Supporting Information

Single-Entity $Ti_3C_2T_x$ MXene Electro-oxidation

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Section 1: Experimental Section

(a) Chemicals

Titanium aluminum carbide (Ti_3AlC_2, 98%, 200 mesh) powders were purchased from Beijing HWRK Chem Co., Ltd. Hydrofluoric acid (HF, AR, 40%) was obtained from Shanghai Macklin Biochemical Co., Ltd. Sulphuric acid (H_2SO_4), were purchased from Sigma-Aldrich, Dorset, UK. All solutions were prepared with ultrapure water from Millipore, with a resistivity of 18.2 MΩcm at 298 K.

(b) Synthesis of $Ti_3C_2T_x$

$Ti_3C_2T_x$ was prepared by using a typical selective etching method. Specifically, 2 g Ti_3AlC_2 powders were added into 60 ml HF and stirred for 24 h at 60 °C. The etched powders were then centrifuged at 3500 rpm for 30 min and washed repeatedly with deionized water until a pH of approximately 7, followed by drying in the oven under vacuum at 80 °C for 12 h to obtain the delaminated $Ti_3C_2T_x$.

(c) MXene characterization

The scanning electron microscopy (SEM) images were obtained using a Zeiss Sigma 300 FEG-SEM with an accelerating voltage of 2.0 kV. The MXene dispersion from Sample A and Sample B was drop-casted (5 µl) onto a cleaned glassy carbon stub. The stub containing the drop-cast samples was dried overnight before the SEM imaging. The particle sizing was performed in ImageJ freeware. X-ray photoelectron spectroscopy studies were carried out in a Thermo Scientific NEXSA (Thermo Fisher) spectrometer equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) operating at 15 kV, under a vacuum of $\sim 5 \times 10^{-9}$ mbar. The survey and high-resolution spectra were collected at fixed analyzer pass energies and the spectral de convolution was done using CASA XPS software. Raman spectra were recorded using a Renishaw Raman microscope with LEICA CTR6000 setup with 633 nm laser, 1200 lines mm^{-1} grating at 10% laser power and a 50X objective. Spectra were acquired with a dwell time of 60 s with 2 accumulations.

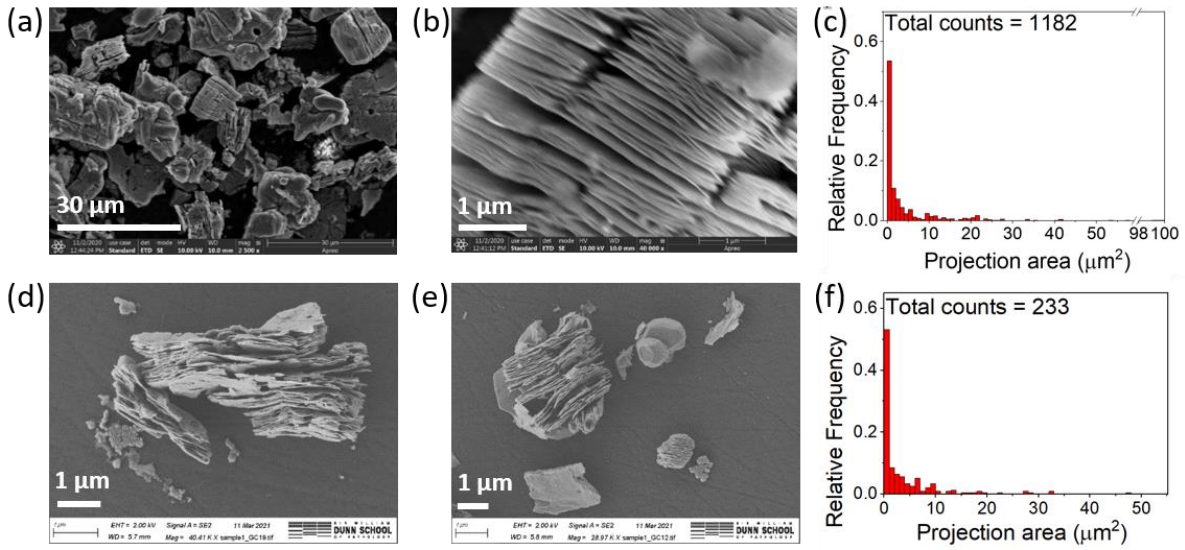


Fig. S1 Field emission scanning electron microscopy (FESEM) images and size distribution plot for as-prepared $Ti_3C_2T_x$ MXene particles (a-c) and Sample B MXene particles (d-f).

