



Aptamer-based colorimetric sensing of acetamiprid in soil samples: Sensitivity, selectivity and mechanism



Huijie Shi^a, Guohua Zhao^{a,b,*}, Meichuan Liu^{a,b}, Lifang Fan^a, Tongcheng Cao^{a,b}

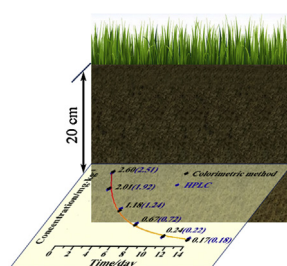
^a Department of Chemistry, Tongji University, Shanghai 200092, PR China

^b Key Laboratory of Yangtze River Water Environment, Ministry of Education, Tongji University, Shanghai 200092, PR China

HIGHLIGHTS

- A simple, sensitive and selective colorimetric detection of acetamiprid is achieved.
- ABA is employed as recognition element and improves the selectivity remarkably.
- High selectivity comes from the specific interaction between acetamiprid and ABA.
- Acetamiprid detection in real soil samples exhibits good reliability and stability.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and selective aptamer-based colorimetric method was developed for highly sensitive detection of acetamiprid, taking advantages of the sensitive target-induced colour changes that arise from the interparticle plasmon coupling during the aggregation of Au nanoparticles (NPs). The results showed that the established method could be applied to detect acetamiprid in the linear range between 75 nM to 7.5 μ M, with a low detection limit of 5 nM. Meanwhile, by employing an “artificial antibody” acetamiprid-binding aptamer (ABA) as recognition element, highly selective and specific colorimetric visualization of acetamiprid was obtained. It indicated that pesticides which may coexist with acetamiprid could not interfere with the detection of acetamiprid even that had similar structure with acetamiprid, such as imidacloprid and chlorpyrifos. Mechanism study suggested that it could be attributed to the specific supramolecular interaction between ABA and acetamiprid, as well as the resulted target-binding event induced conformation changes of ABA from random coil to hairpin structure. The practical application of the colorimetric method was realized for detecting acetamiprid in real soil samples and monitoring its natural degradation process.

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1. Introduction

Acetamiprid is a kind of systemic and contact insecticide which belongs to the chloronicotine class. It is widely used as replacement insecticide of organophosphorus and other conventional insecticides to control sucking-type insects on leafy vegetables, fruits

and tea trees by acting as the agonist of the nicotinic acetylcholine receptors (nAChRs) of the postsynaptic membrane of nerve cells and inhibiting the normal conduction of central nerves [1]. Although it is noted as relatively low acute and chronic mammalian toxicity, acetamiprid released in the surface or ground water and accumulated in the soil will still cause potential risk of human health exposed to the contaminated environment, owing to its frequent and extensive usage [2–4]. Therefore, development of a highly sensitive and selective analytical method for acetamiprid determination is significant to keep people from potential health risk. Many analytical methods including liquid chromatography

* Corresponding author at: Department of Chemistry, Tongji University, Shanghai 200092, PR China. Tel.: +86 21 65981180; fax: +86 21 65982287.

E-mail address: g.zhao@tongji.edu.cn (G. Zhao).

(LC) [5], gas chromatography (GC) [6,7], and high performance liquid chromatography (HPLC) [8,9] have been established for detecting acetamiprid. Although with distinct advantages, these methods also suffer from its own limitations such as complex sample preparation, and usage of large and expensive instruments. As a result, looking for a more simple and sensitive method for fast and convenient acetamiprid determination is meaningful and has application prospect for practical environmental monitoring.

As we all know, colorimetric method is a kind of direct and sensitive strategy with theoretical simplicity and low technical demands which makes use of the sensitive colour change that arises from the interparticle plasmon coupling during the aggregation of Au nanoparticles (NPs) [10,11]. It has been successfully applied for detecting a large variety of targets, such as nucleic acids [12], proteins [13], small molecules [14], and metal ions [15]. So we are considering developing a colorimetric method to detect acetamiprid simply and sensitively. However, this work is still challenging because that a simple colorimetric method lacks of selectivity, which makes it not suitable for the selective detection of acetamiprid in a complex sample environment. It is because that nowadays the contaminants in water have presented the characteristics of low concentration and species diversity, and acetamiprid always coexist with other contaminants. Many molecules such as that containing N, S atoms, would interact with Au NPs and induce Au NPs aggregation, leading to severe interferences on the colorimetric detection.

