Supporting Information: Investigation and Understanding of the Mechanical Properties of MXene by High-Throughput Computations and Interpretable Machine Learning

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Supplementary Notes

1. The definition of thickness

The interlayer distance d can be obtained by optimizing the bilayer 2D materials and calculating the vertical distance between two layers. Using the Föppl-von Karman plate theory, the thin-shell thickness t_{s} can be determined from the tensile stiffness K, the bending stiffness D and the in-plane Poisson's ratio ν as,[S1]

$$t_{\mathrm{s}} = [12(1-\nu^2)D/K]^{1/2}$$

In addition, the geometric thickness h is defined as,

$$h = d_{\mathrm{T\text{-}B}} + r_{\mathrm{T}} + r_{\mathrm{B}}$$

where $d_{\mathrm{T\text{-}B}}$ is the sum of the vertical distance between the topmost and bottommost atoms, r_{T} and r_{B} is the van der Waals radius of the topmost and bottommost atoms, respectively. The geometric thickness can be obtained without extra DFT calculation and thus is used in this work.

Supplementary Tables

Table S1. The thickness of MXenes and other 2D materials using different definitions (units in Å), including the geometric thickness t_g, (van der Waals) effective thickness t_s, and interlayer distance (of the 3D bulk counterpart). The illustrations can be found in Figure S2. In our work, the thickness is defined as t_s.

Formula	t_g	t_s	d
Graphene	0	3.44	3.34[S1]
h-BN	0	3.60	3.34[S1]
Silicene	0.46	4.66	3.19[S1]
h-MoS_2	3.12	6.72	6.15[S1]
α-Black phosphorus	2.11	5.71	5.30[S1]
Sc_2CO_2	4.87	7.97	5.72[S2]
Ti_2CO_2	4.44	7.44	6.77[S2]
Ti_2CF_2	4.80	7.74	6.95[S2]
Zr_2CO_2	4.62	7.66	6.19[S2]
Ti_3C_2	4.66	8.96	7.35[S3]
$Ti_3C_2F_2$	7.25	10.19	9.35[S3]
$Ti_3C_2(OH)_2$	9.22	11.42	9.64[S3]
$Ti_3C_2O_2$	7.01	10.05	9.29[S3]

Table S2. Bond energy (E, in the unit of eV), bond length (l, in the unit of Å), and bond stiffness (k, in the unit of eV/Å^2) of M-X bonds. The bond energy data comes from reported[S4] work. The M-X bond length can be approximated by using the length of a single covalent σ-bond[S5] between M and X, and the equation to calculate bond stiffness[S6] is $k_{\mathrm{M-X}} = 16 \times E_{\mathrm{M-X}}/l^2_{\mathrm{M-X}}$.

	M-C bonds			M-N bonds		
M	$E_{\mathrm{M-C}}$	$l_{\mathrm{M-C}}$	$k_{\mathrm{M-C}}$	$E_{\mathrm{M-N}}$	$l_{\mathrm{M-N}}$	$k_{\mathrm{M-N}}$
Sc	4.62	2.23	14.88	4.83	2.19	16.12
Ti	4.41	2.11	15.84	4.96	2.07	18.51
V	4.41	2.09	16.14	5.45	2.05	20.74
Cr	3.80	1.97	15.67	3.94	1.93	16.90
Mn	4.61	1.94	19.60	4.70	1.90	20.83
Y	4.35	2.38	12.30	4.97	2.34	14.51
Zr	5.16	2.29	15.76	5.89	2.25	18.60
Nb	5.46	2.22	17.71	4.40	2.18	14.81
Mo	5.02	2.13	17.70	3.53	2.09	12.93
Hf	5.62	2.27	17.46	5.57	2.23	17.93
Ta	5.99	2.21	19.62	6.32	2.17	21.48
W	3.95	2.12	14.05	3.27	2.08	12.10

Table S3. Bond energy (E), bond length (l), and bond stiffness (k) of M-T$_x$ bonds. The units are the same as Table S2.

	M-F bonds			M-O bonds		
M	$E_{\mathrm{M-F}}$	$l_{\mathrm{M-F}}$	$k_{\mathrm{M-F}}$	$E_{\mathrm{M-O}}$	$l_{\mathrm{M-O}}$	$k_{\mathrm{M-O}}$
Sc	6.24	2.19	22.21	6.99	2.23	25.13
Ti	5.93	2.18	23.71	6.94	1.98	28.05
V	6.14	2.15	25.08	6.63	1.97	27.36
Cr	5.45	2.11	25.19	4.80	1.93	22.45
Mn	4.64	2.11	22.16	3.77	1.94	18.21
Y	7.14	2.35	22.16	7.44	2.39	23.30
Zr	6.53	2.33	21.99	8.08	2.12	27.46
Nb	4.71	2.11	16.92	7.57	2.10	27.45
Mo	4.83	2.02	18.95	5.23	2.01	20.71
Hf	6.77	2.16	23.22	8.34	2.15	28.88
Ta	5.02	2.10	18.21	8.74	2.09	32.01
W	5.67	2.01	22.44	7.50	2.00	30.00

Table S4. The ratio $\sigma_{\mathrm{s}}^{\mathrm{MX-T}}/\sigma_{\mathrm{s}}^{\mathrm{MX}}$ of H-$M_3X_2T_x$ MXenes. It can be seen that most functionalized MXenes possess higher σ_{s} than that of bare counterparts in both armchair and zigzag directions.

