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Turn-on sensor for quantification and imaging of acetamiprid residues based on quantum dots functionalized with aptamer

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ABSTRACT

In this paper, a novel turn-on sensor was constructed for quantification and imaging of acetamiprid. Acetamiprid aptamer-modified ZnS:Mn probe (ZnS:Mn-Aptamer) was obtained by conjugating ZnS:Mn QDs with acetamiprid binding aptamer. The fluorescence of the probe was turn off by multi-walled carbon nanotubes (MWCNTs) based on fluorescence resonance energy transfer (FRET) between ZnS:Mn-Aptamer and MWCNTs. After acetamiprid was introduced, the fluorescence was turn on because ZnS:Mn-Aptamer specifically binded with acetamiprid. Based on the above-mentioned principle, the quantitative detection and imaging of acetamiprid in real samples were achieved. The linear equation could be described as $F/F_0 = 1.101 + 0.0312C_A$ (C_A represented the concentration of acetamiprid, nM) in a linear range of 0–150 nM with a detection limit of 0.7 nM. The results suggested this method had remarkable sensitivity, selectivity, and was very simple without complex operation. Meanwhile, this novel turn-on sensor has the potential of in situ visual determination for pesticide residues in complex system.

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1. Introduction

Pesticides play an important role in agricultural production, but also inevitably lead to pesticide residues [1]. Ecotope and food safety problems caused by the pesticide residues have drawn the attention of the whole society in recent years [2,3]. Traditional detection methods of pesticide residues include chromatography, mass spectrometry [4–7], etc. However, these methods, which involve complex sample preparation and usage of expensive instruments, are not suitable for on-site [8] and visualization detection [9]. A sensitive, selective and speed method for in situ visible determination of pesticide residues has application prospect towards on-site assay of food safety.

There were abundant reports on detection of pesticide residues content by chromatography and mass spectrometry, while few were reported on visual detecting methods of pesticide residues [10]. Among these few methods, UV–vis absorption [11,12] and fluorescence spectrophotometry [13–15] were used. Yan et al. [16] reported the photoluminescence (PL) intensity of CdTe quantum dots (QDs) was quenched by Au nanoparticles (NPs). Acetamiprid could adsorb on the surface of Au NPs, which could induce the aggregation of Au NPs accompanying color change from red to blue, and the PL intensity of QDs recovered accordingly. The detection method of acetamiprid was established with a detection limit of 75 nM. Not only acetamiprid, all micromolecules containing cyano or other groups which could coordinate to Au NPs could be detected. Zhang et al. [17] demonstrated that dithizone which was coordinated with cadmium of CdTe QDs surface could strongly quench the emission of CdTe QDs. Upon the addition of organophosphorous pesticides with a P═S bond, the dithizone ligands on the CdTe QD surface were replaced by the hydrolyzate of organophosphorous pesticides, and the fluorescence was turned on, thus total content of various organophosphorous pesticides was detected.

Aptamer is single-stranded DNA or RNA. It can specifically bind to various targets. Ensafi et al. [18] described a fluorimetric aptasensor and applied it for determination of ars. Wang and Si [19] developed a aptamer biosensor to detect Hg^{2+}, Ag^{2+} and Pb^{2+} in homogeneous solution. In recent years, aptamer was used to analyzed pesticides. Shi et al. [20] used Au NPs whose surface absorbed acetamiprid binding aptamer to bind with their target acetamiprid specifically. when acetamiprid was added, Au NPs would aggregate and the colour was changed from red to purple blue. The detection of acetamiprid was realized with a detection limit of 5 nM.

The absorption spectrum of carbon nanostructures spans over a wide range of wavelengths, significantly overlapping with the

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fluorescence spectra of various fluorophores [21]. This allows fluorescence resonance energy transfer between them. Thus carbon nanostructures such as multi-walled carbon nanotubes can be used as fluorescence quenchers due to their strong π–π stacking interactions with double bond groups. Mn-doped ZnS (ZnS:Mn) QDs have excellent flourescent properties and lower toxicity than CdTe QDs, and aptamer can specifically identify various targets. But the fluorescence of ZnS:Mn-Aptamer probe is always turning on, and the targets detection will be influenced by excessive probes. Multi-walled carbon nanostructures can act as fluorescence quencher, thus the fluorescence is turned on only when analyte exists.

In this paper, ZnS:Mn QDs were synthesized by a hydrothermal process. With acetamiprid as the analyte, a fluorescence probe was designed by coupling acetamiprid binding aptamer with ZnS:Mn QDs. Multi-walled carbon nanotubes could turn off the fluorescence of the probe. After introduced into the system, acetamiprid binded with aptamer over ZnS:Mn surface, and the fluorescence was turned on. Thus, a biosensor based on "turn-on" mechanism was established for specific detection of acetamiprid (shown in Scheme 1). The detection limit of this method was as low as 0.7 nM. The method was simple and rapid without complex sample preparation. Excessive probes had no interference of background fluorescence. What is more, the sensor had good potential for on-site visual assay.

2. Material and methods

2.1. Materials and instruments

$ZnSO_4 \cdot 7H_2O$ was purchased from Sinopharm Chemical Reagent Co., Ltd. $MnCl_2 \cdot 4H_2O$, $Na_2S \cdot 9H_2O$, NaOH and NaCl were purchased from Damao Reagent (Tianjin, China). *N*-Hydroxysuccinimide (NHS) and 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC.HCl) were obtained from Aladdin. Multi-walled carbon nanotubes (MWCNTs), carbon dots (CDs) and graphene oxide (GO) were purchased from Xfnano materials technologh Co., Ltd. (Nanjing, China). The acetamiprid binding aptamer was purchased from Sangon Biological Engineering Technology & Co., Ltd. (Shanghai, China) with the following sequences: 5′-CTGAC ACCAT ATTAT GAAGA-3′ [22]. And the amine group was introduced in 5′ of aptamer. Mercaptopropionic acid (MPA) was purchased from Sigma–Aldrich. All reagents used were of analytical grade unless otherwise stated. All solutions were prepared with double-distilled water.

