Supporting Information to

Direct Electrochemical Analysis in Complex Samples Using ITO Electrodes Modified with Permselective Membranes Consisting of Vertically Ordered Silica Mesochannels and Micelles

*Fei Yan, Wenjing Zheng, Lina Yao and Bin Su**

Institute of Microanalytical Systems, Department of Chemistry & Center for Chemistry of High-Performance and Novel Materials, Zhejiang University, Hangzhou, 310058, China

* Corresponding author. E-mail: *subin@zju.edu.cn*

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S1. Chemicals and Materials

All chemicals were used as received without further purification and all aqueous solutions were prepared with ultrapure water (18.2 MΩ·cm). Tetraethoxysilane (TEOS, ≥99.0%) and hexaammineruthenium(III) chloride ($Ru(NH_3)_6Cl_3$, 98%) were obtained from Sigma. Hydroxymethylferrocene (FcMeOH, 97%) and cetyltrimethylammonium bromide (CTAB, ≥98%) were bought from Alfa Aesar. Concentrated ammonia aqueous solution (25 wt%), potassium ferricyanide ($K_3[Fe(CN)_6]$), poasium hydrogen phthalate (KHP), paraoxon, 1-chloro-3-nitrobenzene(*m*-NCB, 98%) and chloramphenicol (CAP, 98%) were ordered from Aladdin. The stock solutions of paraoxon, *m*-NCB and CAP were prepared with ethanol and stored at 4 °C for use. ITO coated glasses (surface resistivity < 17 ohm/square, thickness 100 ± 20 nm) were first treated by 1 M NaOH, followed by sonication in acetone, ethanol and deionized water sequentially, prior to use.

S2. Preparation of the OSM@SM/ITO Electrode

The OSM@SM/ITO electrodes were prepared using the Stöber-solution growth approach as previously reported.[1] Typically, CTAB (0.16 g) was dissolved in ethanol (30 mL) and water (70 mL), to which the concentrated ammonia aqueous solution (10 μL, 25 wt. %) and TEOS (80 μL) were subsequently added under stirring. Then the ITO electrodes were immersed into above solution for 24 h under quiescent condition at 60 °C. After rinsing away the loosely adsorbed chemicals from the surface and further aging at 100 °C overnight, the OSM@SM/ITO electrode was obtained. As exemplified in **Scheme 1**, the OSM/SM film retains the CTAB micelles in the silica mesochannels. By immersing the OSM@SM/ITO

electrode in ethanol containing 0.1 M HCl under moderate stirring for 5 min, the CTAB micelles could be excluded from the vertical silica mesochannels to get the SM/ITO electrode.

S3. Measurements and Instrumentations

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a CH-920 electrochemical workstation (CH Instrument, Shanghai). A conventional three-electrode system was used, with a bare or modified ITO electrode as the working electrode, an Ag/AgCl electrode (saturated with KCl) as the reference electrode and a platinum wire as the auxiliary electrode. For electrochemical analysis of organic analytes, the solutions were deoxygenated by argon for 20 min before each measurement, and protected by the argon blanket during the measurement. The DPV parameters used were as follows: increment potential 0.01 V, amplitude 0.05 V, pulse width 0.05 s and pulse period 0.5 s. The measurements were performed at ambient temperature (25 ± 2 °C).

Scanning electron microscopy (SEM) image was taken on a SU8010 field-emission scanning electron microscope (Hitachi, Japan) at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) measurements were performed on a HT7700 microscope (Hitachi, Japan) operated at 100 kV. The TEM specimens were prepared by mechanically scraping OSM@SM films from the ITO surface, dispersing them in ethanol before dropping onto the copper grids.

