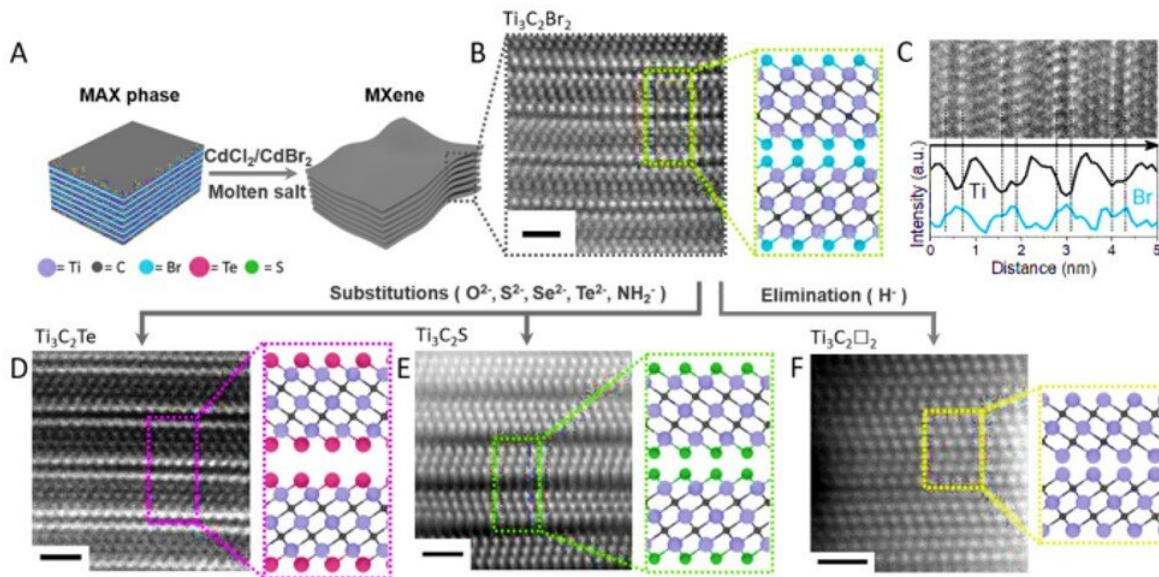


# A new strategy to synthesize 2-D inorganic materials used in capacitors, batteries, and composites

July 15 2020, by Thamarasee Jeewandara

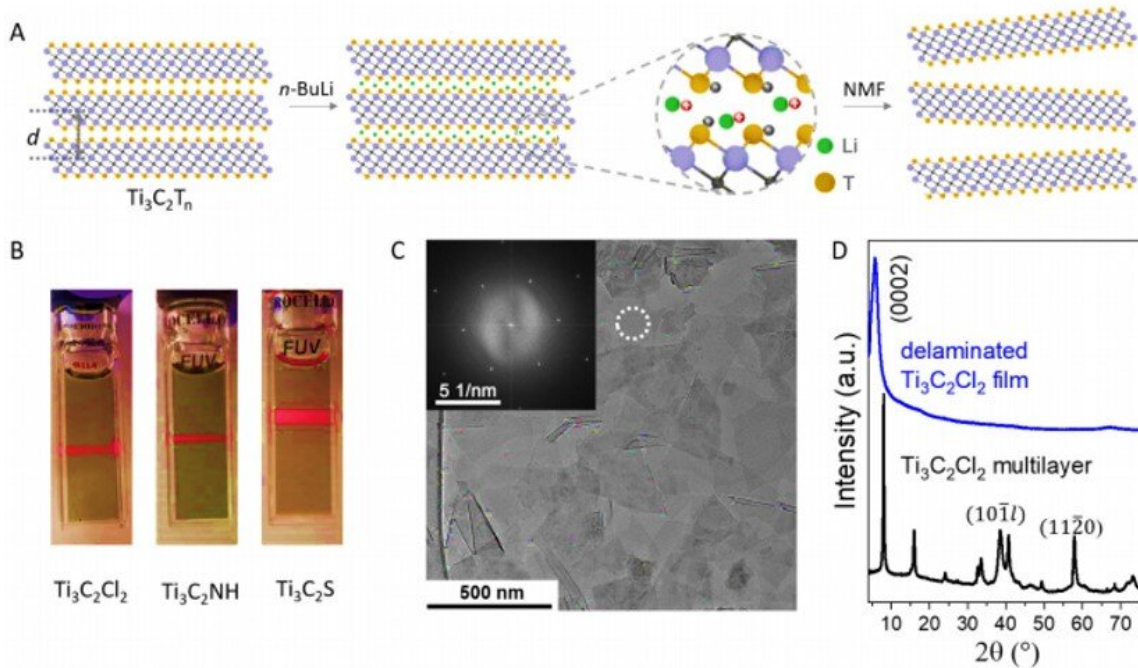


Surface reactions of MXenes in molten inorganic salts. (A) Schematics for etching of MAX phases in Lewis acidic molten salts. (B) Atomic resolution high-angle annular dark-field (HAADF) image of  $Ti_3C_2Br_2$  MXene sheets synthesized by etching  $Ti_3AlC_2$  MAX phase in  $CdBr_2$  molten salt. The electron beam is parallel to  $[110]$  zone axis. (C) Energy dispersive X-ray (EDX) elemental analysis (line scan) of  $Ti_3C_2Br_2$  MXene sheets. HAADF images of (D)  $Ti_3C_2Te$  and (E)  $Ti_3C_2S$  MXenes obtained by substituting Br for Te and S surface groups, respectively. (F) HAADF image of  $Ti_3C_2\Box_2$  MXene ( $\Box$  stands for the vacancy) obtained by reactive elimination of Br surface groups. All scale bars are 1 nm. Credit: Science Advances, doi: 10.1126/science.aba8311

Surface functional groups in two dimensional (2-D) [transition-metal carbides](#) can undergo versatile chemical transformations to facilitate a broad class of [MXene materials](#). In a new report on *Science*, Vladislav Kamysbayev, and a team of scientists in chemistry, physics and nanoscale materials at the James Franck Institute, the University of Chicago and the Argonne National Laboratory in the U.S. introduced a general strategy to synthesize MXenes. Using the method, they installed and removed surface groups via substitution and elimination reactions within molten