Section 2: Preparation of stable MXene dispersions

A sedimentation-based separation technique under a centrifugal field was adopted to prepare a stable suspension of $Ti_3C_2T_x$ MXene. A calculated amount (for 0.5 mg/ml dispersion) of $Ti_3C_2T_x$ MXene powder was dispersed in DI water by ultrasonication (power 80 W, frequency 50/60 Hz) for five minutes (Fig. S2 a, b). The dispersion was allowed to stand for five more minutes to settle the larger particles (Fig. S2c). The supernatant dispersion was then collected in a centrifuge tube and centrifuged at 4000 rpm for five minutes (Fig. S2d, e). As observed,

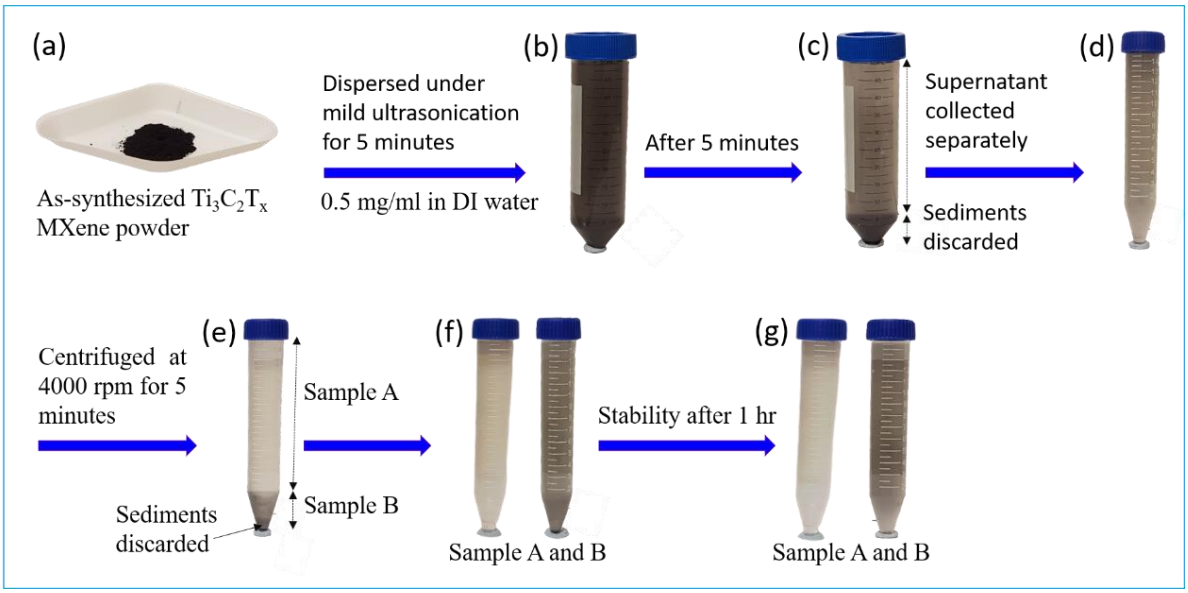


Fig. S2 Schematic representation of the synthesis root for preparing stable MXene dispersion

the particles are divided into visibly three bands in the centrifuge tube. The upper supernatant dispersion was collected and named Sample A. The middle band was collected and named Sample B and the third band containing the sedimented particles was discarded. As depicted in Fig. S2 f,g, the $Ti_3C_2T_x$ MXene particles dispersion sample A and B are seen to be stable over an hour.

Section 3: Calculation of MXene concentrations

The concentration of $Ti_3C_2T_x$ MXene particles in the dispersion of samples A and B are calculated by vacuum filtration. In a typical step, a calculated amount of the dispersion (in ml) was filtrated over a membrane filter paper (pore size 0.22 μm) and was allowed to dry at 60 ºC overnight. The weight of the material was calculated by weighing the filter paper before and after filtration using Sartorius QUINTIX 35-1S Analytical Balance, which can precisely measure from 10 μg to 30 g. The concentration was determined to be 23 μg/ml and 103 μg/ml for Sample A and Sample B respectively.

