Analytica Chimica Acta 916 (2016) 84–91

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

“Turn-off” fluorescent data array sensor based on double quantum dots coupled with chemometrics for highly sensitive and selective detection of multicomponent pesticides

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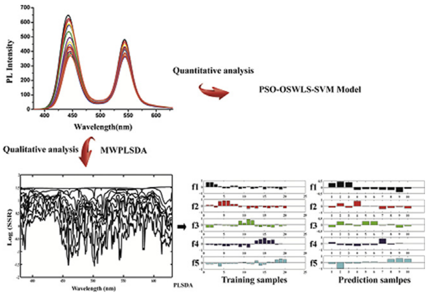
HIGHLIGHTS

- A new model based on double QDs is established for pesticide residues detection.
- The fluorescent data array sensor is coupled with chmometrics methods.
- The sensor can be highly sensitive and selective detection in actual samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 December 2015
Received in revised form
16 February 2016
Accepted 17 February 2016
Available online 22 February 2016

Keywords:
Double quantum dots
Turn-off
Chemometrics methods
Qualitative and quantitative analysis of various pesticides

ABSTRACT

As a popular detection model, the fluorescence “turn-off” sensor based on quantum dots (QDs) has already been successfully employed in the detections of many materials, especially in the researches on the interactions between pesticides. However, the previous studies are mainly focused on simple single track or the comparison based on similar concentration of drugs. In this work, a new detection method based on the fluorescence “turn-off” model with water-soluble ZnCdSe and CdSe QDs simultaneously as the fluorescent probes is established to detect various pesticides. The fluorescence of the two QDs can be quenched by different pesticides with varying degrees, which leads to the differences in positions and intensities of two peaks. By combining with chemometrics methods, all the pesticides can be qualitative and quantitative respectively even in real samples with the limit of detection was 2×10^{-8} mol L^{-1} and a recognition rate of 100%. This work is, to the best of our knowledge, the first report on the detection of pesticides based on the fluorescence quenching phenomenon of double quantum dots combined with chemometrics methods. What's more, the excellent selectivity of the system has been verified in different mediums such as mixed ion disruption, waste water, tea and water extraction liquid drugs.

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http://dx.doi.org/10.1016/j.aca.2016.02.021
0003-2670/

1. Introduction

As a common method, pesticides have been widely used in various combinations at different stages of crop cultivation, such as during postharvest storage to protect crops against a range of pests and fungi [1] or provide quality preservation [2]. Unfortunately, pesticide residues, which might pose a potential risk for human health due to their subacute and chronic toxicity [3,4], could possibly remain in crops such as fruits [3], tea [4] and even traditional Chinese medicines [5]. Thus, it is important to monitor their levels for compliance so as to ensure the safety of the food and pharmaceuticals supply [6–9]. Many methods have been used to distinguish pesticides, such as gas chromatography (GC) coupled with selective detectors [10], electron capture or mass spectrometer (MS) [11,12] and GC–MS [13,14] continues to be a key tool to analyze pesticides because it can satisfy the requirement of sensitivity and selectivity for both qualitative and quantitative analysis. Although these methods are sensitive and reliable, they are too time-consuming and highly costly. Moreover, they can only be performed by well-trained technicians and are not convenient for on-site or in-field detection. Therefore, a rapid, convenient and sensitive assay deserved to be developed for detecting pesticide residues in real samples.

The detection mode based on “turn-off” fluorescence change (quenching) of quantum dots (QDs) have always been magnetic to the researchers due to their importance in sensitive detection of anticancer drugs [15,16], metal ions [17,18], DNA hybridization [19,20], aromatic [21], amino acids [22] and especially pesticides [23,24]. However, the traditional detection methods based on one-direction signal change (either fluorescence quenching or recovery) of the probe [25] can be easily interfered by many factors and have little useful information. In addition, the qualitative process relying on the similar concentrations of materials can not be used in the practical application. On the other hand, by using two different QDs with different properties and maximum emission wavelengths, the fluorescence of them can be quenched or raised by different materials with varying degrees, which may lead to the differences in positions and intensities of two peaks. This model requires no specific modification, and thus keeps the high fluorescence efficiency and stability of QDs, together with additional information for qualitative analysis. However, when it comes to the qualitative diagnosis of various samples with different concentrations, the spectra may be seriously overlapped, which made the accurate assignment of characteristic peaks quite difficult. Therefore, chemometric methods were required to extract useful information for the recognition of samples.

