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Analytical Methods

Gold-nanoparticle-based fluorescent "turn-on" sensor for selective and sensitive detection of dimethoate

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ABSTRACT

A simple approach to fabricate a highly selective and sensitive dimethoate probe was developed based on Rhodamine B (RB)-functionalized gold nanoparticles (AuNPs). The quenching of RB fluorescence in the presence of AuNPs in the solution, mediated by fluorescence resonance energy transfer, was observed. In the presence of dimethoate, the fluorescence intensity of the RB-AuNP solution is gradually recovered when dimethoate molecules displace RB molecules on the surface of the AuNPs, which significantly increased the fluorescence intensity of RB. Fluorescence is proportional to the dimethoate concentration in the range of 0.005–1.0 ppm ($R^2 = 0.989$), and the LOD was 0.004 ppm. The recoveries of dimethoate in water and fruit samples were 86–116% with a good RSD (< 9.3%). Because of its high sensitivity, excellent selectivity, and convenient fabrication process, this method is a promising candidate for dimethoate screening.

1. Introduction

Modern agriculture depends heavily on the use of agrochemicals, which include different organic toxic compounds to control insects, fungi, bacteria, weeds, nematodes, rodents, and other pests and to maximize the potential harvest (Chang, Hsieh, & Chiu, 2016; Handford, Elliott, & Campbell, 2015; Jeschke, 2016). Among these agrochemicals, organophosphorus (OP) compounds have been used worldwide because of their low persistence and high insecticidal activity (Songa & Okonkwo, 2016). However, these compounds are toxic, mobile and capable of bioaccumulation. Long-term exposure to contaminated environmental samples such as food, water and soil is associated with serious ecological pollution and food safety issues (Kim, Kabir, & Jahan, 2017; Mostafalou & Abdollahi, 2017). OPs can inhibit the activity of acetylcholinesterase, which is an important enzyme that hydrolyzes acetylcholine and causes its accumulation in cholinergic clefts (Karami-Mohajeri & Abdollahi, 2013; Lockridge, Norgren, Johnson, & Blake, 2016). Excessive acetylcholine can cause serious impairment of the nerve function and potentially death. Therefore, developing a sensitive and inexpensive detection method to monitor OPs in environmental and biological samples is important.

To date, several methods based on various chemical or biological mechanisms, e.g., liquid or gas chromatography with mass spectrometry, electrochemical analysis, and fluorescent probes, have been used to analyze and detection of OPs (Hassani et al., 2017; Kumar, Kim, & Deep, 2015; Sharma, Nagpal, Pakade, & Katnoria, 2010). These methods are highly selective, sensitive, and reliable. However, most of these methods have limitations such as high cost, time-consuming nature, and requirement of expensive instruments, complicated operation procedures, tedious sample pretreatment, and expertise. Therefore, the development of a simple, facile, sensitive, selective, and reliable method to detect OPs is in high demand.

Nanoparticles, particularly gold nanoparticles (AuNPs), are attractive materials in sensing applications for various target species because of their unique size-dependent optical and electronic properties (Priyadarshini & Pradhan, 2017; Wang, Lin, Su, & Tang, 2017; Yuan, Hu, Chang, & Lu, 2016). To date, AuNPs have been used as ideal color reporters for colorimetric sensors (Bai et al., 2016; Dar, Walia, & Acharya, 2016; Kailasa & Rohit, 2017; Wen et al., 2016; Wu, et al., 2017). The high molar extinction coefficients (up to $10^8\,M^{-1}\,cm^{-1}$) and broad adsorption spectra enable AuNPs to act as quenchers through efficient energy- and/or electron-transfer processes between fluorescent molecules and AuNPs (Huang & Chang, 2006). Chromophore-functionalized AuNPs have been used in fluorescence "turn-on" sensing systems to detect various analytes based on the fluorescence resonance energy transfer (FRET) between fluorescent dyes and AuNPs (Cai, et al., 2011; Wang, Wang, Zhang, & Chen, 2015; Xu, et al., 2014; Xu, Yu, Hu, Chen, & Shao, 2016). Recently, a highly sensitive turn-on fluorescence method to detect clenbuterol in swine feed using Rhodamine B (RB)-functionalized AuNPs as the probes has been reported (Xu et al., 2014).

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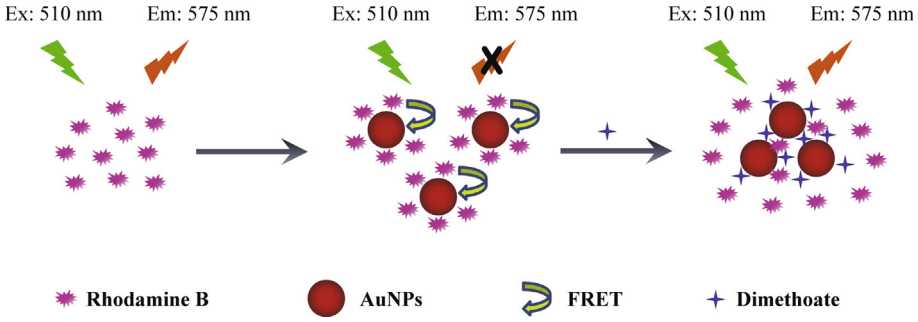

Scheme 1. Schematic of the fluorescent assay for dimethoate detection based on RB-AuNPs.

