Supporting Information

Fabricating an acetylcholinesterase modulated UCNPs-Cu^{2+} fluorescence biosensor for ultrasensitive detection of organophosphorus pesticides-diazinon in food

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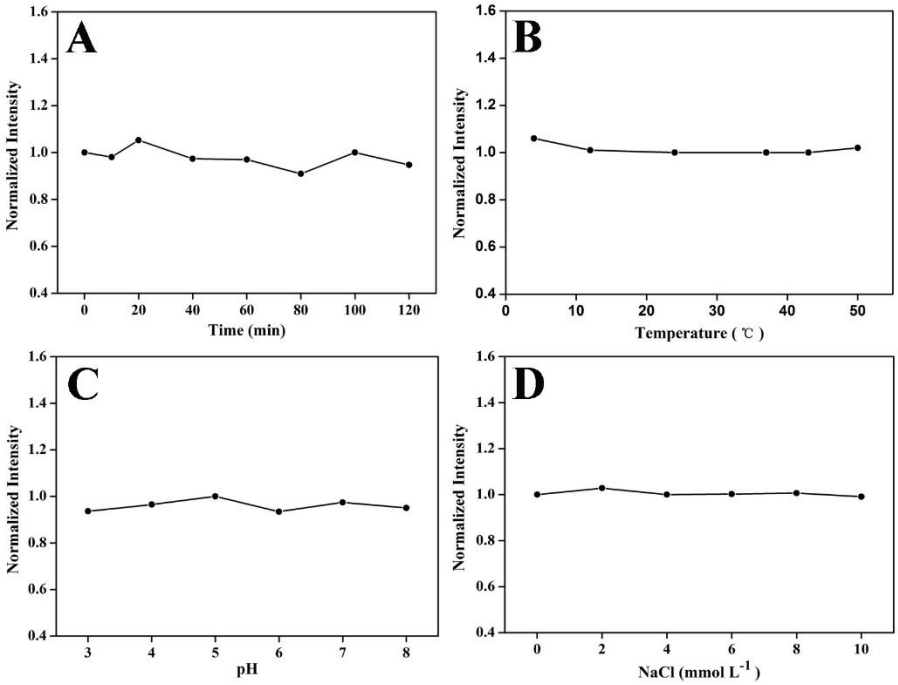

Figure S1. (A) Effect of Time on the FL intensity of UCNPs. (B) Effect of Temperature on the FL intensity of UCNPs. (C) Effect of pH on the FL intensity of UCNPs. (D) Effect of NaCl concentration on the FL intensity of UCNPs. Conditions: 0.18 mg/mL UCNPs; excitation at 980 nm.

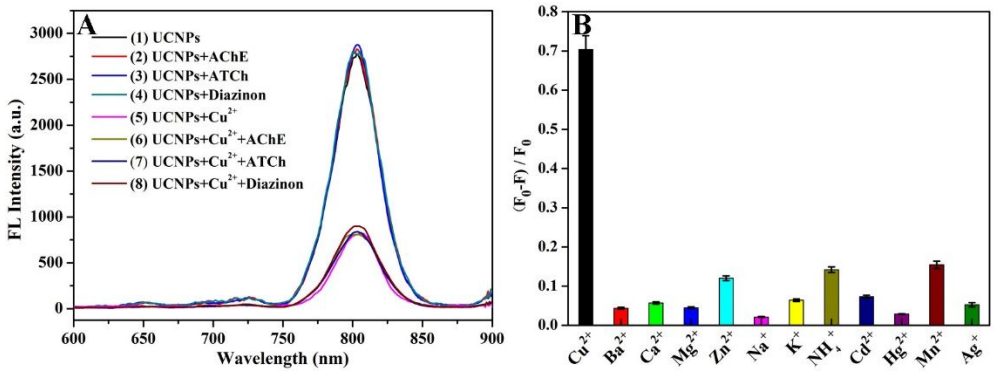

Figure S2. (A) Fluorescence spectra of UCNPs solution. (1) only UCNPs, (2) UCNPs + 25 mU/mL AChE, (3) UCNPs+10 mM ATCh, (4) UCNPs+50 ng/mL Diazinon, (5) UCNPs+5 μM Cu^{2+}, (6) UCNPs+5 μM Cu^{2+} +25 mU/mL AChE, (7) UCNPs+5 μM Cu^{2+} +20 mM ATCh and (8) UCNPs+5 μM Cu^{2+} +50 ng/mL Diazinon, respectively. (B) The luminescence quenching efficiency of the UCNPs in the presence of 5 μM of different cations including, Cu^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Na^{+}, K^{+}, NH_4^{+}, Cd^{2+}, Hg^{2+}, Mn^{2+}, Ag^{+} respectively. F_0 and F stand for the fluorescent intensities of UCNPs in the absence and presence of cations respectively. Conditions: 0.18 mg/mL UCNPs; excitation at 980 nm.

