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Covalent surface modifications and superconductivity of two-dimensional metal carbide MXenes

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Versatile chemical transformations of surface functional groups in 2D transition-metal carbides (MXenes) open up a new design space for this broad class of functional materials. We introduce a general strategy to install and remove surface groups by performing substitution and elimination reactions in molten inorganic salts. Successful synthesis of MXenes with O, NH, S, Cl, Se, Br, and Te surface terminations, as well as bare MXenes (no surface termination) was demonstrated. These MXenes show distinctive structural and electronic properties. For example, the surface groups control interatomic distances in the MXene lattice, and $Ti_{n+1}C_n$ ($n = 1, 2$) MXenes terminated with Te^{2-} ligands show a giant, (>18%) in-plane lattice expansion compared to the bulk TiC lattice. Nb_2C MXenes exhibited surface-group-dependent superconductivity.

Two-dimensional (2D) transition-metal carbides and nitrides (MXenes) (1) have been actively studied for applications in supercapacitors (2), batteries (3), electromagnetic interference shielding (4), composites (5, 6), and catalysts (7). MXenes are typically synthesized from the corresponding MAX phases (Fig. 1A), where M stands for the transition metal (e.g., Ti, Nb, Mo, V, W, etc.) and X stands for C or N, by selectively etching the main group element A (e.g., Al, Ga, Si, etc.). The etching is usually performed in aqueous HF solutions rendering MXenes terminated with a mixture of F, O, and OH functional groups, commonly denoted as T_x . These functional groups can be chemically modified, unlike the surfaces of other 2D materials such as graphene and transition-metal dichalcogenides. Recent theoretical studies predict that selective terminations of MXenes with different surface groups can lead to remarkable properties, such as opening or closing bandgap (8), room-temperature electron mobility exceeding 10^4 cm²/V·s (9), widely tunable work functions (10), half-metallicity, and 2D ferromagnetism (11). Covalent functionalization of MXene surfaces is expected to uncover new directions for rational engineering of 2D functional materials.

The surface of MXene sheets is defined during MAX phase etching. Electrochemical and hydrothermal methods have been recently applied for etching MAX phases without resorting to HF, but the use of aqueous solutions introduces a mixture of Cl, O, and OH surface groups (12, 13). The etching of Ti_3AlC_2 MAX phase in molten $ZnCl_2$ and several other Lewis acidic molten salts above 500°C results in $Ti_3C_2Cl_2$ MXene with a pure Cl termination (14, 15). Because etching of MAX phases in molten salts eliminates undesired oxidation and

hydrolysis, we used a variation of this method for synthesis of $Ti_3C_2Cl_2$, Ti_2CCl_2 , and Nb_2CCl_2 MXenes in $CdCl_2$ molten salt (figs. S1 to S5). Moreover, the use of Lewis acidic $CdBr_2$ allowed us to extend the molten salt etching route beyond chlorides to prepare the first Br-terminated $Ti_3C_2Br_2$ and Ti_2CBr_2 MXenes (Fig. 1, B and C, and figs. S6 and S7). The morphology, structure, and composition of all new MXenes were characterized using high-resolution scanning transmission electron microscopy (STEM), Raman spectroscopy, and a combination of x-ray methods, including energy-dispersive elemental mapping, diffraction (XRD), atomic pair distribution function (PDF), fluorescence (XRF), extended x-ray absorption fine structure (EXAFS), and photoelectron spectroscopy (XPS).

We show that Cl- and, especially, Br-terminated MXenes can efficiently engage in a new type of surface reactions where halide ions exchange for other atoms and functional groups. It enables unprecedented control over the surface chemistry, structure, and properties of MXene materials.

The transition-metal atoms from the outer layers of MXene sheets (Ti, Mo, Nb, V) form relatively weak M-Cl and M-Br bonds, in comparison to M-F and M-OH bonds typical for MXenes with T_x surface groups. This point can be demonstrated by the enthalpies of formation for $TiBr_4$ (−617 kJ mol^{−1}) and $TiCl_4$ (−804 kJ mol^{−1}) versus TiF_4 (−1649 kJ mol^{−1}), as well as by direct comparison of the bond energies (table S1). Strong Ti-F and Ti-O bonds make it difficult to perform any postsynthetic covalent surface modifications of MXenes (16). In contrast, Cl- and Br-terminated MXenes with labile surface bonding act as versatile synthons for further chemical transformations.

MXene surface exchange reactions typically require temperatures of 300° to 600°C, which are difficult to achieve using traditional solvents. Instead, we used molten alkali metal halides as solvents with unmatched high-temperature stability, high solubility of various ionic compounds, and wide electrochemical windows (17–19). For example, $\text{Ti}_3\text{C}_2\text{Br}_2$ MXene (Fig. 1B) dispersed in CsBr/KBr/LiBr eutectic (m.p. 236°C) reacted with Li_2Te and Li_2S to form new $\text{Ti}_3\text{C}_2\text{Te}$ (Fig. 1D and figs. S8 to S10) and $\text{Ti}_3\text{C}_2\text{S}$ (Fig. 1E and fig. S11) MXenes, respectively. The reactions of $\text{Ti}_3\text{C}_2\text{Cl}_2$ and $\text{Ti}_3\text{C}_2\text{Br}_2$ with Li_2Se , Li_2O , and NaNH_2 yielded $\text{Ti}_3\text{C}_2\text{Se}$, $\text{Ti}_3\text{C}_2\text{O}$, and $\text{Ti}_3\text{C}_2(\text{NH})$ MXenes, respectively (figs. S12 to S16). The multilayers of $\text{Ti}_3\text{C}_2\text{T}_n$ MXenes ($\text{T} = \text{Cl}, \text{S}, \text{NH}$) were further treated with *n*-butyl lithium resulting in Li^+ intercalated sheets (fig. S17) with a negative surface charge (Fig. 2A and fig. S18). Subsequent dispersion in a polar organic solvent such as *N*-methyl formamide (NMF) resulted in stable colloidal solutions of single-layer flakes (Fig. 2, B and C). Raman spectroscopy and elemental analysis show that delaminated MXenes preserve their original T_n surface groups (figs. S18 to S20). X-ray diffraction pattern of spin-coated films showed a single (0002) diffraction peak corresponding to the center-to-center separation (d) between two adjacent MXene sheets (Fig. 2D). The absence of $(10\bar{1}l)$ and $(11\bar{2}0)$ reflections is consistent with the alignment of delaminated flakes parallel to the substrate (20), which is also confirmed by the grazing incidence wide angle X-ray scattering patterns (fig. S19).

