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基于电化学生物传感器检测有机磷农药的应用进展

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摘要

有机磷农药应用广泛，残留率高，对人体健康有严重危害，其残留检测技术的发展有着重要的科学研究意义。传统检测方法价格昂贵、复杂且耗时，而基于电化学生物传感器检测有机磷农药简单、快速、便携、高效且有广泛的应用。本文主要综述介绍近五年基于电化学生物传感器检测有机磷农药的种类、原理，将不同类型传感器性能进行对比，分析传感器优点和局限性，对其发展方向进行展望。

关键词

有机磷农药，电化学生物传感器，食品安全检测

Detection of Organophosphorus Pesticides Based on Electrochemical Biosensor: Application Progress

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Abstract

Organophosphorus pesticides are widely used. But it does serious harm to human health due to its high residual rate. Therefore, it's of scientific significance to develop the residual detection technology. Traditional detection methods, such as AA, BB and CC, are expensive, complicated and

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time-consuming. Detection methods based on electrochemical biosensors are simple, fast, portable, efficient and widely used. This paper mainly introduces the types and principles of detecting organophosphorus pesticides based on electrochemical biosensors in the past five years. Performance of different types of sensors is compared, as well as the advantages, limitations, and prospects of its development.

Keywords

Organophosphorus Pesticides, Electrochemical Biosensor, Food Safety Testing

1. 引言

杀虫剂包括有机(有机氯、有机磷、有机硫制剂和氨基甲酸酯类与拟除虫菊酯类)、无机、植物性和矿物油和微生物等。其中，有机磷农药(Organophosphorus pesticides，简写为 OPPs)因其低成本、高毒性和良好的持久性[1]在杀虫剂中应用广泛[2]。但 OPPs 残留率高，例如 Verger Philippe 等做过一项关于 22 个国家农药残留的研究，发现 OPPs 残留种类最多(5 种：毒死蜱、二嗪、乐果、马拉硫磷和丙磷) [3]。2021 年 9 月，《食品安全国家标准食品中农药最大残留限量》(GB 2763-2021)正式实施，规定了 564 种农药在 376 种(类)食品中 10,092 项最大残留限量，标志着我国农药残留限量的标准迈上新台阶。

OPPs 是指含有碳磷键的有机化合物，化学结构如图 1 所示。OPPs 残留对人体健康的危害主要体现在：可以破坏胆碱酯酶的活性从而导致呼吸系统疾病和神经系统疾病的发生。据报道，接触 OPPs 的不良反应的分子机制之一是氧化应激导致细胞水平的改变，慢性会影响器官和组织的功能[4]。如当马拉硫磷、对硫磷和雌激素存在时会导致抑癌基因失活和致癌基因激活[5]；暴露于混合 OPPs 中可以导致人体代谢紊乱从而引起代谢综合征[6]，除此之外，还与儿童智力发育损害、注意力缺陷、多动综合征、行为过失的有密切关联[7]。因此，OPPs 残留检测技术的发展有着重要的科学研究意义。

OPPs 的传统检测方法主要有色谱法、质谱法、光谱法等，这些方法虽然灵敏度和准确度高，但是设备昂贵、费时费力且需要检测人员有一定的知识，除此之外，传统的分析方法样品处理复杂耗时，在分析前化合物有分解的可能性，所以，迫切需要一种简单、快速、便携、高效的检测技术[8]。目前电化学生物传感器以其操作简单、成本低、现场检测快速等优点在农残检测中得到了广泛的应用[9]。

本文主要说明阐述基于电化学生物传感器检测 OPPs 的应用进展，综述近五年发展的各类型电化学生物传感器及其在实际检测中的应用展望。

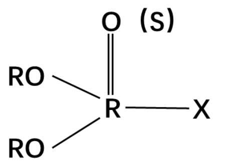

Figure 1. Chemical structure diagram of OPPs (R group is methoxyl or ethoxyl, X is alkoxy, aryl or other substituted group)
图 1. OPPs 化学结构图(其中 R 基团是甲氧基或乙氧基，X 为烷氧基、芳氧基或其它取代基团)

