



Development and application of a novel fluorescent nanosensor based on FeSe quantum dots embedded silica molecularly imprinted polymer for the rapid optosensing of cyfluthrin

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ABSTRACT

A novel molecularly imprinted silica layer appended to FeSe quantum dots (MIP-FeSe-QDs) was fabricated and utilized as a recognition element to develop a selective and sensitive fluorescent nanosensor for cyfluthrin (CYF) determination. The MIP-FeSe-QDs were characterized by fluorescence spectrometry, scanning electron microscopy, transmission electron microscopy, and Fourier transform infrared spectroscopy. Excellent selectivity and high sensitivity of MIP-FeSe-QDs to CYF molecules were observed based on the fluorescence quenching of FeSe-QDs. Under optimal conditions, a good linear relationship was found between fluorescence quenching effect and increased CYF concentration within 0.010–0.20 mg/L, with a correlation coefficient of 0.9911. The practicality of the developed sensor method for CYF detection in fish and sediment samples was further validated. Good recoveries ranging from 88.0% to 113.9% with < 6.8% relative standard deviations were obtained. The detection limits of CYF in sediment and fish samples were 1.3 and 1.0 µg/kg, respectively. This study established a novel, rapid fluorescent nanosensor detection method based on MIP-QDs for successfully analyzing CYF in fish and sediment samples.

1. Introduction

Pyrethroid insecticides are important broad-spectrum pesticides widely used to control insects due to their higher efficiency and lower toxicity to mammals than organochlorine and organophosphate insecticides (Li et al., 2017; Saillenfait and Ndiaye, 2015). However, the persistent and massive usage of pyrethroid insecticides has resulted in serious environment and organism-safety problems. Cyfluthrin (CYF) is a type II pyrethroid widely used to control insects in agriculture and has been reportedly detected in coastal sediments collected in California (Lao et al., 2012; Hu et al., 2014). Moreover, long-term exposure to CYF impairs the respiratory system, reproductive function, nervous and immune systems of humans, and non-target organisms, such as aquatic organisms (fish, shrimp, etc.) and bees (Brander et al., 2016; Hughes et al., 2016). Meanwhile, the high stability of CYF in the environment results in the accumulation of their residues in aquatic organisms, which generates adverse effects on aquatic food safety and human health. Therefore, the maximum residue of CYF in food has

been stipulated in many countries, with EU and Japan being the most stringent (Zhang et al., 2016). Developing a rapid, facile, sensitive and reliable quantification method for detection of trace CYF residue is necessary.

Nowadays, high-performance liquid chromatography (HPLC) and gas chromatography (GC) coupled with mass spectrometry are the most important determination methods for target analytes due to their high sensitivity and identification capability (Machado et al., 2017; Mao et al., 2012). However, these methods usually require long operation time, high cost, and tedious sample preparation procedure (Domínguez et al., 2016). Therefore, establishing a simple, rapid, and effective method to detect CYF in environmental and biology samples is urgent.

Quantum dots (QDs) as semiconductor fluorescent nanocrystals are attracting increased attention due to their remarkable optical and electrical properties of stability, broad absorption spectra, sharp symmetric emission band, and high resistance to photo-bleaching, and are thus considered as an excellent signal response candidate for

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designing sensors (Liu et al., 2016; Medintz et al., 2005). Meanwhile, molecular imprinting is an attractive strategy to fabricate tailor-made binding site materials (molecularly imprinted polymers, MIPs) with high selectivity for target molecules similar to the properties of biological antibodies (Panagiotopoulou et al., 2017). Typically, the highly selective MIPs are synthesized through the co-polymerization of functional monomers and cross-linkers in the presence of template molecule. After removal of the template, the complementary imprinting cavities in the shape, size and functional groups to the target molecule onto MIPs were fabricated and allowed specific rebinding to the template. Meanwhile, MIPs are more cost saving, easier to prepare, and possess stronger mechanical and thermal stability compared with biology antibodies (Cumbo et al., 2013). Recently, surface MIPs have been successfully applied as promising recognition elements in sensors, and have exhibited high selectivity for detecting trace contaminants (Shahar et al., 2017; Uzun and Turner, 2016). After surface functionalization of QDs with molecular imprinting, the obtained molecularly imprinted quantum dot materials (MIP-QDs) exhibited a high selectivity to target molecules and excellent fluorescence properties (Chantada-Vázquez et al., 2016). Therefore, the development of the fluorescent nanosensor based on the MIP-QDs has gained considerable attention for the detection of target molecules. Several fluorescent-nanosensor-based MIP-QDs have recently been reported to contain some contaminants, such as organophosphates, phenolic compounds, prilocaine, chlorophenol, and clenbuterol (Ensafi et al., 2017; Ye et al., 2011; Huy et al., 2014). However, many QDs based on semiconductor heavy metals (such as CdTe, CdSe) are potential threats to humans and the environment. Therefore, in the present work, novel ecofriendly MIP-QDs based on FeSe-QDs were successfully fabricated and a sensitive fluorescent nanosensor to selectively quench the fluorescence by CYF was initially constructed. The MIP-FeSe-QDs characteristics of morphology, optical stability, and selective fluorescence quenching were investigated. Finally, the application capability of the constructed fluorescent nanosensor based on the MIP-QDs was fully evaluated. The results indicated that the fabricated fluorescent nanosensor-based MIP-FeSe-QDs demonstrated ecofriendly, convenient, rapid, and accurate determination of trace CYF contaminants in sediment and fish samples.

