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RESEARCH PAPER

A simple colorimetric probe based on anti-aggregation of AuNPs for rapid and sensitive detection of malathion in environmental samples

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Abstract

In this study, a simple colorimetric probe was developed for rapid and highly sensitive detection of malathion based on gold nanoparticles (AuNPs) anti-aggregation mechanism. A certain amount of NaOH can cause the aggregation of citrate-stabilized AuNPs due to the electrostatic interactions, and the color of AuNP solution changes from wine-red to gray. While in the presence of malathion, malathion is easily hydrolyzed in a strong alkali environment (pH > 9), followed by the production of a mass of negative charges, and thus the aggregated AuNPs turns to well-dispersed and the color of AuNP solution changes from gray to wine-red. This characteristic change can be visualized with the naked eye and quantitatively detected by an ultraviolet-visible (UV-Vis) spectrometer. Under optimized conditions, this probe exhibited a linear response to malathion in the concentration range of 0.05–0.8 μM with a limit of detection (LOD) down to 11.8 nM. The probe also showed good specificity for malathion detection in the presence of other interfering pesticide residues. Furthermore, the probe was successfully employed to detect malathion in environmental samples, with a recovery of 94–107% and a relative standard deviation (RSD) less than 8%. The results demonstrated that the proposed colorimetric probe based on anti-aggregation of AuNPs could be used for quantitative analysis of malathion and provided great potential for malathion determination in environmental samples.

Keywords Colorimetric probe · Gold nanoparticles · Anti-aggregation · Malathion · Environmental samples

Introduction

Malathion, as one kind of organophosphate pesticide, has been widely used for pest control on rice (such as rice planthopper), cotton (Lugus lucorum), vegetables (such as cabbage caterpillar), fruit trees (such as aphis), and tea plants (such as Myllocerinus aurolineatus Voss) to improve the production. However, the pesticide residues in the plant, soil, and water caused by the extensive usage could bring a serious public health problem due to their toxicity and potential carcinogenicity [1], which should be paid attention to ensure the food safety and protect the health of consumers. In the United States (US), Environmental Protection Agency (EPA) establishes a specific tolerance of 8 mg/kg for malathion residues in most of fruits and vegetables [2]. In China, National Standard of the People's Republic of China (GB) specifies a malathion maximum residue limit (MRL) of 0.5 mg/kg in vegetables and 2 mg/kg in fruits [3]. Although the governments have issued the standard for malathion residue, it frequently occurred that malathion residues exceed the standard mostly in fruits and vegetables, especially in the developing countries. Therefore, it is very important to achieve highly sensitive detection of malathion in food and drinking water.

Many efforts have been performed to develop various of analytical methods for detection of malathion pesticide residue, such as gas chromatography (GC) [4, 5], high-performance liquid chromatography (HPLC) [5], gas chromatography-mass spectrometry (GC-MS) [6], liquid chromatography-mass spectrometry (HPLC-MS) [7], enzyme-linked immunosorbent assay

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(ELISA) [8], chemiluminescence [9], and colorimetric sensing [10–13]. Each method has its advantages and disadvantages, where GC, HPLC, and HPLC-MC are the standard detection methods with high sensitivity and good accuracy, while they need a time-consuming process and expensive instruments. ELISA is a rapid detection method with good specificity due to the antibody-antigen specific binding, but antibodies are difficult to obtain and expensive. Chemiluminescence has the advantages of simple instruments, fast detection, low limits of detection, and wide dynamic range, while the selectivity and stability of which are poor. Among all these analytical methods, colorimetric method has received great attention owing to its simplicity, rapidity, good sensitivity, high selectivity, and potential on-site detection ability. Nobel metal nanoparticles such as gold nanoparticles (AuNPs) have been commonly used as the sensing probe in many colorimetric sensors due to the intrinsic optical characteristics determined by the phenomenon of localized surface plasmonic resonance (LSPR) [14]. The shape of LSPR spectrum is tunable, which depends on not only the shape, size, and composition [15], but also the surrounding dielectric environment of nanoparticles [16, 17]. Therefore, based on the sensitive response of nanoparticles to the refractive index variation of the surrounding medium, AuNP-based colorimetric methods have been widely employed in various biosensing fields, such as biomedical research [18–20], photocatalysis [21, 22], environment monitoring [23–25], and food safety detection [26–28]. In recent years, AuNP-based analytical methods have been developed for rapid detection of malathion residues. Kohzadi et al. [10] reported that a rapid and sensitive colorimetric detection of malathion based on AuNP aggregation was achieved, with a detection limit down to 0.15 μM. Bala et al. [11, 12] have developed AuNP-based aptamer biosensors for rapid and sensitive detection of malathion in water and real samples, where an ultra-low limit of detection of 0.5 pM was obtained. Despite the fact that AuNP aptamer–based colorimetric sensor can provide a fast, highly specific, and ultrasensitive detection of malathion, the experimental process is relatively more complicated and the cost is more expensive when compared with pure AuNP-based biosensors.