Formula	Increase ratio (ac)	Increase ratio (zz)
$Hf_3C_2F_2$	1.03	1.32
$Hf_3C_2(OH)_2$	1.25	1.40
$Hf_3C_2O_2$	1.49	1.67
$Nb_3C_2O_2$	1.63	1.65
$Sc_3C_2(OH)_2$	1.03	1.79
$Ta_3C_2O_2$	1.51	1.52
$Ti_3C_2F_2$	1.17	1.48
$Ti_3C_2(OH)_2$	1.31	1.53
$Ti_3C_2O_2$	1.28	1.52
$V_3C_2O_2$	0.99	1.26
$Y_3C_2F_2$	1.22	2.33
$Y_3C_2(OH)_2$	1.23	1.67
$Zr_3C_2F_2$	1.20	1.41
$Zr_3C_2(OH)_2$	1.34	1.46
$Zr_3C_2O_2$	1.53	1.56
$Hf_3N_2O_2$	1.63	1.61
$Sc_3N_2F_2$	0.78	1.75
$Sc_3N_2(OH)_2$	0.81	1.79
$Sc_3N_2O_2$	0.78	1.02
$Ti_3N_2O_2$	2.06	1.65
$V_3N_2O_2$	1.94	2.26
$Y_3N_2F_2$	1.55	1.51
$Y_3N_2(OH)_2$	1.57	1.54
$Y_3N_2O_2$	1.51	0.98
$Zr_3N_2O_2$	2.11	2.09

Table S5. The ideal strength σ_s of H-$M_3X_2T_x$ MXenes (unit: N/m) in armchair and zigzag directions, respectively.

Carbide MXenes			Nitride MXenes		
Formula	σ_s (ac)	σ_s (zz)	Formula	σ_s (ac)	σ_s (zz)
$Cr_3C_2F_2$	15.25	29.15	Hf_3N_2	15.98	26.54
$Cr_3C_2(OH)_2$	14.64	30.3	$Hf_3N_2O_2$	26.04	42.62
Hf_3C_2	23.82	27.55	Nb_3N_2	24.38	22.32
$Hf_3C_2F_2$	24.63	36.42	$Sc_3N_2F_2$	22.40	29.72
$Hf_3C_2(OH)_2$	29.77	38.61	$Sc_3N_2(OH)_2$	23.18	30.49
$Hf_3C_2O_2$	35.66	46.01	Sc_3N_2	28.84	17.01
$Mn_3C_2F_2$	16.04	26.05	$Sc_3N_2O_2$	22.51	17.27
$Mn_3C_2(OH)_2$	16.45	25.45	Ta_3N_2	24.81	30.45
$Mn_3C_2O_2$	17.82	21.72	Ti_3N_2	13.40	24.58
Nb_3C_2	18.78	26.27	$Ti_3N_2O_2$	27.62	40.56
$Nb_3C_2O_2$	30.62	43.49	V_3N_2	12.59	15.9
Sc_3C_2	14.63	12.98	$V_3N_2O_2$	24.48	36.04
$Sc_3C_2(OH)_2$	15.14	23.36	$Y_3N_2F_2$	18.49	25.45
Ta_3C_2	20.51	30.41	$Y_3N_2(OH)_2$	18.76	26.02
$Ta_3C_2O_2$	30.93	46.31	Y_3N_2	11.91	16.87
Ti_3C_2	22.34	25.3	$Y_3N_2O_2$	17.95	16.47
$Ti_3C_2F_2$	26.08	37.38	Zr_3N_2	12.29	18.78
$Ti_3C_2(OH)_2$	29.23	38.73	$Zr_3N_2O_2$	25.96	39.26
$Ti_3C_2O_2$	28.62	38.38			
V_3C_2	20.44	24.24			
$V_3C_2O_2$	20.34	30.67			
Y_3C_2	12.59	10.38			
$Y_3C_2F_2$	15.34	24.16			
$Y_3C_2(OH)_2$	15.47	17.39			
Zr_3C_2	21.07	24.86			
$Zr_3C_2F_2$	25.41	35.01			
$Zr_3C_2(OH)_2$	28.20	36.35			
$Zr_3C_2O_2$	32.24	38.69			

Table S6. The ideal strength σ_s of T-$M_3X_2T_x$ MXenes (unit: N/m) in armchair and zigzag directions, respectively.

Carbide MXenes			Nitride MXenes		
Formula	σ_s (ac)	σ_s (zz)	Formula	σ_s (ac)	σ_s (zz)
$Cr_3C_2F_2$	18.38	26.29	Hf_3N_2	17.47	25.44
$Cr_3C_2(OH)_2$	27.76	24.38	$Hf_3N_2O_2$	24.06	40.81
Hf_3C_2	23.4	25.51	Nb_3N_2	18.73	21.14
$Hf_3C_2F_2$	23.67	35.56	$Sc_3N_2F_2$	23.49	31.83
$Hf_3C_2(OH)_2$	27.71	37.73	$Sc_3N_2(OH)_2$	23.72	32.29
$Hf_3C_2O_2$	34.83	50.52	Sc_3N_2	18.17	22.13
$Mn_3C_2F_2$	14.58	26.29	$Sc_3N_2O_2$	24.48	21.33
$Mn_3C_2(OH)_2$	14.14	24.40	Ta_3N_2	14.09	26.13
$Mn_3C_2O_2$	17.76	26.25	Ti_3N_2	19.25	23.37
Nb_3C_2	22.21	24.82	$Ti_3N_2O_2$	25.54	39.36
$Nb_3C_2O_2$	30.53	44.20	V_3N_2	16.94	18.32
Sc_3C_2	16.12	16.79	$V_3N_2O_2$	13.35	26.91
$Sc_3C_2(OH)_2$	18.83	30.33	$Y_3N_2F_2$	19.59	25.51
Ta_3C_2	24.08	27.24	$Y_3N_2(OH)_2$	18.99	26.01
$Ta_3C_2O_2$	33.86	43.11	Y_3N_2	12.73	16.87
Ti_3C_2	22.59	23.99	$Y_3N_2O_2$	17.96	16.4
$Ti_3C_2F_2$	24.01	36.69	Zr_3N_2	18.76	22.36
$Ti_3C_2(OH)_2$	26.91	37.93	$Zr_3N_2O_2$	21.14	37.02
$Ti_3C_2O_2$	33.21	42.98			
V_3C_2	22.91	19.51			
$V_3C_2O_2$	20.42	41.37			
Y_3C_2	13.63	13.92			
$Y_3C_2F_2$	14.16	24.19			
$Y_3C_2(OH)_2$	15.89	25.28			
Zr_3C_2	21.28	22.96			
$Zr_3C_2F_2$	23.08	34.64			
$Zr_3C_2(OH)_2$	26.33	35.55			
$Zr_3C_2O_2$	32.59	40.57			

