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Fabricating a novel label-free aptasensor for acetamiprid by fluorescence resonance energy transfer between NH_2-$NaYF_4$: Yb, Ho@SiO_2 and Au nanoparticles

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ABSTRACT

Rare earth-doped upconversion nanoparticles have promising potential in the field of pesticide detection because of their unique frequency upconverting capability and high detection sensitivity. This paper reports a novel aptamer-based nanosensor for acetamiprid detection using fluorescence resonance energy transfer (FRET) between NH_2-$NaYF_4$: Yb, Ho@SiO_2 (UCNPs) and gold nanoparticles (GNPs). Herein, GNPs as acceptors efficiently quench the fluorescence of UCNPs and acetamiprid specifically interacts with acetamiprid binding aptamer (ABA), causing the conformation changes of ABA from random coil to hairpin structure. Accordingly, ABA no longer stabilizes the GNPs in salt solution, leading to the varying aggregation extent of GNPs. Thus, the fluorescence of UCNPs are proportionally recovered. Under the optimized conditions, the enhancement efficiency was observed to increase linearly with the concentration of acetamiprid from 50 nM to 1000 nM, resulting in a relatively low limit of 3.2 nM. Additionally, the aptasensor demonstrated high selectivity to similar structure pesticides such as imidacloprid and chlorpyrifos, and further confirmed its application capacity in adulterated tea samples.

1. Introduction

Pesticides have emerged as an indispensable component of modern crop management practices as they are believed to improve the nutritional value of food and minimize the loss in agricultural productivity caused by insects and pests. During the past decades, a myriad of pesticides including diverse classes of organophosphates, pyrethroids, and neonicotinoids have been used to protect crops from insect infestation (Kumar et al. 2015; Pabudi et al. 2014). In particular, acetamiprid (AC), a chloropyridinyl neonicotinoid, is widely used in agriculture and garden markets for its low toxicity and high insecticidal activity. They act as potent agonists on the level of neurotransmission of the insects by blocking the receptors on postsynaptic membranes to cause the paralysis or the death of the insects (Jeschke et al. 2010; Zbiljić et al. 2015). However, pollution from the uncontrolled use of acetamiprid could also lead to dangerous levels of residues in food, or even the exposure of non-target organisms. Considering the extensive application and toxicological impacts of acetamiprid, there is a need for developing a method for acetamiprid determination and removal. Different analytical approaches have been used for acetamiprid residue detection, such as high performance liquid chromatography (Xie et al. 2011), gas chromatography (Zhang et al. 2008), liquid/gas chromatography–mass spectrometry (López-Fernández et al. 2015), enzyme-linked immunosorbent assays (Eiki et al. 2006). Nevertheless, all the above mentioned classic methods have the demerits of multi-steps pretreatment of samples, time-consuming immobilizing processes, laborious synthetic procedures and sophisticated instrumentations, which outweighs the merits of high precision and selectivity. Thus, developing a more simple and sensitive method for acetamiprid determination is meaningful in food monitoring.

Aptamers are DNA or RNA sequences selected in vitro through a systematic evolution of ligands by exponential enrichment (SELEX), which can be sensitive to target molecule with high affinity, specificity and selectivity binging (Mairal et al. 2014). They have raised considerable attentions due to their superior characteristics and promising prospect. Especially, the nature of easy structure-controlled design, cost-effectiveness, and good stability during long-time storage make aptamer an ideal recognition element in acetamiprid determination. Generally, aptamer-based analytical strategies for the sensitive and selective sensing of acetamiprid rely on signal transductions of fluorescence, colorimetry, electrochemistry, and so on (Guo et al. 2015; Shi et al. 2013; Xu et al. 2011, 2015). These methods emerge with the advantages of reliable, simple instruments, easiness for

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operation, but they are still limited by their own drawbacks. For example, organic dyes used in the colorimetric assays are subject to photobleaching, photodamage and autofluorescence issues; Quantum dots (QDs), which are widely used in the fluorescence detection, remain concerns for background autofluorescence and biological applications, which are caused by the shorter excitation wavelength for nanoparticles exciting and the heavy metal components in them (Long et al. 2015).

Recently, rare earth (RE)-doped upconversion nanoparticles have aroused considerable attentions for their unique upconverting capabilities. These nanoparticles can convert a long wavelength radiation (e.g. near-infrared light) to a short wavelength fluorescence (e.g., visible light) via a two-photon or multiphoton mechanism (Dong et al. 2012; Wang et al. 2010). Hence, compared to the traditional fluorescent labels, the rare earth-doped upconversion nanoparticles possess several advantages, such as long fluorescence lifetimes, low photobleaching, high quantum yields, narrow emission peak, and large stokes shifts. Furthermore, their low toxicities, high chemical stability, and tunable optical property by varying lanthanide dopants make such nanoparticles suitable for fluorescence labeling (Long et al. 2015; Wang et al., 2011). Up to now, the feasibility of biological detection using different schemes with upconversion nanoparticles have been reported with remarkable results (Long et al. 2015; Wang et al. 2013; Wu et al. 2013a, 2013b). However, most of them are chemical bonding demanded and multi-residue analytical approaches with complex sample processes. Few studies have reported regarding to aptamer-based upconversion nanosensors that overcoming the stated limitations.

