

Supplementary information

## Sulfur atom doped three-dimensional porous MXene assisted efficient sodium ion batteries

Linlin Zhang<sup>a,b,†</sup>, Yiguang Chen<sup>b,†</sup>, Lianghao Yu<sup>b\*</sup>, Xin Tao<sup>c</sup>, Lan Tang<sup>a,b</sup>, Liangzheng Ye<sup>b</sup>, Yu Liu<sup>b</sup>, Lu Han<sup>b</sup>, Hengzheng Li<sup>b</sup>, Yihan Ling<sup>d\*</sup>, Guang Zhu<sup>b\*</sup>, Huile Jin<sup>c</sup>

<sup>a</sup> School of Mechanics and Optoelectronic Physics, Anhui University of Science and Technology, Huainan 232001, China

<sup>b</sup> Key Laboratory of Spin Electron and Nanomaterials of Anhui Higher Education Institutes, School of Mechanical and Electronic Engineering, Suzhou University, Suzhou 234000, China

<sup>c</sup> Key Laboratory of Leather of Zhejiang Province, College of Chemistry and Materials Engineering, College of Chemistry & Materials Engineering, Wenzhou University, Wenzhou 325035, China

<sup>d</sup> School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, China

\* Corresponding authors.

E-mail address: lhyu@ahszu.edu.cn; lyhyy@cumt.edu.cn; guangzhu@ahszu.edu.cn.

† These authors contributed equally to this work.

### 1 Experimental

#### 1.1 Preparation of delaminated $Ti_3C_2T_x$ MXene suspension:

The  $Ti_3C_2T_x$  MXene was synthesized through a series of steps involving the etching of  $Ti_3AlC_2$  using LiF and HCl. Firstly, a reaction kettle was used to combine 17.5 mL of hydrochloric acid, 2.5 mL of deionized water, and 1g of LiF. The mixture was then heated to 35°C and rotated at 400 rpm for 30 minutes. Subsequently, 1 g of less MAX was slowly added to the solution, and the etching reaction was allowed to proceed for 24 hours. Afterward, the mixture was centrifuged to achieve neutralization, followed by the passage of argon gas for 5 minutes. To further process the sample, ultrasonication was performed for 2 hours, and the upper suspension was collected through a 1 hour centrifugation. Finally, the collected solution was stored in an inert gas environment to maintain its stability.

## **1.2 Preparation of SPM:**

Take 3.2 g of sodium thiosulfate in 32 mL of deionized water and add 5.48 mg of polyvinylpyrrolidone (PVP) for stirring. Prepare a dilution of hydrochloric acid by mixing 1.25 mL of hydrochloric acid with 3.75 mL of water. Then, slowly add the prepared hydrochloric acid solution drop by drop to the previous mixture and allow it to react for half an hour.

After the reaction, neutralize the mixture to a neutral pH using NaOH solution while continuously measuring the pH value. Once neutralized, prepare the MXene solution and dilute it to 50 mL. Create three different proportions of solutions by varying the amount of MXene added. Sonicate the solutions for 10 minutes and then slowly add the MXene solution drop by drop to the stirred sulfur ball solution. Following a 30-minute reaction time, the mixture is briefly left undisturbed and subsequently centrifuged at 6000 rpm for 5 minutes. The resulting sample undergoes three consecutive rounds of centrifugation before undergoing a freeze-drying process lasting 48 hours. Finally, the sample is annealed by gradually heating it to 300°C at a rate of 5°C per minute for a duration of 3 hours, thereby completing the preparation process.

## **1.3 Preparation of Na-PM:**

The colloidal suspension was mixed with a 2 M NaOH solution at room temperature, leading to the rapid flocculation of MXene nanosheets. The resulting flocculated precipitate was separated from the solution using centrifugal separation. Subsequently, it was washed with water until neutral, without vigorous shaking. Finally, the material was dried using a freeze dryer and named Na-PM.

