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Review of optical sensors for pesticides

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ABSTRACT

Sensors for pesticides with high sensitivity have been urgently required to control food safety, protect ecosystem and prevent disease. In this review, we provide an overview of recent advances and new trends in optical sensors for the detection of pesticide based on fluorescence, colorimetric and surface enhanced Raman scattering, surface plasmon resonance and chemiluminescent strategies. These methods will be classified by the types of recognition elements, including enzyme, antibody, molecularly-imprinted polymers, aptamer and host-guest reaction. This review explores the basic features of established strategies through assessment of their performance. In addition, we provide brief summary of the entire review, the drawbacks of present sensor and future prospects, as well as the ongoing efforts to pesticide optical sensors.

1. Introduction

Pesticide are primarily used to prevent, control, or eliminate pests and weeds for boosting agricultural productivity in modern agricultural practices [1,2]. According to the literatures [3,4], the use of pesticides helps in securing almost one-third of crop production globally. However, the residue of pesticide even at trace levels not only seriously cause food contamination, but also severely breakdown the ecosystem, posing a great danger to people's daily life [5–7]. As a result, pesticide pollution has attracted more and more concern and become one of the most alarming challenges. For proper management of pesticide, Governments have set lots of policies for guiding pesticide use and have regulated maximum residue levels on foods and agricultural commodities [2,8,9]. Although most pesticide were detected to be within recommended limits, the bioaccumulation effect and continuous exposure can rise safety risks to human health [10]. In addition, some new types of pesticides with highly effective activity, whose toxic mechanism have not clear understood, are being continuously brought into market [11]. Therefore, the analysis of pesticide residues is an urgent demand to ensure food quality and safety, safeguard the ecosystem and protect human health from possible hazards.

Pesticide detection have traditionally been carried out by employing conventional chromatographic techniques, including high-performance liquid chromatography (HPLC) [12–14], gas chromatography (GC) [15–17] and mass spectrometry (MS) [18–20]. Although these techniques offer powerful trace analysis with excellent sensitivity and high reproducibility, many drawbacks, such as sophisticated equipment, time consuming, tedious sample preparation and purification steps, obviously limited their on-site and real-time application, particularly emergency cases. Thus, vast endeavors have been devoted to investigating alternative strategies for realizing pesticide in a facile, speedy, sensitive, selective, accurate and user-friendly manner. In fact, significant attention has been drawn to the fabrication of optical sensors for pesticide detection. For pesticide analysis, myriad optical strategies have been established utilizing recognition elements, such as enzyme, antibody, molecularly-imprinted polymers, aptamer and host-guest recognizer, which employed to directly capture and identify the target pesticide. Moreover, the integration of recognition elements and nanomaterials possess high sensitivity and excellent selectivity in terms of real-time analysis, which is in high demand for pesticide detection.

This Review focuses on the recent development of sensitive pesticide optical sensor, with a particular emphasis on the fluorescence (FL), colorimetric (CL), surface-enhanced Raman

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scattering (SERS), and other strategies including surface plasmon resonance (SPR) sensor and chemiluminescence strategy (Fig. 1), which provide comprehensive coverage of current standings of pesticide detection. Rather than summarizing either enzyme-based sensors [1,2,21,22] or nanomaterials-based strategies [4,11,23–26] as performed in other excellent reviews, we highlight the latest achievements in pesticide optical sensor and provided readers with a high-impact recent advances in the developing field from our point of view. Enzyme, antibody, and host-guest chemistry as recognizer have been frequently employed in pesticide optical sensor to achieve high sensitivity and good selectivity, which exhibited great superiority. Additionally, new advances in the application of aptamer and molecularly-imprinted polymers have been reviewed herein. Beyond a discussion of the recent development of emerging pesticide optical sensors, we also address existing deficiencies and current challenges, as well as the future perspectives that might impact in commercialization opportunities and point-of-care detection. Because of the explosion of scientific researches in the field of pesticide analysis, we sincerely apologize to authors for overlooking their important contributions. We will endeavor to picture major research efforts in the field and to review the wide and varied section of the relevant literature.

2. Typical optical sensing strategies

Optical sensor provides a facile, rapid and low-cost approach for sensitive detection of pesticide based on FL, UV–vis, Raman, SPR or chemiluminescence signal variations. Generally, an optical sensor contains recognition unit that can interact specially with desired target pesticide and transducer component that is employed for signaling the binding event. Recognition elements including enzyme, antibody, molecularly-imprinted polymers, aptamer, and host-guest recognizer, draw increasing attention of scientific researcher to improve analytical performance of sensor. By combining the recognition units-assisted target response, the current well-established optical probes can be divided into four broad categories based on signal output formats: FL, CL, SERS, SPR and chemiluminescence sensor. In the following section, we will highlight the optical sensor for pesticide detection based on various optical detection modes.

