A Dual-Mode Foam Sensor Employing Ti₃C₂T_x/In₂O₃ Composites for NH₃ Detection with Memory Function and Body Movement

Monitoring for Kidney Disease Diagnosis

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1. Experimental section

1.1 Materials

 Ti_3AlC_2 was obtained from Jilin 11 Technology Co. (3-aminopropyl) triethoxysilane (APTES) and LiF were purchased from Shanghai Macklin Biochemical Technology Co. Hydrochloric acid, In(NO₃)₃-4.5H₂O, and N,N-Dimethylformamide (DMF) were purchased from China National Pharmaceutical Chemical Reagent Co. Polyvinyl pyrrolidone (PVP) was obtained from Aladdin Reagent (Shanghai) Co. Multi-walled carbon nanotubes were purchased from Nanjing Xianfeng Nanomaterials Technology Co. Thermoplastic polyurethane elastomer (TPU) was obtained from Suzhou Liu Yuqi Plastic Chemical Co. The flat electrodes used in this work were purchased from the Yu Xin Fork Finger Electrode Store. The standard NH₃ (1000 ppm) used in this experiment was purchased from Dalian Dart Gas Co., Ltd. All chemicals were of analytical grade and used without further purification. The water used in all experiments was purified using a Millipore system.

1.2 Preparation of Ti₃C₂T_x nanoflakes

Ti₃C₂T_x MXene nanoflakes were synthesized through a process involving the etching of the Ti₃AlC₂ bulk phase with LiF/HCl and subsequent ultrasound-assisted delamination. Initially, 2 g of LiF was added to 20 mL of 9 M HCl and stirred at 35°C in a water bath for 15 minutes. Once the LiF was completely dissolved, 1 g of Ti₃AlC₂ was gradually introduced into the mixed solution and further stirred in a water bath at 35°C for 24 h. After the reaction, the product was washed via centrifugation until the supernatant reached a neutral pH. Subsequently, the precipitate was dispersed in water and subjected to 1 hour of sonication in an ice bath. To eliminate any unetched Ti₃AlC₂ and multilayered Ti₃C₂T_x MXene that hadn't undergone sonication and layering, the mixed solution was centrifuged at 3500 r/min for 30 minutes, and the resulting supernatant was collected. The concentration of the Ti₃C₂T_x nanoflakes colloidal solution was maintained at 4 mg/mL.

1.3 Preparation of In₂O₃ nanotubes

In₂O₃ nanotubes were synthesized using PVP as a sacrificial template via electrostatic spinning. Initially, 0.6 g of In(NO₃)₃-4.5H₂O was dissolved in 10 mL of DMF and magnetically stirred for 2 h. Subsequently, 1.66 g of PVP powder was added and vigorously stirred for 10 h to obtain a colorless precursor solution suitable for electrostatic spinning. The prepared precursor solution was then loaded into a 10 mL syringe and extruded through a metal nozzle connected to a high voltage power supply at a rate of 0.04 mm/min. During the electrostatic spinning process, an applied voltage of 15 kV was used, and the distance between the metal needle and the electrostatic grounding collector was set at 17 cm. Finally, after drying in a drying tower for 12 h, the spun nanofibers were calcined in air at a heating rate of 1°C/min for 180 min at 600°C, resulting in the formation of In₂O₃ nanotubes.

1.4 Preparation of TPU foams

TPU foams were prepared using the salt template method. Initially, 10 g of TPU pellets were mixed with 40 mL of DMF and stirred at 70°C for 48 h to ensure complete dissolution of the TPU. Subsequently, 100 mg of multi-walled carbon nanotube powder was added and stirred for 4 h to achieve a uniform distribution within the TPU system. Then, 37.8 g of NaCl powder was added and manually stirred before being placed in an oven at 80°C to facilitate complete solvent evaporation. Finally, the NaCl powder was washed out of the system with hot water and dried to obtain the TPU foam. The resistance of the foam was measured using a resistance meter to verify its disconnection when no sensing material was loaded.

