Electronic Supplementary Information

A simple and rapid chemosensor for colorimetric detection of dimethoate pesticide based on peroxidase-mimic catalytic activity of gold nanoparticles

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Materials and methods

Preparation of AuNPs

During the preparation of gold nanoparticles, all the glass instruments were soaked with newly configured aqua regia (HCl: HNO_3, 3:1), then thoroughly cleaned with bidistilled water, and finally dried in the oven for standby. Citrate-coated gold nanoparticles (cc-AuNPs) were prepared by the citrate reduction method reported previously[1]. Firstly, solid $HAuCl_4$ is accurately weigh and dissolved in 100 mL of bidistilled the water to form 1.04 mM $HAuCl_4$ solution, which was heated to boil. Afterward, 10 mL of 38.8 mM sodium citrate solution is rapidly added to the solution under continuous stirring. The mixed solution was boiled for 15 min and a color change was observed from initial pale grey to wine-red, then the heater was removed after stirring for 15 min. Finally, the solution was cooled to room temperature and filtered using an ultrafiltration membrane (250 nm aperture), and was packed in a brown reagent bottle and then stored at 4°C before use.

Cysteamine-stabilized gold nanoparticles (cs-AuNPs) were synthesized according to previous publication with some modification. Firstly, 1.2 mL of 213 mM cysteamine and 1.42 mM $HAuCl_4$ were mixed, and then the mixture was blended under ambient temperature for 20 min[2]. Subsequently, 30 mL 10 mM $NaBH_4$ solution was add to the above solution, and the solution was continuously stirred for about 25 min in the dark. Finally, the solution display wine red, and then cooled to room temperature and ultrafiltred using membrane (250 nm aperture) filter store in the 4°C before use.

As for unmodified gold nanoparticles (um-AuNPs), according to the borohydride reduction method, 1.5 mL of 29.43 mM $HAuCl_4$ solution was diluted with 118.5 mL bidistilled water[3]. Subsequently, the 3 mL of 264.34 mM $NaBH_4$ solution was injected drop by drop solution under intense mixing and the solution was left overnight. The resulting wine-red colloidal solution was further stirred continuously for 30 minutes and the solution was left overnight. At last the um-AuNPs solutions were stored in a refrigerator at 4°C.

The determination of AuNPs concentration was carried out using the Bouguer-Lambert-Beer law: A = kcd (where A is the absorption, k is the molar extinction coefficient, c is the sample concentration and d is the optical path length). $C = A_{450} / \varepsilon_{450}$, of which the C per liter of mol, to 1 cm standard path length, using A 450 nm absorption value[4]. Unless otherwise mentioned, cc-AuNPs were used throughout in the experiments.

Preparation of AgNPs

According to the literature[5], the AgNPs was synthesized. Briefly, 5 mL of $AgNO_3$ (10 mM) and 5 mL of sodium citrate solution (10 mM) were mixed with 89 mL of bidistilled water for 20 min in the flask. Subsequently, the 8.8 mg of $NaBH_4$ was rapidly added to the above solution, and the reaction was performed for 2 h in the room temperature. Finally, the AgNPs solution was obtained and stored at 4 °C for further study.

