

## Electronic Supporting Information

# Carbon nanotube cross-linked phosphorus-doped MXene for capacitive pressure microsensor

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## 1 Materials

Hydrochloric acid and sulfuric acid are purchased from Sinopharm Chemical Reagent. Lithium fluoride, poly vinyl alcohols ( $M_w = 89,000-98,000$ ), poly dimethyl diallyl ammonium chloride ( $M_w < 10,000$ , 100-200 cP) are purchased from Aladdin. Carbon nanotubes, sodium hypophosphite monohydrate, titanium aluminum carbide are purchased from Macklin. All chemicals are used without any further purification.

## 2 Experimental

### 2.1 Preparation of MXene powder

The MXene is prepared through selectively etching Al layer from  $Ti_3AlC_2$ . 1.0 g  $Ti_3AlC_2$  (MAX) powders are gradually added to the mixture of LiF (1.6 g) and 9 M HCl (20 mL). The above solution is kept at 35 °C for 24 h with continuous stirring. The black muddy deposits are repeatedly centrifuged at 3500 rpm, washed with deionized water to adjust the pH = 6. Then, it is vacuum dried at 60 °C for 48 h and ground to obtain MXene powder.

### 2.2 Preparation of P-MXene ink

The obtained MXene is subsequently converted to P-MXene via a phosphatization procedure using  $NaH_2PO_2 \cdot H_2O$  as the P source. 0.3 g MXene and 1.5 g  $NaH_2PO_2 \cdot H_2O$  are placed in a quartz tube and heated under  $N_2$  flow at 350 °C for 2 h. P-MXene powder is collected and ultrasonically treated in distilled water under  $N_2$  atmosphere to obtain P-MXene ink.

### 2.3 Preparation of P-MXene/CNT ink

PDDA-CNT suspension is obtained by adding 5  $\mu$ L PDDA solution to 50 mL CNT suspension (1.0 mg/mL) and stirring for 2 hours. Then, 5 mL PDDA-CNT suspension is added to 50 mL P-MXene ink (1.0 mg/mL) and stirred for 6 hours to obtain P-MXene/CNT ink.

### 2.4 Preparation of a PVA/ $H_2SO_4$ gel electrolyte.

For the preparation of the gel electrolyte, 5 g of PVA and 5 g of  $H_2SO_4$  are added in 50 mL of deionized water. The solution is mixed at 80 °C for 2 h with vigorous stirring until it became clear.

### 2.5 Fabrication of P-MXene/CNT MSCs electrodes

The water-based microporous membrane and the interdigital mask are placed on the vacuum filter bottle in turn. Start the vacuum pump. 3ml P-MXene/CNT ink with the concentration of 1mg/mL is slowly added to the interdigital mask. Under the pressure of vacuum, the interdigital electrode is separated on the microporous membrane. The interdigital electrode is peeled off to PET by applying pressure. Coating 0.5ml PVA/ $H_2SO_4$  gel electrolyte in the center of the interdigital electrode. Connect the aluminum foil to the pin of the electrode.

## 3 Material characterizations

X-ray diffraction (XRD, Ultima IV) is used to examine the crystal structure with Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm). The morphology and fine structure are detected by scanning electron microscopy (SEM, FEI F50) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2T20) with selected area electron diffraction (SAED, Gatan) patterns. The elemental analysis is investigated by an X-ray energy dispersive spectrometer. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) is conducted to analyze the surface valence state.

## 4 Electrochemical measurements

The electrochemical performances of the products are determined using an electro-chemical workstation (CHI660e) in a three-electrode set up using a 1M  $H_2SO_4$  solution as the electrolyte. The three-electrode configuration is composed of the working electrode, reference electrode ( $Hg/Hg_2Cl_2$ ) and counter electrode (platinum sheet). The working electrode is fabricated by adding the sample, acetylene black and PVDF with a mass ratio of 8:1:1 into NMP under sonication for 30min. The obtained mixture is then coated on carbon cloth and dried at 70°C in vacuum for 24h. The electrochemical performances included the cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The EIS measurement is carried out in the frequency range of  $10^{-2}$ - $10^5$  Hz at an amplitude of 5 mV. The measurement of the cycling stability is conducted using a LAND battery test instrument (LANHECT3001A).

