Supporting Information

Dual-Readout Immunochromatographic Assay by Utilizing MnO_2 Nanoflowers as the Unique Colorimetric/Chemiluminescent Probe

Hui Ouyang,[†,‡] Qian Lu,[†] Wenwen Wang,[‡] Yang Song,[†] Xinman Tu,[†] Chengzhou Zhu,[†] Jordan N. Smith,[§] Dan Du,[†,*] Zhifeng Fu,[‡,*] Yuehe Lin[†,*]

[†]School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington 99164, United States

[‡]Key Laboratory of Luminescence and Real-Time Analytical Chemistry (Ministry of Education), College of Pharmaceutical Sciences, Southwest University, Chongqing 400716, China

[§]Health Impacts & Exposure Science, Pacific Northwest National Laboratory, Richland, Washington 99352, United States

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* E-mail address: annie.du@wsu.edu

* E-mail address: fuzf@swu.edu.cn.

* E-mail address: yuehe.lin@ wsu.edu.

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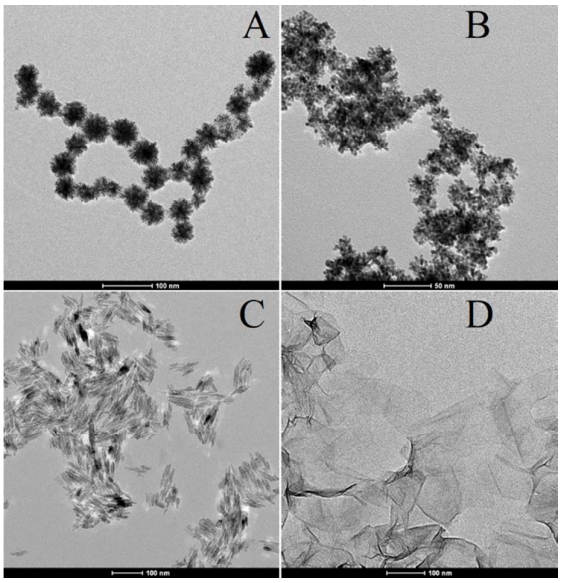

Figure S1 TEM images of (A) PtAu BNPs, (B) PtPd BNPs, (C) PB NRs and (D) GO.

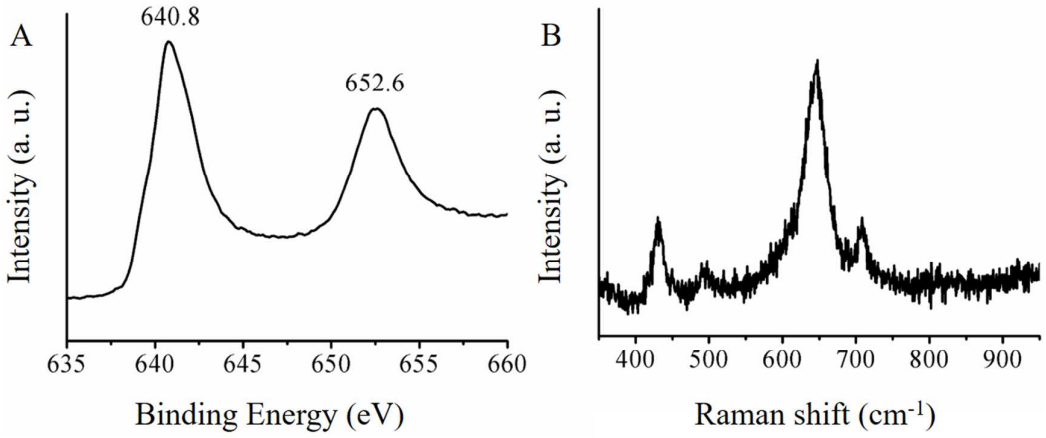

Figure S2 (A) XPS spectrum and (B) Raman spectrum of MnO_2 NFs.

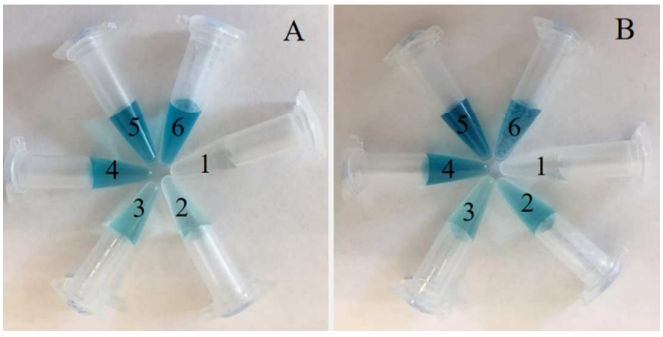

Figure S3 Photograph showing the color evolution of TMB Liquid Substrate System in the presence of (1) ultrapure water, (2) GO, (3) PB NRs, (4) PtPd BNPs, (5) PtAu

BNPs and (6) MnO_2 NFs all at 10 μg/mL within (A) 3 min and (B) 5 min.

