

## Electronic Supplementary Material

### Microfluidic ratiometric electrochemical aptasensor for highly sensitive and selective detection of 3,3',4,4'-tetrachlorobiphenyl

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**Materials and reagents.** Polychlorinated biphenyls (PCB 77, PCB 163, PCB 198), Chlorobenzene and Bisphenol A were purchased from Dr. Ehrenstorfer. Nb<sub>2</sub>AlC

powder was purchased from Adamas-Beta Reagent Co., Ltd. (Shanghai, China), Methylene blue (MB), CH<sub>3</sub>CH<sub>2</sub>OH (99.5%), Lithium fluoride (LiF), hydrochloric acid (HCl, 37 %), Graphene oxide (GO), potassium hexacyanoferrate III (K<sub>3</sub>[Fe(CN)<sub>6</sub>]), potassium hexacyanoferrate II (K<sub>4</sub>[Fe(CN)<sub>6</sub>]), sodium dihydrogen phosphate dihydrate (NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O), disodium hydrogen phosphate dodecahydrate (Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O), Sodium chloride (NaCl), potassium chloride (KCl) and Nafion® perfluorinated resin solution (Nafion, 5 wt%) purchased from Sigma-Aldrich. Hydrogen Tetrachloroaurate (III) Trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O), trisodium citrate, Ethylene Diamine Tetraacetic Acid (EDTA), tris (2-carboxyethyl) phosphine hydrochloride (TCEP), Tris (hydroxymethyl) aminomethane (Tris) were obtained from Adamas-Beta Reagent Co., Ltd. (Shanghai, China). Au nanoparticle solution was purchased from XFNANO Materials Tech Co., Ltd. (Nanjing, China). Bovine Serum Albumin (BSA) was obtained from Shanghai Beyotime Biotechnology Co., Ltd (Shanghai, China). 4,4'-Isopropylidenediphenol and Chlorobenzene were obtained from Adamas-Beta Reagent Co., Ltd. (Shanghai, China). Trivalent iron ion standard solution (Fe<sup>3+</sup>) was obtained from Ncs Testing Technology Co., Ltd. Divalent magnesium ions (Mg<sup>2+</sup>) purchased from Standard Sample Research Institute of Shandong Metallurgical Research Institute Co., Ltd. (Shandong, China). The screen-printed carbon electrode (SPCE, 3.4 cm×1.2 cm) was purchased from Wave Carbon Technology Co., Ltd. (Qingdao, China). All other reagents are analytical grade and can be used directly without further purification. Freshly prepared TE buffer (pH 7.4, 50 mM Tris-HCl buffer + 1.0 mM EDTA) was used as aptamer stock solutions. All the solutions in the experiment were prepared with ultrapure water (18.2 MΩ×cm). Ultrapure water was obtained from a Millipore water purification system (18.2 MΩ×cm, Milli-Q, Germany).

The oligonucleotide sequence was synthesized from Shanghai Sangon Biotechnology

Co. Ltd. (Shanghai, China) and purified by high-performance liquid chromatography (HPLC). Oligonucleotide sequences are shown as follows:

cDNA 5'-COOH-TTC-GTA-GCC-CCG-CCT-TTT-TTT-TTT-TT-(CH<sub>2</sub>)<sub>6</sub>-SH-3'

PCB 77 aptamer (Fc) 5'-(CH<sub>2</sub>)<sub>6</sub>-GGC-GGG-GCT-ACG-AAG-TAG-TGA-TTT-TTT-CCG-ATG-GCC-CGT-G-Fc-3'

**Apparatus.** The morphology and structure of the synthesized samples were analyzed using a scanning electron microscope (SEM, JEOL JSM-7800F, Japan) with a 10 kV accelerating voltage. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM), and energy-dispersive X-ray spectroscopy (EDS) measurements were conducted on a JEM-2100F (Japan) microscope at 200 kV acceleration voltage. X-ray diffraction (XRD) spectra were obtained using a Cu K $\alpha$  radiation source with a Bruker-AXS D8 Advance diffractometer (Germany). Raman spectroscopy (Horiba LabRAM HR, Japan) was performed with an excitation wavelength of 532 nm. Surface elements were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha) with monochromatic Al K $\alpha$  radiation (1486.6 eV). All high-resolution XPS spectra was used to charge-correct all binding energies with C1s peaks at 284.6 eV. Background subtraction and curve fitting were carried out using XPS Peak 4.1 software. Fourier transform infrared spectroscopy (FTIR, IRTracer-100, Shimadzu) was used to detect the functional groups and chemical structures present in the samples. The Brunauer-Emmett-Teller (BET) specific surface area was obtained using a specific surface area and porosity analyzer (ASAP 2460, USA).

