Template-free 3D titanium carbide ($Ti_3C_2T_x$) MXene particles crumpled by capillary forces

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Supporting Information

Methods & Materials:

All chemicals were used as received.

Synthesis of Ti_3AlC_2 MAX phase

Commercial Ti (44 μm average particle size, 99.5% purity), Al (44 μm average particle size, 99.5% purity) and TiC powders (2 – 3 μm average particle size, 99.5% purity), (all from Alfa Aesar, MA, USA), were used as starting raw materials to synthesize Ti_3AlC_2 MAX phase. To prepare homogeneous powder mixtures, Ti, Al and TiC powders were first weighed to achieve Ti:Al:C=3.0:1.2:1.8 ratio and mixed together using ball-milling with zirconia beads in a glass jar at the speed of 300 rpm for 24 hours. Then, the bulk high-purity Ti_3AlC_2 samples were sintered at temperature of 1510 ^oC for 15 mins with a loading of 50 MPa using Pulsed Electric Current System (PECS)[i]. To fabricate high-purity Ti_3AlC_2 powder, the PECSed sample was first drill-milled and sieved to obtain powder with particle sizes below 44 μm.

Synthesis of $Ti_3C_2T_x$ MXene clay

$Ti_3C_2T_x$ MXene clay was synthesized by etching aluminum from the MAX phase using technique described by Ghidiu et.al.[1] Concentrated hydrochloric acid (HCl, ACS reagent, 37% w/w Sigma-Aldrich) was diluted with DI water to obtain 30 mL of 6 M HCl solution. This solution was transferred to a polypropylene (PP) beaker and 1.98 gm of lithium fluoride (LiF, 98+% purity, Alfa Aesar) was added to it. This dispersion was stirred for 5 minutes using a Teflon (PTFE) magnetic stirrer at room temperature. Ti_3AlC_2 MAX phase powder was slowly added to the HCl+LiF solution to prevent overheating as the reaction is exothermic. The PP beaker was capped to prevent evaporation of water and a hole was made in the cap to avoid buildup of hydrogen gas. The reaction mixture was stirred at 40 ºC for about 45 hours. The slurry product was filtered and washed with deionized (DI) water in a polyvinyl-difluoride (PVDF) filtration unit with pore size of 0.22 μm (Millipore® SCGVU10RE Stericup™ GV) to remove the unreacted HF and water soluble salts. This washing process was repeated until pH of the filtrate reached a value of about 6. Reaction product collected over the PVDF filter is extracted as $Ti_3C_2T_x$ MXene clay.

Intercalation and delamination of $Ti_3C_2T_x$ MXene clay

$Ti_3C_2T_x$ MXene clay was intercalated with dimethyl sulfoxide (DMSO) and eventually bath sonicated to obtain an aqueous dispersion of delaminated $Ti_3C_2T_x$ MXenes following procedure described in more detail by Mashtalir et.al.[2] DMSO (ReagentPlus, >99.5%, Sigma-Aldrich) was added to $Ti_3C_2T_x$ MXene clay (dried in vacuum oven for about 24 hours at 40 ˚C) to form a 60 mg/ml suspension followed by about 18 hours of stirring at room temperature. After intercalation, excess DMSO was removed by several cycles of washing with DI water and centrifugation at 5000 rpm for 4 hours. The intercalated $Ti_3C_2T_x$ MXene clay suspension in DI water was bath sonicated for 1 hour at room temperature followed by centrifugation at 3500 rpm for 1 hour to separate the heavier components.

Crumpling of $Ti_3C_2T_x$ MXene nanosheet dispersion

Crumpling of $Ti_3C_2T_x$ MXene nanosheets was achieved by spray drying delaminated MXene dispersion.[3] Aqueous dispersion of delaminated $Ti_3C_2T_x$ MXene was diluted to a concentration of 1 mg/ml, and processed in Buchi B-290 mini spray dryer, **Figure S1**. The spray drying procedure involved conveying the dispersion using a peristaltic pump to an atomizer where it was mixed with in house air to form micrometer sized droplets. For our experiments, we used a pump flow rate of 10 % (of maximum possible flow rate) and atomizer air pressure of 60 psi. The droplets formed by the atomizer were carried and dried by co-currently flowing hot air in the drying chamber. This airflow was created by an aspirator pump by induced draft mechanism and heating occurred via a heating coil. For our experiments, the highest drying air flow rate was used by operating aspirator at 100% power, and inlet air temperature was maintained at 220 ˚C. Carrier gas loses its heat to droplets causing water to evaporate and the dispersion to dry. The dried particles are eventually collected in a cyclone separator and are stored for further analysis. Above mentioned procedure was also carried out at a starting concentration of 0.1 mg/ml to analyze the effect of concentration on morphology of dried MXenes.