2.1. Fluorescence sensing strategy

With high sensitivity and simplification, fluorescence-based sensors as one of the most commonly used sensing candidate, have been widely applied in broad fascinating fields, ranging from biomedical diagnosis [27–30] to environmental monitoring [31–33], food safety and quality control [34,35], as the signal change can be collected vis spectrofluorophotometer and observed by naked eye on-site [36–38]. As the development of advancing technologies, various kinds of materials have been widely employed for the fabrication of FL sensing platform, including fluorescent dyes [39], semiconductors nanomaterials [40], metal nanomaterials [41,42], carbon materials [43], and rare earth materials [44]. Meanwhile, it is very critical to choose and design a proper recognition unit that combined with FL probe for responding the fluorescent “turn off”, “turn on”, or “ratiometric” signal. Nsibande and Forbes reviewed the development of quantum dots-based FL probe for pesticide detection in terms of enzyme, molecularly-imprinted polymers (MIPs) and host-guest recognizer [11]. On the basis of the application of recognition elements, FL sensing strategies can be typically classified into several types: enzyme-mediated methods, antibody-assisted methods, MIPs-based methods, aptamer-based methods, host-guest complexes probe and other approach.

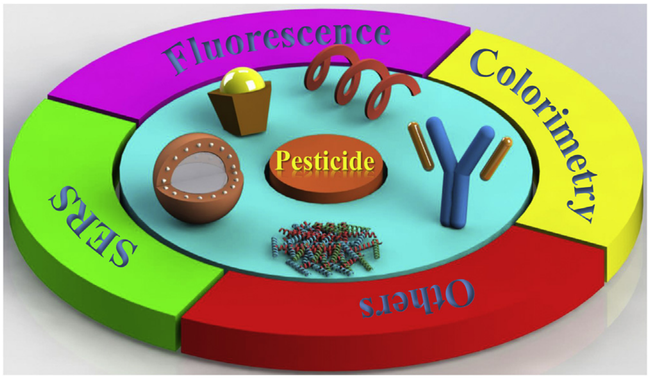

Fig. 1. Schematic illustration for various optical sensors in the detection of pesticide based on different recognition elements.

2.1.1. Enzyme-mediated methods

The enzymatic FL sensors, as popular emerging tools, have been greatly possess excellent sensitivity and promising selectivity for detecting target analyte [45–47]. In the case of enzyme-mediated sensors, pesticide was employed as inhibitor that can suppress the activity of enzyme or served as substrate that play an important role in enzymatic reaction, indirectly inducing the responds of FL signal. As expected, by incorporating the specificity of enzyme, great success was made in fabricating facile and cost-effective FL sensors for the highly accurate detection of pesticide. As one of the most popular enzyme, acetylcholinesterase (AChE) has been exploited extensively for the enzymatic detection of pesticides. In the AChE-based platforms, acetylthiocholine (ATCh) can catalytically hydrolyzed to produce thiocholine containing the chemically reactive group thiol which specifically react with metal cations [48,49], fluorophore [50–52] and nanomaterials [53–55]. Tang's group fabricated nanostructured multilayers of the enzyme AChE and CdTe quantum dots (QDs) vis the layer-by-layer assembly technique [56]. Organophosphorus pesticides (OPs) are well-known inhibitors that can significantly suppress the catalytic activity of AChE and prevent the generation of enzymatic hydrolyzate (thiocholine), thus accompanying the FL signal response of the system, which results in the sensitive analysis of OPs. Our group designed a label-free system for sensitive detection of OPs based on AChE-controlled the hydrolysis of ATCh and thiocholine-triggered the quenching of FL emission of carbon dots (CDs) [57]. On the basis of the behavior of thiocholine, Yu's group developed AChE-based fluorometric assay toward OPs with a detection limit of 5.0 pg mL^{-1} [58]. In the designed platform, squaraine dye can be bleached by thiocholine, showing obviously FL quenching (Fig. 2A). Owing to the inhibition effect of OPs, the enzymatic capacity was blocked, preventing the decomposition of squaraine derivative and resulting in strong FL intensity. In another study, Chang et al. reported a simple FL sensor for rapid naked-eye monitoring of OPs based on the aggregation-induced emission enhancement property between tetraphenylethylene dye and thiocholine [59]. Liao et al. described a FL “turn-on” approach for the sensitive sensing of 3-hydroxycarbofuran based on positively charged perylene probe [60]. Positively charged metal coordination polymer which formed through the interaction between thiocholine and Ag(I) can induce the aggregation of polyanion, resulting in the release of the free perylene probe with strong FL signal. The proposed protocol with “turn-on” mode is quite simple and convenient, which could considerably reduce the false-positive signals.

The combination of fluorophore and novel functional nanomaterials significantly attracted increasing attention in the