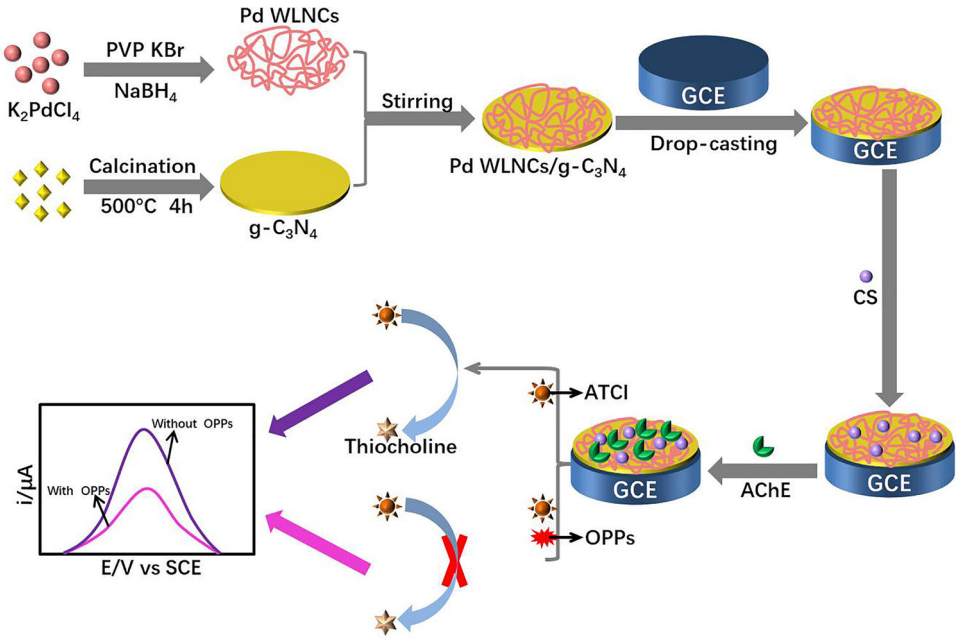

Figure 10. Synthesized process of Pd WLNCs/g-C_3N_4 nanocomposites and schematic description of the fabrication of modified biosensor and response mechanism.

Metal-based other materials

Although noble metal nanomaterials and multi-metal synergistic composite materials could improved the sensitivity and stability of assembled electrochemical biosensors by signal amplification, they were scarce in the natural world and possess higher cost limiting the large-scale application. Compared with precious metal nanomaterials, metal-based other compounds have attracted much attention due to the ease of preparation and low cost.[107] Some new transition metal compounds have also been found and applied to the construction of electrochemical biosensors.

For example, Zhao et al. reported the application of transition metal disulfide nanosheets in electrochemcial sensors for pesticide detection.[24] In this work, a portable and disposable enzyme-based biosensor was developed, which adopted MoS_2 nanosheets modified SPE to detect paraoxon. The peeled ultra-thin MoS_2 nanosheets could accelerate electron transfer on the electrode surface, and also assisted AChE to immobilized via the glutaraldehyde as a cross-linking agent. The MoS_2 nanosheets were immobilized on the SPE surface through the Au-S interaction. The electrochemical biosensor showed a good linear relationship with the concentration of paraoxon in the range of 1.0-1000 μg L^{-1}, and the detection limit of 0.013 μg L^{-1}. The biosensor was successfully applied for the determination of paraoxon in pretreated apple and cabbage samples, which provided a reliable method for the rapid analysis of OPPs in agricultural products.

Nasir et al. developed single layer or multilayer lithium stripped two-dimensional 1 T phase transition metal disulfide (TMDs)-AChE electrochemical biosensor.[59] TMDs as a nanocarrier could enhance and stabilize the enzyme activity, and the sensitive detection of fenitrothion was realized indirectly through the enzyme inhibition pathway. Similarly, Peng et al. adapted the one-pot solvothermal method to prepare a reticulated hollow spherical cobalt-nickel sulfide ($NiCo_2S_4$) with the rod-like structure.[60] Then $NiCo_2S_4$ was used to assemble an AChE-based electrochemical biosensor for the detection of parathion methyl and paraoxon due to its special structure, superior conductivity and abundant reaction active sites. The biosensor demonstrated a wide linear range of 1.0×10^{-13}-1.0×10^{-10} g mL^{-1} with the detection limit of 3.5×10^{-14} g mL^{-1} for paraoxon, and 1.0×10^{-12}-1.0×10^{-8} g mL^{-1} with the detection limit of 4.2×10^{-13} g mL^{-1} for methyl parathion, respectively.

In addition to metal nanoparticles and metal oxides, two-dimensional transition metal halogen compounds are also popular, such as TMDs and $NiCo_2S_4$, TDMs have excellent characteristics such as ultra-fast electronic conductivity, large surface area and ultra-high electrocatalytic activity in 1 T phase nanosheets, which made them be extensively applied in electrochemical sensing. The chemical properties of TMDs can be further improved by peeling them into monolayer or multilayer sheets. However, the stability and sensitivity of the prepared products need to be improved in electrochemical sensing, and now there are new peeling methods (mechanical peeling, chemical stripping and electroablation) for TMDs, which facilitates the use of two-dimensional transition metal halides in electrochemical sensor.

Carbon materials

Carbon nanomaterials are often selected as modified sensitizers of solid electrodes due to their high conductivity, large specific surface area and good biocompatibility.[108] The frequently-used carbon nanomaterials mainly include zero-dimensional materials such as carbon quantum dot (CQD), one-dimensional materials such as carbon nanofiber (CNF) and CNTs, and two-dimensional materials such as graphene nanosheets.[109] They can provide more loading sites for the biological recognition element. In the electrochemical

sensor, carbon nanomaterials play a role in the signal transmission to promote the electron transfer between the electroactive substance and the electrode, and further improve the sensitivity of electrochemical detection.[110–114]

Carbon nanotubes

CNTs are a kind of one-dimensional carbon material with special seamless and hollow structure, which composed of hexagonal planar layers of carbon atoms around concentric axes to be rolled into a nanosheet of SP^2 hybrid carbon.[115] CNTs can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Since CNTs were discovered by Iijima in 1991, they are always one of the hotspots of carbon materials and widely used in many fields.[61,116] CNTs have excellent physical and chemical properties, especially large surface area, to increase active sites, enhance the adsorption capacity, and improve the catalytic efficiency. The preparation methods of CNTs mainly include arc discharge method, chemical vapor deposition (CVD) method and laser evaporation method. Arc discharge method is the earliest method, but CVD is the most widely used commercial preparation method, which is a simple, universal and economic manufacturing technology. Because the process of preparing CNTs is easier to control and the cost of raw materials is lower, it is more suitable for the large-scale production.[117]

Many electrochemical sensors based on CNTs have been developed, including paste electrodes, thin film electrodes, composite electrodes and functionalized CNTs electrodes, due to the advantages of CNTs such as fast charge transfer and good compatibility and synergy with other electrode materials. An electrochemical sensor based on CuO nanoflowers (CuO NFs) and SWCNTs nanocomposites for the reproducible and selective detection of chlorpyrifos was first developed by Xu et al.[62] CuO NFs were used as potential substrates to enlarge the surface area of the electrode due to the 3 D nanostructure and excellent chemical stability. SWCNTs have excellent electrical properties to improve the electron transfer rate and amplify the sensing signal. In this work, SWCNTs were used to enhance the immobilization ability of the aminated probe and the hybridization ability of the aptamer and the aminated probe. In addition, the aptamer sensor can be easily regenerated from urea to achieve repeatable and continuous application of a single electrode for the detection of trace chlorpyrifos. Under the optimal conditions, the linear range of the biosensor for chlorpyrifos was 0.1-150 ng mL^{-1}, and the limit of detection was 70 pg mL^{-1}. The sensor exhibited high selectivity and good repeatability, and it was also successfully applied to the determination of chlorpyrifos in apple and celery cabbage samples with satisfactory recoveries. Yao et al. constructed a honeycomb porous microparticles of CNTs (*h*-CNT-μPs) using droplet microfluidics combined with SiO_2 NPs as sacrificial nanoparticles, in which droplet size and composition could be tunable via the fluidic phases.[63] The prepared *h*-CNT-μPs/Nafion/GCE electrode showed high specific surface area and electrocatalytic activity. Under optimized conditions, the h-CNT-μPs/Nafion/GCE-based sensor showed linear response to methyl parathion in the concentration range of 0.3-20.0 μM and 20.0-150.0 μM. The limit of detection was 0.092 μM, which indicated that the sensor possessed good sensitivity, selectivity, reproducibility and anti-interference performance. This sensor was also used to determine methyl parathion in tomatoes and cabbages, and results were comparable to those measured using high performance liquid chromatography. It provided a reliable method for monitoring pesticides and other active ingredients in fruits, vegetables and other scenarios.

In order to improve the sensing performance of electrochemical sensors, carbon nanotubes and some nanostructured clay minerals have been successfully combined as modified materials and applied to sensors. prepared a simple and efficient halloysite (Hal) Hal-MWCNTs nanocomposite for the determination of MP.[64] Hal was a kind of aluminosilicate clay mineral with hollow nanotube structure of 1:1 type. The clay material had two chemical groups (Si-O-Si and Al-OH), which distributed on the outer surface and the inner surface of the hollow nanotube structure, respectively, so that the prepared Hal-MWCNTs/GCE exhibited good biocompatibility, high recognition capability, large specific surface area and chemical stability. The detection limit was 0.034 μM and the linear range was 0.5-11 μM. The method was applied to the detect MP in real samples (romaine lettuce and kiwi fruit juice) with satisfactory results. The relative standard deviations were 2.46-3.08%, and recoveries were in the range of 98.8-101.8%. The results showed that the coating of Hal-MWCNTs nanocomposites on the surface of GCE was beneficial for the preparation of high-performance MP electrochemical sensor.

CNTs materials have significant mechanical strength, excellent conductivity, high specific surface area and good chemical stability. The application of CNTs in electrochemical sensors improves the electrochemical analysis performance such as the intensity and resolution of the signal. It is a promising electrocatalyst. However, the production cost of high-purity CNTs is high, which limits their large-scale industrial application. Therefore, the synthetic routes and purification methods need to be improved, and new low-cost and effective technologies need to be developed. These research results will contribute to the construction of reliable and repeatable CNT-based electrochemical sensors, and expand the application of sensors in various fields.