In this work, we developed a rapid and highly sensitive colorimetric probe for malathion detection based on AuNP anti-aggregation mechanism, which relies on the fact that malathion can be easily hydrolyzed under strong alkaline conditions. Normally, due to the electrostatic interactions, AuNPs are aggregated after adding a certain amount of NaOH and the color of AuNPs changes to gray. While after the addition of the same amount of NaOH and malathion mixture, the AuNPs are well-dispersed due to the strong negative charges from the hydrolysis product of malathion. The anti-aggregation of AuNPs leads to a distinct color change of AuNP solution from gray to red and an obvious blue shift of the UV-Vis absorption spectrum. This colorimetric probe can provide a simple, rapid, highly sensitive, and selective method for malathion detection. Furthermore, the proposed detection strategy can be applied to determine the malathion in environmental samples such as tap water, apple, and green vegetable.

Experimental

Materials and instruments

Malathion, ethoprophos, fenvalerate, and hexachlorocyclohexane were bought from Aladdin Reagent Co. Ltd. (Shanghai, China). Tetrachloroauric (III) acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) and trissodium citrate were purchased from Sigma-Aldrich (USA). NaOH and methanol were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the reagents were of analytical grade and used without further purification. Milli-Q water was utilized in the whole experiments.

The ultraviolet-visible (UV-Vis) absorption spectrum was recorded by using a UV-Vis spectrophotometer (Nanjing Philes Instruments Co., Ltd., China). Transmission electron microscopy (TEM) images were obtained on a JEM-2100 high-resolution microscopy operated at 200 kV.

Preparation of AuNPs

The citrate-stabilized AuNPs with an average diameter of 13.5 nm were synthesized by the citrate reduction of chloroauric acid [29, 30]. First, 25 mL of $HAuCl_4$ aqueous solution (1 mM) was placed in a round-bottom flask with a capacity of 100 mL and heated to boiling for 2 min. Then, 2.5 mL sodium citrate solution (1%) was quickly added into the boiling solution and boiled until the color of the solution changed into wine-red. Finally, the solution was cooled down to room temperature and then stored in a clean tube at 4 °C for further use. The morphology and particle size of prepared AuNPs were characterized by a JEM-2100 high-resolution transmission electron microscopy (TEM). The synthesized AuNPs showed an absorption maximum at 520 nm with an absorbance of 0.407 (5 times dilution) and a typical extinction coefficient of about $2.7 \times 10^8\ M^{-1}\ cm^{-1}$ [29]. The concentration of AuNP solution was determined to be about 7.5 nM from the formula $A = \varepsilon bc$, where A is the absorbance, ε is the extinction coefficient, b is the optical pathlength (i.e., the length of cuvette, 1 cm), and c is the concentration of AuNPs.

Colorimetric detection of malathion

For rapid colorimetric detection of malathion, a stock solution of malathion (100 mM) was prepared and stored at 4 °C. First, dilutions of malathion with different concentrations were prepared and mixed with 40 mM NaOH. The mixtures were kept at room temperature for 20 min, making the malathion completely hydrolyzed. Subsequently, AuNPs were added

into the mixture and the solution was again incubated for another 20 min at room temperature, followed by the UV-Vis spectral measurements.