The so-called “artificial antibody” aptamers are single-stranded DNA or RNA sequences obtained from *in vitro* selection technique named systematic evolution of ligands by exponential enrichment (SELEX) [16], which can bind their target molecule with high affinity, specificity and selectivity. They not only have found important application in the areas of therapy, drug discovery, and target validation [17], but also have been widely applied as recognition elements in sensors for various targets such as proteins [18], toxins [19], and bio-related small molecules [20]. Meanwhile, the aptamers possess a variety of other advantages, including their small size, easier artificial synthesis and modification, as well as chemical robustness compared to the well-known antibodies [17,21]. Therefore, we attempt to use aptamer as recognition element to achieve the selective functionalization of Au NPs, and consequently a selective colorimetric sensing method would be achieved. However, it is worth noting that the application of aptamers as recognition elements in the sensors for pesticides residue detection is still limited and the number of aptamers selected for the pesticides is not enough in comparison to the demand. Recently, an aptamer for acetamiprid (denoted as S18 in the paper) is newly selected [22] which shows excellent recognition ability to acetamiprid. In this work, a 20mer A- and T-rich sequence of S18 which is stated as the “target-binding region” of S18 [22] for acetamiprid was applied as the recognition element (acetamiprid binding aptamer, ABA) considering the ease of chemical synthesis and low cost. By combination of the colorimetric method with the selectivity of the aptamer, it is believed that a highly selective and simple colorimetric method can be obtained, which will be adaptable for the selective detection of acetamiprid.

Thus, in the present work, a highly sensitive and selective colorimetric method was established employing unmodified Au NPs as optic probes and ABA as recognition element for convenient acetamiprid detection. Utilizing the specific supramolecular interaction between ABA absorbed on the Au NPs surface and acetamiprid of different concentrations, the electrostatic repulsion between Au NPs was well adjusted, leading to different extent of Au NPs aggregation, by which the acetamiprid was conveniently quantified. The detection conditions such as the concentration of aptamer and salt (NaCl in this work) and incubation time are carefully optimized and controlled in order to obtain the best sensitivity

and selectivity. Furthermore, the mechanism of the highly selective colorimetric performance as well as the selective binding ability of ABA towards different pesticides is investigated in detail by monitoring the UV absorption and circular dichroism changes of ABA upon binding of different kinds of pesticides. The established colorimetric method has also been applied in the detection of acetamiprid in real soil samples in order to monitor the natural degradation process of acetamiprid, and satisfactory results have been obtained. This work will provide meaningful information for understanding the specific interaction between the aptamer and the target, along with the conformation changes in the target-binding event, and is helpful for the construction and application of aptamer-based analytical methods in environmental monitoring.

2. Experimental

2.1. Chemicals and apparatus

All the chemicals were commercially available as analytical reagent grade and used as received unless otherwise stated. Chloroauric acid (50% Au basis) was obtained from Adamas Reagent Co., Ltd. Acetamiprid (99%) was purchased from Aladdin Chemistry Co. Ltd. The 20-mer acetamiprid-binding aptamer (ABA) with the sequence of 5'-CTGAC ACCAT ATTAT GAAGA-3' was adopted from the literature [22] and synthesized by Genscript Biotechnology Co. Ltd. (Nanjing, China) and purified by the method of PAGE. The concentration of ABA was determined by measuring the UV absorption at 260 nm with an extinction coefficient of $204,600 \text{ M}^{-1} \text{ cm}^{-1}$. All the solutions were prepared by double distilled water.

UV-vis spectroscopy (Agilent 8453, USA) was used to record the alteration of the localized surface plasmon resonance (LSPR) properties of Au nanoparticles under different conditions as well as the interaction between ABA and different pesticides. High resolution transmission electron microscope (JEM-2100, Japan) was applied to characterize the morphology changes of Au NPs in the absence and presence of acetamiprid. The colour change of Au NPs was photographed by a domestic digital camera (Panasonic DMC-FX2, Japan). The secondary structure changes of ABA under different conditions were monitored by a Circular Dichroism Spectropolarimeter (Jasco J-715, Japan) over the wavelength range from 220 to 300 nm and the scanning speed was 200 nm/min. 10 mM Tris buffer containing 10 mM NaCl and 5 mM MgCl_2 was used to control the acidity and ionic strength in the investigation of the interaction between ABA and acetamiprid as well as other pesticides.

2.2. Synthesis of Au NPs

Au NPs of 13 nm was prepared according to the literature [23] and used as optic probe considering its sensitive SPR and colour changes from dispersion to aggregation state. Briefly, 50 ml of 1 mM HAuCl_4 aqueous solution was heated to boiling under stirring. Then 5 ml of 38.8 mM trisodium citrate was added rapidly and the solution remained boiling for another 30 min. Then, the solution was cooled to room temperature slowly, and filtered with 0.22 μm filter membrane. The Au NPs was diluted to 5 nM and stored in an Amber Laboratory Bottle and kept under 4 °C in the refrigerator. The diameter of the Au NPs synthesized was about 13 nm according to the result of TEM (not shown). The concentration of Au NPs was determined according to the UV-vis absorption at 520 nm with the extinction coefficient of $2.7 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ for 13 nm nanoparticles [24].

2.3. Colorimetric detection of acetamiprid

For acetamiprid determination, a general procedure could be described as follows. 28 μL acetamiprid solution of different

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