A chromophore-modified AuNP sensor to detect thiols in aqueous solutions based on the modulation of fluorescence between the chromophore and AuNPs has also been developed (Xu et al., 2016). This sensor was successfully applied to monitor and image intracellular thiols in HeLa cells.

In this study, a highly selective and sensitive turn-on fluorescent assay method has been designed to detect dimethoate in water and fruit samples based on the modulation of the fluorescence quenching efficiency between the RB chromophore and AuNPs in the presence of dimethoate (Scheme 1). The dimethoate molecules compete with RB molecules to adsorb on the surface of AuNPs, which induces further aggregation of AuNPs. Therefore, the fluorescence of RB is restored because of the FRET processes. Based on this strategy, dimethoate can be easily and sensitively detected. Moreover, the designed detection system can be applied to determine dimethoate in water and fruit samples.

2. Experiment

2.1. Materials

Sodium tetrachloroaurate(III) dehydrate (99%), dimethoate, thiodicarb, acetamiprid, methomyl, imidacloprid, dicofol, bendiocarb, trichlorfon, monocrotophos, chlorpyrifos, metolcarb, pirimicarb, dichlorvos, and propoxur were obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium tetraborate (98%) was obtained from Acros Organics (Geel, Belgium). Sodium citrate was obtained from J.T. Baker (Phillipsburg, NJ, USA). RB was obtained from Tokyo Chemical Industry (Tokyo, Japan). Lake water samples were collected from the University Lake at the National Taitung University. Tangerine, lemon, bamboo shoot, Formosan lambsquarter, rice, and green tea leaf samples were purchased from a local supermarket. All chemical reagents were of analytical reagent grade and used without further purification. Deionized (DI) water was used to prepare all aqueous solutions.

2.2. Apparatus

All optical measurements were performed at 25 °C under ambient conditions. The fluorescence and absorption spectra were recorded using an F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) and a Lambda EZ210 spectrophotometer (Perkin Elmer, USA), respectively. The IR spectra were obtained using an FT-IR spectrometer with an attenuated total reflection attachment in the range of 500–4000 cm^{-1} (Perkin Elmer, USA). Dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano ZS90 particle size analyzer (Malvern Instruments Ltd., Worcestershire, UK). Transmission electron microscopy (TEM) measurements were conducted using a JEM-2100 transmission electron microscope (JEOL Ltd.).

2.3. Preparation of AuNPs

Monodispersed AuNPs were prepared in the presence of trisodium citrate by reducing $NaAuCl_4$, as described in the literature (Frens, 1973). An aqueous solution (50 mL) of $NaAuCl_4$ (1 mM) was brought to a vigorous boil in a round-bottom flask fitted with a reflux condenser under continuous stirring. Then, trisodium citrate (38.8 mM; 5 mL) was rapidly added to the solution, which changed the color from pale yellow to deep red. The solution was heated under reflux for 10 min and cooled to room temperature under continuous stirring. After cooling to room temperature, the solution was stored at 4 °C for further use.

2.4. Preparation of RB-functionalized AuNPs

A stock solution of RB (1 mM) was prepared in DI water. An aliquot of RB solution (1 mM; 10 μL) was added to a solution of AuNPs (4 mL) and sodium tetraborate buffer (10 mM; 5 mL) under stirring. The solution was equilibrated at ambient temperature for 30 min to ensure self-absorption of RB onto the surface of AuNPs. Finally, the newly synthesized RB-AuNPs were purified by centrifugation at 16,099*g* for 10 min to remove excess RB and redispersed in a tetraborate buffer (10 mM; pH 9.2). The prepared RB-functionalized AuNPs were stored at 4 °C for further use.

2.5. Detection of dimethoate

Samples of dimethoate solutions (100 μL), which contained dimethoate at different concentrations (0.01–10 ppm), were added to a sample of RB-AuNPs (900 μL) in a 1.5-mL tube, and the obtained mixtures were equilibrated at room temperature for 10 min. Each mixture was subsequently centrifuged at 16,099*g* for 10 min, and the supernatant was collected. The fluorescence profile of the supernatant was measured at an excitation wavelength of 510 nm, where both excitation and emission slits were set at 5 nm. The fluorescence intensities at 575 nm were recorded as F and F_0 in the presence and absence of dimethoate, respectively. The calibration curve for dimethoate was established according to the fluorescence recovery efficiency, which was monitored using $[(F - F_0)/F_0]$.

2.6. Sample pretreatment

All samples were analyzed by LC–MS/MS to confirm the absence of pesticides. The water samples were filtered through a 0.22-μm membrane and centrifuged at 16,099*g* for 10 min. The supernatant was collected and spiked with various concentrations (5 and 10 ppm) of dimethoate. The other samples were prepared using the QuEChERs extraction method (Rahman, et al., 2017). The whole sample matrices were chopped and homogenized before the preliminary test. 10*g* of the homogenized samples was accurately weighted in 50-mL centrifuge tubes followed by spike 200 μL of 5.0 ppm dimethoate and kept in a ventilation hood for 20 min. Then, 10 mL of acetonitrile, 4.0*g* of $MgSO_4$ and 1.0*g* of CH_3COONa were sequentially added. The mixtures were vigorously shaken and extracted for 1 min, and each solution was centrifuged at 3000*g* for 1 min. Next, 6 mL of the supernatant extract was transferred to another 15-mL centrifuge tube, which included 0.3*g*