

Electronic Supplementary Information for:

***In situ* fabrication of dry/gel bilayer  $Ti_3C_2T_x$  film for high-rate micro-supercapacitors †**

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## **1. Experimental Section**

### **Materials**

$Ti_3AlC_2$  powders (99wt%, pure) were purchased from Jilin 11 tech. Inc. HCl (Sinopharm Chemical Reagent Company, 35-38% concentration), HF (Sigma Aldrich, 40%), and LiCl (MERYER, 99%) were commercially procured. All the chemicals were used without further treatments.

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## Synthesis of $Ti_3C_2T_x$ nanosheets

The  $Ti_3C_2T_x$  nanosheets were synthesized by etching Al from the precursor  $Ti_3AlC_2$  using HF/HCl reported previously.<sup>1</sup> Firstly, 6 ml deionized water, 12 mL of hydrochloric acid and 2.5 ml hydrofluoric acid were mixed in turn by stirring to form a uniform solution. Then, 1 g  $Ti_3AlC_2$  powder was added into the mixed solution in batches, followed by magnetic stirring for 24 h at the temperature of 35 °C. The obtained suspension was washed by deionized water via centrifugation (5000 rpm, 3 min per cycle) several times until the  $pH \geq 6$ . Subsequently, the collected sediment was re-dispersed in 30 ml deionized water, then added into LiCl solution containing 30 ml deionized water and 1 g LiCl for delamination. After being stirred for 4 h at the temperature of 35 °C, the delaminated  $Ti_3C_2T_x$  dispersion was washed by deionized water via centrifugation at 8000 rpm for 3 mins. Further, the supernatant was discarded and the sediment was washed again by centrifugation at 10000 rpm for 5 mins. Afterwards, 20 ml deionized water was added into the centrifuge tube containing the precipitate, followed by vigorous manual shaking until the  $Ti_3C_2T_x$  nanosheets were uniformly dispersed.  $Ti_3C_2T_x$  colloidal solution with a high concentration of 42 mg  $mL^{-1}$  was obtained for further usage.

## Preparation of $H_2SO_4$ - $Ti_3C_2T_x$ ion-gel film

Bilayer  $Ti_3C_2T_x$  films were prepared via a blade-coating method. Firstly,  $Ti_3C_2T_x$  colloidal solution was dropped on the polyimide substrate, followed by removing the blade on it with the height of 200 $\mu$ m. After vacuum drying, the bottom layer of  $Ti_3C_2T_x$

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film designed as an electron-transport layer was prepared. Next, the top layer of wet  $\text{Ti}_3\text{C}_2\text{T}_x$  with a width of 5 mm (the width was limited by the tape) was fabricated on the totally dried  $\text{Ti}_3\text{C}_2\text{T}_x$  film using the same way of blade-coating, closely followed by being immersed in 3 M  $\text{H}_2\text{SO}_4$  for 10 seconds.  $\text{H}_2\text{SO}_4$ -induced  $\text{Ti}_3\text{C}_2\text{T}_x$  ion-gel film (named as  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$ ) was formed from fluid solution  $\text{Ti}_3\text{C}_2\text{T}_x$  solution. For comparison, another set of samples was directly vacuum-dried without being immersed in sulfurous acid (named as  $\text{Ti}_3\text{C}_2\text{T}_x$ -dried).

### **Fabrication of the interdigital micro-supercapacitors**

For the fabrication of interdigital MSCs, the as-obtained double-layer  $\text{Ti}_3\text{C}_2\text{T}_x$  films were cut into strips for being used as electrodes of the symmetric supercapacitor. Using the direct laser writing technique, a pulse laser (wavelength of 1064 nm; power of 12 W; pulse duration of 100 ns; repeat rate of 20 kHz; scanning speed of 800 mm s<sup>-1</sup>) was focused on the  $\text{Ti}_3\text{C}_2\text{T}_x$  film and patterned it into interdigital electrodes. Subsequently, 3 M  $\text{H}_2\text{SO}_4$  aqueous solution as electrolyte was dripped onto the area of interdigital electrodes of  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  and  $\text{Ti}_3\text{C}_2\text{T}_x$ -dried. Then the  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  MSCs and  $\text{Ti}_3\text{C}_2\text{T}_x$ -dried MSCs were obtained.

### **Material characterizations**

The morphologies of  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets and electrodes were characterized by scanning electron microscope (SEM) (Hitachi SU8230). X-ray diffraction (XRD) patterns were measured by powder X-ray diffractometer (Bruke D8, Copper  $\text{K}\alpha$

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radiation,  $\lambda=1.540598 \text{ \AA}$ ). Raman spectrum was obtained by Horiba Raman microscope with 532 nm laser, 600 lines  $\text{mm}^{-1}$  grating at 10% laser power and a 50X objective.