2. 酶电化学传感器

如图 2(a)所示，酶传感器检测 OPPs 最常见的是抑制型，该传感器以胆碱酯酶为识别原件，可以催化底物乙酰胆碱(acetylcholinesterase，简称 AChE)或丁酰胆碱(butyrylcholinesterase，简称 BChE)分解产生胆碱和酸。当存在 OPPs 时，胆碱酯酶受到抑制，底物分解受到限制从而产生电信号差[10]。研究者将一些拥有特殊性能的材料作为媒介更好的固定 AChE。Kai Niu 等[11]用硝基内酯石墨二炔(nitrogen-doped graphdiyne，简称 NGDY)固定 AChE，使酶附着力和传感器电子转移能力更强。Sheying Dong 等[12]通过利用间苯三酚基 MOF (OH-POF)、AChE 和 Nafion 之间的 π-π 相互作用和氢键作用固定化 AChE。然而，抑制型酶电化学传感器也存在着一定的局限性，酶本身的稳定性较低，易受到外界因素(温度、pH、重金属离子等)的干扰，缺乏选择性，且抑制不可逆使得 AChE 的再活化不可行[13]。所以针对此原理需要更多新的方法和深入研究。

酶传感器检测 OPPs 另一种是水解型，如图 2(b)所示，该类型传感器以磷酸水解酶为识别原件，OPPs 水解后产生对硝基苯酚(p-nitrophenol，简称 PNP)，PNP 可以产生电化学信号。常用的是碱性磷酸酶(alkaline phosphatase，简称 ALP)，但选择性并不高。近几年出现一种新型的由大肠杆菌重组表达得到的有机磷水解酶[14] (organophosphorus hydrolase，简称 OPH)，其选择性优于 ALP。Fengnian Zhao 等[15]在三维多孔石墨烯表面修饰了金纳米颗粒和 OPH 发明了一种植物可穿戴式传感器，选择性地捕获和识别甲基对硫磷，为农作物上农药残留的原位分析提供一种新的方法。

还有一种是竞争型酶电化学传感器(如图 2(c)所示)，Guozheng Zhao 等[16]报道一种竞争型酶电化学传感器，利用 Au-S 键将纳米金和巯基甲胺磷修饰在电极上，巯基甲胺磷可以结合 AChE 产生相互作用在电极上形成磷酸化的 AChE 阻碍电子传输，当 OPPs 存在时与巯基甲胺磷竞争结合 AChE，其浓度越高结合巯基甲胺磷的 AChE 越少，传感器产生的电信号就越大。该传感器具有较好的稳定性和重现性，并且可以实现对一大类(11 种)有机磷农药进行高灵敏度快速检测。

酶基电化学发光 ECL (electrochemiluminescence，简称 ECL)传感器也受到了很大的关注(如图 2(d)所示)。Ying He 等[17]将 AChE 和胆碱氧化酶(cholineoxidase，简称 ChOx)结合形成 AChE-ChOx 并以 PFBT PNPs 为基底修饰在电极表面，AChE-ChOx 催化底物乙酰硫代胆碱产生过氧化氢导致 PFBT PNPs 处于信号关闭状态，当 OPPs 存在时 AchE-ChOx 失活无法进行酶促反应继续产生过氧化氢，PFBT PNPs 便会产生 ECL 信号。这种传感器为 OPPs 快速检测提供了一种新的途径，ECL 相比化学发光有着更好的可控性，但是仍然因为酶的选择性、稳定性较低而存在一定的局限性。

