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Review

Nanomaterial-based biosensors for environmental and biological monitoring of organophosphorus pesticides and nerve agents

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ABSTRACT

Due to the large amounts of organophosphorus (OP) pesticides commonly used and their impact on the environment and health, it is important to develop a prompt, accurate method of pesticide analysis. This review gives an overview of recent advances and new trends in nanomaterial-based biosensors for environmental and biological monitoring of OP pesticides and nerve agents. We provide background information and a general overview of electrochemical and immunoassay detection techniques. Nanomaterials function as signal transducers to mediate current flow or as recognition agents. We present electroactive tags to indicate the detection of analytes. In addition, we discuss future considerations and opportunities for advancing the use of biosensors for environmental and health studies.

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1. Introduction

Organophosphorus (OP) compounds are primarily used as insecticides (e.g., paraoxon, parathion and coumaphos) [1,2] and developed as chemical-weapon nerve agents (e.g., sarin and soman) [3,4] worldwide. The large amounts of residues of OP pesticides in the environment, such as air, soil, water and food, and terrorist attacks with nerve-agent gas are major public health and national security concerns. Due to the toxicity of OP pesticides and nerve agents, and the danger presented by their accidental or intentional release in populated areas, the development of rapid, sensitive, inexpensive diagnosis tools for environmental and biological monitoring is currently a research area of great interest.

Currently, the method for pesticide detection usually involves liquid or gas chromatography coupled to mass spectrometry detection (HPLC-MS, GC-MS) due to their sensitivity and reliability, but requires meticulous sample preparation and highly qualified technicians [5–9]. By contrast, electrochemical and immunoassay techniques are very attractive for developing simple, inexpensive

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biosensors for rapid and on-site monitoring of OP pesticides and nerve agents. A biosensor is a self-contained device that integrates an immobilized biological element (e.g., enzyme or antibody) that recognizes the analyte (e.g., enzyme substrate or antigen) and a transduction element is used to convert the (bio)chemical signal resulting in an electronic or optical interaction of the analyte with the bioreceptor. Because of their simplicity, low cost, high sensitivity and ease of miniaturization, electrochemical and optical biosensors have been widely used for detection of OP pesticides [10–16].

Despite electrochemical and optical biosensors providing great advantages, their emergence from the research laboratory to the marketplace has been slow. The obstacles to exploitation have been fundamentally related to the presence of biomaterial in the biosensor, the development of the sensor device and the integration of biosensors into complete systems. Major fundamental and technological advances need to be made towards enhancing the sensitivity, the selectivity and the reliability of OP-pesticide biosensors, and the emergence of nanotechnology may open new horizons and satisfy the above targets. Nanomaterials are attractive because of their unique electrical, chemical and physical properties (i.e. size, composition, conductivity, magnetism, mechanical strength, and light-absorbing and emitting). The most studied nanomaterials, carbon nanotubes (CNTs), graphene, metal nanoparticles (NPs), and quantum dots (QDs) have been especially targeted for developing novel biosensors [17–22]. By utilizing nanomaterials, the biosensors have shown great promise for the detection of chemical markers and biomarkers of exposure, primarily because the nanomaterials are used as signal transducers to mediate current flow or as recognition agents and electroactive tags to indicate the detection of analyte. Nanotechnology can be expected to be an effective approach to develop more sophisticated multi-analyte detection systems with low costs.

This review summarizes recent advances in the development of analytical systems for rapid, sensitive monitoring of OP pesticides

Table 1
Nanomaterial-based biosensors for detection of organophosphorus pesticides

Enzyme /Biomarker	Target analytes	Substrate type	Nanomaterials	Detection limit	Samples	Ref.
AChE	Paraoxon	GCE	CNT, Au/cr-Gs	0.4 pM, 0.1 pM		**[18, 33]**
AChE	Monocrotophos	SPE	PBNCs/rGO	0.1 ng mL^{-1}	Cucumber	**[34]**
AChE	Malathion, Chlorpyrifos, Monocrotophos, Endosulfan	Au electrode	Fe_3O_4/MWCNT	0.1 nM, 0.1 nM, 1 nM, 10 nM	Milk and water	**[41]**
AChE+CHO	Methyl parathion	SPE	CNT	0.05 μM		**[43]**
AChE+CHO	Dichlorvos	Liquid phase	CdTe QDs	4.49 nM	Apple	**[44]**
OPH	Paraoxon	GCE	CNT, MC/CB	0.15 μM, 12 μM		**[47, 51]**
OPH	Methyl parathion	GCE, SPE	CdTe/Au/MWCNT, Fe_3O_4/Au	1.0 ng mL^{-1}, 0.1 ng mL^{-1}		**[48, 49]**
	Methyl parathion	Au electrode	ZrO_2	3 ng mL^{-1}		**[59]**
	Methyl parathion	GCE	Graphene/ZrO_2	0.1 ng mL^{-1}	Garlic	**[60]**
	Paraoxon-ethyl	GCE	Au/ZrO_2/SiO_2	0.5 ng mL^{-1}		**[61]**
TCP	TCP	Test strip	Au, CdS@ZnS QD	0.47 ng mL^{-1}, 1.0 ng mL^{-1}	Human saliva, rat plasma	**[75, 76]**
BAM	BAM	Microarray substrates	Au	20 ng L^{-1}	Water	**[83]**
AChE Activity	Paraoxon	SPE/Flow inject system	CNT	2 pM	Rat saliva	**[95, 96]**
OP-AChE	Paraoxon	SPE	CdS@ZnS QD, ZrO_2	8.0 pM, 0.15 ng mL^{-1}, 0.02 nM	Human plasma, rat plasma	**[86, 99, 100]**
OP-AChE	Chlorpyrifos	Test strip/SPE	CNT	0.02 nM	Human RBCs	**[102]**
OP-BChE	Diisopropylfluorophosphate	SPE	ZrO_2	0.03 nM	Human plasma	**[106]**
OP-BChE	Paraoxon	SPE	Fe_3O_4@ TiO_2, QD	0.01 nM	Human plasma	**[107]**

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