Compared with quantified by the value of a single peak, using optimized sample-weighted least-squares support vector machine based on particle swarm optimization (PSO-OSWLS-SVM) model [26] can perfectly extract full spectra information of fluorescence spectra and provide a better quantitative result. On the other hand, as classical chemical pattern recognition methods, partial least squares discriminant analysis (PLSDA) [27] and moving window partial least squares discriminant analysis (MWPLSDA) [28] models were widely used in several spectral analysis of different sample groups, such as near-infrared spectroscopy [29], mid-infrared spectroscopy [30] and fluorescence spectroscopy [31,32]. By combined with pattern recognition methods, the spectral data can be effectively filtered and only useful principal components can be involved in linear regression which can provide a much better discriminant result. However, based on the available literature, the “turn-off” fluorescent based on double quantum dots combined with chemometrics methods have not been reported to be used in any field.

In this paper, the fluorescence “turn-off” model based on double QDs, for the first time, has been combined with chemometrics methods and employed to study the qualitative and quantitative analysis of five common pesticides (paraquat, dursban, dipterex, methyl thiophanate and cartap). The ZnCdSe and CdSe QDs are put into use to simultaneously provide more available spectra information for quantitative analysis of all the pesticides by using PSO-OWLS-SVM model. Compared with PLSDA, all the pesticides are recognized perfectly by using MWPLSDA. In addition, this is the first time for a fluorescent data array sensor to distinguish different pesticides with various concentrations successfully and reach a discriminant accuracy rate of 100%. What is more, fluorescent data array sensor shows excellent selectivity and stability in the practical application, such as the detection of pesticide residue in no matter tea, water extract of Chinese medicines, mixed ion disruption or waste water.

2. Experimental

2.1. Experimental materials and reagents

Se, $NaBH_4$, $ZnCl_2$, $CdCl_2$, KCl, NaCl, $MgSO_4$, and $CaCl_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd. N-Acetyl-L-cysteine (NAC) was purchased from Aladdin Chemistry Co., Ltd. Water-soluble NAC-capped ZnCdSe and CdSe QDs via the hydrothermal route were synthesized in our laboratory by altering the amount of Cd with Se:Zn = 0.01:1 fixed. All the pesticide residues were bought from Shanghai Pesticide Research Institute Co., Ltd. Deionized distilled water prepared from a Milli-Q-RO4 water purification system (Millipore) was used.

2.2. Apparatus and procedures

The fluorescence spectra were acquired by a LS55 luminescence spectrometer (Perkin–Elmer Company). According to physicochemical properties of the five pesticides which will keep stable in neutral water environment under room temperature, samples containing same concentrations of ZnCdSe QDs, CdSe QDs and different concentrations of pesticides were made up to 1 mL in Deionized distilled water and all optical measurements were performed at room temperature under ambient conditions with the excitation wavelength (λ_{ex}) at 380 nm for convenient practical applications. The concentration of ZnCdSe QDs was set at 4.2×10^{-9} mol L^{-1} while the concentration of CdSe QDs was set at 3.0×10^{-9} mol L^{-1}. The emission spectrum of the solution was then measured 3 min later.

2.3. Method of chemometrics

All original spectra were pre-processed by second-order derivative (2nd derivative) and multiple scatter correction (MSC). Pre-processed methods, PLSDA, MWPLSDA and PSO-OWLS-SVM programs were written and performed using a Matlab 2010a (Math Works, Natick, MA. USA).

3. Results and discussion

3.1. Effective quenching of fluorescence of QDs by pesticides: “turn-off” process

To study the interactions between QDs and different pesticide residues, two QDs with different emission peaks (QD_1 with λ_{em} at 440 nm and QD_2 with λ_{em} at 540 nm) have been tested to examine the quenching ability of different pesticides towards different QDs. Fig. 1.1 shows the images of the emission color of NAC-capped ZnCdSe and CdSe QDs under the white lamp (left) and the radiation of UV lamp (right). With increasing concentration of pesticides