3. 免疫电化学传感器

免疫电化学传感器是利用抗原与抗体的特异性识别将 OPPs 抗体作为识别原件固定在电极表面，OPPs 与抗体结合后电信号发生改变(图 3)。如何增强电信号成为改进这种传感器的热点问题，Haowei Dong 等[18]将金纳米粒子(Gold nanoparticles, AuNPs)与广谱抗体(broad-spectrum antibodies)偶联形成 AuNP-Ab，然后采用电沉积的方法在 SPCE 表面修饰 AuNP-Ab 和普鲁士蓝(Prussian blue，简称 PB)。由于金纳米粒子的修饰该传感器提高了抗体的固定化效果、拥有了更好的导电性能，通过 AuNPs 与广谱抗体偶联有效简化了免疫传感器的制备过程，降低了成本，可用于多种 OPPs 的检测。除此之外，免疫电化学传感器与酶电化学传感器一样容易受到外界因素的干扰导致其稳定性低，还需要更多研究进行优化改进。

4. 适配体电化学传感器

适配体电化学传感器是以适配子(DNA 链)为识别原件的一种传感器(图 4)，通常是将能够产生电信号

发夹适配子修饰在电极表面，通过特异性识别并结合 OPPs，使得发夹适配子打开，从而改变传感器电信号的大小。Jiayun Fu 等[19]使用发夹适配子作为信号供体，其 5′端和 3′端分别用氨基和氧化还原探针二茂铁修饰，他们运用氧化石墨烯和壳聚糖组成的纳米复合材料(GO-CHIT)通过形成酰胺键来固定适配子使其拥有了更好的导电性，该适配传感器对丙溴磷、甲胺磷、水胺硫磷和氧乐果的检测下限分别为 0.01、0.1、0.01 和 0.1 nmol/L。

