



# A colorimetric sensor based on citrate-stabilized AuNPs for rapid pesticide residue detection of terbuthylazine and dimethoate

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## ABSTRACT

A new colorimetric sensor based on citrate-stabilized AuNPs was proposed for the rapid pesticide residue detection of both terbuthylazine (TBA) and dimethoate (DMT) with ultra-sensitivities and high selectivities. The detection mechanisms have been verified via FT-IR, UV-vis spectra, Zeta Potential, TEM and DLS. Under the optimized experimental conditions, 30 kinds of potential environmental pollutants have no interference on the TBA or DMT detection indicating the high selectivities of our AuNP-based colorimetric sensor. The limit of detections (LODs) of TBA and DMT by eye vision are respectively 0.3  $\mu\text{M}$  and 20 nM, and those based on calculation ( $3\sigma/S$ ) are 0.02  $\mu\text{M}$  and 6.2 nM, respectively. The minimum detectable concentrations of TBA or DMT are much lower than the maximum residue limit (MRL) regulated by the governments of EU and China. The linear relationships of the UV-vis spectrometry demonstrate that our AuNP-based colorimetric sensor can be used for the quantitative analysis of TBA in the range of 0.1–0.9  $\mu\text{M}$ , and DMT in the range of 1–40 nM. Finally, our AuNP-based colorimetric sensor is also verified to have a good practical applicability for TBA or DMT detection in the real environmental samples.

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## 1. Introduction

In the process of agricultural production, herbicides and insecticides are two special agricultural chemicals, and have been widely used to ensure the harvest [1–3]. Terbuthylazine (TBA) is a widely used pre- and post- bud herbicide, which is mainly used for the removal of broad-leaved weeds and annual weeds [4,5]. Dimethoate (DMT) is a member of the most common organic phosphorus insecticides (i.e. a group of broad-spectrum insecticidal agents). The DMT is widely used for treatment of plant diseases and insect pests [6,7]. However, TBA and DMT are the primary source of environmental pollution and food toxicity. They bring some nega-

tive effects to the safety and health of the people, and the situation continues to deteriorate [8,9]. In 2015, the European Union (EU) listed 74 pesticides (including the TBA and DMT) that have chronic toxicity to humans. The maximum residue limits (MRL) of TBA and DMT in water or food have been respectively regulated to 0.05 mg/kg and 0.02 mg/kg (i.e. 0.22  $\mu\text{M}$  for TBA and 87 nM for DMT) by the governments of EU and China (GB2763–2014) [10–12].

To ensure the food safety and protect the health of consumers, there have been lots of efforts to develop various strategies for the detection and quantification of TBA and DMT in environmental samples, such as gas chromatography (GC) [13–15], high performance liquid chromatography (HPLC) [16,17], fluorescence spectrometry [18,19] and other related technologies [20–22]. Although these methods have high sensitivity, many of them are complicated and time-consuming, require bulky instrumentation, and have to be performed by highly trained technicians. Moreover, these big instruments cannot be used on site for detection of real environmental samples.

Recently, noble metal-based nanomaterials have emerged as powerful tools for simple and rapid pesticide residue detection

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with high sensitivity and specificity, such as quinalphos insecticide, malathion and glyphosate [23–25]. However, there is little research reported on rapid pesticide residue detection of DMT based on the noble metal-based nanomaterials. Lang et al. developed a sensitive amperometric acetylcholinesterase biosensor based on gold nanorods (AuNRs) for the detection of DMT. This method is highly sensitive and the limit of detection (LOD) is 3.9 nM. However, the synthesis of the biosensor is cumbersome and the storage requires a high criterion (in dark and dry place at 0 °C) [26]. Dar et al. explored a colorimetric chemo-sensor based on gold nanoparticles (AuNPs), and obtained a linear relationship between the fluorescence intensity and DMT concentration, which could be used for the quantitative analysis of DMT. The LOD is 16.4 μM. But this method is based on fluorescence spectrometry, and cannot be used for on-site detection of real environmental samples [27]. Lodha's group proposed a facile strategy for preparing highly stable *p*-sulphonatocalix resorcinarene modified silver nanoprobe in aqueous media for DMT detection. Although the sensitivity is high with the LOD of 80 nM, only 6 kinds of pesticides were used as the interfering substances to clarify the specificity [28].

In addition, to the best of our knowledge, noble metal-based colorimetric nanosensor has not yet been reported for the rapid pesticide residue detection of TBA. Furthermore, it is rarely reported that one noble metal-based nanosensor could be used for colorimetric detection of two environmental pollutants.

In this study, we developed a new colorimetric sensor based on citrate-stabilized AuNPs, which could be used for the rapid pesticide residue detection of both TBA and DMT with ultrasensitivities and high selectivities. The schematic illustration is shown in Scheme 1.

