Korean J. Chem. Eng., **30**(10), 1825-1832 (2013)
DOI: 10.1007/s11814-013-0156-y

INVITED REVIEW PAPER

Toxic chemical monitoring of agricultural bioproducts using nanomaterials-based sensors

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(*Received 18 June 2013 • accepted 15 August 2013*)

Abstract−Owing to the fast growth of the agricultural bioproducts industry, which requires its products to be fresh and visibly appealing, the increased use of imidacloprid pesticides has raised deep concerns about environmental effects, food quality, and the toxicity of residues. This has led to the development of various extraction methods of biochemicals and chemicals and their effective sensors for monitoring pesticide residues. We review the current commercial and nanotechnology-adopted techniques available in order to draw attention to the primary issues in the development of novel extraction and sensing systems using nanotechnology.

Key words: Imidacloprid, Chloronicotinic Pesticides, Agriculture, Chemical Sensor, Nanotechnology, Extraction

ADVERSE EFFECTS OF PESTICIDES USE

The widespread and frequent use of chloronicotinic pesticides in agriculture has resulted in their residual presence in crops, livestock, and poultry products, raising a number of environmental concerns [1-3]. In particular, owing to the fast growth of the agricultural bioproducts industry, chloronicotinic pesticides, such as nitroguanidine imidacloprid or simply imidacloprid, have been used extensively because of the need for product freshness and esthetics, especially for use in salads and food decorations. The nitroguanidine imidacloprid, 1-[(6-chloro-3-pyridinyl)methyl]-4,5-dihydro-N-nitro-1H-imidazol-2-amine, is a systemic insecticide and a nitromethylene derivative synthesized by Nihon Bayer Agrochem K. K. (Tokyo, Japan) in 1985. Products containing imidacloprid have been used in approximately 120 countries and are marketed for use in over 140 agricultural crops, making it a top-selling product. They are extremely effective against sucking insects such as rice leafhoppers, aphids, thrips, and mealybugs, and are very effective against the whitefly [4]. Therefore, imidacloprid is a widely used insecticide with relatively low human toxicity. However, its use has raised concerns because of the possible impact on bee populations and its ability to cause eggshell thinning in birds, resulting in reduced egg production and hatching. Furthermore, this toxic pesticide has raised environmental concerns due to its chemical properties, such as relatively high solubility (0.58 g L^{-1}) and stability in water and its minimal degradation by photolysis. This contaminant poses serious to fatal health hazards, such as asthma, birth defects, and death after exposure to residues on agricultural bioproducts [5-8]. Other parts of the world have already experienced serious pesticide poisoning: China, the largest producer, exporter, and end user of pesticides, reported various contamination levels of pesticide pollution in the air, water bodies, and main land soil, resulting in fetal deaths in past years [9,10]. Many countries lawfully restrict the use of this chemical. For example, according to European Union (EU) regulations [11-13], some agricultural bioproducts such as tomatoes, peppers, cucumbers, and green beans should contain no more than 0.05-0.5 mg kg^{-1} of imidacloprid. Because of the growing concern about the subsequent non-target effects of imidacloprid in the environment, there is a need for the development of sensitive and selective analytical methods to measure imidacloprid residue in water, plants, and soil. Therefore, many sensing methods for low concentrations of pesticides have been developed. Furthermore, because pesticides present usually at trace levels, the extraction and preconcentration steps are so far essential to enrich the target analytes before instrumental determination. For neonicotinoid pesticides (thiamethoxam, imidacloprid, acetamiprid and thiacloprid), sample pretreatment techniques basically comprise liquid-liquid extraction (LLE) [14,15], solid-phase extraction (SPE) [16,17], solid-phase micro-extraction (SPME) [18] and some relatively new techniques, e.g., matrix solid phase dispersion (MSPD) [19], pressurized liquid extraction (PLE) [20], stir-bar sorptive extraction (SBSE) [21,22], dispersive solid-phase extraction DSPE [23], dispersive liquid-liquid microextraction (DLLME) [24-26]. However, these techniques are still tedious, time-consuming, and relatively expensive. To overcome these disadvantages, a new mode for extraction of analytes is needed.