Freeze Drying

Delaminated $Ti_3C_2T_x$ MXene dispersion was frozen in a freezer overnight and freeze dried for roughly 48 hours in Labconco FreeZone benchtop freeze dryer to obtain dry MXene nanosheet powder.

Transmission Electron Microscopy (TEM)

TEM images were obtained using FEI Tecnai G2 F20 field emission transmission electron microscope (FE-TEM). All samples were deposited on 200 mesh holey carbon-coated copper grids of 100 µm (HC200-CU-100, Electron Microscopy Sciences) for imaging. Powdered crumpled $Ti_3C_2T_x$ MXene samples from spray dryer were directly placed on the grid for imaging. Water rehydrated crumpled MXenes were drop casted on the grid followed by air drying for about 5 minutes.

Scanning Electron Microscopy (SEM)

SEM images were obtained using FEI Quanta 600 field emission scanning electron microscope (FE-SEM). For imaging, delaminated native $Ti_3C_2T_x$ MXene samples were prepared by drop casting their dispersion on a silicon wafer. Crumpled MXene samples were prepared by directly placing spray dried powder on carbon tape.

X-Ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed using an Omicron XPS system with Mg x-ray source. Sample preparation for XPS was done by drop casting moistened crumpled $Ti_3C_2T_x$ MXene powder on hydrophilic (oxygen plasma treated) silicon wafer followed by drying in a vacuum oven overnight at 40 °C. Deconvolution was performed using CasaXPS software version 2.3.16.

X-Ray Diffraction (XRD)

Bruker D8 powder X-Ray diffractometer fitted with LynxEye detector, in a Bragg Brentano geometry with CuKα (λ: 1.5418 Å) radiation was used to obtain XRD patterns of powder samples. Freeze dried $Ti_3C_2T_x$ MXene powder was placed on a zero background holder to obtain its XRD pattern. Similarly, crumpled MXene powder was also placed on the same holder to measure its XRD pattern. The X-ray scan was performed with a step size of 0.02º and a scan rate of 1 s per step.

UV-Visible Spectroscopy

Absorbance spectra of $Ti_3C_2T_x$ MXene dispersions were measured using Shimazdu UV-vis spectrophotometer 2550 (Wavelength range: 200 - 800 nm). Samples were placed in a quartz cell with path length of 1 cm, and DI water was used as a blank. Concentrations of MXene dispersions were determined using Beer-Lambert law. The extinction coefficient of MXene dispersions was calculated to be 1167.2 $ml.(mg.m)^{-1}$ at 580 nm. See **Figure S2** for more detail.

Zeta Potential

Malvern Zetasizer ZS90 and the appropriate capillary cell (DTS1070) was used to measure the zeta potential of the stable $Ti_3C_2T_x$ MXene dispersions.

