

Supporting Information

A Label-free Si Quantum Dots-based Photoluminescence Sensor for Ultrasensitive Detection of Pesticides

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The fluorescence quantum yields measurements: Photoluminescence (PL) quantum yields of the silicon quantum dots were obtained by using the comparative method of Williams et al.¹ The quantum yield of SiQDs, Q_x , is calculated according to the equation 1:

$$Q_x = Q_R \cdot \frac{A_R}{A_x} \cdot \frac{F_x}{F_R} \cdot \left(\frac{n_x}{n_R} \right)^2 \quad (1)$$

where Q_R is the quantum yield of the standard, A is the absorbance of the solution, F is the corrected emission intensity and n is the average refractive index of the solution. Subscripts R and X refer to the reference and SiQDs, respectively. Quinine sulfate is used as the standard for the quantum yield correction. Fletcher² reported that the relative fluorescence quantum yield of quinine sulfate have no unexplainable deviations from a constant value with the excitation range set from 240 to 400 nm. The maximum excitation wavelengths of silicon quantum dots are at ~360 nm. Therefore, we chose 360 nm as the excitation wavelength. The quinine sulfate ($Q_R = 0.54$) was dissolved in 0.1 M H_2SO_4 (refractive index (n_R) of 1.33) and the SiQDs was dissolved in absolute ethanol ($n_x = 1.003$).³ To minimize re-absorption effects, the absorbances of SiQDs and quinine sulfate solution were adjusted never exceed 0.1 at the excitation wavelength. The measurement results are as follows: $A_R=0.051$, $A_x=0.049$, $F_x=2382$, $F_R=7895$, $\frac{n_x}{n_R} = 0.7541$. The PL quantum yields of SiQDs were up to ~9.6%.

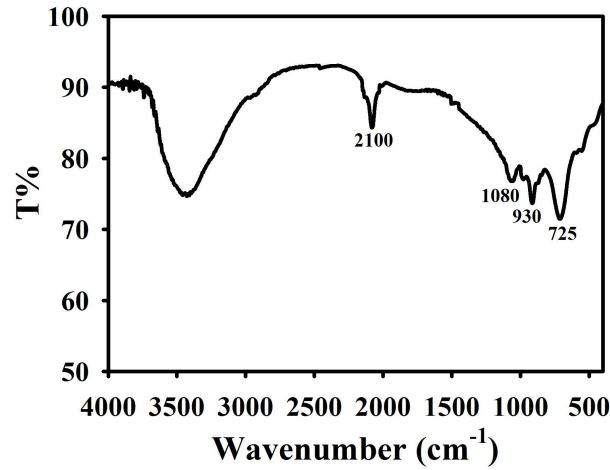


Figure S1. FTIR spectra of SiQDs.

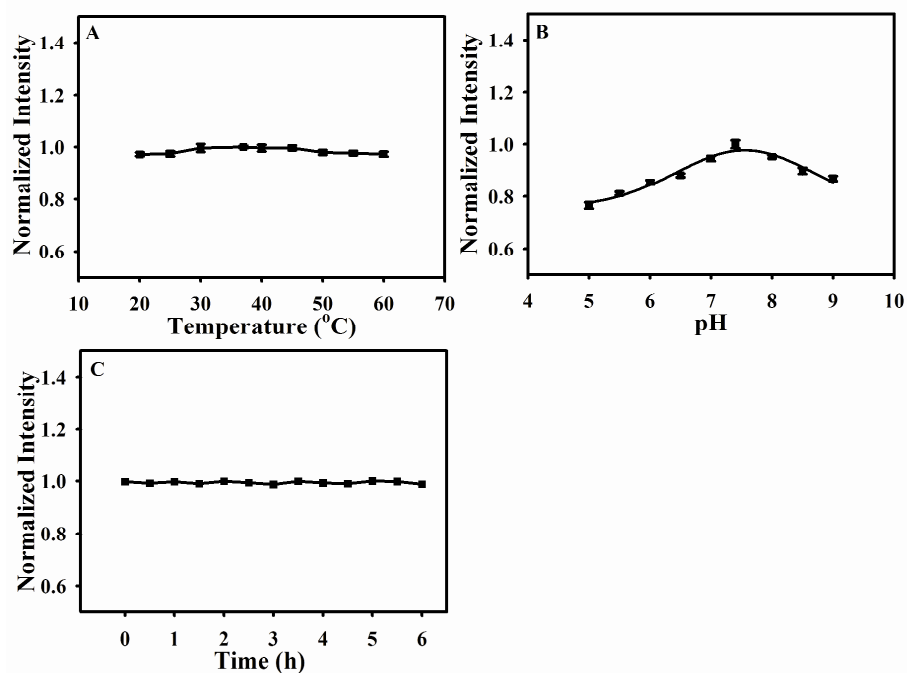


Figure S2. Effects of temperature (A), pH (B) and photostability (C) on the PL intensity of SiQDs solution.