Table S7. Independent calculations of E^{2D} for some MXenes and other typical 2D crystals in comparison with these calculated using the data from C2DB (unit: N/m). Our results of E^{2D} are consistent with that calculated from C_{ij} supplied by C2DB, which confirms the data in C2DB is reliable.

Formula	E^{2D} (C2DB)	E^{2D} (This work)
graphene	331.23	328.76
h-BN	276.20	282.03
h-MoS_2	123.13	140.59
Sc_2C	90.76	90.17
Hf_2C	157.17	159.89
Hf_2N	149.63	147.77
T_2C	142.63	143.16
T_2CO_2	247.73	248.38
Ti_3C_2	243.75	246.01
$Ti_3C_2O_2$	328.26	328.64
T_4C_3	354.52	338.58
$T_4C_3O_2$	467.53	470.36

Table S8. The $E_{\mathrm{H}}^{2\mathrm{D}}$ of H-phase MXenes (that in C2DB) and $E_{\mathrm{T}}^{2\mathrm{D}}$ of T-phase MXenes that calculated in this work. The unit is N/m.

Formula	$E_{\mathrm{H}}^{2\mathrm{D}}$	$E_{\mathrm{T}}^{2\mathrm{D}}$	Formula	$E_{\mathrm{H}}^{2\mathrm{D}}$	$E_{\mathrm{T}}^{2\mathrm{D}}$
$Cr_3C_2F_2$	205.96	220.63	Hf_3N_2	271.04	266.92
$Cr_3C_2(OH)_2$	183.41	249.41	$Hf_3N_2O_2$	389.38	382.55
Hf_3C_2	264.22	265.50	Nb_3N_2	250.46	253.32
$Hf_3C_2F_2$	306.94	314.74	$Sc_3N_2F_2$	261.95	293.55
$Hf_3C_2(OH)_2$	320.35	351.17	$Sc_3N_2(OH)_2$	259.25	299.87
$Hf_3C_2O_2$	361.64	383.02	Sc_3N_2	193.44	184.62
$Mn_3C_2F_2$	219.86	285.26	$Sc_3N_2O_2$	223.98	241.43
$Mn_3C_2(OH)_2$	216.98	175.88	Ta_3N_2	266.29	306.07
$Mn_3C_2O_2$	235.79	248.64	Ti_3N_2	225.21	200.01
Nb_3C_2	262.11	231.29	$Ti_3N_2O_2$	367.84	364.59
$Nb_3C_2O_2$	366.21	370.28	V_3N_2	222.65	289.17
Sc_3C_2	145.83	182.45	$V_3N_2O_2$	338.78	228.41
$Sc_3C_2(OH)_2$	196.84	235.81	$W_3N_2(OH)_2$	511.29	522.99
Ta_3C_2	284.54	271.06	$Y_3N_2F_2$	212.68	237.97
$Ta_3C_2O_2$	385.02	458.63	$Y_3N_2(OH)_2$	206.89	246.24
Ti_3C_2	243.75	248.67	Y_3N_2	149.97	162.90
$Ti_3C_2F_2$	280.94	311.80	$Y_3N_2O_2$	174.65	173.84
$Ti_3C_2(OH)_2$	301.04	319.12	Zr_3N_2	235.83	214.47
$Ti_3C_2O_2$	328.27	374.73	$Zr_3N_2O_2$	368.14	317.93
V_3C_2	256.85	271.91			
$V_3C_2O_2$	342.37	382.29			
Y_3C_2	122.16	108.19			
$Y_3C_2F_2$	139.48	213.83			
$Y_3C_2(OH)_2$	108.58	202.16			
$Y_3C_2O_2$	59.89	164.11			
Zr_3C_2	240.23	249.75			
$Zr_3C_2F_2$	279.10	284.48			
$Zr_3C_2(OH)_2$	292.02	292.19			
$Zr_3C_2O_2$	329.18	356.89			