### Electrochemical measurements

The electrochemical performance of  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  MSCs and  $\text{Ti}_3\text{C}_2\text{T}_x$ -dried MSCs was evaluated in a two-electrode system by CHI 660e electrochemical workstation. 3 M  $\text{H}_2\text{SO}_4$  was served as the electrolyte. Cyclic voltammetry (CV) was carried out from 5 to 200  $\text{mV s}^{-1}$ . Galvanostatic charge–discharge (GCD) was measured ranging from 1 to 10  $\text{mA cm}^{-2}$ . EIS was performed in the frequency range from 100 kHz to 0.01 Hz at 0 V.

### Electrochemical calculations

Areal specific capacitance  $C_A$  ( $\text{mF cm}^{-2}$ ) of the MSCs devices was calculated from the CV curves by integrating the discharge portion using the following equation:

$$C_A = \frac{1}{VA\nu} \int i dV$$

Areal specific capacitance  $C_A$  ( $\text{mF cm}^{-2}$ ) of the MSCs devices was calculated from the GCD profiles based on the following equation:

$$C_A = (I \times \Delta t) / (A \times \Delta V)$$

where  $i$  is the current (mA),  $V$  is the potential (V),  $\nu$  is the scan rate (mV/s) and  $A$  is the area of the MSC ( $\sim 0.4 \text{ cm}^2$ ).

Areal specific energy density  $E_A$  ( $\text{mW h cm}^{-2}$ ) of MSCs device:

$$E_A = \frac{1}{A} \int iV dt$$

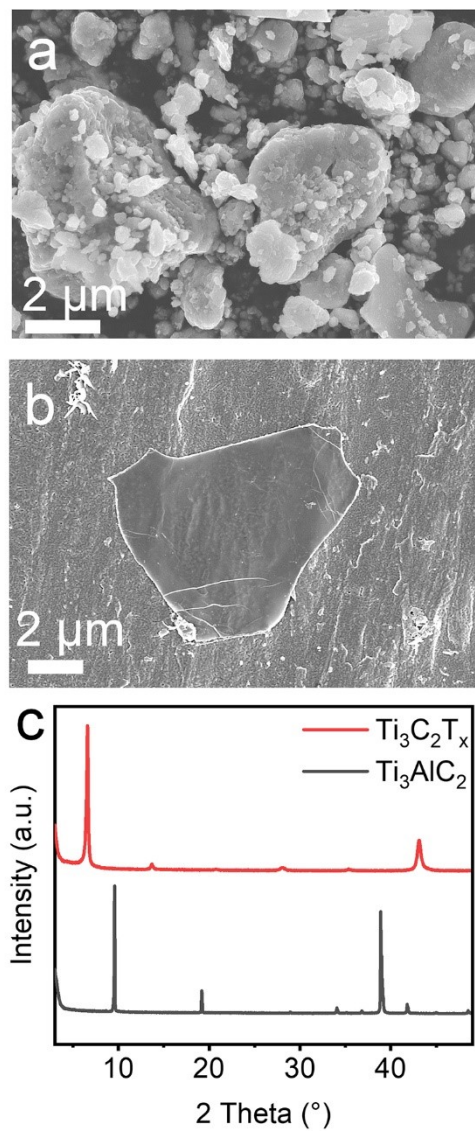
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$$E_A = \frac{C \times V^2}{2 \times 3600}$$

