Supplementary Materials

Molecularly imprinted sensor based on CS/MXene/AuNPs synergy for ultra-trace detection of PFOS in water

Xuanxiu Da[1, #], Miao Zhou[1, #], Bolu Sun[1, #, *], Haoye zou[1], Wenya Wang[1], Zhen Liu[1], Hongxia Shi[2], Jia Zhou[3], Lin Yang[1], Yonggang Wang[1]

[1] School of Life Science and Engineering, Key Laboratory of Herbal-Tibetan Drug Screening and Deep Processing of Gansu Province, Gansu Industrial Technology Center for Food and Pharmaceutical Resources Development and Biomanufacturing, Lanzhou University of Technology, Lanzhou 730050, People's Republic of China.

[2] Lanzhou CAIQTEST Co., Ltd, Lanzhou 730000, Gansu.

[3] Gansu Provincial Institute for Food Inspection, Lanzhou 730030, Gansu, China.

[#] These authors contributed equally to this work.

[*] Corresponding authors. Tel.: +86-18219816572.

E-mail addresses: sunbl@lut.edu.cn (B. Sun);

yanglin-401@163.com (L. Yang);

wanyg@lut.edu.cn (Y. Wang).

Conditions

1.Experimental apparatus and reagents

2.Number of cycles of pyrrole polymerization

3.Optimization of experimental conditions

4.Calculation Method for Detection Limit

5.Determination of Association Constant

1. Experimental apparatus and reagents

Electrochemical workstation (CHI760E, Shanghai Huachen Instrument Co.).Ultrasonic cleaner (SB-5200DTD, Ningbo Xinzhi Biotechnology Co., Ltd.), Fourier transform infrared spectrometer (NicoletIs5, Shanghai Powerchip Scientific Instrument Co., Ltd.), cold field emission scanning electron microscope (JSM-6701F, Japan Electronic Optics Co., Ltd.), electronic analytical balance (SHZ-D (III), Shanghai Qiuzuo Scientific Instrument Co., Ltd.), pH meter (PHS-3D, Shanghai Yidian Scientific Instrument Co., Ltd.).

Perfluorooctane sulfonic acid (20 mg, ≥99 %, Shanghai Macklin Biochemical Technology Co., Ltd.); pyrrole (100 mL, ≥99 %, Beijing inokai technology co., Ltd.); Chitosan (10 g, ≥99 %, Nanjing Xianfeng Nanomaterial Technology Co., Ltd.); MXene (5 g, ≥95 %, Nanjing Xianfeng Nanomaterial Technology Co., Ltd.); Tetrachloroauric acid (100 mg, ≥99.9 %, Shanghai Macklin Reagent Co., Ltd.); PFOS (100 mg, Guangzhou Jiatu Technology Co., Ltd.); methanol (500 mL, Tianjin Fuyu Fine Chemical Co., Ltd.); acetic acid (500 mL, Tianjin Guangfu Fine Chemical Research Institute); potassium ferricyanide (500 g, Shanghai Aladdin Biochemical Technology Co., Ltd.); potassium ferrocyanide (500 g, Shanghai Yien Chemical Technology Co., Ltd.).