Graphene

Graphene is a kind of carbon nanomaterials with two-dimensional honeycomb structure assembled by sp^2 hybrid carbon atoms, which has high specific surface area, excellent mechanical strength and stability, extraordinary photoelectric properties, good thermal conductivity, and excellent electronic conductivity. Since the discovery, many scalable, cost-effective and high-volume production methods have been developed, mainly including mechanical exfoliation, CVD, chemical oxidation, liquid exfoliation, electrochemical method.[118–122] It is widely used in biosensors, fuel cells, catalysts, energy storage and electronic devices and other

fields.[123,124] Nowadays, heteroatom-doped graphene and graphene-based nanocomposites have been widely synthesized to improve the related performance. Introduction of heteroatoms in graphene can cause the changes of charge transport, band gap, thermal stability, optics and magnetism to increase its active sites and improve catalytic performance.[125]

Graphene-based nanocomposites combine the advantages of both nanomaterials and graphene, which posses various structures, diverse types, higher conductivity and catalytic activity. These excellent physicochemical and electrical properties make graphene an attractive candidate material for the fabrication of electrochemical sensor, which can improve the signal response and analytical performance of electrochemical sensors. However, there are also many defects of graphene and its functional derivatives, such as easy agglomeration, high doping amount, poor dispersion etc., and their excellent functional properties could not be fully utilized. In order to solve the above defects and broaden the application of graphene and its derivatives, it is necessary to functionalize graphene. In order to further improve the performance of graphene nanomaterials and improve their electrical conductivity, many researchers start with material synthesis methods Chen et al successfully developed a high-performance nitrogen-doped porous graphene (N-HG) to prepare an electrochemical sensor for detecting methyl parathion.[65] N-HG with hierarchical macro and nano-porous three-dimensional structures was synthesized via a hydrothermal method. HG could open mass transport channels and edge activity. Compared with pyridinic N and graphitic N-based N-HG, N-HG with high pyrrolic N showed the largest electron transfer rate and the best sensing performance (ultra-low limit of detection: 3.5 pg mL^{-1}, wide linear range: 1 ng mL^{-1} to 150 μg mL^{-1}), which indicated that the pyrrolic N in N-HG played a key role in the electrochemical process and in enhanced electrocatalysis resulted from more active sites and electron transfer rate. With the increase of pyrrolic N content, N-HG provided excellent conductivity and mass transfer path to achieve efficient electron and ion transfer and further bring lower overpotential and higher current response. The established sensor exhibited excellent selectivity and freedom from interference, good detecting accuracy and satisfactory recoveries for the detection of MP in river water, fruit and vegetable samples with recoveries in the range of 99-102%.

Fu et al. prepared an electrochemical aptasensor of for the specially identification and detection of four OPPs (profenofos, phorate, isocarbophos and omethoate) via the one-step coelectrodepostion of aptamers and GO-CuNPs nanocomposite materials.[38] Aptamers were immobilized on the sensing interface through GO modified with NH_2 as a connecter. During the electrodeposition, GO was electrochemically reduced to reduced GO with better electrical conductivity. Besides, CuNPs were introduced to enhance the film conductivity of electrodeposited nanomaterials. Under the optimum conditions, the detection limits of phorate, profenofos, isocarbophos and omethoate were 0.003 nM, 0.3 nM, 0.03 nM and 0.3 nM, respectively. In addition, the selectivity of the aptamer biosensor was evaluated by using other five pesticides (carbaryl, malathion, methamidophos, monocrotophos and chlorpyrifos) as interferents. The results showed that the response of the aptamer/GO-CuNPs electrode to the interferents was not obvious, which indicated that the aptamer/GO-CuNPs electrode had good selectivity. The sensor had simple preparation process, good stability, high selectivity and high sensitivity. It was also successfully applied to the analysis of phorate in vegetables, which had broad application prospects in other field.

Kaur et al. proposed a rapid electrochemical sensing tool based on a novel bioelectrode of the redox-active protein hemoglobin (Hb) for the detection of MP.[66,67] The bioelectrode was designed through the immobilization of Hb on an electrochemically reduced graphene oxide-chitosan-based biocompatible coating (ERGO-CS/Hb/FTO). Hb was low cost, easy availability and good electrocatalytic performance. However, the direct electron transfer between Hb and the electrode was very laborious, due to the complex and unstable surface structure of the electrode. In order to prevent the electrode passivation and retain the structure, CS with relatively low conductivity was introduced. RGO had excellent electrocatalytic activity based on the strong π-π stacking interaction between the large delocalized π-electron system and the double bond of benzene ring or OPPs, which not only improved the low conductivity of CS, but also combined with CS through the amide bond, thus contributing to synthesize dispersed and stable composite materials. In this study, the biocompatible ERGO-CS matrix facilitated the direct electron transfer from the protein to the bottom electrode without loss of the original protein structure. The detection limit of the biosensor was 79.77 nM, and the sensitivity was 45.77 $Acm^{-2}\,\mu M^{-1}$. The biosensor had high reliability for the detection of MP in vegetable samples, and recoveries were in the range of 94-101%. The biosensor would be a promising method for the identification of MP.

Graphitic carbon nitride

g-C_3N_4 composed of carbon and nitrogen atoms, is a new 2 D graphene analogue. It can be synthesized by solid state reaction, solvothermal synthesis, CVD, and thermal decomposition. Compared to the lengthy procedure of graphene, the preparation of g-C_3N_4 was relatively easy and economical. Besides, it possesses another advantage of the electronic band-gap structure easily controlled by chemical function or doping. The electrocatalytic activity for redox reaction of g-C_3N_4 made it an excellent choice for desirable electrode material.

As shown in Figure 10, Wang et al. constructed a Pd wormlike nanochains (Pd WLNCs)/g-C_3N_4 nanocomposite and AChE-based electrochemical biosensor platform for the detection of OPPs.[68] g-C_3N_4 could enlarged the electrode surface due to the sheet structure. It was as a carrier for Pd WLNCs, which exhibited highly conductive performance and electrocatalytic activity due to the small diameter (approxomately 5 nm). The Pd WLNCs/g-C_3N_4 could effectively immobilize AChE and enhance the signal

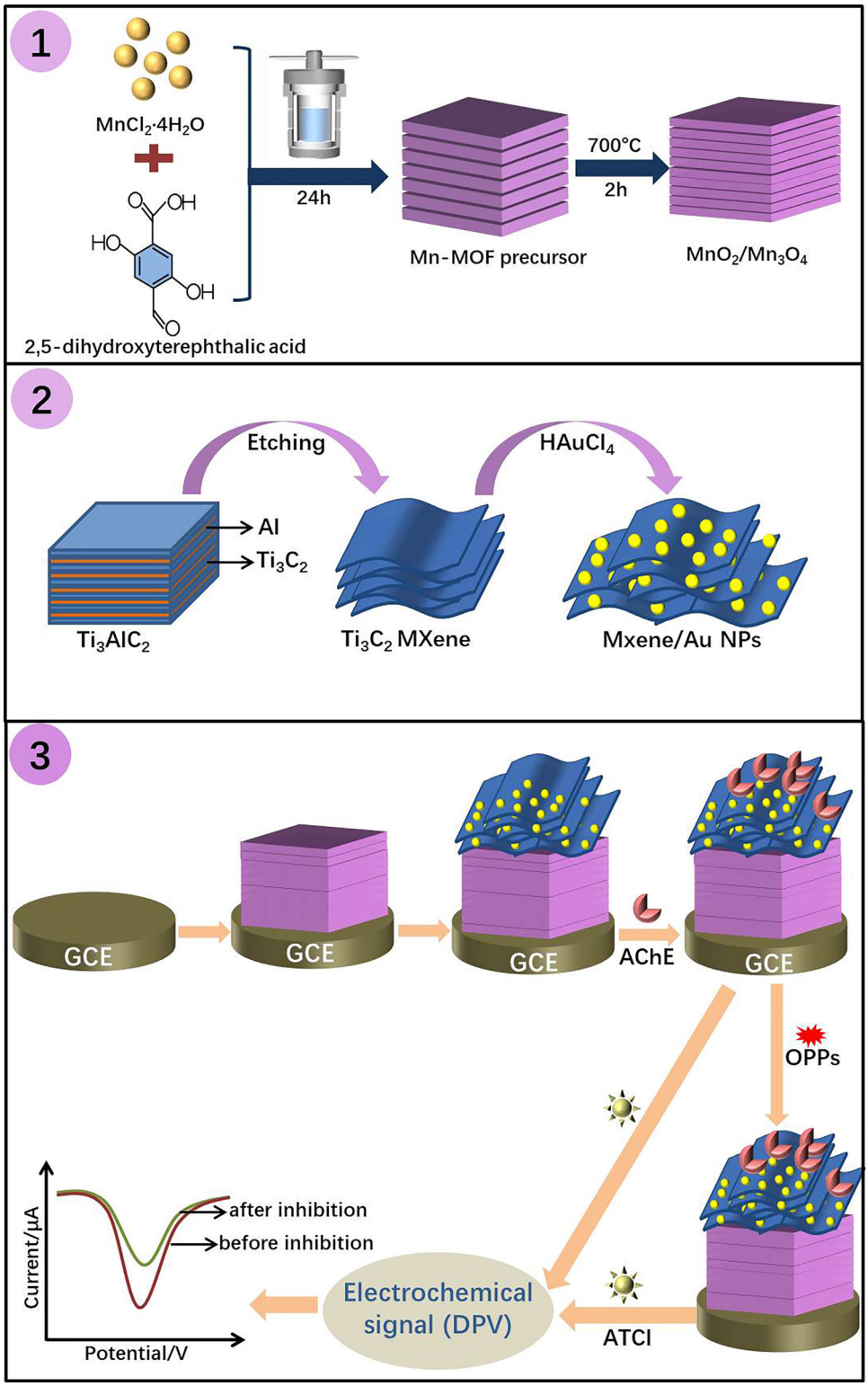

Figure 11. Illustration of the formation of MnO_2/Mn_3O_4 composite (1), MXene/Au NPs (2), the fabrication process of AChE-Chit/MXene/Au NPs/MnO_2/Mn_3O_4/GCE biosensor for methamidophos assay (3).

amplification. The linear range for the determination of OPPs was from 1.00 nM-14.96 μM, and the limit of detection was 0.33 nM.

Tungsten trioxide (WO_3) is a direct bandgap semiconductor with a bandgap of 2.5-2.8 eV with the good electron transfer property of 12 cm^2 V^{-1} s^{-1}. Bilal et al. integrated WO_3 with g-C_3N_4 for the fabrication of Tribolium castaneum (Red flour beetle) (Tc) AChE-based electrochemical biosensor to detect phosmet in stored grains.[69] The WO_3/g-C_3N_4 nanomaterial was nontoxic, biocompatible and easily immobilize Tc-AChE on the electrode surface. The kinetic parameters, obtained from the binding interactions of phosmet with Tc-AChE using a modified AutoDock LGA algorithm and an AMBER03 force field in YASARA,