1.5 Characterization

The scanning electron microscopy (SEM) images were captured using a JSM-6700F electron microscope (JEOL, Japan). Transmission electron microscopy (TEM) images were obtained using a JEM-2100F transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were obtained using a Rigaku TTR III X-ray diffractometer (Tokyo, Japan) with a monochromatized Cu target as the radiation source. Raman spectroscopy was conducted with a LabRAM HR Evolution instrument (Jobin-yvon, Horiba, France) excited by a He-Ne laser operating at a wavelength of 532 nm. Fourier transform infrared (FT-IR) spectra were recorded using a PerkinElmer spectrometer, covering the range of 400 to 4000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB MK II X-ray photoelectron spectrometer to analyze the composition of C, O, Ti, and In elements.

1.6 NH₃ sensing performance measurement

In this study, the evaluation of NH₃ sensing performance was carried out at a relative humidity of 30%, and the test system is shown in Fig. S1. The system comprises a digital multimeter (Fluke 8846A) and two 1L glass vials. The Fluke 8846A is equipped with an internal power supply of 5V specifically for resistance measurements. One glass vial contains air, while the other vial holds the target gas for measurement. In the breath test experiment, NH₃ is diluted to 1.5 ppm using the breath of a healthy person. Subsequently, one glass bottle (1L) is filled with ambient air, while the other glass bottle (1L) contains NH₃ diluted with the exhaled breath. Initially, the sensor is placed in the glass vial containing air, allowing its resistance to stabilize. Subsequently, the sensor is promptly transferred to the glass vial containing the target gas for measurement. The change in resistance is continuously recorded in real-time using the Fluke 8846A digital multimeter. The response value of the sensor to NH₃ (R₁) is defined by equation (1), where R_g and R₀ are the resistance of the device in the target gas and air respectively.

$$R_1 = \frac{R_g - R_0}{R_0} \times 100\%$$
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1.7 Pressure sensing performance measurement

During the pressure test, a linear motor (LPS-1) is utilized to apply a specific pressure to the sensor. The sensor is positioned between the two squeeze plates of the linear motor, ensuring complete coverage. The software accompanying the linear motor allows for adjustment of test conditions such as pressure and frequency. To monitor real-time changes in the sensor's resistance, a digital multimeter (Fluke 8846A) is connected to the sensor using wires positioned at the top and bottom. The pressure

response (R_2) is calculated using Equation (2), where ΔR represents the steady resistance change between the pressure release and loading states, and R_0 denotes the steady resistance of the sensor without pressure loading. In addition, the response and recovery time of the pressure was measured using an electrochemical workstation (CHI-660E, Shanghai Chenhua Apparatus Co., Shanghai, China).

$$R_2 = \frac{\Delta R}{R_0} \times 100\% \tag{2}$$

The response / recovery time are defined as the time duration from the initial resistance value to 90% of the final equilibrium state.



Figure S1. Schematic diagram of the gas sensing test system.

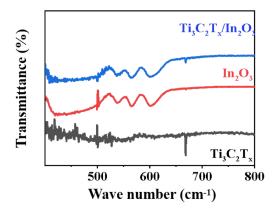


Figure S2. FTIR of $Ti_3C_2T_x$ nanoflakes, In_2O_3 nanotubes, $Ti_3C_2T_x/In_2O_3$ composites in the wave number range of 400-800 cm⁻¹.

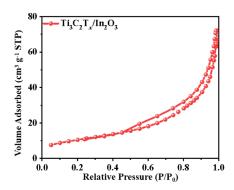


Figure S3. N₂ isothermal adsorption/desorption curve of $Ti_3C_2T_x/In_2O_3$ composites.

