

Self-assembled $Ti_3C_2T_x$ MXene film with high gravimetric capacitance

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Experimental Section

1. Materials

1.1 Porous Ti_3AlC_2 monolith

The porous Ti_3AlC_2 monolith (porosity, ~40%) used in this work was prepared in the authors' laboratory by the solid-liquid reaction synthesis method¹ using elemental powders of Ti (99%, -300 mesh), Al (99%, $D_{50} = 10 \mu m$) and graphite (99%, $D_{90} = 6.5 \mu m$) in a molar ratio of 3:1.1:1.88. Briefly, the powders were mixed for 12 hours with agate balls and absolute alcohol in an agate jar, followed by drying at 70 °C for 8 hours in air. The homogenized mixture was then uniaxially cold pressed into a green compact in a graphite mould. Subsequently, the green compact together with the mould was heated in a furnace up to 1550 °C and hold at that temperature for 2 h in a flowing Ar atmosphere. Finally, the sample was naturally cooled down to room temperature. The prepared porous monolith is phase-pure as determined by X-ray diffraction (XRD) examination.

1.2 Synthesis of $Ti_3C_2T_x$ MXene

A piece of the prepared Ti_3AlC_2 monolith (1 g) was immersed in an aqueous HF solution (10 mL, 6 mol L⁻¹) for 48 h at room temperature. With this treatment, the monolith turned into

particulate-like sediment. The resulting particulates were separated by vacuum filtration with a porous membrane filter (0.22 μm pore size) and washed with deionized water until the pH of the supernatant reached approximately 4.0. The separated wet sediment was immersed in deionized water, after which the mixture was sonicated in a pulse mode for 1 h by using an ultrasonic homogenizer (JY96-IIN, Scientz) to obtain a suspension. The suspension was then centrifuged for 30 min at 2,000 rpm to remove the large particulates. Finally, a black $\text{Ti}_3\text{C}_2\text{T}_x$ MXene colloidal supernatant with a nominal concentration of about 20 g L^{-1} was obtained after decantation.

2. Characterization

The thickness distribution of 1 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ supernatant was evaluated by using an acoustic and electroacoustic spectrometer (DT-1200, Dispersion Technology Inc.). The acoustic spectrometer utilizes a longitudinal ultrasound wave (1–100 MHz) that propagates through a dispersion, measuring raw parameters such as the sound speed and the attenuation coefficients at multiple frequencies, and takes into account certain loss mechanisms (thermal, viscous, scattering, structural, and intrinsic loss)². XRD data were collected on an X-ray diffractometer (D/max-2400, Rigaku) using Cu K_α radiation. Brunauer–Emmett–Teller (BET) specific surface areas were measured with nitrogen as adsorption gas at 77 K on a physisorption analyzer (ASAP 2020, Micromeritics). The film for BET specific surface area measurement was prepared by spreading the suspension on an aluminum foil covered on a hot plate (50 °C). After mild baking, the film was peeled off. Prior to the measurement, the sample was outgassed under vacuum at 150 °C for 4 h. The adsorption isotherms of the samples were analyzed, and the relative pressure P/P_0 values between 0.05 and 0.2 were used to calculate the specific surface area using the BET equation. Microstructural characterization of $\text{Ti}_3\text{C}_2\text{T}_x$ material was conducted by transmission electron microscopy (TEM) on an analytic transmission electron microscope (Tecnai G2 F20, FEI) working at 200 kV. Scanning electron microscopy (SEM) characterization was conducted on a scanning electron microscope (LEO Supra35, Zeiss) with an energy dispersive system (EDS).

3. Density measurement of $Ti_3C_2T_x$ MXene film

As for the density of $Ti_3C_2T_x$ MXene film, it's difficult to measure accurately the area of Ni foam. Alternatively, three films which have comparable thicknesses with the films deposited on nickel foam were prepared by depositing on flat Al foils. Briefly, $Ti_3C_2T_x$ suspension was dropped uniformly on a flat Al foil with a determined area (a circle with a diameter of 0.8 cm) to form a $Ti_3C_2T_x$ MXene film on the foil. The weight and thickness of $Ti_3C_2T_x$ MXene film were determined by weighing and measuring the Al foil before and after film formation, respectively. Then the density was obtained by the weight divided by the volume of the $Ti_3C_2T_x$ MXene film.