Detection of malathion in environmental samples

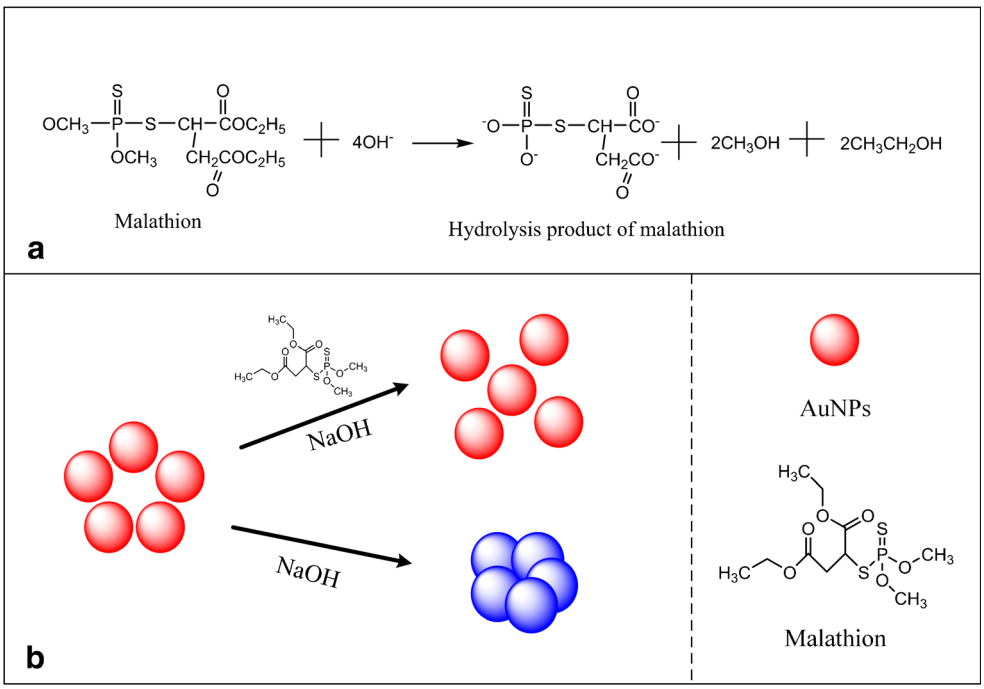
To evaluate the feasibility of the AuNP anti-aggregation–based colorimetric probe for malathion detection in environmental samples, the analysis was also performed in tap water, apple, and green vegetable. First, apple and green vegetable were cut and squeezed into juice with a juice extractor. Then these samples were filtered repeatedly using syringe filters with 0.22 μm of membrane until the colored solution became clear and colorless. Subsequently, the purified samples were spiked with different concentrations of malathion standard solutions, and then detected using the proposed colorimetric probe.

Results and discussion

Detection principle of malathion

The principle for colorimetric detection of malathion using AuNP anti-aggregation is illustrated in Scheme 1. The AuNP anti-aggregation mechanism is mainly based on the hydrolysis of malathion in a strong alkaline environment (pH > 9), as shown in Scheme 1(a); the hydrolysis reaction is followed by a mass of negative charges appearing [31–33]. Normally, the originally synthesized AuNPs with an average diameter of 13.5 nm were stable and well-distributed due to the repulsion interactions between citrate anions coated onto the surface of AuNPs, visually appearing a wine-red color (see Fig. 1), the size and well-dispersion status of pure AuNPs was verified by the TEM image and the particle size distribution profile (see Electronic Supplementary Material ESM Fig. S1). Once a high concentration of NaOH solution was added, the high ionic strength would screen the electrostatic repulsion between citrate anions absorbed the surface of AuNPs, thus leading to that the AuNPs were aggregated and exhibited a gray color. However, after adding a mixture of NaOH and malathion, the AuNPs become well-dispersed and the color of AuNP solution still remains wine-red due to the presence of strong negative charges that significantly increase the electrostatic repulsion. The anti-aggregation effect leads to a clear color grade of AuNPs from gray to red, which is dependent on the concentration of malathion. Therefore, the proposed colorimetric method can be employed for detecting the presence of malathion with naked eyes.

Figure 1 shows the photographic images and UV-Vis absorption spectra of the AuNP solution in the absence and presence of malathion with a concentration of 0.7 μM, where the AuNP solution added with pure NaOH was used as a control. From the UV-Vis spectra, two obvious absorption bands peaking at about 520 nm and 640 nm were obtained. While for the AuNPs added with malathion, the absorption peak at 640 nm disappeared and the 520 nm peak increased. This is mostly caused by the fact that the negatively charged hydrolysis product of malathion significantly increases the electrostatic repulsion between the negative charges of citrate absorbed the surface of AuNPs, resulting in the anti-aggregation of AuNPs. The anti-aggregation effect is further validated by the TEM images shown in Fig. 1b, c; it can be