NOVEL EXTRACTION METHODS USING NANOTECHNOLOGY

Discoveries of novel nanomaterials with unique properties have significant impact on their use in extraction techniques. Nanosized magnetic materials have attracted much interest in the research community due to their unique size and physical properties. Since these nanoparticles are superparamagnetic, they can be attracted by a magnet but do not retain magnetism after the field is removed. For this reason, the magnetic nanoparticles tagged with organic contaminants can be separated from the matrix by applying a magnetic field, but

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they do not agglomerate after the removal of the field. Hence, the nanoparticles can be reused or recycled. Recently, much attention has been specially paid to the study of magnetic solid-phase extraction (MSPE), which is based on the use of magnetic or magnetically modified adsorbents. In MSPE, magnetic nanoparticles (MNPs) are used as sorbents. After adsorption, the separation process between the magnetic solid sorbents and the liquid samples can be performed directly by using an external magnetic field without additional centrifugation or filtration procedures, which makes separation easier and faster. In this novel separation technology, functionalized adsorption materials with magnetic properties are of great interest to researchers because the adsorption material in the extraction process is crucial for the efficient extraction. For example, the Wang group [27] prepared graphene magnetic nanoparticle (G-Fe_3O_4) and used as the adsorbent for the preconcentration of the four neonicotinoid insecticides (thiamethoxam, imidacloprid, acetamiprid and thiacloprid) from environmental water samples. The limits of detection (S/N=3) of the method for thiamethoxam (TMX), imidacloprid (ICL), acetamiprid (ACT) and thiacloprid (TCL) were 0.01, 0.006, 0.004 and 0.006 ng ml^{-1}, respectively. The method has been successfully applied to the analysis of the neonicotinoid insecticides in real water samples and found good accuracy.

The G-Fe_3O_4 sorbent combines the advantages of large surface area of the nanoparticle and the strong adsorption ability of carbon material. The sorbent could be easily and quickly isolated from water samples with an external magnetic field, which could avoid the time-consuming column passing or filtration operations encountered in SPE. However, such magnetic Fe_3O_4 particles will expose themselves out to the sample solution during extraction, and therefore they can be oxidized and lose their magnetism under harsh experimental conditions. To solve the above problems, a suitable protective coating on a magnetic core could be used and G could be confined on the surface of the magnetic microsphere. To address such kind of particles, the same group (Wang group) [28] synthesized graphene grafted silica-coated Fe_3O_4 (Fe_3O_4@SiO_2-G) by chemical bonding. To evaluate the adsorption performance of the new magnetic nanoparticles, Fe_3O_4@SiO_2-G was used as a magnetic solid-phase extraction (MSPE) adsorbent for the first time to simultaneously extract the four most commonly used neonicotinoid pesticides (thiamethoxam, imidacloprid, acetamiprid and thiacloprid) in pear and tomato samples from the local area followed by high performance liquid chromatography-diode array detection (HPLC-DAD). The limits of detection (S/N=3) of this method for the neonicotinoids ranged from 0.08 to 0.15 ng g^{-1} and the repeatability of the method was acceptable. Compared with magnetic adsorbent G-Fe_3O_4, Fe_3O_4@SiO_2-G was more stable for long-term use and analysis of the neonicotinoid pesticides in real samples.