Similar covalent surface modifications were achieved for Ti_2CCl_2 , Ti_2CBr_2 , and Nb_2CCl_2 MXenes (Fig. 3A and figs. S21 to S34). The ability to perform surface exchange reactions on the thinnest MXenes demonstrated that the 2D sheets remained intact during all stages of the transformation. The exact metal/surface group elemental ratios for new MXenes were near the expected values as summarized in table S2.

The reactions of $\text{Ti}_3\text{C}_2\text{Br}_2$ and Ti_2CBr_2 with LiH at 300°C produced bare $\text{Ti}_3\text{C}_2\Box_2$ (Fig. 1F and fig. S14) and $\text{Ti}_2\text{C}\Box_2$ MXenes (fig. S21), where $\Box$ stands for the vacancy site. Because H-terminations are difficult to observe by STEM and other methods, we based this conclusion on the experimental value of the center-to-center distance between the Ti_3C_2 sheets (7.59 Å), which was substantially smaller than the theoretical prediction for $\text{Ti}_3\text{C}_2\text{H}_2$ MXene (8.26 Å) and near the smallest theoretically possible spacing of 7.23 Å (21). Because XPS showed reduction of Ti (fig. S16), this process could be formally described as a reductive-elimination of the hydride groups following the exchange reaction.

The chemical transformations of solids are generally impeded by slow diffusion, which severely limits the scope of synthesizable solid-state compounds (22). The complete exchange of surface groups in stacked MXenes is also expected to be kinetically cumbersome, especially if the entering ions

are bulkier than the leaving ones, as in the case of Cl^- (the ionic radius, $R_i = 1.81$ Å) exchanged for Te^{2-} ($R_i = 2.21$ Å). Counterintuitively, the reactions of $\text{Ti}_3\text{C}_2\text{Cl}_2$ and Ti_2CCl_2 MXenes with O^{2-} , S^{2-} , Se^{2-} , and Te^{2-} occurred at similar temperatures and with comparable reaction rates.

To understand this reactivity, we followed the evolution of the (0002) diffraction peak during surface exchange reactions. In the initial state, $\text{Ti}_3\text{C}_2\text{Cl}_2$ sheets formed stacks (fig. S1) with $d = 11.25$ Å, and the van der Waals (vdW) gap between MXenes is ~ 2.8 Å (table S3), which is smaller than the dimensions of entering or leaving ions. No measurable changes of the d -spacing were detected upon heating $\text{Ti}_3\text{C}_2\text{Cl}_2$ in KCl-LiCl molten salt to 500°C (fig. S35). However, heating MXene in the same molten salt but in the presence of Li_2O resulted in $d = 13.2$ Å (fig. S36), which corresponds to a 4.7 to 6.3 Å vdW gap between the surface atoms on adjacent MXene sheets, depending on the local surface terminations (see supplementary materials). A similar $d = 13.5$ Å was observed during reaction of $\text{Ti}_3\text{C}_2\text{Cl}_2$ MXene with Li_2Se , although with a larger disorder (fig. S37).

The unstacking of MXene sheets in molten salts greatly facilitated diffusion of ions and made MXene surfaces sterically accessible. The interaction potential of MXenes in a molten salt was likely defined by surface-templated ion layering which created an exponentially decaying oscillatory interaction energy (23). We speculate that the free energy released in the surface exchange reaction caused MXene sheets to “swell” into one of the energy minima and stay in this state during chemical transformation.

Moreover, the nature of the surface groups had an unusually strong impact on the MXene structure. The XRD patterns of $\text{Ti}_3\text{C}_2\text{T}_n$ and majority of Ti_2CT_n MXenes were modeled using the space group of the parent Ti_3AlC_2 and Ti_2AlC MAX phases ($P6_3/mmc$) (24). Due to the simpler structure of thinner Ti_2CT_n MXenes, their representative XRD patterns were further modeled using the Rietveld refinement. The fitting of the experimental Fourier-transformed EXAFS functions of Ti_2CT_n MXenes (fig. S26) demonstrated that the local structure around Ti atoms was consistent with the respective crystallographic models. The real space interatomic PDFs, $G(r)$, showed systematic shifts of Ti-T and Ti-Ti2 distances to larger values in S to Te series of Ti_2CT_n MXenes (Fig. 3, A and B, and fig. S27). In MXenes, Ti-Ti2 distance is equal to the nearest-neighbor distance between Ti atoms in the basal (0001) plane and hence it represents the in-plane a lattice constant (Fig. 3, B and C). For example, for Ti_2CBr_2 the Rietveld, EXAFS, and PDF methods converged on $a = 3.32$ Å. After exchanging Br^- for O^{2-} , the resultant MXene showed $a = 3.01$ Å, and the reaction with Te^{2-} produced MXene with $a = 3.62$ Å (Fig. 3C). The simulated XRD patterns of Ti_2CT_n MXenes (figs. S38 and S39) suggest that large Te^{2-} groups are likely positioned on top of the neighboring Ti atoms (Fig. 3D). This is distinctively

different from the MXenes with smaller surface groups which are positioned between hexagonally packed Ti surface atoms, on top of the opposite Ti atoms of the same Ti_2CT_n sheet (Fig. 3B), in accordance with recent theoretical studies (25).