Supplementary Figures

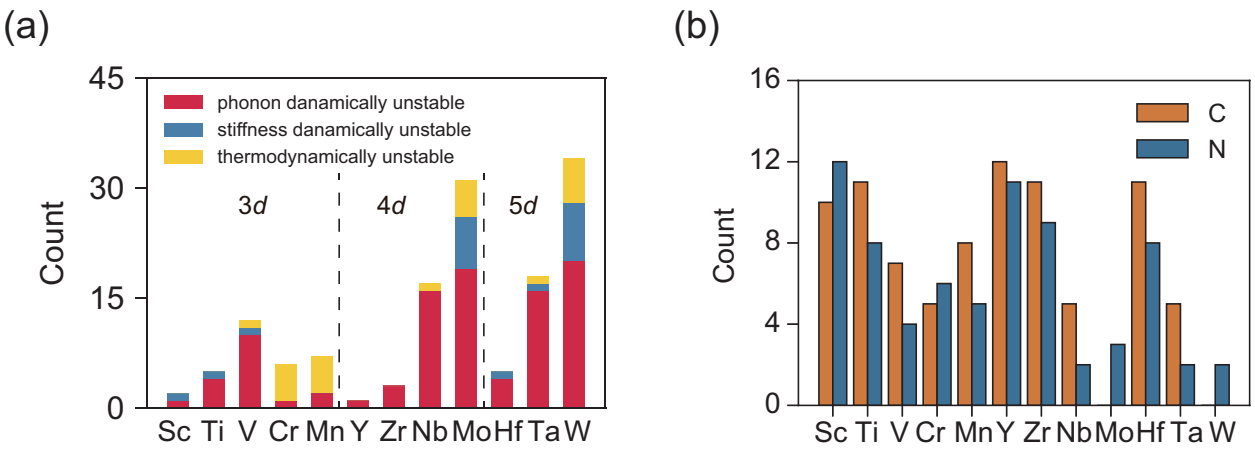

Fig. S1. (a) The number of filtered-out MXenes due to phonon dynamical, stiffness dynamical, and thermodynamic instability. We found that the amount of both phonon and stiffness dynamically unstable MXenes for Mn and Cr is abnormally small. (b) The number of stable carbide and nitride MXenes. Our results show that there are more carbide MXenes than nitride MXenes generally among all the stable MXenes (85 carbides and 72 nitrides). One point should be noted that W and Mo only have stable nitride forms.

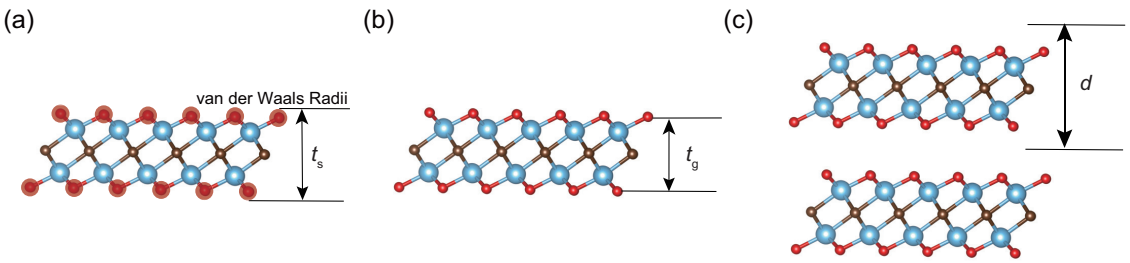

Fig. S2. The definitions of (a) (van der Waals) effective thickness and (b) geometric thickness and (c) interlayer distance (of the 3D bulk counterpart).

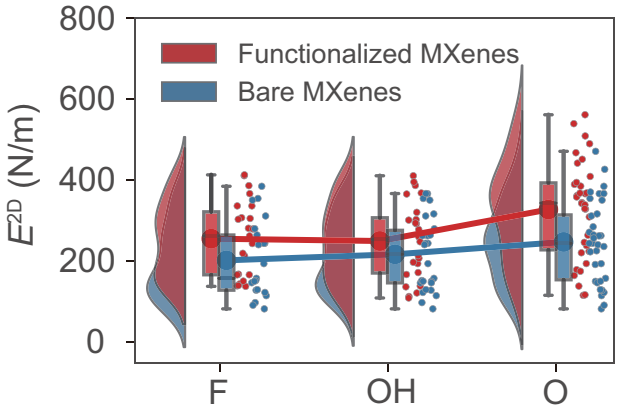

Fig. S3. A raincloud plot for the E^{2D} of bare MXenes and functionalized MXenes. The density plots indicate the data distribution and the boxplots show the quartiles (1st to 3rd quartile) and the median, respectively. The whiskers denote 1.5 times the interquartile range. Here the bare MXenes are only counted that these have functionalized counterparts. It can be seen that the improvement of OH and F groups are quite similar while is smaller than O groups.