## 5 The calculation equations

The specific capacities of the electrodes ( $C_s, F g^{-1}$ ) tested by three-electrode configuration are calculated according to equation S1. For the micro-supercapacitor devices, the area capacities ( $C_a, mF cm^{-2}$ ) are calculated according to equation S2. The energy density ( $E_a, \mu Wh cm^{-2}$ ) and power density ( $P_a, \mu W cm^{-2}$ ) of the devices are calculated according to equations S3 and S4.

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (S1)$$

$$C_a = \frac{I\Delta t}{S\Delta V} \quad (S2)$$

$$E_a = \frac{C_a\Delta V^2}{2 \times 3.6} \quad (S3)$$

$$P_a = \frac{3600E_a}{\Delta t} \quad (S4)$$

Where  $I$  is the discharging current ( $A$ ),  $\Delta t$  is the discharging time ( $s$ ),  $m$  is the weight ( $mg$ ) of the electroactive materials,  $S$  is the area of the electrode ( $cm^2$ ) and  $\Delta V$  is the voltage window ( $V$ ).

## 6 Supplementary figures

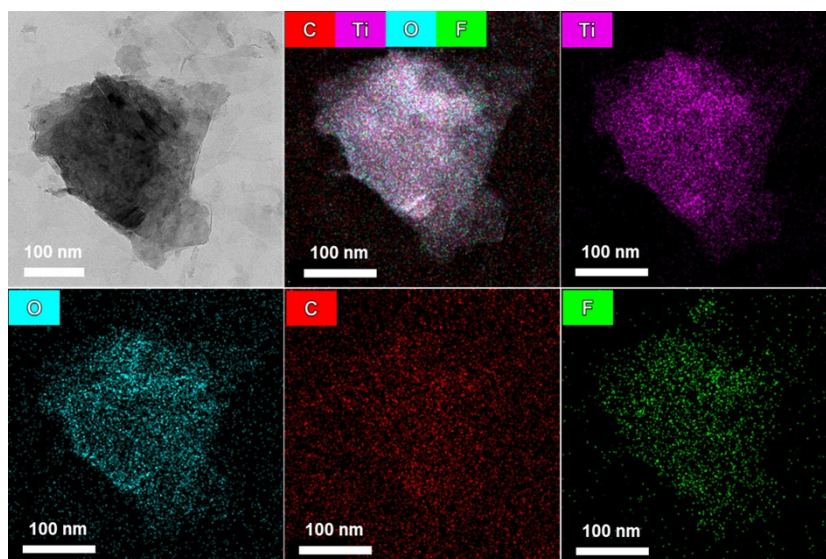


Fig. S1 TEM and elemental mapping images of MXene.

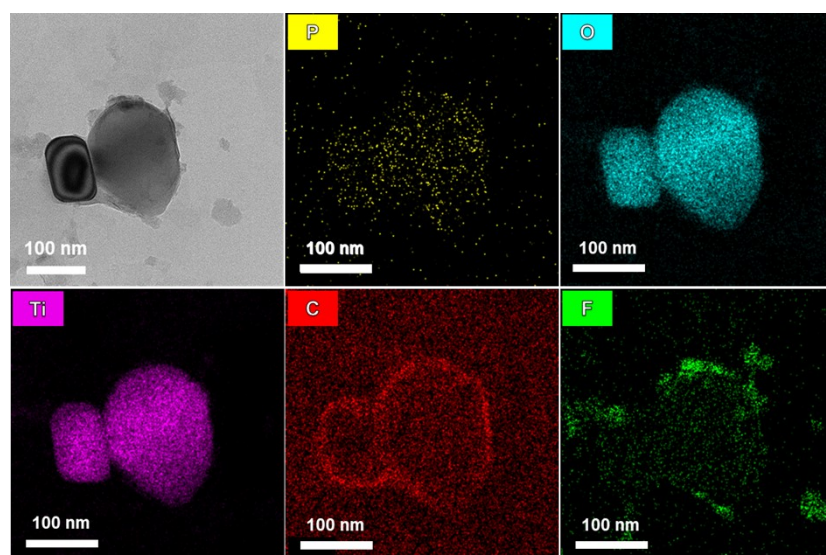


Fig. S2 TEM and elemental mapping images of P-MXene.