The vdW radii and packing density of surface atoms had a huge effect on a (Fig. 3C), and fig. S40 compares these values with available computational predictions. For comparable ion radii, e.g., S versus Cl and Se versus Br, halido-terminated MXenes showed larger a , likely because of the smaller number of chalcogenide ions required for charge compensation of the MXene surface. To estimate the in-plane strain ($\varepsilon_{||}$) imposed on the titanium carbide lattice by surface groups in the new MXene species, we compared a to the nearest-neighbor distance between Ti atoms in (111) plane of bulk cubic TiC that is structurally equivalent to the basal (0001) MXene plane. For $\text{Ti}_3\text{C}_2\text{T}_n$ and Ti_2CT_n MXene families, the mixed ($\text{T}_x = \text{F}, \text{O}, \text{OH}$) and pure O^{2-} terminations resulted in a compressive $\varepsilon_{||}$. Bare ($\square$) and NH-terminated MXenes were nearly strain-free, whereas Cl, S, Se, and Br-terminated MXenes all had tensile $\varepsilon_{||}$. The thinner Ti_2CT_n MXenes had, on average, a slightly larger in-plane expansion or contraction with respect to the bulk TiC lattice, compared to the thicker $\text{Ti}_3\text{C}_2\text{T}_n$ MXenes. The Ti_2CTe MXene (Fig. 3, A and C, and fig. S24) had the largest magnitude of tensile $\varepsilon_{||}$ of 18.2% in accordance with Te^{2-} having the largest vdW radius among all groups used in this study. This degree of lattice expansion in a crystalline solid is very unusual. For comparison, the lattice of bulk TiC expands by “only” 2.5% when heated from room temperature to 2700°C (26).

Since the out-of-plane c lattice constant is strongly affected by the intercalation of ions and solvent molecules between MXene sheets (27), we used high-resolution STEM images to assess the distances between the Ti planes along the c axis of the unit cell (table S3). The magnitude of the out-of-plane strain in the MXene core ($\varepsilon_{\perp}$) was calculated by referencing experimental distances between Ti planes inside the MXene sheets ($M_{\perp}$) to the distance between the (111) planes of bulk TiC (table S3). Figure 3E shows that the expansion of the a -lattice parameter in $\text{Ti}_3\text{C}_2\text{T}_n$ MXenes functionalized with S, Cl, Se, Br, and Te atoms was accompanied by the corresponding contraction of the Ti_3C_2 layers along the c axis.

This observation is consistent with the behavior of the Ti_3C_2 layers as an elastic 2D sheet under tensile stress imposed by the surface atoms (Fig. 3E). The Poisson effect can account for the relations between the stress and the strain components reflected by observed changes of a and $M_{\perp}$ distances. Unfortunately, our atomic-resolution STEM images of MXenes measured $M_{\perp}$ values with relatively large error bars (caused by projection effects and bending of the MXene sheets), which complicated an accurate estimation of the Poisson's ratio (ν) for new MXenes. A simple elastic model (see supplementary materials) applied to $\text{Ti}_3\text{C}_2\text{T}_n$ yields

$\nu \sim 0.22$ for $\text{T} = \text{S}$ and Br , which is comparable to the recently predicted ν value for $\text{Ti}_3\text{C}_2\text{T}_x$ (21). However, $\text{Ti}_3\text{C}_2\text{Te}$ showed $\nu = 0.16 \pm 0.06$, likely caused by the additional stiffening of the Ti_3C_2 layers under very large in-plane stress.

The above examples show that the composition and structure of MXenes can be engineered with previously unattainable versatility. Chemical functionalization of MXene surfaces is expected to impact nearly every property of these materials, and we found that the surface groups defined the nature of electronic transport in Nb_2CT_n MXenes. Figure 4, A and B, shows temperature-dependent four-probe resistivity (ρ) measured on cold-pressed pellets of Nb_2CT_n ($\text{T} = \square, \text{Cl}, \text{O}, \text{S}, \text{Se}$) MXenes (fig. S41), all synthesized by the procedures described above. Figure 4A also compares the conductivity of the parent Nb_2AlC MAX phase with that of Nb_2CCl_2 MXene. Above 30 K, both MAX phase and MXene samples showed similar specific resistivity, which decreased when the sample is cooled. This temperature dependence is often associated with metallic conductivity. The ultraviolet photoelectron spectroscopy (UPS) confirmed nonzero density of electronic states at the Fermi energy E_F (fig. S42), which is also consistent with a metallic state.

However, when the Nb_2CCl_2 MXene was cooled below 30 K, the resistivity started increasing, possibly indicating the onset of localization. A sharp drop of resistivity by several orders of magnitude occurred at a critical temperature $T_c \sim 6.0$ K (Fig. 4A), which is reminiscent of a superconductive transition. The magnetic susceptibility measurements showed the development of a strong diamagnetism below 6.3 K that we interpreted as the Meissner effect (Fig. 4A). From the magnitude of zero-field-cooled data at 1.8 K, we estimated the lower bound for the superconducting volume fraction of Nb_2CCl_2 MXene as $\sim 35\%$. Consistent with superconductivity, the transition broadened, and T_c shifted to lower temperatures with the application of external magnetic field (Fig. 4B and fig. S43). In contrast, the parent Nb_2AlC MAX phase exhibited normal metal behavior down to the lowest measured temperature (1.8 K), which is consistent with $T_c \sim 0.44$ K previously reported for Nb_2AlC (28). For reference, Nb_2CT_x MXene with mixed O, OH, F termination prepared by the traditional aqueous HF etching route shows two orders of magnitude higher resistivity and no superconductivity (fig. S44) (29).