4. Fabrication of $Ti_3C_2T_x$ electrodes

Nickel foam (thickness: 1.65 mm, areal pore density: 480 ppi, Heze Tianyu Technology Development Co., LTD, China) was first rolled into 0.32 mm-thick foam sheet and then cut into required size (1 cm \times 1 cm) using scissors, followed by rinsing in alcohol to clean the foam surface. The $Ti_3C_2T_x$ colloidal suspension was loaded dropwise with a pipette on the pretreated nickel foam sheet that was placed on a hot plate kept at 50 °C. To prevent the hot plate surface from contamination, a hydrophobic polytetrafluoroethylene (PTFE) film was placed between the nickel foam and the hot plate. The $Ti_3C_2T_x$ content of the whole electrode can be easily controlled by adjusting the volume of the suspension. Upon mild baking, water in the suspension evaporated and the remaining flakes self-assembled into a coating on the skeleton of the nickel foam. The mass of the $Ti_3C_2T_x$ loaded on the nickel foam was determined by measuring the weight change after the mild baking. The electronic balance (BP 211D, SARTORIUS) used for the weight measurement has a resolution of 0.01 mg.

5. Assembly of two-electrode supercapacitor

Two pieces of the prepared $Ti_3C_2T_x$ /nickel foam composite electrode were assembled face-to-face, between which a porous filter membrane (pore size: 0.22 μ m, thickness: 140 μ m, Shanghai Xinya Purification Device Factory, China) was placed. Note that an insulating room-temperature

curable silicone rubber paste was filled into the pores of the nickel foam to block the acidic electrolyte from diffusing upward (Fig. S7, ESI†). By doing so, the clamps connecting the prepared electrodes and the electrochemical analyzer's electrodes, were effectively prevented from corrosion by the acidic electrolyte.

6. Electrochemical measurements

The electrochemical performance of the $\text{Ti}_3\text{C}_2\text{T}_x$ material was evaluated using a two-electrode test cell at room temperature. The electrolyte was aqueous H_2SO_4 solution ($1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were all performed on an electrochemical workstation (PARSTAT 2273, Princeton Applied Research). The voltage ramp rates ranged from 2 to 100 mV s^{-1} . The gravimetric capacitance was calculated from the CV curves according to $C_g = 4 (\int i dV) / (vMV)$, where i is the current, v the voltage scan rate, M the total mass of $\text{Ti}_3\text{C}_2\text{T}_x$ in both electrodes, and V the voltage window. EIS spectra were recorded from 10 mHz to f 200 kHz at 0 V with an amplitude of 10 mV. Galvanostatic cycling tests were performed using a cycler (BT2013S, Rambts) at 1, 5 and 10 A g^{-1} with a voltage window of 0 to 0.35 V.

References

1. X. H. Wang and Y. C. Zhou, *J. Maters. Chem.*, 2002, **12**, 455.
2. A. S. Dukhin and P. J. Goetz, *Characterization of Liquids, Nano- and Microparticulates, and Porous Bodies using Ultrasound*, Elsevier, Amsterdam, 2010.

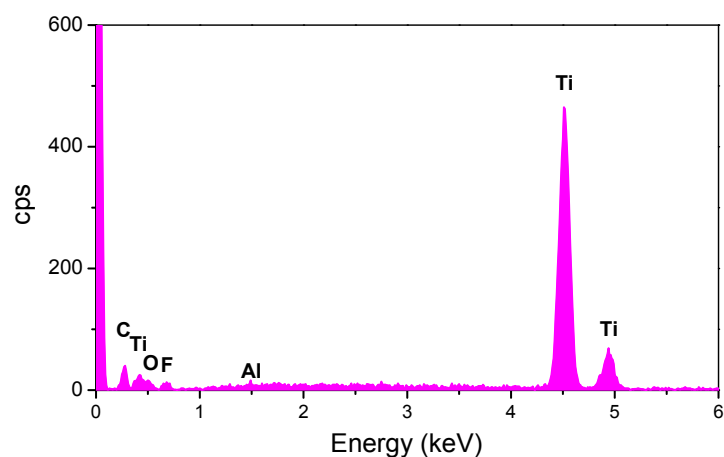


Fig. S1 EDS spectrum of the as-prepared $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Atomic percentage of C, O, F, Al and Ti is 31.28, 13.38, 10.02, 0.39 and 44.93, respectively.

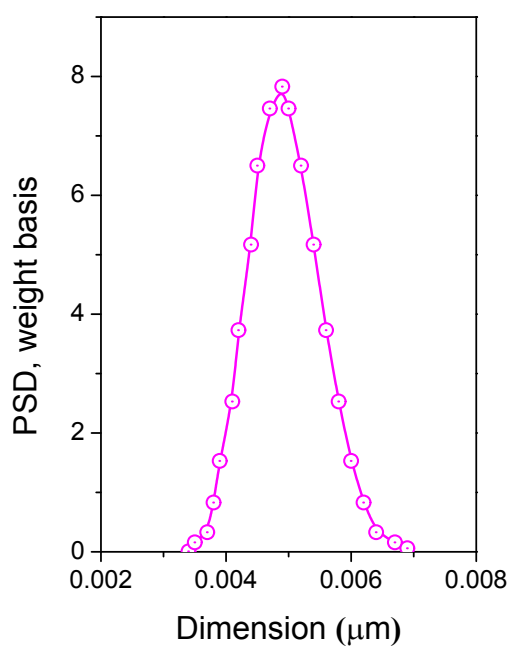


Fig. S2 Particle size distribution profile of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes. The dimension that substantially focused on ~ 5 nm relates to the thickness of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, considering that the width of the flakes is much larger than 5 nm (see Fig.1d). 5 nm represents that the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes statistically consist of five $\text{Ti}_3\text{C}_2\text{T}_x$ unit sheets.