S4. Characterization of the OSM@SM Film

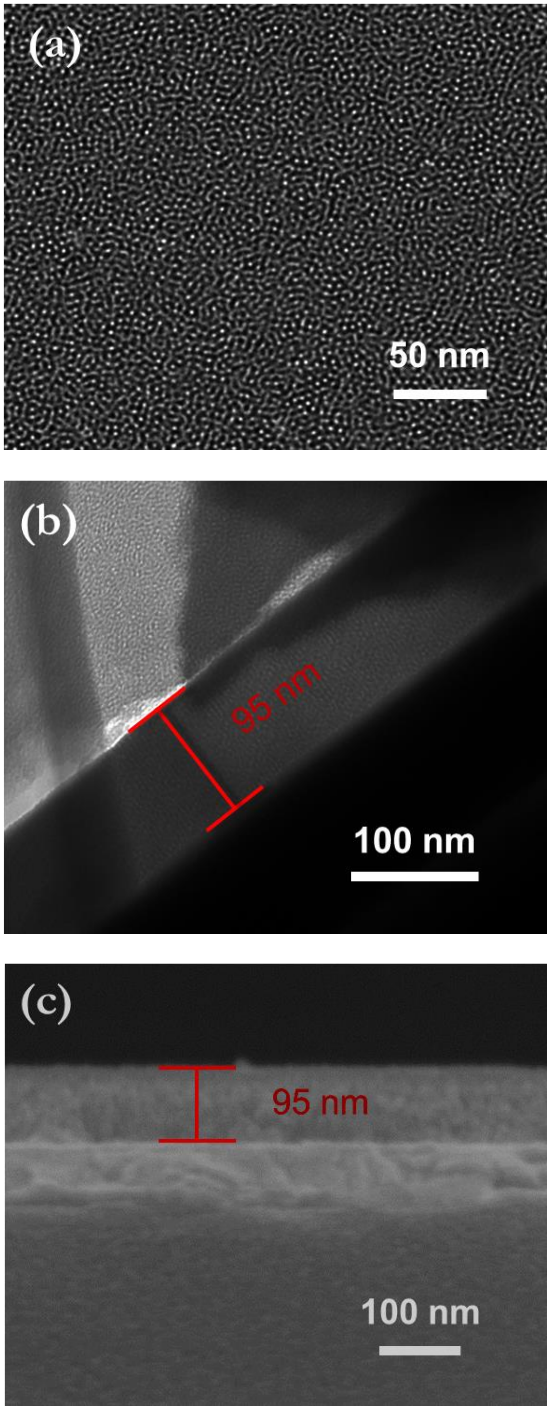

Fig. S1 Top-view (a) and cross-sectional view (b) TEM images of OSM@SM film showing the mesopores as the bright spots. (c) Cross-sectional SEM image illustrating the OSMs layer on the ITO electrode surface with a thickness of ca. 95 nm.

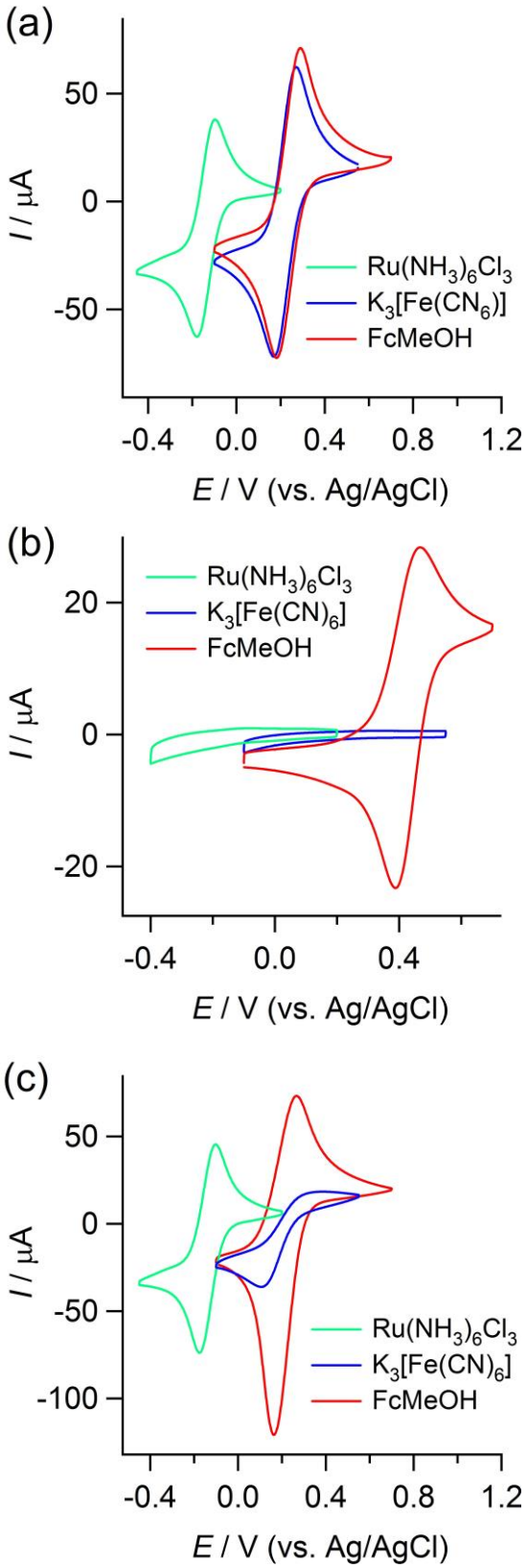

Fig. S2 CVs obtained at the bare ITO (a), OSM@SM/ITO (b), and SM/ITO electrodes in a 0.05 M KHP solution containing 0.5 mM $K_3[Fe(CN)_6]$, $Ru(NH_3)_6Cl_3$ or FcMeOH, respectively. The scan rate was 50 mV s^{-1}.

