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A thin shell and "sunny shape" molecular imprinted fluorescence sensor in selective detection of trace level pesticides in river

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ABSTRACT

This investigation presented a novel strategy for the preparation of hybrid structure silica/ZnO/molecularly imprinted polymers (SiO_2/ZnO/MIPs) to fluorescence recognization and detection of the pyrethroids. Firstly, carboxylated SiO_2 nanoparticles (Si-NPs) and amino-functionalized ZnO quantum dots (QDs) were linked together by the function of amination under the assistance of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and 1-hydroxy-5-pyrrolidinedione (NHS). Next, the "sunny shape" molecular imprinted polymers (MIPs) layers were anchored on the surface of SiO_2/ZnO QDs by the technique of atom transfer radical polymerization (ATRP) and surface molecular imprinting. The resulting nanoparticles were characterized by TEM, FT-IR, fluorescence spectra and the adsorptive properties were detected by the UV–vis spectrophotometer. Through the results, the strategy shortened the preparation time and presented more rapid and sensitive detection performance than the traditional methods. The fluorescence detection results demonstrated this material owned special recognition property to the templates, which contributed that the fluorescence intensity decreased linearly with the variation of pyrethroids in the concentration range 1.0–80 μmol L^{-1} under the optimized conditions and the detection limit was 0.13 μmol L^{-1}. Moreover, the successful applications in practical samples indicated that the synthesis method in this investigation provided a novel way to the pyrethroids detection in river.

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1. Introduction

Recently, a myriad of pesticides such as carbamates, triazines, pyrethroids and other organophosphates were used to keep plants from disoperation of the insects and pests all over the world. The pesticides could effectively prevent and control the spread of insects and pests, but the long-term usage could cause a serious of contamination to the water, soil and a mass of agricultural products and eventually being harmfulness to a majority of biological species in the food chain including humans [1–3]. Among these pesticides, due to owing the excellent properties of the relatively low persistence under natural conditions and high effectiveness for insect pests eradication, pyrethroids were considered as a class of insecticides which were routinely used to control a wide range of plant diseases and insect pests in both agriculture and city [4,5]. According to the survey, pyrethroids not only could cause neurotoxicity and central nervous system intoxication, but also were considered to have endocrine-disrupting effects through dermal absorption or ingestion [6]. Hence, the sensitive and accurate detection of pyrethroids were regarded as the concerns of the public safety and environmental protection.

In the past decades, a large number of analysis and testing technology techniques, such as high-performance liquid chromatography (HPLC) [7], gas chromatography/mass spectrometry (GC/MS) [8], electrochemical analysis [9] and immunochips [10,11] were introduced into the detection of pyrethroids in the water environment and daily foods. These techniques made a certain progress in the detection of pyrethroids, but they all existing some problems. Such as required complicated operational program, expensive detecting costs and skilled manpower, so it was considered that

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these drawbacks would restrict the evolution of pyrethroids detection. Hence, developing an effective method for rapid and sensitive detection of trace pyrethroids in daily foods and drinking water had become a great challenge.

In recent years, quantum dots (QDs) acted as the semiconductor fluorescence sensors had drawn attractive attention in the field of chemical and biological substances detection [12,13]. The QDs owned significant advantages, such as high luminescence efficiency, size-dependent emission wavelengths, narrow symmetric emission and excellent photostability [14,15]. However, traditional semiconductor QDs, such as CdS, CdTe, CdSe, contained toxicities and easily caused heavy metal pollution. Compared with the traditional semiconductor QDs, ZnO QDs acted as the novel fluorescence materials which owned some extra merits, such as environment-friendly, less expensive and biocompatible to the biological systems [16,17]. Moreover, ZnO QDs possessed high quantum yield, quantum size effects, broad absorption spectrum and narrow emission spectrum [18]. It was acknowledged well that ZnO QDs had been applied in many fields, such as live cell imaging, UV photodetector, drug delivery, gas sensors and solar cells [19–23]. Thanks to the unique optical and electrical properties, ZnO QDs gradually got wide attention [24–26] and could effectively solve the problems presented in the traditional semiconductor QDs. Taking these information into consideration, it was decided that use ZnO QDs into the pyrethroids fluorescence detection.