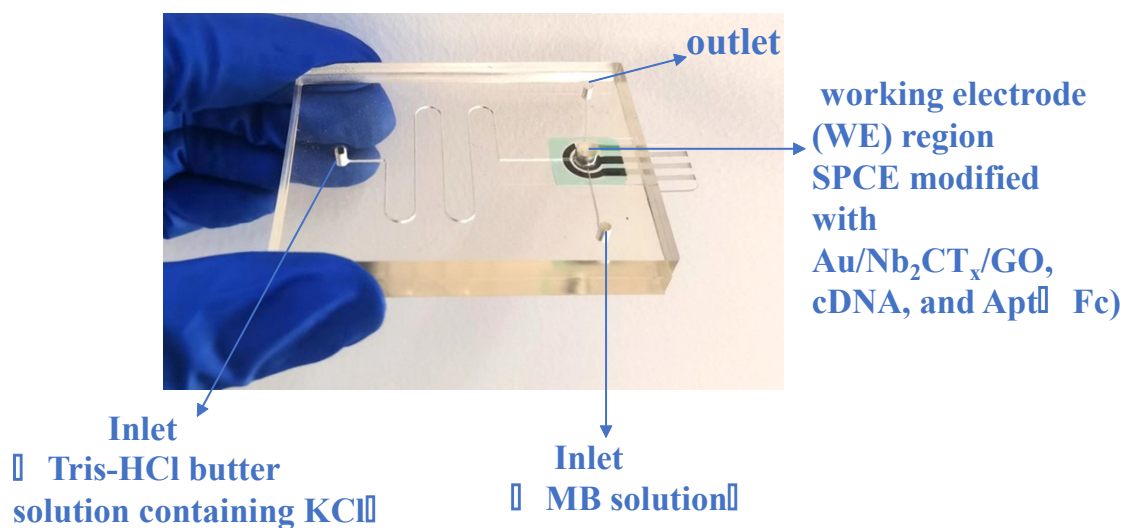
**Preparation of Nb<sub>2</sub>CT<sub>x</sub> MXene.** We prepared a solution of Nb<sub>2</sub>CT<sub>x</sub> MXene using a

method that was previously described. In summary, 2 g of lithium fluoride (LiF) and a hydrochloric acid (HCl) solution with a concentration of 9 M were mixed and agitated for a duration of 30 minutes.<sup>1,2</sup> Subsequently, a quantity of 2 g of Nb<sub>2</sub>AlC was gradually introduced into the mixture at a temperature of 35 °C, while maintaining constant stirring for a duration of 24 hours. Subsequently, the samples underwent a thorough rinsing process using ultrapure water until the pH level of the resulting liquid after centrifugation reached 6. Ultrapure water was introduced into the sediment and subjected to sonication for a duration of 1 hour while being exposed to a flow of nitrogen gas. The samples underwent centrifugation, and the resulting liquid above the sediment was collected to obtain the Nb<sub>2</sub>CT<sub>x</sub> solution.

