Supporting Information

Ligand replacement induced chemiluminescence for selective detection of an organophosphorus pesticide using bifunctional Au-Fe_3O_4 dumbbell-like nanoparticles

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Experimental Section

1.1 Materials. Iron chloride ($FeCl_3 \cdot 6H_2O$, 98%), hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$), H_2O_2 (30 wt%), methionine (>99%), sodium hydroxide (NaOH, >99%), sodium periodate ($NaIO_4$, >99%), and ruthenium(III) chloride ($RuCl_3$, >99%), cyclohexane (99.95%), and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Luminol (>99%), oleylamine (>80%), oleic acid (90%), 1-octadecene (90%) and the typical pesticides including parathion-methyl (PM), ethoprophos (EP), 2,4-dichlorophenoxyacetic acid (2,4-D), profenofos (PF), and methamidophos (MP) were supplied from Sigma-Aldrich. All of these reagents were used without further purification. Ultrapure water (18.2 MΩ cm) was produced using the Millipore water purification system. Luminol solution in CL reactions was freshly prepared by diluting the mother solution (50 mM, keeping in dark for at least 1 week) in 0.1 M NaOH solutions.

1.2 Preparation of Water-Soluble Au NPs, Fe_3O_4 NPs, Au-Fe_3O_4 dumbbell-like Nanoparticles (DBNPs).

1.2.1 Synthesis of 12 nm Gold NPs. A solution of 1-octadecene (10 mL), oleic acid

(1 mL), oleylamine (1 mL) and $HAuCl_4 \cdot 3H_2O$ (60 mg) were prepared in air at room temperature. The mixture was allowed to be kept at 130 °C for 30 min with magnetically stirred and the color of the solution changed from light yellow to deep red purple. Then the solution was cooled to room temperature. Ethanol was added to precipitate the Au NPs. The Au NPs were collected by centrifugation, washed with the mixture solution of ethanol and cyclohexane (V/V: 2:1), and redisposed in cyclohexane.

1.2.2 Synthesis of 18nm Fe_3O_4 NPs. Fe-oleate was prepared according to the reported method[1]. 1-octadecene (8 mL), oleic acid (1 mL), oleylamine (1.5 mL) and 0.12 g Fe-oleate were mixed with magnetically stirred and degassed under a nitrogen flow for 60 min at 100 °C. Then the solution was heated to 320 °C and kept for 40 min before it was cooled to room temperature. The mixture was exposed to air for one hour to ensure the formation of Fe_3O_4. Ethanol was added to precipitate the product, followed by centrifugation. The precipitated products were washed by the mixture of ethanol and cyclohexane (V/V: 2:1) solution, and this process was repeated for two times.

1.2.3 Synthesis of Au-Fe_3O_4 DBNPs. 1-octadecene (8 mL), oleic acid (1 mL), oleylamine (1.5 mL), 0.08 g Fe-oleate and 0.03 g Au NPs were mixed with magnetically stirred and degassed under a nitrogen flow for 60 min at 100 °C. Then the solution was heated to 320 °C and kept for 40 min before it was cooled to room temperature. The mixture was exposed to air for one hour to ensure the formation of Fe_3O_4. Ethanol was added to precipitate the product, followed by washing with the mixture solution of ethanol and cyclohexane (V/V: 2:1), and this process was repeated for two times.

1.2.4 Preparation of Water-Soluble Au NPs, Fe_3O_4 NPs, Au-Fe_3O_4 DBNPs. 20 mg of Au NPs, Fe_3O_4 NPs, or Au-Fe_3O_4 DBNPs were dried and added into a solution containing 8 mL cyclohexane, 8 mL ethyl acetate, and 8 mL acetonitrile. Then, 12 mL aqueous solution containing 496 mg $NaIO_4$ and 2.6 mg $RuCl_3$ was dropping added into the organic solution. After reaction of 120 min, the Au NPs, Fe_3O_4 NPs, Au-Fe_3O_4 DBNPs were separated and washed with deionized water three times. The

particles were then dissolved in deionized water.