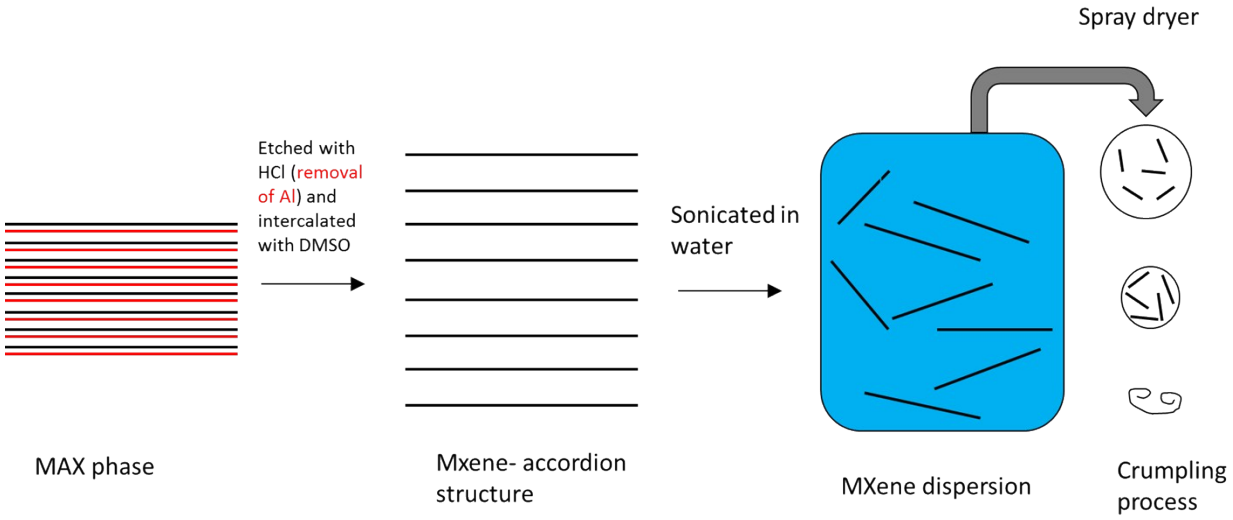

Figure S1. Schematic showing synthesis of $Ti_3C_2T_x$ nanosheets from parent MAX phase to nanosheet crumpling via spray drying. Layered MAX phase (Ti_3AlC_2) is etched using HCl + LiF to obtain $Ti_3C_2T_x$ clay. This clay is intercalated with DMSO and sonicated to obtain delaminated $Ti_3C_2T_x$ nanosheet dispersion. This dispersion is spray dried to obtain crumpled $Ti_3C_2T_x$ nanosheets. The crumpling process on the far right of the figure shows possible crumping mechanism for $Ti_3C_2T_x$ nanosheets.

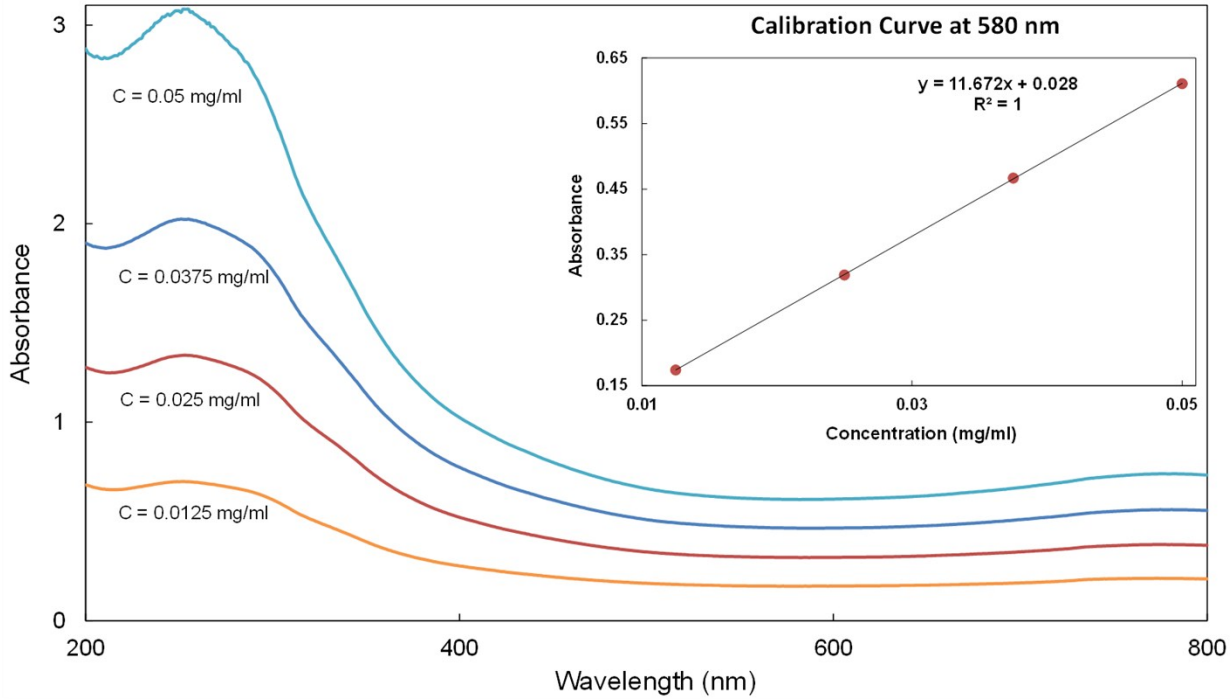

Figure S2. UV-Vis absorbance spectra are shown for $Ti_3C_2T_x$ dispersions at different concentrations (measured using vacuum filtration). Calibration curve (inset) was made

using the absorbance values at 580 nm to measure concentration of subsequent $Ti_3C_2T_x$ dispersions.