Scheme 1 A schematic illustration of the principle for malathion detection based on the anti-aggregation mechanism of gold nanoparticles

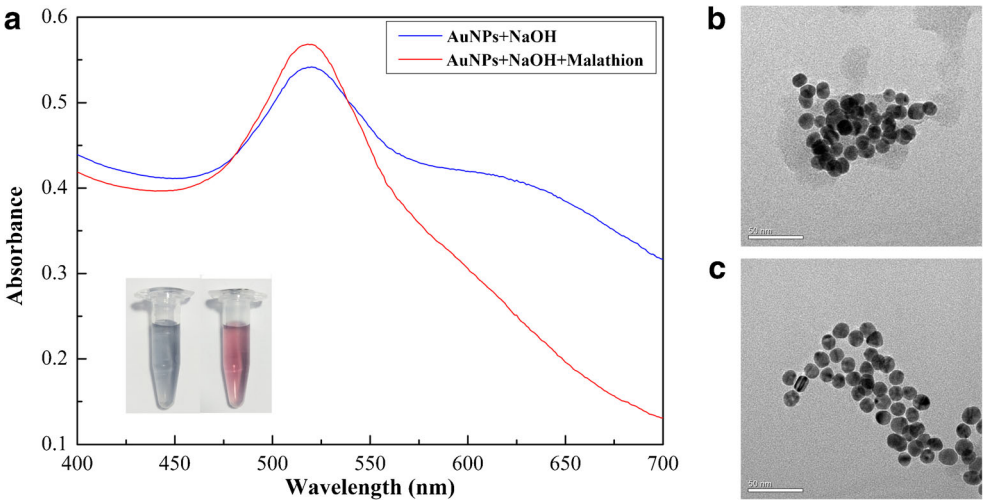


Fig. 1 **a** Photographic images and UV-Vis absorption spectra of AuNPs in the absence and presence of 0.7 μM malathion. **b**, **c** TEM images of AuNPs in the absence and presence of malathion, scale bars = 50 nm

apparently observed that the particles are aggregated after the AuNPs incubated with NaOH, while the treatment of AuNPs with the mixture of NaOH and malathion bring the particles back to mono-dispersed. Therefore, in this work, the aggregated AuNPs were used as a colorimetric probe for malathion detection.

Optimization of experimental conditions

As described above, a high concentration of NaOH solution can make well-dispersed AuNPs aggregated, while a low concentration of NaOH cannot induce the AuNPs aggregated (see inset (a) in ESM Fig. S2), thus minimum concentration of NaOH that is sufficient enough to aggregate AuNPs needs to be determined for malathion detection. Besides, the hydrolysis time of malathion and the incubation time of AuNPs in the presence of malathion also play a very important role for the sensitive and specific detection of malathion. Therefore, the experimental conditions including NaOH concentration, hydrolysis time, and incubation time were optimized to achieve a stable sensing performance.

For the optimization of NaOH concentration, AuNPs were treated with different concentrations of NaOH ranging from 20 to 60 mM (see ESM Fig. S2), including the visual and UV-Vis spectral detection of AuNPs incubated with pure NaOH (control group) and a mixture of NaOH plus malathion. For the control group, when the NaOH concentration reached to 40 mM, the color of AuNPs changed from red to gray, indicating that the AuNPs began to aggregate. While it was opposite for the AuNPs with the addition of NaOH and malathion, the color changed from gray to red when NaOH concentration was increased to 40 mM. In addition, according to the UV-Vis spectra, the ratio of absorbance value at 520 nm between the mixture of NaOH plus malathion (A(520)) and pure NaOH (A_0(520)), i.e., A(520)/A_0(520), as a function of NaOH concentration were plotted, from which the ratio A(520)/A_0(520) reached its maximum when the NaOH concentration was 40 mM. Therefore, 40 mM NaOH was selected as the optimal concentration for colorimetric detection of malathion.