Section 4: Electrochemical Apparatus and Method

(a) Drop-cast measurements

The electrochemical experiments were performed with a three-electrode system comprising glassy carbon (3mm diameter, ALS, Tokyo, Japan) as working electrode, saturated calomel reference electrode (SCE), and Pt wire counter electrode mounted within a thermostated (25±0.5 ºC) Faraday cage. All the potentials reported in this work were with respect to the SCE unless otherwise specified. The drop-cast electrochemical measurements were performed using a computer-controlled Autolab PGSTAT128N potentiostat (Metrohm Autolab, Utrecht, Netherlands) equipped with GPES software.

Before use, the GCE was polished to a mirror-like finish using alumina slurries in a sequence of decreasing sizes: 1.0, 0.3, and 0.05 μm (from Buehler, Lake Bluff, IL), followed by rinsing and sonicating with DI water to remove the slurry residues. The as-prepared MXene samples were vortexed for about 5 minutes to maintain homogeneity. A calculated aliquot of the suspension was then drop-casted over a previously clean GCE and the solvent was left in the

air to evaporate at room temperature to yield an electrode surface modified with a film of the MXene particles. The modified electrode is denoted $Ti_3C_2T_x$@GCE. Before the electrochemical measurements, the electrolyte was purged with N_2 (98 % purity) to remove the dissolved gases. Cyclic voltammetry was performed over a scan range from -1 to 1.8 V (100 mV/s scan rate) with multiple scans as needed.

(b) Nano-impact measurements

To perform Nano-impact experiments, a home-built low-noise three-electrode potentiostat system equipped with a low-noise current amplifier (LCA-4K-1G, FEMTO Messtechnik GmbH, Germany) and a homemade thermostat system was used. [32] The signal was digitized at 100 KS/s via a USB data acquisition device (USB-6003, National Instruments, Texas, USA), which was filtered digitally by a four-pole Bessel filter to100 Hz. The potentiostat conserves the charge passed during the impact even at a short duration. All the impact measurements were performed in thermostated (25±0.5 ºC) Faraday cage. For measurements, a homemade carbon fiber microelectrode (7 µm diameter and 1 mm length) was used as the WE, SCE as RE, and a Pt wire as CE respectively. Chronoamperometry was performed using $Ti_3C_2T_x$ NPs dispersed in 0.1 M H_2SO_4 at a range of potentials from 0 - 1.3 V. The obtained Nano-impact steps were identified, analyzed and individual step charge was determined using Origin and "Signal Counter" software (developed by Dr. Dario Omanovic, Centre for Marine and Environmental Research, Zagreb, Croatia). [33]

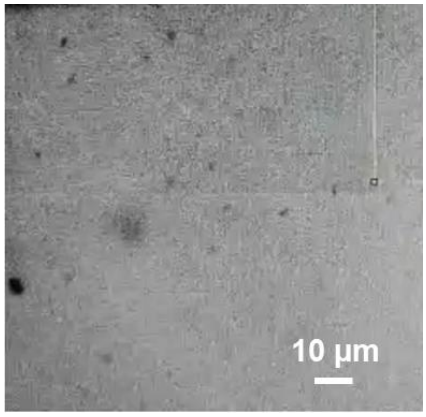


Fig. S3 Image captured through optical microscope showing MXene particles under Brownian motion in solution.