1.3 CL from Au NPs, Fe_3O_4 NPs, Au-Fe_3O_4 DBNPs on luminol-H_2O_2 System. 50 μL of Au-Fe_3O_4 colloid (50 μg/mL) and 50 μL of H_2O_2 (2.5×10^{-4} M) were first added into the well of a 96-well plate. After shaking for 60 s, 100 μL of luminol solution(1×10^{-4} M, pH=12) was added, followed by collecting the CL signals. The catalytic activity of Au NPs, Fe_3O_4 NPs and Fe_3O_4/Au NPs mixture were similarly carried out only that the Au-Fe_3O_4 DBNPs solution was replaced with the same concentration of other nanoparticles solution.

1.4 Preparation of me-Au-Fe_3O_4 DBNPs CL Probe. To prepare CL switching-on probe based on the bifunctional Au-Fe_3O_4 DBNPs, the CL of the purified Au-Fe_3O_4 DBNPs on luminol-H_2O_2 system was first quenched by surface grafting of a special ligand methionine (me), according to the following procedure. 100 μL of methionine solution (50 μM) was injected into 10 mL of the purified Au-Fe_3O_4 DBNPs solution (50 μg/mL) at room temperature. After reaction of 120 min, me-Au-Fe_3O_4 DBNPs were separated by a magnet and washed with deionized water two times.

1.5 CL Detection of Pesticide. A 10^{-2} M PM solution in acetonitrile was prepared and then diluted with water to the desired concentration. The me-Au-Fe_3O_4 DBNPs solution was spiked with PM pesticide to form a purple red homogeneous suspension at pH=11.00. After the mixture was incubated on a rocking table with shaking for 10 min, the Au-Fe_3O_4 DBNPs were drawn to the wall of the vial through adding a small magnet. After discarding the supernatant, the magnet was taken away and the vial was shaken gently after adding a certain amount of deionized water. The black aggregates were again redisposed, and the colloidal solution was used to measure CL emission. For detecting pesticide, 50 μL of Au-Fe_3O_4 colloid (50 μg/mL) and 50 μL of H_2O_2 (2.5×10^{-4} M) were first added into the well of a 96-well plate. After shaking for 60 s, 100 μL of luminol solution(1×10^{-4} M, pH=12) was added, followed by collecting the CL signals. The detection selectivity was further investigated using various kinds of pesticides at the same concentration as controls. The same process was carried out for

detection of PM in real sample of green tea.

1.6 Characterizations. CL signals were recorded in a 96 well polypropylene microtiter plate using a Berthold LB 960 microplate luminometer. Transmission electron microscopy (TEM) images were obtained on a JEOL 2011microscope operated at 120 kV. The X-ray diffraction pattern (XRD) was recorded on a MAC Science Co. Ltd. MXP 18 AHF X-ray diffractometer with monochromatized Cu Kα radiation (λ=1.54056 Å). Magnetic measurements were carried out using a superconducting quantum interference device magnetometer (SQUID MPMS5, Quantum Design Inc.) with a maximum applied continuous field of 10 000 G at room temperature. The infrared spectra were recorded with Nicolet Nexus-670 FT-IR spectrometer.

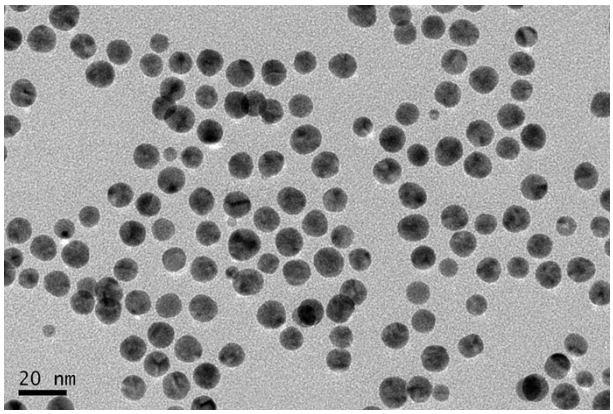


Fig. S1 Typical TEM image of Au NPs in water.

