

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.

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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 via spectrophotometer 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.

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) via 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



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

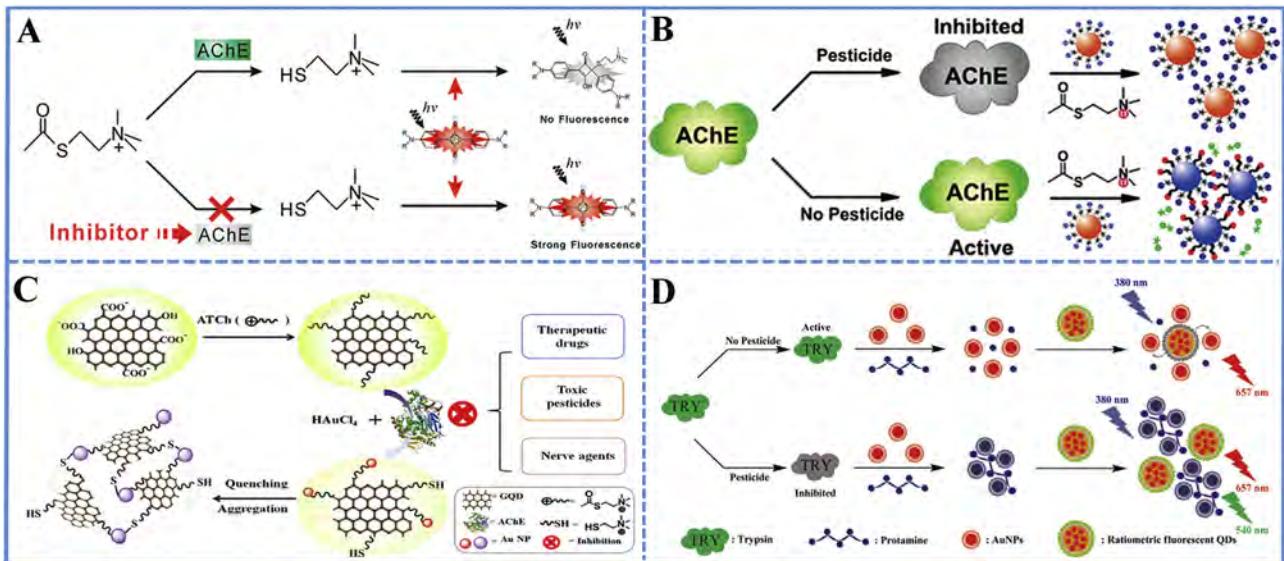


Fig. 2. (A) Description of the signal-on fluorometric strategy for acetylcholinesterase inhibitors (reproduced from Ref. [58] with permission). (B) Design of the dual-readout (colorimetric and fluorometric) assay for pesticides (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [62] with permission). (C) Schematic illustration of GQD-ATCh/AuNPs fluorometric detection of AChE and its inhibitors (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [68] with permission). (D) Illustration of the fluorescent detection of OPs through the inner-filter effect of gold nanoparticles on RF-QDs (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [72] with permission).

construction of ideal sensors. By virtue of the Förster resonance energy transfer (FRET) between CDs and manganese dioxide (MnO_2) nanosheets, our group established fluorometric platform for accurate quantitative of OPs [61]. In this process, enzymatic hydrolyzate (thiocholine) can efficiently induce the decomposition of MnO_2 nanosheets, causing the recovery of FL emission of CDs. OPs as enzyme inhibitors can block the generation of thiocholine and the decomposition of MnO_2 nanosheets, accompanying the FL “turn-off” of the system. Gold nanoparticles (AuNPs) with distinct physical and optical properties have also been employed for developing pesticide sensor. As depicted in Fig. 2B, Liu et al. synthesized rhodamine B-functionalized gold nanoparticles (RB-AuNPs) to fabricate a highly sensitive probe for monitoring carbamate pesticides and OPs [62]. RB was applied as an FL reporter to adsorb onto the surface of AuNPs through electrostatic interactions, which results in the FL quenching. Due to its active thiol group, thiocholine show stronger binding interaction with AuNPs, leading to recover the FL of RB. In the presence of carbamate pesticides or OPs, the activity of AChE was inhibited, preventing the generation of thiocholine and resulting in the quenching of RB. The strategy showed good sensitivity for the sensing of carbaryl and malathion with low detection limit of 0.1 and 0.3 $\mu\text{g L}^{-1}$, respectively. Enlightened by the above strategy, Lin's group combined CDs with AuNPs for the sensitive analysis of OPs [63]. This sensing strategy contains FRET process between CDs (donor) and AuNPs (acceptor), the catalytic hydrolysis event of AChE and the inhibition procedure caused by pesticide. Under the optimal conditions, the proposed platform showed excellent linearity for paraoxon in the range of 0.05–50 $\mu\text{g L}^{-1}$. Many other FL nanomaterials have been employed for the fabrication of AuNPs-based enzyme platforms, such as QDs [64], upconversion nanoparticle [65], graphitic carbon nitride [66], and fluorophore dye [67].

Enzymatic modulation of the in-situ generation of AuNPs, which can address the drawback of background signal in analytical systems, opens new vistas in the field of biosensor. Li et al. constructed a ‘mix-and-detect’ fluorometric sensor for sensitive detection of pesticide based on graphene quantum dots (GQDs) [68]. As shown

in Fig. 2C, the authors successfully synthesized ATCh-modified GQDs through electrostatic interaction. With the assistance of AChE, the enzymatic hydrolyzate (thiocholine) with thiol group can potently reduce Au^{3+} ions to generate AuNPs that can efficiently quench the FL of GQDs by FRET effect. In addition, the free thiocholine also can link with neighboring GQDs through Au–S covalent bonding, causing aggregation of GQDs and further PL quenching. Subsequently, the FL could be recovered again by the addition of OPs that can inhibit the activity of AChE.

Tyrosinase (TYR), a typical polyphenol oxidase, can efficiently catalyze phenolic substrates to yield catechol derivatives, and then oxidized to produce orthoquinone. Compared with AChE-based biosensor, TYR-mediated strategies possess a better tolerance for high temperatures and organic solvents, as well as the faster operation. Inspired by the advantage of TYR biosensor, Hou et al., investigated a facile and sensitive FL strategy for OPs based on L-tyrosine methyl ester modified carbon dots (Tyr-CDs) [69]. In this sensing format, due to its oxidation activity, TYR catalyze the oxidation of tyrosine methyl ester on the surface of CDs to corresponding quinone units that can obviously quench the FL of CDs. Presence of the pesticide results in the FL restore of CDs because the activity of TYR is inhibited, thereby parathion-methyl (PM, as a model of OPs) was detected. This proposed system was further successfully used for real samples detection (cabbage, milk and fruit juice). Our group prepared a dual-emission ratiometric FL probe via hybridizing two differently colored QDs for the analysis of pesticide with a detection limit of 0.45 ng L^{-1} [70]. The ratiometric FL probe was fabricated by embedding red-emissive QDs in the silica nanoparticle as reference signal and covalently linking green-emissive QDs to the surface of silica nanoparticle as report signal. Subsequently, dopamine was conjugated to ratiometric FL probe surface through a simple covalent bonding. In the presence of TYR, dopamine was oxidized to produce dopamine quinone that triggered electron transfer process between dopamine quinone (acceptor) and ratiometric probe (donor), leading to the variation of system FL intensity ratio. Owing to the inhibition effect OPs, the established platform possessed good performance for the

quantitative assessment of PM in the range from 0.001 to 10 $\mu\text{g mL}^{-1}$. In another design, a fluorimetric system was constructed for OPs detection based on TYR-controlled quenching of chicken egg white-encapsulated gold nanoclusters (AuNCs) [71]. Utilizing the proposed FL platform, a detection limit was achieved down to 0.1 ng mL^{-1} . Significantly, AuNCs have been successfully employed to construct cost-effective and rapid response test strips for visual detection of paraoxon, offering a promising potential on-site application toward pesticide monitoring.

A few other enzymes have been applied to fabricate biosensor for pesticide detection. Trypsin that can catalyze the hydrolysis of some proteins into small pieces was employed to develop FL probe for pesticide detection. Recently, our group integrated trypsin-based enzyme reaction and inner-filter effect between AuNPs and ratiometric probe to efficiently estimate the concentration of PM [72]. As revealed in Fig. 2D, the FL of ratiometric probe could be quenched by AuNPs through inner-filter effect (IFE). Protamine induce the aggregation of AuNPs via electrostatic attraction and weaken the IFE, accompanying the recovery of system FL. Trypsin specifically catalyzes the hydrolysis of protamine to small protein fragments, causing sufficient quenching of fluorescent signal. Subsequently, the FL could be recovered again by the addition of PM which can block the activity of trypsin. By collecting the FL ratio of probe, the concentration of PM was evaluated. Under the optimized conditions, the ratiometric sensor exhibited a wide dynamic working range from 0.04 to 400 ng mL^{-1} , with a low detection limit of 0.018 ng mL^{-1} . Compared with conventional technologies, the proposed FL probe based on ratiometric QDs possess a built-in correction which can eliminate false signals emanating from environmental effects, obviously improving sensitivity and accuracy of sensor. Thanks to the catalytic activity of enzyme and pesticide-induced inhibition of the enzyme, acid phosphatase (ACP) was successfully applied to establish biosensor for the analysis of pesticide. Enlightened by the characteristic of ACP, our group reported a convenient and label-free FL sensing system for sensitive detection OPs [73]. In this work, cysteamine-capped CdTe QDs, as an FL reporter, can form both electrostatic and hydrogen bonding with adenosine triphosphate, causing significant FL enhancement of QDs. ACP specially catalyze the hydrolysis of adenosine triphosphate to adenosine and phosphate fragments under acidic environment. As a typical inhibitor, PM can reduce the ACP activity and recover the FL intensity of QDs. The proposed ACP-based sensor was successfully applied to detect OPs with a detection limit of 0.5 ng mL^{-1} .

The above inhibition sensors based on AChE, TYR, trypsin and ACP are not selective to one kinds of pesticide, for example, the activity of AChE can inhibit by carbamates pesticide and OPs. Furthermore, enzyme inhibition in these systems is irreversible which cannot be utilized for repetitive detection. Differing from these enzymes, organophosphorus hydrolase (OPH) display special capability of hydrolysis OPs to produce low-toxicity compounds. Thus, OPH-based sensor with high selectivity and fast response time have drawn increasing attention in OPs detection [23,74–77]. Ji et al. conjugated (CdSe)ZnS QDs and OPH through electrostatic interaction for the detection of paraoxon [78]. The FL intensity was directly quenched in the presence of paraoxon by influencing the degree of surface passivation of OPH/QDs bioconjugate. The change of FL can be used to analyze paraoxon with a detection limit of 10^{-8} mol L^{-1} . On the basis of a similar scheme, our group reported sensitive and facile OPH sensor for PM detection based on ET effect between QDs and the hydrolyzate of PM (*p*-nitrophenol) [79]. PM can be hydrolyzed by OPH to yield *p*-nitrophenol, which can absorb on the surface of cetyltrimethylammonium bromide (CTAB)-decorated QDs based on the strong hydrophobic interaction between the long alkyl chain of CTAB and aromatic ring of *p*-nitrophenol.

Due to its strong electron-withdrawing effect, *p*-nitrophenol can efficiently quenched the FL of QDs through ET mechanism, thereby indirectly reflected PM concentration. For the hydrolyzate of PM (di-methylthiophosphoricacid, DMPA), we fabricated a label-free FL sensor based on CuInS₂ QDs and lead ions [80]. The FL intensity of CuInS₂ QDs was quenched in the presence of lead ions. Subsequently, DMPA with a P=S bond exhibited strong coordinative interaction with lead ions, resulting in the FL recovery of the CuInS₂ QDs system. The established strategy had been successfully used for monitoring PM residues in water, banana and rice samples with satisfactory results.

Bi-enzyme systems with the advantages of multi-signal amplification have been generally considered as sensitive and selective technique for the construction of biosensors. Tang's group ingeniously designed bi-enzyme of AChE and choline oxidase (ChOx) assembly multilayers for optical detection of OPs [81]. AChE can hydrolyze acetylcholine to form choline that is in turn catalytically oxidized by choline oxidase (ChOx) to generate hydrogen peroxide, which can quench the FL of QDs. OPs can interact with AChE and suppress the enzyme activity, leading to the decrease of quenching rate. By measuring the quenching rate, the concentration of OPs was evaluated. On the basis of bi-enzyme format, a series of nanomatrixes, Mn-doped ZnSe dot [82], CdTe QDs [83], silicon quantum dots [84], CDs [85] and fluorescent dye [86], were considered as FL reporter to construct sensing platform for quantitative detection of pesticide.

Despite the high sensitivity and selectivity of enzyme-based sensor, some serious drawbacks still limited their widely utilization. For example, enzyme possess poor stability under high temperature and strong acidic/alkaline conditions. In addition, enzyme as a biomaterial need tedious production and time-consuming purification.

2.1.2. Antibody-assisted methods

Antibody, as biorecognition element, brings new tools in the fabrication of immunosensor in the biochemical, clinical and environmental fields [87–89]. Due to its extremely high equilibrium association constants, antibody can sensitively and selectively recognize its corresponding antigen. Currently, antibody has been widely applied in pesticide immunoassay that have become potentially alternative methods for routine analysis [90]. With the development of nanomaterials and nanotechnology, new opportunities have been brought for the development of advanced FL immunosensor. Shen's group successfully combined QDs with secondary antibody as FL label in the construction of indirect competitive FL-activated immunosensor for sensitive sensing of sulfamethazine in chicken muscle tissue [91]. Enlighten by the above strategy, Vinayaka et al. presented a competitive fluorescence immunoassay based biosensor for rapid and sensitive detection of 2,4-dichlorophenoxyacetic acid (2,4-D) [92]. In this sensing system, mercaptopropionic acid capped CdTe QDs and 2,4-D molecule were orderly conjugated with alkaline phosphatase (ALP) to form 2,4-D-ALP-CdTe composite as a competitor of analyte. The analyzing of 2,4-D was carried out by utilizing competitive binding between 2,4-D-ALP-CdTe composite and free 2,4-D in an antibody immobilized immunoreactor column. In addition, many other antibodies have been labeled with nanomaterials as signal reporter for the quantitative analysis of pesticide, such as chlorpyrifos [93], glyphosate [94] and parathion [95]. The miniaturization of immunosensor can not only overcome the requirement for large volumes of reagents and the consumption of long analysis times, but also provide a promising idea for point-of-care tools. Lin's group proposed a portable immunochromatographic test strip for rapid analysis of an organophosphorus pesticide metabolite

(3,5,6-trichloropyridinol, TCP) [96]. On the basis of an antigen-based antibody capture strategy and QDs-served signal vehicles, the competitive immunochromatographic test strip performed good selectivity and sensitivity for the monitoring of TCP with a detection limit of 1.0 ng mL^{-1} , which was finished within 15 min. Poly(dimethylsiloxane) sheet as an outstanding solid support have been introduced to eliminate the fluorescence interference, concentrate trace analyte and enhance the detection sensitivity for the fabrication of immunosensor. Zhou et al. synthesized a fluorescent immunoassay probe to develop in-situ visual and semi quantitative analysis strategy of phosmet on the poly(dimethylsiloxane) sheet [97]. The polymer dots-antibody probe can recognize phosmet as detector and output fluorescent signal as reporter. Interestingly, the probe can be directly used for visual detection of phosmet residue on apple surfaces.

Incorporating nanomaterials with antibody have paved the way for the fabrication of sensitive and selective immunoassays with excellent performance. Nevertheless, there are several significant challenges to the utilization of fluoroimmunoassay. In particular, the biocompatibility of nanoprobes, uniformity of synthesize nanomaterials and the linking efficiency between antibody and materials should be improved for the establishment of immunoassay.

2.1.3. Molecularly-imprinted polymers (MIPs)-based methods

Molecularly-imprinted polymers (MIPs), called plastic antibodies, with specific recognition capacity are easily prepared by in-situ co-polymerization of functional monomers around a template molecule. Owing to its high stability and remarkable mechanical properties, MIPs can be widely applied to improve the separation efficacy and enhance the detection sensitivity in sensor development, especially they were reusable in different applications. Moreover, in case of biological recognizers (enzyme and antibody) are not available, MIPs have great potential to be employed as tailor made polymers in the fabrication of biosensor. Based on the above-mentioned advantages, MIPs are gaining popularity in biosensor development, separation, environmental remediation, and drug delivery [98–100]. In this section, we would like to review the recent development of pesticide sensor based on MIPs as artificial receptor.

For the easiest way, the MIPs nanoparticles were directly employed as alternate of antibody for the construction of enzyme-linked immunosorbent assay. In the study of Xiao et al., MIP layer was capped to the surface of QDs to fabricate MIP-QDs composite that were served as sensing nanomaterials in preparing enzyme-linked immunosorbent assay-like method for the specific detection of cypermethrin [101]. Typically, by constructing a suitably tailored MIPs on the surface of fluorophore, FL sensing platforms with the advantages of high selectivity of MIPs and good sensitivity of fluorophore were established for target pesticides detection in a target concentration-dependent manner. Li et al. grafted silica nanospheres embedded CdSe QDs with MIPs layer via surface molecular imprinting process [102]. The molecularly imprinted silica nanospheres as a sensitive optical probe was applied to analyze trace λ -cyhalothrin residues and eliminate interferences by coexisting substances in environmental samples. Hollow-particle imprinted polymers which possess high binding capacity and site accessibility were employed to shorten the response time and improve the chemical stability. Wang et al. engineered a fluorescent polymeric hollow nanoparticle for rapid FL detection of pyrethroid pesticides [103]. The analyte-imprinted fluorescent hollow nano-sensor exhibit excellent sensitivity, appreciable selectivity and rapid detection rate, as well as attractive regeneration ability. Thus, hollow-particle imprinted polymers can be performed in good binding kinetics and capacity manner form overcoming slow response and poor chemical stability.

The above-mentioned strategies require several steps and usually a huge amount of reaction compounds. Ultrasonication-assisted encapsulation method which demonstrated short synthesis time, and few number of reaction reagents has been utilized to synthesize QDs-MIPs fluorescent composites by Wang's group in 2012 [104]. They introduced poly-styrene-co-methacrylic acid copolymer and QDs into imprinted pesticide solution to form QDs-MIPs fluorescent nanospheres within 6 min (Fig. 3A). Relying on van der Waals forces and hydrophobic forces, the nanospheres demonstrated fast adsorption and desorption ability to target pesticides (diazinon) with the recognition cavities. On the base of energy transfer (ET) from QDs (donor) to diazinon (acceptor), the QDs-MIPs fluorescent composites were successfully applied to the direct FL quantification of diazinon with the detection limit down to 38.6 ng mL^{-1} . Besides diazinon, MIP-coated single fluorophore composite had also been developed for sensitive detection of paraquat [105], cyphenothrin [106], λ -cyhalothrin [107], carbaryl [108], sulfamethazine [109], and 2,4-D [110].