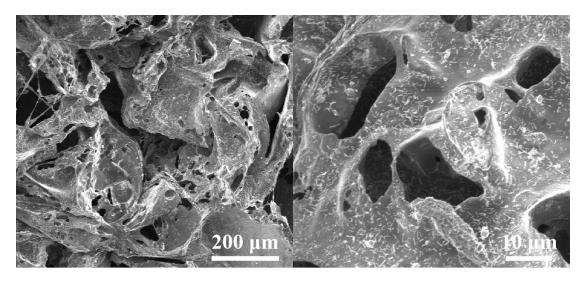


Figure S4. SEM image of $Ti_3C_2T_x/In_2O_3$ foam sensor in different scale.

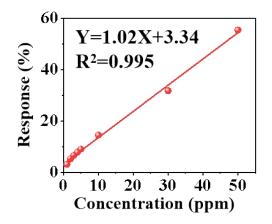


Figure S5. Linear plot of $Ti_3C_2T_x/In_2O_3$ foam sensor: response values versus NH₃ gas concentration.

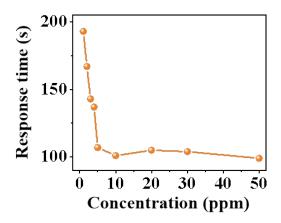


Figure S6. Response time of $Ti_3C_2T_x/In_2O_3$ foam sensor to NH₃ gas in different concentrations.

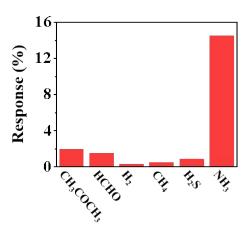


Figure S7. Selectivity of $Ti_3C_2T_x/In_2O_3$ foam sensor for various common breath gases at a concentration of 10 ppm.

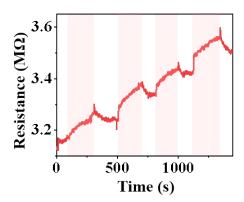


Figure S8. Four consecutive injections of 1.5 ppm NH_3 gas into the $Ti_3C_2T_x/In_2O_3$ foam sensor.

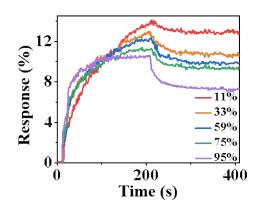


Figure S9. Dynamic response curves of $Ti_3C_2T_x/In_2O_3$ foam sensors to 5 ppm NH₃ at different humidity levels.

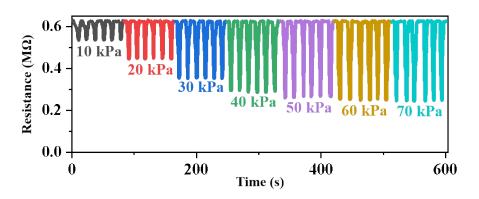


Figure S10. The dynamic response curve of the $Ti_3C_2T_x$ foam sensor to different pressures.

Table S1. Comparison of NH₃ gas sensing performance of some typical MXene based NH₃ gas sensor in compassion with the as-proposed planer $Ti_3C_2T_x/In_2O_3$ in this work at room temperature.

materials	Conc.	Tres/Trec	Response	Ref.
Metallic $Ti_3C_2T_x$	100 ppm	5/10 min	0.8%	1
MXene/SnO ₂	50 ppm	36/44 s	40%	2
MXene/TiO ₂	10 ppm	60/750 s	3.1%	3
Ti ₃ C ₂ T _x /SnO	10 ppm	61/119 s	67%	4
PEDOT:PSS/MXene	100 ppm	116/40 s	36.6%	5
CPAM/Ti ₃ C ₂ T _x	200 ppm	12.7/14.6 s	12.7/14.6%	6
Mxene/GO/CuO/ZnO	100 ppm	26/25 s	59.9%	7
Ti ₃ C ₂ T _x /In ₂ O ₃	50 ppm	34/337s	86%	This work

Where Tres/Trec is the response/recovery times; Conc.: Concentration; Ref.: Reference.

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