inorganic salts. The team successfully synthesized MXenes with oxygen (O), [imidogen](#) (NH), sulfur (S), chlorine (Cl), selenium (Se), bromide (Br) and tellurium (Te) surface terminations. They also designed and developed bare MXenes without surface terminations and with distinctive structures and electronic properties. The surface groups could also control the interatomic distances in the MXene lattice to exhibit surface group-dependent [superconductivity](#).

Scientists have studied MXenes for applications in [supercapacitors](#), [batteries](#), [electromagnetic interference shielding](#) and [composites](#). The substrates can be typically synthesized from corresponding MAX phases where M stands for the [transition metal](#), X stands for carbon or nitrogen, by selectively etching the main group element A, which can include aluminum (Al), gallium (Ga), silicon (Si) and other elements. Researchers typically perform etching in aqueous hydrogen fluoride (HF) solutions that render MXenes with a mixture of fluoride (F), oxygen (O) and hydroxide (OH) [functional groups](#), commonly denoted as  $T_x$ . The functional groups can also be chemically modified, unlike the surfaces of other 2-D materials such as graphene and [transition dichalcogenides](#). Previous research had shown that selective terminations of MXenes with different [surface](#) groups can lead to remarkable properties, including tunable work functions and [2-D ferromagnetism](#). Covalent functionalization of the substrate will lead to uncover new

directions to rationally engineer 2-D functional materials.



