Silver nanoparticles-based colorimetric array for the detection of Thiophanate-methyl

Mingda Zheng, Yingying Wang, Chenge Wang, Wei Wei, Shuang Ma, Xiaohan Sun, Jiang He *

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

ARTICLE INFO

ABSTRACT

A simple and selective colorimetric sensor based on citrate capped silver nanoparticles (Cit-AgNPs) is proposed for the detection of Thiophanate-methyl (TM) with high sensitivity and selectivity. The method based on the color change of Cit-AgNPs from yellow to cherry red with the addition of TM to Cit-AgNPs that caused a red-shift on the surface plasmon resonance (SPR) band from 394 nm to 525 nm due to the hydrogen-bonding and substitution. The density functional theory (DFT) method was also calculated the interactions between the TM and citrate ions. Under the optimized conditions, a linear relationship between the absorption ratio (A_{525nm}/A_{394nm}) and TM concentration was found in the range of 2–100 μM with correlation coefficient (R^2) of 0.988. The detection limit of TM was 0.12 μM by UV–vis spectrometer. Moreover, the applicability of colorimetric sensor is successfully verified by the detection of TM in environmental samples with good recoveries.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

In the last few years, pesticides play an irreplaceable role in modern agriculture through the control of pests to achieve high productivity [1,2]. However, most pesticides are highly toxic, often towards non-target organisms and their extra release into the environment will cause serious environmental consequences [3–5]. Their indispensable use has resulted in serious contamination of air, water, land and posing huge threat to humans [6]. Thiophanate-methyl (TM), as systemic pesticides belonging to benzimidazole fungicides are widely employed in agriculture and fruit farming for the control of pathogens [7,8]. TM has been reported that can be capable of causing endocrine disruption, long-term exposure to the TM may lead to the degradation of seminiferous epithelium. An inhibition of the expression of steroid receptors was also observed and may cause infertility [9]. TM would induce DNA damage in human lymphocytes was reported by Saquibet al. [10], Ben Amara et al. [11] was also reported Genotoxic and oxidative properties in 2014. Therefore, designing an inexpensive, rapid and sensitive approach for the detection of TM is becoming urgent. Thus the pollution of TM has become a global problem, it is urgent to develop a highly sensitive assay for sensing pesticides in environmental samples to prevent the ecosystem from being destroyed. Various techniques have been undertaken to detect and identify pesticide residues, including high-performance liquid chromatography (HPLC) [12], fluorescence assay (FL) [13,14], high-performance liquid chromatography-ultraviolet (HPLC-UV) [15], high-performance liquid chromatography-mass spectrometry/mass spectrometry (HPLC–MS/MS) [16], electrochemical assay (EC) [17,18], Surface-Enhanced Raman Spectroscopy (SERS) [19] and gas chromatography/mass spectrometry (GC/MS) [20,21]. Although most of the methods exhibit reasonable sensitivity and lower detection limits, some inherent shortcomings of instrumental techniques such as sophisticated instrumentation, time-consuming and tedious experimental process were also existed. Compared with above methods, colorimetric assays have attracted increasing attention because it is simple, quick, low-cost and convenient [22–24]. Thus, the colorimetric sensors have great potential for on-site detection. The noble metal nanomaterials based on colorimetric assays have gained more attention for the quantification of pesticides [25,26]. In recent years, various colorimetric sensors have been designed, AuNPs and AgNPs have been utilized for the detection of metal ions and pesticides. For example, Rohit's group [27] developed for colorimetric detection of quinalphos using *p* nitroaniline dithiocarbamate capped gold nanoparticles. Bala et al. [28] developed gold nanoparticles-based aptasensor for the colorimetric detection of organophosphorus pesticide phorate. Our group [29] described the 4 aminothiophenol functionalized silver nanoparticles for the sensing of 6 benzylaminoadenine. Imene et al. [30] illustrated 4 Amino 3 mercaptobenzoic acid functionalized gold nanoparticles as a colorimetric sensor for the detection of cyhalothrin. However, a lot of work mainly focused on gold nanoparticles (AuNPs) and very few literatures have been reported towards silver nanoparticles. Compared with AuNPs, AgNPs possess certain advantages [31,32], for example, higher molar extinction coefficient can result in increased sensitivity and improved visibility in optical brightness. Owing to the lower cost of silver compared to gold, AgNPs as a more economical candidate to replace widely employed AuNPs in colorimetric assays.

* Corresponding author.
  E-mail address: hejiang@lzu.edu.cn (J. He).

Herein, we propose a new colorimetric and visual read-out system for the detection of TM using Cit-AgNPs as signaling probe. This method is based on the aggregation of Cit-AgNPs induced by TM, yielding a color change from yellow to cherry reddish. In this system, citrate acts not only as a stabilizer but also as a functional reagent on the surface of Cit-AgNPs. In the presence of citrate, it enhances the interaction ability of Cit-AgNPs with TM. Thus a visual sensor can be applied to sensing of TM in complex samples, such as environmental water and vegetable samples.

2. Experimental

2.1. Chemicals

Thiophanate-methyl (TM) and silver nitrate ($AgNO_3$) were purchased from Tianjin Kermel Chemical Reagent Co. Ltd (Tianjin, China), sodium borohydride ($NaBH_4$) was obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China), trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) was purchased from Tianjin Guangfu Chemical Reagent Factory (Tianjin, China). H_3PO_4, HAc, H_3BO_3 and NaOH (B-R buffer) were purchased from Tianjin Guangfu Chemical Reagent Factory (Tianjin, China). All chemical reagents were analytical reagent grade without any further purification. All aqueous solutions were prepared with Milli-Q-purified distilled water.