Combining MIPs with two or more nanomaterials in multi-function format is considered to be attractive protocol for pesticide sensing. Yang et al. ingeniously fabricated an imprinted silica matrix loaded with Fe_3O_4 nanoparticles and QDs, which performed superparamagnetic property and bright FL characteristic [111]. They introduced Fe_3O_4 nanoparticles as separator to selectively extract analyte under complex sample matrix and encapsulated QDs as an output signal to sensitively monitor the amount of pentachlorophenol. Thus, the MIPs composite nanomaterials possess tri-functions as recognition unit, separation channel and signal tag for pentachlorophenol detection. In general, MIPs based single-FL sensing platform only can display the change of FL brightness by "turn-on" or "turn-off" toward analytes, easily influencing by false signals and greatly limiting their quantitative capability. To overcome such drawbacks, ratiometric scheme contains two or more kinds of fluorophore were proposed to perform precise measurement based on their self-referencing capability [112]. Inspired by preceding work, Chen's group applied the ratiometric FL probe for the construction of MIPs dual-emission sensor through a facile sol-gel polymerization (Fig. 3B) [113]. The ratiometric FL probe by hybridizing two differently colored fluorophores, the red emissive QDs were loaded in silica nanoparticles as reference while the green emissive nitrobenzoxadiazole (NBD) served as a signal report unit. The detection mechanism was based on ET process between NBD and the amine groups of functional monomers. In the presence of 2,4-D, the amine groups of MIPs composite could bind 2,4-D via hydrogen bond, which blocked the ET process, consequently resulting in dramatic FL recovery of NBD and continuous changes of ratiometric FL intensity. The as-proposed MIPs dual-emission sensor possessed high sensitivity with the detection limit of $0.14 \mu\text{mol L}^{-1}$. Moreover, the variations of the two FL intensity ratios display gradual FL color changes from orange-red to green upon response to different concentration of 2,4-D. A similar approach was used by Amjadi et al. for sensitive ratiometric detection of diniconazole [114]. In such a system, they prepared mesoporous molecularly imprinted polymer containing CDs and QDs. CDs-doped silica as an internal reference unit provided a built-in self-calibration for correction of environmental effects and increased sensor accuracy. And QDs were encapsulated in the pores of mesoporous silica and possessed signal report unit. The ratiometric FL probe was highly reactive toward diniconazole, which obviously quenched the FL of the green QDs, accompanying a visual green-to-blue color switch.

Although MIPs nanoparticles are widely applicable and ideally suitable for integration in practical applications, some challenges including poor reproducibility, lack understand of binding mechanism and complex extraction of template molecules from the

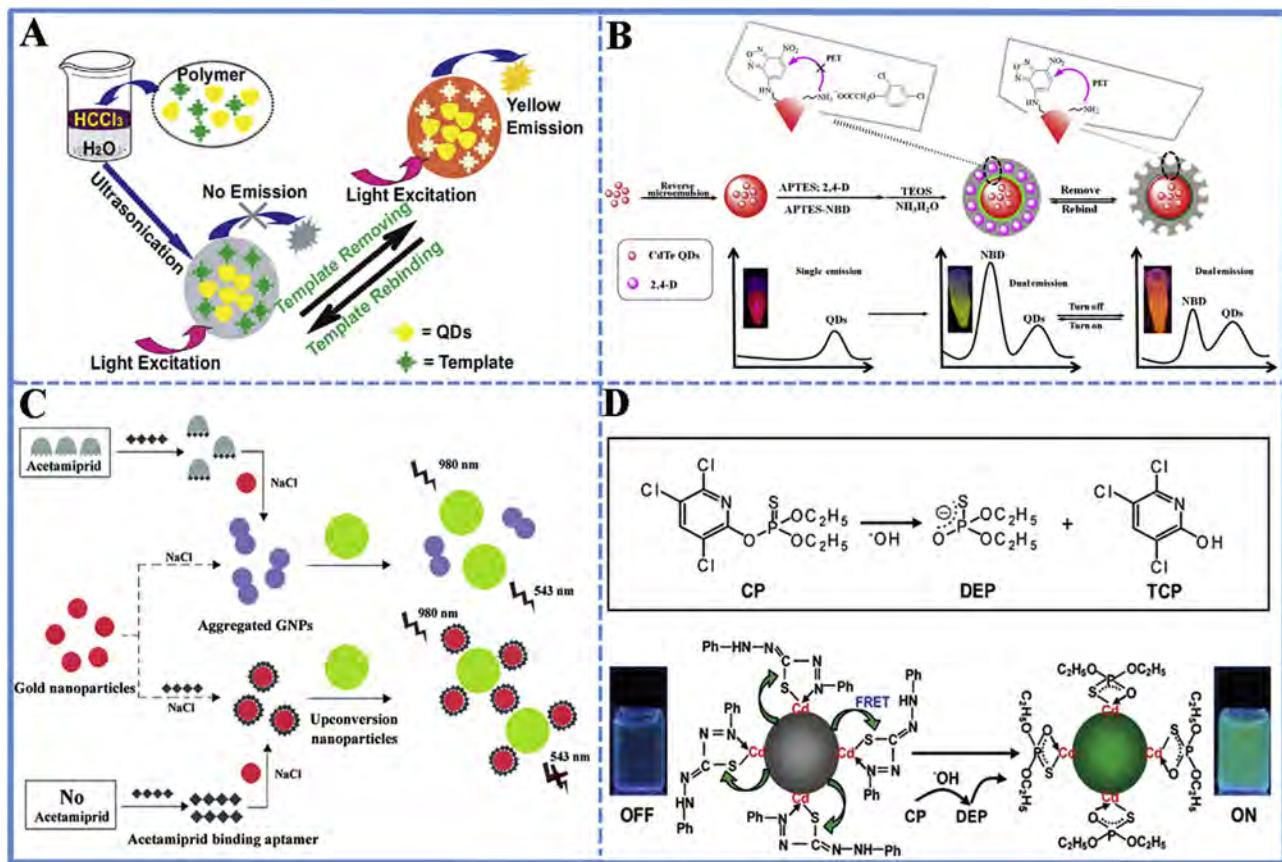


Fig. 3. (A) The preparation of QDs-MIP nanospheres and the FL quenching detection of analytes upon specific recognition (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [104] with permission). (B) The molecular imprinting-based turn-on ratiometric fluorescence sensor for detection of 2,4-D (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [113] with permission). (C) The UCNPs-AuNPs fluorescence aptamer-based nanosensor for the detection of acetamiprid (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [124] with permission). (D) Ligand replacement-induced FL switch of QDs for ultrasensitive detection of chlorpyrifos (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [146] with permission).

polymers have limited their application. Overcoming those drawbacks is crucial to design efficiency sensor and pave the way for further practical application.

2.1.4. Sensor based on aptamer

Aptamer, as typical molecular recognition element, are single-stranded nucleic acids molecules that can be generated via systematic evolution of ligands by exponential enrichment (SELEX) approach from a sequence library. Unlike natural antibodies, aptamers with low molecular weight are generally facile and low-cost to synthesize, and possess good stability, sustainable to repetitive denaturation and renaturation [115]. In particular, aptamers can be controllably decorated with various fluorophore by fine-tuning the functionalization processes, which would not influence their affinity [116]. Furthermore, aptamers directly recognize and bind to corresponding targets as “lock-and-key” by molecular shape complementarities, stacking of aromatic rings, electrostatic and van der Waals interactions as well as hydrogen bonding, which holds their detection much more efficiency and convenient [117]. Recently, Crivianu-Gaita et al. systematically compared antibody and aptamers in aspect of synthesis/engineering, immobilization techniques and application, suggesting that aptamers hold higher affinity, stronger stability and well regenerability [118]. Given these properties, aptamers have been considered as promising recognition elements for sensing strategies from biomedical diagnosis to environmental monitoring [119,120]. For pesticide recognition, Liu's group firstly applied SELEX strategy to select aptamer

response to acetamiprid from single-stranded DNA library in 2011 [121]. Subsequently, aptamers against OPs were isolated from an immobilized random single-stranded DNA library, possessing high affinities and specificities to the four OPs [122]. Thus, the utilization of aptamers in establishment of pesticide sensor aroused significant investigative attention from researcher [123]. The mechanism of designed platform was mainly based on physical adsorption of aptamers on nanomaterials and excellent quenching efficiency of nanomaterials to fluorophore. Based on the above-mentioned mechanism, Hu et al. rationally established aptamer-based nanosensor for the detection of acetamiprid through FRET between NH₂-NaYF₄:Yb, Ho@SiO₂ upconversion nanoparticles (UCNPs) and AuNPs [124]. As displayed in Fig. 3C, acetamiprid binding aptamer can adsorb on the surface of AuNPs through coordination interaction, which protect AuNPs from salt-induced aggregation, boosting efficient FRET process between UCNPs and AuNPs. As aptamer hold high affinity toward acetamiprid to form hairpin structure, the uncovered AuNPs were low tolerance to salt and showed aggregative state in the salty solution, so the FRET-weakened FL of UCNPs was regenerated with the presence of acetamiprid. The FL enhancement efficiency was driven by acetamiprid concentration. Similar to AuNPs, carbon nanotubes are also an outstanding FRET acceptor. On the basis of a similar scheme, Lin et al. constructed a turn-off-on sensor for quantification and imaging of acetamiprid using aptamer-modified QDs and multi-walled carbon nanotubes (MWCNTs) [125]. Due to strong π-π stacking interaction, aptamer-modified QDs were close to MWCNTs, triggering the FRET possess

and FL quenching of probe. In the presence of acetamiprid, the binding of aptamer-pesticide made the two materials stay away from each other and blocked the FRET effect. This sensing protocol could achieve a detection limit of 0.7 nmol L^{-1} for acetamiprid. In addition, Dou et al. prepared a gold-based nanobeacon probe as a signal indicator for the analysis of OPs based on the affinity of aptamer and the FL switch of fluorophore [126]. Abnous et al. applied three kinds of materials, including fluorophore, AuNPs and carbon nanotubes, for the fabrication of acetamiprid sensor with high selectivity [127].

In these strategies, the aptamer governs the specificity and sensitivity of sensing system. Even though great achievements have been made in current pesticide detection, there are still some important challenges and obstacles. For example, due to the difficulty of aptamer screening, aptamer-based nanosensor could only recognize several kinds of pesticide, which limited their wide application. Additionally, the detection mode was mainly based on the interaction between nanomaterials and fluorophore, thus the stability of nanomaterials directly affects the performance of sensor. AuNPs were often susceptible to be influenced by chemicals, such as cyanide and melamine, which maybe caused false positive results.

2.1.5. Sensor based on host-guest interaction

Host-guest recognition chemistry, as the branch of supramolecular chemistry, refers to the formation of inclusion complexes between macrocyclic hosts and suitable guests in a highly-controlled and cooperative manner. Typically, a host is a macrocyclic molecule that holds high cavity volume such as crown ethers, cucurbiturils, cyclodextrins, calixarenes, and pillararenes. Guests with complementary shape can selectively interact with host via various non-covalent interactions. The interaction between host and guest endue these polymers with good selectivity and convenient environmental responsiveness. Therefore, host-guest chemistry can provide new perspective into multifunctional biointerfaces, heterocatalysis, electronics, gas storage as well as fluorescence sensing [128–131]. Combined with FL signal tag, guest-host system as recognition elements can be utilized for pesticide detection. Li's group successfully coated QDs-silica spheres with Calix [4]arene to form C [4]/SiO₂/QDs nanoparticles via the sol-gel technique [132]. The as-synthesized nanocomposites with high FL intensity and good stability can serve as sensing probe for sensitive determination of methomyl. The intercalation of methomyl suppress the calixarene-cavity distort, forming an ordered orientation and uniform arrangement. Such change of calixarene-group shell structure blocked the quenching path via effective core protection, thereby increasing the FL intensity. Enhancement of the FL intensity emitted by the nanocomposites afford the selective detection of methomyl as low as $0.08 \mu\text{mol L}^{-1}$. Subsequently, the authors utilized *p*-sulfonatocalix [4]arene doped QDs for sensitive response to acetamiprid [133]. The *p*-sulfonatocalixarene cavities showed high affinity with ionized state of acetamiprid to form supramolecular complex, which effectively protect the core of composite and increased the FL intensity. Very recently, the same group adopted naphthol-appended calix [4]arene to selective recognition of metolcarb [134]. Motivated by previous study, Sun et al. introduced methylene blue (MB) and cucurbit [8]uril (CB [8]) as host-guest pairs to construct paraquat sensor [135]. MB with a single positive charge easily formed a head to tail dimer within the CB [8] cavity, inducing the FL quenching of MB. In the presence of paraquat, MB were replaced by paraquat immediately due to the two positive charges of paraquat, leading to a strong FL enhancement. Meanwhile, the 2MB@CB [8] based sensor also occurred in living cells for in-situ monitoring paraquat.

By transferring host-guest chemistry into pesticide sensing, many detection nanosensors were successfully achieved with high

selectivity. However, the fully understand molecular recognition in sensing and markedly improve anti-interference ability of host-guest system should be tackle in fabrication sensor.

2.1.6. Other approaches

With the achievements of recognition units, FL sensing strategies have performed outstanding sensitivity and selectivity for pesticide detection. Apart from the above recognition elements-based sensor, some novel FL detection strategies and technologies based on the direct utilization of fluorophore as recognition and response elements have been skillfully exploited for pesticide detection, which simplified the detection steps, saved the reaction time and avoided the modification process. Chow et al. designed a new bimetallic complex (Re(I)-NCS-Pt(II)) for directly quantitative detection of pesticides with aliphatic mercapto functionality [136]. Owing to the bridging linkage between the Re(I) and Pt(II) centers, the bimetallic complex demonstrated high selectivity to phorate, demeton, and aldicarb. Guan et al. purified protein-protected AuNCs via co-precipitation separation process for the fabrication of pesticides nanosensor [137]. Based on the quenching ability of pesticide, the FL color of AuNCs evidently changed with the addition of dithizone, 2,4-dichlorophenoxyacetic acid, paraoxon and fenitrothion, which allows a visual perception of pesticide. Similar to the direct-response manner of FL assays, our group conveniently synthesized CdS QDs for directly response to paraquat [138]. More importantly, the total time of analysis preparation of QDs and fluorescent measurement was only of 20 min. Furthermore, OPs [139,140], sulfonylurea herbicides [141] and bi-pyridine herbicides [142,143] were also determined by the directly reaction with QDs.

On the base of development of bioengineering technology, living organisms and its secretions are also used for pesticide monitoring. Yin et al. extracted and purified pyoverdine with bright FL from *Pseudomonas aeruginosa* strain PA1 [144]. The FL intensity of pyoverdine could be efficiently quenched by furazolidone based on ET mechanism. Interestingly, the fluorescent biosensor with good sensitivity completed within few seconds, which provided a potential candidate for real-time and on-site application. Tahirbegi et al. incubated metabolism/photosynthesis of chlamydomonas reinhardtii algal cells in microfluidic device for in-situ analysis of pesticide [145]. In the initial state, algal with bright FL grown in glass based microfluidic chip. Pesticides damage the integrity of the photosystems and inhibit photosynthesis, therefore affecting the FL intensity emitted from algae. This optical sensor could be used for fast quantification of atrazine, diuron and simazine in less than 10 min.

It is worth mentioning that ligand-replacement system has also been explored for sensitive pesticide analysis in “turn-off-on” mode. Zhang's group presented a facile and on-site method for OPs detection based on coordination-originated FRET [146]. Dithizone ligands were employed to modify QDs in basic media, which strongly quench emission FL of QDs by FRET process. In the presence of OPs, the ligands on the QDs surface were replaced by the hydrolyzate of OPs, immediately inducing the enhancement of probe (Fig. 3D). Importantly, the FRET based nanosensor can directly analyze chlorpyrifos in apple samples with a limit of $5.5 \mu\text{g L}^{-1}$. Latterly, the authors proposed an ratiometric FL response platform on the basis of ET process between fluorophore and dopamine dithiocarbamate using intrinsic dual-emitting QDs as signal reporter [147]. The ET pathway from QDs to ligands could be suppressed upon addition of diethylphosphorothioate due to its strongly coordinative interaction, resulting in continuous color changes from blue to red.

The specific coordination property between pesticide and metal, which improved the selectivity of recognition, brought new sight for the development of pesticide detection system. Mei et al.

conjugated Cu²⁺ on the surface of polymer-coated UCNPs via electrical attraction as a signal probe, which can generate specific coordination property to thiram [148]. After forming thiram-Cu²⁺ coordination complex, the blue luminescence of UCNPs can be quenched through luminescence resonance energy transfer mechanism. The coordination-induced recognition strategy that uses UCNPs as a FL reporter possesses excellent performance for thiram with a detection limit of 0.1 μmol L⁻¹. Enlightened by the above method, Fang et al. synthesized fluorescent ligand-Hg²⁺ complex for facile determination of OPs with satisfactory sensitivity [149]. Latterly, a “switch off” protocol with octahedral nickel complexes was presented by Raj et al. for the detection of phosmet and chlorpyrifos [150].

In addition to the mentioned sensor, the introduction of metal nanomaterials as recognition unit and nanoquencher has been demonstrated to be an attractive approach to enhance the analytical performance of pesticide detection. Our group designed dual-output optical (fluorometric and colorimetric) scheme that combined ratiometric fluorescent QDs as a FL sensor and AuNPs as capture material, nanoquencher and colorimetric reporter in the development of acetamiprid sensor [151]. In the initial state, the FL of ratiometric fluorescent QDs could be quenched by AuNPs via IFE. Acetamiprid with cyano group can specifically adsorb on the surface of AuNPs, which induced the aggregation of AuNPs, accompanying the weakened IFE and enhancement of FL. Thus, the presence of acetamiprid can qualitative screening via color change and quantitative assessment by FL sensor. On the base of the affinity between metal nanoparticles and pesticide, a series of dual-signal probe were fabricated for the monitoring of pesticide, such as fenamithion [152], glyphosate [153,154] and cyanazine [155].

2.2. Colorimetric sensing strategy

Owing to its convenience and simplicity, colorimetric (CL) sensing strategy has proven to be a powerful analytical approach for the analysis of variety of analyte, including ions [156], chemical warfare agents [157], small organic molecules [158] and biomarkers [159]. A prominent merit of CL sensing is that their direct visualization output makes them promising candidates for point-of-care assays. Therefore, the key challenge for fabricating CL platform is transforming response behavior into visual color change. Reviewed the remarkable achievements of nanomaterials, AuNPs as fascinate signal transducer have been widely utilized to design CL sensors for pesticide detection. Xu et al. developed AuNPs-based probe for the directly monitoring of acetamiprid based on the strong affinity between cyano group and gold [160]. The sensing mechanism was based on the state change of AuNPs from dispersion to aggregation. The concentration of acetamiprid can be qualitatively estimated from the color change (red to blue). The color change during nanoparticle aggregation is highly dependent on their distance and concentration. Shen et al. used citrate-stabilized AuNPs for the rapid detection of terbutylazine and dimethoate by visualizing the color change [161]. This AuNPs-based CL sensor showed high selectivity and good sensitivity for pesticide detection in real environment samples. Recently, a CL sensor array was constructed for identifying five OPs based on the dispersion-aggregation behavior of AuNPs by Fahimi-Kashani and Hormozi-Nezhad [162]. Apart from unmodified AuNPs, functionalized AuNPs have been utilized to improve selectivity for CL detection of pesticide as well. Sun et al. displayed p-amino benzenesulfonic acid functionalized AuNPs as signal reporter for detecting carbaryl [163]. Based on the similar protocol, Kim et al. introduced imidazole into AuNPs-based probe to improve the sensitivity and shorten the detection time for quantitative analysis of diazinon [164]. In addition, melamine [165], p-nitroaniline dithiocarbamate [166] and guanidine acetic acid

[167] were also served as ligand to decorate AuNPs for selective CL detection of pesticide. Despite many advantages of those aggregate sensors including easy-to-use and cost-effective, more endeavors are still needed to improve the sensitivity and selectivity. The combination of recognition elements is preferred as they address the above limitations. Thus, numerous efforts have been devoted to integrating the specific affinity of recognition units with the optical properties of metal nanoparticles for realizing pesticide analysis in a sensitive, selective and accurate manner. From perspective of recognition elements, CL sensing strategies can be typically summarized as four types: enzyme strategies, antibody assays, aptamer-based methods and other approaches.