This study attempted to quantify acetamiprid in food using a novel label-free aptamer-based upconversion nanosensor with fluorescence resonance energy transfer (FRET) between NH_2-$NaYF_4$: Yb, Ho@SiO_2 (UCNPs) and gold nanoparticles (GNPs). As seen in Scheme 1, utilizing the specific supramolecular interaction between acetamiprid binding aptamer (ABA) that are absorbed on the GNPs surface and varying concentrations of acetamiprid, the electrostatic repulsion between gold nanoparticles was well adjusted, resulting in different aggregation states of GNPs in salty solution. Accordingly, FRET was proportionally inhibited and the fluorescence intensity of UCNPs linearly recovered with the concentration of acetamiprid. The specific procedures are outlined as follows. (1) The preparation of functionalized upconversion nanoparticles and the synthesis of gold nanoparticles. (2) The setup of an upconversion fluorescence spectrometer. (3) The fabrication and optimization of the novel aptamer-based upconversion nanosensor. (4) The tests of independent food samples.

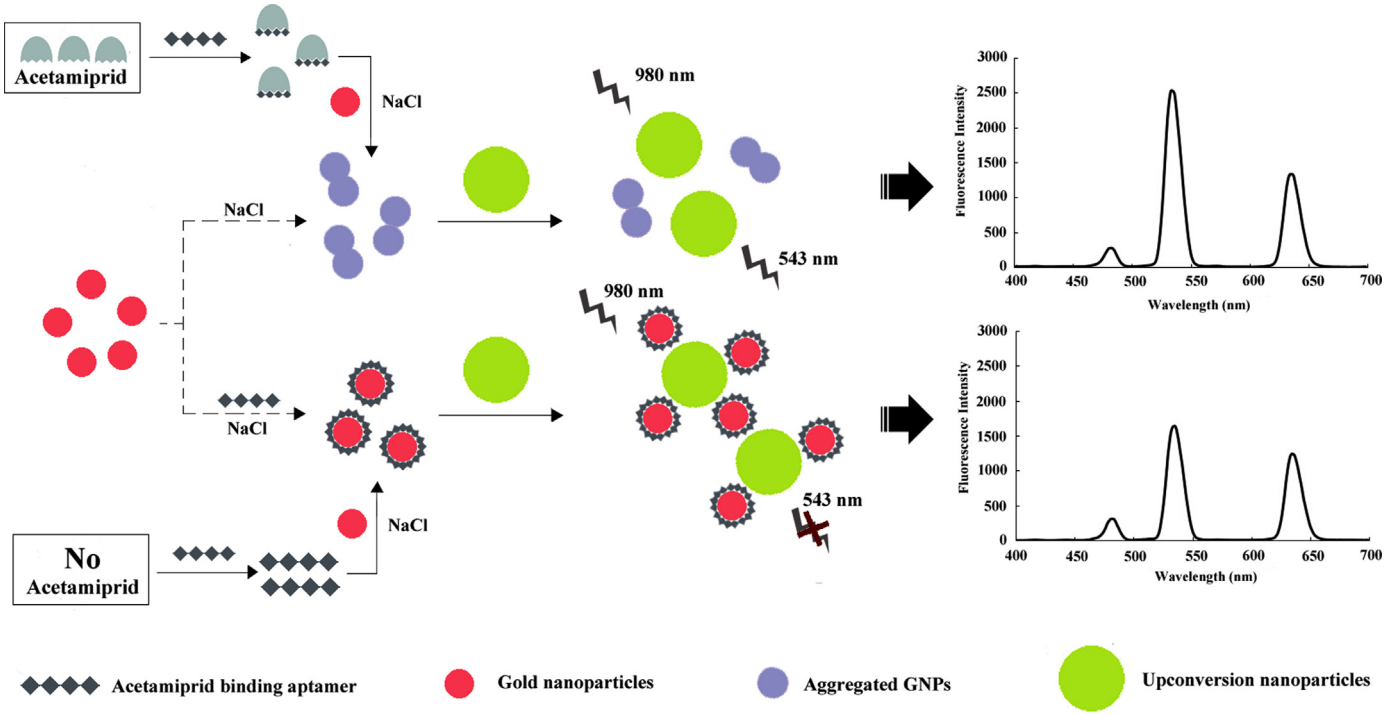
2. Experimental sections

2.1. Materials

Rare-earth metal chloride hydrates used in this work, including Yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$), Ytterbium (III) chloride hexahydrate ($YbCl_3 \cdot 6H_2O$), and Holmium chloride hexahydrate ($HoCl_3 \cdot 6H_2O$), were purchased from Aladdin (Shanghai, China), and used without further purification. Chloroauric acid ($HAuCl_4$) and sodium citrate tribasic dihydrate were obtained from Sinopharm Chemical Reagent (Shanghai, China). The 20-mer acetamiprid-binding aptamer (ABA) with the following sequence: 5′-CTGAC ACCAT ATTAT GAAGA-3′ was adopted from the literature (He et al. 2011) and purchased from Sangon Biotech Co.,Ltd (Shanghai, China). The concentration of ABA was determined by measuring the UV absorption at 260 nm with an extinction coefficient of 204,600 $M^{-1}\,cm^{-1}$. All the other chemicals were commercially available as analytical reagent grade and Millipore Milli-Q ultrapure water was used throughout the experiments.

2.2. Apparatus

Transmission electron microscopy (TEM) images were taken with the JEOL 2100 TEM (TEM, JEOL, Ltd.). The crystalline phases of UCNPs were characterized by the Rigaku 2500 X-ray diffractometer (Bruker AXS Ltd.). Fourier transform infrared spectra (FT-IR) with the wavenumber range of 4000–500 cm^{-1} were collected by the Nicolet Nexus 470 Fourier transform infrared spectrophotometer (Thermo



Scheme 1. Schematic representation of the UCNPs–GNPs fluorescence aptamer-based nanosensor for the detection of acetamiprid.