Supplementary Materials:

Carboxylic silica nanosheets-platinum nanoparticles modified glass carbon electrode for pesticides detection

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Preparation process of SNS

Briefly, 3.0 g of montmorillonite was dissolved by 5.0 ml of DI water, and then 20 ml of nitric acid, 20 ml of hydrochloric acid and 5.0ml of perchloric acid were added to the montmorillonite aqueous solution respectively. In succession, the above mixture solution was heated to the temperature of 150℃ on an electric hot plate for 5 h. As

approximately dried, the solution was added to 10 ml of hydrochloric acid. Sequentially heated 10-min then the white suspension was separated by centrifuging at 12,000 rpm for 20 min, washed with DI water for several cycles, dried in an oven at 50℃ to gain SNS.

Optimization of the preparation of the biosensor

Optimization of volume of Pt NPs–CSNS–NF

The current response of the biosensor to ATCl was affected by the modified dosage of Pt NPs–CSNS–NF. During the dosage of Pt NPs–CSNS–NF ranged from 2 to 10 μl, the current response increased along with the modified dosage. When the dosage exceeded 5 μl, the current response did not significantly increase and the base line turned high, possibly because of increased resistance and double layer capacitance of the modified electrode. Hence, the optimal dosage of Pt NPs–CSNS–NF was 5 μl.

Optimization of ratio of Pt NPs in Pt NPs–CSNS

The current response of the biosensor to ATCl was also affected by the ratio of Pt NPs in Pt NPs–CSNS, when the ratio of Pt NPs was from 2 wt% to 8 wt%, the current response increased with the ratio of Pt NPs. As the ratio of Pt NPs exceeded 5 wt%, current response did not significantly increase and the base line turned high, possibly

because of Pt NPs aggregation and not well separated at CSNS. Then, the optimal ratio was selected as 5 wt%.

Optimization of pH

The bioactivity of the immobilized AChE depended on the pH of the ATCl solution. **Fig. S1** showed the relationship between the current response of the biosensor and the pH of the ATCl solution. The current response increased with increasing pH and reached a maximum at pH 7.4. Further increase of the pH of the ATCl solution led to a gradual decrease of the current response in the pH range from 6.8 to 8.0. Obviously, the maximum current response was obtained at pH 7.4. This result indicated that pH 7.4 was the optimum pH for catalytic behavior of the NF/AChE–CS/Pt NPs–CSNS–NF/GCE biosensor.