S5. Collection of Complex Samples

Three analytes of interest, paraoxon, *m*-NCB and CAP, in complex media, namely soil dispersion, human blood serum and milk, were electrochemically determined to examine the performance of OSM@SM/ITO electrodes in practical analytical applications.

Preparation of soil dispersion: First, the soil sample was collected from the Zijin'Gang campus of Zhejiang University and dried at 60 °C overnight, 1.0 g of which was subsequently spiked with 15 mL of 0.1 M NaCl solution by stirring for 20 min. Then different volumes of paraoxon or *m*-NCB stock solution were added.

Preparation of human blood serum and milk solutions: Human blood serum and fresh milk were directly diluted by 100 and 10 times with 0.1 M NaCl without any other pretreatment. The different volumes of CAP stock solution were added.

S6. CVs of Paraoxon at the OSM@SM/ITO Electrode

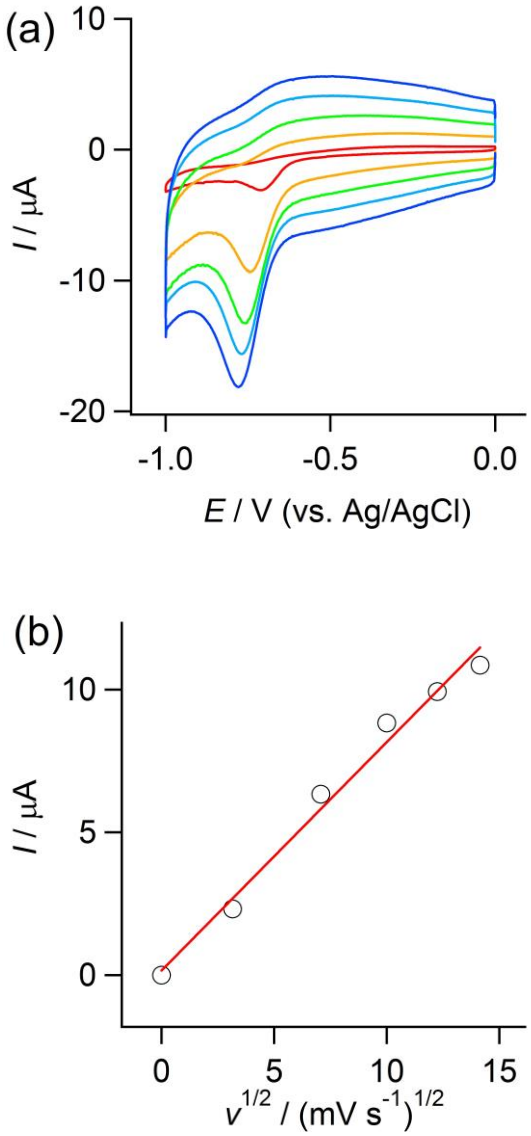

Fig. S3 (a) CVs of the OSM@SM/ITO electrode in a soil dispersion containing 1 ppm paraoxon at different scan rates (from inner to outer: 10, 50, 100, 150, 200 $mV \cdot s^{-1}$); (b) The dependence of the reduction peak currents on the square root of the scan rate.

S7. Optimized Preconcentration Time for Electrochemical Detection

Mechanical stirring was used as the preconcentration method in this work and optimal preconcentration time for each analyte in respective complex samples was studied. As shown in **Fig. S4**, the current maximum was reached at 30 s for paraoxon in soil, while 10 s was found to get the current plateau for m-NCB, CAP in soil, human blood serum and milk, respectively, indicating a rapid extraction by the OSMs.