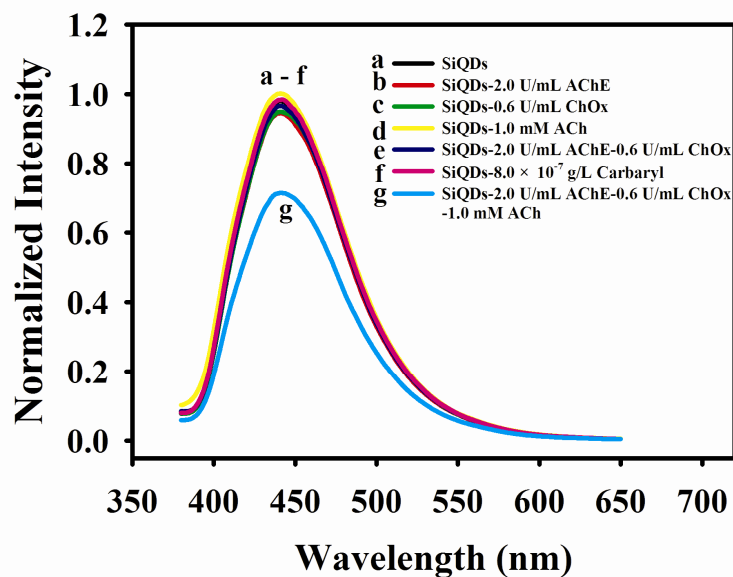


Figure S3. PL spectra of SiQDs solution. (a) only SiQDs and buffer, (b) SiQDs +2 U/mL AChE, (c) SiQDs + 0.6 U/mL ChOx, (d) SiQDs + 1.0 mM ACh, (e) SiQDs + 2 U/mL AChE + 0.6 U/mL ChOx, (f) SiQDs + 8.0×10^{-7} g/L carbaryl and (g) SiQDs + 2 U/mL AChE + 0.6 U/mL ChOx + 1.0 mM ACh, respectively.

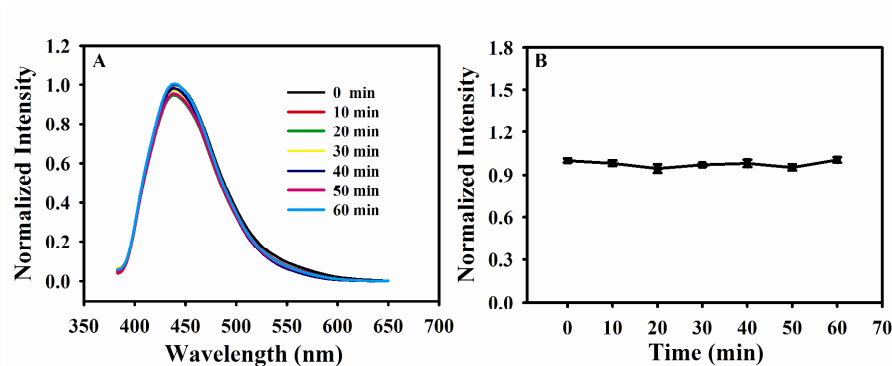


Figure S4. (A) Time-dependent PL spectra of SiQDs-AChE-ChOx system in the saturated oxygen atmosphere. (B) Effects of reaction time (0-60 min) on the PL intensity of SiQDs-AChE-ChOx system. The measurements were performed at 40 °C in PBS (pH 8.0) and enough oxygen was passed. The concentrations of AChE and ChOx are 2 U/mL and 0.6 U/mL, respectively.