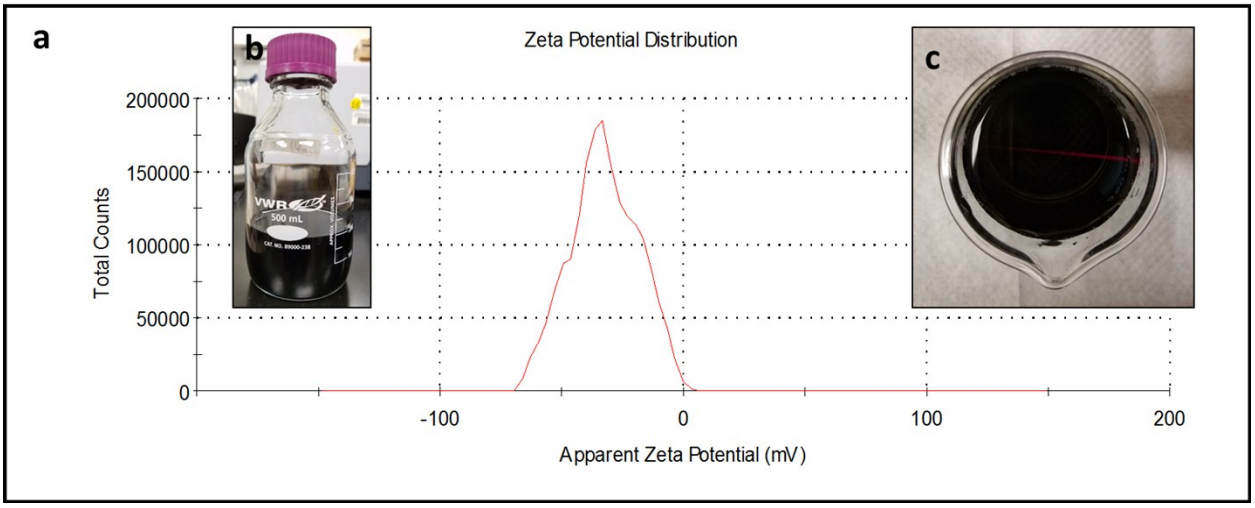

Figure S3. (a) Zeta potential of (b) aqueous $Ti_3C_2T_x$ nanosheet dispersion being stored in glass container shows its colloidal stability. (c) Colloidal nature of the dispersion can be verified by Tyndall effect (laser being scattered by dispersed MXene nanosheets).

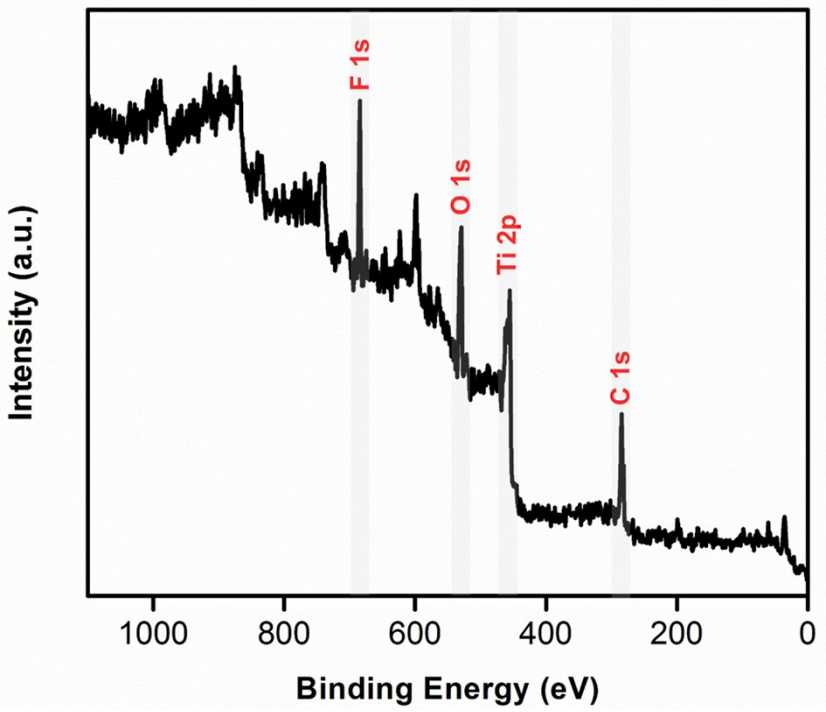

Figure S4. XPS spectrum of crumpled $Ti_3C_2T_x$ MXenes labelled with characteristic peaks of Ti, C, O and F.