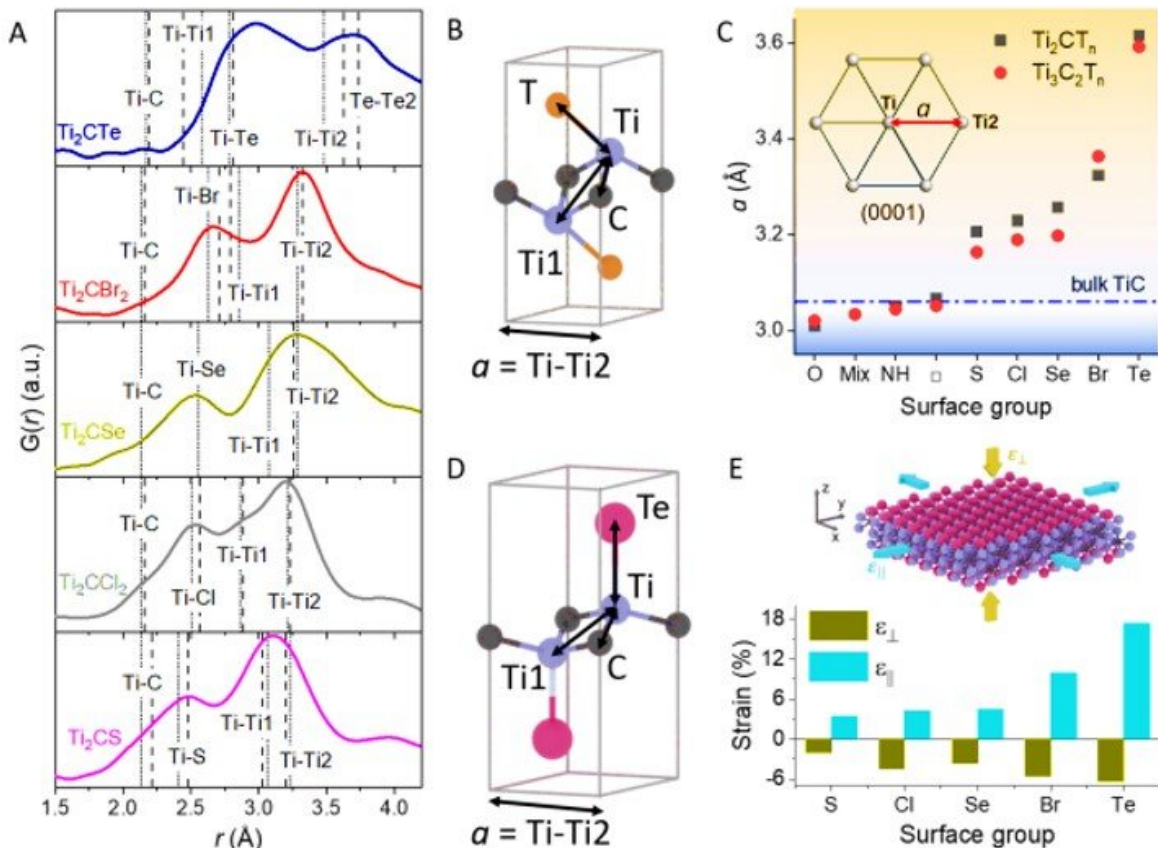
Delamination of multilayer  $Ti_3C_2T_n$  MXenes. (A) Schematic of delamination process. (B) Photographs of stable colloidal solutions of  $Ti_3C_2T_n$  MXenes ( $T = Cl, S, NH$ ) in NMF exhibiting Tyndall effect. (C) TEM image of  $Ti_3C_2Cl_2$  MXene flakes deposited from a colloidal solution. (Inset) 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. Credit: Science Advances, doi: 10.1126/science.aba8311

By etching MAX phases in molten salts in the lab, the scientists eliminated undesired oxidation and hydrolysis reactions to synthesize the new MXenes. Kamysbayev et al. characterized the samples using [high-resolution scanning transmission electron microscopy](#) (STEM), [Raman](#)