## **1.4 Material Characterization:**

The composition and crystal structure of the sample were analyzed using X-ray diffraction (XRD, Bruker D8 Advance with Cu K $\alpha$  radioactive source, Karlsruhe, Germany). The XRD measurements were conducted in an angle

range of 3° to 80°. The morphology and microstructure of the prepared samples were examined using scanning electron microscopy (SEM, Nova Nanosem 200 system, 10 kV FEI, Hillsboro, USA.). For a more detailed examination of the surface morphology, transmission electron microscopy (TEM, JEOL-2100, accelerating voltage 200 keV, GeoLu (Beijing) Science and Technology Co., Ltd., Beijing, China) was utilized. To determine the surface composition, monochromatic X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, Kratos, Manchester, UK) was employed. The XPS measurements were conducted with 22.4 W Al K $\alpha$  radiation (1486.7 eV). The acquired XPS data were processed using XPS Peak software. The pyrolysis behavior of the material under argon atmosphere of 50°C-500 °C was studied by using a NETZSCH thermogravimetric analyzer (STA 409 PC/4/H Luxx). Raman spectroscopy was carried out using a Horiba Jobin Yvon 800 Raman spectrometer (Kyoto, Japan, 10 mW, diffraction grating 600/1800 mm, wavelength LASER excitation equal to 532 nm). The nitrogen adsorption/desorption isotherms were measured using a physisorption instrument, specifically the Micrometrics ASAP 2020 from Micromeritics Instrument Corporation in Norcross, GA, USA. The specific surface area was analyzed using the Brunauer-Emmett-Teller (BET) method within the P/P<sub>0</sub> range of 0.05–0.3. Additionally, the pore distribution was determined using the density flooding theory (DFT) method, which utilizes the N<sub>2</sub>-DFT model.

### **1.5 Electrochemical measurements:**

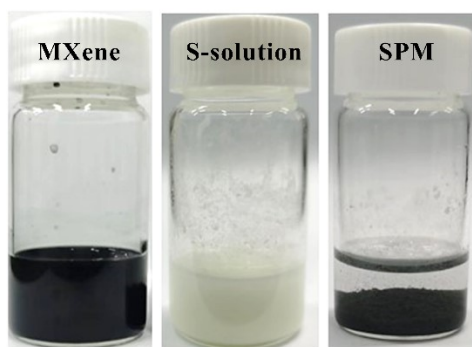
To investigate the sodium storage performance, three-dimensional porous Mxene, pleated MXene, and stacked MXene were directly used as anodes for sodium-ion batteries. The working electrodes were prepared by mixing 70 wt% of the active material, 20 wt% Super P (conductive agent), and 10 wt% polyvinylidene fluoride (binder) soluble in N, N methylpyrrolidone (NMP) to form a homogeneous slurry. This slurry was then coated onto copper foil. The working electrode was dried at 80°C under vacuum overnight and cut into 12

mm round pole pieces.

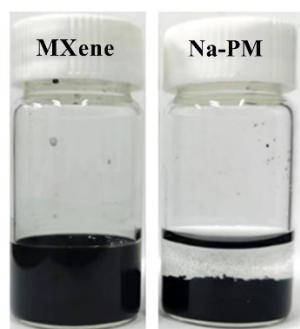
In a glove box filled with argon gas ( $\text{H}_2\text{O} < 0.1$  ppm,  $\text{O}_2 < 0.1$  ppm), a half-cell CR-2025 coin cell was assembled. The prepared anode served as the working electrode, while a sodium sheet with a diameter of 13 mm, made by rolling a sodium block and using a punching device, was used as the counter electrode. A glass microfiber filter acted as the separator. The electrolyte used was 1.0 M  $\text{NaPF}_6$  in DME = 100 Vol%. Cyclic voltammetry (CV) measurements were conducted at a scan rate of  $0.1 \text{ mV s}^{-1}$  within the voltage range of 0.01-3.0 V vs Na/Na<sup>+</sup>. Electrochemical impedance spectroscopy (EIS) was performed from 0.01 Hz to 100 kHz with the bias voltage set to the open-circuit voltage and an AC amplitude of 5 mV using the same electrochemical workstation (CHI760E, Shanghai Chenhua Instruments Co.). Constant current charge/discharge tests were carried out at room temperature over the potential range of 0.01-3.0 V (vs Na/Na<sup>+</sup>) using the CT-4008-5V6A Sunway battery system from Shenzhen Neware Technology Co.