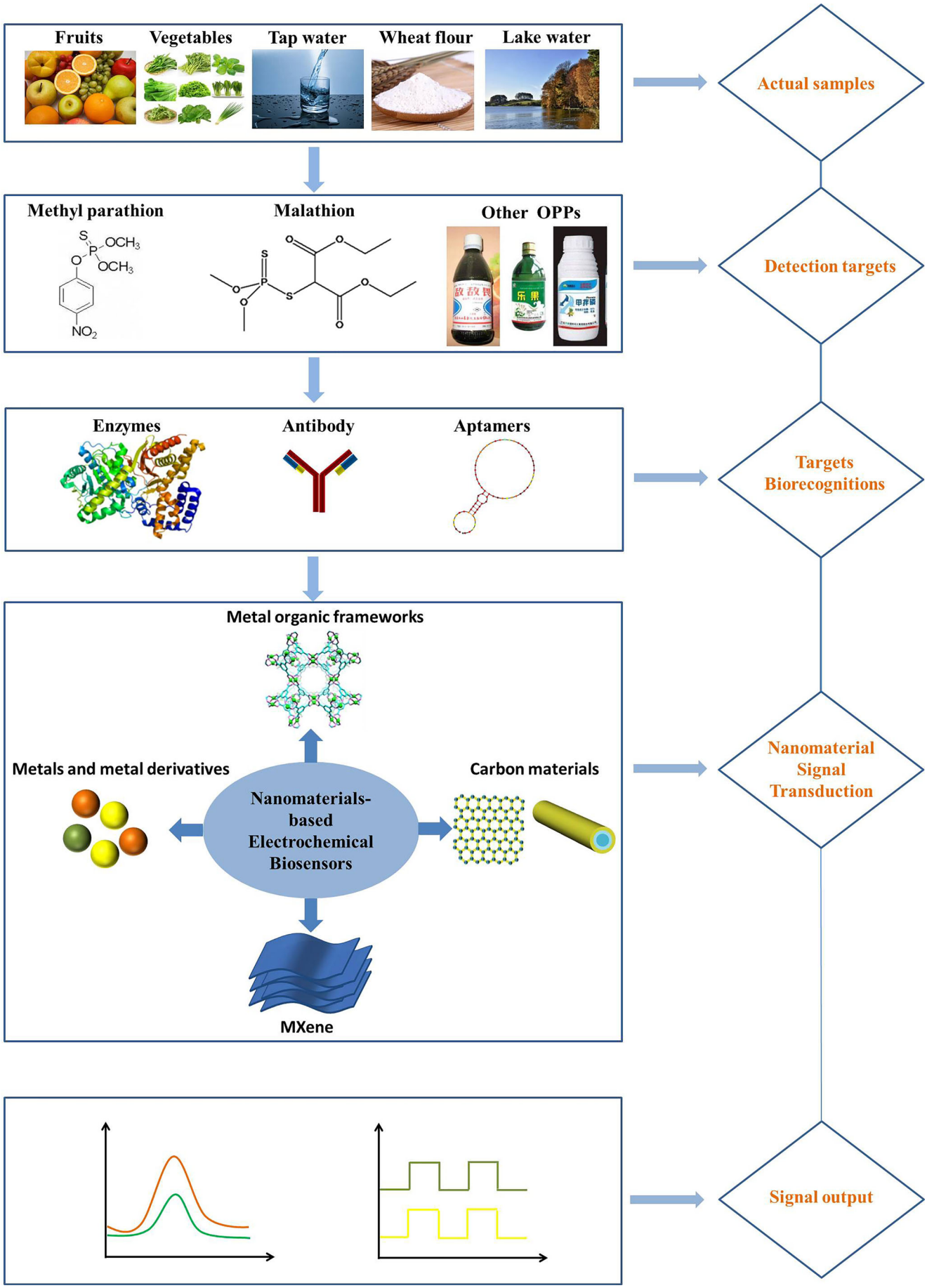

Figure 12. The bio-recognized and responsive process of OPPs on the nanomaterials-based electrochemical platform.

displayed the high potency of inhibitor with Tc-AChE. This method provided the desirable recoveries of phosmet up to 99% in spiked wheat flour samples, and the result agreed with the result of HPLC analysis.

g-C_3N_4 is a kind of early two-dimensional semiconductor material. Its nanostructure has extraordinary physical and chemical properties, excellent catalytic performance, and the price is relatively cheap. Therefore, the integration of the g-C_3N_4 structure improves the sensitivity of the electrochemical sensor and makes the development of a new generation of electrochemical sensor possible.

Quantum dots

Quantum dots (QDs) are considered as an emerging sensing tool for electrochemical sensing strategies. They have large surface area, volume ratio, good interface properties, high surface reactivity and electron transfer efficiency, and excellent biological phases.[126]

In addition, metal QDs are also a viable option. Therefore, electrochemical sensors involving the use of these QDs have been used for the determination of pollutants in food and the environment. However, the toxicity of heavy metal quantum dots has inevitably led to the research of new nanomaterials to replace them. For example, graphene quantum dot (GQD) (graphene sheets with GQDs less than 100 nanometers) was low toxicity, excellent electronic properties, strong chemical inertness, large specific surface area, good biocompatibility and low cost. Elshafey et al. used GO and GQDs nanocomposites (GO@GQDs) to detect ds-DNA-dimethoate (DMT) at trace level.[127] GQDs were electrodeposited on the GCE, and then the GO layer was cast. This platform was used to adsorb ds-DNA to make DNA biosensors (ds-DNA/GO@GQDs/GCE). The microscopic and electrochemical characterization of the modified electrode was carried out. Studies proved that the ds-DNA-GO@GQDs/GCE sensor had fast response, reproducibility, low detection limit and high selectivity. Dong et al. reported an innovative method for sensitive and simple electrochemical detection of non-electroactive OPPs.[70] The new strategy emphasized the manufacture of oxime-based sensors by attaching phosphatidylamine (PAM) to GQD modified GCE. The introduction of GQDs significantly increased the effective electrode active area, thereby expanding the fixed amount of PAM. Therefore, the oxidation current of PAM increased significantly. Based on the nucleophilic substitution reaction between oxime and OPPs, PAM was used as an electroactive probe to detect fenthion. Under optimal conditions, the difference in oxidation current of PAM was proportional to the concentration of fenthion, ranging from 1.0×10^{-11}-5.0×10^{-7} M, and the detection limit was 6.8×10^{-12} M (S/N = 3).

Mxene

MXene, a two-dimensional transition metal carbide or carbonitride, is a new graphene-like layered two-dimensional crystal material. The unique structure, composition and physical and chemical properties of MXene make it as a popular material in the field of 2 D material after graphene.[128,129] MXene was widely used in energy storage, catalysis, electromagnetic shielding and other fields due to its good conductivity and hydrophilicity, excellent mechanical properties and mature and controllable preparation process.[130] Through the control of the prepared conditions, 2 D MXene could be assembled into various morphologies, such as irregular particles, nanofibers and so on, which provided more possibilities for the design of microstructured material.[131,132] In the electrochemical biosensor, MXene were mainly used as immobilization substrates for proteins, biological enzymes, bioluminescent materials to improved the electron transfer rate resulted from their large specific surface area and high conductivity.[133,134] However, the conductivity of MXene was affected by the functional groups on the surface, and different functional groups have different effects on the conductivity of MXene.[135] Therefore, other materials (i.e., metal nanoparticles, carbon nanotubes, etc.) were assembled with MXene to enhance the conductivity.[136–139]

Embedded with metal nanoparticles could significantly improve conductivity and enhance the electrochemical property. Zhao et al. fabricated a sensing platform for the detection of paraoxon based on the Au-Pd bimetallic nanoparticles on MXene nanosheets.[71] Ti_3C_2MXene was prepared by the selective etching of Al layer from the Ti_3AlC_2 powder to generated an opened interspace. It exhibited an accordion-like structure with multilayer nanosheets. The shape-controlled Au-Pd bimetallic nanoparticles were prepared by the self-reduction process at room temperature using ultra-thin MXene nanosheets as the natural reducing agent and support. The prepared multi-dimensional MXene/Au-Pd was benefit for the AChE immobilization and could well enhance the catalytic performance, conductivity and stability. The fabricated biosensor showed a good linear relationship with the concentration of paraoxon in the range of 0.1-1000 μg L^{-1}, and the limit of detection was 1.75 ng L^{-1}.

Two-dimensional MXene nanosheets have become a key material for the construction of highly sensitive biosensor devices due to their large hydrophilic surface, low framework density, high electrochemical performance and good conductivity, which is conducive to their potential applications in the electrochemical field. Generally, there are two common methods to synthesize MXene, which are CVD and top-down method. The top-down method is mostly used to prepare layered materials, which are obtained from bulk solids through various exfoliation methods, but due to the uncontrollability of the synthesis method, the production will cause the stacking of nanomaterials. MXene is more promising than other two-dimensional materials due to its strong interaction between Ti and C bond. Song et al. prepared a MOF-dervied MnO_2/Mn_3O_4 and Ti_3C_2 MXene/Au NPs composite for the loading of AChE to fabricate the electrode, and the fabricated process was shown in Figure 11.[73] The exfoliated multilayers of MXene were less than 50 nm. The MnO_2/Mn_3O_4 derived from MOF with 3 D structure of hierarchical microcuboids was composed of

vertically aligned and highly ordered nanosheets. Compared with the bare GCE (410 Ω), the MnO_2/Mn_3O_4 and Ti_3C_2 MXene/Au NPs modified electrode possessed a much smaller Ret (12 Ω), which revealed that the composite acted as transducer could accelerate electron transfer. It showed outstanding performance for the detection of methamidophos with widely linear range from 10^{-12}-10^{-6} M, a low limit of detection was 1.34×10^{-13} M. Good recoveries (95.2-101.3%) were also obtained in fresh fruits. Although ultra-thin two-dimensional nanomaterials have been widely used to construct electrochemical sensors, they also have their shortcomings. These ultra-thin two-dimensional materials have relatively poor stability. The ultra-thin structure also makes nanosheets prone to be stacking, which will also cause the loss of nanosheets

In this study, a multi-layer structure composed of highly orderly stacked nanosheets and MXene/Au NPs were used to construct a sensing platform to achieved a synergistic signal amplification effect. The composite of this nanomaterial could make the AChE sensor exhibited excellent performance, and achieved the advantages of long-term stability of the MXene layered structure.

Sample treatment and real sample analysis

The quantitative and qualitative analysis of OPPs in environmental and food samples requires a process of sample preparation which will decrease the interference of sample matrices. In the process of food analysis, sample preparation is a crucial issue in the accurate detection of pesticides. Typically, the procedure of sample preparation require several steps, consist of sample collection, target analytes extracted from the sample, clean-up and analysis. Considering the high complexity of food samples, it is necessary to evaluate the lipid composition of food composition, sample state (liquid, granule, powder) and sample type (meat, tissue, fruit, vegetable), etc. Besides, it is of necessity to avoid the use of harmful organic solvents in the sample preparation to interfere the detected result. Therefore, an appropriate method of sample preparation should be selected and used before the detection.[140]

Nowadays, some miniaturized extraction and preconcentration techniques (i.e., QuEChERS, dispersion-liquid microextraction, solid-phase microextraction, stir-bar adsorption extraction, membrane-assisted solvent extraction, and single drop microextraction etc.) have been used for the trace analysis of pesticides in food samples.[141,142] In the case of the detection of pesticides using biosensors, the collected samples must be simply processed for the on-site and fast detection.

As listed in Table 2, the detected OPPs mostly existed in water (tap water, lake water), fruits and vegetables. The tap water analysis required a simple pretreatment, which usually involved diluting the sample with a buffer solution to facilitate the electrochemical analysis of OPPs.[143] For liquid matrices with high complexity, including juice, processing steps are different, including dilution with buffer solution, pH adjustment, and filtration through filters to ensure the proper program in the extraction of pesticides.[144,145] When the tested samples were solid, and due to the high complexity of solid matrices, a large amount of processing steps were introduced to homogenize the samples to obtain liquid extracts for the continuous analysis. In general, the detection of OPPs in the stock solution from actual samples required slicing, breaking, and homogenizing the solid matrix, and then removing solid impurities through the centrifugation and filter before the detection using electrochemical (bio)sensors.