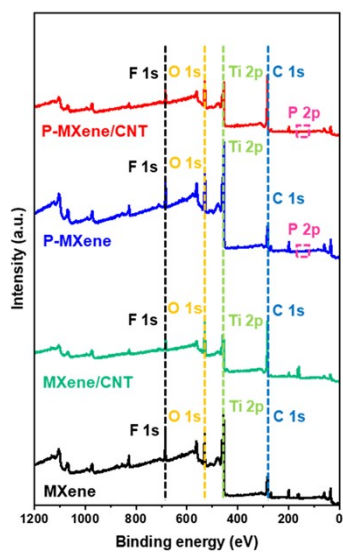


Fig. S3 XPS survey curves of MXene, MXene/CNT, P-MXene, and P-MXene/CNT.

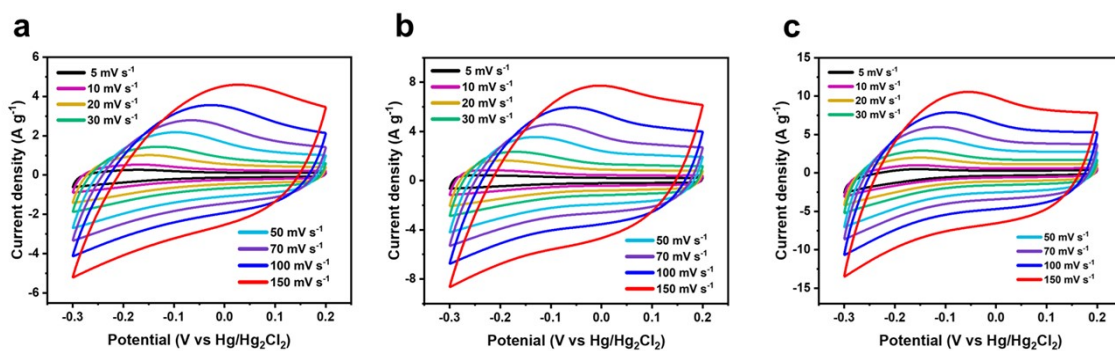


Fig. S4 CV curves of (a) MXene, (b) MXene/CNT, and (c) P-MXene.

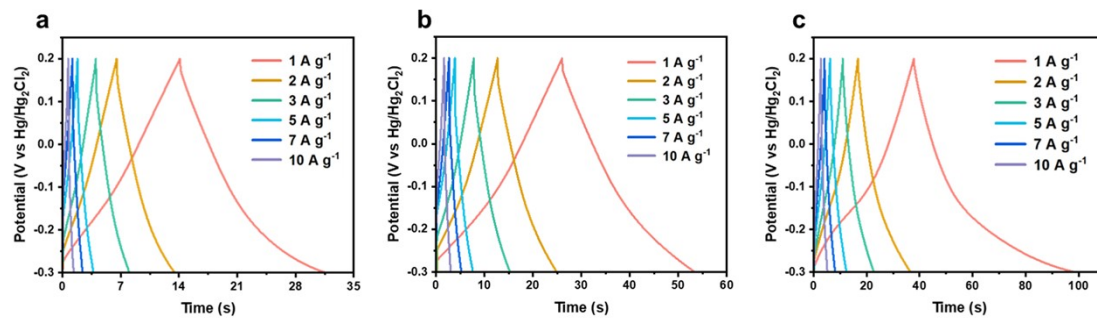


Fig. S5 GCD curves of (a) MXene, (b) MXene/CNT, and (c) P-MXene.