COMMERCIAL SENSING TECHNIQUES AND THEIR CHALLENGES

Conventional techniques that have been used commonly for pesticide monitoring include gas chromatography (GC) and high-performance liquid chromatography (HPLC). GC is an advanced technology used to separate and selectively detect raw materials. In particular, specific physical properties of pesticides with similar chemical backbone structures and functional groups can be effectively separated through a long channel column. Since GC is a separation technique, the choice of detector is rather important. For chlorinated pesticide monitoring, a dry electrolytic conductivity detector (DELCD) has been used, because it effectively detects low levels of chlorinated and brominated solvents in environmental samples and other trace analyses. However, a number of compounds cannot be analyzed directly by GC owing to their poor volatility, polarity, and/or thermal instability [29-31]. Hence, the use of HPLC has become a suitable alternative owing to the sensitivity of the diode-array detection (DAD) and its suitability in selecting the optimum wavelength for maximum sensitivity using UV spectral information. However, its application in residue analysis is hampered by the necessity for proper sample preparation due to the lack of DAD sensitivity and the large amounts of UV interferents in vegetable extracts [31-34]. Currently, the determination of pesticide residues requires the use of the aforementioned chromatographic techniques coupled to mass spectrometry (MS) analysis (quadrupole, time of flight (TOF) or hybrid instrumentation) as a detection system. In general, MS is widely used in trace analysis laboratories due to its intrinsic characteristics, such as selectivity, sensitivity and effective identification. Originally, GC coupled to MS (GC-MS) was primarily used, but this technique had been expanded to include liquid chromatography coupled to MS (LC-MS) [7,35,36]. Many pesticides are highly polar and have a specific mode of action; thus, they require a derivatization step prior to GC analysis. Currently, advances in LC technology (especially in ionization sources) have increased the popularity of LC-MS as a method for detecting pesticides because it is more sensitive and selective than GC-MS for such analyses [7,37-40]. Phytochemical screening can also facilitate the accurate identification in morphological, in genetic and in chemical characteristics of agroforestry. Once optimal source genotypes have been identified, in vitro tools may be applied to mass propagate from seeds or vegetative materials. Phytochemical screening and antibacterial activity of few plants were studied against *Xanthomonas campestris* (Table 1) [41].

Overall, traditional pesticide detection methods have been used to analyze the presence of compounds in environmental samples. However, these methods are unsuitable for screening large volumes of samples, and owing to their cost, such methods are limited; in

Table 1. Antibacterial activity of leaves extracts of some plants

Plant samples	Extracts (100 μg/ml)	Xanthomonas campestris (inhibition zone in mm)
L. aspera	Methanol	14.00nolao
C. gigantia	Methanol	10.00nolti
O. sanctum	Methanol	16.00nolum
A. vasica	Methanol	24.33nolam
H. suaveolens	Methanol	20.30nolns
T. purpurea	Methanol	14.66nolre
C. gynandra	Methanol	10.33noldr
C. viscosa	Methanol	7.60anols
Kanamycin (30amycin)	Antibiotic	15.00iotic
Neomycin (10sone i)	Antibiotic	16.33iotic
Control aqueous	Blank	0.00kol a
Control methanol	Blank	0.00kol m

particular, developing countries do not readily have access to such methods, even though these areas are facing the fallout of pesticide use. Thus, researchers have been investigating alternative detection and screening methods that are cheaper, can be used to monitor large-scale pesticide operations, and are more user-friendly. In recent years, the use of enzyme-linked immunosorbent assays (ELISAs) has grown rapidly as a tool for pesticide measurement. As many pesticides are designed to inhibit various enzymes within insects and other pests, utilizing these enzymes for pesticide detection in water and other matrices such as soil, food, and beverages seemed logical. Consequently, most of these enzymes have been incorporated into biosensors for this purpose. Enzymatic methods allow hundreds of samples to be screened in a short period of time. For accurate determination, chromatographic techniques for multistage sample pretreatment procedures before analysis are often required. In contrast, an ELISA provides a sensitive response to only one or a few trace pesticides in various matrices and is therefore a promising method for pesticide residue analysis. Grennan et al. [42] described an amperometric immunosensor for the analysis of atrazine by using recombinant single-chain antibody (scAb) fragments. The sensor was based on carbon paste, screen-printed electrodes incorporating the conducting polymer, which enables direct mediator-less coupling to take place between the redox centers of antigen-labeled horseradish protein (HRP) and the electrode surface (Fig. 1).

However, some essential improvements are required. Since a number of pesticides have a similar mode of action affecting the activity of the enzyme, most enzyme-based biosensors are used for screening purposes and are nonspecific for individual pesticides. From the investigation, it is clear that enzymatic methods are not able to achieve the sensitivity of traditional chromatographic methods and therefore should not be regarded as a means of replacing existing, traditional methods of analysis. This method does not have the ability to function in a highly contaminated environment. Additionally, very limited studies have been conducted to investigate compounds that may inhibit enzyme activity and thus interfere with pesticide detection. Limited work also has been conducted on the identification of individual pesticides from mixtures, and this needs to be further explored. Enzyme-based methodologies can detect only total pesticide content and do not provide specific information about a particular pesticide [1,43-46].

