Support Information

MXene Decorated 3D-Printed Carbon Black-based Electrodes for Solid-State Micro-Supercapacitors

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Experimental Section

Preparation of MXene suspension

MXene nanosheets ($Ti_3C_2T_x$) were synthesized by etching aluminum from the MAX phase. The etchant was prepared by dissolving 1.2 g LiF in 20 mL of 9 M HCl. Subsequently, 1 g of Ti_3AlC_2 was added to the etchant and continuously stirred for 24 hours at 42℃. The resulting etching suspension was washed with deionized (DI) water through centrifugation at 5000 rpm (5 minutes per cycle) several times, until the pH of the supernatant reached approximately 6. The centrifuged multilayer MXene nanosheets were collected and freeze-dried for 24 hours. Finally, 50 mg of MXene nanosheets were added to deionized water and sonicated for 30 minutes. The concentration of the as-prepared MXene suspension was approximately 1 mg mL^{-1}.

Preparation of conductive filaments for 3D printing

A mixture of PLA/TPU (PLA with a molecular weight of 200,000 and TPU with a molecular weight of 200,000) powders in a weight ratio of 1:5 was initially prepared. Carbon black was then added to the mixture at 25% and mixed for 30 minutes. The mixture was subsequently added to ethanol and continuously stirred for 60 minutes. Afterward, the mixture was dried at 90℃ for 2 hours. The conductive PLA/TPU/CB (PTC) filaments, with a diameter of 1.7 mm for 3D printing, were prepared using a Wellzoom B single-screw extruder (Mistar Technology Co. Ltd., Shenzhen, China) at 190 °C and a rate of 50 r/min.

Fabrication of 3D-printed electrodes

The cylindrical and interdigital shapes of the electrodes were designed using Sketch UP and Ultimaker Cura software. The designed electrodes were then prepared using a commercial PLA/MWCNT filament and the as-prepared conductive PTC filament, using an FDM 3D printer (Anycubic Technology Co. Ltd., Hong Kong, China). The print parameters for all specimens were set uniformly to a nozzle temperature of 220 °C, bed temperature of 60 °C, 100% filling volume, and a layer height of 0.15 mm.

Fabrication of MXene decorated 3D-printed electrodes.

The as-printed electrodes (PTC and PM electrodes) were activated by immersing them in N,N-dimethylformamide (DMF) for different durations (2 hours and 12 hours). They were then washed with deionized water to remove residual DMF and polymers from the electrode surfaces, followed by drying in a vacuum oven at 60 °C for 24 hours. Next, the activated 3D-printed electrodes were immersed in a 1.0 mg mL^{-1} MXene solution for 12 hours and then dried in a vacuum oven at 60 °C for 24 hours. The MXene-decorated 3D-printed electrodes were denoted as MXene@PTC-12h and MXene@PM-12h.

Preparation of micro-supercapacitor

A micro-supercapacitor was prepared by assembling two identical interdigital electrodes with a PVA/H_2SO_4 gel electrolyte. The PVA/H_2SO_4 gel serves as both the electrolyte and the separator between the two electrodes. The gel electrolyte was prepared by dissolving 4 g of PVA in 40 mL of H_2O, heating the solution to 90℃ until it became clear, and then adding 2.27 mL of concentrated sulfuric acid. After cooling the PVA/H_2SO_4 solution to room temperature, it was stored in a glass bottle.

Material characterization

The morphologies of the conductive filaments and 3D-printed electrodes were characterized using scanning electron microscopy (SEM) with a GeminiSEM 300. The Transmission electron microscopy (TEM) images and energy dispersive X-ray spectroscopy (EDX) measurements were

conducted on a JEOL JEM-2100F at 200 kV. The structures of the 3D-printed electrodes were investigated using X-ray diffraction (XRD) patterns obtained with a D/teX Ultra 250 detector and Cu Kα radiation (λ = 0.15406 nm). The compositions of the 3D-printed electrodes were examined using Fourier transform infrared spectroscopy (FT-IR) with a Bruker model VECTOR-22 Fourier transform spectrometer. Raman spectroscopy was performed using a Raman spectrometer (Horiba HR Evolution) equipped with the laser wavelength of 532 nm.