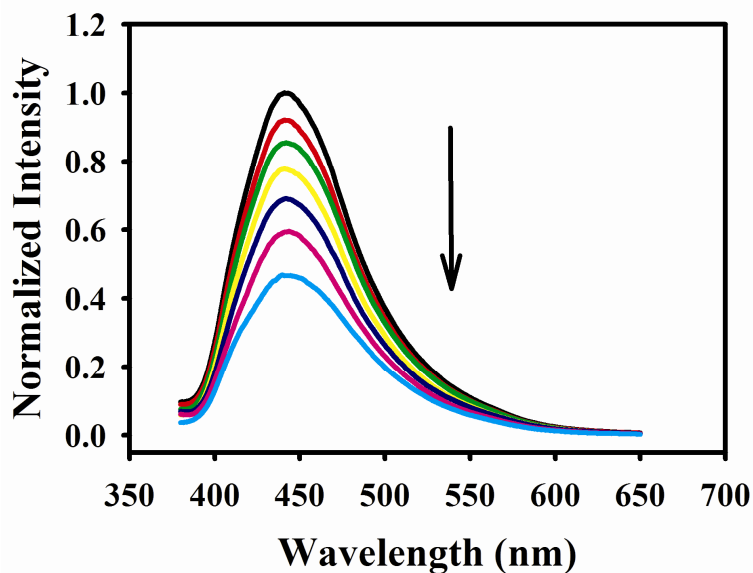


Figure S5. PL spectra of SiQDs upon stepwise addition of H_2O_2 (from top to bottom, the final concentration of H_2O_2 is 0, 35, 120, 200, 300, 450 and 600 μ M, respectively).

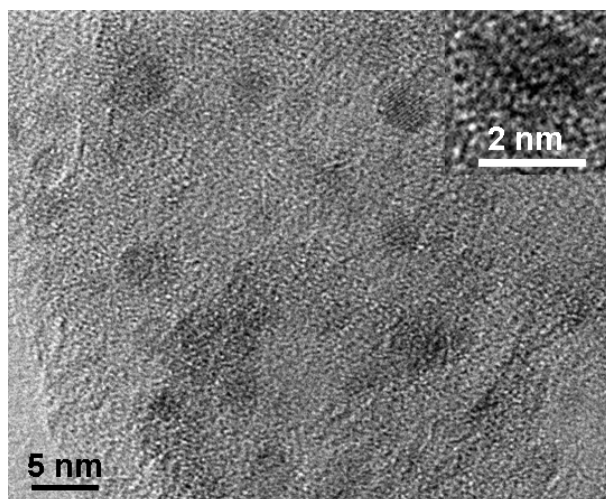


Figure S6. Transmission electron microscopy image of SiQDs-AChE-ChOx system in the present of 1.0 mM ACh; the insert shows the high-resolution transmission electron microscopy image of SiQDs-AChE-ChOx system in the present of 1.0 mM ACh.

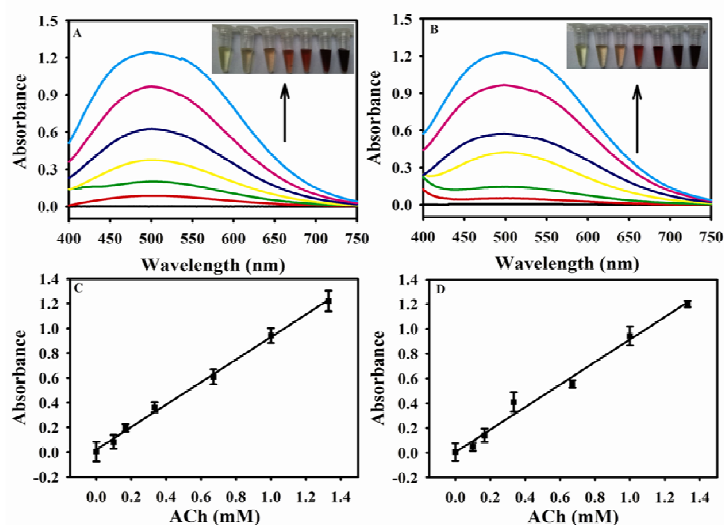


Figure S7. (A, B): Absorbance spectra of variable concentrations of ACh upon the interaction with AChE, ChOx and alkaline hydroxylamine in the presence (A) and absence (B) of SiQDs; The insert shows the color change with increasing concentrations of ACh from left to right (0-1.33 mM). (C, D) : Plots of the absorption band at 520 nm vs ACh concentrations in the presence (C) and absence (D) of SiQDs.

