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REVIEW ARTICLE

# Optical and electrical nano eco-sensors using alternative deposition of charged layer

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**ABSTRACT: This review focuses on layer by layer (LBL) assembly-based nano ecological sensor (hereafter, eco-sensor) for pesticide detection, which is one of the most versatile methods. The effects of pesticides on human health and on the environment (air, water, soil, plants, and animals) are of great concern due to their increasing use. We highlight two of the most popular detecting methods, i.e., fluorescence and electrochemical detection of pesticides on an LBL assembly. Fluorescence materials are of great interest among researchers for their sensitivity and reliable detection, and electrochemical processes allow us to investigate synergistic interactions among film components through charge transfer mechanisms in LBL film at the molecular level. Then, we noted some prospective directions for development of different types of sensing systems.**

**KEYWORDS: pesticides, fluorescence, electrochemistry, layer by layer (LBL)**

## 1 Introduction

Uses of optical and electrochemical detection in biologic science are greater now than at any other time. The most important uses of these analytical methods in biosensors include (1) sensitivity; (2) specificity; (3) short time detection; (4) simplicity; (5) low cost, and (6) wide concentration range [1–2]. General sensors are composed of three main components: sensing part, physical transducer, and detectors. Many trials have been conducted for improvement of sensing activity using nanomaterials, biologic moieties, etc. Mostly, versatile detection methods are composed of optical and electronic analysis due to their robustness of reproducibility. For example, a fluorescent material absorbs light of one color and then emits light of a second color, which attracts the researcher for its use in many biologic sciences for targeting of compounds with high specificity. Meanwhile, electrochemical analysis is a robust and trusted method for application in complicated biologic environments. In general, sensitivity of fluorescence detection is in parts per billion or even trillion, which allows reliable detection of fluorescent materials using a small sample size, while electrochemical analysis presents similar and higher levels of sensitivity in most experimental reports. No doubt is arrived at in selection of the most reliable detection methods, i.e., optical (in particular, fluorescence) and electrochemical analysis in fabrication of nano eco-sensors for environmentally hazardous materials.

One important step is to build a physical transducer, which is a main base component of sensors to flow signals from sensing parts to a designated detector, whether the

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signal is electrical, optical, or chemical. There are many different means for construction of the base component through nanomaterials such as carbon nanotube, quantum dot (QD), metallic nanomaterials, etc. Mainly, the targeting goal in building the physical component is to gain higher signals from sensing parts with less noise and to deliver sensing signals to the detector without any loss in short period. To satisfy such a peculiar requirement, nanomaterials have been adopted for composition of the base component. In the review, the layer by layer (LBL) method is introduced for construction of the base component. The most important reason for use of LBL would be its simplicity and wide adoption of nanomaterial candidates. Detailed methods of LBL will be described in Section 2.

In our review, four keywords have been selected in worldwide experimental reports, i.e., optical and electrochemical analysis, LBL, and pesticide. In other words, current research and tendency toward use of optical and electrochemical nano eco-sensors using LBL are reviewed, and we have provided some further direction for research, which will be valuable reading for potential researchers in development of bio-/environmental sensors.