2. Number of cycles of pyrrole polymerization

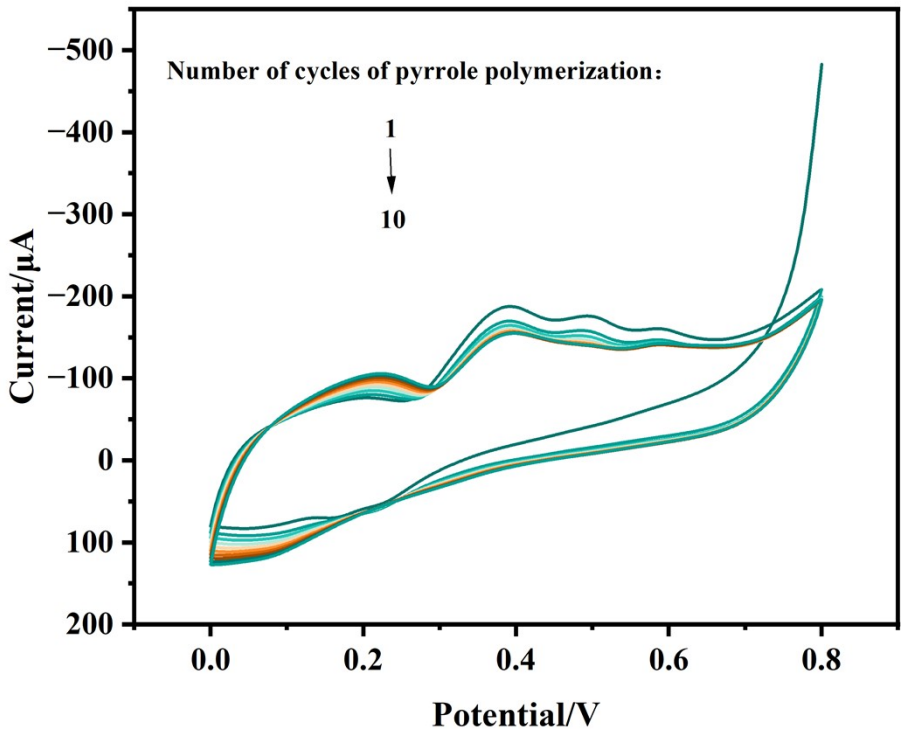

Fig. S1 Number of cycles of pyrrole polymerization (1~10)

3. Optimization of experimental conditions

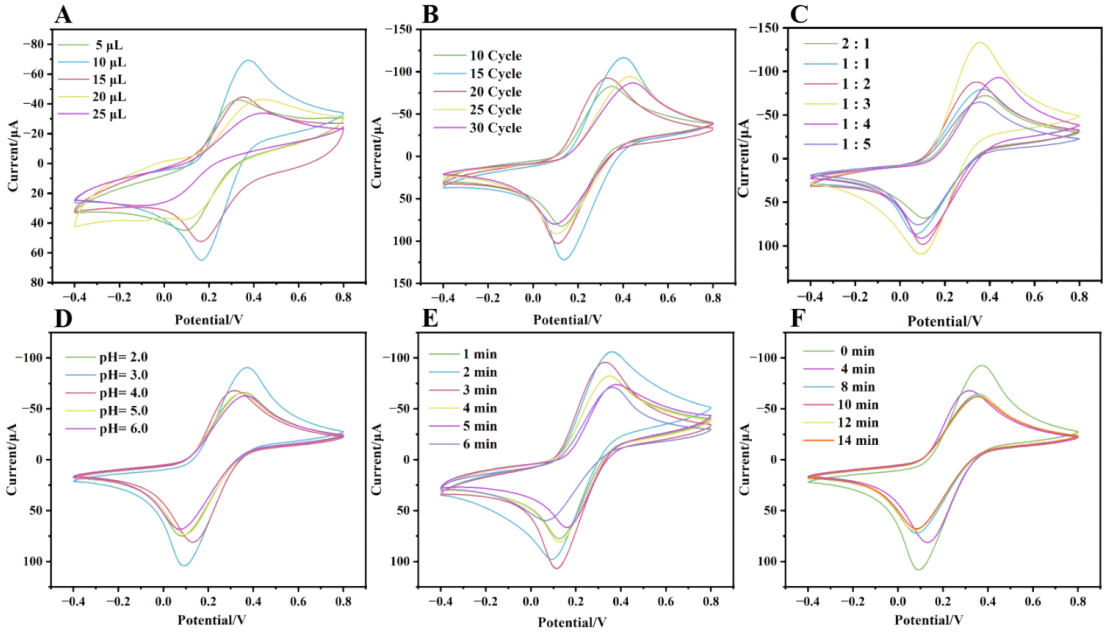

Fig. S2 (A) CV curves of different amounts of MXene modification, (B) CV curves of different number of electrodeposited AuNPs turns, (C) CV curves of different molar ratios of template molecules to functional monomers, (D) CV curves of different number of electropolymerization turns, (E) CV curves of different elution times of MIP, (F) CV curves of different adsorption times of template molecules.

4. Calculation Method for Detection Limit

The calibration curve for PFOS detection was constructed by plotting the current difference (ΔI) against the logarithm of PFOS concentration (log C), as shown in **Fig. S3C**. The linear regression equation derived from this plot is:

$$\Delta I\ (\mu A) = 3.03\ \log C\ (pg\ mL^{-1}) + 4.49\ (R^2 = 0.991)$$

The limit of detection (LOD) was calculated according to the IUPAC recommendation using the formula:

$$LOD = 10^{(3\sigma/S)}$$

Where σ is the standard deviation of ten blank measurements (σ = 0.91μA), and S is the slope of the calibration curve (S = 3.03μA · (log[pg/mL]$^{-1}$)).