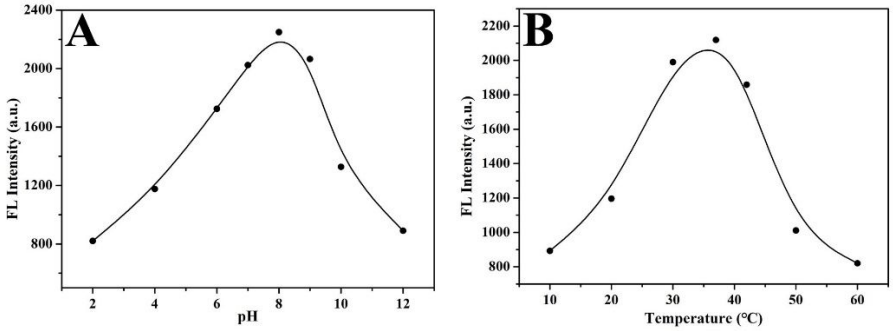

Figure S3. (A) The fluorescent emission intensity of UCNPs-Cu^{2+}-AChE-ATCh system at different pH. (B) The fluorescent emission intensity of UCNPs-Cu^{2+}-AChE-ATCh system at different Temperature. Conditions: 0.18 mg/mL UCNPs; 5 μM Cu^{2+}; 25 mU/mL AChE; 20 mM ATCh.

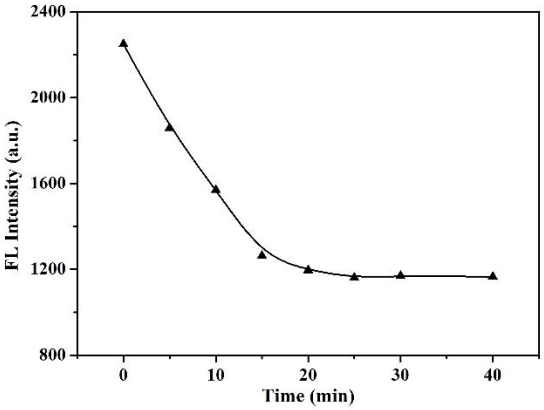

Figure S4. Effects of incubation time on the fluorescence responses of UCNPs-Cu^{2+}-AChE-ATCh system to pesticides detection. Conditions: 0.18 mg/mL UCNPs; 5 μM Cu^{2+}; 25 mU/mL AChE; 20 mM ATCh; 50 ng/mL Diazinon.

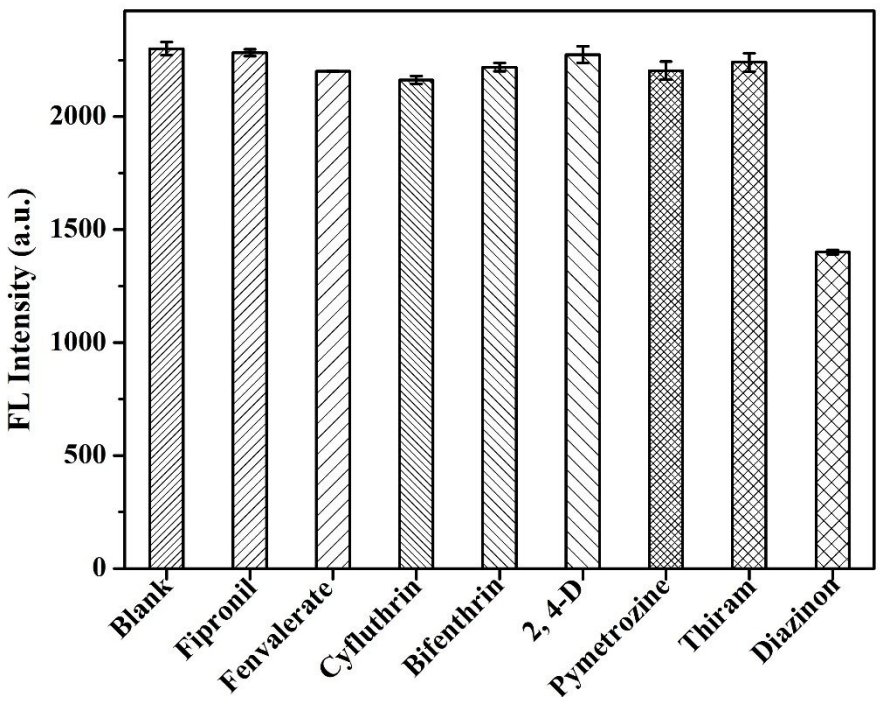

Figure S5. Selectivity of the proposed UCNPs-Cu^{2+}-AChE-ATCh system toward OPs against other pesticides. Conditions: 0.18 mg/mL UCNPs; 5 μM Cu^{2+}; 25 mU/mL AChE; 20 mM ATCh; 10 ng/mL Pesticides.