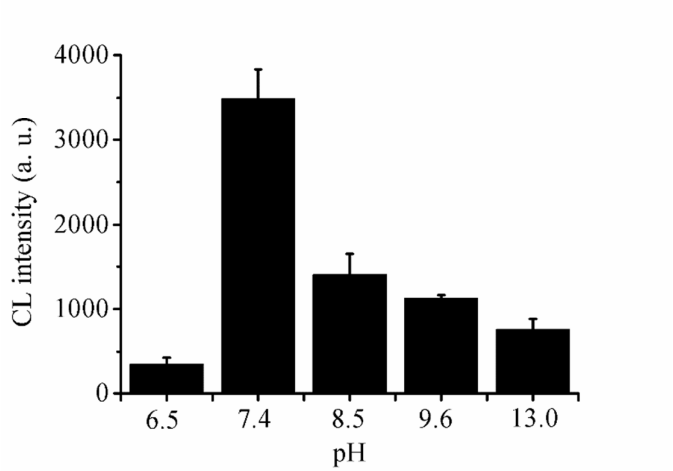

Figure S4 Effect of pH value on the CL signal of MnO_2 NFs-enhanced luminol-H_2O_2 CL reaction. The concentration of luminol, H_2O_2 and MnO_2 NFs were 5.0×10^{-7} M, 0.20 M and 10 μg/mL, respectively.

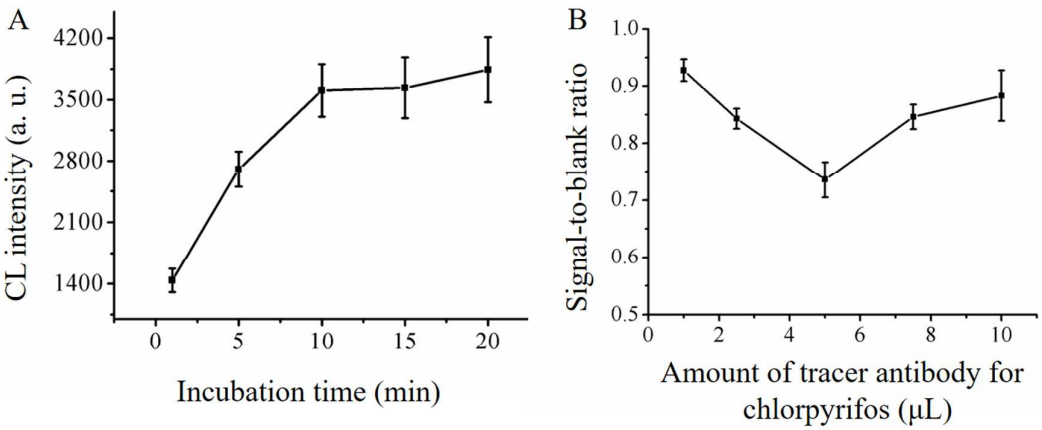

Figure S5 (A) Effect of the incubation time on the CL signal of MnO_2 NFs-enhanced luminol-H_2O_2 CL reaction (n = 3). (B) Effect of the amount of the tracer antibody on the signal-blank-ratio, where the concentration of chorpyrifos was 5 ng/mL (n = 3).

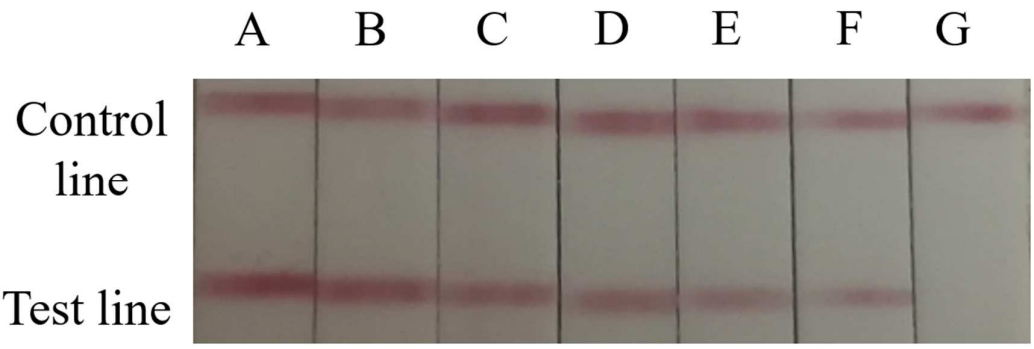

Figure S6 Photograph of different red colors in the gold-nanoparticles-based ITS assay for chlorpyrifos at (A) 0 ng/mL, (B) 0.3 ng/mL, (C) 1.0 ng/mL，(D) 5.0 ng/mL，(E) 10 ng/mL, (F) 50 ng/mL and (G) 100 ng/mL.