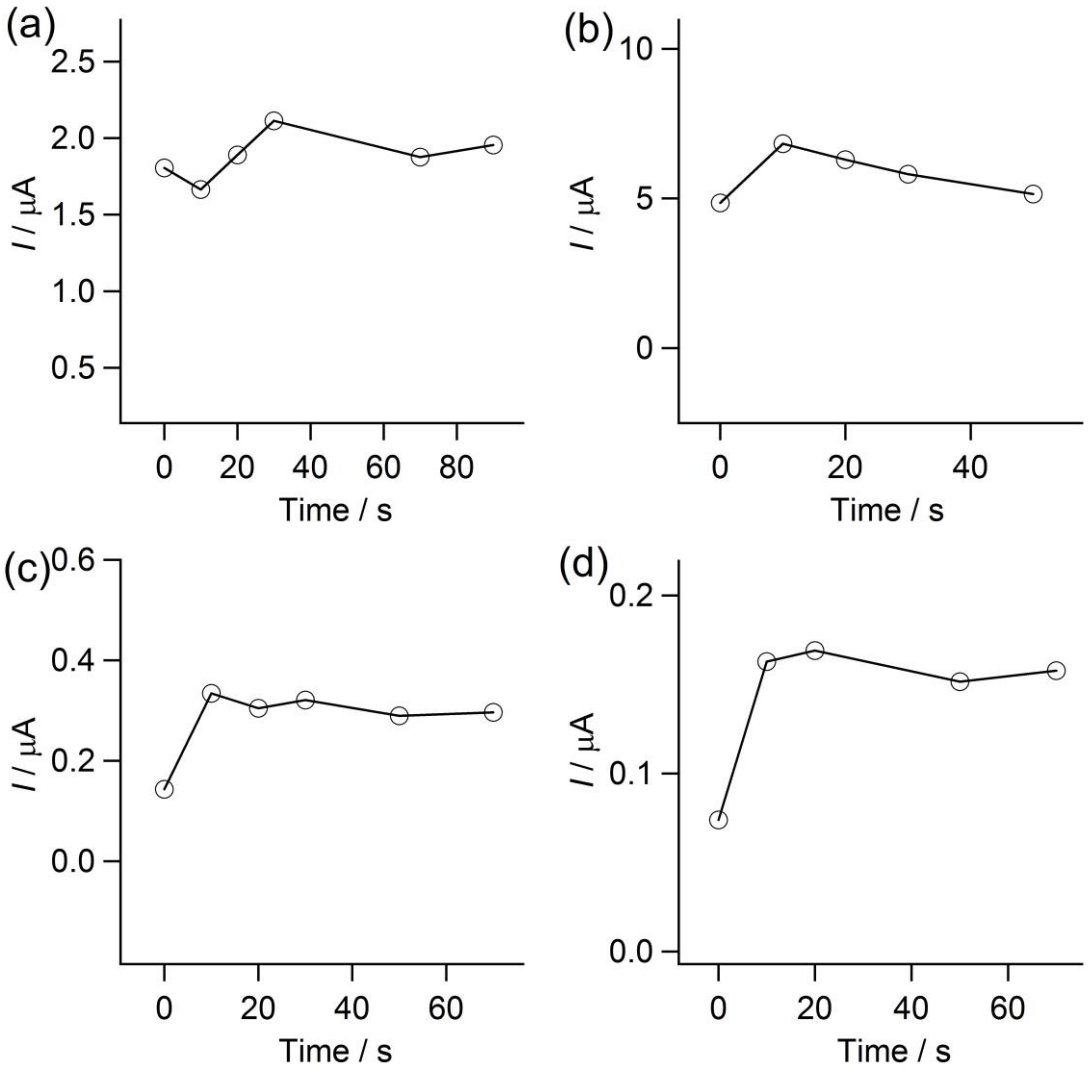

Fig. S4 Influence of the stirring time on the current response of 0.5 ppm paraoxon in the soil dispersion (a), *m*-NCB in the soil dispersion (b), CAP in human blood serum (c), and CAP in milk (d).