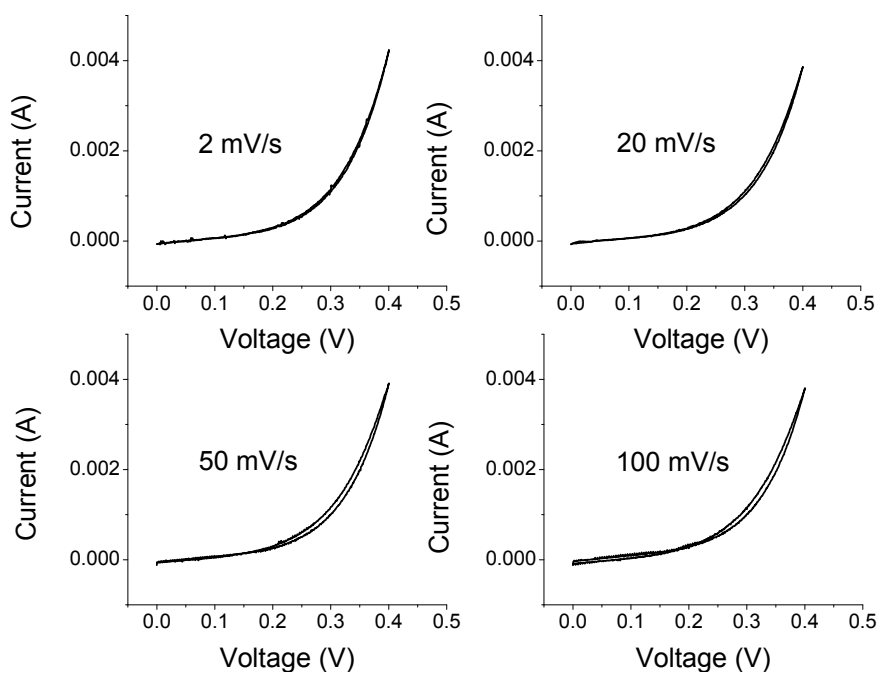


Fig. S3 CV curves of bare nickel foam at various scanning rates, showing the negligible capacitance.

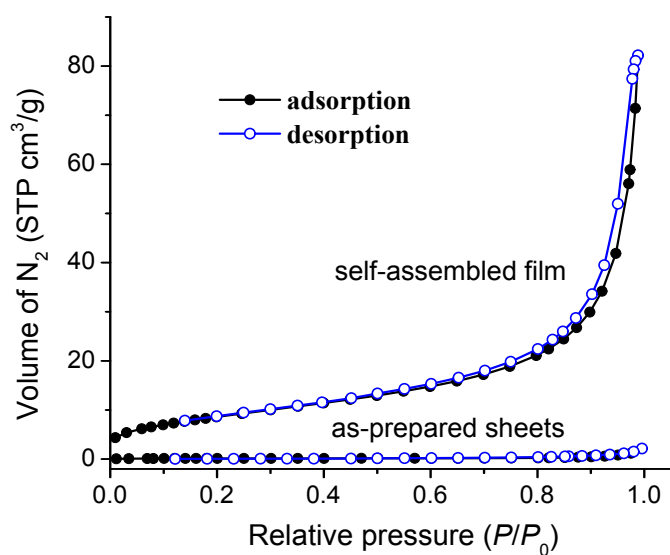


Fig. S4 Nitrogen adsorption/desorption isotherms of as-prepared $\text{Ti}_3\text{C}_2\text{T}_x$ sheets and self-assembled $\text{Ti}_3\text{C}_2\text{T}_x$ film. The BET specific surface areas of as-prepared sheets and self-assembled film are 0.5 and $32 \text{ m}^2 \text{ g}^{-1}$ respectively.