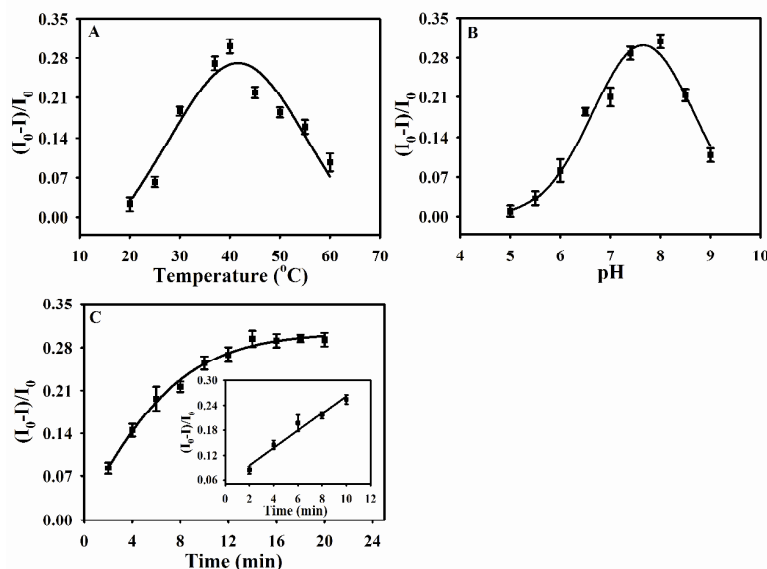


Figure S8. The effect of pH, temperature and time on the PL quenching of SiQDs-AChE-ChOx system in the absence and presence of 1.0 mM ACh. The insert shows a linear response of the PL intensity of SiQDs-AChE-ChOx system vs the incubation time from 0 to 10 min. I_0 and I represent the PL intensity of the SiQDs-ChOx-AChE system before and after incubating with ACh, respectively.

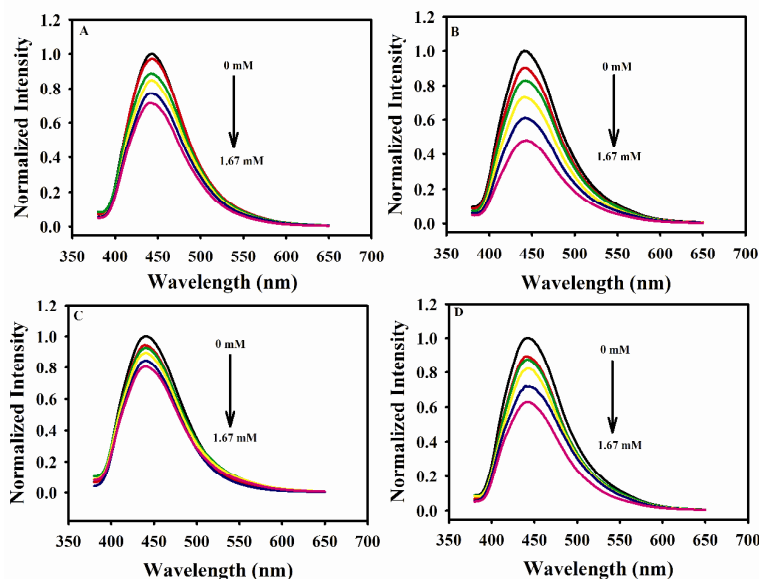


Figure S9. The PL spectra of SiQDs in the presence of varying concentrations of AChE, ChOx and ACh. (A): The concentrations of AChE and ChOx are 2 U/mL and 2 U/mL, respectively; (B): The concentrations of AChE and ChOx are 2 U/mL and 0.6 U/mL, respectively; (C): The concentrations of AChE and ChOx are 5 U/mL and 0.3 U/mL, respectively; (D): The concentrations of AChE and ChOx are 0.3 U/mL and 2 U/mL, respectively. The concentrations of ACh: 0, 0.33, 0.5, 0.67, 1.33, 1.67 mM.