2.2.1. Sensor based on enzyme

Enzyme-based sensors take advantage of selectively catalytic behavior of enzyme and outstandingly optical properties of nanomaterials, which are the most common high-efficiency strategies in the CL field of pesticide detection. The application of enzyme-mediated signal amplification has been indicated by employing the enzymatic hydrolyzate as an initiator to trigger the aggregation or self-assembly of metal nanoparticle, which can assist in signal transformation and amplification. Thanks to the binding affinity toward pesticide, AChE act as one of the most widely used enzyme for CL detection of pesticide. For example, lipoic acid-capped AuNPs as the colorimetric reporter have been prepared by Sun et al. to devise a sensitive sensor for OPs with the participation of AChE-induced catalytic reaction [168]. TCh can efficiently trigger the aggregation of lipoic acid functionalized AuNPs to produce clearly color change. When OPs exist as enzyme inhibitor, the activity of AChE can be blocked, which consequently diminished the generation of TCh, inducing the color change of probe. The proposed platform was successfully applied for spiked fruit sample with satisfactory results, thus representing great potential for on-site screening without more technical demand. To improve the sensor performance, Xia's group described an ultrahigh sensitively CL strategy for the sensing of OPs based on end-to-end (EE) assembly modulation of gold nanorods (AuNRs) by enzymatic reaction [169]. As shown in Fig. 4A, the two-point electrostatic interaction between cysteine molecules assisted the EE assembly of AuNRs, which resulted in the formation of one-dimensional superstructure. TCh preoccupied on the AuNRs binding sites via S–Au conjunction, preventing the EE self-assembly. In the presence of OPs, the enzymatic activity is suppressed, correspondingly observing the cysteine-induced AuNRs assembly again. The detection limit was estimated to be 0.039 pmol L⁻¹ with a linear range of 0.12–40 pmol L⁻¹. In combination with copper catalyzed click chemistry, Jiang's group developed AChE-assisted CL procedure for monitoring OPs by using azide- and alkyne-functionalized AuNPs [170]. In this sensing system, Cu (I) as the catalyst to trigger cycloaddition click chemistry and aggregation of AuNPs was released from CuO nanoparticles in the presence of enzymic hydrolyzate (acetic acid) and reductant (sodium ascorbate). OPs could control the production of acetic acid through inhibited AChE activity, thus influencing the click chemistry and aggregation of AuNPs. The involvement of Cu (I)-catalyzed click chemistry as signal amplification process greatly enhanced the sensitivity. Furthermore, horseradish peroxidases (HRP) [171], OPH [172], ALP [173], plant-esterase [174] and dual enzyme of AChE and HRP [175] are also worked as potential candidates for pesticide detection.

Owing to its single or multiple enzyme-like catalytic properties, nanozyme (artificial enzymes) attracts significant investigative interest as the alternative of natural enzyme. Yan's group firstly discovered HRP-like activities of Fe₃O₄ magnetic nanoparticles to catalyze different enzyme substrates in 2007 [176]. After this pioneering work, a significant number of materials such as hemin-

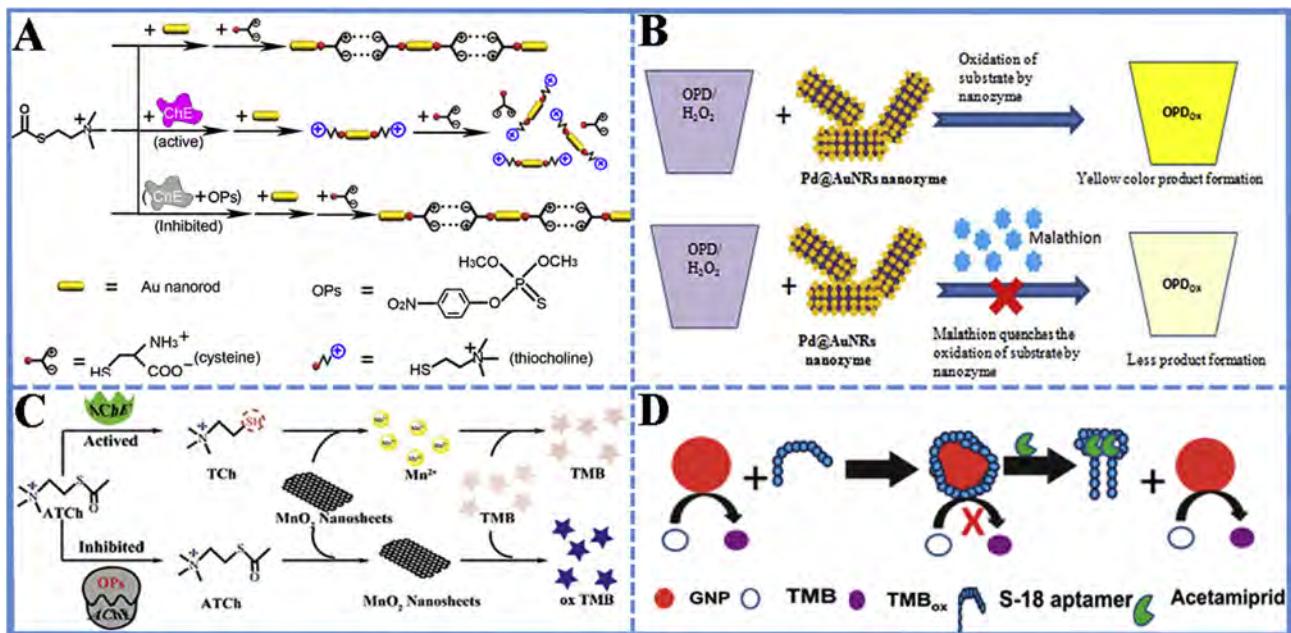


Fig. 4. (A) Schematic illustration of colorimetry for the assays of OPs based on the modulation of AuNRs EE self-assembly (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [169] with permission). (B) The principle of Pd@AuNR nanzyme assay for malathion (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [184] with permission). (C) Schematic of colorimetric platform for OPs detection based on MnO₂-TMB probe (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [187] with permission). (D) Schematic representation of the reversible inhibition of the nanzyme activity of AuNPs using an acetamiprid-specific aptamer (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [217] with permission).

graphene hybrid nanosheets [177], gold nanoclusters [178], graphene oxide nanoparticles [179], Prussian blue nanoparticles [180], CDs [181], AuNPs [182] and nanoceria [183], have investigated to hold similar activities as different enzymes. As peroxidase mimetic, palladium-gold bimetallic nanzyme is proposed response to malathion in the presence of hydrogen peroxide and *o*-phenylenediamine by Singh et al. (Fig. 4B) [184]. Palladium-gold bimetallic nanzyme with excellent peroxidase mimetic activity can catalytic *o*-phenylenediamine to form yellow-color oxidation product in the presence of hydrogen peroxide. It is interesting to discover that the addition of malathion could selectively inhibited the enzyme mimic activity of nanomaterials. Furthermore, the author also studied gold nanorods with peroxidase mimetic activity for developing a simple CL inhibition assay in the monitoring of malathion [185].

In addition to the above designs, the joint application of nanomaterials and natural enzyme as “dual-/tri-enzyme” has been proved to be a fascinating approach for amplifying the response signal of the CL sensor. An “tri-enzyme” strategy designed for OPs recognition was presented by Liang et al., which make use of the peroxidase mimetic property of Fe₃O₄ nanoparticles and the catalysis activity of AChE/ChOx [186]. In this study, with the consumption of acetylcholine, AChE and ChOx were utilized to generate hydrogen peroxide, which activates Fe₃O₄ nanoparticles to oxidase substrates, accompanying color change. After incubation with OPs, AChE activity was blocked, causing a decreased color intensity. As shown above, the developed enzyme sensor was convenient to implement and rapidly monitored acephate with the detection limit of 5 nmol L⁻¹. Based on this principle, our group constructed a novel CL sensing platform for quantitative analysis of OPs by monitoring the absorption of manganese dioxide nanosheets/3,3',5,5'-tetramethylbenzidine (MnO₂/TMB) probe [187]. As revealed in Fig. 4C, we prepared dual-function of ultrathin MnO₂ nanosheets to serve as enzyme with oxidase-mimicking activity which can directly oxidize TMB into blue-colored oxTMB in the absence of hydrogen peroxide, and to employ as recognizer for

distinguishing the enzymic hydrolyzate of AChE. Thanks to the inhibition effect of OPs, the enzymatic activity of AChE was blocked, then reducing the formation of TCh and resulting in the absorbance increase of MnO₂/TMB probe in a concentration-dependent manner. The integration of MnO₂ nanosheets and AChE not only improved the selectivity and sensitivity of the CL strategies but also introduced a novel insight for OPs detection. Likewise, enzyme-based CL assays were carried out by using cerium oxide nanoparticles whose oxidase mimic activity was rationally modulated via proton or TCh producing for the detection of OPs [188,189].

Apart from the above aggregation-based approach and mimic enzyme-assisted methods, nanoparticle morphology-mediated tool (change in nanoparticle size) is a promising strategy for designing CL sensors. The signal generation of the morphology transition of nanoparticles was depend on enzymatic control of AuNPs growth [190]. For instance, a CL sensing mechanism based on AChE catalytic growth of the AuNPs was utilized for ultrasensitive detection of OPs [191]. In this approach, the enzyme hydrolyzate (TCh) stimulated the catalytically reductive enlargement of gold seeds with the participation of AuCl₄, that is, enzyme can modulate the growth of the AuNPs. The target molecule can block the activity of AChE and subsequently decrease the production of TCh, resulting in the color change. The generation of colored solutions with characteristic property is responded to detect OPs with naked eye. Based on this principle, Pavlov's group introduced ascorbic acid to reduce Ag⁺ on the surface of gold seeds, promoting the catalytic growth of Au–Ag bimetallic nanoparticles with characteristical absorbance peaks at 400 nm [192]. Owing to the affinity between –SH and Au, TCh can bind to the surface of the gold seeds, hindering the deposition of silver (Ag⁰) in the presence of ascorbic acid and AgNO₃ (Ag⁺). Inhibition of AChE by paraoxon produces lower yields of TCh, consequently triggering the growth of Au–Ag nanoparticles. Recently, coupling of enzymes to the biocatalytic growth of AuNPs, a simple CL sensor was established for OPs detection in Au³⁺-cetyltrimethylammonium bromide environment

[193]. Interestingly, the author fabricated a CL test paper for visual detecting OPs by naked eyes within 20 min.

Some important chromogenic substrates, such as Ellman's agent and indophenyl acetate, are also utilized as signal reporter for pesticide detection [194–196]. Ellman's agent, 5,5-dithiobis (2-nitrobenzoic acid) (DTNB), specially reacted with thiol groups to produce yellow-colored product, which provides a practical means of designing CL sensors for AChE and its inhibitors (pesticide). Hossain et al. fabricated a paper-based CL strips by sandwiching the AChE within two layers of sol gel-derived silica on detection zone, which triggered the Ellman's test [197]. The bioactive test strip can be applied for the quantitative detection of OPs by monitoring the residual activity of enzyme. Latterly, the author employed indophenyl acetate as AChE hydrolysis of the substrate that can be catalyzed to yield blue-colored indigo for screening and monitoring enzyme inhibitor [198]. This CL strategy can detect pesticide with rapid response times of 5 min. From a sensing perspective, those strategies with rapid analysis capability do not need complex synthesis and modification of nanomaterials, suggesting that the convenient strategy could serve as an attractive protocol for the point-of-care detection of pesticide.

2.2.2. Sensor based on antibody

By combining antibody with CL strategy, enzyme-linked immunoassays (EIA) have been developed for pesticide detection [199–201], which become potentially attractive approaches for routine analysis. In the traditional immunoassay, HRP or alkaline phosphatase labeled detection antibody as signal reporter can specifically recognize the target for screening pesticides. For instance, our group developed a bi-enzyme tracer competitive EIA for the analysis of thiacloprid and imidaclothiz [202]. We directly coated two kinds of antibody on analysis plate, which can capture enzyme-functionalized tracers for pesticide detection based on competitive format. This detection format held excellent superiority in saving detection time and workload. Latterly, we also offered mini reviews of multi-pesticide detection based on immunoassays in 2014 [203]. Nanomaterials bring exciting opportunities for the establishment of advanced CL immunoassay for pesticide [204,205]. To achieve this goal, Wang et al. presented a lateral flow immunoassay for the monitoring of three kinds of pesticide based on AuNPs-labeled monoclonal antibody [206]. The performance of assay in cabbage and soil samples was satisfactory, particular in detection time within 7 min. To obtain high-throughput application, a nitrocellulose membrane-based CL immunochip assay for simultaneous detection of seven pesticides by using seven kinds of AuNPs-labeled antibodies [207]. Xu's group employed Fe₃O₄ nanoparticle aggregates as color reagents for fabricating lateral flow immunochromatographic assay [208]. Poly-(ethylene glycol) coated Fe₃O₄ nanoparticle were firstly modified with poly-L-lysine, then coupled with anti-PM polyclonal antibody, which can serve as color reagents for analyzing pesticide residue. The signal amplification strategy endowed by the controlled aggregation of Fe₃O₄ nanoparticles were recorded by absorption intensity analysis, greatly improving visual detection limit. In addition to their function as signal reporter, nanomaterials have been extensively used as nanocarriers to load enzyme and antibody. Du et al. designed a competitive CL triazophos immunoassay by employing Fe₃O₄ nanoparticles and multi-labeled AuNPs [209]. In this platform, AuNPs were utilized to conjugate anti-triazophos antibody and enzyme, which was served as signal amplifier when the immuno-reaction occurred. Meanwhile, Fe₃O₄ microparticle modified with ovalbumin-hapten complex to competitively bind antibody on the surface of AuNPs, further separated from reaction solution using a magnet. The quantitative detection of pesticide was depended on the enzyme-catalyzed color reaction.

2.2.3. Sensor based on aptamer

Attributed to design flexibility, cost-effectiveness, and promising stability under extreme experimental, nucleic acid aptamers have attracted tremendous concern in the fields of bioanalysis and biomedical applications [210–212]. From perspective of pesticide analysis, aptamers cooperated with nanomaterials as signal unit or catalysis element accomplish the transduction of recognition event with suitable affinity and selectivity toward pesticide [213,214]. By employing an "artificial antibody" aptamer, Shi et al. adapted AuNPs aggregation-based methods for sensitive recognition of acetamiprid, taking advantages of the selective target-induced color response [215]. Aptamer with random coil structure could be absorbed on the surface of AuNPs through coordination bonds, making AuNPs more stable against salt medium. Aptamer specifically bind with acetamiprid to form aptamer-target complexes, which induced the conformation changes of aptamer. The unprotected AuNPs would aggregate under proper amount of salt, accompanying the color change from red to purple blue. This CL strategy was realized for monitoring the natural degradation process of acetamiprid in soil. Motivated by this platform, Bala et al. employed unmodified AuNPs and aptamer for OPs detection based on pesticide-controlled aggregation of AuNPs [216]. By monitoring the signal change in the absorbance, the aptasensor showed a wide linear range from 0.5 to 1000 pmol L⁻¹ toward malathion with a detection limit of 0.06 pmol L⁻¹.

Nanomaterial served as peroxidase-mimicking catalyst has also been introduced into aptasensor for improving analysis performance. Combining peroxidase-like nanozyme activity of AuNPs, Weerathunge et al. demonstrated a facile CL sensor for acetamiprid detection in a specific and sensitive manner (Fig. 4D) [217]. In this design, the nanozyme activity of AuNPs can be suppressed via surface passivation with aptamer molecules. In the presence of target pesticide, the aptamer undergoes structural changes followed by desorption from the AuNPs surface to participate in an aptamer-target binding event, subsequently reactivating nanozyme activity of AuNPs. The residue of pesticide can either be directly visualized recognition on the base of color change or be quantified detection using UV-visible absorbance spectroscopy. Latterly, the well-dispersed hemin-functionalized reduced graphene oxide (hemin-rGO) composites possessed both peroxidase-like activity to catalyze reaction substrate and physical adsorption property to capture aptamer, which were used to fabricate CL aptasensor for acetamiprid detection [218]. The adsorbed aptamer on hemin-rGO composites can increase individual hemin-rGO electrostatic repulsion, making the composites coagulate vanish. Once aptamers were specifically bind with acetamiprid, the conformation changes of aptamers desorpted from the surface of hemin-rGO, accordingly losing the ability to protect composites in salt medium. As a consequence, the nanozyme activity was blocked, which produced low absorbance in the presence of TMB and hydrogen peroxide.

2.2.4. Other approaches

Other recognition unit, such as MIP and host-guest interaction, also open attractive window for pesticide analysis. It is well-known that MIP, as a fantastic recognition molecule, can be skillfully exploited to decorate sensing probes for fabrication of the high-performance CL sensor [219,220]. Wu et al. prepared MIPs with the special hierarchical porous structure for rapid recognition of atrazine, then they directly transformed recognition events into a readable color changes [221]. The MIP-based sensor exhibited good sensitivity (10^{-8} ng mL⁻¹) with a response time that was less than 30 s. Host-guest interactions also possess excellent recognition function for pesticide detection. As an example, Rohit et al. made use of dithiocarbamate-*p*-tertbutylcalix [4]arene capped AuNPs (DTC-PTBCA-AuNPs) as a capture material for the detection of

metsulfuron-methyl herbicide based on pesticide-assisted state change of AuNPs [222]. In this sensing strategy, DTC-PTBCA contains calixarene ring cavities that can selectively capture metsulfuron-methyl via host-guest interactions and π - π stacking, inducing a red-shift of absorption peak of AuNPs. The detection performance in a target concentration-dependent manner can be visual recognition by the naked-eye.

Microbial cells expressing enzyme, which are inspired by nature, offer a favorable chance for fabrication of sensor. Mishra et al. integrated polyethyleneimine functional silica nanoparticles with *Sphingomonas* sp. cell to synthesize a stable biohybrid material that express OPH enzyme activity to hydrolyze OPs [223]. By directly measuring the absorption intensity of PM hydrolyzate (*p*-nitrophenol), the optical biosensor can achieve PM detection in the range of 0.1–1.0 mg L⁻¹. In this platform, the utilization of silica nanoparticles not only save the cost of sensor, also enhance the storage stability of biohybrid.

2.3. Surface enhanced Raman scattering strategies

Raman spectroscopy can identify the chemical content of different molecular species via the collection of molecular vibrations, that is, Raman spectroscopy possess the capability of molecular “fingerprint” recognition for distinct molecule/analyte. Surface enhanced Raman scattering strategy (SERS) essentially integrated the molecular specificity of Raman spectroscopy with optical properties of plasmonic nanostructures [224]. Owing to optical resonance properties of coinage-metal nanostructures, the local electromagnetic field can be significantly enhanced, accompanying the improvement of the SERS signal. Taking advantages of ultrafast analysis capabilities, label-free, high stability and non-destructive characterization, the application of SERS received numerous concern in the field from biomedical diagnosis to environmental monitoring [225–227]. By means of coinage-metal nanostructures, SERS can even achieve an ultra-sensitivity down to the single-molecule level, which offered new opportunities toward obtaining single molecule recognition [228,229]. Recently, He et al. reviewed the development of SERS technique for pesticide detection in the aspect of sensitivity, reproducibility, selectivity and portability [230]. The following are recent achievements in pesticide SERS strategy as a powerful analytical tool that have focused on the development of metal nanostructures-enhanced amplification. In this section, according to the coinage metal nanoparticles-based solid substrates, SERS nanoprobes are typically designed as gold substrate, silver substrate and Au@Ag bimetallic substrate.