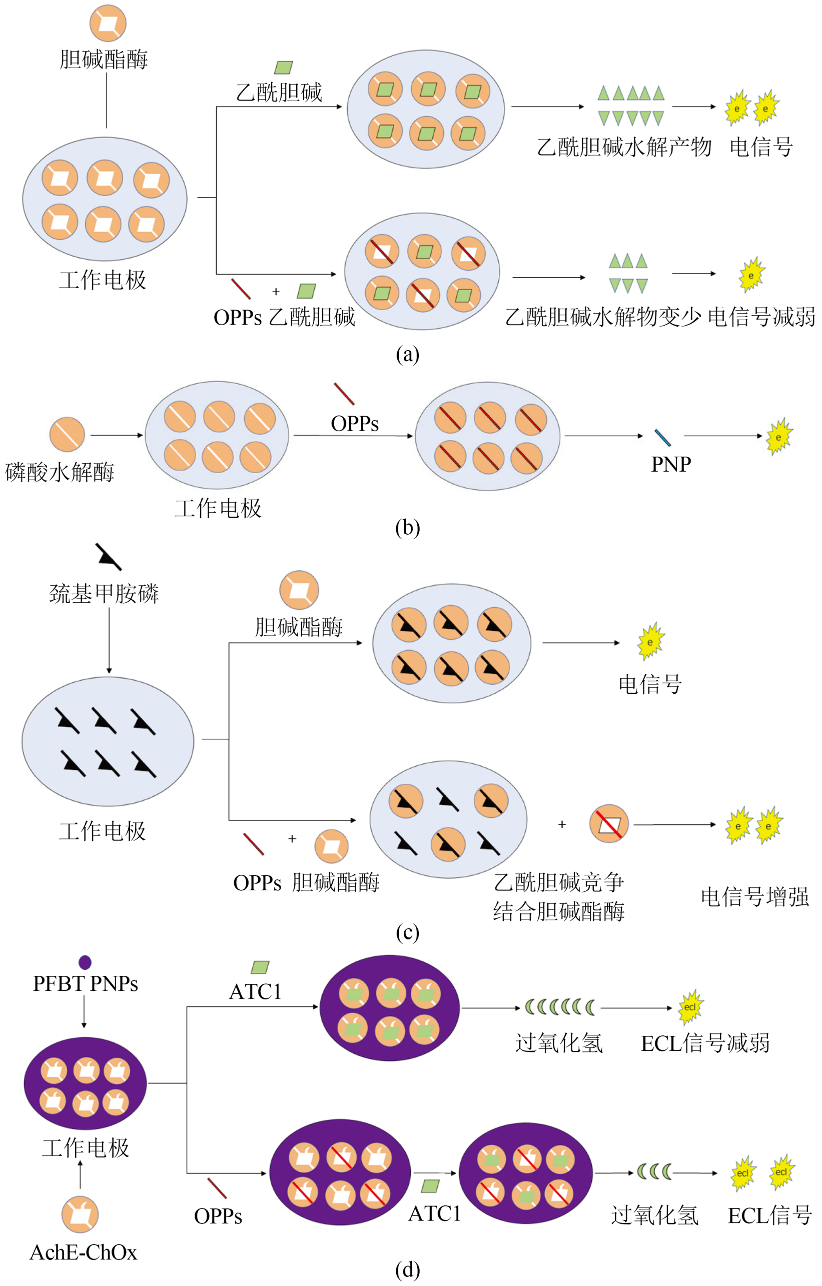

Figure 2. Principle of enzyme electrochemical sensor detection: (a) Principle of inhibitory enzyme electrochemical sensor detection; (b) Principle of hydrolytic enzyme electrochemical sensor detection; (c) Principle of competitive enzyme electrochemical sensor detection; (d) Principle of enzymatic ECL electrochemical sensor detection

图 2. 酶电化学传感器检测原理：(a) 抑制型酶电化学传感器检测原理；(b) 水解型酶电化学传感器检测原理；(c) 竞争型酶电化学传感器检测原理；(d) 酶基 ECL 电化学传感器检测原理

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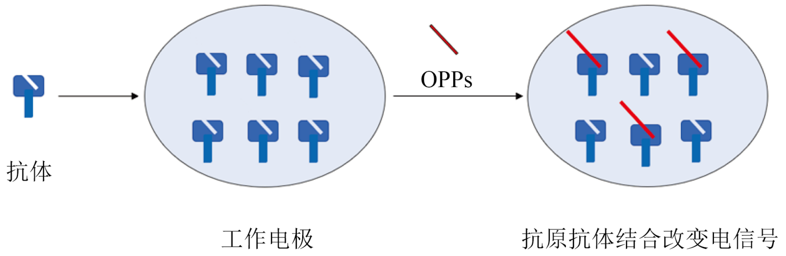

Figure 3. Principle of immunoelectrochemical sensor detection
图 3. 免疫电化学传感器检测原理

5. 分子印迹电化学传感器

该传感器一般是将分子印迹聚合物(molecularly imprinted polymer，简称 MIP)固定在电极，通过模板 OPPs 分子的融合与去除使得 MIP 具有识别并结合 OPPs 的功能，传感器的电信号强度随 MIP 与 OPPs 结合程度呈反比，据此来检测 OPPs 浓度(图 5)。该传感器具有更高的选择性、稳定性和重现性，不容易受到外界环境因素的干扰，但是单纯的不加修饰的电极会出现电信号微弱等情况，所以现在很多研究者通过放大其电信号来提高灵敏度和准确度，而纳米材料在该传感器的研究中受到广泛应用。Liping Xu 等[20]将锆基金属-有机骨架催化剂(Pt-UiO-66)修饰在自制的碳糊微电极上(carbon paste microelectrode, CPME)以放大电信号，研制出了一种用于检测伏杀磷的基于 MIP/(Pt-UiO-66)/CPME 的一次性分子印迹电化学传感器，该传感器检测下限为 0.078 nmol/L。

