



Lanthanum-functionalized gold nanoparticles for coordination–bonding recognition and colorimetric detection of methyl parathion with high sensitivity

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ABSTRACT

A novel and sensitive colorimetric sensor for determination of methyl parathion (MP) was developed based on a lanthanum (La^{3+}) functionalized gold nanoparticles (Au NPs-La) probe. In this assay, a new type of crosslinking molecule- La^{3+} , possessing strong coordination effect on oxygen-containing functional groups, was first applied in the Au NPs-based colorimetric assay. On account of the oxygen-containing thiophosphate, MP could combine with La^{3+} and induce the aggregation of Au NPs-La probes through coordination–bonding interactions, resulting in a variation of the solution color from red to blue. Further, the color change was in situ monitored with ultraviolet visible (UV–vis) spectrophotometer for the quantitative detection of MP. In contrast with the commonly designed Au NPs-based colorimetric assays, a novel Au NPs-La probe, which equipped with the same type of binding sites with Au NPs and analyte molecules, was explored and used for optical detection of MP. Under optimized conditions, the colorimetric assay exhibited a linear correlation to the concentration of MP in the range from 0.5 nM to 0.5 μM with a detection limit of 0.1 nM ($S/N=3$). The developed sensor is simple, without using complicated instruments, and has enormous potential applications in rapid and on-site monitoring for MP in real samples.

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1. Introduction

Organophosphate pesticides (OPs), which have played an important role in agriculture [1], are widespread used as pesticides across the world [2,3]. However, OPs residues can attack central nervous system through irreversible phosphorylation and inactivation of acetylcholinesterase (AChE), often leading to perturbation of the nerve conduction system and rapid paralysis of vital functions of living systems [4]. Therefore, it is necessary to establish sensitive and accurate analytical methods for analysis of OPs. Traditional analytical protocols used to determine OPs are mainly based on gas chromatography (GC), high performance liquid chromatography (HPLC) or coupled to mass spectrometry (MS) [5–9]. These methods are of highly efficiency, but very expensive, time consuming, and not appropriate for real-time analysis. In contrast, enzyme/antibody-based [10–13] biosensors are commonly used recently, and can offer a simple and inexpensive approach for

rapid and on-site monitoring of OPs exposure. Although high sensitivity can be achieved, the poor chemical/physical stability of the antibodies or enzymes prevents their applications in harsh environments such as acids, organic solvents, and high temperatures [14]. A great challenge remains to develop a fast, reliable and real-time biological monitoring system.

Recently, gold nanoparticles (Au NPs) based colorimetric assays have attracted considerable interests [15–19] because molecular events can be directly monitored through color changes. Apparently, no sophisticated instruments are involved in the detection procedure, and the fast and real-time monitoring is facile to achieve. Furthermore, Au NPs have high extinction coefficients (3–5 orders of magnitude higher than those of organic dye molecules), so the limit of detection can be as low as nM level [17]. Interparticle crosslinking aggregation is, so far, a commonly used mechanism for colorimetric analysis of target analytes, in which Au NPs can be chemically programmed by the use of specific crosslinking molecules. To the best of our knowledge, nearly all the crosslinking molecules contain two different types of binding sites, with one modified on Au NPs and another bonded with analyte molecules. It is noteworthy that, in the same ambient environment (e.g. pH,

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temperature, stirring or no stirring), with two different types of interactions, it is very difficult for the crosslinking molecule to achieve the best binding performance, hence resulting in low efficiency. Nonetheless, the best binding performance is relatively easier to accomplish if the crosslinking molecule is linked with Au NPs and analyte molecules through the same kind of interaction. In this regard, our group attempted to explore a new type of crosslinking molecule, equipped with the same type of binding sites with Au NPs and OPs molecules.

Given all this, we focused our attention on the use of lanthanum, one of the most typical rare earth elements. At present, lanthanum has attracted more and more attention due to its high phosphate adsorption capacity, nontoxicity and environment-friendly property [20–22]. The lanthanum doped substrate has proved to be ideal for improving phosphate adsorption efficiency and enrichment or separation of phosphorylated protein [23]. For instance, Zhang et al. [24] fabricated lanthanum onto diamino modified MCM-41, and investigated the adsorption behavior to phosphate. Cheng et al. [25] synthesized lanthanum silicate coated magnetic microspheres, and explored the property of phosphopeptide enrichment. All the results indicated excellent adsorptive properties of lanthanum doped materials. Lately, activated carbon fiber (ACF) loaded with lanthanum oxide was synthesized and used to adsorb phosphate from water [22]. It was indicated that lanthanum has a very high affinity to oxygen-containing functional groups on the ACF.