2.3.1. Sensor based on gold nanomaterial

Thanks to the enhancement of the electric field, gold nanomaterial as one of the widely used SERS substrates, can absorb target analyte, obviously strengthening SERS intensity. The Raman scattering amplification phenomenon are mainly dependent on the size, shape, orientation, and aggregation of nanomaterials, which can greatly influence the electromagnetic and chemical enhancement effects. Thus, vast endeavors have been undertaken to synthesis different morphology of gold nanomaterial or modify/coat recognition unit on the surface of gold nanomaterial [231–234]. Guo's group presented SERS strategy for directly extracting and rapidly detecting of target pesticides by using AuNPs as substrate and adhesive tape as nanocarrier (Fig. 5A) [235]. Thanks to the interaction between AuNPs and pesticide, the SERS strategy achieved the qualitative detection of PM, thiram, and chlorpyrifos in various sample as a practical application. Khlebtsov et al. fabricate centimeter-scale gold nanoisland films with strong electromagnetic coupling as substrate to improve SERS sensitivity and reproducibility by using wet-chemical approach [236]. A point-of-care

application of the proposed SERS sensor is exemplified by thiram analysis in the linear range of 5–250 ng mL⁻¹. Especially, this SERS technology can recognize thiram down to level of 5 ng cm⁻² on apple peel. For improving the selectivity of approach, modification of gold material received researcher's interests. Wang et al. performed trace SERS sensor by decorating AuNPs with mono-6-thio-b-cyclodextrin as substrate to efficiently capture PM [237]. Incorporating host-guest reaction between the hybridized cavity and pesticide, the Raman approach for identifying PM can be observed at picomolar level with high selectivity. To overcome roughened surfaces caused by aggregation or formation of nanoparticles and weak signal of tips area, Tian's group reported shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) whose signal amplification was provided by silica/alumina-coated AuNPs (Fig. 5B) [238]. In their design, AuNPs were capped with ultrathin shell of silica or alumina as “smart dust” to spread over the target surface, and then measured in-situ for inspecting pesticide residues on real-life sample, demonstrating that SHINERS can be employed as a simple-to-use and field-portable analyzer for pesticide screening.

2.3.2. Sensor based on silver nanomaterial

Compared with solid gold, solid silver shows simpler preparation process and stronger plasmon resonance property, which created more “hot spots” to achieve higher Raman enhancement, commonly fabricating of SERS platform [239]. Taking advantage of the silver nanoparticles (AgNPs)-induced enhancement of Raman signal, a “surface spray” SERS approach was introduced to achieve the sensitive monitoring of pesticide residues on sample skins [240]. The author sprayed the AgNPs to cover the surface of pear or apple skin, which showed interaction with paraquat molecules, followed by detecting via SERS signal. On the basis of the above principle, a high sensitivity for paraquat was reached the order of magnitude of 10⁻⁹ mol L⁻¹. Owing to its controllable of optical spectra, silver nanoshells (NSs) that consist of dielectric silica nanoparticles coated with a silver shell were utilized as SERS-active nanostructures for quantitative determination of thiram residue (Fig. 5C) [241]. In this study, under the reduction of octylamine at room temperature, a uniform layer of silver shells directly grown on the surface of silica nanoparticles without predeposition of seed metals. Through strongly enhanced Raman signals, this label-free approach successfully recognized thiram down to 38 ng cm⁻² in a rapid and sensitive manner on apple peel.

In addition to the focus on the morphology of nanomaterials, significant effort has been devoted to the modification of material in order to overcome the inherent drawback of low affinity. Kubackova et al. carried out the 1,8-octanedithiol functionalized AgNPs not only to create a specific nanogap which was suitable for assembly, also to induce interparticle junctions where sensitive hot spots were presented to attach the pesticide [242]. By means of SERS technique, organochlorine pesticides (aldrin, α -endosulfan, dieldrin, and lindane) can be sensitively detected because they are inserted in dithiol multilayer to induce signal change.

On account of their easy-to-cut or conformal surfaces, flexible substrates can be wrapped onto curved surfaces for the efficient extraction of target molecules, exhibiting impressive merits in sampling and rapid analysis with excellent efficiency. Kumar et al. fabricated large area SERS-active and flexible substrate for rapid tracing pesticide residues by embedding silver nanorods (AgNRs) into polydimethylsiloxane polymer [243]. The AgNRs arrays were deposited on Si wafer, followed by embedding in low index polydimethylsiloxane polymer, which enhanced portability and mechanical stability of substrate. The in-situ SERS measurements on flexible substrates were performed by directly extracting trace amount of thiram on fruit peels. Fan et al. used sandpaper as

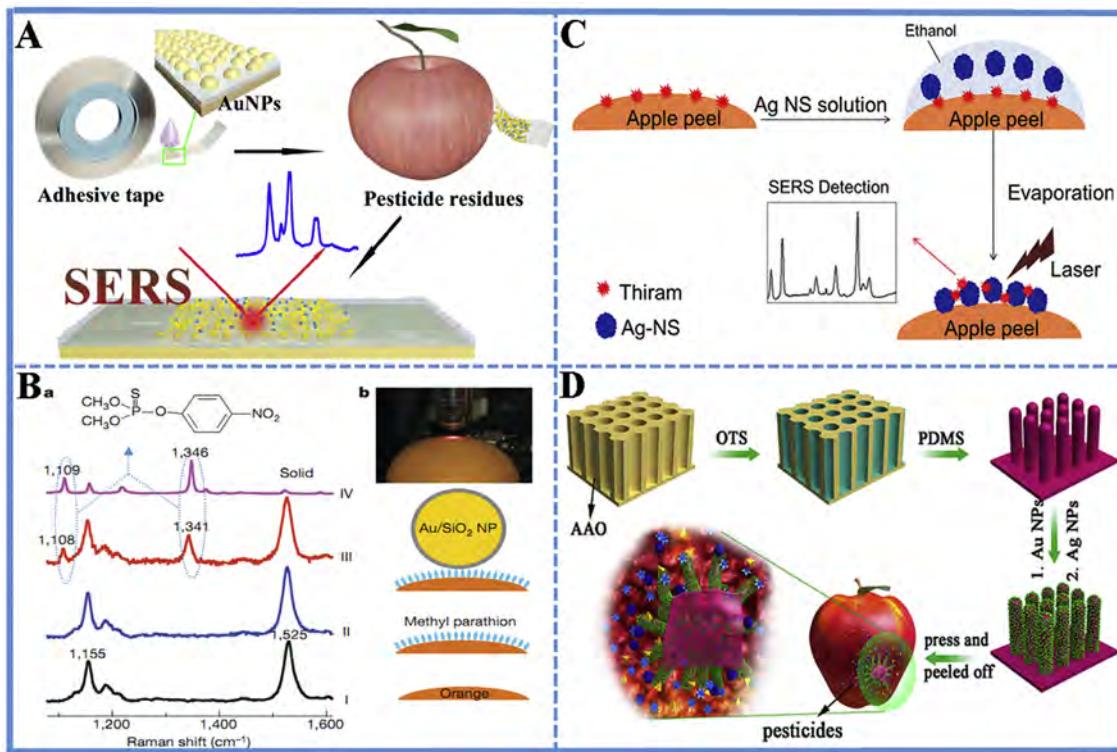


Fig. 5. (A) Schematic illustration of the fabrication of SERS tape and extraction of targets from fruit peel surface (apple) for SERS analysis (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [235] with permission). (B) In-situ inspection of pesticide residues on food/fruit based on SHINERS spectrum (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [238] with permission). (C) On-site detection of thiram on an apple peels using AgNSs (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [241] with permission). (D) Schematic demonstration of preparation of SERS substrate and SERS measurement for pesticide (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [250] with permission).

template for deposition of silver for constructing flexible SERS substrate [244]. By swabbing real-life sample surfaces, the proposed SERS sensor with low-cost (less than 10 cents) is suitable for rapid screening triazophos.

2.3.3. Sensor based on bimetallic nanomaterial

It has been confirmed that key nanomaterial structural compositions play a significant role in determining SERS performance [245]. Compared to single-element nanomaterials, bimetallic materials possess the richer combination of material-dependent and size/shape-dependent manner to get more plasmonic modes. In particular, silver-coated gold nanoparticles (Au@Ag NPs) were synthesized for fabricating SERS sensor in the detection of thiram residues [246]. The proposed sandwich nanostructure with good uniformity was fabricated by composing of graphene oxide nanosheets and Au@Ag NPs via a simple self-assembly process, which employed as SERS-active substrate for producing highly enhanced Raman signals. On account of plenty of hot spots and unique structure of sandwich nanomaterial, the SERS platform can be exploited to determine thiram in grape juice with a detection limit down to 0.1 mmol L⁻¹. This approach opened an attractive avenue for utilizing core-shell particle in the identification and detection of pesticide residues. Motivated by above strategy, Guo et al. prepared monodisperse Au@Ag nanocubes (NCs) and Au@Ag nanocuboids (NBs) in well controlled sizes and shapes manner as SERS substrates for thiram detection [247]. With the optimized particle size, the sensing method achieved a detection limit of 80 pmol L⁻¹ for thiram in the utilization of NBs substrates.

Most of SERS substrates are two dimensions (2D) planar systems, which are limited SERS active area to a single Cartesian plane.

Meanwhile, Laser confocal volume is a 3D space for measurement, demonstrating that excitation source needs to be closely concentrated on the correct location (plane) and 2D SERS substrates are under-utilizing confocal volume [248]. 3D nanostructures, which can overcome low sampling efficiency on complex surface, were also introduced in the construction of SERS approach [249]. A gecko-inspired nanotentacle SERS strategy is proposed for the monitoring of pesticide via “press and peeled-off” approach, as shown in Fig. 5D [250]. The flexible 3D “tentacle” array was constructed by absorbing AuNPs and seeding deposition of AgNPs on high density of 3D poly(dimethylsiloxane) nanotentacle, which can freely approach the microarea and achieve efficient pesticide recognition and collection, making it suitable for directly in-situ enrichment and sampling from cucumber, apple and grape surfaces. More importantly, the sensing platform which hold unique molecular “fingerprint” is proposed for simultaneous analysis of three kinds of pesticides (thiram, PM and malachite green) in a complex system.

2.4. Other detection strategies

Other detection techniques, such as surface plasmon resonance (SPR) strategy and chemiluminescence strategy, have also gained strong driving forces in the detection of pesticide due to their convenient manipulation and high efficiency. By taking advantage of the outstanding distinguish ability provided by recognition unit, SPR and chemiluminescence strategy possessed excellent sensitivity and selectivity for real-time monitoring. Here, we focus on some of the attractive research on SPR and chemiluminescence strategy.

2.4.1. Surface plasmon resonance sensor

Surface Plasmon Resonance (SPR) strategy as a label-free tool have received significant attention due to their ability to detect target compounds in sensitivity, automation and real-time manner [251]. The SPR sensor with outstanding reutilization performance and excellent reproducibility has become increasingly popular in drug discovery, food safety and environmental monitoring, especially for point-of-care diagnostics [252]. Commonly, SPR sensors employ antibodies as receptors to capture its corresponding target due to their superior performance. For example, Mauriz et al. presented a useful portable analytical method based on SPR strategy by combining competitive immunoassay format for on-line monitoring of carbaryl [253]. In this platform, alkanethiol self-assembled monolayer was formed on the surface of gold substrate to improve the reusability of sensor, followed by immobilizing hapten-carrier protein conjugate to capture antibody. In the presence of carbaryl, a competitive immunoassay was immediately performed within 10 min, which reflected mass change on the transducer surface and finally converted to a digital signal output by multielement photodiode. On the basis of above principle, a SPR-based indirect competitive immunoassay has been fabricated for thiabendazole analysis in whole orange sample based on specific monoclonal antibodies [254]. Under the optimal conditions, the detection limit of SPR-based immunosensor was able to reach $0.16 \mu\text{g L}^{-1}$ by monitoring mass variation.

MIPs represent a new class of materials that hold high stability and outstanding mechanical properties. By combining MIPs with sensor transducers, Dong et al. designed SERS sensor for quantitatively detecting profenofos in sensitive and selective manner [255]. The author synthesized MIP ultrathin films on the surface of 11-mercaptopoundecanoic acid-functionalized SPR gold chips via surface-initiated thermal polymerization, which worked as sensing material for recognizing profenofos. On the basis of target-induced mass change, the MIP-modified SPR sensor showed good linearity in the range of 1.0×10^{-4} – $1.0 \mu\text{g mL}^{-1}$ for detecting profenofos. For the signal output of sensor, in most cases, the physical response (mass variation) on the surface of metal substrates caused by binding a target analyte often led to relatively low sensitivity [256]. To overcome this drawback, Qiu et al. introduced SPR angle shift-based output into sensing platform by integrating MIPs recognition property with magnetic separation ability for amplifying SPR response [257]. As shown in Fig. 6A, the obtained magnetic MIPs

nanosphere possess excellent magnetic properties to directly capture, concentrate, and separate of pesticide in complex samples in virtue of an external magnetic field. In sensing strategy, the magnetic MIPs nanoparticles with template-imprinting sites were integrated on a SPR chip via the specific interactions between the immobilized AChE and chlorpyrifos rebound in the recognition cavities, resulting in a significant signal amplification due to the high molecular weights, high refractive indices and excellent imprinted effect. The biosensor obtained good sensitivity and acceptable selectivity for chlorpyrifos with a dynamic linear range from 0.001 to $10 \mu\text{mol L}^{-1}$ and a detection limit of 0.76 nmol L^{-1} .

2.4.2. Chemiluminescence strategy

Chemiluminescence strategy has grown into a well-established luminometry assay, which not require light excitation, greatly improving signal-to-noise ratio because of the reduction or elimination of background signal [258,259]. Chemiluminescence approach as an attractive technique possess inherent merits, such as simplicity of operation, cost-effectiveness, rapid response and superior sensitivity, that make them excellent scaffolds for the construction of optical probes in various scientific fields range from food analysis to diagnosis of disease [260,261]. In the light of these advantages, chemiluminescence techniques have been successfully applied to the determination of pesticide by combining with recognition elements. Fu's group designed a chemiluminescence assay with high sensitivity for PM and imidacloprid detection based on a bi-enzyme competitive immunoreaction in the utilization of bispecific monoclonal antibody (BsMcAb) [262]. In this platform, BsMcAb as the unique recognition unit that can specially capture PM and imidacloprid in complex samples was produced by a hybrid hybridomas approach, which were coated on the surface of microplate. As displayed in Fig. 6B, enzyme (HRP and ALP) tagged haptens of the two pesticides can competitively bound to the BsMcAb, simultaneously triggering the chemical reaction by adding the chemiluminescence co-reactants. By collecting the chemiluminescence signal at 0.6 s (for PM detection) and 1000 s (for imidacloprid detection), good linear ranges were obtained in the range of 1.0 – 500 ng mL^{-1} for both PM and imidacloprid. Compared to time-resolved fluorescent assay, the proposed chemiluminescence immunoassay were easy-manipulation which collected signals at much wider time windows. Very recently, the same group constructed multiplexed immunochromatographic test

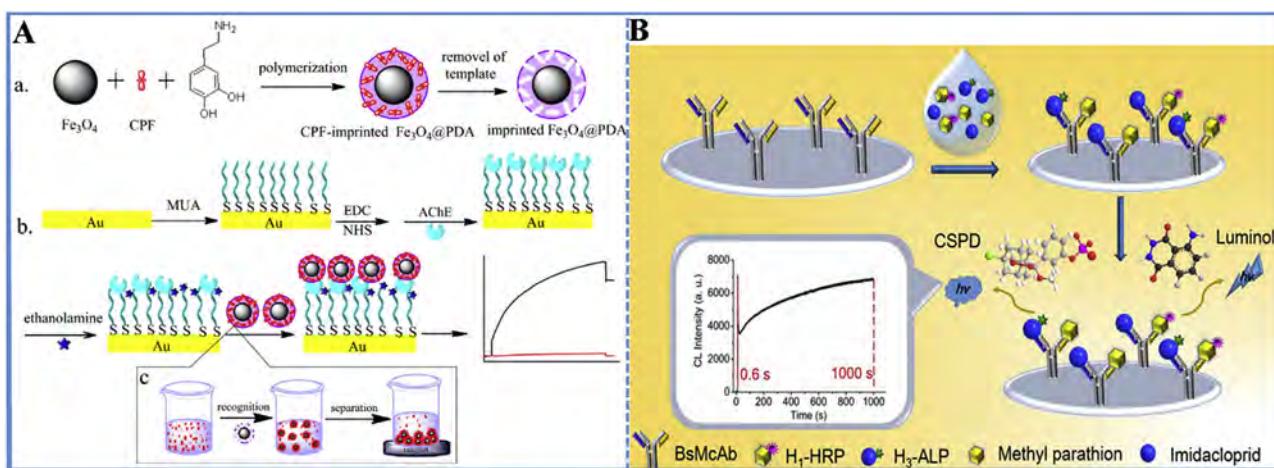


Fig. 6. (A) SPR sensor based on magnetic MIPs nanosphere for pesticide recognition (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [257] with permission). (B) Schematic illustration of the CL Strategy for PM and imidacloprid detection (reproduced from Ref. <http://www.sciencedirect.com/science/article/pii/S0165993617301516> [262] with permission).

strip by using BsMcAb-based chemiluminescence probe for simultaneously detection PM and imidacloprid [263]. The assay exhibited low-cost and user-friendliness with analysis time that was less than 22 min.

Recent developments in mimicking enzyme have approved new sight in the establishment of chemiluminescence sensor. By taking advantage of peroxidase-like activity of AuNPs, Khajvand et al. presented a chemiluminescence procedure for the detection of hexythiazox residues with the luminol-H₂O₂ system [264]. The bare AuNPs with intrinsic peroxidase-like activity can catalyze luminol and H₂O₂ to produce hydroxy-hydroperoxide, leading to enhancement of chemiluminescence intensity. The slight change of AuNPs state, such as aggregation, can cause the significant change of catalytic properties. Hydrolyzate of hexythiazox can trigger the aggregation of AuNPs, which reduced mimicking enzyme activity of AuNPs in the luminol-H₂O₂ system. According to the chemiluminescence signal, hexythiazox can be analyzed in the range of 0.017–0.42 µg mL⁻¹. Inspired by preceding work, Lin's group synthesized graphitic carbon nitride/bismuth ferrite nanocomposites (g-C₃N₄/BiFeO₃ NCs) as a peroxidase-like catalyst in the construction of chemiluminescent immunochromatographic assay for detection of chlorpyrifos and carbaryl [265]. By coupling with high binding affinity of pesticide aptamer, an amplified chemiluminescence strategy was reported for ultrasensitive and selective detection of acetamiprid by Qi et al. [266]. The conformational change of aptamers can significantly influence the state of AuNPs (from dispersed state to aggregated state) in salt solution, further inducing the catalytic capability of AuNPs in luminol-H₂O₂ chemiluminescence reaction. On the base of specific affinity of aptamer and catalytic property of AuNPs, the aptamer-based chemiluminescence sensing system revealed good performance for acetamiprid detection with a detection limit of 62 pmol L⁻¹.

Another approach to nanoparticle-based chemiluminescence assay is direct synthesis of luminol-functionalized material in chemiluminescence sensing. He et al. prepared luminol-modified AgNPs (Lum-AgNPs) for fabricating chemiluminescence sensor array with triple-channel properties for recognizing and discriminating of OPs and carbamate pesticides [267]. Luminol as a reducing agent can reduce silver nitrate to form Lum-AgNPs which can react with H₂O₂ to produce a chemiluminescence emission. Owing to the different affinity of AuNPs for pesticide, distinct chemiluminescence responses could obtain with the addition of different pesticides. Based on this phenomenon, this sensor array has well distinguished dimethoate, dipterex, carbaryl, chlorpyrifos, and carbofuran, thereby greatly simplifying the operation procedure. This sensing array opens a new avenue for pesticide identification in simple, facile and high-throughput manner.