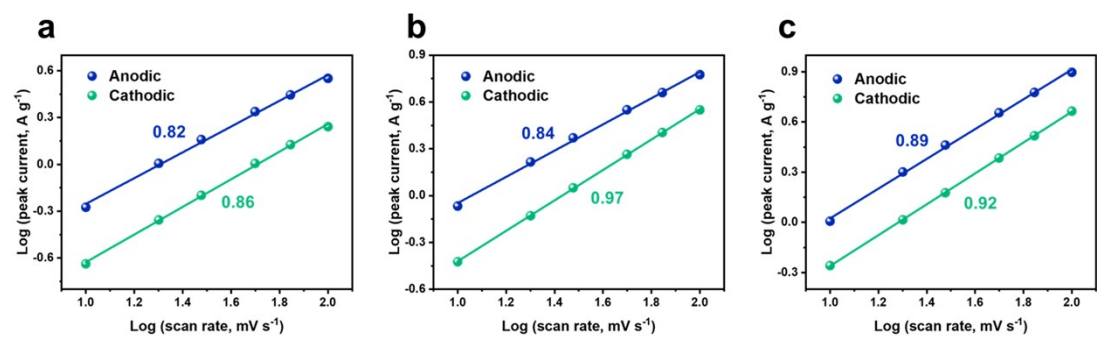
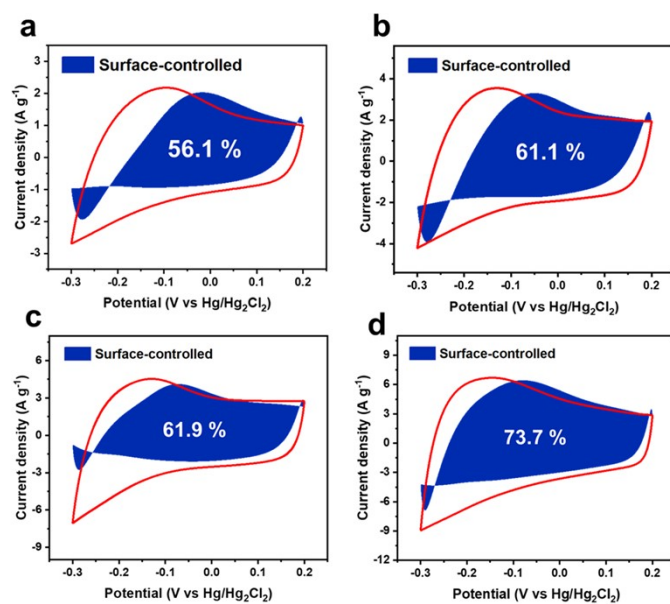
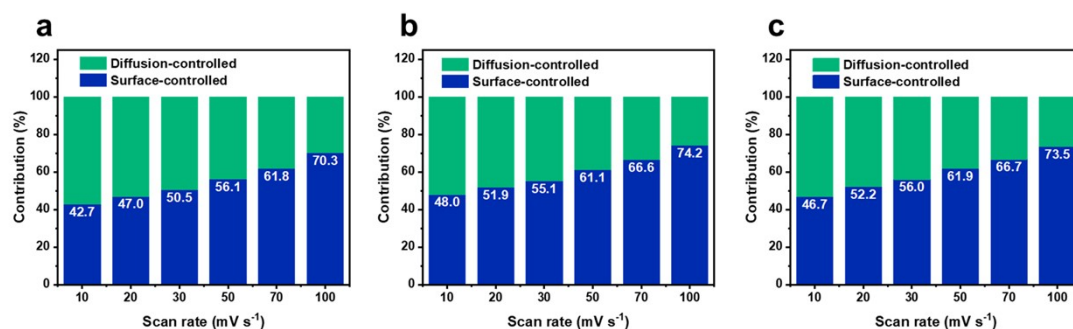


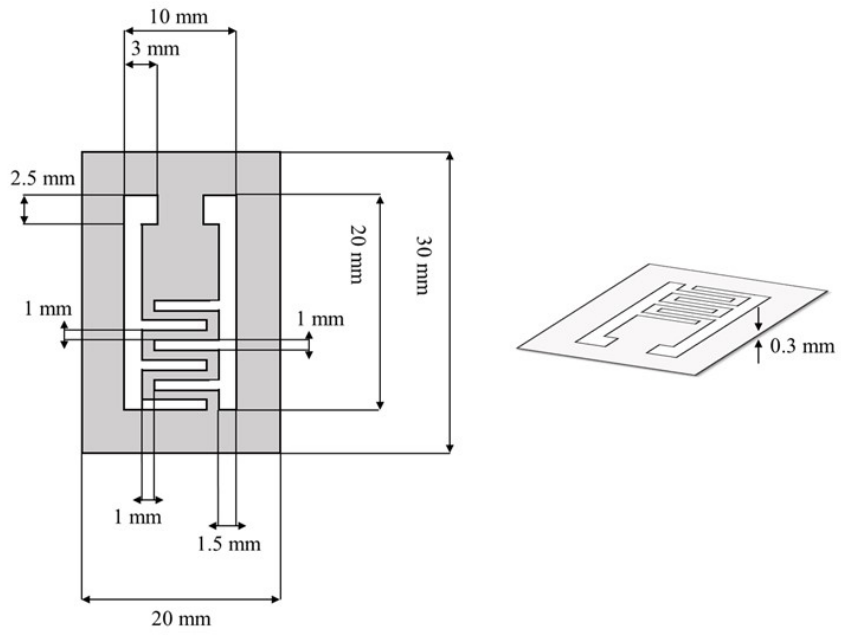
Fig. S6 Plots of  $\log i$  vs  $\log v$  of (a) MXene, (b) MXene/CNT, and (c) P-MXene.