## 2 Layer by layer techniques

For preparation of LBL film, there are many technical publications on drastic advancement of LBL techniques [3–10]. There is literally no limitation in the use of materials for LBL, such as inorganic molecular clusters, nanoparticles [11], nanotubes and nanowires [12], nanoplates [13], dendrimers [14], porphyrin [15], polysaccharides [16–17], polypeptides [18], nucleic acids and DNA [19], proteins [20–21], and viruses [22], and the application areas have been expanded to superhydrophobic surfaces [23–24], drug, and biomolecular delivery systems [25–27], optical active and responsive films [28–31], cell and protein adhesion-resistant coatings [32], electrochemical sensing [33–36], biomimetic and bio-responsive coatings [37–38], and semiconductors [39–40]. Here, we provide a very short description of LBL, since many review papers have provided detailed descriptions [3–10]. Wide use of materials and application is based on the simplicity and robustness of LBL techniques. The charged layers (each positively and negatively) are deposited alternatively one to another on glass slides by dipping in colloidal solutions, and the layers are bound with the assistance of electrostatic forces. Typical LBL assemblies consist of a series of four basic steps: (i) immersion of the substrate into a solution of a polymer or other high molecular weight material, (ii) rinsing for removal of excess of the first component on a substrate, (iii) immersion into a solution of a different high molecular weight material, and (iv) rinsing for removal of excess of the second LBL component. The adsorption step for each component can take anywhere between a few seconds to hours, while rinsing steps can take between a few seconds and 10 min [41]. These basic steps are then repeated as many times as necessary in order to reach a desired thickness of the film. Film thickness in LBL is in nanoscale and can be precisely controlled by adjustment of processes such as pH and immersion time [42]. In our review, we focus on relatively novel fields, including environmental sensing using LBL techniques with nanomaterials via fluorescence, and electrochemistry.

### 2.1 Fluorescence-based pesticide nano eco-sensors using the LBL technique

Due to high specificity and accuracy, use of fluorescence materials for sensing has increased. Many receptors focus their work on fluorescence-based sensing for glucose biosensors [43–46], DNA biosensors [47–53] and environmental monitoring, such as phenols [54–55], polycyclic aromatic hydrocarbons [56–58], total trihalomethanes (THMs), and haloacetic acids (HAAs) [59], pesticides [60–63], and metal ions [64–72].

Use of pesticides in crop fields, walls of houses, and in other fields has become increasingly widespread day by day, which raises a number of environmental concerns, including air, water, soil pollution, and food contamination. Accurate detection and highly sensitive determination of pesticides in environmental samples are therefore of great importance. Many methods are available, including thin-layer chromatography (TLC), high-performance chromatography (HPLC), and gas chromatography (GC) for pesticide detection [73–75]; however, these are not applicable for *in situ* application and are also problematic with regard to rapid and sensitive measurement. Some authors featured in Table 1 have developed *in situ* detection methods of pesticides [76–84]. For example, Garcia-Reyes et al. used desorption electrospray ionization mass spectroscopy to characterize ultra trace agrochemicals in foodstuffs, but this technique has limitation on heavy requirement of sample manipulation and long processing time [76]. Xiong et al. utilized a simple colorimetric detection means. In general, this technique is relatively easy and ultrasensitive to detect a targeting analyte species. However, cross-talking of data might be a substantial

**Table 1** Important experimental studies of pesticide detection

| Researchers | Methods | Characteristics / Detection limit | Refs. |
|---|---|---|---|
| J. F. Garcia-Reyes, et al. | Desorption Electrospray Ionization Mass Spectrometry | These techniques are usually exhaustive and provide compressive data but they require considerable sample manipulation such extraction and as a consequence take considerable time and effort | [76] |
| D. Xiong, et al. | Colorimetric detection | Relatively easy and ultrasensitive to detect but result may be influenced by impurities in solution | [77] |
| T. Henriksen, et al. | Solid-phase microextraction (SPME) method | Method is less labor-intensive and automated but one of the important things detection limit which is not so impressive (0.16–2.3 micro g/L) and instrument is also expansive | [78] |
| S. Schlücker, et al. | Nonlinear Raman Spectroscopy | Nonlinear Raman techniques are an ideal tool for *in situ* diagnostics but not suitable for trace level analysis. It needs costly laser sources for excitation to improve sensitivity | [79] |
| S. Lacorte, et al. | Stir bar sorptive extraction and gas chromatography coupled to mass spectrometry | Detection limit is down to low pg/L but it needs long time treatment for sample extraction, chromatographic separation, high effort and also trained person | [80] |
| D. A. Alvarez, et al. | Polar organic chemical integrative sampler (POCIS) | POCIS technique has the potential to become the standard for global water quality monitoring but preparation and construction of POCIS is very complex and also time consuming | [81] |
| M. Janotta, et al. | Attenuated total reflection (ATR) spectroscopy | Detection of pesticides down to the sub-ppm concentration range but disadvantages are high cost of raw materials and long processing times | [82] |
| S. Hassoon, et al. | Fluorimetric detection | Detection limit is within ng but only two pesticides are possible to detect and chemical (e.g. pH) and physical effects may influence the calibration graphs as well | [83] |
| H. P. Li, et al. | Microwave-assisted headspace solid-phase microextraction (MA-HS-SPME) | Method is fast and solvent free procedure but need highly trained person to operate, expensive instrument and detection limit varied from 0.002 to 0.070 micro g/L | [84] |