3. Conclusions and perspectives

Continuous concerns over pesticide residues have provided a long-driven force to develop novel techniques. In the past decade years, thousands of research literatures have been published for the routine and convenient monitoring of pesticide to meet increasing market and social requirements. Herein, we have reviewed various kinds of optical strategy that were ingeniously designed and successfully applied for the detection of pesticide, with a specific focus on the fluorescence, colorimetric and surface-enhanced Raman scattering sensing strategies. With the emergence of high affinity of recognition elements, as well as various novel signal transduction approaches, optical assay reveal good performance to quantify pesticide residues in complex environment and food matrices, especially in the simplification and visualization design, making them ideally suitable for on-site application.

On the basis of the discussed research, the stability, accuracy, sensitivity and selectivity of optical sensor can be improved as follows: (1) the development of recognition units with excellent distinguish capacity to offer selectivity and sensitivity toward targeted analytes. For example, bi-enzyme cascade catalytic format has the merit of multi-signal amplification, greatly improving the sensitivity. (2) the utilization of novel nanomaterials that employ as signal reporters, substrates and catalysts. Ratiometric probe with dual-emission can provide built-in correction to eliminate environmental effects, exhibiting advantage in terms of enhanced sensitivity and accuracy. Nanozymes possess lower cost, higher stability, and excellent recyclability in comparison with natural enzymes, which improved the stability of sensor. Furthermore, the integration of optical strategy into paper-based analytical devices can be constructed in simplicity and miniaturization, further promoting the commercialization of devices.

Even though optical sensor has a promising future in pesticide determination, there are sustainable challenges to be addressed in the field. Particularly, most optical sensors still retain at laboratory level of testing and verifying proof-of-concept, which have not been exploited in practical applications. In the aspect of recognition events, the stability of recognition units (such as enzymes, antibody and aptamer) can be easily influenced by environmental conditions, such as temperature and pH. Furthermore, the integration of recognition event into the analytical system is a vital step in the fabrication of a successful sensor. The conjugation between recognition elements and functionalized nanomaterials will inevitably increase the complexity, cost and time of optical sensor, especially suppress the distinguish ability of recognition elements. From the perspective of nanomaterials, nanomaterials-based analytical platforms are in the starting stage of development. The specificity and catalytic activity of current nanozymes are lower than that of natural enzymes, in turn impeding the use of nanozymes. The synthesis of functional materials/nanomaterials with relatively narrow size distribution will seriously influence the performance of sensor because inhomogeneous distribution of nanoprobe can reduce analysis accuracy. Thus, future endeavors should directly focus on addressing above obstacles.

While remarkable progress has been made toward the design of optical sensor for pesticide detection, tremendous opportunities and new trends are emerging. Coupling newly developed recognition elements (nanobodies, peptide aptamers and so on) with functional materials/nanomaterials will afford exciting opportunities for the monitoring of pesticide, which can improve the performance of sensor. On the other hands, the integration of field-deployable devices with optical sensor perform promising on-site applications, with the aid of 3D printing technologies, improving the reproducibility and stability of sensor. By taking advantage of miniaturized device and wire-less networking, the recognition event of pesticide can be transformed into a measurable digital signal by hand-held devices, such as smartphone, then the detection results can deliver to the servers. Thus, the portable detecting platforms can be carried out outside of laboratory setting with minimal user involvement, paving the way for a new generation of analytical devices in real-time detection. We envision that, therefore, optical sensors will assuredly act significant roles in future on-site monitoring of pesticide.

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References

- [1] E.A. Songa, J.O. Okonkwo, Recent approaches to improving selectivity and sensitivity of enzyme-based biosensors for organophosphorus pesticides: a review, *Talanta* 155 (2016) 289–304.
- [2] C.S. Pandir, N. Chauhan, Acetylcholinesterase inhibition-based biosensors for pesticide determination: a review, *Anal. Biochem.* 429 (2012) 19–31.
- [3] M. Eddleston, N.A. Buckley, P. Eyer, A.H. Dawson, Management of acute organophosphorus pesticide poisoning, *Lancet* 371 (2008) 597–607.
- [4] P. Kumar, K.H. Kim, A. Deep, Recent advancements in sensing techniques based on functional materials for organophosphate pesticides, *Biosens. Bioelectron.* 70 (2015) 469–481.
- [5] E.Y. Long, C.H. Krupke, Non-cultivated plants present a season-long route of pesticide exposure for honey bees, *Nat. Commun.* 7 (2016) 11629.
- [6] C. Rowe, R. Gunier, A. Bradman, K.G. Harley, K. Kogut, K. Parra, B. Eskenazi, Residential proximity to organophosphate and carbamate pesticide use during pregnancy, poverty during childhood, and cognitive functioning in 10-year-old children, *Environ. Res.* 150 (2016) 128–137.
- [7] A.I. Sankoh, R. Whittle, K.T. Semple, K.C. Jones, A.J. Sweetman, An assessment of the impacts of pesticide use on the environment and health of rice farmers in Sierra Leone, *Environ. Int.* 94 (2016) 458–466.
- [8] U.E.P.A. USEPA, Setting Tolerances for Pesticide Residues in Foods, 2016.
- [9] N.P.I.C. NPIC, International Pesticide Regulations, 2016.
- [10] S.B. Bird, T.D. Sutherland, C. Gresham, J. Oakeshott, C. Scott, M. Eddleston, OpdA, a bacterial organophosphorus hydrolase, prevents lethality in rats after poisoning with highly toxic organophosphorus pesticides, *Toxicology* 247 (2008) 88–92.
- [11] S.A. Nsibande, P.B.C. Forbes, Fluorescence detection of pesticides using quantum dot materials - a review, *Anal. Chim. Acta* 945 (2016) 9–22.
- [12] E. Watanabe, K. Baba, Highly sensitive quantification of pyrethroid insecticide etofenprox in vegetables with high-performance liquid chromatography and fluorescence detection, *J. Chromatogr. A* 1385 (2015) 35–41.
- [13] M.Y. Yang, X.F. Xi, X.L. Wu, R.H. Lu, W.F. Zhou, S.B. Zhang, H.X. Gao, Vortex-assisted magnetic beta-cyclodextrin/attapulgite-linked ionic liquid dispersive liquid-liquid microextraction coupled with high-performance liquid chromatography for the fast determination of four fungicides in water samples, *J. Chromatogr. A* 1381 (2015) 37–47.
- [14] T.T. Liu, P. Cao, J.P. Geng, J.Q. Li, M.Z. Wang, M.L. Wang, X.Y. Li, D.L. Yin, Determination of triazine herbicides in milk by cloud point extraction and high-performance liquid chromatography, *Food Chem.* 142 (2014) 358–364.
- [15] M.T. Jafari, M. Saraji, H. Sherafatm, Polypyrrole/montmorillonite nanocomposite as a new solid phase microextraction fiber combined with gas chromatography-corona discharge ion mobility spectrometry for the simultaneous determination of diazinon and fenthion organophosphorus pesticides, *Anal. Chim. Acta* 814 (2014) 69–78.
- [16] X.H. Hou, X. Zheng, C.L. Zhang, X.W. Ma, Q.Y. Ling, L.S. Zhao, Ultrasound-assisted dispersive liquid-liquid microextraction based on the solidification of a floating organic droplet followed by gas chromatography for the determination of eight pyrethroid pesticides in tea samples, *J. Chromatogr. B* 969 (2014) 123–127.
- [17] X.S. Zhao, W.J. Kong, J.H. Wei, M.H. Yang, Gas chromatography with flame photometric detection of 31 organophosphorus pesticide residues in Alpinia oxyphylla dried fruits, *Food Chem.* 162 (2014) 270–276.
- [18] E.T. Rodrigues, M.A. Pardal, N. Salgueiro-Gonzalez, S. Muniategui-Lorenzo, M.F. Alpendurada, A single-step pesticide extraction and clean-up multi-residue analytical method by selective pressurized liquid extraction followed by on-line solid phase extraction and ultra-high-performance liquid chromatography-tandem mass spectrometry for complex matrices, *J. Chromatogr. A* 1452 (2016) 10–17.
- [19] Q.S. Zhong, L.L. Shen, J.Q. Liu, D.B. Yu, S.M. Li, J.T. Yao, S. Zhan, T.H. Huang, Y. Hashi, S. Kawano, Z.F. Liu, T. Zhou, Pre-column dilution large volume injection ultra-high performance liquid chromatography-tandem mass spectrometry for the analysis of multi-class pesticides in cabbages, *J. Chromatogr. A* 1442 (2016) 53–61.
- [20] M.E.S. Synaridou, V.A. Sakkas, C.D. Stalikas, T.A. Albanis, Evaluation of magnetic nanoparticles to serve as solid-phase extraction sorbents for the determination of endocrine disruptors in milk samples by gas chromatography mass spectrometry, *J. Chromatogr. A* 1348 (2014) 71–79.
- [21] J.S. Van Dyk, B. Pletschke, Review on the use of enzymes for the detection of organochlorine, organophosphate and carbamate pesticides in the environment, *Chemosphere* 82 (2011) 291–307.
- [22] I.V. Lyagin, E.N. Efremenko, S.D. Varfolomeev, Enzymatic biosensors for determination of pesticides, *Russ. Chem. Rev.* 86 (2017) 339–355.
- [23] W.Y. Zhang, A.M. Asiri, D.L. Liu, D. Du, Y.H. Lin, Nanomaterial-based biosensors for environmental and biological monitoring of organophosphorus pesticides and nerve agents, *Trends Anal. Chem.* 54 (2014) 1–10.
- [24] G. Aragay, F. Pino, A. Merkoci, Nanomaterials for sensing and destroying pesticides, *Chem. Rev.* 112 (2012) 5317–5338.
- [25] N. Verma, A. Bhardwaj, Biosensor technology for pesticides-a review, *Appl. Biochem. Biotech.* 175 (2015) 3093–3119.
- [26] N. Xia, Q.L. Wang, L. Liu, Nanomaterials-based optical techniques for the detection of acetylcholinesterase and pesticides, *Sensors* 15 (2015) 499–514.
- [27] Y. Du, S.J. Guo, Chemically doped fluorescent carbon and graphene quantum dots for bioimaging, sensor, catalytic and photoelectronic applications, *Nanoscale* 8 (2016) 2532–2543.
- [28] J.J. Zhang, F.F. Cheng, J.J. Li, J.J. Zhu, Y. Lu, Fluorescent nanoprobes for sensing and imaging of metal ions: recent advances and future perspectives, *Nano Today* 11 (2016) 309–329.
- [29] L.W. He, B.L. Dong, Y. Liu, W.Y. Lin, Fluorescent chemosensors manipulated by dual/triple interplaying sensing mechanisms, *Chem. Soc. Rev.* 45 (2016) 6449–6461.
- [30] A.B. Chinen, C.M. Guan, J.R. Ferrer, S.N. Barnaby, T.J. Merkel, C.A. Mirkin, Nanoparticle probes for the detection of cancer biomarkers, cells, and tissues by fluorescence, *Chem. Rev.* 115 (2015) 10530–10574.
- [31] L.Y. Li, Y.L. Wen, L. Xu, Q. Xu, S.P. Song, X.L. Zuo, J. Yan, W.J. Zhang, G. Liu, Development of mercury (II) ion biosensors based on mercury-specific oligonucleotide probes, *Biosens. Bioelectron.* 75 (2016) 433–445.
- [32] Y.M. Guo, L.F. Zhang, S.S. Zhang, Y. Yang, X.H. Chen, M.C. Zhang, Fluorescent carbon nanoparticles for the fluorescent detection of metal ions, *Biosens. Bioelectron.* 63 (2015) 61–71.
- [33] P. Wu, T. Zhao, S.L. Wang, X.D. Hou, Semiconductor quantum dots-based metal ion probes, *Nanoscale* 6 (2014) 43–64.
- [34] K.V. Ragavan, N.K. Rastogi, M.S. Thakur, Sensors and biosensors for analysis of bisphenol-A, *Trends Anal. Chem.* 52 (2013) 248–260.
- [35] V. Scognamiglio, F. Arduini, G. Palleschi, G. Rea, Biosensing technology for sustainable food safety, *Trends Anal. Chem.* 62 (2014) 1–10.
- [36] S. Paterson, R. de la Rica, Solution-based nanosensors for in-field detection with the naked eye, *Analyst* 140 (2015) 3308–3317.
- [37] P. Wu, X.D. Hou, J.J. Xu, H.Y. Chen, Ratiometric fluorescence, electrochemiluminescence, and photoelectrochemical chemo/biosensing based on semiconductor quantum dots, *Nanoscale* 8 (2016) 8427–8442.
- [38] K. Zhang, H.B. Zhou, Q.S. Mei, S.H. Wang, G.J. Guan, R.Y. Liu, J. Zhang, Z.P. Zhang, Instant visual detection of trinitrotoluene particulates on various surfaces by ratiometric fluorescence of dual-emission quantum dots hybrid, *J. Am. Chem. Soc.* 133 (2011) 8424–8427.
- [39] M. Strobl, A. Walcher, T. Mayr, I. Klimant, S.M. Borisov, Trace ammonia sensors based on fluorescent near-infrared emitting aza-BODIPY dyes, *Anal. Chem.* 89 (2017) 2859–2865.
- [40] P. Wu, X.P. Yan, Doped quantum dots for chemo/biosensing and bioimaging, *Chem. Soc. Rev.* 42 (2013) 5489–5521.
- [41] L.Y. Chen, C.W. Wang, Z.Q. Yuan, H.T. Chang, Fluorescent gold nanoclusters: recent advances in sensing and imaging, *Anal. Chem.* 87 (2015) 216–229.
- [42] P.L. Wang, Z.Y. Lin, X.O. Su, Z.Y. Tang, Application of Au based nanomaterials in analytical science, *Nano Today* 12 (2017) 64–97.
- [43] F.L. Yuan, S.H. Li, Z.T. Fan, X.Y. Meng, L.Z. Fan, S.H. Yang, Shining carbon dots: synthesis and biomedical and optoelectronic applications, *Nano Today* 11 (2016) 565–586.
- [44] X.M. Li, F. Zhang, D.Y. Zhao, Lab on upconversion nanoparticles: optical properties and applications engineering via designed nanostructure, *Chem. Soc. Rev.* 44 (2015) 1346–1378.
- [45] A. Amine, F. Arduini, D. Moscone, G. Palleschi, Recent advances in biosensors based on enzyme inhibition, *Biosens. Bioelectron.* 76 (2016) 180–194.
- [46] S. Kumar, W. Ahlawat, R. Kumar, N. Dilbaghi, Graphene, carbon nanotubes, zinc oxide and gold as elite nanomaterials for fabrication of biosensors for healthcare, *Biosens. Bioelectron.* 70 (2015) 498–503.
- [47] H.X. Li, X. Yan, S.P. Qiao, G.Y. Lu, X.G. Su, Yellow-emissive carbon dots based optical sensing platform: cell imaging and analytical applications for biocatalytic reactions, *ACS Appl. Mater. Interfaces* 10 (2018) 7737–7744.
- [48] T. He, L. Qi, J. Zhang, Y.L. Huang, Z.Q. Zhang, Enhanced graphene quantum dot fluorescence nanosensor for highly sensitive acetylcholinesterase assay and inhibitor screening, *Sens. Actuators B* 215 (2015) 24–29.
- [49] J.Y. Hou, G.J. Dong, Z.B. Tian, J.T. Lu, Q.Q. Wang, S.Y. Ai, M.L. Wang, A sensitive fluorescent sensor for selective determination of dichlorvos based on the recovered fluorescence of carbon dots-Cu(II) system, *Food Chem.* 202 (2016) 81–87.
- [50] E. Caballero-Diaz, S. Benitez-Martinez, M. Valcarcel, Rapid and simple nanosensor by combination of graphene quantum dots and enzymatic inhibition mechanisms, *Sens. Actuators B* 240 (2017) 90–99.
- [51] N. Zhang, Y.M. Si, Z.Z. Sun, S. Li, S.Y. Li, Y.H. Lin, H. Wang, Lab-on-a-drop: biocompatible fluorescent nanoprobe of gold nanoclusters for label-free evaluation of phosphorylation-induced inhibition of acetylcholinesterase activity towards the ultrasensitive detection of pesticide residues, *Analyst* 139 (2014) 4620–4628.
- [52] J. Chen, D.L. Liao, Y. Wang, H.P. Zhou, W.Y. Li, C. Yu, Real-time fluorometric assay for acetylcholinesterase activity and inhibitor screening through the pyrene probe monomer-excimer transition, *Org. Lett.* 15 (2013) 2132–2135.
- [53] D. Zhao, C.X. Chen, J. Sun, X.R. Yang, Carbon dots-assisted colorimetric and fluorometric dual-mode protocol for acetylcholinesterase activity and inhibitors screening based on the inner filter effect of silver nanoparticles, *Analyst* 141 (2016) 3280–3288.
- [54] R. Zhang, N. Li, J.Y. Sun, F. Gao, Colorimetric and phosphorimetric dual-signaling strategy mediated by inner filter effect for highly sensitive assay of organophosphorus pesticides, *J. Agr. Food Chem.* 63 (2015) 8947–8954.
- [55] J.J. Deng, D.K. Lu, Z.L. Xiaolei, G.Y. Shi, T.S. Zhou, Highly sensitive GQDs-MnO₂ based assay with turn-on fluorescence for monitoring cerebrospinal acetylcholinesterase fluctuation: a biomarker for organophosphorus pesticides poisoning and management, *Environ. Pollut.* 224 (2017) 436–444.
- [56] Z.Z. Zheng, Y.L. Zhou, X.Y. Li, S.Q. Liu, Z.Y. Tang, Highly-sensitive organophosphorous pesticide biosensors based on nanostructured films of