In contrast to Nb_2CCl_2 MXene, the resistivity of MXenes terminated with chalcogenide ions (O, S, Se) gradually increased when the sample was cooled (Fig. 4B), consistent with the activated transport regime. Given that UPS showed the finite density of states at E_F in Nb_2CS_2 (fig. S42), we hypothesized that the localization was controlled by the tunneling rates for charge carriers between metallic MXene sheets. The oxo-terminated Nb_2CT_n MXene showed the highest resistivity, and the seleno-terminated MXene the lowest resistivity, consistent with the reduction of the tunneling barrier

heights between the MXene sheets.

In the low-temperature region, we observed superconducting transitions in Nb₂CS₂ ($T_c \sim 6.4$ K), Nb₂CSe ($T_c \sim 4.5$ K), and Nb₂C(NH) ($T_c \sim 7.1$ K, fig. S34), whereas Nb₂CO_x did not enter the superconducting state (fig. S45). In granular metals, the development of macroscopic superconductivity can be suppressed by weak coupling of individual superconducting domains, which is also reflected by the high resistivity in the normal state (30). The upper critical field ($\mu_0 H_{c2}$) showed a strong dependence on the surface functional group. For example, Nb₂CS₂ MXene exhibited higher $\mu_0 H_{c2}$ compared to Nb₂CCl₂ (Fig. 4B, inset, and fig. S46). Interestingly, bare Nb₂C₂ MXenes showed no transition to the superconducting state down to 1.8 K (Fig. 4B). Thus, surface groups were not spectators but active contributors to the MXene superconductivity, which is consistent with surface groups affecting biaxial lattice strain, phonon frequencies, and the strength of electron-phonon coupling.

The MXene exchange reactions represent an exciting counter example to traditional perception of solids as hard to post-synthetically modify entities. We showed that chemical bonds inside an extended MXene stack can be rationally designed in a way more typical for molecular compounds. Other MXene structures could be enabled by the combinations of etching and substitution reactions using Lewis acidic and Lewis basic molten salts, respectively.