Electrochemical characterization

The electrochemical performance and capacitance measurements of the 3D-printed electrodes and micro-supercapacitors were characterized using cyclic voltammetry (CV) and galvanostatic charge–discharge curves on a CHI 760E electrochemical workstation (Chenhua, Shanghai). In the three-electrode setup, the as-prepared 3D-printed electrodes, Pt wire, and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. The electrolyte used was 2 M H_2SO_4. The corresponding electrochemical impedance spectroscopy (EIS) experiments were conducted at frequencies ranging from 100 kHz to 100 mHz with a low sinusoidal amplitude alternating voltage of 10 mV. The specific areal capacitance Cs ($mF \cdot cm^{-2}$) was calculated from discharge curves using the following equation:

$$Cs = (I \cdot t) \cdot (\Delta U \cdot s)^{-1}$$

Where I (A) represents the discharge current, t (s) is the discharge time, ΔU (V) is the voltage range during discharging, and S (cm^2) corresponds to the area of the working electrode. For micro-supercapacitors (MSCs), the electrochemical performance was evaluated in a two-electrode configuration. The interdigitate area was 1.5 cm^2. The energy density (E) and power density (P) were calculated using the following equations:

$$E = (\frac{1}{2})(\frac{1}{3.6}) \cdot C \cdot (\Delta U)^2$$

$$P = 3600 \cdot E \cdot t^{-1}$$

Where E ($\mu Wh\ cm^{-2}$) and P ($\mu W\ cm^{-2}$) are the energy density and power density of the MSC, respectively. C ($mF \cdot cm^{-2}$) is the capacitance calculated from the Equation.

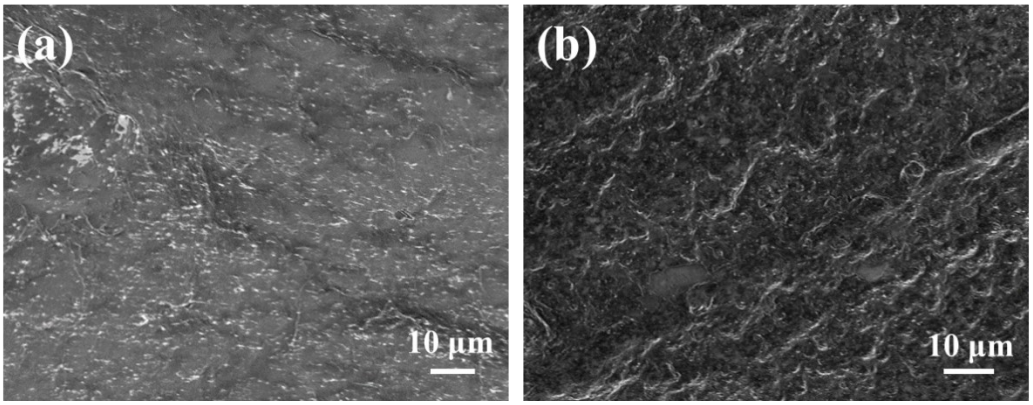

Fig. S1. SEM images of (a) commercial PLA/MWCNT filament, and (b) PLA/TPU/CB conductive filament.

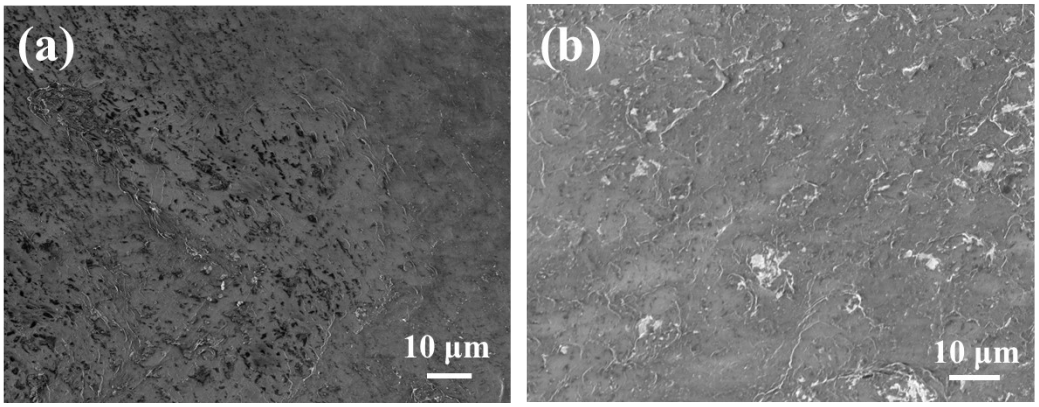

Fig. S2. SEM images of (a) DMF-activated PM-2h electrode, and (b) DMF-activated PM-12h electrode.