Although several studies have applied electrochemical (bio)sensors in actual samples, few articles describe the detailed validation of electrochemical (bio)sensors compared to the standard laboratory technique, such as chromatography. Besides, there is also a lack of real-time monitoring technology in the processing of food raw materials, which is still to be developed in future studies.

Conclusion and future perspectives

OPPs have been widely used in farmland. Incomplete utilization of OPPs leads to residues in soil, food, surface water and groundwater, which can enter into human body and seriously endanger human health. Therefore, the development of detection methods for OPPs for environmental monitoring and food safety applications has become very important. Among these methods, the development of highly sensitive electrochemical (bio)sensors occupies a leading position in analytical chemistry. With the remarkable development of nanotechnology and nanoscience, electrochemical signal amplification based on nanomaterials has the potential to improve the sensitivity and selectivity of electrochemical (bio)sensors. This review classifies the mechanisms involved in OPPs through electrochemical (bio)sensors based on sensing elements of various nanomaterials.

This paper also reviews the recent progress in the design of electrochemical (bio)sensor platforms, and summarizes the unique electrochemical properties of different nanomaterials, which promotes the development of their advanced application. Biological recognition and response processes of OPPs on electrochemical platforms based on different nanomaterials are summarized in Figure 12. The unique physical and chemical properties, synthesis methods, integration strategies and recent trends of electrochemical (bio)sensor platforms based on the most advanced nanomaterials (such as MOFs, metals and metal derivatives, carbon materials (CNTs, graphene, g-C_3N_4), MXene) are evaluated. Emphasis is placed on the selected sensing applications and future prospects of these nanostructured materials in the design of some advanced sensor platforms. However, up to now, the analysis of OPPs using electrochemical (bio)sensing strategies based on different nanomaterials still has unsatisfactory stability and selectivity problems, which are attracting the attention of many researchers around the world. In order to achieve the goal of long-term application of electrochemical (bio)sensors, the stability and reusability of these nanomaterials still need to be further improved to meet the key requirements of actual sample applications. Some of the

unsolved problems include: (1) sensing materials: with the help of advanced nano-modified materials, the performance of electrochemical (bio)sensors is expected to be greatly improved through precise nano-structures. Nanomaterials are substances that act as a bridge between electrodes and biologically active substances to generate and transmit signals. Further research is needed to control the morphology of nanomaterials to enhance the reaction signal between nanomaterials and electrodes. (2) component interference: in real samples, various ions and organics can easily cause huge damage. In order to meet on-site and on-site detection, the stability and reliability of the biosensor should be considered. (3) equipment development: the general three-electrode system is complicated, and the actual detection process is cumbersome to operate. More attention should be paid to the development of portable devices. It is expected that the progress of electrochemical (bio)sensor platforms based on nanomaterials will become a powerful driving force for new technologies and a major development to ensure the human environment and food safety.

Funding

This work was supported by the National Natural Science Foundation of China (No. 31901766), Financial support from the Talents of High Level Scientific Research Foundation, Qingdao Agricultural University (No. 1119014, 1120023), and Breeding Plan of Shandong Provincial Qingchuang Research Team (2019).

ORCID

Wei Wu http://orcid.org/0000-0002-1772-3841

References

[1] Cha, E. S.; Chang, S. S.; Choi, Y.; Lee, W. J. Trends in Pesticide Suicide in South Korea, 1983-2014. *Epidemiol. Psychiatr. Sci.* **2019**, *29*, e25. DOI: 10.1017/S2045796019000118.

[2] Kumar, P.; Kim, K. H.; Deep, A. Recent Advancements in Sensing Techniques Based on Functional Materials for Organophosphate pesticides. *Biosens. Bioelectron.* **2015**, *70*, 469–481. DOI: 10.1016/j.bios.2015.03.066.

[3] Hernandez, A. F.; Gil, F.; Lacasana, M. Toxicological Interactions of Pesticide Mixtures: An Update. *Arch. Toxicol.* **2017**, *91*, 3211–3223. DOI: 10.1007/s00204-017-2043-5.

[4] Song, D.; Wang, Y.; Lu, X.; Gao, Y.; Li, Y.; Gao, F. Ag Nanoparticles-Decorated Nitrogen-Fluorine co-Doped Monolayer MoS_2 Nanosheet for Highly Sensitive Electrochemical Sensing of Organophosphorus Pesticides. *Sens. Actuators, B.* **2018**, *267*, 5–13. DOI: 10.1016/j.snb.2018.04.016.

[5] Sun, L.; Xu, W.; Peng, T.; Chen, H.; Ren, L.; Tan, H.; Xiao, D.; Qian, H.; Fu, Z. Developmental Exposure of Zebrafish Larvae to Organophosphate Flame Retardants Causes Neurotoxicity. *Neurotoxicol. Teratol.* **2016**, *55*, 16–22. DOI: 10.1016/j.ntt.2016.03.003.

[6] Mishra, A.; Kumar, J.; Melo, J. S.; Sandaka, B. P. Progressive Development in Biosensors for Detection of Dichlorvos Pesticide: A Review. *J. Environ. Chem. Eng.* **2021**, *9*, 105067. DOI: 10.1016/j.jece.2021.105067.

[7] Barker, Z.; Venkatchalam, V.; Martin, A. N.; Farquar, G. R.; Frank, M. Detecting Trace Pesticides in Real Time Using Single Particle Aerosol Mass Spectrometry. *Anal. Chim. Acta.* **2010**, *661*, 188–194. DOI: 10.1016/j.aca.2009.12.031.

[8] Masia, A.; Suarez-Varela, M. M.; Llopis-Gonzalez, A.; Pico, Y. Determination of Pesticides and Veterinary Drug Residues in Food by Liquid Chromatography-Mass Spectrometry: A Review. *Anal. Chim. Acta.* **2016**, *936*, 40–61. DOI: 10.1016/j.aca.2016.07.023.

[9] Pelajic, M.; Pecek, G.; Mutavdzic Pavlovic, D.; Vitali Cepo, D. Novel Multiresidue Method for Determination of Pesticides in Red Wine Using Gas Chromatography-Mass Spectrometry and Solid Phase Extraction. *Food Chem* **2016**, *200*, 98. DOI: 10.1016/j.foodchem.2016.01.018.

[10] Pico, Y.; Alfarhan, A. H.; Barcelo, D. How Recent Innovations in Gas Chromatography-Mass Spectrometry Have Improved Pesticide Residue Determination: An Alternative Technique to Be in Your Radar. *Trac, Trends Anal. Chem.* **2020**, *122*, 115720. DOI: 10.1016/j.trac.2019.115720.

[11] Amali, R. K. A.; Lim, H. N.; Ibrahim, I.; Huang, N. M.; Zainal, Z.; Ahmad, S. A. A. Significance of Nanomaterials in Electrochemical Sensors for Nitrate Detection: A Review. *Trends Environ. Anal. Chem.* **2021**, *31*, e00135. DOI: 10.1016/j.teac.2021.e00135.

[12] Anu Prathap, M. U.; Kaur, B.; Srivastava, R. Electrochemical Sensor Platforms Based on Nanostructured Metal Oxides, and Zeolite-Based Materials. *Chem. Rec.* **2019**, *19*, 883–907. DOI: 10.1002/tcr.201800068.

[13] Bo, X.; Zhou, M.; Guo, L. Electrochemical Sensors and Biosensors Based on Less Aggregated Graphene. *Biosens. Bioelectron.* **2017**, *89*, 167–186. DOI: 10.1016/j.bios.2016.05.002.

[14] Liu, T.; Chu, Z.; Jin, W. Electrochemical Mercury Biosensors Based on Advanced Nanomaterials. *J. Mater. Chem. B.* **2019**, *7*, 3620–3632. DOI: 10.1039/C9TB00418A.

[15] Pundir, C. S.; Malik, A. Preety Bio-Sensing of Organophosphorus Pesticides: A Review. *Biosens Bioelectron* **2019**, *140*, 111348. DOI: 10.1016/j.bios.2019.111348.

[16] Liu, G.; Lin, Y. Electrochemical Sensor for Organophosphate Pesticides and Nerve Agents Using Zirconia Nanoparticles as Selective Sorbents. *Anal. Chem.* **2005**, *77*, 5894–5901. DOI: 10.1021/ac050791t.

[17] Gannavarapu, K. P.; Ganesh, V.; Thakkar, M.; Mitra, S.; Dandamudi, R. B. Nanostructured Diatom-ZrO_2 Composite as a Selective and Highly Sensitive Enzyme Free Electrochemical Sensor for Detection of Methyl Parathion. *Sens Actuators B Chem ..* **2019**, *288*, 611–617. DOI: 10.1016/j.snb.2019.03.036.

[18] Shanmugam, R.; Manavalan, S.; Chen, S.-M.; Keerthi, M.; Lin, L.-H. Methyl Parathion Detection Using SnS_2/N, S–Co-Doped Reduced Graphene Oxide Nanocomposite. *ACS Sustainable Chem. Eng.* **2020**, *8*, 11194–11203. DOI: 10.1021/acssuschemeng.0c02528.

[19] Liao, C.; Mak, C.; Zhang, M.; Chan, H. L.; Yan, F. Flexible Organic Electrochemical Transistors for Highly Selective Enzyme Biosensors and Used for Saliva Testing. *Adv. Mater.* **2015**, *27*, 676–681. DOI: 10.1002/adma.201404378.

[20] Stoytcheva, M.; Zlatev, R.; Montero, G.; Velkova, Z.; Gochev, V. A Nanotechnological Approach to Biosensors Sensitivity Improvement: application to Organophosphorus Pesticides Determination. *Biotechnology & Biotechnological Equipment* **2018**, *32*, 213–220. DOI: 10.1080/13102818.2017.1389618.

[21] Amine, A.; Arduini, F.; Moscone, D.; Palleschi, G. Recent Advances in Biosensors Based on Enzyme Inhibition. *Biosens. Bioelectron.* **2016**, *76*, 180–194. DOI: 10.1016/j.bios.2015.07.010.

[22] Zhang, Y.; Arugula, M. A.; Wales, M.; Wild, J.; Simonian, A. L. A Novel Layer-by-Layer Assembled Multi-Enzyme/CNT Biosensor for Discriminative Detection between Organophosphorus and Non-Organophosphrus Pesticides. *Biosens. Bioelectron.* **2015**, *67*, 287–295. DOI: 10.1016/j.bios.2014.08.036.

[23] He, L.; Cui, B.; Liu, J.; Song, Y.; Wang, M.; Peng, D.; Zhang, Z. Novel Electrochemical Biosensor Based on Core-Shell Nanostructured Composite of Hollow Carbon Spheres and Polyaniline for Sensitively Detecting Malathion. *Sens. Actuators, B.* **2018**, *258*, 813–821. DOI: 10.1016/j.snb.2017.11.161.

[24] Zhao, F.; Yao, Y.; Li, X.; Lan, L.; Jiang, C.; Ping, J. Metallic Transition Metal Dichalcogenide Nanosheets as an Effective and Biocompatible Transducer for Electrochemical Detection of Pesticide. *Anal. Chem.* **2018**, *90*, 11658–11664. DOI: 10.1021/acs.analchem.8b03250.