REFERENCES AND NOTES

1. B. Anasori, M. R. Lukatskaya, Y. Gogotsi, 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* **2**, 16098 (2017). [doi:10.1038/natrevmats.2016.98](https://doi.org/10.1038/natrevmats.2016.98)
2. Y. Xia, T. S. Mathis, M.-Q. Zhao, B. Anasori, A. Dang, Z. Zhou, H. Cho, Y. Gogotsi, S. Yang, Thickness-independent capacitance of vertically aligned liquid-crystalline MXenes. *Nature* **557**, 409–412 (2018). [doi:10.1038/s41586-018-0109-z](https://doi.org/10.1038/s41586-018-0109-z) [Medline](#)
3. C. J. Zhang, S.-H. Park, A. Seral-Ascaso, S. Barwich, N. McEvoy, C. S. Boland, J. N. Coleman, Y. Gogotsi, V. Nicolosi, High capacity silicon anodes enabled by MXene viscous aqueous ink. *Nat. Commun.* **10**, 849 (2019). [doi:10.1038/s41467-019-08383-y](https://doi.org/10.1038/s41467-019-08383-y) [Medline](#)
4. F. Shahzad, M. Alhabeab, C. B. Hatter, B. Anasori, S. Man Hong, C. M. Koo, Y. Gogotsi, Electromagnetic interference shielding with 2D transition metal carbides (MXenes). *Science* **353**, 1137–1140 (2016). [doi:10.1126/science.aag2421](https://doi.org/10.1126/science.aag2421) [Medline](#)
5. V. Kamysbayev, N. M. James, A. S. Filatov, V. Srivastava, B. Anasori, H. M. Jaeger, Y. Gogotsi, D. V. Talapin, Colloidal gelation in liquid metals enables functional nanocomposites of 2D metal carbides (MXenes) and lightweight metals. *ACS Nano* **13**, 12415–12424 (2019). [doi:10.1021/acs.nano.9b06207](https://doi.org/10.1021/acs.nano.9b06207) [Medline](#)
6. J. Guo, B. Legum, B. Anasori, K. Wang, P. Lelyukh, Y. Gogotsi, C. A. Randall, Cold sintered ceramic nanocomposites of 2D MXene and zinc oxide. *Adv. Mater.* **30**, e1801846 (2018). [doi:10.1002/adma.201801846](https://doi.org/10.1002/adma.201801846) [Medline](#)
7. J. Zhang, Y. Zhao, X. Guo, C. Chen, C.-L. Dong, R.-S. Liu, C.-P. Han, Y. Li, Y. Gogotsi, G. Wang, Single platinum atoms immobilized on an MXene as an efficient catalyst for the hydrogen evolution reaction. *Nat. Catal.* **1**, 985–992 (2018). [doi:10.1038/s41929-018-0195-1](https://doi.org/10.1038/s41929-018-0195-1)
8. M. Khazaei, M. Arai, T. Sasaki, C.-Y. Chung, N. S. Venkataramanan, M. Estili, Y. Sakka, Y. Kawazoe, Novel electronic and magnetic properties of two-dimensional transition metal carbides and nitrides. *Adv. Funct. Mater.* **23**, 2185–2192 (2013). [doi:10.1002/adfm.201202502](https://doi.org/10.1002/adfm.201202502)
9. L. Zhou, Y. Zhang, Z. Zhuo, A. J. Neukirch, S. Tretiak, Interlayer-decoupled Sc-based MXene with high carrier mobility and strong light-harvesting ability. *J. Phys. Chem. Lett.* **9**, 6915–6920 (2018). [doi:10.1021/acs.jpclett.8b03077](https://doi.org/10.1021/acs.jpclett.8b03077) [Medline](#)
10. Y. Liu, H. Xiao, W. A. Goddard 3rd, Schottky-barrier-free contacts with two-dimensional semiconductors by surface-engineered MXenes. *J. Am. Chem. Soc.* **138**, 15853–15856 (2016). [doi:10.1021/jacs.6b10834](https://doi.org/10.1021/jacs.6b10834) [Medline](#)
11. C. Si, J. Zhou, Z. Sun, Half-metallic ferromagnetism and surface functionalization-induced metal–insulator transition in graphene-like two-dimensional Cr₂C crystals. *ACS Appl. Mater. Interfaces* **7**, 17510–17515 (2015). [doi:10.1021/acsami.5b05401](https://doi.org/10.1021/acsami.5b05401) [Medline](#)
12. S.-Y. Pang, Y.-T. Wong, S. Yuan, Y. Liu, M.-K. Tsang, Z. Yang, H. Huang, W.-T. Wong, J. Hao, Universal strategy for HF-free facile and rapid synthesis of two-dimensional MXenes as multifunctional energy materials. *J. Am. Chem. Soc.* **141**, 9610–9616 (2019). [doi:10.1021/jacs.9b02578](https://doi.org/10.1021/jacs.9b02578) [Medline](#)
13. T. Li, L. Yao, Q. Liu, J. Gu, R. Luo, J. Li, X. Yan, W. Wang, P. Liu, B. Chen, W. Zhang, W. Abbas, R. Naz, D. Zhang, Fluorine-free synthesis of high-purity Ti₃C₂T_x (T=OH, O) via alkali treatment. *Angew. Chem. Int. Ed.* **57**, 6115–6119 (2018). [doi:10.1002/anie.201800887](https://doi.org/10.1002/anie.201800887) [Medline](#)