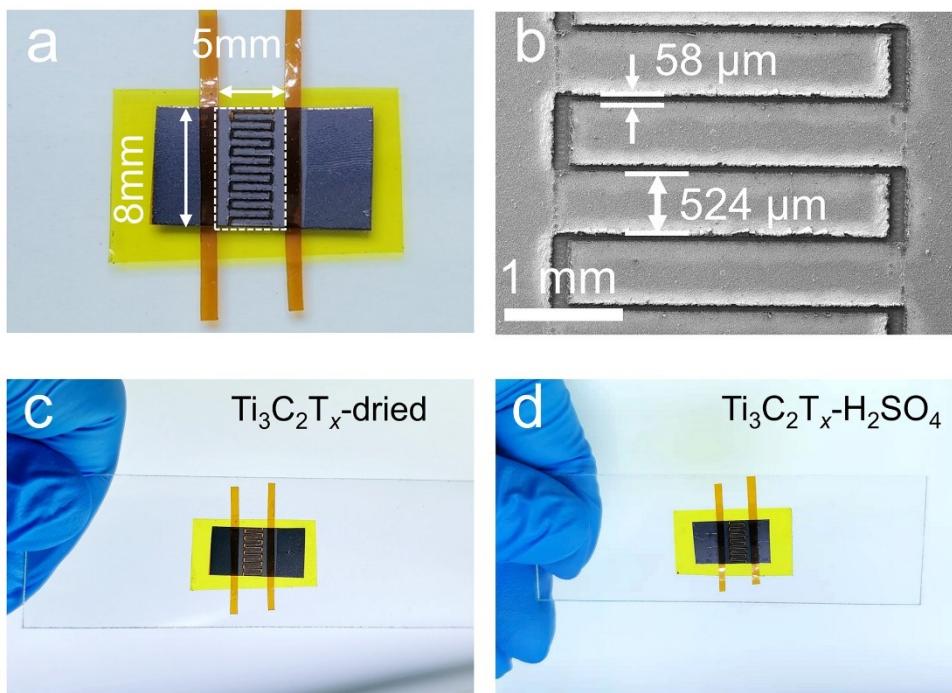
Areal specific power density  $P_A$  ( $\text{mW cm}^{-2}$ ) of MSCs device:

$$P_A = \frac{E_A \times 3600}{\Delta t}$$

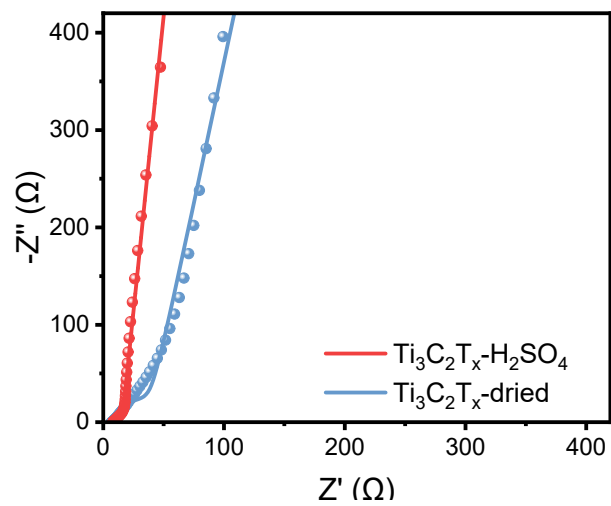
where  $A$  is the area of the MSC device and  $\Delta t$  is the discharge time.



**Fig. S1** SEM of (a)  $\text{Ti}_3\text{AlC}_2$ , (b)  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheet (the substrate is copper foil); (c) XRD of  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{C}_2\text{T}_x$ .

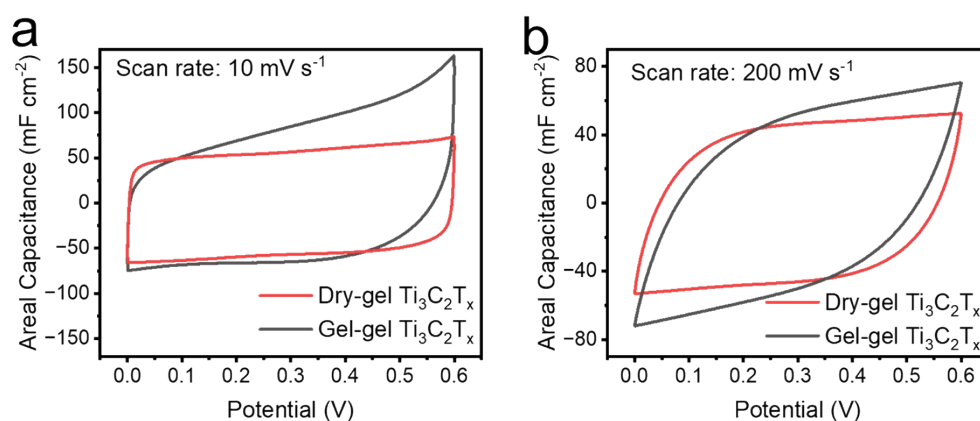


**Fig. S2** (a) Photograph shows the effective area of the device; (b) SEM of interdigital electrodes; Photographs of (c)  $\text{Ti}_3\text{C}_2\text{T}_x\text{-dried}$  MSCs and (d)  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  MSCs.