Further, the influence of hydrolysis time and incubation time for the detection of malathion was investigated. In the experiments, the mixture of 0 μM (blank), 0.4 μM, and 0.7 μM malathion plus 40 mM NaOH was added to AuNP solution, respectively. To quantify the relative change of absorbance value at 520 nm and 640 nm, the ratio between absorbance at 520 nm and 640 nm (A_{520}/A_{640}) was used. As shown in ESM Fig. S3(a), both for the addition of 0.4 μM and 0.7 μM malathion, the A_{520}/A_{640} reached to a maximum at about 20 min of hydrolysis time, which indicated that 20 min was sufficient to make the malathion completely hydrolyzed. From ESM Fig. S3(b), it was clearly found that the A_{520}/A_{640} of UV-Vis spectra for the blank, 0.4 μM, and 0.7 μM malathion was almost stable when the incubation time reached to 20 min, which meant that 20 min was enough to reach the reaction equilibrium. Therefore, 20 min of hydrolysis time and 20 min of incubation time were chosen as the optimal time for further experiments.

Colorimetric detection of malathion

Under the optimized conditions described above, the sensitivity of the proposed colorimetric method for malathion detection was evaluated by treating the colorimetric probe with different concentrations of malathion in the range of 0.05 to 0.8 μM. As displayed in Fig. 2, it can be seen by naked eyes that the colorimetric probe presented an obvious color gradient from gray to red after adding with different concentrations of malathion. From the UV-Vis absorption spectra, the absorption peak approximating at 520 nm increased gradually with the increasing malathion concentration, which indicated that more and more AuNPs became dispersed from the aggregated status. Based on the evident variation of absorption peak

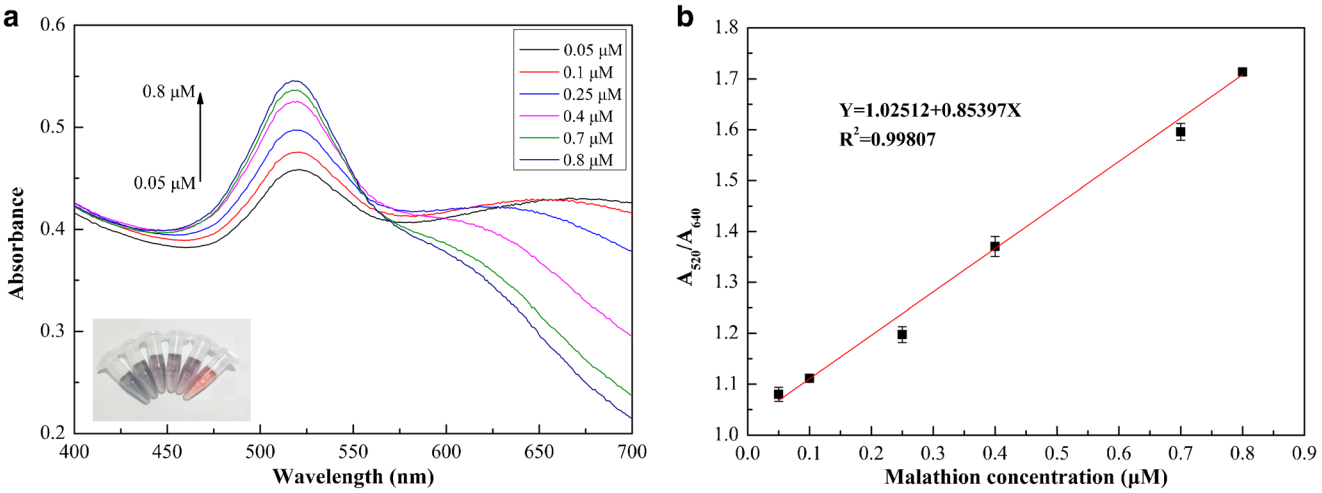


Fig. 2 Sensitivity of the proposed colorimetric probe for malathion detection. UV-Vis absorption spectra (**a**) and calibration curve (**b**) of the colorimetric probe in the presence of different concentrations of malathion in the range of 0.05–0.8 μM. Inset shows the images of AuNPs added with increasing malathion concentration

intensity of AuNPs, the ratio between absorbance at 520 and 640 nm (A_{520}/A_{640}) was used for the quantitative analysis of malathion. Figure 2b showed the plot of A_{520}/A_{640} as a function of malathion concentration ranging from 0.05 to 0.8 μM, a good linear relationship with a regression coefficient R^2 = 0.998 was obtained. From the calibration curve, the limit of detection (LOD) of this colorimetric probe was found to be 11.8 nM, which was determined by the formula 3σ/slope, where σ is the standard deviation of instrument and slope can be obtained from the linear calibration curve [34]. Apparently, the LOD was much lower than the maximum residue limit (MRL) regulated by the governments. Besides, when compared with other previously reported methods, except for the ultrasensitive aptamer-based colorimetry, the LOD and linearity obtained by the proposed colorimetric probe were clearly superior (see ESM Table S1) [10–13, 35]. The results demonstrated that the proposed colorimetric probe can be used for rapid and highly sensitive detection of malathion residues.