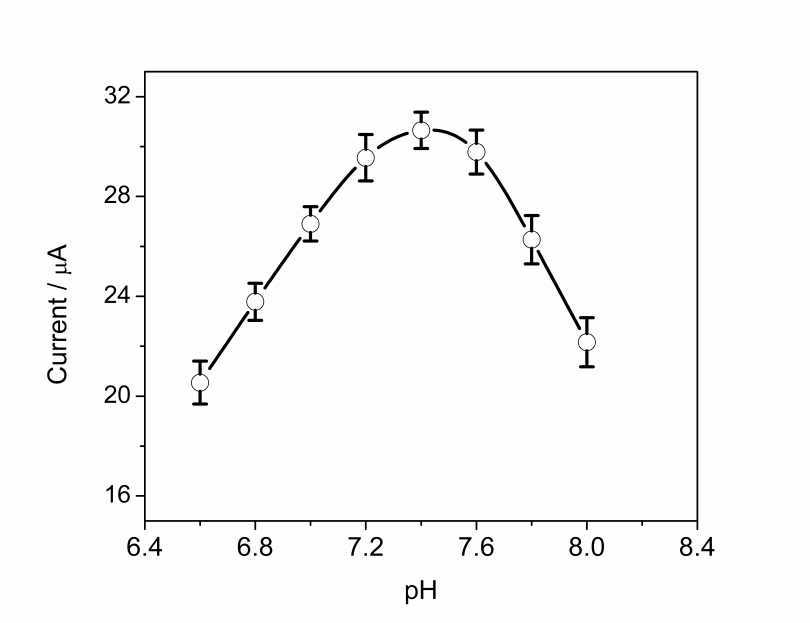

Fig. S1

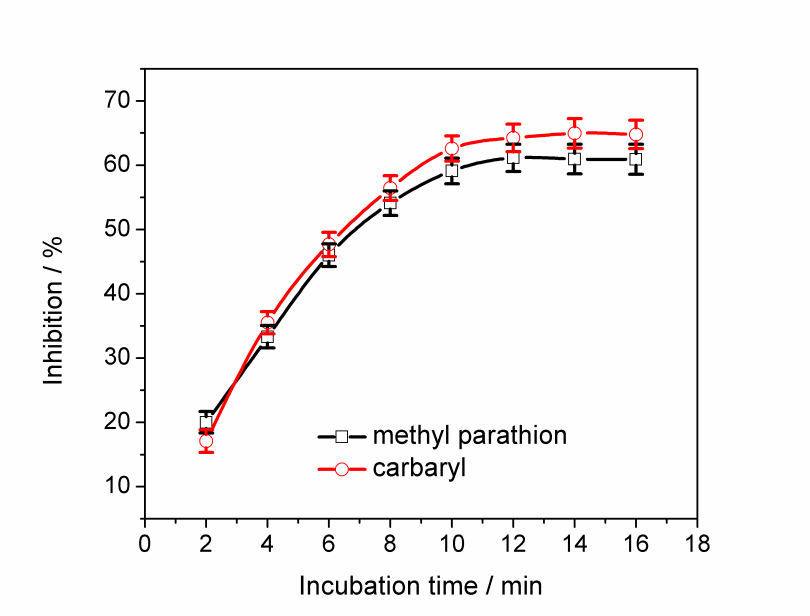

Fig. S2

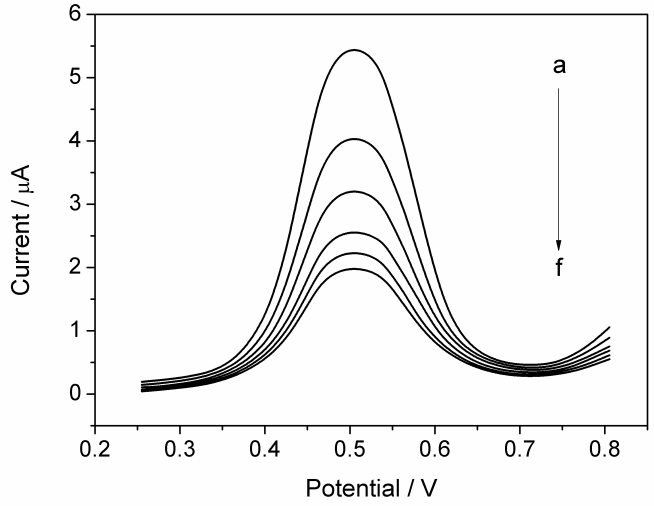

Fig. S3

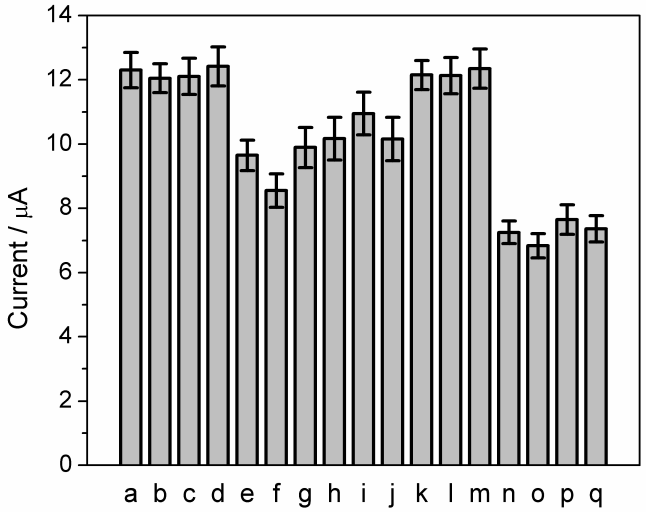

Fig. S4

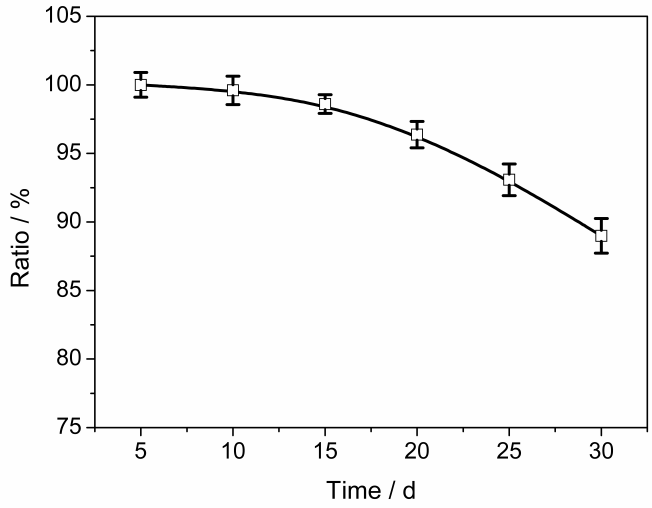

Fig. S5

Fig. S1. Effect of pH on current response of the NF/AChE–CS/Pt NPs–CSNS–NF/GCE biosensor in 0.5 mM ATCl. Scan rate: 0.10V/s at 25 ^{o}C.

