Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Mechanically Strong and Electrically Conductive Multilayered MXene Nanocomposites

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Experimental methods

Preparation of Ti_3C_2 delaminated flakes: The precursor Ti_3AlC_2 (MAX phase) and Ti_3C_2 were synthesized following protocols described in detail elsewhere.[25] Aluminum (Al) was selectively etched from Ti_3AlC_2 using the minimally intensive layer delamination (MILD) method. Using plastic bottle, 4.8 g lithium fluoride (LiF) was added to 60 ml of 9 M hydrochloric acid (HCl) and the mixture was stirred for 5 min. Then, 3 g of Ti_3AlC_2 (MAX phase) was gradually added to the etchant solution and the reaction was allowed to proceed at ambient temperature (~23 °C) for 24 h. The acidic product was brought to neutral pH by washing with deionized water (DI H_2O) for multiple cycles of centrifugation at 3500 rpm (5 min per cycle). After each cycle, the water-like supernatant was decanted into waste and the black MXene sediment was re-dispersed with DI H_2O. These washing cycles were repeated until a stable dark-green supernatant solution of Ti_3C_2 flakes, with a pH of ~ 6, was obtained and collected. A concentration of 2 mg mL^{-1} of colloidal solution of Ti_3C_2 MXene flakes was used to fabricate composites by LbL.

Materials for dip-LbL: PVA was purchased from Sigma-Aldrich with a molecular weight of 85,000-124,000 g mol^{-1}. MTM, under commercial name Closite-Na^+, was procured from BYK USA, inc. Glass slides used as substrates were 1” x 3” x 1mm, purchased from Thermo Scientific. Sulfuric acid (98%) was purchased from J.T. Baker. 30% Hydrogen Peroxide was purchased from Sigma-Aldrich. Deionized water was obtained using a Millipore Elix 20 TOC system.

Tensile strength measurements: Freestanding films were cut into rectangular pieces 3 mm wide and 2 cm long. Stress-strain curves were obtained using an Instron 5940 Microtester, using a 10 N load cell and an extension rate of 0.6 mm min^{-1}. Tests were repeated with different samples, made using different solutions to ensure repeatable results. Samples used for mechanical testing were 10 bilayer composite films. The modulus is calculated by computing the derivative of the linear part of the stress-strain curve.

Characterization: SEM was performed using a Hitachi SU-70 and Hitachi SU8230. Film thickness was determined using cross-sectional SEM. EDS was performed using Bruker FlatQuad EDS. Sheet resistance measurements were performed using a four-point probe and a Keithley 2400. Four silver contacts were deposited for sheet resistance measurements at $\sim 2\times10^{-6}$ torr using a thermal evaporator. TGA was performed using a TA Instruments TGA Q50 under compressed air flow. Zeta potential and DLS measurements were performed in a Malvern Nano ZS90 at 25 ºC. Measurements were averaged from 3 trials at pH = 6. For zeta potential measurements, all solutions were diluted by a factor of 5 with water of the same pH to have high enough transmission for a measurement. For DLS measurements, a 0.01 mg/mL MXene solution was used to obtain the intensity distribution particle size distributions.

EMI Shielding Effectiveness: Electromagnetic interference (EMI) shielding measurements of the composite films were carried out in a WR-90 rectangular waveguide using a 2-port network analyzer (E5071C, Agilent Technologies, USA), photograph shown in **Figure S3**. X-band frequency range (8-12.4 GHz) was selected as the test range. The dynamic range of network analyzer was 80 dB. A standard calibration before the test was performed using short offset, short and load on both ports, 1 and 2. The samples were placed into the sample holder which was tightened around the sample with screws. The effect from glass slide was subtracted by the controlled experiment. The S parameters (i.e., S11 and S21) of each sample were recorded and were then used to calculate the EMI shielding effectiveness, calculation methods are discussed in **Equation (S12) -(S16)** in the supporting information.