[spectroscopy](#) and a combination of X-ray methods. They showed how chloride ( $\text{Cl}^-$ ) and bromide ( $\text{Br}^-$ ) terminated MXenes could efficiently engage in new types of surface reactions. The process allowed unprecedented control across the surface chemistry, structure and properties of MXene materials. Chloride and bromide-based MXenes with labile (easy to alter) surface bonding acted as versatile [synthons](#) for additional chemical transformations. The MXene surface exchange reactions required temperatures of 300 degrees Celsius to 600 degrees Celsius, which are difficult to achieve through traditional solvents. The team therefore used [molten alkali metal halides](#) in solvents with unmatched high-temperature stability and high solubility. For example, halogenated MXenes such as  $\text{Ti}_3\text{C}_2\text{Br}_2$  dispersed in alkali halides such as caesium bromide, potassium bromide or lithium bromide ( $\text{CsBr}/\text{KBr}/\text{LiBr}$ ) could react with [dilithium telluride](#) ( $\text{Li}_2\text{Te}$ ) and [lithium sulfide](#) ( $\text{Li}_2\text{S}$ ) to form MXenes with a telluride or sulfide-based group.

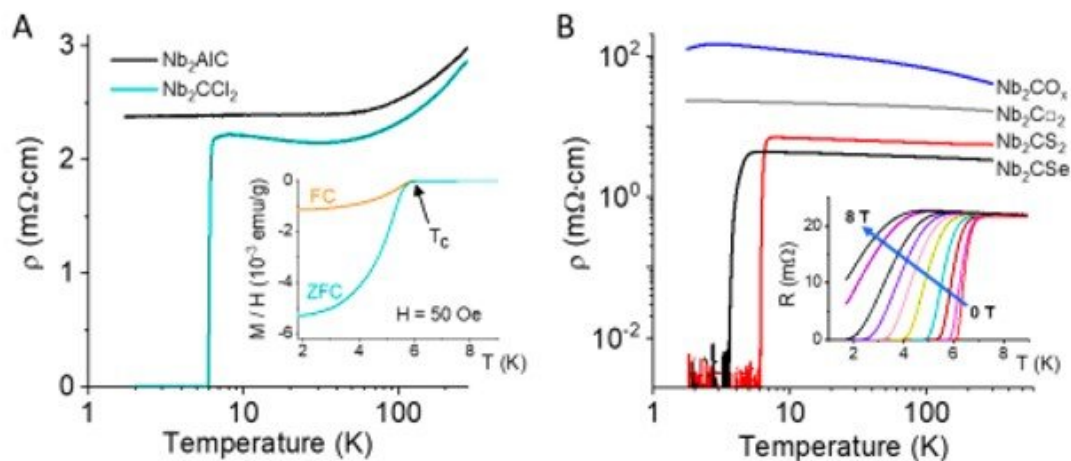
Kamysbayev et al. then synthesized  $\text{Ti}_2\text{CCl}_2$ ,  $\text{Ti}_2\text{CBr}_2$ , and  $\text{Nb}_2\text{CCl}_2$  (denoted in brief as chloride-MXenes and bromide-MXenes) based on similar covalent surface modifications. They performed surface exchange reactions on the MXenes to demonstrate the intact 2-D sheets during all stages of transformation. For example, during reactions of bromide-MXenes with lithium hydride at 300 degrees Celsius, the team produced bare MXenes with vacancy sites and described the process as a reductive-elimination of the hydride groups. Chemical transformations of solids are typically impeded by slow diffusion to severely limit the [scope of synthesizing solid-state compounds](#), therefore completely exchanging the surface groups in stacked MXenes was a kinetically cumbersome process.