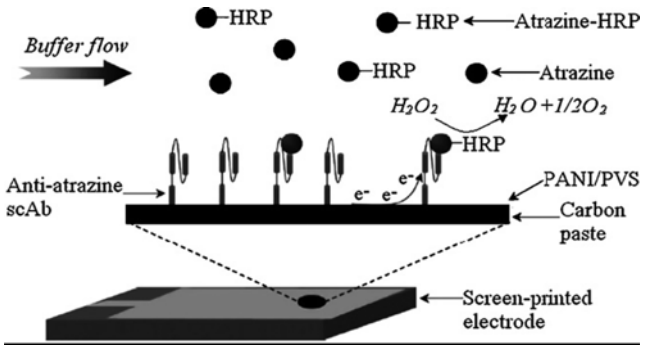

Fig. 1. Schematic of the electrochemical real-time sensing process for atrazine detection. Free and HRP-labeled atrazine compete for binding to immobilized scAb fragments (Reproduced with permission from Ref. [42], Copyright Clearance Center ("CCC"), Elsevier).

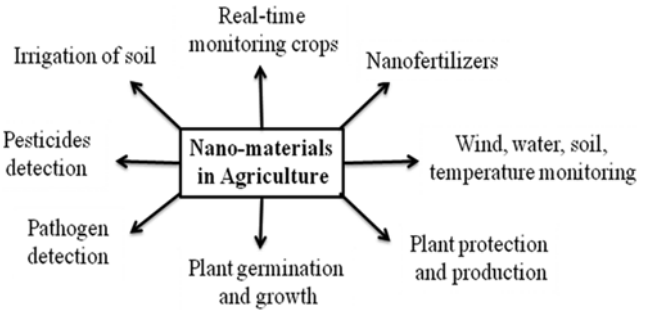

Fig. 2. Schematic presentation of nanomaterials applications in agriculture fields.

Traditional analytical methods for pesticides usually require sampling, extraction, and concentration of the pollutants before quantitative evaluation. These types of multi-step procedures are not only time consuming but may also introduce significant errors caused by adsorption losses, contamination, or even decomposition of the components of interest. Therefore, these methods are not suitable for *in-situ* and real-time monitoring. Novel advances in fast and simple analytical methods should be introduced for environmental monitoring of these compounds, especially when low-cost field results are required [1,6-8,46,47].

SENSING TECHNIQUES USING NANOTECHNOLOGY

Nanotechnology is gradually shifting from the experimental to the practical and is making its presence known in the field of agriculture (Fig. 2). Nanoparticle-based sensors are promising candidates for the detection of pesticide residues. With increased nanotechnology innovations in the agricultural sector, one could envision the major economic driving forces and benefits to consumers and farmers with no detrimental effects on the ecosystem. These sensors have superior properties over existing chromatographic techniques (i.e., HPLC or GC), because they can provide rapid, sensitive, simple, and low-cost on-field detection [48,49].

A major portion of the research in agricultural nanotechnology concerns harmful pesticide degradation by converting pesticides into harmless and useful components such as minerals and water. This is possible through photocatalysis, a property exhibited by semiconducting oxides, whereby photons are absorbed that initiate redox reactions that can break up complex organic molecules into smaller fragments [50-58]. In recent years, nanomaterials have provided novel opportunities for developing a new generation of pesticide biosensors [59-62]. Some nanomaterials can be readily functionalized, which can then be prepared as nanosensors or nanodevices for ultrasensitive pollution detection, such as CNTs or silicon nanowires (SiNWs). CNTs and graphene possess excellent electrical conductivity and can facilitate electron transfer between electrodes and electro-active species. Many sensors have been developed for detecting environmental pollution based on these characteristics. Those sensors exhibit a rapid response and high sensitivity toward a series of pesticides [63-66]. Silicon-based nanomaterials, particularly silicon nanowires (SiNWs), have shown great promise in pesticide detection. Su et al. [67] worked on gold nanoparticle-coated silicon nano-