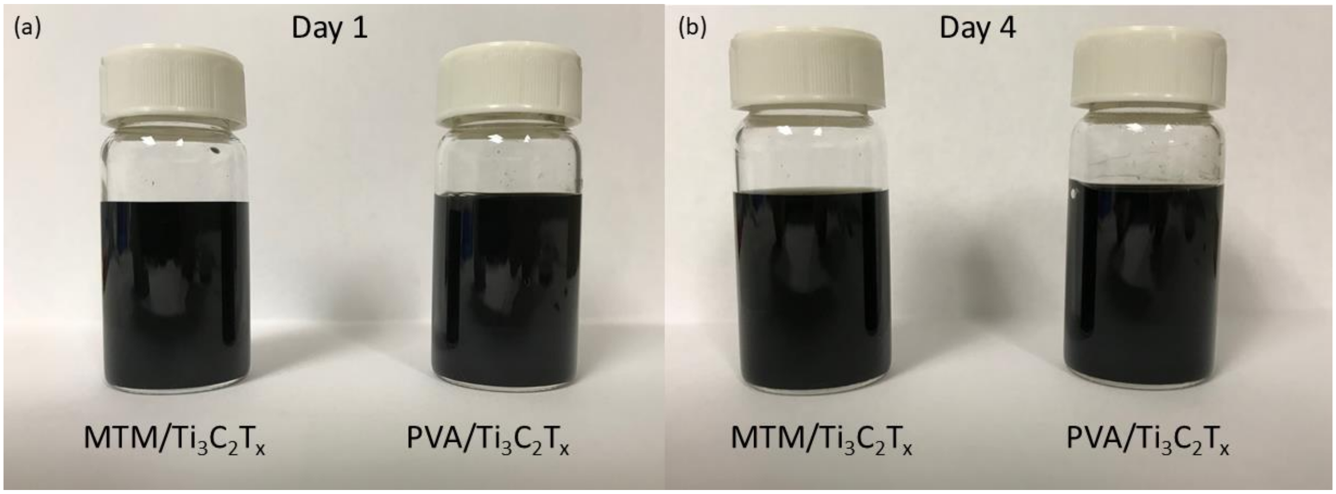

Figure S1. (a) MTM/MXene and PVA/MXene dispersions immediately after preparation. (b) The same dispersions as in (a) after 4 days.

Table S1: Zeta Potential Data for LbL Suspensions at a neutral pH (pH=6)

Material	Zeta Potential (mV)
Ti_3C_2 + PVA	-10.5±1.7
Ti_3C_2 + MTM	-47.3±1.6
Ti_3C_2	-53.6±2.7
MTM	-25.8±0.6

We note that solubilized polymers do not have a zeta potential by definition, therefore, we have not shown any data on PVA alone in Table S1.

TGA Calculations

To determine the mass of all 3 components in the composite using TGA data we evaluated Equation (S1)-(S3) with three unknowns, using the raw data to obtain coefficients. Equation (1) is a relation for the initial mass of the composite. Equation (S2) relates the fractional change in mass of each component to the change in overall mass of the composite from 100º C to 800º C. Equation S3 relates the weight percent of each component remaining at 800º C to the mass of the composite remaining at 800º C.

$$m_{MTM} + m_{MXene} + m_{PVA} = m_{i,composite} \tag{S1}$$

$$f_{MTM} * m_{MTM} + f_{MXene} * m_{MXene} + f_{PVA} * m_{PVA} = \Delta m_{composite} \tag{S2}$$

$$wp_{MTM} * m_{MTM} + wp_{MXene} * m_{MXene} + wp_{PVA} * m_{PVA} = m_f, composite \tag{S3}$$

$$f_j = \frac{m_{j,800} - m_{j,100}}{m_{j,100}} \tag{S4}$$

$$wp_j = \frac{m_{j,800}}{m_{j,100}} \tag{S5}$$

Where:

- $m_{i,\ composite}$ is the mass of the composite at 100º C
- $m_{f,\ composite}$ is the mass of the composite at 800º C
- $\Delta m_{composite}$ is the change in mass of the composite between 100º C and 800º C
- f_{MTM}, f_{MXene}, f_{PVA}, are the fractional mass change of each component between 100º C and 800º C

- wp_{MTM}, wp_{MXene}, and wp_{PVA} are the weight percent of the components remaining at 800º C
- The subscript j is an index representing PVA, MXene, or MTM

We note that f_{MXene}, fractional mass change after testing, is a positive number because the MXene sample increased in mass by 15.31% during thermogravimetric analysis.