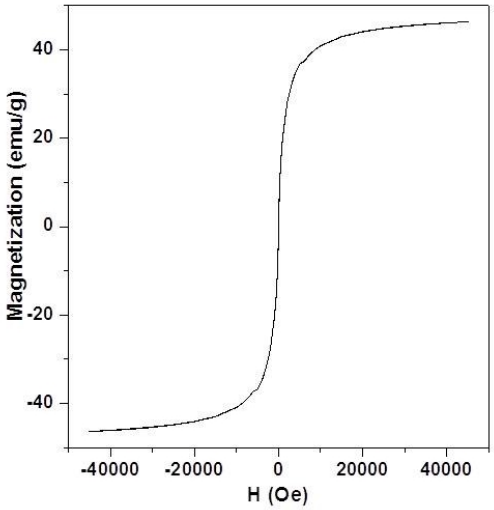


Fig. S2 Room-temperature magnetization curve of pure Fe_3O_4 NPs.

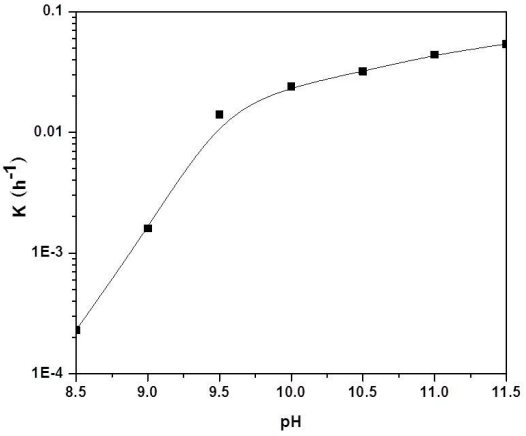


Fig. S3 The pH effect on the hydrolysis of dimethylphosphorothioate.

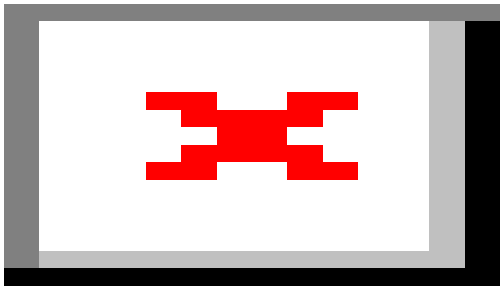


Fig. S4 Effects of reaction conditions on the CL intensity: A) the concentrations of Au-Fe_3O_4 DBNPs; B) the pH values of Au-Fe_3O_4 DBNPs solution. The maximum CL intensity was obtained when the Au-Fe_3O_4 DBNPs concentration was 50 μg/mL, above which CL intensity decreased due to the self-absorption of emission by Au-Fe_3O_4 DBNPs.