14. M. Li, J. Lu, K. Luo, Y. Li, K. Chang, K. Chen, J. Zhou, J. Rosen, L. Hultman, P. Eklund, P. O. Å. Persson, S. Du, Z. Chai, Z. Huang, Q. Huang, Element replacement approach by reaction with Lewis acidic molten salts to synthesize nanolaminated MAX phases and MXenes. *J. Am. Chem. Soc.* **141**, 4730–4737 (2019). [doi:10.1021/jacs.9b00574](https://doi.org/10.1021/jacs.9b00574) [Medline](#)
15. Y. Li, H. Shao, Z. Lin, J. Lu, L. Liu, B. Duployer, P. O. Å. Persson, P. Eklund, L. Hultman, M. Li, K. Chen, X. H. Zha, S. Du, P. Rozier, Z. Chai, E. Raymundo-Piñero, P. L. Taberna, P. Simon, Q. Huang, A general Lewis acidic etching route for preparing MXenes with enhanced electrochemical performance in non-aqueous electrolyte. *Nat. Mater.* (2020). [Medline](#)
16. D. Kim, T. Y. Ko, H. Kim, G. H. Lee, S. Cho, C. M. Koo, Nonpolar organic dispersion of 2D Ti₃C₂T_x MXene flakes via simultaneous interfacial chemical grafting and phase transfer method. *ACS Nano* **13**, 13818–13828 (2019). [doi:10.1021/acs.nano.9b04088](https://doi.org/10.1021/acs.nano.9b04088) [Medline](#)
17. V. Srivastava, V. Kamysbayev, L. Hong, E. Dunietz, R. F. Klie, D. V. Talapin, Colloidal chemistry in molten salts: Synthesis of luminescent In_{1-x}Ga_xP and In_{1-x}Ga_xAs quantum dots. *J. Am. Chem. Soc.* **140**, 12144–12151 (2018). [doi:10.1021/jacs.8b06971](https://doi.org/10.1021/jacs.8b06971) [Medline](#)
18. A. Dash, R. Vaßen, O. Guillon, J. Gonzalez-Julian, Molten salt shielded synthesis of oxidation prone materials in air. *Nat. Mater.* **18**, 465–470 (2019). [doi:10.1038/s41563-019-0328-1](https://doi.org/10.1038/s41563-019-0328-1) [Medline](#)
19. X. Liu, N. Fechner, M. Antonietti, Salt melt synthesis of ceramics, semiconductors and carbon nanostructures. *Chem. Soc. Rev.* **42**, 8237–8265 (2013). [doi:10.1039/C3CS60159F](https://doi.org/10.1039/C3CS60159F) [Medline](#)
20. M. Ghidui, M. W. Barsoum, The {110} reflection in X-ray diffraction of MXene films: Misinterpretation and measurement via non-standard orientation. *J. Am. Ceram. Soc.* **100**, 5395–5399 (2017). [doi:10.1111/jace.15124](https://doi.org/10.1111/jace.15124)
21. Z. H. Fu, Q. F. Zhang, D. Legut, C. Si, T. C. Germann, T. Lookman, S. Y. Du, J. S. Francisco, R. F. Zhang, Stabilization and strengthening effects of functional groups in two-dimensional titanium carbide. *Phys. Rev. B* **94**, 104103 (2016). [doi:10.1103/PhysRevB.94.104103](https://doi.org/10.1103/PhysRevB.94.104103)
22. M. Jansen, A concept for synthesis planning in solid-state chemistry. *Angew. Chem. Int. Ed.* **41**, 3746–3766 (2002). [doi:10.1002/1521-3773\(20021018\)41:20<3746::AID-ANIE3746>3.0.CO;2-2](https://doi.org/10.1002/1521-3773(20021018)41:20<3746::AID-ANIE3746>3.0.CO;2-2) [Medline](#)
23. H. Zhang, K. Dasbiswas, N. B. Ludwig, G. Han, B. Lee, S. Vaikuntanathan, D. V. Talapin, Stable colloids in molten inorganic salts. *Nature* **542**, 328–331 (2017). [doi:10.1038/nature21041](https://doi.org/10.1038/nature21041) [Medline](#)
24. M. Sokol, V. Natu, S. Kota, M. W. Barsoum, On the chemical diversity of the MAX phases. *Trends Chem.* **1**, 210–223 (2019). [doi:10.1016/j.trechm.2019.02.016](https://doi.org/10.1016/j.trechm.2019.02.016)
25. Y. Qin, X.-H. Zha, X. Bai, K. Luo, Q. Huang, Y. Wang, S. Du, Structural, mechanical and electronic properties of two-dimensional chlorine-terminated transition metal carbides and nitrides. *J. Phys. Condens. Matter* **32**, 135302 (2019). [doi:10.1088/1361-648X/ab6048](https://doi.org/10.1088/1361-648X/ab6048) [Medline](#)
26. J. H. Richardson, Thermal expansion of three group IVA carbides to 2700°C. *J. Am. Ceram. Soc.* **48**, 497–499 (1965). [doi:10.1111/j.1151-2916.1965.tb14647.x](https://doi.org/10.1111/j.1151-2916.1965.tb14647.x)
27. O. Mashtalir, M. Naguib, V. N. Mochalin, Y. Dall'Agnese, M. Heon, M. W. Barsoum, Y. Gogotsi, Intercalation and delamination of layered carbides and carbonitrides. *Nat. Commun.* **4**, 1716 (2013). [doi:10.1038/ncomms2664](https://doi.org/10.1038/ncomms2664) [Medline](#)
28. T. H. Scabarozi, J. Roche, A. Rosenfeld, S. H. Lim, L. Salamanca-Riba, G. Yong, I. Takeuchi, M. W. Barsoum, J. D. Hettinger, S. E. Lofland, Synthesis and