Example equations with numbers are as follows:

$$m_{MTM} + m_{MXene} + m_{PVA} = 5.67789\ mg \tag{S6}$$

$$-0.02904 * m_{MTM} + 0.15313 * m_{MXene} - 0.96405 * m_{PVA} = -1.65272\ mg \tag{S7}$$

$$0.97096 * m_{MTM} + 1.15313 * m_{MXene} + 0.03595 * m_{PVA} = 4.02517\ mg \tag{S8}$$

$$\frac{m_{MTM}}{m_{i,composite}} \cdot 100\ = 17.613\% \tag{S9}$$

$$\frac{m_{MXene}}{m_{i,composite}} \cdot 100\ = 45.497\% \tag{S10}$$

$$\frac{m_{PVA}}{m_{i,composite}} \cdot 100\ = 36.890\% \tag{S11}$$

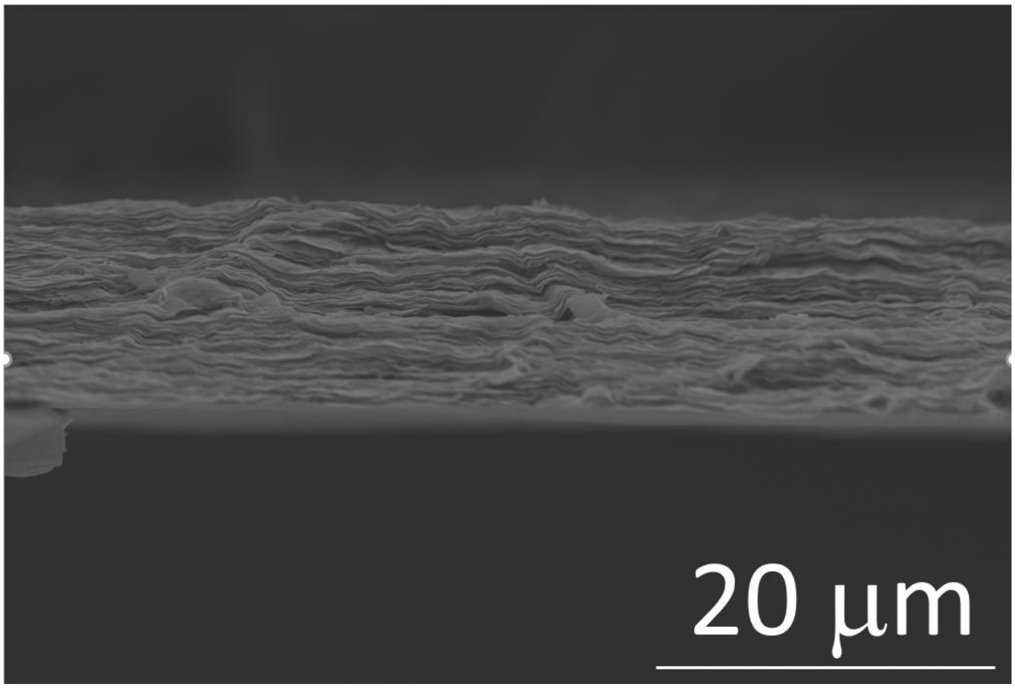

Figure S2. SEM image of 40 bilayer (11 μm) MTM-Ti_3C_2-PVA LbL composite.