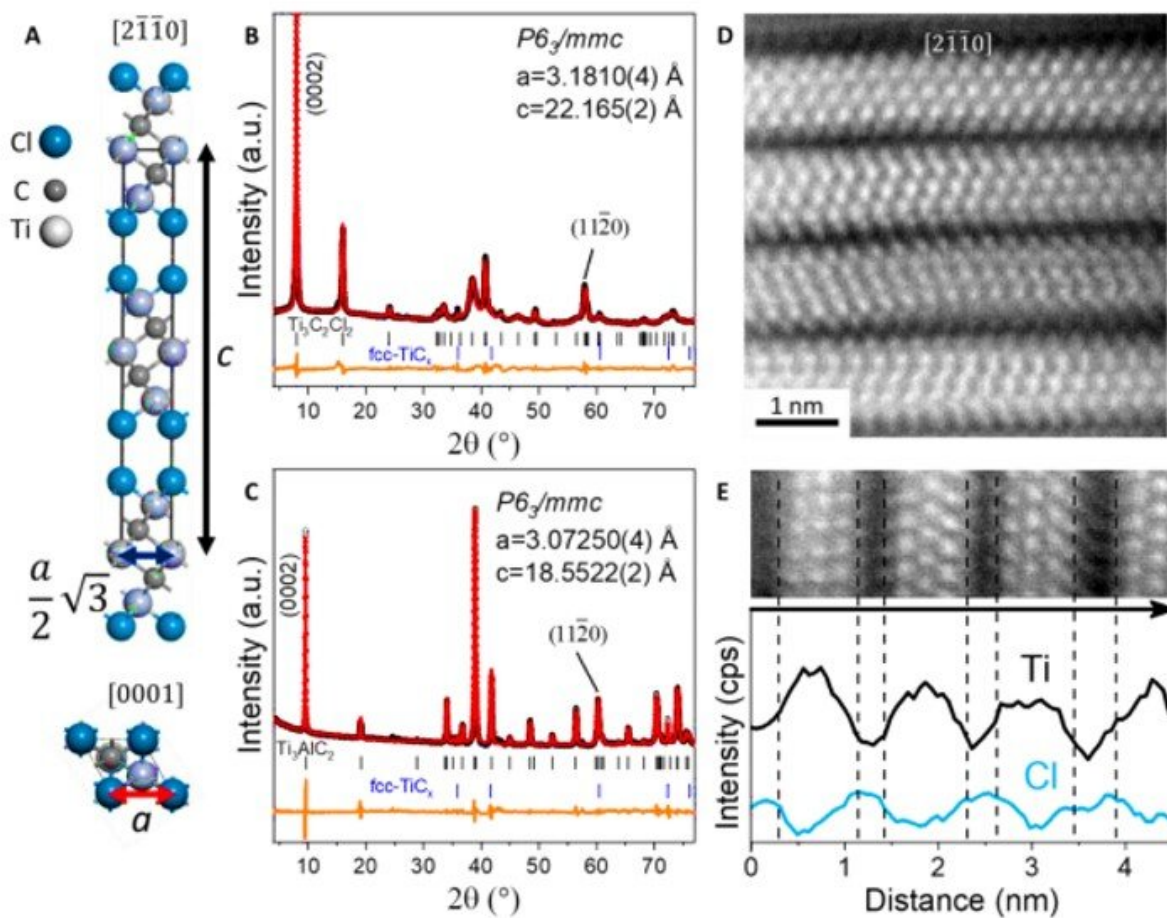
Surface groups can induce giant strain in the MXene lattice. (A) Local interatomic distances in  $Ti_2CT_n$  MXenes ( $T = S, Cl, Se, Br$  and  $Te$ ) probed by small  $r$  region of the atomic pair distribution functions,  $G(r)$ . The vertical lines show the Ti-C, Ti-T bond lengths and Ti-Ti1 and Ti-Ti2 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 ( $T = S, Cl, Se, Br$ ) 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  $Ti_3C_2T_n$  MXenes on the chemical nature of the surface group ( $T_n$ ). (D) Proposed unit cell of  $Ti_2CTe$  MXene. (E) Biaxial straining of  $Ti_3C_2T_n$  MXene lattice induced by the surface groups. The in-plane ( $\epsilon_{||}$ ) and out-of-plane ( $\epsilon_{\perp}$ ) strain components are evaluated with respect to the bulk cubic TiC lattice with  $a_{TiC} = 4.32 \text{ \AA}$ . Credit: Science Advances, doi: 10.1126/science.aba8311