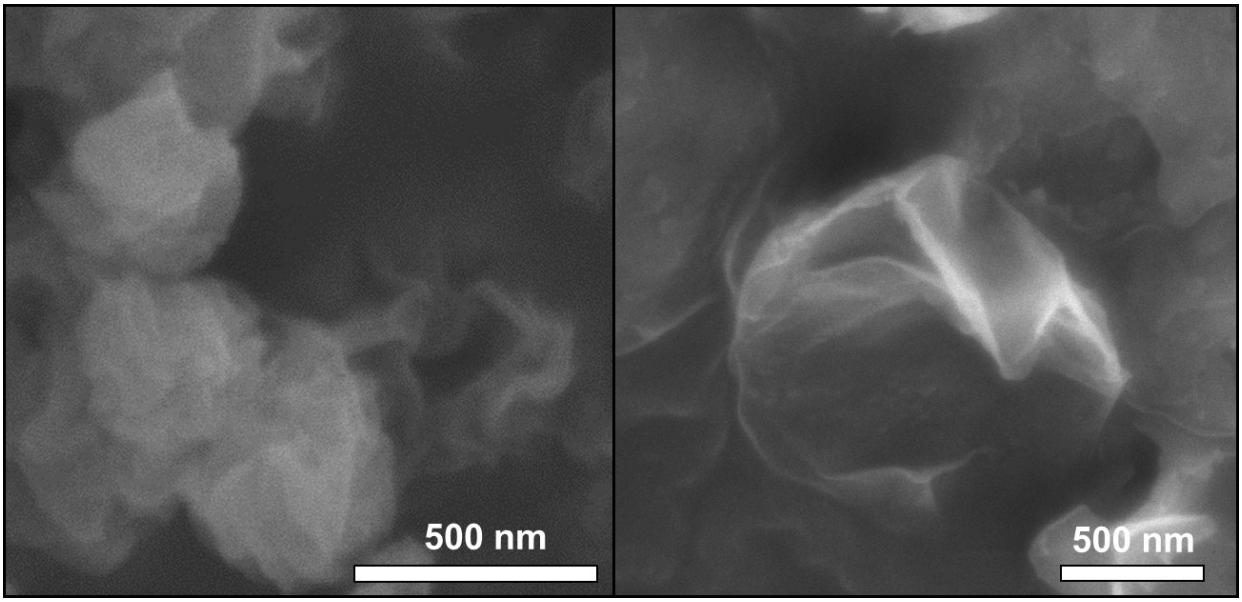

Figure S5. SEM/TEM images of (a) crumpled GO and (b) crumpled $Ti_3C_2T_x$. Crumpled GO shows significant amount of ridges whereas crumpled $Ti_3C_2T_x$ shows folds with relatively larger local radius of curvature.