[25] He, Y.; Du, J.; Luo, J.; Chen, S.; Yuan, R. Coreactant-Free Electrochemiluminescence Biosensor for the Determination of Organophosphorus Pesticides. *Biosens. Bioelectron.* **2020**, *150*, 111898. DOI: 10.1016/j.bios.2019.111898.

[26] Bao, J.; Hou, C.; Chen, M.; Li, J.; Huo, D.; Yang, M.; Luo, X.; Lei, Y. Plant Esterase-Chitosan/Gold Nanoparticles-Graphene Nanosheet Composite-Based Biosensor for the Ultrasensitive Detection of Organophosphate Pesticides. *J Agric Food Chem* .. **2015**, *63*, 10319–10326. DOI: 10.1021/acs.jafc.5b03971.

[27] Cho, I. H.; Lee, J.; Kim, J.; Kang, M. S.; Paik, J. K.; Ku, S.; Cho, H. M.; Irudayaraj, J.; Kim, D. H. Current Technologies of Electrochemical Immunosensors: Perspective on Signal Amplification. *Sensors (Basel)* **2018**, *18*, 207. DOI: 10.3390/s18010207.

[28] Lim, S. A.; Ahmed, M. U. Electrochemical Immunosensors and Their Recent Nanomaterial-Based Signal Amplification Strategies: A Review. *RSC Adv.* **2016**, *6*, 24995–25014. DOI: 10.1039/C6RA00333H.

[29] Chen, H. M.; Jheng, K. R.; Yu, A. D. Direct, Label-Free, Selective, and Sensitive Microbial Detection Using a Bacteriorhodopsin-Based Photoelectric Immunosensor. *Biosens. Bioelectron.* **2017**, *91*, 24–31. DOI: 10.1016/j.bios.2016.12.032.

[30] Liu, G.; Song, D.; Chen, F. Towards the Fabrication of a Label-Free Amperometric Immunosensor Using SWNTs for Direct Detection of Paraoxon. *Talanta* **2013**, *104*, 103–108. DOI: 10.1016/j.talanta.2012.11.039.

[31] Sun, X.; Cao, Y.; Gong, Z.; Wang, X.; Zhang, Y.; Gao, J. An Amperometric Immunosensor Based on Multi-Walled Carbon Nanotubes-Thionine-Chitosan Nanocomposite Film for Chlorpyrifos Detection. *Sensors (Basel)* **2012**, *12*, 17247–17261. DOI: 10.3390/s121217247.

[32] Dong, H.; Zhao, Q.; Li, J.; Xiang, Y.; Liu, H.; Guo, Y.; Yang, Q.; Sun, X. Broad-Spectrum Electrochemical Immunosensor Based on One-Step Electrodeposition of AuNP-Abs and Prussian Blue Nanocomposite for Organophosphorus Pesticide Detection. *Bioprocess Biosyst Eng* **2021**, *44*, 585–594. DOI: 10.1007/s00449-020-02472-9.

[33] Zhou, J.; Zhao, Y.; Bao, J.; Huo, D.; Fa, H.; Shen, X.; Hou, C. One-Step Electrodeposition of Au-Pt Bimetallic Nanoparticles on MoS_2 Nanoflowers for Hydrogen Peroxide Enzyme-Free Electrochemical Sensor. *Electrochim. Acta* **2017**, *250*, 152–158. DOI: 10.1016/j.electacta.2017.08.044.

[34] Peltomaa, R.; Benito-Pena, E.; Gorris, H. H.; Moreno-Bondi, M. C. Biosensing Based on Upconversion Nanoparticles for Food Quality and Safety Applications. *Analyst* **2021**, *146*, 13–32. DOI: 10.1039/d0an01883j.

[35] Huo, B.; Hu, Y.; Gao, Z.; Li, G. Recent Advances on Functional Nucleic Acid-Based Biosensors for Detection of Food Contaminants. *Talanta* **2021**, *222*, 121565. DOI: 10.1016/j.talanta.2020.121565.

[36] Selvolini, G.; Băjan, I.; Hosu, O.; Cristea, C.; Săndulescu, R.; Marrazza, G. DNA-Based Sensor for the Detection of an Organophosphorus Pesticide: Profenofos. *Sensors (Basel)* **2018**, *18*, 2035. DOI: 10.3390/s18072035.

[37] Yang, Y.; Liu, X.; Wu, M.; Wang, X.; Hou, T.; Li, F. Electrochemical Biosensing Strategy for Highly Sensitive Pesticide Assay Based on Mercury Ion-Mediated DNA Conformational Switch Coupled with Signal Amplification by Hybridization Chain Reaction. *Sens. Actuators, B.* **2016**, *236*, 597–604. DOI: 10.1016/j.snb.2016.06.044.

[38] Fu, J.; An, X.; Yao, Y.; Guo, Y.; Sun, X. Electrochemical Aptasensor Based on One Step co-Electrodeposition of Aptamer and GO-CuNPs Nanocomposite for Organophosphorus Pesticide Detection. *Sens. Actuators, B.* **2019**, *287*, 503–509. DOI: 10.1016/j.snb.2019.02.057.

[39] C, G. A.; Varghese, A.; M, N. Recent Advances in Nanomaterials Based Molecularly Imprinted Electrochemical Sensors. *Crit Rev Anal Chem* **2021**. DOI: 10.1080/10408347.2021.1937925.

[40] Wang, W.; Wang, X.; Cheng, N.; Luo, Y.; Lin, Y.; Xu, W.; Du, D. Recent Advances in Nanomaterials-Based Electrochemical (Bio)Sensors for Pesticides Detection. *Trac, Trends Anal. Chem.* **2020**, *132*, 116041. DOI: 10.1016/j.trac.2020.116041.

[41] Wang, B.; Hong, J.; Liu, C.; Zhu, L.; Jiang, L. An Electrochemical Molecularly Imprinted Polymer Sensor for Rapid β-Lactoglobulin Detection. *Sensors* **2021**, *21*, 8240. DOI: 10.3390/s21248240.

[42] Zheng, X.; Khaoulani, S.; Ktari, N.; Lo, M.; Khalil, A. M.; Zerrouki, C.; Fourati, N.; Chehimi, M. M. Towards Clean and Safe Water: A Review on the Emerging Role of Imprinted Polymer-Based Electrochemical Sensors. *Sensors (Basel)* **2021**, *21*, 4300. DOI: 10.3390/s21134300.

[43] Motaharian, A.; Motaharian, F.; Abnous, K.; Hosseini, M. R.; Hassanzadeh-Khayyat, M. Molecularly Imprinted Polymer nanoparticles-based electrochemical sensor for determination of diazinon pesticide in well water and apple fruit samples . *Anal. Bioanal. Chem.* **2016**, *408*, 6769–6779. DOI: 10.1007/s00216-016-9802-7.

[44] Xu, G.; Huo, D.; Hou, J.; Zhang, C.; Zhao, Y.; Hou, C.; Bao, J.; Yao, X.; Yang, M. An Electrochemical Aptasensor of Malathion Based on Ferrocene/DNA-Hybridized MOF, DNA Coupling-Gold Nanoparticles and Competitive DNA Strand Reaction. *Microchem. J.* **2021**, *162*, 105829. DOI: 10.1016/j.microc.2020.105829.

[45] Karimi-Maleh, H.; Yola, M. L.; Atar, N.; Orooji, Y.; Karimi, F.; Senthil Kumar, P.; Rouhi, J.; Baghayeri, M. A Novel Detection Method for Organophosphorus Insecticide Fenamiphos: Molecularly Imprinted Electrochemical Sensor Based on Core-Shell Co_3O_4@MOF-74 Nanocomposite. *J Colloid Interface Sci* . **2021**, *592*, 174–185. DOI: 10.1016/j.jcis.2021.02.066.

[46] Cao, Y.; Wang, L.; Shen, C.; Wang, C.; Hu, X.; Wang, G. An Electrochemical Sensor on the Hierarchically Porous Cu-BTC MOF Platform for Glyphosate Determination. *Sens. Actuators, B.* **2019**, *283*, 487–494. DOI: 10.1016/j.snb.2018.12.064.

[47] Ma, L.; He, Y.; Wang, Y.; Wang, Y.; Li, R.; Huang, Z.; Jiang, Y.; Gao, J. Nanocomposites of Pt Nanoparticles Anchored on UiO66-NH_2 as Carriers to Construct Acetylcholinesterase Biosensors for Organophosphorus Pesticide Detection. *Electrochim. Acta* **2019**, *318*, 525–533. DOI: 10.1016/j.electacta.2019.06.110.

[48] Li, X.; Gao, X.; Gai, P.; Liu, X.; Li, F. Degradable Metal-Organic Framework/Methylene Blue Composites-Based Homogeneous Electrochemical Strategy for Pesticide Assay. *Sens. Actuators, B.* **2020**, *323*, 128701. DOI: 10.1016/j.snb.2020.128701.

[49] Chen, P.; Liu, Z.; Liu, J.; Liu, H.; Bian, W.; Tian, D.; Xia, F.; Zhou, C. A Novel Electrochemiluminescence Aptasensor Based CdTe QDs@NH_2-MIL-88(Fe) for Signal Amplification. *Electrochim. Acta* **2020**, *354*, 136644. DOI: 10.1016/j.electacta.2020.136644.

[50] Wang, Z.; Ma, B.; Shen, C.; Cheong, L. Z. Direct, Selective and Ultrasensitive Electrochemical Biosensing of Methyl Parathion in Vegetables Using Burkholderia cepacia Lipase@MOF Nanofibers-Based Biosensor. *Talanta* **2019**, *197*, 356–362. DOI: 10.1016/j.talanta.2019.01.052.

[51] Zhao, G.; Zhou, B.; Wang, X.; Shen, J.; Zhao, B. Detection of Organophosphorus Pesticides by Nanogold/Mercaptomethamidophos Multi-Residue Electrochemical

Biosensor. *Food Chem.* **2021**, *354*, 129511. DOI: 10.1016/j.foodchem.2021.129511.

[52] Lu, X.; Tao, L.; Li, Y.; Huang, H.; Gao, F. A Highly Sensitive Electrochemical Platform Based on the Bimetallic Pd@Au Nanowires Network for Organophosphorus Pesticides Detection. *Sens. Actuators, B.* **2019**, *284*, 103–109. DOI: 10.1016/j.snb.2018.12.125.

[53] Pajooheshpour, N.; Rezaei, M.; Hajian, A.; Afkhami, A.; Sillanpää, M.; Arduini, F.; Bagheri, H. Protein Templated Au-Pt Nanoclusters-Graphene Nanoribbons as a High Performance Sensing Layer for the Electrochemical Determination of Diazinon. *Sens. Actuators, B.* **2018**, *275*, 180–189. DOI: 10.1016/j.snb.2018.08.014.

[54] Gao, N.; He, C.; Ma, M.; Cai, Z.; Zhou, Y.; Chang, G.; Wang, X.; He, Y. Electrochemical co-deposition synthesis of Au-ZrO2-graphene nanocomposite for a nonenzymatic methyl parathion sensor. *Anal. Chim. Acta.* **2019**, *1072*, 25–34. DOI: 10.1016/j.aca.2019.04.043.