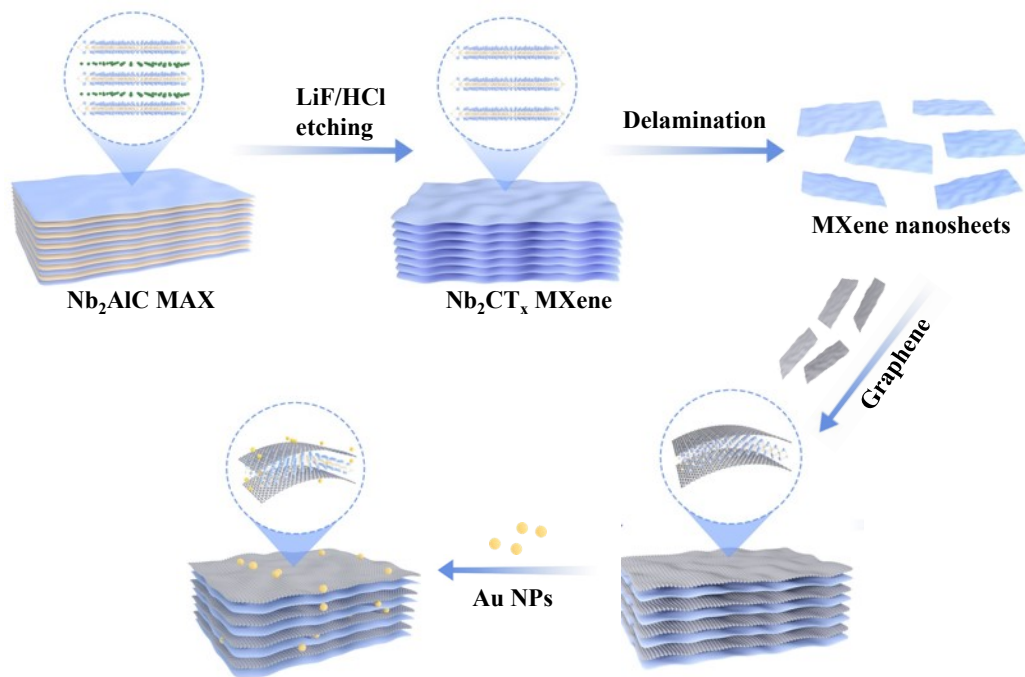
**Preparation of the Au/ Nb<sub>2</sub>CT<sub>x</sub> /GO hybrid.** The Au/Nb<sub>2</sub>CT<sub>x</sub>/GO nanohybrids were synthesized via electrostatic adsorption and the process of depositing gold particles. The Nb<sub>2</sub>CT<sub>x</sub>/GO composite was synthesized by the electrostatic adsorption technique. At first, 4 milligrams of graphene oxide (GO) were dispersed in 10 milliliters of ethanol. This mixture was subjected to ultrasonic treatment for a duration of 30 minutes. Following that, a 10 ml solution of MXene (2 mg/ml) was added to the GO solution that had been prepared, and the mixture was subjected to 30 minutes of ultrasound to form a uniform mixture. The Nb<sub>2</sub>CT<sub>x</sub> MXene nanosheet solution was uniformly dispensed multiple times while being subjected to sonication. Following a 30-minute sonication procedure, the solution was subjected to magnetic stirring at a temperature of 75 °C and a speed of 450 revolutions per minute until the material underwent complete evaporation. Ultimately, the mixture underwent vacuum filtration and subsequent natural air-drying to yield the Nb<sub>2</sub>CT<sub>x</sub> /GO material.

20 mg of Nb<sub>2</sub>CTx /GO was distributed in 20 mL of 100% ethanol and sonicated for 30 minutes. Next, a volume of 10 mL of gold nanoparticle solution with a concentration of 0.1 mg/mL was subjected to sonication for a duration of 10 minutes. Afterwards, the solution that had been subjected to sonication was added slowly and cautiously to the Nb<sub>2</sub>CTx/GO. This was followed by an additional sonication period of 10 minutes. Subsequently, the heterogeneous solution is agitated using a magnetic stirrer until it reaches a state of dryness. Subsequently, the solution undergoes calcination in a tube furnace, which operates at a temperature of 250°C, for a period of 60 minutes in the presence of a helium (He) atmosphere.