drawback, influenced by impurities in solution [77]. Henriksen et al. adopted solid-phase microextraction (SPME) method which is less labor-intensive and automated, but one of the important things is detection limit that is not so impressive (0.16–2.3 micro g/L) and the instrument is either expansive or not portable [78]. In total, these suggested methods in Table 1 still require pretreatment of samples, highly trained personnel for operation, bulky scale of sensing instruments, and careful clean-up step. Then, they are somehow time consuming, labor intensive, and often result in derivatization of target compounds, high cost of raw materials, and complex sample preparation. In addition, several chemicals and toxic solvents are also used. Therefore, requirement on cheap and handy techniques are of crucial importance.

Such difficulties can be overcome by use of the LBL technique, which is inexpensive, simple, sensitive, and does not require a long period of time; in addition, massive levels of pesticides can be detected quickly for industrial processes and environmental monitoring [85]. Many researchers are now focusing their research on the use of fluorescence materials & LBL techniques for detection of pesticides. Paraoxons, which are contained in pesticides, have been reported by several epidemiological studies in association with the incidence of some hormone-dependant diseases [86–87]. Fluorescence spectroscopy is particularly sensitive to small quantities of analytes and has been used for sensing paraoxon interaction with LBL films that were composed of chitosan (CS) and organophosphorus hydrolase polycations (OPH) along with thioglycolic acid capped (TGA) CdSe QDs as the polyanion (Fig. 1) [88].

Step-by-step self-assembly of oppositely charged layers provides quantitative evidence for an increase in template particle diameter, and the morphology, as well as the increase in size of individual particles, will change after deposition. Fluorescence spectroscopy qualitatively demonstrates the increase in fluorescence intensity of individual particles with increasing layer number. This key characteristic allows incorporation of QDs into a biosensing assembly system. Leblanc and his coworkers reported on the change in fluorescence intensity in colloidal solution and in LBL film (Fig. 2). Exposure of the film on paraoxon solution immediately decreased the photoluminescence intensity. The photoexcited electron or hole interacts with OPH in a donor-acceptor charge transfer manner, which ultimately leads to a decrease in photoluminescence.

Due to its great sensitivity, fluorescence detection is very useful in pesticide analysis; however, due to its selectivity,