[55] Cui, H. F.; Wu, W. W.; Li, M. M.; Song, X.; Lv, Y.; Zhang, T. T. A Highly Stable Acetylcholinesterase Biosensor Based on chitosan-TiO_2-Graphene Nanocomposites for Detection of Organophosphate Pesticides. *Biosens. Bioelectron.* **2018**, *99*, 223–229. DOI: 10.1016/j.bios.2017.07.068.

[56] Xie, Y.; Tu, X.; Ma, X.; Fang, Q.; Liu, G.; Dai, R.; Qu, F.; Yu, Y.; Lu, L.; Huang, X. A CuO-CeO_2 Composite Prepared by Calcination of a Bimetallic Metal-Organic Framework for Use in an Enzyme-Free Electrochemical Inhibition Assay for Malathion. *Mikrochim. Acta.* **2019**, *186*, 567. DOI: 10.1007/s00604-019-3684-2.

[57] Gu, C.; Wang, Q.; Zhang, L.; Yang, P.; Xie, Y.; Fei, J. Ultrasensitive Non-Enzymatic Pesticide Electrochemical Sensor Based on HKUST-1-Derived Copper Oxide @ Mesoporous Carbon Composite. *Sens. Actuators, B.* **2020**, *305*, 127478. DOI: 10.1016/j.snb.2019.127478.

[58] Tian, X.; Liu, L.; Li, Y.; Yang, C.; Zhou, Z.; Nie, Y.; Wang, Y. Nonenzymatic Electrochemical Sensor Based on CuO-TiO_2 for Sensitive and Selective Detection of Methyl Parathion Pesticide in Ground Water. *Sens. Actuators, B.* **2018**, *256*, 135–142. DOI: 10.1016/j.snb.2017.10.066.

[59] Nasir, M. Z. M.; Mayorga-Martinez, C. C.; Sofer, Z.; Pumera, M. Two-Dimensional 1T-Phase Transition Metal Dichalcogenides as Nanocarriers to Enhance and Stabilize Enzyme Activity for Electrochemical Pesticide Detection. *ACS Nano.* **2017**, *11*, 5774–5784. DOI: 10.1021/acsnano.7b01364.

[60] Peng, L.; Dong, S.; Wei, W.; Yuan, X.; Huang, T. Synthesis of Reticulated Hollow Spheres Structure $NiCo_2S_4$ and Its Application in Organophosphate Pesticides biosensor. *Biosens. Bioelectron.* **2017**, *92*, 563–569. DOI: 10.1016/j.bios.2016.10.059.

[61] Zhang, Y.; Kang, T.-F.; Wan, Y.-W.; Chen, S.-Y. Gold Nanoparticles-Carbon Nanotubes Modified Sensor for Electrochemical Determination of Organophosphate Pesticides. *Microchim. Acta* **2009**, *165*, 307–311. DOI: 10.1007/s00604-008-0134-y.

[62] Xu, G.; Huo, D.; Hou, C.; Zhao, Y.; Bao, J.; Yang, M.; Fa, H. A Regenerative and Selective Electrochemical Aptasensor Based on Copper Oxide Nanoflowers-Single Walled Carbon Nanotubes Nanocomposite for Chlorpyrifos Detection. *Talanta* **2018**, *178*, 1046–1052. DOI: 10.1016/j.talanta.2017.08.086.

[63] Yao, J.; Liu, Z.; Jin, M.; Zou, Y.; Chen, J.; Xie, P.; Wang, X.; Akinoglu, E. M.; Zhou, G.; Shui, L. Uniform Honeycomb CNT-Microparticles Prepared via Droplet-Microfluidics and Sacrificial Nanoparticles for Electrochemical Determination of Methyl Parathion. *Sens. Actuators, B.* **2020**, *321*, 128517. DOI: 10.1016/j.snb.2020.128517.

[64] Zhao, H.; Ma, H.; Li, X.; Liu, B.; Liu, R.; Komarneni, S. Nanocomposite of Halloysite Nanotubes/Multi-Walled Carbon Nanotubes for Methyl Parathion Electrochemical Sensor Application. *Appl. Clay Sci.* **2021**, *200*, 105907. DOI: 10.1016/j.clay.2020.105907.

[65] Chen, Z.; Zhang, Y.; Yang, Y.; Shi, X.; Zhang, L.; Jia, G. Hierarchical Nitrogen-Doped Holey Graphene as Sensitive Electrochemical Sensor for Methyl Parathion Detection. *Sens. Actuators, B.* **2021**, *336*, 129721. DOI: 10.1016/j.snb.2021.129721.

[66] Kaur, R.; Rana, S.; Lalit, K.; Singh, P.; Kaur, K. Electrochemical Detection of Methyl Parathion via a Novel Biosensor Tailored on Highly Biocompatible Electrochemically Reduced Graphene Oxide-Chitosan-Hemoglobin Coatings. *Biosens. Bioelectron.* **2020**, *167*, 112486. DOI: 10.1016/j.bios.2020.112486.

[67] Khosropour, H.; Rezaei, B.; Rezaei, P.; Ensafi, A. A. Ultrasensitive Voltammetric and Impedimetric Aptasensor for Diazinon Pesticide Detection by VS_2 Quantum Dots-Graphene Nanoplatelets/Carboxylated Multiwalled Carbon Nanotubes As A New Group Nanocomposite For Signal Enrichment. *Anal. Chim. Acta.* **2020**, *1111*, 92–102. DOI: 10.1016/j.aca.2020.03.047.

[68] Wang, B.; Ye, C.; Zhong, X.; Chai, Y.; Chen, S.; Yuan, R. Electrochemical Biosensor for Organophosphate Pesticides and Huperzine-A Detection Based on Pd Wormlike Nanochains/Graphitic Carbon Nitride Nanocomposites and Acetylcholinesterase. *Electroanalysis* **2016**, *28*, 304–311. DOI: 10.1002/elan.201500339.

[69] Bilal, S.; Mudassir Hassan, M.; Fayyaz Ur Rehman, M.; Nasir, M.; Jamil Sami, A.; Hayat, A. An Insect Acetylcholinesterase Biosensor Utilizing WO_3/g-C_3N_4 Nanocomposite Modified Pencil Graphite Electrode for Phosmet Detection in Stored Grains. *Food Chem.* **2021**, *346*, 128894. DOI: 10.1016/j.foodchem.2020.128894.

[70] Dong, J.; Hou, J.; Jiang, J.; Ai, S. Innovative Approach for the Electrochemical Detection of Non-Electroactive Organophosphorus Pesticides Using Oxime As Electroactive Probe . *Anal. Chim. Acta.* **2015**, *885*, 92–97. DOI: 10.1016/j.aca.2015.05.033.

[71] Zhao, F.; Yao, Y.; Jiang, C.; Shao, Y.; Barcelo, D.; Ying, Y.; Ping, J. Self-Reduction Bimetallic Nanoparticles on Ultrathin MXene Nanosheets as Functional Platform for Pesticide Sensing. *J. Hazard. Mater.* **2020**, *384*, 121358. DOI: 10.1016/j.jhazmat.2019.121358.

[72] Jiang, Y.; Zhang, X.; Pei, L.; Yue, S.; Ma, L.; Zhou, L.; Huang, Z.; He, Y.; Gao, J. Silver Nanoparticles Modified Two-Dimensional Transition Metal Carbides as Nanocarriers to Fabricate Acetycholinesterase-Based Electrochemical Biosensor. *Chemical Engineering Journal* **2018**, *339*, 547–556. DOI: 10.1016/j.cej.2018.01.111.

[73] Song, D.; Jiang, X.; Li, Y.; Lu, X.; Luan, S.; Wang, Y.; Li, Y.; Gao, F. Metal-organic Frameworks-derived MnO2/Mn3O4 Microcuboids with Hierarchically Ordered Nanosheets and Ti3C2 MXene/Au NPs Composites for Electrochemical Pesticide Detection. *J. Hazard. Mater.* **2019**, *373*, 367–376. DOI: 10.1016/j.jhazmat.2019.03.083.

[74] Wang, B.; Li, Y.; Hu, H.; Shu, W.; Yang, L.; Zhang, J. Acetylcholinesterase Electrochemical Biosensors with Graphene-Transition Metal Carbides Nanocomposites Modified for Detection of Organophosphate Pesticides. *PLoS One.* **2020**, *15*, e0231981. DOI: 10.1371/journal.pone.0231981.

[75] Devic, T.; Serre, C.; Audebrand, N.; Marrot, J.; Férey, G. MIL-103, a 3-D Lanthanide-Based Metal Organic Framework with Large One-Dimensional Tunnels and a High Surface Area. *J. Am. Chem. Soc.* **2005**, *127*, 12788–12789. DOI: 10.1021/ja053992n.

[76] He, C.; Lu, K.; Liu, D.; Lin, W. Nanoscale metal-Organic Frameworks for the Co-delivery of Cisplatin and Pooled siRNAs to Enhance Therapeutic Efficacy in Drug-resistant Ovarian Cancer Cells. *J. Am. Chem. Soc.* **2014**, *136*, 5181–5184. DOI: 10.1021/ja4098862.

[77] Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. *Science* **2002**, *295*, 469–472. DOI: 10.1126/science.1067208.

[78] Liu, Y.; Eubank, J. F.; Cairns, A. J.; Eckert, J.; Kravtsov, V.; Luebke, R.; Eddaoudi, M. Assembly of Metal-Organic Frameworks (MOFs) Based on Indium-Trimer Building Blocks: A Porous MOF with Soc Topology and High Hydrogen Storage. *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 3278–3283. DOI: 10.1002/anie.200604306.

[79] Xiong, C. Y.; Wang, H. J.; Liang, W. B.; Yuan, Y. L.; Yuan, R.; Chai, Y. Q. Luminescence-Functionalized Metal-Organic Frameworks Based on a Ruthenium(II) Complex: A Signal Amplification Strategy for Electrogenerated Chemiluminescence Immunosensors. *Chemistry* **2015**, *21*, 9825–9832. DOI: 10.1002/chem.201500909.

[80] Zhao, X.; Wang, Y.; Li, D. S.; Bu, X.; Feng, P. Metal-Organic Frameworks for Separation. *Adv. Mater.* **2018**, *30*, e1705189. DOI: 10.1002/adma.201705189.

[81] Vikrant, K.; Tsang, D. C. W.; Raza, N.; Giri, B. S.; Kukkar, D.; Kim, K. H. Potential Utility of Metal-Organic Framework-Based Platform for Sensing Pesticides. *ACS Appl Mater Interfaces* **2018**, *10*, 8797–8817. DOI: 10.1021/acsami.8b00664.

[82] Aguilera-Sigalat, J.; Bradshaw, D. Synthesis and Applications of Metal-Organic Framework–Quantum Dot (QD@MOF) Composites. *Coord. Chem. Rev.* **2016**, *307*, 267–291. DOI: 10.1016/j.ccr.2015.08.004.

[83] Bennett, T. D.; Sotelo, J.; Tan, J.-C.; Moggach, S. A. Mechanical Properties of Zeolitic Metal–Organic Frameworks: mechanically Flexible Topologies and Stabilization against Structural Collapse. *CrystEngComm* **2015**, *17*, 286–289. DOI: 10.1039/C4CE02145B.

[84] Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. Metal-Organic Framework Materials as Chemical Sensors. *Chem. Rev.* **2012**, *112*, 1105–1125. DOI: 10.1021/cr200324t.