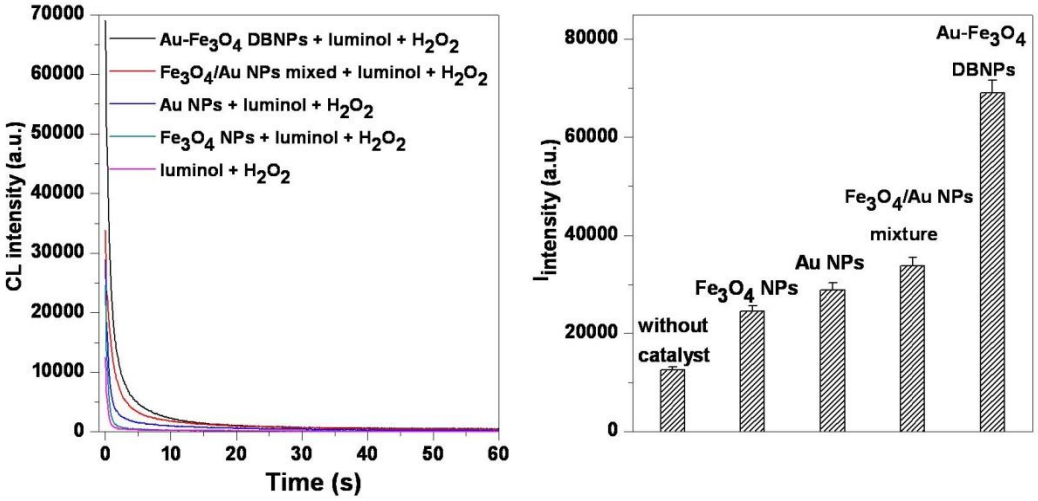


Fig. S5 The enhanced CL signals of various nanoparticles on luminol-H_2O_2 CL system.

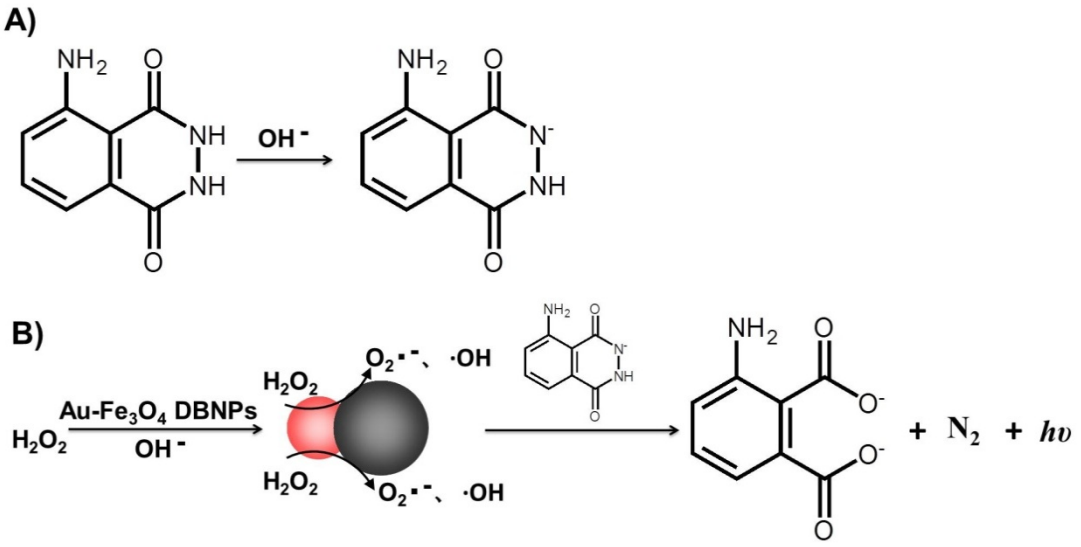


Fig. S6 The mechanism for the Au-Fe_3O_4 DBNPs enhanced the CL efficiency of luminol-H_2O_2 system: A) luminol molecules transform into luminol anions under alkaline condition; B) oxygen-related radicals are generated at surface of Au-Fe_3O_4 DBNPs and react with luminol anions to yield electronically excited 3-aminophthalate anions (3-APA*) and the excited 3-APA* emits light when it is relaxed to the ground state.

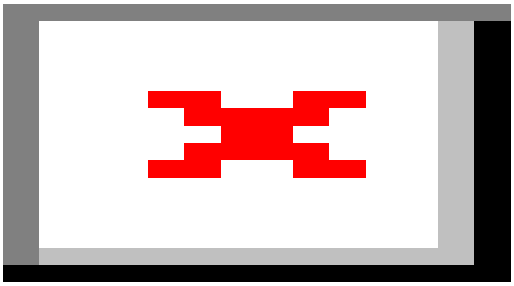


Fig. S7 The linear correlations of CL enhancement vs PM concentrations. The PM concentration ranges are A) 10 nM ~ 500 nM and B) 500 nM ~ 10 μM, respectively.