S8. More Electrochemical Detection Data in Complex Media

S8.1. Paraoxon in Soil

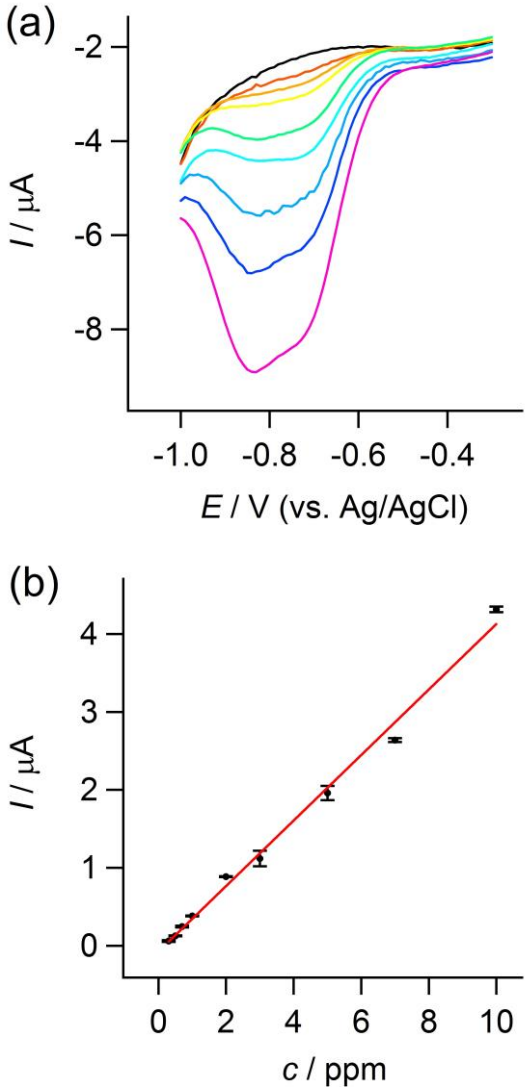

Fig. S5 (a) DPV responses of a bare ITO electrode in a soil dispersion containing various concentrations of paraoxon. (b) The calibration curve. Error bars represent the standard deviations of three measurements.

S8.2. *m*-NCB in Soil

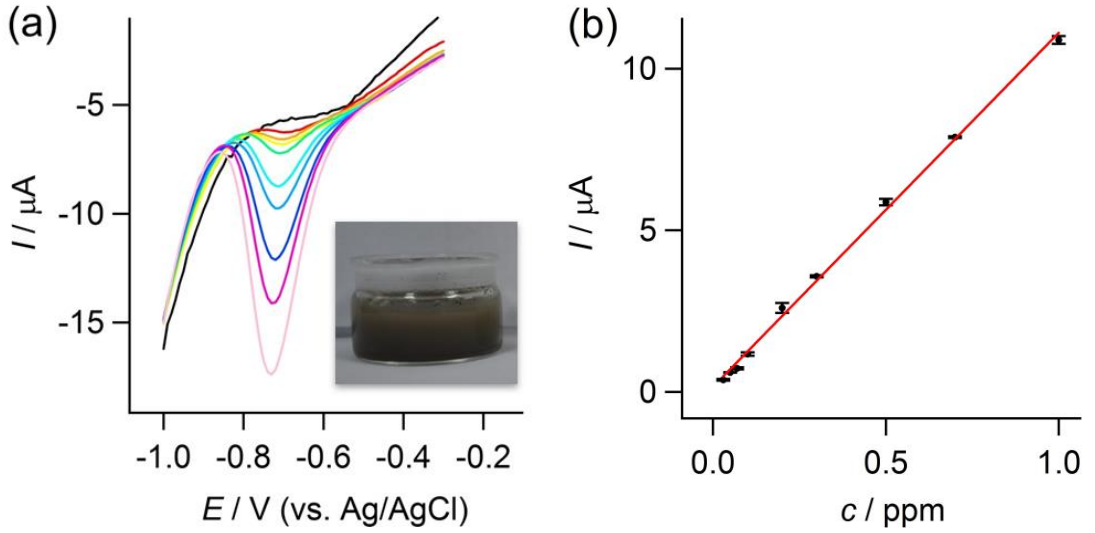

Fig. S6 (a) DPV responses of an OSM@SM/ITO electrode in a soil dispersion containing various concentrations of *m*-NCB. The inset shows the photograph of soil dispersion for direct electrochemical analysis. (b) The calibration curve. Error bars represent the standard deviations of three measurements.