- acetylcholinesterase and CdTe quantum dots, *Biosens. Bioelectron.* 26 (2011) 3081–3085.
- [57] H.X. Li, X. Yan, G.Y. Lu, X.G. Su, Carbon dot-based bioplatform for dual colorimetric and fluorometric sensing of organophosphate pesticides, *Sens. Actuators B* 260 (2018) 563–570.
- [58] S.Z. Liao, W.T. Han, H.Z. Ding, D.X. Xie, H. Tan, S.Y. Yang, Z.Y. Wu, G.L. Shen, R.Q. Yu, Modulated dye retention for the signal-on fluorometric determination of acetylcholinesterase inhibitor, *Anal. Chem.* 85 (2013) 4968–4973.
- [59] J.F. Chang, H.Y. Li, T. Hou, F. Li, Paper-based fluorescent sensor for rapid naked-eye detection of acetylcholinesterase activity and organophosphorus pesticides with high sensitivity and selectivity, *Biosens. Bioelectron.* 86 (2016) 971–977.
- [60] D.L. Liao, J. Chen, H.P. Zhou, Y. Wang, Y.X. Li, C. Yu, In situ formation of metal coordination polymer: a strategy for fluorescence turn-on assay of acetylcholinesterase activity and inhibitor screening, *Anal. Chem.* 85 (2013) 2667–2672.
- [61] X. Yan, Y. Song, C.Z. Zhu, H.X. Li, D. Du, X.G. Su, Y.H. Lin, MnO₂ nanosheet-carbon dots sensing platform for sensitive detection of organophosphorus pesticides, *Anal. Chem.* 90 (2018) 2618–2624.
- [62] D.B. Liu, W.W. Chen, J.H. Wei, X.B. Li, Z. Wang, X.Y. Jiang, A highly sensitive, dual-readout assay based on gold nanoparticles for organophosphorus and carbamate pesticides, *Anal. Chem.* 84 (2012) 4185–4191.
- [63] X.L. Wu, Y. Song, X. Yan, C.Z. Zhu, Y.Q. Ma, D. Du, Y.H. Lin, Carbon quantum dots as fluorescence resonance energy transfer sensors for organophosphate pesticides determination, *Biosens. Bioelectron.* 94 (2017) 292–297.
- [64] J.J. Guo, H.K. Li, M. Xue, M.W. Zhang, X.Y. Cao, Y.L. Luo, F. Shen, C.Y. Sun, Highly sensitive detection of organophosphorus pesticides represented by methamidophos via inner filter effect of Au nanoparticles on the fluorescence of CdTe quantum dots, *Food Anal. Methods* 7 (2014) 1247–1255.
- [65] Q. Long, H.T. Li, Y.Y. Zhang, S.Z. Yao, Upconversion nanoparticle-based fluorescence resonance energy transfer assay for organophosphorus pesticides, *Biosens. Bioelectron.* 68 (2015) 168–174.
- [66] H.Z. Xie, F. Bei, J.Y. Hou, S.Y. Ai, A highly sensitive dual-signaling assay via inner filter effect between g-C₃N₄ and gold nanoparticles for organophosphorus pesticides, *Sens. Actuators B* 255 (2018) 2232–2239.
- [67] Y.D. Zhang, T.T. Hei, Y.A. Cai, Q.Q. Gao, Q. Zhang, Affinity binding-guided fluorescent nanobiosensor for acetylcholinesterase inhibitors via distance modulation between the fluorophore and metallic nanoparticle, *Anal. Chem.* 84 (2012) 2830–2836.
- [68] N. Li, X.W. Wang, J. Chen, L. Sun, P. Chen, Graphene quantum dots for ultrasensitive detection of acetylcholinesterase and its inhibitors, *2D Mater.* 2 (2015) 034018.
- [69] J.Y. Hou, J. Dong, H.S. Zhu, X. Teng, S.Y. Ai, M.L. Mang, A simple and sensitive fluorescent sensor for methyl parathion based on L-tyrosine methyl ester functionalized carbon dots, *Biosens. Bioelectron.* 68 (2015) 20–26.
- [70] X. Yan, H.X. Li, W.S. Zheng, X.G. Se, Visual and fluorescent detection of tyrosinase activity by using a dual-emission ratiometric fluorescence probe, *Anal. Chem.* 87 (2015) 8904–8909.
- [71] X. Yan, H.X. Li, T.Y. Hu, X.G. Su, A novel fluorimetric sensing platform for highly sensitive detection of organophosphorus pesticides by using egg white-encapsulated gold nanoclusters, *Biosens. Bioelectron.* 91 (2017) 232–237.
- [72] X. Yan, H.X. Li, X.S. Han, X.G. Su, A ratiometric fluorescent quantum dots based biosensor for organophosphorus pesticides detection by inner-filter effect, *Biosens. Bioelectron.* 74 (2015) 277–283.
- [73] J. Wang, Y. Yan, X. Yan, T.Y. Hu, X.J. Tang, X.G. Su, Label-free fluorescent assay for high sensitivity and selectivity detection of acid phosphatase and inhibitor screening, *Sens. Actuators B* 234 (2016) 470–477.
- [74] Y.T. Zhao, W.Y. Zhang, Y.H. Lin, D. Du, The vital function of Fe₃O₄@Au nanocomposites for hydrolase biosensor design and its application in detection of methyl parathion, *Nanoscale* 5 (2013) 1121–1126.
- [75] X.H. Cao, S.V. Mello, R.M. Leblanc, V.K. Rastogi, T.C. Cheng, J.J. DeFrank, Detection of paraoxon on immobilized organophosphorus hydrolase in a Langmuir-Blodgett film, *Colloid. Surface. A* 250 (2004) 349–356.
- [76] S. Thakur, P. Kumar, M.V. Reddy, D. Siddavattam, A.K. Paul, Enhancement in sensitivity of fluorescence based assay for organophosphates detection by silica coated silver nanoparticles using organophosphate hydrolase, *Sens. Actuators B* 178 (2013) 458–464.
- [77] N. Kamelipour, A. Mohsenifar, M. Tabatabaei, T. Rahmani-Cherati, K. Khoshnevisan, A. Allameh, M.M. Milani, S. Najavand, B. Etemadikia, Fluorometric determination of paraoxon in human serum using a gold nanoparticle-immobilized organophosphorus hydrolase and coumarin 1 as a competitive inhibitor, *Microchim. Acta* 181 (2014) 239–248.
- [78] X.J. Ji, J.Y. Zheng, J.M. Xu, V.K. Rastogi, T.C. Cheng, J.J. DeFrank, R.M. Leblanc, (CdSe)ZnS quantum dots and organophosphorus hydrolase bioconjugate as biosensors for detection of paraoxon, *J. Phys. Chem. B* 109 (2005) 3793–3799.
- [79] X. Yan, H.X. Li, X.Y. Wang, X.G. Su, A novel fluorescence probing strategy for the determination of parathion-methyl, *Talanta* 131 (2015) 88–94.
- [80] X. Yan, H.X. Li, Y. Yan, X.G. Su, Selective detection of parathion-methyl based on near-infrared CuInS₂ quantum dots, *Food Chem.* 173 (2015) 179–184.
- [81] Z.Z. Zheng, X.Y. Li, Z.F. Dai, S.Q. Liu, Z.Y. Tang, Detection of mixed organophosphorus pesticides in real samples using quantum dots/bi-enzyme assembly multilayers, *J. Mater. Chem.* 21 (2011) 16955–16962.
- [82] X. Gao, G.C. Tang, X.G. Su, Optical detection of organophosphorus compounds based on Mn-doped ZnSe d-dot enzymatic catalytic sensor, *Biosens. Bioelectron.* 36 (2012) 75–80.
- [83] X.W. Meng, J.F. Wei, X.L. Ren, J. Ren, F.Q. Tang, A simple and sensitive fluorescence biosensor for detection of organophosphorus pesticides using H₂O₂-sensitive quantum dots/bi-enzyme, *Biosens. Bioelectron.* 47 (2013) 402–407.
- [84] Y.H. Yi, G.B. Zhu, C. Liu, Y. Huang, Y.Y. Zhang, H.T. Li, J.N. Zhao, S.Z. Yao, A label-free silicon quantum dots-based photoluminescence sensor for ultrasensitive detection of pesticides, *Anal. Chem.* 85 (2013) 11464–11470.
- [85] H.T. Li, C.H. Sun, R. Vijayaraghavan, F.L. Zhou, X.Y. Zhang, D.R. MacFarlane, Long lifetime photoluminescence in N, S co-doped carbon quantum dots from an ionic liquid and their applications in ultrasensitive detection of pesticides, *Carbon* 104 (2016) 33–39.
- [86] Y.M. Shen, F.M. Yan, X. Huang, X.Y. Zhang, Y.Y. Zhang, C.X. Zhang, J.L. Jin, H.T. Li, S.Z. Yao, A new water-soluble and colorimetric fluorescent probe for highly sensitive detection of organophosphorus pesticides, *RSC Adv.* 6 (2016) 88096–88103.
- [87] X.L. Fu, L.X. Chen, J. Choo, Optical nanoprobe for ultrasensitive immunoassay, *Anal. Chem.* 89 (2017) 124–137.
- [88] W. Wen, X. Yan, C.Z. Zhu, D. Du, Y.H. Lin, Recent advances in electrochemical immunosensors, *Anal. Chem.* 89 (2017) 138–156.
- [89] Z. Farka, T. Jurik, D. Kovar, L. Trnkova, P. Skladal, Nanoparticle-based immunochemical biosensors and assays: recent advances and challenges, *Chem. Rev.* 117 (2017) 9973–10042.
- [90] Y.F. Li, Y.M. Sun, R.C. Beier, H.T. Lei, S. Gee, B.D. Hammock, H. Wang, Z.H. Wang, X.L. Sun, Y.D. Shen, J.Y. Yang, Z.L. Xu, Immunochemical techniques for multianalyte analysis of chemical residues in food and the environment: a review, *Trends Anal. Chem.* 88 (2017) 25–40.
- [91] S.Y. Ding, J.X. Chen, H.Y. Jiang, J.H. He, W.M. Shi, W.S. Zhao, J.Z. Shen, Application of quantum dot-antibody conjugates for detection of sulfamerazine residue in chicken muscle tissue, *J. Agr. Food Chem.* 54 (2006) 6139–6142.
- [92] A.C. Vinayaka, S. Basheer, M.S. Thakur, Bioconjugation of CdTe quantum dot for the detection of 2,4-dichlorophenoxyacetic acid by competitive fluorimmunoassay based biosensor, *Biosens. Bioelectron.* 24 (2009) 1615–1620.
- [93] Y.P. Chen, H.L. Ren, N. Liu, N. Sai, X.Y. Liu, Z. Liu, Z.X. Gao, B.A. Ning, A fluorimmunoassay based on quantum dot-streptavidin conjugate for the detection of chlorpyrifos, *J. Agr. Food Chem.* 58 (2010) 8895–8903.
- [94] D. Wang, B.X. Lin, Y.J. Cao, M.L. Guo, Y. Yu, A highly selective and sensitive fluorescence detection method of glyphosate based on an immune reaction strategy of carbon dot labeled antibody and antigen magnetic beads, *J. Agr. Food Chem.* 64 (2016) 6042–6050.
- [95] P. Kumar, K.H. Kim, V. Bansal, A.K. Paul, A. Deep, Practical utilization of nanocrystal metal organic framework biosensor for parathion specific recognition, *Microchim. J.* 128 (2016) 102–107.
- [96] Z.X. Zou, D. Du, J. Wang, J.N. Smith, C. Timchalk, Y.Q. Li, Y.H. Lin, Quantum dot-based immunochromatographic fluorescent biosensor for biomonitoring trichloropyridinol, a biomarker of exposure to chlorpyrifos, *Anal. Chem.* 82 (2010) 5125–5133.
- [97] L.N. Zhou, Y.J. Cao, B.X. Lin, S.H. Song, Y. Yu, L.L. Shui, In-situ visual and ultrasensitive detection of phosmet using a fluorescent immunoassay probe, *Sens. Actuators B* 241 (2017) 915–922.
- [98] Z.J. Zhang, X.H. Zhang, B.W. Liu, J.W. Liu, Molecular imprinting on inorganic nanzymes for hundred-fold enzyme specificity, *J. Am. Chem. Soc.* 139 (2017) 5412–5419.
- [99] J. Wackerlig, R. Schirhagl, Applications of molecularly imprinted polymer nanoparticles and their advances toward industrial use: a review, *Anal. Chem.* 88 (2016) 250–261.
- [100] R. Schirhagl, Bioapplications for molecularly imprinted polymers, *Anal. Chem.* 86 (2014) 250–261.
- [101] T.T. Xiao, X.Z. Shi, H.F. Jiao, A.L. Sun, H. Ding, R.R. Zhang, D.D. Pan, D.X. Li, J. Chen, Selective and sensitive determination of cypermethrin in fish via enzyme-linked immunosorbent assay-like method based on molecularly imprinted artificial antibody-quantum dot optosensing materials, *Biosens. Bioelectron.* 75 (2016) 34–40.
- [102] H.B. Li, Y.L. Li, J. Cheng, Molecularly imprinted silica nanospheres embedded CdSe quantum dots for highly selective and sensitive optosensing of pyrethroids, *Chem. Mater.* 22 (2010) 2451–2457.
- [103] J.X. Wang, H. Qiu, H.Q. Shen, J.M. Pan, X.H. Dai, Y.S. Yan, G.Q. Pan, B. Sellergren, Molecularly imprinted fluorescent hollow nanoparticles as sensors for rapid and efficient detection lambda-cyhalothrin in environmental water, *Biosens. Bioelectron.* 85 (2016) 387–394.
- [104] Y. Zhao, Y. Ma, H. Li, L. Wang, Composite QDs@MIP nanospheres for specific recognition and direct fluorescent quantification of pesticides in aqueous media, *Anal. Chem.* 84 (2012) 386–395.
- [105] Z.H. Chen, M. Alvarez-Perez, F. Navarro-Villoslada, M.C. Moreno-Bondi, G. Orellana, Fluorescent sensing of "quat" herbicides with a multifunctional pyrene-labeled monomer and molecular imprinting, *Sens. Actuators B* 191 (2014) 137–142.
- [106] X.H. Ren, L.G. Chen, Quantum dots coated with molecularly imprinted polymer as fluorescence probe for detection of cyphenothrin, *Biosens. Bioelectron.* 64 (2015) 182–188.