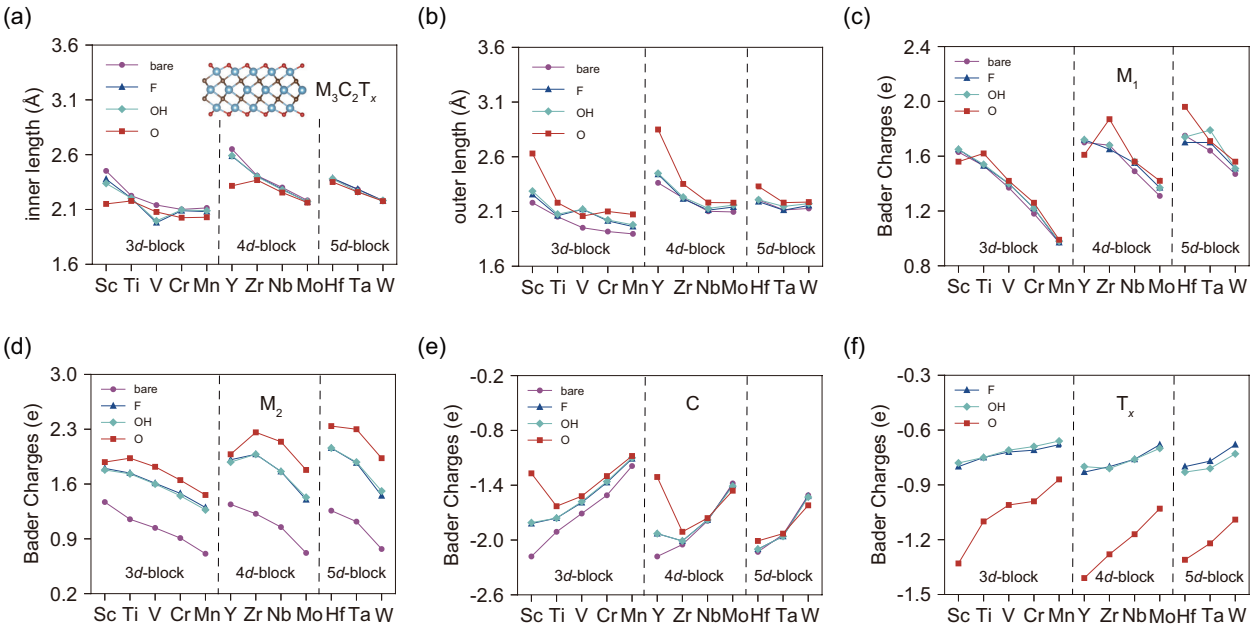

Fig. S4.(a) The *inner* M-C bond length and (b) the *outer* M-C bond length of $M_3C_2T_x$ MXenes, and the Bader charges of MXenes with and without surface terminations for (c) M_1, (d) M_2, (e) C, and (f) T_x.

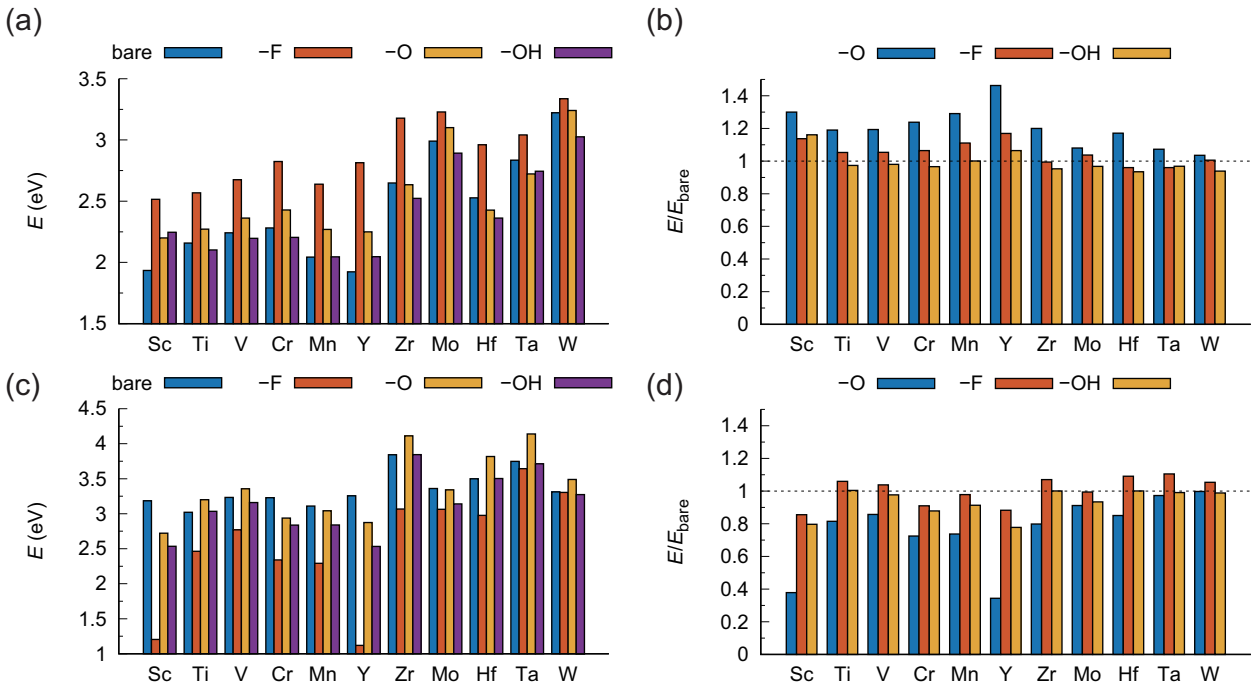

Fig. S5. (a) The bond strength (E) of inner M-C bonds calculated by crystal orbital Hamilton population (COHP).[S7] (b) The change of bond strength comparing to bare MXenes. (c)-(d) The results of outer M-C bonds.