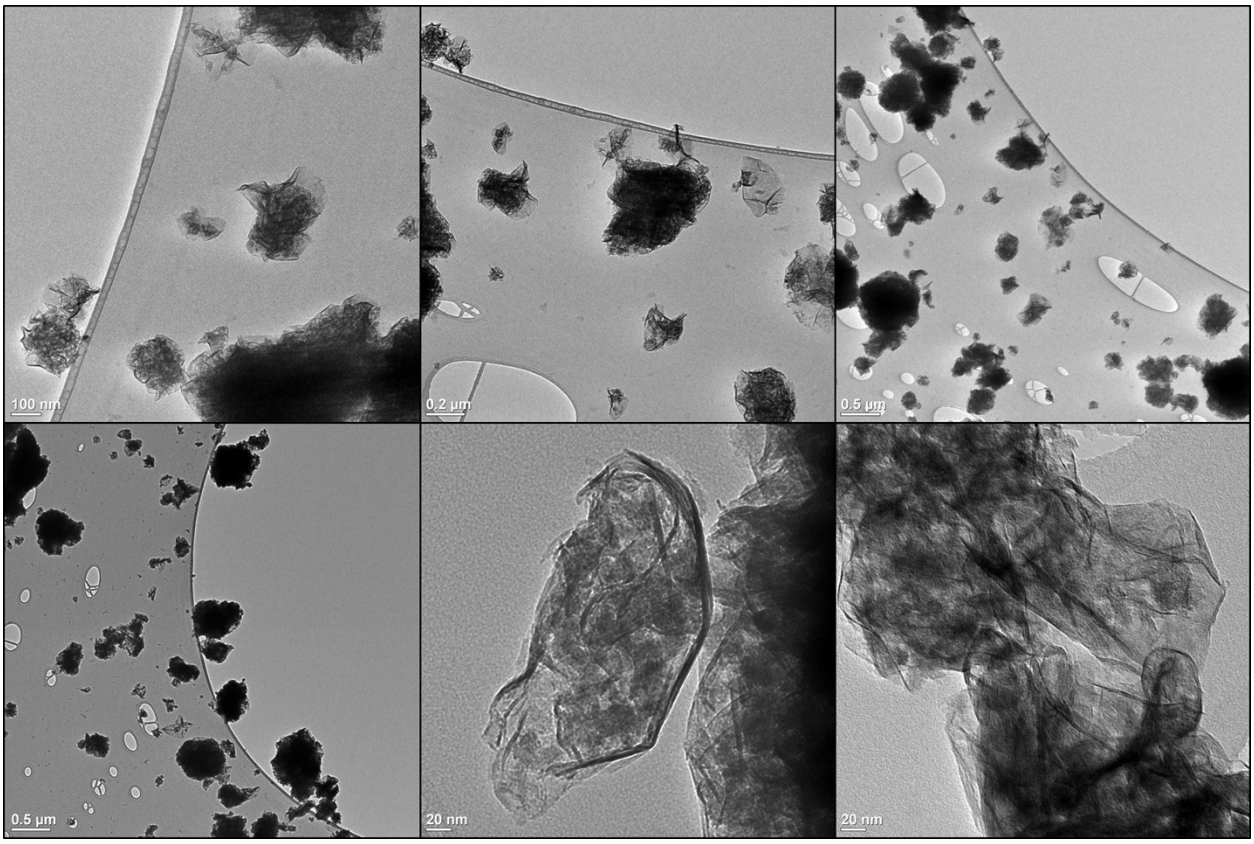

Figure S6. TEM images of crumpled $Ti_3C_2T_x$ spray dried at a concentration of 0.1 mg/ml.

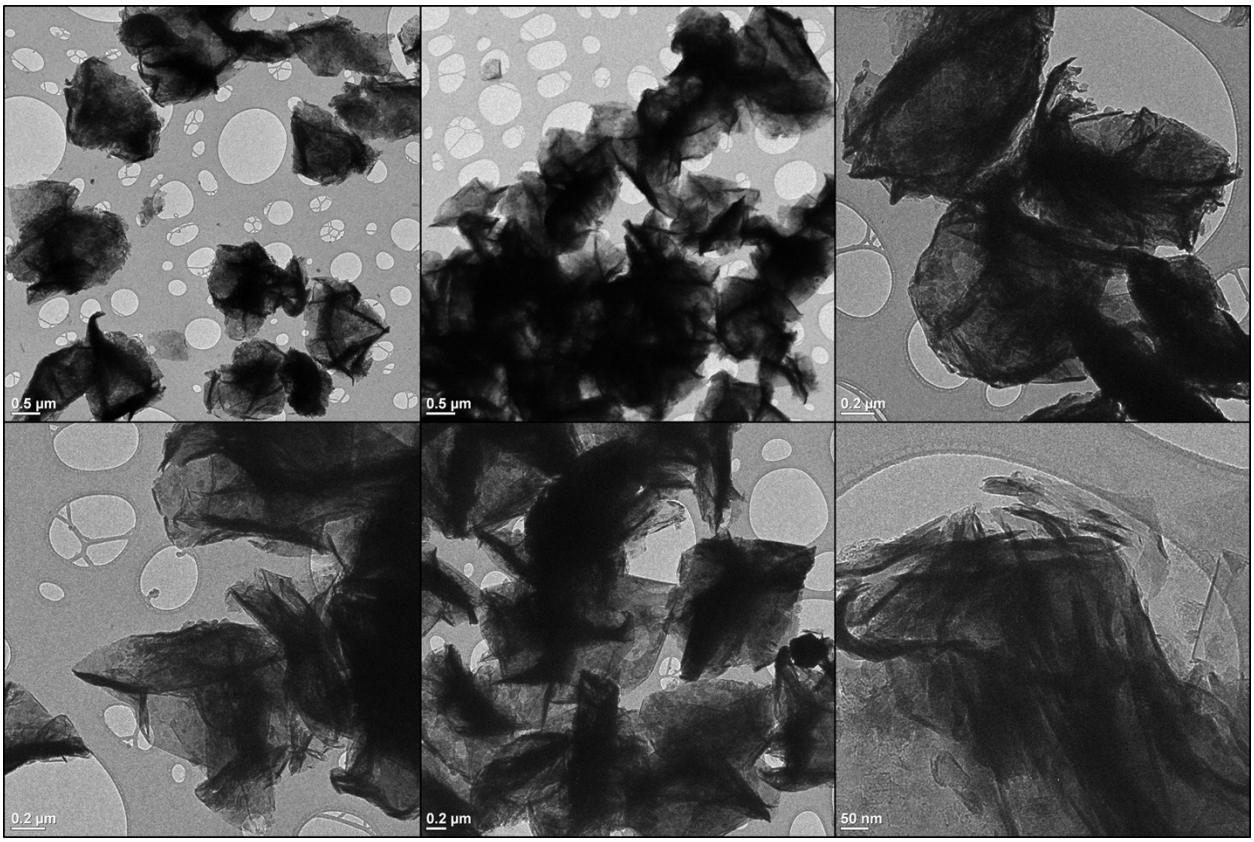

Figure S7. TEM images of crumpled $Ti_3C_2T_x$ spray dried at a concentration of 1 mg/ml.