2.2. Apparatus

Transmission electron microscopy (TEM) images of Cit-AgNPs were obtained using a Tecnai G2F30 instrument. Dynamic light scattering (DLS) data were acquired using Zetasizer Nano BI-200SM instrumentation. The UV–vis spectra were taken on a Lambda 35 UV–visible spectrometer.

2.3. Synthesis of Cit-AgNPs

The AgNPs solutions were synthesized by the reduction of $AgNO_3$ using $NaBH_4$ as the reducing agent and tri sodium citrate as the stabilizer agent according to published method [33] with some modifications. Briefly, 10 mL freshly prepared $NaBH_4$ (2.7×10^{-3} M) was added dropwise to 20 mL $AgNO_3$ (1.0×10^{-3} M) in 250 mL round-bottom flask, then tri sodium citrate (5 mL 1.0×10^{-2} M) was rapidly added and 50 mL H_2O was mixed with solution. Finally, the solution stirred for 48 h at room temperature.

2.4. Cit-AgNPs as a Sensor for Colorimetric Detection of TM

To investigate the applicability of Cit-AgNPs, 0.5 mL Cit-AgNPs solutions were exposed to different concentrations of TM (1 μM–100 μM) solutions. Then 0.5 mL Britton-Robinson (B-R) buffer solution (pH = 5.0) and 1 mL H_2O were added to this solution at room temperature. The color changes were observed with naked eyes and spectra were also recorded by UV–vis spectrometer.

2.5. Analysis of TM in Environmental Samples

Water samples including the Yellow River and tap water were received from Lanzhou, China. These water samples were spiked with certain concentrations of TM, and then centrifuged and sonicated for 15 min finally they were filtrated through a syringe membrane (0.45 μm). For vegetable samples, extraction procedure was performed in accordance with previous method [34] with some modifications. Firstly, 5 g tomato sample was chopped and homogenized with blander for 10 min, secondly, it was spiked with different concentrations of TM and stand for 10 min, then 25 mL ethyl alcohol was added to sample and sonicated for 10 min, finally the supernatant of sample was filtered

through 0.45 μm. All sample extracts were stored at 4 ± 2 °C prior to use.

3. Results and Discussion

3.1. Characterization of the Cit-AgNPs

Fig. 1 showed the Cit-AgNPs and Cit-AgNPs in presence of 5.0×10^{-5} M Thiophanate-methyl (TM) were characterized by DLS data and TEM images. As showed in Fig. 1c, with the absence of TM, Cit-AgNPs were spherical and highly dispersed with the average size around 8 nm, which was consistent with DLS measurement (Fig. 1a). However, in the presence of TM, Cit-AgNPs were aggregated, in which many irregular clusters were seen and the average size increased to 53 nm. The DLS results (Fig. 1b) further revealed the size of the Cit-AgNPs in addition of TM. All above results confirmed that the colorimetric sensing assay was absolutely feasible for TM detection.

To investigate the mechanism between Sodium citrate and TM, FT-IR spectroscopy was performed. As depicted in Fig. 2, these results showed that —O—H vibration of sodium hydroxide (Fig. 2a) appeared at 3271 cm^{-1}, 1305–1271 cm^{-1} belonged to —C=O Groups. While the band about 3350 cm^{-1}, 1174 cm^{-1} and 1710 cm^{-1} due to the stretching vibrations of —NH, —C=S and —C=O groups of TM (Fig. 2b) was completely revealed. Meanwhile, the band at 3433 cm^{-1} assigned to —O—H vibration of sodium hydroxide was broaden and the bands at 1173 cm^{-1} assigned to —C=S vibration and 3195 cm^{-1} assigned to —N—H vibration of TM (Fig. 2c) disappeared, which further indicating the hydrogen-bonding interaction between TM and —N—H protons of sodium hydroxide.

To investigate the feasibility of the proposed method for TM analysis, the UV–visible spectra was presented in Fig. 3. The well-dispersed Cit-AgNPs exhibited a typical absorption peak at 394 nm and appeared yellow by naked-eyes, which was ascribed to the surface plasmon resonance (SPR) of the Cit-AgNPs. After addition of TM, the absorption intensity at 394 nm was greatly decreased and a new absorption peak at 525 nm was increased, leading to the aggregation of Cit-AgNPs and the color changed from faint yellow to cherry red (Fig. 3 inset).

3.2. Mechanism of the Colorimetric Sensor

The mechanism is represented in Scheme 1. The citrate ions were absorbed on AgNPs to prevent the aggregation. At optimal conditions, it provided suitable condition for forming the hydrogen bonding between TM and citrate ions, —COOH of citrate can be simultaneously form hydrogen bondings with —NH, —C=S, —C=O, —CH₃ of TM. At the same time, the Mercapto groups of TM would replace carboxyl groups of citrate. The addition of TM to the Cit-AgNPs solution leaded to the aggregation of Cit-AgNPs with color change from yellow to cherry red *via* strong substitution and hydrogen bonding. The mechanism illustrates that TM induces the aggregation of Cit-AgNPs, The changes of the optical property can be observed by naked eyes and monitored by UV–vis spectrometer.

To further confirm the mechanism, we also utilize density functional theory (DFT) method to verify the hypothesis. Fig. 4(a) and (b) showed optimized geometry structure of the TM molecule and citrate ions towards AgNPs, which induced the aggregation of Cit-AgNPs. All calculations were carried out using Gaussian 09 [29] software package, C, O, S and H atoms was calculated by standard hf/3–21 g basis set, while the lanl2dz basis set was used for Ag atom. The interactions between TM molecule and citrate were also investigated as shown in Fig. 4(c) and (d). It revealed that the carboxyl group of citric could form hydrogen bondings with TM. Based on these simulated results, the aggregation of Cit-AgNPs induced by TM through the hydrogen bonding and substitution were identified.