- [107] X. Wei, T.F. Hao, Y.Q. Xu, K. Lu, H.J. Li, Y.S. Yan, Z.P. Zhou, Facile polymerizable surfactant inspired synthesis of fluorescent molecularly imprinted composite sensor via aqueous CdTe quantum dots for highly selective detection of lambda-cyhalothrin, *Sens. Actuators B* 224 (2016) 315–324.
- [108] C. Zhang, H.Y. Cui, J.R. Cai, Y.Q. Duan, Y. Liu, Development of fluorescence sensing material based on CdSe/ZnS quantum dots and molecularly imprinted polymer for the detection of carbaryl in rice and Chinese cabbage, *J. Agr. Food Chem.* 63 (2015) 4966–4972.
- [109] J.H. Tian, J.L. Bai, Y. Peng, Z.W. Qie, Y.F. Zhao, B.A. Ning, D. Xiao, Z.X. Gao, A core-shell-structured molecularly imprinted polymer on upconverting nanoparticles for selective and sensitive fluorescence sensing of sulfamethazine, *Analyst* 140 (2015) 5301–5307.
- [110] Mengfan Jia, Zhong Zhang, Jinhua Li, Hongjun Shao, Lingxin Che, Xingbin Yang, A molecular imprinting fluorescence sensor based on quantum dots and a mesoporous structure for selective and sensitive detection of 2,4-dichlorophenoxyacetic acid, *Sens. Actuators B* 252 (2017) 934–943.
- [111] M. Yang, A.J. Han, J.L. Duan, Z.P. Li, Y.C. Lai, J.H. Zhan, Magnetic nanoparticles and quantum dots co-loaded imprinted matrix for pentachlorophenol, *J. Hazard. Mater.* 237 (2012) 63–70.
- [112] Y.J. Zhou, X.Y. Huang, C. Liu, R.L. Zhang, X.L. Gu, G.J. Guan, C.L. Jiang, L.Y. Zhang, S.H. Du, B.H. Liu, M.Y. Han, Z.P. Zhang, Color-multiplexing-based fluorescent test paper: dosage-sensitive visualization of arsenic(III) with discernable scale as low as 5 ppb, *Anal. Chem.* 88 (2016) 6105–6109.
- [113] X.Y. Wang, J.L. Yu, X.Q. Wu, J.Q. Fu, Q. Kang, D.Z. Shen, J.H. Li, L.X. Chen, A molecular imprinting-based turn-on Ratiometric fluorescence sensor for highly selective and sensitive detection of 2,4-dichlorophenoxyacetic acid (2,4-D), *Biosens. Bioelectron.* 81 (2016) 438–444.
- [114] M. Amjadi, R. Jalili, Molecularly imprinted mesoporous silica embedded with carbon dots and semiconductor quantum dots as a ratiometric fluorescent sensor for diniconazole, *Biosens. Bioelectron.* 96 (2017) 121–126.
- [115] L. Lan, Y. Yao, J. Ping, Y. Ying, Recent progress in nanomaterial-based optical aptamer assay for the detection of food chemical contaminants, *ACS Appl. Mater. Interfaces* 9 (2017) 23287–23301.
- [116] A. Dhiman, P. Kaira, V. Bansal, J.G. Bruno, T.K. Sharma, Aptamer-based point-of-care diagnostic platforms, *Sens. Actuators B* 246 (2017) 535–553.
- [117] N. Duan, S.J. Wu, S.L. Dai, H.J. Gu, L.L. Hao, H. Ye, Z.P. Wang, Advances in aptasensors for the detection of food contaminants, *Analyst* 141 (2016) 3942–3961.
- [118] V. Crivianu-Gaita, M. Thompson, Aptamers, antibody scFv, and antibody Fab' fragments: an overview and comparison of three of the most versatile biosensor biorecognition elements, *Biosens. Bioelectron.* 85 (2016) 32–45.
- [119] Y. Du, S.J. Dong, Nucleic acid biosensors: recent advances and perspectives, *Anal. Chem.* 89 (2017) 189–215.
- [120] L. Zhou, J.S. Ren, X.G. Qu, Nucleic acid-templated functional nanocomposites for biomedical applications, *Mater. Today* 20 (2017) 179–190.
- [121] J.A. He, Y.A. Liu, M.T. Fan, X.J. Liu, Isolation and identification of the DNA aptamer target to acetamiprid, *J. Agr. Food Chem.* 59 (2011) 1582–1586.
- [122] L. Wang, X.J. Liu, Q. Zhang, C.Z. Zhang, Y. Liu, K. Tu, J. Tu, Selection of DNA aptamers that bind to four organophosphorus pesticides, *Biotechnol. Lett.* 34 (2012) 869–874.
- [123] A. Verdian, Apt-a-nanosensors for detection and quantitative determination of acetamiprid – a pesticide residue in food and environment, *Talanta* 176 (2018) 456–464.
- [124] W.W. Hu, Q.S. Chen, H.H. Li, Q. Ouyang, J.W. Zhao, Fabricating a novel label-free aptasensor for acetamiprid by fluorescence resonance energy transfer between NH₂-NaYF₄: Yb, Ho@SiO₂ and Au nanoparticles, *Biosens. Bioelectron.* 80 (2016) 398–404.
- [125] B.X. Lin, Y. Yu, R.Y. Li, Y.J. Cao, M.L. Guo, Turn-on sensor for quantification and imaging of acetamiprid residues based on quantum dots functionalized with aptamer, *Sens. Actuators B* 229 (2016) 100–109.
- [126] X.W. Dou, X.F. Chu, W.J. Kong, J.Y. Luo, M.H. Yang, A gold-based nanobeacon probe for fluorescence sensing of organophosphorus pesticides, *Anal. Chim. Acta* 891 (2015) 291–297.
- [127] K. Abnous, N.M. Danesh, M. Ramezani, M. Alibolandi, P. Lavaee, S.M. Taghdisi, Aptamer based fluorometric acetamiprid assay using three kinds of nanoparticles for powerful signal amplification, *Microchim. Acta* 184 (2017) 81–90.
- [128] P.F. Wei, X.Z. Yan, F.H. Huang, Supramolecular polymers constructed by orthogonal self-assembly based on host-guest and metal-ligand interactions, *Chem. Soc. Rev.* 44 (2015) 815–832.
- [129] H. Yang, B. Yuan, X. Zhang, O.A. Scherman, Supramolecular chemistry at interfaces: host-guest interactions for fabricating multifunctional bioInterfaces, *Acc. Chem. Res.* 47 (2014) 2106–2115.
- [130] D. Shetty, J.K. Khedkar, K.M. Park, K. Kim, Can we beat the biotin-avidin pair?: cucurbit[7]uril-based ultrahigh affinity host-guest complexes and their applications, *Chem. Soc. Rev.* 44 (2015) 8747–8761.
- [131] Y.W. Yang, Y.L. Sun, N. Song, Switchable host-guest systems on surfaces, *Acc. Chem. Res.* 47 (2014) 1950–1960.
- [132] H.B. Li, F.G. Qu, Synthesis of CdTe quantum dots in sol-gel-derived composite silica spheres coated with calix[4]arene as luminescent probes for pesticides, *Chem. Mater.* 19 (2007) 4148–4154.
- [133] F.G. Qu, X.F. Zhou, J. Xu, H.B. Li, G.Y. Xie, Luminescence switching of CdTe quantum dots in presence of p-sulfonatocalix[4]arene to detect pesticides in aqueous solution, *Talanta* 78 (2009) 1359–1363.
- [134] X. Zeng, J. Ma, L. Luo, L. Yang, X. Cao, D. Tian, H. Li, Pesticide macroscopic recognition by a naphthol-appended calix[4]arene, *Org. Lett.* 17 (2015) 2976–2979.
- [135] S.G. Sun, F.S. Li, F.Y. Liu, J.T. Wang, X.J. Peng, Fluorescence detecting of paraquat using host-guest chemistry with cucurbit[8]uril, *Sci. Rep.* 4 (2014) 3570.
- [136] C.F. Chow, K.Y.F. Ho, C.B. Gong, Synthesis of a new bimetallic Re(I)-NCS-Pt(II) complex as chemodosimetric ensemble for the selective detection of mercapto-containing pesticides, *Anal. Chem.* 87 (2015) 6112–6118.
- [137] G.J. Guan, S.Y. Zhang, Y.Q. Cai, S. Liu, M.S. Bharathi, M. Low, Y. Yu, J.P. Xie, Y.G. Zheng, Y.W. Zhang, M.Y. Han, Convenient purification of gold clusters by co-precipitation for improved sensing of hydrogen peroxide, mercury ions and pesticides, *Chem. Commun.* 50 (2014) 5703–5705.
- [138] H.X. Li, J.J. Liu, X.H. Yang, Facile synthesis of glutathione-capped CdS quantum dots as a fluorescence sensor for rapid detection and quantification of paraquat, *Anal. Sci.* 31 (2015) 1011–1017.
- [139] M.M.F. Chang, I.R. Ginjom, S.M. Ng, Single-shot “turn-off” optical probe for rapid detection of paraoxon-ethyl pesticide on vegetable utilising fluorescence carbon dots, *Sens. Actuators B* 242 (2017) 1050–1056.
- [140] Y. Fan, L. Liu, D.L. Sun, H.Y. Lan, H.Y. Fu, T.M. Yang, Y.B. She, C. Ni, “Turn-off” fluorescent data array sensor based on double quantum dots coupled with chemometrics for highly sensitive and selective detection of multicomponent pesticides, *Anal. Chim. Acta* 916 (2016) 84–91.
- [141] G.M. Duran, M.R. Plata, M. Zougagh, A.M. Contento, A. Rios, Microwave-assisted synthesis of water soluble thiol capped CdSe/ZnS quantum dots and its interaction with sulfonylurea herbicides, *J. Colloid Interface Sci.* 428 (2014) 235–241.
- [142] C. Carrillo-Carrión, B.M. Simonet, M. Valcarcel, Rapid fluorescence determination of diquat herbicide in food grains using quantum dots as new reducing agent, *Anal. Chim. Acta* 692 (2011) 103–108.
- [143] G.M. Duran, A.M. Contento, A. Rios, Use of CdSe/ZnS quantum dots for sensitive detection and quantification of paraquat in water samples, *Anal. Chim. Acta* 801 (2013) 84–90.
- [144] K. Yin, W.W. Zhang, L.X. Chen, Pyoverdine secreted by *Pseudomonas aeruginosa* as a biological recognition element for the fluorescent detection of furazolidone, *Biosens. Bioelectron.* 51 (2014) 90–96.
- [145] I.B. Tahirbegi, J. Ehgartner, P. Sulzer, S. Zieger, A. Kasjanow, M. Paradiso, M. Strobl, D. Bouwes, T. Mayr, Fast pesticide detection inside microfluidic device with integrated optical pH, oxygen sensors and algal fluorescence, *Biosens. Bioelectron.* 88 (2017) 188–195.
- [146] K. Zhang, Q.S. Mei, G.J. Guan, B.H. Liu, S.H. Wang, Z.P. Zhang, Ligand replacement-induced fluorescence switch of quantum dots for ultrasensitive detection of organophosphorothioate pesticides, *Anal. Chem.* 82 (2010) 9579–9586.
- [147] K. Zhang, T. Yu, F. Liu, M.T. Sun, H. Yu, B.H. Liu, Z.P. Zhang, H. Jiang, S.H. Wang, Selective fluorescence turn-on and ratiometric detection of organophosphate using dual-emitting Mn-doped ZnS nanocrystal probe, *Anal. Chem.* 86 (2014) 11727–11733.
- [148] Q.S. Mei, H.R. Jing, Y. Li, W. Yisibashaer, J. Chen, B.N. Li, Y. Zhang, Smartphone based visual and quantitative assays on upconversion paper sensor, *Biosens. Bioelectron.* 75 (2016) 427–432.
- [149] Y.C. Lü, Q.Q. Sun, B.L. Hu, X.L. Chen, R. Miao, Y. Fang, Synthesis and sensing applications of a new fluorescent derivative of cholesterol, *New J. Chem.* 40 (2016) 1817–1824.
- [150] P. Raj, A. Singh, K. Kaur, T. Aree, A. Singh, N. Singh, Fluorescent chemosensors for selective and sensitive detection of phosmet/chlorpyrifos with octahedral Ni²⁺ complexes, *Inorg. Chem.* 55 (2016) 4874–4883.
- [151] X. Yan, H.X. Li, Y. Li, X.G. Su, Visual and fluorescent detection of acetamiprid based on the inner filter effect of gold nanoparticles on ratiometric fluorescence quantum dots, *Anal. Chim. Acta* 852 (2014) 189–195.
- [152] Z.M. Cui, C.P. Han, H.B. Li, Dual-signal fenamithion probe by combining fluorescence with colorimetry based on rhodamine B modified silver nanoparticles, *Analyst* 136 (2011) 1351–1356.
- [153] J.J. Guo, Y. Zhang, Y.L. Luo, F. Shen, C.Y. Sun, Efficient fluorescence resonance energy transfer between oppositely charged CdTe quantum dots and gold nanoparticles for turn-on fluorescence detection of glyphosate, *Talanta* 125 (2014) 385–392.
- [154] L. Wang, Y.D. Bi, J. Hou, H.Y. Li, Y. Xu, B. Wang, H. Ding, L. Ding, Facile, green and clean one-step synthesis of carbon dots from wool: application as a sensor for glyphosate detection based on the inner filter effect, *Talanta* 160 (2016) 268–275.
- [155] L. Dong, C.J. Hou, M. Yang, H.B. Fa, H.X. Wu, C.H. Shen, D.Q. Huo, Highly sensitive colorimetric and fluorescent sensor for cyanazine based on the inner filter effect of gold nanoparticles, *J. Nanopart. Res.* 18 (2016) 164.
- [156] F. Wang, L. Wang, X. Chen, J. Yoon, Recent progress in the development of fluorometric and colorimetric chemosensors for detection of cyanide ions, *Chem. Soc. Rev.* 43 (2014) 4312–4324.
- [157] G.Z. Yue, S. Su, N. Li, M.B. Shuai, X.C. Lai, D. Astruc, P.X. Zhao, Gold nanoparticles as sensors in the colorimetric and fluorescence detection of chemical warfare agents, *Coord. Chem. Rev.* 311 (2016) 75–84.
- [158] D. Liu, Z. Wang, X. Jiang, Gold nanoparticles for the colorimetric and fluorescent detection of ions and small organic molecules, *Nanoscale* 3 (2011) 1421–1433.

- [159] J.S. Sun, Y.L. Xianyu, X.Y. Jiang, Point-of-care biochemical assays using gold nanoparticle-implemented microfluidics, *Chem. Soc. Rev.* 43 (2014) 6239–6253.
- [160] Q. Xu, S. Du, G.D. Jin, H.B. Li, X.Y. Hu, Determination of acetamiprid by a colorimetric method based on the aggregation of gold nanoparticles, *Microchim. Acta* 173 (2011) 323–329.
- [161] N.Y. Chen, H.Y. Liu, Y.J. Zhang, Z.W. Zhou, W.P. Fan, G.C. Yu, Z.Y. Shen, A.G. Wu, A colorimetric sensor based on citrate-stabilized AuNPs for rapid pesticide residue detection of terbutylazine and dimethoate, *Sens. Actuators B* 255 (2018) 3093–3101.
- [162] N. Fahimi-Kashani, M.R. Hormozi-Nezhad, Gold-nanoparticle-based colorimetric sensor array for discrimination of organophosphate pesticides, *Anal. Chem.* 88 (2016) 8099–8106.
- [163] Z.Y. Sun, Z.M. Cui, H.B. Li, p-Amino benzenesulfonic acid functionalized gold nanoparticles: synthesis, colorimetric detection of carbaryl and mechanism study by zeta potential assays, *Sens. Actuators B* 183 (2013) 297–302.
- [164] M.S. Kim, G.W. Kim, T.J. Park, A facile and sensitive detection of organophosphorus chemicals by rapid aggregation of gold nanoparticles using organic compounds, *Biosens. Bioelectron.* 67 (2015) 408–412.
- [165] G.Y. Liu, X. Yang, T.F. Li, H.L. Yu, X.W. Du, Y.X. She, J. Wang, S.S. Wang, F. Jin, M.J. Jin, H. Shao, L.F. Zheng, Y.X. Zhang, P. Zhou, Spectrophotometric and visual detection of the herbicide atrazine by exploiting hydrogen bond-induced aggregation of melamine-modified gold nanoparticles, *Microchim. Acta* 182 (2015) 1983–1989.
- [166] J.V. Rohit, H. Basu, R.K. Singhal, S.K. Kailasa, Development of p-nitroaniline dithiocarbamate capped gold nanoparticles-based microvolume UV-vis spectrometric method for facile and selective detection of quinalphos insecticide in environmental samples, *Sens. Actuators B* 237 (2016) 826–835.
- [167] J.R. Bhambore, P. Ganguly, S.K. Kailasa, Molecular assembly of 3-mercaptopropionic acid and guanidine acetic acid on silver nanoparticles for selective colorimetric detection of triazophos in water and food samples, *Sens. Actuators B* 233 (2016) 486–495.
- [168] J. Sun, L. Guo, Y. Bao, J. Xie, A simple, label-free AuNPs-based colorimetric ultrasensitive detection of nerve agents and highly toxic organophosphate pesticide, *Biosens. Bioelectron.* 28 (2011) 152–157.
- [169] L.L. Lu, Y.S. Xia, Enzymatic reaction modulated gold nanorod end-to-end self-assembly for ultrahigh sensitively colorimetric sensing of cholinesterase and organophosphate pesticides in human blood, *Anal. Chem.* 87 (2015) 8584–8591.
- [170] G.L. Fu, W.W. Chen, X.L. Yue, X.Y. Jiang, Highly sensitive colorimetric detection of organophosphate pesticides using copper catalyzed click chemistry, *Talanta* 103 (2013) 110–115.
- [171] S. de Marcos, E. Callizo, E. Mateos, J. Galban, An optical sensor for pesticide determination based on the autoindicating optical properties of peroxidase, *Talanta* 122 (2014) 251–256.
- [172] J.A. Hondred, J.C. Breger, N.T. Garland, E. Oh, K. Susumu, S.A. Walper, I.L. Medintz, J.C. Claussen, Enhanced enzymatic activity from phosphotriesterase trimer gold nanoparticle bioconjugates for pesticide detection, *Analyst* 142 (2017) 3261–3271.
- [173] B.J. Lv, M. Wei, Y.J. Liu, X. Liu, W. Wei, S.Q. Liu, Ultrasensitive photometric and visual determination of organophosphorus pesticides based on the inhibition of enzyme-triggered formation of core-shell gold-silver nanoparticles, *Microchim. Acta* 183 (2016) 2941–2948.
- [174] L.M. Yang, J. Han, W. Liu, J.Q. Li, L. Jiang, Conversion of inhibition biosensing to substrate-like biosensing for quinalphos selective detection, *Anal. Chem.* 87 (2015) 5270–5277.
- [175] L. Saa, R. Grinyte, A. Sanchez-Iglesias, L.M. Liz-Marzan, V. Pavlov, Blocked enzymatic etching of gold nanorods: application to colorimetric detection of acetylcholinesterase activity and its inhibitors, *ACS Appl. Mater. Interfaces* 8 (2016) 11139–11146.
- [176] L.Z. Gao, J. Zhuang, L. Nie, J.B. Zhang, Y. Zhang, N. Gu, T.H. Wang, J. Feng, D.L. Yang, S. Perrett, X. Yan, Intrinsic peroxidase-like activity of ferromagnetic nanoparticles, *Nat. Nanotechnol.* 2 (2007) 577–583.
- [177] Y.J. Guo, L. Deng, J. Li, S.J. Guo, E.K. Wang, S.J. Dong, Hemin-graphene hybrid nanosheets with intrinsic peroxidase-like activity for label-free colorimetric detection of single-nucleotide polymorphism, *ACS Nano* 5 (2011) 1282–1290.
- [178] Y. Tao, Y.H. Lin, Z.Z. Huang, J.S. Ren, X.G. Qu, Incorporating graphene oxide and gold nanoclusters: a synergistic catalyst with surprisingly high peroxidase-like activity over a broad pH range and its application for cancer cell detection, *Adv. Mater.* 25 (2013) 2594–2599.
- [179] S. Wang, R. Cazelles, W.C. Liao, M. Vazquez-Gonzalez, A. Zoabi, R. Abu-Reiq, I. Willner, Mimicking horseradish peroxidase and NADH peroxidase by heterogeneous Cu²⁺-modified graphene oxide nanoparticles, *Nano Lett.* 17 (2017) 2043–2048.
- [180] M. Vazquez-Gonzalez, R.M. Torrente-Rodriguez, A. Kozell, W.C. Liao, A. Cecconello, S. Campuzano, J.M. Pingarron, I. Willner, Mimicking peroxidase activities with prussian blue nanoparticles and their cyanometalate structural analogues, *Nano Lett.* 17 (2017) 4958–4963.
- [181] M. Vazquez-Gonzalez, W.C. Liao, R. Gazelles, S. Wang, X. Yu, V. Gutkin, I. Willner, Mimicking horseradish peroxidase functions using Cu²⁺-modified carbon nitride nanoparticles or Cu²⁺-modified carbon dots as heterogeneous catalysts, *ACS Nano* 11 (2017) 3247–3253.
- [182] P.J. Ni, H.C. Dai, Y.L. Wang, Y.J. Sun, Y. Shi, J.T. Hu, Z. Li, Visual detection of melamine based on the peroxidase-like activity enhancement of bare gold nanoparticles, *Biosens. Bioelectron.* 60 (2014) 286–291.
- [183] A.A. Vernekar, T. Das, G. Mugesh, Vacancy-engineered nanoceria: enzyme mimetic hotspots for the degradation of nerve agents, *Angew. Chem. Int. Ed.* 55 (2016) 1412–1416.
- [184] S. Singh, P. Tripathi, N. Kumar, S. Nara, Colorimetric sensing of malathion using palladium-gold bimetallic nanozyme, *Biosens. Bioelectron.* 92 (2017) 280–286.
- [185] S. Biswas, P. Tripathi, N. Kumar, S. Nara, Gold nanorods as peroxidase mimetics and its application for colorimetric biosensing of malathion, *Sens. Actuators B* 231 (2016) 584–592.
- [186] M.M. Liang, K.L. Fan, Y. Pan, H. Jiang, F. Wang, D.L. Yang, D. Lu, J. Feng, J.J. Zhao, L. Yang, X.Y. Yan, Fe₃O₄ magnetic nanoparticle peroxidase mimetic-based colorimetric assay for the rapid detection of organophosphorus pesticide and nerve agent, *Anal. Chem.* 85 (2013) 308–312.
- [187] X. Yan, Y. Song, X.L. Wu, C.Z. Zhu, X.G. Su, D. Du, Y.H. Lin, Oxidase-mimicking activity of ultrathin MnO₂ nanosheets in colorimetric assay of acetylcholinesterase activity, *Nanoscale* 9 (2017) 2317–2323.
- [188] S.X. Zhang, S.F. Xue, J.J. Deng, M. Zhang, G.Y. Shi, T.S. Zhou, Polyacrylic acid-coated cerium oxide nanoparticles: an oxidase mimic applied for colorimetric assay to organophosphorus pesticides, *Biosens. Bioelectron.* 85 (2016) 457–463.
- [189] H.J. Cheng, S.C. Lin, F. Muhammad, Y.W. Lin, H. Wei, Rationally modulate the oxidase-like activity of nanoceria for self regulated bioassays, *ACS Sens.* 1 (2016) 1336–1343.
- [190] R. de la Rica, M.M. Stevens, Plasmonic ELISA for the ultrasensitive detection of disease biomarkers with the naked eye, *Nat. Nanotechnol.* 7 (2012) 821–824.
- [191] V. Pavlov, Y. Xiao, I. Willner, Inhibition of the acetylcholine esterase-stimulated growth of Au nanoparticles: nanotechnology-based sensing of nerve gases, *Nano Lett.* 5 (2005) 649–653.
- [192] A. Virel, L. Saa, V. Pavlov, Modulated growth of nanoparticles. application for sensing nerve gases, *Anal. Chem.* 81 (2009) 268–272.
- [193] S. Wu, D.D. Li, J.M. Wang, Y.Q. Zhao, S.J. Dong, X.Y. Wang, Gold nanoparticles dissolution based colorimetric method for highly sensitive detection of organophosphate pesticides, *Sens. Actuators B* 238 (2017) 427–433.
- [194] Z. Han, C.S. Chi, B. Bai, G. Liu, Q.X. Rao, S.J. Peng, H. Liu, Z.H. Zhao, D.B. Zhang, A.B. Wu, Chromogenic platform based on recombinant Drosophila melanogaster acetylcholinesterase for visible unidirectional assay of organophosphate and carbamate insecticide residues, *Anal. Chim. Acta* 720 (2012) 126–133.
- [195] Y. Wu, Y.F. Sun, F.B. Xiao, Z.Y. Wu, R.Q. Yu, Sensitive inkjet printing paper-based colorimetric strips for acetylcholinesterase inhibitors with indoxyl acetate substrate, *Talanta* 162 (2017) 174–179.
- [196] X.J. Meng, C.W. Schultz, C. Cui, X.C. Li, H.Z. Yu, On-site chip-based colorimetric quantitation of organophosphorus pesticides using an office scanner, *Sens. Actuators B* 215 (2015) 577–583.
- [197] S.M.Z. Hossain, R.E. Luckham, A.M. Smith, J.M. Lebert, L.M. Davies, R.H. Pelton, C.D.M. Filipe, J.D. Brennan, Development of a bioactive paper sensor for detection of neurotoxins using piezoelectric inkjet printing of sol-gel-derived bioinks, *Anal. Chem.* 81 (2009) 5474–5483.
- [198] S.M.Z. Hossain, R.E. Luckham, M.J. McFadden, J.D. Brennan, Reagentless bidirectional lateral flow bioactive paper sensors for detection of pesticides in beverage and food samples, *Anal. Chem.* 81 (2009) 9055–9064.
- [199] X. Yan, H.Y. Shi, M.H. Wang, Development of an enzyme-linked immunosorbent assay for the simultaneous determination of parathion and imidacloprid, *Anal. Methods* 4 (2012) 4053–4057.
- [200] H.Y. Zhang, S. Wang, G.Z. Fang, Applications and recent developments of multi-analyte simultaneous analysis by enzyme-linked immunosorbent assays, *J. Immunol. Methods* 368 (2011) 1–23.
- [201] Y.J. Wang, M.M.A. Zeinhom, M.M. Yang, R.R. Sun, S.F. Wang, J.N. Smith, C. Timchalk, L. Li, Y.H. Lin, D. Du, A 3D-printed, portable, optical-sensing platform for smartphones capable of detecting the herbicide 2,4-dichlorophenoxyacetic acid, *Anal. Chem.* 89 (2017) 9339–9346.
- [202] H.X. Li, X. Yan, H.Y. Shi, X.H. Yang, Development of a bi-enzyme tracer competitive enzyme-linked immunosorbent assay for detection of thiacloprid and imidaclothiz in agricultural samples, *Food Chem.* 164 (2014) 166–172.
- [203] X. Yan, H.X. Li, Y. Yan, X.G. Su, Developments in pesticide analysis by multi-analyte immunoassays: a review, *Anal. Methods* 6 (2014) 3543–3554.
- [204] X.X. Ge, A.M. Asiri, D. Du, W. Wen, S.F. Wang, Y.H. Lin, Nanomaterial-enhanced paper-based biosensors, *Trends Anal. Chem.* 58 (2014) 31–39.
- [205] M.M. Yang, Y.T. Zhao, L.M. Wang, M. Paulsen, C.D. Simpson, F.Q. Liu, D. Dan, Y.H. Lin, Simultaneous detection of dual biomarkers from humans exposed to organophosphorus pesticides by combination of immunochromatographic test strip and ellman assay, *Biosens. Bioelectron.* 104 (2018) 39–44.
- [206] L.M. Wang, J. Cai, Y.L. Wang, Q.K. Fang, S.Y. Wang, Q. Cheng, D. Du, Y.H. Lin, F.Q. Liu, A bare-eye-based lateral flow immunoassay based on the use of gold nanoparticles for simultaneous detection of three pesticides, *Microchim. Acta* 181 (2014) 1565–1572.
- [207] M.J. Lan, Y.R. Guo, Y. Zhao, Y.H. Liu, W.J. Gui, G.N. Zhu, Multi-residue detection of pesticides using a sensitive immunochip assay based on nano-gold enhancement, *Anal. Chim. Acta* 938 (2016) 146–155.