The logarithmic LOD is calculated as:

$$\text{Log(LOD)} = \frac{3 \times 0.91}{3.03} = 0.90$$

Converting from logarithmic to linear concentration gives:

LOD = $10^{0.90}$pg·mL^{-1} = 7.9 pg·mL^{-1} (or 7.9 × 10^{-3} ng·mL^{-1})

This LOD value corresponds to the concentration at which the signal is three times the standard deviation of the blank.

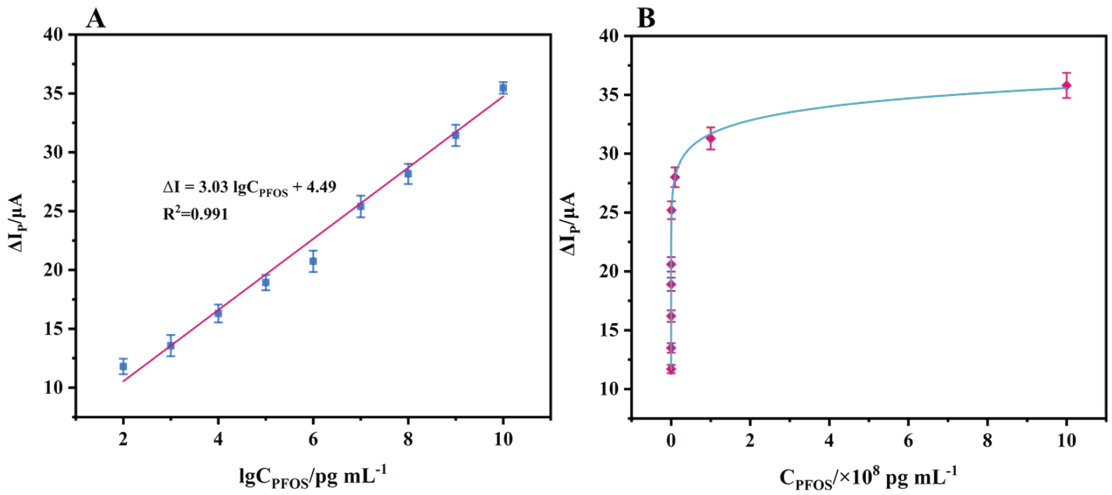

Fig. S3 (A) Calibration curve of current difference (ΔI) versus logarithm of PFOS concentration (log C). The red line represents the linear fit with the equation ΔI (μA) = 3.03 logC (pg mL^{-1}) + 4.49 (R^2 = 0.991). (B) Binding isotherm of the MIP sensor for PFOS.

5. Determination of Association Constant

Fig. S3B presents the binding isotherm of a molecularly imprinted polymer sensor for the target compound PFOS. The scatter points represent experimental signal values (e.g., DPV peak current) measured at different PFOS concentrations, while the solid red line shows the nonlinear fitting of the experimental data using an extended Langmuir model. The model equation is expressed as $y = \frac{a \cdot b \cdot x^{1-c}}{1 + b \cdot x^{1-c}}$, where y is the DPV current change value (ΔI), x is the PFOS concentration, parameter a is the maximum saturation response signal (ΔI_{max}), parameter b is the apparent binding constant K_a, and parameter c is related to the heterogeneity of the binding site (with c = 1 in the ideal Langmuir model) [1]. Through nonlinear least-squares fitting, the fitted value of parameter b is obtained directly, which corresponds to K_a in the concentration units used. For comparison, this value has been uniformly converted to the apparent binding constant in molar concentration (M^{-1}).

The fitting results demonstrate a high degree of agreement between the

experimental data and the model ($R^2 = 0.998$). Among the fitted parameters, parameter b corresponds to the apparent binding constant K_a, with a value of 6.40×10^{10} M^{-1}.

[1] P. Ugo, P. Marafini, M. Meneghello, Bioanalytical Chemistry-from Biomolecular Recognition to Nanobiosensing, 2nd edition, De Gruyter, 2025, pp.210-215.