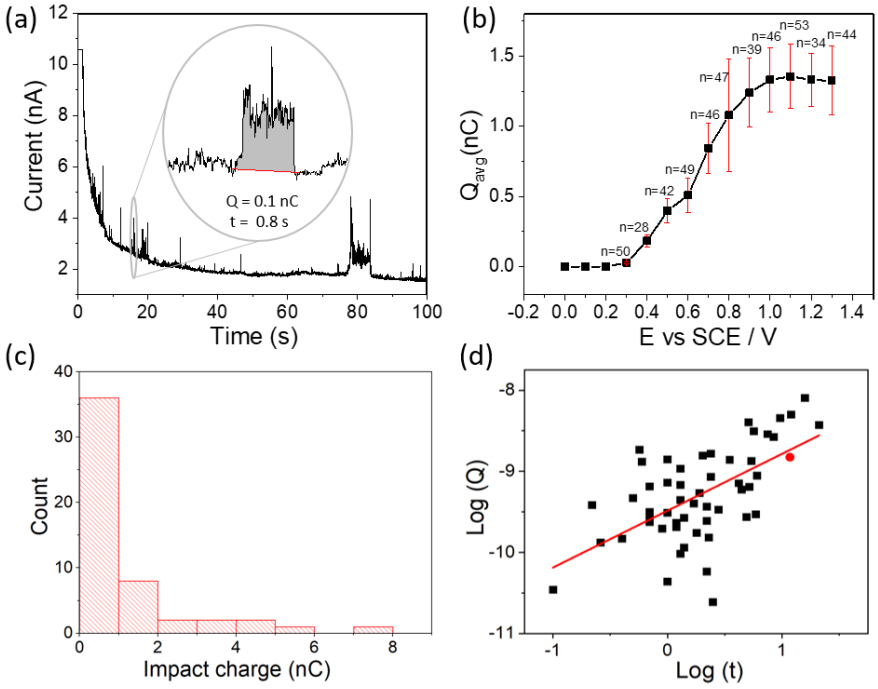


Fig. S4 (a) Chronoamperogram recorded at a carbon fibre micro wire electrode in a 103 mg/ml $Ti_3C_2T_x$ MXene suspension in 0.1 M H_2SO_4 at 1.3 V applied potential vs. SCE, (b) Plot of Q_{avg} as a function of applied potential E; the error bars are derived from $SD/(n)^{1/2}$, where SD is the standard deviation and n is the number of the spikes. (c) Distribution of charge from oxidation of single particles spikes by analysis of 52 current spikes at 1.3 V applied potential vs. SCE, (d) linear fit (red line) of the natural logarithm of individual spike charge (Q) vs. logarithm of time. The red dot indicates the logarithm of average charge per particle vs logarithm of time from the drop-cast.

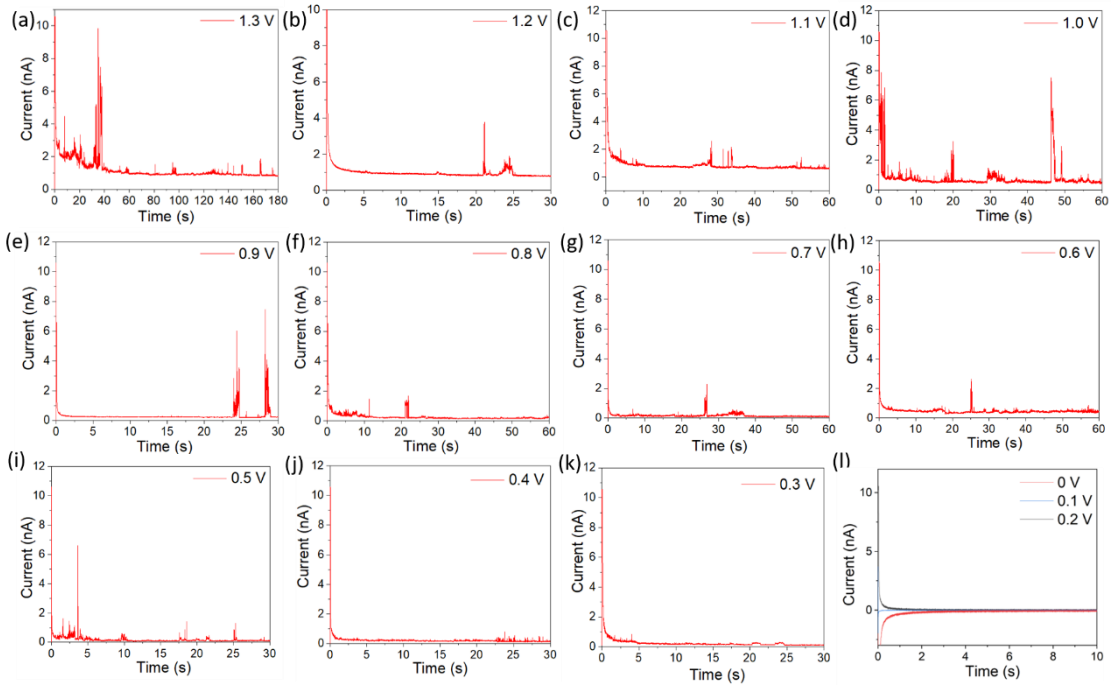


Fig. S5 Chronoamperograms recorded at different electrode potentials (0-1.3 V) for Sample A.