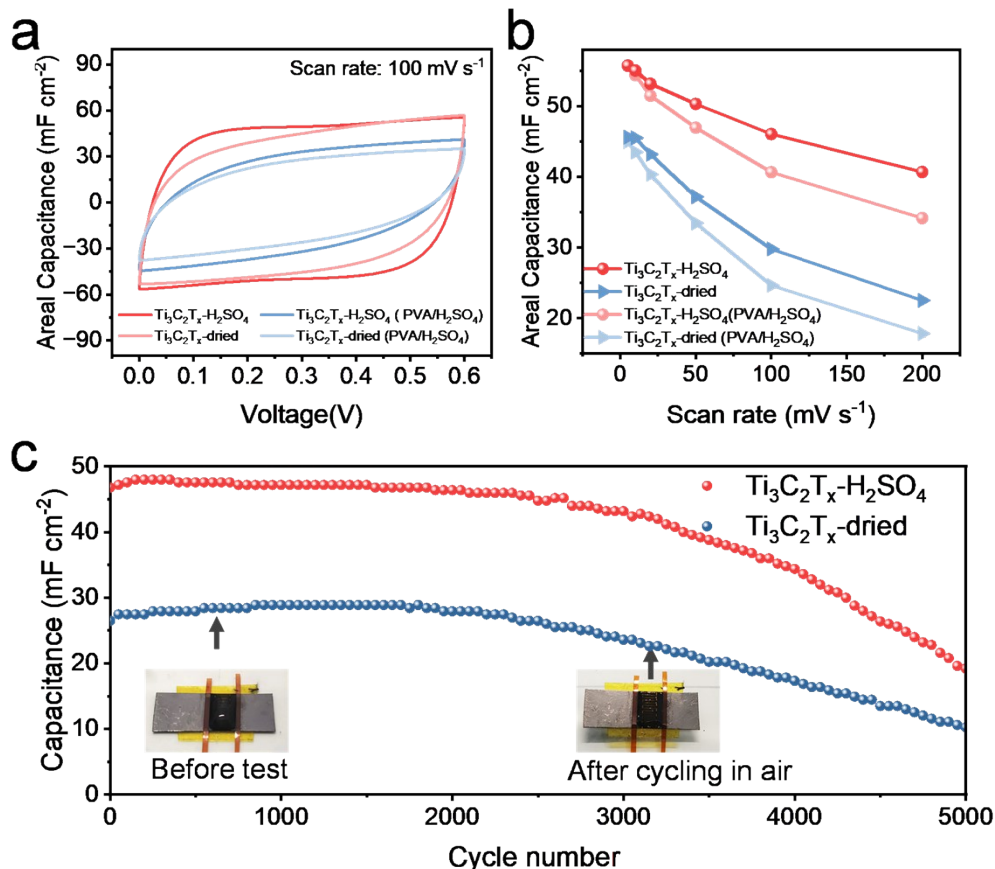


**Fig. S3** EIS spectra with the fitting results of the  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  and  $\text{Ti}_3\text{C}_2\text{T}_x\text{-dried}$  MSCs.

In order to investigate the performance improvement contributed from the bottom dry  $\text{Ti}_3\text{C}_2\text{T}_x$  film, electrochemical measurements of double-layered ion-gel  $\text{Ti}_3\text{C}_2\text{T}_x$  MSCs (named as Gel-gel  $\text{Ti}_3\text{C}_2\text{T}_x$ ) were performed in the same test conditions. Fig.S4a and S4b show the cyclic voltammeter (CV) profiles of Gel-gel  $\text{Ti}_3\text{C}_2\text{T}_x$  and Dry-gel  $\text{Ti}_3\text{C}_2\text{T}_x$  MSCs at various scanning rates. The black lines referring to Gel-gel  $\text{Ti}_3\text{C}_2\text{T}_x$  MSCs deviate from the rectangle both at the scan rate of 10 mV/s and 200 mV/s, indicating a worse capacitive performance and large resistance of Gel-gel MSCs. As a comparison, the CV curves of the dry-gel MSCs display a near rectangle in shape, which reveals an ideal capacitor behaviour.<sup>2</sup> Consequently, the CV curves prove that the bottom layer of dry  $\text{Ti}_3\text{C}_2\text{T}_x$  plays an important role for excellent capacitance performance.



**Fig. S4** CV curves of the Dry-gel and gel-gel  $\text{Ti}_3\text{C}_2\text{T}_x$  at the scan rate of (a)10 mV/s and (b) 200 mV/s.