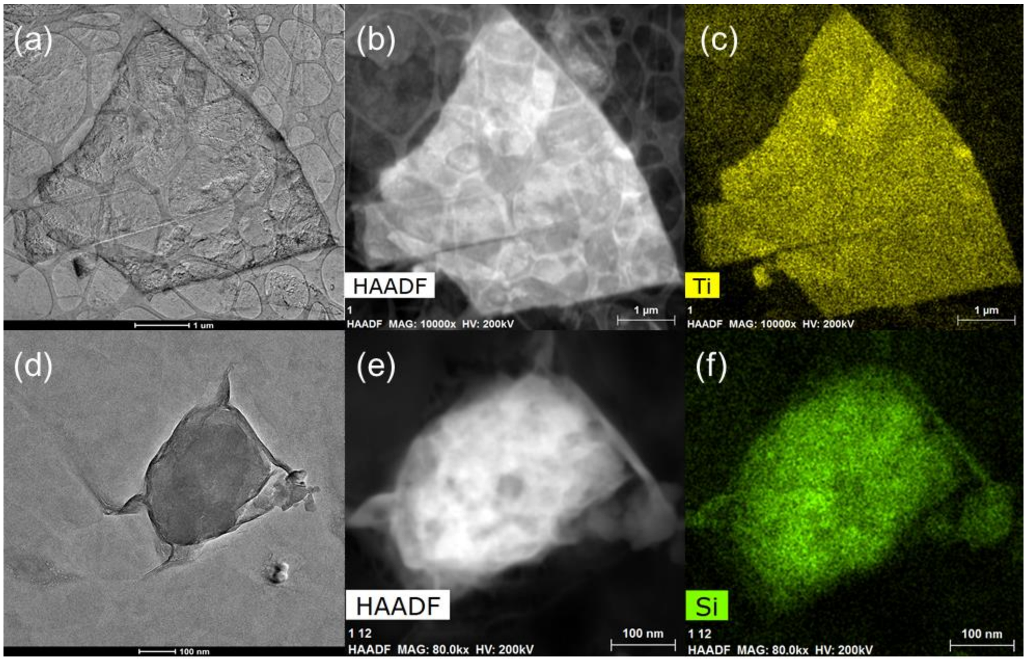

Figure S3. (a-c) Ti_3C_2 MXene TEM, STEM, and Ti EDS Map, respectively. (d-f) MTM clay platelet TEM, STEM, and Si EDS map, respectively.

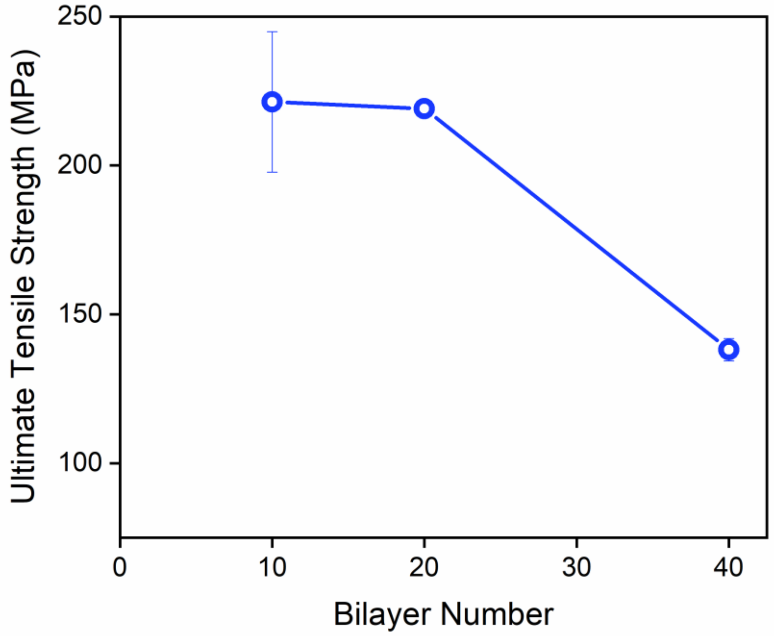

Figure S4. Ultimate tensile strength of PVA-MTM-Ti_3C_2 as a function of bilayer.

