

## *Supporting Information*

### **Template protection of gold nanocluster for detection of organophosphorus pesticides**

Huan Li, Hongyu Chen, MingxiaLi, Qiujun Lu, Youyu Zhang\* and Shouzhuo Yao

*Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education), College  
of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, PR China*

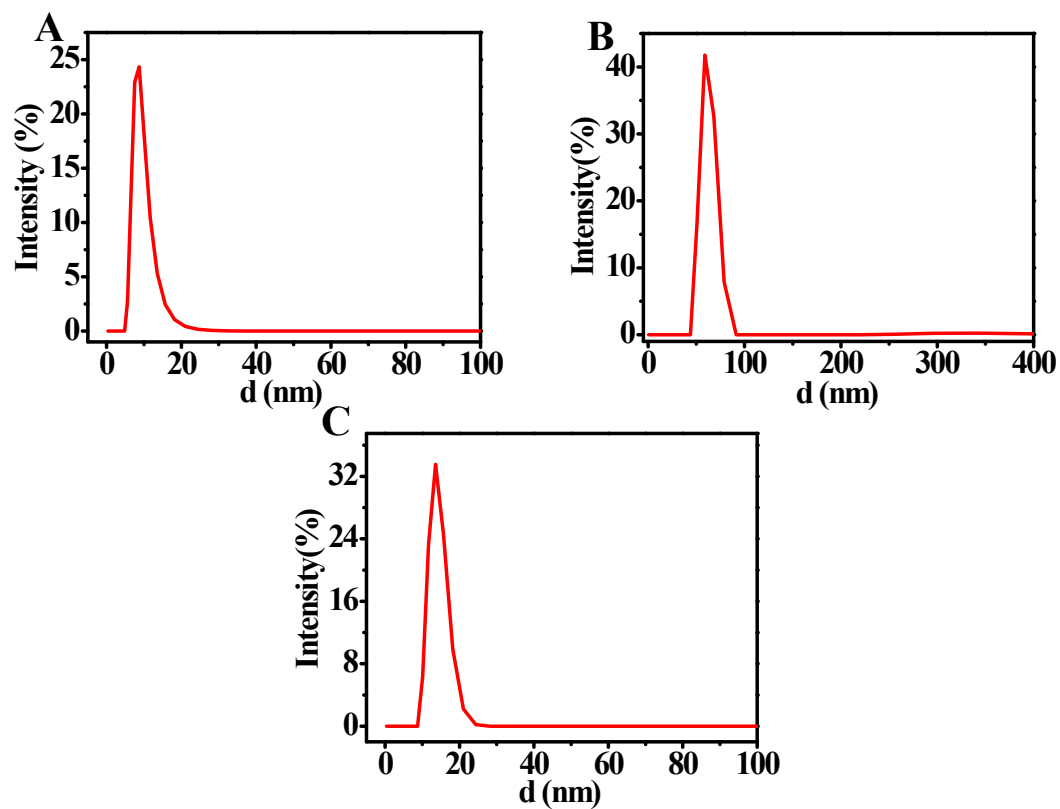
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\* Corresponding author: Tel: +86-731-88865515; fax: +86-731-88865515;