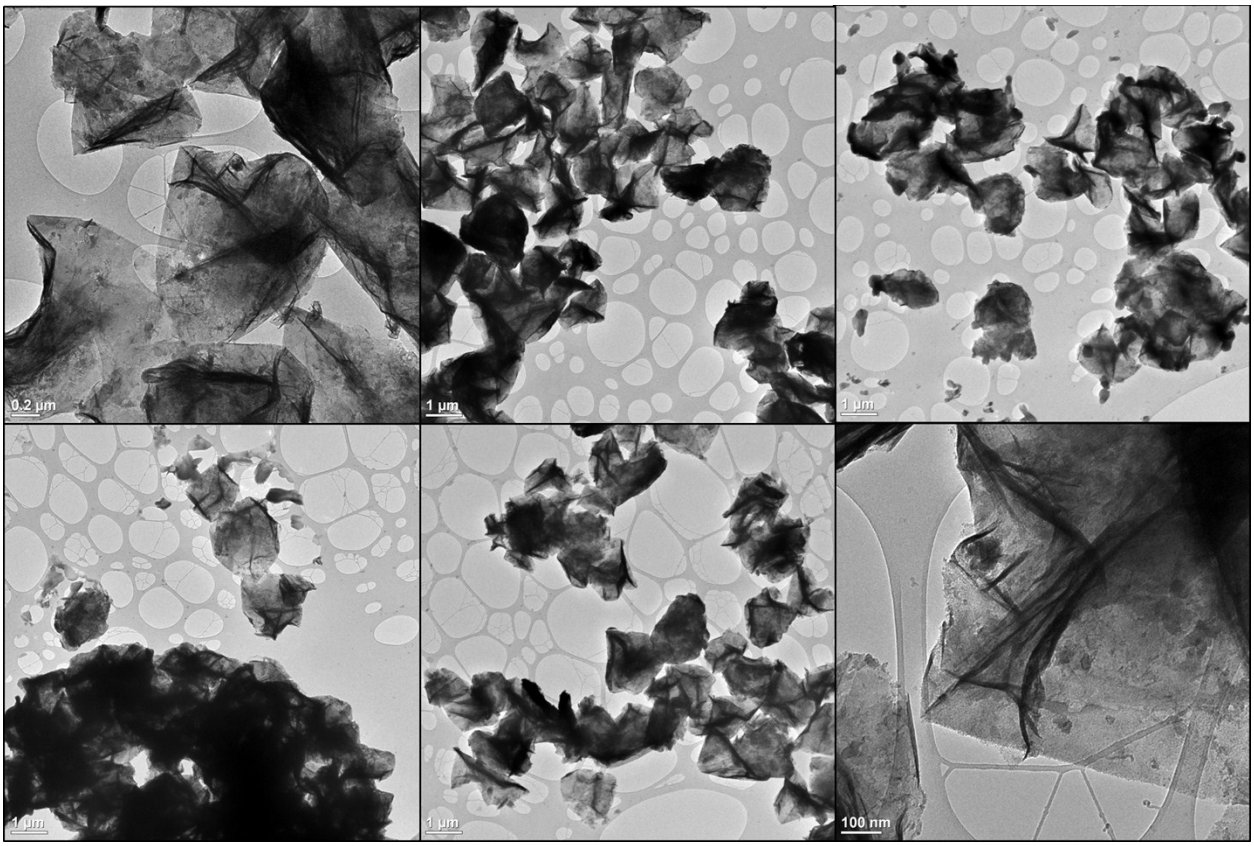

Figure S8. TEM images of "rehydrated" $Ti_3C_2T_x$ MXene nanosheets from spray dried 1 mg/ml crumpled $Ti_3C_2T_x$ dispersion (**Figure S7**).