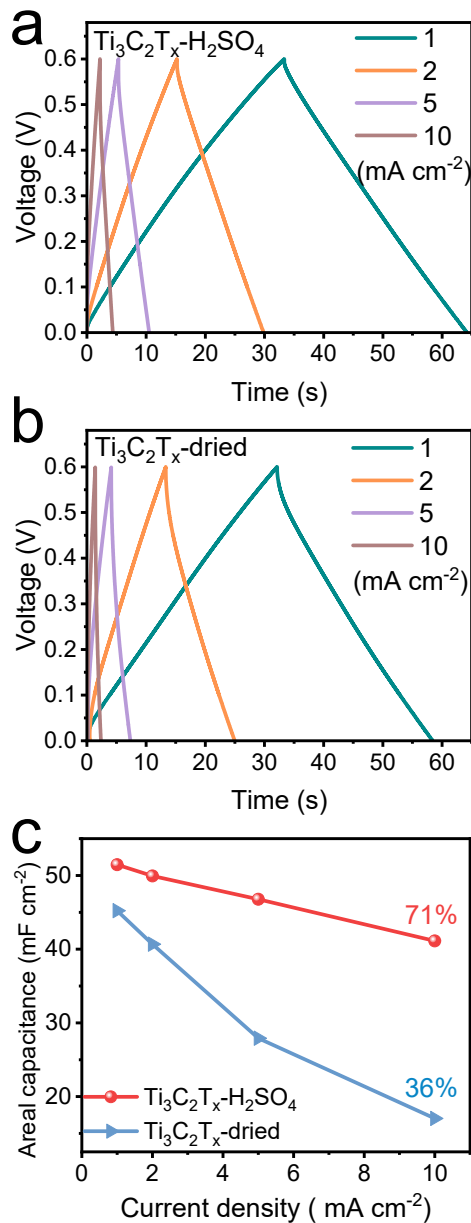
**Fig. S5** (a) CV curves and (b) rate performance of  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  and  $\text{Ti}_3\text{C}_2\text{T}_x\text{-dried}$  MSCs in 3M  $\text{H}_2\text{SO}_4$  and 3M PVA/ $\text{H}_2\text{SO}_4$ ; (c) Cycling stability tested at  $5 \text{ mA cm}^{-2}$  in 3M  $\text{H}_2\text{SO}_4$ , the inserted pictures show the state of the electrolyte before and after the cycling test respectively.

The cycle stability of the  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  MSCs was tested in the 3M  $\text{H}_2\text{SO}_4$  in the very beginning (Fig.S5). However, since the device was exposed to the air, the electrolyte of 3M  $\text{H}_2\text{SO}_4$  solution gradually evaporates during the long-time cycling test. As a result, the concentrated  $\text{H}_2\text{SO}_4$  with hardly electric severely affected the performance of MSCs. Besides, we have tested the CV of  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  and  $\text{Ti}_3\text{C}_2\text{T}_x\text{-dried}$  MSCs in the electrolyte of 3M  $\text{H}_2\text{SO}_4$  and 3M PVA/ $\text{H}_2\text{SO}_4$  respectively. It is worth noting that as shown in Fig.S5a and S5b, there are obvious enhancements of  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  compared with  $\text{Ti}_3\text{C}_2\text{T}_x\text{-dried}$  both in 3M  $\text{H}_2\text{SO}_4$  and 3M PVA/ $\text{H}_2\text{SO}_4$ .



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All of them reflect the effectiveness of using ion-gel to improve performance. Moreover, the performances of  $\text{Ti}_3\text{C}_2\text{T}_x\text{-H}_2\text{SO}_4$  in 3M  $\text{H}_2\text{SO}_4$  and 3M PVA/ $\text{H}_2\text{SO}_4$  are similar, the same is true for  $\text{Ti}_3\text{C}_2\text{T}_x$ -dried MSCs. Consequently, considering the similar performance in 3M  $\text{H}_2\text{SO}_4$  and 3M PVA/ $\text{H}_2\text{SO}_4$ , we chose the 3M PVA/ $\text{H}_2\text{SO}_4$  to ensure the stability of the electrolyte. And 3M PVA/ $\text{H}_2\text{SO}_4$  can also reflect the effective improvement of performance and reflect the stability of the capacitor more truly.



**Fig. S6** GCD profiles of (a) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-H<sub>2</sub>SO<sub>4</sub> and (b) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-dried MSCs at different current densities; (c) Areal capacitance versus current density.

## Refences

1. A. Sarycheva, A. Polemi, Y. Liu, K. Dandekar, B. Anasori and Y. Gogotsi, *Sci Adv*, **4**, eaau0920.
2. Y.-Y. Peng, B. Akuzum, N. Kurra, M.-Q. Zhao, M. Alhabeab, B. Anasori, E. C. Kumbur, H. N. Alshareef, M.-D. Ger and Y. Gogotsi, *Energy Environ. Sci.*, 2016, **9**, 2847-2854.