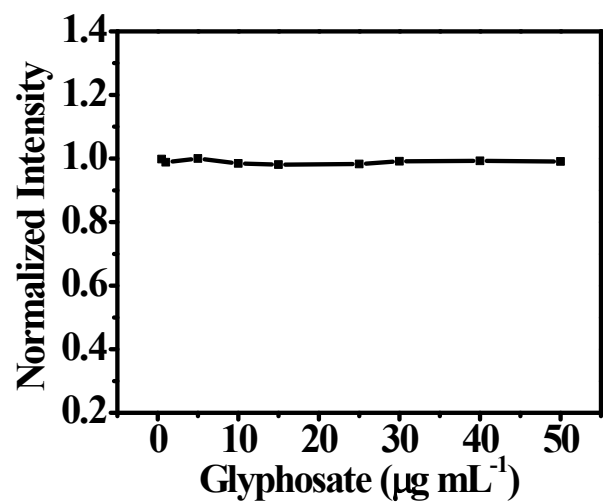
E-mail address: zhangyy@hunnu.edu.cn

## **1. Preparation of the BSA-AuNCs**

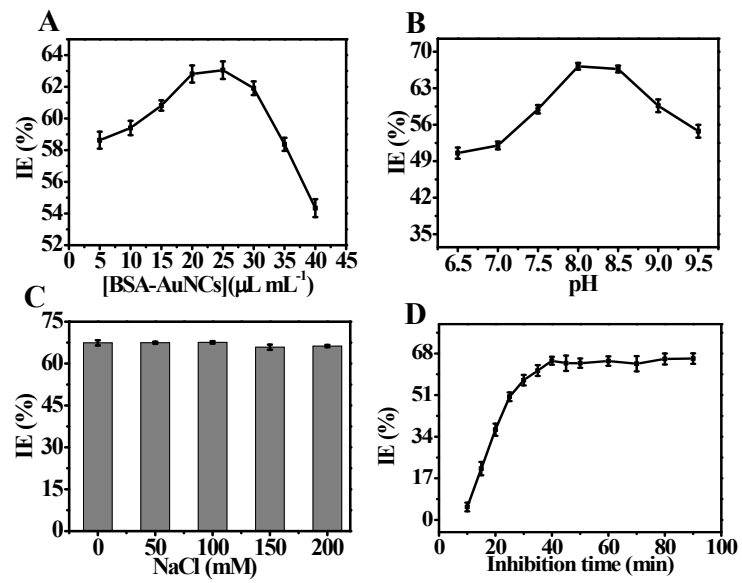
BSA-AuNCs were prepared following previous method. Briefly, 5 mL BSA solution (50 mg mL<sup>-1</sup>, 37 °C) was mixed 5 mL aqueous HAuCl<sub>4</sub> solution (10 mM, 37 °C). 2 min later, adding 1 M NaOH solution (0.5 mL). The final solution was incubated at 37 °C for 12 h then stored at 4 °C.



**Fig. S1.** DLS of (A) BSA-AuNCs; (B) BSA-AuNCs was incubated with  $10 \mu\text{g mL}^{-1}$  trypsin in Tris-HCl (50 mM, pH 8.5) for two hours in  $37^\circ\text{C}$  bath; (C) BSA-AuNCs/ trypsin incubated with  $5 \mu\text{g mL}^{-1}$  glyphosate.



**Fig. S2.** The influence of different concentration (0.5, 1.0, 5.0, 10.0, 15.0, 25, 30, 40, and 50 µg mL<sup>-1</sup>) of glyphosate on the fluorescent intensity of BSA-Au NCs.



**Fig. S3.** Effect of (A) the concentration of BSA-AuNCs, (B) pH, ionic strengths (ionic strengths were controlled by various concentrations of NaCl) and (D) inhibition time and on inhibition efficiency of BSA-AuNCs/trypsin/glyphosate. The slit widths of emission and excitation were 5 nm.