Procedures for GC analysis of dimethoate in actual samples

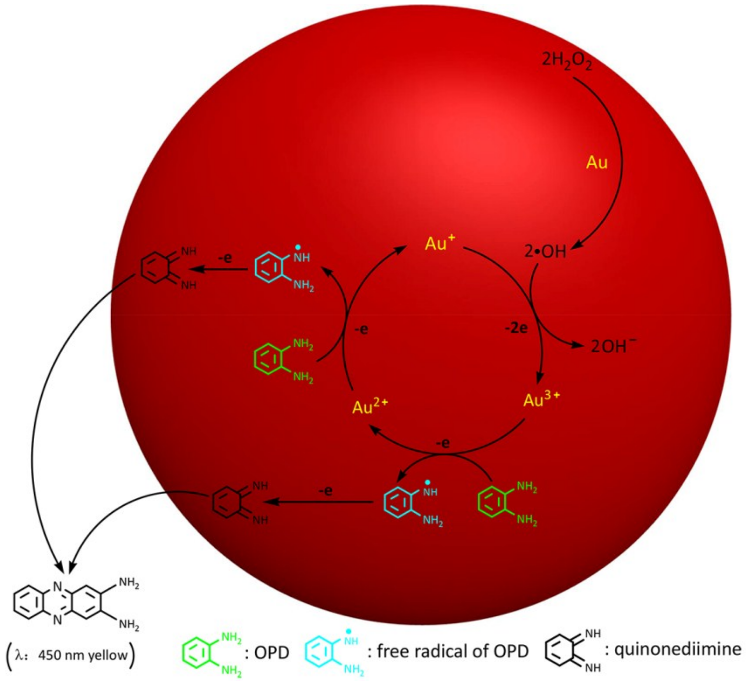
The procedures for detection of dimethoate pesticide were referenced to the previous reports[6-9]. The analyses were performed by using a gas chromatograph (Agilent 7890B, USA) equipped with flame photometric detector (FPD). Separation was carried out on an Agilent 19091Z-416 column (60 m × 320 μm × 0.25 μm). The conditions for GC analysis were referenced to the previous literatures [6-9]. Nitrogen (purity 99.999%) was used as carrier gas at a constant flow-rate of 1 mL/min. Hydrogen and air were applied for FPD at a respective flow rate of 75 mL/min and 100 mL/min. Detector temperature was set at 250°C. The injection volume was 2.0 μL in split mode with an inlet temperature of 220°C. The column temperature was programmed as follows: the initial oven temperature was set at 150°C for 2 min, increased to 250°C at 8 °C/min (hold 12 min).

Supplementary Table

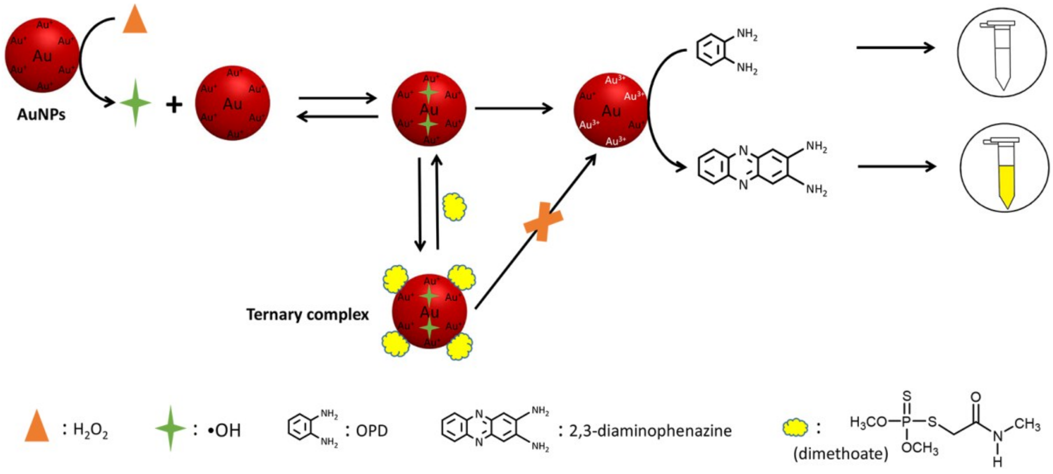
Table S1 Comparison with earlier reported methods for dimethoate detection