Specificity of the colorimetric detection

The specificity of the proposed colorimetric method for malathion detection was evaluated in the presence of possible interfering pesticide residues such as ethoprophos (organic thiophosphate pesticide), fenvalerate (pyrethroid pesticide), and δ-hexachlorocyclohexane (δ-HCH, organochlorine pesticide), which are three other categories of insecticides commonly used in agricultural fields except for organophosphorus pesticides. In the experiment, the concentration of malathion was kept to 0.5 μM, while the interfering pesticides were 5 μM. As shown in Fig. 3, AuNPs incubated with malathion showed a distinct absorbance ratio (A_{520}/A_{640}), while the absorbance ratio for AuNPs incubated with other pesticides was almost identical to the blank. The results confirmed that the proposed colorimetric method presents high selectivity towards malathion, while other potential environmental insecticides have no interference towards malathion detection. As a matter of fact, it can be said that this colorimetric method based on anti-aggregation of AuNPs is highly selective to organophosphorus pesticides, since most of the organophosphorus pesticides have the chemical structure of phosphate which can be easily hydrolyzed by strong alkali. Besides, the specificity of the proposed colorimetric method could also be a major concern when malathion measurements were performed in the environmental water where the pH value could reach up to 8~9. Therefore, the proposed method is primarily limited to the practical applications involving environmental samples with the pH less than 7.

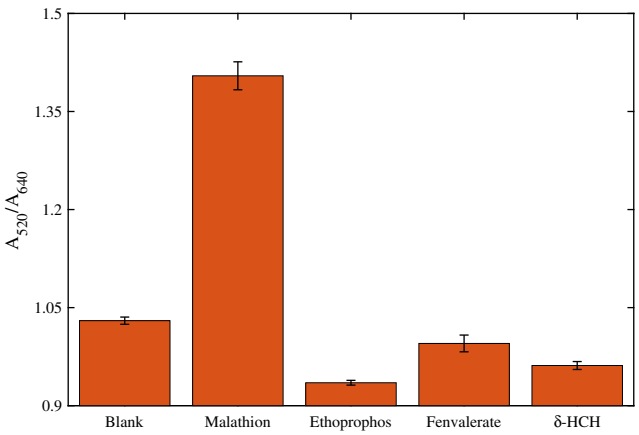


Fig. 3 Selectivity of the colorimetric probe for malathion detection. The absorbance ratio A_{520}/A_{640} of the probe in the absence and presence of various pesticides including malathion, ethoprophos, fenvalerate, and δ-HCH with a concentration of 0.5 μM, 5 μM, 5 μM, and 5 μM, respectively

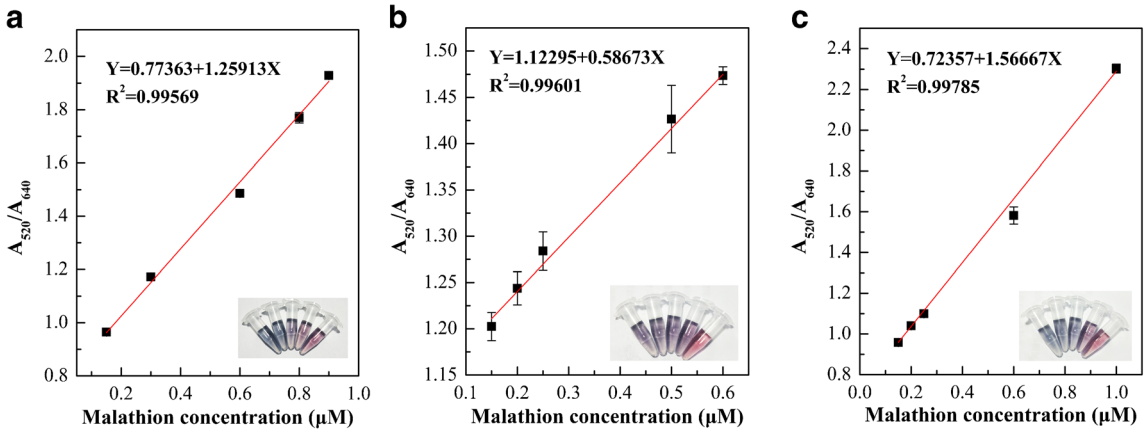


Fig. 4 Detection of malathion in environmental samples with the proposed colorimetric probe. Calibration curves in tap water (**a**), apple (**b**), and green vegetable (**c**) with a regression coefficient of 0.996, 0.996, and 0.998 were established, respectively