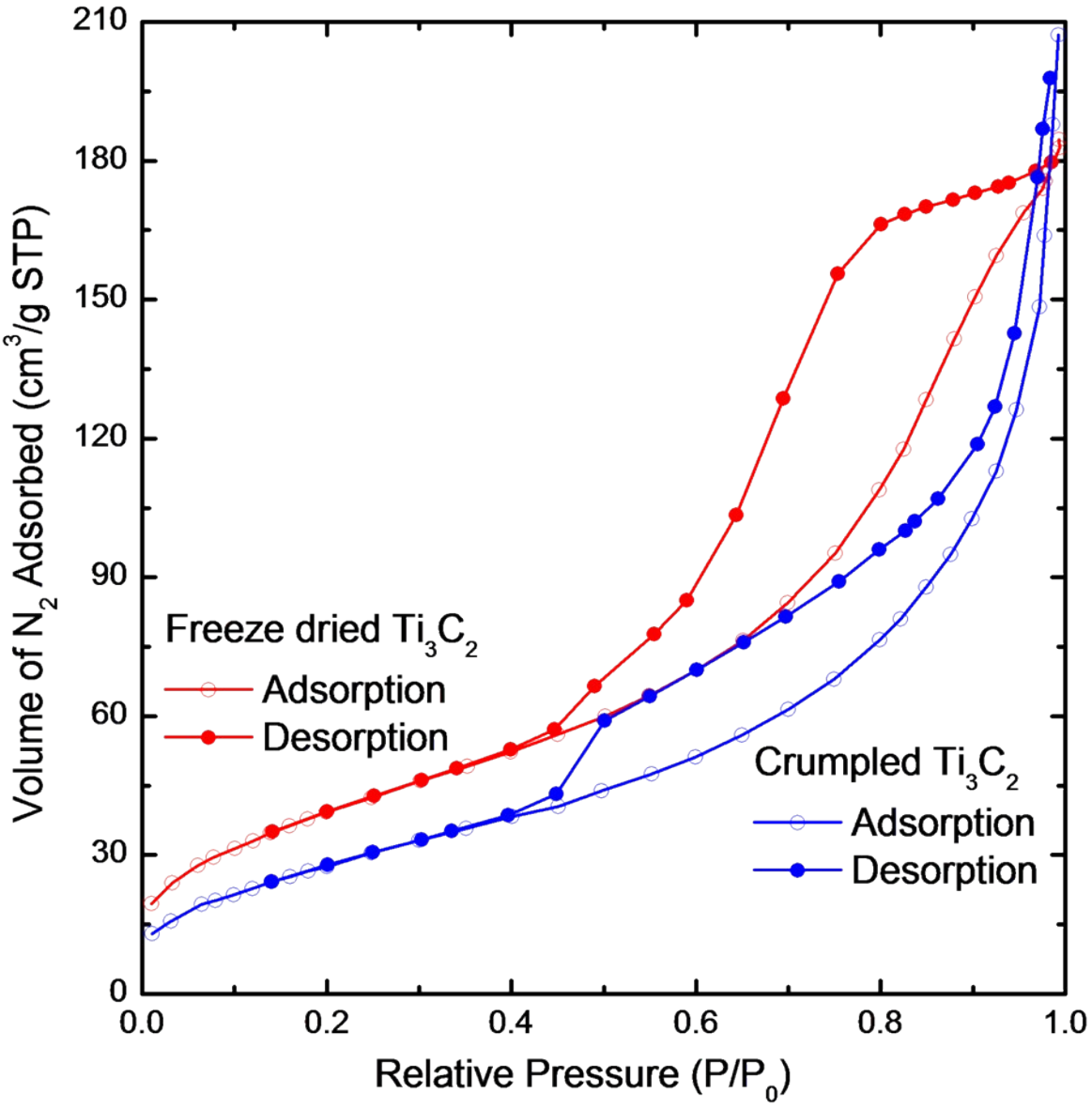

Figure S9. N_2 sorption and desorption measurements conducted using ASAP 2010 (Micrometrics) at 77.35 K. The samples were degassed at 373.15 K for 12 hours prior to the measurements. Brunauer–Emmett–Teller (BET) surface area for freeze dried and crumpled Ti_3C_2 powder was calculated to be 147.40 m^2/g and 105.52 m^2/g respectively.

Reference:

(1) Ghidiu, M.; Lukatskaya, M. R.; Zhao, M.-Q.; Gogotsi, Y.; Barsoum, M. W. Conductive two-dimensional titanium carbide /`clay/' with high volumetric capacitance. *Nature* **2014**, *516*, 78-81.

(2) Mashtalir, O.; Naguib, M.; Mochalin, V. N.; Dall'Agnese, Y.; Heon, M.; Barsoum, M. W.; Gogotsi, Y. Intercalation and delamination of layered carbides and carbonitrides. *Nat Commun* **2013**, *4*, 1716.

(3) Parviz, D.; Metzler, S. D.; Das, S.; Irin, F.; Green, M. J. Tailored Crumpling and Unfolding of Spray-Dried Pristine Graphene and Graphene Oxide Sheets. *Small* **2015**, *11*, 2661-2668.

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[i] This method is commonly, but inaccurately referred to as spark plasma sintering (SPS)