Fluorescence spectra were recorded using an F-2500 spectrofluorometer (Hitachi, Japan) with voltage of 400 V, slit of 5 nm and scanning speed of 300 nm/min. Infrared spectra were recorded using Prestige-21 FT-IR spectrometer (SHIMADZU, Japan). Transmission electron micrographs were carried out on TEM-2100HR microscope (JEOL, Japan). Dynamic light scattering (DLS) samples were characterized with Malvern Zetasizer Nano ZS nanometer particle size analyzer (Malvern, UK). Confocal fluorescence imagings were performed with a Nikon Digital Eclipse C1 plus Laser Scanning Confocal Microscope (Nikon, Japan).

2.2. Synthesis of ZnS:Mn-Aptamer probe

ZnS:Mn QDs were prepared according to previous methods with some modifications [23]. 5 mL of 0.1 M $ZnSO_4$ and 300 μL of MPA were dissolved in 40 mL double-distilled water and then transferred into a 100 mL three-necked flask. The mixed solution was adjusted to pH 10.8 with NaOH (2 M) and deaerated with N_2 bubbling for 10 min under stirring at room temperature. Then 0.15 mL of 0.1 M $MnCl_2$ was added with N_2 bubbling for 20 min and 5 mL of 0.1 M Na_2S was added by dropwise into the flask. The resulting solution was stirred accompanying by bubbling nitrogen for another 20 min and then kept in water bath at 50 °C for 12 h. Thus ZnS:Mn QDs were successfully obtained.

The obtained ZnS:Mn QDs were precipitated with the same volume of absolute ethanol, separated by centrifuging for 3 min at the speed of 12,000 r/min, washed with absolute ethanol 3 times, and finally dried in vacuum.

0.4 mg of ZnS:Mn QDs modified by MPA were dispersed in 2.5 mL of PBS buffer (pH 7.2). 20.9 μL of 0.1 M EDC and 20.9 μL of 0.1 M NHS were added into the solution and reacted for 30 min under stirring. Thereafter, 50 μL of acetamiprid binding aptamer was added and the mixture was stirred gently for 12 h at room temperature. The resulting solution was put in the refrigerator to impede further reaction and dialyzed (MWCO: 3500 Da) to remove redundant reactants. Finally, the probe modified with acetamiprid binding aptamer was obtained and kept at 4 °C in the refrigerator. The conjugation rate of the aptamer in QDs-aptamer was about 1.6% which was measured by thermogravimetry analysis.

2.3. Synthesis of hydrosoluble carbon nanotube

Hydrosoluble carbon nanotubes were prepared as indicated in a previous study [24]. Briefly, 0.2 g of multi-walled carbon nanotubes were dissolved in 50 mL of mixed acid (the volume ratio of concentrated HNO_3 to H_2SO_4 was 3:1), followed by sonicated for 0.5 h. Then the mixture was refluxed at 80 °C for 6 h, filtered with 0.22 μm filter membrane, washed repeatedly with ultrapure water until pH neutral, and finally dried in vacuum at 60 °C for 24 h. Thus the MWCNTs modified with carboxyl groups were acquired. 10 mg of the modified MWCNTs were dissolved in 10 mL of ultrapure water. A black aqueous solution was acquired, and the concentration of MWCNTs was 1 mg/mL.

2.4. Quantification and imaging of acetamiprid residues

The linear working plot was described as follows: 3.0 mL of ZnS:Mn-Aptamer (0.16 mg/mL), 1 mL of PBS buffer (pH 7.2) and 200 μL of MWCNTs (1 mg/mL) were added into a series of colorimetric tubes, mixed uniformly and placed statically. After 15 min, the fluorescence intensity (F_0) was recorded. Then acetamiprid standard solutions at a series of concentrations were added, mixed uniformly and diluted accurately to 5.0 mL with double-distilled water, finally placed statically. After 40 min. the fluorescence intensities (F) of the resulting solutions were determined. The linear relationship was formulated with the fluorescence intensity change (F/F_0) and the acetamiprid amount (C_A). All the fluorescence spectra were recorded at $\lambda_{ex}/\lambda_{em}$ = 310/580 (nm).

Pearl river water (Guangzhou, China) and Chinese cabbage leaves were chosen as the samples to evaluate the probe for the quantitative detection of acetamiprid residues in actual samples. Water samples were treated as follows: Pearl River water (45 mL) was filtered to remove insoluble impurities, then added with acetamiprid solution and diluted accurately to 50 mL. The extractions of leaves were obtained as follows: Chinese cabbage leaves (5 g) were cut into small pieces and sprayed by acetamiprid solution. Then the leaf pieces were air-dried and extracted with 20 mL of acetonitrile for 10 min under ultrasonic conditions (KQ-300DE, 500 W, 40 kHz). Finally the extractions were filtered with 0.22 μm microporous membrane.

The samples were also performed following the same procedure as describing linear working plot above. 10.0 μL of water samples (the final spiked concentrations were 0, 40, 90 nM) or leaf extractions (the final spiked concentrations were 0, 40, 90 nM) were added instead of acetamiprid standard solutions. The resulting fluorescence enhancement (F/F_0) was determined, and the acetamiprid

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