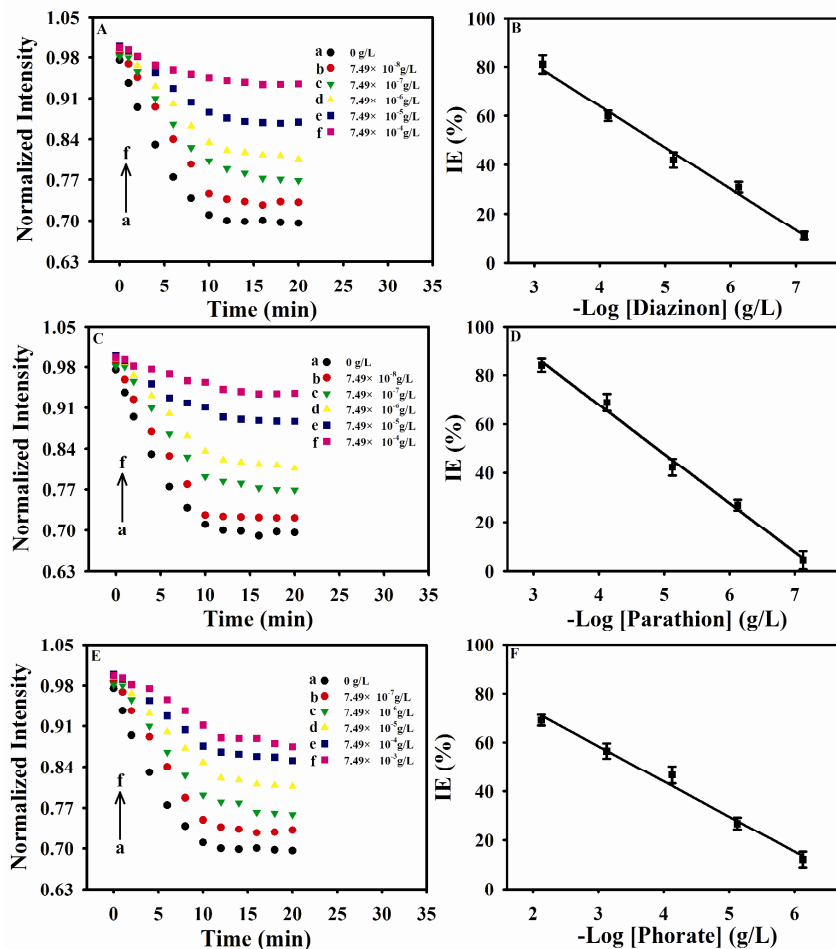


Figure S10. (A, C, E): Incubation time dependence of the PL intensity of SiQDs-AChE-ChOx system in the present of 1.0 mM ACh and variable concentrations of diazinon (A), parathion (C) and phorate (E), respectively. (B, D, F): Inhibition efficiency vs the logarithm of diazinon (B), parathion (D) and phorate (F) concentrations. All measurements were performed in PBS, pH= 8.0. The concentrations of AChE and ChOx are 2 U/mL and 0.6 U/mL, respectively.

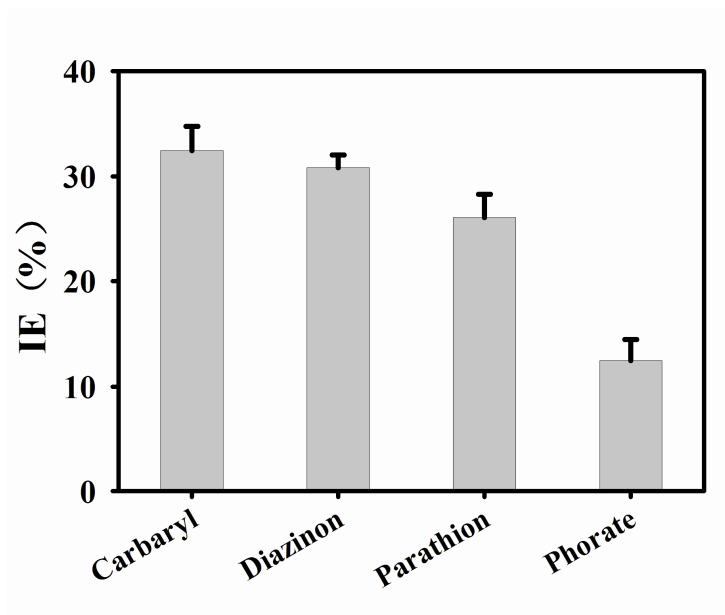


Figure S11. Inhibition efficiency of 8.0×10^{-7} g/L of different pesticide toward SiQDs-AChE-ChOx-ACh system. (Each data point is an average of five measurements.).

Table S1. Comparison of various approaches to pesticides detection.