[85] Stavila, V.; Talin, A. A.; Allendorf, M. D. MOF-Based Electronic and Opto-Electronic Devices. *Chem. Soc. Rev.* **2014**, *43*, 5994–6010. DOI: 10.1039/c4cs00096j.

[86] Liu, Y.; Liu, Z.; Huang, D.; Cheng, M.; Zeng, G.; Lai, C.; Zhang, C.; Zhou, C.; Wang, W.; Jiang, D.; et al. Metal or Metal-Containing Nanoparticle@MOF Nanocomposites as a Promising Type of Photocatalyst. *Coord. Chem. Rev.* **2019**, *388*, 63–78. DOI: 10.1016/j.ccr.2019.02.031.

[87] Kempahanumakkagari, S.; Kumar, V.; Samaddar, P.; Kumar, P.; Ramakrishnappa, T.; Kim, K. H. Biomolecule-Embedded Metal-Organic Frameworks as an Innovative Sensing Platform. *Biotechnol. Adv.* **2018**, *36*, 467–481. DOI: 10.1016/j.biotechadv.2018.01.014.

[88] Nagabooshanam, S.; Roy, S.; Mathur, A.; Mukherjee, I.; Krishnamurthy, S.; Bharadwaj, L. M. Electrochemical Micro Analytical Device Interfaced with Portable Potentiostat for Rapid Detection of Chlorpyrifos Using Acetylcholinesterase Conjugated Metal Organic Framework Using Internet of Things. *Sci. Rep.* **2019**, *9*, 19862. DOI: 10.1038/s41598-019-56510-y.

[89] Fenzl, C.; Hirsch, T.; Baeumner, A. J. Nanomaterials as Versatile Tools for Signal Amplification in (Bio)Analytical Applications. *Trac, Trends Anal. Chem.* **2016**, *79*, 306–316. DOI: 10.1016/j.trac.2015.10.018.

[90] Maduraiveeran, G.; Sasidharan, M.; Ganesan, V. Electrochemical Sensor and Biosensor Platforms Based on Advanced Nanomaterials for Biological and Biomedical applications. *Biosens. Bioelectron.* **2018**, *103*, 113–129. DOI: 10.1016/j.bios.2017.12.031.

[91] Chang, C. C.; Chen, C. P.; Wu, T. H.; Yang, C. H.; Lin, C. W.; Chen, C. Y. Gold Nanoparticle-Based Colorimetric Strategies for Chemical and Biological Sensing Applications. *Nanomaterials (Basel)* **2019**, *9*, 861. DOI: 10.3390/nano9060861.

[92] Peng, Y.; Rabin, C.; Walgama, C. T.; Pollok, N. E.; Smith, L.; Richards, I.; Crooks, R. M. Silver Nanocubes as Electrochemical Labels for Bioassays. *ACS Sens.* **2021**, *6*, 1111–1119. DOI: 10.1021/acssensors.0c02377.

[93] Chang, Y. T.; Liao, P. Y.; Sheu, H. S.; Tseng, Y. J.; Cheng, F. Y.; Yeh, C. S. Near-Infrared Light-Responsive Intracellular Drug and siRNA Release Using au Nanoensembles with Oligonucleotide-Capped Silica Shell. *Adv. Mater.* **2012**, *24*, 3309–3314. DOI: 10.1002/adma.201200785.

[94] Wolfrum, B.; Katelhon, E.; Yakushenko, A.; Krause, K. J.; Adly, N.; Huske, M.; Rinklin, P. Nanoscale Electrochemical Sensor Arrays: Redox Cycling Amplification in Dual-Electrode Systems. *Acc. Chem. Res.* **2016**, *49*, 2031–2040. DOI: 10.1021/acs.accounts.6b00333.

[95] Fang, S.; Li, C.; Lin, J.; Zhu, H.; Cui, D.; Xu, Y.; Li, Z. Gold Nanorods-Based Theranostics for Simultaneous Fluorescence/Two-Photon Luminescence Imaging and Synergistic Phototherapies. *J. Nanomater.* **2016**, *2016*, 1. DOI: 10.1155/2016/1082746.

[96] Wang, J.; Yang, B.; Zhong, J.; Yan, B.; Zhang, K.; Zhai, C.; Shiraishi, Y.; Du, Y.; Yang, P. Dopamine and Uric Acid Electrochemical Sensor Based on a Glassy Carbon Electrode Modified with Cubic Pd and Reduced Graphene Oxide Nanocomposite. *J Colloid Interface Sci* . **2017**, *497*, 172–180. DOI: 10.1016/j.jcis.2017.03.011.

[97] Yang, L.; Xu, B.; Ye, H.; Zhao, F.; Zeng, B. A Novel Quercetin Electrochemical Sensor Based on Molecularly Imprinted Poly(Para-Aminobenzoic Acid) on 3D Pd Nanoparticles-Porous Graphene-Carbon Nanotubes Composite. *Sens. Actuators, B.* **2017**, *251*, 601–608. DOI: 10.1016/j.snb.2017.04.006.

[98] Kumar, J. V.; Karthik, R.; Chen, S. M.; Muthuraj, V.; Karuppiah, C. Fabrication of Potato-like Silver Molybdate Microstructures for Photocatalytic Degradation of Chronic Toxicity Ciprofloxacin and Highly Selective Electrochemical Detection of H_2O_2. *Sci. Rep.* **2016**, *6*, 34149. DOI: 10.1038/srep34149.

[99] Lebegue, E.; Anderson, C. M.; Dick, J. E.; Webb, L. J.; Bard, A. J. Electrochemical Detection of Single Phospholipid Vesicle Collisions at a Pt Ultramicroelectrode. *Langmuir* **2015**, *31*, 11734–11739. DOI: 10.1021/acs.langmuir.5b03123.

[100] Rismetov, B.; Ivandini, T. A.; Saepudin, E.; Einaga, Y. Electrochemical Detection of Hydrogen Peroxide at Platinum-Modified Diamond Electrodes for an Application in Melamine Strip Tests. *Diamond Relat. Mater.* **2014**, *48*, 88–95. DOI: 10.1016/j.diamond.2014.07.003.

[101] Sepunaru, L.; Plowman, B. J.; Sokolov, S. V.; Young, N. P.; Compton, R. G. Rapid Electrochemical Detection of Single Influenza Viruses Tagged with Silver nanoparticles. *Chem. Sci.* **2016**, *7*, 3892–3899. DOI: 10.1039/c6sc00412a.

[102] Zhang, R.; Sun, C. L.; Lu, Y. J.; Chen, W. Graphene Nanoribbon-Supported PtPd Concave Nanocubes for Electrochemical Detection of TNT with High Sensitivity and Selectivity. *Anal. Chem.* **2015**, *87*, 12262–12269. DOI: 10.1021/acs.analchem.5b03390.

[103] Bansal, P.; Bhanjana, G.; Prabhakar, N.; Dhau, J. S.; Chaudhary, G. R. Electrochemical Sensor Based on ZrO_2 NPs/Au Electrode Sensing Layer for Monitoring Hydrazine and Catechol in Real Water Samples. *J. Mol. Liq.* **2017**, *248*, 651–657. DOI: 10.1016/j.molliq.2017.10.098.

[104] Huang, X.; Zhao, G.; Liu, M.; Li, F.; Qiao, J.; Zhao, S. Highly Sensitive Electrochemical Determination of 1-Naphthol Based on High-Index Facet SnO_2 Modified Electrode. *Electrochim. Acta* **2012**, *83*, 478–484. DOI: 10.1016/j.electacta.2012.08.008.

[105] Wang, P.; Ge, L.; Li, M.; Li, W.; Li, L.; Wang, Y.; Yu, J. Photoelectrochemical Sensor Based on Molecularly Imprinted Polymer-Coated TiO_2 Nanotubes for Lindane Specific

Recognition and Detection. *J. Inorg. Organomet. Polym.* **2013**, *23*, 703–711. DOI: 10.1007/s10904-013-9836-7.

[106] Yu, X.-Y.; Liu, Z.-G.; Huang, X.-J. Nanostructured Metal Oxides/Hydroxides-Based Electrochemical Sensor for Monitoring Environmental Micropollutants. *Trends Environ. Anal. Chem.* **2014**, *3-4*, 28–35. DOI: 10.1016/j.teac.2014.07.001.

[107] Terzi, F.; Pigani, L.; Zanardi, C. Unusual Metals as Electrode Materials for Electrochemical Sensors. *Curr. Opin. Electrochem.* **2019**, *16*, 157–163. DOI: 10.1016/j.coelec.2019.05.005.

[108] Yang, Y.; Yang, X.; Yang, Y.; Yuan, Q. Aptamer-Functionalized Carbon Nanomaterials Electrochemical Sensors for Detecting Cancer Relevant Biomolecules. *Carbon* **2018**, *129*, 380–395. DOI: 10.1016/j.carbon.2017.12.013.

[109] Liu, R.; Wan, L.; Liu, S.; Pan, L.; Wu, D.; Zhao, D. An Interface-Induced Co-Assembly Approach towards Ordered Mesoporous Carbon/Graphene Aerogel for High-Performance Supercapacitors. *Adv. Funct. Mater.* **2015**, *25*, 526–533. DOI: 10.1002/adfm.201403280.

[110] Eguilaz, M.; Villalonga, R.; Rivas, G. Electrochemical Biointerfaces Based on Carbon Nanotubes-Mesoporous Silica Hybrid Material: Bioelectrocatalysis of Hemoglobin and Biosensing Applications. *Biosens. Bioelectron.* **2018**, *111*, 144–151. DOI: 10.1016/j.bios.2018.04.004.

[111] Lu, X.; Yim, W.-L.; Suryanto, B. H. R.; Zhao, C. Electrocatalytic Oxygen Evolution at Surface-Oxidized Multiwall Carbon Nanotubes. *J. Am. Chem. Soc.* **2015**, *137*, 2901–2907. DOI: 10.1021/ja509879r.

[112] Suryanto, B. H. R.; Chen, S.; Duan, J.; Zhao, C. Hydrothermally Driven Transformation of Oxygen Functional Groups at Multiwall Carbon Nanotubes for Improved Electrocatalytic Applications. *ACS Appl Mater Interfaces* **2016**, *8*, 35513–35522. DOI: 10.1021/acsami.6b14090.

[113] Wang, D. Y.; Gong, M.; Chou, H. L.; Pan, C. J.; Chen, H. A.; Wu, Y.; Lin, M. C.; Guan, M.; Yang, J.; Chen, C. W.; et al. Highly Active and Stable Hybrid Catalyst of Cobalt-Doped FeS_2 Nanosheets-Carbon Nanotubes for Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2015**, *137*, 1587–1592. DOI: 10.1021/ja511572q.

[114] Yang, Y.; Yang, X.; Chen, S.; Zou, M.; Li, Z.; Cao, A.; Yuan, Q. Rational Design of Hierarchical Carbon/Mesoporous Silicon Composite Sponges as High-Performance Flexible Energy Storage Electrodes. *ACS Appl Mater Interfaces* **2017**, *9*, 22819–22825. DOI: 10.1021/acsami.7b05032.