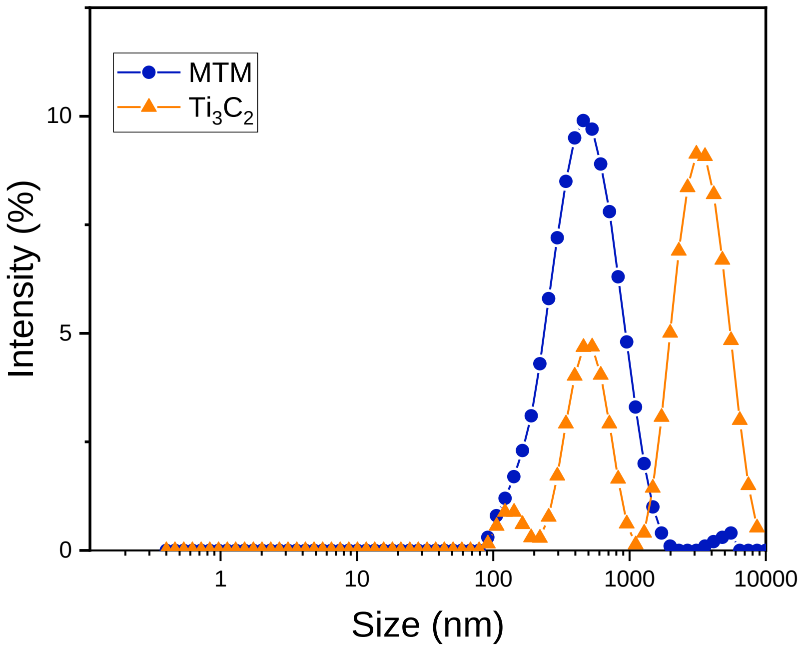

Figure S5. Dynamic light scattering (DLS) size distribution data for Ti_3C_2 (orange), and MTM (blue).

Table S2. Comparison of Tensile Strength and Sheet Resistance of LbL composites in literature

Material	Ultimate Tensile Strength (MPa)	Sheet Resistance ($k\Omega\ sq^{-1}$)	Thickness (µm)	Reference
MXene/MTM/PVA	**225**	**0.855**	**3 - 12**	**This Work**
MXene/PVA/CNT/PSS	25	0.45	0.025 – 0.225	1
PVA/MTM	400	N/A	1.0 - 1.5	2
CNT/PEI	220	N/A	0.75 – 1.0	3
$CaCO_3$/PDDMA	106	N/A	1.2 – 4.9	4
PVA/GO	110	N/A	78 – 120	5
MTM/PDDMA	150	N/A	N/A	6
MWCNT/PEI	150	N/A	1.5	7
PU/PAA	86	N/A	10 – 70	8
PDDMA/PAA/SWCNT	70	N/A	N/A	9
Silk Fibroin	100	N/A	0.02 – 0.12	10
PSS/PAH	30	N/A	N/A	11
Laponite/PVA	108	N/A	3 - 10	12
MXene/PVA (not LbL)	91	2,083	3.3 - 13	13

MXene/CNF (not LbL)	135	N/A	47	35
MXene/MWNT/PCL	3	5	60	14
GO	N/A	2.5	0.005 – 0.015	15
PSS/PAA	N/A	1.2	0.01 – 0.10	16
CNT/Graphene	N/A	8	0.011	17
PANI/rGO	N/A	5.3	0.01 – 0.13	18
AgNP/rGO	N/A	0.8	0.5	19
Graphene/azo-poyelectrolyte	N/A	1,000	0.04	20
Grapene/PANI	N/A	6	0.01 – 0.05	21
Graphene/DWNT/PANI	N/A	0.02	0.1 – 0.75	22
rGO	N/A	4.92	0.05 – 0.25	23
MXene/TAEA	N/A	0.154	0.090	36

Abbreviations:

- PDDMA- Poly(diallyldimethylammonium chloride)
- MTM – Montmorillonite
- PVA – Poly(vinyl alcohol)
- CNT – carbon nanotubes
- SWCNT – single wall carbon nanotubes

- MWCNT – multiwall carbon nanotubes
- DWCNT – double wall carbon nanotubes
- GO -Graphene oxide
- PEI – poly(ethylenimine)
- PU – polyurethane
- PAA – poly(acrylic acid)
- PAH – poly(allylamine hydrochloride)
- PCL – Poly(caprolactone)