To understand the material reactivity, the scientists followed the evolution of surface exchange reactions using  $\text{Ti}_3\text{C}_2\text{Cl}_2$  sheets. Unstacking the MXene sheets in molten salts greatly assisted the diffusion of ions to make MXene surfaces sterically accessible. The [van der Waals](#) (vdW) radii and packing density of surface atoms in the material had a huge effect on the lattice constant denoted  $a$ . The work showed how the composition and structure of MXenes could be engineered with unprecedented versatility, while chemical functionalization of MXenes affected nearly every property of the materials and influenced the nature of electronic transport in MXenes. Above a temperature of 30 K, the MAX phase and MXene samples showed similar specific resistivity, which decreased on cooling the sample. The team associated the temperature dependence with conductivity and a metallic state.



Electronic transport and superconductivity in Nb<sub>2</sub>CT<sub>n</sub> MXenes. (A) Temperature-dependent resistivity for the cold-pressed pellets of Nb<sub>2</sub>AlC MAX phase and Nb<sub>2</sub>CCl<sub>2</sub> MXene. (Inset) Magnetic susceptibility of Nb<sub>2</sub>CCl<sub>2</sub> 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 Nb<sub>2</sub>CTn MXenes. (Inset) Resistance as a function of temperature at different applied magnetic fields (0 to 8 T) for the cold-pressed pellets of Nb<sub>2</sub>CS<sub>2</sub> MXene. Credit: Science Advances, doi: 10.1126/science.aba8311



Structure of Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> MXene. (A) The structure of Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> MXene can be approximated using P6<sub>3</sub>/mmc space group with the two lattice parameters: in-plane, a, and out of plane, c. Experimental XRD patterns (Cu K $\alpha$ , reflection, black curve), Le Bail fits (red curve) and the corresponding residues (orange curves) of (B) Ti<sub>3</sub>C<sub>2</sub>Cl<sub>2</sub> MXene derived from (C) Ti<sub>3</sub>AlC<sub>2</sub> MAX phase. The successful MXene synthesis can be visualized from the shift of (0002) and

(1120) peaks to lower angles compared to that of the parent MAX phase. In the direct space these changes are reflected by the increase of both a and c lattice parameters. Initial  $\text{Ti}_3\text{AlC}_2$  MAX phase contains small amounts of bulk fcc- $\text{TiC}_x$  (Fm-3m space group) impurity which propagates into the final MXene product. (D) Atomic-column resolved HAADF image of  $\text{Ti}_3\text{C}_2\text{Cl}_2$  MXene. The electron beam is parallel to  $[2\bar{1}10]$  zone axis. (E) The EDX elemental line scans of  $\text{Ti}_3\text{C}_2\text{Cl}_2$  MXene using Ti  $K\alpha$  and Cl  $K\alpha$  suggest presence of Cl surface groups on each  $\text{Ti}_3\text{C}_2$  sheet. Due to their low Z contrast, C atoms could not be observed. Credit: Science Advances, doi: 10.1126/science.aba8311

Kamysbayev et al. noted a sharp drop of resistivity at a critical temperature of 6.0 K, to indicate superconductive transition in the material. Comparatively, oxygen, hydroxide and fluoride-based MXenes prepared through the traditional etching route (in aqueous HF) showed two orders of magnitude higher resistivity [without displaying superconductivity](#). The oxo-terminated MXenes showed the highest-resistivity, while the seleno-terminated MXene showed the lowest resistivity. In this way, the surface groups were not mere spectators but active contributors to MXene superconductivity, affecting biaxial strain, phonon frequencies and the strength of [electron-phonon](#) coupling in the material. The MXene exchange reactions represent an exciting counter-example to the traditional view of solids that are generally considered hard to modify post-synthesis. Using extensive characterization studies, Vladislav Kamysbayev and colleagues showed how chemical bonds inside an extended MXene stack could be designed rationally to form a broad class of functional materials.

**More information:** Vladislav Kamysbayev et al. Covalent surface modifications and superconductivity of two-dimensional metal carbide MXenes, *Science* (2020). [DOI: 10.1126/science.aba8311](https://doi.org/10.1126/science.aba8311)

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