For in-situ XRD cells, the working electrode consisted of an active material, the counter electrode was a sodium sheet, and a beryllium window served as an X-ray window. The in-situ battery assembly took place in a glove box filled with argon gas ( $\text{H}_2\text{O} < 0.1$  ppm,  $\text{O}_2 < 0.1$  ppm). After standing for 10 hours, the assembled in-situ battery was placed in an XRD test equipment, and an external electrochemical workstation (CHI760E, Shanghai Chenhua Instrument Co., Ltd.) was connected for constant current charge and discharge (GCD) tests. The GCD test was conducted at room temperature with a current density of  $0.05 \text{ A g}^{-1}$  and a voltage range of 0.01-3.0 V. The XRD angle test range was set to  $3^\circ \leq 2\theta \leq 45^\circ$ . The XRD test continued until the GCD test was completed after configuring the test parameters.

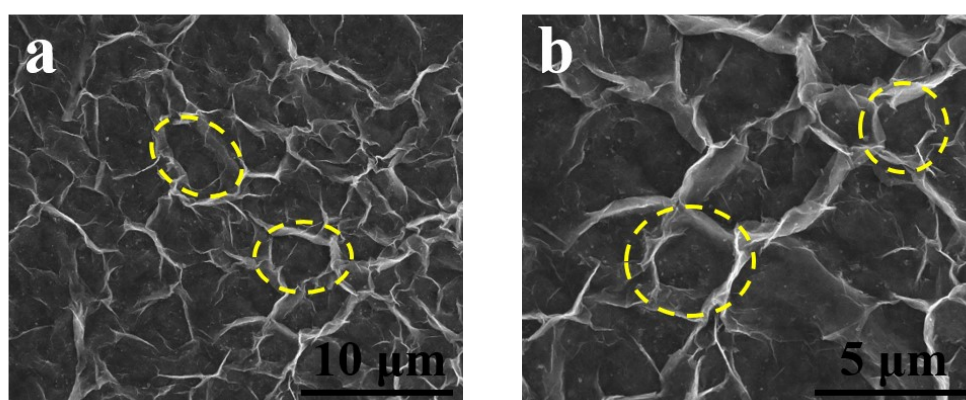
## 2. Supporting figures



**Fig. S1** Digital photo of the  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene colloidal suspensions (left), Sulfur sphere solution with white color (middle) and flocculation SPM solution (right).



**Fig. S2** Photographs of  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene colloidal suspensions (left), and Na-PM after flocculation (right).



**Fig. S3** SEM image of the Na-PM.

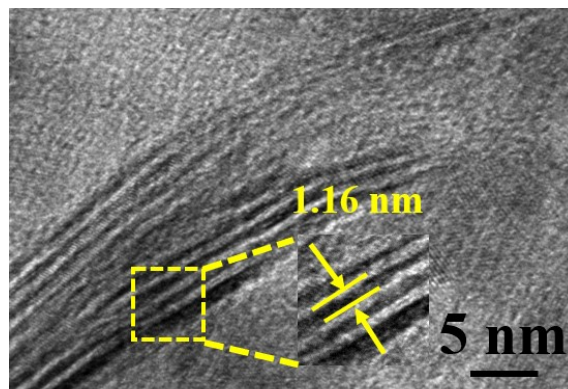


Fig. S4 HRTEM image of MXene.

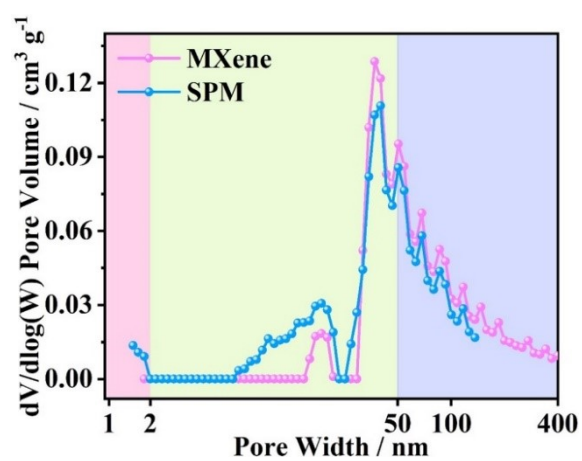


Fig. S5 Pore size distribution of pure MXene and SPM.