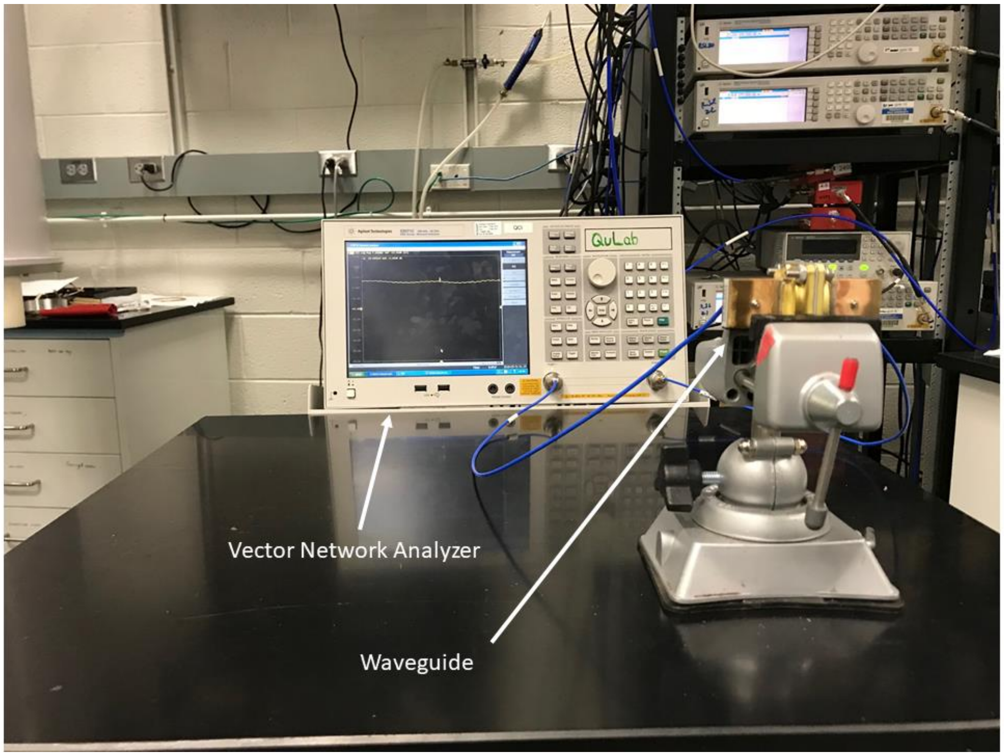

Figure S6. Photograph of testing setup for EMI shielding effectiveness. Behind the table is the vector network analyzer, and in the vice is the sample holder and waveguide.

EMI Shielding Calculations

EMI SE can also be written theoretically in Simon Formalism as shown in Equation (4).[35]

$$SE = 50 + 10\log\left(\frac{\sigma}{f}\right) + 1.7t(\sigma f)^{\frac{1}{2}} \tag{S12}$$

The total EMI SE (SE_T) can be written as the sum of the contributions from reflection (SE_R) and absorption (SE_A). SE_R and SE_A, and thus SE_T can be expressed as in Equation (5), (6), and (7).

$$SE_R = 10\log\left[\frac{1}{1-|S_{11}|^2}\right] \tag{S13}$$

$$SE_A = 10\log\left[\frac{1-|S_{11}|^2}{|S_{21}|^2}\right] \tag{S14}$$

$$SE_T = 10\log\left[\frac{1}{|S_{21}|^2}\right] \tag{S15}$$

EMI SSE/t is the EMI shielding efficiency normalized to the thickness and density, expressed in equation (16) where *t* represents thickness and *ρ* represents mass density.

$$EMI\ SSE/t = \frac{SE_T}{t\rho} \tag{16}$$

Table S3. Literature comparison of EMI SSE/t.

Material	Thickness (μm)	SSE/t (dB cm^2 g^{-1})	SSE/t†	Reference
MXene/MTM/PVA	**3**	**24,550**	**Reported**	**This Work**
AgNW	500	2416	Calculated	24
Al Foil	8	30555	Reported	25
Cu Foil	0.1	7812	Reported	25
rGO	80	11712	Calculated	26
Graphene Foam	300	1395800	Calculated	27
Graphene	30	14000	Calculated	27
Graphene	100	3330	Calculated	28
MWCNT	100	5410	Calculated	29
CNT-Sponge	240	4622	Calculated	30
Carbon	200	1705	Calculated	31
Carbon foam	200	1250	Calculated	32
CuNi-CNT	150	1580	Calculated	33
Ti_3C_2	11	25863	Reported	25
Ti_3C_2	8	30830	Reported	25
MXene Foam	6	136752	Calculated	34
Mxene Foam	18	69444	Calculated	34
MXene Foam	6	53030	Calculated	34
Ti_3C_2/CNF	47	2647	Reported	35
MXene/MWCNT	0.170	58187	Reported	1
MXene/SWCNT	0.207	49912	Reported	1

†Notes: this data is directly reported or calculated.

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