Fluorescence sensors owned the properties of sensitive detection [27], but these materials absented selectivity to the specific target molecules. To improve the specific selectivity of ZnO QDs-based fluorescence sensors, the molecularly imprinted polymers (MIPs) synthesized by molecular imprinting technique (MIT) were introduced to selective detection of environment pollutant [28]. More recently, MIPs were gradually developed as a splendid mimetic materials owned specific recognition cavities which were complementary in chemical and geometrical to the target molecules [29–31]. Generally, MIPs were prepared by the copolymerization of functional monomers and cross-linkers in the presence of template molecules [32] and there would be specific recognition cavities formed which could be complemented to the template molecules in the size, shape and functionality after removing the templates [33]. However, the traditional imprinted materials owned lots of disadvantages, such as they had to be crushed, ground and sieved to obtain the desired particles. To overcome these disadvantages, surface molecular imprinted technique (SMIT) had been introduced, which fabricated and assembled specific binding sites on the surface or in the proximity of materials to improve mass transfer and reduce permanent entrapment of the template [34]. Moreover, compared with the traditional radical polymerization, atom transfer radical polymerization (ATRP) had been presented as a novel imprinting technology to improve the imprinting properties of MIPs. It was based on the successive transfer of halogen atom from initiator to the monomer and to the polymer chain. This process was catalyzed by a transition-mental complex which could mediate the propagation [35]. This technique presented the advantages in the synthesis of predictable molecular weights, low polydispersities and specific functionalities. Furthermore, many kinds of initiators, catalysts and monomers could be utilized in this process [36]. Recently, ATRP had successfully used into the preparation of surface-imprinted polymers, MIP nanotube membranes and microspheres [37].

Herein, in this investigation, a highly selective and sensitive fluorescence sensor was first prepared in relatively moderate temperature (50 °C) and was used into pyrethroids detection in the river. The SiO_2/ZnO/MIPs were prepared by two steps. Firstly, the ZnO QDs were anchored on the surface of SiO_2 and they were fabricated by ethyl-2-bromoisobutyrate (EBiB), which could let the polymerization occur on the surface of SiO_2/ZnO QDs. Secondly, it was combined the SMIT and the ATRP technique, under the existence of cyhalothrin (LC), acrylamide (AM), divinylbenzene (DVB), 2,2′-Bipyridyl and cuprous chloride (CuCl) to prepare "sunny shape" fluorescence sensor for the pyrethroids detection at ultra-trace level (μmol L^{-1}). The characterization, adsorption capacity, fluorescence stability, fluorescence sensitivity and selectivity of the sensor were investigated in detail. Also, the performance of the sensor for the extraction of LC in the river sample was assessed. By integrating fluorescence detection with the universal sample preparation process, the demand for a rapid, sensitive and specific LC detection from river samples can be fulfilled.

2. Experimental section

2.1. Chemicals and reagents

Cyhalothrin (LC), cyfluthrin (BC), fenvalerate (FE) and bifenthrin (BI) were purchased from Yingtianyi standard sample company (Beijing, China). Zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$), potassium hydroxide (KOH), acrylamide (AM), divinylbenzene (DVB), succinic anhydride (SA), ethyl-2-bromoisobutyrate (EBiB), tetramethoxysilane (TEOS), ammonium hydroxide ($NH_3 \cdot H_2O$), triethylamine (TEA), 2-morpholino-ethanesulfonic acid (MES), 1-hydroxy-5-pyrrolidinedione (NHS), 3-Aminopropyltriethoxysilane (APTES) were obtained from Aladdin-reagent (Shanghai, China). 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and 2,2′-Bipyridyl were obtained from Macklin (Shanghai, China). Cuprous chloride (CuCl), methanol, ethanol, *N*,*N*-Dimethylformamide (DMF) and toluene were received from Sinopharm Chemical Reagent (Shanghai, China). All chemicals used were of analytical grade. Ultra-pure water was used for preparing all aqueous solutions and cleaning processes.

2.2. Apparatus

Transmission electron microscopy (TEM) images were recorded by a JEM-2100 (HR) electron microscope. Infrared spectra (4000-400 cm^{-1}) were collected on a Nicolet NEXUS-470 FT-IR apparatus (U.S.A.) using KBr disks. Fluorescence spectra were taken on a Cary Eclipase fluorescence spectrometer (USA). UV–vis adsorption spectra were carried out on a UV–vis spectrophotometer (UV-2450, Shimadzu, Japan).

2.3. Synthesis of Amino-Functionalized ZnO QDs

The process of synthesis of amino-functionalized ZnO QDs according to the suggestions in the literature [38] was separated into two-step procedures. Typically, in the first step, 1.0 mmol of $Zn(OAc)_2 \cdot 2H_2O$ was dissolved in 50 mL ethanol and the KOH solution was else prepared in the same time by dissolving 3.0 mmol of KOH in 8.0 mL of ethanol. Then, the obtained KOH solution was added drop by drop into the $Zn(OAc)_2$ solution and continued stirring for extra 6.0 h under the room temperature. The ZnO QDs were gathered by following centrifugation, washed with pure water and ethanol three times and dried in vacuum under the room temperature.

In the second step, the prepared ZnO QDs were aminated with APTES. 2.0 g ZnO QDs were dispersed into 50 mL anhydrous toluene solution. Under continuous stirring, 3.0 mL APTES solution was added into the ZnO QDs solution drop by drop and sealed vigorous stirring for 24 h under the temperature of 90 °C. The product was gathered by centrifugation and washed with absolute ethanol for several times to remove the unreacted materials. The final particles were dried in vacuum under the room temperature. These steps

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