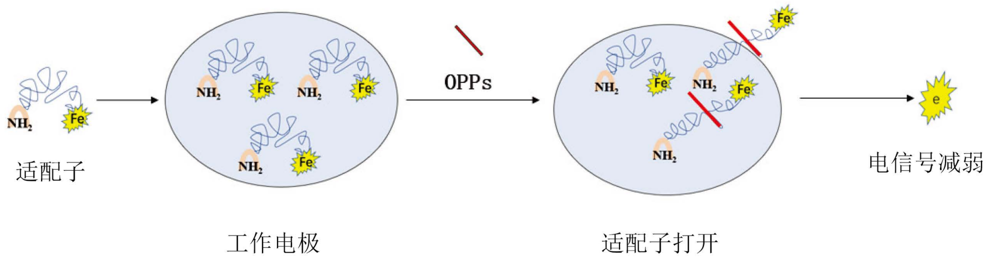

Figure 4. Principle of aptamer electrochemical sensor detection
图 4. 适配体电化学传感器检测原理

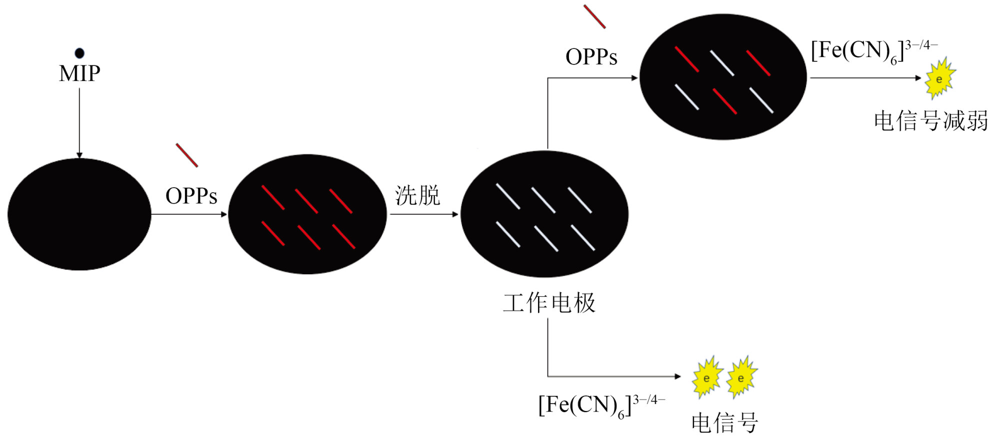

Figure 5. Detection principle of molecularly imprinted electrochemical sensor
图 5. 分子印迹电化学传感器检测原理

6. 可抛型电化学生物传感器

随着丝网印刷技术的发展和对快速、简便检测 OPPs 方法的需求，可抛型的电化学生物传感器受到研究者们的青睐[21]。目前市面上存在商业化有机磷农药的快速检测方法主要集中在速测卡和速测仪，这种存在着检测精度不够、操作繁琐、数据不便于传输保存等缺点，一次性可抛纸基传感器装置轻巧、携带方便并且拥有一定的灵敏度和准确度，能够弥补速测卡和速测仪的不足，更加适合用于现场快速检测，而且在实验室制作传感器的步骤有人工操作影响精度，商业化大规模批量生产可以改善这一缺点[22]。

Ning Yang [23]等提出了一种用来检测 OPPs 的纸基的微流控芯片和电化学分析装置，结果表明，该快速检测方法具有良好的稳定性和特异性，准确率稳定在 93%。Alessia Cioffi 等[24]以办公用纸为基底实现了一种分散化、小型化、可持续、便携的检测有机磷农药的酶抑制型电化学传感器。该便携式传感器的检测限为 1.3 ng/mL，在不同基质中的回收率为 90%~110%。Fengnian Zhao 等[25]提出 MXene 纳米片作为天然还原剂和载体能够很好地控制双金属纳米粒子和固定胆碱酯酶，使得其具有高比表面积的同时还拥有者良好的催化能力，在优化条件下，他们制备的生物传感器在对氧磷浓度 0.1~1000.0 μg/L 之间呈良好的线性关系，检出限低至 1.75 ng/L。