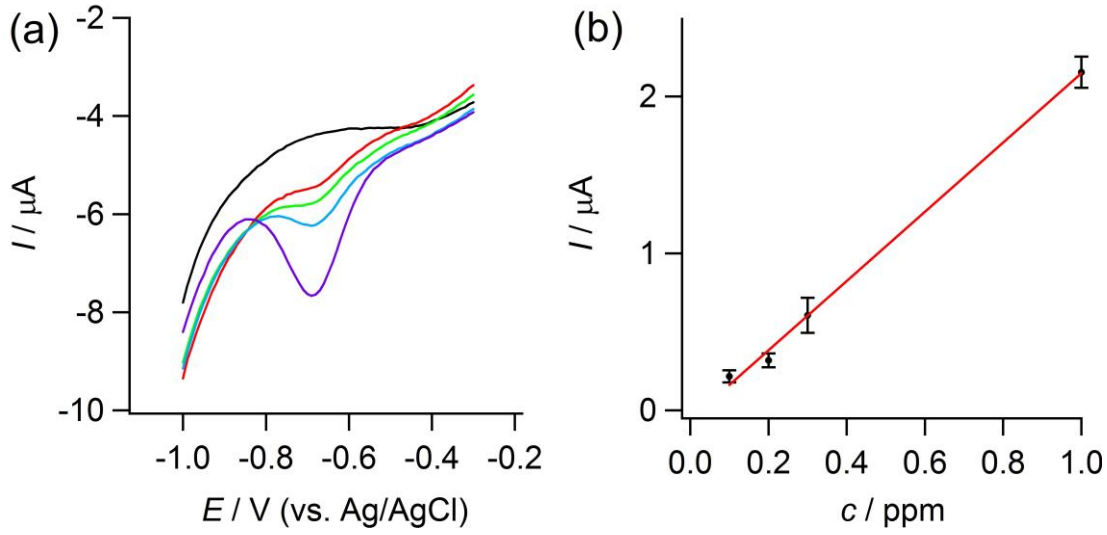

Fig. S7 (a) DPV responses of a bare ITO electrode in a soil dispersion containing various concentrations of *m*-NCB. (b) The calibration curve. Error bars represent the standard deviations of three measurements.

S8.3. CAP in Human Blood Serum

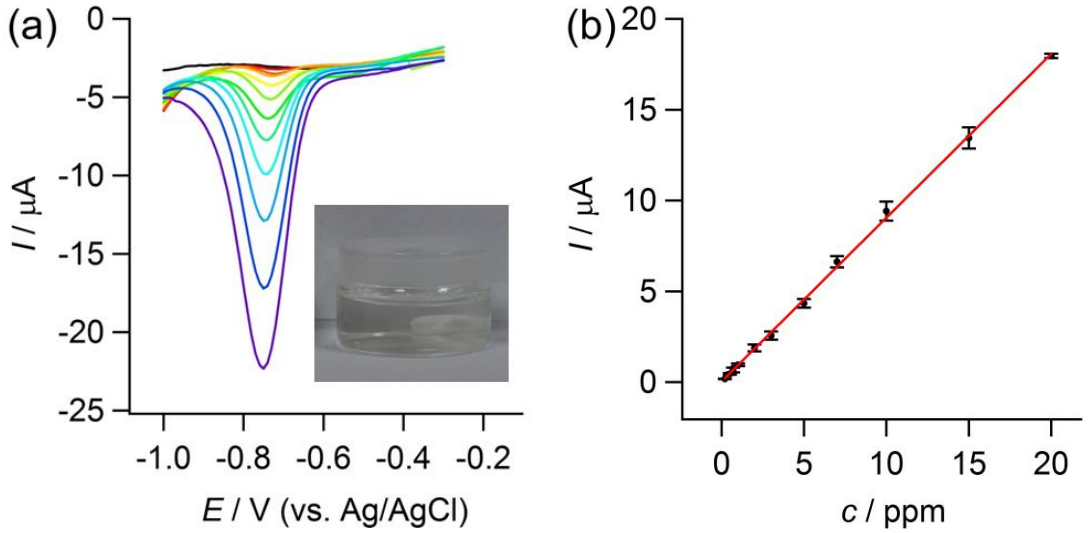

Fig. S8 (a) DPV responses of an OSM@SM/ITO electrode in human blood serum containing various concentrations of CAP. The inset shows the photograph of diluted human blood serum for direct electrochemical analysis. (b) The calibration curve. Error bars represent the standard deviations of three measurements.