- [208] C.Y. Liu, Q.J. Jia, C.H. Yang, R.R. Qiao, L.H. Jing, L.B. Wang, C.L. Xu, M.Y. Gao, Lateral flow immunochromatographic assay for sensitive pesticide detection by using Fe_3O_4 nanoparticle aggregates as color reagents, *Anal. Chem.* 83 (2011) 6778–6784.
- [209] P.F. Du, M.J. Jin, G. Chen, C. Zhang, X.Y. Cui, Y.D. Zhang, Y.X. Zhang, P. Zou, Z.J. Jiang, X.L. Cao, Y.X. She, F. Jin, J. Wang, Competitive colorimetric triazophos immunoassay employing magnetic microspheres and multi-labeled gold nanoparticles along with enzymatic signal enhancement, *Microchim. Acta* 184 (2017) 3705–3721.
- [210] J. Li, C.Y. Hong, S.X. Wu, H. Liang, L.P. Wang, G.M. Huang, X. Chen, H.H. Yang, D.H. Shangguan, W.H. Tan, Facile phase transfer and surface bio-functionalization of hydrophobic nanoparticles using janus DNA tetrahedron nanostructures, *J. Am. Chem. Soc.* 137 (2015) 11210–11213.
- [211] F.J. Huang, W.C. Liao, Y.S. Sohn, R. Nechushtai, C.H. Lu, I. Willner, Light-responsive and pH-responsive DNA microcapsules for controlled release of loads, *J. Am. Chem. Soc.* 138 (2016) 8936–8945.
- [212] L. Ma, C.L. Tu, P. Le, S. Chitoor, S.J. Lim, M.U. Zahid, K.W. Teng, P.H. Ge, P.R. Selvin, A.M. Smith, Multidentate polymer coatings for compact and homogeneous quantum dots with efficient bioconjugation, *J. Am. Chem. Soc.* 138 (2016) 3382–3394.
- [213] Y. Tian, Y. Wang, Z. Sheng, T.T. Li, X. Li, A colorimetric detection method of pesticide acetamiprid by fine-tuning aptamer length, *Anal. Biochem.* 513 (2016) 87–92.
- [214] R. Bala, R.K. Sharma, N. Wangoo, Development of gold nanoparticles-based aptasensor for the colorimetric detection of organophosphorus pesticide phorate, *Anal. Bioanal. Chem.* 408 (2016) 333–338.
- [215] H.J. Shi, G.H. Zhao, M.C. Liu, L.F. Fan, T.C. Cao, Aptamer-based colorimetric sensing of acetamiprid in soil samples: sensitivity, selectivity and mechanism, *J. Hazard. Mater.* 260 (2013) 754–761.
- [216] R. Bala, M. Kumar, K. Bansal, R.K. Sharma, N. Wangoo, Ultrasensitive aptamer biosensor for malathion detection based on cationic polymer and gold nanoparticles, *Biosens. Bioelectron.* 85 (2016) 445–449.
- [217] P. Weerathunge, R. Ramanathan, R. Shukla, T.K. Sharma, V. Bansal, Aptamer-controlled reversible inhibition of gold nanzyme activity for pesticide sensing, *Anal. Chem.* 86 (2014) 11937–11941.
- [218] Z.T. Yang, J. Qian, X.W. Yang, D. Jiang, X.J. Du, K. Wang, H.P. Mao, K. Wang, A facile label-free colorimetric aptasensor for acetamiprid based on the peroxidase-like activity of hemin-functionalized reduced graphene oxide, *Biosens. Bioelectron.* 65 (2015) 39–46.
- [219] L. Uzun, A.P.F. Turner, Molecularly-imprinted polymer sensors: realising their potential, *Biosens. Bioelectron.* 76 (2016) 131–144.
- [220] J. Liu, T. Qian, M. Wang, X. Liu, N. Xu, Y. You, C. Yan, Molecularly imprinted polymer enables high-efficiency recognition and trapping lithium polysulfides for stable lithium sulfur battery, *Nano Lett.* 17 (2017) 5064–5070.
- [221] Z. Wu, C.A. Tao, C.X. Lin, D.Z. Shen, G.T. Li, Label-free colorimetric detection of trace atrazine in aqueous solution by using molecularly imprinted photonic polymers, *Chem. Eur. J.* 14 (2008) 11358–11368.
- [222] J.V. Rohit, R.K. Singhal, S.K. Kailasa, Dithiocarbamate-calix[4]arene functionalized gold nanoparticles as a selective and sensitive colorimetric probe for assay of metsulfuron-methyl herbicide via non-covalent interactions, *Sens. Actuators B* 237 (2016) 1044–1055.
- [223] A. Mishra, J. Kumar, J.S. Melo, An optical microplate biosensor for the detection of methyl parathion pesticide using a biohybrid of *Sphingomonas* sp cells-silica nanoparticles, *Biosens. Bioelectron.* 87 (2017) 332–338.
- [224] N.L. Gruenke, M.F. Cardinal, M.O. McAnalley, R.R. Frontiera, G.C. Schatz, R.P. Van Duyne, Ultrafast and nonlinear surface-enhanced Raman spectroscopy, *Chem. Soc. Rev.* 45 (2016) 2263–2290.
- [225] D. Cialla-May, X.S. Zheng, K. Weber, J. Popp, Recent progress in surface-enhanced Raman spectroscopy for biological and biomedical applications: from cells to clinics, *Chem. Soc. Rev.* 46 (2017) 3945–3961.
- [226] A.I. Henry, B. Sharma, M.F. Cardinal, D. Kurouski, R.P. Van Duyne, Surface-enhanced Raman spectroscopy biosensing: *in vivo* diagnostics and multimodal imaging, *Anal. Chem.* 88 (2016) 6638–6647.
- [227] M.R. Ali, Y. Wu, T. Han, X. Zang, H. Xiao, Y. Tang, R. Wu, F.M. Fernandez, M.A. El-Sayed, Simultaneous time-dependent surface-enhanced Raman spectroscopy, metabolomics, and proteomics reveal cancer cell death mechanisms associated with gold nanorod photothermal therapy, *J. Am. Chem. Soc.* 138 (2016) 15434–15442.
- [228] S.Y. Ding, J. Yi, J.F. Li, B. Ren, D.Y. Wu, R. Panneerselvam, Z.Q. Tian, Nanostructure-based plasmon-enhanced Raman spectroscopy for surface analysis of materials, *Nat. Rev. Mater.* 1 (2016) 16021.
- [229] A.B. Zrimsek, N.H. Chiang, M. Mattei, S. Zaleski, M.O. McAnalley, C.T. Chapman, A.I. Henry, G.C. Schatz, R.P. Van Duyne, Single-molecule chemistry with surface- and tip-enhanced Raman spectroscopy, *Chem. Rev.* 117 (2017) 7583–7613.
- [230] S.T.R. Pang, T.X. Yang, L.L. He, Review of surface enhanced Raman spectroscopic (SERS) detection of synthetic chemical pesticides, *Trends Anal. Chem.* 85 (2016) 73–82.
- [231] R.Y. Hou, Z.Y. Zhang, S. Pang, T.X. Yang, J.M. Clark, L.L. He, Alteration of the nonsystemic behavior of the pesticide ferbam on tea leaves by engineered gold nanoparticles, *Environ. Sci. Technol.* 50 (2016) 6216–6223.
- [232] T.X. Yang, Z.Y. Zhang, B. Zhao, R.Y. Hou, A. Kinchla, J.M. Clark, L.L. He, Real-time and *in situ* monitoring of pesticide penetration in edible leaves by surface-enhanced Raman scattering mapping, *Anal. Chem.* 88 (2016) 5243–5250.
- [233] Q. Xu, X.Y. Guo, L. Xu, Y. Ying, Y.P. Wu, Y. Wen, H.F. Yang, Template-free synthesis of SERS-active gold nanopopcorn for rapid detection of chlorpyrifos residues, *Sens. Actuators B* 241 (2017) 1008–1013.
- [234] C.D.L. Albuquerque, R.J. Poppi, Detection of malathion in food peels by surface-enhanced Raman imaging spectroscopy and multivariate curve resolution, *Anal. Chim. Acta* 879 (2015) 24–33.
- [235] J.M. Chen, Y.J. Huang, P. Kannan, L. Zhang, Z.Y. Lin, J.W. Zhang, T. Chen, L.H. Guo, Flexible and adhesive surface enhance Raman scattering active tape for rapid detection of pesticide residues in fruits and vegetables, *Anal. Chem.* 88 (2016) 2149–2155.
- [236] B.N. Khlebtsov, V.A. Khanadeev, E.V. Panfilova, D.N. Bratashov, N.G. Khlebtsov, Gold nanoisland films as reproducible SERS substrates for highly sensitive detection of fungicides, *ACS Appl. Mater. Interfaces* 7 (2015) 6518–6529.
- [237] J. Wang, L.T. Kong, Z. Guo, J.Y. Xu, J.H. Liu, Synthesis of novel decorated one-dimensional gold nanoparticle and its application in ultrasensitive detection of insecticide, *J. Mater. Chem.* 20 (2010) 5271–5279.
- [238] J.F. Li, Y.F. Huang, Y. Ding, Z.L. Yang, S.B. Li, X.S. Zhou, F.R. Fan, W. Zhang, Z.Y. Zhou, D.Y. Wu, B. Ren, Z.L. Wang, Z.Q. Tian, Shell-isolated nanoparticle-enhanced Raman spectroscopy, *Nature* 464 (2010) 392–395.
- [239] K. Kneipp, H. Kneipp, J. Kneipp, Surface-enhanced Raman scattering in local optical fields of silver and gold nanoaggregates: from single-molecule Raman spectroscopy to ultrasensitive probing in live cells, *Acc. Chem. Res.* 39 (2006) 443–450.
- [240] H. Fang, X. Zhang, S.J. Zhang, L. Liu, Y.M. Zhao, H.J. Xu, Ultrasensitive and quantitative detection of paraquat on fruits skins via surface-enhanced Raman spectroscopy, *Sens. Actuators B* 213 (2015) 452–456.
- [241] J.K. Yang, H. Kang, H. Lee, A. Jo, S. Jeong, S.J. Jeon, H.I. Kim, H.Y. Lee, D.H. Jeong, J.H. Kim, Y.S. Lee, Single-step and rapid growth of silver nanoshells as SERS-active nanostructures for label-free detection of pesticides, *ACS Appl. Mater. Interfaces* 6 (2014) 12541–12549.
- [242] J. Kubackova, G. Fabriciova, P. Miskovsky, D. Jancura, S. Sanchez-Cortes, Sensitive surface-enhanced Raman spectroscopy (SERS) detection of organochlorine pesticides by alkyl dithiol-functionalized metal nanoparticles-induced plasmonic hot spots, *Anal. Chem.* 87 (2015) 663–669.
- [243] S. Kumar, P. Goel, J.P. Singh, Flexible and robust SERS active substrates for conformal rapid detection of pesticide residues from fruits, *Sens. Actuators B* 241 (2017) 577–583.
- [244] M.K. Fan, Z.G. Zhang, J.M. Hu, F.S. Cheng, C. Wang, C.Y. Tang, J.H. Lin, A.G. Brolo, H.Q. Zhan, Ag decorated sandpaper as flexible SERS substrate for direct swabbing sampling, *Mater. Lett.* 133 (2014) 57–59.
- [245] J.B. Jackson, N.J. Halas, Surface-enhanced Raman scattering on tunable plasmonic nanoparticle substrates, *PNAS* 101 (2004) 17930–17935.
- [246] L.L. Zhang, C.L. Jiang, Z.P. Zhang, Graphene oxide embedded sandwich nanostructures for enhanced Raman readout and their applications in pesticide monitoring, *Nanoscale* 5 (2013) 3773–3779.
- [247] P.Z. Guo, D. Sikdar, X.Q. Huang, K.J. Si, W. Xiong, S. Gong, L.W. Yap, M. Premaratne, W.L. Cheng, Plasmonic core-shell nanoparticles for SERS detection of the pesticide thiram: size- and shape-dependent Raman enhancement, *Nanoscale* 7 (2015) 2862–2868.
- [248] Q. Zhang, Y.H. Lee, I.Y. Phang, C.K. Lee, X.Y. Ling, Hierarchical 3D SERS substrates fabricated by integrating photolithographic microstructures and self-assembly of silver nanoparticles, *Small* 10 (2014) 2703–2711.
- [249] W. Xie, B. Walkenfort, S. Schlucker, Label-free SERS monitoring of chemical reactions catalyzed by small gold nanoparticles using 3D plasmonic superstructures, *J. Am. Chem. Soc.* 135 (2013) 1657–1660.
- [250] P. Wang, L. Wu, Z.C. Lu, Q. Li, W.M. Yin, F. Ding, H.Y. Han, Gecko-inspired nanotentacle surface-enhanced Raman spectroscopy substrate for sampling and reliable detection of pesticide residues in fruits and vegetables, *Anal. Chem.* 89 (2017) 2424–2431.
- [251] E. Mauriz, M.C. Garcia-Fernandez, L.M. Lechuga, Towards the design of universal immunosurfaces for SPR-based assays: a review, *Trends Anal. Chem.* 79 (2016) 191–198.
- [252] P. Singh, SPR biosensors: historical perspectives and current challenges, *Sens. Actuators B* 229 (2016) 110–130.
- [253] E. Mauriz, A. Calle, A. Abad, A. Montoya, A. Hildebrandt, D. Barcelo, L.M. Lechuga, Determination of carbaryl in natural water samples by a surface plasmon resonance flow-through immunosensor, *Biosens. Bioelectron.* 21 (2006) 2129–2136.
- [254] M.C. Estevez, J. Belenguer, S. Gomez-Montes, J. Miralles, A.M. Escuela, A. Montoya, L.M. Lechuga, Indirect competitive immunoassay for the detection of fungicide Thiabendazole in whole orange samples by Surface Plasmon Resonance, *Analyst* 137 (2012) 5659–5665.
- [255] J.W. Dong, N. Gao, Y. Peng, C. Guo, Z.Q. Lv, Y. Wang, C.H. Zhou, B.A. Ning, M. Liu, Z.X. Gao, Surface plasmon resonance sensor for profenofos detection using molecularly imprinted thin film as recognition element, *Food Contr.* 25 (2012) 543–549.
- [256] L. Ye, K. Mosbach, Polymers recognizing biomolecules based on a combination of molecular imprinting and proximity scintillation: a new sensor concept, *J. Am. Chem. Soc.* 123 (2001) 2901–2902.
- [257] G.H. Yao, R.P. Liang, C.F. Huang, Y. Wang, J.D. Qiu, Surface plasmon resonance sensor based on magnetic molecularly imprinted polymers amplification for pesticide recognition, *Anal. Chem.* 85 (2013) 11944–11951.
- [258] N. Hananya, A.E. Boock, C.R. Bauer, R. Satchi-Fainaro, D. Shabat, Remarkable enhancement of chemiluminescent signal by dioxetane-fluorophore

- conjugates: turn-on chemiluminescence probes with color modulation for sensing and imaging, *J. Am. Chem. Soc.* 138 (2016) 13438–13446.
- [259] Z.J. Hai, J.D. Li, J.J. Wu, J.C. Xu, G.L. Liang, Alkaline phosphatase-triggered simultaneous hydrogelation and chemiluminescence, *J. Am. Chem. Soc.* 139 (2017) 1041–1044.
- [260] M. Iranifam, Analytical applications of chemiluminescence methods for cancer detection and therapy, *Trends Anal. Chem.* 59 (2014) 156–183.
- [261] J.F. Huertas-Perez, D. Moreno-Gonzalez, D. Airado-Rodriguez, F.J. Lara, A.M. Garcia-Campana, Advances in the application of chemiluminescence detection in liquid chromatography, *Trends Anal. Chem.* 75 (2016) 35–48.
- [262] H. Ouyang, L.M. Wang, S.J. Yang, W.W. Wang, L. Wang, F.Q. Liu, Z.F. Fu, Chemiluminescence reaction kinetics-resolved multianalyte immunoassay strategy using a bispecific monoclonal antibody as the unique recognition reagent, *Anal. Chem.* 87 (2015) 2952–2958.
- [263] Q. Shu, L.M. Wang, H. Ouyang, W.W. Wang, F.Q. Liu, Z.F. Fu, Multiplexed immunochromatographic test strip for time-resolved chemiluminescent detection of pesticide residues using a bifunctional antibody, *Biosens. Bioelectron.* 87 (2017) 908–914.
- [264] T. Khajvand, M.J. Chaichi, A.H. Colagar, Sensitive assay of hexythiazox residue in citrus fruits using gold nanoparticles-catalysed luminol-H₂O₂ chemiluminescence, *Food Chem.* 173 (2015) 514–520.
- [265] H. Ouyang, X.M. Tu, Z.F. Fu, W.W. Wang, S.F. Fu, C.Z. Zhu, D. Du, Y.H. Lin, Colorimetric and chemiluminescent dual-readout immunochromatographic assay for detection of pesticide residues utilizing g-C₃N₄/BiFeO₃ nanocomposites, *Biosens. Bioelectron.* 106 (2018) 43–49.
- [266] Y.Y. Qi, F.R. Xiu, M.F. Zheng, B.X. Li, A simple and rapid chemiluminescence aptasensor for acetamiprid in contaminated samples: sensitivity, selectivity and mechanism, *Biosens. Bioelectron.* 83 (2016) 243–249.
- [267] Y. He, B. Xu, W.H. Li, H.L. Yu, Silver nanoparticle-based chemiluminescent sensor array for pesticide discrimination, *J. Agr. Food Chem.* 63 (2015) 2930–2934.