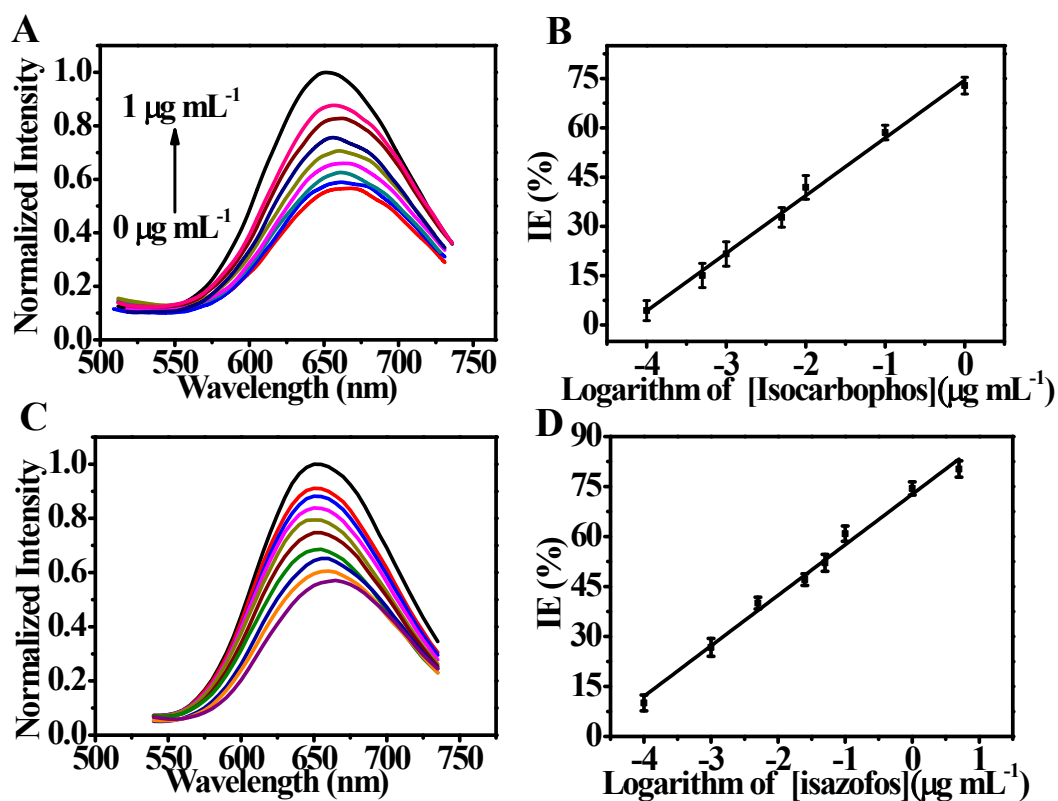


Fig. S4. (A, C) Fluorescence spectra of BSA-AuNCs/trypsin system in the presence of various concentration of isocarbophos (from bottom:  $0.1 \text{ ng mL}^{-1}$  to  $1 \text{ }\mu\text{g mL}^{-1}$ ) and isazofos (from bottom:  $0.1 \text{ ng mL}^{-1}$  to  $5 \text{ }\mu\text{g mL}^{-1}$ ). (B, D) the linear plot of the inhibition efficiency versus the logarithm concentration of isocarbophos and isazofos. The slit widths of emission and excitation were 5 nm.

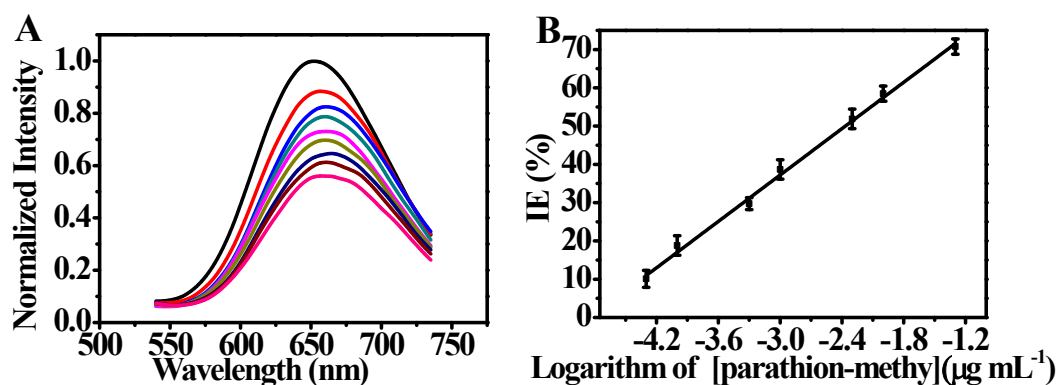


Fig. S5. (A) Fluorescence spectra of BSA-AuNCs/trypsin system in the presence of various concentration of parathion-methyl (from  $0.05 \text{ ng mL}^{-1}$  to  $50 \text{ ng mL}^{-1}$ ). (B) the linear plot of the inhibition efficiency versus the logarithm concentration of parathion-methyl. The slit widths of emission and excitation were 5 nm.

**Table S1.** Comparison of different typical techniques for the determination of organophosphorus pesticides.

<b>analyte</b>	<b>Method</b>	<b>Linear range</b>	<b>Detection limit</b>	<b>Ref.</b>
parathion	Fluorescence	—	$1.3 \times 10^{-6} \mu\text{g mL}^{-1}$	1
parathion	Cyclic voltammetric	$4.0 \times 10^{-1} - 6.0 \mu\text{g mL}^{-1}$	—	2
parathion	Fluorescence	$7.49 \times 10^{-5} - 7.49 \times 10^{-1} \mu\text{g mL}^{-1}$	$6.76 \times 10^{-5} \mu\text{g mL}^{-1}$	3
parathion	Fluorescence	$2.0 \times 10^{-5} - 2.0 \times 10^{-2} \mu\text{g mL}^{-1}$	$6.7 \times 10^{-6} \mu\text{g mL}^{-1}$	4
monocrotophos	Electrochemical	$10^{-11} - 10^{-6} \text{ M}$ ( $2.2 \times 10^{-6} - 2.2 \times 10^{-1} \mu\text{g mL}^{-1}$ )	$2.7 \times 10^{-12} \text{ M}$ ( $6.0 \times 10^{-7} \mu\text{g mL}^{-1}$ )	5
monocrotophos	Electrochemical	1–50 nM ( $2.2 \times 10^{-4} - 1.1 \times 10^{-2} \mu\text{g mL}^{-1}$ )	1.0 nM ( $2.2 \times 10^{-4} \mu\text{g mL}^{-1}$ )	6
dimethoate	Colorimetric	$2.5 \times 10^{-7} - 1 \times 10^{-4} \text{ M}$ ( $5.7 \times 10^{-2} - 23 \mu\text{g mL}^{-1}$ )	0.3 ppm ( $0.3 \times 10^{-3} \mu\text{g mL}^{-1}$ )	7
dimethoate	Chemiluminescent	—	$5 \times 10^{-5} \mu\text{g mL}^{-1}$	8
Paraoxon	Fluorescence	$5.0 \times 10^{-5} - 5.0 \times 10^{-2} \mu\text{g mL}^{-1}$	$5.0 \times 10^{-5} \mu\text{g mL}^{-1}$	9
parathion-methyl	Fluorescent	$4 \times 10^{-5} - 4 \times 10^{-3} \mu\text{g mL}^{-1}$	$1.8 \times 10^{-5} \mu\text{g mL}^{-1}$	10
paraoxon	Fluorescent	$2.5 \times 10^{-4} - 5.0 \times 10^{-2} \mu\text{g mL}^{-1}$	$1.0 \times 10^{-4} \mu\text{g mL}^{-1}$	11
methyl parathion	Fluorescent	$2.63 \times 10^{-5} - 2.63 \times 10^{-1} \mu\text{g mL}^{-1}$	$1.263 \times 10^{-5} \mu\text{g mL}^{-1}$	12
Glyphosate	Surface-enhanced Raman scattering	0.0001-10 ppm ( $0.0001 \mu\text{g mL}^{-1} - 10 \mu\text{g mL}^{-1}$ )	0.1 ppb ( $0.0001 \mu\text{g mL}^{-1}$ )	13
Glyphosate	Fluorescent	$1.0 \times 10^{-4} - 5 \mu\text{g mL}^{-1}$	$3.7 \times 10^{-4} \mu\text{g mL}^{-1}$	Present work