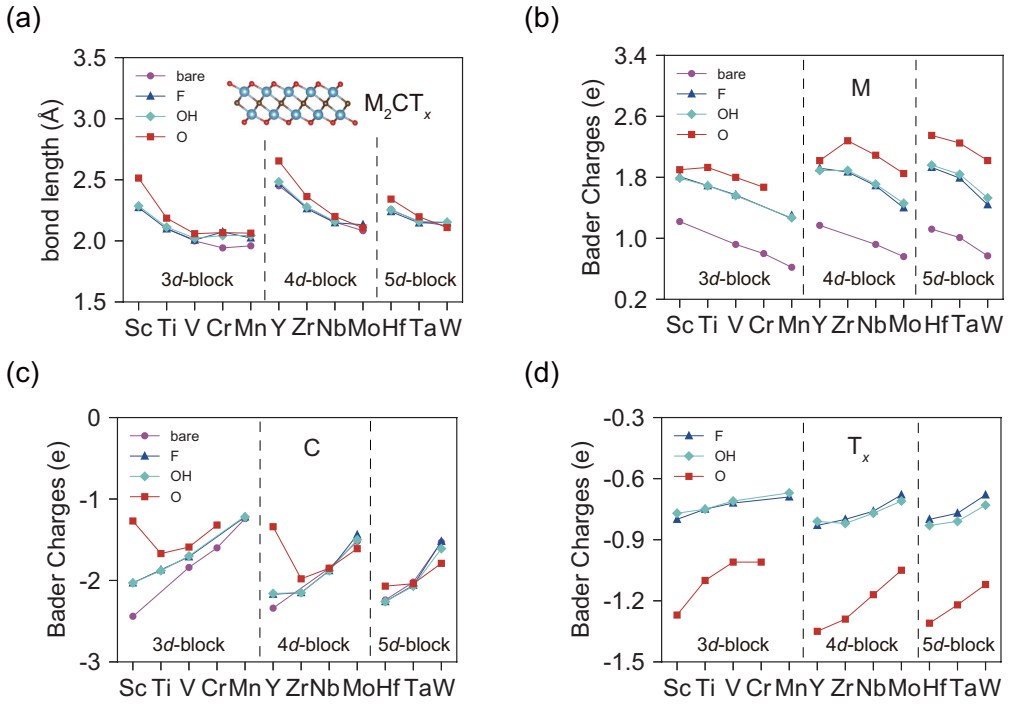

Fig. S6. (a) The M-C bond length of M_2CT_x MXenes, and the Bader charges of M_2CT_x MXenes with and without surface terminations for (b) M, (c) C, and (d) T_x. The Bader charges for T=-OH is the sum of O and H atoms.

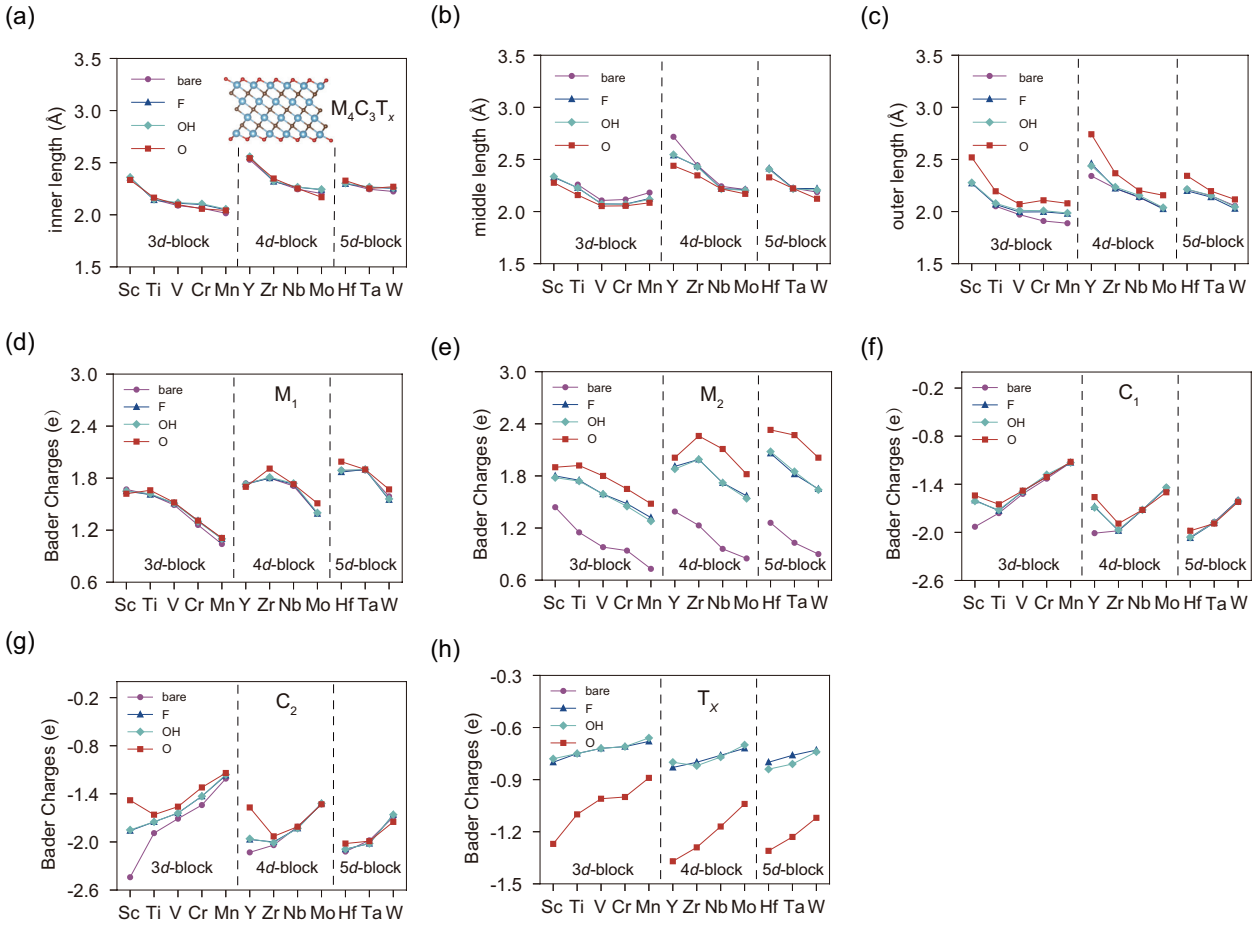

Fig. S7. (a) The inner bond length and (b) the middle bond length and (c) the outer bond length of $M_4C_3T_x$ MXenes. It can be seen that the surface terminations have a relatively large influence on the outer and middle bonds, but they have almost no effect on the inner bonds. and the Bader charges of MXenes with and without surface terminations for (d) M_1, (e) M_2, (f) C_1, (g) C_2, and (h) T_x.