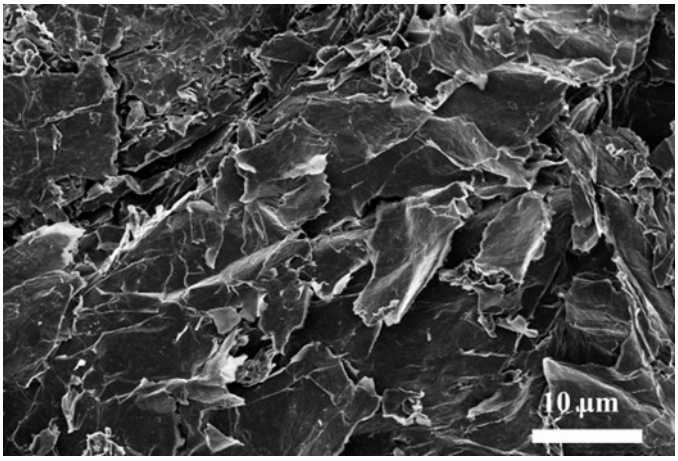

Fig. S3. SEM image of the as-prepared MXene nanosheets.

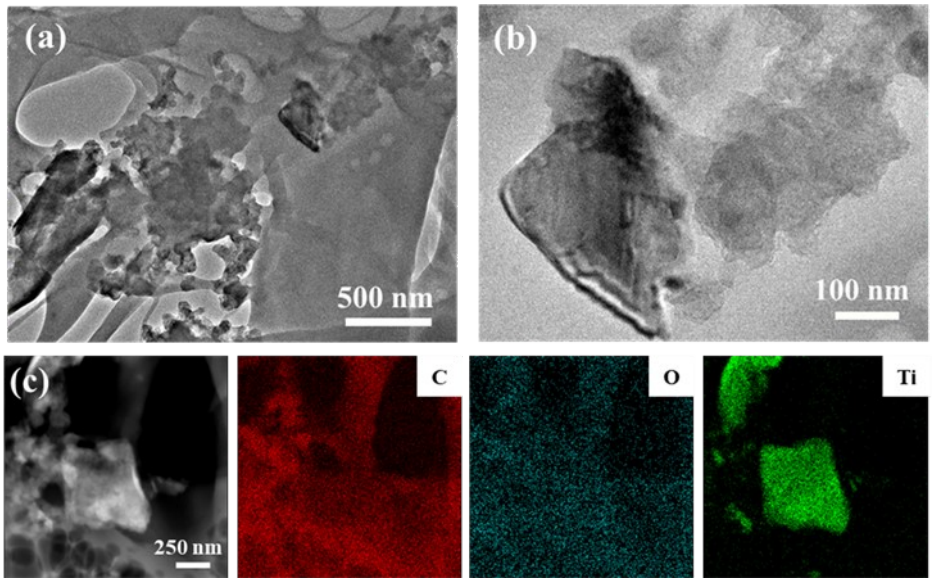

Fig. S4. (a, b) TEM images of the MXene@PTC-12h composites. (c) Elemental mappings (C, O and Ti elements) of the MXene@PTC-12h composites.

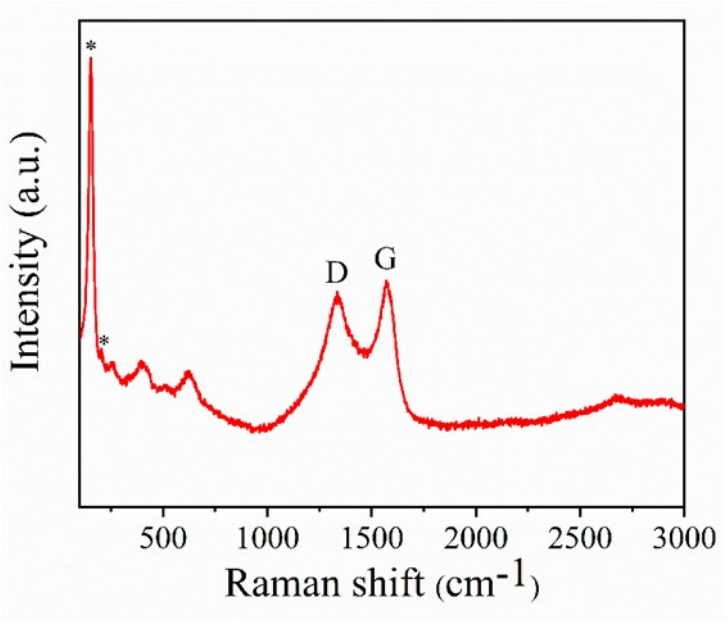

Fig. S5. Raman spectrum of the MXene@PTC-12h composites.