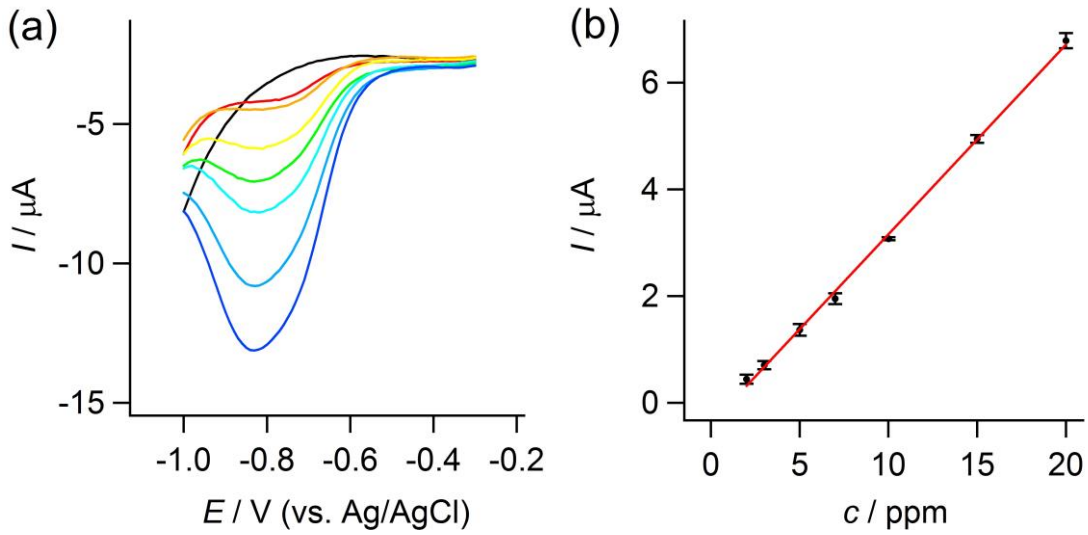

Fig. S9 (a) DPV responses of a bare ITO electrode in human blood serum containing various concentrations of CAP. (b) The calibration curve. Error bars represent the standard deviations of three measurements.

S8.4. CAP in Milk

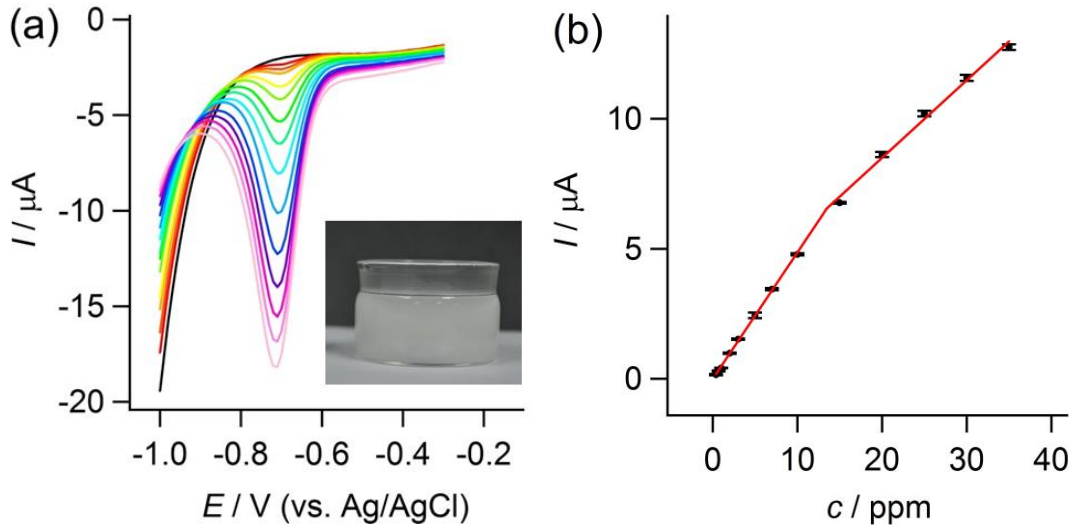

Fig. S10 (a) DPV responses of an OSM@SM/ITO electrode in milk containing various concentrations of CAP. The inset shows the photograph of diluted milk for direct electrochemical analysis. (b) The calibration curve. Error bars represent the standard deviations of three measurements.