**Table S2. Recovery ratios of parathion-methyl in real samples.**

<b>Determination methods</b>		<b>BSA-AuNCs/trypsin sensor</b>			<b>Chromatography</b>		
<b>Samples</b>	<b>Added</b>	<b>Measured</b>	<b>Recovery</b>	<b>RSD</b>	<b>Measured</b>	<b>Recovery</b>	<b>RSD</b>
	<b>(ng mL<sup>-1</sup>)</b>	<b>(ng mL<sup>-1</sup>)</b>	<b>(%)</b>	<b>(n = 3 %)</b>	<b>(ng mL<sup>-1</sup>)</b>	<b>(%)</b>	<b>(n = 3 %)</b>
<b>Pakchoi</b>	5	4.94	98.8	4.26	5.21	104	2.92
	50	51.6	103	1.28	48.8	97.6	1.62
<b>Tomato</b>	5	4.82	96.4	2.92	4.86	97.2	2.79
	50	48.5	97.0	3.98	49.1	98.2	2.17
<b>Wheat Flour</b>	5	5.41	108	2.81	5.30	106	2.62
	50	49.8	99.6	1.92	49.8	99.6	3.42



## References

- 1 Z. Zheng, Y. Zhou, X. Li, S. Liu and Z. Tang, *Biosens. Bioelectron.*, 2011, **26**, 3081-3085.
- 2 Y. Zhao, Y. Ma, H. Li and L. Wang, *Anal. Chem.*, 2011, **84**, 386-395.
- 3 Y. Yi, G. Zhu, C. Liu, Y. Huang, Y. Zhang, H. Li, J. Zhao and S. Yao, *Anal. Chem.*, 2013, **85**, 11464-11470.
- 4 Q. Long, H. Li, Y. Zhang and S. Yao, *Biosens. Bioelectron.*, 2015, **68**, 168-174.
- 5 Y. Liu and M. Wei, *Food Control*, 2014, **36**, 49-54.
- 6 N. Chauhan and C. S. Pundir, *Anal. Chim. Acta*, 2011, **701**, 66-74.
- 7 N. Ben Oujji, I. Bakas, G. Istamboulié, I. Ait-Ichou, E. Ait-Addi, R. Rouillon and T. Noguier, *Food Control*, 2014, **46**, 75-80.
- 8 M. Catalá-Icardo, J. L. López-Paz, C. Choves-Barón and A. Peña-Bádena, *Anal. Chim. Acta*, 2012, **710**, 81-87.
- 9 X. Wu, Y. Song, X. Yan, C. Zhu, Y. Ma, D. Du and Y. Lin, *Biosens. Bioelectron.*, 2017, **94**, 292-297.
- 10 X. Yan, H. Li, X. Han and X. Su, *Biosens. Bioelectron.*, 2015, **74**, 277-283.
- 11 X. Yan, H. Li, T. Hu and X. Su, *Biosens. Bioelectron.*, 2016, **91**, 232-237.
- 12 J. Hou, J. Dong, H. Zhu, X. Teng, S. Ai and M. Mang, *Biosens. Bioelectron.*, 2015, **68**, 20-26.
- 13 M. J. Tan, Z. Y. Hong, M. H. Chang, C. C. Liu, H. F. Cheng, X. J. Loh, C. H. Chen, C. D. Liao and K. V. Kong, *Biosens. Bioelectron.*, 2017, **96**, 167-172.