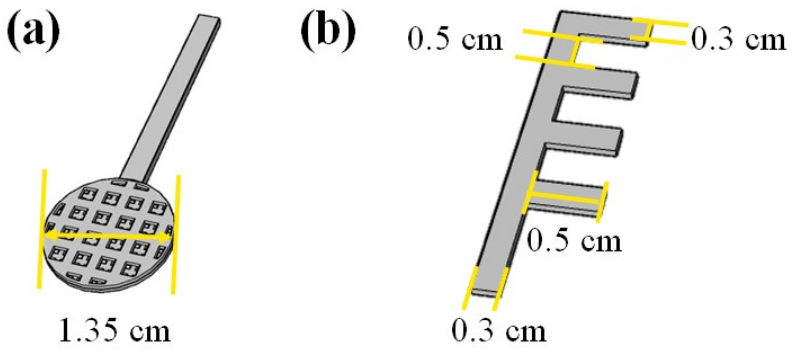

Fig. S6. 3D-printed electrode structures. (a) cylindrical shaped electrode, and (b) interdigital shaped electrode.

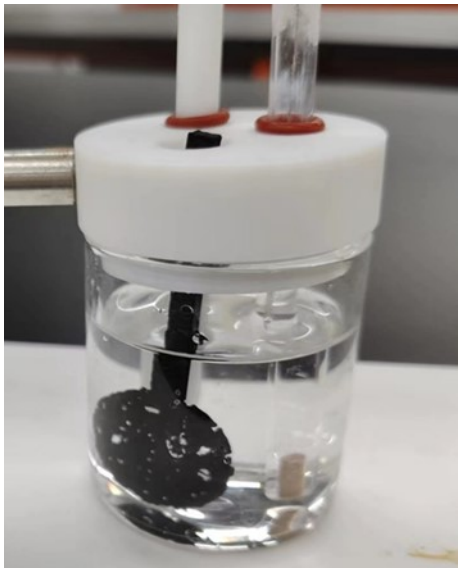

Fig. S7. Cylindrical electrode in three-electrode system.