Methods	Transduction principle	Linear range (μg L^{-1})	LOD (μg L^{-1})	Reference
Electrochemistry	Dimethoate inhibited acetylcholinesterase using the modified electrode as signal	1.145×10^{-3}-22.9	2.29×10^{-5}	10
	Dimethoate inhibited acetylcholinesterase using electrocatalytic activity of gold nanorods as signal	1.145-229.12	0.89	11
	Dimethoate enhanced the reduction current of a new organic molecule containing -SH and oxime	2.29×10^{-4}-9.17	1.99×10^{-4}	12
Fluorescence	Dimethoate specifically quenched the fluorescence of MIP-coated ZnO quantum dots	20-320	6	13
	Dimethoate inhibited the catalytic activity of AgNPs composites causing no conversion of Amplex red to produce fluorescent substances	10-350	3	14
	Dimethoate removed the inhibitory effect of AuNPs on the fluorescence of Rhodamine B	5-1000	4	15
Colorimetry	Dimethoate inhibited the catalytic activity of α-naphthyl acetate esterase	0.51-50.83	960	16
	Dimethoate inhibited the catalytic activity of soybean esterase	None	31.25	17
	Dimethoate inhibited the peroxidase-mimic catalytic activity of AuNPs	10-400	4.74	This work

Supplementary Schemes and Figures



Scheme S1 The peroxidase catalytic oxidation mechanism of AuNPs to substrate OPD.



Scheme S2 Illustration of the anticompetitive inhibitory mechanism of dimethoate on the peroxidase-mimic catalytic activity of AuNPs.

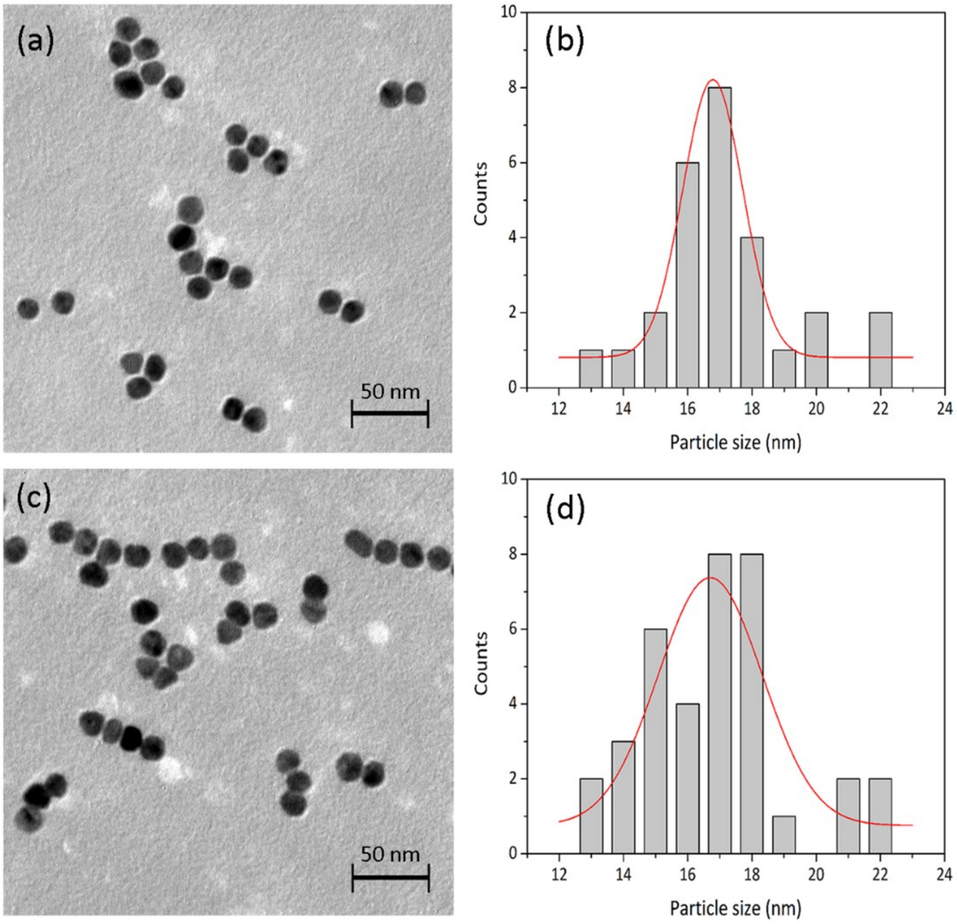


Fig. S1 TEM observation and particle distribution of AuNPs solutions in the absence (a-b) and presence of 5 mg/L dimethoate (c-d).