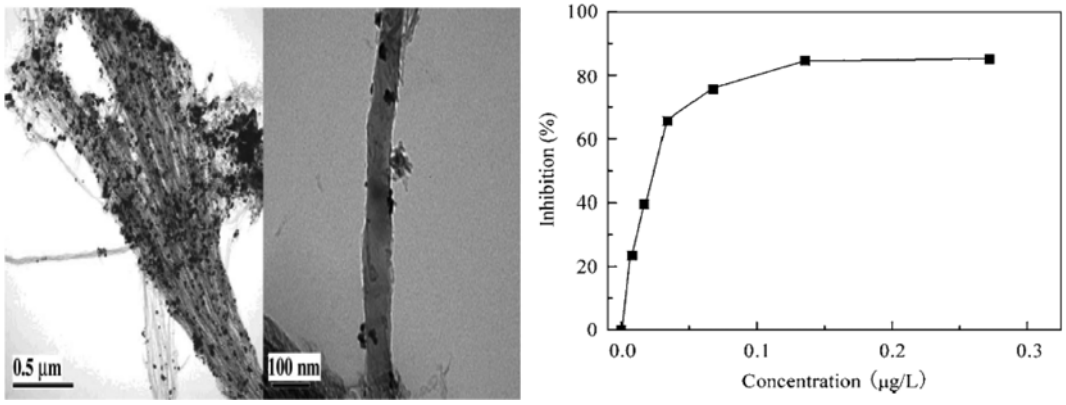

Fig. 3. (Left) Transmission electron microscopy images of the AuNPs/SiNWs nanocomplex. (Right) Effect of DDV concentration on inhibition (g L^{-1}) (Reproduced with permission from Ref. [67], Copyright Clearance Center ("CCC"), American Physics Letters).

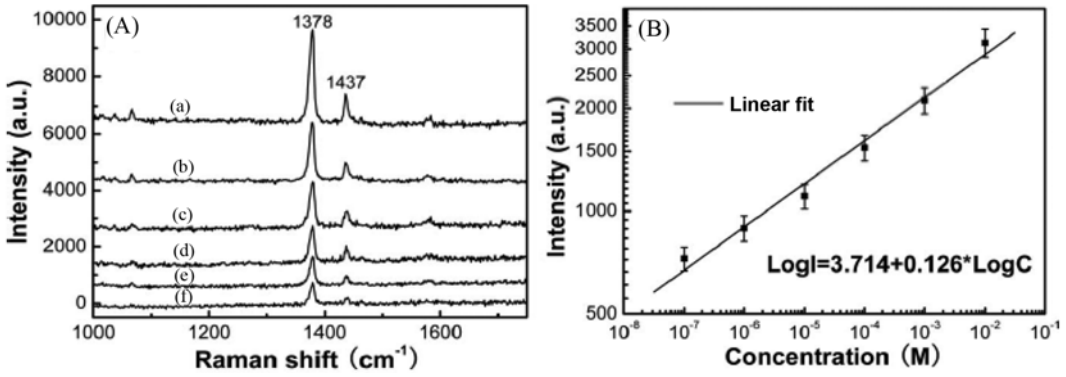

Fig. 4. (A) SERS spectra of carbaryl obtained at different concentrations, curve (a) 10^{-2} M, curve (b) 10^{-3} M, curve (c) 10^{-4} M, curve (d) 10^{-5} M, curve (e) 10^{-6} M, and curve (f) 10^{-7} M. (B) The linear relationship between the logarithmic intensities at 1,378 cm^{-1} and the concentrations. Each data point indicates an average of five samples, and each error bar indicates the standard deviation (Reproduced with permission from Ref. [68], Copyright Clearance Center ("CCC"), American Physics Letters).

wires for pesticide detection and found that the SiNW-based electrochemical sensor was suitable for the rapid and sensitive detection of pesticides at concentrations as low as 8 ng L^{-1} (Fig. 3).