Fig.S2. Inhibition on 10^{-9} M methyl parathion and 10^{-9} M carbaryl at different exposure time.

Fig. S3. DPV of the NF/AChE–CS/Pt NPs–CSNS–NF/GCE in 0.1 M PBS containing 0.5 mM ATCl after incubation with 0 (a), 10^{-12} M (b), 10^{-11} M (c), 10^{-10} M (d), 10^{-9} M (e) and 10^{-8} M (f) methyl parathion for 10 min. Pulse amplitude: 0.05 V; pulse width: 0.05 s.

Fig.S4 Current response in 0.1 M PBS containing 0.5 mM ATCl in the absence (a) and presence of 0.5 mM glucose (b), 0.5 mM citric acid (c), 0.5 mM oxalic acid (d), 0.5 mM p-nitrophenol (e), 0.5 mM nitrobenzene (f), 0.5 mM p-nitroaniline (g), 0.5 mM trinitrotoluene (h), 0.5 mM toluene (i), 0.5 mM p-toluenesulfonic acid (j), 0.5 mM PO_4^{3-} (k), 0.5 mM SO_4^{2-} (l), 0.5 mM NO_3^{-} (m) 10^{-9} M malathion (n), 10^{-9} M acephate (o), 10^{-9} M chlorpyrifos (p), and 10^{-9} M carbofuran (q) after incubated by 10^{-9} M methyl parathion for 10 min.

Fig. S5. The retained ratio of its initial current response (in 0.1 M PBS containing 0.5 mM ATCl) of the biosensor with time. Scan rate: 0.10 V/s at 25 ^{o}C.

Table S1

Linear relationships between inhibition percentage and the concentration of pesticides

Sample	Linearization equation	Liner range (M)	Detection limit (M)	R[c]
methyl parathion[a]	I(%)=13.51 lgC + 188.78	10^{-12} -10^{-10}	5.52×10^{-13}	0.993
methyl parathion[b]	I(%)=5.39 lgC + 107.13	10^{-10} -10^{-8}	–	0.995
carbaryl[a]	I(%)=17.73 lgC + 233.93	10^{-12} -10^{-10}	5.65×10^{-13}	0.996
carbaryl[b]	I(%)=5.17 lgC + 108.86	10^{-10} -10^{-8}	–	0.992

[a] low concentration; [b] high concentration; [c] correlation coefficient

Table S2

Inhibition of intra-assay and inter-assay for 6 assays

Assay number	1	2	3	4	5	6
Inhibition (%)[a]	52.92	53.28	51.85	50.38	49.85	49.52
Inhibition (%)[b]	51.93	49.28	52.85	52.25	49.38	48.52

[a] intra-assay; [b] inter-assay

Table S3

Recovery studies of spiked practical samples (n=6)

Sample	pesticide	Added (M)	Found (M)	Recovery (%)	RSD (%)
Tap water	methyl parathion	0.00	Not detected	–	–
		5.00×10^{-11}	4.82×10^{-11}	96.4	3.9
		1.00×10^{-10}	0.933×10^{-10}	93.3	4.2
		5.00×10^{-10}	4.77×10^{-10}	95.4	6.5
	carbaryl	0.00	Not detected	–	–
		5.00×10^{-11}	4.76×10^{-11}	95.2	4.4
		1.00×10^{-10}	0.957×10^{-10}	95.7	4.5
		5.00×10^{-10}	4.68×10^{-10}	93.6	4.8
Lake water	methyl parathion	0.00	Not detected	–	–
		5.00×10^{-11}	5.27×10^{-11}	105.4	3.6
		1.00×10^{-10}	0.966×10^{-10}	96.6	4.8
		5.00×10^{-10}	5.16×10^{-10}	103.2	3.8
	carbaryl	0.00	Not detected	–	–
		5.00×10^{-11}	5.32×10^{-11}	106.4	4.7
		1.00×10^{-10}	0.987×10^{-10}	98.7	4.3
		5.00×10^{-10}	4.86×10^{-10}	97.2	6.6
Apple	methyl parathion	0.00	Not detected	–	–
		5.00×10^{-11}	4.76×10^{-11}	95.2	4.6
		1.00×10^{-10}	0.935×10^{-10}	93.5	4.1
		5.00×10^{-10}	4.88×10^{-10}	97.6	6.3
Cabbage	carbaryl	0.00	Not detected	–	–
		5.00×10^{-11}	5.26×10^{-11}	105.2	3.7
		1.00×10^{-10}	0.963×10^{-10}	96.3	4.6
		5.00×10^{-10}	5.17×10^{-10}	103.4	3.9