- characterization of Nb₂AlC thin films. *Thin Solid Films* **517**, 2920–2923 (2009). [doi:10.1016/j.tsf.2008.12.047](https://doi.org/10.1016/j.tsf.2008.12.047)
29. J. Halim, I. Persson, E. J. Moon, P. Kühne, V. Darakchieva, P. O. Å. Persson, P. Eklund, J. Rosen, M. W. Barsoum, Electronic and optical characterization of 2D Ti₃C₂ and Nb₂C (MXene) thin films. *J. Phys. Condens. Matter* **31**, 165301 (2019). [doi:10.1088/1361-648X/ab00a2](https://doi.org/10.1088/1361-648X/ab00a2) [Medline](#)
 30. I. S. Beloborodov, A. V. Lopatin, V. M. Vinokur, K. B. Efetov, Granular electronic systems. *Rev. Mod. Phys.* **79**, 469–518 (2007). [doi:10.1103/RevModPhys.79.469](https://doi.org/10.1103/RevModPhys.79.469)
 31. A. N. Beecher, X. Yang, J. H. Palmer, A. L. LaGrassa, P. Juhas, S. J. L. Billinge, J. S. Owen, Atomic structures and gram scale synthesis of three tetrahedral quantum dots. *J. Am. Chem. Soc.* **136**, 10645–10653 (2014). [doi:10.1021/ja503590h](https://doi.org/10.1021/ja503590h) [Medline](#)
 32. M. Alhabeb, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin, Y. Gogotsi, Guidelines for synthesis and processing of two-dimensional titanium carbide (Ti₃C₂T_x MXene). *Chem. Mater.* **29**, 7633–7644 (2017). [doi:10.1021/acs.chemmater.7b02847](https://doi.org/10.1021/acs.chemmater.7b02847)
 33. M. Naguib, J. Halim, J. Lu, K. M. Cook, L. Hultman, Y. Gogotsi, M. W. Barsoum, New two-dimensional niobium and vanadium carbides as promising materials for Li-ion batteries. *J. Am. Chem. Soc.* **135**, 15966–15969 (2013). [doi:10.1021/ja405735d](https://doi.org/10.1021/ja405735d) [Medline](#)
 34. P. Stephens, Phenomenological model of anisotropic peak broadening in powder diffraction. *J. Appl. Cryst.* **32**, 281–289 (1999). [doi:10.1107/S0021889898006001](https://doi.org/10.1107/S0021889898006001)
 35. E. B. Deeva, A. Kurlov, P. M. Abdala, D. Lebedev, S. M. Kim, C. P. Gordon, A. Tsoukalou, A. Fedorov, C. R. Müller, In situ XANES/XRD study of the structural stability of two-dimensional molybdenum carbide Mo₂CT_x: Implications for the catalytic activity in the water–gas shift reaction. *Chem. Mater.* **31**, 4505–4513 (2019). [doi:10.1021/acs.chemmater.9b01105](https://doi.org/10.1021/acs.chemmater.9b01105)
 36. B. H. Toby, R. B. Von Dreele, GSAS-II: The genesis of a modern open-source all purpose crystallography software package. *J. Appl. Cryst.* **46**, 544–549 (2013). [doi:10.1107/S0021889813003531](https://doi.org/10.1107/S0021889813003531)
 37. X. Qiu, J. W. Thompson, S. J. L. Billinge, PDFGetX2: A Gui-driven program to obtain the pair distribution function from X-ray powder diffraction data. *J. Appl. Cryst.* **37**, 678 (2004). [doi:10.1107/S0021889804011744](https://doi.org/10.1107/S0021889804011744)
 38. B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **12**, 537–541 (2005). [doi:10.1107/S0909049505012719](https://doi.org/10.1107/S0909049505012719) [Medline](#)
 39. J. J. Rehr, R. C. Albers, Theoretical approaches to X-ray absorption fine structure. *Rev. Mod. Phys.* **72**, 621–654 (2000). [doi:10.1103/RevModPhys.72.621](https://doi.org/10.1103/RevModPhys.72.621)
 40. J. Halim, M. R. Lukatskaya, K. M. Cook, J. Lu, C. R. Smith, L.-Å. Näslund, S. J. May, L. Hultman, Y. Gogotsi, P. Eklund, M. W. Barsoum, Transparent conductive two-dimensional titanium carbide epitaxial thin films. *Chem. Mater.* **26**, 2374–2381 (2014). [doi:10.1021/cm500641a](https://doi.org/10.1021/cm500641a) [Medline](#)
 41. A. Sarycheva, Y. Gogotsi, Raman spectroscopy analysis of the structure and surface chemistry of Ti₃C₂T_x MXene. *Chem. Mater.* **32**, 3480–3488 (2020). [doi:10.1021/acs.chemmater.0c00359](https://doi.org/10.1021/acs.chemmater.0c00359)
 42. N. Zhang, Y. Hong, S. Yazdanparast, M. Asle Zaeem, Superior structural, elastic and electronic properties of 2D titanium nitride MXenes over carbide MXenes: A comprehensive first principles study. *2D Materials* **5**, 045004 (2018). [doi:10.1088/2053-1583/aa8fb3](https://doi.org/10.1088/2053-1583/aa8fb3)
 43. Y.-R. Luo, *Comprehensive Handbook of Chemical Bond Energies* (CRC Press, 2007).
 44. M. A. Hope, A. C. Forse, K. J. Griffith, M. R. Lukatskaya, M. Ghidui, Y. Gogotsi, C. P. Grey, NMR reveals the surface functionalisation of Ti₃C₂ MXene. *Phys. Chem. Chem. Phys.* **18**, 5099–5102 (2016). [doi:10.1039/C6CP00330C](https://doi.org/10.1039/C6CP00330C) [Medline](#)
 45. J. Palisaitis, I. Persson, J. Halim, J. Rosen, P. O. Å. Persson, On the structural stability of MXene and the role of transition metal adatoms. *Nanoscale* **10**, 10850–10855 (2018). [doi:10.1039/C8NR01986J](https://doi.org/10.1039/C8NR01986J) [Medline](#)
 46. I. Persson, L.-Å. Näslund, J. Halim, M. W. Barsoum, V. Darakchieva, J. Palisaitis, J. Rosen, P. O. Å. Persson, On the organization and thermal behavior of functional groups on Ti₃C₂ MXene surfaces in vacuum. *2D Materials* **5**, 015002 (2017). [doi:10.1088/2053-1583/aa89cd](https://doi.org/10.1088/2053-1583/aa89cd)
 47. S. I. Troyanov, E. M. Snigireva, V. B. Rybakov, X-ray diffraction study of phase transition in alpha-TiCl₃. *Zh. Neorg. Khim.* **36**, 1117–1122 (1991).
 48. S. I. Troyanov, V. M. Ionov, V. B. Rybakov, Synthesis and crystal structures of TiBr₄, TiBr₃ and Ti(AlBr₄)₂. *Zh. Neorg. Khim.* **35**, 882–887 (1990).
 49. P. Ehrlich, W. Gutsche, H.-J. Seifert, Darstellung und kristallstruktur von titandibromid. *Z. Anorg. Allg. Chem.* **312**, 80–86 (1961). [doi:10.1002/zaac.19613120112](https://doi.org/10.1002/zaac.19613120112)
 50. T. Hu, J. Wang, H. Zhang, Z. Li, M. Hu, X. Wang, Vibrational properties of Ti₃C₂ and Ti₃C₂T₂ (T = O, F, OH) monosheets by first-principles calculations: A comparative study. *Phys. Chem. Chem. Phys.* **17**, 9997–10003 (2015). [doi:10.1039/C4CP05666C](https://doi.org/10.1039/C4CP05666C) [Medline](#)
 51. N. C. Saha, H. G. Tompkins, Titanium nitride oxidation chemistry: An X-ray photoelectron spectroscopy study. *J. Appl. Phys.* **72**, 3072–3079 (1992). [doi:10.1063/1.351465](https://doi.org/10.1063/1.351465)
 52. P. Ehrlich, Über titanselenide und -telluride. *Zeitschrift für anorganische Chemie* **260**, 1–18 (1949). [doi:10.1002/zaac.19492600102](https://doi.org/10.1002/zaac.19492600102)
 53. M. Onoda, H. Wada, The titanium-sulphur system: Structures of Ti₆S₉(18H) and Ti_{8.2}S₁₁(33R) and the unit cells of 45R and 57R types of titanium sulphide. *J. Less Common Met.* **132**, 195–207 (1987). [doi:10.1016/0022-5088\(87\)90576-5](https://doi.org/10.1016/0022-5088(87)90576-5)
 54. T. Hu, M. Hu, B. Gao, W. Li, X. Wang, Screening surface structure of MXenes by high-throughput computation and vibrational spectroscopic confirmation. *J. Phys. Chem. C* **122**, 18501–18509 (2018). [doi:10.1021/acs.jpcc.8b04427](https://doi.org/10.1021/acs.jpcc.8b04427)
 55. J. Lu, I. Persson, H. Lind, J. Palisaitis, M. Li, Y. Li, K. Chen, J. Zhou, S. Du, Z. Chai, Z. Huang, L. Hultman, P. Eklund, J. Rosen, Q. Huang, P. O. Å. Persson, Ti_{n+1}C_n MXenes with fully saturated and thermally stable Cl terminations. *Nanoscale Adv.* **1**, 3680–3685 (2019). [doi:10.1039/C9NA00324J](https://doi.org/10.1039/C9NA00324J)
 56. G. R. Berdiyrov, Optical properties of functionalized Ti₃C₂T₂ (T = F, O, OH) MXene: First-principles calculations. *AIP Adv.* **6**, 055105 (2016). [doi:10.1063/1.4948799](https://doi.org/10.1063/1.4948799)
 57. Q. Meng, J. Ma, Y. Zhang, Z. Li, C. Zhi, A. Hu, J. Fan, The S-functionalized Ti₃C₂ MXene as a high capacity electrode material for Na-ion batteries: A DFT study. *Nanoscale* **10**, 3385–3392 (2018). [doi:10.1039/C7NR07649F](https://doi.org/10.1039/C7NR07649F) [Medline](#)
 58. D. Wang, F. Li, R. Lian, J. Xu, D. Kan, Y. Liu, G. Chen, Y. Gogotsi, Y. Wei, A general atomic surface modification strategy for improving anchoring and electrocatalysis behavior of Ti₃C₂T₂ MXene in lithium–sulfur batteries. *ACS Nano* **13**, 11078–11086 (2019). [doi:10.1021/acs.nano.9b03412](https://doi.org/10.1021/acs.nano.9b03412) [Medline](#)
 59. R. Ibragimova, M. J. Puska, H.-P. Komsa, pH-dependent distribution of functional groups on titanium-based MXenes. *ACS Nano* **13**, 9171–9181 (2019). [doi:10.1021/acs.nano.9b03511](https://doi.org/10.1021/acs.nano.9b03511) [Medline](#)