The TBA detection is based on an aggregation mechanism (Scheme 1a). NaOH only play a role in regulating the pH of the detection solution for better recognition of TBA. Moreover, citrate-stabilized AuNP dispersions are stable incubated with NaOH (20 μL, 1.0 M). After addition of a mixture of NaOH (20 μL, 1.0 M) and TBA (100 μL, >0.02 μM) into our AuNP-based colorimetric sensor (0.88 mL,  $C_{Au} = 0.25$  mM), the ionic interaction between the strong positive charge of TBA and negative charge of citrate on the surface of AuNPs results in the AuNPs' aggregation. However, the AuNPs of the colorimetric sensor are well-dispersed after addition of the same amount of NaOH without TBA, which are used as the control for the TBA detection. The aggregation of AuNPs leads to obvious red shift of the UV–vis spectrum and clear color change of the colorimetric sensor from red to blue. Based on this aggregation mechanism, the pesticide residue of TBA could be rapidly detected by visualizing the color change of the sensor or measuring the UV–vis spectrum. Our AuNP-based sensor has an ultra-sensitivity and a high selectivity for the TBA detection because the extinction coefficient of AuNPs is high and the positive charge of TBA is very strong compared with other pesticides and normal substances in real environmental samples.

On the contrary, the DMT detection is built on an anti-aggregation mechanism (Scheme 1a). Because DMT belongs to acid pesticide that is easily hydrolyzed in a strong alkaline environment, NaOH is used to hydrolyze the DMT to realize the detection. After mixing of NaOH (40 μL, 1.0 M) and DMT (100 μL, >6.2 nM), the DMT is hydrolyzed quickly and the hydrolysis product is negatively charged (Scheme 1b). Therefore, after addition of a mixture of NaOH and DMT into our AuNP-based colorimetric sensor (0.88 mL,  $C_{Au} = 0.25$  mM), the AuNPs of the colorimetric sensor are well-dispersed under stabilization of the DMT hydrolysis product with strong negative charges. In addition, the AuNPs of the colorimetric sensor are aggregated after addition of same amount of NaOH without DMT due to the high ionic strength, which are used as the control for the DMT detection. The anti-aggregation of AuNPs leads to obvious blue shift of the UV–vis spectrum and clear color

change of the colorimetric sensor from grey to red. Based on this anti-aggregation mechanism, the pesticide residue of DMT can also be rapidly detected by visualizing the color change of the sensor or measuring the UV–vis spectrum. Our AuNP-based sensor also has an ultra-sensitivity and a high selectivity for the DMT detection because of the high extinction coefficient of AuNPs and the specific reaction of DMT at strong alkaline conditions.

The applicability of our AuNP-based colorimetric sensor is also verified by detection of TBA and DMT in real environmental samples.

## 2. Experimental

### 2.1. Materials and instrumentation

Gold(III) chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O), sodium citrate dihydrate (Na<sub>3</sub>Ct·2H<sub>2</sub>O), HCl, HNO<sub>3</sub> and NaOH were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Atrazine and glyphosate were obtained from J&K Scientific Ltd. (Beijing, China). Melamine iprodione, dipterex, regent, indoxacarb, fenobucarb, pretilachlor, isoprocarb, pymetrozine were purchased from Aladdin-Reagent Co.,Ltd. (Shanghai, China). MCPA-Na was obtained from Sigma-Aldrich (Shanghai, China). Chemicals of analytical reagent grade were used without further purification and all solutions were prepared with Milli-Q water.

Transmission electron microscopy (TEM) images were obtained on a JEOL 2100 microscope operated at 200 kV. Dynamic light scattering (DLS) and Zeta potential measurements were made on a Zetasizer instrumentation (Nano ZS, Malvern Instruments Ltd). Fourier transform infrared (FT-IR) spectroscopy was recorded on a Nicolet 6700 spectrophotometer (Thermo Scientific, USA). UV–vis spectra were obtained on an ultraviolet and visible spectrophotometer (T10CS, PERSEE, China).

### 2.2. Preparation of the citrate-stabilized AuNPs

The citrate-stabilized AuNPs with an average diameter of 16 nm were prepared according to previously published protocols [29–31]. Typically, 5.0 mL of HAuCl<sub>4</sub> aqueous solution (5.0 mM) was added to 92.5 mL of Milli-Q water in a round-bottom flask. The solution was then heated to be boiling under vigorous magnetic stirring. After that, 2.0 mL of Na<sub>3</sub>Ct solution (10 mg/mL) was charged, which results in a solution color change from pale yellow to deep red. After this color change, the heating was stopped immediately. The obtained AuNP dispersion was cooled down at room temperature and kept in the refrigerator (4 °C) until use.

### 2.3. Rapid colorimetric detection of TBA and DMT

For the rapid colorimetric detection of TBA, 100 μL of TBA aqueous solutions with various concentrations (0.1–5.0 μM) were first mixed with various volume of NaOH (1.0 M). The mixture was then added into the above obtained AuNP-based colorimetric sensor (0.88 mL,  $C_{Au} = 0.25$  mM). The mixtures were kept at room temperature for 1.0–30 min before the colorimetry observation or spectrometry measurement. Addition of the same amount of NaOH without TBA into the AuNP-based sensor was used as the control of TBA detection.

For rapid colorimetric detection of DMT, 100 μL of DMT aqueous solutions with different concentrations (1–5000 nM) were first mixed with different volume of NaOH (1.0 M). Then, the mixture was added into the AuNP-based colorimetric sensor (0.86 mL,  $C_{Au} = 0.25$  mM). The mixtures were kept at room temperature for 1.0–30 min before the colorimetry observation or spectrometry detection. Addition of the same amount of NaOH

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