Wang et al. utilized a surface-enhanced Raman scattering (SERS) sensor made of Ag nanoparticle-coated SiNW arrays that was fabricated for the quantitative detection of 1-naphthyl methylcarbamate, also called carbaryl. This SiNW array exhibited high sensitivity, reproducibility, and stability in the detection of carbaryl. Significantly, the linear relation between the logarithmic concentrations and Raman peak intensities provided quantitative detection of carbaryl (Fig. 4). The detection limit of the SiNW-based sensor was as low as 10^{-7} M (0.02 ppm), which is lower than the maximum residue standard of farm produce (10 ppm) [68].

Metallic nanoparticles, especially gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs), have received much attention owing to their potential applications as chemical and biological sensors. It is well known that the plasmonic coupling effect of metallic nanoparticle dimers and aggregates induces enormous electromagnetic enhancement that allows surface-enhanced Raman scattering (SERS) signals to be detected with single-molecule sensitivity. Zhang and co-workers reported the shell thickness-dependent Raman enhancement of silver-coated gold nanoparticles for the identification and detection of pesticide residues in various fruit peels, such as apple, grape, mango, pear, and peach. By casting the particle sensors onto fruit peels, several types of pesticide residues (e.g., thiocarbamate and organophosphorus compounds) have been rapidly detected [69]. The sensors can detect 1.5 ng/cm^2 of thiram in apple peels under unoptimized conditions. However, the application of nanobiosensors for the detection of pesticides is still in the early stages. Thus, the design of new sensors with improved analyte selectivity and sensitivity is of paramount importance in this area.

Fluorescence-based detection is the most common method utilized in chemical sensing because of its high sensitivity, and simplicity. Since their discovery, quantum dots (QDs) have been subjected to intensive investigations because of their unique tunable photoluminescence (PL) properties and potential applications [48]. Quantum dots have significant advantages over traditional fluorescent dyes, including better stability, stronger fluorescent intensity, and different colors, which are adjusted by controlling the size of the dots. Therefore, quantum dots provide a new functional platform for chemical and environmental analysis [70]. For example, a layer-by-layer (LbL) film of CdTe quantum dots (QDs), polymers, and ascorbate has been designed as a rapid, highly selective, and sensitive fluorescence probe for $^1O_2$ detection in many chemical and biological systems as an environmental sensor [71]. Upon reaction with $^1O_2$, the probe exhibits a strong photoluminescence (PL) response