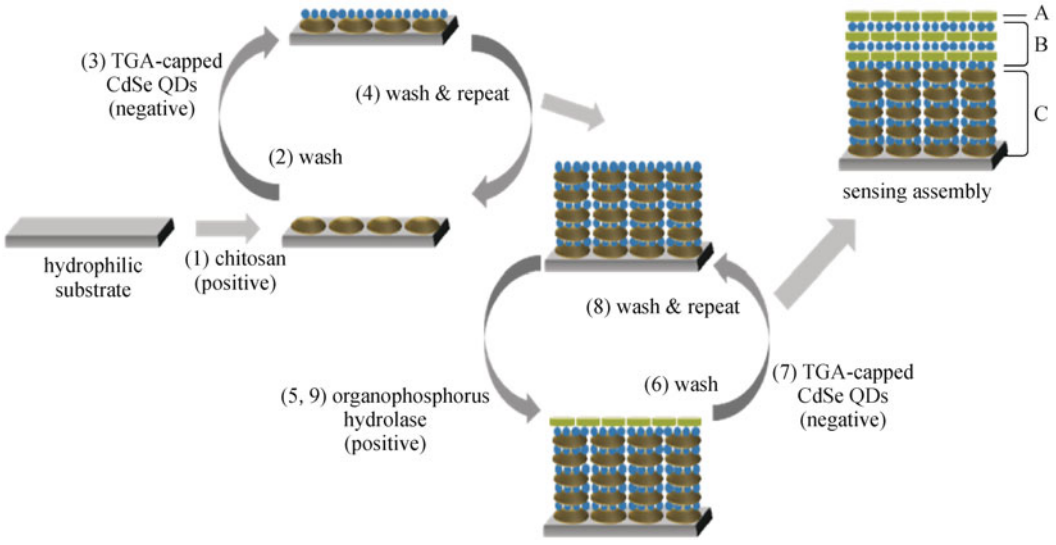


**Fig. 1** Sensing assembly: top layer of OPH (A); two bilayers OPH/TGA-capped CdSe QDs (B); five bilayers CS/TGA-Capped CdSe QD (C). (Reproduced with permission from Ref. [88], Copyright 2003 American Chemical Society)

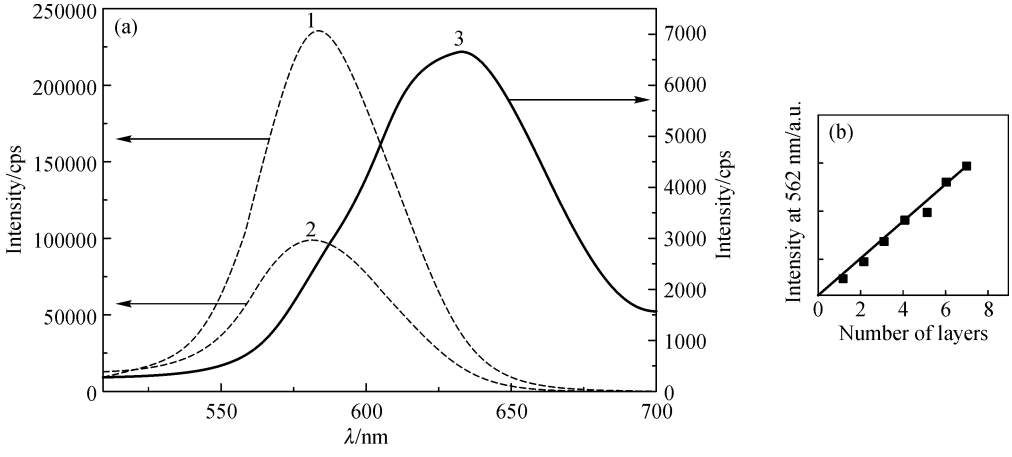


**Fig. 2** **(a)** Photoluminescence spectra of the TGA-capped CdSe QDs: (1) in the LBL film before paraoxon exposure; (2) in the LBL film after paraoxon exposure; (3) ($1.6 \times 10^{-4}$ mol·L$^{-1}$) in solution. **(b)** Intensity of photoluminescence at $\lambda_{em}$ versus the number of layers. (Reproduced with permission from Ref. [88], Copyright 2003 American Chemical Society)

it cannot be the recommended method for pesticide screening or early-warning procedures. Nevertheless, fluorescence detection is an important aid in environmental analysis, especially when monitoring specific analytes. However, since relatively few pesticides are naturally fluorescent, fluorimetric analysis requires pre-treatment of these compounds or conversion to fluorescent species. Hydrolysis, heat treatment, and derivatization are some of the methods used for fluorescence enhancement in pesticide analysis. Electrochemical analysis of pesticides using the LBL technique may be another important procedure due to its inherent sensitivity and selectivity toward electroactive species. Also, it is a fast, accurate, compact, field portable and inexpensive technique.