[115] Hermann, S.; Schulze, S.; Ecke, R.; Liebig, A.; Schaefer, P.; Zahn, D. R. T.; Albrecht, M.; Hietschold, M.; Schulz, S. E.; Gessner, T. Growth of Carbon Nanotube Forests between a bi-Metallic Catalyst Layer and a SiO_2 Substrate to Form a Self-Assembled Carbon–Metal Heterostructure. *Carbon* **2012**, *50*, 4765–4772. DOI: 10.1016/j.carbon.2012.05.034.

[116] Ramnani, P.; Saucedo, N. M.; Mulchandani, A. Carbon Nanomaterial-Based Electrochemical Biosensors for Label-Free Sensing of Environmental Pollutants. *Chemosphere* **2016**, *143*, 85–98. DOI: 10.1016/j.chemosphere.2015.04.063.

[117] Yan, Y.; Miao, J.; Yang, Z.; Xiao, F. X.; Yang, H. B.; Liu, B.; Yang, Y. Carbon Nanotube Catalysts: recent Advances in Synthesis, Characterization and Applications. *Chem. Soc. Rev.* **2015**, *44*, 3295–3346. DOI: 10.1039/c4cs00492b.

[118] Hou, D.; Liu, Q.; Wang, X.; Quan, Y.; Qiao, Z.; Yu, L.; Ding, S. Facile Synthesis of Graphene via Reduction of Graphene Oxide by Artemisinin in Ethanol. *J. Materiomics* **2018**, *4*, 256–265. DOI: 10.1016/j.jmat.2018.01.002.

[119] Jin, S.; Chung, B.; Park, H. J.; Cunning, B. V.; Lee, J. H.; Yoon, A.; Huang, M.; Seo, H.; Lee, D.; Lee, Z.; et al. Ultrahigh Strength and Modulus Graphene-Based Hybrid Carbons with AB-Stacked and Turbostratic Structures. *Adv. Funct. Mater.* **2020**, *30*, 2005381. DOI: 10.1002/adfm.202005381.

[120] Low, C. T. J.; Walsh, F. C.; Chakrabarti, M. H.; Hashim, M. A.; Hussain, M. A. Electrochemical Approaches to the Production of Graphene Flakes and Their Potential Applications. *Carbon* **2013**, *54*, 1–21. DOI: 10.1016/j.carbon.2012.11.030.

[121] Roldan, R.; Chirolli, L.; Prada, E.; Silva-Guillen, J. A.; San-Jose, P.; Guinea, F. Theory of 2D Crystals: graphene and beyond. *Chem. Soc. Rev.* **2017**, *46*, 4387–4399. DOI: 10.1039/c7cs00210f.

[122] Zhang, W.; Zhu, S.; Luque, R.; Han, S.; Hu, L.; Xu, G. Recent Development of Carbon Electrode Materials and Their Bioanalytical and Environmental Applications. *Chem. Soc. Rev.* **2016**, *45*, 715–752. DOI: 10.1039/c5cs00297d.

[123] Pakapongpan, S.; Poo-Arporn, R. P. Self-Assembly of Glucose Oxidase on Reduced Graphene Oxide-Magnetic Nanoparticles Nanocomposite-Based Direct Electrochemistry for Reagentless Glucose Biosensor. *Mater Sci Eng C Mater Biol Appl …* **2017**, *76*, 398–405. DOI: 10.1016/j.msec.2017.03.031.

[124] Vilian, A. T. E.; Chen, S.-M.; Ali, M. A.; Al-Hemaid, F. M. A. Direct Electrochemistry of Glucose Oxidase Immobilized on ZrO_2 Nanoparticles-Decorated Reduced Graphene Oxide Sheets for a Glucose Biosensor. *RSC Adv* **2014**, *4*, 30358–30367. DOI: 10.1039/C4RA04350B.

[125] Lyu, L.; Seong, K-d.; Ko, D.; Choi, J.; Lee, C.; Hwang, T.; Cho, Y.; Jin, X.; Zhang, W.; Pang, H.; Piao, Y. Recent Development of Biomass-Derived Carbons and Composites as Electrode Materials for Supercapacitors. *Mater. Chem. Front.* **2019**, *3*, 2543–2570. DOI: 10.1039/C9QM00348G.

[126] Pedrero, M.; Campuzano, S.; Pingarron, J. M. Quantum Dots as Components of Electrochemical Sensing Platforms for the Detection of Environmental and Food Pollutants: A Review. *J AOAC Int .* **2017**, *100*, 950–961. DOI: 10.5740/jaoacint.17-0169.

[127] Elshafey, R.; Abo-Sobehy, G. F.; Radi, A.-E. Graphene Oxide/Graphene Quantum Dots: A Platform for Probing ds-DNA-Dimethoate Interaction and Dimethoate Sensing. *Electroanal. Chem.* **2021**, *899*, 115678. DOI: 10.1016/j.jelechem.2021.115678.

[128] Gogotsi, Y.; Huang, Q. MXenes: Two-Dimensional Building Blocks for Future Materials and Devices. *ACS Nano.* **2021**, *15*, 5775–5780. DOI: 10.1021/acsnano.1c03161.

[129] Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. H. 2D Materials and Van Der Waals Heterostructures. *Science* **2016**, *353*, aac9439. DOI: 10.1126/science.aac9439.

[130] Dong, Y.; Mallineni, S. S. K.; Maleski, K.; Behlow, H.; Mochalin, V. N.; Rao, A. M.; Gogotsi, Y.; Podila, R. Metallic MXenes: A New Family of Materials for Flexible Triboelectric Nanogenerators. *Nano Energy* **2018**, *44*, 103–110. DOI: 10.1016/j.nanoen.2017.11.044.

[131] Jiang, Q.; Lei, Y.; Liang, H.; Xi, K.; Xia, C.; Alshareef, H. N. Review of MXene Electrochemical Microsupercapacitors. *Energy Storage Mater.* **2020**, *27*, 78–95. DOI: 10.1016/j.ensm.2020.01.018.

[132] Shahzad, F.; Iqbal, A.; Zaidi, S. A.; Hwang, S.-W.; Koo, C. M. Nafion-Stabilized Two-Dimensional Transition Metal Carbide (Ti_3C_2Tx MXene) as a High-Performance Electrochemical Sensor for Neurotransmitter. *J. Ind. Eng. Chem.* **2019**, *79*, 338–344. DOI: 10.1016/j.jiec.2019.03.061.

[133] Murugan, N.; Jerome, R.; Preethika, M.; Sundaramurthy, A.; Sundramoorthy, A. K. 2D-Titanium Carbide (MXene) Based Selective Electrochemical Sensor for Simultaneous Detection of Ascorbic Acid, Dopamine and Uric Acid. *Journal of Materials Science & Technology* **2021**, *72*, 122–131. DOI: 10.1016/j.jmst.2020.07.037.

[134] Zhang, R.; Liu, J.; Li, Y. MXene with Great Adsorption Ability toward Organic Dye: An Excellent Material for Constructing a Ratiometric Electrochemical Sensing Platform. *ACS Sens.* **2019**, *4*, 2058–2064. DOI: 10.1021/acssensors.9b00654.

[135] Tu, X.; Gao, F.; Ma, X.; Zou, J.; Yu, Y.; Li, M.; Qu, F.; Huang, X.; Lu, L. Mxene/carbon nanohorn/β-cyclodextrin-Metal-organic Frameworks as High-performance Electrochemical Sensing Platform for Sensitive Detection of Carbendazim

Pesticide. *J. Hazard. Mater.* **2020**, *396*, 122776. DOI: 10.1016/j.jhazmat.2020.122776.

[136] Medetalibeyoglu, H.; Beytur, M.; Akyıldırım, O.; Atar, N.; Yola, M. L. Validated Electrochemical Immunosensor for Ultra-Sensitive Procalcitonin Detection: Carbon Electrode Modified with Gold Nanoparticles Functionalized Sulfur Doped MXene as Sensor Platform and Carboxylated Graphitic Carbon Nitride as Signal Amplification. *Sens. Actuators, B.* **2020**, *319*, 128195. DOI: 10.1016/j.snb.2020.128195.

[137] Shen, L.; Zhou, X.; Zhang, X.; Zhang, Y.; Liu, Y.; Wang, W.; Si, W.; Dong, X. Carbon-Intercalated $Ti_3C_2TxMXene$ for High-Performance Electrochemical Energy Storage. *J. Mater. Chem. A.* **2018**, *6*, 23513–23520. DOI: 10.1039/C8TA09600G.

[138] Wang, R.; Chang, Z.; Fang, Z.; Xiao, T.; Zhu, Z.; Ye, B.; Xu, C.; Cheng, J. Pt Nanowire/Ti_3C_2Tx-CNT Hybrids Catalysts for the High Performance Oxygen Reduction Reaction for High Temperature PEMFC. *Int. J. Hydrogen Energy* **2020**, *45*, 28190–28195. DOI: 10.1016/j.ijhydene.2020.03.068.

[139] Zheng, J.; Wang, B.; Ding, A.; Weng, B.; Chen, J. Synthesis of MXene/DNA/Pd/Pt Nanocomposite for Sensitive Detection of Dopamine. *Electroanal. Chem.* **2018**, *816*, 189–194. DOI: 10.1016/j.jelechem.2018.03.056.

[140] Arduini, F.; Cinti, S.; Scognamiglio, V.; Moscone, D. Nanomaterials in Electrochemical Biosensors for Pesticide Detection: Advances and Challenges in Food Analysis. *Microchim. Acta* **2016**, *183*, 2063–2083. DOI: 10.1007/s00604-016-1858-8.

[141] Delińska, K.; Yavir, K.; Kloskowski, A. Ionic Liquids in Extraction Techniques: Determination of Pesticides in Food and Environmental Samples. *Trac, Trends Anal. Chem.* **2021**, *143*, 116396. DOI: 10.1016/j.trac.2021.116396.

[142] Boulanouar, S.; Mezzache, S.; Combes, A.; Pichon, V. Molecularly Imprinted Polymers for the Determination of Organophosphorus Pesticides in Complex Samples. *Talanta* **2018**, *176*, 465–478. DOI: 10.1016/j.talanta.2017.08.067.

[143] Kalhor, H.; Hashemipour, S.; Yaftian, M. R. Ultrasound-Assisted Emulsification-Microextraction/Ion Mobility Spectrometry Combination: Application for Analysis of Organophosphorus Pesticide Residues in Rice Samples. *Food Anal. Methods* **2016**, *9*, 3006–3014. DOI: 10.1007/s12161-016-0492-8.

[144] Musarurwa, H.; Chimuka, L.; Tavengwa, N. T. Green Pre-Concentration Techniques during Pesticide Analysis in Food Samples. *J. Environ. Sci. Health. B.* **2019**, *54*, 770–780. DOI: 10.1080/03601234.2019.1633213.

[145] Elencovan, V.; Joseph, J.; Yahaya, N.; Abdul Samad, N.; Raoov, M.; Lim, V.; Zain, N. N. M. Exploring a Novel Deep Eutectic Solvents Combined with Vortex Assisted Dispersive Liquid-Liquid Microextraction and Its Toxicity for Organophosphorus Pesticides Analysis from Honey and Fruit Samples. *Food Chem.* **2022**, *368*, 130835. DOI: 10.1016/j.foodchem.2021.130835.