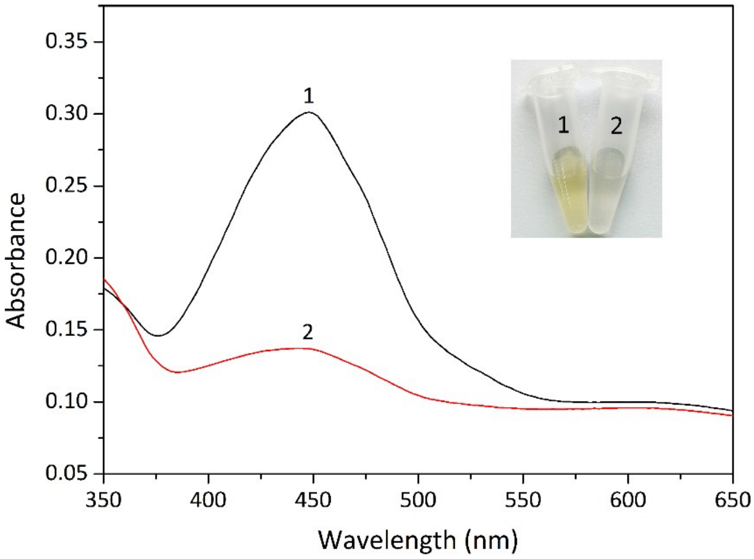


Fig. S2 UV absorption spectra and visual colors of chemosensor constructed by AgNPs. Sample 1: AgNPs + buffer + H_2O_2 + OPD; Sample 2: AgNPs + dimethoate (500 μg/L) + buffer + H_2O_2 + OPD.