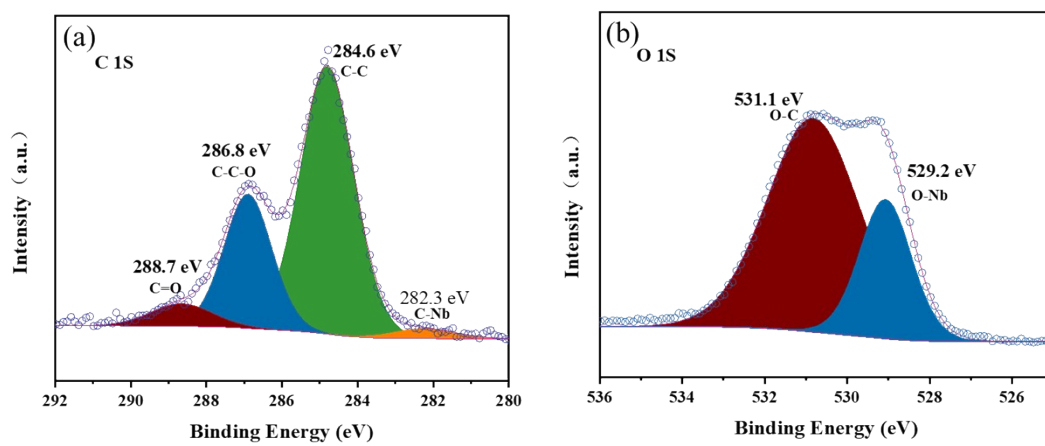
**Assembling instructions :** The portable potentiometer is made by means of the circuit diagram in Figure S6 and then connected with Figure S1 in the supplementary data. Our screen-printed electrodes plug into a homemade portable potentiometer and finally receive signal data through the blue pressure of a mobile phone.