## 2.2 Electrochemistry of LBL film for pesticide nano eco-sensor

Electrochemical biosensors currently hold a leading position in the task of environmental monitoring. Electrochemical detection is a simple, sensitive, and environmentally friendly detection method that is even suitable for analysis of colored or turbid samples. Several electrodes, including sulfite [89–90], nitrate [91], organonitriles [92], cyanide [93], formaldehyde [94], organophosphates [95–97], and carbamate pesticide [97–98] detection, have already proven useful for the task of environmental monitoring. Pesticide contamination of soil, food, and water has become a serious problem. Pesticides and

herbicides are widely used for control of insects, fungi, bacteria, weeds, nematodes, rodents, and other pests. Accurate detection and highly sensitive determination of pesticides in environmental samples are therefore of great importance [99]. LBL-nanostructured thin films comprised of naturally-occurring humic acid (HA) and poly(allylamine hydrochloride) (PAH) displayed a well-defined electroactivity for detection of pentachlorophenol (PCP) pesticides [100]. Although chromatographic methods, such as HPLC/UV and GC/ECD, have been previously used [101–102], methods using LBL have certain advantages, including chemically stable films that can be easily prepared; LBL films do not require a pretreatment stage of the sample, which makes the method of detection less costly than chromatographic methods; LBL film also offers the advantage of a lesser amount of material employed in the sensing unit in addition to allowing fine-tuning of film thickness and film architecture. One of the main challenges in the use of biologic films or nanostructured films containing biomolecules is the preservation of bioactivity, particularly because these films are used in their dry state. In this context, the LBL method has been proven excellent for immobilization of biomolecules with preserved activity for long periods because film fabrication is performed under mild conditions, and one can choose various materials as templates or scaffolds. Oliveira and his coworkers [100] developed LBL films of HA and PAH, which were deposited onto ITO electrodes and used as modified electrodes for detection of pentachlorophenol. One important characteristic of these films was their smoothness, with average roughness varying from 0.89 to 1.19 nm. HA/PAH films displayed electroactivity and could be used for detection of pesticides, as illustrated in Figs. 3 and 4 for PCP. Sensitivity was very high, with a detection limit of $1.6 \times 10^{-9}$ mol·L$^{-1}$. It is worth noting that at this concentration, the PCP oxidation peak was not observed with a bare ITO electrode. Indeed, the presence of HA molecules improved adsorption of PCP at the electrode surface and enhanced electron transfer between PCP and the electrode.

### 2.3 Prospective techniques for better accessibility, selectivity, and sensitivity

Due to the increasing use of pesticides in many fields, an *in situ* detector is important for continuous monitoring of pollutants. Electrochemical detection of pesticides is suitable for this purpose. However, one of the main disadvantages of electrochemical detection is that it can only be used for electrochemically active compounds. Other limitations include electrochemically active interference in the sample, weak long-term stability, and troublesome electron-transfer pathways. Future work will be required in order to overcome this limitation. For fast response, conductive polymers may be used for development of the conductivity of electroactive substances. Recently, immunoassay detection of organophosphorylated acetylcholinesterase (OP-AChE) has been successfully performed using magnetic particles (MPs) and QDs in order to avoid interference and increased sensitivity [103]. This paper used two types of antibodies (termed Ab1 & Ab2) to facilitate specific recognition of OP-AChE. Amorphous MPs with a large surface-to-volume ratio were chosen for loading of Ab1 to capture the OP-AChE from the sample matrixes by binding the phosphoserine moieties, and, second, recognition of Ab2 labeled with QDs serving as the signal-amplifying tags. This new electrochemical immunoassay is demonstrated to be a simple, selective, sensitive, and field-deployable alternative tool for OP pesticide detection. This novel work can be further developed by use of the LBL technique for achievement of higher benefits. Those developments can

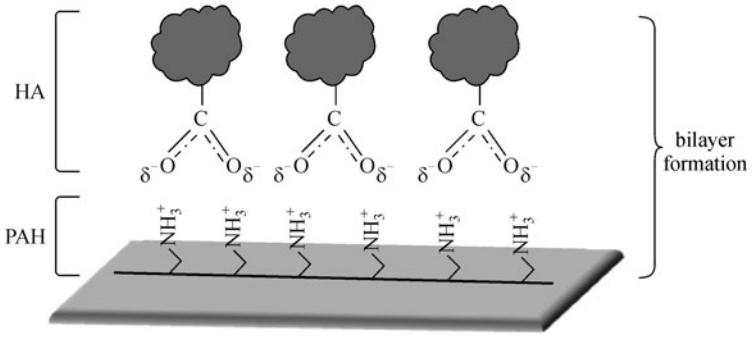


**Fig. 3** Schematic fabrication of LBL films comprising HA and PAH. (Reproduced with permission from Ref. [100], Copyright 2005 American Chemical Society)