**Fig. S7** Diffusion-controlled and surface-controlled contribution of (a) MXene, (b) MXene/CNT, (c) P-MXene, and (d) P-MXene/CNT at a scan rate of  $50 \text{ mV s}^{-1}$ .



**Fig. S8** Surface-controlled contribution ratios of (a) MXene, (b) MXene/CNT, and (c) P-MXene at various scan rates.



**Fig. S9** Schematic diagram of interdigital mask.



## 7 Supplementary tables

**Table S1.** Summary of the atomic ratio (%) of C, Ti, O, F, and P by XPS analysis.

Sample	C (%)	Ti (%)	O (%)	F (%)	P (%)
MXene	38.56	28.73	21.04	11.66	—
MXene/CNT	61.17	14.63	18.64	5.55	—
P-MXene	40.96	27.22	20.98	9.82	1.02
P-MXene/CNT	59.25	15.47	18.25	6.06	0.97

**Table S2.** The electrochemical performance comparison in this job.

Electrodes	Current density	Capacitance	Rate capability	Electrolytes
MXene	1 A g <sup>-1</sup>	35.0 F g <sup>-1</sup>	40.0%@10 A g <sup>-1</sup>	1M H <sub>2</sub> SO <sub>4</sub>
MXene/CNT	1 A g <sup>-1</sup>	54.8 F g <sup>-1</sup>	51.1%@10 A g <sup>-1</sup>	1M H <sub>2</sub> SO <sub>4</sub>
P-MXene	1 A g <sup>-1</sup>	121.4 F g <sup>-1</sup>	41.5%@10 A g <sup>-1</sup>	1M H <sub>2</sub> SO <sub>4</sub>
P-MXene/CNT	1 A g <sup>-1</sup>	166.1 F g <sup>-1</sup>	56.3%@10 A g <sup>-1</sup>	1M H <sub>2</sub> SO <sub>4</sub>

**Table S3.** The fitted parameters for the Nyquist plots using the equivalent circuit.

Electrodes	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$R_w$ ( $\Omega$ )
MXene	1.52	0.36	2.91
MXene/CNT	1.25	0.35	1.85
P-MXene	1.32	0.27	1.67
P-MXene/CNT	1.13	0.19	1.04

**Table S4.** Performance comparison of various MSCs.

Materials	Testing conditions	$\Delta V$ (V)	$C_a$ (mF $cm^{-2}$ )	$E_a$ ( $\mu Wh$ $cm^{-2}$ )	$P_a$ ( $\mu W$ $cm^{-2}$ )	Ref.
P-MXene/CNT	0.2 mA $cm^{-2}$	0.6	162.4	8.12	60.02	This work
P-MXene/CNT	0.5 mA $cm^{-2}$	0.6	135.33	6.76	150	This work
P-MXene/CNT	1 mA $cm^{-2}$	0.6	97.5	4.88	300	This work
MXene/Graphene	20 $\mu A$ $cm^{-2}$	1	3.84	0.53	10	[1]
MXene/graphene aerogel	0.1 mA $cm^{-2}$	0.6	—	2.18	60	[2]
Polyester@MXene nanofibers-based yarn	0.25 mA $cm^{-2}$	0.6	13.23	0.67	90	[3]
Inkjet printed MXene MSC	—	0.5	12	0.32	11.4	[4]
GQDs//MnO <sub>2</sub>	15 $\mu A$ $cm^{-2}$	1	1.11	0.15	7.51	[5]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> /CNF/PC	0.1 mA $cm^{-2}$	0.7	143	2.4	17.5	[6]

## References

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