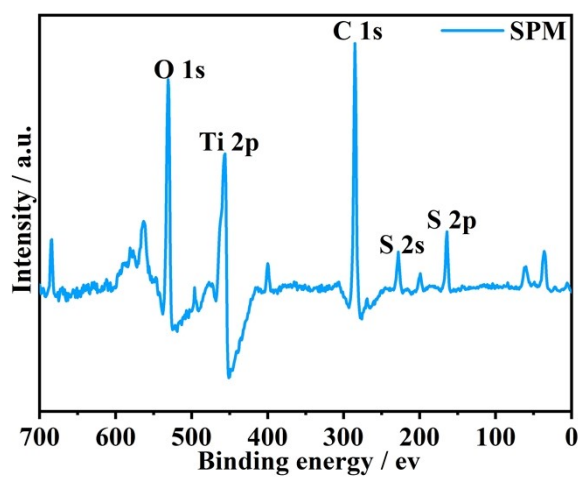


Fig. S6 XPS spectra of SPM.

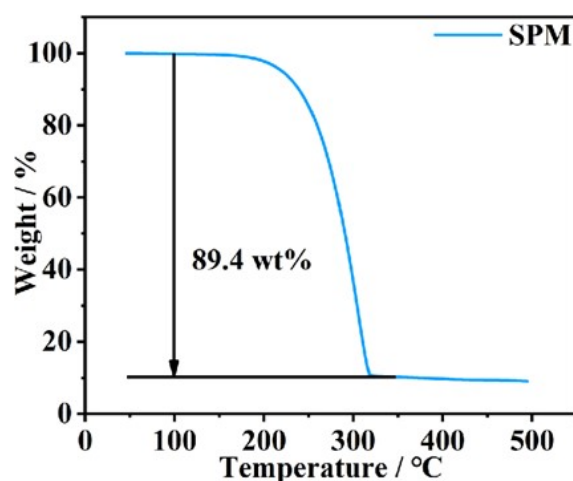


Fig. S7 TGA curves of SPM.

