# 1 Conductive imprinted polymeric interfacially modified

- 2 electrochemical sensors based on covalently bonded layer-by-
- 3 layer assembly of Gr/Au flower-like for sensitive detection of

# 4 **2,4,6-TCP**

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## 13 1.1. Apparatus

Electrochemical measurements were performed on IGS6030 electrochemical 14 workstation (Guangzhou Ingsens sensor technology, China) and controlled by 15 IGS4030CN software to register the data. All measurements were performed at room 16 temperature and data were collected using a three-electrode system with screen-printed 17 carbon electrodes. Carbon ink (Three seven international Co., Ltd., Shaoguan, China), 18 silver/silver chloride ink (Tenghui Co., Ltd., Huizhou, China), insulating ink (Tenghui 19 Co., Ltd., Huizhou, China), and polypropylene synthetic paper (PP-paper, NANYA, 20 Taiwan). Screen printed carbon electrodes (SPCEs) were fabricated on a EPL-21 YS4060D screen printer (Ebolia precision technology, Zhongshan, China), the working 22 electrode area is about 4.9 mm<sup>2</sup>. 23

Drying oven (DHG, Jinghong Experimental Equipment Co., Ltd., Shanghai,
China), pH meter (FE20, Mettler-Toledo Instruments Co., Ltd., Shanghai, China); Mini

Mixer (MIX-2500, Hangzhou Union Instrument Co., Ltd., China); Beijing-made
electronic balance No. 00000246 (Sartorius Scientific Instruments Beijing Co., Ltd.);
KQ5200E Ultrasonic Cleaner Kunshan Ultrasonic Instrument Co., Ltd.

#### 29 1.2. Materials and Reagents

All solutions were prepared with ultrapure water (18.25 M $\Omega$ ) obtained from a 30 MilliQ water purification system (Millipore, Bedford, MA, USA). Analytical grade 31 reagents were used in the present study. Hydrochloric acid, acetic acid, glutaraldehyde, 32 potassium ferrocyanide (K<sub>4</sub>[Fe(CN)<sub>6</sub>]), potassium ferricyanide (K<sub>3</sub>[Fe(CN)<sub>6</sub>]), 2-33 chlorophenol (2-CP, 99%), 2,4-dichlorophenol (2,4-DCP, 99%), 2,6-dichlorophenol 34 (2,6-DCP, 99%), 2,4,6-trichlorophenol (2,4,6-TCP, 99%), 2,4,5-trichlorophenol (2,4,5-35 TCP, 99%), o-phenylenediamine (o-PD, 99.5%). 2,5-dihydroxybenzoic acid (DBH) 36 was obtained from Shanghai Macklin Biochemical Co., Ltd. Amino-modified 37 Monolayer graphene dispersion (Gr, 1 mg/mL) were purchased from Nanjing XFNano 38 Materials Tech Co.. KCl, NaCl, Na<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> and chlorauric acid (HAuCl<sub>4</sub>) 39 were obtained from Sigma Aldrich. Phosphate buffer solution (PBS) used in all 40 experiments were prepared as follows: 1×PBS (2.6 mM KCl, 135 mM NaCl, 10 mM 41 Na<sub>2</sub>HPO<sub>4</sub>, 10 mM KH<sub>2</sub>PO<sub>4</sub>, pH 7.4) 42

### 43 2.1. Optimization of the ratio of polymerized monomer to template molecule

The surface properties of MIP membranes are an important factor affecting the recognition of template molecules by MIP sensors. The construction of SPCE/Gr/Au-F/MIP was optimized by studying the ratio of polymerized monomer to template molecule. The analytical response of 25  $\mu$ M 2,4,6-TCP was used to display the sensor performance.

The ratio of polymerized monomer to template molecule can affects the imprinting efficiency. The ratio of template to polymerized monomer was investigated to optimize from 2:1 to 1:8 (2:1, 1:1, 1:2, 1:4, 1:6, 1:8), where the concentration of o-PD was maintained at 5 mM. As the proportion of polymerized monomers in the mixed solution increased, the detection signal first increased (Fig. S1B). The reason is that the amount of the polymerized monomer in the appropriate ratio is conducive to the formation of the polymer membrane network skeleton, and sufficient molecular imprinting space is 56 ensured, so that enough 2,4,6-TCP molecules can be captured. When the ratio of 1:4, 57 the value of oxidation peak current reaches the maximum and then decreases. This may 58 be due to the fact that the ratio of o-PD increased to a certain extent, too few target 59 molecules resulted in a small number of template pores in the imprinted membrane. At 60 the same time, there is incomplete elution of the template molecule, resulting in a 61 decrease in the binding capacity of the final 2,4,6-TCP. Eventually, 1:4 is considered 62 the optimal ratio for subsequent MIP membrane preparation.



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Fig. S1. (A) Electropolymerization of MIP from a solution containing 5 mM o-PD and 1.25 mM
2,4,6-TCP in 0.1 M phosphate buffer pH 5.0; (B) Optimize the ratio of template molecule to
polymerized monomer.

### 67 2.2. The characterization of SPCE/Gr/Au-F/MIP stability

In order to assess the durability of conductive molecularly imprinted polymerized electrodes assembled layer-by-layer by covalently bonded structures and their ability to withstand repeated cleaning processes over long periods of time, we tested the electrodes using microfluidic techniques with different flow rates. The signals generated by the binding reaction of 2,4,6-trichlorophenol at the same concentration before and after rinsing were also compared. Recovery comparisons were made based on the signals generated, which in turn assessed the stability of these electrodes.

75 The recovery was calculated using the following formula:

76 Recovery =  $I_b/I_a \times 100\%$ 

Here,  $I_b$  represents the response value of 10  $\mu$ M TCP measured at the electrode after rinsing the chip using microfluidic transfer buffer, and  $I_a$  represents the response value of 10  $\mu$ M concentration of TCP measured at the electrode before rinsing.





Fig. S2 Physical representation of microfluidic-electrochemical chip







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Fig. S3 Stability of electrodes flushed at different flow rates

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Fig. S4 SWV response values of the prepared sensors at different times in 250  $\mu$ M 2,4,6-TCP solution





Fig. S5 Determination of 64 standard samples of sVOCs containing 2,4,6trichlorophenol 210 ng/L (a) , 30 ng/L(b) and Pearl River samples (c), Haizhu lake
samples (d) by standard methods using GC-MS