Electronic Supplementary Information for:

Large-Scale Delamination of Multi-Layers Transition Metal Carbides and Carbonitrides "MXenes"

Michael Naguib,*[a] Raymond R. Unocic,[b] Beth L. Armstrong,[a] and Jagjit Nanda [a]

I. MAX phases Synthesis:

To synthesis V_2AlC, elemental powders of vanadium (-325 mesh, 99.5%, Alfa Aesar, Ward Hill, MA, USA), aluminum (-325 mesh, 99.5%, Alfa Aesar, Ward Hill, MA, USA) graphite (7-11µm , 99%, Alfa Aesar, Ward Hill, MA, USA) with the atomic ratio of 2.0:1.3:1.0, respectively, were mixed in a high-density polyethylene (HDPE) jars with zirconia balls using a TURBULA shaker-mixer for 4 h. The mixture was placed in an alumina crucible that was then placed in a tube furnace, heated at a rate of 10°C/minute to 1500 °C, and held at that temperature for 4h before cooling to room temperature (RT). The entire heating and cooling cycle was carried out under a continuous flow of argon, Ar. For Ti_3AlCN, titanium (-325 mesh, 99.5%, Alfa Aesar, Ward Hill, MA, USA), aluminum nitride (10µm, ≥98%, Sigma Aldrich, St. Louis, MO, USA), and graphite with atomic ratio of 3.0:1.0:1.0, respectively, were mixed and heated using the same procedures described above for V_2AlC, but the soaking time at 1500 °C was 2 h for Ti_3AlCN instead of 4 h for V_2AlC. In both cases, the resulted materials were in the form of partially sintered bricks, which were ground using a titanium nitride coated stainless steel milling bit, to produce powders. The latter were then sieved, and powders with particle size less than 38µm were used to synthesis MXenes.

II. MXenes Synthesis:

The MXenes were synthesized by immersing the MAX phase powders slowly in a HDPE jar contained an aqueous hydrofluoric acid, HF (48% Macron Fine Chemicals – Avantor Performance Materials, Center Valley, PA, USA) solution with a certain concentration at RT. Then, a Teflon coated magnet was put in the jar and the jar was moved to a stir plate, and stirred at a speed of 400 rpm for a specific time at RT. Afterword, the solution with the reacted powders were moved to centrifuging vials, and centrifuged. The concentrated HF solutions were decanted and fresh deionized (DI) water was added to wash the powders from HF and reaction products, and centrifuged again. The washing step was repeated many times till the pH of the top liquid reached values higher than 4. Finally, the washed powders were vacuum filtered to facilitate drying at RT. The HF concentrations and reaction times were 48% for 92 h, and 30% for 18 h, for V_2AlC and Ti_3AlCN, respectively.

III. Delamination of MXenes after Tetrabutylammonium Hydroxide (TBAOH) Treatment:

After centrifuging the TBAOH treated MXenes, the settled powders were highly packed at the bottom of the centrifuging tubes. Thus, in case of extracting the settled powders using DI water, many cycles of partially filling the tubes with DI water, and hand shaking for 2 minutes then decanting the black suspension into a large glass bottle was required. This procedure was repeated several times until the entirety of the settled powders were extracted from the tubes and transferred to the bottle.

Once in the bottle, extra DI water was added to reach a ratio of 400 mL of DI water for each 1 g of MXene. The whole mixture was then hand-shaken for 2 minutes in the case of V_2CT_x, or sonicated for 20 minutes in the case of Ti_3CNT_x. Finally, the solution was centrifuged at 2000 rpm for 0.5 h, and the black supernatant was decanted and used for further investigation. More delaminated MXene could be recovered from the settled powders using the same procedure described above to extract the latter from the tubes, and hand-shacked/sonicated, then centrifuged again to separate the black supernatant from non-delaminated MXenes. This cycle was repeated 3-4 times before the supernatant started to be diluted turning from opaque black to transparent. The concentration of the supernatant was in range of 0.2-0.3 mg/mL, and the overall percentage of delaminated MXene was about 30 wt.%. The resulted multi-layered MXene sediment after several cycles of sonicating and centrifuging could be reused again for other purposes and even for retreatment using TBAOH.

IV. Other Organic Bases Treatments:

Samples of multi-layers V_2CT_x were treated using n-butylamine (99+%, ACROS Organics, NJ, USA), and 50% aqueous choline hydroxide (pure, ACORS Organics, NJ, USA) each for 4 h at room temperature each at room temperature. Each treatment was carried out by immersing 0.3 g of V_2CT_x in a vial contained 10 mL of the solution, then a Teflon coated magnet was put in the vial. Then, the vial was placed on a stirrer plate, and was stirred at 400 rpm. After 4 h, the solutions with the powders were moved to centrifuging tubes, and centrifuged for 20 minutes at

2000 rpm. The liquids were then decanted from the tubes and the settled powders were investigated using X-ray diffraction (XRD). To delaminate the V_2CT_x treated with either n-butylamine or choline hydroxide, DI water was added with a ratio of 0.3g V_2CT_x powder : 40 mL of DI water and hand shaken for 2 minutes then centrifuged at 2000 rpm for 30 minutes. After centrifuging, the supernatant were found to be black similar to what was achieved using tetrabutylammounium hydroxide.

V. Characterization Techniques:

A Cu K-alpha Scintag X1 diffractometer (Scintag, Cupertino, CA, USA) was used to collect the XRD patterns (with scanning steps of 0.02° of 2Theta, and 1 s dwell time at each step) for samples investigated in this study. Scanning electron microscopy (SEM) images were captured using Zeiss Merlin VP microscope (Carl Zeiss Microscopy GmbH, Oberkochen, Germany) equipped with an energy dispersive X-ray spectroscopy (EDS) system. High resolution transmission electron microscopy was performed using a Hitachi HF-3300 S/TEM that was operated at 300 keV.