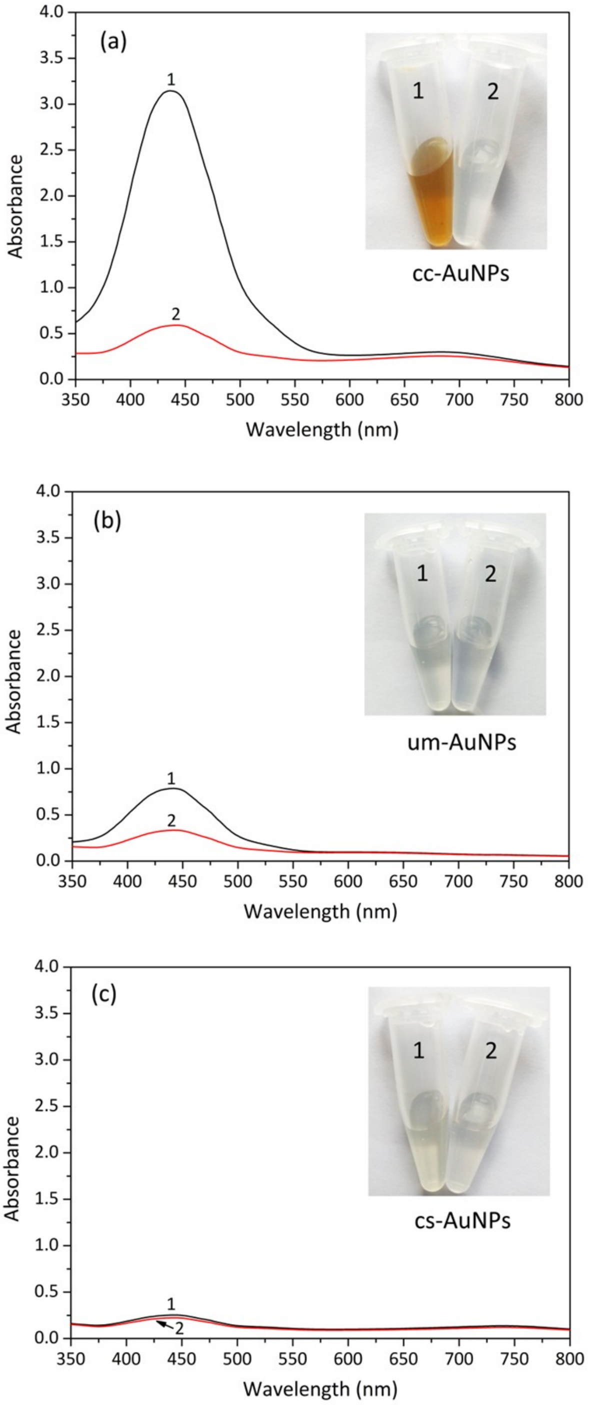


Fig. S3 UV absorption spectra and visual colors of different chemosensors constructed by cc-AuNPs (a), um-AuNPs (b) and cs-AuNPs (c), respectively. Sample 1: AuNPs + buffer + H_2O_2 + OPD; Sample 2: AuNPs + dimethoate (500 μg/L) + buffer + H_2O_2 + OPD.

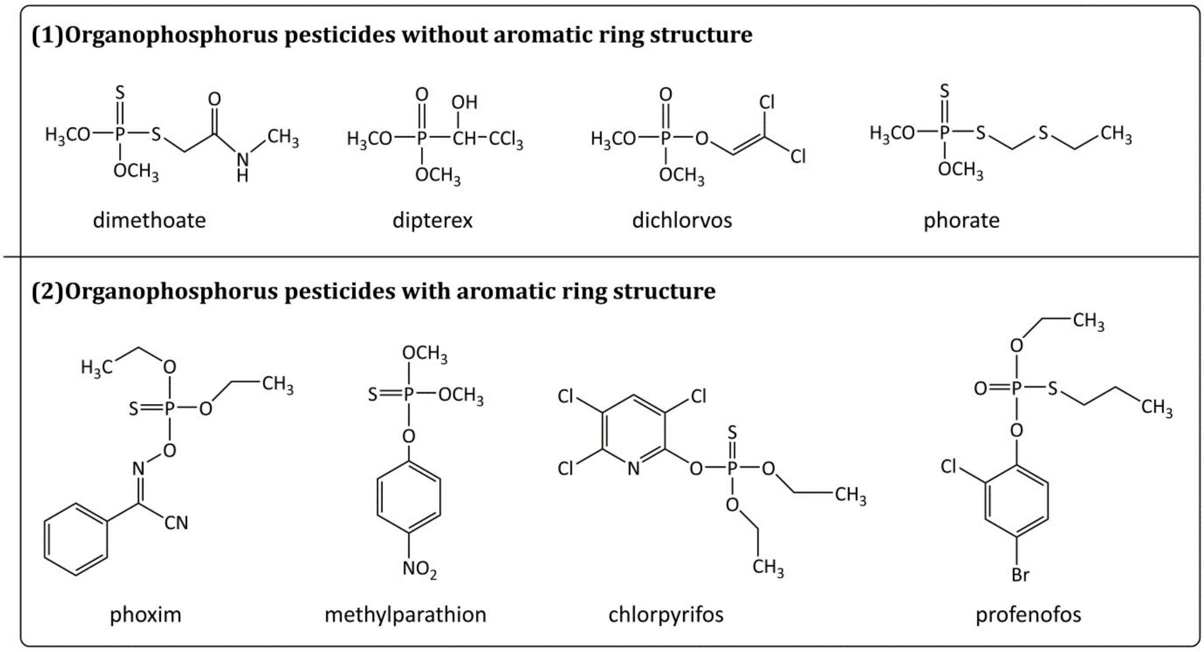


Fig. S4 Structures of dimethoate and other competitive organophosphorus pesticides.

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