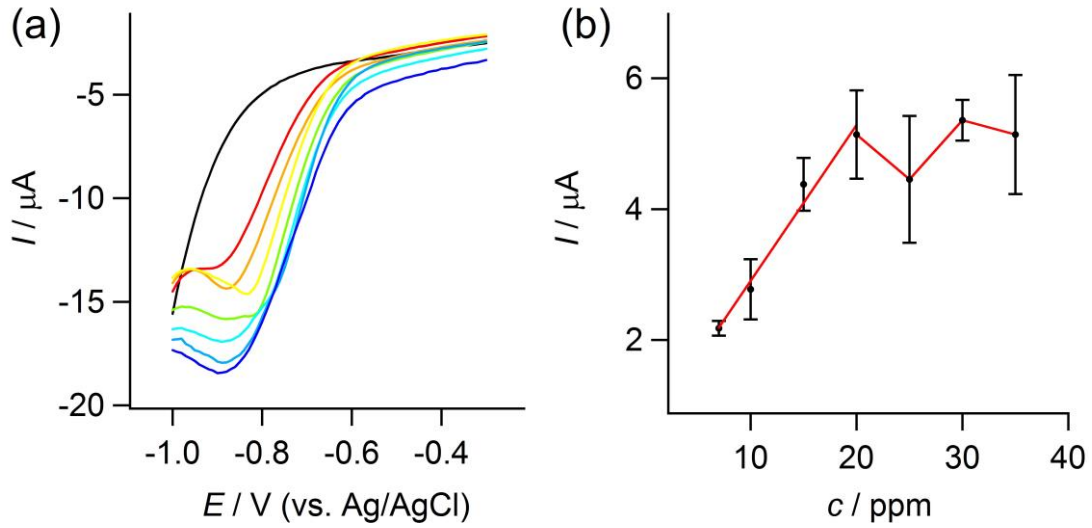

Fig. S11 (a) DPV responses of a bare ITO electrode in milk containing various concentrations of CAP. (b) The calibration curve. Error bars represent the standard deviations of three measurements.

Table S1. Summary of analytical performance of bare ITO electrodes in complex media

Analyte	**Sensitivity (μA/ppm)**	**Dynamic Range (ppm)**	**Lowest Detection Concentration (ppm)**	**LOD (ppb)**	***R***
Paraoxon in soil	0.42 ± 0.01	0.3 – 10	0.3	103.57 ± 2.53	0.9967
m-NCB in soil	2.21 ± 0.13	0.1 – 1	0.1	37.38 ± 2.38	0.9965
CAP in blood serum	0.36 ± 0.01	2 – 20	2	1022.54 ± 23.58	0.9987
CAP in milk	0.24 ± 0.04	7 – 20	7	1235.29 ± 249.56	0.9895

Table S2. Comparison of analytical performance of the proposed OSM@SM/ITO sensor in the complex media with other sensors in the buffer solution

Analyte	Method	Sensitivity	Dynamic Range	LOD	Ref
paraoxon	MC/CB/GCE	0.198 μA/μM	0.2 – 8 μM	36 ppb	2
	Au/ZrO_2/SiO_2/GCE	/	0.001 – 0.5 ppm	0.5 ppb	3
	MWCNT-$(PEI/DNA)_2$ OPH/AChE bi-enzymatic biosensor	0.021 μA/μM	0.5 – 50 μM	0.5 μM	4
	OSM@SM/ITO (in soil dispersion)	4.23 μA/ppm (1.164 μA/μM)	0.02 –1.9 ppm (72.67 nM – 6.90 μM) 1.9 – 10 ppm (6.90 – 36.34 μM)	10.20 ppb (37.06 nM)	This work
m-NCB	*β*-CD/AgNP/SAM/ITO	/	0.1 – 100 μM	/	5
	OSM@SM/ITO (in soil dispersion)	10.96 μA/ppm (1.72 μA/μM)	0.03 – 1 ppm (0.19 –6.35 μM)	14.23 ppb (90.32 nM)	This work
CAP	single-use sensor strip	0.05 μA/μM	up to 100 μM	0.42 μM	6
	Au/N-G/GCE	2.13 μA/μM	2 –80 μM	0.59 μM	7
	Based on the reaction of CAP and zinc in HCl solution to form a new substance	0.03375 μA/ppm	0.8 – 30 ppm	/	8
	aptamer/N-GOD/FTO	128.18 μA/μM	0.005 – 0.5 μM 0.5 – 4 μM	0.1 nM	9
	OSM@SM/ITO (in blood serum)	0.90 μA/ppm (0.29 μA/μM)	0.2 – 20 ppm (0.62 – 61.89 μM)	130.38 ppb (0.40 μM)	This Work
	OSM@SM/ITO (in milk)	0.49 μA/ppm (0.16 μA/μM)	0.4 –13.5 ppm (1.24 – 41.78 μM) 13.5 – 40 ppm (41.78 – 123.79 μM)	197.14 ppb (0.61 μM)	This work

MC, mesoporous carbon; CB, carbon black; MWCNT, multiwalled carbon nanotubes; PEI, polyethyleneimine; OPH, organophosphate hydrolase; AChE, Acetylcholine esterase; *β*-CD, *β*-Cyclodextrin; SAM, self-assembled monolayers; N-G, nitrogen-doped graphene nanosheets; N-GOD, nitrogen-doped graphene quantum dots; FTO, F-doped SnO_2

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