2. Experimental

2.1. Reagents and materials

CYF, bifenthrin (BIF), deltamethrin (DEL), cypermethrin (CYP), and fenvalerate (FEN) were obtained from Shanghai Pesticide Research Institute Co., Ltd (Shanghai, China). Azobisisobutyronitrile (AIBN) was bought from Shanghai Shisihewei Chemical Co., Ltd (Shanghai, China). 3-Aminopropyl-triethoxysilane (APTES), tetraethoxysilane (TEOS), triton X-100, methacrylic acid (MAA), and ethyleneglycol dimethacrylate (EGDMA) were purchased from Sigma-Aldrich (Steinheim, Germany). Ammonia, acetone, chloroform, acetic acid, triethylamine, and cyclohexane were obtained from Sinopharm Group Co., Ltd (Shanghai, China), and all the reagents were of analytical grade.

2.2. Synthesis of FeSe-QDs

The FeSe-QDs were synthesized using the modified method as previously reported (Mao et al., 2014). In a typical experiment, an iron oleate precursor solution was prepared by placing acetylacetone iron, oleic acid, and octadecene in a three-necked flask and evacuated for 1 h at 100 °C. The temperature was increased to 120 °C at 10 °C/min and held until the color of the solution turns from yellow to colorless. Then, it underwent natural cooling to 50 °C. Meanwhile, the appropriate amount of selenium powder and octadecene were quickly added to another three-necked flask and heated at 100 °C for 1 h. The tempera-

ture was then increased to 310 °C at 10 °C/min under nitrogen atmosphere. A 1.0 mL iron oleate precursor solution was injected, and after 0.5 h, a certain amount of chloroform and ethanol were added and centrifuged at 3000 g for 10 min. Finally, the precipitate was redispersed in chloroform to obtain FeSe-QDs.

2.3. Fabrication of MIP-FeSe-QDs

MIP-FeSe-QDs for CYF were synthesized by the modified reverse micro-emulsion method. A total of 40.0 mg of AIBN and 1.8 mL of Triton-X 100 were dissolved in 7.5 mL of cyclohexane in a two-necked flask and stirred for 15 min at 200 rpm. Subsequently, 400 µL of QDs (1 nmol), 50 µL of TEOS, and 100 µL of ammonia were sequentially added and the solution was stirred for 2 h. Meanwhile, the solution mixture containing 4.3 mg of CYF, 21.8 µL of APTES, 3.4 µL of MAA, and 38.1 µL of EGDMA were prepared by stirring for 2 h. Then, the mixture solution was poured into the two-necked flask and stirred for 2 h. Afterwards, the flask was immersed in a 60 °C water bath and allowed to react for 10 h. After polymerization, the MIP-FeSe-QDs were purified by adding 10.0 mL of acetone to the reaction mixture and centrifuged at 8000g for 10 min. After the supernatant was discarded, 6.0 mL of ultrapure water was added and centrifuged at 8000g for 20 min to remove the unreacted crosslinking agent and functional monomer. Finally, the template was removed with ethanol in acetonitrile (8:2, v/v) until the fluorescence value of MIP-FeSe-QDs was not changed as measured by a fluorescence spectrophotometer. Non-imprinted quantum dot materials (NIP-QDs) were simultaneously synthesized in the same process without the addition of template molecules.

2.4. Fluorescent measurements

Fluorescence measurements were performed using a F-4600 fluorescence spectrophotometer (Hitachi, Japan) equipped with a cuvette (1 cm × 1 cm). MIP-FeSe-QDs or NIP-QDs solution was added to the cuvette and mixed with a certain concentration of standard samples for 5 min, and then tested. The parameters for the detection of FL were as follows: the excitation wavelength was 365 nm, the emission wavelength was 450 nm, the slit widths of excitation and emission were both 5 nm, and the photomultiplier voltage was 350 eV. Generally, the determination was performed in triplicate to ensure the measurement accuracy.

2.5. Evaluation of MIP-FeSe-QDs selectivity

Under optimal conditions, the chemical analogs of CYF including BIF, DEL, CYP, and DEL at appropriate concentrations were applied to evaluate the selectivity of the obtained MIP-FeSe-QDs. Furthermore, the selective fluorescence quenching ability of MIP-FeSe-QDs was analyzed by comparing their fluorescence changes after adding different substances. Meanwhile, this system was evaluated by the Stern-Volmer fluorescence quenching equation: $F_0/F = 1 + K_{sv}[Q]$, where F_0 and F in the equation represent the fluorescence values before and after the addition of the quencher, K_{sv} is the quenching constant of the quenching equation, and Q is the concentration of the quencher (Xiao et al., 2016). The values of $\Delta F (F_0 - F)$ were calculated as a response function to evaluate the FL quenching characteristics. The specificity of the MIP-FeSe-QDs was evaluated by the competitive quenching method by fixing CYF concentration and increasing FEN concentration.

2.6. Sample preparation

Marine sediment samples were obtained from Ningbo offshore. The samples were freeze-dried for 24 h and ground. A total of 8 g of sediment samples were weighed and placed in a centrifuge tube; then, 1.0 g of copper powder and 15.0 mL of *n*-hexane in acetone (2: 1, v/v)

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