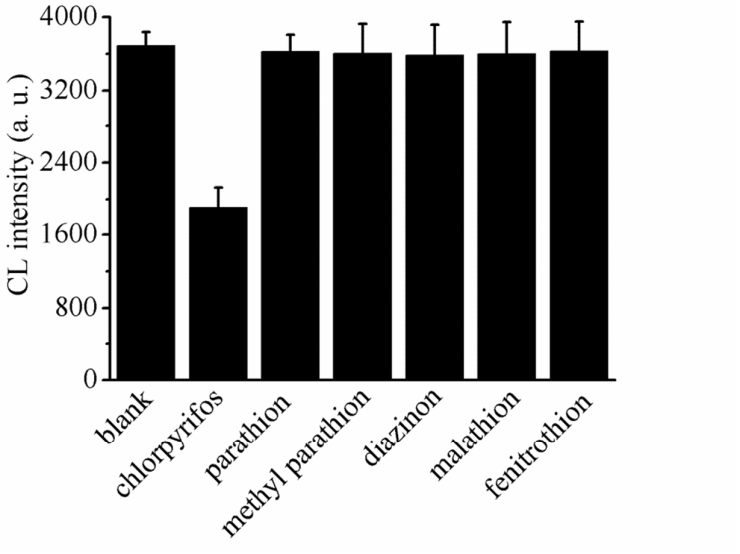

Figure S7 CL signals of six pesticides using the proposed ITS. All the tests are conducted under the optimal conditions (n = 3).

Preparation of PtAu BNPs and PtPd BNPs

PtAu BNPs and PtPd BNPs were synthesized according to a method with minor modification.[1] Pluronic F127 (10 mg) was dissolved in 1.0 mL of an aqueous mixed solution containing 18 mM K_2PtCl_4 and 2 mM $HAuCl_4$ (or Na_2PdCl_4), and 130mM HCl. After that, 1.0 mL of 100 mM ascorbic acid as a reducing agent was added to the

solution, and then the mixture was continuously sonicated in a water bath at 30 °C for 3 h. The final product was rinsed with acetone five times and water twice and then a PtAu BNPs (or PtPd BNPs) aqueous dispersion (2 mg/mL) was obtained for further use.

Preparation of PB NRs

PB NRs were prepared by a modified procedure.[2] In brief, 20 mL of 1.0 mM $FeCl_3$ was heated to 60 °C and then 0.5 mmol of citric acid was added to the solution with stirring for a homogenous mixed solution. Afterwards, to the mixture 20 mL 1.0 mM aqueous K_4[Fe(CN)6] solution containing 1.0 mM citric acid was added. Immediately, the dispersion turned a clear bright blue. The pH value of this dispersion was adjusted to 2.8. After 1 min, the solution was cooled to room temperature with the stirring continued for another 5 min at room temperature. Acetone (40 mL) was added to the dispersion and stirred for 1min. The blue precipitation was collected after a centrifugation at 10 000 rpm for 15 min resulted in the formation and washed three times with the mixture of ultrapure water-acetone (v/v=1:1). Finally, a PB NRs solution (0.1 mg/mL) was obtained for further use.

Preparation of GO

Based on a modified Hummers method,[3] the graphite oxide was synthesized from natural graphite powder. Then, graphene oxide was achieved through the exfoliation of graphite oxide by a ultrasonication process for 40 min. Finally, a homogeneous GO aqueous dispersion (0.5 mg/mL) was obtained and stored at room temperature until use.

DPBF quenching studies

DPBF was adopted as a reactive oxygen species trapping reagent in ethanol

solution.[4] In the investigation, 1.0 mL ethanol solution containing 0.5 mg/mL DPBF was mixed thoroughly with 160 μL ultrapure water containing 5.0 μg/mL nanomaterials 50 mM H_2O_2. After 1-min incubation, the absorbance of the mixture at 410 nm was measured using a UV-visible spectrophotometer.

Table S1. Comparison of analytical parameters resulting from different methods for the detection of chlorpyrifos.

Method	LOD	Reference
ELISA	0.2 ng/mL	5
Microimmunoassay	0.11 ng/mL	6
HPLC	0.25 ng/mL	7
LC–MS/MS	10 ng/mL	8
Photoelectrochemical sensor	0.0074 ng/mL	9
Surface-enhanced Raman scattering spectroscopy	351 ng/mL	10
Surface-enhanced Raman scattering spectroscopy	64 ng/g	11
Electrochemical aptasensor	0.033 ng /mL	12
Non-enzyme electrochemical sensor	6.3 ng/mL	13
Fluorescent assay	5.2 ng/mL	14
Colorimetric/CL ITS assay	0.033 ng/mL	The proposed method

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