**Figure S1** Photo of the microfluidic chip.

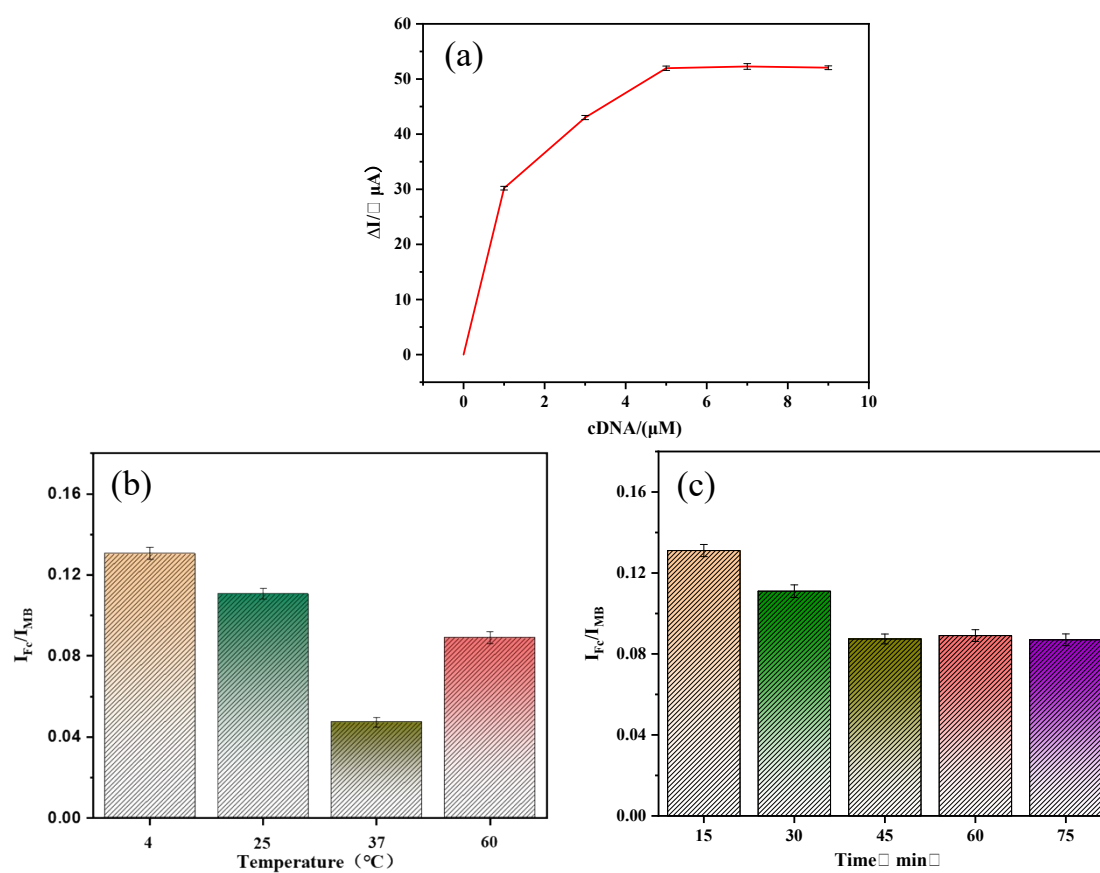


**Figure S2** The Schematic illustration for the preparation of Au/Nb<sub>2</sub>CT<sub>x</sub>/GO.



**Figure S3** High-resolution XPS spectrum of (a) C 1s and (b) O 1s of Au/Nb<sub>2</sub>CT<sub>x</sub>/GO.





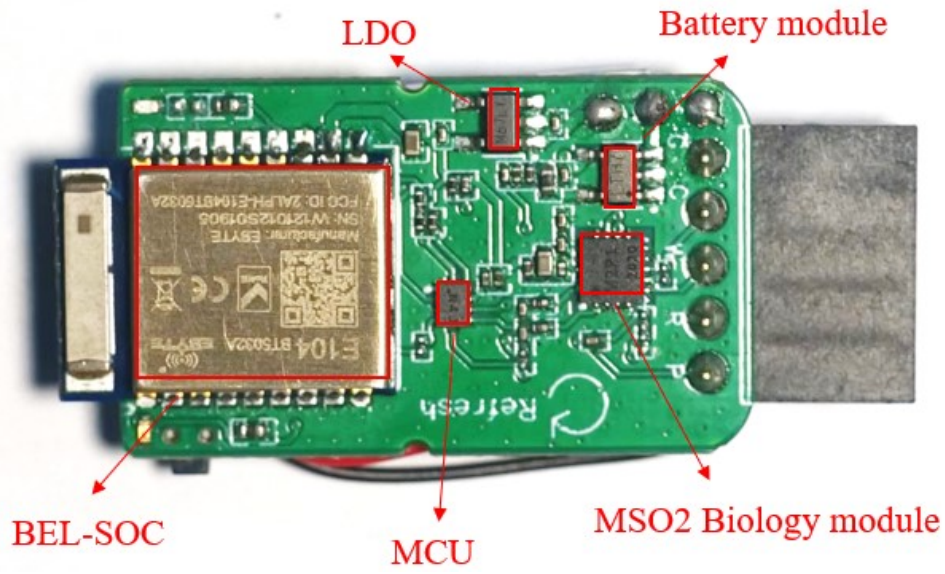
**Figure S4** Optimization of the amounts of cDNA, the temperature at which PCB77 is incubated, and the duration of the binding between the aptamer and PCB77.

**Table S1** Comparison of reported methods for the detection of PCB77.

<b>Materials</b>	<b>Method</b>	<b>Linear range(ng/mL)</b>	<b>LOD (ng/mL)</b>	<b>Ref.</b>
MXene/GO/AuNPs	Ratiometric Electrochemical	$10^{-4}$ - $10^3$	$1.56 \times 10^{-5}$	<b>This Work</b>
BiVO <sub>4</sub> -TiO <sub>2</sub>	Photoelectrochemical	$1 \times 10^{-3}$ -0.5	$2.3 \times 10^{-4}$	3
CdTe@CdsQDs-TiO <sub>2</sub>	Photoelectrochemical	$1 \times 10^{-4}$ -0.5	$3 \times 10^{-5}$	4
NiHCF NPs/rGO	Electrochemical	$1 \times 10^{-3}$ - $1 \times 10^{-1}$	$2.2 \times 10^{-4}$	5
CoxP-AuNR	Electrochemical	$1 \times 10^{-5}$ - $1 \times 10^2$	$5.9 \times 10^{-5}$	6
Cu <sub>2</sub> O-rGO/CeO <sub>2</sub> -AuPt	Electrochemical	$1 \times 10^{-4}$ -1	$6.9 \times 10^{-5}$	7

**Table S2** Detection of PCB77 in Lake water, Tap water samples (n=3)

Sample	Added(ng/L)	Microfluidic electrochemical aptasensor		
		Found(ng/L)	Recovery(%)	RSD(%)
	0	Undetected		
Lake water	10	10.09	100.9	2.5
	50	49.36	98.72	2.8
	100	99.13	99.13	3.3
	0	Undetected		
Tap water	10	10.01	100.1	1.8
	50	49.05	98.10	3.1
	100	99.67	99.67	2.7



**Figure S5** Physical diagram of portable potentiometer



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