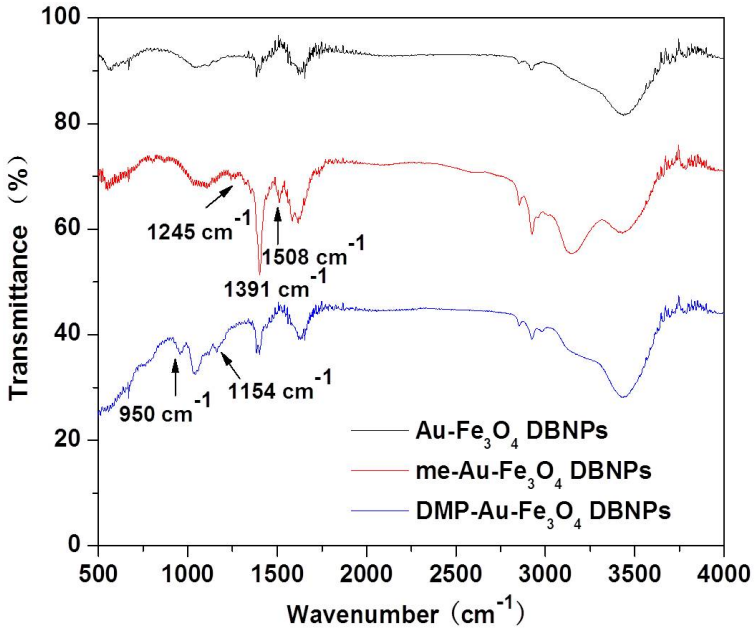
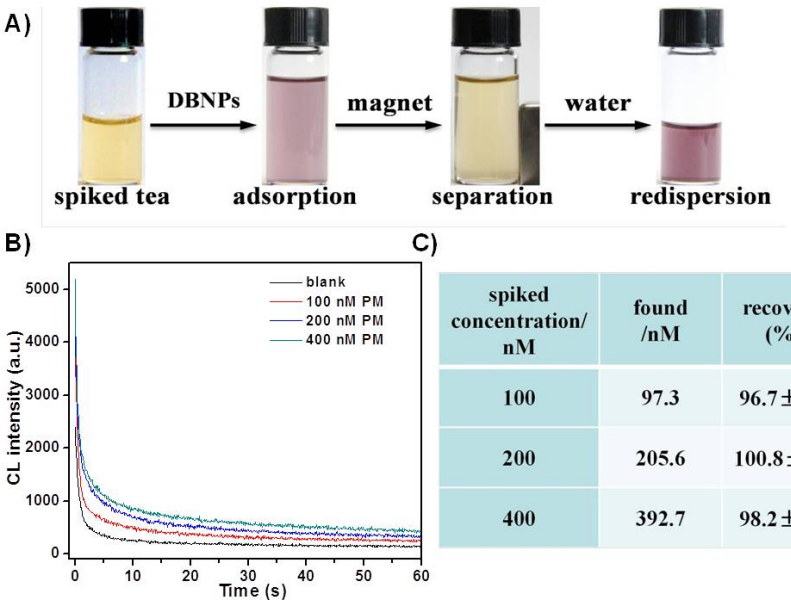


Fig. S8 FT-IR spectra of Au-Fe_3O_4 DBNPs, the methionine modification of Au-Fe_3O_4 DBNPs and after ligand replacement using DMP.



C)

spiked concentration/ nM	found /nM	recovery (%)
100	97.3	96.7±1.4
200	205.6	100.8±2.5
400	392.7	98.2±2.8

Fig. S9 CL detection of pesticide PM in real samples. A) Schematic drawing of the magnetic separation/redispersion process for overcoming the interfering effect in green tea. B) CL response resulted from PM molecules in green tea after carrying out the separation/redispersion process two times. C) Table of analytical results by the application of me-Au-Fe_3O_4 DBNPs probes to the determination of PM in green tea samples.

Reference

1. J. Park, K. J. An, Y. S. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park, N. M. Hwang, T. Hyeon, *Nat. Mater.,* 2004, **3**, 891.