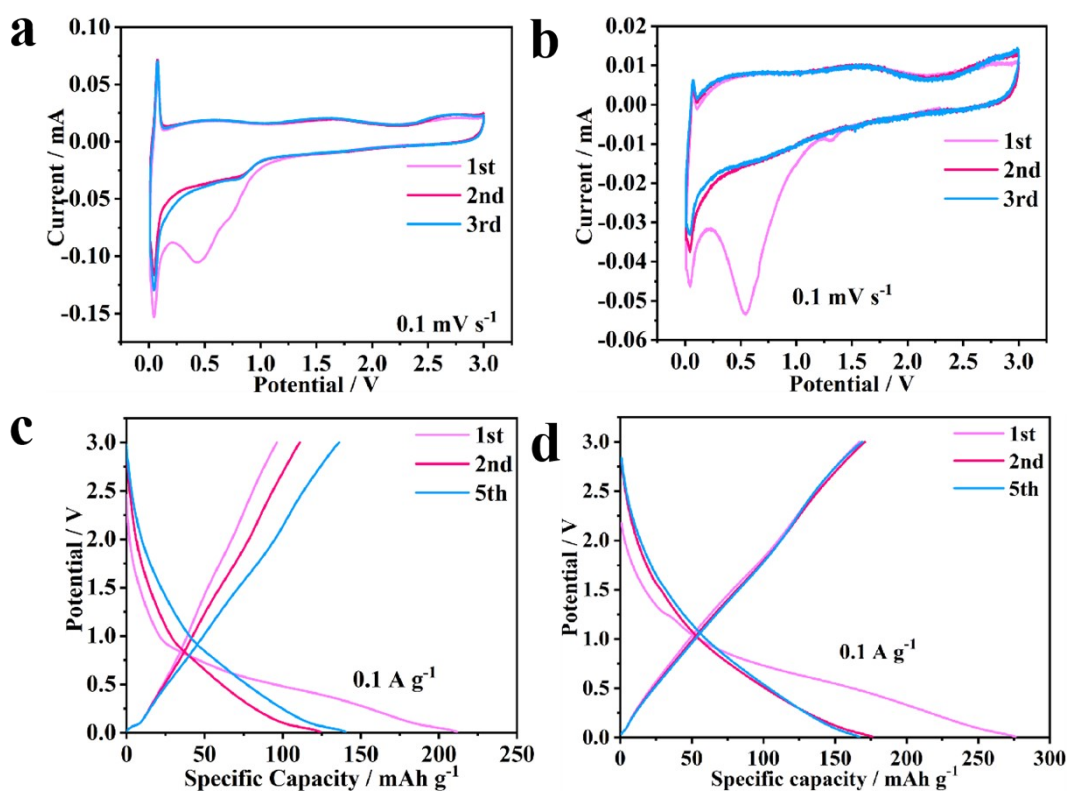
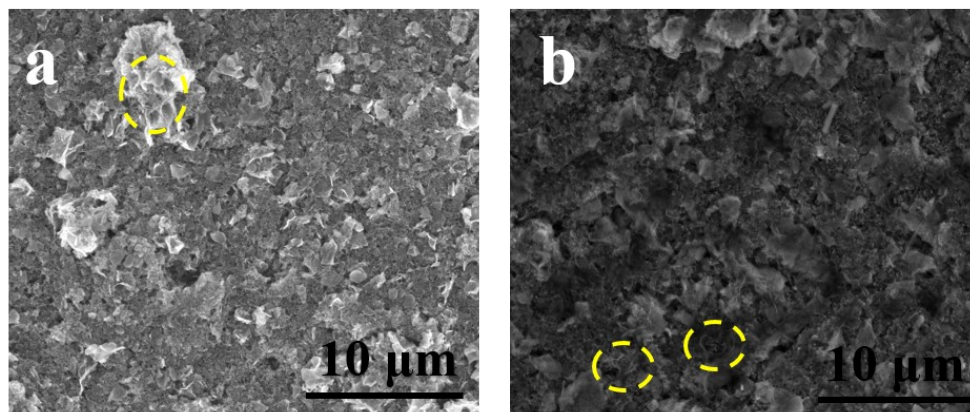
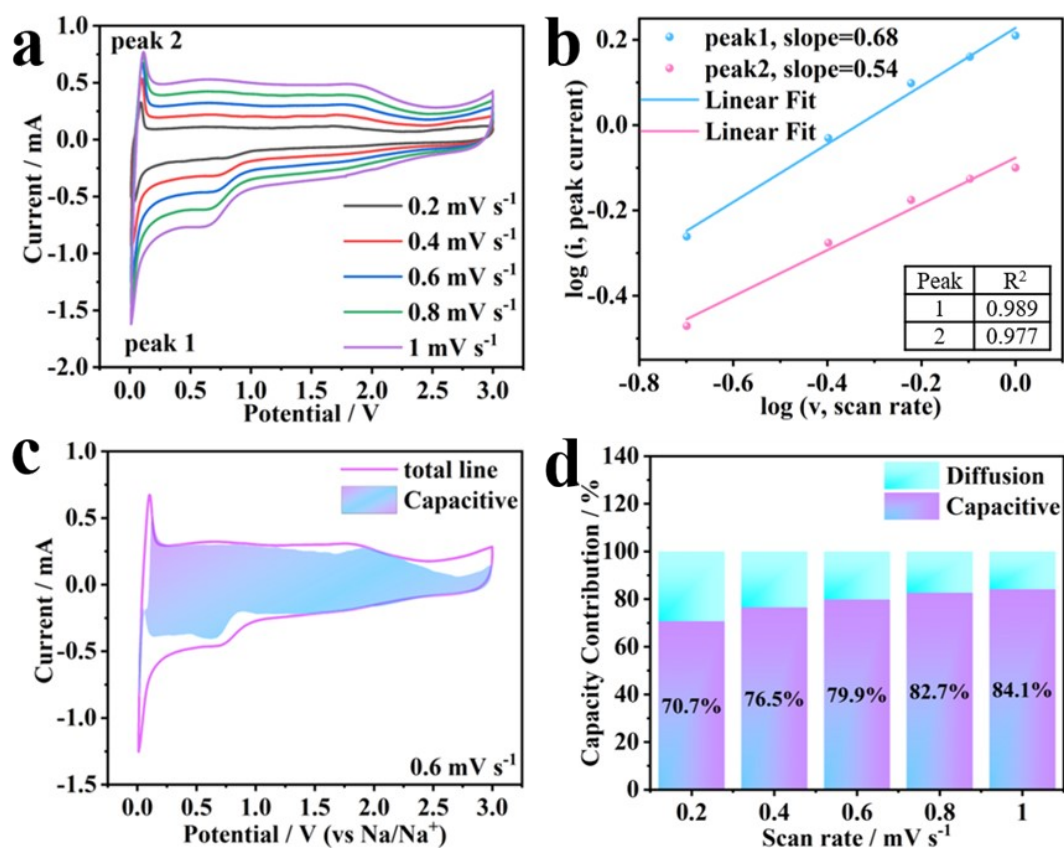


Fig. S8 CV curves of a) pure MXene and b) Na-PM at  $0.1 \text{ mV s}^{-1}$  in a potential window of 0.01-3 V; c) charge-discharge curves of pure MXene and d) Na-PM at a current density of  $0.1 \text{ A g}^{-1}$ .