Target analyte	Detection technique	System			Linear range (g/L)	Detect limit (g/L)	Reference
carbaryl	Colorimetric & fluorometric	Rhodamine nanoparticle	B-covered	gold	1.0×10^{-7} - 1.0×10^{-4}	1.0×10^{-7}	⁴
carbaryl	colorimetric	Sol gel derived silica inks			Not given	$\sim 2.0 \times 10^{-6}$	⁵
carbaryl	Amperometric	Cobalt(II) phthalocyanine modified cellulose-graphite composite			1.0×10^{-5} - 5.0×10^{-5}	Not given	⁶
carbaryl	Amperometric	CdS-decorated nanocomposite		graphene	2.0×10^{-6} - 2.0×10^{-3}	7×10^{-7}	⁷
carbaryl	Cyclic voltammetric	Self assembled modified electrode		gold	4.0×10^{-4} - 6.0×10^{-3}	Not given	⁸
carbaryl	Fluorescence	Label-free SiQDs			7.49×10^{-9} - 7.49×10^{-4}	7.25×10^{-9}	This work
diazinon	Fluorescence	CompositeQDs@MIPNanospheres			5.0×10^{-5} - 6.0×10^{-4}	3.86×10^{-5}	⁹
diazinon	Colorimetric & fluorometric	Rhodamine nanoparticle	B-covered	gold	1.0×10^{-7} - 1.0×10^{-4}	1.0×10^{-7}	⁴
diazinon	Amperometric	Cobalt(II) phthalocyanine (CoPc)modified cellulose-graphite			1.9×10^{-5} - 5.0×10^{-5}	Not given	⁶
diazinon	Fluorescence	Label-free SiQDs			7.49×10^{-8} - 7.49×10^{-4}	3.25×10^{-8}	This work
parathion	Amperometry	CNTs			5.8×10^{-7} - 1.2×10^{-5}	4.4×10^{-6}	¹⁰
parathion	Fluorescence	(PAH/CdTe QDs)x multilayers			Not mentioned	1.3×10^{-9}	¹¹
parathion	Amperometric	Cobalt(II) phthalocyanine (CoPc)modified cellulose-graphite			6.0×10^{-6} - 1.0×10^{-4}	Not given	⁶
parathion	Cyclic voltammetric	Self assembled modified electrode		gold	4.0×10^{-4} - 6.0×10^{-3}	Not given	⁸
parathion	Fluorescence	Label-free SiQDs			7.49×10^{-8} - 7.49×10^{-4}	6.76×10^{-8}	This work
phorate	Colorimetric & fluorometric	Rhodamine nanoparticle	B-covered	gold	1.0×10^{-6} - 1.0×10^{-3}	1.0×10^{-6}	⁴
phorate	Two-step technique	Sensitive equipment materials			1.5×10^{-5} - 1.0×10^{-3}	1.2×10^{-5}	¹²
phorate	Fluorescence	Label-free SiQDs			7.49×10^{-7} - 7.49×10^{-3}	1.9×10^{-7}	This work

Reference:

- (1) Williams, A. T. R.; Winfield, S. A.; Miller, J. N. *Analyst* **1983**, *108*, 1067-1071.
- (2) Fletcher, A. N. *Photochem. Photobiol.* 1969, *9*, 439-444.
- (3) Zhao, Q.-L.; Zhang, Z.-L.; Huang, B.-H.; Peng, J.; Zhang, M.; Pang, D.-W. *Chem. Commun.* **2008**, 5116-5118.
- (4) Liu, D.; Chen, W.; Wei, J.; Li, X.; Wang, Z.; Jiang, X. *Anal. Chem.* **2012**, *84*, 4185-4191.
- (5) Hossain, S. M. Z.; Luckham, R. E.; McFadden, M. J.; Brennan, J. D. *Anal. Chem.* **2009**, *81*, 9055-9064.
- (6) Tanimoto de Albuquerque, Y. D.; Ferreira, L. F. *Anal. Chim. Acta* **2007**, *596*, 210-221.
- (7) Wang, K.; Liu, Q.; Dai, L.; Yan, J.; Ju, C.; Qiu, B.; Wu, X. *Anal. Chim. Acta* **2011**, *695*, 84-88.
- (8) Pedrosa, V.; Caetano, J.; Machado, S.; Bertotti, M. *Sensors* **2008**, *8*, 4600-4610.
- (9) Zhao, Y.; Ma, Y.; Li, H.; Wang, L. *Anal. Chem.* **2011**, *84*, 386-395.
- (10) Chough, S. H.; Mulchandani, A.; Mulchandani, P.; Chen, W.; Wang, J.; Rogers, K. R. *Electroanalysis* **2002**, *14*, 273-276.
- (11) Zheng, Z.; Zhou, Y.; Li, X.; Liu, S.; Tang, Z. *Biosens. Bioelectron.* **2011**, *26*, 3081-3085.
- (12) Blinov, V.; Volchek, K.; Kuang, W.; Brown, C. E.; Bhalerao, A. *Ind. Eng. Chem. Res.* **2012**, *52*, 1405-1413.