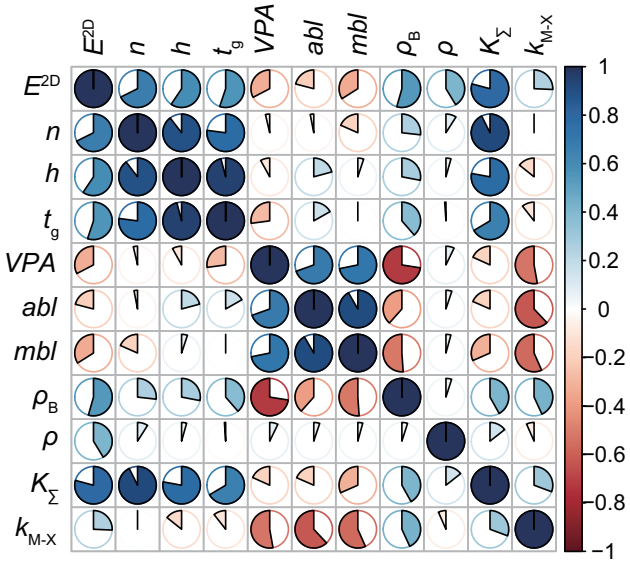

Fig. S8. Correlation plot for the associations between E^{2D} and the number of X layers n, the effective thickness h, the geometric thickness t_g, the volume per atom VPA, the average bond length abl, the minimum bond length mbl, the bond density ρ_B, the density ρ, the sum of the M-X and M-T_x bond stiffness K_Σ, and the bond stiffness of M-X bonds $k_{M\text{-}X}$. Blue and red colors indicate positive and negative correlations, and the filled fraction of the circle in each pie chart corresponds to the absolute value of the Pearson correlation coefficient. There are significant positive correlations between E^{2D} and n, h, t_g, ρ_B, and K_Σ, while VPA is negatively correlated with ρ_B.

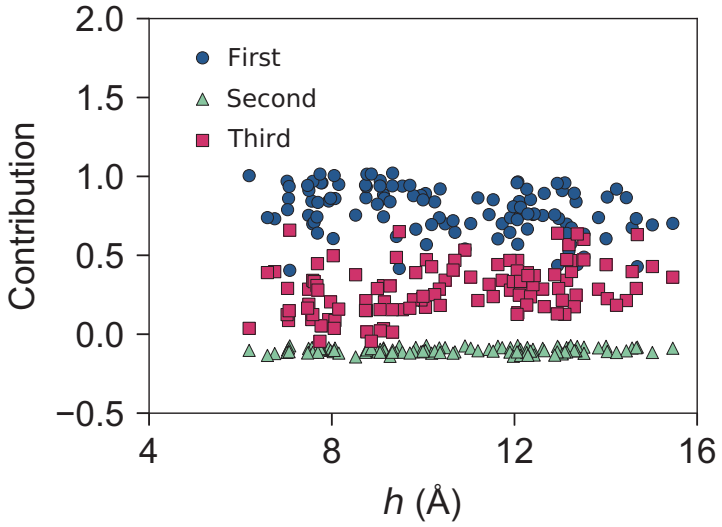

Fig. S9. The contribution of each term in the formula obtained by SISSO. The contribution of the second term to the E^{2D} ranges from -7.1% to -14.3%, while the contribution of the third term is quite small (below 7%) for some MXenes such as $Zr_2N(OH)_2$ and Ti_2NF_2, which lead to a smaller E^{2D} compared to their counterparts.

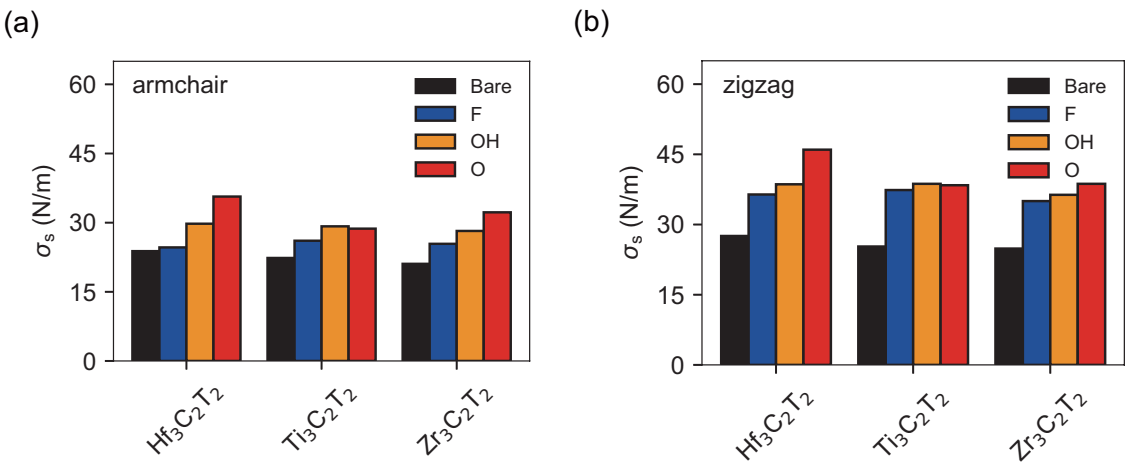

Fig. S10. The σ_s of $Hf_3C_2T_x$, $Ti_3C_2T_x$, $Zr_3C_2T_x$, and $Sc_3N_2T_x$ MXenes. We can find the MXenes with oxygen group generally shows the most enhancement of strength.