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submitted by the University of Chicago that covers surface modifications of MXenes and methods. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper or the supplementary materials.

SUPPLEMENTARY MATERIALS

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Materials and Methods

Supplementary Text

Figs. S1 to S46

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Fig. 1. Surface reactions of MXenes in molten inorganic salts. (A) Schematics for etching of MAX phases in Lewis acidic molten salts. (B) Atomic resolution high-angle annular dark-field (HAADF) image of Ti₃C₂Br₂ MXene sheets synthesized by etching Ti₃AlC₂ MAX phase in CdBr₂ molten salt. The electron beam is parallel to $[2\bar{1}\bar{1}0]$ zone axis. (C) Energy dispersive X-ray (EDX) elemental analysis (line scan) of Ti₃C₂Br₂ MXene sheets. HAADF images of (D) Ti₃C₂Te and (E) Ti₃C₂S MXenes obtained by substituting Br for Te and S surface groups, respectively. (F) HAADF image of Ti₃C₂□₂ MXene (□ stands for the vacancy) obtained by reactive elimination of Br surface groups. All scale bars are 1 nm.

Fig. 2. Delamination of multilayer $\text{Ti}_3\text{C}_2\text{T}_n$ MXenes. (A) Schematic of delamination process. (B) Photographs of stable colloidal solutions of $\text{Ti}_3\text{C}_2\text{T}_n$ MXenes ($\text{T} = \text{Cl}, \text{S}, \text{NH}$) in NMF exhibiting Tyndall effect. (C) TEM image of $\text{Ti}_3\text{C}_2\text{Cl}_2$ MXene flakes deposited from a colloidal solution. (Inset) Fast Fourier transform of the highlighted region showing crystallinity and hexagonal symmetry of the individual flake. (D) XRD patterns of multilayer MXene and delaminated flakes in a film spin casted on a glass substrate.

Fig. 3. Surface groups can induce giant strain in the MXene lattice. (A) Local interatomic distances in Ti_2CT_n MXenes ($T = \text{S, Cl, Se, Br}$ and Te) probed by small r region of the atomic pair distribution functions, $G(r)$. The vertical lines show the Ti-C, Ti-T bond lengths and Ti-Ti1 and Ti-Ti2 interatomic distances obtained from the Rietveld refinement of powder XRD patterns (dashed lines) and EXAFS analysis (dotted lines). (B) The unit cells of Ti_2CT_n MXenes ($T = \text{S, Cl, Se, Br}$) obtained from the Rietveld refinement. (C) Dependence of the in-plane lattice constant a [equivalent to Ti-Ti2 distance in (A)] for Ti_2CT_n and $\text{Ti}_3\text{C}_2\text{T}_n$ MXenes on the chemical nature of the surface group (T_n). (D) Proposed unit cell of Ti_2CTe MXene (see fig. S39). (E) Biaxial straining of $\text{Ti}_3\text{C}_2\text{T}_n$ MXene lattice induced by the surface groups. The in-plane ($\epsilon_{\parallel}$) and out-of-plane ($\epsilon_{\perp}$) strain components are evaluated with respect to the bulk cubic TiC lattice with $a_{\text{TiC}} = 4.32$ Å.

Fig. 4. Electronic transport and superconductivity in Nb₂CT_n MXenes. (A) Temperature-dependent resistivity for the cold-pressed pellets of Nb₂AlC MAX phase and Nb₂CCl₂ MXene. (Inset) Magnetic susceptibility of Nb₂CCl₂ MXene as a function of temperature. FC and ZFC correspond to the field cooled and zero-field cooled measurements, respectively. (B) Temperature-dependent resistivity for the cold pressed pellets of Nb₂CT_n MXenes. (Inset) Resistance as a function of temperature at different applied magnetic fields (0 to 8 T) for the cold-pressed pellets of Nb₂CS₂ MXene.