7. 讨论

我们将上述各种类型的电化学生物传感器的性能进行对比，如表 1 所示，其中水解型酶电化学传感器相比其它传感器检测限较高；对于不同的抑制型酶电化学传感器其性能也有一定差异；但总体来说各种类型的传感器都能够实现良好的线性范围和较低的检测限。然而在对灵敏度和准确度有着要求的同时，传感器的快速性和便携性的需求也越来越高，纸基可抛型传感器能够满足这种要求，目前纸基可抛型传感器大都是酶电化学传感器，其它类型的纸基传感器指日可待。

Table 1. Performance comparison of various OOPs sensors
表 1. 各种 OOPs 传感器的性能对比

OPPs 名称	传感器类别	线性范围	检测限	参考文献
对氧磷	抑制型酶电化学传感器	0.1~1000.0 μg/L	1.75 ng/L	[11]
甲基对硫磷	抑制型酶电化学传感器	5.0×10^{-13}~1.0×10^{-8} g/mL	1.5×10^{-13} g/mL	[12]
对氧磷	抑制型酶电化学传感器	1.0×10^{-13}~1.0×10^{-9} g/mL	3.4×10^{-14} g/mL	
敌敌畏	抑制型酶电化学传感器	11.31 μmol/L~22.6 nmol/L	14.45 nmol/L	[27]
敌敌畏	抑制型酶电化学传感器	10^{-6}~10^{-10} mol/L	3×10^{-10} mol/L	[28]
马拉硫磷	抑制型酶电化学传感器	0.001~100 ng/mL	0.68 pg/mL	[29]
甲基对氧磷、甲基对硫磷、乙基对氧磷	水解型酶电化学传感器	1~100 μmol/L	0.5 μmol/L	[30]
甲基对硫磷	水解型酶电化学传感器	20~500 μmol/L	0.01 μmol/L	[15]
含 11 类有机磷农药	竞争型酶电化学传感器	0.1~1500 ng/mL	0.019~0.077 ng/mL	[16]
有机磷农药	酶基 ECL 传感器	1.0×10^{-12}~1.0×10^{-7} mol/L	1.5×10^{-13} mol/L	[17]
对硫磷、鱼腥草素、喹硫磷、甲基对硫磷四种标准溶液等量混合	免疫电化学传感器	1.82×10^{-3}~3.29×10^{-4} ng/mL	0.003 ng/mL	[18]

Continued

马拉硫磷	免疫电化学传感器	0.1×10^{-12}~1×10^{-6} mol/L	1.1×10^{-15} mol/L	[31]
丙溴磷	适配体电化学传感器	0.01~1000 nmol/L	0.01 nmol/L	[19]
甲胺磷	适配体电化学传感器	0.1~800 nmol/L	0.1 nmol/L	
水胺硫磷	适配体电化学传感器	0.01~1000 nmol/L	0.01 nmol/L	
氧乐果	适配体电化学传感器	0.1~100 nmol/L	0.1 nmol/L	
马拉硫磷	适配体电化学传感器	0.006~600 ng/mL	2 pg/mL	[32]
杀螨磷	分子印迹电化学传感器	1.0×10^{-11}~1.0×10^{-9} mol/L	3.0×10^{-12} mol/L	[33]
伏杀磷	分子印迹电化学传感器	0.50 nmol/L~20 nmol/L	0.078 nmol/L	[20]
丙溴磷	分子印迹电化学传感器	1.0×10^{-9}~5.0×10^{-6} mol/L	1.0 nmol/L	[34]
对氧磷乙酯	纸基可抛型电化学生物传感器	定性分析	1.3 ng/mL	[24]

8. 结论

目前用于检测 OPPs 的各类电化学生物传感器中基于酶的电化学生物传感器已经有着非常良好的发展，然而由于酶本身的稳定性较低、缺乏选择性、AChE 再活化有限等因素，抗体、核酸适配体和分子印迹聚合物等识别性高的非酶生物传感器诞生成为后起之秀[26]。在形式上以纸基为电化学平台的一次性可抛型电化学生物传感器由于其轻巧便携受到研究者的青睐。将有机磷传感器进行改进优化，研发出一种价格低廉、快速、便捷、更高灵敏度和准确性的传感器是其发展大方向。

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