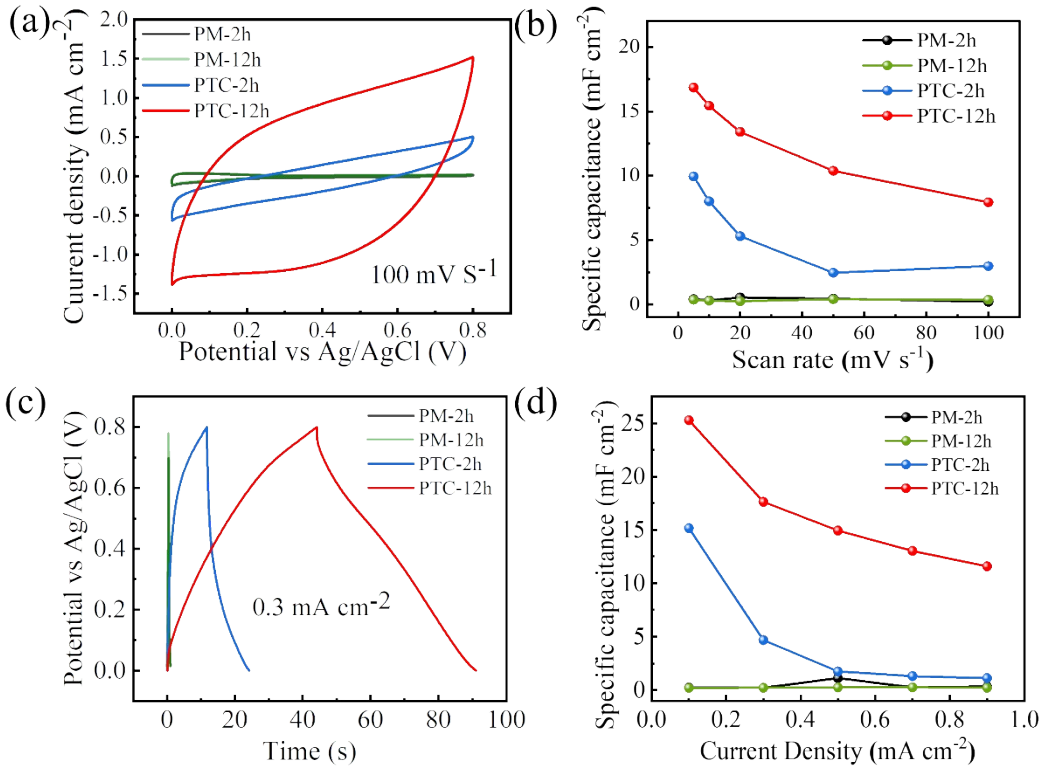

Fig. S8. The electrochemical performance of different DMF-activated electrodes. (a) CV curves; (b) Specific capacitance at different scan rates; (c) GCD curves; and (d) Specific capacitances calculated from GCD curves as a function of current density.

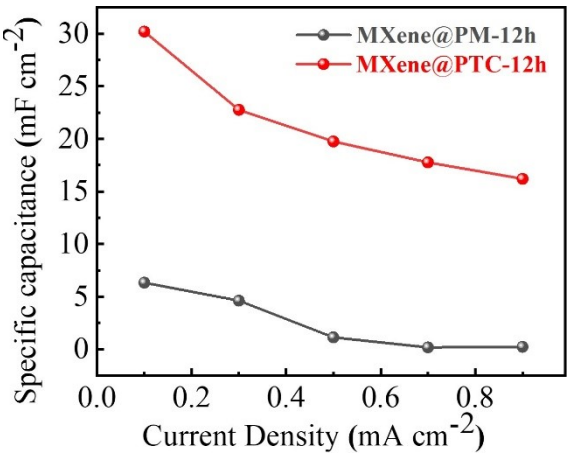

Fig. S9. Specific capacitances of MXene@PM-12h and MXene@PTC-12h electrodes calculated from GCD curves as a function of current density.

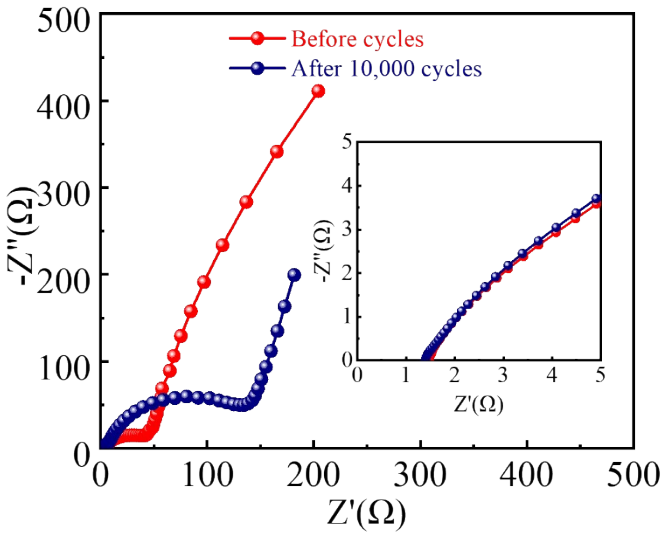

Fig. S10. Nyquist plots of the MXene@PTC-12h electrodes before and after 10,000 cycles.

Table.S1. Comparison of the electrochemical performance of MXene@PTC-12h based MSC with other reported MSCs

Samples	Specific capacitance (mF cm^{-2})	Cycle life	Energy density (μWh cm^{-2})	Power density (μW cm^{-2})	Ref.
MXene@PTC-12h	**20.8**	**95.0% after 10,000 cycles**	**1.04**	**30**	**This work**
MoS_x@3D-PE	4.15	90.0% after 10,000 cycles	0.2	16.26	22
$Ti_3C_2T_X$/CNF	25.3	86.8% after 10,000 cycles	0.08	145	44
I-$Ti_3C_2T_x$	56.8	93.7% after 10,000 cycles	0.76	6.17	45
Graphene	0.7	77% after 11,000 cycles	0.092	25	46
MXene-Graphene	3.26	82% after 2,500 cycles	0.48	4	47
Wet Jet Milling Graphene:SWCNTs	5.296	98% after 10,000 cycles	0.361	10	48
polyaniline-wrapped multi-walled carbon nanotube	0.67	67.4% after 10,000 cycles	0.13	0.012	49
PU coating-PPy	2.64	97% after 10,000 cycles	0.09	19.1	50