Herein, in order to decrease the contaminants and harm caused by OPs residues, a novel and sensitive visualized method was developed for the detection of OPs based on lanthanum ions (La^{3+}) functionalized Au NPs (Au NPs-La) probe using methyl parathion (MP), a common used OPs as a model. Lanthanum ions are used as “molecular bridge” between Au NPs and MP, leading to the aggregation of Au NPs via the strong coordination effect between lanthanum and oxygen-containing functional groups. It is noted that, La^{3+} can also result in the aggregation of Au NPs in the absence of MP, which is ascribed to the coordination integration between lanthanum and citrate-stabilized Au NPs. As a consequence, the concentration of La^{3+} is a key factor to be discovered. Under optimal conditions, the Au NPs-La probe can be crosslinked in the presence of certain amount of MP. Thus, quantitative determination of MP is realized through the distinct color change (from red to blue).

2. Experimental

2.1. Reagents and apparatus

Sodium citrate and sodium chloride were purchased from Tianjin Kaitong Chemicals Company (Tianjin, China). $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ was obtained from Shanghai Chemical Reagent Company (Shanghai, China). MP was supplied by Aladdin (Shanghai, China). Lanthanum chloride was from Shanghai Mountain Pu Chemical Co., LTD. 0.01 M acetate buffer solution (ABS) (pH varying from 3.5 to 7.0) was prepared by mixing the stock solutions of 0.01 M CH_3COOH and 0.01 M CH_3COONa and adjusting the pH with 0.01 M CH_3COOH or 0.01 M NaOH. Other chemicals were analytical reagent grade and all solutions were prepared using double-distilled deionized water from quartz. All the reagents were used without further purification.

DMF-101B Collector constant temperature heating magnetic stirrer was supplied by Gongyi Yuhua Instrument Company (Henan, China). Absorption spectra were recorded using UV-2450 Shimadzu Vis-spectrometer (Japan). The photographs were taken with FinePix F200EXP digital camera. The pH measurement was carried out on model PHS-3CT digital ion analyzer (Shanghai Instruments,

Shanghai, China). Transmission electron microscopy (TEM) observations were obtained using the 100CX II (JEM; Japan) transmission electron microscope. All the measurements were carried out at room temperature ($25.0 \pm 0.5^\circ\text{C}$).

2.2. Preparation of citrate-stabilized Au NPs

Colloidal Au NPs of 13 nm in diameter were synthesized by the reported citrate reduction method [26,27]. Typically, all glassware used in the procedure was dipped in aqua regia (HCl/HNO_3 , volume ratio 3:1) for 30 min, rinsed thoroughly with double-distilled water and then dried in vacuum dryer at 60°C . 100 mL of HAuCl_4 (1 mM) solution was heated to reflux with vigorous stirring, and then 10 mL of 38.8 mM sodium citrate was quickly added into above solution. The color of the solution changed from pale yellow to wine red within 1 min. The solution was heated under reflux for another 20 min. Then the heating source was removed and the solution was continuously stirred until it had cooled to room temperature (25°C). The resultant citrate-stabilized Au NPs colloids were stored in 4°C .

2.3. Preparation of lanthanum-functionalized Au NPs

Firstly, the acquired Au NPs colloids were diluted in ABS to a quarter. Then, a certain amount of lanthanum chloride and NaCl solution with a final concentration of 0.10 mM and 1.50 mM respectively were added into the colloidal Au NPs solution. The claret-red product was stirred evenly and Au NPs-La were obtained and stored for use.

2.4. Detection of MP

Different amount of MP was added into the Au NPs-La solution with moderate stirring. After 2 min, the color change was observed by the naked eyes and the absorbance spectra were recorded with UV-vis spectrometer.

2.5. Preparation of real samples

Water and soil samples were pretreated according to the previous report [28]. Briefly, the water sample was collected from river in Taian (Shandong, China) and filtered using glass fiber filter to remove particles large than $0.22 \mu\text{m}$. Then, a certain concentration of MP was added into. For recovery studies, the treated water sample was adjusted to pH 5.0 using 0.01 M ABS and kept at 4°C until analysis.

The soil used was collected from dry land of Taian (Shandong, China). The sample was ground to a fine powder before use. Then, a certain concentration of MP was added into 10 g soil sample. After 24 h, the mixture was shaken by sonication for 30 min and the slurry was centrifuged at 4000 rpm for 10 min. For recovery studies, the treated soil sample was adjusted to pH 5.0 using 0.01 M ABS and kept at 4°C until analysis.

3. Results and discussion

3.1. Colorimetric sensing strategy

As shown in Scheme 1, citrate-stabilized Au NPs were synthesized by a typically used method. The redundant citrate ions were absorbed on Au NPs to prevent the aggregation. Based on the character that lanthanum has a very high affinity to the oxygen-containing functional groups, the lanthanum ions are bond to the surfaces of negatively charged Au NPs via the coordination–bonding interactions. With this, the Au NPs-La probe based colorimetric detection system was realized. The obtained Au

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