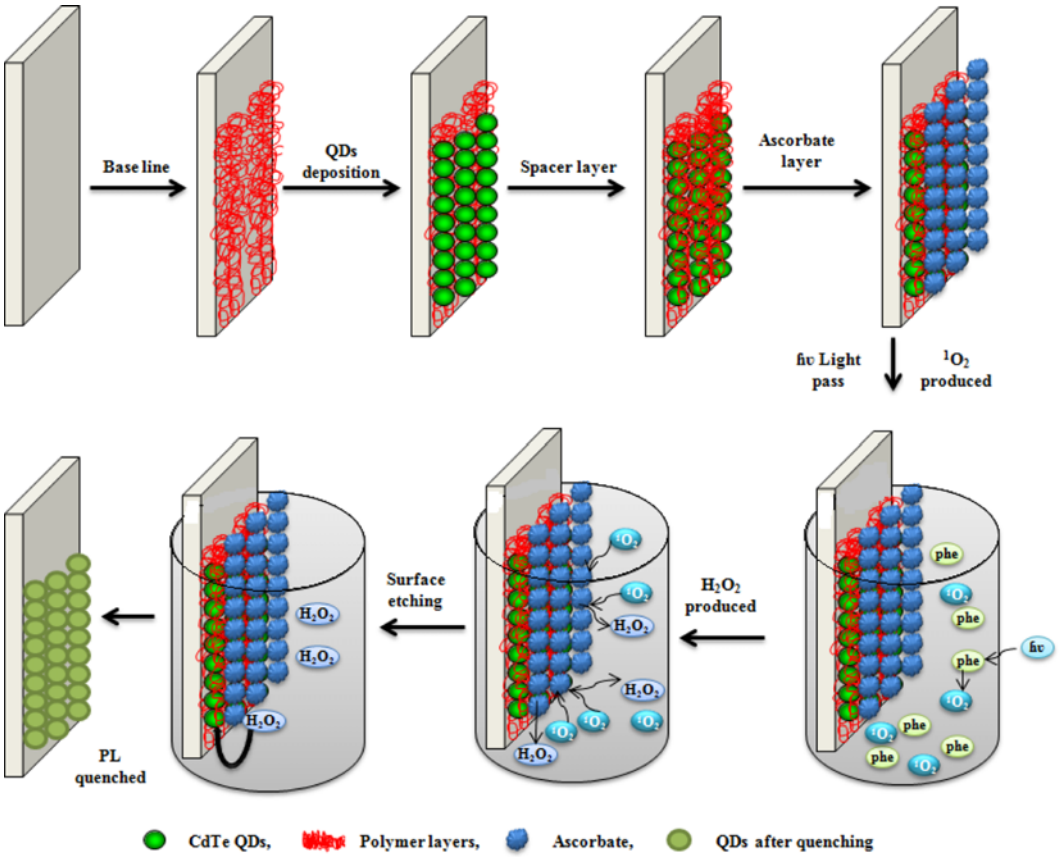

Fig. 5. Schematic diagram of sensing assembly: (a) Cleaned glass slides to make LbL film; (b) Polymer layers deposited on glass slides to make base line; (c) QDs deposited on polymer layer; (d) Polymer layers deposited on QDs to give a space between fluorophore and ascorbate; (e) Deposited ascorbate at the top of the LbL film; (f) LbL film immersed in phenylalanine solution and UV light passed through the solution which produced $^1O_2$; (g) $^1O_2$ rapidly react with ascorbate and H_2O_2 produced; (h) H_2O_2 chemically etches the QDs and surface defects generated; (i) QDs quenched and lost its brightness (Reproduced with permission from Ref. [71], Copyright © 2005 KCSNET).

Table 2. Detection limits, calibration curves, linear dynamic ranges, recoveries, and RSDs of spiked samples (n=3)

Pesticides	Detection limit (mg/kg)	Calibration curve	r	Linear dynamics range (mg/L)	Added (mg/L)	Carrot		Cucumber		Tomato	
						Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Thiamethoxam	0.05	Y=0.420X +0.128	0.9910	0.5-30.0	0.5	74.3	5.1	96.8	4.9	78.5	3.7
					1.0	72.0	5.6	92.7	5.3	81.5	3.6
					2.0	86.4	3.1	100.3	4.1	90.5	3.4
					5.0	79.6	4.6	99.1	4.5	83.6	2.8
					10.0	90.1	3.3	101.2	3.7	89.9	3.1
Acetamiprid	0.01	Y=0.420X +0.128	0.9960	0.1-30.0	0.1	100.8	4.1	80.1	3.9	81.5	4.3
					0.5	106.7	3.4	74.0	3.5	79.1	5.1
					1.0	104.9	2.9	74.5	3.7	77.5	5.1
					5.0	104.6	3.3	78.5	4.2	75.9	4.5
					10.0	98.5	3.1	87.7	3.3	84.8	3.7
Imidacloprid	0.009	Y=0.420X +0.128	0.9980	0.1-30.0	0.1	80.4	3.9	105.1	4.2	85.7	4.5
					0.5	79.5	4.6	103.5	4.1	78.5	5.7
					1.0	79.0	4.9	98.5	3.9	81.3	5.5
					5.0	85.1	4.3	101.9	4.3	77.8	5.6
					10.0	89.7	3.2	99.8	3.7	83.9	3.9

Y is the peak height, X is the concentration (mg/L) (Reproduced with permission from Ref. [72], Copyright Clearance Center ("CCC"), John Wiley and Sons)