107 **Table S1.** Comparison of the analytical performances of the developed method with

108 that of the reported methods for diazinon detection

Method	Analytical range (ng/mL or ng/g or nM)	LOD (ng/mL or ng/g or nM)	References
Enzyme sensor	0.01-10000	0.2	*1*
Gold nanoprobe	0.30-17.30	0.2	*2*
Fluorescent chemosensor	500-10000	378	*3*
HPLC-DAD	0.8-800	0.3	*4*
UV-vis spectrophotometric	10-60	11	*5*
GC-flame ionization	0.55 – 5000	0.17	*6*
GC-MS system	50–1000	3	*7*
HPLC-HRMS	0.1-20	0.1	*8*
ELISA assays	0.9-6	0.9	*9*
Fluorescent sensor	1.05-206	0.13	*10*
Fluorescent sensor	0.1-100000	6.7	*11*
The developed method	0.1-50	0.05	This work

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122 **Table S2.** Comparison of the results from GC-MS and the developed method for

123 diazinon detection in authentic apple samples

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Sample	Amount ± SD (ng/g)	
	GC-MS	The developed method
Sample 1	ND	ND
Sample 2	1.23±0.11	1.19±0.20
Sample 3	8.72±0.83	8.90±0.75
Sample 4	24.62±2.45	23.81±1.87
Sample 5	15.19±1.36	16.08±1.59
Sample 6	61.42±3.11	62.11±3.02
Sample 7	43.45±3.05	45.03±2.71

125 ND, not detected

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127 **References**

128 1. Lee, H. S.; Kim, Y. A.; Cho, Y. A.; Yong, T. L. Oxidation of organophosphorus

129 pesticides for the sensitive detection by a cholinesterase-based biosensor. *Chemosphere*

130 **2002**, *46,* 571-576.

131 2. Satnami, M. L.; Korram, J.; Nagwanshi, R.; Vaishnav, S. K.; Karbhal, I.; Dewangan,

132 H. K.; Ghosh, K. K. Gold Nanoprobe for Inhibition and Reactivation of

133 Acetylcholinesterase: An Application to Detection of Organophosphorus Pesticides.

134 *Sensors & Actuators B Chemical* **2018**, *267*, 155-164.

135 3. Azab, H. A.; Kamel, R. M. Sensitive and selective fluorescent chemosensor for the

136 detection of some organophosphorus pesticides using luminescent Eu(III) complex.

137 *Journal of Photochemistry & Photobiology A Chemistry* **2016**, *321*, 33-40.

138 4. Behbahani, M.; Veisi, A.; Omidi, F.; Badi, M. Y.; Noghrehabadi, A. R.; Esrafily, A.;

139 Sobhi, H. R. Conjunction of a new ultrasonic assisted dispersive soild phase extraction

140 method with HPLC-DAD for trace determination of diazinon in biological and water
141 media. *New Journal of Chemistry* **2018**, *42*, 4289-4296.
142 5. Cao, H.; Nam, J.; Harmon, H. J.; Branson, D. H. Spectrophotometric detection of
143 organophosphate diazinon by porphyrin solution and porphyrin-dyed cotton fabric.
144 *Dyes & Pigments* **2007**, *74*, 176-180.
145 6. Mir Ali Farajzadeh, A. S. H.; Mogaddam, M. R. A. Development of a new
146 temperature-controlled liquid phase microextraction using deep eutectic solvent for
147 extraction and preconcentration of diazinon, metalaxyl, bromopropylate, oxadiazon,
148 and fenazaquin pesticides from fruit juice and vegetable samples followed by gas
149 chromatography-flame ionization detection. *Journal of Food Composition and Analysis*
150 **2017,** *66*, 90-97.
151 7. Vera, R.; Insa, S.; Fontàs, C.; Anticó, E. A new extraction phase based on a polymer
152 inclusion membrane for the detection of chlorpyrifos, diazinon and cyprodinil in natural
153 water samples. *Talanta* **2018**, *185*, 291–298.
154 8. Hu, T. T.; Lu, C. M.; Li, H.; Zhang, Z. X.; Zhao, Y. H.; Li, J., Determination of Eleve
155 Organophosphorus Pesticide Residues in Textiles by Using HPLC-HRMS. *Analytical*
156 *Sciences* **2017**, *33*, 1027–1032.
157 9. Lee, E. K.; Kim, Y. J.; Park, W. C.; Chung, T.; Yong, T. L., Monoclonal antibody-
158 based enzyme-linked immunosorbent assays for the detection of the organophosphorus
159 insecticide diazinon. *Analytica Chimica Acta* **2005**, *530*, 143-153.
160 10. Arvand, M.; Mirroshandel, A. A. An efficient fluorescence resonance energy
161 transfer system from quantum dots to graphene oxide nano sheets: Application in a

162 photoluminescence aptasensing probe for the sensitive detection of diazinon. *Food*
163 *Chem* **2019**, *280*, 115-122.
164 11. Cheng, N.; Song, Y.; Fu, Q.; Du, D.; Luo, Y.; Wang, Y.; Xu, W.; Lin, Y. Aptasensor
165 based on fluorophore-quencher nano-pair and smartphone spectrum reader for on-site
166 quantification of multi-pesticides. *Biosens Bioelectron* **2018**, *117*, 75-83.