Malathion detection in environmental samples

To evaluate the potential practical applicability, the proposed colorimetric probe was employed for malathion detection in environmental samples such as tap water, apple, and green vegetable. Since no malathion was present in the environmental samples, they were spiked with various concentrations of malathion standard solution. As displayed in Fig. 4, the colorimetric detection with naked eyes for different concentrations of malathion was achieved, where the color of colorimetric probe gradually changed from gray to red with the increasing malathion concentration. The absorbance ratio A_{520}/A_{640} of UV-Vis absorption spectra was used for quantitative determination of malathion in spiked environmental samples, from which the calibration curves were established with a regression coefficient (R^2) of 0.996, 0.996, and 0.998 separately for tap water, apple juice, and vegetable juice. The LOD of malathion in tap water, apple juice, and vegetable juice was determined to be 8.25 nM, 49 nM, and 10.6 nM, respectively.

Further, based on the calibration curve shown in Fig. 4a–c, two different concentrations of malathion were separately spiked to the tap water, apple juice, and vegetable juice to perform the recovery measurements. Table 1 shows the recovery results based on the anti-aggregation of AuNPs for determination of malathion in environmental samples. The obtained recovery was ranged from 94 to 107%, with a relative standard deviation (RSD) ranging from 1 to 8%. The results demonstrated that the AuNP anti-aggregation–based colorimetric probe can be used for practical applicability for malathion detection in real environmental samples.

Indeed, there are some challenges for the detection of the colored samples when using colorimetric methods. In this work, vegetable juice was originally green, after several times filtering using syringe filters with 0.22 μm of membrane, the solution became clear and colorless. While for heavy pigment samples that filtering does not work, activated charcoal or decolorizing carbon can be used to decolorize the solution. Therefore, in the case of analyzing colored samples, the pretreatment process of decolorization should be adopted to eliminate the possible interference.

Conclusions

In this work, a colorimetric probe based on AuNP anti-aggregation effect was developed for rapid, selective, and high-sensitive detection of malathion pesticide residue. The anti-aggregation mechanism is based on the fact that malathion is easily hydrolyzed in a strong alkaline environment (pH > 9), leading to the colorimetric probe well-dispersed due to the presence of the strong negative charges. To improve

Table 1 Determination of malathion in tap water, apple juice, and vegetable juice

Samples	Spiked (μM)	Detected (μM)	Recovery (%)	RSD (%)
Tap water	0.5	0.534 ± 0.007	106.74	1.36
	0.7	0.678 ± 0.001	96.90	1.42
Apple juice	0.3	0.283 ± 0.013	94.46	4.27
	0.55	0.526 ± 0.042	95.58	7.63
Vegetable juice	0.4	0.385 ± 0.009	96.25	2.30
	0.8	0.809 ± 0.020	101.1	2.49

the sensitivity of malathion detection, the experimental conditions including NaOH concentration, hydrolysis time, and incubation time were optimized. Under the optimal conditions, a linear relationship between absorbance ratio A_{520}/A_{640} and the malathion concentration in the range of 0.05–0.8 μM with a regression coefficient R^2 of 0.998 was obtained, and then a LOD of 11.8 nM was determined, which was much lower than MRL regulated by the governments. The proposed colorimetric probe also showed excellent selectivity for malathion against other three kinds of insecticides (ethoprophos, fenvalerate, and δ-hexachlorocyclohexane). Besides, the detection of malathion based on the proposed colorimetric probe was also achieved in environmental samples including tap water, apple, and green vegetable with a recovery of 94–107% and a relative standard deviation (RSD) < 8%, achieving a LOD of 8.25 nM, 49 nM, and 10.6 nM, respectively. As a consequence, due to its advantages of low cost, rapid detection, good selectivity, and high sensitivity, the proposed colorimetric probe can provide enormous potential for on-site detection of malathion in environmental samples.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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