Section 5: Voltammetry results for drop-cast MXene particles

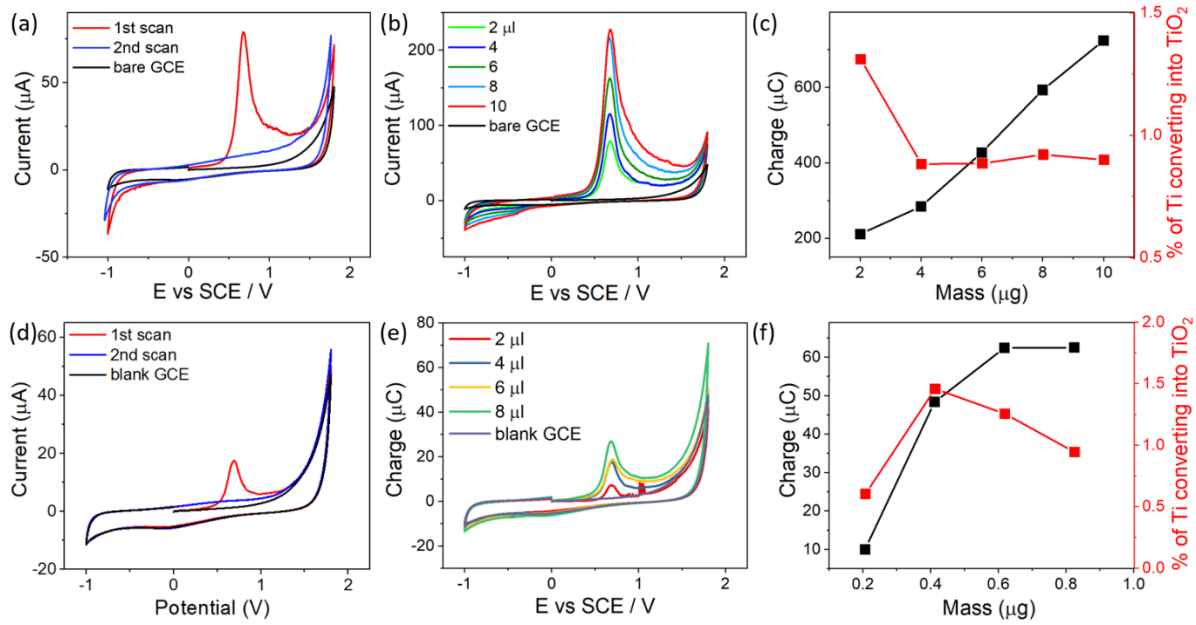


Fig. S6 Voltammograms at GCE modified with as-prepared MXene (a, b) and Sample B (d, e) for repeated scans and for different aliquot of MXene drop-cast. Plot of charge and % of Ti converting into TiO_2 for different aliquots of drop-cast for as-prepared (c) and Sample B MXene. Scan rate 100 mV/s, SCE as RE.

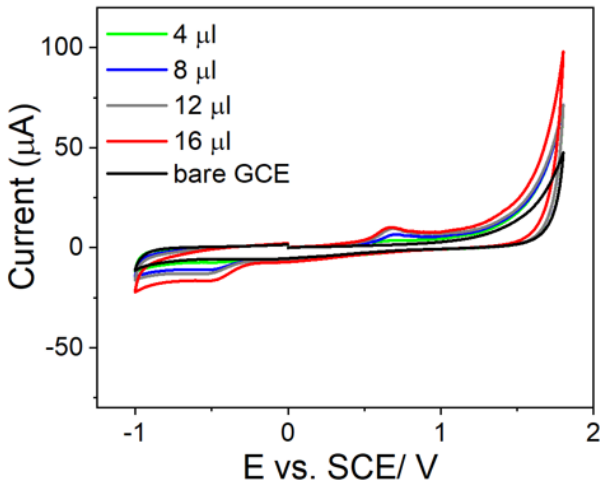


Fig. S7 Voltammograms at GCE modified with Sample A for different aliquot of MXene drop-cast. Scan rate 100 mV/s, SCE as RE.

Section 6: Calculation of average charge per particle from drop-cast

The average projection area for Sample A, Sample b, and as-prepared MXene is calculated from FESEM images and the same are 2.21 μm^2, 3.59 μm^2, and 4 μm^2 respectively.