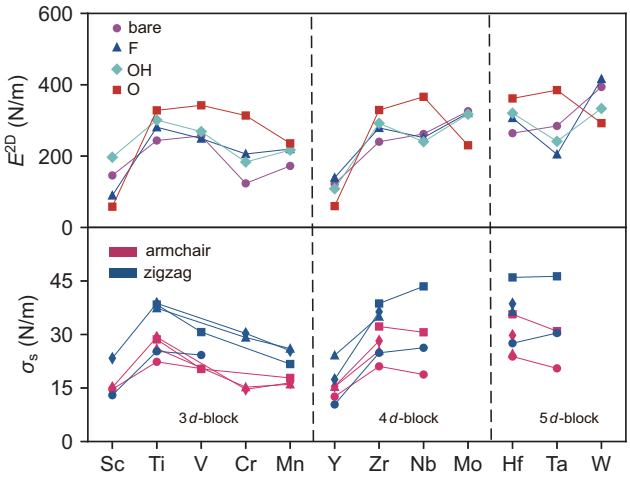

Fig. S11. The σ_s and E^{2D} of $M_3C_2T_x$. We can find the σ_s and E^{2D} exhibit similar periodicity.

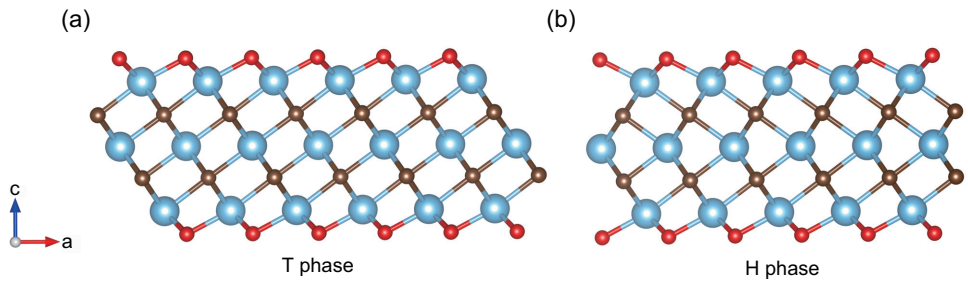

Fig. S12. Two structures of MXenes in C2DB. (a) T phase. (b) H phase. The T phase is widely investigated and could be directly fabricated by experiments while the H phase is also stable for some MXenes. Here the MXene is $Ti_3C_2O_2$.

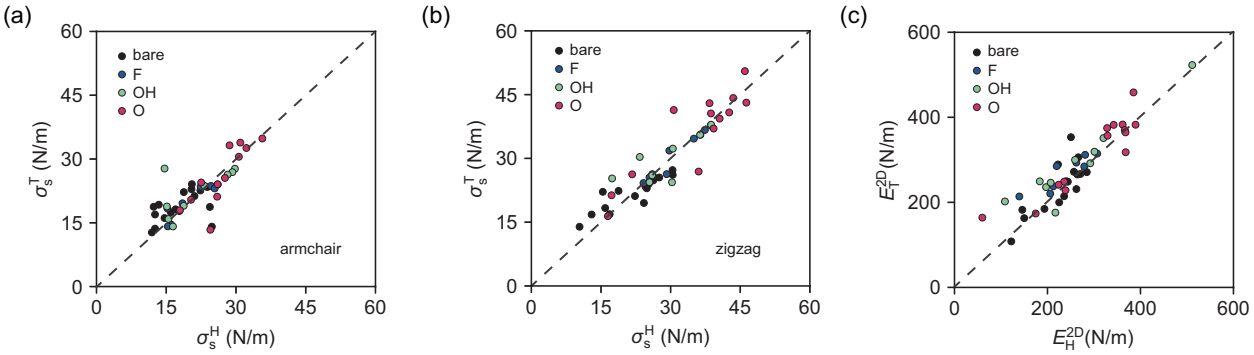

Fig. S13. Comparison of mechanical properties of T phase and H phase of $M_3X_2T_x$ MXenes (see Figure S12). (a) The σ_s in armchair direction and (b) in zigzag direction. (c) The E^{2D}. The results show that both σ_s and E^{2D} of these two phases are very close.

References

(S1) Gao, E.; Xu, Z. Thin-shell thickness of two-dimensional materials. *J. Appl. Mech.* **2015**, *82*, 121012.

(S2) Zha, X.-H.; Luo, K.; Li, Q.; Huang, Q.; He, J.; Wen, X.; Du, S. Role of the surface effect on the structural, electronic and mechanical properties of the carbide MXenes. *Europhys. Lett.* **2015**, *111*, 26007.

(S3) Hu, T.; Yang, J.; Li, W.; Wang, X.; Li, C. M. Quantifying the rigidity of 2D carbides (MXenes). *Phys. Chem. Chem. Phys.* **2020**, *22*, 2115–2121.

(S4) Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies*; CRC press, 2007.

(S5) Pyykkö, P.; Atsumi, M. Molecular single-bond covalent radii for elements 1–118. *Chem. Eur. J.* **2009**, *15*, 186–197.

(S6) Barsoum, M. *Fundamentals of Ceramics*; CRC press, 2019.

(S7) Dronskowski, R.; Bloechl, P. E. Crystal orbital Hamilton populations (COHP): energy-resolved visualization of chemical bonding in solids based on density-functional calculations. *J. Phys. Chem.* **1993**, *97*, 8617–8624.