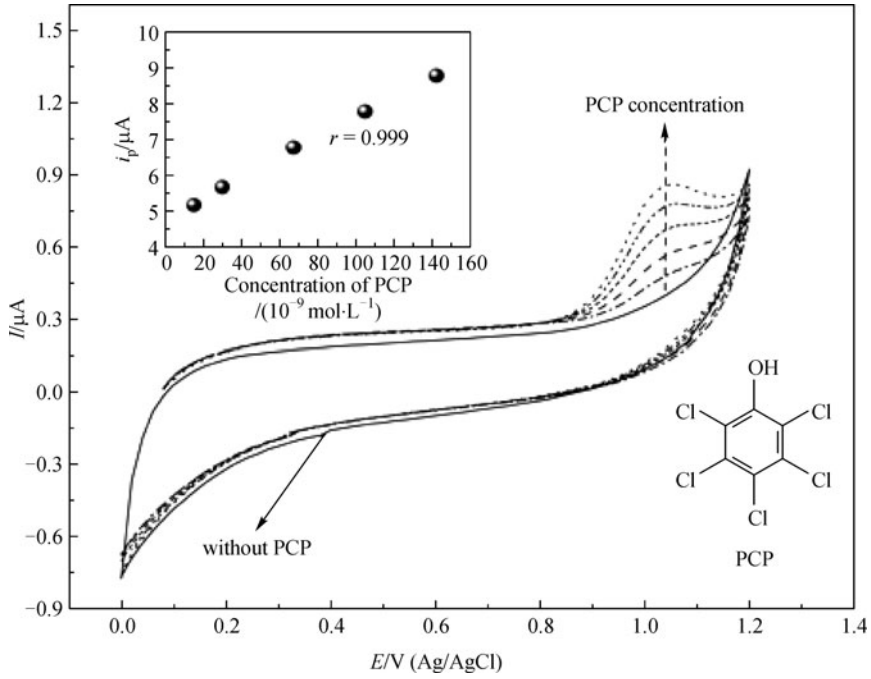


**Fig. 4** Analytical curve showing the electrochemical response of an ITO/$(PAH/HA)_6$ film obtained in aqueous solution containing different concentrations of PCP. The inset shows the linear dependence of the oxidation peak as a function of the amount of PCP in the electrolytic solution. Electrolyte: NaCl 0.5 mol·$L^{-1}$ (pH = 4.0). Scan rate: 50 mV·$s^{-1}$. (Reproduced with permission from Ref. [100], Copyright 2005 American Chemical Society)

lead to exciting new uses of LBL film for pesticide detection at the field level.

## 3 Conclusions

In recent decades, numerous developments have been achieved for detection of pesticides. Each technique has its own advantages and disadvantages. However, more importance should be given to a simple, cheap, sensitive, selective, and field portable detector. LBL is an effective method and offers many advantages for pesticide detection; however, it is still under use. Currently, we are in the initial state of this type of sensor. We hope that, in the near future, many researchers will take an interest in this field. In this review paper, we want to leave some direction for future researchers: 1) High intense and longer fluorescence resonance energy transfer (FRET) will increase selectivity and sensitivity for detection of trace amounts; 2) 3D conformal structure using the advantages of LBL will be another challenge; 3) Magnetic separation of electroactive ions will avoid interference; 4) Use of conductive polymers in the LBL technique will increase the conductivity of electroactive ions. Currently, we are in the beginning stages of development of a new generation of pesticide detectors using the LBL technique, which is likely to provide enabling technologies for rapid, accurate, selective, sensitive, and low-cost performance, and the most important one is field-portable.

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