Converting the average projection area into the area of a side of a cubical layered particle (ca. a Fig. S6) results for Sample A, $a^2 = 2.21\ \mu m^2$

So, the volume of the cube = 3.28 μm^3

Taking density of $Ti_3C_2T_x$ MXene as 2.71 g/cm^3, average mass per particle = 8.9 x 10^{-12} g

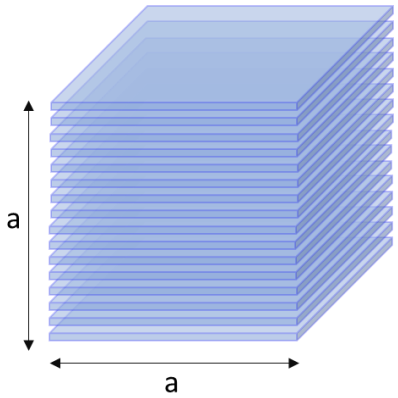


Fig. S8. Schematic model of a layered cubical cell

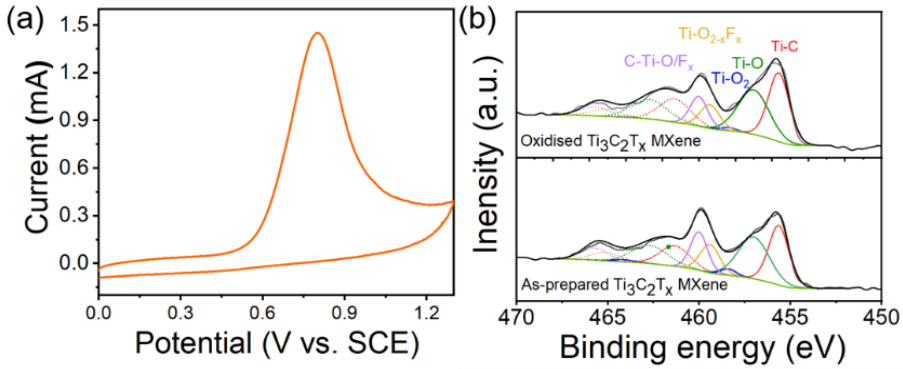
Now, the mass of $Ti_3C_2T_x$ from drop cast (ca. 8 µl of Sample A) = 0.18 µg

The average number of particles in 8 µl = $\frac{0.18\ \mu g}{8.9 \times 10^{-12}\ g} \approx 2$ x 10^4 numbers

Taking the charge under oxidation peak for 8 µl drop-cast and the above-average number of particles in the drop-cast, the average charge per particle

$$= \frac{\text{total charge from CV}}{\text{number of particles}} = \frac{3.10 \times 10^{-12}\ C}{2 \times 10^4\ g} = 1.5 \text{ x } 10^{-9} \text{ C}$$

Similarly, the average charge per single-particle for Sample B and the as-prepared MXene for different aliquots of drop-cast.



(c)

Atomic %	Ti-C	Ti-O	$Ti-O_2$	$Ti-O_{2-x}F_x$	$C-Ti-O/F_x$
Oxidized MXene	37.6	35.93	1.25	13.61	11.6
As-prepared MXene	31.8	34.28	2.63	14.05	17.25

Fig. S9 (a) Voltammogram at as-prepared drop-cast $Ti_3C_2T_x$ MXene in 0.1 M, Scan rate 100 mV/s, SCE as RE. (b) High resolution XPS spectra of Ti 2p for oxidised $Ti_3C_2T_x$ compared with as-prepared $Ti_3C_2T_x$ MXene. (c) Tabulation of atomic % of Ti bonded with C, O, and F.

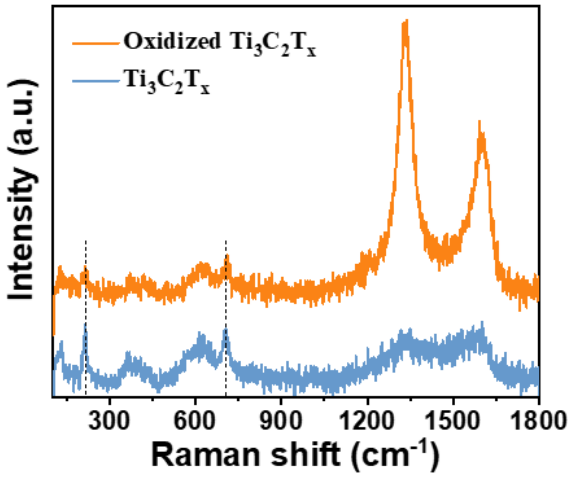


Fig. S10 Raman spectra of oxidised $Ti_3C_2T_x$ compared to as-prepared $Ti_3C_2T_x$.