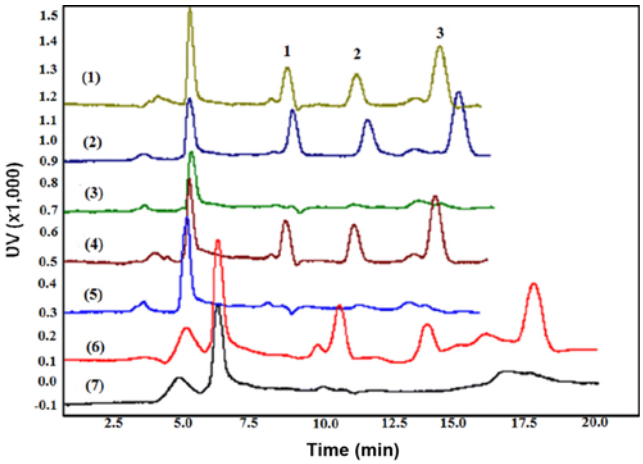

Fig. 6. Standard chromatogram using MWCNTs as packing materials with spiked purified water and chromatograms from real world water samples. Spiked level: 0.8 ng mL^{-1}; methanol volume: 4 ml; pH of sample solution: 4; flow rate: 5 mL min^{-1}; sample volume: 500 mL. 1 Thiamethoxam, 2 imidacloprid, 3 acetamiprid. (1) Spiked purified water, (2) spiked tap water, (3) blank of tap water, (4) spiked groundwater, (5) blank of groundwater, (6) spiked reservoir water, and (7) blank of reservoir water (Reproduced with permission from Ref. [76], Copyright Clearance Center ("CCC"), Analytical and Bioanalytical Chemistry).

even at trace levels.

Chen et al. developed a new assay for the detection of thiamethoxam, acetamiprid, and imidacloprid residues in vegetables by micellar electrokinetic capillary chromatography with indirect laser-induced fluorescence (LIF). CdTe QDs were used as a fluorescent background substance and their excitation and emission wavelengths were matched with the LIF detector by engineering their size. The detection limits of thiamethoxam, acetamiprid, and imidacloprid pesticides are shown in Table 1, and these potentially meet the requirements for maximum residue limits in vegetables under the regulations of the European Union and Japan [72].

Since the discovery of carbon nanotubes (CNTs) in 1991, they have attracted enormous interest due to their many novel properties such as unique mechanical, physical, chemical properties. CNTs have great potential in applications such as nanoelectronics, biomedical engineering, and biosensing and bioanalysis [73-75]. Taking into account the widespread interest in carbon nanostructures, it is not surprising that they are also found some application in analysis of pesticides. Because of their advantageous characteristics (high adsorption capacity, good thermal stability, wide pH range of application), carbon nanostructures have been employed in the extraction techniques such as solid-phase extraction (SPE) and solid phase microextraction (SPME). The use of CNTs as SPE sorbents for the extraction of both organic and inorganic compounds is also a relatively important field of application, which has especially emerged in the last five years when the number of works has greatly improved. SPE is widely accepted for analyte extraction and preconcentration as an alternative to time consuming and laborious liquidorganic compounds. Zhou et al. [76] described a novel method for sensitive determination of thiamethoxam, imidacloprid and acetamiprid based on solid-phase extraction with multi-walled CNTs as the packed materials. Under the optimized conditions, the detection limits of thiamethoxam, imidacloprid and acetamiprid were 6.1, 5.4 and 6.7 ng L^{-1}, respectively. The proposed method has been applied to the analysis of real-world water samples, with satisfactory achievements obtained. The average spiked recoveries were in the range of 87.5-109.8%. According to the obtained results, the method is sensitive, simple, rapid and easy to perform as well as repeatable.

FUTURE PERSPECTIVES

In recent years, nanomaterials such as gold nanoparticles, carbon nanotubes, magnetic nanoparticles, and quantum dots have been investigated for their potential as biosensors, and such an investigation has become a new interdisciplinary frontier between biological detection and material science. Owing to the large amount of pesticides currently being used in agricultural fields, there is an increased interest in developing rapid screening systems for their detection. However, nanotechnology applications in agriculture are still in the beginning stages and many more applications can be expected in the future. Here, we discussed the advantages and disadvantages of traditional pesticide-sensing systems. Future research is focused on the development of small, portable, easy, cost-effective, and automated systems that could be applied to a large number of species simultaneously. Self-assembly techniques are particularly well suited for fulfilling these requirements and are the most promising for developing future composite nanostructures that could exhibit interesting pesticide sensing. In addition, the introduction of biofriendly synthesis of new materials in biosensors would increase their range of applications [77,78].

ACKNOWLEDGEMENT

This work was supported by a 2-Year Research Grant of Pusan National University.

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