The zeta potential was measured using a Brookhaven Instruments ZetaPALs instrument (Brookhaven Instruments Corp., Holtsville, NY, USA). This instrument utilizes phase analysis light scattering which is a modified electrophoretic light scattering technique to measure the electrophoretic mobility and subsequently calculate the zeta potential. The pH for the solutions of MXenes in deionized (DI) water (1 mg of MXene / mL of DI water) was adjusted using HNO_3 and NH_4OH. At each pH value, ten measurements were collected for the zeta potential and the mean value was reported.

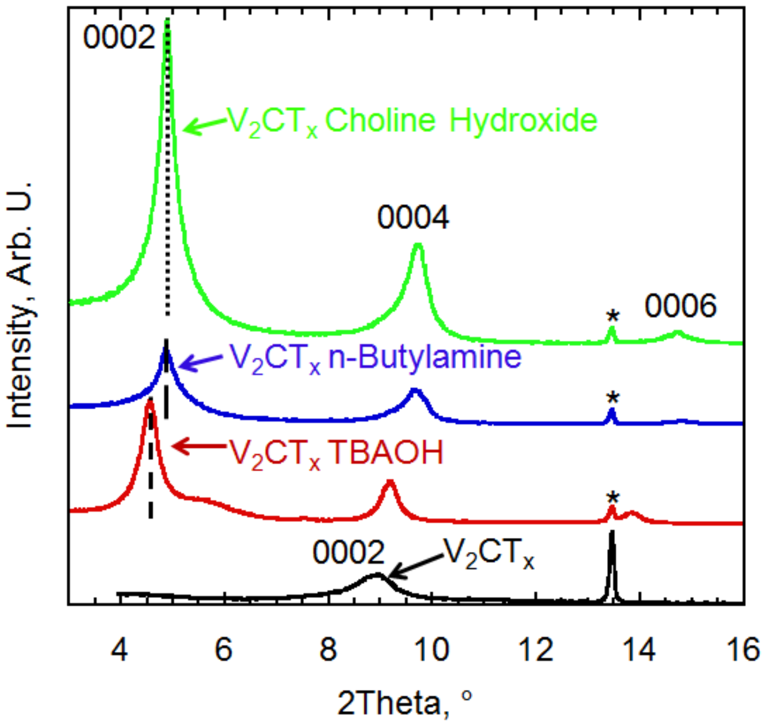

Fig. S1. XRD patterns for V_2CT_x samples before and after treatments with different organic bases; tetrabutylammonium hydroxide (TBAOH), n-butylamine, and choline hydroxide for 4 hours each at room temperature. The * symbols indicate the 0002 peak position of unreacted V_2AlC in MXene samples.

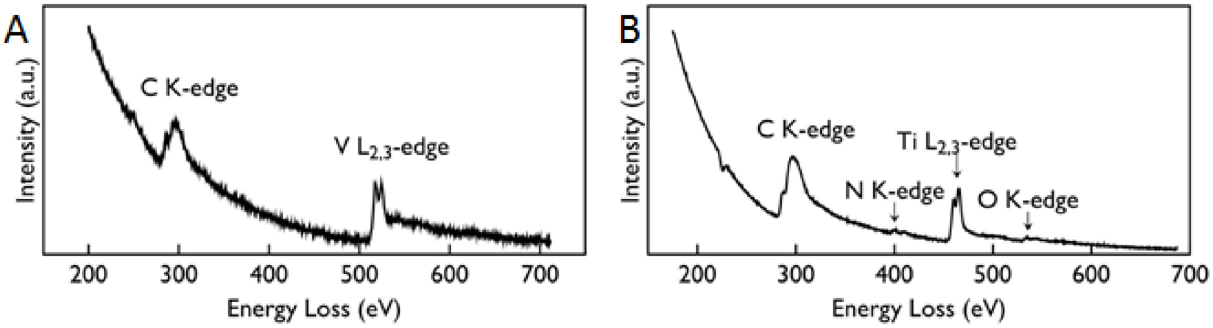

Fig. S2. Electron energy loss spectra of delaminated flakes of (A) V_2CT_x, and (B) Ti_3CNT_x

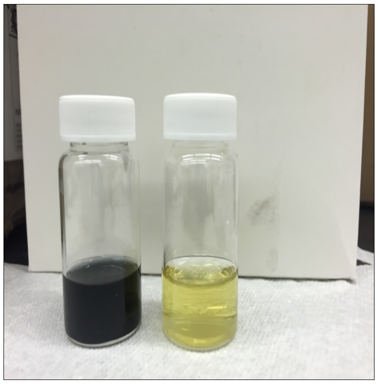

Figure S3. Photograph for two vials contain freshly delaminated V_2CT_x in water (the black liquid in the left vial) and V_2CT_x solution that was kept in air for 48 h (the yellow solution at the right).

Table S1. Energy-dispersive X-ray spectroscopy analysis for V_2CT_x and Ti_3CNT_x before and after delamination:

Sample	Atomic ratio (normalized to M = 2 for V_2CT_x, and 3 for Ti_3CNT_x)					
	M *	Al	C	N	O	F
V_2CT_x as synthesized powder	2	0.16	1.11	------	1.07	0.95
V_2CT_x paper of delaminated MXene	2	0.01	4.96	0.35	3.14	0.003
Ti_3CNT_x as synthesized powder	3	0.06	1.56	0.99	1.53	2.05
Ti_3CNT_x paper of delaminated MXene	3	0.02	2.95	1.63	3.65	0.77

* M stands for V in case of V_2CT_x and Ti in case of Ti_3CNT_x.