**Fig. S9** SEM images of SPM electrode a) before cycle and b) after 400 cycles at 5 A  $\text{g}^{-1}$ .



**Fig. S10** The MXene electrode (a) CV curve at different scan rates, (b) plot of logarithmic peak current and logarithmic scan rate, (c) pseudocapacitance contribution at a scan rate of  $0.6 \text{ mV s}^{-1}$ , and (d) capacitance contribution at different scan rates.



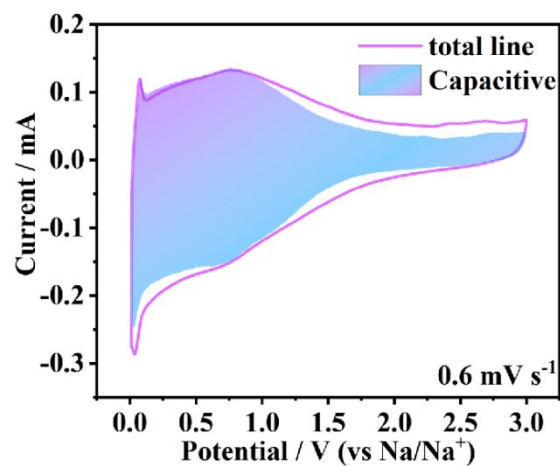


Fig. S11 CV profile at  $0.6 \text{ mV s}^{-1}$  with shaded portion showing the capacitive contribution.

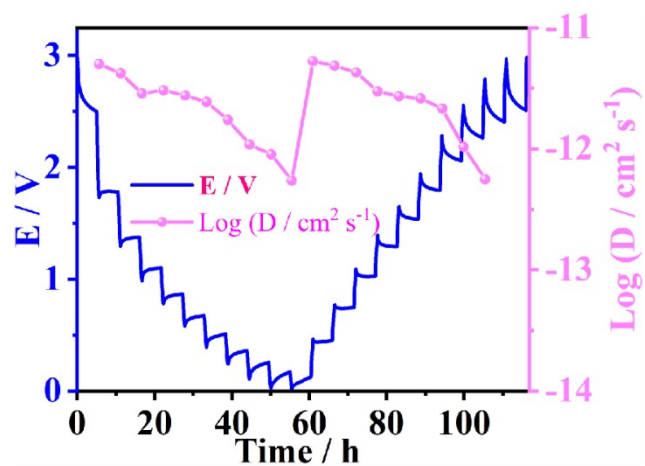


Fig. S12 GITT potential and Na<sup>+</sup> diffusion coefficients profile of the Na-PM electrodes.

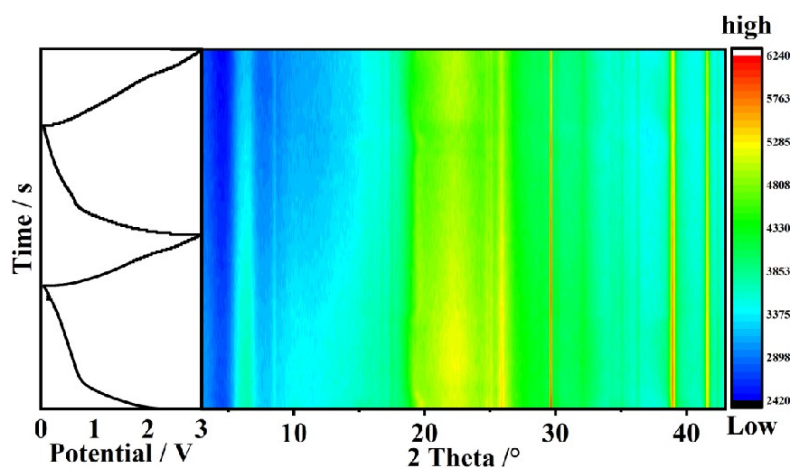


Fig. S13 In situ XRD data of MXene.