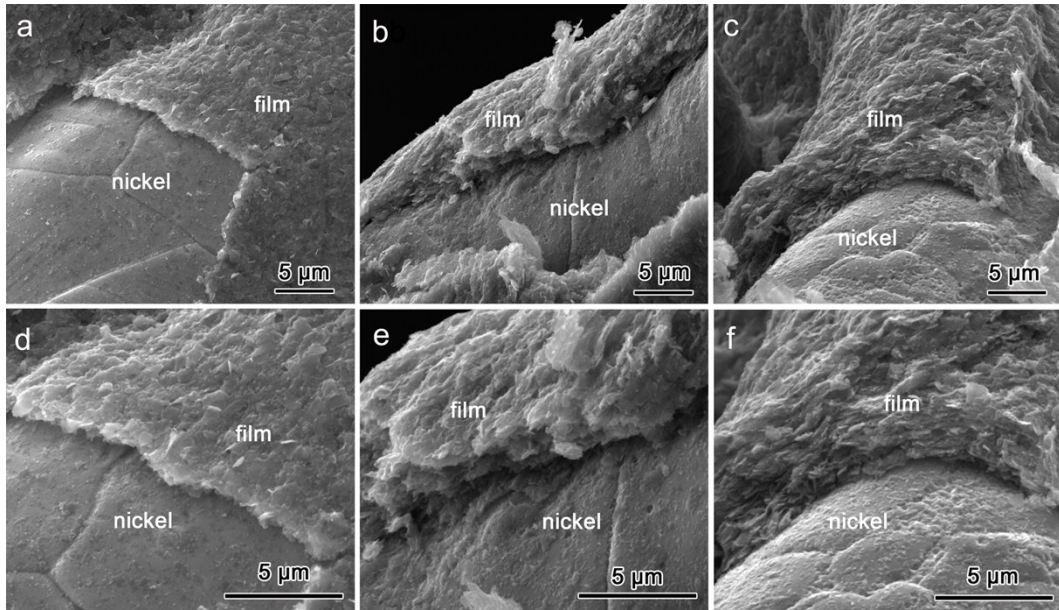


Fig. S5 SEM images of the cross sections of $Ti_3C_2T_x$ -coated nickel foam. (a) and (d) 1.1 mg, (b) and (e) 3.0 mg, (c) and (f) 5.0 mg. Note that the $Ti_3C_2T_x$ film is adhered to the nickel substrate even at the corner where the curvature is large. In addition, the film thickness uniformity is good.

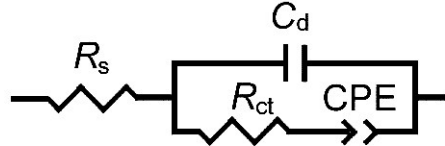


Fig. S6 Equivalent circuit adopted in the simulation of EIS spectra. R_s : electrolyte resistance; C_d : electrical double layer capacitor; R_{ct} : charge transfer resistance; CPE: constant phase angle element.

Table S1 Simulation results of the EIS spectra in Fig.3c

Element	1.1 mg		3.0 mg		5.0 mg	
	Values	Error/%	Values	Error/%	Values	Error/%
R_s /ohm	0.2512	0.8697	0.2739	1.265	0.2754	1.484
C_d /F	0.0466	8.29	0.05187	8.727	0.06112	9.409
R_{ct} /ohm	0.1259	8.205	0.1848	6.038	0.2083	6.537
CPE-T	0.1633	2.393	0.4501	1.574	0.6382	1.894
CPE-P	0.9166	0.4163	0.8783	0.7521	0.8518	1.03

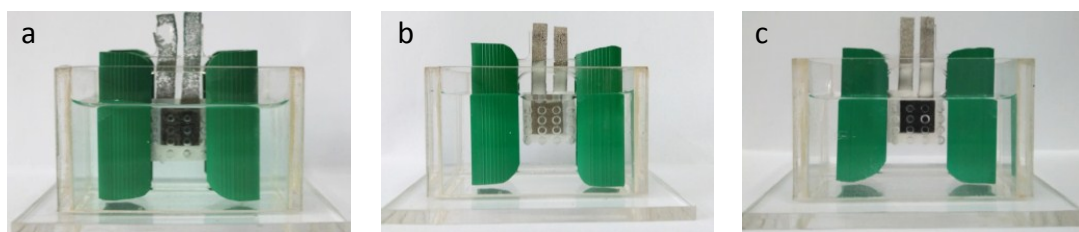


Fig. S7 Photographs of two-electrode cells showing the effect of oxygen (or air) on the corrosion of nickel foam in H_2SO_4 solution. (a) Nickel foam exposed directly to air without rubber filling. (b) and (c) Nickel foam with rubber filling to prevent the acid electrolyte from diffusing upward. Due to the porous nature of the nickel foam, the capillary effect gave rise to diffusing upward of the acid electrolyte which caused the serious corrosion of the foam exposed directly to air (see Fig.S7a). In contrast to the exposed part, the part immersion in the electrolyte survived. With filling of a room temperature curable silicone rubber in the pores of the foil, the electrolyte was blocked from diffusing upward. As a result, the part exposed directly to air was prevented from corrosion (see Fig.S7b-c).